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Poster Abstracts

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**Importance of particulate organic matter in singlet oxygen mediated photochemistry**Elena Appiani<sup>1</sup>, Kristopher McNeill<sup>1</sup> \*<sup>1</sup>ETH Zurich

Organic matter is known to be one of the most relevant photosensitizers in aquatic environments. Dissolved organic matter (DOM) has been widely studied and its role in the production of reactive oxygen species is well understood [1]. Particulate organic matter (POM) is known to play an important role in pollutant degradation both by transportation of hydrophobic pollutants, and due to the ability of particles to scatter light enhancing the photo transformation of organic molecules[2,3]. In addition to those known properties, the capacity of POM to photo produce reactive oxygen species is still a matter of debate. If this was the case, the molecules adsorbed on the particles could interact with the reactive oxygen species where they are formed. In this study, among the reactive oxygen species, we focus on  $^1\text{O}_2$  because of its widely accepted microheterogeneous distribution due to the high quenching rate with the solvent. [4] This property of singlet oxygen offers the best condition to assess the particles contribution. The  $^1\text{O}_2$  formation upon irradiation of solution containing POM and DOM was monitored using two different selective probe molecules: furfuryl alcohol (FFA), a hydrophilic probe molecule, widely used as reference in environmental studies and 2-[(1-(3-*tert*-butyldimethylsiloxy)phenyl)-1-methoxy-methylene]tricyclo[3.3.1.1]decane,(TPMA), a hydrophobic probe molecule, which better simulate the behavior of pollutants bound to DOM.

We used model particles synthesized by loading a known amount of organic matter to an homogeneous spherical silica support as POM sources. The dependence of size and aggregation state to the  $^1\text{O}_2$  photo production was investigated.

Our experiments show comparable  $^1\text{O}_2$  steady state concentrations ( $[^1\text{O}_2]_{ss}$ ), experienced by TPMA, photosensitized by POM- and DOM-containing solutions. We confirmed that our synthetic model simulates the natural particles by comparing the results obtained with the one obtained using particles isolated from a lake sediment. During this study the affinity of the two probes for hydrophobic and hydrophilic environments respectively was confirmed in both the DOM and POM containing systems, by observing up to four order of magnitude difference in  $[^1\text{O}_2]_{ss}$  detected by different probes.

[1] R. G. Zepp, N. L. Wolfe, G. L. Baughmann, R. C. Hollins, *Nature* **1977**, 267, 421.

[2] G. C. Miller, R. G. Zepp, , *Water Res.* **1979b**, 13, 453.

[3] G. C. Miller, R. G. Zepp, *Env. Sci. Tech.* **1979a**, 13, 860-863.

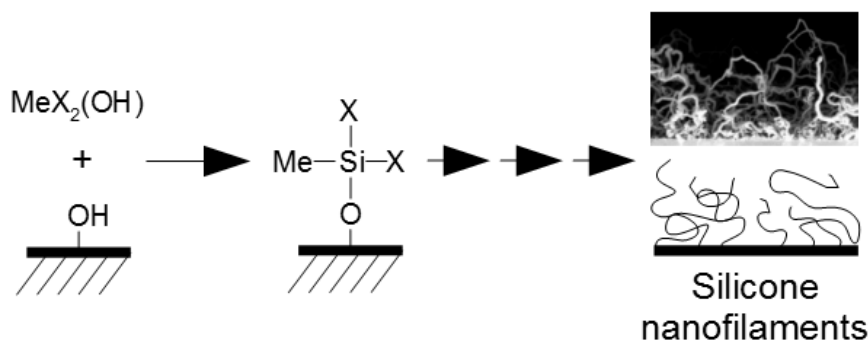
[4] Latch, D.E.; McNeill, K., *Science* **2006**, 311, 1743-1747.

## Superficial Doping Allows Growth of Silicone Nanostructures on Hydroxyl-free Substrates

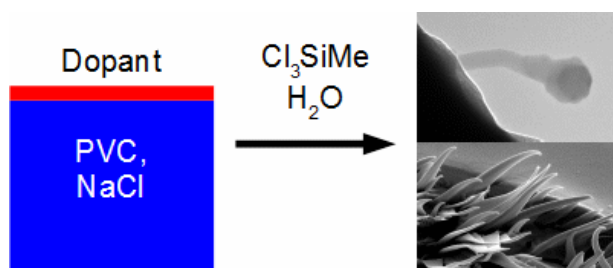
Georg Artus<sup>1</sup>, Laurent Bigler<sup>1</sup>, Stefan Seeger<sup>1</sup> \*

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The current understanding of the growth of one-dimensional silicone nanofilaments on substrates is based on two fundamental assumptions: First, a hydrophilic substrate with a high density of terminating hydroxyl groups is believed to be necessary, and second, covalent bonding of the silane to the substrate via these hydroxyl groups is presupposed.[1,2]



We show that these two pre-conditions are invalid by the growth of silicone nanofilaments on hydrophobic poly(vinyl chloride) which was superficially doped with the detergent Span®20, and on sodium chloride which was superficially doped with dibutyl phthalate. Both substrate materials are inherently free of hydroxyl groups and therefore do not bind covalently to a silane. These results question the currently discussed mechanisms for the growth of one-dimensional silicone nanofilaments.[2] Furthermore, we introduce new types of silicone nanostructures: filaments with a raveled end and silicone nano-teeth.

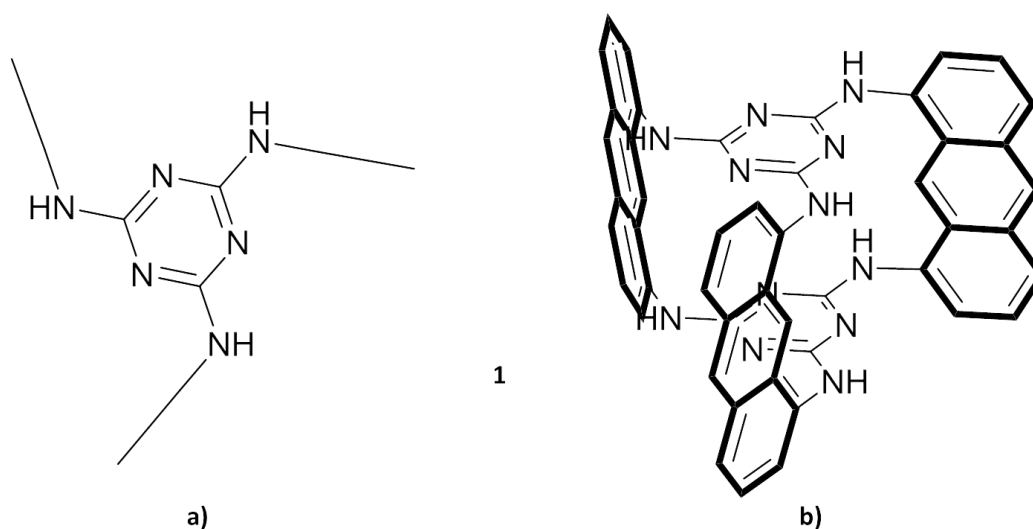


[1] D. Rollings, J. Veinot, J. *Langmuir* **2008**, 24, 13653–13662.

[2] G. R. J. Artus, S. Seeger, *Adv. Colloid Interface Sci.* **2014**, doi 10.1016/j.cis.2014.03.007

**Towards 2D-Polymers: Synthesis of a Rotor-shaped Monomer**Simon T. Cerqua<sup>1</sup>, Max J. Kory<sup>1</sup>, A. Dieter Schlüter<sup>1</sup> \*<sup>1</sup>Laboratory of Polymer Chemistry, Institute of Polymers, Department of Materials, ETH Zurich

The organic synthesis of a 2D polymer by single crystal transformation has recently been achieved [1]. The synthesis of a triazine-based double-decker monomer, its polymerization and depolymerization process characterized via single crystal XRD measurement is another example for a 2D polymer [2-4]. One of the major challenges, in the above cases, is reaching single sheets by exfoliation. Here synthesis and a potential crystal structure of amine bearing monomer **1** is presented. The presence of the amine groups is likely to make the exfoliation process by the wet chemistry approach more versatile. Furthermore it should allow the functionalization of both, the monomer and polymer, by chemical modification of the amine groups.

**Figure:** Top (a) and side view (b) of monomer **1**

[1] P. Kissel, R. Erni, W. B. Schweizer, M. D. Rossell, B. T. King, T. Bauer, S. Götzinger, A. D. Schlüter, J. Sakamoto, *Nat. Chem.* **2012**, 4, 287-291.

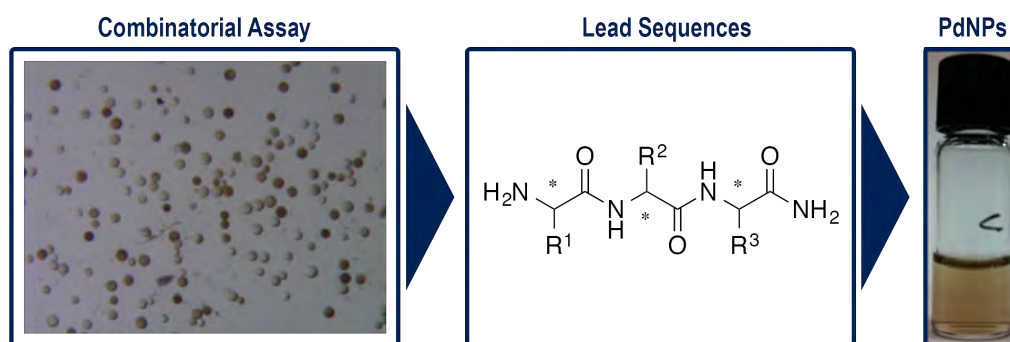
[2] M. J. Kory, M. Bergeler, M. Reiher, A. D. Schlüter, *Chem. Eur. J.* **2014**, 20, accepted for publication. DOI:10.1002/chem.201400364

[3] J. Sakamoto, J. van Heijst, O. Lukin, A. D. Schlüter, *Angew. Chem. Int. Ed.* **2009**, 48, 1030-1069.

[4] M. J. Kory, M. Wörle, T. Weber, P. Payamyar, J. Dschemuchadse, N. Trapp, A. D. Schlüter, submitted.

**Tripeptides as Additives for the Controlled Formation of Palladium Nanoparticles**Stefano Corrà<sup>1</sup>, Helma Wennemers<sup>1</sup> \*<sup>1</sup>ETH Zurich

Nature uses interactions between metals and proteins for a variety of purposes ranging from catalysis (enzymes) to biomineralization. The modularity of peptides renders them attractive as additives for the formation of nanoparticles (NPs) and opens attractive avenues for the preparation of novel materials with specific functions and for a broad range of applications. [1] Our group has previously developed a combinatorial assay for the identification of peptides that control the formation of silver NPs within one-bead-one-compound libraries. [2] We have now used this combinatorial assay for the identification of peptides that control the formation of palladium (Pd) NPs. Evaluation of the identified lead sequences in solution phase revealed that the resulting PdNPs have an average diameter of ~2 nm and are highly monodisperse. [3]



Detailed analysis of the structural and molecular properties of the peptide, the peptide-Pd(II) complex and the resulting PdNPs are currently ongoing.

[1] Dickerson, M. B.; Sandhage, K. H.; Naik, R. R. *Chem. Rev.* **2008**, *108*, 4935.

[2] Belser, K.; Vig-Slenter, T.; Pfumbidzai, C.; Upert, G.; Mirolo, L.; Fromm, K. M.; Wennemers, H. *Angew. Chem. Int. Ed.* **2009**, *48*, 3661.

[3] Corrà, S.; Wennemers, H. *manuscript in preparation*.

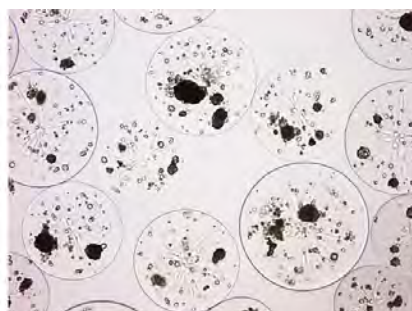
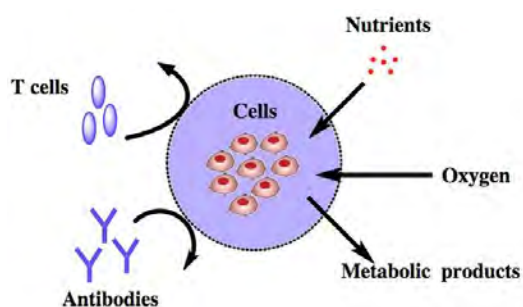
## Engineering alginate-based hydrogels for cell microencapsulation

Virginia Crivelli<sup>1</sup>, Françoise Borcard<sup>1</sup>, Redouan Mahou<sup>1</sup>, Elisa Montanari<sup>2</sup>, Raphael P.H. Meier<sup>2</sup>, Sandrine Gerber<sup>1</sup>, Léo Bühler<sup>2</sup>, Christine Wandrey<sup>1</sup> \*

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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.

Hydrogels composed of covalently and electrostatically crosslinked combinations of sodium alginate (Na-alg), poly(ethylene glycol) derivatives (PEG), and functionalized Na-alg favorably mimic the natural environment of cells. One- and two-component hydrogel microspheres were produced by combining the ionotropic gelation of Na-alg using calcium ions with covalent crosslinking of either vinyl sulfone-terminated multi-arm PEG<sup>1</sup> or thiol end groups grafted onto Na-alg. In a one-step microsphere formation process, the fast ionotropic gelation ensures the spherical shape of the microspheres. Controlled simultaneously but slowly occurring covalent crosslinking reinforces the hydrogel mechanically and adjusts its permeability. The physical properties of series of microspheres are presented<sup>2</sup> and the feasibility of cell microencapsulation is demonstrated.<sup>3</sup>



[1] R. Mahou, C. Wandrey, *Macromolecules*, **2010**, 43, 1371-1378.

[2] R. Mahou, G. Kollarikova, C. Gonelle-Gispert, R. Meier, F. Schmitt, N.M. Tran, M. Dufresne, I. Altimari, I. Lacik, L. Bühler, L. Juillerat-Jeanneret, C. Legallais, C. Wandrey, *Macromol. Symp.*, **2013**, 329, 49-57.

[3] R. Mahou, R. Meier, L. Bühler, C. Wandrey, *Materials*, **2014**, 7(1), 275-286.

## Poly(*m,p*-phenylene) based Materials via Suzuki Polycondensation

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Poly(*m,p*-phenylene)s bearing solubilizing side chains were shown to be tough amorphous materials with outstanding thermal stability and chemical resistance.<sup>1</sup> Removing the side chains should lead to further improved mechanical properties as a negative influence of solubilizing side chains for rigid backbone materials is reported.<sup>2</sup> As the increased solubility is necessary for synthesizing and processing the materials, a concept including cleavable silyl side chains was developed.<sup>3</sup> We synthesized *meta*-dibromomonomers bearing these solubilizing chains in a multi gram scale which was then used in a AA-BB-type Suzuki polycondensation with 1,4-benzenediboronic acid bis(pinacol)ester to result in a soluble high molecular weight poly(*m,p*-phenylene) with a weight average molecular weight of about 100`000 g×mol<sup>-1</sup>. After processing, the side chains were cleaved by acid treatment to result in a highly insoluble material with excellent mechanical properties (Figure 1c) even under thermal and chemical stress. The poster will also discuss where we see the future of these novel and promising materials.

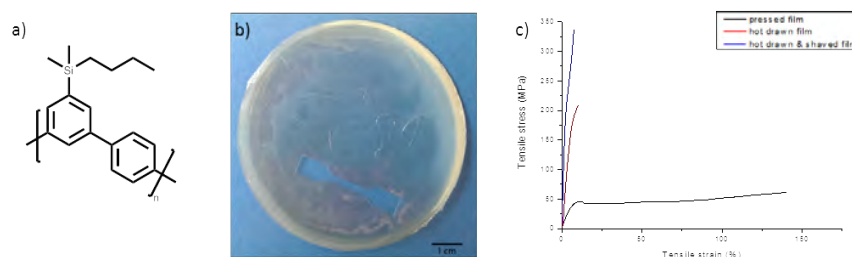


Figure 1. a) Structure of a poly(*m,p*-phenylene) bearing a cleavable side chain. b) Hot pressed film of this polymer. c) Stress-strain curves of differently treated films.

[1] R. Kandre, K. Feldman, H. E. H. Meijer, P. Smith, A. D. Schlüter, *Angew. Chem. Int. Ed.* **2007**, 46, 4956.

[2] A. R. Postema, K. Liou, F. Wudl, P. Smith, *Macromolecules* **1990**, 23.

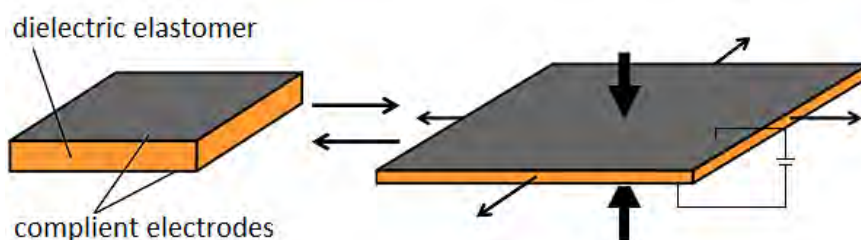
[3] S. Jakob, A. Moreno, X. Zhang, L. Bertschi, P. Smith, A. D. Schlüter, J. Sakamoto, *Macromolecules* **2010**, 43, 7916.

**Polar silicones to be used in dielectric elastomer actuators**

Simon Dünki<sup>1</sup>, Adrian Bele<sup>2</sup>, Maria Cazacu<sup>2</sup>, Carmen Racles<sup>2</sup>, Frank Nüesch<sup>3</sup>, Dorina Opris<sup>3</sup> \*

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Dielectric elastomer actuators (DEA) are stretchable capacitors that are able to convert electrical energy directly into mechanical work.<sup>[1]</sup> They consist of a non-conductive, elastomeric film sandwiched between two compliant electrodes. When a voltage is applied, electrostatic pressure is created between the two electrodes, which then attract each other. Since elastomers conserve their volume, the electrostatic pressure compressing the film results in a reduction of the thickness and increasing of the area of the actuator.



Silicones have many interesting properties, such as broad usable temperature range, inert chemical behaviour, good electric insulation and low viscoelastic losses.<sup>[2]</sup> Besides these unique properties, silicones lack of a low relative permittivity, which decreases the efficiency of DEA.<sup>[3]</sup> A possible way to enhance the relative permittivity of a material is the introduction of dipoles. In this presentation, the synthesis of silicone elastomers with good elastic properties and increased relative permittivity by attaching polar pendant groups to the silicon backbone is presented.

[1] Ron Pelrine, Roy Kornbluh, Qibing Pei, Jose Joseph, *Science*, **2000**, 287, 836.

[2] Dorina Opris, Martin Molberg, Christian Walder, Yee Song Ko, Beatrice Fischer, Frank Nüesch, *Advanced Functional Materials*, **2011**, 21, 3531-3539.

[3] Carmen Racles, Maria Cazacu, Beatrice Fischer, Dorina Opris, *Smart Materials and Structures*, **2013**, 22, 104004.



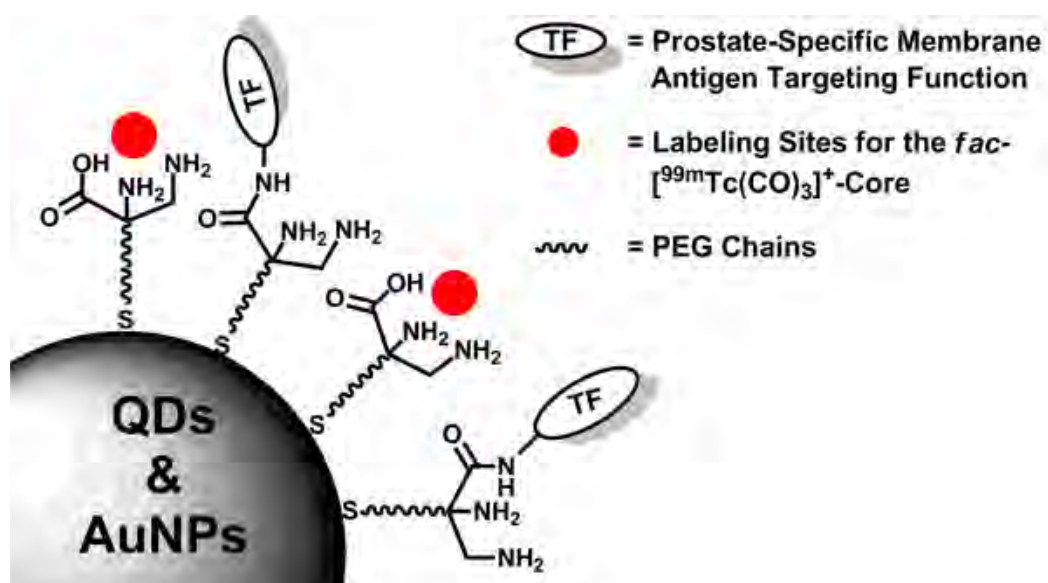
## Radiolabeling of Functionalized Nanoparticles with $\text{fac-}[^{99\text{m}}\text{Tc}(\text{OH}_2)_3(\text{CO})_3]^+$

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Nanoparticles (NPs) attracted much attention in the last decade for both therapeutic and diagnostic applications. Most of the NPs are used for drug delivery and contrast agents, especially for magnetic resonance imaging (MRI).<sup>[1]</sup> In order to study the pharmacokinetics and *in vivo* tumor targeting capability, the NPs can be labeled with a radionuclide for a quick, quantitative and reliable evaluation of their biodistribution.<sup>[2]</sup> Furthermore, the radiolabeling of gold nanoparticles AuNPs (computed tomography), quantum dots QDs (optical imaging), superparamagnetic iron oxide NPs (MRI) or Silica NPs (ultrasound) affords multi-modality imaging agents.

In this work, CdSe/ZnS QDs and spherical AuNPs were quantitatively coated with a novel bifunctional coating ligand that allows a direct labeling with  $[\text{fac-}^{99\text{m}}\text{Tc}(\text{OH}_2)_3(\text{CO})_3]^+$ . This bifunctional coating ligand consists of a thiol group for the attachment on the NPs, a polyethylene glycol (PEG) linker and the 2,3-diamino propionic acid (DAP) moiety as a small and potent chelator for the  $\text{fac-}[\text{fac-}^{99\text{m}}\text{Tc}(\text{CO})_3]^+$ -core. Moreover, the coating ligand was conjugated with a lysine-glutamate urea to target the prostate-specific membrane antigen (PSMA) which is over-expressed in prostate cancer and its metastases.<sup>[3]</sup> The cellular uptake of the NP-conjugates was investigated with LNCaP cells based on a transmission electron microscopy (TEM) study. Additionally, the *in vivo* behavior was evaluated with tumor bearing mice.<sup>[4]</sup>



[1] Sanjiv S. Gambhir *et al.*, *Acc. Chem. Res.*, **2011**, 44, 1050-1060. [2] Younan Xia *et al.*, *ACS Nano*, **2012**, 6, 5880-5888. [3] Martin G. Pomper *et al.*, *J. Med. Chem.*, **2008**, 51, 4504-4517. [4] Michael Felber, Roger Alberto *et al.*, *in preparation*.

## Enzyme-catalyzed Atom Transfer Radical Polymerization of Heterocyclic Aromatic Vinyl Compounds

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<sup>1</sup>University of Fribourg

Polymers based on heterocyclic aromatic vinyl monomers have unique properties that render them interesting for applications in gene delivery systems, as fuel cell membranes, or as ingredients of pharmaceutical and cosmetic formulations. Living/controlled radical polymerizations, such as atom transfer radical polymerization (ATRP) usually allow tailoring the architecture of polymers, their molecular weight and, as a result of this, the polymers' properties. Unfortunately, many heterocyclic aromatic vinyl monomers cannot be polymerized by ATRP. The nitrogen-containing monomers and polymers strongly bind metal ions, such as copper ions and therefore strip the Cu-complexes, which are used as ATRP catalysts, of their active center. Moreover, the radicals involved in this polymerization are often too reactive to allow for a good degree of control by these catalysts. Last but not least, the copper-based catalysts are very difficult to remove from the polymer products and could easily contaminate the polymer. Even in low amounts, the residual copper can have enormous negative influence on the properties of the polymer.

The presented work will discuss the synthesis of tailor-made vinyl polymers that contain N-heterocyclic aromatic side chains by biocatalytic ATRP. Controlled polymerization of these monomers was achieved by replacing the commonly used catalysts with macromolecules from nature, i.e. with metalloproteins. The enzymes strongly bind their metal ions within their native three-dimensional structure, so that metal ion-free polymers with predetermined molecular weight, structure and relatively low molecular weight distribution could be prepared.

[1] Severin J. Sigg, Farzad Seidi, Kasper Renggli, Tilana B. Silva, Gergely Kali, Nico Bruns, *Macromol. Rapid Commun.*, **2011**, 32,21, 1710-1715.

[2] Gergely Kali, Tilana B. Silva, Severin J. Sigg, Farzad Seidi, Kasper Renggli, Nico Bruns, *ACS Symp. Ser.*, **2012**, 1100, 171-181.

[3] Tilana B. Silva, Mariana Spulber, Marzena C. Kocik, Farzad Seidi, Himanshu Charan, Martin Rother, Severin J. Sigg, Kasper Renggli, Gergely Kali, Nico Bruns, *Biomacromolecules*, **2013**, 14, 2703-2712.

[4] Kasper Renggli, Mariana Spulber, Jonas Pollard, Martin Rother, Nico Bruns, *ACS Symp. Ser.* **2013**, 1144, 163-171.

## Nano-Handling of Individual Dendronized Polymers

Lucie Grebikova<sup>1</sup>, Plinio Maroni<sup>1</sup>, Baozhong Zhang<sup>2</sup>, A. Dieter Schlüter<sup>2</sup>, Michal Borkovec<sup>1</sup> \*

<sup>1</sup>University of Geneva, <sup>2</sup>ETH Zurich

A novel atomic force microscopy (AFM) nano-handling technique is presented that can precisely measure force-extension relations of individual polymer molecules. The technique was used to study the mechanical response of amino-functionalized dendronized polymers (DP). Because of their dendritic structure DPs provide a perfect tool to study a scaling behaviour with respect to the number of monomers in the side chain [1].

DPs of different generations were adsorbed on a chemically modified substrate and then imaged in solution. A single polymer chain was picked up with the AFM cantilever and the force curves were recorded by stretching an individual polymer molecule many times. The fact that one deals with one single molecule was verified by AFM imaging of the polymer chain in question before and after the nano-handling experiment (Fig. 1).

The force response of individual DP molecules could be accurately described with the freely jointed chain model with a linear elasticity term. Monotonic dependence of mechanical properties of these polymers was found. The effective Kuhn length increased with generation at high salt concentrations and remained constant at low salt levels. The elastic constant was found to be independent of the generation and solution composition.

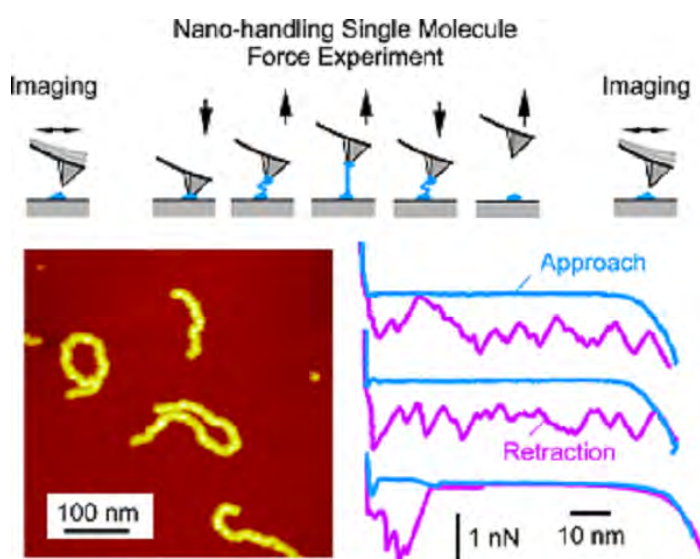


Figure 1: Principle of single-molecule nano-handling force experiments [2].

[1] Yifei Guo, Jacco D. van Beek, Baozhong Zhang, Martin Colussi, Peter Walde, Afang Zhang, Martin Kröger, Avraham Halperin, A. Dieter Schlüter, *Journal of the American Chemical Society*, **2009**, 131, 11841-11845.

[2] Lucie Grebikova, Plinio Maroni, Baozhong Zhang, A. Dieter Schlüter, Michal Borkovec, *ACS Nano*, **2014**, 8 (3), 2237-2245.

## Self-Assembly of Magnetic Janus Dumbbells

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In the last decade, many scientists in the field of nanoparticles focused on creating anisotropic nanoparticles, also called Janus nanoparticles. These special types of particles have very interesting properties and self-assembling behavior, as compared to simple isotropic particles.

In this work, we created magnetic Janus dumbbells, and studied their self-assembling behavior under a magnetic field. Dumbbells of different size and aspect ratio have been synthesized using a two-step swelling procedure. The use of 3-trimethoxysilylpropylmethacrylate (MPS) in the second step brings some silane group to the surface of the nanoparticles, which can be used for asymmetric functionalization afterward. After swelling and polymerizing one more time, one ends up with a dumbbell nanoparticle which is asymmetrically functionalized, as the silane groups are indeed only present on the surface of the first hemisphere and not on the second one [1]. Silane coupling chemistry can be then performed selectively. By reacting a silane with an amino or an ammonium group, positive charge are brought to the first hemisphere, while the second remains negatively charged due to the presence of Sodium Dodecyl Sulfate (SDS) used as surfactant. The resulting dumbbells are then dipolar under the right pH condition.

Beside the Janus dumbbells, negatively charged superparamagnetic iron oxide nanoparticles (SPIONS) have been synthesized, either by co-precipitation of two iron salts in water or by thermal decomposition of iron oleate in high boiling point solvents [2]. For the SPIONS synthesized in water, citric acid can be directly used as a surfactant. For the SPIONS made in organic solvents, oleic acid is used as a surfactant. In order to make them negatively charged, it is necessary to exchange the surfactant or to oxidize the double bond of oleic acid. Many approaches have been tested to transfer the SPIONS to water.

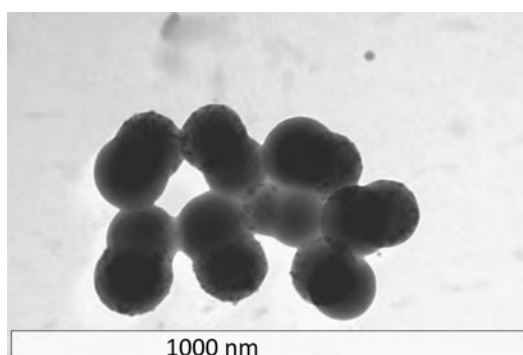


Figure 1 : Citrate-coated SPIONS selectively heteroaggregated with dipolar dumbbell polystyrene nanoparticles

[1] F. Guignard, M. Lattuada, *Chimia (Polymer and Colloid Highlights)*, 67, 829 (**2013**)

[2] Hyeon et. al., *Nature Materials* 3, 891 - 895 (**2004**)

[3] Hu, Y., He, L. and Yin, Y., *Angew. Chem. Int. Ed.*, 50: 3747–3750 (**2011**)

### Hybrid bio-responsive nanocapsules

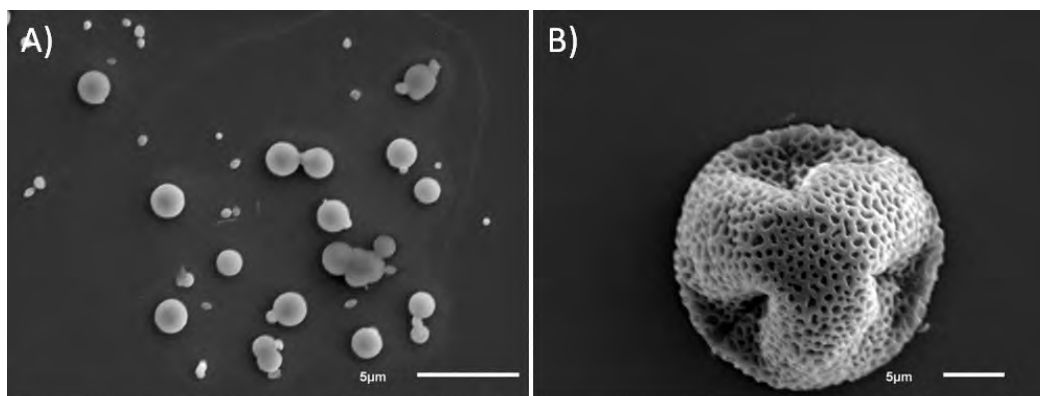
Dawid Kedracki<sup>1</sup>, Plinio Maroni<sup>1</sup>, Helmut Schlaad<sup>2</sup>, Corinne Vebert<sup>1</sup> \*

<sup>1</sup>University of Geneva, <sup>2</sup>Max Plank Institute of Colloids and Interfaces, Potsdam

**Introduction:** Herein we describe the synthesis of DNA-copolymers, being the nucleotide sequence an aptamer selected in vitro to bind to the target with high specificity [1]. Subsequent to coupling to poly(2-alkyl-2-oxazoline) with N-protected amino acid side chains, the resulting amphiphilic DNA-polymer hybrid composed of the water soluble DNA fragment grafted to the hydrophobic polymer segment can be regarded as a high molecular weight analogue of a surfactant.

**Results:** The aptamer polymer hybrid has been successfully synthesized by solid phase synthesis according to well established chemistry routes. This macromolecule can be regarded as a high molecular weight analogue of a surfactant with the major advantage of being constituted of a bioinspired biocompatible synthetic polymer segment coupled to a biological stimulus-responsive nucleotide sequence [2]. Results obtained from CLSM, AFM and reflectometry evidence that the aptamer remains functional subsequent to coupling to the polymer and engagement in the stabilization of the emulsion and shows high specificity.

**Discussion and Conclusions:** The resulting amphiphilic copolymer-aptamer efficiently stabilizes oil-in-water and water-in-oil emulsions. Engagement of the aptamer in the emulsion stabilization does not hinder its specificity of binding to its target, which paves the way for further developments of capsules for sustained and targeted delivery through the synergistic combination of site specific aptamer recognition of the encapsulated load [3].



*Fig. 1: Scanning electron micrographs of PBOX-aptamer capsules after cross-linking by irradiation with UV light A) Cross-linkage is performed subsequent to filtration B) Large porous structures are observed when no extrusion is performed to reduce the size: fusion of the droplets might occur.*

[1] Nimjee et al, *Annu Rev Med.*, **2005**, 56, 555-583.

[2] Schlaad et al, *Macromolecular Rapid Communications*, **2010**, 31, 511-525

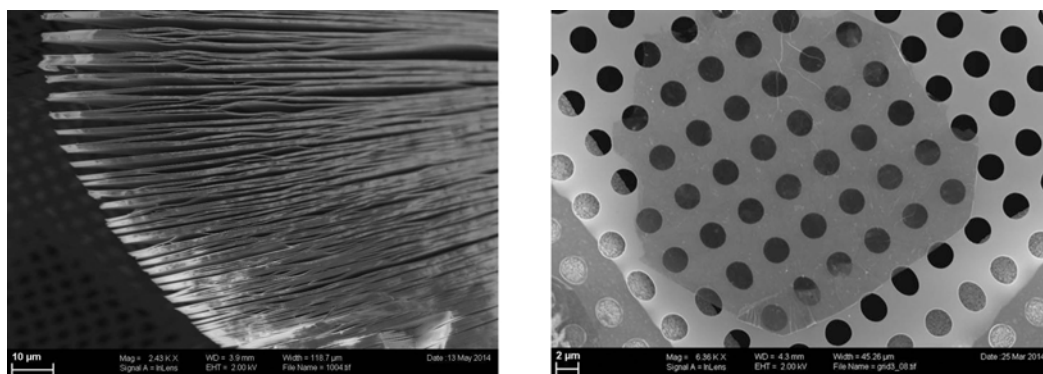
[3] Kedracki et al., *Adv. Funct. Mater.*, **2014**, 24, 1133-1139

## Gram-Scale Synthesis of Organic Two-Dimensional Polymer Crystals and Exfoliation into Nanometer-Thin Sheets

Max J. Kory<sup>1</sup>, Michael Wörle<sup>1</sup>, Thomas Weber<sup>1</sup>, Carsten Becher<sup>1</sup>, A. Dieter Schlüter<sup>1</sup> \*

<sup>1</sup>ETH Zurich

Ever since the discovery of graphene, a natural two-dimensional polymer (2DP), it has become evident that macromolecular sheets consisting of covalently bonded repeating units bear many interesting prospects for nanotechnology. Up until recently, a bottom-up preparation of such structures based on a carbon scaffold has not been achieved [1]. Here we report that noncentrosymmetric, enantiomorphic single crystals of a simple-to-make[2] monomer can be photochemically converted into chiral 2DP crystals on the multigram scale, and by thermal treatment also cleanly reversed back to monomer[3]. The crystal structure of the two-dimensional polymer was elucidated by single crystal XRD which provides unequivocal structural proof of this synthetic macromolecule. The highly robust monomer crystals can be grown to sizes larger than 1mm and the 2DP crystals can be exfoliated to nanometer-thin sheets. Both monomer and polymer crystals show pronounced second-harmonic generation which makes them interesting materials for applications in the field of nonlinear optics.



SEM images (2kV) of a swollen two-dimensional polymer crystal (left) and a nanometer-thin two dimensional polymer sheet (right), the original hexagonal shape of the crystal it was exfoliated from, is still visible.

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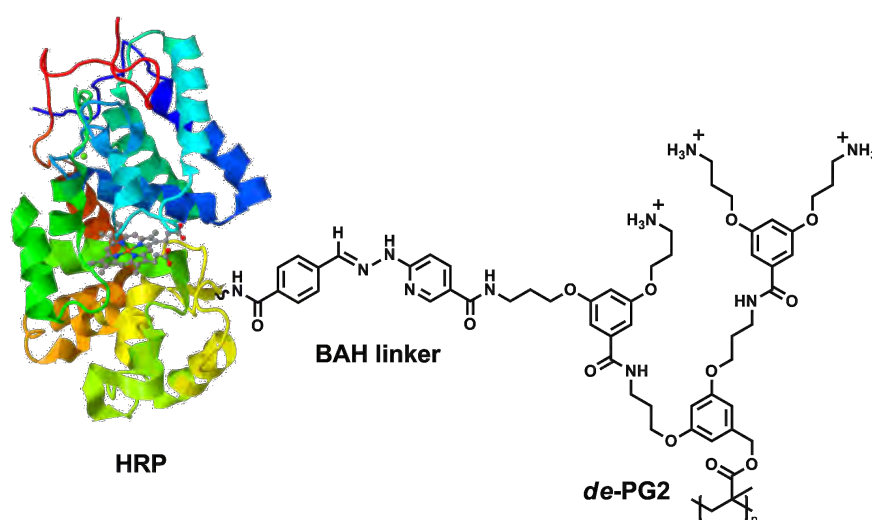
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## Enzyme Immobilization with Dendronized Polymer-Enzyme Conjugates for Localized Cascade Reactions

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Conjugates between the second generation dendronized polymer (denpol) *de*-PG2 and either *Aspergillus niger* glucose oxidase (GOD) or horseradish peroxidase (HRP) were prepared in aqueous solution. The enzymes were bound *via* a stable, spectrophotometrically quantifiable bis-aryl hydrazone linker (BAH) [1,2]. Adsorption of these conjugates (*de*-PG2-BAH-HRP (Figure) and *de*-PG2-BAH-GOD) on SiO<sub>2</sub> surfaces was monitored with the transmission interferometric adsorption sensor (TInAS) and atomic force microscopy (AFM). With a *sequential immobilization* of the two conjugates the continuous formation of products of a two enzyme cascade reaction was monitored (oxidation of D-glucose with GOD and dissolved O<sub>2</sub> yielding glucono-δ-lactone and H<sub>2</sub>O<sub>2</sub>, and subsequent HRP catalyzed oxidation of ABTS<sup>2-</sup> (2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonate)) to ABTS<sup>•-</sup> by the H<sub>2</sub>O<sub>2</sub> formed).



A conjugate containing both enzymes, GOD and HRP, was also prepared and adsorbed under retention of enzymatic activity. In this case, GOD and HRP were *co-immobilized*. Overall, the used denpol was found to be a very useful macromolecular linker for simple and stable enzyme immobilization on silicates.

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**pH-dependent Degradation Kinetics of Polylactic Acid**

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Polylactic acid (PLA) is a biodegradable and biocompatible polymer. Due to its properties it raised significant interest in the biomedical field, where it is often employed in drug delivery applications. The knowledge of the degradation kinetics of PLA has a key role when designing such drug releasing devices, as it allows modulating their release profiles. Among the different parameters affecting the PLA degradation kinetics, pH is one of the most relevant ones. While previous studies clarified the pH-dependent degradation mechanisms occurring (acid-, base- and non-catalyzed), the values of the corresponding kinetic constants were actually provided only at specific pH values.<sup>[1-3]</sup>

In this frame, the aim of this work is to study the degradation of lactic acid oligomers as a function of pH in a wide range of values of interest for biomedical applications. In particular, the degradation of oligomers with chain length varying from 2 to 8 repeating units was followed at 37°C for pH values equal to 1, 3.5, 5.7 and 7.4. These experimental data, along with those previously reported at pH = 2<sup>[1]</sup>, are used to develop a detailed kinetic scheme and evaluate the corresponding kinetic constants. The resulting deterministic, pH-dependent model is able to describe the experimental data with reasonable accuracy and an average error of about 5%. The following values of the kinetic constants have been estimated: , (acid-catalyzed), , (base-catalyzed) and (non-catalyzed). Notably, these kinetic constants can be used to study also the degradation of PLA polymer chains, as the values have been found to be chain-length independent from the tetramer on. Taking advantage of the results of this kinetic analysis and accounting for the diffusion limitations typical of PLA biomedical devices (e.g. nano- and microparticles), a predictive modeling of the degradation behavior becomes possible for a wide range of pH conditions.

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**Synthesis of oriented nano-wires on a microfluidic platform**

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Oriented nano-wires offer novel building blocks for next-generation electronic devices. Localized formation of well-defined nano-wires in bulk is challenging due to limited control. Control of reaction and also localization is provided by microfluidic systems with volumes of a few hundreds picoliter. Controlled and reproducible orientation of formed nanowires however remains challenging today but is essential for further applications.

Here, we analyze the controllability and reproducibility of position and orientation on the bottom-up formation of metal-organic nano-wires.

Here, in a microfluidic channel system of polydimethylsiloxane polymer with pneumatic valves, silver is electroless deposited after reduction of a Ag(I) salt and reacts with tetracyanoquinodimethane (TCNQ). Consequently, AgTCNQ wires are formed by diffusion-controlled self-assembly which are influenced by narrow microchannel or additional confined geometries in the reaction vessel.

Controlling the position and orientation of newly formed structures provides enhanced possibilities of application of AgTCNQ but also other metal-organic nano-wires for synthesis and *in-situ* application for microelectronic circuits that could be used as gas-sensing elements.[1]

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**Poly (N-isopropylacrylamide-co-tris-nitrilotriacetic acid acrylamide) for a combined study of molecular recognition and distance constraints in protein binding and interactions**

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Many biological processes require precise regulation and synergy of proteins, and consequently involve molecular recognition and spatial constraints between biomolecules. Here, a library of poly (N-isopropylacrylamide-co-tris-nitrilotriacetic acid acrylamide) (PNTs) has been synthesized and complexed with  $\text{Cu}^{2+}$  in order to serve as models for investigation of the combined effects of molecular recognition and distance constraints in biomolecular interactions. The distance between  $\text{Cu}^{2+}$ -trisNTA binding sites in PNTs polymers was varied from 2 nm to 13.3 nm by adjusting their trisNTA contents. His tag ( $\text{His}_6$ ), his-tagged enhanced yellow fluorescent protein ( $\text{His}_6$ -eYFP) and his<sub>6</sub>-tagged collagenase G ( $\text{His}_6$ -ColG), with sizes ranging from 1 to 11 nm, were used as models to assess whether the binding ability is influenced by a cooperative topology based on molecular recognition interaction with  $\text{Cu}^{2+}$ -trisNTA binding sites, and distance constraints between trisNTAs. His-tagged molecules bound to all PNTs polymers due to their molecular recognition interaction involving histidines and  $\text{Cu}^{2+}$ -trisNTA pockets, but with a binding ability that was highly modulated by the distance between the trisNTA binding sites. Small molecular mass molecules ( $\text{His}_6$ ) exhibit a high binding ability to all PNTs polymers, whereas his-tagged proteins bind to PNTs efficiently only when the distance between trisNTA binding sites is at least equal to the protein dimensions.

**Mass spectrometric analysis of the enzymatic polymerization of p - aminodiphenylamine (PADPA) in the presence of vesicles as templates**

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<sup>1</sup>ETH Zurich

The aniline dimer *p*-aminodiphenylamine (PADPA) was polymerized in high yield with *Trametes versicolor* laccase in the presence of negatively charged vesicles consisting of sodium bis(2-ethylhexyl)sulfocuccinate (AOT) at pH = 3.5, analogous to the polymerization of aniline with the same type of enzyme and vesicles [1]. The vesicles act as 'reaction regulators' for both polymerization reactions, *i.e.* the outcome of the reactions strongly depends on the presence of the vesicles. The vesicles are soft interfaces which "steer" the course of the reactions towards the desired end products. In the case of the polymerization of PADPA, it was found that intermediary reaction products can be extracted and analyzed by UV/Vis/NIR absorption and mass spectroscopy. ESI-MS measurements indicate that the presence of AOT vesicles has a significant influence on the chemical structure of these intermediates which form during the polymerization reaction. Comparative measurements were carried out in the absence of vesicles but otherwise identical conditions.

Acknowledgements: We thank Louis Bertschi from the MS Service Lab, LOC, ETHZ for his support in the analysis of the reaction intermediates with ESI-MS, and the Swiss National Science Foundation for financial support (SNF project number: 200020\_150254)

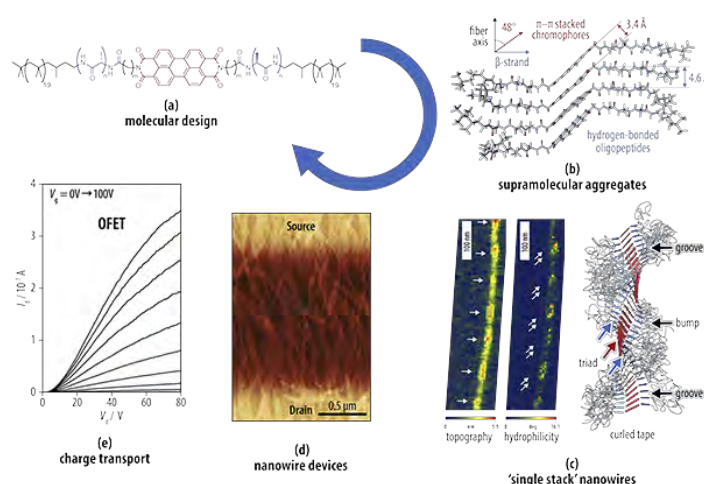
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## Structure-Property Relationships in Self-Assembled Perylene Bisimide Nanowires

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One-dimensional nanowires and microfibers from small molecules or  $\pi$ -conjugated polymers are important building blocks for the fabrication of nanoelectronic devices and provide model systems for charge transport in organic semiconductors under nanoscopic confinement. We investigated the relationship between molecular structure, supramolecular arrangement of the chromophores, and charge transport within self-assembled nanowires from perylene bisimides with oligopeptide-polymer side chains. The preparation of hierarchically structured microfibers of aligned nanofibrils allowed for a comprehensive structural characterization on all length scales with molecular level precision.<sup>[1]</sup> We prove that conformational flexibility between the hydrogen-bonded oligopeptides and the  $\pi$ - $\pi$  stacked chromophores is a key requirement for synergistically enhanced  $\pi$ - $\pi$  interactions and hydrogen bonding. The combination of beneficial  $\pi$ - $\pi$  stacking, long-range order of the  $\pi$ -conjugated segments, and the directionality of the nanowires within thin films result in remarkably high conductivity after n-type doping. Moreover, we show that the capability to efficiently transport charge carriers through such nanowires ultimately depends on a delicate balance between  $\pi$ - $\pi$  and other supramolecular interactions.<sup>[2]</sup> Our results show that there is a complex interplay between the universal translation of molecular chirality into supramolecular helicity and the molecules' inherent propensity to form  $\beta$ -sheet-like aggregates. The result is a twofold odd-even effect in electronic circular dichroism spectra, depending on both the number of L-alanine units in the oligopeptides and the length of the alkylene spacer between the chromophores and oligopeptide substituents. We demonstrate that even derivatives with similar molecular structures and self-assembly behavior can have significantly different electron mobilities that appear to correlate with the nature of their electronic CD spectra. It is, hence, not generally sufficient to prepare one-dimensional aggregates of  $\pi$ -conjugated molecules in order to obtain self-assembled nanowires. Instead, the exact molecular arrangement within the aggregates and, consequently, even supposedly minor details of the molecular structure may play an important role.



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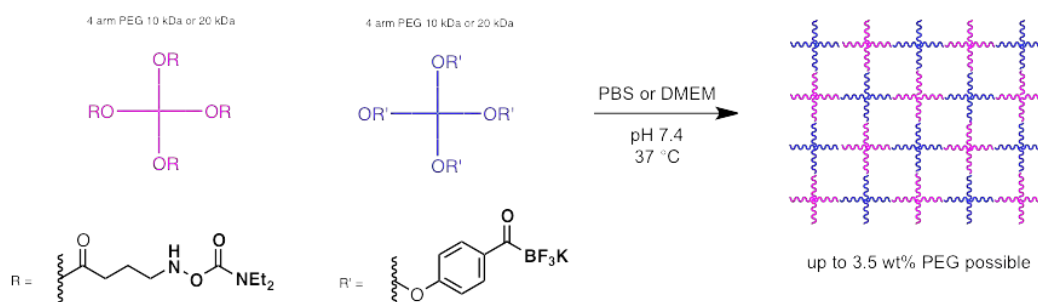
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## Synthesis of biocompatible PEG-based hydrogel by Potassium Acyltrifluoroborate (KAT) Amide-Formation

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<sup>1</sup>ETH Zurich

A novel ligation reaction forming a native amide bond was exploited to synthesize a PEG-based hydrogel under physiological conditions (37 °C and pH 7.4) and shown to be biocompatible. Additionally, the formation of the hydrogel is pH sensitive and allow to tune finely the gelation time by small changes in pH (from pH 2 to pH 7.4). These advantages, combined with a straightforward synthesis of both building blocks could provide a new bio-orthogonal reaction.



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**Charging Behavior of Negatively Charged Particles in Presence of Multivalent Cations**

Mohsen Moazzami Gudarzi<sup>1</sup>, Plinio Maroni<sup>1</sup>, Michal Borkovec<sup>1</sup> \*

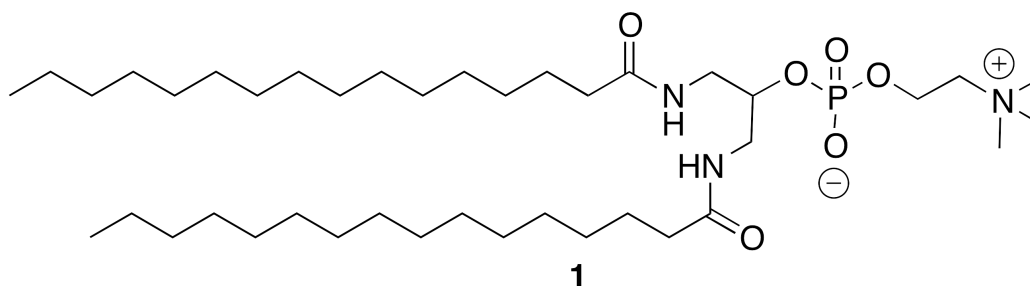
<sup>1</sup>University of Geneva

The surface forces between negatively charged colloidal particles interacting through aqueous medium containing organic multivalent cations, oligoamine (mono to hexamers), are measured using atomic force microscopy. In the line with classical expectation, the power of cations for neutralization and screening the surface charges is determined by the valence of cations. Moreover, in the case of tetra, penta and hexamer inversion of charge from negative to positive is observed due to ion adsorption. The adsorption of ions is reversible and no saturation level in charge inversion is detected in the case of high valence oligomers, even at concentration of four orders magnitudes higher than charge reversal point.

The core finding of this study is the surface forces between the particles can be interpreted by DLVO theory at large distances (typically 5nm). This actually implies multivalent ions screen the electrical double layer similar to what predicted by Poisson-Boltzmann theory, whether as counter ions or coions. In addition, these results indicate non-DLVO interactions are not in action at long range.

**1,3-Diamidophospholipids and Analogous Lipids: Synthesis and Characterization**Dennis Müller<sup>1</sup>, Andreas Zumbühl<sup>1</sup> \*<sup>1</sup>University of Fribourg

We are interested in exploring the frontiers of phospholipid chemistry. Therefore we are focusing in the rearrangement and modification of natural phospholipids. A shift of the natural substitution pattern to an artificial 1,3-substitution at the backbone leads to a membrane stabilization through leaflet interdigitation. Herein we report the synthetic strategies and biophysical properties of selected phospholipids with a 1,3-substitution pattern. Pad-PC-Pad **1**, a phospholipid with a 1,3-substitution pattern and an amide linker between the tails and the backbone, was recently synthesized in the group.<sup>[1]</sup> In aqueous solution **1** self-assembles into vesicles that are mechanosensitive: they release their content, if they are exposed to shear stress.<sup>[2]</sup> This property is unique and allows the use of this type of vesicles as drug-carriers in targeted drug delivery for e.g. first-line treatment of acute heart attack patients.



The mechanism of the mechanosensitivity has however not been investigated. Here we aim to modify **1** in specific positions to address this question. We evaluate the influence of different tail length, which directly influences the transition temperature of the vesicles. Further experiments aim to test the impact of different linker groups between backbone and tail of the phospholipid on the ability to form hydrogen bonds. In the future, the availability of artificial phospholipid vesicles with a defined mechanosensitivity will allow to generate drug delivery systems which meets the needs of individual patient.<sup>[3]</sup>

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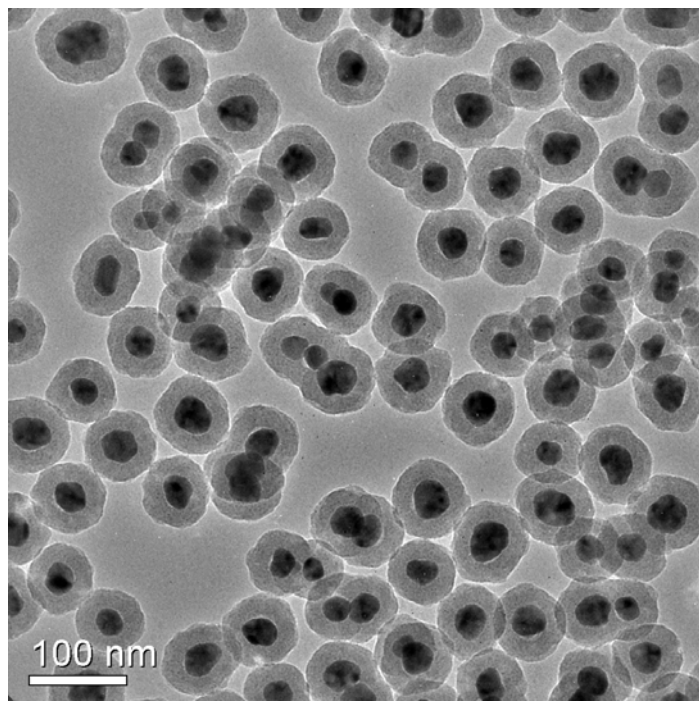


## Preparation of PDMS/AgNPs nanocomposites with enhanced electromechanical properties

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The blending of inorganic nanoparticles into polymers allows access to a large variety of materials which show enhanced electrical, thermal, mechanical, magnetical or optical properties. In particular, silver nanoparticles (AgNPs) have gained a lot of attraction for its array of properties that can be tuned through the control of size and morphology offered by the *polyol synthesis*.<sup>1</sup> The high polarizability of the AgNPs allows to increase the dielectric constant  $\epsilon$  of polymer based nanocomposites such as polydimethylsiloxane (PDMS)/AgNPs. In this work, Ag nanostructures of different size and shape were subjected to surface functionalization which consists of silica-coating<sup>2</sup> (see picture below) and surface hydrophobization<sup>3</sup> followed by blending into the polymeric PDMS matrix in order to give polymer/metal nanocomposites with improved dielectric properties.



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**Characterization of Artificial Phospholipids and Interactions with Cholesterol**

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Phospholipid vesicles can be used as biocompatible drug carriers. Today 13 liposomal drug formulations are approved for in human use.<sup>[1]</sup>

Recently, we introduced a new approach in targeted drug-delivery: mechano-sensitivity.<sup>[2]</sup> Vesicles formulated from the artificial phospholipid Pad-PC-Pad release their payload when they are exposed to shear stress but stay tight when they are at rest.

Monolayer and bilayer studies showed that the mechano-sensitivity is induced by an interplay of intermolecular forces such as van der Waals forces and hydrogen bonding acting on the structure of the bilayer. This hypothesis is based on a high elasticity of the monolayer and the lentil-shape of large unilamellar vesicles (bilayers). Moreover, contrary to DPPC:cholesterol mixtures, Pad-PC-Pad:cholesterol mixtures show no main phase transition above 30 mol% cholesterol content. Pad-PC-Pad fatty acyl tails interdigitate, leading to a strong membrane ordering by itself and therefore reducing the amount of cholesterol necessary for inducing a liquid ordered phase.

In this contribution we provide an update on Pad-PC-Pad:cholesterol interactions measured in mono- and bilayers.

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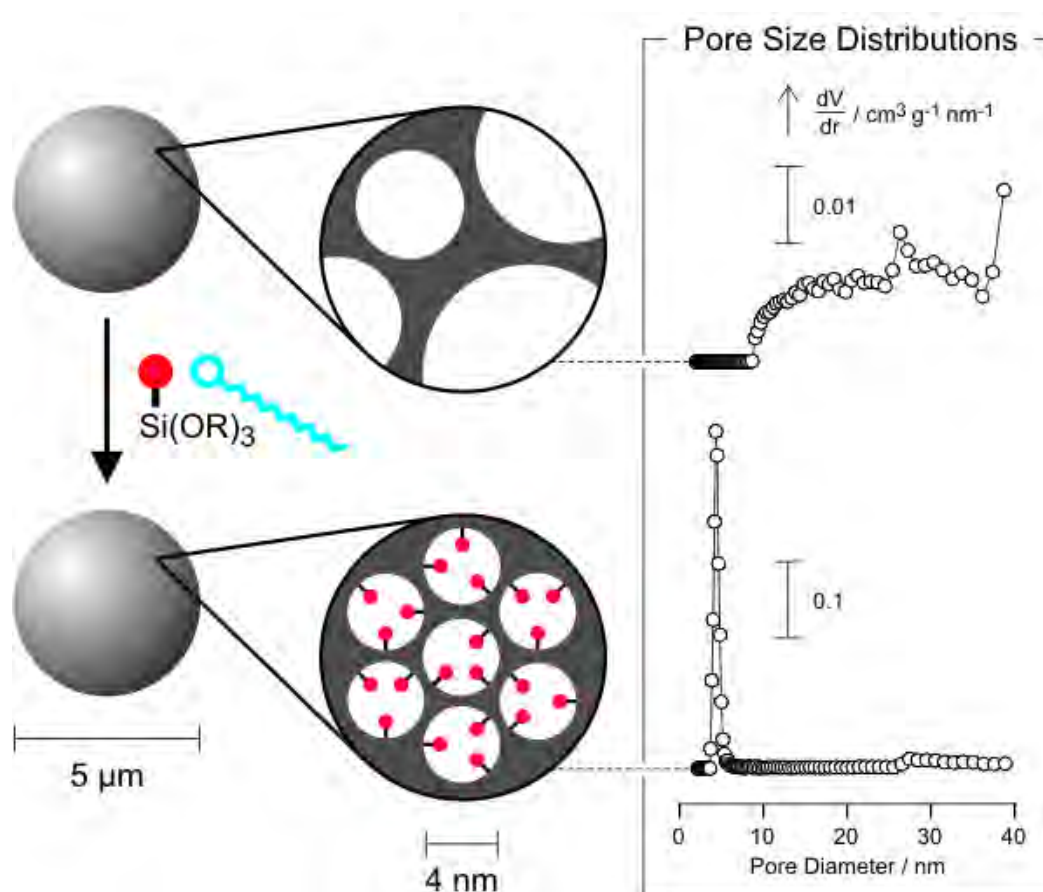
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## Pseudomorphic transformation and simultaneous functionalization of silica microspheres

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Amino-functionalized mesoporous silica microspheres are synthesized by a one-pot synthesis from a parent silica gel.[1] Narrow pore size distributions are obtained with alkyltrimethylammonium structure-directing agents. By following the pseudomorphic transformation pathway [2], the particle size distribution and spherical morphology of the parent silica gel are retained during the synthesis. The products contain accessible and uniformly distributed amino groups. The ratio of small uniform mesopores (diameter less than 5 nm) to larger mesopores and macropores can be controlled by adjusting the concentration of the amino-functionalized silane precursor, leading to a variety of meso-macroporous hybrid materials. The external surface of the predominantly mesoporous spherical particles can be selectively functionalized by postsynthetic grafting.[3]



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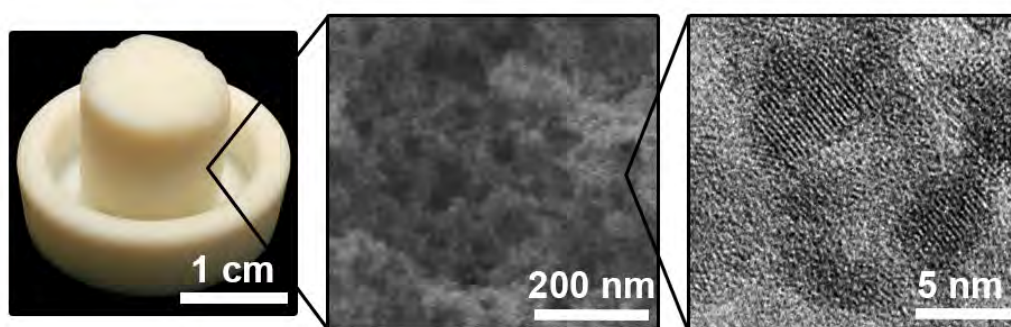
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## Assembly of BaTiO<sub>3</sub> Nanocrystals into Macroscopic Aerogel Monoliths with High Surface Area

Felix Rechberger<sup>1</sup>, Florian Heiligttag<sup>1</sup>, Martin Süess<sup>1</sup>, Markus Niederberger<sup>1</sup> \*

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Aerogels with their low density and high surface area are fascinating materials with great application potential.[1] Replacing the sol-gel process by a particle-based assembly route represents a powerful alternative to expand the accessible functionalities of aerogels, to increase the compositional variety and to improve the crystallinity. We present a strategy of assembling nanocrystalline BaTiO<sub>3</sub> building blocks into cylindrically shaped monolithic gels, thereby combining the inherent properties of ternary oxides with the highly porous microstructure.[2]



The gelation mechanism is based on a rapidly induced destabilization of a highly concentrated BaTiO<sub>3</sub> nanoparticle dispersion. After supercritical drying the obtained aerogels showed a homogenous and open-porous percolating BaTiO<sub>3</sub> network and an unprecedentedly high surface area of over 300 m<sup>2</sup> g<sup>-1</sup>.

Starting from nanoscale building blocks and ending with centimeter sized bodies, the proposed bottom-up approach expands over seven orders of length scales, and the use of perovskite nanoparticles introduces another level of potential functionality.

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## **Influence of the Potential Barrier on the Breakage of Colloidal Aggregates under External Shear Flows**

Zhiqiang Ren<sup>1</sup>, Marco Lattuada<sup>1</sup> \*

<sup>1</sup>University of Fribourg

In this work the effect of interactions on the breakage of colloidal clusters was investigated. The understanding of this is of crucial importance to better design nanoparticles redispersion and coagulation processes. The colloidal aggregates under simple shear and elongational flows were analyzed in this paper by means of Stokesian Dynamics simulation. A library of clusters made of identical spherical particles covering a broad range of masses and fractal dimension values (from 1.8 to 3) have been generated by means of a combination of several Monte-Carlo methods. The hydrodynamic interactions among the particles have been accounted for by Stokesian Dynamics. DLVO theory has been used to describe the interparticle interactions, while contact forces, described by means of discrete element method, have been included to provide the clusters with realistic structural rigidity. The aggregates breakage process was investigated by exposing them into a well-defined shear forces, generated under both simple shear conditions and elongational flow. To investigate the evolution of aggregate size and morphology, respectively, the mean radius of gyration and the cluster fractal dimension were monitored during the breakup process. Considerable attention has been given to understand the effect of electrostatic repulsive interactions on both the breakage rate and cluster fragment mass distribution. It has been found that the breakage rate of clusters was controlled by the potential barrier between particles that was dominated by DLVO theory. A semiempirical exponential equation that related to potential barrier and the breakage rate has been proposed.

**Preparation of composite materials from aqueous nanoparticles mixed suspensions**

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<sup>1</sup>University of Fribourg

Since the term 'nanocomposites' has been introduced in 1970, numerous procedures for the preparation of nanocomposite materials have been investigated in order to generate materials with controlled features, which is still one of the great challenges in nanotechnology.

The purpose of this work is to use the extended and large knowledge of self-assembly behavior of spherical nanoparticles in aqueous solutions and its dependence on interparticle interactions for the preparation of various polymeric nanoparticles and the investigation of their self-assembly, to generate hybrid nanostructured composites.

The nanocomposites are prepared by blending together two colloidal suspensions made of charged particles. The first one is a suspension of hard silica nanoparticles (20 nm diameter) at different concentrations, while the second one consists of soft poly(butyl acrylate/methyl methacrylate) copolymer particles (80 nm diameter). The advantage of working in aqueous suspensions is that interparticles interactions of charged nanoparticles can be controlled. In order to investigate the specific role of such interactions on the final structure and mechanical properties of the materials, the nanocomposites have been synthesized following three different assembly strategies. The first one consists of simply mixing of stable particle suspensions with same surface charge. In the second case, instead, the filler particles were subject to aggregation and gelation while the matrix particles remained in stable suspension. The last case is that of hetero-aggregation of silica and rubber particles suspensions bearing opposite surface charges.

The solvent (i.e., water) was removed from all samples, which have been annealed, giving rise to nanostructured polymeric composites. All samples structure and mechanical properties have been characterized using different techniques (SAXS, AFM, SEM, tensile tests).

**Protein cage-polymer conjugates synthesized by atom transfer radical polymerization as a delivery platform for siRNA**

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The thermosome (THS) from *Thermoplasma acidophilum* is a protein complex with two cavities. It is composed of two hemispheres. Each hemisphere is assembled from alternating  $\alpha$ - and  $\beta$ -subunits. Its size is around 16 nm in diameter. THS has gated pores that enable macromolecules to enter and exit the cavities. A genetically modified variant of THS was used, which had cysteine residues on the inside of every  $\beta$ -subunit for site-selective attachment of thiol-specific ATRP-initiators<sup>1</sup>. 2-(Dimethylaminoethyl) methacrylate (DMAEMA) was used as monomer for polymerization under Activator ReGenerated by Electron Transfer (ARGET) ATRP conditions, using 1,1,4,7,10,10-hexamethyltriethylene tetramine as ligand and sodium ascorbate as reducing agent. Poly(DMAEMA) is cationic at physiological conditions and can therefore interact with negatively charged molecules like siRNA<sup>2</sup>. THS-Poly(DMAEMA) was used to encapsulate siRNA and deliver it to cells. Protein cage-polymer conjugate protect siRNA from degradation by RNases. In addition the cage structure shields positive charges of polycationic polymers from cells, which reduces toxicity.

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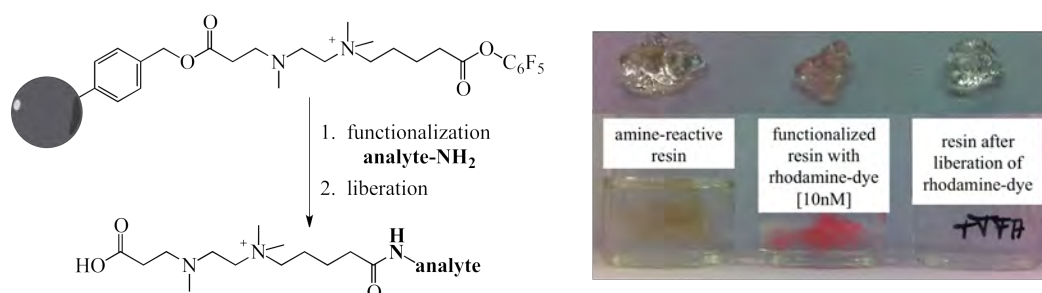
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## Functional Polymeric Resins for the Improved Detection of Drugs and Quantification of Neurotransmitters

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In most physiological systems both, the concentration of neurotransmitters as well as of a broad variety of drugs is in the nano-molar range. Even today, performing the detection as well as the quantification of an analyte in this concentration regime is extremely challenging and requires extensive sample preparations.<sup>[1]</sup> Additionally, these analyses are mostly limited to one single analyte at a time. Previously, a robust synthetic technique allowing for multiple orthogonal post-polymerization modifications of highly functionalized Ring-Opening Metathesis Polymers has been developed in our group.<sup>[2]</sup> Taking advantage of this model, an amine-reactive polymeric resin is utilized in order to analyze samples collected from animal brains, regarding their composition of mono-amine neurotransmitters. With this method, a variety of analytes can be detected all at the same time.



Due to the incorporation of a quaternary ammonium group into the linker unit, permanently charged analytes are created. During subsequent mass spectrometric analysis, this intrinsic charge causes not only a higher sensitivity but additionally, an improved signal-to-noise ratio and thereby facilitates their detection in the nano-molar concentration range. The same polymeric resin is currently under investigation for its application in improved drug usage screening in order to test for the abuse of amphetamines, methylhexanamine (DMAA) and other illegal substances containing amino groups.

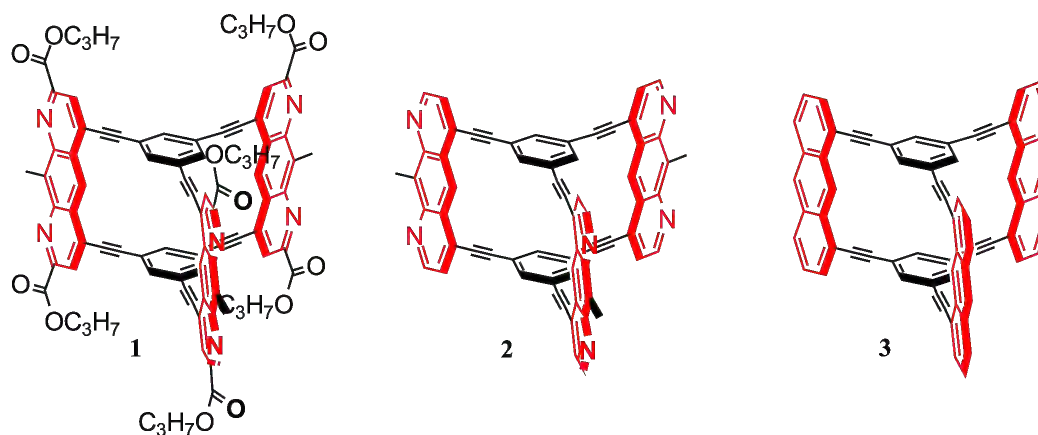
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**Propeller-shaped macrocycles with three 1,8-diazaanthracene and three anthracene blades as monomers for topochemical 2D-polymerisation**Marco Servalli<sup>1</sup>, Junji Sakamoto<sup>1</sup>, A. Dieter Schlüter<sup>1</sup> \*<sup>1</sup>ETH Zurich

The so called “single crystal approach” has proven to be a reliable tool for synthesizing two-dimensional polymers (2DP) [1]. This method involves the crystallization of a photoreactive monomer into lamellar single crystals. In every layer of the crystal, the monomers are packed, so that the photoreactive units (anthracene moieties) can react with each other topochemically upon photoirradiation, converting each layer into a two-dimensional polymer. By solvent-induced exfoliation, the single molecular sheets can then be isolated. While the size of the 2DP is limited by the size of the single crystals, this method allows a facilitated characterization: information on the periodical internal structure can be obtained by conventional techniques such as SC-XRD [2, 3]. The synthesis of suitable monomers, which have to be rationally designed, can be however challenging and therefore much effort has been put into reducing the overall synthetic effort and number of steps.



We here present a set of propeller-shaped monomers: 1,8-diazaanthracene-based monomers **1** and **2** and the hydrocarbon anthracene-based monomer **3**. These macrocycles were synthesised by Sonogashira cross-coupling chemistry from accessible building blocks. While **1** and **2** offer the possibility of functionalization (post-polymerisation modification) and ensure that the photoreactive units will stack face-to-face in the crystal due to the methyl group at the **9**-position, **3** displays a higher crystallizability with single crystals being formed from a variety of solvents, according to which, face-to-face or edge-to face interactions are preferred. An overview on the synthetic strategy and different crystal structures will be shown, providing an insight into the challenges of this fascinating topic.

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**Immobilization of Biomimetic Block Copolymer Membranes on Solid Supports**

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The functionalization of surfaces through biomimetic block copolymer membranes aims at developing smart surfaces for biotechnological applications such as biosensing. Amphiphilic block copolymer membranes were chosen instead of lipid membranes as mimics of biological membranes because of their properties, such as thickness, chemical and mechanical stability, lower permeability, fluidity, mobility, etc. Upon insertion of membrane proteins, these systems could allow for the preparation of mechanically and chemically robust and air-stable biosensor devices.

Surface-initiated atom transfer radical polymerization (ATRP) provides a good control of the brush thickness by controlling polymer molecular weight and by initiating polymerization of a second monomer from the chain end of the first. Poly(2-hydroxyethyl methacrylate)-b-poly(*n*-butyl methacrylate)-b- poly(2-hydroxyethyl methacrylate), PHEMA-b-PBMA-b-PHEMA block copolymers were synthesized with the first PHEMA block anchored to a self-assembled monolayer on the gold surface while the other PHEMA block exposed to the outer surface. To this end, a self-assembled monolayer of (BrC-(CH<sub>3</sub>)<sub>2</sub>COO(CH<sub>2</sub>)<sub>11</sub>S)<sub>2</sub>) initiator was formed through a covalent binding of disulfides to gold. Then, HEMA monomer was polymerized by ATRP. The first PHEMA block initiated the polymerization of BMA. Subsequently, the second PBMA block again initiated HEMA polymerization, thus resulting in a triblock copolymer membrane anchored to the gold substrate. Block copolymer brushes were prepared with different block lengths and characterized on the gold surfaces using different characterization methods.

The formation of the self-assembled monolayer was successfully characterized by AFM, contact angle and X-ray photoelectron spectroscopy (XPS), providing information on the presence of chemical elements and their binding energies, and therefore on the structure of the initiator on the surface. Contact angle, ATR-FTIR, and AFM measurements were taken to monitor the ATRP synthesis. PHEMA brushes render the surface smoother and more hydrophilic, whereas PBMA brushes result in a rougher, more hydrophobic surface. The thickness was measured layer by layer by surface plasmon resonance (SPR), with an overall thickness of 12 nm.

The thickness was well-tuned in order to obtain a suitable model for the use as a biomimetic membrane. Moreover, to predict a suitable model, the grafting density was varied by mixing the ATRP initiator with a molecule inert to ATRP reaction. It was shown that lowering the grafting density contributes to decrease the layer thickness. Therefore, a grafting density higher than 70% of the brushes on surfaces can be used as models for further protein insertion experiments. The polymer brushes with a hydrophilic-hydrophobic-hydrophilic sequence can be regarded as the first example of solid supported, biomimetic block copolymer membranes prepared by a "grafting-from" approach.

**Forces Between Silica Particles in Ionic Liquids and Ionic Liquid-Water Mixtures**

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In recent years, Ionic Liquids (ILs) have attracted considerable interest among the scientific community in account of their unique physicochemical properties, and the advantage to tune them by systematic choice of cation's and anion's molecular structure and combination. Indeed, ILs emerged as great candidates for many interesting applications, such as solar cells, fuel cells and batteries, dispersants, solvents for organic synthesis, catalysis and nanoparticle synthesis [1].

Relatively little has been done to study the behavior of particle suspensions in ILs as well as the IL-solid interface, and even less to study IL-water mixtures [2, 3]. Our work is addressed to characterize forces between particles in pure ILs and in the whole dilution range of IL-water mixtures, giving a qualitative and eventually quantitative interpretation of the data acquired.

Forces between 5  $\mu\text{m}$  silica particles have been measured using Atomic Force Microscopy (AFM) colloidal probe technique [4] in three different imidazolium based ILs.

For the ILs studied, the force curves in IL-water mixtures show qualitatively similar features. At very low concentrations (up to 10mM), the forces are electrostatic in nature, where the double layer repulsion decreases with the IL concentration. The fitted Debye length can be predicted by Poisson-Boltzmann theory, suggesting that ILs behave like classical electrolytes over this concentration range. Increasing further the IL concentration, the resulting force is attractive due to dispersion forces. In pure ILs, step-like force profiles are observed, showing layering of ILs molecules on the surface, whose order decreases going from the surface to the bulk.

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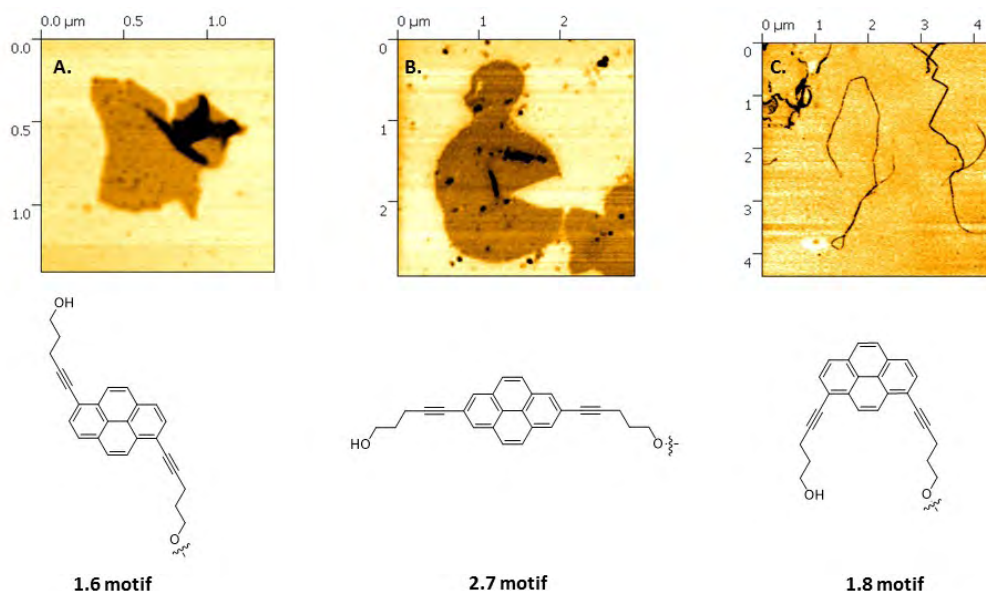
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## Morphological diversity of supramolecular polymers formed by amphiphilic pyrene oligomer

Mykhailo Vybornyi<sup>1</sup>, Robert Häner<sup>1</sup> \*

<sup>1</sup>University of Berne

We demonstrate that a substitution pattern of phosphodiester-linked pyrene building blocks in short amphiphilic oligomers (trimers) determines the morphology of the formed supramolecular assemblies. Thus, 1.6- and 2.7-linkages lead to a formation of micrometer-sized 2D supromolecular polymers with a constant thickness 2 nm (see Figure below, pictures A and B) [1]. These assemblies possess a high degree of an internal order: the interior consists of hydrophobic pyrenes and alkyl chains, whereas the exterior exists as a net of hydrophilic negatively charged phosphates. But, a 1.8-linkage exclusively leads to a formation of long nanometer thick helical supramolecular polymers (picturee C) [2]. These structures tend to form more complex assemblies (bundles, superhelices). Moreover, for all samples the supramolecular polymerization process proceeds via a nucleation-elongation mechanism. To study Py<sub>3</sub> self-assembly, we carried out a whole set of spectroscopic (UV/vis, fluorescence, DLS) and microscopic experiments (AFM).



**Figure:** AFM pictures illustrating the morphological diversity of supramolecular polymers formed by differently linked pyrene oligomers.

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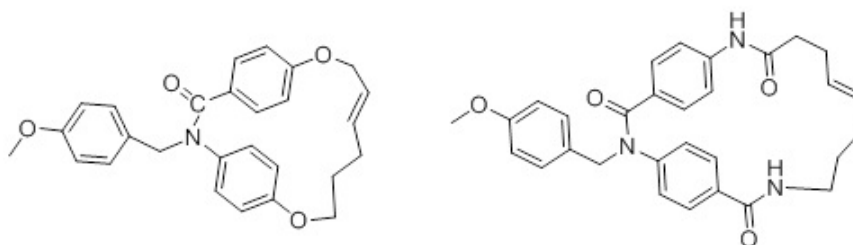
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**Strained Aramide Macrocycles for Ring-Opening Metathesis Polymerization**

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Polycondensation methods are usually used for synthesizing polyamides which fail to provide well defined and high molecular weight polymers. Our intention is to replace conventional polycondensation methods with Ring-Opening Metathesis Polymerization (ROMP)<sup>[1]</sup> to obtain polymers with higher molecular weight and narrow polydispersity and even block copolymers. In order to perform ROMP, strain can be induced in the macrocycles by controlling the geometry of the amide bonds. The open monomer unit is fixed to *cis*-conformation with respect to phenyl rings by amide N-protection<sup>[2]</sup> which also allows the Ring Closing Metathesis (RCM)<sup>[3]</sup> to obtain the cyclic monomer. Acid cleavable *p*-methoxybenzyl (PMB) protecting group is a suitable option for this synthesis. The unprotected amide has been proved to isomerize to the *trans*-conformer<sup>[4]</sup> thereby inducing a ring strain needed to perform ROMP. These polymers are expected to have semicrystalline nature.



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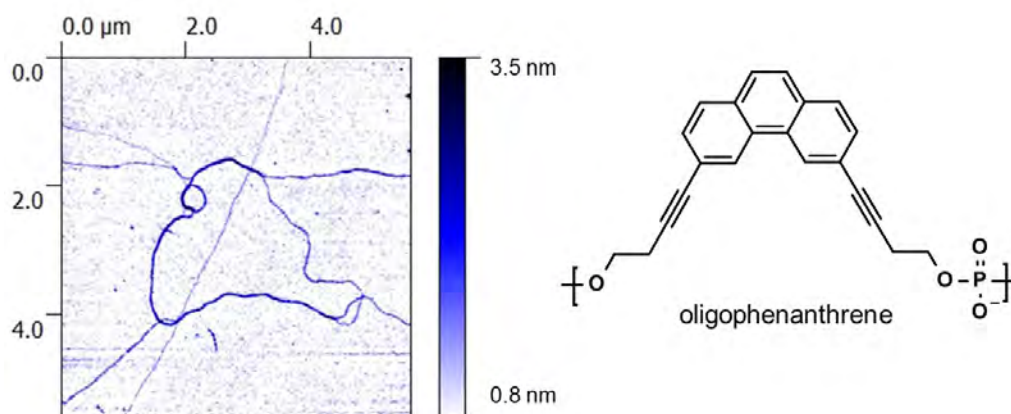
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## Building Polymer Light Harvesting Antennas

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Photosynthesis is the key process which enables life on earth. In photosynthesis, specialized pigment-complexes collect light and transform it into electronic excited states which are delivered to reaction centers to initiate charge separation<sup>1</sup>. Building artificial light harvesting systems is a brainteaser and many groups came up with ideas to mimic the outstanding scopes of light harvesting systems. This current work combines two of our recent projects to design powerful artificial light harvesting antennas. Garo et al. reported on phenanthrene and pyrene molecules to build DNA based light harvesting antennas<sup>2</sup>. In another project linear water soluble polymers based on polyaromatic hydrocarbons (PAH) and a DNA-like phosphate backbone were successfully built<sup>3</sup>.



We will report on the preparation of phenanthrene oligomers and their formation of supramolecular polymers in aqueous conditions. We will present the spectroscopic properties (absorption and fluorescence spectra) as well as morphological studies (AFM) of the formed polymers. Furthermore, the effect of acceptor chromophores will be described.

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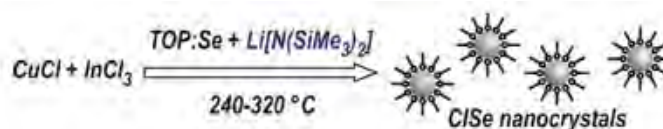
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## Generalizable amide-promoted approach for high-quality multicomponent semiconductor nanocrystals

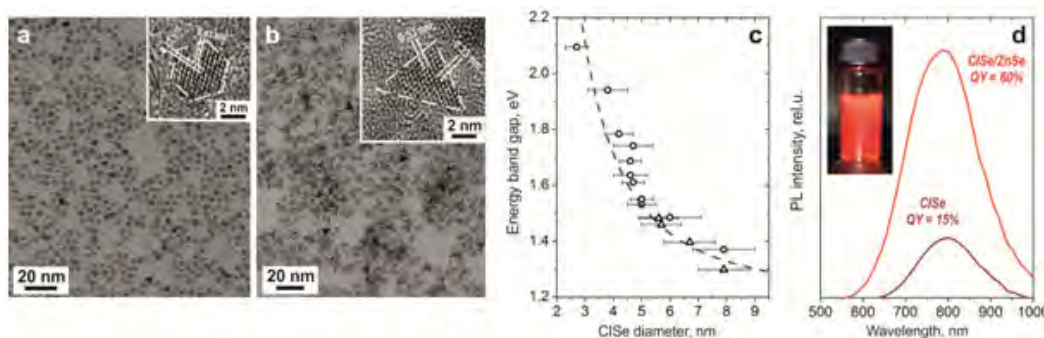
Olesya Yarema<sup>1</sup>, Maksym Yarema<sup>1</sup>, Vanessa Wood<sup>1</sup>

<sup>1</sup>ETH Zurich

Because of suitable band gaps, high luminescence efficiencies, and relatively low toxicity, multicomponent chalcopyrite nanocrystals are considered perspective candidates for thin film photovoltaics, lighting devices, and medical applications.<sup>1</sup> However, the synthesis of colloiddally-stable I-III-VI and I-(II;IV)-VI materials remains under-developed. Here, we present a simple, high-yield colloidal synthesis of multicomponent chalcopyrite nanocrystals based on an amide-promoted approach.<sup>2</sup> This approach differs from conventional hot-injection syntheses of nanocrystals by the presence of (silyl)amide-anions in the reaction mixture, which notably speed up the reaction rate on the nucleation stage (See scheme below). Nearly quantitative reaction yields, balanced reactivities of cations, and precise composition control are among the benefits of this amide-promoted synthesis. While this strategy was successfully applied to make various binary chalcogenides,<sup>3</sup> here we will present the first use of (silyl)amide-promoted synthesis to achieve high performance ternary and quaternary compounds.



Here, I will discuss results for copper indium selenide (CISE), silver indium selenide (AISE), and quaternary complexes with zinc (CIZSe and AIZSe). The figure below shortly summarizes the results for the case of CISE nanocrystals.<sup>2</sup> By introducing a specific concentration of silylamide-anions in the reaction mixture, the shape of CISE nanocrystals can be preselected to be nearly spherical or tetrahedral (a,b). The size of the CISE nanocrystals is precisely controlled to be between 2.7 and 7.9 nm with size distributions down to 9–10%. Most importantly, CISE nanocrystals possess size-tunable emission, which, after the ZnSe shell protection, can reach the record values of 50-60% (c,d).



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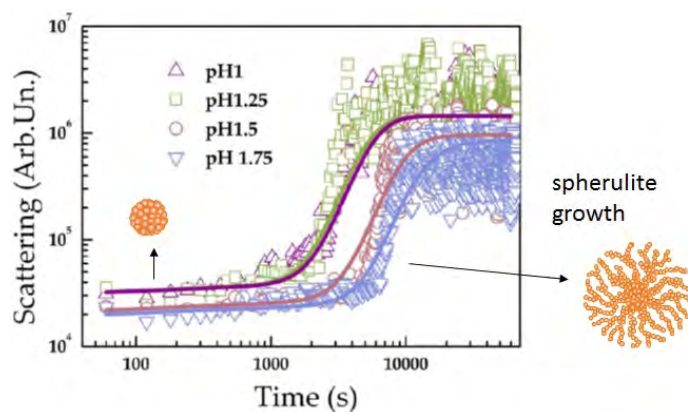
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**Linking self-assembly, rheology and critical behaviour in chemical and colloidal gels**Alessio Zaccone<sup>1</sup>, Matthias Ballauff<sup>2</sup>, Henning Winter<sup>3</sup><sup>1</sup>University of Cambridge, <sup>2</sup>Humboldt University Berlin, <sup>3</sup>University of Massachusetts, Amherst

We propose a microscopic framework based on nonequilibrium statistical mechanics to connect the microscopic level of particle self-assembly with the macroscopic rheology of colloidal gelation. The method is based on the master kinetic equations for the time evolution of the colloidal cluster size distribution, from which the relaxation time spectrum during the gelation process can be extracted. The relaxation spectrum is a simple stretched-exponential for irreversible diffusion-limited colloidal aggregation gelation, with a stretching exponent  $df/3$ , where  $df$  is the mass fractal dimension. As opposed to glassy systems, the stretched-exponential relaxation does not result from quenched disorder in the relaxation times, but from the self-assembly kinetics in combination with the fractal character of the process. As the master kinetic equations for colloidal aggregation do not admit bond-percolation solutions, the arrest mechanism is driven by the interconnection among fractal clusters when excluded volume becomes active, i.e., at sufficiently high packing of clusters. The interconnections between rigid clusters decrease the soft modes of the system and drive a rigidity-percolation transition at the cluster level. Using the Boltzmann superposition principle, the creep and the full rheological response can be extracted for both irreversible and thermoreversible colloidal aggregation. In the case of thermoreversible gelation, the attraction energy is finite and plays the role of the control parameter driving a nonequilibrium phase transition into a nonequilibrium steady-state (the gel). A power-law spectrum coexisting with a stretched-exponential cut-off is predicted leading to power-law rheology at sufficiently high frequency. Our theory is in good agreement with experimental data of different systems published by other authors, for which no theory was available.



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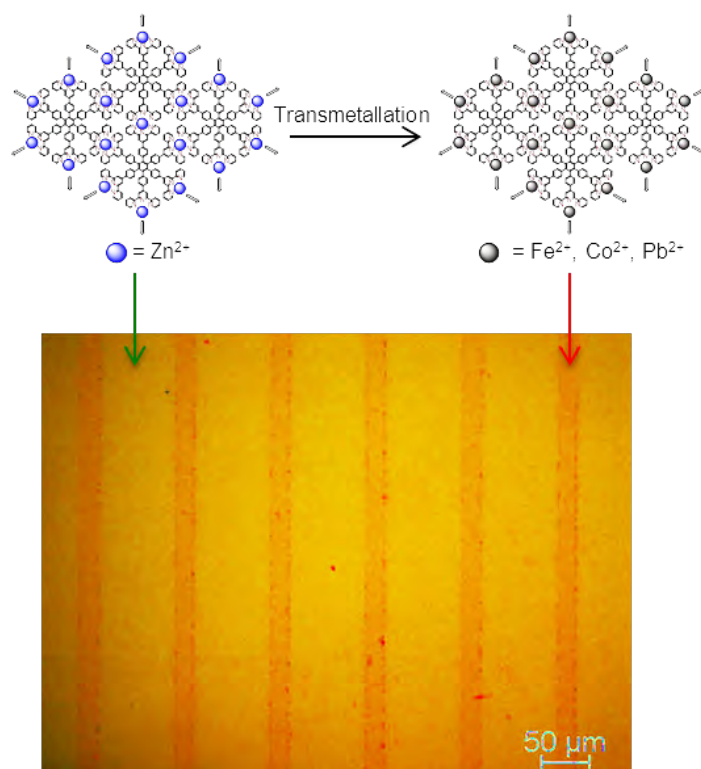


## Synthesis of Monolayer Metal-organic Sheets

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Monolayer sheets such as graphene, hexagonal boron nitride and the like have gained intensive interest both from academy and industry. However, these sheets cannot be accessible through mild organic synthesis processes that would allow rational design and precise control. Here we present a general method for rational synthesis of metal-organic sheets under mild conditions.<sup>1,2</sup> It rests on the connection of monomers at air-water interface with metal ions. These sheets obtained are one-monomer unit thick and are mechanically stable enough to be spanned over  $20 \times 20 \mu\text{m}^2$  holes. Interestingly, site-to-site transmetalation of  $\text{Zn}^{2+}$  in Zn-based sheets to  $\text{Fe}^{2+}$  ( $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ ) can be achieved on the  $\text{cm}^2$ -sized scale.<sup>3</sup> This novel transformation was done both randomly and at predetermined patterns defined by photolithography to create monolayer sheets comprised of different metal ions-based netpoints. Such transmetalated sheets with random and patterned netpoints can be considered as two-dimensional analogues of linear copolymers. Their nanoscale synthesis presents an advance in monolayer/polymer chemistry with applications in fields such as surface coating, molecular electronics, device fabrication, imaging and sensing.



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