Electronic Supplementary Material (ESI) for Chemical Communications

Stability improvement of $Cu_3(BTC)_2$ metal-organic framework under steaming conditions by encapsulation of Keggin polyoxometalate

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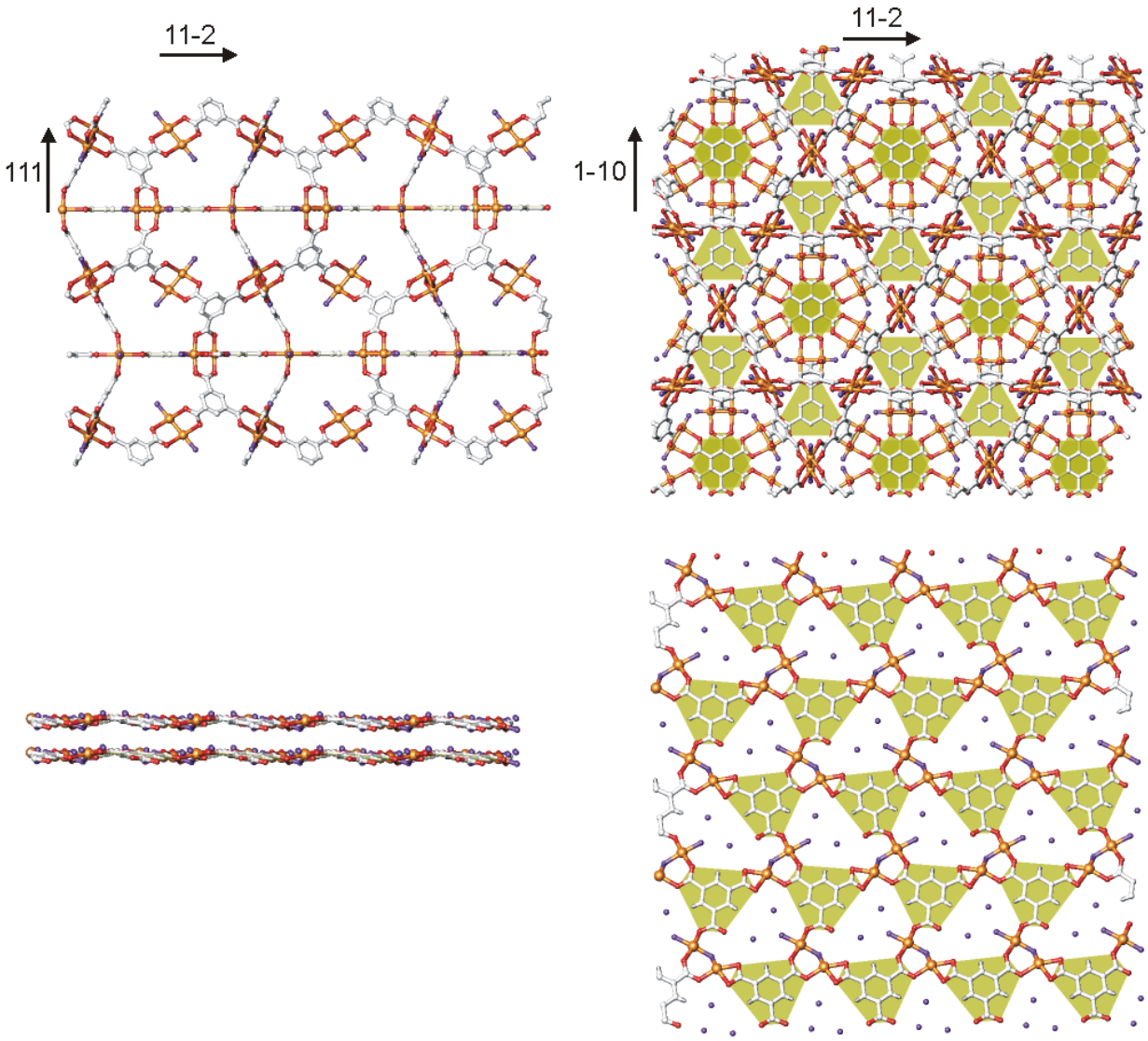
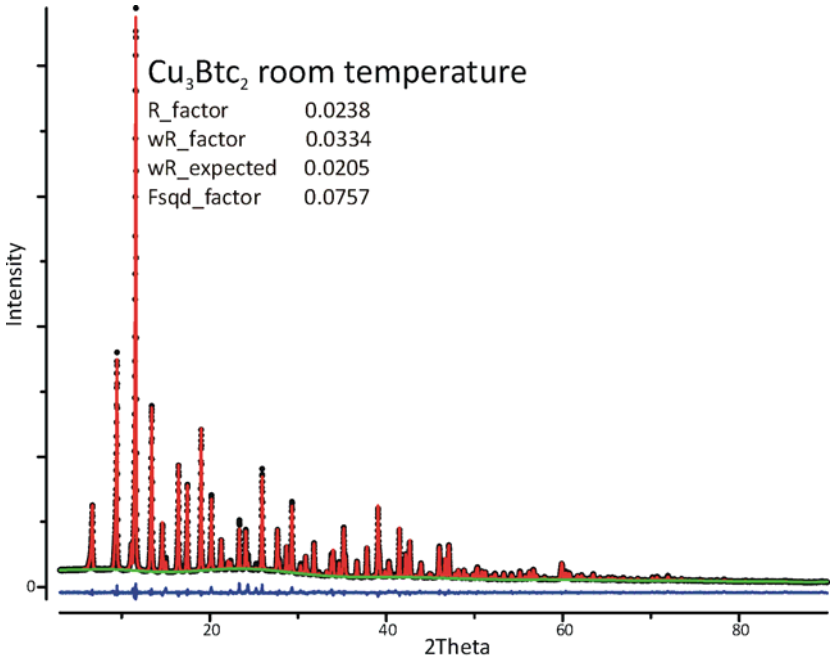


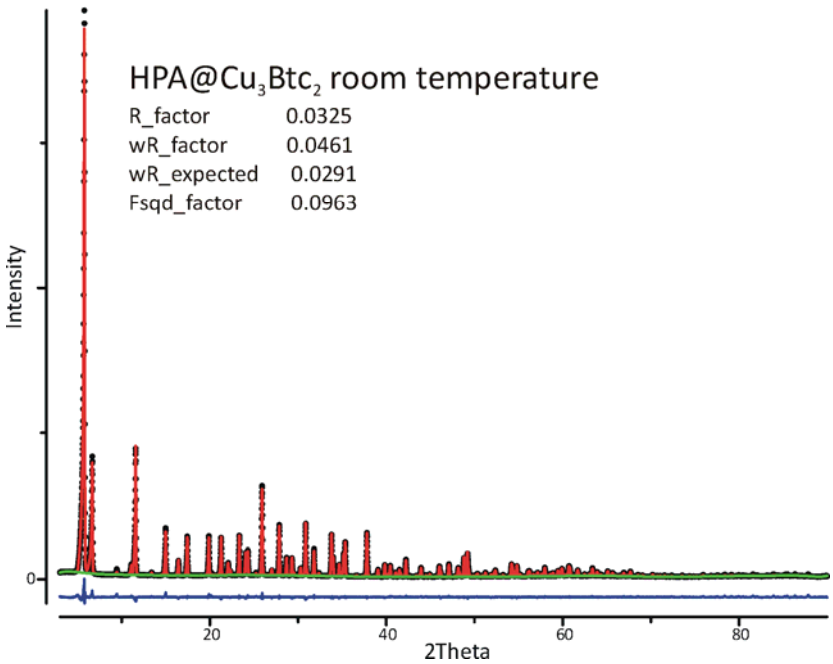
The upper image shows two views of the HKUST-1 crystal structure in different orientations. The lower left image shows the $[Cu_2OH(BTC)(H_2O)]_n.2nH_2O$ material composed by densely packed layers with distance (±3.5Å) and altered sheet structure compared to the layers present in HKUST-1. The lower right is a view on the layers in the same material.

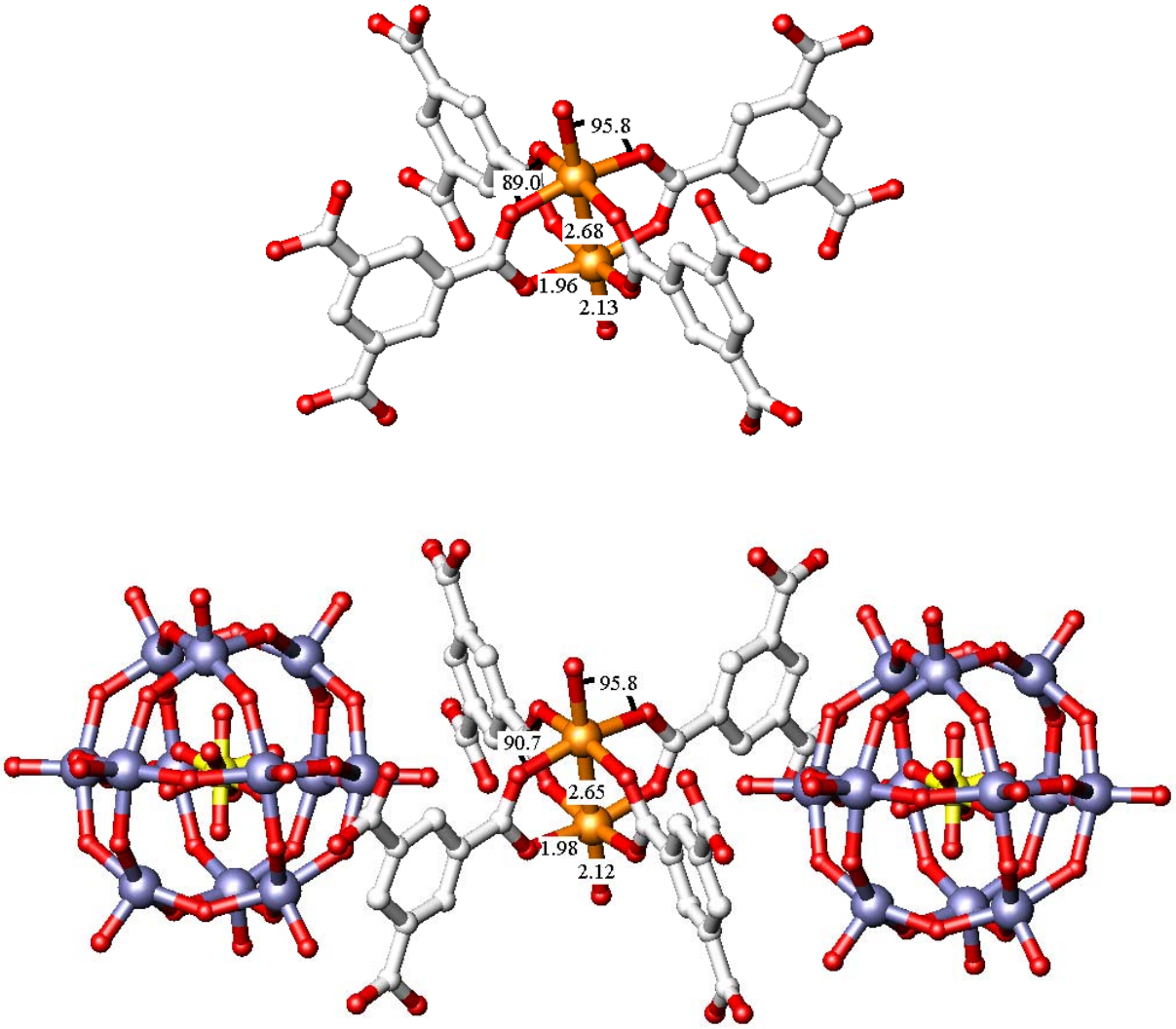
Rietveld refinement of HPW@Cu_3Btc_2 and Cu_3Btc_2

Refinement strategy

As starting models for both structures served the coordinates reported in [17]. Background and profile were refined in a Le Baile fit before the atomic positions were Rietveld refined. Occupation numbers of framework atoms were kept at 100%. Occupation numbers of atoms of Keggin ions were refined together and constrained to account for the chemical composition of the HPA. Initially, the organic linker was inserted as rigid body where of the position and orientation was freely refined. In a next step the observed and difference electron density maps were inspected for residual intensity. The latter was throughout assumed as water molecules, which were added successively to the coordinate lists. Positions and occupation of water were freely refined. After reasonably good fits were obtained the rigid body of the organic linker was replaced by individual atoms and the isotropic temperature factors were refined together with the positions of all atoms. Several occupation numbers of water molecules approached unity and were fixed. This strategy resulted in both cases in reasonable structures, sensible temperature factors and acceptable profile fits. The occupation factor of Keggin ions in HPA@ Cu_2Btc_3 refined to a value very close to unity, strongly indicating 100% occupation of one of the two types of large cavities in the framework.







The comparison between the structures with and without Keggin included in one type of the large cages shows the local environments of Cu in Cu_2Btc_3 do not significantly differ. The framework structure is in no way affected by the presence of the HPA.

Thermo Gravimetric Analysis of HPW@Cu_3Btc_2 and HKUST-1

TG was measured on a TGA Q500 V6.7 Build 203, heating at 5.00°C/min to 450.00°C in N_2.