

**Experiment title:**

Molecular domino - nanoscale positioning of TMs during self-assembly of MOFs: Cu – btc interaction

**Experiment number:**

26-01 894

**Beamline:**

BM26A

**Date of experiment:**

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**Shifts:**

9

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**Report:**Introduction:

Metal organic Frameworks (MOF) are a new family of hybrid, hierarchical porous materials exhibiting interesting properties for the chemical industry. Similar to zeolite synthesis, most MOF recipes utilize hydrothermal conditions to facilitate the formation of the highly coordinated TM centers necessary for self-assembly of the hierarchical framework. Recently it was shown that molecular level, direct templation with heteropolyacids (HPA) allows to replace the hydrothermal synthesis of the well-known HKUST-1 framework [1]  $[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]^1$  by a quick, room temperature self-assembly procedure [2]. HPA's not only enable the room temperature synthesis of the  $\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3.n\text{H}_2\text{O}$  framework, the direct templation in addition provides elegant way to systematically include the HPA molecules into MOFs. Within minutes after mixing an acidic ethanol/water based solution of Cu-decorated Keggin anions ( $\text{H}_{8-x}\text{XM}_{12}\text{O}_{40}$ );  $\text{X} = \text{P}^{5+}/\text{Si}^{4+}$  and  $\text{M} = \text{W}^{6+}/\text{Mo}^{6+}$  with the organic linker 1,3,5-benzene-tri-carboxylic-acid (BTC), micron-sized, highly crystalline  $\text{Cu}_3(\text{BTC})_2$  containing Keggin ions can be collected.

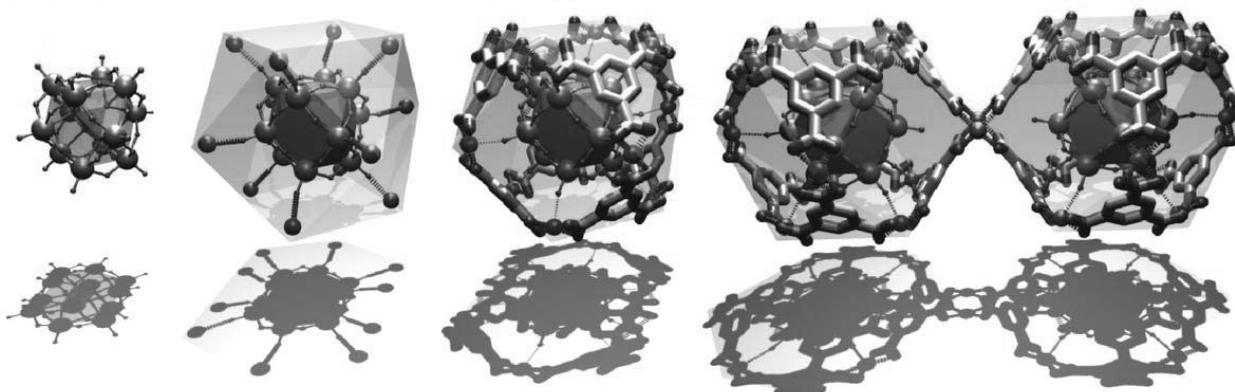


Figure 1: Structure directing behaviour of HPA on  $\text{Cu}^{2+}$  during self-assembly of HKUST-1 (animated visualization available online [2]).

<sup>1</sup> BTC - 1,3,5 – benzenetricarboxylic acid

## Experimental Details

Fully characterized solutions (UV-VIS-NIR, ESR, pH, SAXS, Raman, NMR) containing Cu-decorated non-lacunary Keggin colloid assemblies were prepared as function of HPA:Cu:ratio, solution pH and HPA concentration. After preparation these decorated colloid assemblies were contacted with BTC in order to create Cu-HPA-BTC ternary complexes expected to be the precursors of room temperature MOF assemblies. The Cu-HPA precursor solutions were measured concurrently in transmission and fluorescence mode, both in cryo conditions (15K) and at room temperature at the Cu K and the W-L3 edges. For the cryo measurements, PTFE sample liners were designed to allow flash-freezing the sample solutions in order to disturb the chemical equilibria in the systems as little as possible. The new sample liners in combination with an adapted cryostat sample rod, allowed to easily mount the samples in the cryostat, hence ensuring that the transfer of the flashfrozen samples from the liquid nitrogen to the cryostat could occur in optimal conditions. Room temperature measurements were performed in flow mode to inhibit beam induced speciation changes of Cu<sup>++</sup>. These measurements were performed on an identical sample geometry as compared to the PTFE liners in cryo conditions, using a flow rate of 300µl per minute in order to ensure that the complete sample volume was renewed every 120s, thereby preventing any beam induced sample alterations.

## Results

High quality W-L3 edge data was obtained for all samples up to k=14. The virtually noise-free W data allows to extract information on the local chemical information of W up to 7Å for the heavy backscatterers and up to 4Å for the lighter elements such as O and C. Contrary to the W L3 data, the Cu K-edge spectra had a significantly lower signal to noise ratio. This only allowed to obtain usefull EXAFS data up to k=11, thus limiting the information content of these spectra to the 1<sup>st</sup> oxygen shell around the Cu centers.

## Data analysis.

The initial analysis of the obtained spectra allowed to confirm both the specific interaction of Cu<sup>++</sup> cations with the heteropolyacids molecules and undisputably verify the stability of these high molecular weight species in the Cu<sub>3</sub>Btc<sub>2</sub> precursor solutions. In addition a lowered the first shell coordination environment for Cu<sup>++</sup> could also be demonstrated. In the next phase of the data analysis Iterative Target transform Factor Analysis [3] will be utilised to extract the EXAFs spectra of the pure components in the synthesis solutions from the recorded spectral series. This should allow to elucidate the exact chemical structure of the intermediate Cu-HPA species serving as direct template for the Cu<sub>3</sub>Btc<sub>2</sub> framework formation.

## Publications

Combination of the information obtained from initial data analysis of the XAS spectra with the data obtained from UV-VIS-NIR, pH measurements and chemical analysis on related samples resulted in the submission of a manuscript to Journal of Material Chemistry:

*'The impact of Keggin ions on Cu-speciation and its consequences for metal organic framework synthesis.* Bajpe, S.R.; Breynaert\*, E.; Mustafa,D.; Jobbágy, M.; Maes, A.; Martens J.A. and Kirschhock, C.E.A Journal of Materials Chemistry, 2011, DOI:10.1039/C1JM10947B' [4]

## References

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- [3] Breynaert, E. Scheinost, A.C., Dom, D., Rossberg, A., Vancluysen, J., Gobechiya, E., Kirschhock, C.E. A. and Maes, A., *ES&T*, **2010**, 44(17), 6649-55
- [4] Bajpe, S.R.; Breynaert\*, E.; Mustafa,D.; Jobbágy, M.; Maes, A.; Martens J.A. and Kirschhock, C.E.A Journal of Materials Chemistry, **2011**, DOI:10.1039/C1JM10947B