Electronic Supplementary Information

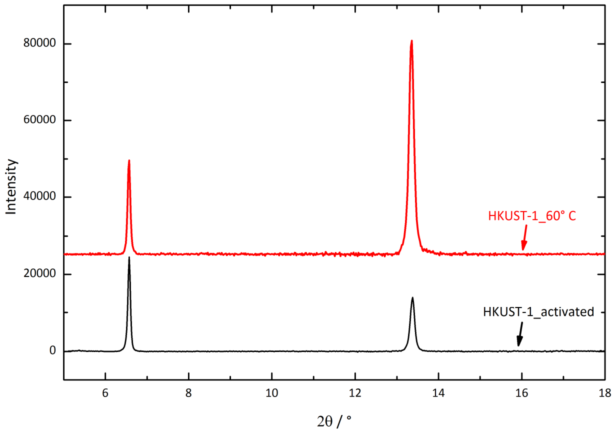

Fig. S1: XRD of a ferrocene-loaded HKUST-1 sample (HKUST-1_60° C) compared to a pristine HKUST-1 after activation at 60° C (HKUST-1_activated). The intensity is normalized to the 6.5 ° signal.

Fig. S1 shows the diffraction peaks of a pristine sample activated at 60° C (HKUST-1_activated) that are expected for HKUST-1[16] and thereby confirms the structure. Changes in X-ray scattering are induced by the uptake of ferrocene (Fc) into the HKUST-1 pore system as shown for HKUST-1_60° C. The crystal structure remains unchanged but the signal intensity is changed by an increased scattering intensity caused by the high scattering yield of Fe atoms in Fc. Fc uptake is thereby confirmed, consistent with an estimated uptake of about 1 Fc per pore as also shown earlier for MOF samples[17].

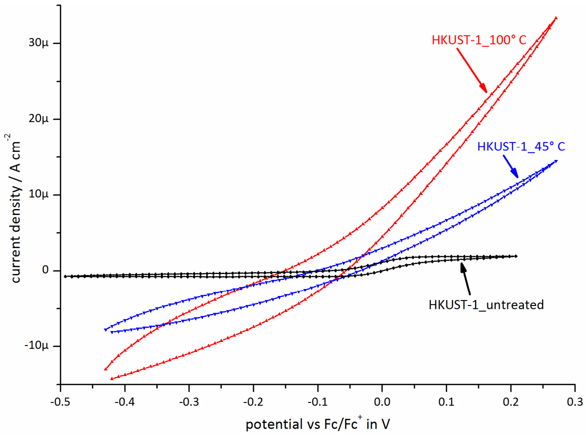

Fig. S2: Cyclic voltammetry in contact to [BMIM] [NTf_2] with 10 mM Fc at 20 mV s^{-1} for a MHDA- terminated Au surface covered with HKUST-1 and following conditioning of HKUST-1 by soft annealing and exposition to a Fc atmosphere as indicated in the plots.

In Fig. S2, cyclic voltammograms of the Fc redox reaction are shown, obtained for differently pre-treated SURMOF samples. The current obtained at an untreated HKUST-1, almost not detectable in the Fig. 1 of the article, can be analysed in more detail here because of a different scale of the Fig.. The shape of the signal is characteristic for a diffusion-limited current and therefore points at the presence of miniature defects (ca. 1% of the overall electrode area) in the insulating SURMOF layer. Increased current density in the oxidation as well as the re-reduction could already be seen for the sample heated to 45° C (Fig. S2, 15 µA cm^{-2} at the positive end of the scan) but to a significantly smaller degree compared to the sample heated to 60° C (Fig. 1, 133 µA cm^{-2} at the positive end of the scan). Annealing of the SURMOF to an even higher temperature of 100° C before the loading of Fc also led to a clearly smaller current density of 33 µA cm^{-2}, which is attributed to a partial collapse of the HKUST-1 / MHDA-SAM system. Since a similar shape of the cyclic voltammogram was observed as for the optimum HKUST-1_60°C (Fig. 1) we conclude that also after the collapse the electrode is still coated by a solid film with, however, significantly decreased accessibility of the pores for the Fc redox mediator.

As expected, Fc in the IL is a mandatory component as could be seen in a control experiment for a Fc loaded SURMOF without Fc in the electrolyte. The current density dropped to 16 µA cm^{-2} at the anodic end of the experiment for a SURMOF following repeated loading and unloading of Fc (Fig. 3) that had shown 42 µA cm^{-2} in the presence of Fc in the IL. The current recovered to only 22 µA cm^{-2} if Fc finally is added again to the IL. Fc obviously was partly dissolved from the SURMOF into the IL leading to these non-stationary characteristics in this case. Limitation of the current by Fc diffusion in the electrolyte was observed for the bare MHDA-SAM by the shape of the voltammograms, typical for a transport-limited reversible redox reaction (Fig. S3). The inset shows the linear increase of the current with the square root of the scan rate, also characteristic for a diffusion-limited Nernstian reaction.

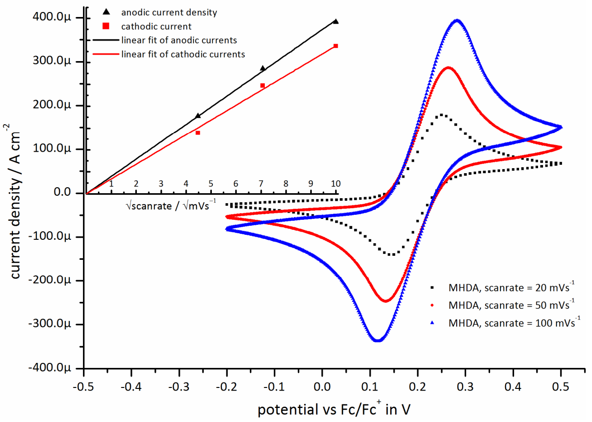

Fig. S3: Cyclic voltammetry under conditions as described in Fig. 1 for scan rates of 20, 50 and 100 mV s^{-1} at the MHDA-SAM on Au. The inset shows the linear dependence of the peak current densities on the square-root of the scan rate.

A current density limited by the electrode kinetics, however, caused by 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 observed by the contrasting scan-rate dependence depicted in Fig. S4. Currents widely independent on scan rate typical for an Ohmic resistor were observed for the Fc-loaded SURMOF. The slightly decreasing currents at the positive end of the scans for the Fc-loaded SURMOF are indicative of a subtle depletion of Fc in the electrolyte at the electrode surface at lower scan rate. Consistently the charge passed in this anodic branch for the bare MHDA-SAM and the Fc-loaded SURMOF were 1.8 mC cm^{-2} or 1.2 mC cm^{-2} (20 mV s^{-1}), 1.1 mC cm^{-2} or 0.5 mC cm^{-2} (50 mV s^{-1}) and 0.8 mC cm^{-2} or 0.3 mC cm^{-2} (100 mV s^{-1}), respectively, showing the resistance caused by the redox mediator Fc as opposed to a completely accessible SAM surface.

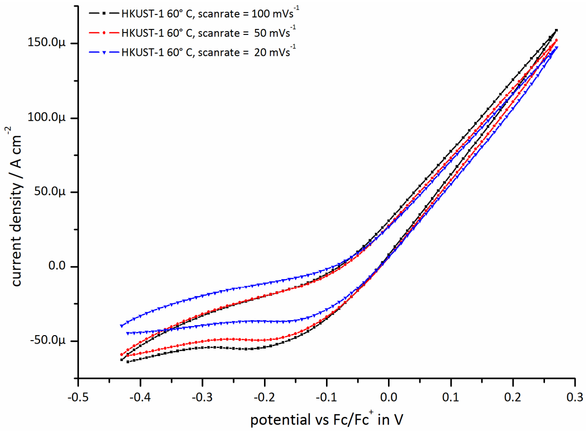

Fig. S4: Cyclic voltammetry under conditions as described in Fig. 1 for scan rates of 20, 50 and 100 mV s^{-1} for the HKUST-1_60° C.