Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Investigating the vapour phase growth of copper terephthalate Metal Organic Framework thin films by atomic/molecular layer deposition

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A. Materials and Methods

All chemical reagents and solvents were acquired from commercial sources and used without further purification.

Ellipsometry

The thickness of the deposited films on Si (100) was measured by ellipsometry spectroscopy at an incidence angle of either 70° or 75°, using a Sopra GES-5E and a SEMILAB SE-2000 spectrometers, respectively. Data fit was realized with the software "Winell II" and "SAM suite" using a Cauchy dispersion law.

X-Ray Diffraction

Thin films and bulk crystals were analyzed by X-Ray diffraction using a PANalytical XpertPro MRD diffractometer with a Cu Kα1 radiation (λ = 1.540598 Å) used with 40 kV and 30 mA settings in θ/θ mode, and a Bruker D8 Advance diffractometer with a Debye-Scherrer geometry. For the thin films, measurements were made using 2θ between 4°and 25° for 12h while for the powder samples, 2θ ranged from 4° to 50° with 1h measurement.

FTIR analysis

Infrared spectroscopy was performed using a SAFAS Monaco spectrometer coupled with attenuated total reflectance (ATR) with diamond crystal accessory.

Electron microscopy

Scanning Electron Microscopy images were recorded on FEI Quanta 250 FEG and on Zeiss Merlin VP compact microscopes, both equipped with EDXS detector, respectively, SDD OXFORD X-Max and SAMx Premium. For bulk samples, the solids were mounted on stainless pads and sputtered with ∼2 nm of carbon to prevent charging during observation. Film samples were analyzed directly without deposition of a metallic coating.

Transmission Electron Microscopy was performed on JEOL 2100F microscope operating at 200 kV and equipped with an 80 mm^2 Oxford EDS analysis detector. The sample was prepared by dry deposition on a gold TEM grid (300 mesh) covered with a holey carbon support film.

Sorption isotherms measurements

Surface areas were measured by N_2 sorption at 77.3 K using a BEL Japan Belsorp Mini apparatus volumetric adsorption analyzer. The sample was pre-activated by heating under vacuum prior to sorption measurement. The BET surface calculations were performed using points at the pressure range $0 < P/P° < 0.15$.

Precursor synthesis

Synthesis of copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate) ($Cu(thd)_2$)

Copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate) ($Cu(thd)_2$) was synthesized according to the reported procedure[1]. Briefly, NaOH (1.821 g, 45.55 mmol) was dissolved in methanol (41.4 mL) while stirring and the resulting solution was cooled to room temperature followed by addition of 2,2,6,6-tetramethyl-3,5-heptanedione(TMHD, 7.06 ml, 7.630 g, 41.40 mmol). A solution of $Cu(NO_3)_2{\cdot}3H_2O$ (5.000 g, 20.70 mmol) in MeOH (41.4 mL) was added to the TMHD containing mixture over a period of 30-40 minutes. The reaction mixture was stirred for 6h and the resulting precipitate was filtered and dried on filter paper. The product is recrystallized in hot methanol, recovered by filtration and washed with water and methanol to remove excess NaOH. The final dark purple single crystals were kept in a Schenck tube and dried under vacuum for 12h at 60 °C before characterization. The final yield is 85.37% (7.6 g). Powder X-Ray diffraction was used to check the purity and FTIR analysis to confirm the presence of the expected chemical bonds vibrations.

Bulk MOF crystals synthesis

Synthesis of CuTPA

Cu(TPA)·DMF was synthesized according to previously published procedure by dissolving $Cu(NO_3)_2{\cdot}3H_2O$ (0.48 g, 2 mmol) and TPA (0.33 g, 2 mmol) in DMF (20 mL)[2] in a 40 mL vial that was sealed and placed in an oven at 110 °C for 24h. The resulting blue powder was collected by filtration, washed with methanol. Then the solid was transferred in a cartridge of a Soxhlet extractor charged with methanol. After 3 days of Soxhlet solvent exchange, the blue powder was recovered and dried in Schlenk line at 150 °C for 12h before further characterization.

Synthesis of DMOF-1

DMOF-1 was synthesized according to the reported procedure[3]. A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (1.0 g, 3.36 mmol), TPA (0.560 g, 3.37 mmol), and DABCO (1,4-diazabicyclo[2.2.2]octane, 0.187 g, 1.67 mmol) was suspended in DMF (40 mL) and heated in a Teflon-lined stainless steel reactor at 120 °C for 2 days. The colorless crystalline precipitate formed was collected, washed with DMF (3 times) and acetone (2 times). The recovered crystals were then dried in Schlenk line at 150 °C for 4h before further characterizations.

B. Characterizations of bulk samples

B1. Copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate) $Cu(thd)_2$ precursor

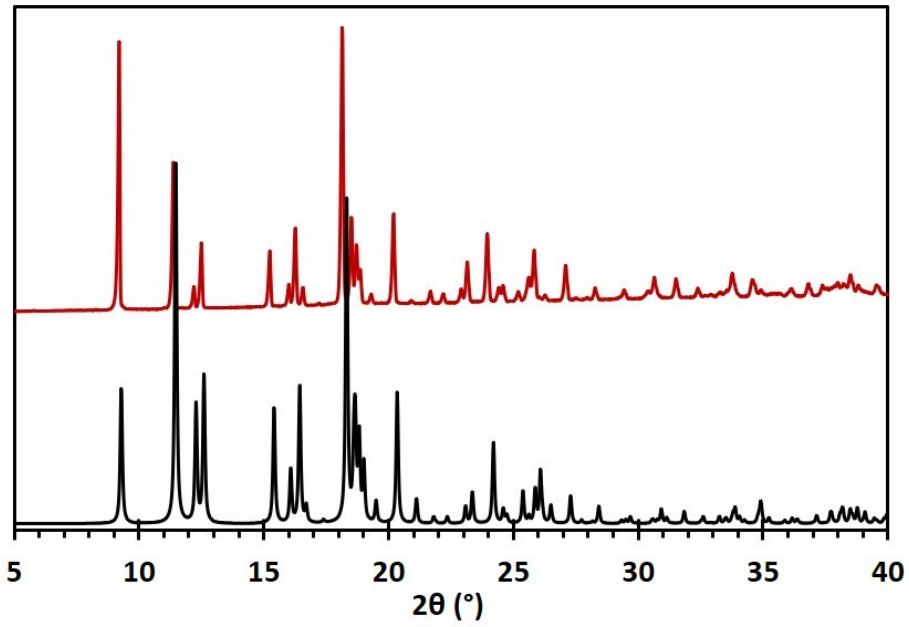

Figure S1 : PXRD pattern of the synthesized $Cu(thd)_2$ (red) and the calculated pattern from the single crystal structure (black).

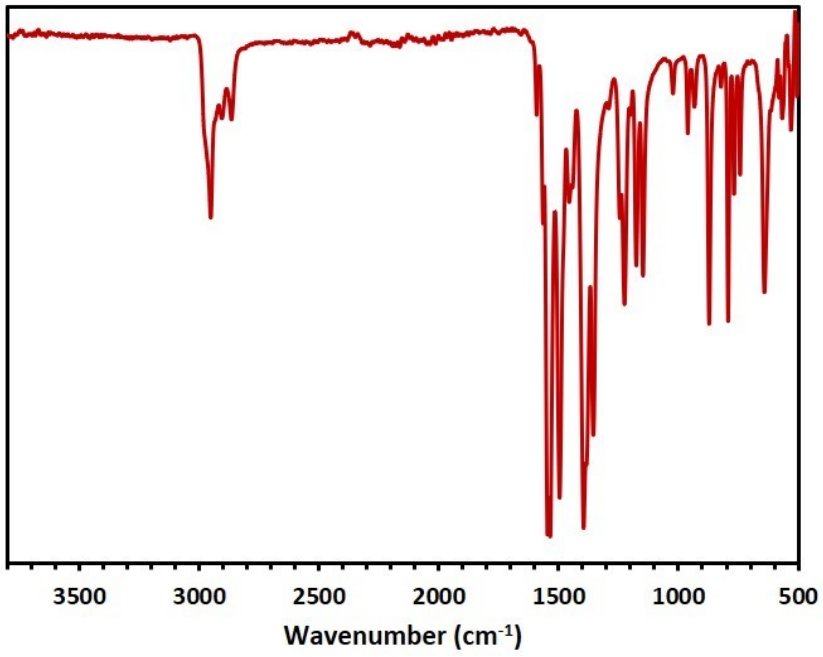

Figure S2 : FTIR spectrum of the synthesized $Cu(thd)_2$.

B2. Bulk CuTPA

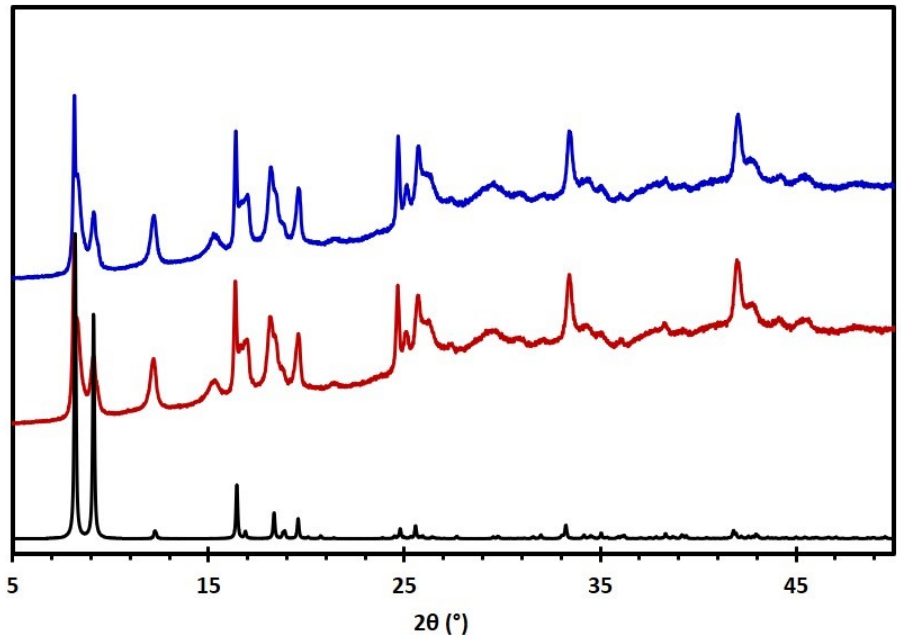

Figure S3 : PXRD patterns of bulk CuTPA after methanol exchange (red) and after activation (blue) as well as the calculated pattern (black) of the triclinic 3D phase.

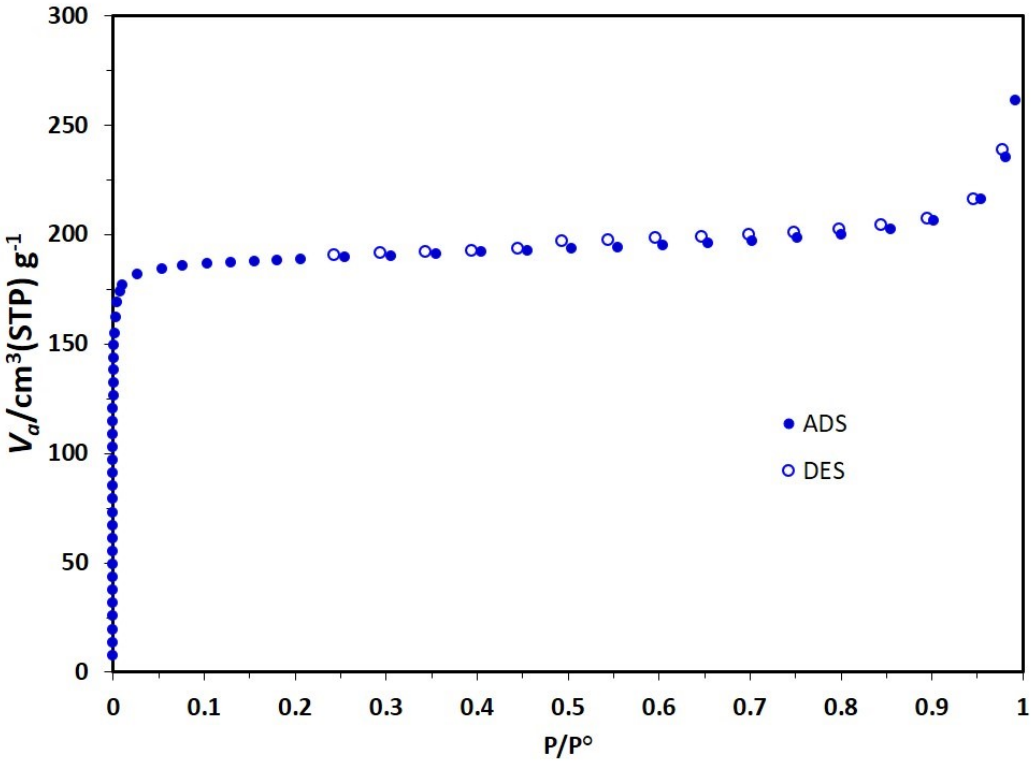

Figure S4 : N_2 sorption isotherm at 77K of bulk CuTPA, the derived BET SA is 770 $m^2.g^{-1}$.

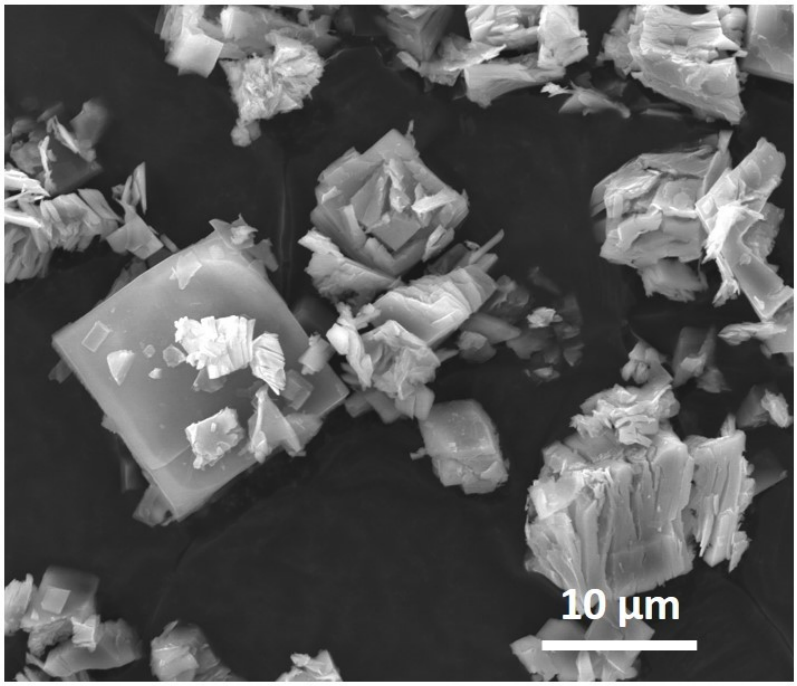

Figure S5 : SEM image of the bulk CuTPA crystallites.

B3. Bulk DMOF-1

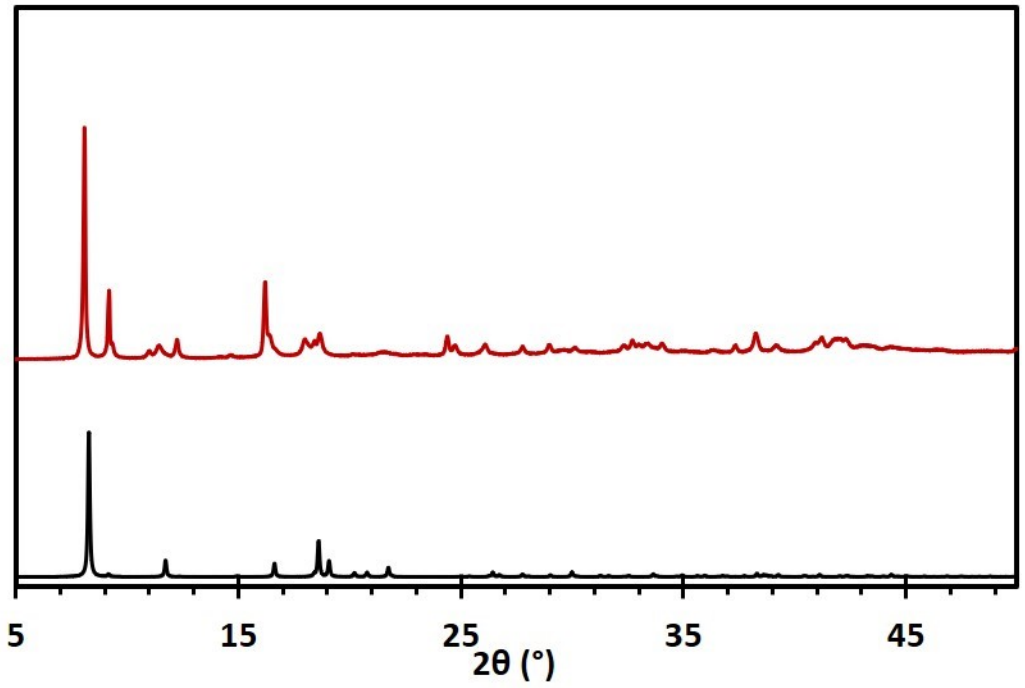

Figure S6 : PXRD pattern of bulk DMOF-1 (red) and the calculated pattern from the single crystal structure (black).

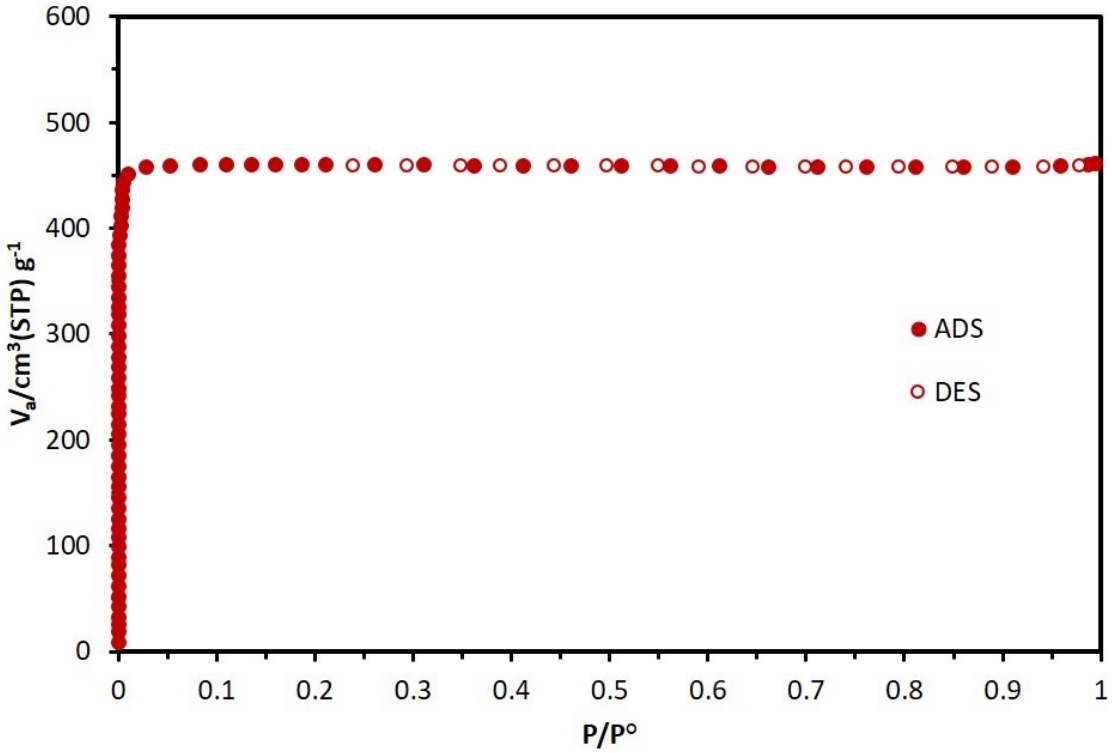

Figure S7 : N_2 sorption isotherm at 77K for bulk DMOF-1, the derived BET SA is 2020 $m^2.g^{-1}$.

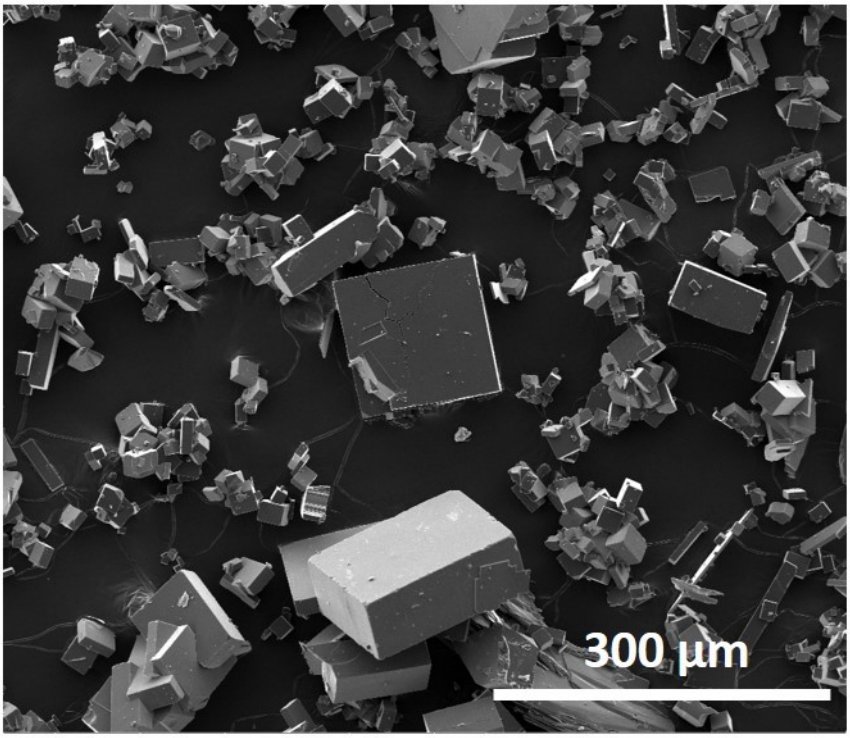

Figure S8: SEM image of bulk DMOF-1 crystals.

C. ALD/MLD deposition of CuTPA

The CuTPA films were deposited on different substrates: FTO, sapphire, DMOF-1 single-crystal, and Si (100) with native oxide, using a home-made manual reactor, depicted in Figure S9. It consists of a stainless steel tube, connected to the reactant canisters on one side and to the exhaust line on the other side. The precursors employed are $Cu(thd)_2$ and TPA, kept separated in stainless-steel canisters, respectively at 110 °C and 180 °C. They were sequentially injected into the reactor using manual valves. To ensure uniform pulses, the argon carrier gas passed though the reactant canisters. The Ar flow is maintained constant and set to have a pressure in the reaction chamber to about 2 mbar during each pulse; a pressure gauge, connected to reactor monitored the reactor pressure. A cold trap was placed between the reaction chamber and the pump to condense the unreacted precursors and avoid their lost inside the pump.

Depositions were performed at 190 °C, in agreement with the reported ALD/MLD window.[4] To determine the pulse parameters that allow saturation of the surface, the pulse duration of each precursor was varied between 1, 2 and 5s, while a purge of 10s was set for both $Cu(thd)_2$ and TPA. The number of ALD/MLD cycles ranged from 160 to 300. To reduce/avoid the presence of unreacted precursors on the surface of the films, 5-micron gasket filter was inserted before the injection valve of $Cu(thd)_2$.

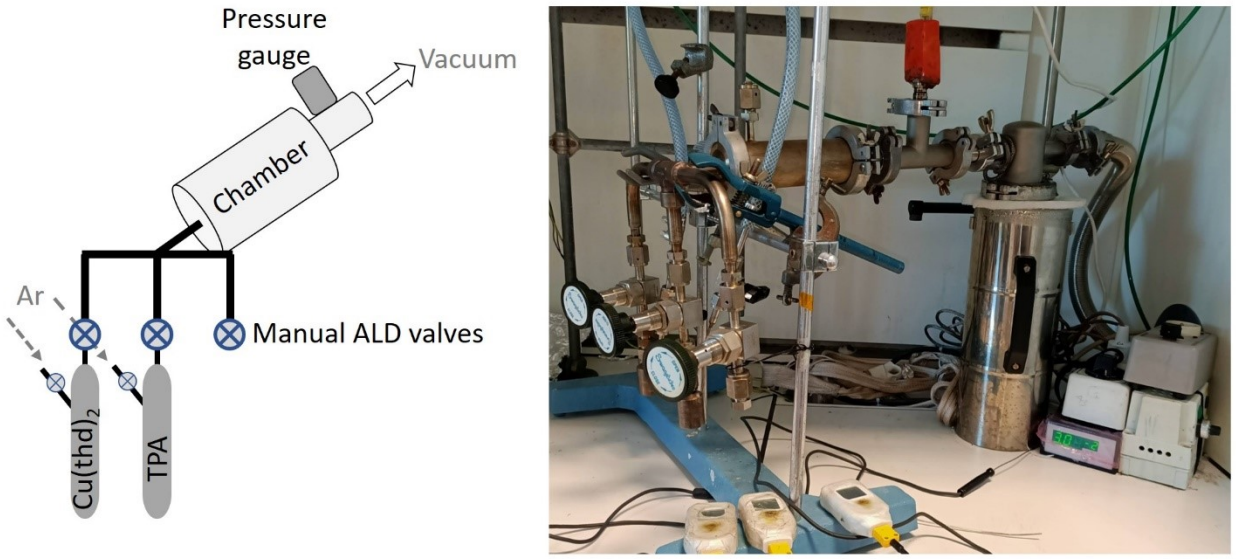

Figure S9 : Scheme (left) and photograph (right) of the home-made ALD/MLD reactor.

D. ALD/MLD of CuTPA thin films characterizations

Oriented thin film growth

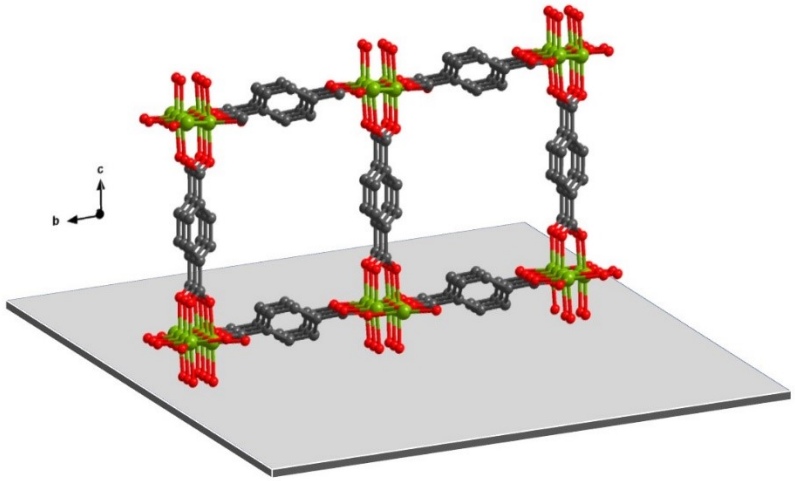

Figure S10 : Schematic representation of oriented CuTPA thin film growth on Si (100), with the c axis perpendicular and the pores running parallel to the substrate.

XRD characterizations

Reproducibility of the thin film growth

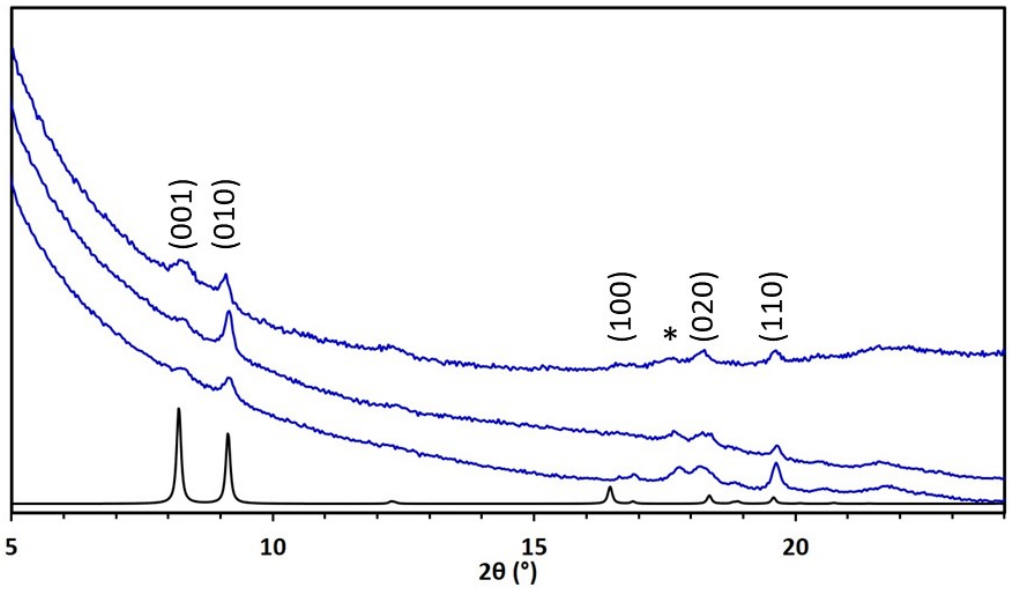

*Figure S11 : PXRD data for CuTPA thin film samples, deposited on Si (100) substrate at 190 °C using 160 cycles and (blue), calculated pattern for CuTPA (black), * corresponds to the free TPA.*

The observed variation in Figure S11 concerns the relative intensity of the diffraction peaks. This can be correlated to a beginning of loss of orientation of the crystallites and to a more isotropic film. Nonetheless, the overall pattern is preserved and the 3D phase is obtained in all cases.

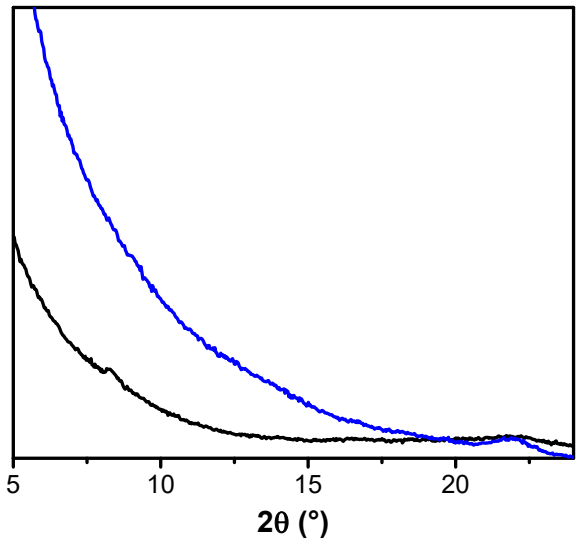

Figure S12: XRD patterns recorded from 152 and 91 nm thick films deposited using, respectively, shorter pulse (blue) and lower temperature for TPA (black).

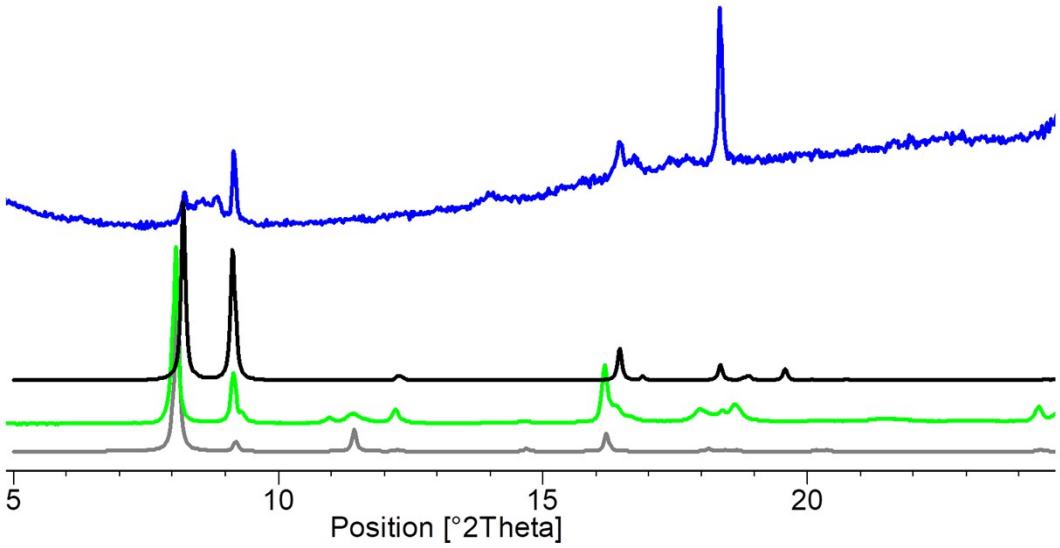

Figure S13: XRD patterns recorded from bulk DMOF-1 crystals (green) and DMOF-1 crystals dispersed on the Si (100) substrate after CuTPA ALD/MLD cycles (blue) compared to the calculated patterns of the 3D phase of CuTPA (black) and the DMOF-1 (grey).

In the experiment of CuTPA ALD/MLD on the DMOF-1 crystals, the deposition occurs both on the Si wafer and on DMOF-1 crystals. This wafer is then used for the X-Ray diffraction analysis. Therefore, it is not possible to record the X-Ray diffraction pattern corresponding solely to the heterostructure (CuTPA@DMOF-1), nonetheless the obtained pattern displays Bragg peaks corresponding to the CuTPA phase.

IR characterization

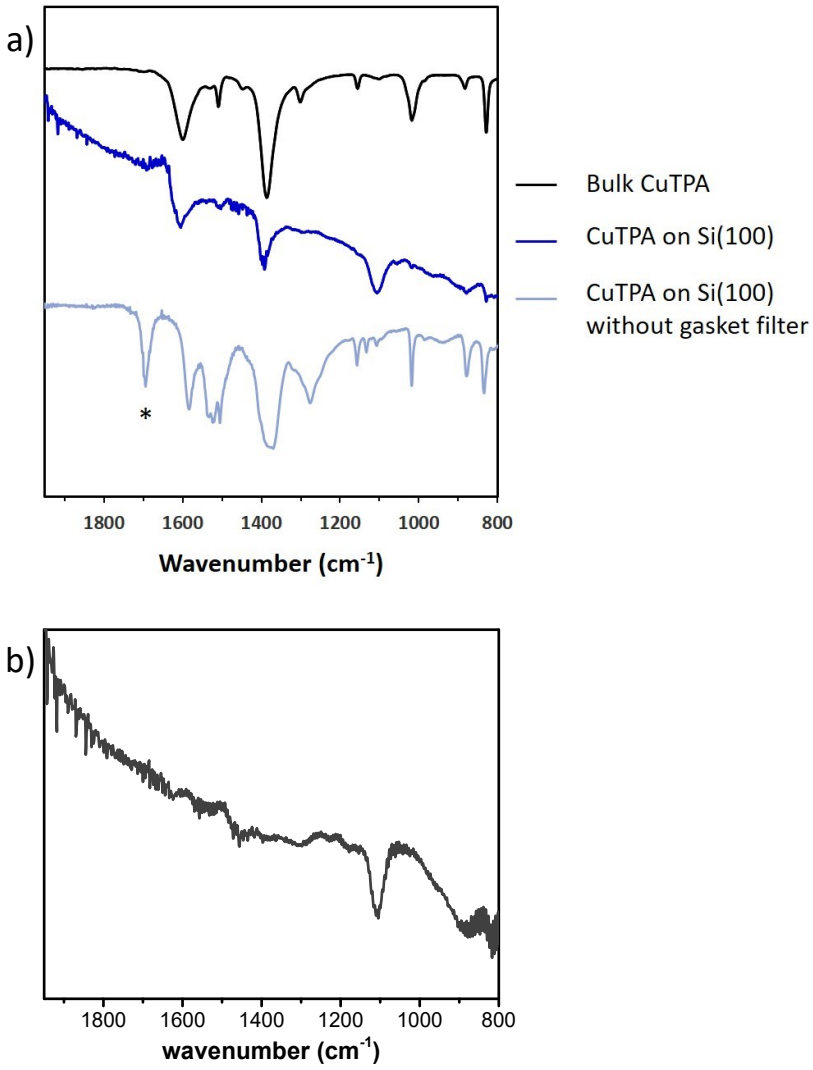

*Figure S14: FTIR spectra of the bulk CuTPA and the corresponding ALD/MLD deposited thin films on Si (100) with and without the use of the filter gasket, *shows the carboxylic acid vibration band (a) and of the bare Si wafer with native oxide (b).*

SEM/EDS characterizations

Film coverage

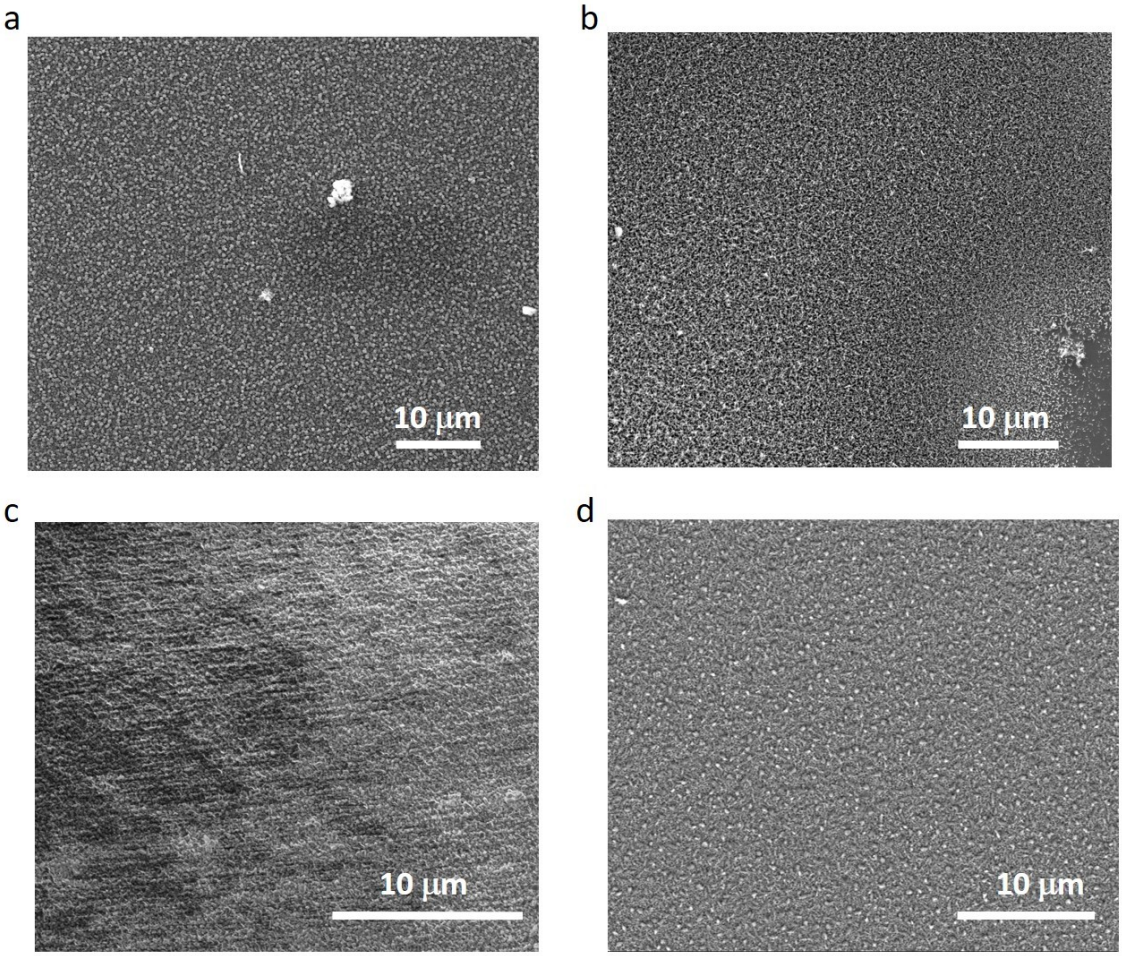

Figure S15: SEM images showing the homogeneity of the film coverage for the different substrates: Si (100) for a 160 cycles ALD/MLD (a), Si(100) for a 250 cycles ALD/MLD (b), sapphire for 250 cycles (c), FTO for 250 cycles ALD/MLD (d).

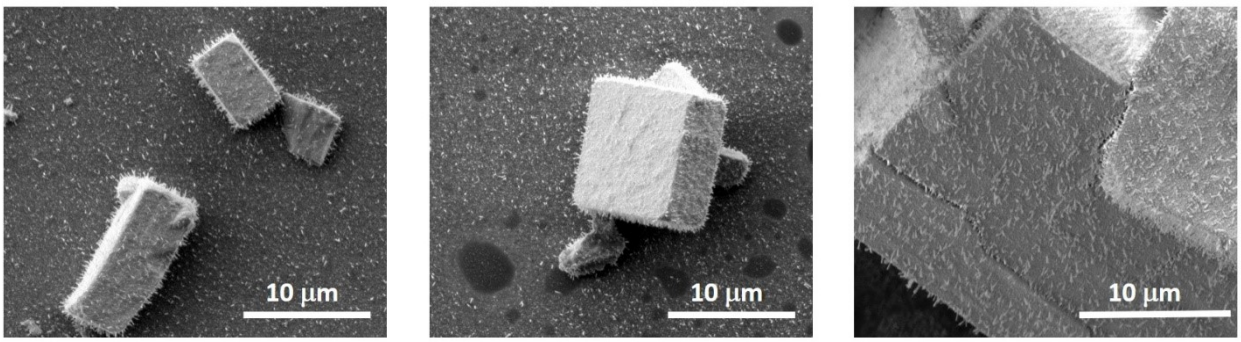

Figure S16: SEM images of several crystallites of DMOF-1 on Si (100), after the ALD/MLD of CuTPA.

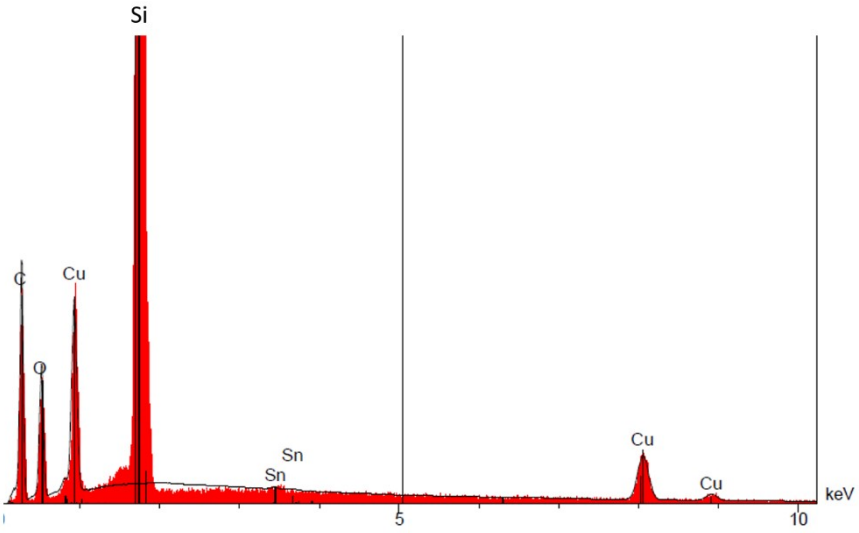

Figure S17. Energy-dispersive X-ray spectrum of CuTPA film obtained after 250 ALD/MLD cycles on Si (100).

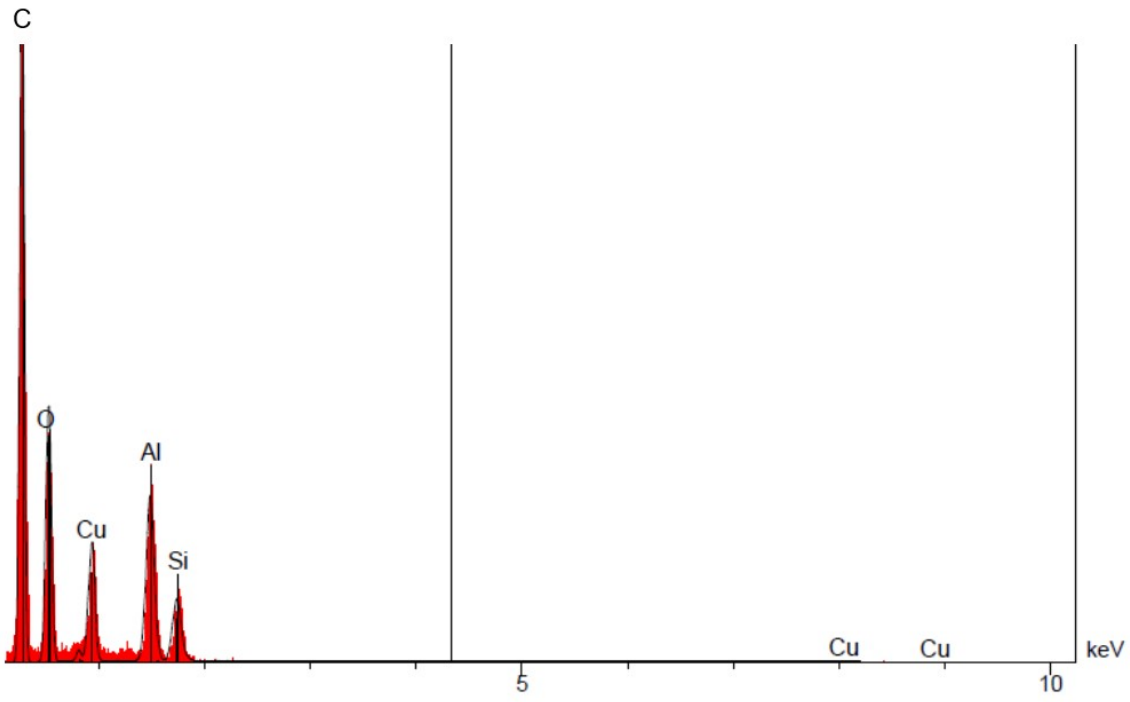

Figure S18: Energy-dispersive X-ray spectrum of CuTPA film obtained after 250 ALD/MLD cycles on sapphire.

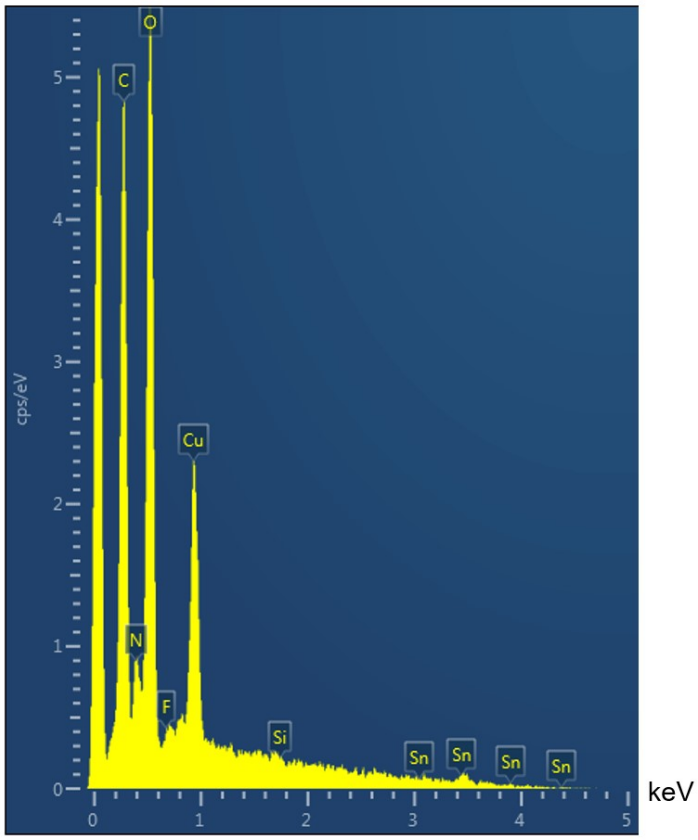

Figure S19: Energy-dispersive X-ray spectrum of CuTPA film obtained after 250 ALD/MLD cycles on FTO.

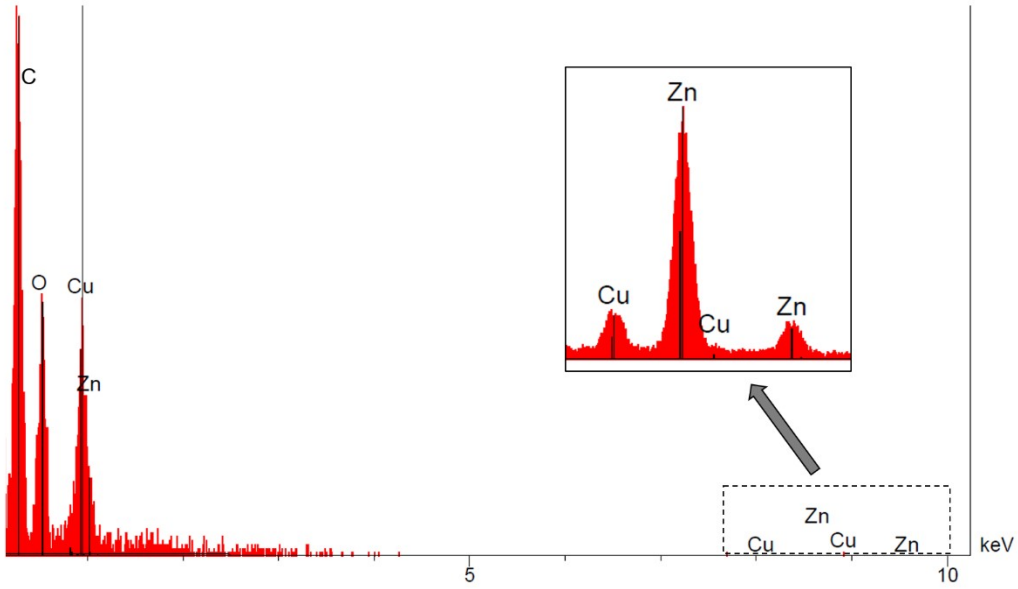

Figure S20: Energy-dispersive X-ray spectrum of CuTPA film grown on DMOF-1 (Zn-TPA-DABCO) single crystal through 250 ALD/MLD cycles.

References

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4. Ahvenniemi, E. & Karppinen, M. Atomic/molecular layer deposition: a direct gas-phase route to crystalline metal–organic framework thin films. *Chem. Commun.* **52**, 1139–1142 (2016).