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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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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 TiO₂ and ZnO [1].

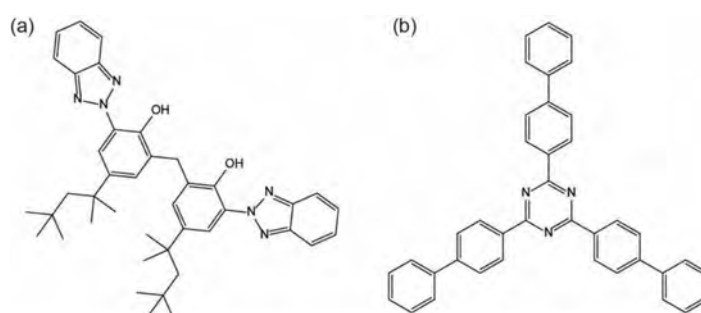


Fig. 1: A new class of organic UV filters. Chemical structures of (a) Methylene bis-benzotriazolyl tetramethyl-butylphenol (MBBT) and (b) Tris-biphenyl triazine (TBT).

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 musclesD. Opris¹¹EMPA 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 expand 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 hinder 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

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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 CO₂ 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

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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 $140 \text{ kg}\cdot\text{mol}^{-1}$, 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.

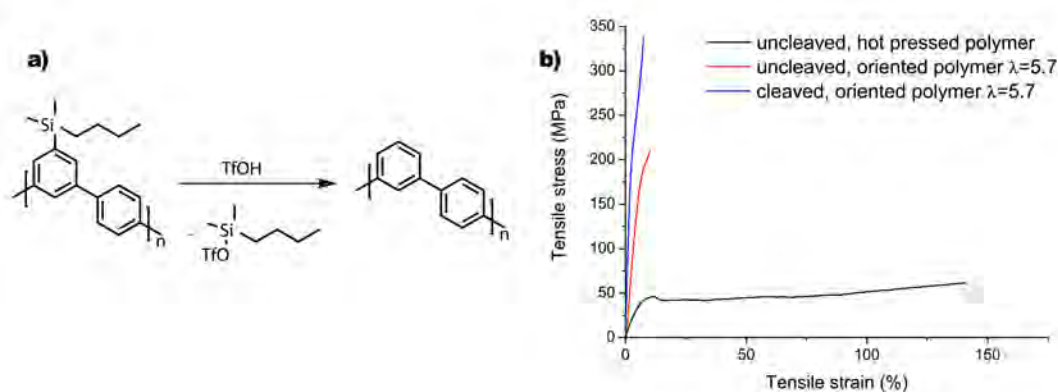


Figure 1. a) Cleaving reaction which furnishes the bare poly(*m,p*-phenylene) b) Stress-strain curves of differently treated polymer samples.

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Functionalized polymersomes inhibit malaria parasite invasion into host red blood cells

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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 lubricantsM. Dow Europe GmbH¹¹Horgen, Switzerland

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 TimeA. deMello¹

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The past 20 years have seen dramatic 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 assays⁶ and DNA amplification.⁷

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Photo-Sensitive Cationic Nanocarriers for Non-Toxic Delivery of Small MoleculesI.A. Dinu¹, J. T. Duskey¹, A. Car¹, W. Meier^{1*}, C. G. Palivan^{1*}¹University of Basel

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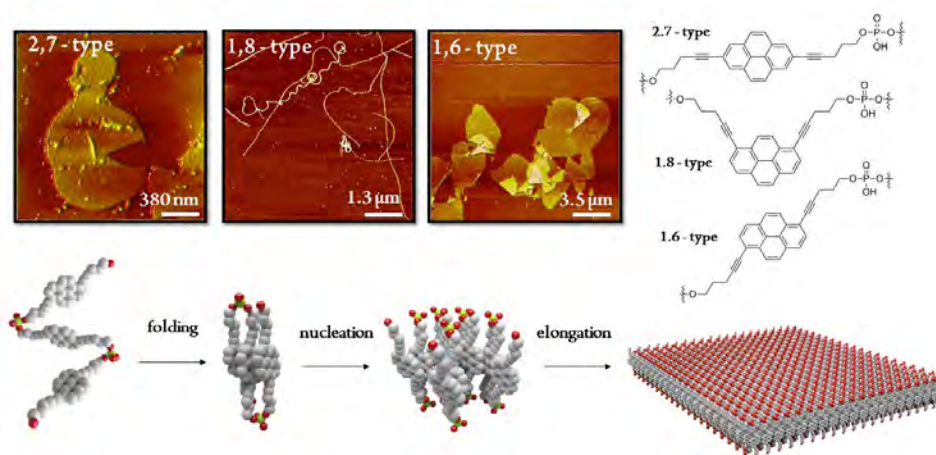
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From supramolecular sheets to fibers and back: establishing the critical parameters that govern the morphology of pyrene-based self-assembled materials

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The precise arraying of functional entities in morphologically well-defined shapes remains one of the 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 (**Py₃**) 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 $\sim 10^7$) 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.

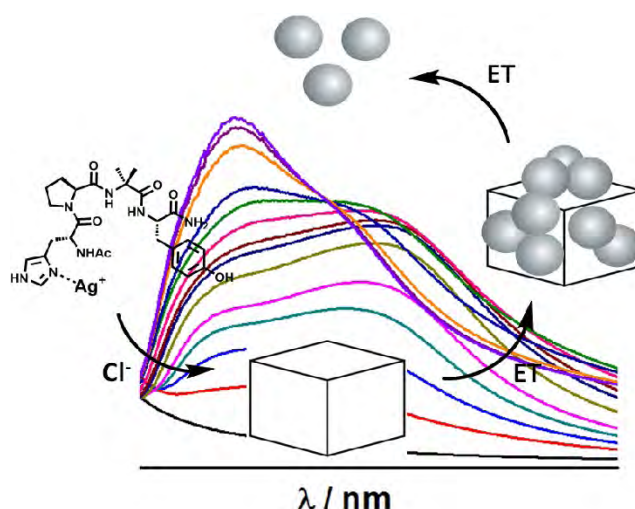


Figure 1. Schematic process of the AgNP formation and transformation.

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 occurred 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 these composites to 15 nm AgNPs.^[2] The nature of the Ag^+ -coordinating amino acid highly influences 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-concentration dispersions 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 by substrate transfer 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 1988¹, 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 assemblies 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.

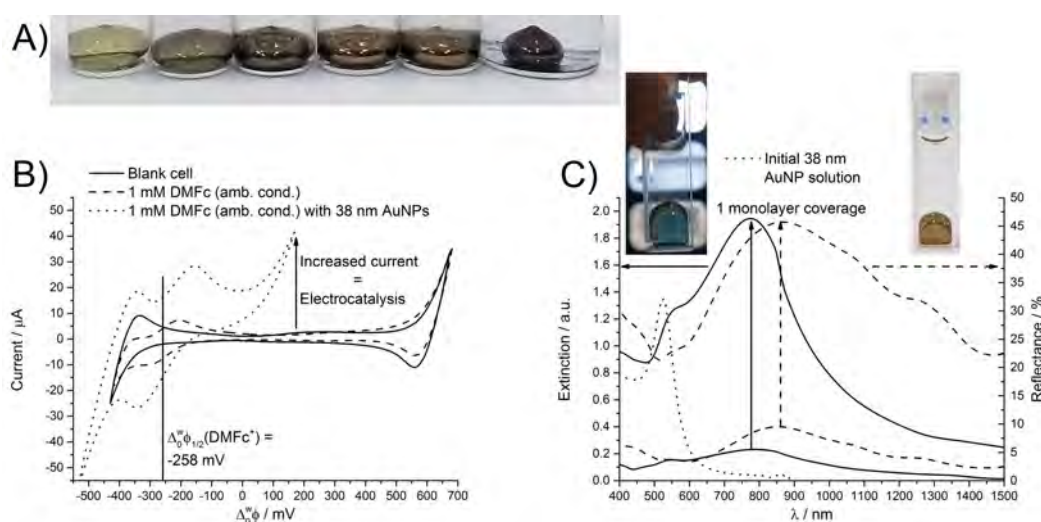


Figure 1. A) Stepwise increasing of AuNP coverage at water|1,2-dichloroethane (1, 2, 4, 6, 8 and 35 ml of 38 nm AuNP solution). B) Electrocatalysis of O₂ reduction by decamethylferrocene (DMFc) on AuNPs at water|trifluorotoluene interface. C) Tuneable optical properties to create filters and mirrors at water|1,2-dichloroethane interface: UV-Vis-IR spectra and corresponding photos.

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