

Supporting Information for

**Controlled Growth of Narrowly Dispersed Nanosize Hexagonal
MOF Rods with Mn(III)-Porphyrin and In(NO₃)₃ and Their
Application in Olefin Oxidation**

by

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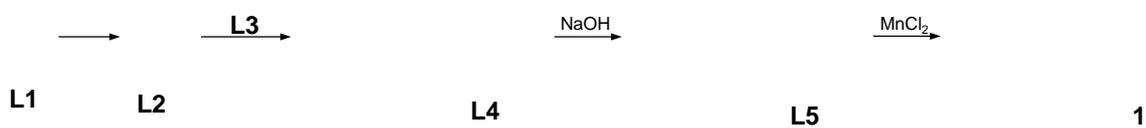
I. Instrumentations

NMR spectra were recorded on a Varian AS400 (399.937 MHz for ¹H and 100.573 MHz for ¹³C) spectrometer. ¹H chemical shifts are referenced to the proton resonance resulting from protic residue in deuterated solvent and ¹³C chemical shift recorded downfield in ppm relative to the carbon resonance of the deuterated solvents. Absorbance and emission spectra were obtained using an Agilent UV-Vis-NIR spectrophotometer using quartz cells. All scanning electron microscopy (SEM) images were obtained using a Jeol JSM-7001F. Energy dispersive X-ray spectroscopy (EDX) was obtained using a Horiba EMAX Gatan at the Korea Basic Science Institute (KBSI) Seoul Center. Matrix-Assisted Laser-Desorption-Ionization Time-of-flight Mass Spectra (MALDI-TOF) were obtained on a Bruker Daltonics LRF20 MALDI-TOF Mass Spectrometer at the Industry-Academic Cooperation Foundation, Yonsei University. Powder X-ray diffraction measurements were recorded with a Rigaku

D/MAX Ultima III using nickel-filtered Cu K α radiation ($\lambda = 1.5418\text{\AA}$) over a range of $2^\circ < 2\theta < 40^\circ$ and X'celerator detector operating at 40 kV and 30 mA. Thermo Gravimetric Analyzer (TGA) measurements were carried out using a Scinco TGA N-1000 in a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ in the temperature range of $25\sim 900^\circ\text{C}$ for particles. Gas chromatography was recorded using a Hewlett Packard HP 6890 series. Ultrapure grade (99.999%) N₂, CO₂, and H₂ gases were used for the gas sorption experiments. The N₂ sorption analysis was performed on a Belsorp-miniII at 77 K (BEL Japan). The low-pressure CO₂ sorption analyses were also performed on a Belsorp-miniII at 196 K (BEL Japan). 2-propanol/dry ice bath was used to maintain 196 K. The Inductively coupled plasma (ICP) mass spectra were obtained on an IRIS XDL Duo (USA) Mass Spectrometer.

II. Materials

2,6-Dietoxybenzaldehyde, ethyl-4-formylbenzoate, and 2-(*tert*-butylsulfonyl)iodosylbenzene were synthesized by according to modified literature procedures.¹ All other chemicals were obtained from commercial sources and used without further purification. All of the reactions and manipulations of the porphyrin building blocks were carried out under N₂ with the use of standard inert-atmosphere and Schlenk techniques unless otherwise noted. Solvent used in inert-atmosphere reactions were dried and degassed using standard procedures. Flash column chromatography was carried out with 230-400 mesh silica gel from Sigma-Aldrich using wet-packing method. All deuterated solvents were purchased from Cambridge Isotope Laboratory.



Scheme S1. Synthesis of Mn(III)-porphyrin.

III. Synthesis

Ethyl-4-formylbenzoate (L1). To a solution 4-formylbenzoic acid (10 g, 66.6 mmol) was dissolved in freshly distilled AcCN and degassed with N₂ for 15 min. Then K₂CO₃ (11 g,

79.6 mmol) and bromoethane (10.9 g, 100.0 mmol) were added and the resulting mixture was refluxed overnight under N₂. The mixture was diluted with ethyl acetate and quenched with 0.1 N NaOH. After washing with water, the organic was dried over anhydrous sodium sulfate. After filtration, the organic was evaporated to dryness using a rotary evaporator. The residue was purified by silica-gel column chromatography (ethyl acetate/hexane 1:4 v/v) to afford pure **L1** as a white solid (6.5 g, 54.0 %). ¹H NMR (CDCl₃): δ 10.1 (s, 1H), 8.20 (d, ³J_{H-H} = 8.79 Hz, 2H), 7.95 (d, ³J_{H-H} = 8.24 Hz, 2H), 4.41 (q, ³J_{H-H} = 7.1 Hz, 2H), 1.14 (t, ³J_{H-H} = 7.14 Hz, 3H).

meso-(4-Carboxyethylphenyl)dipyrromethane (L2). **L1** (5 g, 28.06 mmol) was dissolved in freshly distilled pyrrole (52.5 ml, 756.70 mmol) in a 100-mL round-bottom flask equipped with a magnetic stirbar. The mixture was degassed for 10 min and trifluoroacetic acid (TFA, 0.25 ml, 3.30 mmol) was injected into the reaction solution via syringe. The resulting mixture was stirred for 20 min under N₂. After quenching with aqueous sat. NaOH solution (0.1 N), ethyl acetate was added. The mixture was washed with water (2 x 50 mL), dried over anhydrous MgSO₄, and concentrated to dryness using a rotary evaporator. The resulting oily residue was purified by silica-gel column chromatography (ethyl acetate/dichloromethane 0.2:9.8 v/v) to afford pure **L2** as a white solid (5.2 g, 61.5 %). ¹H NMR (CDCl₃): δ 7.96 (d, ³J_{H-H} = 7.8 Hz, 2H), 7.26 (d, ³J_{H-H} = 7.8 Hz, 2H), 6.69 (dd, ³J_{H-H} = 1.6 Hz, 2H), 6.15 (dd, ³J_{H-H} = 3.1 Hz, 2H), 5.89 (bs, 2H), 5.56 (s, 1H), 4.35 (q, ³J_{H-H} = 7.04 Hz, 2H), 1.37 (t, ³J_{H-H} = 7.04 Hz, 3H), ¹³C NMR (CDCl₃) : δ 166.658, 147.425, 131.851, 130.097, 129.397, 128.609, 117.780, 108.766, 107.725, 61.196, 44.167, 14.580.

2,6-Diethoxybenzaldehyde (L3). To a solution *N,N,N',N'*-Tetramethylethylenediamine (TMEDA, 7.1 mL, 47.66 mmol) and diethoxybenzene (10 g, 60.16 mmol) in distilled diethylether was added *n*-BuLi (2.5 M in hexane, 26.13 mL, 65.30 mmol) at 0 °C over a period of 30 min. The reaction mixture was stirred for 3 hr under N₂. After warming up to room temperature, *N,N*-dimethylformamide (DMF, 8.85 mL, 114.30 mmol) was added dropwise and the resulting reaction was stirred for an additional 2 hr. After quenching with water, the mixture was extracted with ethyl acetate 4-times, the organic was combined and evaporated to dryness using a rotary evaporator to yield a yellow residue, which was purified by silica-gel column chromatography (ethyl acetate/hex 1:5 v/v) to afford pure **L3** as a white

solid (9.1 g, 77.7 %). ^1H NMR (CDCl_3): δ 10.5 (s, 1H), 7.39 (t, $^3J_{\text{H-H}} = 8.07$ Hz, 1H), 6.54 (d, $^3J_{\text{H-H}} = 8.95$ Hz, 2H), 4.11 (q, $^3J_{\text{H-H}} = 7$ Hz, 4H), 1.46 (t, $^3J_{\text{H-H}} = 6.87$ Hz, 6H).

5,15-Bis(4-carboxyethylphenyl)-10,20-bis[2,6-diethoxyphenyl]porphyrin (L4). **L2** (1 g, 3.4 mmol) and **L3** (0.66 g, 3.4 mmol) were dissolved in dichloromethane (600 mL) in a 1-L round-bottom flask equipped with a magnetic stirbar. The mixture was degassed for 15 min and was then allowed to reflux for 4 h under N_2 . 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1g) added and refluxed for another 30 min. After cooling to room temperature, pyridine (3.4 ml) was injected into the reaction mixture via syringe. The resulting mixture was evaporated to dryness using a rotary evaporator to yield a dark residue, which was re-dissolved in dichloromethane. The solution was filtered and washed with dichloromethane. The resulting solution was evaporated to dryness using a rotary evaporator and the residue was purified by silica-gel column chromatography (100% dichloromethane). After recrystallization from the mixture of dichloromethane and methanol, a pure **L4** was obtained as a purple solid (248 mg, 15.6 %). ^1H NMR (CDCl_3): δ 8.82 (d, $^3J_{\text{H-H}} = 4.70$ Hz, 4H), 8.72 (d, $^3J_{\text{H-H}} = 4.70$ Hz, 4H), 8.42 (d, $^3J_{\text{H-H}} = 7.83$ Hz, 4H), 8.32 (d, $^3J_{\text{H-H}} = 7.83$ Hz, 4H), 7.68 (t, $^3J_{\text{H-H}} = 8.61$ Hz 2H), 6.98 (d, $^3J_{\text{H-H}} = 8.61$ Hz, 4H), 4.57 (q, $^3J_{\text{H-H}} = 7.04$ Hz, 4H), 3.88 (q, $^3J_{\text{H-H}} = 7.04$ Hz 8H), 1.55 (t, $^3J_{\text{H-H}} = 7.04$ Hz 6H), 0.60 (t, $^3J_{\text{H-H}} = 7.04$ Hz 12H). ^{13}C NMR (CDCl_3) : δ 167.223, 160.083, 147.574, 134.826, 130.258, 129.784, 127.940, 117.691, 113.407, 105.626, 77.439, 77.077, 76.770, 76.453, 64.436, 61.476, 14.745, 14.611, 1.268. MS (MALDI-TOF): $m/z = 934.360$ for M^+ ; Calcd 935.07.

5,15-Bis(4-carboxyphenyl)-10,20-bis[2,6-diethoxyphenyl]porphyrin (L5). To a solution of **L4** (200 mg, 0.21 mmol) in tetrahydrofuran (THF, 20 mL) was added a 40 % aqueous solution of KOH (20mL) and was degassed with N_2 for 10 min. The mixture was allowed to reflux for overnight. After cooling to room temperature, the resulting mixture was evaporated to dryness and the solid was re-dissolved in methanol and 10 % HCl was added. After extracting the product with dichloromethane, the product was purified by silica-gel column chromatography (methanol/dichloromethane/triethylamine 9:1:0.01v/v/v) to afford pure **L5** as a purple solid (178 mg, 94.6 %). ^1H NMR (DMSO): δ 8.71 (m, 8H), 8.20 (d, $^3J_{\text{H-H}} = 7.04$ Hz, 4H), 8.02 (d, $^3J_{\text{H-H}} = 7.04$ Hz, 4H), 7.71 (t, $^3J_{\text{H-H}} = 8.61$ Hz, 2H), 7.09 (d, $^3J_{\text{H-H}} = 7.83$ Hz, 4H), 3.88 (q, $^3J_{\text{H-H}} = 7.04$ Hz, 8H), 0.47 (t, $^3J_{\text{H-H}} = 7.04$ Hz, 12H). ^{13}C NMR

(DMSO): δ 168.379, 159.725, 139.869, 135.004, 128.532, 125.574, 119.727, 118.387, 113.869, 106.119, 67.684, 64.278, 55.591, 46.026, 31.078, 14.865, 10.204. MS (MALDI-TOF): $m/z=$ 878.191 for M^+ ; Calcd 878.97.

{5,15-Bis(4-carboxyphenyl)-10,20-bis[2,6-diethoxyphenyl]porphyrinato}manganese(III) chloride (1). A solution of **L5** (250 mg, 0.26 mmol) and $MnCl_2 \cdot 4H_2O$ (514 mg, 2.60 mmol) in *N,N*-dimethylformamide (DMF, 12.5 mL) was heated to reflux for 6 h. The reaction was monitored by UV-Vis spectrum. The reaction mixture was allowed to cool to room temperature and then DMF was evaporated under reduced pressure. Then resulting residue was dispersed in water, filtered and dried in vacuum. The crude product was purified by column chromatography (methanol/dichloromethane/triethylamine 1:6:0.01 v/v/v). After recrystallization from dichloromethane and methanol, a pure **1** was obtained as a dark green solid (227 mg, 82.5 %). MS (MALDI-TOF): $m/z=$ 931.298 for $[M-Cl]^+$; Calcd 931.89.

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{5,15-Bis(4-carboxyethylphenyl)-10,20-bis[2,6-diethoxyphenyl]porphyrinato}manganese(III) chloride (2). A solution of **L4** (100 mg, 0.11 mmol) and $MnCl_2 \cdot 4H_2O$ (211 mg, 1.1 mmol) in *N,N*-dimethylformamide (DMF, 10 mL) was heated to reflux for 6 h. The reaction was monitored by UV-Vis spectrum. The reaction mixture was allowed to cool to room temperature and then DMF was evaporated under reduced pressure. Then resulting residue was dispersed in water, filtered and dried in vacuum. The crude product was purified by column chromatography (methanol/dichloromethane 1:9 v/v). After recrystallization from dichloromethane and methanol, a pure **2** was obtained as a dark green solid (92 mg, 87.8 %). MS (MALDI-TOF): $m/z=$ 987.311 for $[M-Cl]^+$; Calcd 987.95.

General synthesis of porphyrin MOF rods. A solution of **1** (3.134 mg, 3.24 μmol) and $\text{In}(\text{NO}_3)_3$ (1.949 mg, 6.48 μmol) in anhydrous *N,N*-dimethylformamide (DMF, 0.45 mL) at a 4 ml vial equipped with a stirbar. The resulting mixture was heated at 120, 100, and 80 °C for 2, 5, 10, 30 and 60 min, respectively. After cooling to room temperature, the MOF rods were collected by centrifugation, and washed several times with DMF.

General reaction condition of styrene epoxidation. Dried Mn(III)-porphyrin MOF rods (3.90 mg, 1.34×10^{-3} mmol) were dispersed to a solution of 2-(*tert*-butylsulfonyl)iodosylbenzene (460 mg, 1.35 mmol), styrene (281 mg, 2.70 mmol) and hexadecane (611 mg, 2.70 mmol) in dichloromethane (5 mL). The reaction mixture was shaken at room temperature for various reaction times. The adequate amount of solution was taken via syringe and filtered through a silica gel plug which was further washed with dichloromethane. The turn of number (TON) of the catalyst was determined by gas chromatography with hexadecane as an internal standard. The Mn(III) loading was determined by ICP-Mass spectroscopy after heating at 120 °C under vacuum (1.9 wt%/mg).

IV. UV-Vis adsorption spectra

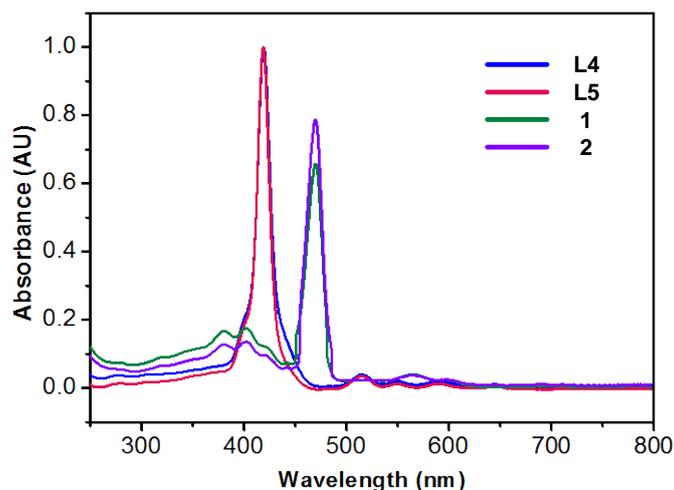


Fig. S1 UV-Vis spectra of porphyrin derivatives taken as a solution (3.3×10^{-6} M) in dichloromethane and methanol mixture (1:1), showing the spectral change before and after the metallation.

V. PXRD Patterns

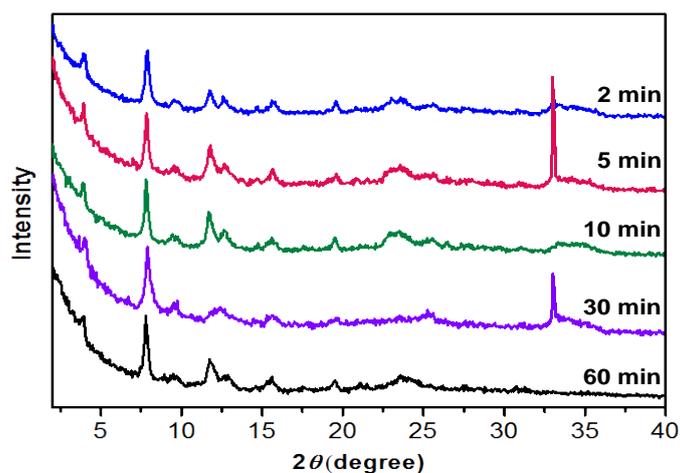


Fig. S2 The PXRD patterns for the MOF rods obtained from various reaction times at 120 °C.

VI. SEM images and EDX data

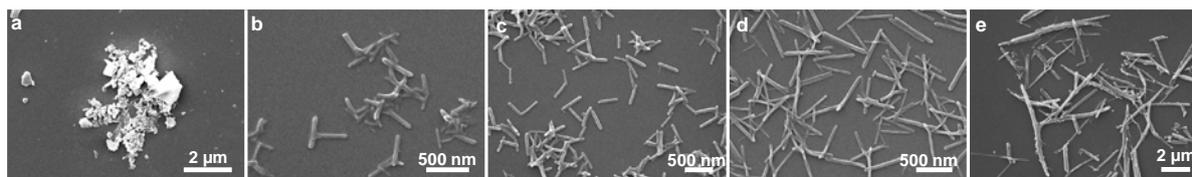


Fig. S3 SEM images of Mn(III)-porphyrin MOF rods obtained from various reaction times at 100 °C; a) 2, b) 5, c) 10, d) 30, and e) 60 min.

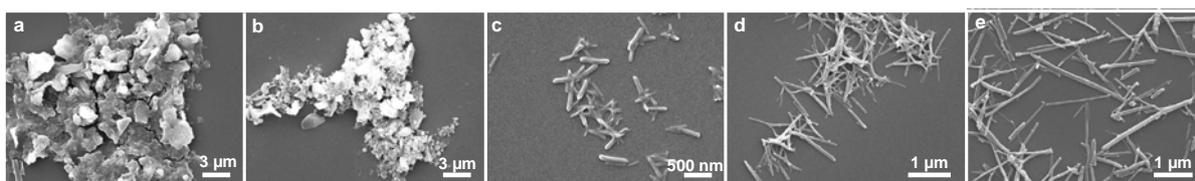


Fig. S4 SEM images of Mn(III)-porphyrin MOF rods obtained from various reaction times at 80 °C; a) 2, b) 5, c) 10, d) 30, and e) 60 min.

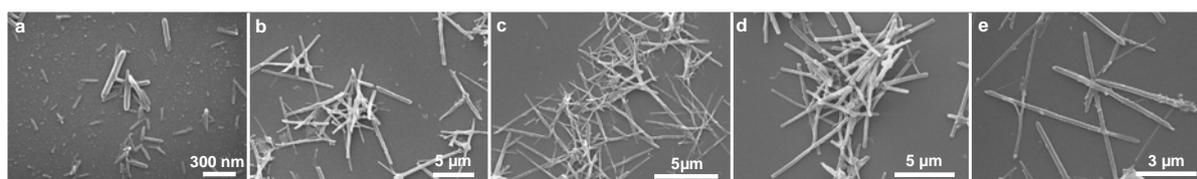


Fig. S5 SEM images of Mn(III)-porphyrin MOF rods obtained from diluted in double and various reaction times at 120 °C; a) 2, b) 5, c) 10, d) 30, and e) 60 min.

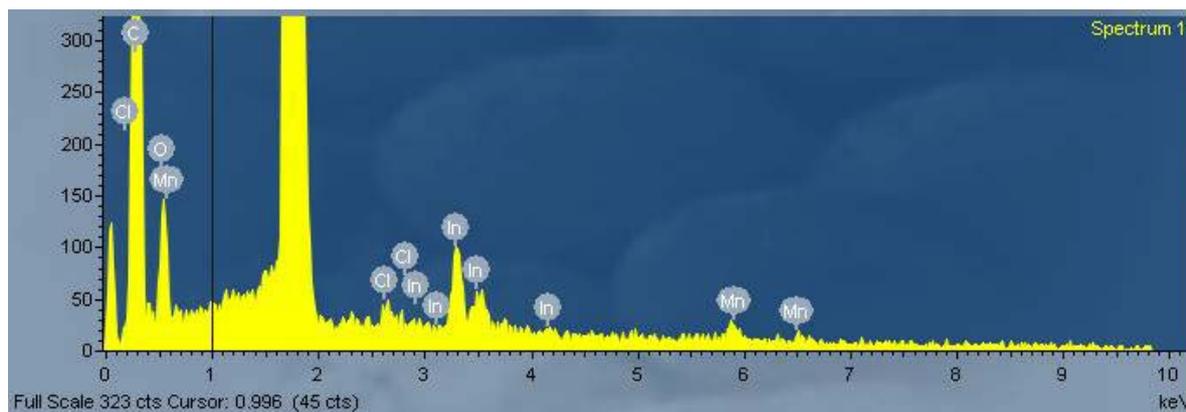


Fig. S6 EDX data of Mn(III)-porphyrin MOF rod.

VII. Thermogravimetric Analysis (TGA)

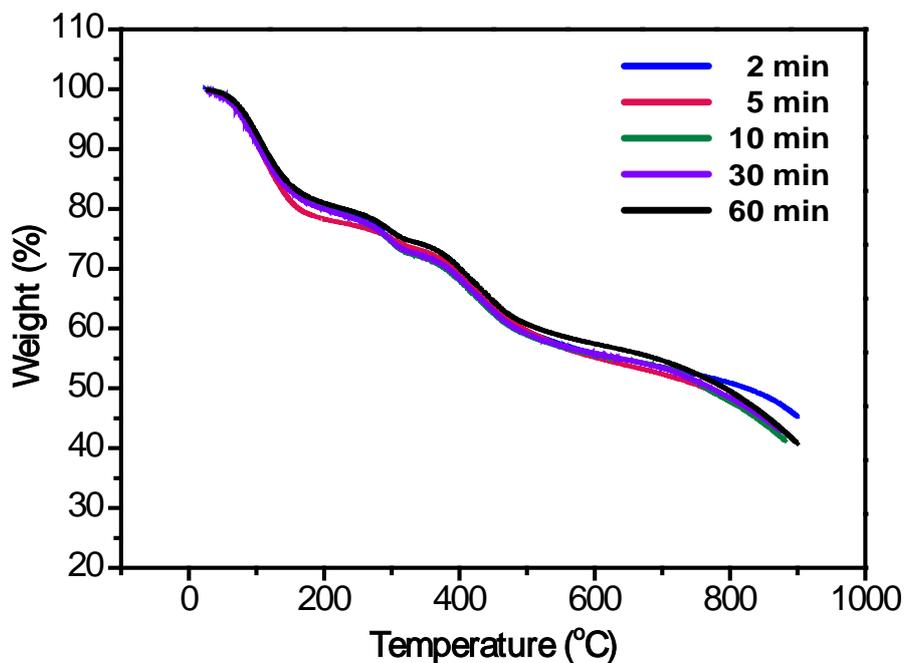


Fig. S7 Thermogravimetric analysis (TGA) of Mn(III)-porphyrin MOF rods synthesized at 120 °C from various reaction times of 2, 5, 10, 30 and 60 min, respectively.

VIII. Gas sorption analysis

Ultrapure grade (99.999%) N₂, CO₂, and H₂ gases were used for the gas sorption experiments. The N₂ sorption analysis was performed on a Belsorp-miniII at 77 K (BEL Japan). The low-pressure CO₂ sorption analyses were also performed on a Belsorp-miniII at 196 K (BEL Japan). 2-propanol/dry ice bath was used to maintain 196 K. A moisture trap was

equipped at the outlet of the CO₂ gas cylinder to avoid moisture contamination during the measurement. The samples soaked in CHCl₃ in a screw-capped vial were shaken for two days. The CHCl₃-exchanged samples were dried at 393 K under high vacuum for 2 h before measurements. Low-pressure H₂ sorption measurements were performed at 77 K on the same equipment. The equipment was calibrated by using Cu-BTC (HKUST-1) as a reference material.²

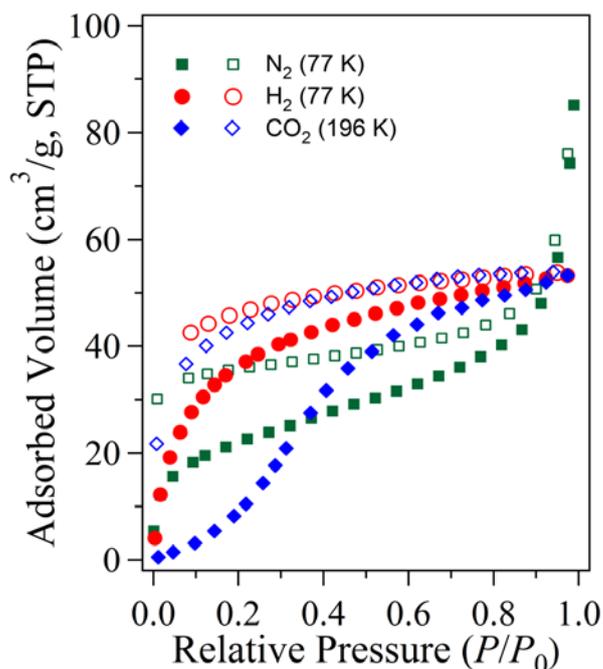


Fig. S8 Gas sorption isotherms measured with MOF rods obtained from 10 min of reaction at 120 °C.

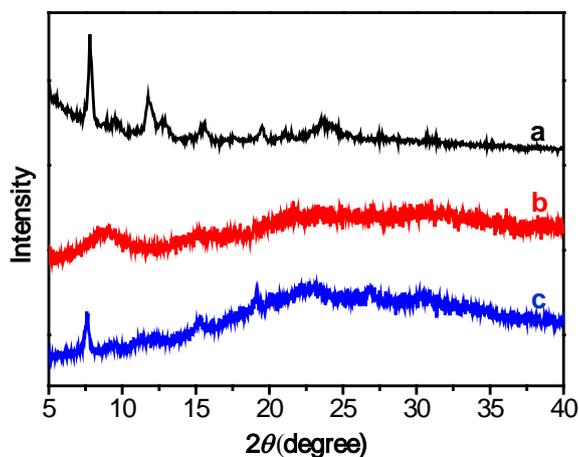


Fig. S9 PAXD patterns of the MOF rod sample obtained from 10 min of reaction at 120 °C before (a) and after (b) gas sorption measurements and after the resolution (c) in DMF.

IX. Additional SEM images

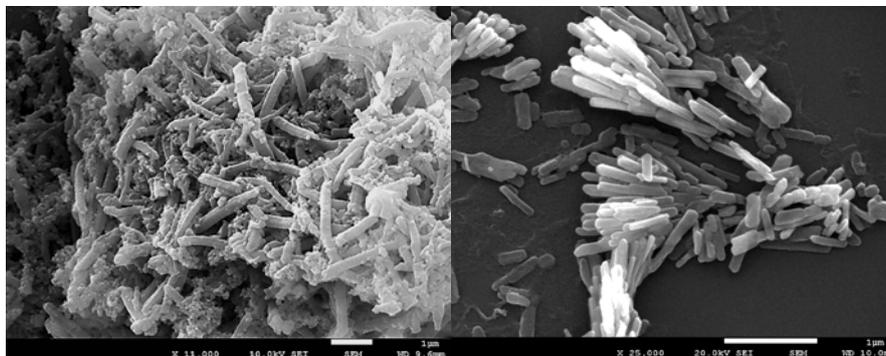


Fig. S10 SEM image of recovered MOF rods after the oxidation: Before (left) and after (right) washing with dichloromethane.

IX. References

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2. S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. Guy Orpen and I. D. Williams, *Science* 1999, **283**, 1148.