Supplementary Information.

Green Scalable Aerosol Synthesis of Porous Metal Organic Frameworks

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1. Materials and Methods:

Iron (III) chloride hexahydrate, Pluronics F-127, hexadecamethyltrimethylammonium bromide (CTAB), copper (II) nitrate hydrated, zinc nitrate hexahydrated and 2-methylimidazole were purchased from Aldrich. 1,3,5-tricarboxybenzene (trimesic acid, H_3BTC) was furnished by BASF chemicals. Absolute ethanol, methanol and other solvents were purchased from Carlo Erba and used as received.

Powder XRD measurements were performed with a Brucker D8 X-ray diffractometer operating in the reflection mode at Cu Ka radiation. The data were collected in the 4–40 range (2θ) with steps of 0.04 and a counting time of 10 s.

Infrared spectra were recorded on a Nicolet 6700 FT-IR Scientific spectrometer with a diamond interface.

TGA measurements were performed on a Perkin Elmer STA 600 simultaneous thermal analyzer. Samples were heated at 2 ºC min^{-1} to 600 ºC.

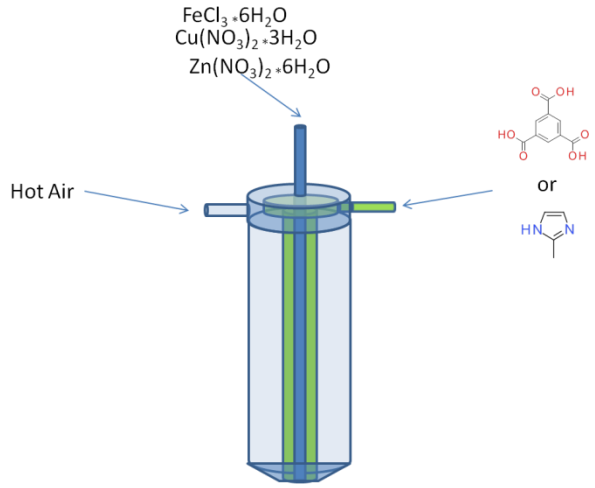
Nitrogen Sorption studies were carried out at 77 K in a Belsorp Max apparatus, specific surface area was calculated both by Brunauer-Emmett-Teller method. Activated materials were degassed at 160ºC for 3 h.

FE-SEM images were recorded on a Hitachi apparatus. Voltages were kept between 1.0 and 3 kV. Samples were prepared by depositing the sample on a carbon tape.

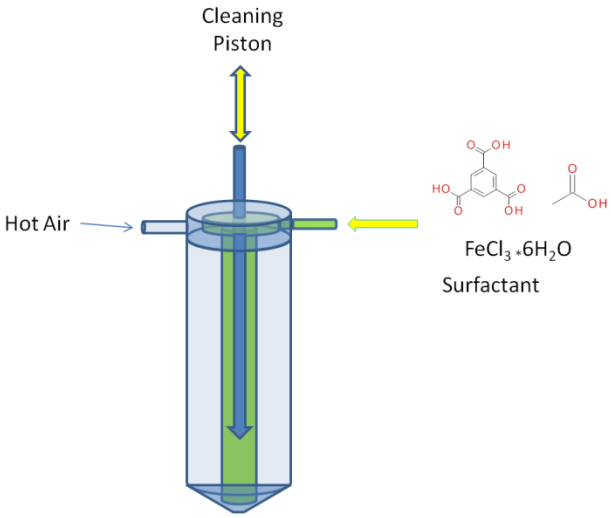
TEM studies were carried out using a JEOL 100CX (100 kV) apparatus equipped with a Gatan Orius camera. Samples were prepared by evaporating a drop of diluted suspension in ethanol on a carbon-coated copper grid.

2. Aerosol processing details

Large scale particle production was carried out on a Büchi mini spray drier B-290 with a glass cyclone and electrically conductive layer and a self-cleaning nozzle. Solution was fed into the nozzle with a built-in peristaltic pump. Air was dried with an air dehumidifier B-296. For experiments using the three fluid nozzle, solutions were placed separately in two syringes, connected to the nozzle and the feed rate was settled by injecting with a dual syringe pump.

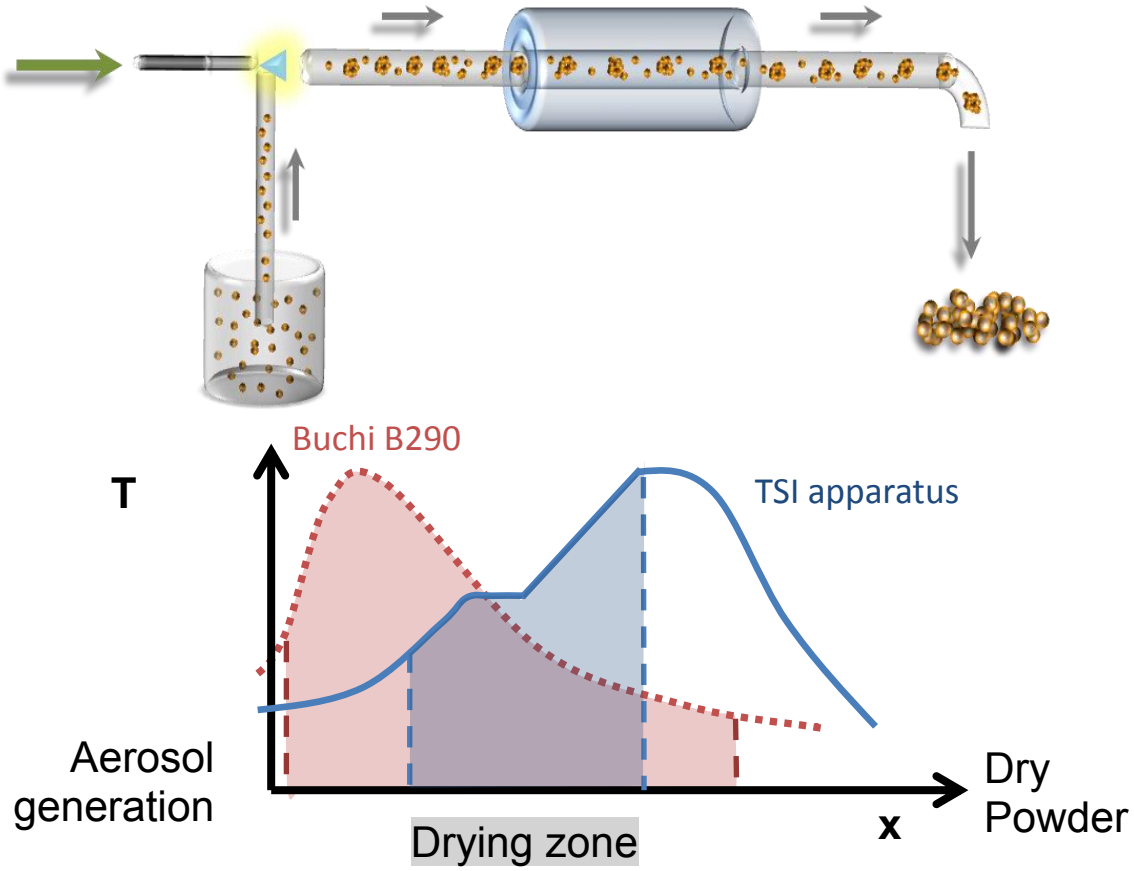


Scheme S1. Three fluid nozzle of Industrial B290 Buchi aerosol apparatus.



Scheme S2. Scheme of the two- fluid nozzle (with cleaning piston) used on B290 Buchi aerosol apparatus.

Aerosol of nano and submicronic particles were carried out on an aerosol device consisting on a 6-Jet 9306A atomizer from TSI with an air pressure of 10 psi the aerosol was dried by passing through a tubular quartz tube heated at 350 ºC.



Scheme S3. (top) Scheme of the drying setup coupled with the 6-Jet 9306A atomizer from TSI for preparing submicron sized spherical MOFs. (down) Temperature profile observed along the drying path from TSI generator-based system (blue) and Büchi industrial spray drier (red).

3. Synthesis and characterization of particles prepared with the three fluid nozzle.

For the preparation of HKUST-1, ZIF-8 and $Fe_3(BTC)_2$ particles, the two solutions or reactants were kept separately and feed injection flow was settled equally.

HKUST-1

Solution A: 1.65 g (7.20 mmol) of copper nitrate trihydrated were dissolved in 20 mL of a mixture water ethanol 1:1 under vigorous stirring.

Solution B: 0.840 g (4.00 mmol) of 1,3,5-tricarboxybenzene were dissolved into 20 mL of a mixture water ethanol 1:1 under vigorous stirring.

Outlet temperature 160 ºC. Dry air pressure 50 bar; vacuum capacity 100%. Injection flow 30 mL/h.

Blue solid 1.93 g h^{-1} of crude product. STY: 494 kg m^{-3} day^{-1} (activation time not taken into account).

Activation: 105 mg of crude product were swollen in 50 mL of absolute ethanol for 1 h. The resulting dispersion was then centrifuged at 10500 rpm for 15 min. The liquid fraction was discarded and 67.3 mg were recovered (64 %).

ZIF-8

Solution A: 2.933 g (9.33 mmol) of zinc (II) nitrate hexahydrate were dissolved in 200 mL of methanol under vigorous stirring.

Solution B: 6.489 g (79.4 mmol) of 2-methylimidazole were dissolved into 200 mL of methanol under vigorous stirring.

Outlet temperature 50 ºC. dry air pressure 50 bar; vacuum capacity 100%. Injection flow 30 mL/h.

1.02 g h^{-1} crude product; STY = 69.4 kg m^{-3} day^{-1}

Activation consisted on three redispersions of 1 g of crude solid in 50 mL of absolute ethanol. 170 mg of product were recovered after the process. (17%)

$Fe_3(BTC)_2$

Solution A: 2.425 g (8.99 mmol) of iron (III) chloride hexahydrated were added in 300 mL of absolute ethanol under vigorous stirring until total solubilization. 1.97 mL of acetic acid were added.

Solution B: 0.845 g (4.02 mmol) of 1,3,5-tricarboxybenzene were dissolved into 300 mL of ethanol under vigorous stirring. Later, 1.97 mL of acetic acid were added.

Outlet temperature: 150 ºC. Dry air pressure: 50 bar; vacuum capacity: 100%. Syringe pump flow: 30 mL/h.

yellow solid.

Activation: 200 mg of crude product were washed once with 30 mL water and then two times with 30 mL of absolute ethanol.

4. Two fluid nozzle production of Fe(BTC) particles (Buchi apparatus).

In a typical synthesis of aerosol produced particles, two precursor solutions namely A and B are prepared and mixed before aerosol processing. Solutions A and B are poured together into a flask. Once mixed, 100 mL of deionized water are then added and the resulting solution is spray dried on the spray drying device by means of a peristaltic pump.

$Fe_3(BTC)_2$:

Solution A : 2.425 g (8.99 mmol) of iron (III) chloride hexahydrate were a in 300 mL of absolute ethanol under vigorous stirring until total solubilization. 1.97 mL of acetic acid were added.

Solution B: 0.845 g (4.02 mmol) of 1,3,5-tricarboxybenzene were dissolved into 300 mL of ethanol under vigorous stirring. Later, 1.97 mL of acetic acid were added.

Outlet temperature: 150 ºC. Dry air pressure: 50 bar; vacuum capacity: 100%. Syringe pump flow: 30 mL/h.

Activation: 200 mg of crude product were washed once with 30 mL water and then two times with 30 mL of absolute ethanol.

F-127 templated $Fe_3(BTC)_2$:

Solution A: 1.60 g (0.13 mmol) of F-127 were dissolved in 300 mL of absolute ethanol under vigorous stirring. 15 minutes later, 2.425 g (8.99 mmol) of iron (III) chloride hexahydrate were added until total solubilization. 1.97 mL of acetic acid were added.

Solution B: 0.845 g (4.02 mmol) of 1,3,5-tricarboxybenzene were dissolved into 300 mL of ethanol under vigorous stirring. Later, 1.97 mL of acetic acid were added.

Outlet temperature: 150 ºC. Dry air pressure: 50 bar; vacuum capacity: 100%. Peristaltic pump flow: 150 mL/h.

Pink Product: 1.39 g/h. kg m^{-3} day^{-1}

Activation: 200 mg of crude product were washed once with 30 mL water and then two times with 30 mL of absolute ethanol. 58.1 mg were recovered (29 %).

CTAB-templated $Fe_3(BTC)_2$:

Solution A: 2.88 g (7.90 mmol) of CTAB were dissolved in 300 mL of absolute ethanol under vigorous stirring. 15 minutes later, 2.43 g (9.00 mmol) of iron (III) chloride hexahydrate were added and let dissolve. 1.97 mL of acetic acid were added.

Solution B: 0.845 g (0.4 mmol) of 1,3,5-tricarboxybenzene were dissolved into 300 mL of ethanol under vigorous stirring. Later, 1.97 mL of acetic acid were added.

1.05 g h^{-1} Orange powder.: STY: 49.5 kg m^{-3} day^{-1}

Activation: 200 mg of crude product were washed once with 30 mL water and then two times with 30 mL of absolute ethanol 49 mg of an orange solid were recovered (24 %).

Characterizations

HKUST-1particles were compared with a simulated spectrum. The Aerosol ZIF-8 was compared with both a colloidal ZIF-8 crystalline structure and a simulated patterns, colloidal ZIF-8 was synthesized as reported.[1]

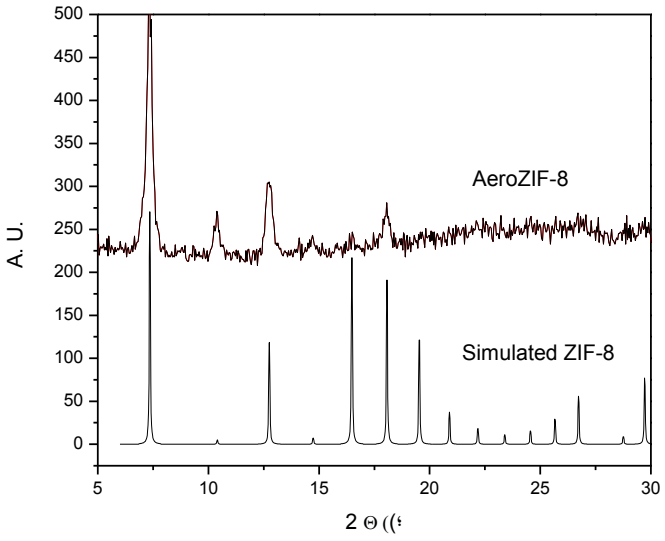


Figure S1. XRPD pattern of ZIF-8 processed with the three fluid nozzle.

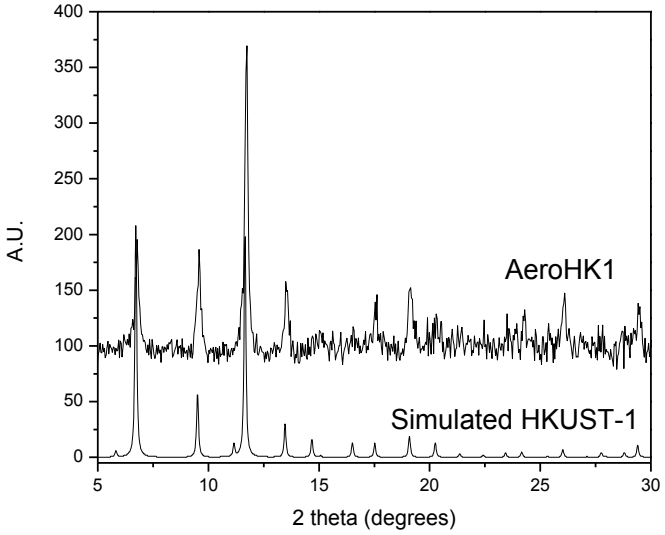


Figure S2. XRPD pattern HKUST-1 processed with the three fluid nozzle

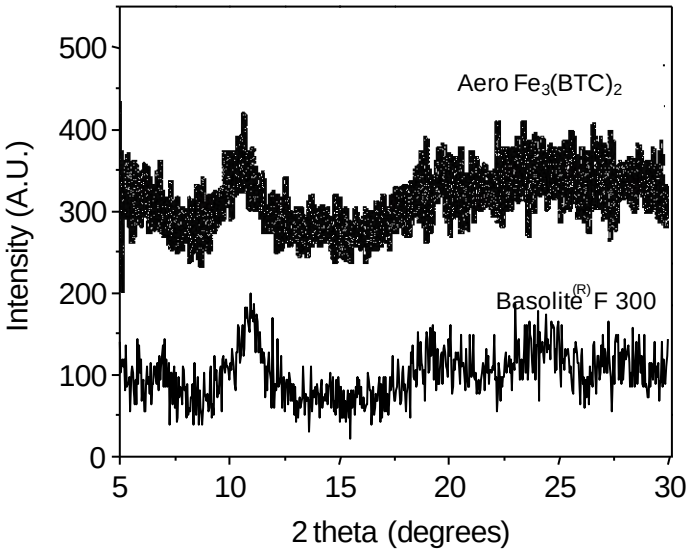


Figure S3. XRPD pattern $Fe_3(BTC)_2$ processed with the three fluid nozzle

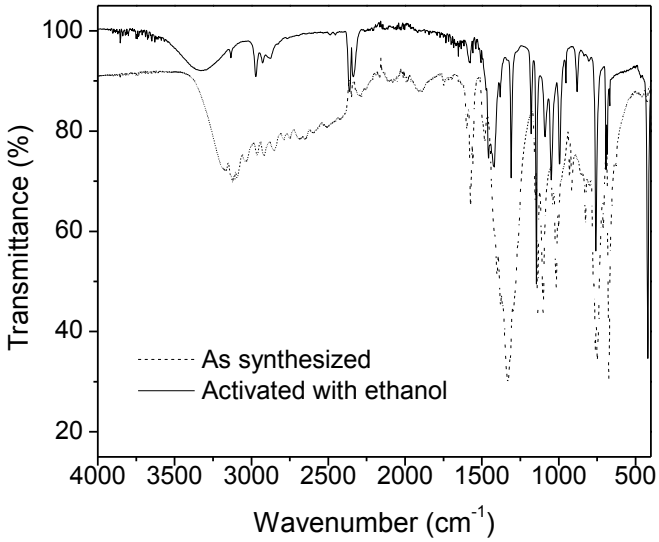


Figure S4. FTIR spectra of 2 ZIF-8 processed with the three fluid nozzle

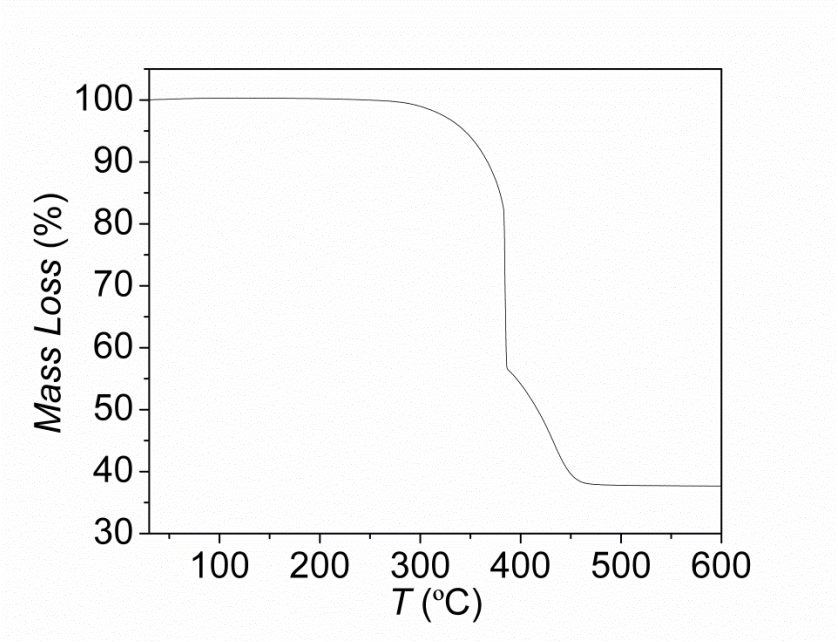


Figure S5. TGA plot of ZIF-8 processed with the three fluid nozzle

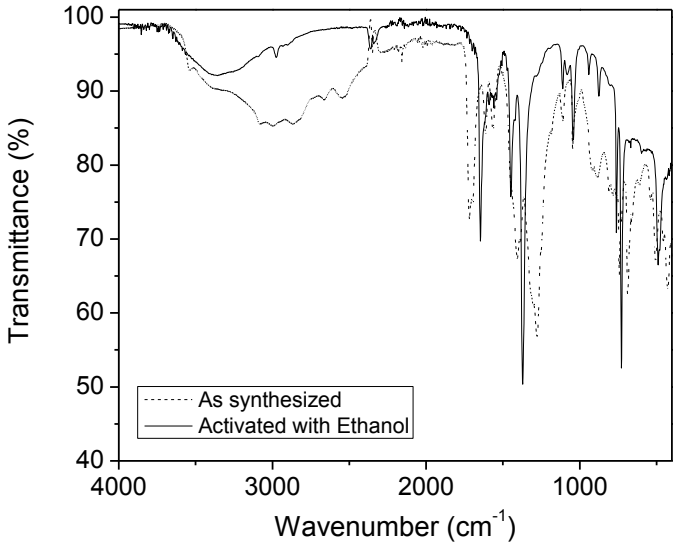


Figure S6. IR spectra of HKUST-1 processed with the three fluid nozzle

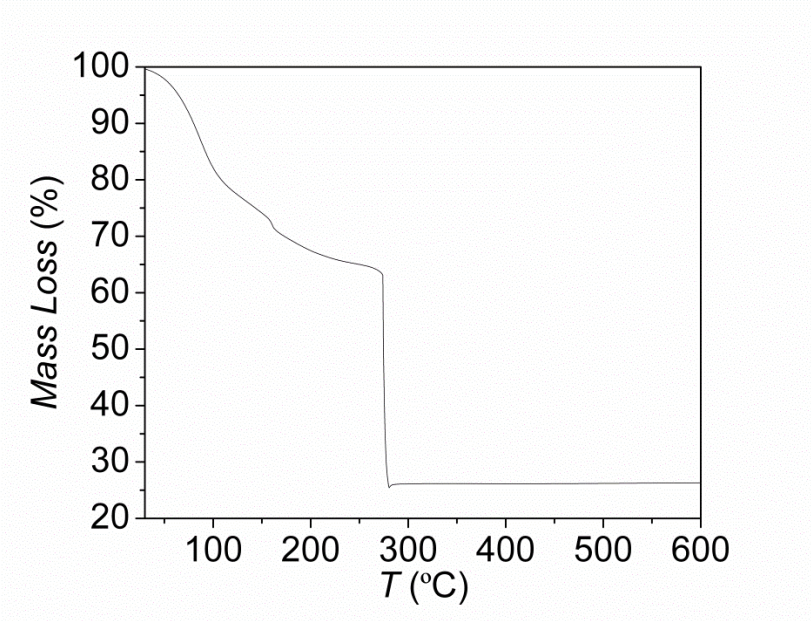


Figure S7. TGA plot of HKUST-1 processed with the three fluid nozzle

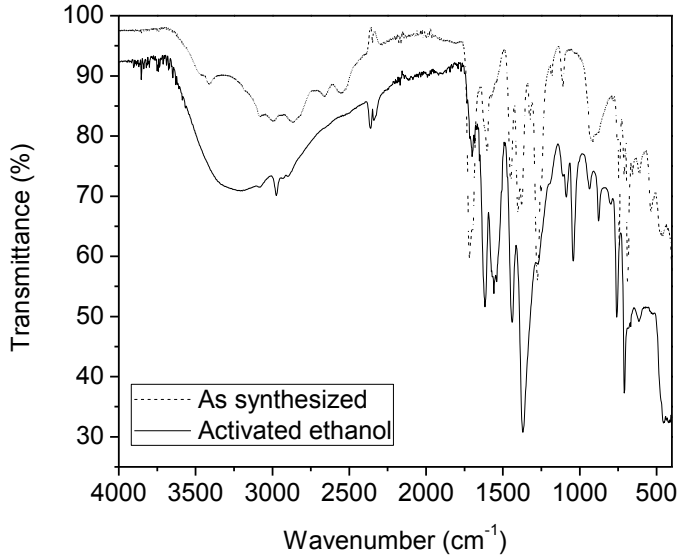


Figure S8. IR spectra of $Fe_3(BTC)_2$ processed with the three fluid nozzle

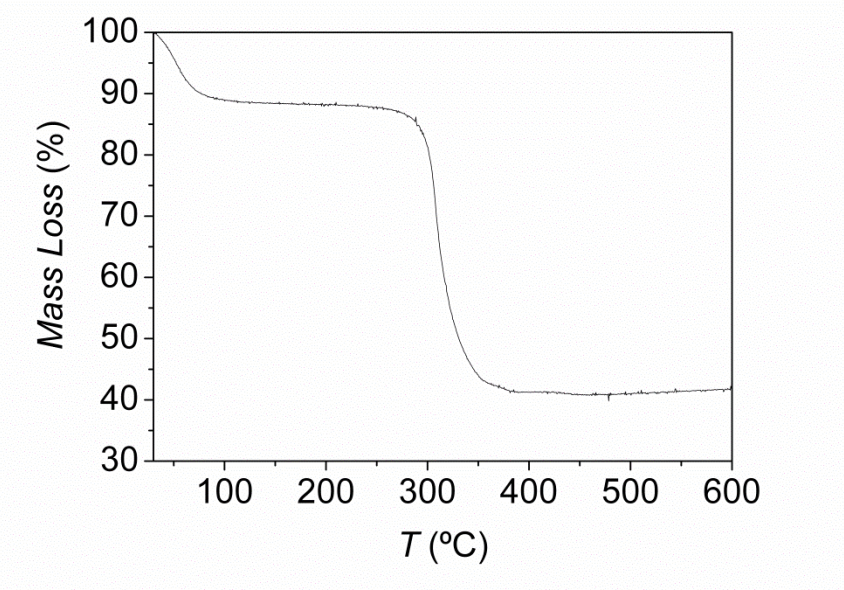


Figure S9. ATG of $Fe_3(BTC)_2$ processed with the three fluid nozzle

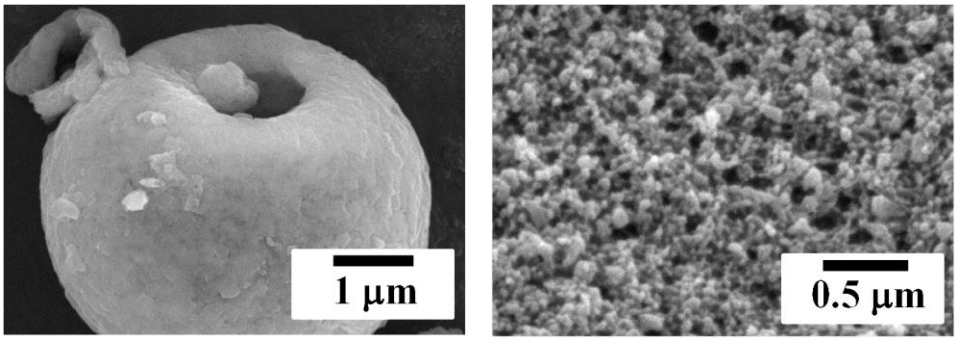


Figure S10: SEM images of aero HK-1 as synthesized (left) and activated (right).

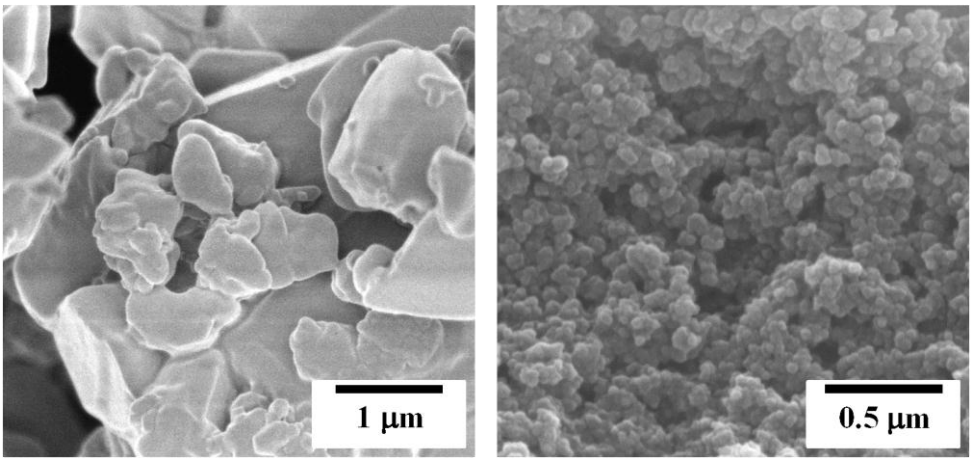


Figure S11: SEM images of aero Z-8 as synthesized (left) and activated (right)

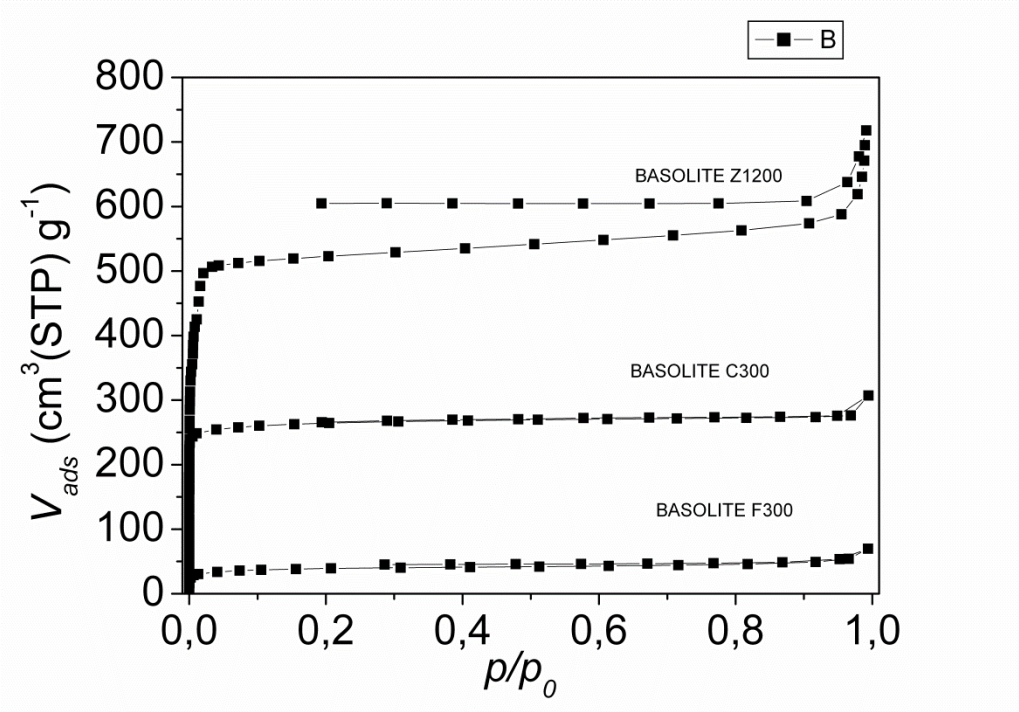


Figure S12. Nitrogen sorption isotherms of commercially available Basolites®.

Figure S13. a) Reacting mixture of single nozzle spray casted $Fe_3(BTC)_2$ after 1 day. b) and c) Gelification of the original reacting mixture ([Fe] = 0.2M) after 2 minutes of water addition.

Table S2. Oxide content of aerosol obtained porous coordination polymers by dual bus.

PCP	% Oxide Observed	%Oxide Calculated
HKUST-1	40.2	39.4
ZIF-8	37.7	35.4
Fe_3BTC_2	46.1	37.9

F-127-tempated Fe_3BTC_2	40.4	37.9
CTAB-templated Fe_3BTC_2	38.0	37.9

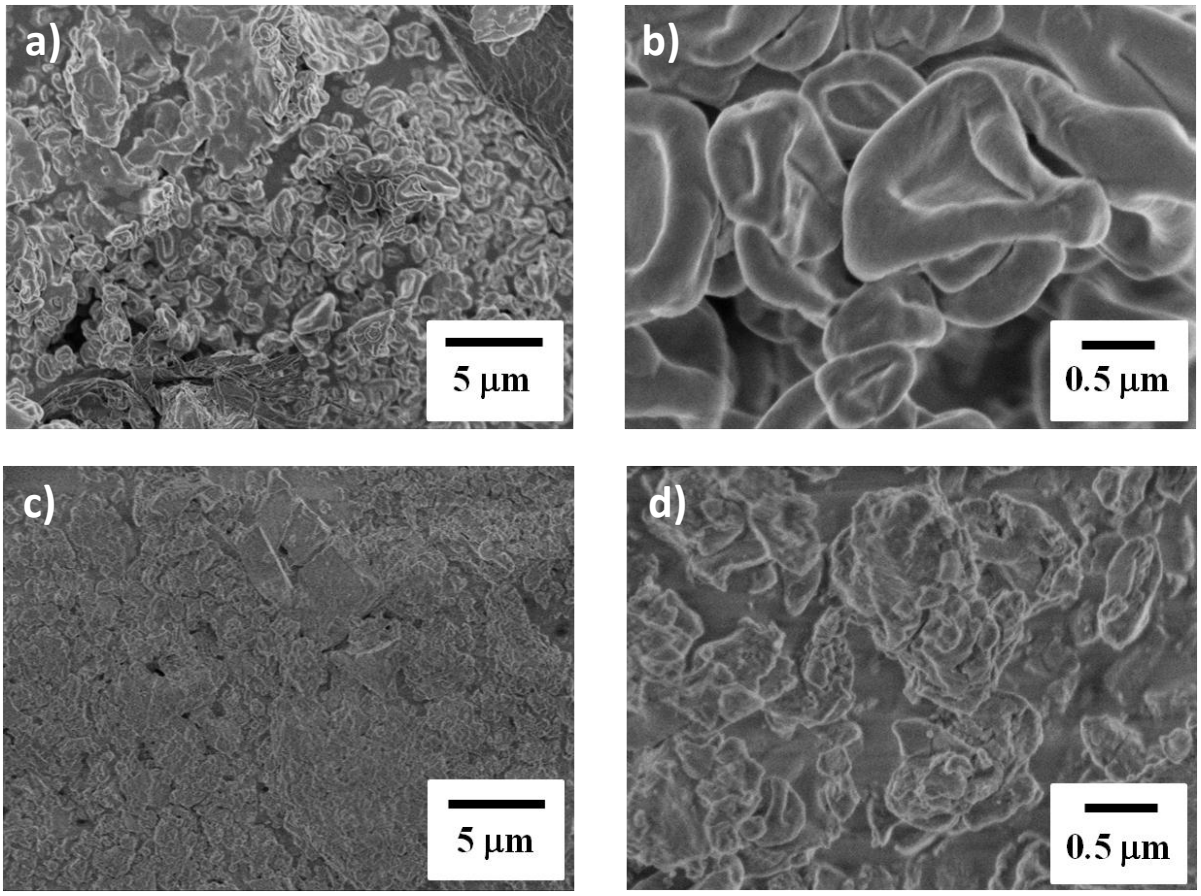


Figure S14. Images of industrially produced templated particles a) as synthesized F-127-templated ; b) activated F-127-templated; c) as synthesized CTAB-templated; d) activated CTAB-templated $Fe_3(BTC)_2$.

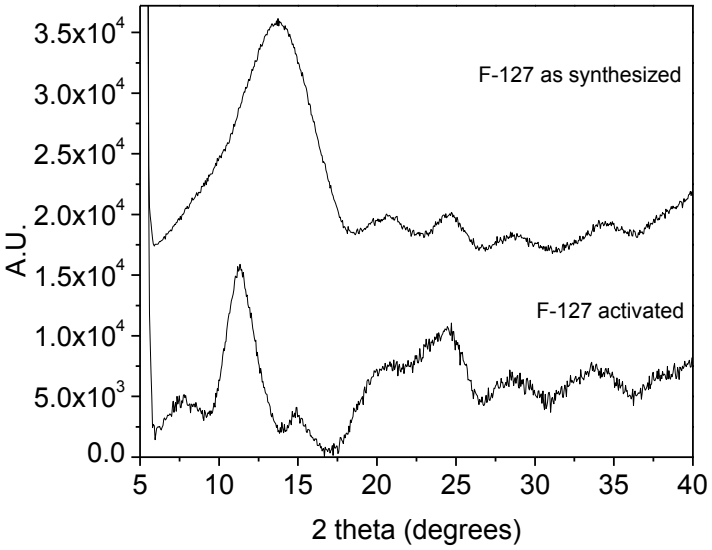


Figure S15. XRPD of F-127-templated $Fe_3(BTC)_2$

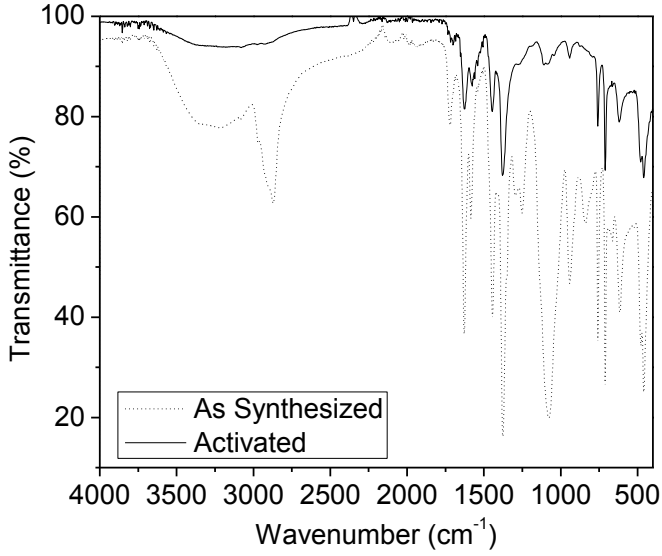


Figure S16. IR spectra of F-127-templated $Fe_3(BTC)_2$

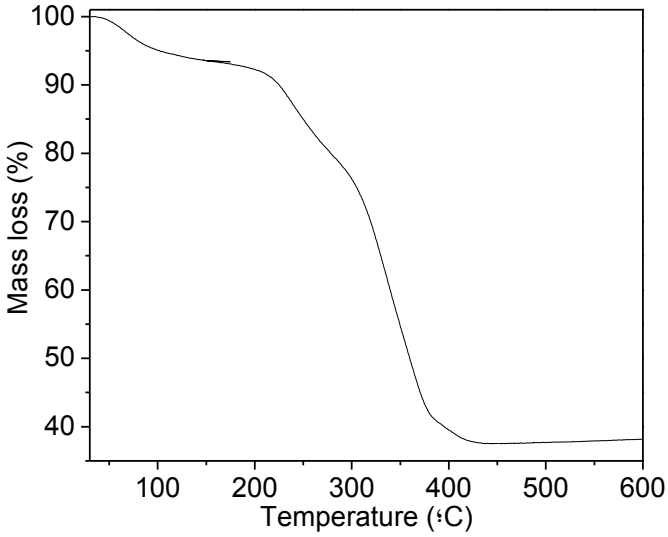


Figure S17. TGA of activated F-127-templated $Fe_3(BTC)_2$

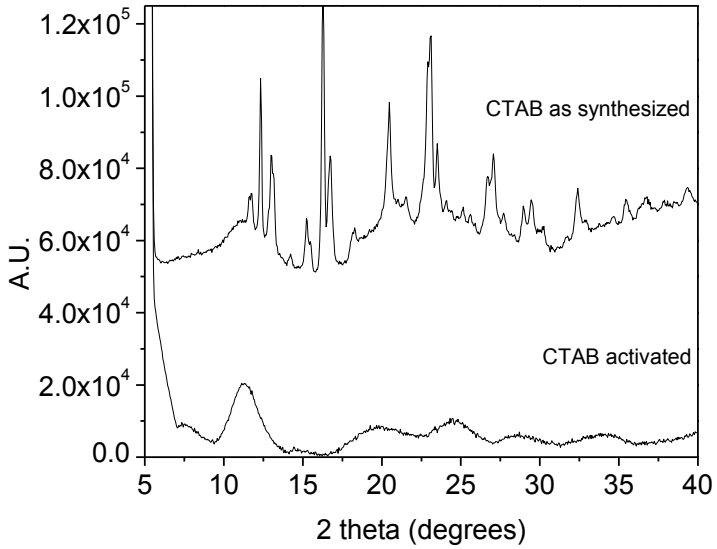


Figure S18. XRPD of CTAB-templated $Fe_3(BTC)_2$

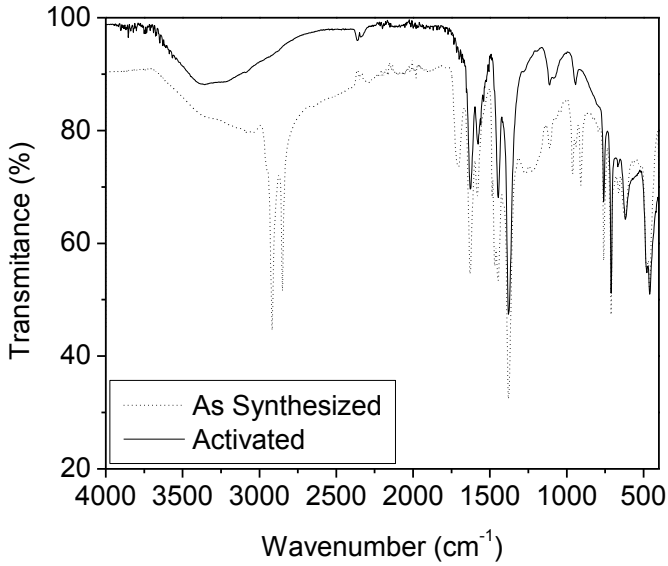


Figure S19. IR spectra of CTAB-templated $Fe_3(BTC)_2$

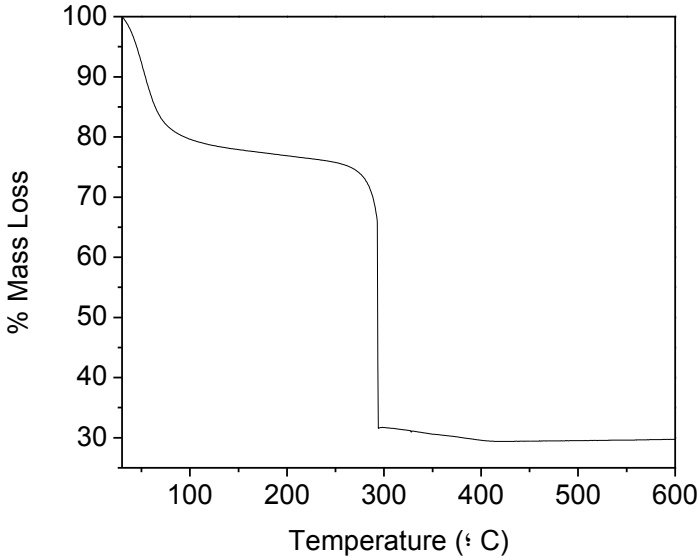


Figure S20. TGA of activated CTAB-templated $Fe_3(BTC)_2$

Table S1. BET specific surfaces area of particles produced with B290 BUCHI device.

PCP	**Aerosols MOFs (m^2 g^{-1})**	**As Reported Basolite materials(m^2 g^{-1}) [2] (*Basolite Materials Measured in our laboratory*)***
HKUST-1	1550	1500-2100 (*1050*)
ZIF-8	1650	1940 (*2100*)
Fe_3BTC_2	0	1500 (*140*)
F-127-tempated Fe_3BTC_2	598	
CTAB-templated Fe_3BTC_2	1011	

*Experimental BET surface measured after activation at 160°C

5. Submicron and nanometric EISA synthesized particles (TSI apparatus).

In a typical synthesis of aerosol produced particles, two precursor solutions namely A and B are prepared and mixed for the process. Solutions A and B are poured together in a flask. Once mixed, 10 mL of deionized water are then added and the resulting solution is thoroughly poured into the device's reservoir for spray drying.

Non templated Fe_3BTC_2.

Solution A: 0.243 g (0.90 mmol) of iron (III) chloride hexahydrate were dissolved in 30 mL of absolute ethanol under vigorous stirring. 15 minutes later, 0.197 mL of acetic acid were added.

Solution B: 0.084 g (0.40 mmol) of 1,3,5-tricarboxybenzene (trimesic acid) were dissolved into 30 mL of ethanol under vigorous stirring. Later, 0.197 mL of acetic acid were added.

160 mg. (33 %) Orange-Brown powder.

F-127-templated Fe_3BTC_2:

Solution A: 0.16 g (0.01 mmol) of F-127 were dissolved in 30 mL of absolute ethanol under vigorous stirring. 15 minutes later, 0.243 g (0.90 mmol) of iron (III) chloride hexahydrate were added and let dissolve. 0.197 mL of acetic acid were added.

Solution B: 0.084 g (0.40 mmol) of 1,3,5-tricarboxybenzene were dissolved into 30 mL of ethanol under vigorous stirring. Later, 0.197 mL of acetic acid were added.

Yield 0.24 g (49 %). Pink powder.

Activation: 100 mg of crude product were washed once with 30 mL water and then two times with 30 mL of absolute ethanol.

CTAB-templated Fe_3BTC_2:

Solution A: 0.288 g (0.79 mmol) of CTAB were dissolved in 30 mL of absolute ethanol under vigorous stirring. 15 minutes later, 0.243 g (0.90 mmol) of iron (III) chloride hexahydrate were added and let dissolve. 0.197 mL of acetic acid were added.

Solution B: 0.084 g (0.04 mmol) of 1,3,5-tricarboxybenzene were dissolved into 30 mL of ethanol under vigorous stirring. Later, 0.197 mL of acetic acid were added.

150 mg (30 %). Orange powder.

Activation: 100 mg of crude product were washed once with 30 mL water and then two times with 30 mL of absolute ethanol.

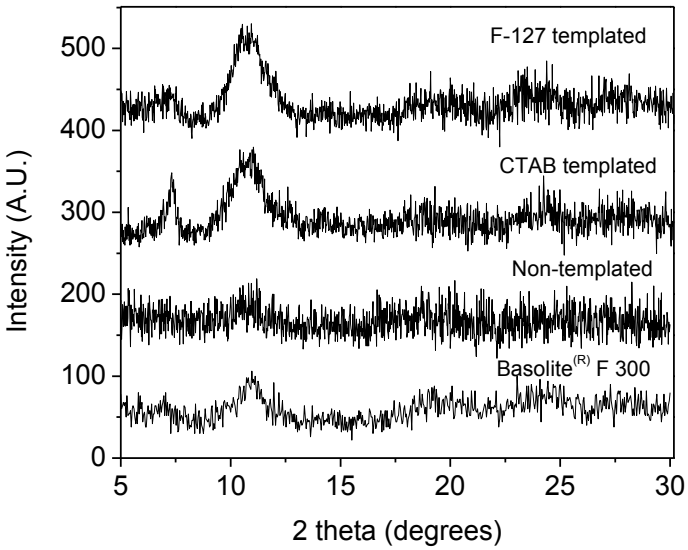


Figure S21. XRPD patterns of commercial Basolite® F300; non-templated, F127-templated and CTAB-templated $Fe_3(BTC)_2$

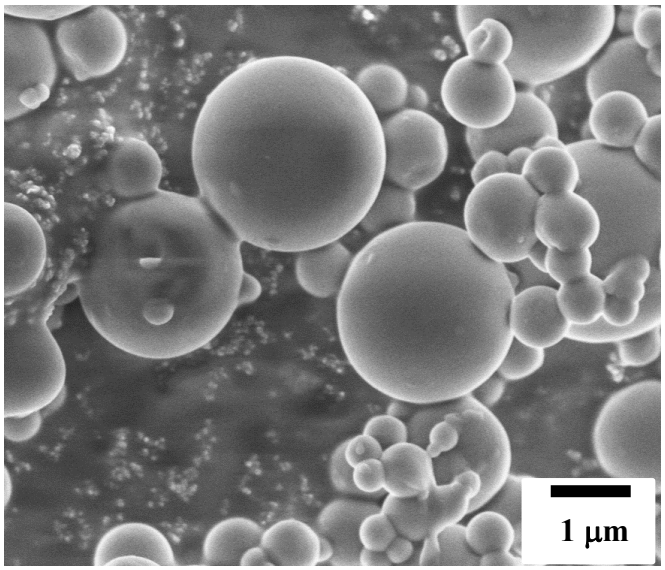


Figure S22. SEM images of as synthesized F-127-templated $Fe_3(BTC)_2$

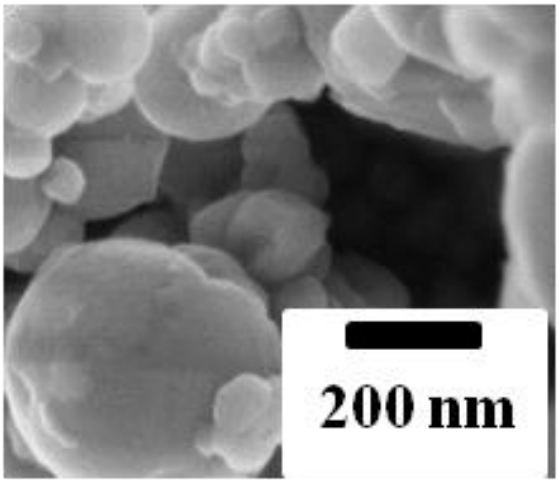


Figure S23. SEM images of activated F-127-templated $Fe_3(BTC)_2$

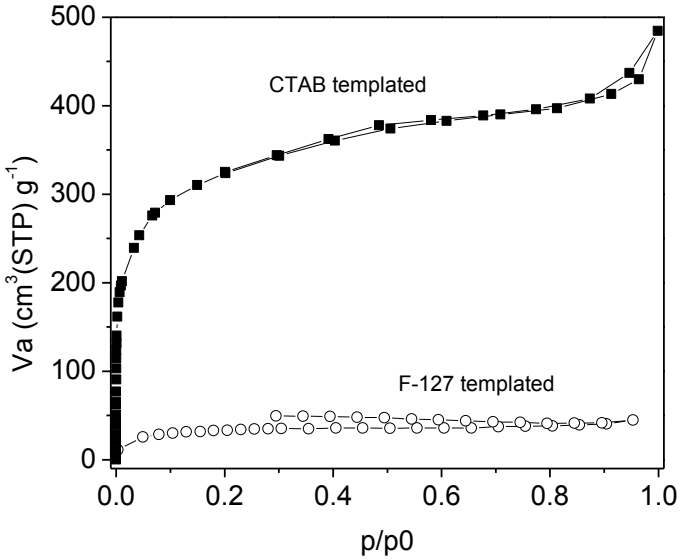


Figure S24. Nitrogen sorption isotherms of activated F-127 AND CTAB-templated $Fe_3(BTC)_2$. Made with TSI apparatus.

[1] Demessense, A.; Boissière, C.; Grosso, D.; Horcajada, P. ; Serre, C. ; Férey, G. ; Soler-Illia, G. J. A. A. ; Sanchez, C. *J. Mater. Chem.* **2010**. *20*, 7676-7681.
[2] Basolite Z1200 : http://www.sigmaaldrich.com/catalog/product/aldrich/691348?lang=fr&region=FR;
Basolite C300 : http://www.sigmaaldrich.com/catalog/product/aldrich/688614?lang=fr&region=FR;

Basolite F300 : http://www.sigmaaldrich.com/catalog/product/aldrich/690872?lang=fr&region=FR