A general and efficient approach for tuning crystal morphology of classical MOFs

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Preparation of bulk Co-MOF-74 crystal

Bulk Co-MOF-74 was synthesized according to the method reported by Matzger and co-workers. In a typical procedure, a solid mixture of H$_4$dhtp (0.198 g, 1 mmol) and Co(NO$_3$)$_2$.6H$_2$O (1.164 g, 4 mmol) was added to 100 mL DMF:EtOH:H$_2$O (1:1:1, v/v/v). The mixture solution was then transferred to a 100 mL Teflon-sealed and placed in an oven at 100 °C for 24 h. After which the solid was isolated by centrifugation and washed with DMF three times, and then two more times with methanol. The solid product was kept immersed in methanol at room temperature for 3 days and 50 °C for 24 h. During this period, fresh solvent was added four times after solid decanting. Methanol was finally removed under high vacuum (<10$^{-8}$ bar) at 100 °C, yielding the bulk Co-MOF-74.

Preparation of microscale Co-MOF-74 crystal using 2-MI

Microcrystal Co-MOF-74 was obtained by adding different concentrations of 2-MI to the reported synthetic methods. In simple terms, different concentrations of 2-MI was dissolved in 10 mL mixture of DMF:EtOH:H$_2$O (1:1:1 (v/v/v))/ DMF:MeOH:H$_2$O (1:1:1 (v/v/v))/ DMF:i-Propyl:H$_2$O (1:1:1 (v/v/v))/ DMF:H$_2$O (1:1:1 (v/v/v)), which was added dropwise to 100 mL DMF:EtOH:H$_2$O (1:1:1 (v/v/v))/ DMF:MeOH:H$_2$O (1:1:1 (v/v/v))/ DMF:i-Propyl:H$_2$O (1:1:1 (v/v/v))/ DMF:H$_2$O (1:1:1 (v/v/v)) solution dissolved Co(NO$_3$)$_2$.6H$_2$O and H$_4$dhtp. The mixture solution was stirred at room temperature for 10 min, and then transferred to a 100 mL Teflon-sealed and heated at different temperature for different time. The resulting precipitates were collected by centrifugation, washed with DMF and MeOH for three more times respectively. The solid product was kept immersed in methanol at room temperature for 3 days and 50 °C for 24 h. During this period, fresh solvent was added four times after solid decanting. Methanol was finally removed under high vacuum (<10$^{-8}$ bar) at 100 °C, yielding the microcrystal Co-MOF-74.

Preparation of nanoscale Co-MOF-74 crystal using 2-MI

2-MI (2 mmol) was dissolved in 10ml of MeOH/ MeOH:H$_2$O (1:1 (v/v))/ EtOH:H$_2$O (1:1 (v/v)), and added dropwise to another solution of H$_4$dhtp (0.5 mmol) and Co(NO$_3$)$_2$.6H$_2$O (1.78 mmol) to
obtained Co-MOF-74 after a few minutes of stirring. After ageing for 24 h, the solid was recovered by centrifugation and washed three times with 20 mL of MeOH. The solid product was kept immersed in methanol at room temperature for 3 days and 50 °C for 24 h. During this period, fresh solvent was added four times after solid decanting. Methanol was finally removed under high vacuum (<10⁻⁸ bar) at 100 °C, yielding the nanocrystals Co-MOF-74.

**Preparation of other MOFs**

MOF-5, HKUST-1, Ni-MOF-74 and H₂N-Fe-MIL-101 was synthesized according to the method reported by Cheng and co-workers;² Yang and co-workers;³ Matzger and co-workers;¹ Guo and co-workers⁴ respectively. The morphology controlled MOFs were obtained by adding 2-MI in the methods reported in the literature. The only difference was that the nanoscale HKUST-1 can be achieved at room temperature for a few minutes, which didn’t need of heating at 85 °C for 20 h described by the literature. The resulting precipitates were collected by centrifugation, washed with DMF and MeOH for three more times respectively. The solid product was kept immersed in methanol at room temperature for 3 days and 50 °C for 24 h. During this period, fresh solvent was added four times after solid decanting. Methanol was finally removed under high vacuum (<10⁻⁸ bar) at 100 °C.

**Materials characterization**

The product was characterized by XRD using a Rigaku D/max-ga X-ray diffractometer at a scan rate of 6 ° min⁻¹ in 2θ ranging from 5 ° to 40 ° with Cu Kα radiation (λ = 1.54178 Å). Scanning electron microscopy (SEM) was conducted on a Hitachi S-8010 with an accelerating voltage of 100 kV. Transmission electron microscopy (TEM) images were obtained with a FEI Tecnai G2 F20. Nitrogen adsorption/desorption isotherms at 77 K were performed on a Micromeritics ASAP2460, USA to obtain the specific surface area, total pore volume and pore size distribution. The specific surface area (SBET) was calculated by the conventional BET (Brunauer–Emmett–Teller) method. The total pore volume (Vₜ) was calculated from the adsorbed N₂ amount at a relative pressure of 0.99. The pore size distribution was calculated by the density function theory (DFT) method using a carbon slit pore equilibrium model. Thermogravimetric analysis (TGA) was performed on a
Shimadzu DTG-50 thermal analyzer from room temperature to 800 °C at a heating rate of 10 °C min⁻¹. Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis held samples at 100 °C for 1 min, heated them from 100 to 280 °C at 20 °C /min, and held them at 280 °C for 5 min. Inlet and detector temperatures were set constant at 280 °C. Toluene was used as an internal standard to calculate GC yield. GC-MS analyses were performed using a Shimadzu GCMS-QP2010 Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC-MS analysis held samples at 100 °C for 1 min, heated samples from 100 to 280 °C at 20 °C /min and held them at 280 °C for 5 min. Inlet temperature was set constant at 280 °C. MS spectra were compared with the spectra gathered in the NIST library.

**Catalytic studies**

The catalytic oxidation was carried out in a glass reactor equipped with a magnetic stirrer. In a typical reaction, the mixture of Co-MOF-74 (5 mg), TBHP (108 μL, 4 equiv.), H₂O (1mL) and 2,3-dihydro-1H-indene (25 μL, 1 equiv.) was added into the reactor, and stirred for 12 h at 60 °C. When the reaction was complete, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate was analyzed using a GC-FID to get the GC yield. The product identity was further confirmed by GC-MS.

**Experimental Data**

Fig. S1 Competitive coordination process. a: Methanol solution of cobalt nitrate; b-c: 2-MI was added dropwise to a solution of cobalt nitrate; d-g: H4dhtp was added dropwise to a solution of c; h: solution g was stirred at room temperature for 30 min; i: solution h was allowed to stand at room temperature for 24 h.
Fig. S2 The simulated PXRD pattern for the Co-MOF-74 created from CIF and PXRD patterns for Co-MOF-74 samples prepared at different molar ratios of H₄dhtp and 2-MI in the DMF: EtOH: H₂O (1:1:1 v/v/v) at 100 °C for 24 h.

Fig. S3 The simulated PXRD pattern for the Co-MOF-74 created from CIF and PXRD patterns for Co-MOF-74 samples prepared at different molar ratios of H₄dhtp and Co II in the DMF: EtOH: H₂O (1:1:1 v/v/v) at 100 °C for 24 h.
Fig. S4 The simulated PXRD pattern for the Co-MOF-74 created from CIF and PXRD patterns for Co-MOF-74 samples prepared at different temperatures.

Fig. S5 The simulated PXRD pattern for the Co-MOF-74 created from CIF and PXRD patterns for Co-MOF-74 samples prepared at different solvents.
Fig. S6 HRTEM image of Co-MOF-74 prepared by the addition of 4 mmol of 2-MI and the distinct lattice fringes of crystal.

Fig. S7 SEM image of the Co-MOF-74 obtained in DMF:EtOH:H$_2$O (1:1:1, v/v/v) at 100 °C for 24 h, and the Co-MOF-74 samples prepared with different molar ratios of H$_4$dhtp and 2-MI. a: in the absence of 2-MI; b: n(H$_4$dhtp):n(2-MI)=1:1; c: 1:2; d: 1:3; e: 1:4; f: 1:6; g: 1:8; h: 1:10; i: 1:20.
Fig. S8 SEM images for Co-MOF-74 samples prepared at different molar ratios of H$_4$dhtp and CoII; a: n(H$_4$dhtp):n(CoII)=1:1; b: n(H$_4$dhtp):n(CoII)=1:3; c: n(H$_4$dhtp):n(CoII)=1:8; d: n(H$_4$dhtp):n(CoII)=1:16.

Fig. S9 SEM images for Co-MOF-74 samples prepared at different temperature; a: 80 °C; b: 100 °C; c: 120 °C; d: 135 °C.
Fig. S10 SEM image for the Co-MOF-74 prepared with different solvents in the presence of 4 mM of 2-MI. a: DMF:MeOH:H$_2$O (1:1:1 v/v/v) at 100 °C for 24 h; b: DMF:i-PrOH:H$_2$O (1:1:1 v/v/v) at 100 °C for 24 h; c: DMF:H$_2$O (1:1 v/v) at 100 °C for 24 h; d: MeOH:H$_2$O (1:1 (v/v)) at 25 °C; e: EtOH:H$_2$O (1:1 (v/v)) at 25 °C; f: MeOH at 25 °C.

Fig. S11 SEM image for the Co-MOF-74 prepared with different times in the presence of 4 mM of 2-MI. a: DMF:MeOH:H$_2$O (1:1:1 v/v/v) at 100 °C for 10 min; b: DMF:MeOH:H$_2$O (1:1:1 v/v/v) at 100 °C for 1 h; c: DMF:MeOH:H$_2$O (1:1:1 v/v/v) at 100 °C for 12 h; d: DMF:MeOH:H$_2$O (1:1:1 v/v/v) at 100 °C for 24 h.
Fig. S12 TGA for Co-MOF-74 prepared under different conditions. Co-MOF-74-1 (absence of 2-MI, DMF:EtOH:H₂O (1:1:1, v/v/v), 100 °C for 24 h), Co-MOF-74-2 (n(H₄dhtp):n(2-MI)=1:4, DMF:EtOH:H₂O (1:1:1, v/v/v), 100 °C for 24 h), Co-MOF-74-3 (n(H₄dhtp):n(2-MI)=1:4, MeOH:H₂O (1:1, v/v), RT for 24 h) and Co-MOF-74-4 (n(H₄dhtp):n(2-MI)=1:4, MeOH, RT for 24 h).

Fig. S13 a: N₂ adsorption/desorption isotherms of the Co-MOF-74 samples prepared under different conditions; b: Brunauer-Emmett-Teller (BJH) pore-size distributions.
Fig. S14 HK method pore size distribution of the Co-MOF-74 samples prepared at different conditions: Co-MOF-74-1 (absence of 2-MI, DMF:EtOH:H₂O (1:1:1, v/v/v), 100 °C for 24 h), Co-MOF-74-2 (n(H₄dhtp):n(2-MI)=1:4, DMF:EtOH:H₂O (1:1:1, v/v/v), 100 °C for 24 h), Co-MOF-74-3 (n(H₄dhtp):n(2-MI)=1:4, MeOH:H₂O (1:1, v/v), RT for 24 h) and Co-MOF-74-4 (n(H₄dhtp):n(2-MI)=1:4, MeOH, RT for 24 h).

Fig. S15 DFT method pore size distribution of the Co-MOF-74-1 (absence of 2-MI, DMF:EtOH:H₂O (1:1:1, v/v/v), 100 °C for 24 h).
Fig. S16 DFT method pore size distribution of the Co-MOF-74-2 (n(H₄dhtp):n(2-MI)=1:4, DMF:EtOH:H₂O (1:1:1, v/v/v).

Fig. S17 DFT method pore size distribution of the Co-MOF-74-3 (n(H₄dhtp):n(2-MI)=1:4, MeOH:H₂O (1:1, v/v), RT for 24 h).
Fig. S18 DFT method pore size distribution of the Co-MOF-74-4 (n(H₄dhtp):n(2-MI)=1:4, MeOH, RT for 24 h).

References