

## Supporting Information

### **Synthesis, size and structural evolution of metal-organic framework-199 via a reaction-diffusion process at room temperature**

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## **Materials**

1,3,5-Benzenetricarboxylic acid (BTC) and Copper Acetate monohydrate were purchased from Acros Organics, Agar from Bacto, N-N-Dimethyl Formamide (DMF), and Ethanol absolute from Sigma Aldrich.

## **Preparation of gel and synthesis of the MOF-199**

Regarding the preparation of MOF-199, the inner portion consists of the ligand BTC mixed with agar gel in an Ethanol/Water (10%/90%) solution. The whole mixture is then heated up to a convenient temperature so that the agar gel becomes clear and directly transferred into a Pyrex test tube filling its two thirds, which is then covered and left until the agar has jellified completely.

The outer portion is formed by dissolving the Copper Acetate metal salt in an Ethanol/Water (10%/90%) mixture. Following this, the obtained solution is added to the congealed inner portion filling by that the remaining volume of the tube. Finally, the tube is covered and left for the reaction-diffusion process.

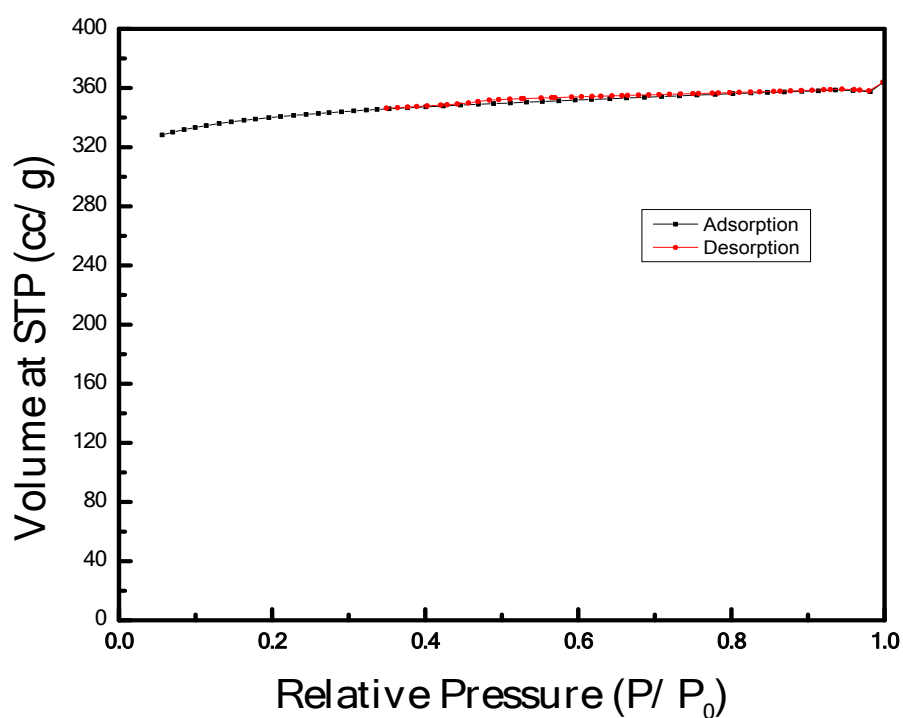
The formed MOF-199 is extracted by heating the agar gel in double distilled water at 60 °C with continuous stirring until the gel becomes clear. Then, the precipitate of the MOF-199 are collected and separated from the supernatant solution through centrifugation. After that, the obtained MOF-199 particles are washed with DMF over 3 days and then with DCM by solvent exchange. Finally, the sample is subjected to freeze drying for 10 hours so that it becomes ready to be characterized with the corresponding techniques.

## Characterization

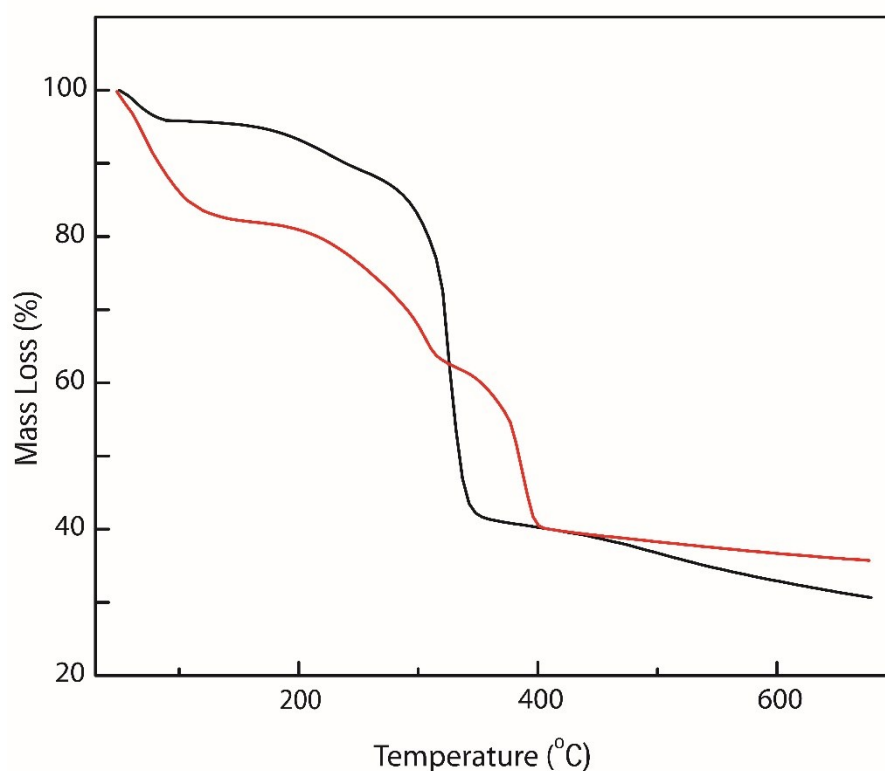
X-Ray Diffraction (XRD) patterns were recorded on a Bruker D8 discover XRD diffractometer using CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 40 mA, with  $2\theta$  ranging between  $5^\circ$  and  $40^\circ$  at a scanning rate of  $0.5^\circ \cdot \text{min}^{-1}$  and a total analysis time of 30 min. The thermogravimetric analysis (TGA) of the precipitates were performed under nitrogen atmosphere with a heating rate of  $5^\circ \text{C} \cdot \text{min}^{-1}$  and a temperature ranging from  $30^\circ \text{C}$  to  $1100^\circ \text{C}$  using a TG 209 F1 Iris (Netzsch, Germany). The  $\text{N}_2$  adsorption/desorption isotherms, surface area and total pore volume were obtained using a Micromeritics ASAP 2420 analyzer. Prior to the  $\text{N}_2$  adsorption/desorption and TGA measurements, the samples were washed for 3 days with DMF followed by 2 washing days with DCM. The morphology of the gold-coated samples was examined using a scanning electron microscope (Tescan Mira), operating at 5 kV with Oxford detector for energy dispersive X-ray (EDX) characterization.



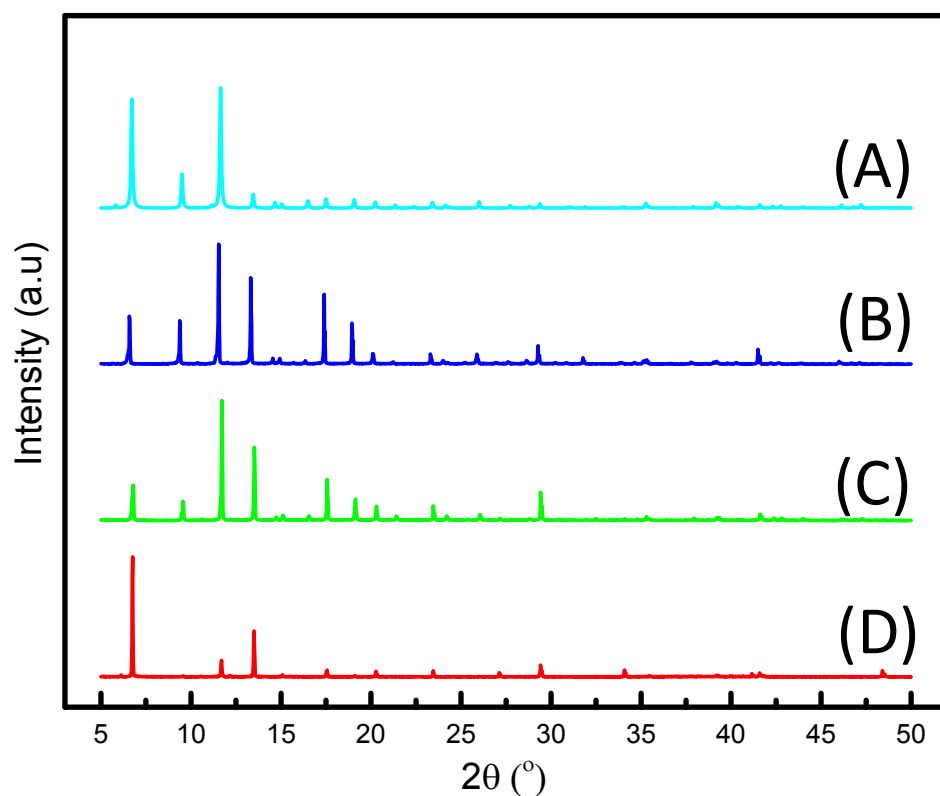
**Fig. S1:** Room-temperature synthesis of MOF-199 using RDF at different scales.



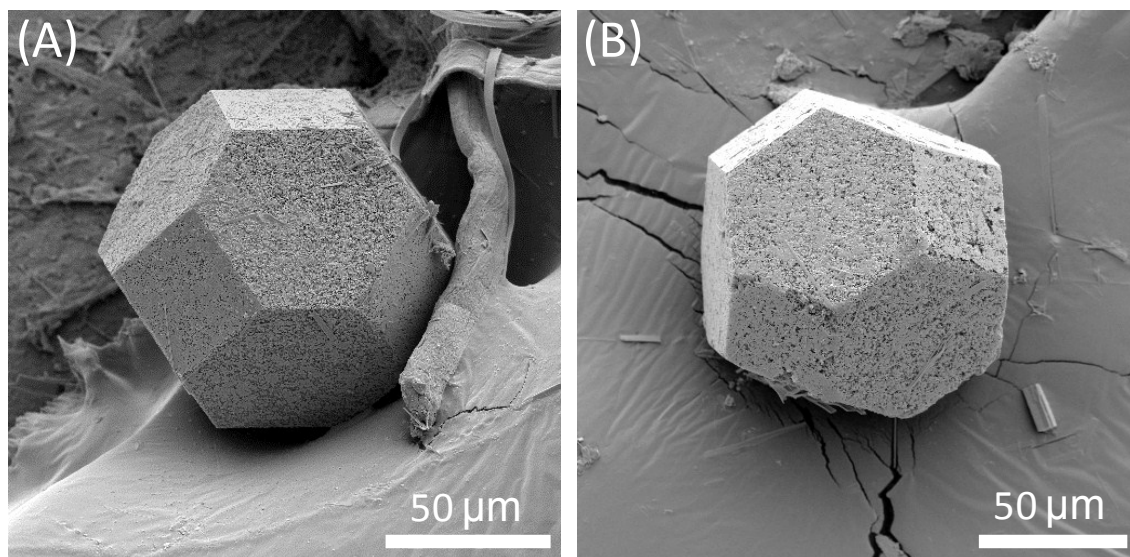
**Fig. S2:** Nitrogen physisorption isotherm of synthesized MOF-199 after extraction using copper acetate as outer electrolyte ( $[\text{Cu}^{2+}] = 100 \text{ mM}$  and  $[\text{BTC}] = 20 \text{ mM}$  at  $25^\circ \text{C}$ ). The sample was degassed at  $80^\circ \text{C}$  under vacuum for 10 h. The BET surface area for MOF-199 is  $1236 \text{ m}^2/\text{g}$ . The  $\text{N}_2$  adsorption-desorption isotherms exhibit a mode of type IV with a pronounced adsorption-desorption hysteresis loop of type  $\text{H}_4$ , corresponding to mesoporous and microporous materials.



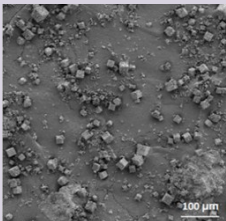
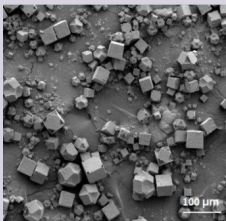
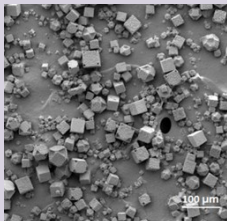
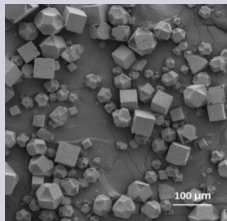
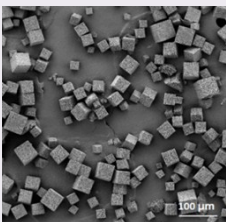
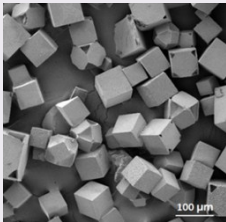
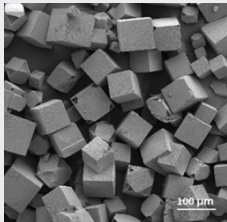
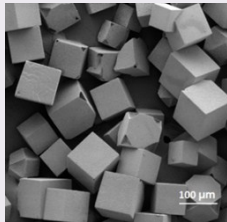
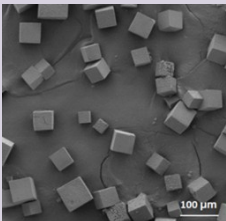
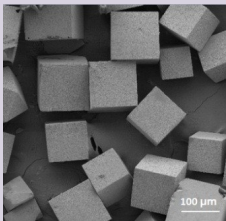
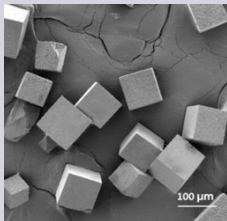
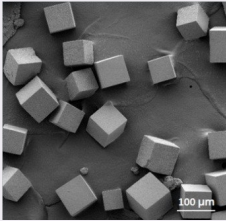
**Fig. S3:** Thermogravimetric curves of the Cu<sub>3</sub>(BTC)<sub>2</sub> under nitrogen atmosphere with a heating rate of 5 °C.min<sup>-1</sup> and a temperature ranging from 30 °C to 700 °C of (a) synthesized MOF-199 (red) (b) activated MOF-199 (black). Weight losses were observed in two steps; the first step is around 100 °C corresponding to the volatilization of the solvent molecules and the decomposition of the organic gel matrix. The second one is around 350 °C conforming to the decomposition of the MOF-199 framework to give CuO.



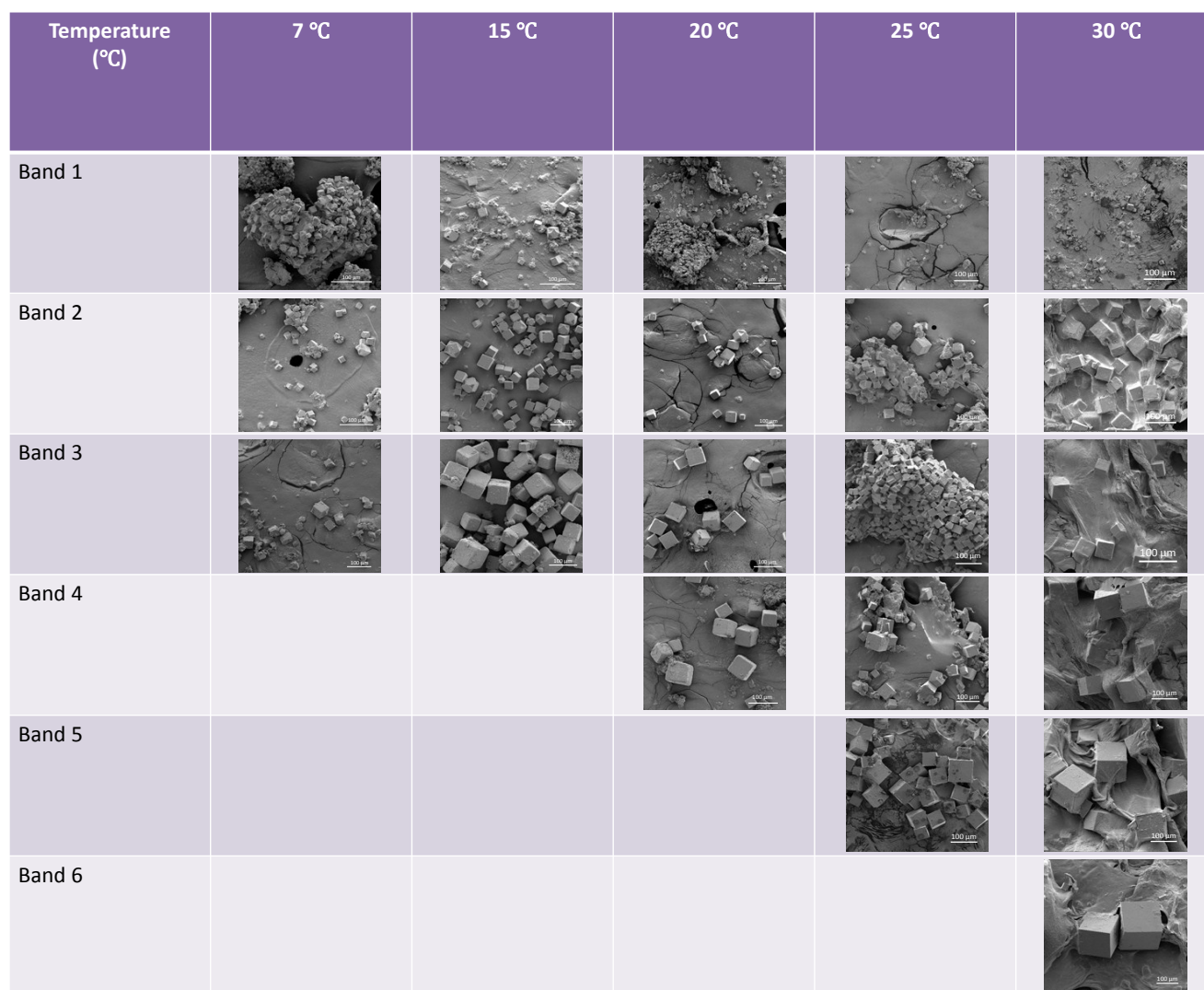
**Fig. S4:** Powder XRD patterns of MOF-199 using different metal salts in the outer, (A) simulated from the single crystal data of MOF-199, (B)  $\text{Cu}(\text{OAc})\cdot\text{H}_2\text{O}$ , (C)  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ , (D)  $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ .



**Fig. S5:** SEM images of MOF-199 crystals prepared at  $[\text{BTC}] = 10 \text{ mM}$ ,  $T = 25 \text{ }^\circ\text{C}$ , 1 % agar gel, and outer electrolyte copper sulfate (100 mM) (A) outer copper nitrate (100 mM) (B).

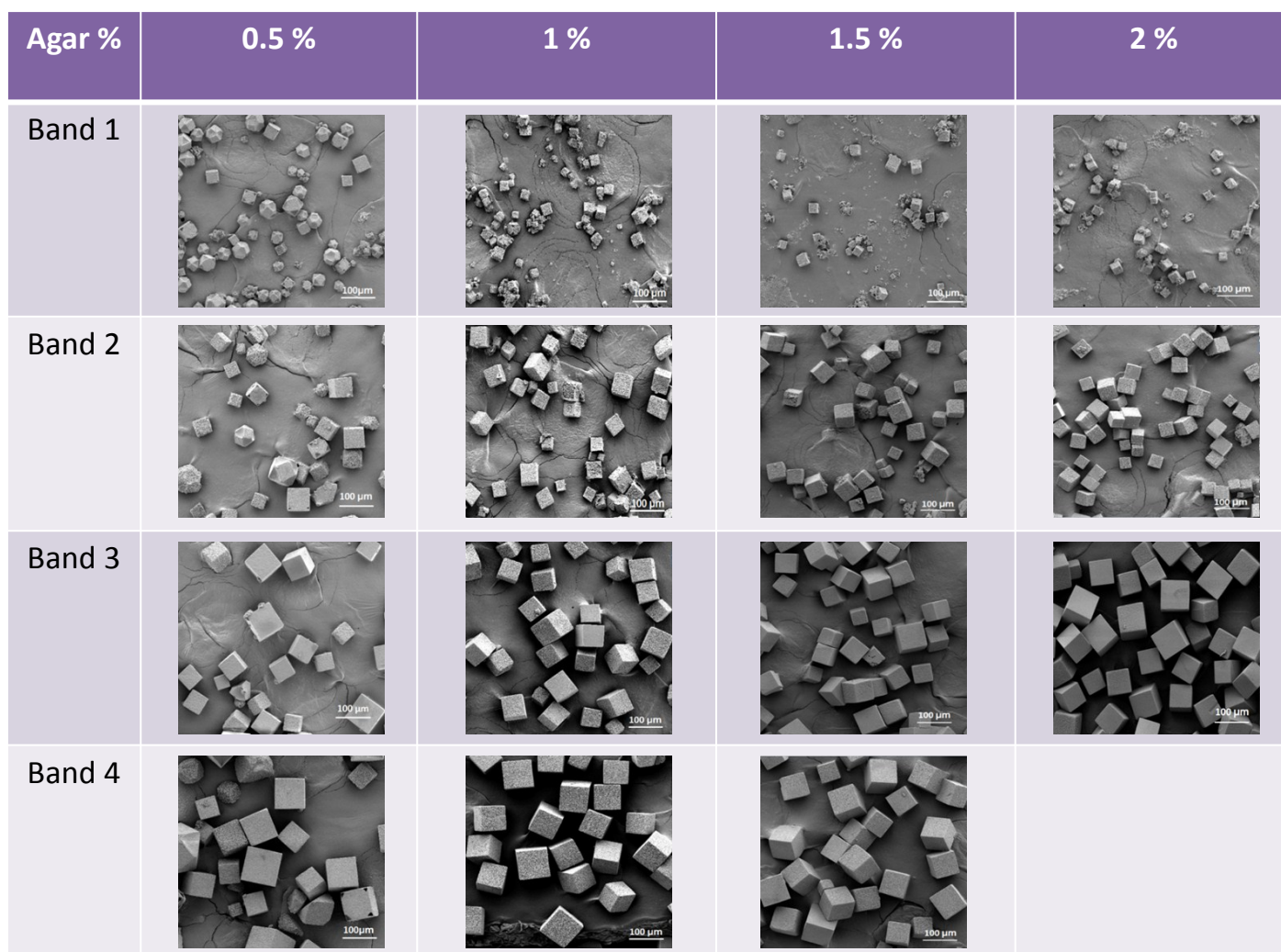
Inner [BTC]	5 mM	10 mM	20 mM	50 mM
Band 1				
Band 2				
Band 3				
Band 4				

**Fig. S6:** SEM images showing the growth pattern of the MOF-199 particles at different inner concentration [BTC] and outer  $[\text{Cu}^{+2}] = 100 \text{ mM}$  in consecutive bands of the tube (0.5 cm each, starting at the gel interface).  $T = 25 \text{ }^{\circ}\text{C}$ , 1 % agar gel.



**Fig. S7:** SEM images showing the growth pattern of the MOF-199 particles at different temperatures and same inner concentration [BTC] = 10mM and outer concentrations  $[Cu^{+2}] = 100 \text{ mM}$  in consecutive bands (0.5 cm each, starting at the gel interface). 1 % agar gel.

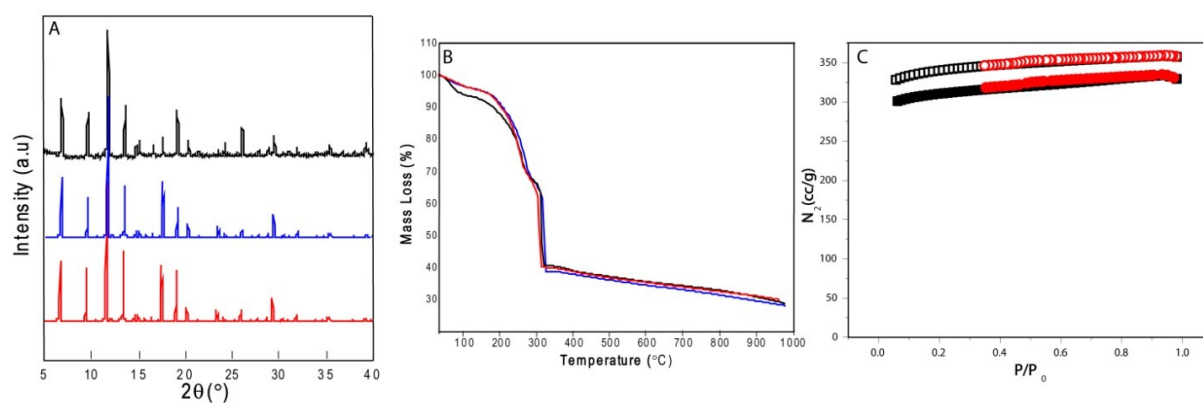




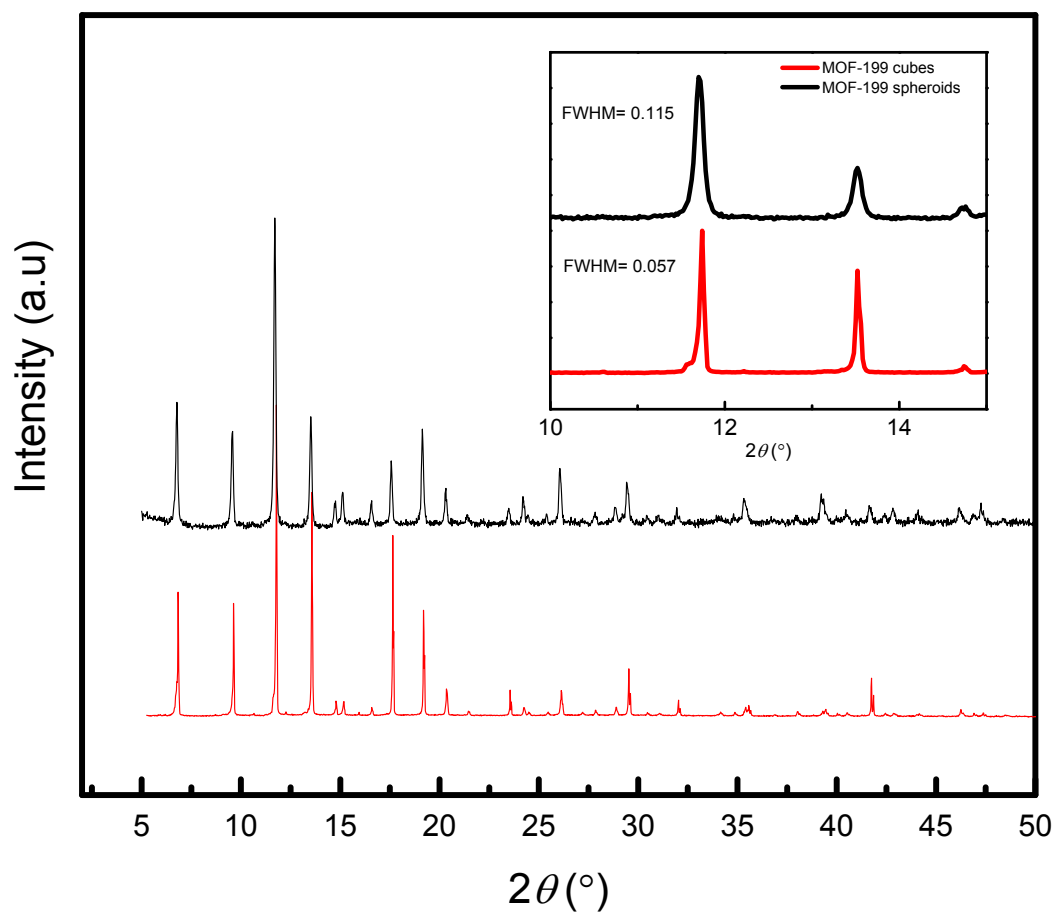
**Fig. S8:** SEM images showing the growth pattern of the MOF-199 particles at different agar gel concentration in consecutive bands (0.5 cm each, starting at the gel interface). Same inner concentration [BTC] = 10mM and outer concentrations [Cu<sup>2+</sup>] = 100 mM. T = 25 °C.







**Fig. S9:** PXRD patterns (A), TGA curves (B) of crystals extracted from 3 consecutive bands the MOF-199 and BET isotherms (C) of crystals extracted from the first and last bands for inner concentration [BTC] = 10mM and outer concentrations  $[\text{Cu}^{+2}] = 100 \text{ mM}$ .  $T = 25^{\circ}\text{C}$ .



**Fig. S10:** PXRD pattern of the MOF-199 spheroid from the interface region after 2 s (Black) compared to that of the cubic crystals after 10 s.