Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Size and Morphology Control over MOF-74 Crystals

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Section S1. Materials

2,5-Dihydroxyterephthalic acid (DOT, Tokyo Chemical Industry, 98%), magnesium (II) nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, Adamas, 99.999%), acetic acid glacial (HOAC, Greagent, 99.5%), formic acid (HCOOH, Alfa Aesar, 98%), chloroacetic acid ($ClCH_2COOH$, Adamas, 98%), sodium hydroxide (NaOH, Aladdin, 96%), Pyridine(Adamas, 99.5%), N,N-dimethylformamide (DMF, Greagent, 99.5%), ethanol (Greagent, 99.7%), and anhydrous methanol (Greagent, 99.5%) were purchased from the mentioned sources and used without further purification.

Section S2. Synthesis

Synthesis of Mg-MOF-74 with various molar ratio of ligand and metal salt

The solution for Mg-MOF-74 was prepared by dissolving a mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (461.52 mg, 1.8 mmol) and 0.6/0.3/0.2 mmol DOT (118.89/59.45/39.63 mg) under sonication in a 1:1:1 (v/v/v) mixture of DMF (5.5 mL), ethanol (5.5 mL), and deionized water (5.5 mL). This mixture solution was defined as the standard solution. 5 equiv. of HOAC (1 mmol) with respect to DOT was added to the solution under stirring. Then NaOH aqueous was used as pH regulator to adjust pH value of reaction solution to 9.55 ± 0.05 at room temperature for reaction solution. The prepared solution was transferred to 20 mL reaction vessels. Then, the reaction vessel was fixed in the microwave reactor (Biotage Initiator+) and reacted at 100 ℃ for 90 min with stirring (600 rpm). After the reaction, the as-synthesized yellow materials were washed with DMF and anhydrous methanol for three times.

Synthesis of Mg-MOF-74 with various amounts of water

The solution for Mg-MOF-74 was prepared by dissolving a mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (461.52 mg, 1.8 mmol) and DOT (39.63 mg, 0.2 mmol) under sonication in a mixture of DMF (5.5 mL), ethanol (5.5 mL), and deionized water (0/1/3/5.5/7.5/8.5/9.5/13 mL). This mixture solution was defined as the standard solution. 5 equiv. of HOAC (1 mmol) with respect to DOT was added to the solution under stirring. Then NaOH aqueous was used as pH regulator to adjust pH value of reaction solution to 9.55 ± 0.05 at room temperature for reaction solution. The prepared solution was transferred to 20 mL reaction vessels. Then, the reaction vessel was fixed in the microwave reactor (Biotage Initiator+) and reacted at 100 ℃ for 90 min with stirring (600 rpm). After the reaction, the as-synthesized yellow materials were washed with DMF and anhydrous methanol for three times.

Synthesis of Mg-MOF-74 with the absences of DMF or ethanol

The solution for Mg-MOF-74 was prepared by dissolving a mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (461.52 mg, 1.8 mmol) and DOT (39.63 mg, 0.2 mmol) under sonication in a mixture of ethanol (5.5 mL) and deionized water (5.5 mL), or a mixture of DMF (5.5 mL) and deionized water (5.5 mL). This mixture solution was defined as the standard solution. 5 equiv. of HOAC (1 mmol) with respect to DOT was added to the solution under stirring. Then NaOH aqueous was used as pH regulator to adjust pH value of reaction solution to 9.55 ± 0.05 at room temperature for reaction solution. The prepared solution was transferred to 20 mL reaction vessels. Then, the reaction vessel was fixed in the microwave reactor (Biotage Initiator+) and reacted at 100 ℃ for 90 min with stirring (600 rpm). After the reaction, the as-synthesized yellow materials were washed with DMF and anhydrous methanol for three times.

Synthesis of Mg-MOF-74 with capping agents of various acidity

The solution for Mg-MOF-74 was prepared by dissolving a mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (461.52 mg, 1.8 mmol) and DOT (39.63 mg, 0.2 mmol) under sonication in a 1:1:1 (v/v/v) mixture of DMF (5.5 mL), ethanol (5.5 mL), and deionized water (5.5 mL). 3 equiv. of HOAC/HCOOH/$ClCH_2COOH$ (0.6 mmol) with respect to DOT was added to the solution under stirring. Then NaOH aqueous was used as pH regulator to adjust pH value of reaction solution to 9.55 ± 0.05 at room temperature for reaction solution. The prepared solution was transferred to 20 mL reaction vessels. Then, the reaction vessel was fixed in the microwave reactor (Biotage Initiator+) and reacted at 100 ℃ for 90 min with stirring (600 rpm). After the reaction, the as-synthesized yellow materials were washed with DMF and anhydrous methanol for three times.

Synthesis of Mg-MOF-74 with various amounts of $ClCH_2COOH$

The solution for Mg-MOF-74 was prepared by dissolving a mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (461.52 mg, 1.8 mmol) and DOT (39.63 mg, 0.2 mmol) under sonication in a 1:1:1 (v/v/v) mixture of DMF (5.5 mL), ethanol (5.5 mL), and deionized water (5.5 mL). 3/4/5 equiv. of $ClCH_2COOH$ (0.6/0.8/1 mmol) with respect to DOT was added to the solution under stirring. Then NaOH aqueous was used as pH regulator to adjust pH value of reaction solution to 9.55 ± 0.05 at room temperature for reaction solution. The prepared solution was transferred to 20 mL reaction vessels. Then, the reaction vessel was fixed in the microwave reactor (Biotage Initiator+) and reacted at 100 ℃ for 90 min with stirring (600 rpm). After the reaction, the as-synthesized yellow materials were washed with DMF and anhydrous methanol for three times.

Synthesis of Mg-MOF-74 with various amounts of pyridine

The solution for Mg-MOF-74 was prepared by dissolving a mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (461.52 mg, 1.8 mmol) and DOT (39.63 mg, 0.2 mmol) under sonication in a 1:1:1 (v/v/v) mixture of DMF (5.5 mL), ethanol (5.5 mL), and deionized water (5.5 mL). 0/5/25/50 equiv. of pyridine (0/1/5/10 mmol) with respect to DOT was added to the solution under stirring. Then NaOH aqueous was used as pH regulator to adjust pH value of reaction solution to 9.55 ± 0.05 at room temperature for reaction solution. The prepared solution was transferred to 20 mL reaction vessels. Then, the reaction vessel was fixed in the microwave reactor (Biotage Initiator+) and reacted at 100 ℃ for 90 min with stirring (600 rpm). After the reaction, the as-synthesized yellow materials were washed with DMF and anhydrous methanol for three times.

Section S3. Characterization

Scanning electron microscope (SEM) images were acquired on a JEOL JSM 7800F Prime SEM. Powder X-ray diffraction patterns (PXRD) were acquired on a Bruker D8 Advance diffractometer with Cu Kα radiation. The pH values were measured with a Mettler Toledo Seven Compact S210 pH meter.

Section S4. Supplemental figures and tables

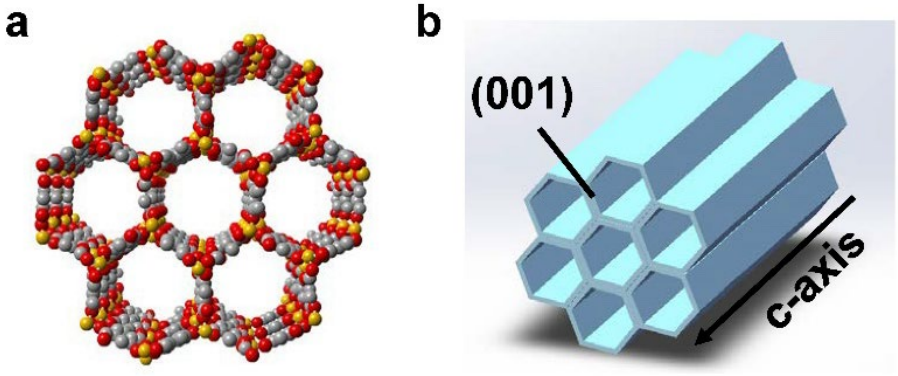

Figure S1. Perspective view of the three-dimensional (3D) open framework of MOF-74 along the c-axis (a) and 1-D hexagonal channel of MOF-74(b).

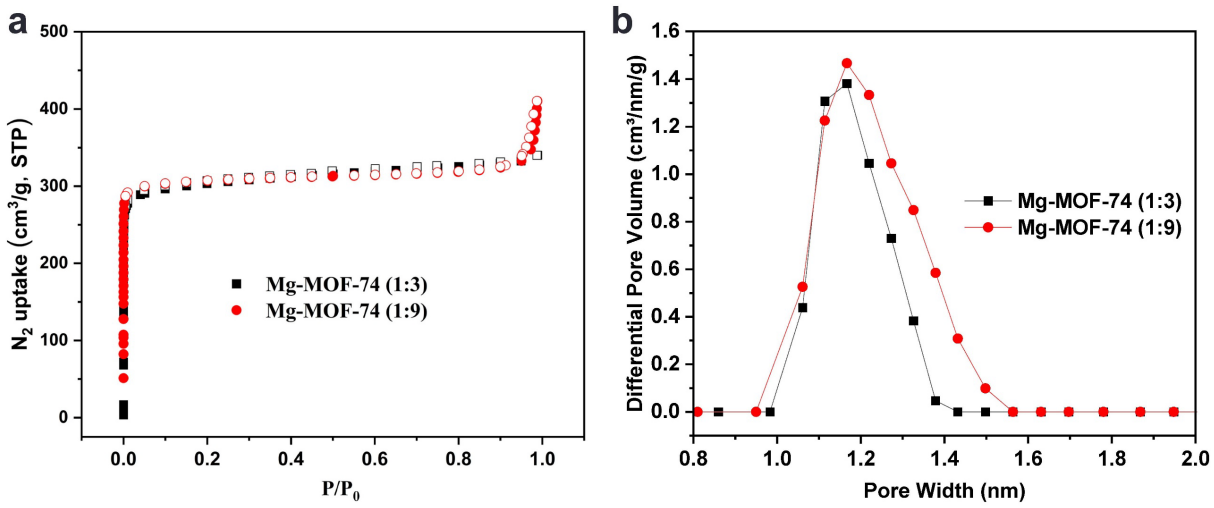

Figure S2. (a) N_2 adsorption-desorption isotherms at 77 K of Mg-MOF-74(1:3) and Mg-MOF-74(1:9). (b) Pore size distribution of Mg-MOF-74(1:3) and Mg-MOF-74(1:9).

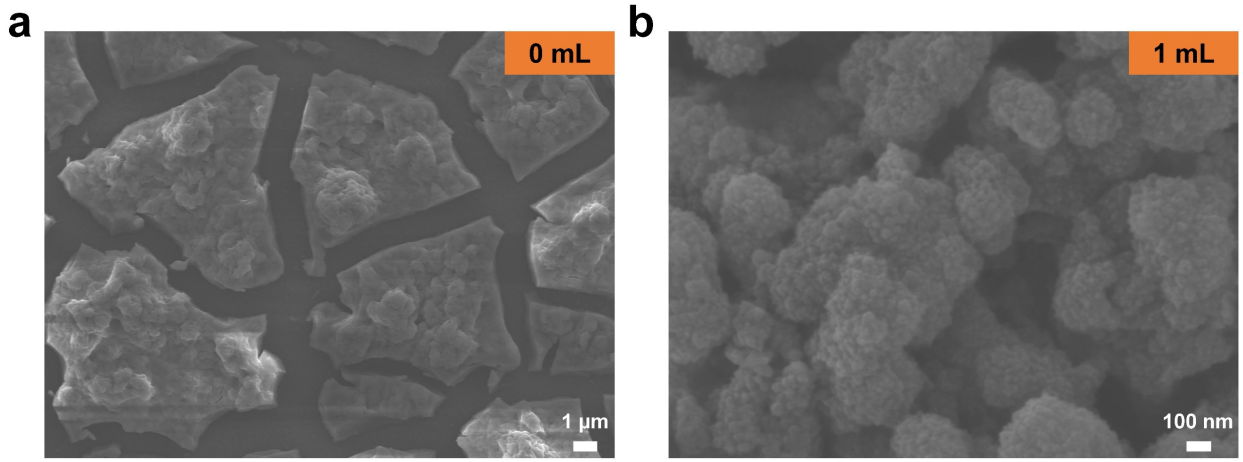

Figure S3. (a-b) SEM images of Mg-MOF-74 synthesized with various amounts of water.

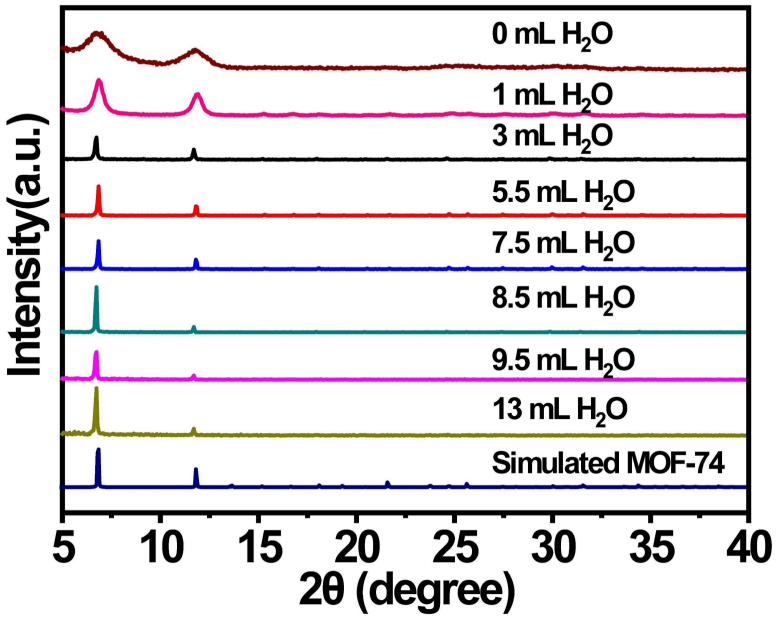

Figure S4. PXRD patterns of Mg-MOF-74 synthesized with various amounts of water.

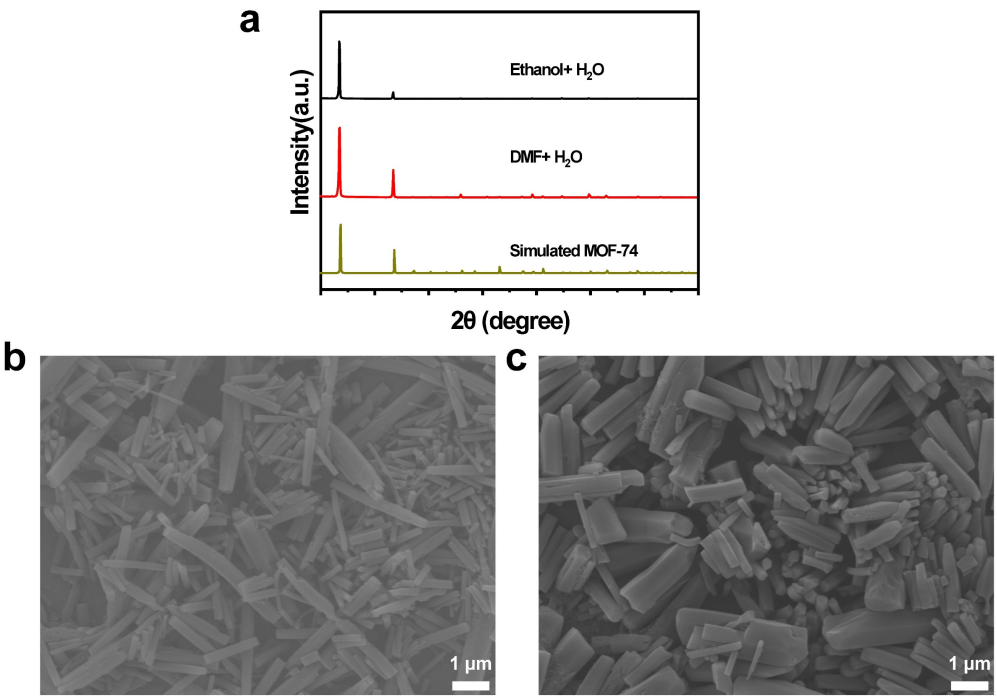

Figure S5. (a) PXRD patterns of Mg-MOF-74 synthesized with the absences of ethanol or DMF. SEM images of Mg-MOF-74 synthesized with the absences of ethanol (b) or DMF (c).

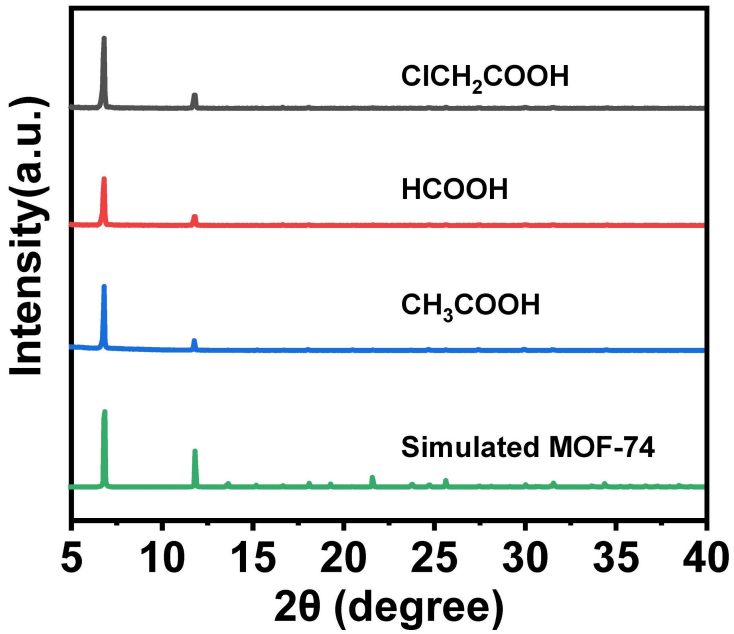

Figure S6. PXRD patterns of Mg-MOF-74 synthesized with capping agents of various acidity.

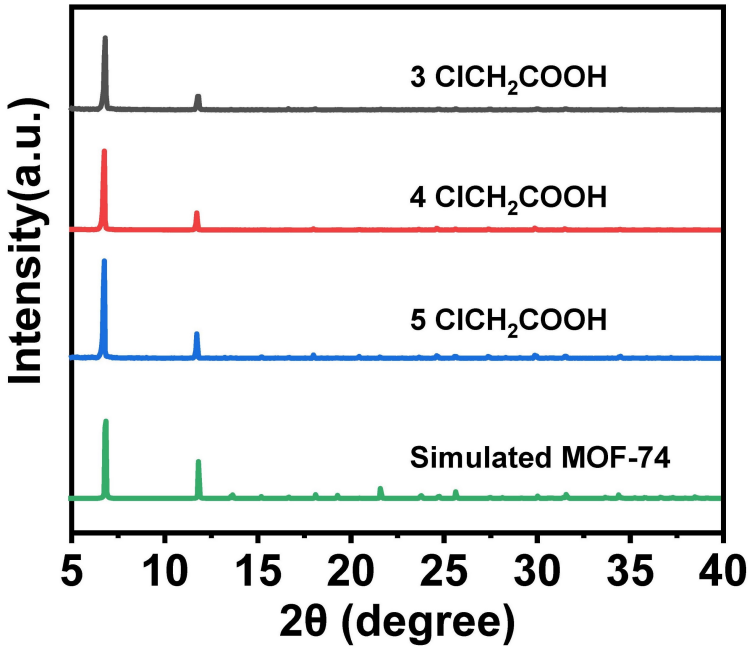

Figure S7. PXRD patterns of Mg-MOF-74 synthesized with different amounts of chloroacetic acid.

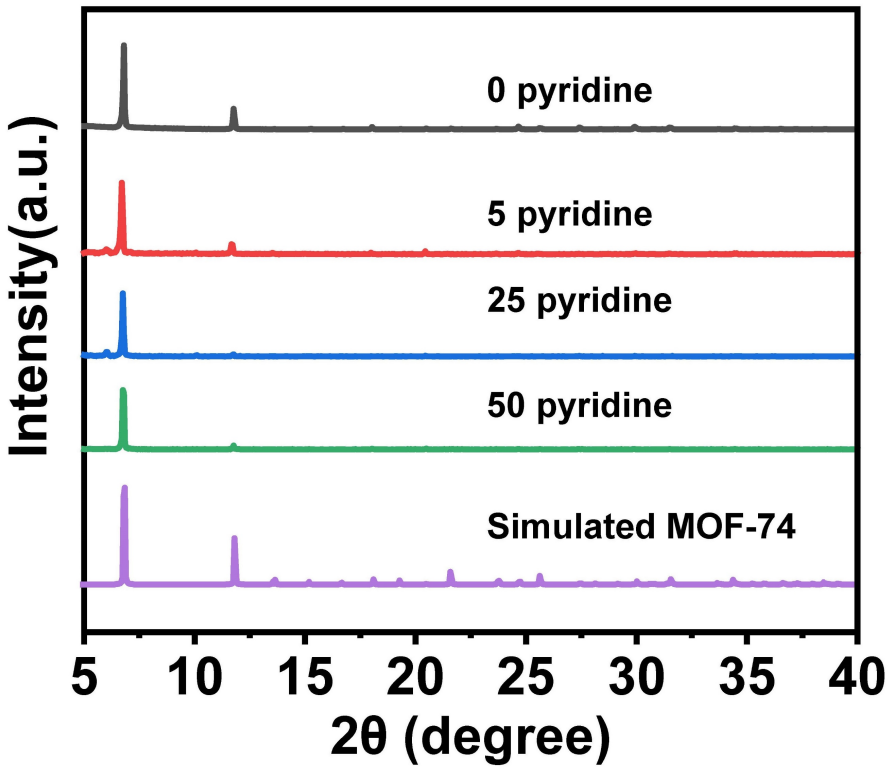

Figure S8. PXRD patterns of Mg-MOF-74 synthesized with different amounts of pyridine.