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Redox mediation enabled by immobilised centres in the pores of a metal–organic framework grown by liquid phase epitaxy†André Dragässer,^a Osama Shekhah,^b Olexandra Zybaylo,^b Cai Shen,^c Manfred Buck,^c Christof Wöll*^b and Derck Schlettwein*^a

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A layer of a metal–organic framework (SURMOF) was prepared on a thiol monolayer on Au. Charge transport across the insulating membrane could be established by using ferrocene as an immobilised redox mediator. Reversibility of the immobilisation and its role in the electrode kinetics are discussed.

The prospect of functionalizing surfaces by deposition of a highly ordered porous material and loading of its open voids with functional molecules is a very attractive method to produce coatings with adjustable properties.¹

The most flexible type of frameworks available today are metal–organic frameworks, MOFs, with more than 1000 different types having already been published.^{2–5} Recently, several protocols have been demonstrated to yield well defined, homogenous coatings with well-defined thicknesses.⁶ Such porous coatings are of interest for gas separation, for chromatography,⁷ and also for electrical and electronic applications, including solar cells, organic electronic devices and electrochemical sensors.^{8,9} In this context, it is of pronounced interest to explore the charge transport characteristics and redox properties of MOFs. Dithiolene-based MOFs, *e.g.*, showed p-type conduction and could be reversibly oxidised.^{10,11}

Proton-conduction was reported for MOFs consisting of carboxylate or sulfonate groups in the framework.^{12–14} A clear influence of molecules embedded in the pores of the MOF was found.^{12,13} Surface photovoltage spectroscopy (PVS) at a MOF based on a manganese phosphonate demonstrated p-type conductivity.¹⁵ With regard to the rather promising properties established for bulk MOFs, an ability to tune the electrical properties of SURMOFs would close a fundamental gap of knowledge and open the door to attractive applications as electrodes.

We have therefore carried out an investigation of the electro-chemical properties of highly ordered, crystalline HKUST-1 films deposited on modified gold substrates using liquid phase epitaxy (LPE).¹⁶ Cyclic voltammetry was used to characterise the charge transport properties of this SURMOF by employing a diluted ionic liquid (IL) as an inert electrolyte and ferrocene (Fc), which can be loaded into the SURMOF from the gas phase,¹⁷ as a suitable inner-sphere redox system.^{18,19}

A self-assembled monolayer (SAM) of mercaptohexadecanoic acid (MHDA)²⁰ was prepared on polycrystalline Au evaporated on Si. The HKUST-1 SURMOF was grown on top of this SAM by immersion in a solution of Cu(CH₃COO)₂·2H₂O and subsequently in a solution of benzenetricarboxylic acid (H3btc). The cycles were repeated to obtain a 40 layer HKUST-1 SURMOF with a thickness of 52 nm (1.3 nm per layer²¹). All HKUST-1 SURMOFs were characterised by X-ray diffraction (XRD) in a θ –2 θ -geometry using Cu K α radiation to prove the structure¹⁶ before all subsequent measurements were carried out (ESI†, Fig. S1). The samples were placed in a petri dish and heated to 45 °C, 60 °C or 100 °C in air for 20 minutes to evaporate excess solvent and were then exposed to a vapour of ferrocene (Fc) to load Fc into the HKUST-1. Based on earlier experiments, about 1 Fc per pore can be estimated.¹⁷ Cyclic voltammograms (CVs) were measured in contact to 10 mM Fc in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][NTf₂] at a scan rate of 20 mV s^{–1} using standard electrochemical equipment in a N₂ glove box. For the removal of Fc, samples treated at 60 °C (see above) were immersed in ethanol for 48 hours. To reload Fc, the loading procedure described above was repeated after heating to 60 °C for 20 minutes. Details of sample preparation and characterisation are described in ESI.†

In Fig. 1 we display cyclic voltammograms recorded for a modified gold substrate coated with an MHDA-SAM as well as for an HKUST-1 SURMOF directly after synthesis. The results recorded for the modified Au substrate were almost identical to experiments on pure Au. The results are in accord with previously published electrochemical data using water-based electrolytes for SAMs deposited on a Au surface.²² These results demonstrate the presence of a facile electron transfer from the electrode to Fc⁺ (reduction, cathodic, negative currents) and *vice versa* from Fc to the Au-electrode through the MHDA-SAM (oxidation, anodic, positive currents). It is remarkable that the peaks are separated by only 100 mV which

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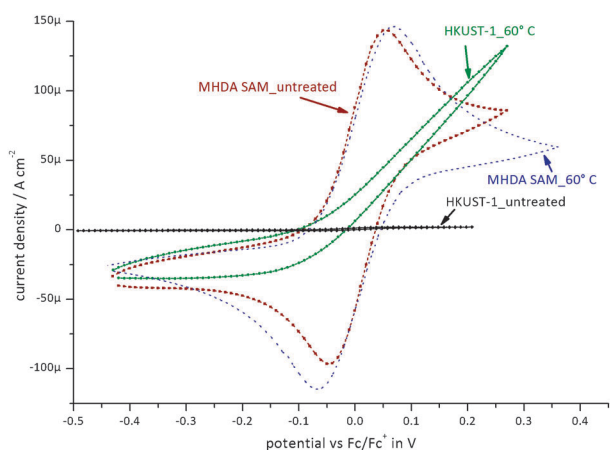


Fig. 1 CV at 20 mV s^{-1} for a MHDA-terminated Au surface in contact with [BMIM][NTf₂] with 10 mM Fc in comparison to an identical surface covered with the SURMOF HKUST-1 and such a surface following conditioning by soft annealing and exposition to a Fc atmosphere.

is close to the 59 mV expected for a diffusion-limited Nernstian reaction.²³ The CVs shown in Fig. 1 reveal that, in contrast, the SURMOF deposited on top of the MHDA-SAM (HKUST-1_untreated) rather effectively blocks the charge flow through the film. This blocking behaviour is in line with the rather large band gap of the HKUST-1 MOF (the HOMO–LUMO gap of the btc-unit amounts to $\sim 2.5 \text{ eV}$). If both IL and Fc could diffuse into the pores of the SURMOF equally well, at least some current would be expected. Since the ionic liquid molecules are fairly small and, therefore, can penetrate the MOF quite well,²⁴ the blocking behaviour strongly suggests that diffusion of ferrocene inside the SURMOF is too slow.

In the next step of experiments we have thus investigated the effect of Fc loaded in the pores of the MOF-lattice. Since it is known that after synthesis the pores inside metal–organic frameworks are frequently occupied by solvent molecules we have activated the SURMOF by placing it in a petri dish and heating it to $60 \text{ }^\circ\text{C}$ for 20 min.

Subsequent to Fc treatment of the activated SURMOF the XRD signals clearly showed a change of the relative intensities in the θ – 2θ scans. Such a change in the form factor clearly shows that Fc, which contains an Fe-atom being a strong X-ray scatterer, has been included into virtually all pores of the HKUST-1 SURMOF (ESI†, Fig. S1).

After exposing the activated SURMOF to Fc vapour at RT, the CVs showed a pronounced difference to those recorded for the empty SURMOF, see Fig. 1 (HKUST-1_60 °C). Instead of the blocking seen for the untreated SURMOF, substantial currents exceeding $100 \mu\text{A cm}^{-2}$ were seen for the Fc-loaded SURMOF. Heating an MHDA SAM to $60 \text{ }^\circ\text{C}$ and exposure to Fc vapour in a control experiment showed no change in the CV compared to the bare SAM (Fig. 1, MHDA SAM_60 °C). Therefore the change in the CVs for the Fc loaded SURMOFs cannot be due to a surface layer of Fc. The increased current density in the reduction as well as the oxidation at the Fc loaded SURMOFs (HKUST-1_60 °C) could already be seen for the sample heated to $45 \text{ }^\circ\text{C}$ (ESI†, Fig. S2, HKUST-1_45 °C) but to a significantly increased degree for the sample heated to $60 \text{ }^\circ\text{C}$ (HKUST-1_60 °C).

Although the current densities reached at the positive and negative ends of the scan (HKUST-1_60 °C) were similar to the current densities observed for the bare MHDA-SAM (MHDA SAM_untreated), the CVs exhibited several significant qualitative differences. Instead of the diffusion-limited Nernstian behaviour seen for the uncoated SAM, several features were observed which are typical for an electrochemical current limited by electrode kinetics or charge transport phenomena within the electrode rather than by reactant diffusion. The anodic current slowly increased for positive potential sweeps as opposed to the steep increase observed for the bare MHDA-SAM. The cathodic currents were found to be considerably smaller than the anodic currents. No characteristic features, typical for diffusion-limited reactions, caused by the depletion of reactant concentration at the electrode surface, were observed in the experimental data. Because of this missing depletion of Fc in the solution caused by slower electrode kinetics at HKUST-1_60 °C, slightly larger currents were observed at the positive end of the scan for HKUST-1_60 °C when compared to a bare MHDA-terminated Au surface.

The linear current–voltage characteristics at current densities smaller than those at the uncovered MHDA-SAM indicate limitation of the overall current by charge transport through the electrode, *i.e.* along the Fc moieties in the SURMOF pore system which act as redox mediators. In these scans 1.8 mC cm^{-2} had passed in the anodic branch from -0.08 V to 0.27 V for the bare SAM and 1.3 mC cm^{-2} for the HKUST-1_60 °C.

These characteristics rule out that the electrochemical current is brought about by the electrolyte reaching the SAM-covered substrate through cracks or leaks but demonstrate that the charge is transported through the Fc-loaded channels and pores of the HKUST-1 SURMOF. From the slope of the plot HKUST-1_60 °C we calculate a resistance of $31 \text{ M}\Omega$. From the known sample area, 0.07 cm^2 , and a film thickness of 52 nm we obtain a specific conductivity for the Fc-loaded SURMOF electrode of $2 \times 10^{-9} \text{ S cm}^{-1}$. This value is about 50 000 times higher than that reported for solid Fc which has a conductivity of about 10^{-14} to $10^{-13} \text{ S cm}^{-1}$.²⁵ Such a strong increase of the conductivity upon oxidation has also been observed for crystals of molecular semiconductors like Pentacene²⁶ or Phthalocyanines.^{27,28} Since the mobility of charge carriers typically is higher for highly ordered crystals, this increase is best understood by an increase of the charge carrier concentration consisting of oxidised Fc moieties (hole conduction). This description is equivalent to propose that the Fc acts as an immobilised redox mediator in the SURMOF. We propose that the electron transfer through the film proceeds by hopping transport between adjacent embedded Fc molecules in the SURMOF matrix, beginning with an oxidation reaction of the Fc molecules in contact to the positive electrode^{23,29} and then progressing along the Fc moieties in the SURMOF, finally leading to oxidation of Fc in solution at the outer SURMOF surface. The experimental findings and the proposed electrochemical mechanism are summarised in Fig. 2.

These Fc-induced changes of the SURMOF conductivity were found to be reversible. Removing the Fc from the lattice by immersing the substrates into ethanol for several hours restored the signal seen to that before loading with Fc (Curve Step 2 in Fig. 3). Just a small current density of diffusion-limited

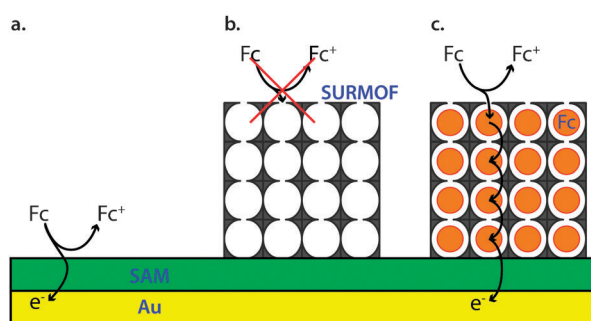


Fig. 2 Schematics of the samples and charge-transfer reactions of the MHD-terminated Au (a), the HKUST-1 on MHD-terminated Au (b) and the HKUST-1 loaded with Fc (c).

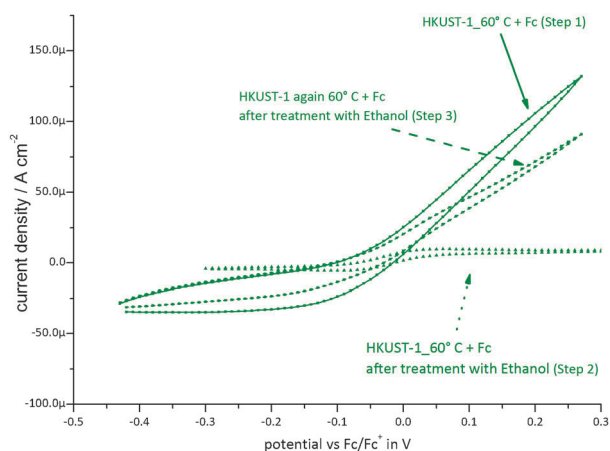


Fig. 3 CVs under conditions as described in Fig. 1 for the HKUST-1 SURMOF on MHD-terminated Au which was heat-treated at 60 °C and loaded with Fc from the gas phase, following desorption of Fc in ethanol solution and following repeated thermal treatment and loading with Fc.

characteristics indicated a minor contact of the redox electrolyte to MHD-SAM or Au. Another cycle of heating to 60 °C and exposure to Fc vapour re-established the redox-mediating characteristics.

The different limitation of the current by either Fc diffusion in the electrolyte observed for the bare MHD-SAM or charge transport along the redox mediator Fc embedded in the SURMOF acting as a series resistance to the electrochemical charge transfer at the interface was confirmed by the contrasting scan rate dependence depicted in Fig. S3 and S4 (ESI†). A typical increase of the current with the square root of the scan rate characteristic for a diffusion-limited Nernstian reaction was observed for the bare MHD-SAM. In contrast, currents widely independent of the scan rate typical for an Ohmic resistor were observed for the Fc-loaded SURMOF.

Annealing of the SURMOF to even higher temperatures of 100 °C before the loading of Fc led to a strong reduction in current which is attributed to a partial collapse of the HKUST-1/MHD-SAM system (ESI†, Fig. S2). Since the characteristic features of the $I(V)$ -curves for the electrolyte in direct contact with the SAM or the bare Au interface are still lacking we conclude that also after the collapse the Au SAM interface is still coated by a solid film. Since the current did not

increase after the loading we conclude that the pores are not accessible for the Fc molecules.

The charge transport properties of a metal–organic framework, MOF, were investigated using electrochemical methods. Whereas thin layers, SURMOFs, of HKUST-1 were observed to be highly insulating, loading with Fc was found to lead to a large increase in conductivity, exceeding that of solid Fc by several orders of magnitude. These findings demonstrate that the charge transport is enabled by the embedded Fc molecules acting as redox-mediators. Our results prove a far reaching potential of high quality thin MOF coatings (SURMOFs) on conducting electrodes for electrochemical and electronic applications.

Notes and references

- 1 A. Götzhäuser and C. Wöll, *Chem. Phys. Chem.*, 2010, **11**, 3201.
- 2 G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191.
- 3 B. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546.
- 4 S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.
- 5 J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3.
- 6 O. Shekhan, J. Liu, R. A. Fischer and C. Wöll, *Chem. Soc. Rev.*, 2011, **40**, 1081.
- 7 Y. S. Li, F. Y. Liang, H. Bux, W. S. Yang and J. Caro, *J. Membr. Sci.*, 2010, **354**, 48.
- 8 C. Janiak, *Dalton Trans.*, 2003, 2781.
- 9 U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastré, *J. Mater. Chem.*, 2006, **16**, 626.
- 10 S. Takaishi, M. Hosoda, T. Kajiwara, H. Miyasaka, M. Yamashita, Y. Nakanishi, Y. Kitagawa, K. Yamaguchi, A. Kobayashi and H. Kitagawa, *Inorg. Chem.*, 2009, **48**, 9048–9050.
- 11 Y. Kobayashi, B. Jacobs, M. D. Allendorf and J. R. Long, *Chem. Mater.*, 2010, **22**, 4120–4122.
- 12 J. Hurd, R. Vaidyanathan, V. Thangadurai, C. I. Ratcliffe, I. L. Moudrakovski and G. K. H. Shimizu, *Nat. Mater.*, 2009, **1**, 705–710.
- 13 S. Bureekaew, S. Horike, M. Higuchi, M. Mizuno, T. Kawamura, D. Tanaka, N. Yanai and S. Kitagawa, *Nat. Mater.*, 2009, **8**, 831–836.
- 14 A. Shigematsu, T. Yamada and H. Kitagawa, *J. Am. Chem. Soc.*, 2011, **133**, 2034–2036.
- 15 D. P. Dong, Z. G. Sun, F. Tong, Y. Y. Zhu, K. Chen, C. Q. Jiao, C. L. Wang, C. Li and W. N. Wang, *Cryst. Eng. Commun.*, 2011, **13**, 3317.
- 16 O. Shekhan, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher, R. A. Fischer and C. Wöll, *J. Am. Chem. Soc.*, 2007, **129**, 15118.
- 17 R. Heck, O. Shekhan, O. Zybalyo, P. G. Weidler, F. Friedrich, R. Maul, W. Wenzel and C. Wöll, *Polymers*, 2011, **3**, 1565–1574.
- 18 D. Podkościelny, S. Gadde and A. E. Kaifer, *J. Am. Chem. Soc.*, 2009, **131**, 12876.
- 19 W. R. Fawcett and M. Opallo, *Angew. Chem., Int. Ed.*, 1994, **33**, 2131.
- 20 R. Arnold, W. Azzam, A. Terfort and C. Wöll, *Langmuir*, 2002, **18**, 3980.
- 21 C. Munuera, O. Shekhan, H. Wang, C. Wöll and C. Ocal, *Phys. Chem. Chem. Phys.*, 2008, **10**, 7257.
- 22 C. E. D. Chidsey, *Science*, 1991, **251**, 919.
- 23 A. J. Bard and L. R. Faulkner, *Electrochemical Methods—Fundamentals and Applications*, John Wiley & Sons, Inc, New York, 2nd edn, 2001, vol. 19.
- 24 O. Zybalyo, O. Shekhan, H. Wang, M. Tafipolsky, R. Schmid, D. Johannsmann and C. Wöll, *Phys. Chem. Chem. Phys.*, 2010, **12**, 8092.
- 25 D. O. Cowan and F. Kaufman, *J. Am. Chem. Soc.*, 1970, **92**, 6198.
- 26 M. Brinkmann, V. S. Videva, A. Bieber, J. J. André, P. Turek, L. Zuppiroli, P. Bugnon, M. Schaer, F. Nuesch and R. Humphry-Baker, *J. Phys. Chem. A*, 2004, **108**, 8170.
- 27 G. D. Sharma, S. G. Sangodkar and M. S. Roy, *Mater. Sci. Eng., B*, 1996, **41**, 222.
- 28 A. Beck, K. Mangold and M. Hanack, *Chem. Ber.*, 1991, **124**, 2315.
- 29 K. Habermüller, M. Mosbach and W. Schuhmann, *Fresenius' J. Anal. Chem.*, 2000, **366**, 560–568.