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COMMUNICATION

Microporous polymer network films covalently bound to gold electrodes

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Daniel Becker,^{†a} Nina Heidary,^{†b,d} Marius Horch,^b Ulrich Gernert,^c Ingo Zebger,^b Johannes Schmidt,^a Anna Fischer^{*b,d} and Arne Thomas^{*a}

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Covalent attachment of a microporous polymer network (MPN) on a gold surface is presented. A functional bromophenyl-based self-assembled monolayer (SAM) formed on the gold surface acts as co-monomer in the polymerisation of the MPN yielding homogeneous and robust coatings. Covalent binding of the films to the electrode is confirmed by SEIRAS measurements.

The possibility to combine the advantages of porous materials with the functionalities found in organic molecules has made microporous polymer networks (MPNs) an emergent research field.¹ The introduction of various functional groups into the backbone of MPNs has led to applications in catalysis,² energy conversion and storage³ or gas sorption⁴ and separation.⁵ Recently also the promising properties of MPNs in organic electronic devices were described.⁶ The first microporous polymers prepared using the concept of rigid, contorted tectons to avoid dense packing of polymer chains (polymers of intrinsic microporosity, PIMs),⁷ were soluble and thus processable from solutions. However, it had been later recognized that very high surface areas and structural stability can be reached when a higher degree of crosslinking is realized, yielding the development of MPNs. Unfortunately, due to their cross-linked structure MPNs are insoluble and inmeltable, which make any processing nearly impossible, a serious drawback for a range of envisaged applications. This is especially true for possible applications in organic electronic devices for which MPNs must be

processed as thin films on electrodes. Other possible applications of MPNs requiring film morphology comprise gas separation membranes and catalytically active coatings.

Consequently, several groups have attempted the synthesis of films or other morphologies of MPNs. The PIM approach was further extended to microporous, conjugated dendrimers,⁸ or MNP nanoparticles⁹ which could be as well processed from solutions. A further improvement was made by the design of novel organic cages, soluble in many solvents and advantageously self-aggregating into porous crystals after solvent removal.¹⁰ Some examples are reported in which MPNs are deposited on surfaces present during synthesis.^{11,6b} Also electropolymerizable films have been grown on surfaces, for example using carbazole functionalized tectons.¹² Naturally, this approach is restricted to monomers which can be electropolymerized (such as carbazole or thiophene functionalized tectons).¹³ However it has been reported that conjugated polymer films made by electropolymerization are not effective for organic electronic applications as some of the electrolyte used during synthesis inevitably stays in the polymer films, thus strongly influencing their electronic properties.¹⁴

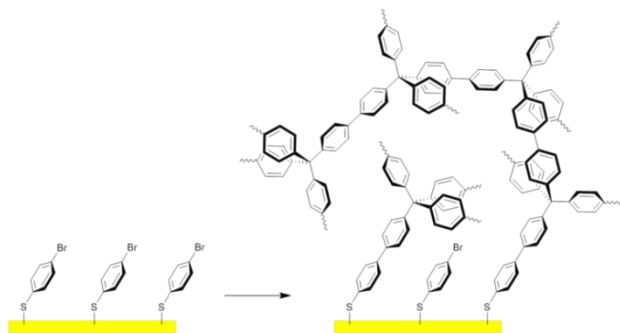
In all these approaches the polymer/electrode interface is not well controlled and it can be assumed that films are attached to the surfaces just by dispersion forces, thus potentially prone to electrode / surface detachment. This would certainly be advantageous in case free-standing films or membranes are targeted. However, for other e.g. electrocatalytic or organic electronic applications formation of stable films on electrodes is an essential requirement.

A more controlled attachment of films to electrode surfaces was developed in the field of metal organic frameworks (MOFs). Surface bonded MOFs (SurMOFs) can be grown from functional self-assembled monolayer by a layer-by-layer process.¹⁵ A similar approach has been used to produce ultrathin films of molecular networks on amine terminated SAMs.¹⁶ In another relevant approach, organic films and later free standing membranes of polymer carpets were fabricated by cross-linking of SAMs.¹⁷

^a Department of Chemistry, Functional Materials, Technische Universität Berlin, Hardenbergstr. 40, 10623 Berlin. ^b Department of Chemistry, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin ^c Center for Electron Microscopy (ZELMI), Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin. ^d Universität Freiburg, Institut für Anorganische und Analytische Chemie, Albertstrasse 21, 79104 Freiburg.

[†] These authors contributed equally to this work

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Scheme 1 Illustration of the synthesis of PPN-6 films on 4-bromophenyl functionalized gold substrates.

Motivated by these works we attempted to grow a MPN onto an electrode surface by first covalently attaching a functional monomer which can take part in the polymerization of the MPN (Scheme 1). A gold surface was chosen as being a superior electrode and amenable to modification by SAMs. The gold surface was functionalized with 4-bromothiophenol since halogenated aromatic compounds are the moieties which are applied in the most frequently used C-C-bonding reactions for the synthesis of MPNs, such as the Sonogashira-Hagihara,¹⁸ Yamamoto¹⁹ or Suzuki²⁰ coupling. Provided that the forming polymer reacts with the exposed bromine atoms of the SAM, the formed MPN should be tightly connected to the surface by covalent bonds. Indeed, formation of homogeneous films of the MPN on the gold surface could be achieved as seen from scanning electron microscopy (SEM) as well as the covalent attachment *via* the SAM to the gold surface, which is proven by surface enhanced infrared absorption (SEIRA) spectroscopic measurements (see SI for synthetic details).

For the generation of covalently bound MPN films on gold electrodes a Yamamoto-type coupling was chosen. This C-C-type coupling reaction, which is frequently used for the generation of MPNs, requires just one type of monomer, namely halogen functionalized aromatic monomers, which can be homo-polymerized into high surface area networks.¹⁹ Tetrakis(4-bromophenyl)methane was applied as monomer. Yamamoto polymerization of this monomer in bulk yields a MPN called “PAF-1” with an extraordinary high BET surface area of 5600 m²g⁻¹.^{21a} The synthetic protocol for PAF-1 was further improved by Zhou et al. thereby renaming PAF-1 to “PPN-6”.^{21b} Since in the present work the latter protocol was applied the here described polymers are as well entitled PPN-6. To prepare bromophenyl functionalized gold films, cleaned gold wafers were immersed in an ethanolic solution of 4-bromothiophenol for 16 hours. It should be noted that the simplicity of SAM formation allow for a broad variety of covalently attached functional groups on gold electrodes, which in principle could be also used for various other polymerization reactions. The synthesis of the microporous polymer network PPN-6 was carried out in presence of these bromophenyl-functionalized gold films. In case the bromophenyl-SAM molecules on the gold surface act as comonomers in the Yamamoto polymerization, it can be expected that films of PPN-6 are growing from the surface and as a result are covalently attached to it. All experiments were carried out using an additional blank, i.e. unfunctionalized gold film, within the same reaction environment. While for the blank samples no change in

appearance was observed after the polymerization reaction, on SAM-functionalized gold surfaces thin coatings have formed (Fig. S1). Before this coating was further analyzed, the reaction protocol was verified by analyzing the bulk polymer powder (PPN-6), which has additionally precipitated from solution by ¹³C solid-state NMR and ATR-FTIR measurements (Fig. S2,3). Nitrogen sorption (Fig. S4) revealed an apparent surface area of 2977 m²/g which is a remarkable high value even though lower than the value of 4023 m²/g reported by Zhou et al. for PPN-6.^{21b} This might be due to slight changes in our reaction protocol compared to the reported procedure. Still the ¹³C-NMR and nitrogen sorption measurements confirm the successful synthesis of PPN-6 using the here applied reaction protocol. Unfortunately, these techniques could not be applied to the polymer films due to the low amount of sample mass (see a discussion on Kr-Sorption measurements in the SI, Figure S5).

To investigate the formed MPN films, SEM analysis was carried out. Fig. 1a) shows a top view of the MPN film grown on the SAM-functionalized gold electrode. For better visibility a location on the substrate was chosen, where the polymer film only partially covers the gold surface. The polymer film is very smooth and homogeneous. However, some larger particles are also found to be located on top of the polymer film. This becomes even more apparent in the cross section SEM picture (Fig. 1b-f).

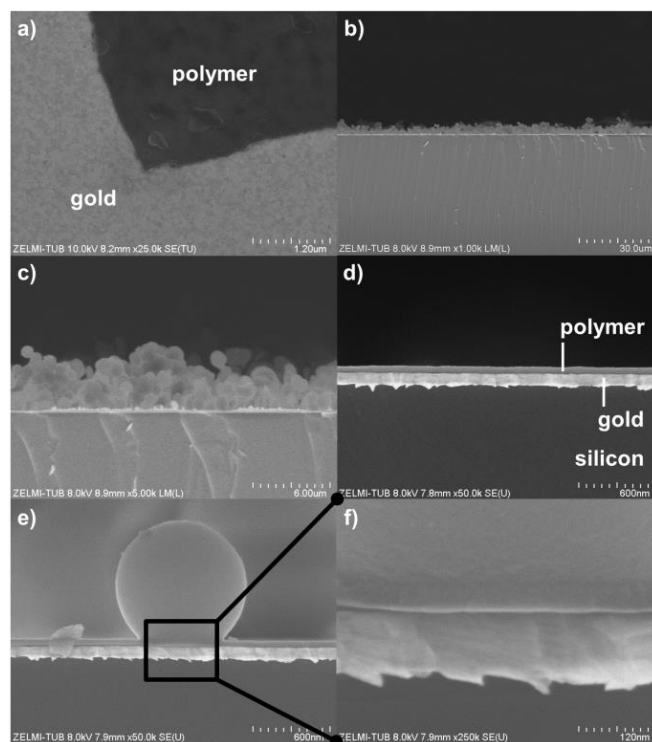


Fig. 1 SEM micrographs of PPN-6 film grown on gold substrate *via* Yamamoto cross coupling reaction. Top view (a) and cross section (b-f) micrographs showing increasing magnification from b to f.

It can be assumed that the homogenous polymer layer is formed by polymerization of monomers in solution with the bromophenyl moieties attached to the gold surface. On top of this dense polymer layer a second open polymer layer has been formed, which consists of agglomerates of polymer spheres. It can be reasoned that this layer consists of polymer particles firstly formed in solution and

subsequently bound to the homogeneous primary polymer layer *via* terminal bromine groups. Fig. 1e clearly shows the primary polymer layer and a polymer particle bound to it. This is further supported by investigating the films after different reaction times (Fig. S6). Already after 18 min reaction time a thin, homogeneous polymer film can be observed on the gold substrate and just a few larger particles can be spotted on top of this film. With ongoing reaction time both the thickness of the film and the number of particles increase (Fig. S7) and after 20 h reaction time, a second, open layer of agglomerated particles is formed. EDX line and spot scans confirm the elemental composition of both the structures that grow atop the homogeneous film and the film itself (Fig. S8). The polymer films cannot be detached from the surface when treated with solvents like THF overnight, which further supports the covalent binding of PPN-6 to the gold substrate. However, swelling yield cracks in the polymer films (Fig. S9), which is consistent with a surface attached polymer film that suffers from structural strain caused by swelling and drying. It should be mentioned that even though in most cases the blank gold films are unaffected by the reaction, in rare occasions the formation of polymer films was also observed on the blank gold substrates. So far we were not able to find a systematical explanation to predict when polymer films are formed on unfunctionalized gold films. Anyway, these films are easily detached from the gold surface by solvent treatment (Fig. S9), confirming again that the surface functionalization by SAMs is necessary to yield MPN films covalently bound to the surface.

To further prove the involvement of the SAM in the polymeric film formation and surface attachment to the gold surface, in-situ SEIRAS measurements were carried out. In this case the thin nanostructured gold film acts also as IR signal amplifier to probe molecules near the gold surface. As the surface enhancement decreases strongly with distance,²² SEIRAS can be applied as a surface sensitive method to study mono- und multilayer formation up to a thickness of about 8 nm. In such way, SEIRAS allows to monitor the covalent binding of the 4-bromothiophenol monolayer to the gold surface.

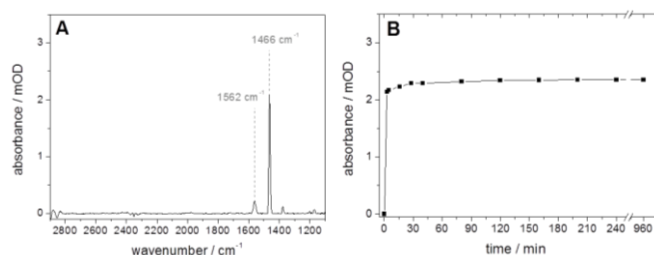


Fig. 2 SEIRA spectrum recorded immediately after incubation of the gold film with SAM solution (A) and time evolution of 4-bromothiophenol monolayer formation over 16 hours monitored by the aromatic C=C stretching band 1466 cm^{-1} (B).

Fig. 2 displays the binding of 4-bromothiophenol to the gold surface directly after incubation of the gold film with the SAM solution, as indicated by the characteristic bands of the aromatic $\nu(\text{C}=\text{C})$ stretching vibrations at 1562 cm^{-1} and 1466 cm^{-1} . The “disappearance” of bands compared to the FTIR bulk reference spectrum (Fig. S10) can be explained considering the SEIRAS selection rule, i.e. only vibrations with predominant dipole moment

changes perpendicular to the surface are enhanced, while vibrations parallel to the surface remain unamplified. Fig. 2B displays the time evolution of the SAM formation during an incubation period of 16 hours. Thereby, the most intensive aromatic band at 1466 cm^{-1} was chosen as marker for the monolayer formation on the gold surface. A biphasic behavior is observed, with a primary, exponential process related to a completed SAM adsorption within the first 30 minutes and an additional, slight but continuous intensity increase over the remaining 16 hours. The secondary process can be potentially attributed to rearrangements of thiol molecules. Therefore, a longer incubation time of SAM solution onto the gold surface leads to a more homogeneous monolayer formation. Subsequent removal of the SAM-containing solution and several rinsing cycles with ethanol did not affect the overall band intensities, indicating a strong binding of thiol to the gold surface *via* covalent Au-S bonding. In addition no remaining S-H modes could be detected. Fig. 3 shows the spectra before and after the Yamamoto coupling reaction and careful rinsing of the SEIRA cell. For clarity we plotted the respective difference spectrum obtained by subtracting the spectrum recorded before from the one taken after the polymerization reaction (Fig. 3C). In such way a decrease of the characteristic bands of the aromatic $\nu(\text{C}=\text{C})$ stretching at 1562 cm^{-1} and 1466 cm^{-1} can be monitored, while new bands at 1602 cm^{-1} and 1492 cm^{-1} appear. These significant band shifts of 40 cm^{-1} and 26 cm^{-1} to higher wavenumbers are a good indication for the ongoing reaction *via* the bromine-groups of the SAM, i.e. the formation of new C-C bonds between the aromatic ring of the SAM and the phenyl groups of tetrakis(4-bromophenyl)methane under elimination of the bromide end groups of the SAM.

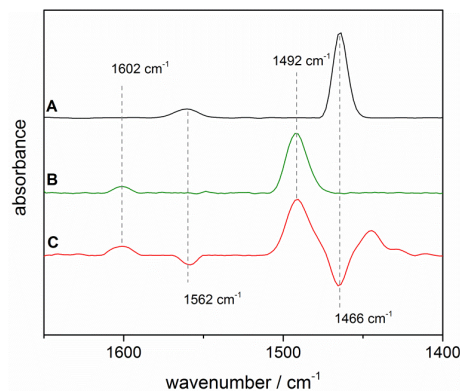


Fig. 3 SEIRA spectra of the SAM recorded in the adsorption equilibrium after 16 hours (black, A), subsequent to the Yamamoto-like coupling reaction (green, B) and difference spectrum (B minus A i.e. after minus before Yamamoto reaction) (red, C). Positive bands are related to the emerging polymer matrix, negative bands are characteristic for the consumed (incorporated) SAM.

Notably, similar shifts to higher wavenumbers of approximately 29 cm^{-1} and 35 cm^{-1} are predicted by DFT calculations for the C=C vibrations of a molecular model system composed of one 4-bromothiophenol molecule linked to one monomer species in vacuum (Fig. S10-12). Thus, it can be concluded, that the film formation is indeed initiated at the $-\text{Br}$ terminated surface, resulting in a covalent attachment of the MPN film to the gold electrode.

Conclusions

Films of the microporous polymer network PPN-6 were grown on SAM-functionalized gold electrodes. SEIRAS measurements confirm the covalent binding of PPN-6 to the gold surface and prove that SAM molecules act as co-monomers in the polymerization reaction. In future this approach will be extended to other cross-coupling reactions. The here presented method has therefore strong implications for the deposition of functional microporous polymers and constitutes an important step to the formation of organic electronic devices.

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