

Supporting Information

Reverse Synthesis of Yolk-Shell Metal-Organic Frameworks

Songwei Zhang,^{abc} Yaqi Fan,^a Lianshun Luo,^a Conger Li,^a Yanhang Ma,^a and Tao Li^{*a}

^aSchool of Physical Science and Technology, ShanghaiTech University, 201210 Shanghai, People's Republic of China

^bShanghai Advanced Research Institute, Chinese Academy of Sciences 201203, Shanghai, People's Republic of China

^cUniversity of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

Experimental Section

Materials

Zinc acetate dihydrate ($\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$, AR, Aladdin), Zinc nitrate hexahydrate ($\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR, Aladdin), Cobaltous Nitrate Hexahydrate ($\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR, Aladdin), Cobalt(II) acetate tetrahydrate ($\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$, AR, Aladdin), 2-Methylimidazole (HMIM, AR, Adamas), Methanol (AR, $\geq 99.5\%$, GENERAL-REAGENT), Acetic acid (HOAc, ACS, $\geq 99.7\%$, Aladdin), Zirconium(IV) chloride (98%, anhydrous, Alfa Aesar), Zirconyl chloride octahydrate (AR, GENERAL-REAGENT), Terephthalic acid (BDC, RG, 99%, Adamas), 2,5-Dihydroxyterephthalic acid (DOBDC, RG, 99%+, Adamas), N,N-Dimethylformamide (DMF, $>99.5\%$, GENERAL-REAGENT), Nitric acid (HNO_3 , AR, GENERAL-REAGENT), Deionized water (DI-water), Ethanol (AR, GENERAL-REAGENT), Dichloromethane (DCM, GENERAL-REAGENT), Petroleum ether (PE, GENERAL-REAGENT), polyvinylpyrrolidone (PVP, $M_w \sim 24000$, aladdin).

Synthesis of MOF

Synthesis of UiO-66-(OH)₂: 1.1424 g PVP was pre-dissolved in 10 mL DMF. 42 mg ZrCl_4 and 35.7 mg DOBDC were added to 2.7 mL DMF. Then 349 μL PVP/DMF solution was added and mixed adequately. 2.56 mL acetic acid and 0.1 mL DI water were added subsequently. The well-mixed solution was left undisturbed for 2 hours in the oven of 120 °C. As-synthesized UiO-66-(OH)₂ was centrifuged and washed with DMF twice. The collected UiO-66-(OH)₂ was dispersed in 4 mL DMF for future use.

Synthesis of UiO-66-(OH)₂@UiO-66: 0.15 mmol BDC was added into a mixed solution of 2 mL DMF and 2 mL acetic acid, and then allowed to react at 90 °C for 5 minutes with stirring. 1 mL as-synthesized UiO-66-(OH)₂ suspension in DMF was added and stirred for another 5 minutes. Finally, 1 mL DMF containing 10.5 mg ZrOCl₂·8H₂O was added and stirred at 90 °C for 4 hours. The obtained UiO-66-(OH)₂@UiO-66 samples were centrifuged and washed with DMF twice. The collected products were dispersed in 4 mL methanol for future use.

Synthesis of hollow UiO-66 (H-UiO-66) by HNO₃: 1 mL as-synthesized UiO-66-(OH)₂@UiO-66 was centrifuged, dried and dispersed in 5 mL 10 M HNO₃. The suspension was stirred for 2 days. The resulting hollow UiO-66 samples were centrifuged and washed with DMF twice. To remedy defects in hollow MOFs generated during etching, the hollow MOFs were incubated in a DMF solution contain excess ligands. Briefly, about 20 mg hollow sample was dispersed in a 25 mL DMF solution containing 50 mM BDC. After stirring at 100 °C for 3 days, the sample was collected and washed with DMF twice.

Synthesis of ZIF-8@H-UiO-66: The ZIF-8 precursor stock solution was first prepared (mol ratio of Zn(OAc)₂: HOAc: HMIM:DI-water= 1:3:4.4:100). 8 mg dried H-UiO-66 samples were dispersed with 90 µl precursor solution of ZIF-8 and 1.2 ml ethanol. Dichloromethane (DCM, 2.4 mL) was added to the mixture and sonicated for 5 min to give a clear solution. After adding 6.0 ml petroleum ether (PE), white precipitate was formed. After drying the precipitate in a 120 °C oven, precursors@H-UiO-66 was

obtained. Then the sample was soaked in the methanol solution of HMIM (100 mg/ml) overnight to obtain ZIF-8@H UiO-66.

Synthesis of ZIF-67@H UiO-66: Similarly, $\text{Zn}(\text{OAc})_2$ was replaced by $\text{Co}(\text{OAc})_2$ with the same molar quantity in the preparation of ZIF-67 precursor solution. Precursors@H UiO-66 was synthesized using the same method above. The samples were then soaked in a water solution of HMIM (100 mg/ml) overnight to obtain ZIF-67@H UiO-66.

Synthesis of ZIF-8¹: 1.05 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2.34 g HMIM were added into 50 ml methanol at room temperature (RT). After 6 hours, a large amount of white precipitate was produced. The obtained ZIF-8 was centrifuged and washed with methanol twice. The collected products were redispersed in 30 mL methanol for future use.

Synthesis of ZIF-67²: 0.45 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 5.5 g HMIM were added into 23 ml DI-water at room temperature (RT). After 6 hours, a large amount of purple precipitate was produced. The obtained ZIF-67 was centrifuged and washed with methanol twice. The collected products were redispersed in 30 mL methanol for future use.

Instrumentation

Powder X-ray diffraction (PXRD) patterns were collected on an X-ray diffractometer (Bruker D8 PHASER) with $\text{Cu K}\alpha$ radiation, operated at 40 kV and 40 mA.

High-resolution scanning electron microscope (HRSEM) images were obtained using a JSM-7800F Prime Scanning Electron Microscopy at 5 kV. The samples were pre-coated with Au for 10 seconds using an SBC-12 sputter coater.

Transmission electron microscope (TEM) images were taken on a JEM 2100 plus (200 kV) or JEM 1400 plus (120 kV). Powder samples were first evenly dispersed in methanol. Then, a 2.0 μl solution droplet was added onto a carbon-coated copper grid.

Gas sorption. N_2 adsorption isotherms were collected by a volumetric gas adsorption analyzer (Quantachrome Instruments Autosorb-iQ-MP-AG). Typically, a 50-80 mg powder sample was loaded in a 6 mm large bulb sample cell and degassed under vacuum at 120 $^\circ\text{C}$ for 8 h.

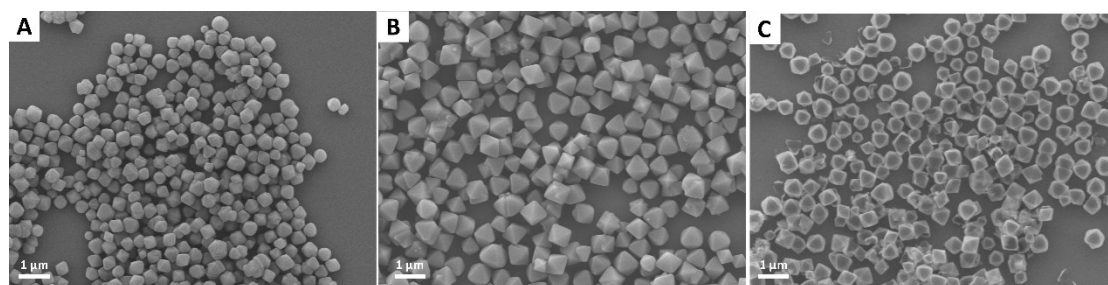


Fig. S1. The SEM images of (A) UiO-66-(OH)_2 , (B) $\text{UiO-66-(OH)}_2@ \text{UiO-66}$, (C) H- UiO-66 .

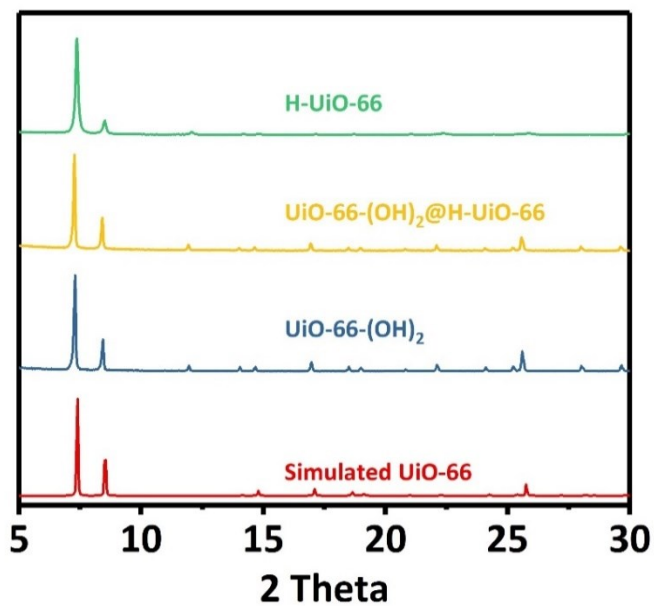


Fig. S2. The PXRD pattern of UiO-66-(OH)₂, UiO-66-(OH)₂@UiO-66, and H-UiO-66.

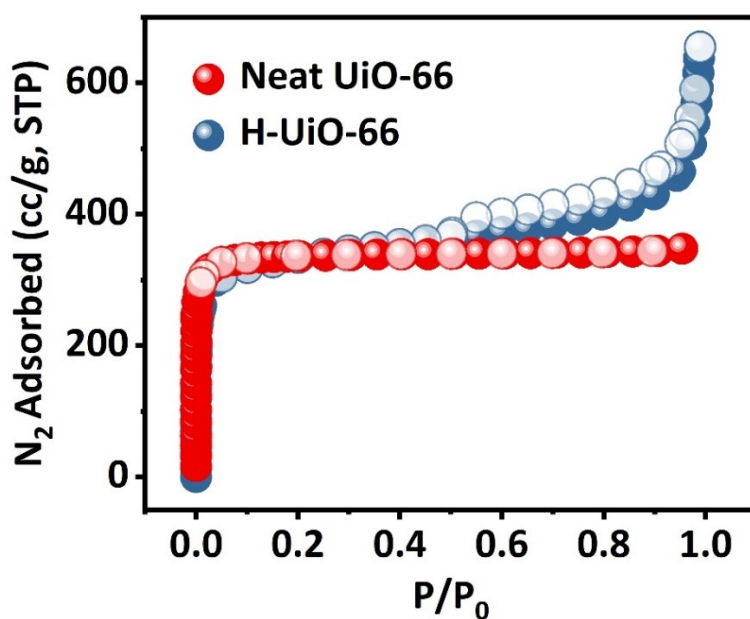


Fig. S3. N₂ sorption isotherms of neat UiO-66 and H-UiO-66 at 77K.

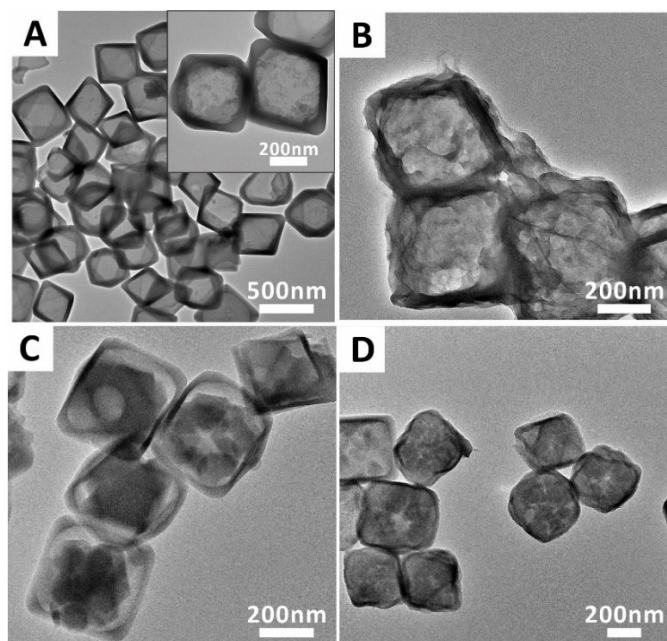


Fig. S4. The TEM image of (A) ZIF-8 precursors@H-UiO-66, (B) ZIF-67 precursors@H-UiO-66, (C) ZIF-8@H-UiO-66, (D) ZIF-67@H-UiO-66.

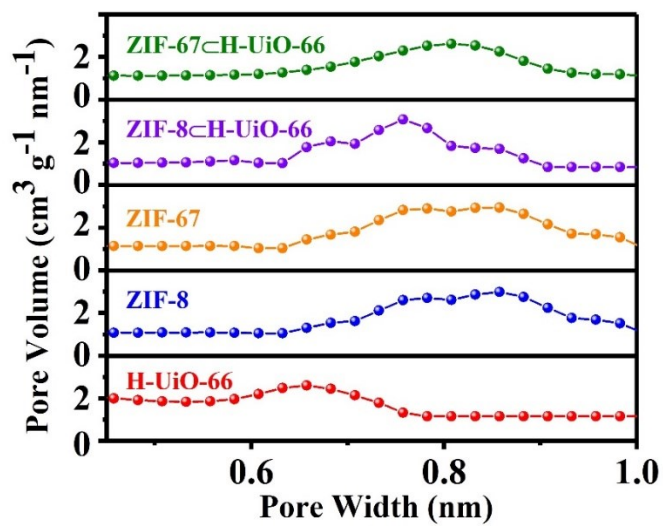


Fig. S5. Pore size distribution of neat MOFs and ZIF-8/67@H-UiO-66 calculated from N_2 adsorption isotherms at 77 K.

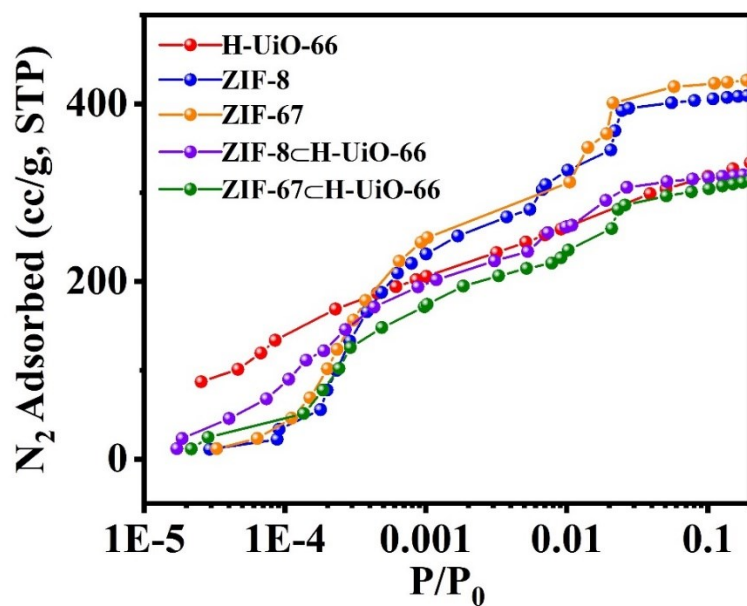


Fig. S6. N₂ sorption isotherms of neat MOFs and ZIF-8/67@H-UiO-66 at 77K.

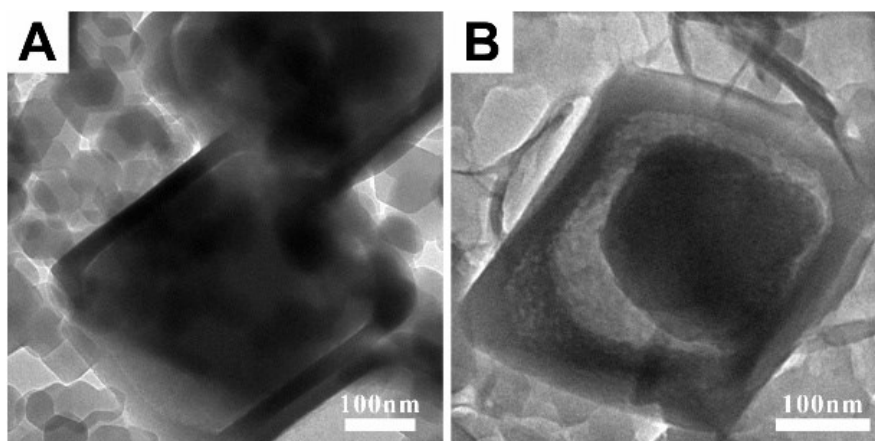


Fig. S7. TEM images of (A) mixture of ZIF-8@H-UiO-66 and ZIF-8, (B) mixture of ZIF-8@H-UiO-66 and ZIF-8 after soaking in 0.5 M gallic acid / ethanol solution at 60 °C for 1 h.

Reference

1. J. Cravillon, S.-J. Lohmeier, A. Feldhoff, K. Huber, and M. Wiebcke, *Chem. Mater.*, 2009, **21**, 1410-1412.
2. J. Qian, F. Sun and L. Qin, *Mater. Lett.*, 2012, **82**, 220-223.

