

**Supporting Information-JA0701208****Step-by-step route for the synthesis of metal organic frameworks**

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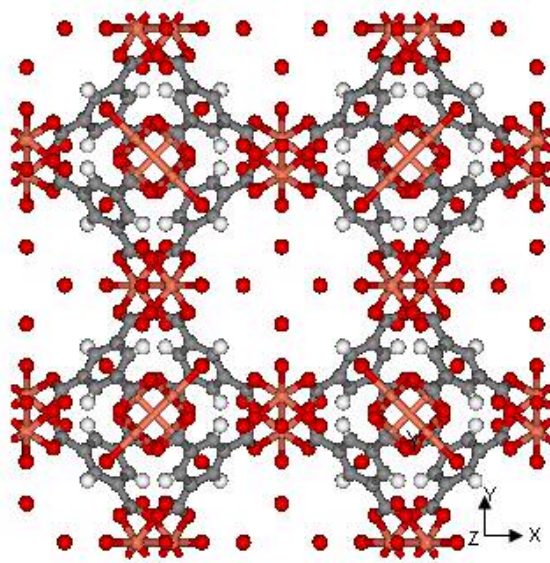
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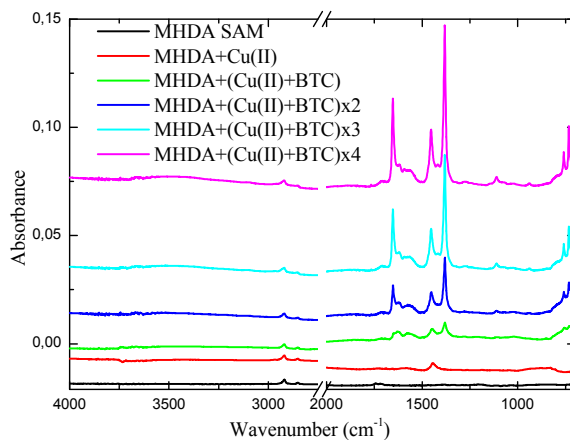
**Experimental:**

The HUKST-1 MOFs were grown on a gold substrates (200-nm Au/2-nm Ti evaporated on Si wafers) that were at first functionalized by self assembled monolayers SAMs of 16 mercaptohexadecanoic acid MHDA, that were prepared as described in [20]. These substrates were then immersed subsequently in a 1 mM of  $(\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O})$  (CuAc) ethanol solution for 30 minutes and then in a 1 mM of benzenetricarboxylic acid (BTC) solution for 1 hour at room temperature. Between each step the substrates were rinsed with ethanol and dried in stream of Nitrogen. After a given number of cycles the samples were characterized with Infra-Red Reflection Absorption Spectroscopy IRRAS, X-ray photoelectron spectroscopy XPS and Near edge X-ray Absorption Fine Structure NEXAFS. The loading exchange experiments were carried out for an 8- cycles Cu(II)-BTC MOF was first exposed to gaseous  $\text{NH}_3$  (step 1) and then immersed in a water/ethanol mixture (1:50) (step 2). IRRAS data were recorded using a Biorad Excalibur FTIR spectrometer (FTS 3000). All spectra were recorded with 2  $\text{cm}^{-1}$  resolution at an angle of incidence of  $80^\circ$  relative to the surface normal and further processed by using boxcar apodization .

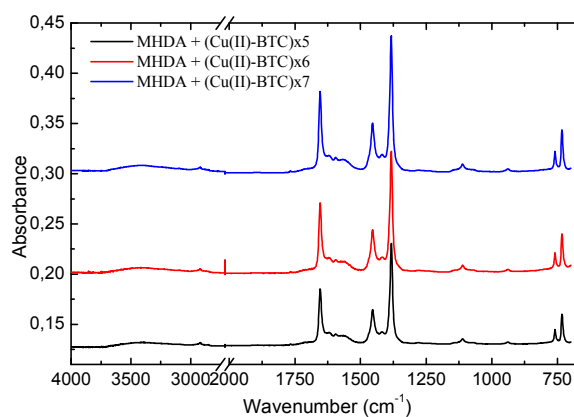


**Figure 1.**  $[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n$  (HKUST-1) polymer framework viewed down the  $[100]$  direction.

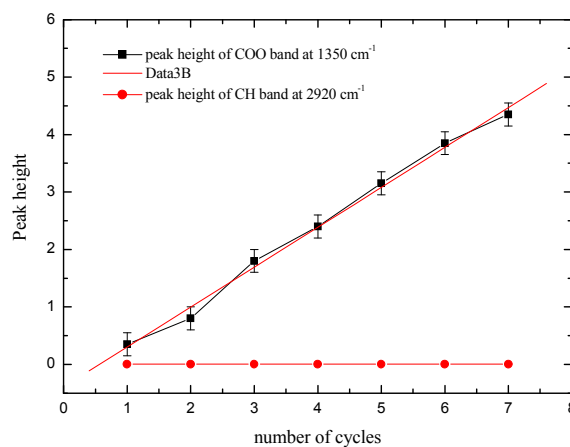
a)



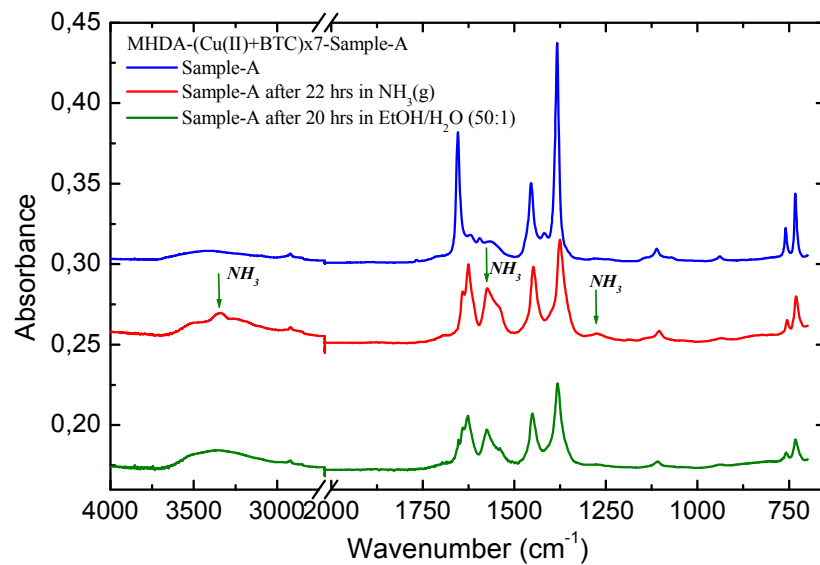
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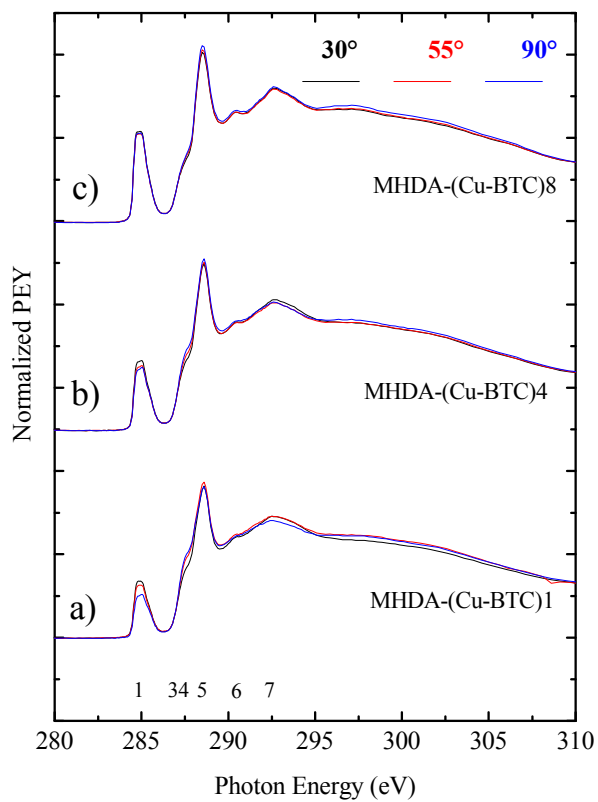
c)



**Figure 2.** a) IRRAS of Mhda SAM, recorded after immersion for 30 min in CuAc solution, d) after immersion for 30 min in CuAc solution and 60 min in BTC solution (1cycle), after 2-4 cycles of immersion in CuAc and BTC solution respectively. b) After 5-7 cycles of immersion in CuAc and BTC solution respectively, c) the correlation between the intensity of the COO band at 1350  $\text{cm}^{-1}$  and the CH<sub>2</sub> band at 2923  $\text{cm}^{-1}$  with the increase in the number of cycles.



**Figure. 3** IR-spectra recorded for a 7-cycle Cu(II)/BTC MOF deposited on a COOH-terminated surface, a) directly after deposition, b) after exposure to NH<sub>3</sub>-vapour for 22 hours and c) after re-immersion in an EtOH/H<sub>2</sub>O-mixture for 20 hours. Note the change of intensities in the OH stretch regime and the appearance of NH<sub>3</sub>-related peaks at around 3300 cm<sup>-1</sup>, 1520 and 1260 cm<sup>-1</sup> (arrows)



**Figure. 4** C-K edge NEXAFS spectra of a) MHDA after immersion for 30 min in CuAc then for 60 min in BTC (acid form), b) MHDA after immersion for 30 min in CuAc then for 60 min in BTC (4 cycles). c) MHDA after immersion for 30 min in CuAc then for 60 min in BTC (8 cycles).