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Template-Free Synthesis of Hierarchical Porous Metal-Organic Frameworks

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The details:

1. Experimental

Materials. The ligand of 2,5-dihydroxy-1,4-benzenedicarboxylic acid (H_2DHBDC) was obtained from Alfa Aesar. Solvents (dimethylformamide, DMF; dimethylacetamide DMA; and N-methylpyrrolidone, NMP) and metal salts (zinc acetate, zinc nitrate, zinc chloride, and zinc sulfate) were purchased from Aldrich Chemical Co. Inc.. All materials were used without further purification.

Synthesis. A 20 mL DMF solution of 2,5-dihydroxy-1,4-benzenedicarboxylic acid (0.099 g, 0.50 mmol) was added to a 20 mL DMF solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.343 g, 1.57 mmol) under stirring. The mixture was stirred for desired time at room temperature, and the resulting yellow precipitate was separated by centrifugation and subsequently washed with dimethylformamide and methanol. The resulting yellow product was dried under vacuum at 60 ^oC overnight and characterized by powder XRD, SEM, TEM, TGA, and nitrogen adsorption-desorption.

TGA measurement. Thermogravimetric analysis (TGA) was carried out by using a TA Instrument 2950 from room temperature to 900 ^oC at a heating rate of 5 ^oC min^{-1} under an air atmosphere.

Powder X-ray Diffraction (XRD). Powder X-ray Diffraction **(**XRD) analysis of the Zn-MOF-74 series was used to confirm the crystallinity as well as the phase purity of the bulk materials. Powder XRD patterns were recorded on a PANalytical Empyrean diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å).

Gas Adsorption Analysis. Gas adsorption studies were done to investigate the porosity of the Zn-MOF-74/*t* series. Gas adsorption experiments were performed on a Micromeritics Tristar 3000 and Quantachrome Autosorb-1 at 77 K. Samples were

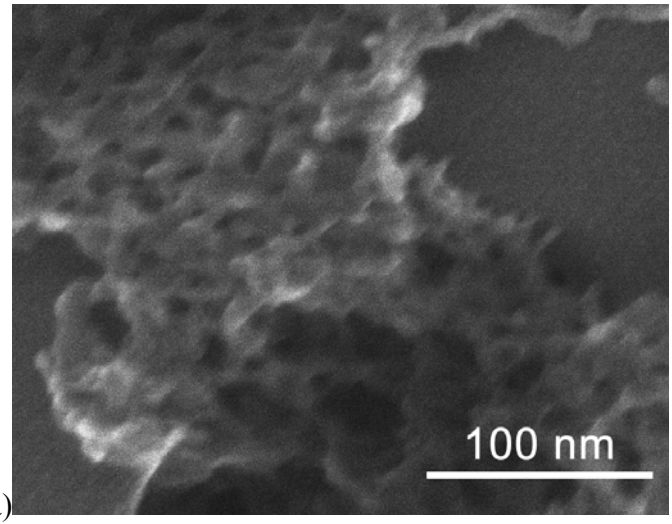
outgassed for 6 hours at 150 °C under nitrogen flow (Tristar) or vacuum (Autosorb-1) prior to adsorption analysis.

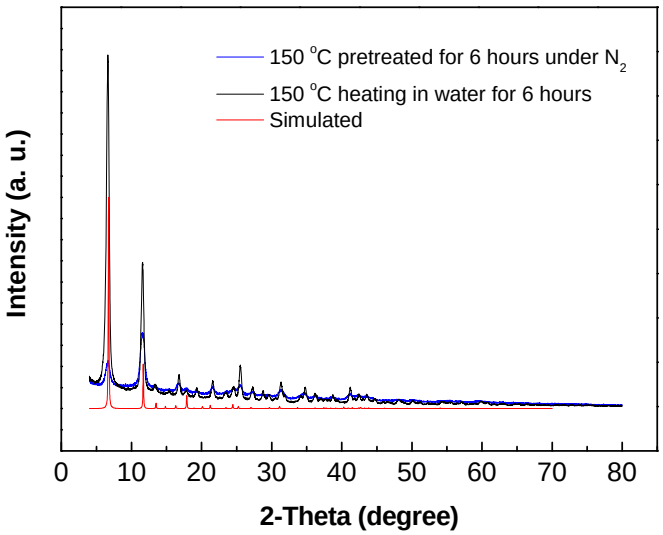
Electron Microscopy (S/TEM). Scanning transmission electron microscope (STEM) images were recorded using a Hitachi HD2000 STEM microscope operating at 200 kV. Samples for STEM analysis were prepared by drop casting: one drop of the sample dispersion in ethanol was dropped onto a copper grid and allowed to dry at ambient temperature before subjection to STEM analysis. Low dose high resolution TEM (HRTEM) images were collected using a Zeiss Libra 120 at 120kV. A minimum dose condition and an emission current of 6μA are used in order to minimize electron-beam-related radiation damage of MOF samples.

Dye Up-Take Measurements. The UV-vis spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer. Fresh made Zn-MOF-74 (0.0109 g), obtained from 18-hour reaction, was dried at an ambient temperature and soaked in a methanol solution of BBR-250 (20 mM, 2 mL). The mixture was stirred for 24 hours and subsequently separated by centrifugation. The supernatant was decanted and solid was washed with methanol to move the dye molecules adsorbed on the external surface, and all the methanol was cumulated and diluted to 4000 mL for the Ultraviolet/Visible spectroscopy measurements. The calibration solutions were prepared with the BBR-250 concentration being 0.01, 0.02, 0.03, 0.04, 0.05 mM, respectively. All the concentrations were calculated based on the biggest adsorption at 587 nm.

2. The SEM image and powder XRD of Zn-MOF-74/18 after thermal and hydrothermal treatments

(a)





(b)

Figure S1. The SEM image (a) and powder XRD (b) of Zn-MOF-74/18 after thermal treatment at 150 °C (blue line) and hydrothermal treatment at 150 ºC (black line), both for 6 hours.

3. TGA measurements of as-made Zn-MOF-74/18

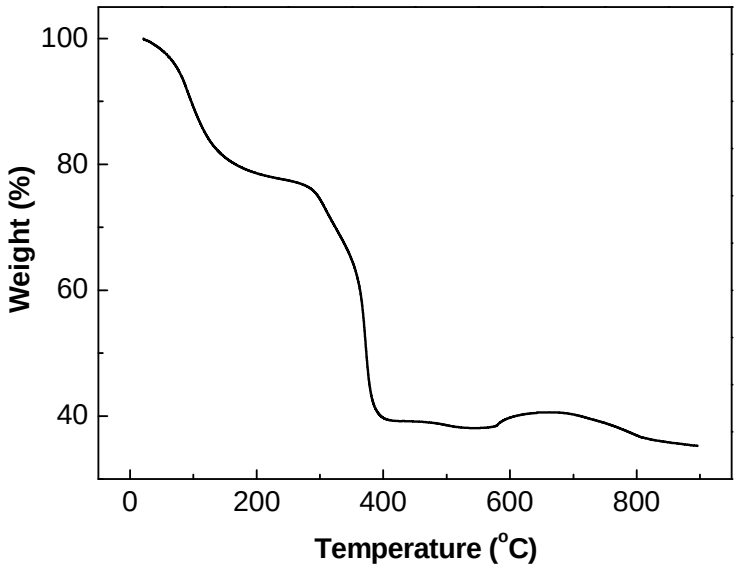
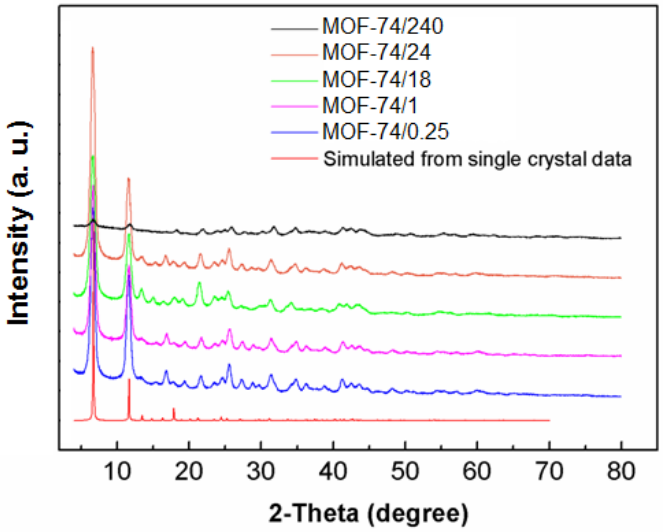
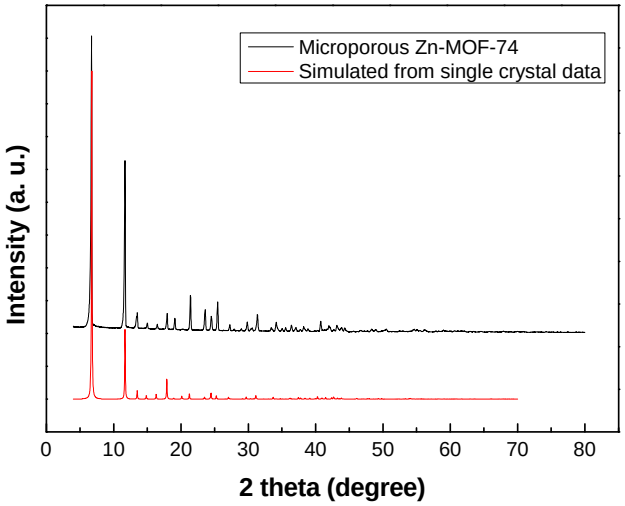


Figure S2. TGA measurement of the as-made Zn-MOF-74/18 under air.

4. Powder XRD patterns of Zn-MOF-74/t obtained with different reaction times



(a)



(b)

Figure S3. (a) Powder XRD patterns of Zn-MOF-74/*t* prepared with different reaction time (0.25 hour, 1 hour, 18 hours, 24 hours, and 10 days); (b) Powder XRD patterns of microporous Zn-MOF-74 prepared through solvothermal method.[1]

1. (a) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* 2005, *127*, 1504–1518; (b) Liu, B.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* 2013, 1419–1421.

5. Powder XRD patterns of Zn-MOF-74/18 obtained with different solvents

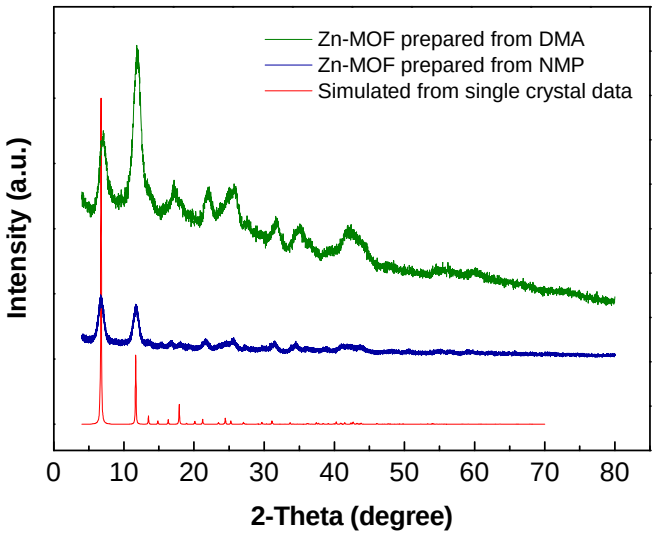


Figure S4. Powder XRD patterns of Zn-MOF-74/18 prepared with dimethylacetamide (DMA) and N-Methylpyrrolidone (NMP) from 18-hour reaction.

6. SEM and TEM images of Zn-MOF-74/*t* series obtained with different solvents

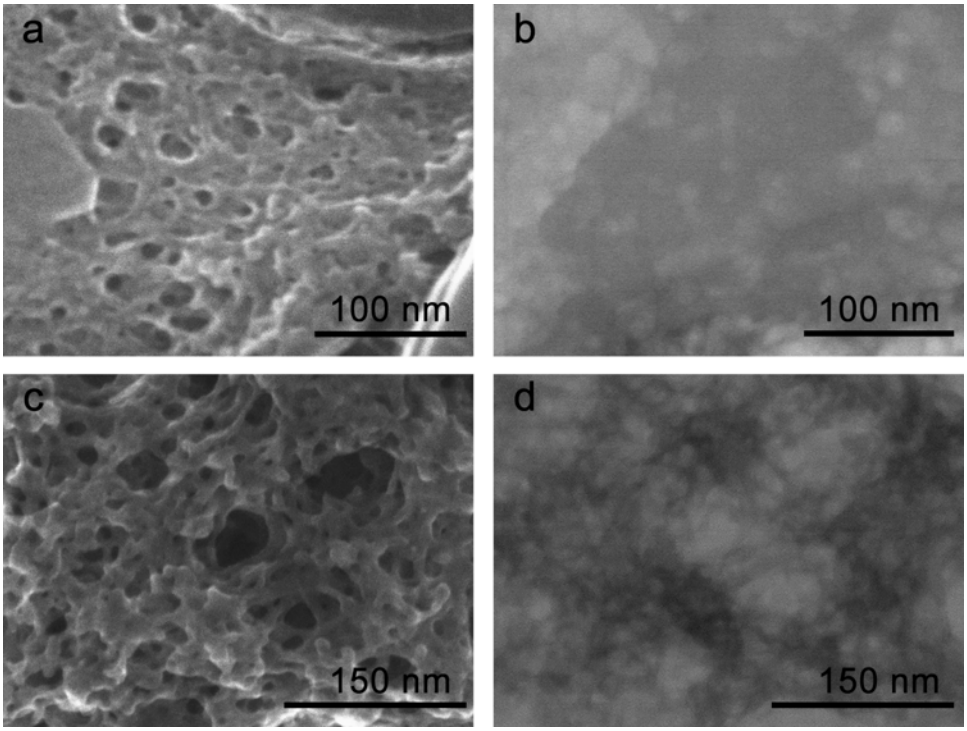
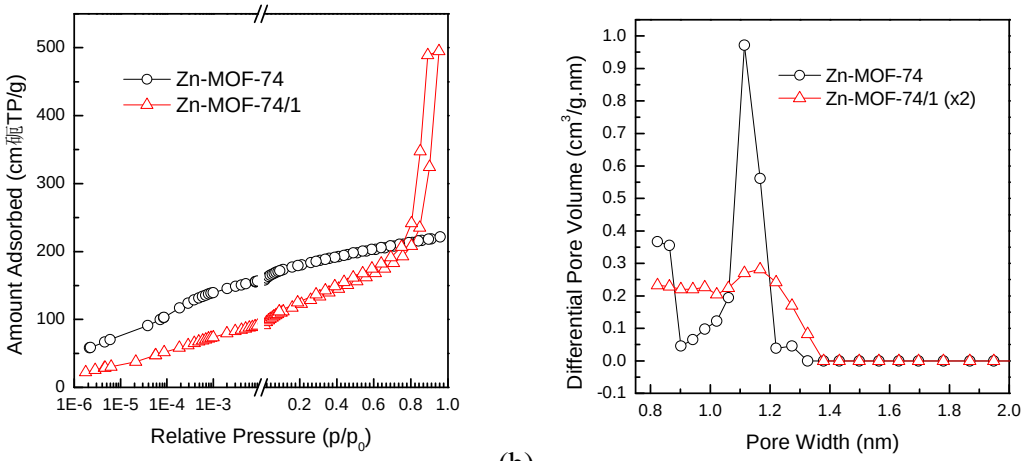


Figure S5. The SEM and TEM images of Zn-MOF-74 prepared with (a, b) N-Methylpyrrolidone (NMP) and (c, d) dimethylacetamide (DMA).

7. N_2 77K isotherms of Zn-MOF-74 and Zn-MOF-74/1 and corresponding PSD



(a) (b)

Figure S6. N_2 77K isotherms for Zn-MOF-74 and Zn-MOF-74/1 materials (a) and corresponding pore size distributions (b). The adsorption isotherms are shown in the logarithmic scale at low relative pressures. The PSDs were calculated using NLDFT method for cylindrical pores based on the adsorption branch of the isotherms.

8. Table 1. Calculated adsorption parameters for Zn-MOF-74 series obtained with various reaction times†

Samples	V_{SP} (cm^3/g)[a]	S_{BET} (m^2/g)[b]	V_{mi} (cm^3/g)[c]	V_t (m^2/g)[d]	$100xV_{mi}/V_t$[e]	w (nm)[f]	d_{XRD} (nm)[g]
Zn-MOF-74	0.35	759	0.35*	0.35*	100	–	>100
Zn-MOF-74/0.25	0.48	638	0.22	0.48	46	8.6	13.2
Zn-MOF-74/1	0.44	431	0.09	0.44	20	6.8	11.5
Zn-MOF-74/18	0.31	314	0.03	0.31	10	8.6	10.3
Zn-MOF-74/24	0.36	287	0.01	0.36	3	6.8	11. 5
Zn-MOF-74/240	0.49	236	0.02	0.49	4	14.8	8.9
Zn-MOF-74/18-DMA	0.24	253	0.03	0.24	13	6.4	6.5
Zn-MOF-74/18-NMP	0.48	318	0.01	0.48	2	8.6	8.8

†[a]Single point pore volume taken at $p/p_0 \sim 0.98$; [b]specific surface area calculated in the p/p_0 range of 0.05 – 0.20; [c]micropore volume and [d]total pore volume calculated in the α_S-plot range of 0.8-1.0 and 2.5-7.5 (*1.6-2.0), respectively; [e]approximate α_S-plot micropore to total pore volume percent ratio; [f]mesopore width from the maximum of the calculated PSDs; [g]the average crystallite size of the Zn-MOF-74/*t* series was calculated by Scherrer equation $d_{XRD} = 0.9\lambda/(B\cdot\cos\theta)$, where, λ is the wavelength of X-ray (0.15406 nm), B is the width of XRD pattern line at half peak height in radians, and θ is the angle between the incident and diffracted beams in degree.

9. N_2 77K isotherms of Zn-MOF-74/*t* obtained with different solvents

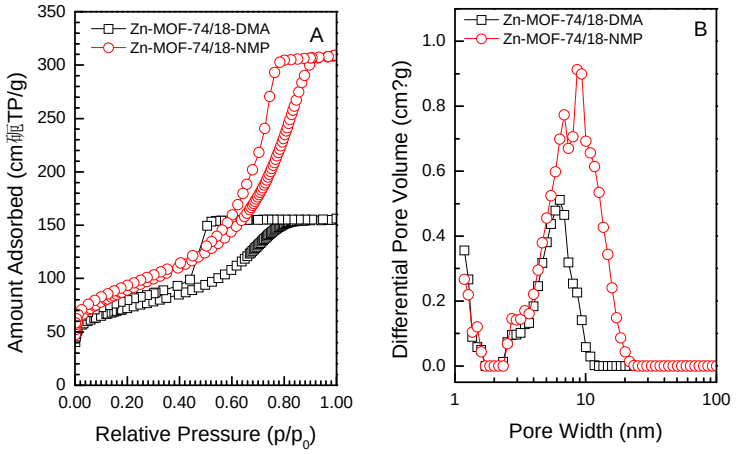


Figure S7. N_2 adsorption-desorption isotherms of Zn-MOF-74 obtained for 18-hour reaction with dimethylacetamide (DMA) and N-methylpyrrolidone (NMP), with BET surface area being 317.09 and 252.68 m^2/g, respectively.

10. UV-vis spectra of BBR-250 methanol solutions after immersing Zn-MOF-74 and Zn-MOF-74/18 for 24hours

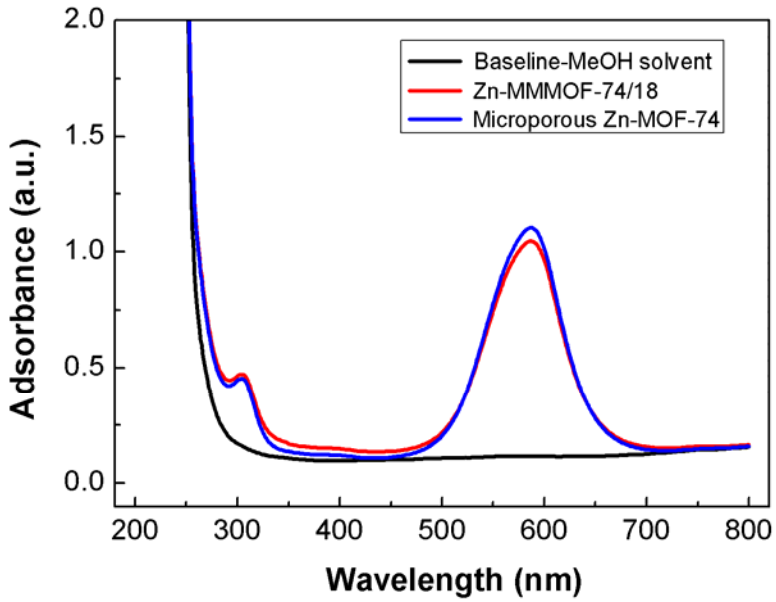


Figure S8. UV-vis spectra of BBR-250 methanol solutions, in which the MOF materials were soaked for 24 hours.