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Transport of calcium ions through thick biomimetic polymer membranes

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Nature represents a fascinating source of inspiration, through its complex and controlled reactions with high specificity. A particular example is reflected by ion-transporters, which mediate ion passage across cellular membranes, in a selective manner, to initiate these complex reactions [1]. An elegant strategy is to mimic biocompartments and cell membranes, through the combination of biological entities and synthetic nanocompartments, for the development of theranostic applications [2]. One approach is to use lipid membranes, which are selectively permeabilized by ion-transporters [3]. Due to their lack of stability, the use of synthetic membranes based on block copolymers provides a better solution for technological applications. They offer enhanced mechanical stability and tunability of their proprieties in terms of flexibility, thickness, or stimuli-responsiveness [4]. Block copolymers, based on poly(2–methyloxazoline)–*block*–poly(dimethylsiloxane)–*block*–poly(2–methyloxazoline ($PMOXA_x$-$PDMS_y$-$PMOXA_x$), were successfully shown to self-assemble in aqueous solutions into polymer vesicles [5, 6], with a membrane which could be successfully permeabilized with ion-transporters [7]. This was surprising, taking into account that the membrane of these vesicles had twice the thickness of a typical membrane of a lipid vesicle (10.7 nm compared with 5 nm). As a model ion-transporter, ionomycin was chosen and it was shown to successfully permeabilize these thick membranes towards divalent cations, such as Ca^{2+}, without any perturbation of the polymer vesicle architecture. This resulted in a stimuli-responsive system, as a support for the development of biosensing platforms with a selective and rapid efficacy.

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Amphiphilic Hexayne Derivatives as Precursors for Atomically Dense Carbon Nanolayers

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Two-dimensional nanostructures (e.g. graphene, molybdenum disulfide, phosphorene) are considered as promising materials for technological progress due to their outstanding thermal, mechanical, and electrical properties [1]. Especially two-dimensional carbon nanomaterials offer new possibilities in the fields of organic electronics, membrane technology, and nanocomposites. The access to two-dimensional carbon nanomaterials remains challenging and synthetic routes follow either top-down or bottom-up strategies [2]. Top-down approaches yield materials with a high degree of structural perfection, but are mostly restricted to small-scale production. Bottom-up approaches have the advantage that they allow to study structure-property relationships in depth. However, these procedures are often synthetically demanding and mostly rely on temperatures above 600°C for the carbonization of low molecular weight precursors. Such high temperatures preclude the chemical functionalization of carbon nanomaterials, which makes further processing difficult.

Recently, we have presented an alternative approach to obtain two-dimensional carbon nanomaterials that is based on the use of hexayne amphiphiles as molecular precursors [3, 4]. The *sp*-hybridized carbons of the hexayne moiety in such amphiphilic precursor molecules show a high reactivity and are susceptible to crosslinking under mild conditions, i.e., irradiation with UV light at room temperature. Notably, the chemical functionality of the precursor translates directly in the functionality of the crosslinked carbon nanostructure. Extending our work on the fabrication of self-supporting carbon nanosheets at the air-water interface, we explore the properties of crosslinked hexayne amphiphiles in detail.

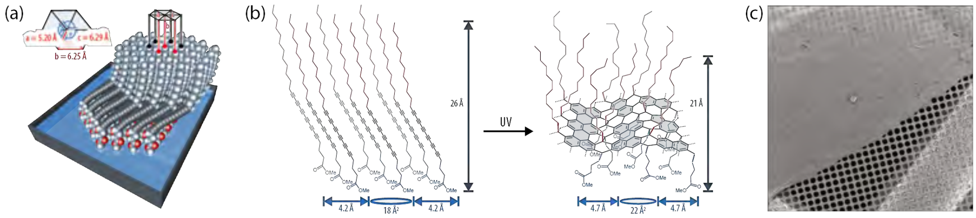

Figure 1. (a) Self-assembly of hexayne amphiphiles at the air-water interface. (b) Crosslinking of the hexayne amphiphiles at room temperature by UV irradiation. (c) Crosslinked carbon nanosheet on a transmission electron microscopy grid.

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Development of functionalized hybrid hydrogels

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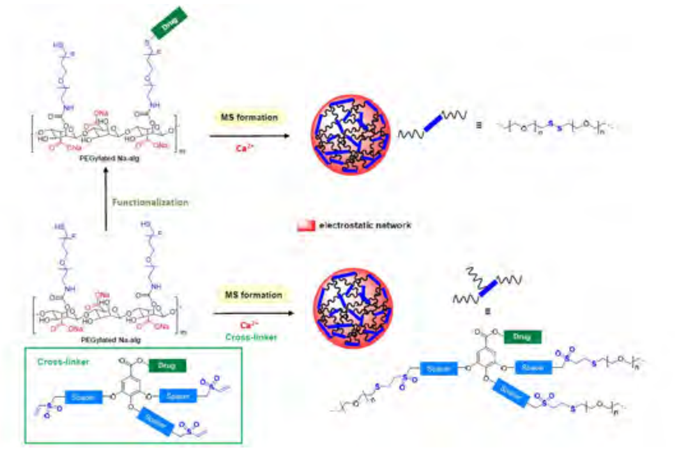
The progress of medical therapies, which rely on the transplantation of microencapsulated cells, depends on the quality of the encapsulating material. Such material has to be biocompatible, its physical characteristics have to be adjustable, and the microencapsulation process must be simple and not harm the cells.

Although great progresses were done concerning the resistance of microspheres[1-4] inevitable inflammation response and fibrosis formation leading to cell asphyxiation is observed for long term experiments[5]. Therefore improving lifetime of microspheres in living organisms by tuning the composition of the polymeric components of the hydrogels is necessary. The strategy used for this purpose relies on the conjugation of anti-inflammatory agents on the polymeric components or cross-linkers involved in hydrogel formation to obtain microspheres with surface functionalization that might be released in a controlled manner around the transplantation site. Depending on the chemical linkage envisaged for the conjugation process, different time scales for local delivery are expected.



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Supramolecular organogels based on boronate esters and imidazolyl ligands

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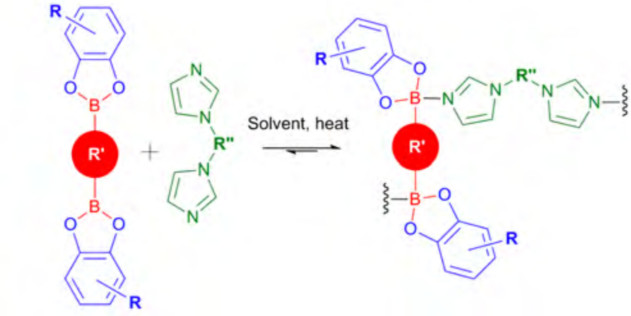
Dative boron-nitrogen bond is a molecular interaction of growing interest in supramolecular chemistry. Previous reports have shown its use for the formation of polymer materials or molecular cages. We demonstrate the use of this reversible covalent binding for the synthesis of organogel via B-N adducts formation of imidazolyl ligands on diboronate ester compounds.[1] A large variety of boronate esters could thus be gelated together with bis(imidazole-1-yl)methane ligands in non-polar solvents such as 1,2-dichlorobenzene, toluene or mesitylene. Those gels all showed the expected solid-like behavior during rheology measurements. Surprisingly gelation could also be achieved in polar solvents as THF or acetone. Some samples were showing very low critical gel concentration, as low as 0.02 percent in weight, which illustrate the strong binding of the gel components, and the large solvent-gelator interaction. Gelation could also be obtained in one-pot reaction upon direct mixing of diboronic acid, catechol and imidazolyl donor. We also reported the formation of a four-component organogel by *in-situ* synthesis of an imine-bridged diboronic acid through condensation of a formyl-benzeneboronic acid with an amino-benzeneboronic acid.[2] This last gel could successfully be post-modified to increase its mechanic resistance.



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PEGylation of sodium alginate for tuning the properties of hydrogel microspheres

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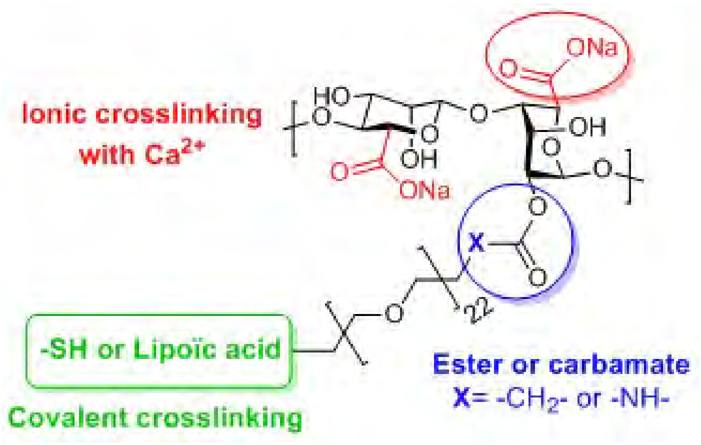
Cells microencapsulation is a promising technology to treat a wide range of diseases through cells transplantation. The scaffold materials for cell immobilization consist of biocompatible hydrogels which require specific physical properties. In particular, long term cell viability and functionality is strongly influenced by the network density, the mechanical stability and permeability of hydrogel microspheres (MS). While the hydrogel calcium alginate (Ca-alg) display favorable biocompatibility for biomedical applications, several limitations including insufficient stability and permselectivity were reported. We present herein the reinforcement of Ca-alg MS by combination of Na-alg with poly(ethylene glycol) (PEG) derivatives to allow hydrogel formation by both electrostatic and covalent crosslinking. Physical properties of the resulting microspheres (MS) will be discussed and compared between the different systems.



Heterobifunctional a-amino-w-mercapto-poly(ethylene glycol) and a-amino-w-lipoyl-poly(ethylene glycol) 1000 were synthetized and grafted to Na-alg hydroxyl functionalities through ester or carbamate linkages. The resulting materials were investigated for their ability to form MS through the combination of fast electrostatic interactions of Na-alg with calcium ions with covalent disulfide crosslinking, in one-step processes. The influence of the chemical composition and formulation of the different polymeric materials on the physical properties of the resulting MS was studied. In addition, the compatibility of these MS for human cells microencapsulation was evaluated *in vitro* and long term MS stability was investigated in animal models.

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Light-Induced Fragrance Release from Microcapsules Containing 2-Oxoacetates

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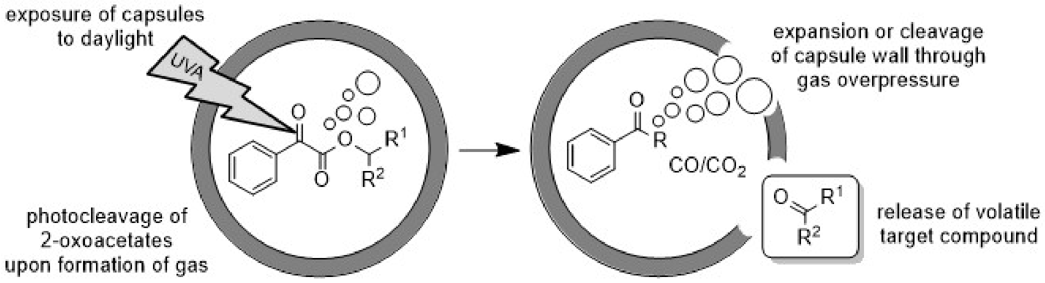
Because of its importance for our everyday life, the UN declared 2015 the International Year of Light. The UVA region of natural daylight provides enough energy to isomerise and cleave covalent bonds. This allows using light as a trigger for the controlled release of a multitude of bioactive compounds from stimuli-responsive materials [1]. To be smelled, fragrances have to evaporate from surfaces that are typically exposed to daylight. Light-sensitive delivery systems are thus particularly suitable to control the release of these compounds [2].



In this context, 2-oxoacetates have been explored as photocleavable fragrance precursors (profragrances) that generate aldehydes or ketones when exposed to light [3]. Depending on whether the photoreaction proceeds in the presence or absence of oxygen, an equivalent of CO_2 or CO is formed as side-product of the reaction. The formation of gas has been reported in the literature, but no advantage has so far been taken from it. We now discovered that photoirradiation of 2-oxoacetates encapsulated in core-shell microcapsules generates CO_2/CO sufficiently fast to build up an overpressure inside the capsules, which cleaves the capsule wall and releases the (co-)encapsulated volatiles [4]. Dynamic headspace measurements confirmed the generation of the gas and the release of the fragrances. Optical microscopy demonstrated the formation of gas bubbles, the cleavage of the capsule wall and the leaking out of the encapsulated oil phase.

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Effect of Reactive Extrusion on the Morphology of Polymer Nanocomposites

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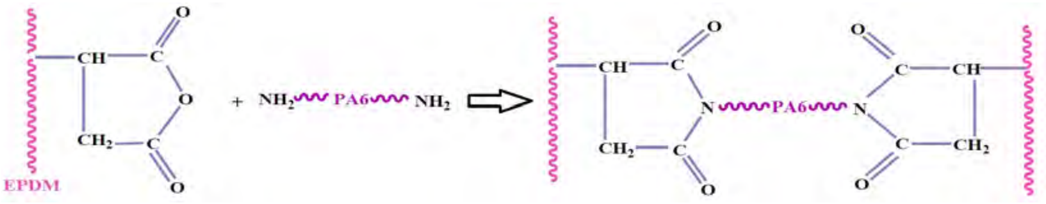
Reactive extrusion of functional groups present on the macromolecular chains of polymer blend constituents including Polypropylene/Polyamide6/Maleic Anhydride-grafted Ethylene Propylene Diene Monomer alters the morphology of corresponding polymer blend/clay nanocomposites. In fact, amine end groups on the polyamide6 chains tend to establish interactions with the succinic functionalities grafted on Ethylene Propylene Diene Monomer (EPDM) affecting the surface tension between the phases[1-2]. In other words, the amphiphilic grafted copolymer, gathers at the EPDM-PA6 interface and decreases the interfacial tension between the two dispersed phases involved [3]. Direct observation of morphology through Scanning Electron Microscope confirms the role of surface tension balance affected through the in-situ reactions which are evidenced by Fourier Transform Infrared Spectroscopy, on the formation of final microstructure.



Dynamic interfacial energy model was used to predict the morphology of samples containing different compositions of functionalized compatibilizing agent. Calculation results were compared with the microstructures observed through microscopy indicating model accuracy of 40%. A new model was developed offering 80% precision through consideration of ignored effective parameters. Results showed that in the investigated polymer blend samples the compatibilizer composition does affect the EPDM shell thickness and also the overall size of composite droplets dispersed within the polypropylene matrix but do not alter the core/shell type of morphology driven by the thermodynamic of investigated ternary system where at the presence of nanoclay, the governing equations fail due to the interactions of involved polar groups with clay gallery surfaces. The phenomena involved at the presence of clay are discussed in this research work.

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An investigation into thermal analysis methods of detection and quantification of oxidative degradation of PVC-coated constructional steel.

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PVC-coated steel used for construction consists of many layers of coatings, which, together with their interfaces, make up a complex system. Model paints have been made using industrial components of this system in order to simplify it and therefore gain a better understanding of the degradation mechanisms present. Different solvents and alternative methods of curing have been tried and the resulting paints tested by thermal analysis. Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Dynamic Mechanical Analysis (DMA) and Gas Chromatography Mass Spectrometry (GC/MS) have been used to analyse the model paints and their degradation products. Organically coated steels, that have been weathered using industry standard accelerated testing have been tested for comparison. The methods show potential to detect early stages of degradation.

Structural characteristics of amyloid-like fibers issued from a human estrogen receptor α-derived peptide

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At 10 mM, the peptide corresponding to the 295-311 sequence of the hinge region of the human estrogen receptor alpha (peptide ERa17p) shares a panel of interesting pharmacological properties [1,2]. It provokes, in physiological conditions, apoptosis and specifically the death of breast cancer cells [1].

Whereas it is random when alone in solution [3], it adopts an a helix conformation when bound to Ca^{2+}-calmodulin [4]. By using circular dichroism (CD) spectroscopy and differential scanning calorimetry (DSC), we have shown that the peptide ERa17p, when used at concentration ≥ 50 mM, adopts a b-sheet secondary structure when associated with anionic membranes (micelles, vesicles), exclusively; no folding was observed with neutral lipids [5,6]. This observation suggests that the folding of the peptide occurs in an anionic environment. Remarkably, transmission electronic microscopy (TEM) showed that this b-sheet conformation was accompanied by the formation of fibers occurring around anionic vesicles [6]. The homogeneity of the anionic vesicles was affected in the presence of the peptide since a calcein leakage was observed.

When alone in water, at neutral pH and at concentrations ≥ 50 mM, this secondary structure was accompanied by the formation of particularly long fibers originating from nucleation regions [6]. It was shown by using TEM that these fibers were twisted, with a periodicity of 45 nm, as commonly observed with amyloid-like fibers [6]. Such observations were supported by nano-infrared spectroscopy (nano-IR) and atomic force microscopy (AFM). In the case of AFM, the fibers were observed with mica, which is a cationic substrate, reinforcing the concept that negative charges are important for the folding of amyloidogenic peptides [6,7]. Also, we observed by using fluorescence spectroscopy that the kinetics of formation of fibers was dramatically increased in the presence of anions such as sulfate.

Cancer cells, rich in phosphatidylserine, may be considered to be anionic. Accordingly, we hypothesize that the apoptotic effects of the peptide ERa17p on cancer cells could be due to its propensity to recognize negative charges and to destabilize cell membranes.
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H-Bonded Supramolecular Polymers Selectively Dispersing and Subsequent Releasing Single-Walled Carbon Nanotubes

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Single walled carbon nanotubes (SWCNTs) have outstanding physical (mechanical and electronic) properties which depend on the arrangement of the carbon atoms when a graphene sheet is rolled into a tube. While chemistry fails so far to synthesize monodisperse tubes with given *n*,*m* indices, impressive steps were made in sorting tubes. In particular, some polymers and copolymers comprising rigid aromatic subunits display excellent selectivity towards specific nanotubes, as they form strong π-π stacking interaction with the nanotube surface, such as fluorene, and carbazole-based polymers.[1-4] A drawback of this approach is that the polymers tightly wrap around the SWCNTs and it becomes extremely difficult to get rid of them. However, various applications require polymer-free SWCNTs. In this research proposal we would like to develop a series of H-bonded supramolecular polymers to disperse reversibly SWCNTs with particular diameters, *n*,*m*-indices and hopefully even chirality. For this purpose we designed a self-complementary structure with a 2,6-di(acetylamino)pyridine on one end and the imidic uracil derivate at the other end. The triple hydrogen bonds formed between both terminal units enables the formation and breaking up of supramolecular polymers. In the middle of the monomer units, various rigid aromatic subunits will be adopted to selectively interact with the SWCNTs. Once the SWCNTs are successfully dispersed, it can be released via addition of a bit polar solvents or acidic solutions, which are very effective in disputing hydrogen bonds.

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Synthetic biocompartments with selective membrane permeability towards protons and monovalent cations

M. Lomora[1], F. Itel[1], I.A. Dinu[1], M. Garni[1], M. Spulber[1], C. G. Palivan[1]*

[1]University of Basel

Regulation of ions across cellular membranes has implications for cell division, cell volume regulation, in maintaining the stability of the cell’s internal environment, or providing specific signaling functions [1]. For a better understanding of the biological processes, the design of models based on synthetic polymer compartments [2] with tuneable proprieties of their membrane is desired. The permeabilization of these membranes with ion channels induces the formation of gates for allowing specific ions to pass through. In this respect, we present biomimetic membranes with selective ion permeability and preserved architecture upon insertion of biopores. The biomimetic membranes consisted of a block copolymer library, composed of poly(2–methyloxazoline)–*block*–poly(dimethylsiloxane)–*block*–poly(2–methyloxazoline) ($PMOXA_x$-$PDMS_y$-$PMOXA_x$) triblock copolymers, with membrane thicknesses in the range of 9.2-16.2 nm, able to self-assemble in aqueous solutions into polymer vesicles (polymersomes) [3]. Their membranes were successfully permeabilized using a model biopore, gramicidin, allowing the passage of protons (H^+) and monovalent ions (Na^+, K^+) [4]. Due to the flexibility of block copolymers, gramicidin (2.5 nm in length) was shown to be functional within the hydrophobic domain, up to a membrane thickness of 12.1 nm. The permeabilization of polymersomes membranes, for protons and ions (Na^+, K^+) passage, is a novel strategy for the development of synthetic biocompartments, with maintained integrity upon insertion of biopores, and selective ion permeability. This biomimetic approach enables the design of ion biosensors, nanoreactors, or specialized artificial organelles, in which the influx of ions is necessary for *in situ* reactions.

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Development of triggered nanoreactor platforms

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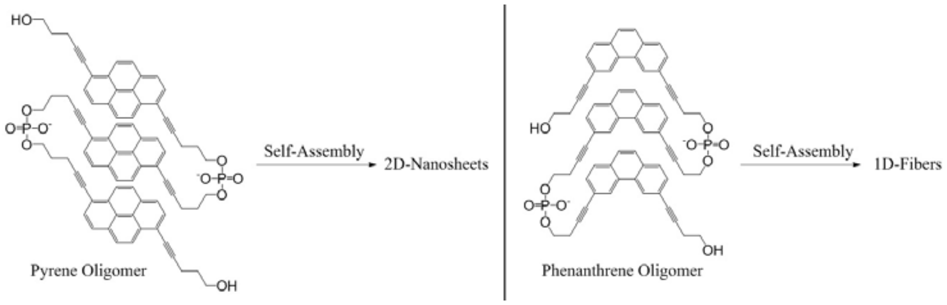
Development of pH-triggered platforms plays a pivotal role in various scientific fields, ranging from nanomedicine to biosensing applications. As an example the pH, temperature and reduction potential in the body often varies, which is especially noticeable in the case of inflamed or cancerous tissue. These differences in environment conditions can be exploited by therapeutic or diagnostic systems that are responsive to the local changes in environment. Here, we introduce polymer nanoreactors with pH and reduction triggered activity. These nanoreactors are based on polymer vesicles, whose membrane permeability is controlled by insertion of chemically modified channel proteins acting as “gates”. The previous concept of nanoreactors, where active compounds are encapsulated inside polymer compartments (proteins, enzymes, mimics) and are able to act in situ, is extended by chemically modification of the membrane protein such to serve as an responsive gate. Only in certain conditions the gate is opened (by releasing its cap) and the enzymatic substrate can enter vesicular compartment. Through this the substrate the enzymatic reaction can take place: the subsequent products of the reaction are released in the nanoreactors environment. Through encapsulation of different enzymes, the nanoreactors can be tailored for purposes of therapy or biosensing.

Phenanthrene Nanotubes

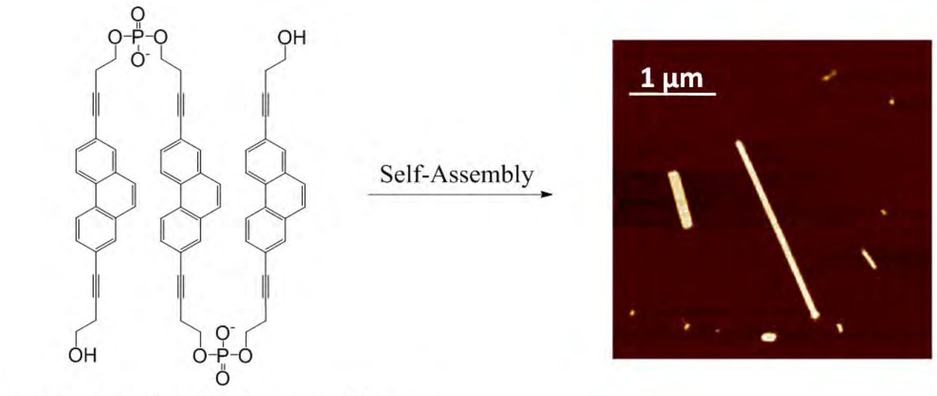
C. D. Bösch[1], S. M. Langenegger[1], R. Häner[1]*

[1]University of Bern

The self-assembly of oligomers into well-defined supramolecular polymers is of large interest in the material sciences [1]. In previous work we showed the formation of two-dimensional supramolecular polymers by pyrene oligomers [2] and the formation of one-dimensional supramolecular polymers by phenanthrene oligomers [3]. The latter is remarkable because the assembled phenanthrene units act as an antenna which effectively transfers its excitation energy to a pyrene acceptor.



The appearance of self-assembled nanostructures seems to depend on the substitution geometry of the phosphodiester-linked monomers. In this poster we will present the findings for a 2,7-disubstituted phenanthrene oligomer which forms tubular structures in aqueous medium. The formation of supramolecular polymers is studied by temperature-dependent absorption and fluorescence measurements and visualized by atomic force microscopy. Further it will be of interest to see if these phenanthrene assemblies also act as a light-harvesting antenna in combination with a suitable acceptor.



2,7-Disubstituted Phenanthrene Oligomer

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The formation of large assemblies through single, non-covalently attached pyrene phosphates

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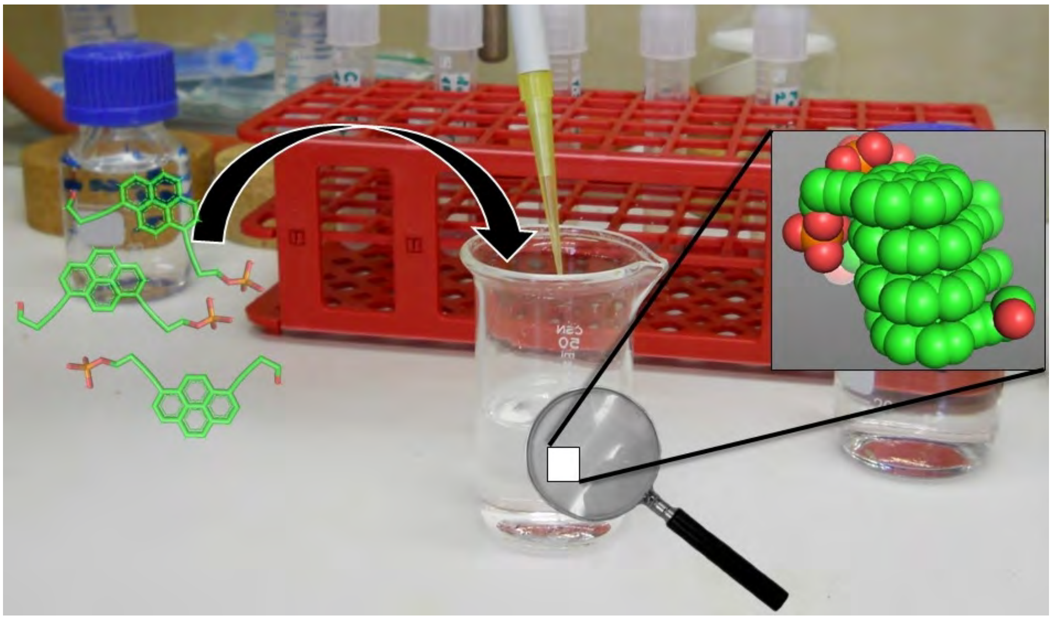
[1]Universität Bern

The precise construction of functional entities with a well-defined morphology is a key challenge in materials science. The process has to be reproducible as well as predictable. In this work, we describe the self-assembly of negatively charged pyrene monomers in aqueous media into supramolecular polymers. The morphology of the aggregates was characterized by AFM. Due the distinct UV-Vis and fluorescence properties of the amphiphilic molecules, spectroscopy revealed important insights into the intermolecular interactions of these building blocks.



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Hierarchical self-assembly of the DNA-grafted supramolecular polymers

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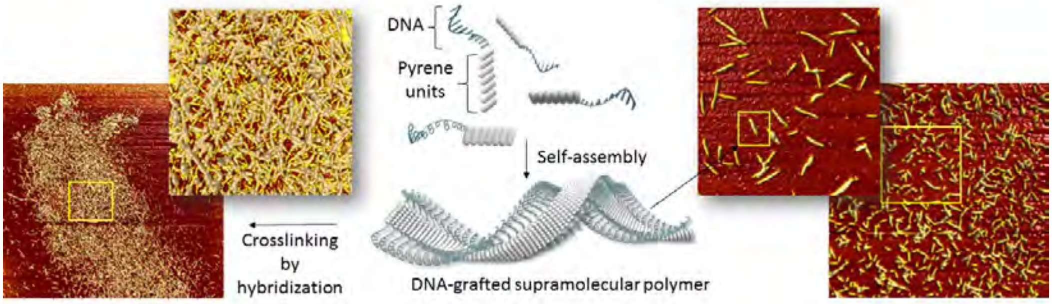
Conjugation of functional entities with a specific set of optical, mechanical or biological properties to DNA strands allows engineering of sophisticated DNA-containing architectures.[1], [2] Among various hybrid systems, DNA-grafted polymers occupy an important place in modern materials science. [3] In this contribution we present the non-covalent synthesis and properties of DNA-grafted linear supramolecular polymers (SPs), which are assembled in a controllable manner from short chimeric DNA-pyrene oligomers. The synthetic oligomers consist of two parts: a 10 nucleotides long DNA chain and a covalently attached segment of variable number of phosphodiester-linked pyrenes. The temperature-dependent formation of DNA-grafted SPs is described by a nucleation-elongation mechanism.

The high tendency of pyrenes to aggregate in water, leads to the rapid formation of SPs. The core of the assemblies consists of stacked pyrenes. They form a 1D platform, to which the DNA chains are attached. Combined spectroscopic and microscopic studies reveal that the major driving forces of the polymerization are π-stacking of pyrenes and hydrophobic interactions, and DNA pairing contributes to a lesser extent. [4] AFM and TEM experiments demonstrate that the 1D SPs appear as elongated ribbons with a length of several hundred nanometers. They exhibit an apparent helical structure with a pitch-to-pitch distance of 50±15 nm.

Since DNA pairing is a highly selective process, the ongoing studies are aimed to utilize DNA-grafted SPs for the programmable arrangement of functional entities. For example, the addition of non-modified complementary DNA strands to the DNA-grafted SPs leads to the cooperative formation of higher-order assemblies. Also, our experiments suggest that the fluorescent pyrene core of 1D ribbons serves as an efficient donor platform for energy transfer applications.



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$Pt^{(0)}$ containing metallosupramolecular polymers

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[1]University of Fribourg

Supramolecular polymers (SP's) are macromolecules formed by monomeric units connected through reversible, non-covalent interactions. SP's can be thus synthesized by self-assembly of molecules containing a variety of supramolecular motifs that are capable of interacting via hydrogen bonding, metal-ligand complexation, ion pairing, or host guest interactions. As a result, SP's combine the advantages of dynamic supramolecular interactions and the physical properties of polymers.

A sub-group of SP's are metallosupramolecular polymers (MSP's), which are assembled through metal-ligand complex formation. Building on our previous work on cross-linked $Pt^{(0)}$-containing MSP's,[1] we have recently developed a synthetic framework for the synthesis of linear $Pt^{(0)}$ containing MSP's. These materials are synthesized by fast ligand exchange between a $Pt^{(0)}(styrene)_3$ complex and diphenyl acetylene-terminated telechelic poly(ethylene-*co*-butylene)(DPA-O-PEB-O-DPA)(Figure 1). This procedure presents clear practical advantages over current examples in the literature, which introduce the metal center by *in situ* reduction of a previously introduced metallic salt.[2]

Homogeneous films of the new polymer were formed by solvent casting and characterized by small angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR), revealing a random nanophase segregation and adequate stability under ambient conditions. The stimuli responsiveness of this material in the context of irreversible Pt nanoparticle formation will also be discussed.

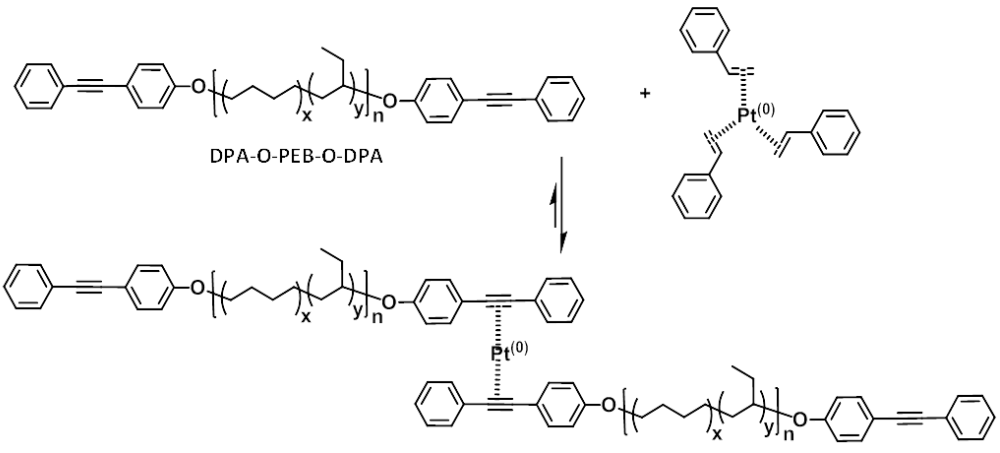

Figure 1: Schematic representation of linear chain extension used for the synthesis of the $Pt^{(0)}$-based MSPs.

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Incorporation of dithiomaleimide as mechanophores into polymers chain.

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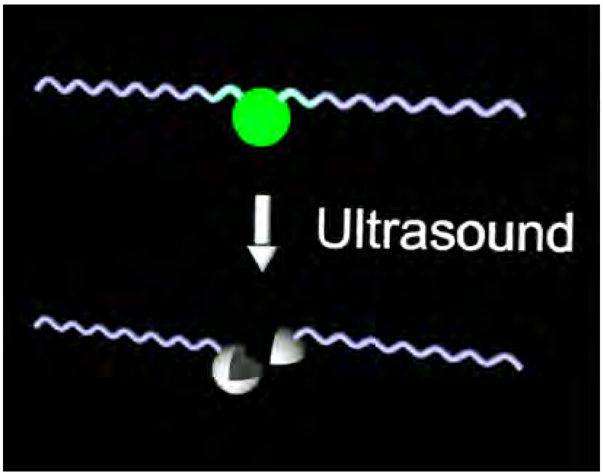
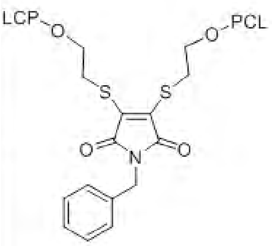
[1]Adolphe Merkle Institute

While mechanical forces are well-known to cause the non-specific breaking of chemical bonds in polymers, the exploitation of targeted chain scission at mechanically weak links has only recently begun to attract considerable attention. It appears, however, that this design approach is useful to create a broad range of possibly useful stimuli-responsive materials, whose response can be tailored via the choice of mechanically weak motifs that are commonly referred to as mechanophores. Dibromomaleimide derivatives are known to react with disulfide bridges present in proteins and the substitution of the two bromine groups by alkylthiols leads to highly fluorescent products. Therefore, dibromomaleimides have been used in protein labeling and self-reporting micelles. Here we show that the dithiomaleimide (DTM) group can serve as a mechanophore, which signals mechanically induced cleavage by a significant change of its fluorescence behavior. DTM-containing poly(ε-caprolactone)s (PCL) were synthesized using a ring-opening polymerization and employing a diol derivative of DTM as initiator. When solutions of high-molecular weight samples of PCL-DTM-PCL were exposed to ultrasonication, an exponential decrease of the molecular weight and the fluorescence emission intensity were observed, as a result of sonochemical chain scission. On the other hand, no changes in molecular weight and optical properties were seen when the same experiment was carried out with a sample whose molecular weight was below the critical limit required for sonochemical dissociation, supporting the conclusion that the activation is indeed the result of a mechanochemical transduction process.





Side reactions in polycondensation of aromatic amino acids

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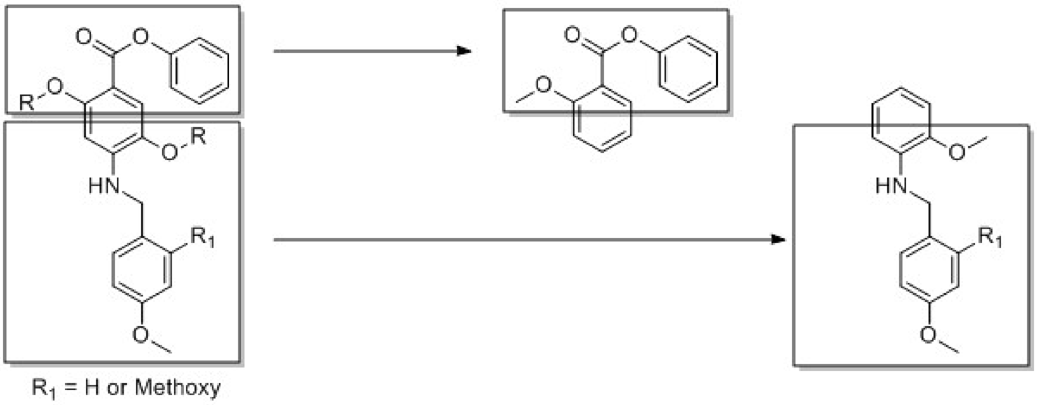
[1]University of Fribourg

Yokozawa et al.[1] have described reaction conditions that have been used for living polymerization yielding aromatic amide polymers (aramides). These conditions rely on the reaction of lithium anilides and 4-aminobenzoic acid esters. We have adopted the "Yokozawa-conditions" for step-growth polymerizations with the aim of achieving high molecular weight aramides of highly substitued 2,5-dialkoxy-4-aminobenzoic acid ester monomers. [2]

Here we describe model reactions (figure) in order to optimize reaction conditions and understand side reactions observed by us. After identifying several side reactions[3], we modified the reported procedure using different protecting groups on the aniline nitrogen and/or replacing the lithium amide base with N-heterocyclic carbenes [4]. The poster presents and rationalizes the best conditions for our highly substituted aminobenzoic acid ester monomers.



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Synthesis of polymer-silver nanocomposites for biomedical applications

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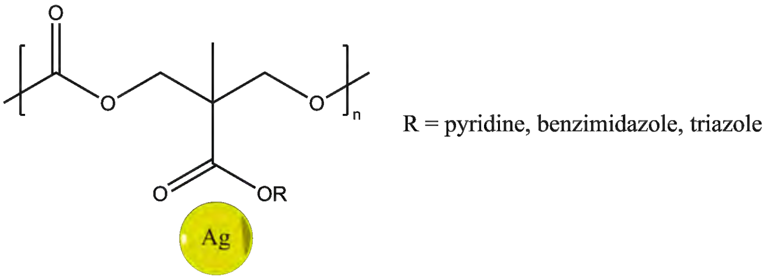
[1]University of Fribourg

In the last decades, polymeric materials have attracted a significant interest in the biomedical field especially in their use as implants. With the emergence of new multi-drug resistant bacteria and despite the advanced sterilization procedures, the contamination of implant surfaces by bacteria is a new challenge to overcome.[1] Then, the designing of new antibacterial/bactericidal surfaces in order to prevent bacterial adhesion and biofilm formation is a serious concern.

Many compounds possess antimicrobial properties such as antimicrobial peptides (AMPs), quaternary ammonium compounds, polycationic polymers and metallic elements.[2] Among the last, silver has already been proved to be effective against bacterial infections even at low concentration (0,1-10 ppm).[3] Furthermore, it has been demonstrated that nano-sized silver could be even more efficient due to a better interaction with bacteria and a more long-term activity compared to ionic silver.[4] For these reasons, silver nanoparticles (NPs) will be exploited in the framework of this project.

The incorporation of silver NPs in a polymer matrix has been shown to allow a higher antibacterial activity[1] and also to prevent aggregation.[5] More importantly, the polymers can be designed in order to enhance the antibacterial properties of the final composite by reducing the bacterial adhesion or incorporating biocidal groups. Hedrick and co-workers highlighted that aliphatic polycarbonates (APCs) functionalized with imidazole or pyridine compounds could provide this biocidal activity.[6]

APCs are very suitable for biomedical applications owing to their good biocompatibility, biodegradability, low toxicity and minimized inflammatory response upon hydrolysis. In addition, monomers can be easily tagged with specific functionalities allowing a fine-tuning of the polymer functionality in line with the targeted application.[7] In this context, ACPs with different side chains will be synthesized in order to bind silver ions and thus enhance antimicrobial properties.



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Design of Ag@SiO$_2$ nanorattles for antimicrobial implant coatings

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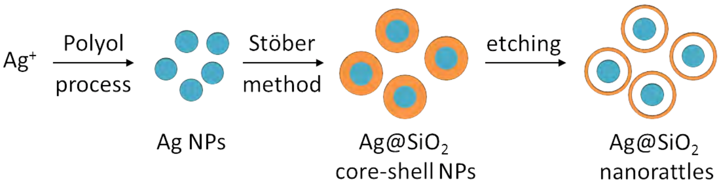
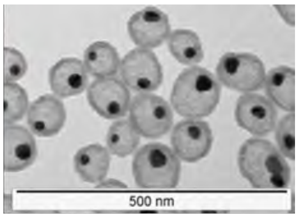
[1]University of Fribourg

Medical progress and an ageing world population have led to an increasing use of foreign materials inside the human body. Consequently also the number of infections related to these implants has grown significantly.[1] Antimicrobial coatings that prevent the formation of infectious biofilms on the surface of the implants could make an important contribution to overcome that issue. Silver is known for its good antimicrobial and biocompatible properties and could therefore play an important role in the fight against implant infections, especially if they are caused by antibiotic resistant bacteria.[2]

This project covers the synthesis of Ag nanoparticles that are encapsulated inside a protective silica shell in order to prevent aggregation or a too fast release of the antimicrobial active Ag$^+$ ions. The silica shell provides reactive sites to covalently attach the antimicrobial nanocontainers to the implant surface. Furthermore it enables the functionalization with biosensor units to create a stimuli responsive release of the Ag$^+$ only in the presence of bacteria.





We have developed a reliable synthesis of well-defined Ag@SiO$_2$ nanorattles that combines the polyol method for synthesizing Ag nanoparticles [3] with a modified Stöber method [4] for growing the silica shell and a surface protected etching protocol [5] for partial removal of the inner part of that shell.

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DNA complexation effect on a cyanine probe studied at liquid/water interfaces by SSHG

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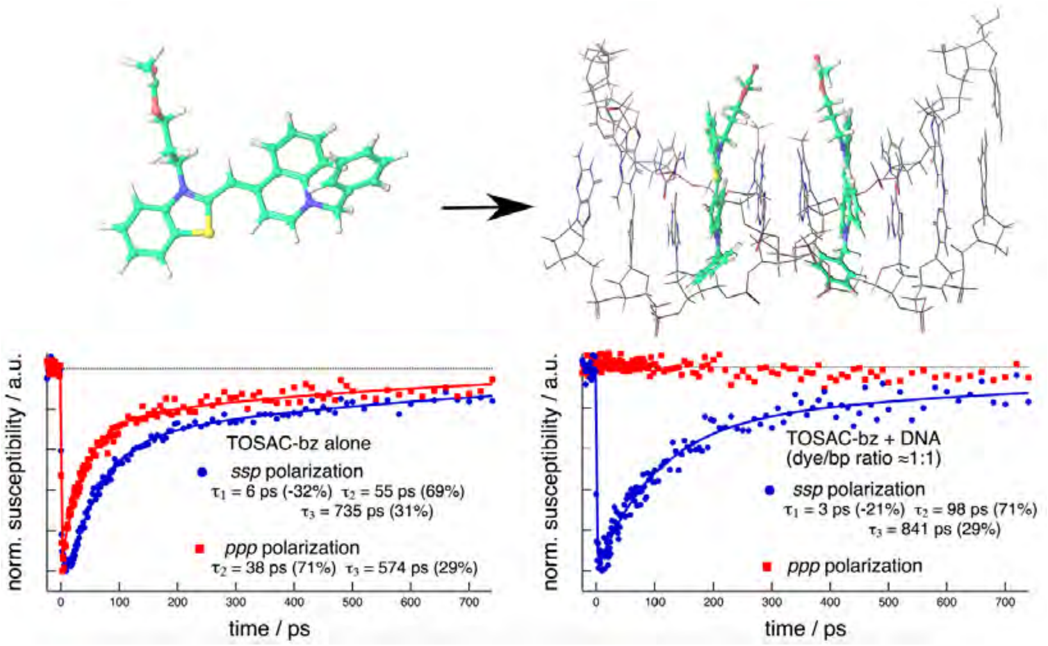
[1]University of Geneva

TOSAC-bz is a monomeric cyanine molecule belonging to the YOPRO1 class[1,2], which is a well-known fluorescent DNA probe, and that displays surfactant properties. The DNA binding properties of this dye make it an attractive tool for studying the dynamics and the orientation of biological molecules at the interface between two different immiscible liquids. Such an environment can be a model of cell membrane. Early studies on the excited-state dynamics of these dyes in solution have revealed an ultrafast nonradiative deactivation with time constants of the order of few picoseconds.

We have measured the ultrafast excited state dynamics of TOSAC-bz in the presence and absence of DNA at the liquid/liquid interface using surface second harmonic generation (SSHG).[3,4] In general, we observe slower dynamics than in bulk solution. Our newly built SSHG setup allows us to probe selectively different second-order susceptibility elements by controlling the polarization of the three interacting beams. Our results reveal a dramatic change upon addition of DNA to the dye solution with the TR-SSHG signal at the *ppp* polarization geometry disappearing (picture below). The lifetime associated with the monomeric dye excited state relaxation is also increasing when DNA is added, showing that the binding of the macromolecule has a strong impact on its dynamics.



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Large-scale self-assembled gold nanoparticle arrays and plasmonic-enhanced fluorescence

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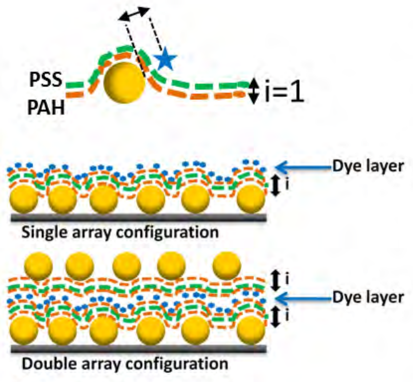
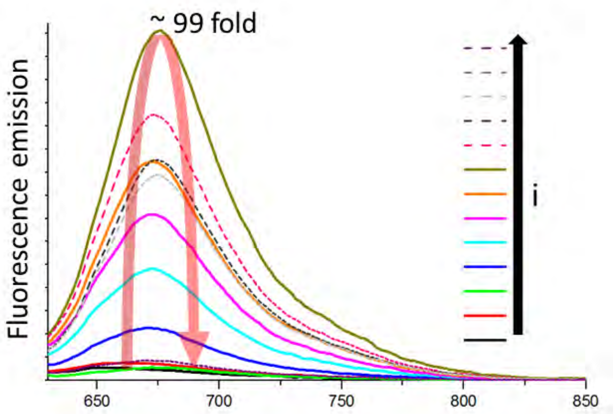
[1]University of Geneva

In recent years potential applications of metallic nanoparticles as an efficient source of light, heat and energetic electrons at the nanoscale regime attract a lot of attention and lead to their extensive study. Nanoparticles’ plasmon resonances can be tuned by altering their size, shape, surrounding medium and even their assemblies and spatial arrangement. Their unique light interaction and recent advances in their syntheses and application paved the way toward their use in chemical, biological and therapeutics fields. Their strong interaction with light (absorption, scattering and electromagnetic field confinement) found application in sensing, detection and enhanced spectroscopy.

The localized surface plasmon resonances of metallic nanoparticles confine the electromagnetic field and cause intense near-fields. The latter can enhance the optical properties of nearby emitters by improving their absorption and emission, especially inside narrow gaps between nanoparticles. Thus the electromagnetic properties of the plasmonic system and its enhancement effect are both distance dependent.

In this work we applied layer-by-layer method (LBL) to provide a well-defined distance between the dye layer and the gold nanoparticles and we investigated the plasmon-enhanced fluorescence of single array and double arrays of gold nanoparticles. A different number of oppositely charged polyelectrolyte bilayers were applied in-between the nanoparticle array and the dye layer and the effect of spatial arrangement and distance dependency on fluorescence enhancement is investigated. Excitation wavelength dependency and the necessity of overlap of plasmon resonance with excitation wavelength are discussed. A maximum of a 99-fold increase in the fluorescence intensity of the dye layer sandwiched between two gold nanoparticle arrays is found. The interaction of the dye layer with the plasmonic system causes a spectral shift in the emission spectrum and fluorescence lifetimes in presence of nanoparticle arrays. However the lifetime increased with increasing distance between the dye and gold nanoparticle arrays.





Dispersion stability of layered double hydroxide particles in the presence of polyelectrolytes

M. Pavlovic[1], V. Prevot[2], M. Adok-Sipiczki[1], C. Nardin[1], I. Szilgyi[1]

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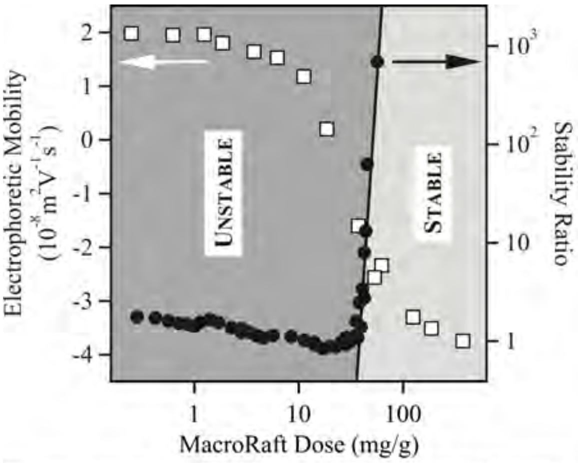
Layered nanomaterials have been in the focus of investigations due to their growing applications ranging from development of sensors through solar cells to catalysis. In many of such applications, these lamellar particles are used in dispersions where aggregation and related colloidal stability is an important issue. Therefore, we have recently studied formulation of layered double hydroxide (LDH) dispersions using polyelectrolytes. Accordingly, electrophoretic mobility measurements were carried out with LDH particles in the presence of the negatively charged MacroRaft polyelectrolyte. The MacroRaft adsorbs strongly on the oppositely charged LDHs leading to surface charge neutralization followed by overcharging at high doses (see figure).



Electrophoretic mobilitiy (square) and stability ratio (circle) values of LDH particles as a function of the MacroRaft dose. Stability ratios close to unity indicate fast aggregation, while higher values more stable dispersions.

Aggregation processes were followed in time-resolved dynamic light scattering experiments to probe the dispersion stability of the system. Stability ratios close to unity indicated fast aggregation at doses lower than the charge neutralization point. Images taken by atomic force and transmission electron microscopy revealed that the nanoplatelets prefer face-to-face orientation in the aggregates. However, the samples were stable at higher MacroRaft concentrations at which the particles were negatively charged. The dispersions showed long-time kinetic stability even at high ionic strengths under these conditions. In summary, colloidal stability of aqueous LDH dispersions can be well tuned by polyelectrolytes, accordingly, the particles can be aggregated, but highly stable dispersions can be also obtained if one applies the appropriate polyelectrolyte dose.

Inverse Schulze-Hardy Rule

T. Cao[1], I. Szilgyi[1], T. Oncsik[1], G. Trefalt[1], M. Borkovec[1]*

[1]University of Geneva

Schulze and Hardy discovered that multivalent ions are more effective in destabilizing colloidal suspensions than monovalent ones.[1, 2] The classical Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory predicts that colloidal suspensions are stable at low salt concentrations and are unstable at higher ones. The transition between these two regimes is referred to as the critical coagulation concentration (CCC). For highly charged particles, the DLVO theory suggests CCC is proportional to $1/z^6$, where z is the counterion valence. This dependence is called the Schulze-Hardy rule.

In this work, the aggregation behavior of positively charged amidine latex particles and negatively charged sulfate latex in salt solutions containing *multivalent coions* and monovalent counterions was studied by time-resolved light scattering techniques. The results show that the CCC is inversely proportional to the *coion valence*. We argue that an analogous the *inverse Schulze-Hardy rule* can be formulated in this situation, namely CCC is proportional to $1/z$. The dependencies of the CCC on the valence predicted by the *inverse Schulze-Hardy rule* and the Debye-Hückel theory (CCC is proportional to $1/\ z(z+1)$) are compared with the experimental data (Fig. 1a). We have also carried out DLVO calculations of the CCCs within the Poisson-Boltzmann theory for different charge densities (Fig. 1b).[3] For high charge densities, the $1/z$ dependence is obtained, while the Debye-Hückel dependence is recovered for low charge densities.

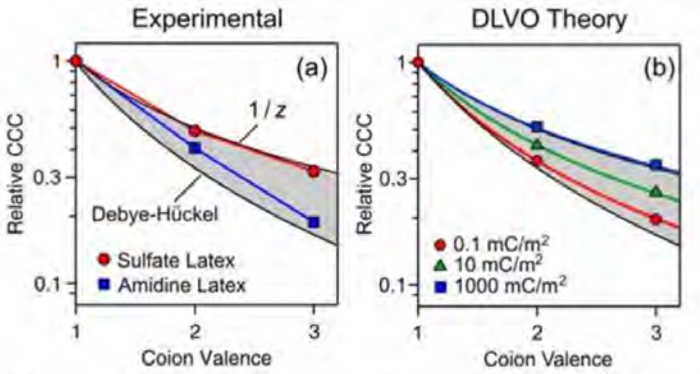


Figure 1: CCC normalized to its value in the monovalent electrolyte versus the valence of the coions in the salt solutions used. The shaded area lies between the Debye-Hückel result and the inverse Schulze-Hardy rule. (a) The present experimental data. (b) Calculations with DLVO theory with the surface charge densities indicated.

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Improved fiber diameter determination of nanofibers through image analysis using a hierarchical scaling approach.

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[1]Zurich University of Applied Sciences, ZHAW

The determination of nanofiber diameters from SEM images is the standard procedure in characterizing the fiber morphology of electrospun materials. Typically, fiber diameter determination is done manually – a time consuming step including subjective factors of the analyst. An automated approach should save time and reduce the subjective part of the operator. However, only very few algorithms for fiber diameter determination have been reported. Recently, Öznergiz et al. reported a robust algorithm based on a radon transformation through which they were able to determine fiber diameters within given boundaries [1]. We improved their approach by adding a hierarchical scaling strategy. The latter operates without boundary conditions for a large variety of fiber structures from straight fibers, through fibers containing beads to coiled fibers. It will not work for parallel fibers.

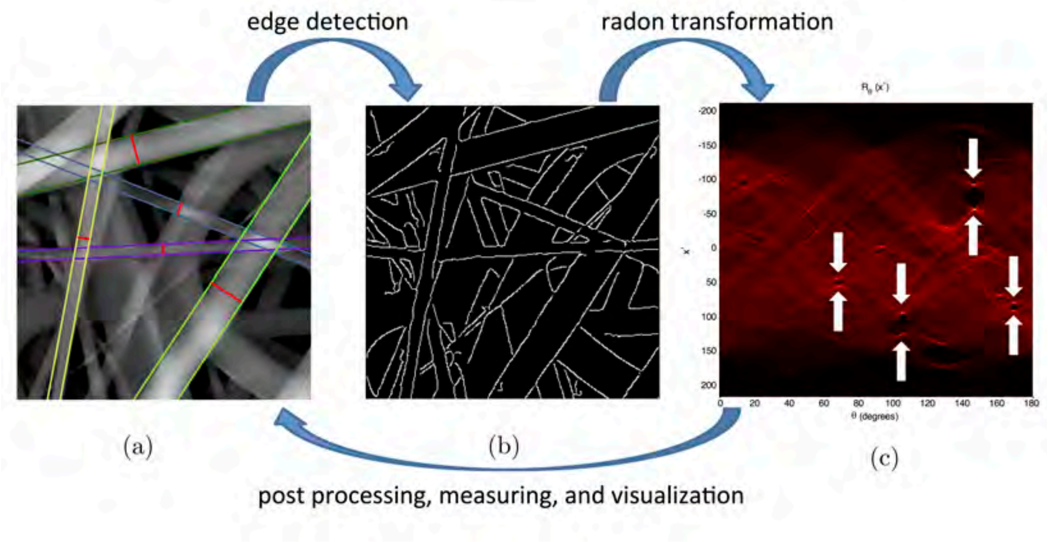

Fig 1. Sample result of the proposed approach. (a) The orginal SEM of electrospun PVP nanofibers; (b) After a Canny edge detection; (c) Radon transformed picture. The arrows are highlighting the found nanofibers.

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Tuning the size and aspect ratio of arrays of silica nanochannels

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Arrays of silica nanochannels (ASNCs) are ordered mesoporous silica particles with hexagonal prismatic shape. The entrances of the well-defined one-dimensional nanochannels are located on the base surfaces of the hexagonal prisms. The aspect ratio of the micrometer-sized particles (length-to-diameter ratio) can be tuned in the range of 0.8 to 2.2 by the addition of KCl or $CaCl_2$ to the liquid crystal templated synthesis and by an adjustment of the relative amounts of silica precursor (tetraethoxysilane) and structure-directing agent (hexadecyltrimethylammonium bromide). In addition to the influence of K^+ and Ca^{2+} on the particle morphology, the pore diameter and the pore wall thickness also depend on the presence of these cations in the synthesis mixture.

Surface Activity of Nanoparticle Suspensions at Interfaces

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The design and development of amphiphilic nanoparticles is of growing interest in the field of nanoscience. The use of novel nanocarriers may be extended beyond the drug delivery, to applications, such as precious and radioactive metal recovery. Some applications may require the nanocarriers to partition at interfaces. The polarity balance needed for this partitioning requires meticulous design of the synthetic and measurement procedures. We have used pendant drop tensiometry to quantitatively characterize the interfacial activity of surfactant-free nanoparticles. The surfactant-free silica and polystyrene-based nanoparticles were synthesized, or post-modified during the experiment so that they acquire varying surface polarities and thus the appropriate amphiphilic balance for interfacial partitioning. Our focus was to verify the accuracy and robustness of the measurement method for further application to other surface-active nanoparticles systems.

Ellipsoid-Shaped Superparamagnetic Nanoclusters through Emulsion Electrospinning

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One-dimensional (1D) organic/inorganic nanomagnets with high saturation magnetization and superparamagnetic properties are difficult to obtain. Nonetheless, they are highly desirable 1D-materials since the properties differ strongly for their spherical counterparts. Common approaches to generate such 1D-stuctures include i) template assistance, [1] ii) self-assembly of the single building blocks,[2-4] or iii) electrospinning. We now developed a process that allows to generate superparamagnetic nanoellipsoids with a high saturation magnetization (Fig. 1 E) by implementing magnetic droplets into electrospinning to obtain stretched iron oxide clusters.[5] In this novel process the aspect ratio of the ellipsoids strongly correlates with the diameter of the spun fibers (Fig. 1 A-C). The aspect ratio of the ellipsoids strongly increases with a decreasing fiber diameter. After spinning, the polymer fibers can easily dissolved in water to obtain an aqueous dispersion of the ellipsoid clusters, which makes them accessible for various biomedical applications (Fig. 1 D).

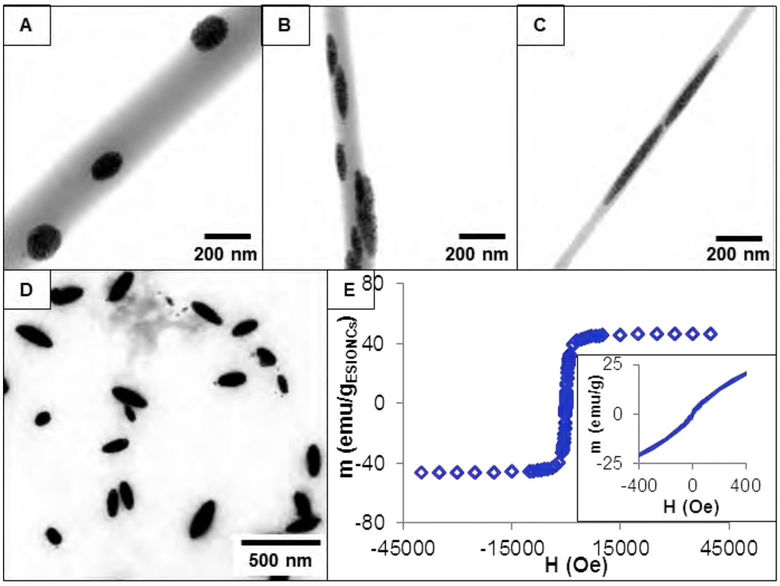

Fig. 1. *TEM images of stretched iron oxide clusters within an electrospun fiber with decreasing fiber diameter and increasing aspect ratio of the clusters (A-C) and ellipsoid-shaped clusters after dissolution of the polymer fibers (D). Vibrating sample magnetometer measurement curve of the ellipsoid-shaped nanoclusters of superparamagnetic particles (E).*

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Long-lived charge carriers in organic Nanowires

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[1]EPF Lausanne

One-dimensional nanostructures of organic semiconductors are expected to become important components for their use as defined charge percolation paths in future nanoelectronic devices, including organic field-effect transistors or organic solar cells. Furthermore, they can serve as excellent model systems for fundamental investigations of charge generation and transport in organic semiconductors. We recently reported how 'well-defined' nanowires that comprise a single stack of π-conjugated segments at their core are obtained from oligopeptide-functionalized quaterthiophenes or perylene bisimide.[1, 2]

Such nanowire systems based on semiconducting molecules exhibit a photo-induced formation of polaron-like charge carriers with unusually long lifetimes. The origin of the formation and stability of these charge carriers was investigated spectroscopically, and related to macroscopic transport in two-point devices.Here, we demonstrate that similar nanowires can be obtained from a variety of different π-conjugated segments, such as quinquethiophene **1**, the corresponding derivatives **2** with diketopyrrolopyrrole cores as well as **3** 1,7-dicyano perylenbisimide, respectively. Our results, thus, provide an example of a universal organic nanowire model system that successfully links molecular design, well-defined supramolecular structure formation, charge carrier generation, and finally macroscopic charge transport.

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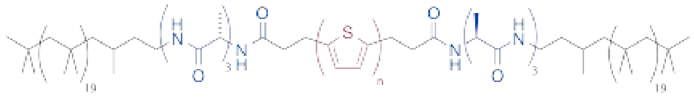

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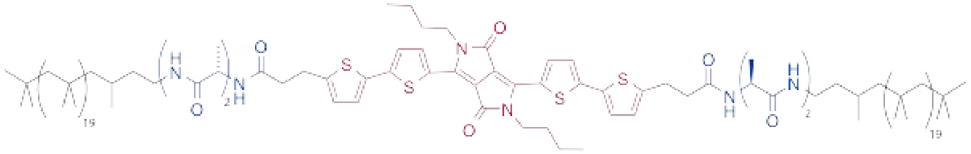

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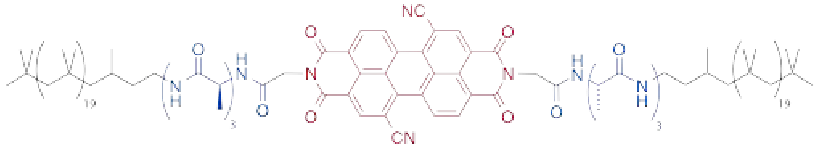

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Porous nitrogen-doped carbon materials generated from fractal gels for CO_2 capture

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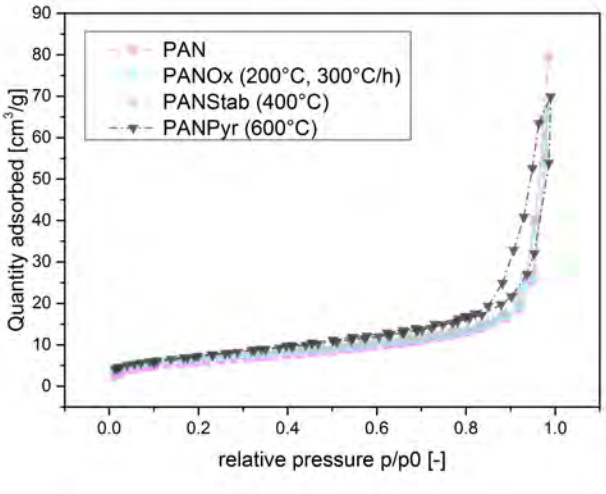
The use of solid sorbents for CO_2 capture has become a real challenge in the last decade. In the aim of achieving target separation performances, well-defined porosity and suitable surface chemistry are needed. In contrast to widely used activated carbons, displaying high CO_2-uptake but rather disadvantageous pore size, polymeric materials containing nitrogen appear to be good candidates to fulfil the task of adsorbing CO_2 selectively and reversibly. [1] This project includes all relevant steps, from the synthesis to the application focusing on the chemistry behind the thermal treatments.

The following process is made of several steps aimed to optimize the material. The first step is the preparation of colloidal dispersions of non-porous nanoparticles made of acrylonitrile by emulsion polymerization. Then, the dispersions are destabilized to form a fractal gel. Large pores are typically obtained during this destabilization (or gelation) step, which permit the introduction of a perfusive behaviour. The third step, intended to produce micropores to increase surface area and to ease the diffusion towards active sites, is partial polymer decomposition by pyrolysis. [2,3] This last treatment is actually a series of multiple thermal steps: oxidation in air to perform stabilization reaction involving cyclization of the cyanide functional groups and dehydrogenation of the backbone with formation of conjugated double bounds, followed by pyrolysis under nitrogen to complete the stabilization and form very small pores by controlled polymer degradation. It appears that cyclization reactions are decisive for further heat treatments. In fact, the thermal stability of the polymer depends very strongly on the oxidation followed by stabilization. The figure below shows the N_2-adsorption isotherms of polyacrylonitrile (PAN) after oxidation (PANOx), stabilization (PANStab) and pyrolysis (PANPyr). It can be observed, that their porous structure is retained along with the thermal treatment steps.



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Synthesis and characterization of homologous (non-)interacting (hybrid) dendronized polymers with tunable bulk properties

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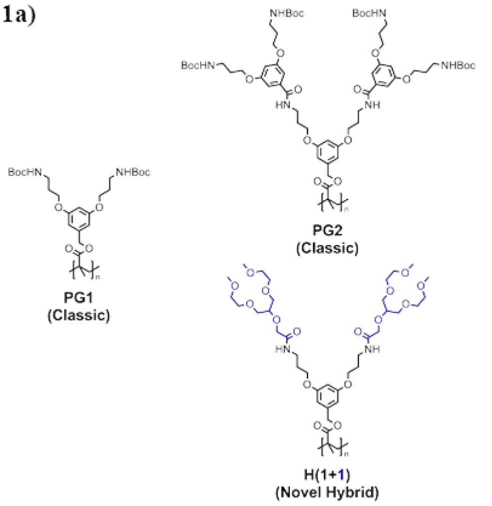
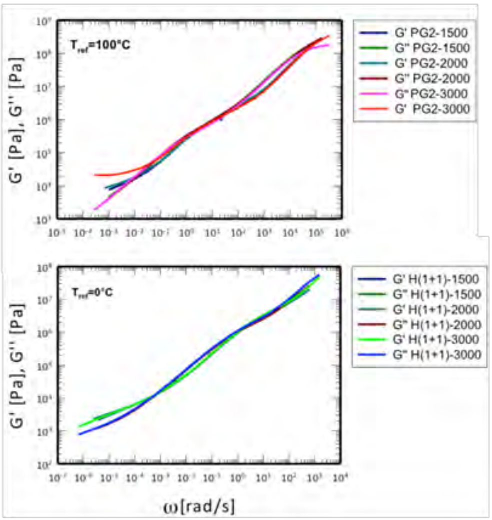
Dendronized polymers (DPs) with thickness and persistence length tunable through the generation number (*g*) hold the potential for applications in membranes, adhesives, chemical and biological sensing or microelectronics [1]. In order to approach the intrinsic properties of these unusual comb polymers, we recently synthesized "hybrid" DPs bearing oligoethylene glycol based dendrons in the periphery. These novel DPs are aimed at switching off the hydrogen bonding and Π-Π stacking interactions that are present in the prototype "classic" DPs [2] of our laboratory (Figure 1a). Here, we present a systematic study of homologous PG1-3, H(1+1) and H(1+2) DPs with various backbone lengths (P_n), whose bulk material properties have been investigated by differential scanning calorimetry and dynamic mechanical measurements. Compared to PG1-3, H(1+1) and H(1+2) show higher segmental mobility, which is reflected in considerably lower glass transition temperatures for these novel DPs. Conversely to the classic DPs, no increase of the low frequency elastic plateau is observed for the hybrid DPs and the moduli follow the same mastercurves irrespective of P_n, as exemplified by the PG2 and H(1+1) series (Figure 1b). For both DP series, interpenetration can provide entanglement-like behavior, albeit with different viscoelastic moduli. Combined with previous measurements [3] and molecular dynamics simulations [4], our results demonstrate remarkable effects of the chemical structure on the rheological response of such highly branched polymers with ultra-high molar mass and pave the way into exciting applications.

1a)



1b)



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Nanocrystals of Cesium Lead Halide Perovskites ($CsPbX_3$, X=Cl, Br, and I) Showing Bright Emission with Wide Color Gamut

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[1]ETH Zurich, [2]University of Bath, [3]EMPA Dubendorf

The emergence of metal halides perovskites, such as hybrid organic-inorganic CH3NH3PbI3, have attracted enormous attention as solution-deposited absorbing layers for solar cells with power conversion efficiencies exceeding 20%, as well as for light emitting deviced, and as lasing materials.[1,2] Herein we present a new avenue for halide perovskites by designing highly luminescent perovskite-based quantum dot materials. Using inexpensive commercial precursors, we synthesized fully inorganic cesium lead halide perovskites (CsPbX3, X=Cl, Br, and I or mixed halide systems Cl/Br and Br/I) in the form of to monodisperse colloidal nanocubes (4-15 nm edge lengths) .[3]

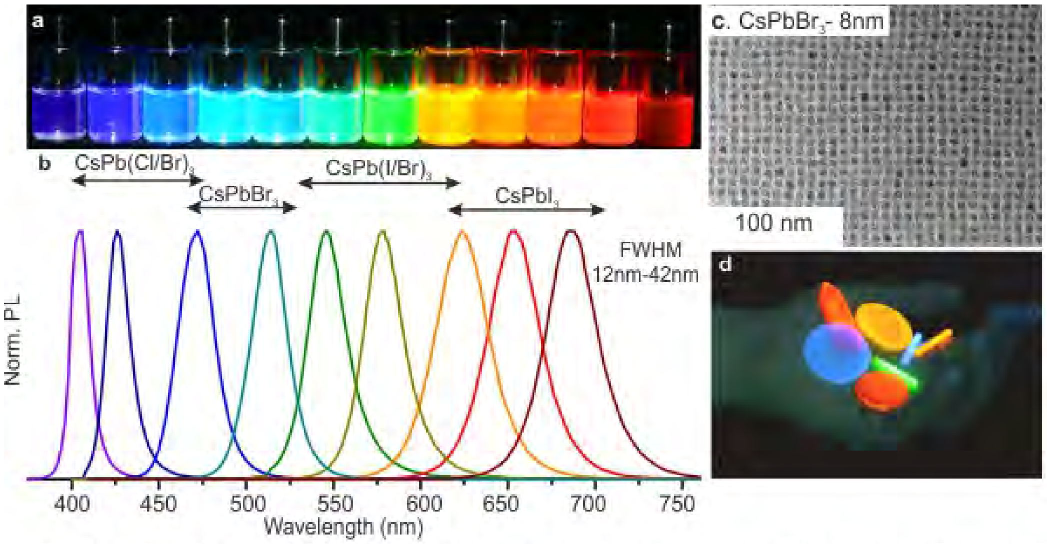

Figure 1. a) Colloidal solutions in toluene, under UV lamp (λ=365 nm); b) representative PL spectra (λ_{exc}=400 nm for all but 350 nm for $CsPbCl_3$ samples); c)typical transmission electron microscopy (TEM) images of $CsPbBr_3$ NCs, d) Photograph (λ_{exc}=365 nm) of highly luminescent $CsPbX_3$ NCs-PMMA polymer monoliths obtained with Irgacure 819 as photo-initiato for polymerization.

Through compositional modulations and quantum size-effects, the bandgap energies and emission spectra are readily tunable over the entire visible spectral region of 410-700nm. The photoluminescence of $CsPbX_3$ nanocrystals is characterized by narrow emission line-widths, wide color gamut covering up to 140% of the NTSC color standard, high quantum yields of up to 90% and radiative lifetimes in the range of 4-29ns (Figure 1).Particularly appealing are highly-stable blue and green emitting $CsPbX_3$ NCs (440-530nm), since the corresponding metal-chalcogenide QDs show reduced chemical and photo-stability at these wavelengths.

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Controlled synthesis and functionalization of AuTTF micro- and nanowire sensors

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Conductive nano- and microwires are very promising sensing elements. In the past years, various approaches to form such wires have been presented. However, most of them are based on reactions in bulk with little control on the reaction conditions of individual wires, and require post-processing such as purification. In addition, it is still challenging to integrate the created structures into a functional analytical device. Recently, we showed the advantage of microfluidic devices for the creation of nanowires made of metal organic compounds or coordination polymers (1-3). We exploited the laminar flow conditions providing a well-defined interface between two streams (1), or used small reaction volumes to allow defined diffusion of the precursors (2).

Here, we demonstrate an improved microchip design for the site-specific formation of single nano- and microwires, where we exploit the increased permeability of the microchip substrate poly(dimethyl)siloxane (PDMS) for organic molecules after swelling caused by an organic solvent. In these devices, two adjacent, but still fully separated microchannel systems are filled with the precursor solutions $HAuCl_4$ and tetrathiafulvalene (TTF) in acetonitrile, respectively. Swelling of PDMS by acetonitrile enables the diffusion of TTF towards the $HAuCl_4$ solution, where the redox reaction to AuTTF takes place yielding extraordinary long wires of several hundred micrometers. The geometry of the channels provides physical constraints with respect to number, orientation and localization of the created wires.

We utilized such wires before for sensing gases (2), In addition, we successfully achieved the functionalization of nanowires for label-free sensing of biomolecules. Binding of dopamine to the functionalized wires could be detected by using Raman spectroscopy. Moreover, we showed in a proof-of-concept experiment that we could immobilize antibodies on the nanowires to enable the binding and detection of analytes with a high specificity. Future work focuses on the realization of conductivity measurements for sensing biomolecules.

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Insight into how vesicles control the course of a laccase – catalysed oligomerization reaction

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Sodium bis-(2-ethylhexyl)sulfosuccinate (AOT) vesicles are used as ‘soft templates’ for the enzymatic oxidation and oligomerization of the aniline dimer, *p*-aminodiphenylamine (PADPA), with *Trametes versicolor* laccase and molecular oxygen to form oligo(PADPA). The products thus formed in the presence of vesicles exhibit a UV-vis-NIR spectrum which is typical for polyaniline in the conductive emeraldine salt form (PANI – ES). The presence of the vesicles was found to be crucial for the formation of the desired products[1]. We attempt to understand the molecular mechanism underlying this ‘template effect’. The reactions were conducted with both conventional PADPA and selectively deuterium – labelled PADPA. The resulting products were then extracted and analysed by reverse phase HPLC – MS. These measurements suggest that there are at least two reaction routes in the presence of vesicles, a major and a minor pathway. Without vesicles, significant side reactions occur, most prominently hydrolysis, which was determined by using $H_2{}^{18}O$.

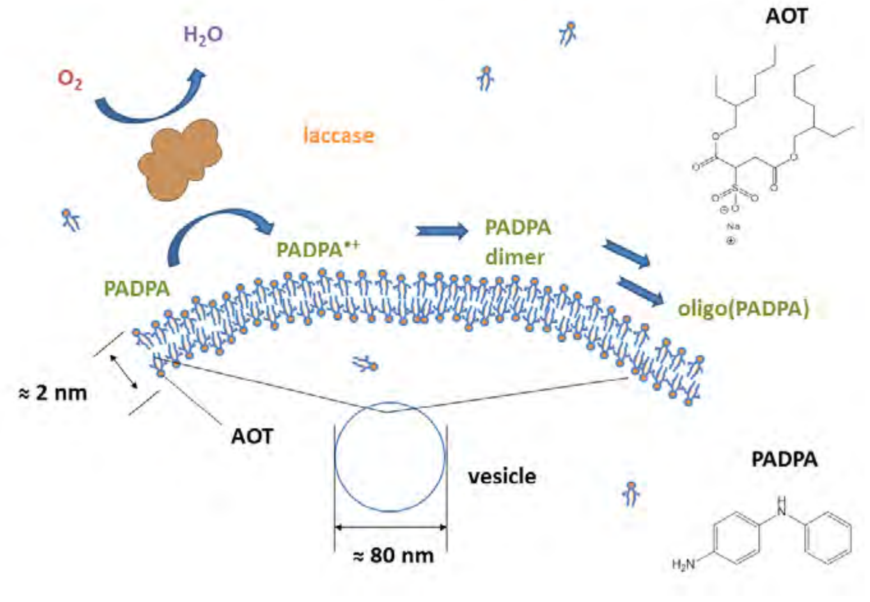

Figure 1: Schematic illustration of the laccase-catalyzed PADPA oxidation and oligomerization reaction occurring on the surface of vesicles with a diameter of about 80 nm.

Acknowledgments: We thank Louis Bertschi, MS Service Lab, LOC, ETHZ for his support in the ESI – MS measurements; SNF project number: 200020_150254.

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Stability of radiation grafted polymer electrolyte membranes for water electrolysis cells

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Radiation grafted membranes are functional polymer membranes that can acts as proton conductor, electric insulator and gas separator for fuel cell and electrolyser application. Despite all the similarities of the fuel cell and electrolyser membranes, the operating condition of both applications is different. Fuel cell membrane works under partially humidified condition, meanwhile electrolyser membrane under fully hydrated condition.

In 2011, Enomoto et al. investigated the degradation manner of radiation grafted membrane in aqueous media. They found out that thepoly (styrenesulfonic acid) (PSSA) radiation grafted membranes undergo swelling-induced detachment of the grafted polymers from the hydrophobic base film in water at 85 °C and 95 °C. From the proposed degradation mechanism it is highly possible that radiation grafted membranes will be unstable for electrolyser application, since the membrane will always in contact with water at elevated temperature.

In our previous study, we synthesised radiation grafted membranes based on the combination of styrene, α-methyl styrene, acrylonitrile, 1,3-diisopropenylbenzene. These membranes showed better properties, such as lower area resistance, lower hydrogen crossover and mechanically more robust than the state of the art electrolyser membranes likes Nafion 115 and 117.

In this work, the stability of these membranes is investigated. The first stability test was performed by immersing the membranes under water at elevated temperature. The membrane before and after the test is characterised in terms of area resistance, hydrogen crossover, swelling, Ion Exchange Capacity (IEC), FTIR and SEM/EDX. The water after the test is investigated by UV-Vis and IC.

The results indicated that the S/AN, S/AN/DiPB radiation grafted membranes are not stable under the first test. This confirms the results of Enomoto et al. However, the AMS/AN/DiPB is stable under this test and contradictory to the mechanism of swelling-induced detachment, because the swelling of AMS/AN/DiPB is similar to that of S/AN/DiPB. Therefore, we conclude that the degradation mechanism of radiation grafted membrane is not only caused by swellingswelling-induced detachment.

The second test was conducted by letting the membranes in a peroxide-rich environment. The membranes are characterised in terms of the area resistance and hydrogen crossover before and after the test. The results showed that S/AN membranes had higher area resistance and hydrogen crossover after the test. By adding the DiPB as crosslinker, S/AN/DiPB and AMS/AN/DiPB membranes had only higher area resistance but not hydrogen crossover, which indicated the stability improvement.

The research leading to these results has received funding from the European Union´s Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n°303484.

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Intact flying nanoparticles for gas-phase investigations

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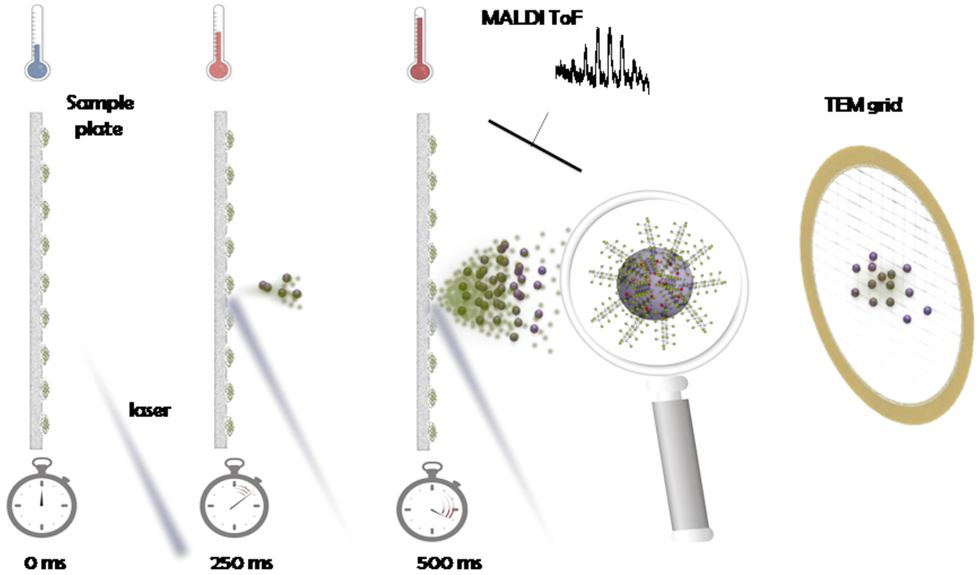
Sublimation of heavy particles as intact entities is a difficult challenge as large particles tend to decompose or fragmentize before the sublimation temperature is reached. However, it is a fundamental requirement when the physical behaviour of isolated entities in the gas-phase is to be investigated. Interferometry experiments of heavy particles are our ultimate goal[1]. Thus, we developed a system that allowed us to achieve the first key step of our research: the sublimation and characterization of intact nanoparticles (NPs). Although some evidences of sublimed NPs were already reported[2,3], its characterization as intact flying entities was not testified.

With this purpose, we synthesize metallic NPs stabilized with perfluorinated ligands in order to reduce the delocalized electron density on the carbon frames of the shell. It generates low-polarized particles and minimizes the particle-particle and particle-surface interactions. The NPs were vaporized with a laser desorption method and characterized with MALDI-ToF spectroscopy. The value of mass detected perfectly correlates with the one previously obtained under standard conditions and its resolution confirms that the ligands remain attached to the core of the NPs.



This experiment not only represents a key stage for the subsequent quantum experiments, but also shows the potential of combining chemical design with an accurate built-up technology, opening a range of new possibilities for energy and/or biological applications.

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Surfactant-Free Polarity Tuned Polymeric Nanoparticles Prepared by Ultrasonic Emulsion-Polymerization

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Abstract: We report the synthesis of sub-100 nm surfactant-free polymeric nanoparticles with varying polarity by highly-effective emulsification of a monomer-oil/water emulsion and subsequent polymerization driven by acoustic radiation. The surface polarity gradient of the nanoparticles was achieved by applying different concentrations of a polar co-monomer during the polymerization under ultrasonic treatment. The influence of dispersion time, emulsion nanodroplet composition, monomer ratio, initiator type and co-stabilizer on the nanoparticles' diameter, polydispersity, morphology and polarity, was investigated by DLS, SEM, FTIR, EDX and zeta potential. Most importantly, the polarity tuned nanoparticles were tested for their ability to partition at liquid-liquid and liquid-vapor interfaces.

Janus Dumbbells: A flexible template for colloidal chemistry

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The recent development of nanotechnology led to an increased amount of scientist working on nanoparticles worldwide. However, most of the studies are focusing on spherical isotropic nanoparticles, which are the easier to prepare. We used a described procedure [1,2] to prepare shape-anisotropic, asymmetrically-functionalized dumbbells nanoparticles covering a good range of size and aspect ratio. We then used the presence of silane groups on one hemisphere of the dumbbells only to selectively functionalize the nanoparticles [1], creating different types of hybrids.

The hydrolysis and condensation of a silane precursor covered one bulb with a thin layer of silica. Upon removal of the polymeric template, we prepared silica nanobowls bearing a well-defined opening in their shell. Calcination of the template at 550 °C led to purely hydrophilic silica nanobowls, while the dissolution of the template in THF gave birth to Janus nanobowls having a thin polymer layer on their inner side. We proved the different reactivity of the inside and outside surfaces by selectively binding oppositely-charged silica nanoparticles. They selectively adhered outside the Janus nanobowls, while they were present both inside and outside the nanobowls prepared by calcination [2].

Magnetic anisotropic nanoparticles were prepared either by attaching negatively charged Superparamagnetic Iron Oxide Nanoparticles (SPIONS) on dipolar dumbbells, or by preparing dumbbells with commercially available magnetic beads as seed nanoparticles. In both cases, we obtained asymmetric dumbbells with magnetic nanoparticles only on one side. We then studied the impact of shape-anisotropy on the directed self-assembly of these nanoparticles in the presence of an external magnetic field. We showed that it is possible to change the types of chain-like structures obtained by tuning the aspect ratio of the dumbbells.

Using the same dipolar dumbbells, we prepared Janus nanomotors by selectively attaching citrate-coated platinum nanocrystals on one hemisphere. The resulting nanoparticles can undergo self-propulsion when place in a solution containing hydrogen peroxide fuel. The catalytic decomposition of the fuel is only taking place on one side of the dumbbells, generating a gradient which leads to effective propulsion.

Finally, we made the dumbbells temperature-responsive by growing some poly-N-isopropylacrylamide brushes on one hemisphere. We first attached an initiator to the dumbbells by silane chemistry, and then used a surface initiated atom transfer radical polymerization (ATRP) to grow the PNIPAM chains. This renders the dumbbells hydrophilic below 32 °C (PNIPAM LCST), and amphiphilic above. We showed that it is possible to induce aggregation between the dumbbells by hydrophobic interactions above LCST. These stimuli-responsive nanoparticles have also been used to prepare multiple Pickering emulsions.

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Stimuli-responsive azo-containing polymeric materials

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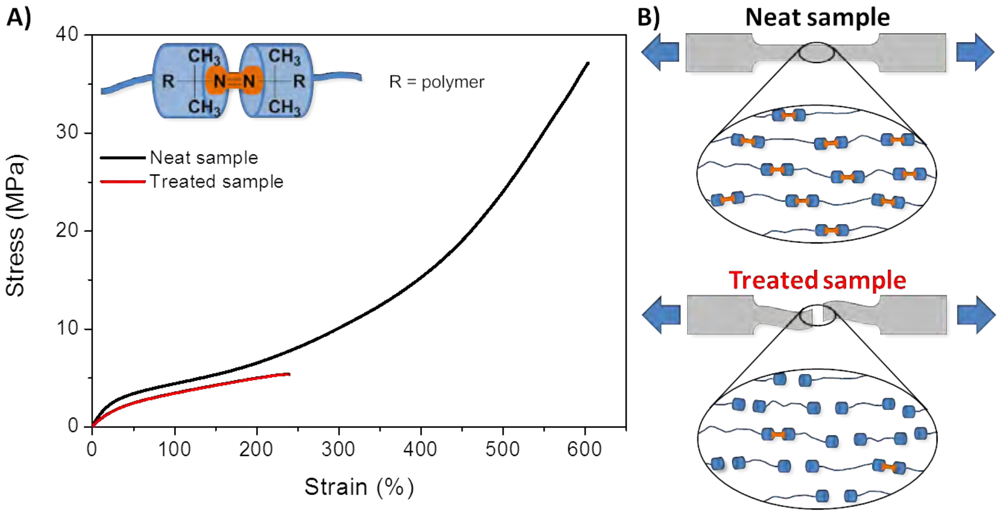
Molecules comprising aliphatic azo moieties have been widely studied as radical polymerization initiators, but interestingly only a few studies have demonstrated their usefulness as stimuli-responsive motifs that are covalently incorporated in macromolecular constructs. The azo motif is well-known to be activated by heat, which results in the cleavage of its C-N bonds, inducing the release of N_2 and producing C-centered tertiary radicals that can further react. These systems were also proven to cleave upon mechanical activation in solution by sonochemistry. However, the solid-state behavior of azo-containing polymers has remained largely unexplored. Here we present the syntheses of linear azo-containing polyurethanes and PVOH organogels in which azo-group containing-motifs serve as cross-links. We report on the thermally and optically induced responses of these materials in solution and the solid state and show that the behavior, quite surprisingly, depends strongly on the nature of the polymer backbone, the state of matter, and in solution also on the nature of the solvent. The solid-state properties of the azo-containing materials may be particularly useful. In this case, irreversible cleavage of the azo motifs is observed. For the linear polyurethanes, this leads to a molecular weight decrease, concomitant with a significant reduction of the elongation at break and the tensile strength. The azo-containing organogels undergo a de-cross-linking reaction, which also causes pronounced changes of the material's mechanical properties. Since N_2 is formed in the process, significant foaming is observed.



A) Stress-strain curves of neat (black line) and heated (red) films of an azo-containing polyurethane; the inset shows the chemical structure of the azo motif employed. **B)** Schematic illustration of the molecular weight decrease caused by treating the samples with heat or light.

ATRPases: Controlling Radical Polymerizations with Enzymes

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[1]University of Fribourg

Controlled/living radical polymerizations enable the synthesis of well-defined functional polymers with complex architectures and predetermined molecular weights, as well as narrow molecular weight distributions. Atom transfer radical polymerization (ATRP) has become one of the most widely used polymerization techniques due to its versatility: it can be applied to polymerize the majority of common monomers, it allows the addition of functional groups and it is compatible with numerous biomolecules. However, some monomers, such as N-vinylimidazole, cannot be polymerized by ATRP because the monomer is incompatible with the copper complexes needed for this reaction. The catalysts also represent a challenge for those monomers that are compatible with ATRP, because they can be toxic and potentially harmful to the environment. Moreover, the catalysts can have a negative impact on the polymer properties if not fully removed from the product. A greener approach involves the use of enzymes as catalysts, so-called “ATRPases”, rather than transition metals. We have discovered that the metalloproteins horseradish peroxidase and hemoglobin catalyze ATRP under activators regenerated by electron transfer (ARGET) conditions. Moreover, copper-containing laccases from tree fungi were found to be excellent catalysts for the controlled radical polymerization of N-vinylimidazole. Enzymatic ATRP can yield polymers with predetermined molecular weight, narrow molecular weight distribution and very low residual metal content. Therefore, it offers new opportunities for synthetic polymer chemistry.

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Cholesterol Interactions with an Artificial Phospholipid

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[1]University of Fribourg

Phospholipid vesicles are attractive biocompatible drug carriers. Nowadays, 13 liposomal drug formulations are approved by the FDA for *in human* use.[1]

We have recently reported on the use of shear stress responsive vesicles for purely physics based targeted drug delivery.[2] Pad-PC-Pad, an artificial phospholipid, forms lentil shaped vesicles that release their payload when the vesicles are exposed to shear stress but not when they are at rest; the vesicles are mechanosensitive.

Bilayer studies show that the mechanosensitivity is induced by interdigitated bilayer membranes. Monolayer experiments corroborate this hypothesis by showing a high fluidity whereas cryo transmission electron micrographs show lenticular large unilamelar vesicles. Clearly, an additional force is present in bilayers that is absent in monolayers: membrane interdigitation.

Here, we have studied the influence of cholesterol on a Pad-PC-Pad 1,3-diamidophospholipid bilayer and monolayer membrane. The addition of cholesterol reduces the stiffness of the membrane and thus leads to spherical membranes. 30 mol% cholesterol is sufficient to completely remove the main phase transition of the bilayer membrane and to lead to a liquid-ordered membrane organization. In DPPC:cholesterol mixtures, the main phase transition is still maintained even after 40 mol% cholesterol.[3] Adding cholesterol to monolayers of Pad-PC-Pad condenses these almost down to the size of a molecule of cholesterol. Overall, cholesterol clearly dominates the forces at play between Pad-PC-Pad and cholesterol.

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Amyloid Fibrils as reinforcement filler of polymeric nanocomposite materials

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[1]University of Fribourg

Fibers have fascinated mankind since the very beginning. Most of textile products are made of fibers, which for centuries have been obtained from natural sources. Many biological materials use nano fibers as building block. One of the best examples is spider webs. The incredible properties of spider silk fibers, with their exceptional toughness, have prompted scientist to investigate their structure in the hope of creating light weight but highly resistant materials. Given the difficulty in working with silk proteins, we used instead amyloid fibrils, which are less known but have similar structure to silk and are much easier to prepare, to create an entire new class of reinforced rubber materials.

In this project, a novel type of composite polymeric materials reinforced by protein fibrils has been prepared. Protein fibrils are self-assembled structures resulting from partial denaturation of certain proteins, and the resulting aggregation mediated by beta-sheets interactions. These structures are characterized by an extremely large aspect ratio, with a diameter that changes depending on the age of the fibrils, and on the degree of association of the different strands. For the fibrils used in our experiments, which are prepared by partial denaturation of beta-lacto globulin at pH 2.0 and 80°C for 24 hours, and at a concentration of 10mg/ml, typical diameters are about 25nm with a length of several micrometers. For the first time high concentrations of fibrils have been incorporated into a polymer. The process used to incorporate fibrils is unique. We started from a suspension of polymer particles in water, which are mixed with the fibrils in the aqueous phase. It has been observed that not only the elastic modulus of composite materials with fibrils is increased, but also the ductility of the materials is enormously improved.

Development of cell membrane mechanosensor for quantitative force detection of peptides

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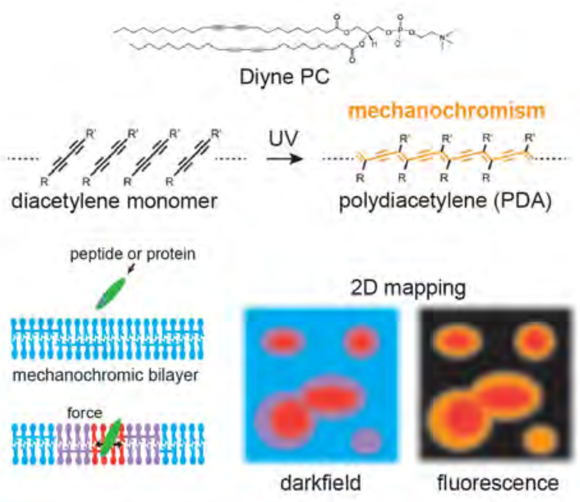
[1]Department of Physical Chemistry, University of Geneva

Membrane forces play pivotal roles in numerous physiological processes such as endocytosis, cell mutations and calcium signalling.

Currently used characterization methods such as atomic force microscope (AFM) or optical tweezers allow for the controlled force application but not for the detection of the forces applied to the bilayers.[1,2,3] Micro-aspiration of giant unilamellar vesicles (GUV) enables the quantification of surface tension, however, its conversion into local forces is difficult.[4]



We develop a mechanosensitive membrane probe that enables direct measurement of molecular forces applied on lipid bilayers. We employ a mechanochromic polymer polydiacetylene (PDA) that changes its colour and fluorescence intensity upon application of forces.[5,6] The biggest challenge is to maintain the homogeneity and fluidity of lipid bilayers after staining the membrane by the probe to increase the biocompatibility without compromising its sensitivity. The probe was calibrated by correlating the fluorescence intensity and the applied forces by AFM. As a proof of principal, pore-forming peptide melittin was incorporated into the probe-stained planar lipid bilayers and its forces distribution within the membrane was studied by fluorescence and dark-field microscopy.

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Characterization of voltage sensitive dyes with free-standing lipid bilayers

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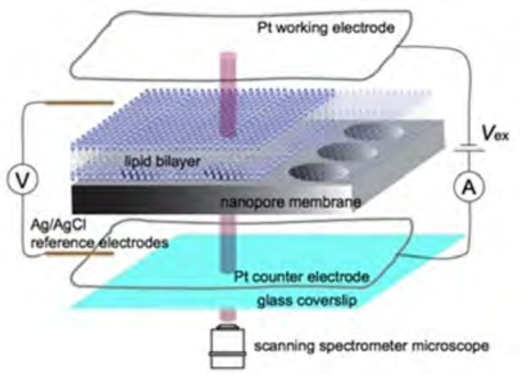
[1]University of Geneva

Voltage sensitive dyes (VSDs) are powerful tools for membrane potential monitoring. The characterization of VSDs is commonly performed either directly with living cells or with vesicles where the membrane potential is established by incorporating ion selective channels. However, both characterization methods lack the possibility to precisely control the voltage sequences, thus are enable to study the kinetics of the dyes. In this work, we demonstrate a new approach for the VSD characterization using free-standing lipid bilayers. First, pores (*f* = 1 mm) were fabricated in silicon nitride thin (200 nm) membranes by focused ion beam (FIB). Second, the membrane with pores was mounted in a home-made electrochemical cell where both sides of the membrane is electrically accessible. Third, free-standing lipid bilayers were formed over the pores by giant unilamellar vesicle (GUV) rupture. After the incorporation of VSDs (*e.g.* di-4-ANNEPS), the fluorescence signal from the bilayer is monitored by fluorescence microscopy while applying different voltage sequences. This platform offers the possibility 1) to apply any voltage sequences, 2) to modify bilayer composition freely, and 3) to acquire two-dimensional mapping of the VSD activities, allowing more detailed studies of VSDs.



Ionic liquids and ion-specific effects in particle aggregation: an experimental study beyond the Hofmeister series

T. Oncsik[1], G. Trefalt[1], I. Szilágyi[1], M. Borkovec[1]*

[1]Department of Inorganic and Analytical Chemistry, University of Geneva

Since the pioneering work of Hofmeister, ion-specific effects are of great interest in many scientific areas such as physical and colloidal chemistry as well as biology [1]. However, most of the studies deal with simple electrolytes, the effect of ionic liquid (IL) constituents on coagulation has not been investigated so far.

In the present work, aggregation of two oppositely charged hydrophobic colloidal particles (sulphate and amidine functionalized polystyrene latices) was investigated in the presence of simple electrolytes and ILs by electrophoresis and time-resolved dynamic light scattering (DLS). In the systems investigated, the simple electrolyte and IL constituent anions and cations were systematically varied. Depending on whether they act as counterion or co-ion, direct and indirect order of the Hofmeister series can be observed. In some cases, no ion-specificity can be seen. These results are in a good agreement with our previous studies [2]. In general, the IL constituent cations tend to adsorb on oppositely charged surface, lowering its charge density, thus the critical coagulation concentration. This effect is more pronounced when increasing the hydrophobicity of the ion by a longer alkyl chain. The electrophoretic mobility measurements confirm the stability behaviors in an excellent fashion. Accordingly, screening, neutralization and overcharging are all possible, in some cases even restabilization can be observed at the concentration range investigated.

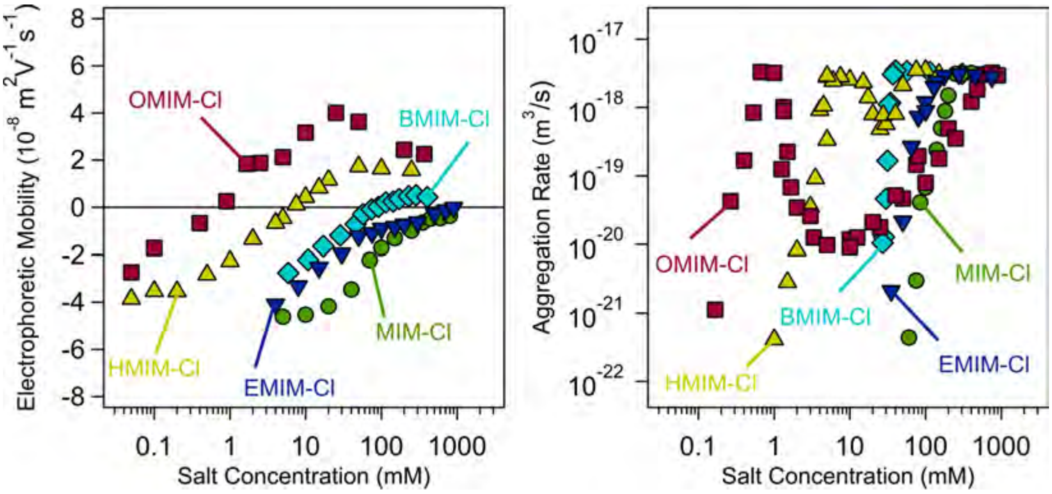


Figure 1: Electrophoretic mobility and stability plots of systems containing sulphate modified latex particles and different types of ionic liquids.

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Tuning the nanostructure and the properties of silica surfaces by heat treatment

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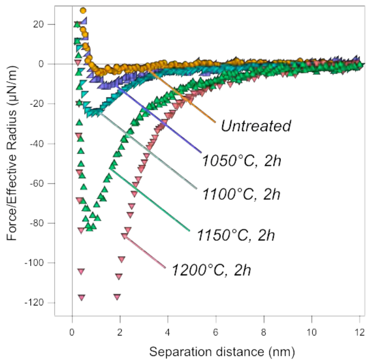
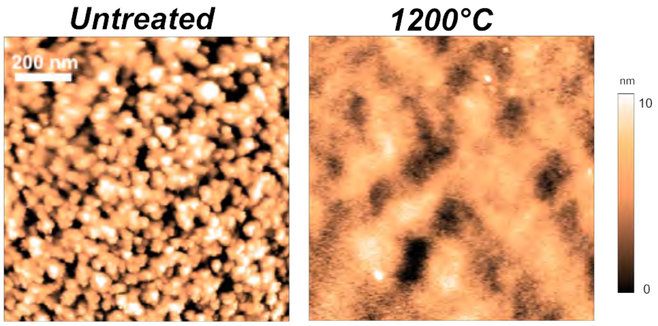
Due to its plain relevance in nature, industry and technology, silica colloids and silica surfaces have been largely investigated, and their behavior is often referred to as “anomalous” because it is not well described by the DLVO theory, especially for their unusual stability at high salt levels and high pH [1,2]. Nevertheless it has been extensively used as a model substrate for surface force studies and some discrepancies still exist within the literature data, mostly due to the different preparation techniques used and the history-dependent characteristic of the surface itself. Our work aims to give some insight into this landscape, trying to quantify the effects of different surface treatments and relate them with actual surface parameters.

5 µm silica colloids have been subjected to heat treatment at different temperatures (from 1050°C to 1300°C, 2h) and then the forces acting between single pairs of colloids have been measured by the Atomic Force Microscopy (AFM) colloidal probe technique in KCl solutions, pH4. From the measurements, surface force parameters such as double layer potential and Hamaker constant have been extrapolated and compared.





The results show that the heat treatment and the temperature at which it is performed affect dramatically the surface forces acting between the colloids. Upon increasing the temperature both the surface potential and the Hamaker constant increase substantially, for the latter a jump from 0.06 to 2.5 * 10^{-21} has been observed going from untreated to 1250°C treated samples. AFM topography and SEM images have been collected in order to verify how the treatment impacts the shape and the topography of the colloids. Our experiments show that the heat treatment decrease substantially the surface roughness, in correlation to the observed variation of surface potential and Hamaker constant.

In conclusion, our work demonstrate how appropriate and controlled heat treatment can be used to tune the nanostructure of silica surfaces and consequently modulate their interfacial behavior.

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Enhancing the Rheological Properties of a Sulfobetaine using a Cationic Surfactant

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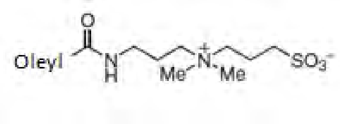
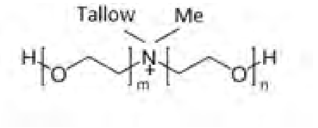
Long chain sulfobetaine surfactants based on Oleyl amidoamines are one of the fantastic topics in recent years, but the synergistic effects between these new surfactants with other ones have been less documented. In this work, comparative studies were examined on a sulfobetaine and a mixture of it with a long-chain cationic surfactant. The chemical structures of two surfactants are shown below. The measured parameter was viscosity .vs. shear rate for individual betaine and mixture of two surfactants [1,2]





The oleyl amidosulfobetaine was obtained through a two-step synthesis method. In the first step, the amidoamine was obtained by gradual addition of N,N-dimethyl propanediamine (DMAPA) to oleic acid. In the second step, the prepared amidoamine was reacted with sodium 3-chloro-2-hydroxypropane sulfonate in a solvent mixture of Ethanol, water and propylene glycol and NaOH was used as a catalyst. The selected solvent mixture prevents the gelling of the product with high active content of 40% [3].

To evaluate the rheological properties of the synthesized sulfobetaine, viscosity .vs. shear rate different compositions containing sulfobetaine and KCl were prepared and the steady shear viscosities as a function of shear rate of each composition was measured at room temperature. Using a mixture of sulfobetaine and long-chain cationic surfactant the stability of viscosity .vs. shear rate was notably enhanced which shows the synergistic effect of cationic surfactant [4].

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Dynamic bonds in fracture of soft materials

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It has been well established that combining self-healing bonds with permanent bonds, can significantly increase the fracture toughness of soft hydrogels. Yet the details of how this actually occurs and in particular the link between bond breaking and healing dynamics and fracture properties, is not yet known. In this work we investigate in detail the rheology in small and large strain and the fracture behavior of a model hydrogel based on polyvinyl alcohol crosslinked both chemically with glutaraldehyde, and physically with a borax solution.

We carried out a series of crack propagation experiments on prenotched gel samples over a wide range of loading rates and measured both the critical energy release rate where the crack propagates, and the average crack propagation velocity for each case. Using a recently proposed 3D mechanical model to describe the breaking and healing of the reversible bonds we can simulate the energy stored and dissipated ahead of the crack and we attempt to explain quantitatively how the physical bonds affect the fracture process of the hybrid hydrogels.

New UV Absorbers for the Photo-protection of Human Skin (KGF-SCS Industrial Science Award Lecture 2015)

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[1]BASF Schweiz AG, Basel, Switzerland

New scientific and public awareness of the risk of premature skin ageing and skin cancer due to exposure to UV-A radiation have created a market need for high SPF (= sun protection factor) sunscreens with superior UV-A protection. Researchers at BASF anticipated future market needs in an early phase and developed three new chemical entities which today define the highest standards in photo-protection of human skin (Tinosorb S, Tinosorb M, Tinosorb A2B).

Tinosorb S represents a new class of oil-soluble cosmetic UV absorbers named Hydroxy-phenyl-triazines (HPT), providing excellent broad-spectrum UV absorbance in combination with high photostability. Today this filter is widely used in all market segments (sun care and day care; from low cost to premium brands).

In search for new oil-soluble UV absorbers, the researchers synthesized many molecules which showed very low solubility. Making a virtue of necessity, UV absorbing molecules with weakest solubility were identified in order to create organic UV absorbers in sub-micrometer pigment form as already known from inorganic filters like TiO_2 and ZnO [1].

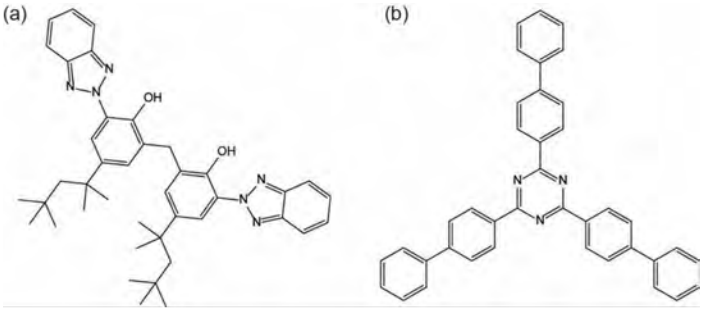

Fig. 1: A new class of organic UV filters. Chemical structures of (a) Methylene bis-benzotriazolyl tetramethyl-butylphenol (MBBT) and (b) Tris-biphenyl triazine (TBT).

Methylene bis-benzotriazolyl tetramethyl-butylphenol (MBBT) was the first representative of this new class of particulate organic UV absorbers. The structure of MBBT is depicted in Figure 1a. The commercial form is produced by a milling process as a 50% aqueous dispersion of colorless organic microfine particles with a size 200 nm ($d_{0.5}$). These small particles are stabilized in their size by a surfactant [2] [3].

With Tris-biphenyl-triazine (TBT) a second UV filter based on organic, sub-micrometer UV absorbing particles has been developed by BASF and recently registered for cosmetic use in the EU [4]. The chemical structure of this filter, which exhibits exceptionally strong photo-protection in the UV-B and UV-A2 range of 290 – 340 nm, is depicted in Fig. 1b.

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High dielectric permittivity elastomers for artificial muscles

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[1]EMPA Dübendorf

Elastomers that respond to an electric field are of great interest for many fields of applications. Dielectric elastomer actuators (DEAs) are stretchable capacitors made of a thin elastic film coated with two compliant electrodes which expend their area when charged. Due to their simple working principle and muscle-like actuation, DEA could find a large variety of applications in engines, optical devices, sensors, energy harvesters, artificial muscles to name a few. However, the high voltages required to induce the mechanical motion hider their use in some applications. Here, new dielectric elastomers with increased permittivity, excellent mechanical properties and increased electromechanical sensitivity are presented.[1] They show a maximum lateral actuation strain of 20.5% at 10.8 MV/m and ability to self-repair after a breakdown. Due to the low actuation voltage and the large actuation strain, applications of this material in commercial products might become reality.

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Surface-initiated controlled radical polymerization from cellulose nanomaterials

J. Zoppe[1], G. Siqueira[2], P. Orsolini[2], P. Tingaut[2], T. Zimmermann[2], H.-A. Klok[1]*

[1]Ecole Polytechnique Fédérale de Lausanne, [2]Swiss Federal Laboratories for Materials Science

Cellulose is the world's most abundant organic compound and is considered a practically inexhaustible source of stored carbon and solar energy. Historically, cellulose has been used primarily for energy, building materials, paper products and textile fibers. As a result of diminishing fossil fuel resources, evolving environmental concerns and the decreasing need of paper, great efforts have been made over the last two decades to produce novel nanomaterials from cellulose. Due to the unique optical, thermo-mechanical properties and low toxicity of cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs or NFC), there is a growing interest in their utility for advanced applications, such as nanomedicine and porous adsorbents. Toward these efforts, surface modification through surface-initiated controlled radical polymerization (SI-CRP) offers a means to tailor their interfacial properties. Here we present our recent work in copper-mediated SI-CRP from CNCs and CNFs for targeted applications, such as adsorbents for CO_2 capture and viral inhibitors. We demonstrate the accelerated nature of copper-mediated SI-CRP from cellulose nanomaterials by analysis of hydrolytically cleaved polymers. Overall, we present surface engineering of cellulose nanomaterials with polymer brushes through SI-CRP as an efficient method to further expand their exemplary properties.

High molecular weight poly(m,p-phenylene)s derived by Suzuki polycondensation: synthesis, processing and testing

B. Deffner[1], A. D. Schlüter[2]*

[1]ETH Zürich, [2]ETH Zurich

Polyphenylenes consisting exclusively of sp^2 hybridized carbon atoms have always been an appealing material to polymer chemists because of its unique properties.[1] Our current research is focused on poly(*m*,*p*-phenylene)s consisting of alternating *meta* and *para* linked phenylene units, because they have been shown to be tough amorphous materials with outstanding thermal stability and chemical resistance.[2] Unfortunately the synthesis of bare polyarylenes holds several challenges, like low reproducibility, low regioselectivity and low solubility of the formed products.[3] These issues were addressed using an AA/BB type Suzuki polycondensation which yielded a soluble precursor with acid cleavable side chains on every repeat unit. This polymer was reproducibly synthesized in a 20 g scale with a molecular weight of 140 $kg \cdot mol^{-1}$, which to our knowledge is among the highest reported values in this field. Having this attractive material in hand it was processed in to fibers by hot drawing. These fibers were subjected to a cleavage protocol,[4] which rendered them insoluble. Interestingly the resulting fibers show both, high stiffness and considerable stretchability of up to 8%. This is an unheard of property combination.

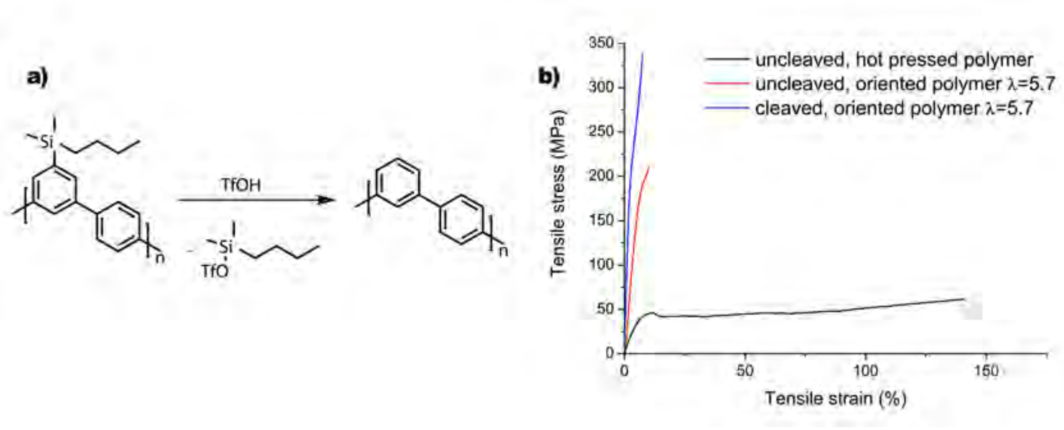

Figure 1. a) Cleaving reaction which furnishes the bare poly(*m*,*p*-phenylene) b) Stress-strain curves of differently treated polymer samples.

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Functionalized polymersomes inhibit malaria parasite invasion into host red blood cells

A. Najer[1,2], C. G. Palivan[1], H. Beck[2], W. Meier[1]

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Malaria is a disease caused by *Plasmodium* parasites that are transmitted by *Anopheles* mosquitos. Today, malaria is still responsible for about 600’000 deaths each year, mainly among African children.[1] There is no vaccine on the market yet and the most advanced vaccine candidate showed only partial protection in children.[2] Current drugs, which constantly lose their activity over time due to the emergence of drug resistant parasites,[3] kill intracellular parasites.

We have now designed heparin-functionalized polymer vesicles (polymersomes) with a size of 130 ± 30 nm in diameter, which served as simple host red blood cell (RBC) nanomimics and efficiently inhibited parasite invasion into RBCs by binding to the parasite surface after their egress from infected RBCs.[4,5] Invasion inhibition was more than two orders of magnitudes more potent when heparin was presented on the nanostructure compared to soluble heparins as tested in suspension culture assays using *Plasmodium falciparum*-infected RBCs and uninfected RBCs.[4] This highlights the potent interruption of the malaria blood stage cycle by nanomimics. Additionally, the mechanism of action is different to conventional drugs; the passive blockage of egressed parasites will expose the whole parasites to the immune system, which might induce a beneficial immune response against the extracellular parasites.[4,5]

We further analyzed the interaction of nanomimics and parasites using high-resolution fluorescence imaging and electron microscopy. The detailed analysis of the interaction of the parasite protein that binds heparin on nanomimics was performed using fluorescence-cross correlation spectroscopy (FCCS) in order to determine the interaction strength that explains the efficient invasion inhibition mechanism by nanomimics.[6]

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Polyalkylene glycols and their role as components of modern industrial and automotive lubricants

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Polyalkylene glycols (PAG) have been known for more than 60 years and are a diverse range of materials produced from downstream derivatives of ethylene oxide and 1,2-propylene oxide building blocks. Many of these polymers have been effective components of water based lubricants. Recently polymers derived from 1,2-butylene oxide have been developed. These materials offer many of the key functionalities of conventional PAGs. However a key difference is their solubility in hydrocarbon base oils. This opens up the application space for their use in industrial and automotive lubricants. Key aspects of their performance benefits will be discussed including their ability to improve friction control of modern lubricants and their ability to control deposits in high temperature application environments. A brief overview of how to optimise their performance by controlling their polymer architecture will be discussed.

Droplet-Based Microfluidics: High-Throughput Experimentation One Drop at a Time

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The past 20 years have seen drmatic progress in the development of microfabricated systems for use in the chemical and biological sciences. Interest in such microfluidic technologies has driven by concomitant advances in the areas of genomics, proteomics, drug discovery, high-throughput screening and diagnostics, with a clearly defined need to perform rapid measurements on small sample volumes. At a basic level, microfluidic activities have been stimulated by the fact that physical processes can be more easily controlled when instrumental dimensions are reduced to the micron scale.[1] The relevance of such technology is significant and characterized by a range of features that accompany system miniaturization. Such features include the ability to process small volumes of fluid, enhanced analytical performance, reduced instrumental footprints, low unit costs, facile integration of functional components within monolithic substrates and the capacity to exploit atypical fluid behaviour to control chemical and biological entities in both time and space.

My lecture will discuss recent studies that are focused on exploiting the spontaneous formation of droplets in microfluidic systems to perform a variety of analytical processes.

Droplet-based microfluidic systems allow the generation and manipulation of discrete droplets contained within an immiscible continuous phase.[2] They leverage immiscibility to create discrete volumes that reside and move within a continuous flow. Significantly, such segmented-flows allow for the production of monodisperse droplets at rates in excess of tens of KHz and independent control of each droplet in terms of size, position and chemical makeup. Moreover, the use of droplets in complex chemical and biological processing relies on the ability to perform a range of integrated, unit operations in high- throughput. Such operations include droplet generation, droplet merging/fusion, droplet sorting, droplet splitting, droplet dilution, droplet storage and droplet sampling.[3-4] I will provide examples of how droplet-based microfluidic systems can be used to perform a range of chemical and biological experiments including nanomaterial synthesis,[5] cell-based assays[6] and DNA amplification.[7]

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Photo-Sensitive Cationic Nanocarriers for Non-Toxic Delivery of Small Molecules

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Cationic polymeric nano-assemblies, such as those based on PDMS-*b*-PDMAEMA [1] are good candidates to protect and deliver proteins, enzymes, nucleic acids, [2] and imaging agents. [3] However, the positive charge of these systems also determines a poor release of the loaded cargo and induces toxicity. By modification of tertiary amine groups to photo-cleavable cationic moieties, it is possible to create a delivery system able to bind, protect, and controlled release small negatively charged molecules. However, unlike the previous PDMS-*b*-PDMAEMA nanoparticles, the quaternized nano-assemblies showed less cell toxicity. Also, these particles shown that upon UV irradiation, convert from cationic macromolecular species into the corresponding polyzwitterions, [4] preserving the non-toxic nature after releasing the cargo. A rapid release of anionic cargo would be expected, due to the conversion into the zwitterionic form. Nevertheless, a slow release over time was observed because the irradiation does not disrupt the particles, and the dye cannot rapidly overcome the special barrier of the pre-assembled structures. These data represent a major advancement in the safe delivery and controlled release mechanism that is needed to produce more efficacious delivery systems.

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From supramolecular sheets to fibers and back: establishing the critical parameters that govern the morphology of pyrene-based self-assembled materials

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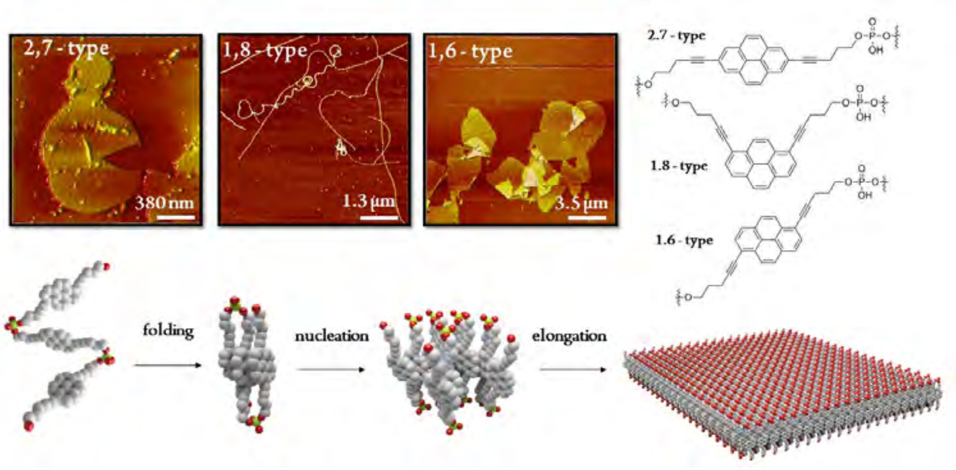
The precise arraying of functional entities in morphologically well-defined shapesremains one ofthe key challenges in the processing of organic molecules [1]. Among various π-conjugated species, pyrene exhibits a set of unique properties, which make it an attractive compound for the utilization in materials science [2]. In this contribution we report on properties of self-assembled structures prepared from amphiphilic pyrene trimers (**Py$_3$**) consisting of phosphodiester-linked pyrenes.



Depending on the geometry of a pyrene core substitution (1.6-, 1.8-, or 2.7- type, see Scheme), the thermally-controlled self-assembly allows the preparation of supramolecular architectures of different morphologies in a bottom-up approach: two-dimensional (2D) nanosheets [3]are formed in case of 1.6- and 2.7-substitution [4A]whereas one-dimensional (1D) fibers are built from 1.8- substituted isomers. The morphologies of the assemblies are established by AFM and TEM, and the results are further correlated with spectroscopic and scattering data. Two-dimensional assemblies consist of an inner layer of hydrophobic pyrenes, sandwiched between a net of phosphates. Due to the repulsion of the negative charges, the 2D assemblies exist mostly as free-standing sheets. An internal alignment of pyrenes leads to strong exciton coupling with an unprecedented observation (simultaneous development of J- and H-bands from two different electronic transitions). Despite the similarity in spectroscopic properties, the structural parameters of the 2D aggregates drastically depend on the preparation procedure. Under certain conditions extra-large sheets (thickness of 2 nm, aspect ratio area/thickness ~10e7) in aqueous solution are formed [4B,C]. Finally, one-dimensional assemblies are formed as micrometer-long and nanometer-thick fibers. Both, planar and linear structures are intriguing objects for the creation of conductive nanowires that may find interest for applications in supramolecular electronics.

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Electron transfer through peptide assemblies

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Some microorganisms use peptide assemblies, so called pili, as a medium for long distance electron transfer (ET). These pili can mediate reduction processes of metal ions outside the cell membrane while the electron is generated in the inner cell membrane. To investigate this ET process through the peptide assemblies we designed a model system, based on previous work,[1] containing histidine as a Ag^+-binding site at the *N*-terminus and tyrosine as a photoinducible electron donor at the *C*-terminus.

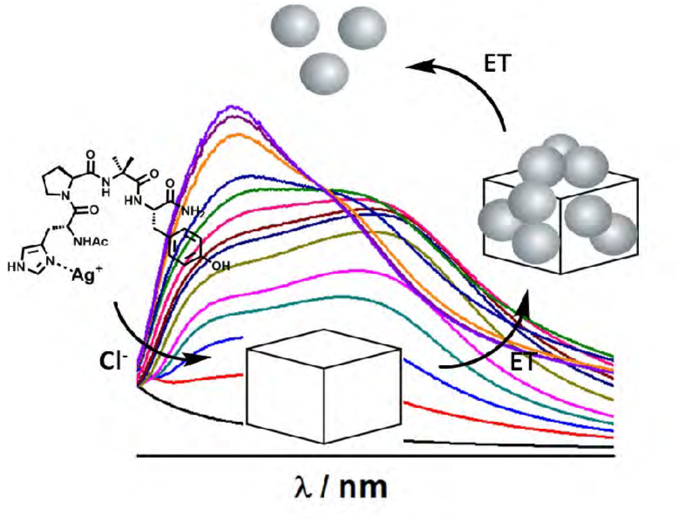

Figure 1. Schematic process of the AgNP formation and tranformation.

Surprisingly ET through the Ag^+-peptide did not reduce the Ag^+ peptide to silver nanoparticles (AgNPs) because the peptide matrix prevented the assembly of reactive Ag atoms to stable Ag aggregates. The synthesis of AgNPs occured when the silver ions were preorganized in the peptide matrix by addition of chloride ions (Figure 1). In these systems ET generated in the first step Ag@AgCl nanocomposites of 100 nm size, as shown in the Figure. Further ET cleaved theses composites to 15 nm AgNPs. [2] The nature of the Ag^+-coordinating amino acid highly influence the binding strength of the silver ion peptide bond and therefore the rate of the AgNP formation. In lowering the bond strength the AgNP formation rate increases.

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Self-assembled 2-D WSe2 Thin Films for Photo-electrochemical Hydrogen production

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WSe2 is a layered semiconductor that can be exfoliated into atomically-thin 2D sheets offering promising characteristics for application in solar energy conversion. However, the lack of controllable and cost-effective methods to scalably fabricate homogeneous thin films of these 2D sheets limits their practical application. Here we present a technique for the preparation of controlled thin-films of 2D WSe2 using our previously-developed method for preparing high-concentrationdispersions of solvent-exfoliated few-layer flakes.[1] Flake self-assembly at a liquid/liquid interface (formed exceptionally from two non-solvents for the WSe2) is followed bysubstratetransfer to afford large-area thin films with superior edge-to-edge particle ordering compared to traditional (liquid/air) interfacial self-assembly techniques.[2] We further demonstrate, for the first time, solar-to-hydrogen energy conversion from solution-processed WSe2 thin films. Photoelectrodes prepared with our liquid/liquid deposition technique at a thickness of ca. 25 nm exhibited sustained p-type photocurrent under simulated solar illumination, and with an added water reduction catalyst (Pt) photocurrent densities of ca. 1.0 mA/cm2 at 0 V versus the reversible hydrogen electrode were observed. The importance of the self-assembled thin-film morphology on the performance was further established by photoelectrochemical and conductivity measurements.

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Self-Recovering Gold Nanoparticle Films and Applications

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Films and coatings of nanoparticles (NPs) are key components in many emerging technologies due to their distinctive opto-electrical, biological and magnetic properties. In this case, soft interfaces, such as liquid-liquid interfaces (LLIs), can serve as a perfect platform to self-assemble 2D as well as 3D films of NPs. Since the discovery of the metal liquid-like films (MELLFs) by Yogev and Efrima in their pioneering work in 1988[1], many attempts have been made to improve the synthetic procedure and investigate the properties of such films.[2-4]

Here, we introduce a novel and facile approach to encapsulate macroscopic droplets with AuNPs in a way that does not require functionalization of AuNPs or covalent linkers. Simply contact between an aqueous citrate stabilized colloidal AuNP solution and an oil phase incorporating tetrathiafulvalene (TTF), with subsequent vigorous shaking of the system, leads to the formation of a continuous shining gold film in a stepwise manner (Fig.1A).[5] The obtained AuNPs assembles are dynamic in nature allowing them to self-heal after re-dispersing process.

Among potential applications there are: facilitated electron transfer across LLIs and electrocatalysis (Fig.1B), optical filters and mirrors with tuneable properties (Fig.1C), as well biphasic SERS and micro-droplets encapsulation to create containers.

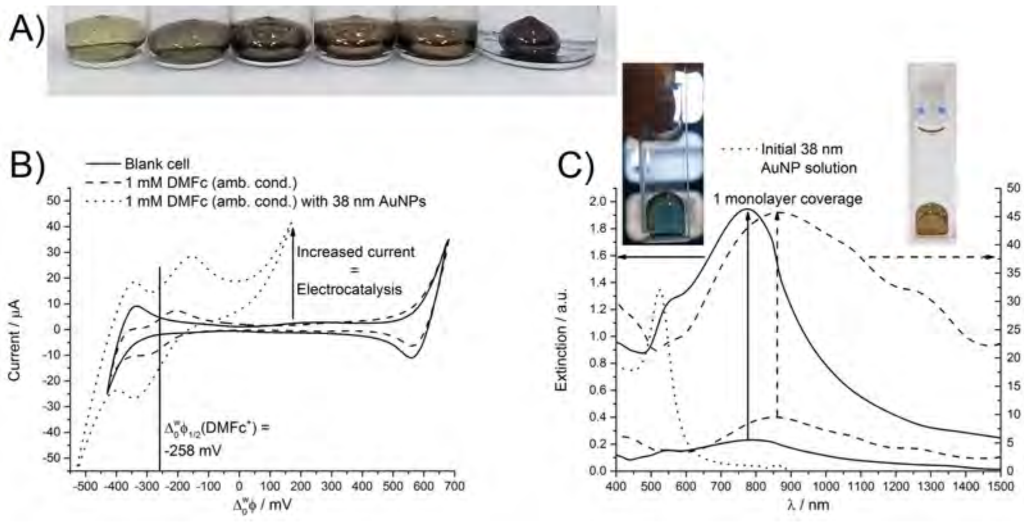

Figure 1. *A) Stepwise increasing of AuNP coverage at water|1,2-dischloroethane (1, 2, 4, 6, 8 and 35 ml of 38 nm AuNP solution). B) Electrocatalysis of O_2 reduction by decamethylferrocene (DMFc) on AuNPs at water|trifluorotoluene interface. C) Tuneable optical properties to create filters and mirrors at water|1,2-dichloroethane interface: UV-Vis-IR spectra and corresponding photos.*

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