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COMMUNICATION

Underlying mechanism of the hydrothermal instability of $Cu_3(BTC)_2$ metal-organic framework

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Supporting Information

Outline:

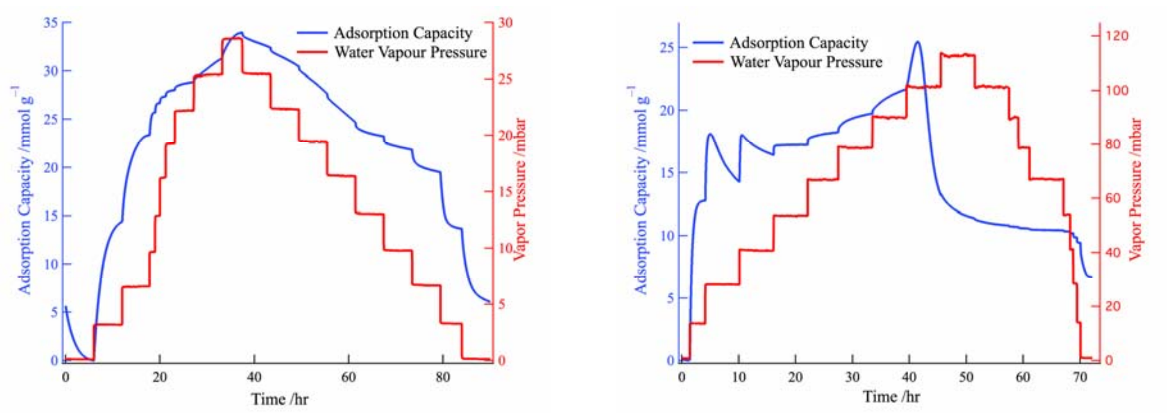
Synthesis and characterisation of $Cu_3(BTC)_2$ MOF

The improved hydrothermal synthesis of $Cu_3(BTC)_2$ MOF [1] was used in this work. All materials, *i.e.* $Cu(NO_3)_2{\cdot}3H_2O$ (99%, Sigma Aldrich), benzene-1,3,5 tricarboxylic acid (BTC, 95%, Sigma Aldrich) and ethanol (absolute, Fisher Scientific) were used as received without further purification. BTC (0.42 g, 2 mmol) was dissolved in 24 mL of 50:50 vol.% mixture of ethanol and deionised water. The mixture was stirred for 10 min until a clear solution was obtained. Then $Cu(NO_3)_2{\cdot}3H_2O$ (0.875 g, 3.62 mmol) was added to the mixture and stirred thoroughly for another 10 min. Once the reactants were completely dissolved in the solvent, the resulting blue solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and heated to 100 °C for the crystallisation to occur. After synthesis, the reactor was cooled to room temperature and a blue crystalline powder was formed. The powder was then filtered and washed thoroughly with a 60 mL mixture of water and ethanol (% v/v of water = 50%). The product was finally activated under vacuum at 120 °C for 16 h and stored in closed vials in an oven at 60 °C. Full characterisation of prepared materials can be found in [1].

Dynamic water vapour adsorption

Dynamic water vapour adsorption on $Cu_3(BTC)_2$ was performed using a dynamic vapour adsorption analyser (Surface Measurements Systems, DVS 1). The analyser was housed inside an environmental chamber at a constant temperature to ensure a stable baseline and the accurate delivery of required relative humidity. Relative humidity values are controlled by mixing dry nitrogen and saturated water vapour in appropriate proportions using mass flow controllers. Prior to the sample loading, dry nitrogen at 2 barG pressure was used to purge the head of the balance (Cahn D200) to prevent vapour condensation in the balance's head and ensure an accurate measurement. All samples were dried at 0% relative humidity (RH) for 6 h before the measurement of adsorption/desorption isotherms at various vapour partial pressures. The water vapour adsorption isotherms of $Cu_3(BTC)_2$ were measured at temperatures of 25 and 50 °C with relative humidity values ranging from 0 to 90%.

The equilibration time for each pressure stage was set as maximum 6 h per stage. The criterion of changing adsorption pressures was determined by the rate of changing mass of the sample (*i.e.* dm/dt) and a critical value of dm/dt = 0.002 was specified in the instrument. When a value of dm/dt is measured as smaller than 0.002, the adsorption of water vapour on the sample is believed to reach the equilibrium at this pressure. Then the system moves to the next pressure stage. Maximum 6 h was used to accommodate the time required for every equilibrium during the adsorption. The total time of an adsorption experiment is the sum of the time required for all equilibria in the adsorption/desorption stage, as shown in Fig. S1.



(a) (b)

Fig. S1 Dynamics of water vapour adsorption on $Cu_3(BTC)_2$ at (a) 25 °C with 90% RH and (b) 50 °C with 90% RH

Powder X-ray diffraction (PXRD) studies

PXRD was carried out on a Rigaku Miniflex diffractometer (Cu*Kα* radiation, 30 kV, 15 mA, $\lambda = 1.5406$ Å) using a step scan mode (0.03° per step) with a range of $5° < 2\theta < 46°$. SEM analyses were carried out using a FEI Quanta 200 ESEM equipment with a high voltage mode of 20 kV. Gold coating of samples was performed using an Emitech K550X sputter coater under vacuum conditions of 1×10^{-4} mbar.

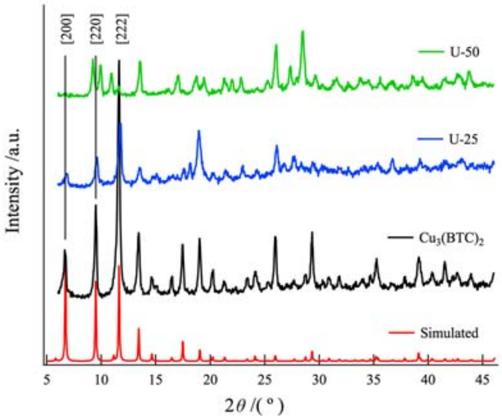


Fig. S2 PXRD patterns for fresh activated $Cu_3(BTC)_2$, U-25 (used $Cu_3(BTC)_2$ after water adsorption at 25 °C with 90% RH) and U-50 (used $Cu_3(BTC)_2$ after water adsorption at 50 °C 90% RH)

Differential Scanning Calorimetry (DSC) studies

Differential Scanning Calorimetric (DSC) analysis was carried out using Mettler DSC30 instrument, with explorer software to perform the peak analysis. The samples were dispensed into aluminium sample-pans and hermetically sealed to prevent samples' loss. The sample pan (with its lid) was weighed before and after sealing to determine the exact weight of the sample. The reference chambers contained an empty pan with its lid. The DSC was calibrated with indium prior to analysis. The accuracy of the enthalpy measurements is ±1%. Samples were heated and cooled at a rate of 5 °C min^{-1}, and the scan was completed over a range of 50 °C to 350 °C.

The comparison of DSC spectrum of the fresh $Cu_3(BTC)_2$ sample with those of reactants for $Cu_3(BTC)_2$ synthesis (copper nitrate trihydrate and benzene-1,3,5 tricarboxylate) is shown in Fig. S3. The results showed that no peaks are related to the melting of pure reactants, indicating the purity of the synthesised $Cu_3(BTC)_2$ sample.

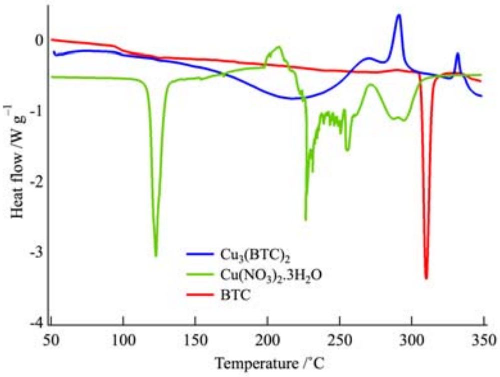


Fig. S3 DSC curves of fresh $Cu_3(BTC)_2$ (solid blue), copper nitrate trihydrate (solid green) and benzene-1,3,5 tricarboxylic acid (solid red)

Small Angle X-ray Scattering (SAXS) studies

Materials were filled to Lindeman capillaries (1mm diameter, quartz capillary) and examined using the Hecus SA X-Ray S3-Micro Pix Camera. SAXS patterns were recorded at a fixed wavelength λ of 1.54 Å. The PSD 50 mol·L^{-1} detectors were used to acquire the data. The long spacing was calculated from the scattering angles according to the Bragg formula, Eq. s1. [2]

$$n\lambda = 2d\sin\theta \tag{s1}$$

where n is an integral number describing the order of reflection, λ is the wavelength of the incident X-ray, d is spacing between the lattice planes and ϑ is the diffraction angle where a maximum in the diffracted intensity occurs.

Data for SAXS experiments were represented in the form of a two dimensional image consisting of 512 vertical and 512 horizontal channels. FTI2D software was used in order to obtain d-spacing from the data. A one dimensional representation of the data was produced from two dimensional images by using the FTI2D to convert the two-dimensional spots to the corresponding scattering angles and then generating a plot of intensity versus 2θ. The analysis was carried out at room temperature.

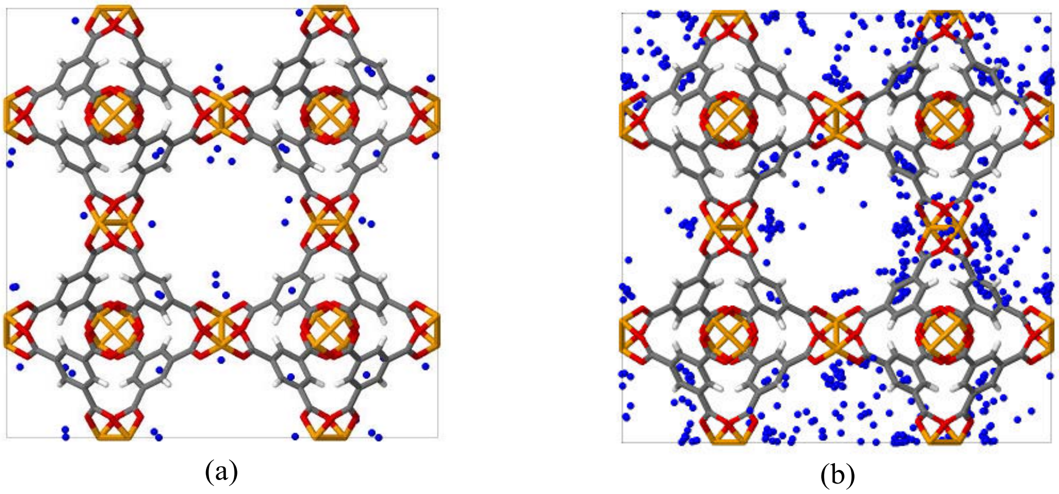
The studies of XRD for crystal structure of $Cu_3(BTC)_2$ that was first reported by Chui et al. [3] indicated that $Cu_3(BTC)_2$ form face-centred-cubic crystal, which is in a good agreement with our SEM image of fresh sample.

Fourier Transform Infrared spectroscopy (FT-IR) studies

The FT-IR analysis was carried out using solid FT-IR Avatar 360 ESP spectrometer instrument in the range of 400–4000 cm^{-1} with ATR accessory that contains a germanium crystal conjointly with Nicolet's OMNIC software.

Grand Canonical Monte Carlo (GCMC) simulation

$Cu_3(BTC)_2$ was modelled as a rigid structure with a cubic unit cell of 26.343 Å length. Lenard-Jones parameters of all atoms were taken from Dreiding force field [4] except those of copper, which were taken from UFF [5]. Partial charges of all atoms were adopted from literatures [6]. Lenard-Jones cross interactions were calculated using Lorentz-Berthelot mixing rules. A cut-off radius of 12 Å radius was used for Lenard-Jones interactions and Ewald sum was used for the electrostatic interactions' computations. H_2O molecule was modelled as a five sites molecule with the Lenard-Jones parameters and partial charges were taken from TIP5P force field [7]. GCMC simulation of pure H_2O adsorption was carried out using MCCCS Towhee code [8]. The chemical potentials that are required for the GCMC simulation were computed using NPT ensemble.



(a) (b)

Fig. S4 GCMC simulation of single-component gas adsorption (H_2O the as probing gas) on $Cu_3(BTC)_2$ framework: (a) 2.7 mbar and (b) 8 mbar

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