Electronic Supplementary Material (ESI) for Chemical Communications

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High performance Metal-Organic-Framework Coatings Obtained via Thermal Gradient Synthesis

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Synthesis

Chemicals

Dimethyl formamide (≥ 99.5%. Carl Roth) was redistilled prior to use. $Cu(NO_3)_2 \cdot 3\ H_2O$ (≥ 98 %, Carl Roth) and trimesic acid (98 %, ABCR) were used without further purification. ETP copper sheets (50 mm x 50 mm x 0.60 mm) were wet sanded (SiC, CAMI grit = 600) and tempered (150 °C, 12 h in air) before use.

Alternatively or in addition the surface was also degreased with acetone before sanding. This was, however, not found necessary and there was no change in the final deposition results with and without degreasing before sanding. Tempering was done in order to ensure reproducibility of the deposition results.

Experimental procedure

The heating block (see Figure S1 for description) was equipped with prepared Cu sheets at both sides and immersed into a solution of 3,36 g (15,99 mmol) of H_3btc and 7,00 g (28,09 mmol) of $Cu(NO_3)_2 \cdot 3\ H_2O$ in 200 ml of DMF in a glass cylinder of 6 cm inner diameter. The whole assembly was immersed into a stirred ice-water bath.

The total heating power was then set in such a way that the temperature at the interface between the Cu sheet and the heater was 150 °C (approx. 225 W). Undesired nucleate boiling had been observed at interface temperatures of > 165 °C in a reference experiment. The conditions were kept for 120 minutes while carefully monitoring the interface temperature and readjusting the heating power, if necessary. For activation, the coated sheet was rinsed with DMF and then immersed into DMF for 12 h. The procedure was repeated twice with redistilled ethanol. The sample was then dried in air at 120 °C overnight and stored under inert conditions.

Temperature control was achieved by placing a thermocouple on the inner side of the heating element and a thermocouple (or thermometer) into the solution at a distance of 5 mm from the outer surface of the heating element.

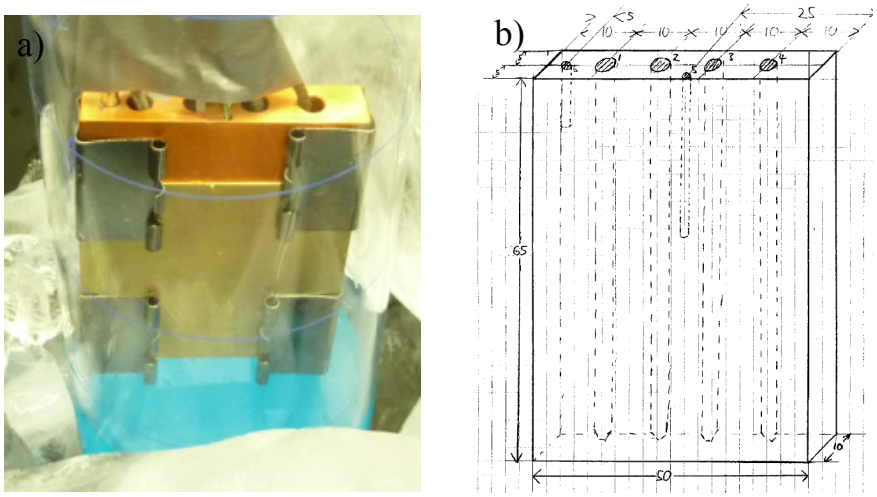

Figure S1: a) experimental setup (before submersion), **b)** geometry of the heater. Bores No. 1-4 were equipped with heating cartridges (100 W, 24 V, connected to a variable power source). Bore No. 5 is located directly at the surface and equipped with a K-type thermocouple for the purpose of monitoring the temperature at the heater/copper sheet interface. Bore No. 5 is for mounting.

SEM/EDX:

Conditions

SEM/EDX measurements were obtained on a FEI Quanta 400 MkII scanning electron microscope. Top down images were obtained under high vacuum, cross sectional images in environmental mode (H_2O, 100 Pa).

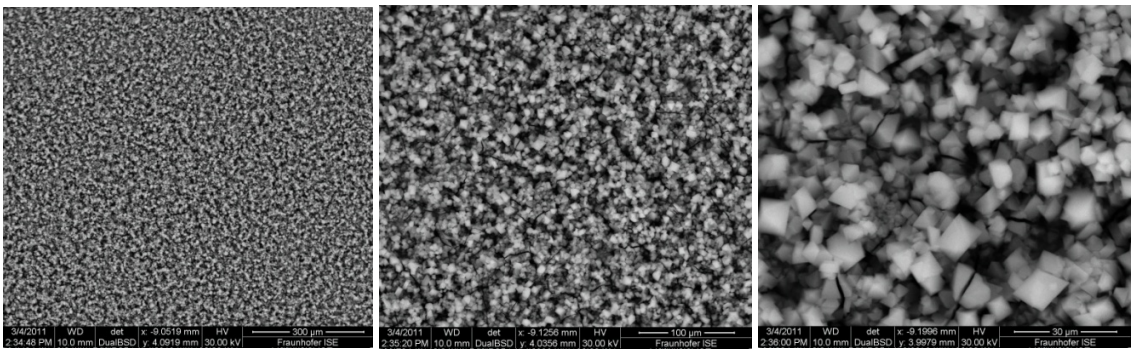

Figure S2: Top-down view SEM/EDX images of the obtained coating

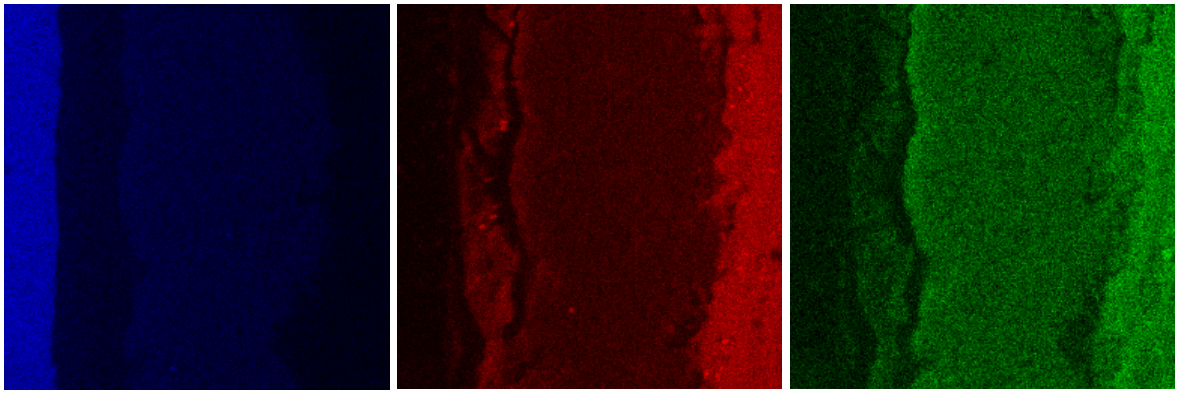

Figure S3: Separate cross-sectional, element-mapping images: Cu (blue), C (red) and O (green).

XPS

X-ray photoelectron spectroscopy was performed on a VG Scientific LTD with monochromatised Al Kα radiation (1486.6 eV). The pass energy for survey spectra from 0 to 1000 eV was 15 eV. Vertical surface composition analysis was performed by sputtering with Ar^+ at 3.5 kV and 4 mA, thereby exposing and analysing different layers down to the bottom layer.

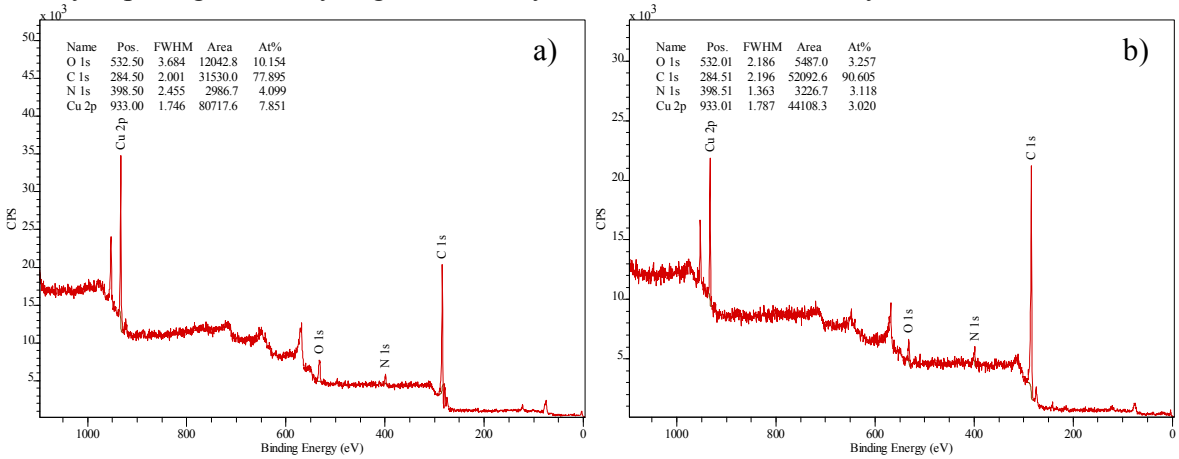

Figure S4: XPS spectra of the bottom layer, after removing 50 nm (a) and 100 nm (b) by sputtering.

N_2 Sorption isotherm

Nitrogen sorption isotherms were obtained on a Quantachrome Nova at 77 K. Samples were de-gassed for 24 h at 120 °C *in vacuo* prior to measurement.

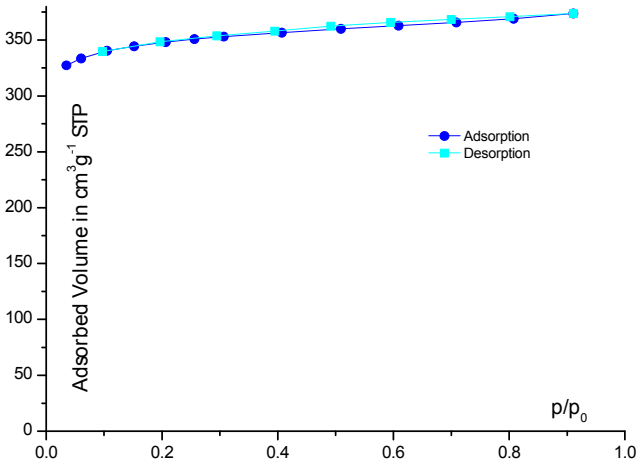

Figure S5: Nitrogen Sorption Isotherm obtained at 77 K.

Heat capacity measurements

The heat capacity of copper trimesate was determined on commercial Basolite™ C-300 using a Setaram™ C-80 calorimeter. The sample was dehydrated under vacuum at 120°C and subject to a preliminary temperature run prior to the measurement. Temperature steps: 25 K / h.

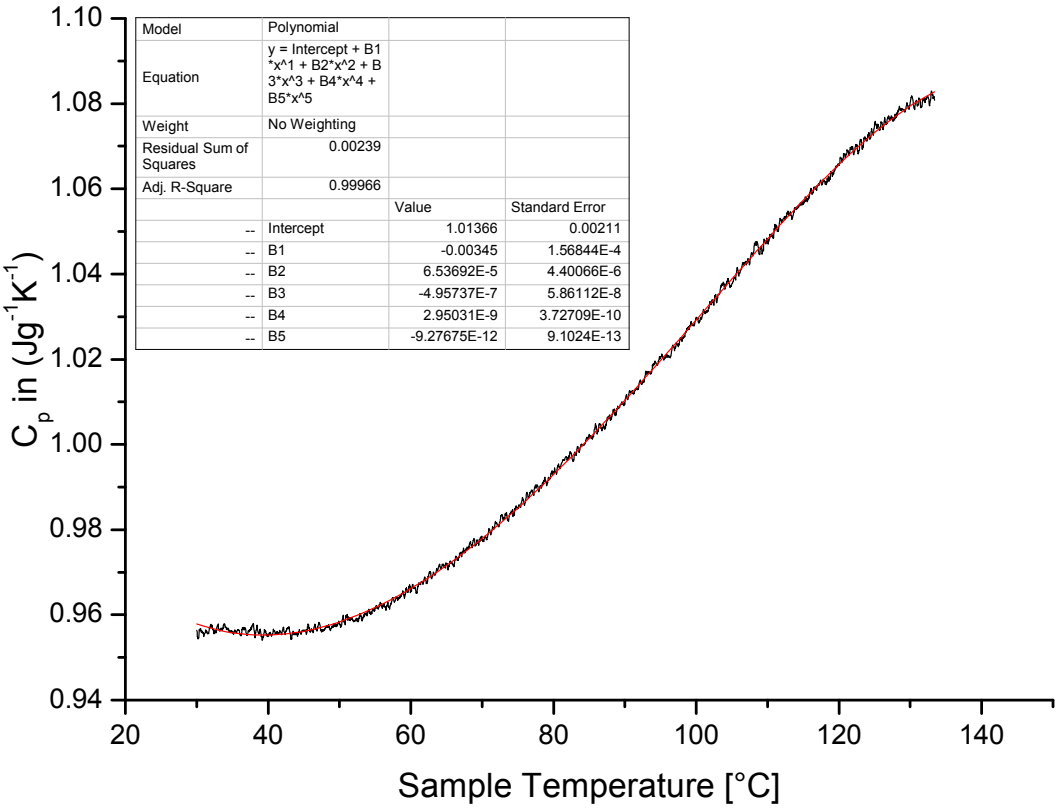

Figure S6: Heat capacity of Basolite™ C-300. For heat conductivity measurements, the polynomial fit (line depicted in red) was used.

Thermal conductivity measurements

Thermal conductivity measurements were obtained on a Netzsch Microflash™ LFA 457 laser flash analysis apparatus on samples of 10 mm x 10 mm under vacuum. Samples were coated with graphite on both sides and dehumidified at 120°C prior to measurement. A Cowan 2-layer approach with regard to heat loss and pulse correction was used. Heat capacity and thermal conductivity of the Cu substrate were obtained from the Netzsch database, the heat capacity of the coating was calculated from the regression function from Figure S6. Three shots per temperature, the given values are calculated as the arithmetic mean. The calculation of the thermal conductivity, diffusivity, and contact resistance were performed using the NETZSCH software algorithm, which is based on the work by Hartmann et al. (*Rev. Sci. Instrum.* **68**, 1510 (1997))

Water vapour cycling

In a vacuum chamber filled with water vapour of 12 mbar, the sample was brought to temperatures alternating between 15 °C and 120 °C for 90 s each. This equals relative vapour pressures of $p/p_0 = 0.73$ or, respectively, $p/p_0 = 6.1 \cdot 10^{-3}$.

This was conducted over 500 cycles. During the first cycles, the colour change between dark blue and turquoise was visible, after 500 cycles however, the colour had changed to green. PXRD measurement showed an almost complete loss of the structure.

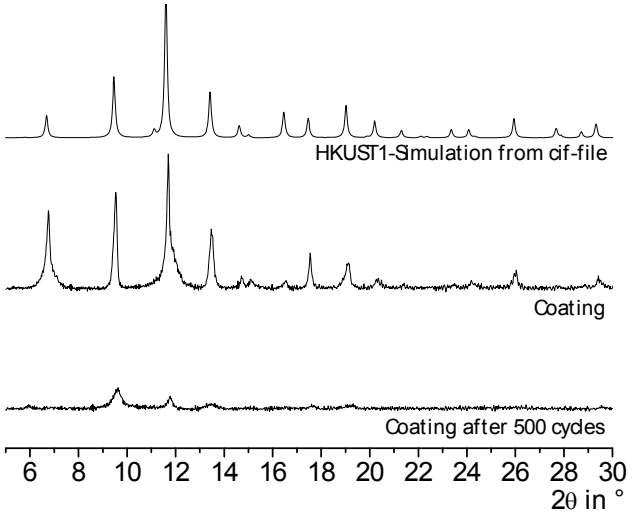

Figure S7: PXRD measurements of the coated sheet before and after cycling. Cu-Kα radiation.

Further details of analytic methods

Powder diffraction patterns were obtained on a Bruker D8 Advance with Cu-Kα radiation and a LYNXEYE detector on a Newport stage, with Bragg-Brentano geometry and 4s/0.01° per step.

Infrared spectra were obtained on a Bruker Alpha FT spectrometer equipped with an ATR unit, 32 scans per spectrum.

Additional optical microscope images

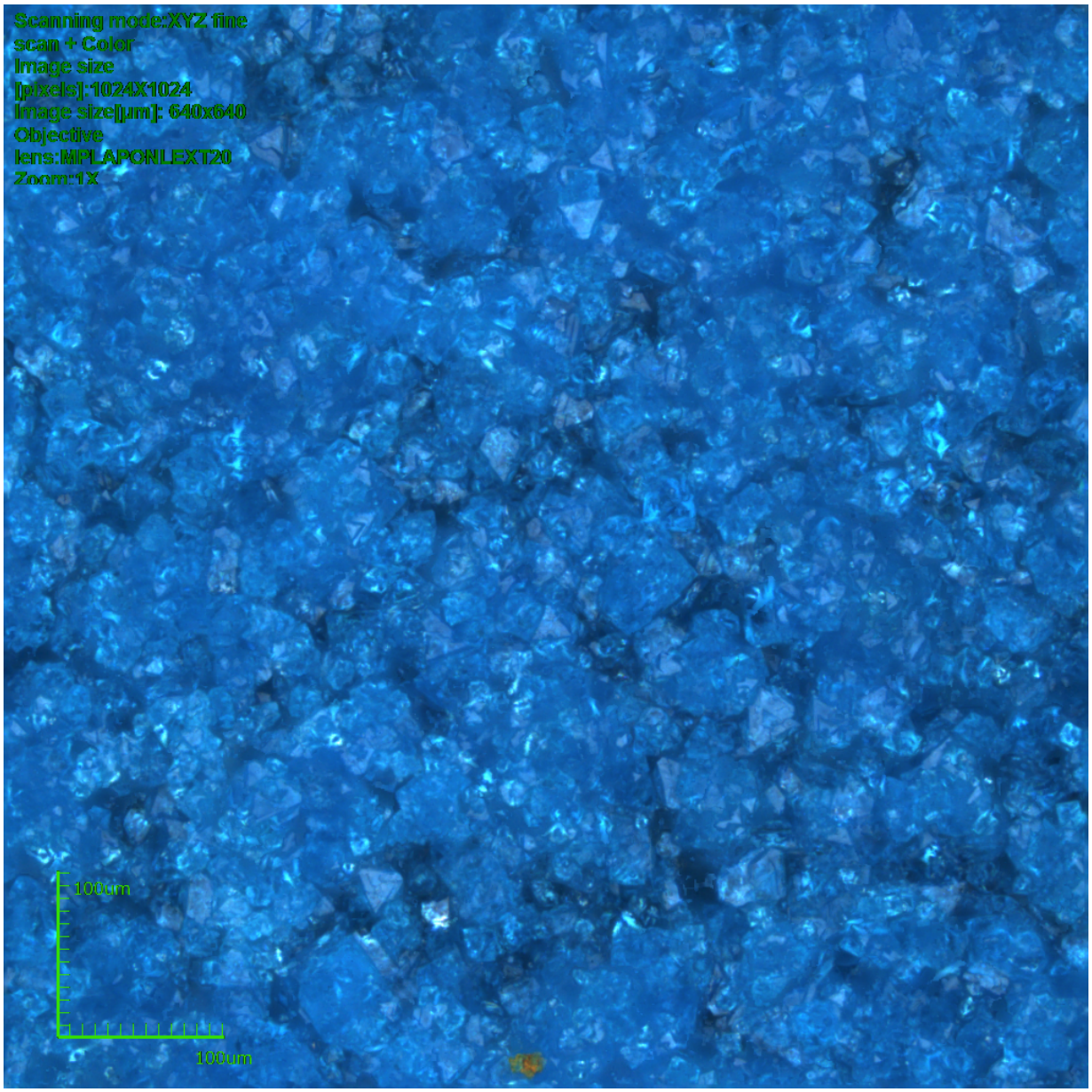

Figure S8: Image from Fig. 2c, enlarged.