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Electrochemical investigation of covalently post-synthetic modified SURGEL coatings†

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Thiol–yne click chemistry is used to covalently link a ferrocenyl derivative to the pore walls of a fully organic porous polymer coating (SURGEL). By cyclic voltammetry, it is demonstrated that the ferrocene bound to the SURGEL via a flexible alkyl linker can be reversibly reduced and oxidised. Surprisingly, when adding ferrocene as an electrolyte, a Nernstian diffusion limited process is observed. We explain this observation in terms of a high permeability of the SURGELS for ferrocene after the post synthetic modification.

Porous coordination polymers (PCPs), such as metal–organic frameworks (MOFs), have been receiving continuously growing attention from organic-, inorganic- and bio-chemists, as well as materials scientists over the past two decades.¹ The interest in these materials comprised of metal nodes connected by organic linkers is largely due to their structural flexibility. Indeed, by the appropriate choice of the inorganic and organic synthons, the properties of PCPs can be tailored and numerous functionalities can be added to these porous materials, paving the way for their use in several different application fields.² For a number of device-oriented applications, *e.g.* where electrical contacts³ or certain optical properties⁴ are required, the controlled deposition of materials such as thin films on solid substrates⁵ represents a crucial step.

A very appealing approach towards the preparation of application-targeted crystalline and porous PCPs is their covalent post-synthetic

modification (PSM)⁶ *via* click-chemistry.⁷ The main advantage of this type of PSM is that it can be carried out under mild conditions, thus avoiding that the porosity and high crystalline order of the starting polymeric material are affected.

In this communication we focus on a particular coating, the SURGEL⁸ which is derived from PCPs but it involves only covalent bonds, *i.e.*, it is free of metal ions and does not exhibit the crystallinity of the initial PCPs. Lacking coordination bonding, this type of material is characterised by a pronounced stability, a striking advantage for applications, in particular in the field of electrochemistry. In addition we herein demonstrate that these SURGEL coatings are well suited for the introduction of functional moieties by covalent PSM *via* thiol–yne click chemistry.⁹

SURGELS are fabricated from surface-anchored metal–organic frameworks (SURMOFs) which are readily obtained by liquid phase epitaxy (LPE) following a stepwise procedure.⁵

The crystalline SURMOFs, anchored to a gold surface through an appropriate self-assembled monolayer (SAM), are thereafter cross-linked using an organic linker whose three alkyne functional groups react with the two azido groups of the SURMOF organic ligand (see ESI1†). Subsequently the metal ions are removed using a complexation agent leading to a porous and amorphous purely organic surface supported coating, the SURGEL.⁸ Since not all three alkyne moieties of the cross-linker can couple to an azido moiety of the SURMOF organic ligand due to spatial and sterical constraints,⁸ unreacted alkyne functional groups are available for additional functionalisation.

Herein, we report on the introduction of a ferrocenyl thiol derivative (6-(ferrocenyl)hexanethiol, Scheme 1) *via* thiol–yne click chemistry PSM into the SURGEL (see the ESI2† for infrared reflection absorption spectra before and after PSM) and the electrochemical characterization by cyclic voltammetry (CV) using a three electrode setup (see Fig. ESI2†). CV was demonstrated to be a simple but efficient way to investigate the electrochemical behaviour of a SURMOF in a previous study.^{3c} 6-(Ferrocenyl)hexanethiol was chosen to post synthetically modify the SURGEL because (a) the ferrocene functional group exhibits well known redox properties¹⁰ and (b) the thiol moiety allows for the covalent

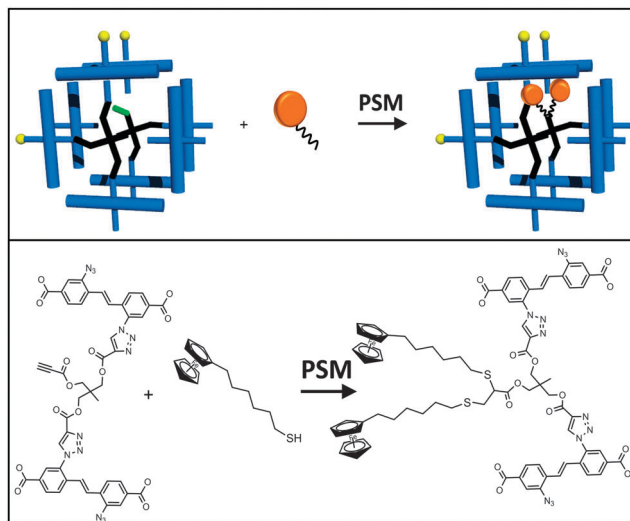
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† Electronic supplementary information (ESI) available: Experimental section with description of SURGEL preparation and a scheme of the electrochemical cell (ESI1); IRRA spectra (ESI2); XP spectra (ESI3); plots of the square root of the current density *vs.* the scan rate for the ferrocene post-synthetic modified SURGEL in Fig. 1 (ESI4) and Fig. 2 (ESI5). See DOI: 10.1039/c4cc03521f



Scheme 1 Top: schematic 3D representation of the reaction between the crosslinked SURGEL unit cell and the ferrocenyl derivative. Bottom: chemical structure of the crosslinked SURGEL tecton and the ferrocenyl derivative. (For details regarding the SURGEL preparation and PSM see the ESI†)

coupling to the residual alkyne groups of the SURGEL. From XPS data (see ESI†), we estimate a stoichiometric ratio of 2 to 1, *i.e.*, two ferrocenyl moieties per SURGEL pore.

We first discuss the CV-data for the SURGEL prior to the thiol-yne post-synthetic modification. The cyclic voltammogram was recorded in a neat supporting electrolyte (1-butyl-3-methylimidazolium bis(trifluoroethylsulfonfyl)-imide ionic liquid, [BMIM][NTf₂]). As expected for the homogeneous, defect-free unmodified SURGEL sample, no current was measured (Fig. 1, filled circles). After PSM, ferrocenyl moieties are covalently attached to the SURGEL framework, and, as shown in Fig. 1 (open circles) their reversible redox behaviour is recorded, analogously to that observed for a PCP where a ferrocene dicarboxylic derivative was used as an organic ligand in the framework.¹¹ However, the low current density ($24 \mu\text{A cm}^{-2}$ at 100 mV s^{-1} , see the ESI† for other

scan rate values) reveals that only a fraction of the ferrocenyl units in the SURGEL are reversibly oxidised and reduced. In addition, the oxidation and reduction of the ferrocene/ferrocenium redox couple occur at 0.12 V (vs. Pt) and at 0.07 V (vs. Pt), respectively. The peak separation of only 45 mV (at 100 mV s^{-1}) – smaller than expected for a diffusion controlled redox reaction – and the low current density suggest that only ferrocene moieties close to the SAM@metal/SURGEL interface are involved in the redox process. However, unlike for self-assembled monolayers of ferrocene thiols which exhibit no separation in the position of the peaks for oxidation and reduction due to the well defined position of the electroactive moiety,¹² the peak splitting observed for the SURGEL indicates a substantial degree of mobility of the covalently attached ferrocenyl moieties. This can be rationalised by the non crystalline structure of the SURGEL in combination with the flexibility of the aliphatic linker.

To further characterize the electrochemical properties of the SURGELs and the quality of this gel-like coating, further CV-experiments^{3c} were carried out using ferrocene dissolved in [BMIM][NTf₂] as an electrolyte. The CV recorded before the PSM, shown in Fig. 2 (filled circles), demonstrates that the supporting gold substrate is not accessible to the ferrocene molecules dissolved in the ionic liquid as no current was recorded. Therefore, the amorphous SURGEL forms a closed and non-porous insulating film for ferrocene sized molecules. A similar blocking behaviour was reported for the crystalline SURMOF HKUST-1.^{3c} However, a striking change in the blocking behaviour occurs upon PSM as evidenced by the cyclic voltammogram of the ferrocenyl modified SURGEL (recorded under the same conditions as the pristine SURGEL) shown in Fig. 2 (open circles). Unexpectedly, the CV now reveals reversible waves assigned to the ferrocene/ferrocenium redox couple with peaks at 0.18 V and 0.104 V . The 76 mV separation of the peaks is close to the theoretical value expected for a Nernstian diffusion limited process.¹³ The plot of the current density vs. the square root of the scan rate (see ESI†) shows a linear behaviour and further suggests that the charge transfer in the redox process is controlled by the diffusion of charges in the SURGEL, as described by the

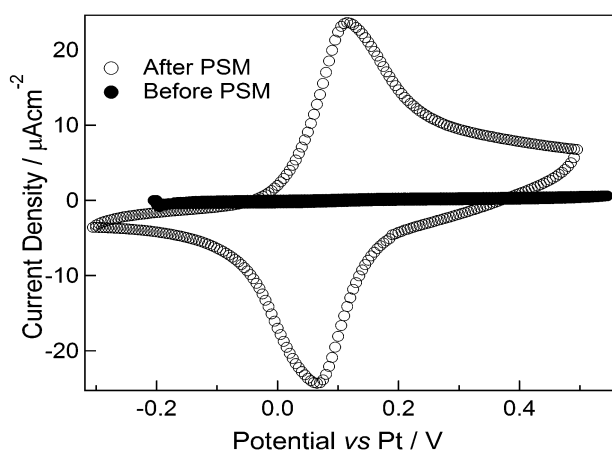


Fig. 1 Current density vs. voltage (range -0.2 – 0.55 V) plot of the ferrocenyl modified SURGEL in the presence of a neat [BMIM][NTf₂] ionic liquid at a scan rate of 100 mV s^{-1} .

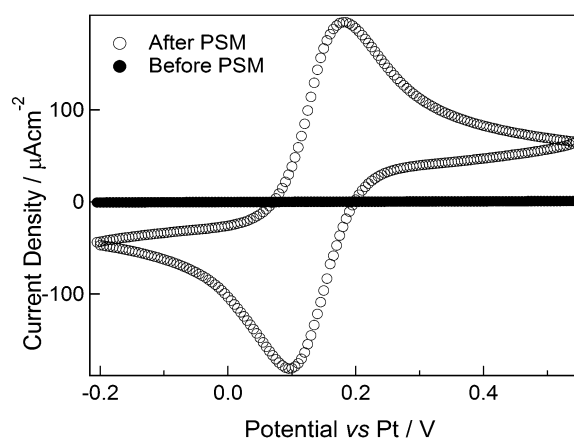


Fig. 2 Current density vs. voltage (range -0.2 – 0.55 V) plot of the as prepared SURGEL (black circles) and the ferrocenyl modified SURGEL (white circles). Electrolyte: ferrocene, 2.85 mM . Supporting electrolyte: [BMIM][NTf₂] ionic liquid (with 4% ethanol). Scan rate of 100 mV s^{-1} .

empirical Randles–Sevcik equation.¹³ Therefore, after PSM with 6-(ferrocenyl)hexanethiol the SURGEL switched from being completely blocked to permeable for the ferrocene molecules. Such a behaviour is in stark contrast to previous studies on the ferrocene loaded SURMOF HKUST-1.^{3c} For this system, upon modification of the film by noncovalent loading of ferrocene, conductivity due to charge hopping involving the ferrocene guests immobilised inside the SURMOF pores had been observed. As the SURGEL lacks any crystalline order⁸ it is reasonable to assume that the ferrocenyl groups decorating the SURGEL pores form an unordered array, thus excluding an electron hopping mechanism as instead proposed for the crystalline SURMOF HKUST-1 fully loaded with ferrocene.

In summary, we have shown that SURGELS are well suited for post-synthesis modification (PSM) employing the alkyne moieties still available after the SURGEL formation. A ferrocenethiol derivative has been successfully incorporated into the SURGELS using thiol–yne click chemistry. The success of this PSM process, as confirmed by a thorough spectroscopic characterization (IRRAS, XPS), demonstrates that SURGELS provide a robust platform for the attachment of functional moieties and hence the fine tailoring of the properties of these 3D open polymeric coatings. By means of cyclic voltammetry, it is demonstrated that the ferrocene, covalently bound to the SURGEL *via* a flexible alkyl linker, can be reversibly oxidised and reduced. The reduction and oxidation peaks appearing at different potentials suggest that these moieties have some degree of mobility, as indeed expected from their rather flexible anchoring chain to the SURGEL framework. In addition, we have demonstrated that the SURGEL is a pin-hole free and insulating coating before PSM but, surprisingly, becomes permeable to the ferrocene electrolyte afterwards. Indeed, in the case of PS modified SURGEL, much higher currents and larger separations of the oxidation/reduction peaks compared to ferrocene-free ionic liquids are observed, fully consistent with Nernstian diffusion of the redox species within the modified SURGELS. This unexpected finding opens the way to the use of PSM to finely tune the permeability of the amorphous SURGEL coatings.

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