

## ESI: Supporting information

# On the electrochemical deposition of Metal-Organic Frameworks

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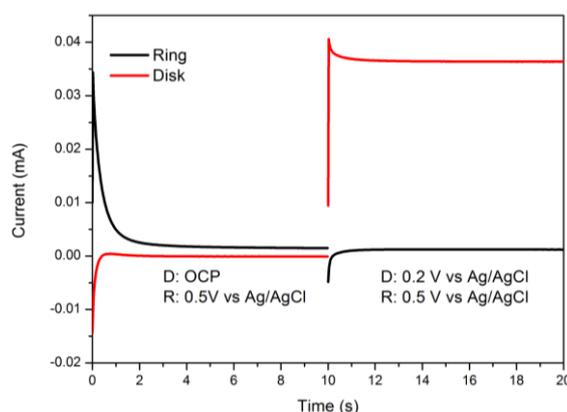
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## Oxidation state of copper in a trimesic acid solution



*Figure S1: Experiment to determine the oxidation state of copper ions released anodically in a trimesic acid solution.*

Using a Rotating Ring Disk Electrode (RRDE) set up, copper metal was deposited on the disk from a copper sulphate solution and the RRDE was then transferred in a beaker containing a trimesic acid solution. The disk was kept at OCP for 10 s, while the ring was at +0.5 V vs ref. (Ag/AgCl homemade electrode). In this phase no current was detected on the ring since no copper ions are present in solution. In the second part of the experiment, a potential of +0.2 V vs ref was applied to the disk for 10 s, releasing copper ions in solution. The ring was kept at +0.5 V vs ref. and even in this case no current was detected. If the copper ions were released as copper(I) from the disk, a positive current would have been observed on the ring, but since this did not occur it can be concluded that the copper ions released from the disk are in the copper(II) state.

## Anodic electrodeposition: Stress evolution on the substrate

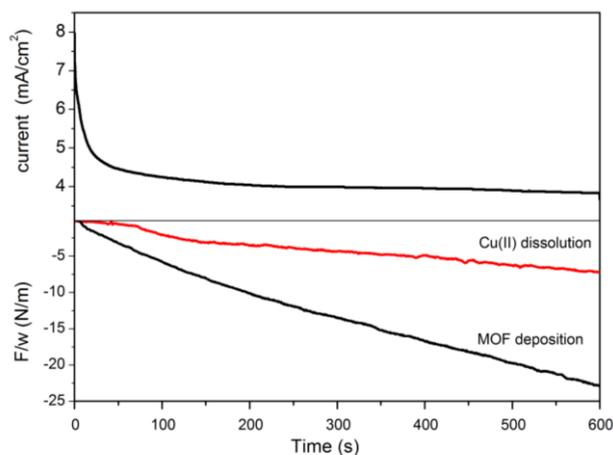


Figure S2: Current and stress measured during an anodic MOF deposition (2 V vs counter) in a solution containing 10 g L<sup>-1</sup> MTBS and 10 L<sup>-1</sup> H<sub>3</sub>BTC with a laser curvature set-up, and stress evolution during copper dissolution in a blank solution (without linker) under the same conditions.

## Anodic electrodeposition: islands growth and edge effect

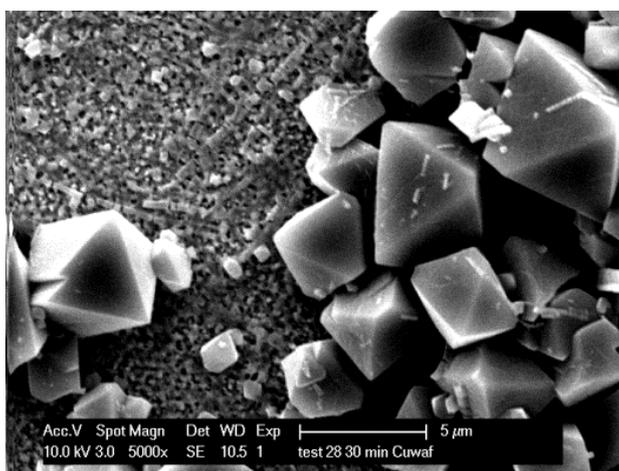
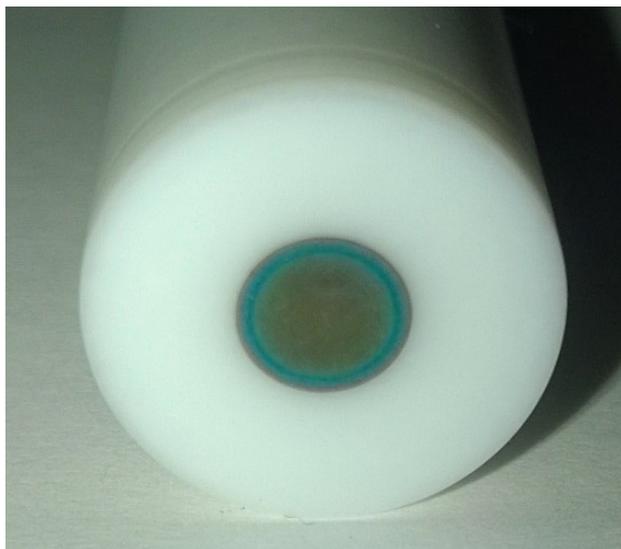


Figure S3: SEM pictures of HKUST-1 deposition after 20 min at 2 V vs counter on a copper-coated wafer.

The growth of islands phase is well shown in Figure S3: large and small crystals lay in agglomerates on the right side of the picture, while areas where copper is still exposed can be noticed on the left side.



*Figure S4: RRDE after MOF electrodeposition at 1.5 V vs ref. for 5 minutes at circa 50 rpm.*

The picture shows that if no mask is used, like in the case of a RRDE, the MOF layer tends to grow at the edge of the electrode, in this case the disk. It is important to point out that the deposit is still on the disk, not on the ring.

## Crystal growth: MOF-solution or MOF-substrate interphase?

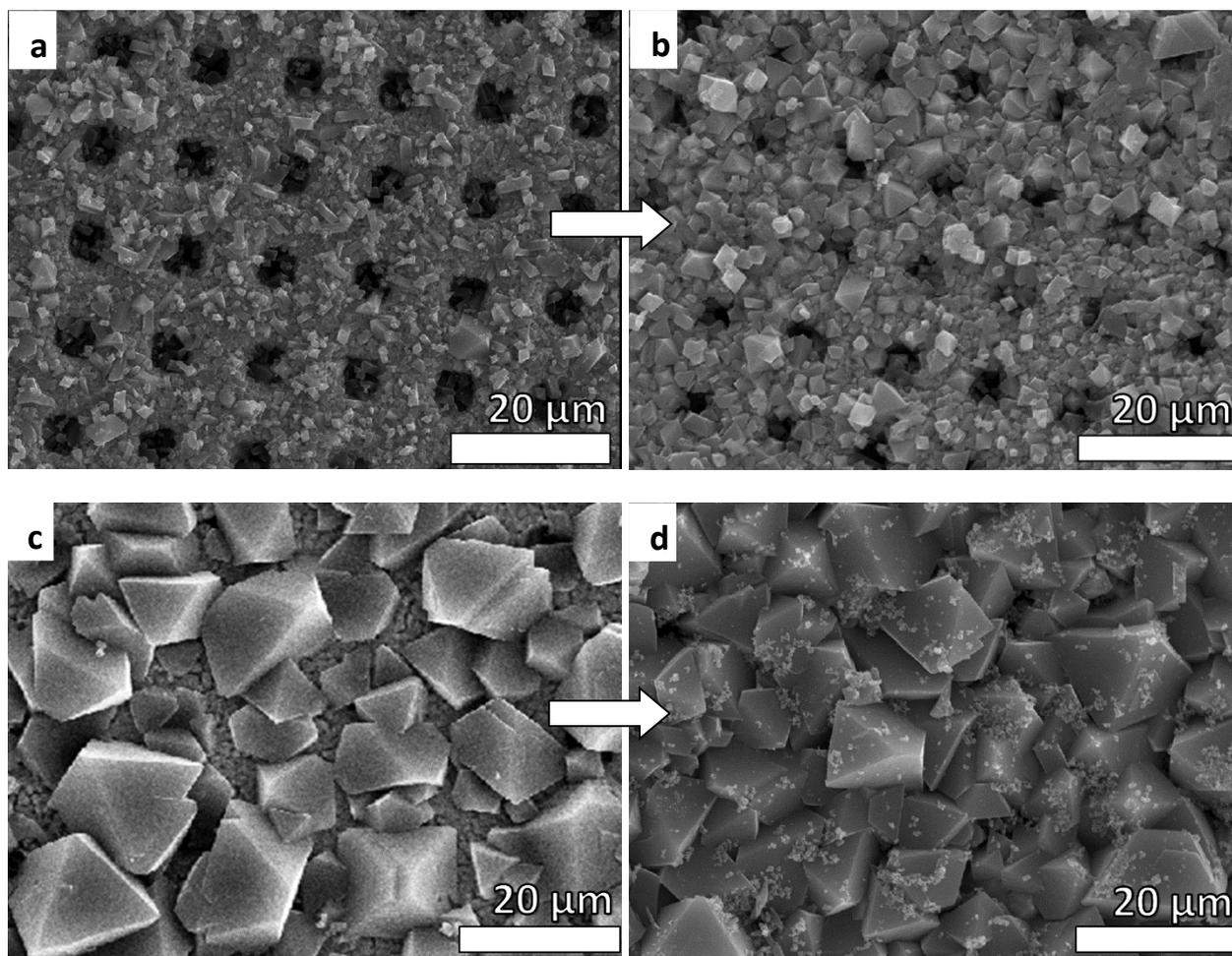


Figure S5: (TOP) HKUST-1 synthesised at 2.7 V vs counter for 20 min on a copper mesh using first a DMSO/methanol (35:65 wt%) mixture (a) and then a water/methanol (35:65 wt%) mixture in a second step (b). (BOTTOM) HKUST-1 synthesised at 2.7 V vs counter for 20 min using a water/methanol (35:65 wt%) mixture and in a second step a DMSO/methanol (35:65 wt%) mixture.

Indications that the MOF layer grows at the MOF-electrolyte interface in the case of HKUST-1 were obtained using different solvents for the synthesis of this MOF, since different solvents lead to MOFs with different crystal size. For example, layers synthesised in DMSO/methanol mixtures are composed of crystals sizably smaller than those synthesised in water/methanol. If a substrate is first subjected to electrodeposition and in one solution, and then in another, the final morphology reflects the two treatments; in particular the crystals expected from the last used of the two electrolytes are found preferentially on top of those expected from the first solvents (Figure S5).

## Cu-INA(X) (X=H, Cl, F) electrodeposition

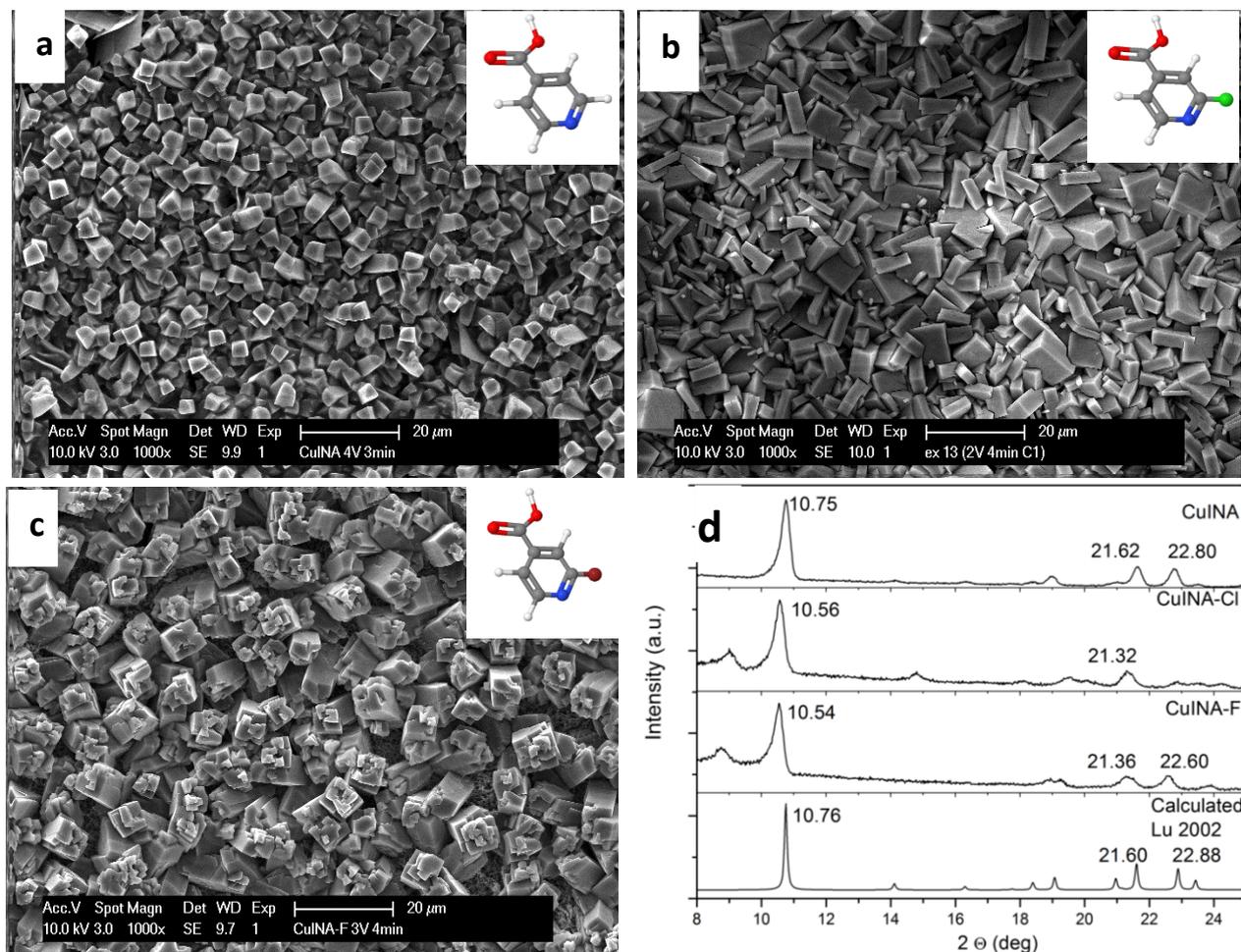
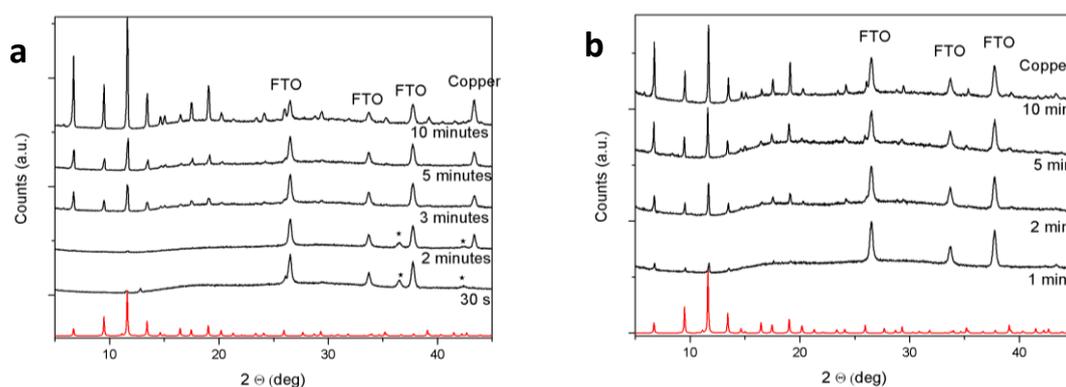


Figure S6: SEM pictures of Cu-INA (a), Cu-INA(Cl) (b) and Cu-INA(F) (c) layers with the sketch of the correspondent linkers. (d) Comparison between the XRD patterns of Cu-INA, Cu-INA(Cl), Cu-INA(F), and the calculated pattern from Lu et al.<sup>1</sup>

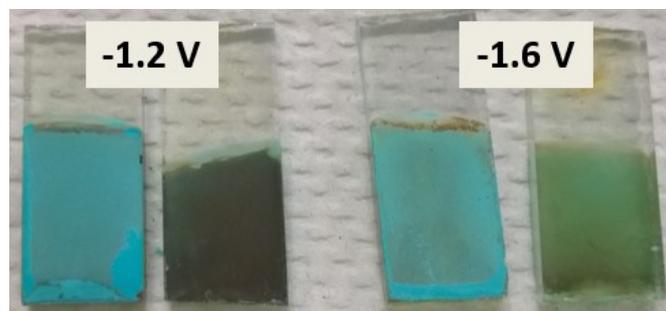
The electrochemical synthesis of Cu-INA layers was already reported by Van de Voorde et al.<sup>2</sup> In comparison to Cu-INA which can be synthesised as a pure phase, in none of the conditions tested for the substituted versions it was possible to avoid the deposition of a needle-shaped pre-phase. This pre-phase can be synthesised pure if low potentials are kept, while at higher potentials the cubic phase reported also for Cu-INA is present. Unfortunately, at too high potentials, detachment of the layers is observed. The shape of the crystals changes with the different linkers: while Cu-INA crystals look like truncated pyramids, Cu-INA(Cl) ones resemble plates, and Cu-INA(F) are more like cubes (Figure S6). All the samples are undistinguishable from the XRD patterns, except for the fact that the layers made by the substituted versions show a small peak shift

to lower angles and also the peak of the pre-phase, see *Figure S6d*. This pre-phase is crystalline and has already been indexed by Tran *et al.* in the P21/n space group,<sup>3</sup> while the more studied and already synthesised phase is also monoclinic but from the CC group.<sup>1</sup>

### Cathodic electrodeposition: different potentials.

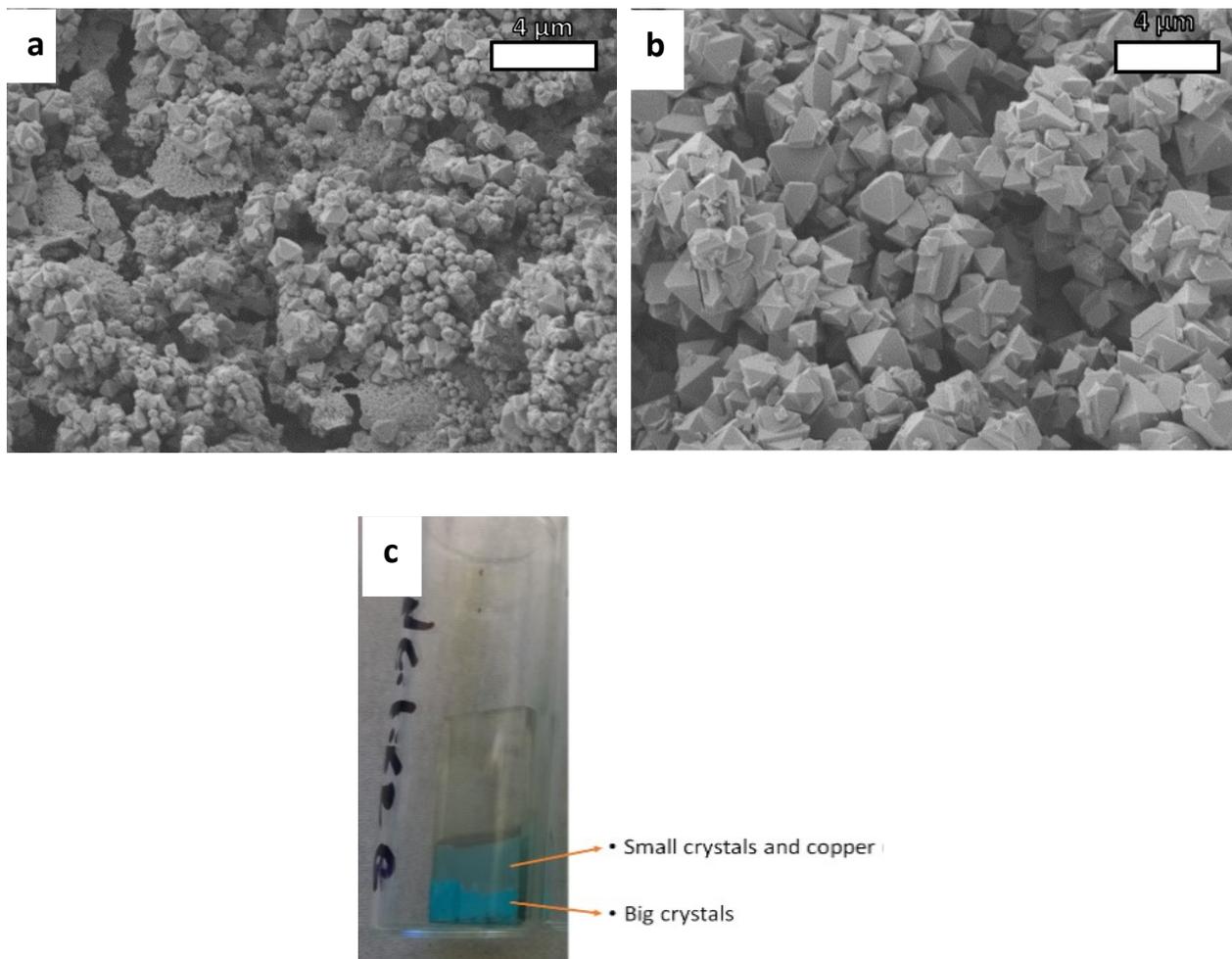


*Figure S7: XRD patterns of HKUST-1 samples synthesised cathodically for different times at: (a) -1.0 V vs Ag/Ag(Crypt)<sup>+</sup> and (b) -1.6 V vs Ag/Ag(Crypt)<sup>+</sup>. In red, the calculated XRD pattern of HKUST-1. (\* Cu<sub>2</sub>O)*



*Figure S8: Front and back pictures of HKUST-1 samples synthesised cathodically by applying -1.2 V and -1.6 V vs ref.*

From the time evolution of the XRD patterns recorded applying different cathodic potentials, it can be observed that copper is first deposited at -1.2 V vs ref, while the deposition starts right away with the MOF if -1.6 V are applied. Looking at the back side of the electrodeposited layers, which is possible thanks to the FTO substrate used, different colours can be observed: samples synthesised at -1.6 V are more transparent-blue due to the prevalent presence of MOFs, while those synthesised at -1.2 V are darker and opaque because of the metallic copper phase.



*Figure S9: SEM (a,b) and optical (c) images of a sample synthesised at -1.2 V for 10 min. The SEM pictures were taken (a) from the top part where the layer is made by MOF co-deposited with copper, and (b) from the bottom part, where the layer is thick and made out of large crystals.*

## Cathodic electrodeposition: CV blank.

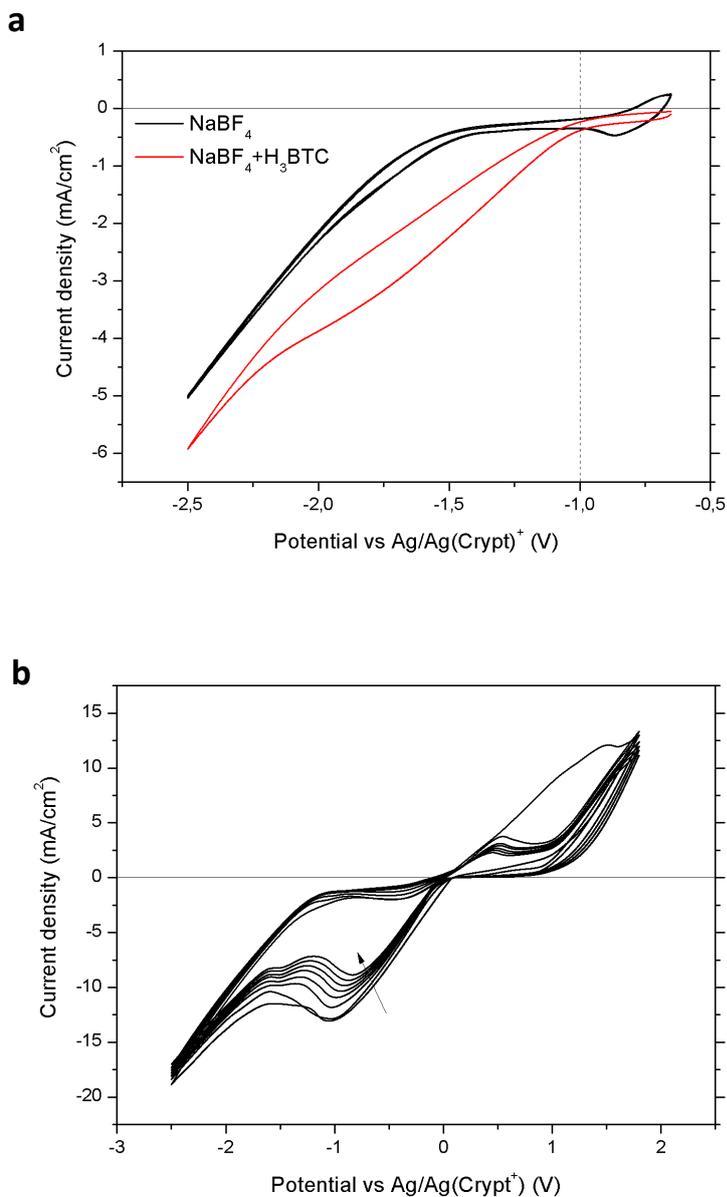
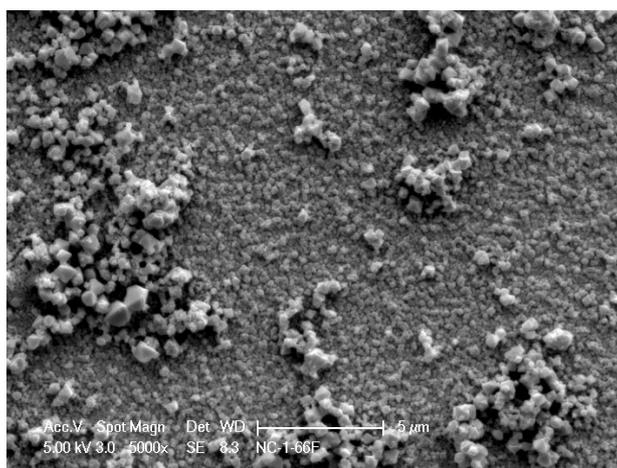


Figure S10: (a) Cyclic voltammetry of a copper plate in a blank solution (100 mM NaBF<sub>4</sub>) and one containing trimesic acid (50 mM H<sub>3</sub>BTC + 100 mM NaBF<sub>4</sub>) at 100 mV s<sup>-1</sup>. (b) as a comparison, CV at 100 mV s<sup>-1</sup> of an FTO plate in a solution containing trimesic acid, conductive salt and copper(II) nitrate.

In absence of trimesic acid the reduction of the water present in the solvent starts at circa -1.5 V vs ref. Adding H<sub>3</sub>BTC the reduction potential shifts to -1.0 V vs ref, which is the potential at which deposition of HKUST-1 was observed during the potential screening shown in the main text. If some free copper ions are released in solution, as in the case of the experiment with the conductive salt alone, the deposition and stripping waves

are visible at more anodic potentials than the reduction of trimesic acid, in agreement with the observation of pure copper metal deposits at potentials less cathodic than -1.0 V vs ref. With the solution normally used in this report for the cathodic deposition it is observable that copper plating starts at 0 V vs ref. and both the anodic and the cathodic waves decrease in intensity due to the presence of a MOF layer which hampers the electrochemical reaction, acting as an apparent resistance, as shown before.

**Cathodic electrodeposition: island growth.**



*Figure S11: SEM picture of an HKUST-1 sample synthesised cathodically on FTO at -1.2 V vs ref for 30 seconds.*

From this SEM image taken in the early stages of the cathodic deposition of a MOF film it can be seen the tendency of the crystals to grow in islands or agglomerates.

## Cathodic electrodeposition: time evolution

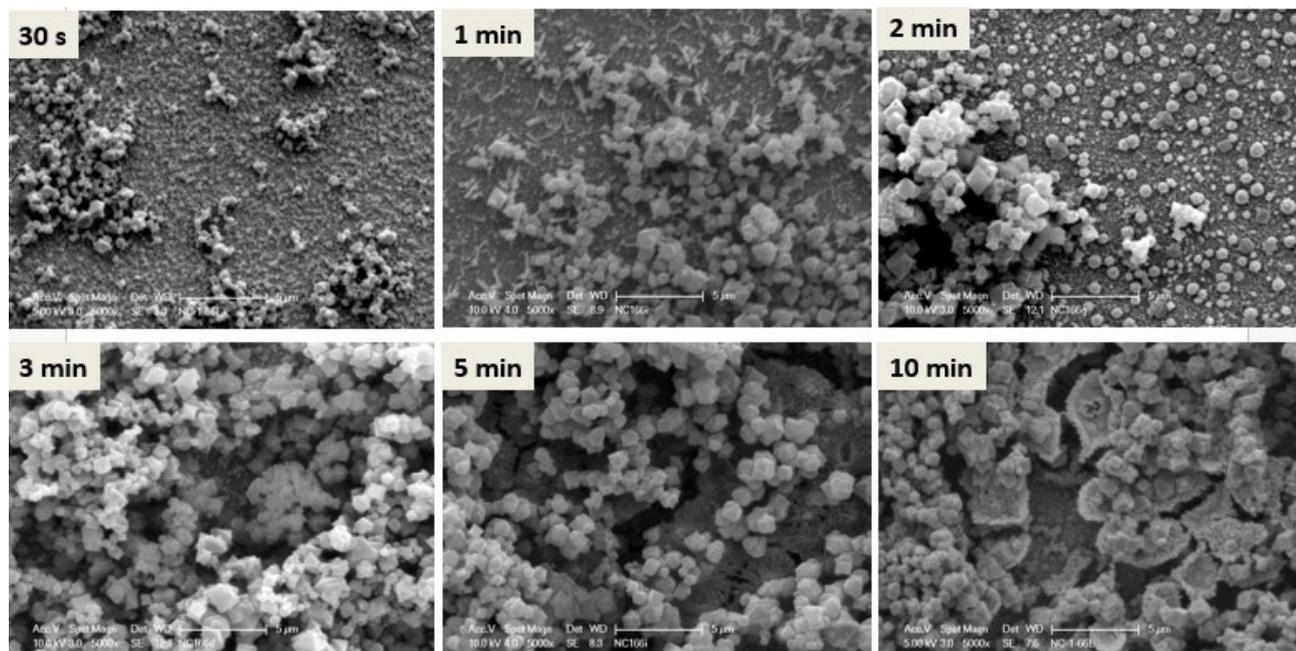


Figure S12: SEM picture of an HKUST-1 sample synthesised cathodically on FTO at -1.2 V vs ref for 30 s, 1, 2, 3, 5, and 10 min.

## Cathodic electrodeposition: FIB+elemental analysis

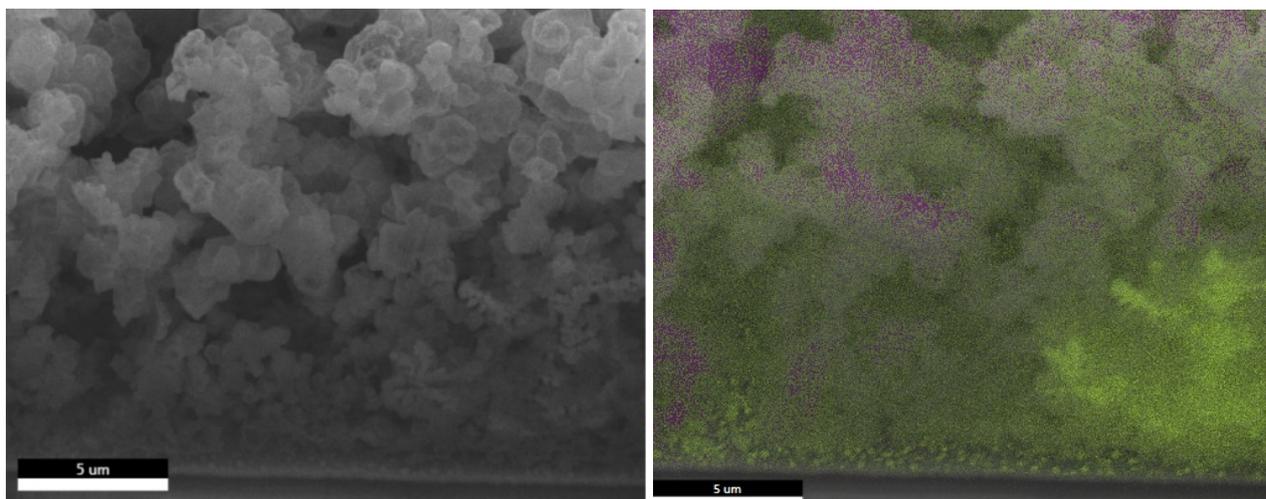


Figure S13: Cross section of a HKUST-1 sample synthesised cathodically on FTO at -1.6 V vs ref for 2 min. Left, SEM image, right elemental contrast (purple = carbon, green = copper).

From the FIB images with and without elemental contrast, the two phases described in the main text can be observed: The lower part of the layer is constituted by smaller aggregates which give high copper signal, but also a carbon signal. A dendritic-like feature can be seen on the right side of the image, among several crystal-shaped features, which is a good indication of the co-deposition of copper and MOF crystals. This is the part called small crystals+copper in the main text. On the other hand, the top part has mostly bigger crystals, often with the well-defined octahedral shape, and the copper signal coming from this areas is weaker.

## References

1. Lu, J. Y.; Babb, A. M., An extremely stable open-framework metal–organic polymer with expandable structure and selective adsorption capability *Chem. Comm.* **2002**, (13), 1340-1341.
2. Van de Voorde, B.; Ameloot, R.; Stassen, I.; Everaert, M.; De Vos, D.; Tan, J.-C., Mechanical properties of electrochemically synthesised metal-organic framework thin films. *Journal of Materials Chemistry C* **2013**, 1, (46), 7716-7724.
3. Tran , D. T.; Fan, X.; Brennan, D. P.; Zavalij, P. Y.; Oliver, S. R., Open metal-organic framework containing cuprate chains. *Inorg. Chem.* **2005**, 44, (18), 6192-6196.