

## Supporting Information

### **Pre-Programed Hydroxy Double Salt Templates for Room-Temperature Controlled Synthesis of Mixed-Metal Zeolitic Imidazolate Frameworks**

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## Experimental Methods

### Synthesis of (Zn, Co) HDS via coprecipitation method

For (Zn, Co) HDS, coprecipitation method was used similar to previous report for synthesizing hydroxy double salts<sup>1</sup>. In general, 5 mL NaOH aqueous solution was added to the reactor vessel prior to coprecipitation to provide an initial pH = 10 condition. Aqueous solution of mixed transition metal salts ( $\text{Co}(\text{NO}_3)_2$  and  $\text{Zn}(\text{NO}_3)_2$ ) with particular concentration listed in **Table S1** and 1M NaOH aqueous solution were added dropwise to the reactor vessel simultaneously using syringe pumps. Magnetic stirring and  $\text{N}_2$  purge were kept throughout the coprecipitation process and maintained for 3 h after the dropwise addition of solutions. The precipitated product was separated by centrifugation (7800 rpm, 3min) and washed twice with ethanol overnight. The (Zn, Co) HDS powders were collected and vacuum dried at 60°C for 3 h.

**Table S1.** Synthesis Conditions for (Zn, Co) HDS with different metal ratios.

Co:Zn in Salt Feed Solution	1:3	2:3	1:1	2:1	5:2	3:1
$\text{Co}^{2+}$ Concentration in Salt Feed Solution (M)	0.25	0.4	0.5	0.67	0.71	0.75
$\text{Zn}^{2+}$ Concentration in Salt Feed Solution (M)	0.75	0.6	0.5	0.33	0.29	0.25
Salt Feed Solution Flow Velocity ( $\mu\text{L}/\text{min}$ )	500					
Salt Feed Solution Total Volume (mL)	10					
NaOH Solution Flow Velocity ( $\mu\text{L}/\text{min}$ )	490	610	710	830	840	850
NaOH Solution Total Volume (mL)	9.80	12.1	14.2	16.5	16.7	16.9
Co:Zn in HDS Determined by ICP-OES	0.32	0.62	0.94	1.99	2.45	3.01

### **Synthesis of bimetallic ZIF-7 from (Zn, Co) HDS**

0.10 g (Zn, Co)HDS was dispersed in 5 ml of deionized water using sonication for 20 min. 0.30 g (2.5 mmol) of benzimidazole (bIM) was dissolved in 10 ml of mixed solvent of DMF and ethanol (v% : v% = 50 : 50), and then added to the HDS suspension under magnetic stirring at room temperature. After 3 h of reaction, the powder product was separated by vacuum filtering and washed with 50 mL of ethanol for three times. The purplish powder was collected and dried in vacuum at 60 °C for 12 h.

### **Synthesis of bimetallic ZIF-8 from (Zn, Co) HDS**

0.050 g (Zn, Co) HDS was dispersed in 10 ml of mixed solvent of deionized water and ethanol (v% : v% = 50 : 50) using sonication for 10 min. 0.50 g (6.1 mol) of 2-methylimidazole was dissolved in 5 ml ethanol, and then added to the HDS suspension under magnetic stirring at room temperature. After 30 min of reaction, the powder product was centrifuged at 6000 rpm for 3 min, and washed with 50 mL of ethanol for three times. The purple powder was collected and dried in vacuum at 60°C overnight.

### **Synthesis of bimetallic ZIF-71 from (Co,Zn) HDS**

0.10 g (Zn, Co) HDS was dispersed in 5 ml of deionized water using sonication for 20 min. 0.30 g (2.5 mmol) of 4,5-dichloroimidazole (dcIM) was dissolved in 10 ml of mixed solvent of DMF and ethanol (v% : v% = 50 : 50), and then added to the HDS suspension under magnetic stirring at room temperature. After 2 h of reaction, the powder product was separated by vacuum filtering and washed with 50 mL ethanol for three times. The purplish powder was collected and dried at 60 °C for 12 h.

### **Synthesis of monometallic ZIF-7 (Zn)**

The synthesis of single-metal ZIF-7(Zn) was adopted from the previous report.<sup>2</sup> 5 ml DMF solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (136 mg, 0.5 mmol) and 5 ml methanol solution of bIm (120 mg, 1 mmol) were prepared separately. Zinc nitrate DMF solution was quickly added into the bIm methanol solution under magnetic stirring. The reaction was kept for 30 min. The ZIF-7 product was collected by centrifugation (7800 rpm, 30 min),

washed by 50 mL of methanol for three times, and then dried in vacuum at 60 °C for 12 h.

### **Synthesis of monometallic ZIF-9(Co)**

The synthesis of single-metal ZIF-9(Co) was adopted from the previous report.<sup>3</sup> 7.2 mmol of bIM and 3.6 mmol of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in 60 mL of DMF. After mixing for 30 min, the mother solution was transferred to a 100 mL Teflon autoclave and heated to 135 °C for 48 h. Purple precipitation was collected by vacuum filtration, washed with 50 mL of methanol for three times, and dried in vacuum at 60 °C for 12 h.

### **Synthesis of bimetallic ZIF-7 via direct one-pot method**

The one-pot synthesis of bimetallic ZIF-7 was attempted by directly adopting the method for synthesizing single-metal ZIF-7(Zn).  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with different ratios (Co:Zn = 1:3, 1:1, 2:1, 5:2, 3:1, respectively; total divalent cation concentration = 0.1 M) were dissolved in 5 ml DMF solution. 5 ml methanol solution of bIm (120 mg, 1 mmol) were prepared separately. The DMF solution of mix nitrate salts was quickly added into the bIm methanol solution under magnetic stirring. The reaction was kept for 30 min. The product was collected by centrifugation (7800 rpm, 30 min), washed by 50 mL of methanol for three times, and then dried in vacuum at 60 °C for 12 h.

### **Synthesis of mixed-matrix membrane**

7.5 wt% Pebax-2533 was dissolved in 1-butanol under heating at 75 °C for 5 h. Bimetallic or monometallic ZIF particles was dispersed in 5 mL of 1-butanol, and then mixed with 10 mL of Pebax-2533 solution. The final concentration of the ZIF particles in the mixed suspension was 15 wt%, while the concentration of Pebax-2533 was 5 wt%. The suspension was further sonicated for 20 min to remove bubbles. During the spin coating process, 1 mL of the mixed suspension was added onto the porous alumina substrate prior to spinning at 1500 rpm for 60s. The membrane samples were dried in ambient environment at room temperature for 12 h, and in vacuum oven at room

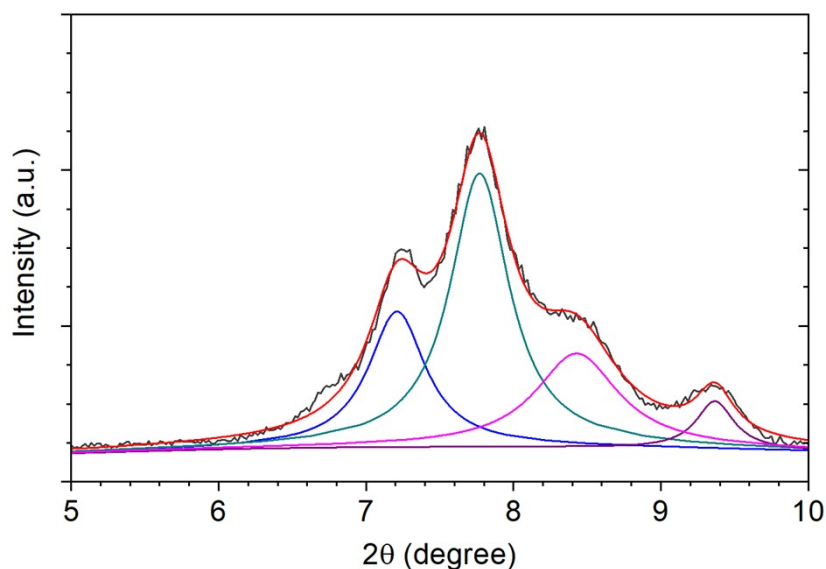
temperature for 10 h and then at 70°C for 12 h. Single gas permeation was tested using a custom-built Wicke-Kallenbach setup with feed pressure of 3.5 bar at 25 °C.

### **Materials Characterization**

X-ray diffraction (XRD) was conducted on a PANalytical X'Pert PRO X-ray diffractometer (Cu K $\alpha$  X-ray source). Scanning electron microscopic (SEM) images were taken by a Hitachi SU-8010 SEM. The powder samples were dispersed in ethanol, drop casted onto the silicon, and sputter coated with platinum for imaging. Energy dispersive X-ray (EDX) analysis was performed using a SU-8010 SEM equipped with an Oxford energy dispersive X-ray spectrometer (X-max80). Transmission electron microscope (TEM) was carried out on a Hitachi HT-7700. The powder samples were dispersed in ethanol and dripped onto carbon support films for imaging. The ratios of Co:Zn in the HDS and the ZIF powders were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Varian-730ES). Typically, 0.020 g powder sample was dissolved in 1 mL HNO<sub>3</sub> (Sinopharm, 65~68%) and diluted to 100 mL (<20 ppm). Before ICP-OES analysis, the analyte solution was filtered with a 0.2  $\mu$ m filter head. UV-Vis spectroscopy was measured using a PerkinElmer Lambda 750 spectrometer. BET surface area was calculated based on N<sub>2</sub> adsorption taken at 77 K using a Quantachrome Autosorb-IQ2-MP gas adsorption analyzer and the CO<sub>2</sub> adsorption was taken at 273k using a Micromeritics ASAP2460 gas adsorption analyzer. FTIR spectroscopy was performed on a Thermo Nicolet 5700 spectrometer. The thermal stability of the sample was determined by a Mettler TGA/DSC3+ synchronous thermal analyzer.

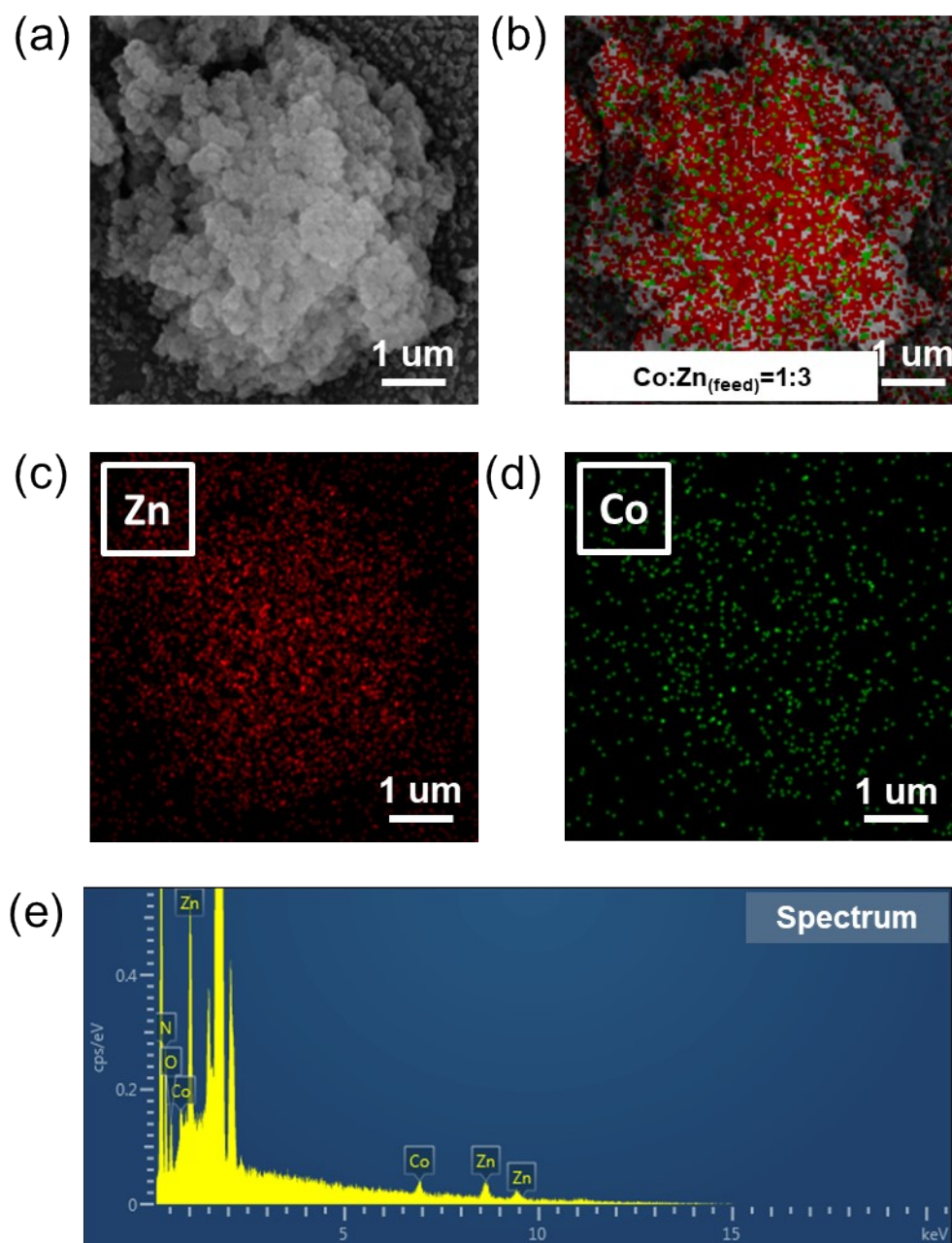
**Table S2.** Co:Zn ratios in the ZIF-7 powders synthesized using direct one-pot method with  $\text{Zn}(\text{NO}_3)_2$  and  $\text{Co}(\text{NO}_3)_2$  as precursors

Feed Ratio	Co:Zn=1:3	Co:Zn=1:1	Co:Zn=2:1	Co:Zn=5:2	Co:Zn=3:1
Co:Zn (EDX)	0.0052	0.0057	0.0093	0.0080	0.0099
Co:Zn (ICP-OES)	0.0024	0.0044	0.0080	0.0092	0.0110

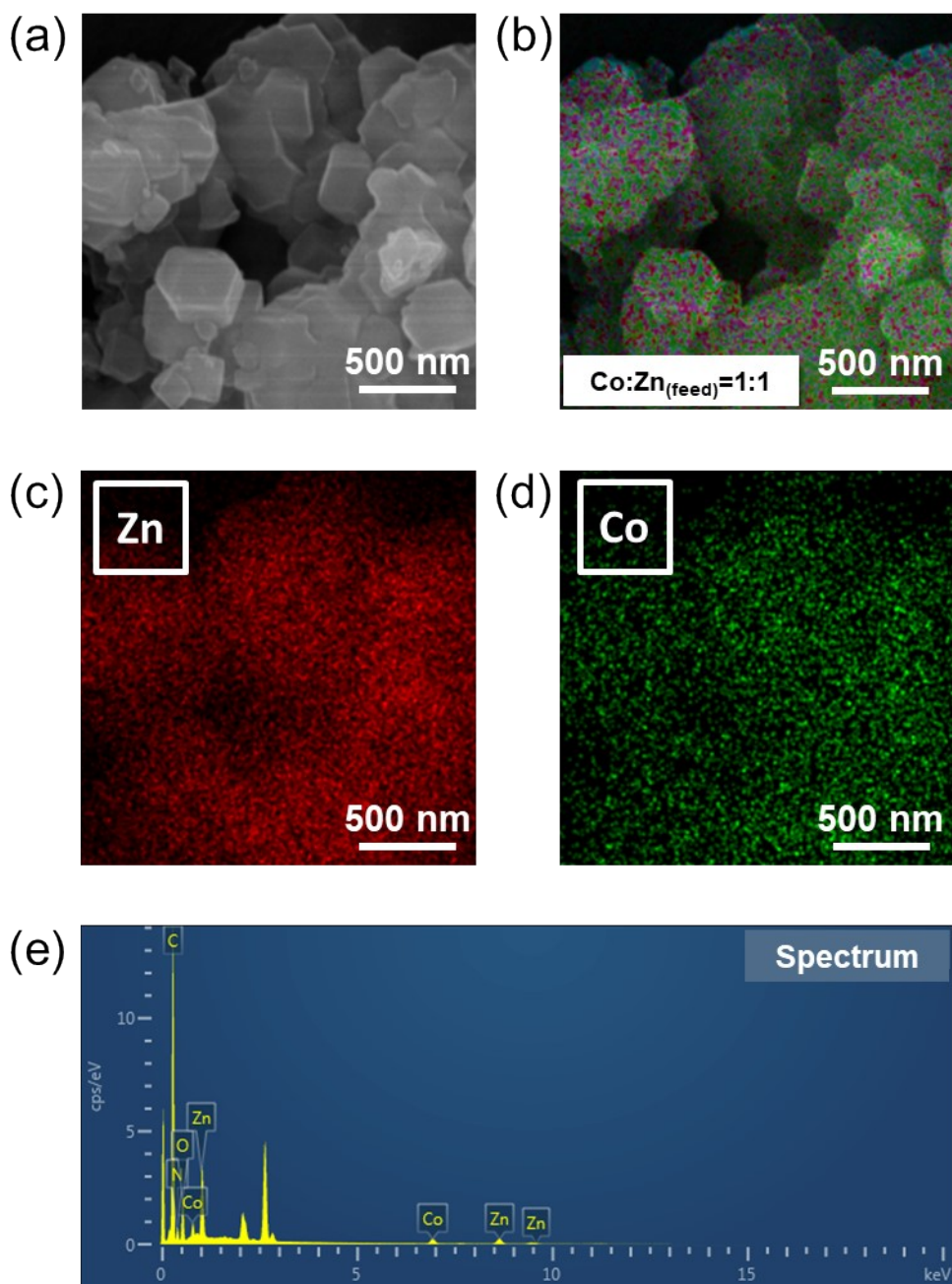


**Figure S1.** Powder XRD for the intermediate species collected after the reaction between (Zn,Co) HDS (Co:Zn=1:1) and bIm linker for 1 h (black). Deconvoluted peaks are at 7.210 (blue), 7.771 (dark cyan), 8.429 (magenta) and 9.366 (purple), while the fitted pattern are shown in red. The former two peaks are associated with the mixed-

metal ZIF-7. The latter two peaks are likely related to the HDS structure during the conversion process to ZIF-7.

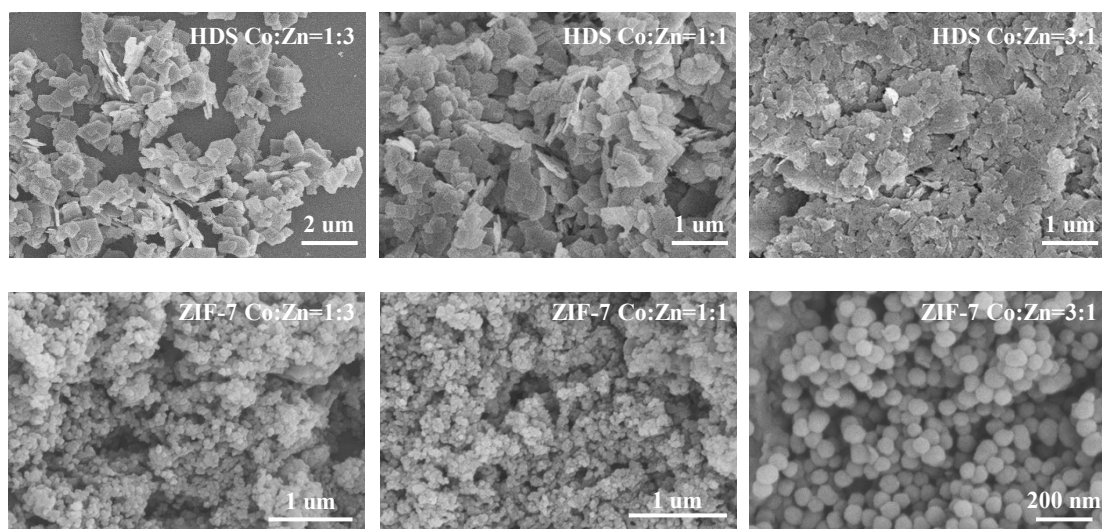


**Figure S2.** (a) SEM image, (b-d) EDX mapping images and (e) EDX spectrum for the ZIF-8 powder synthesized using HDS conversion method with Co:Zn=1:3 ratio in the HDS template. The Co:Zn ratio for the final mmZIF-8 was =1:3.026 as determined by ICP-OES.

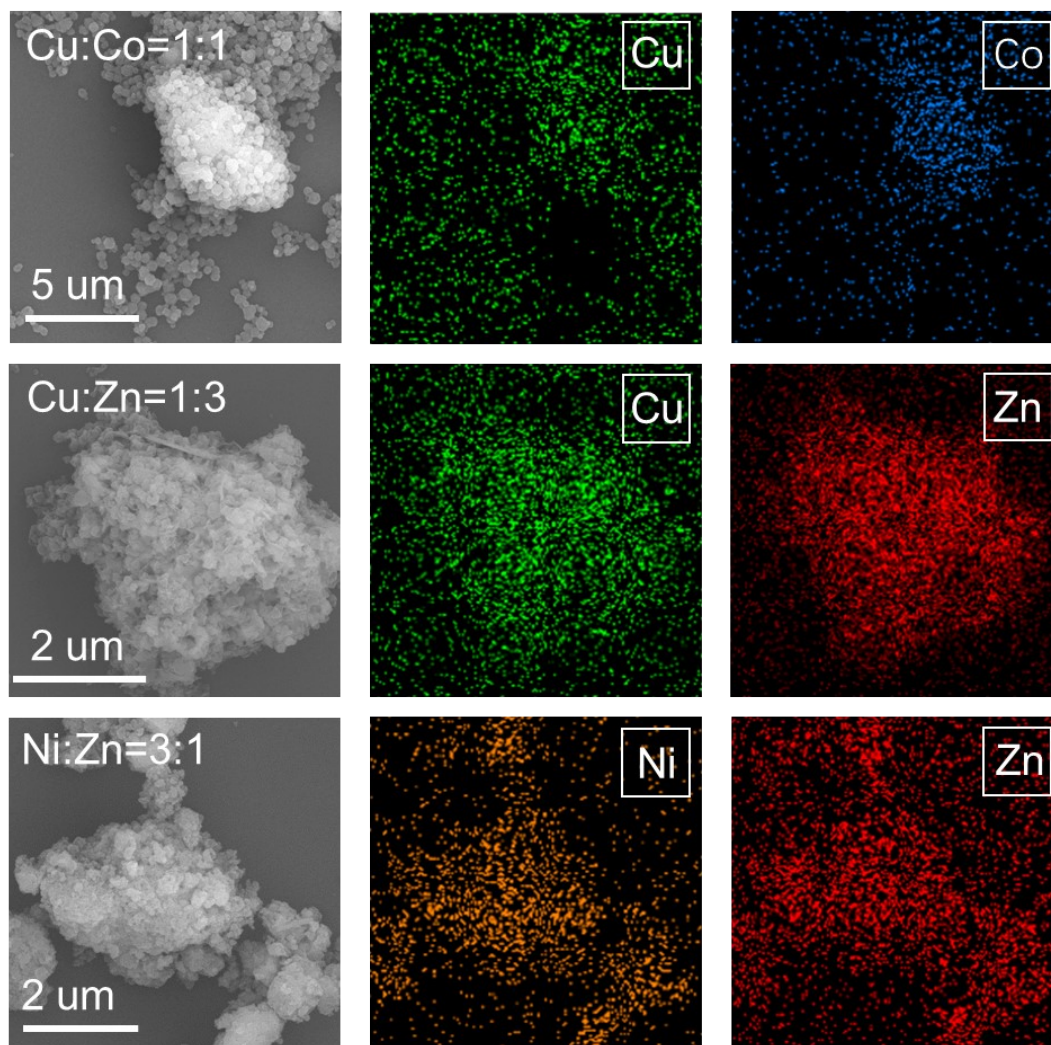


**Figure S3.** (a) SEM image, (b-d) EDX mapping images and (e) EDX spectrum for the ZIF-71 powder synthesized using HDS conversion method with Co:Zn=1:1 ratio in the HDS template. The Co:Zn ratio for the final mmZIF-71 was =1:0.975 as determined by ICP-OES.

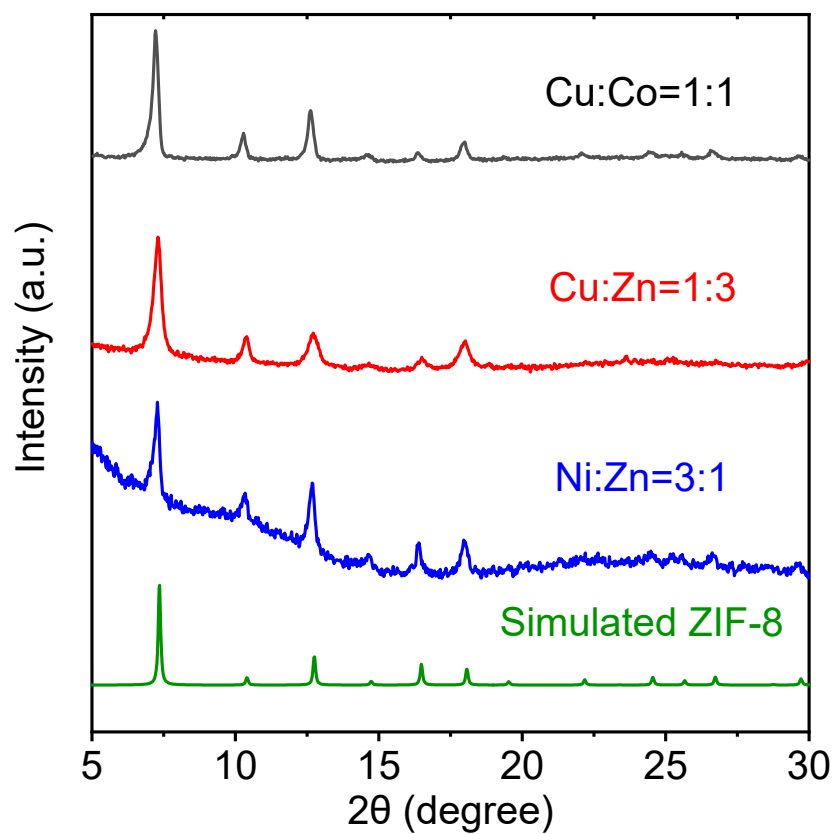




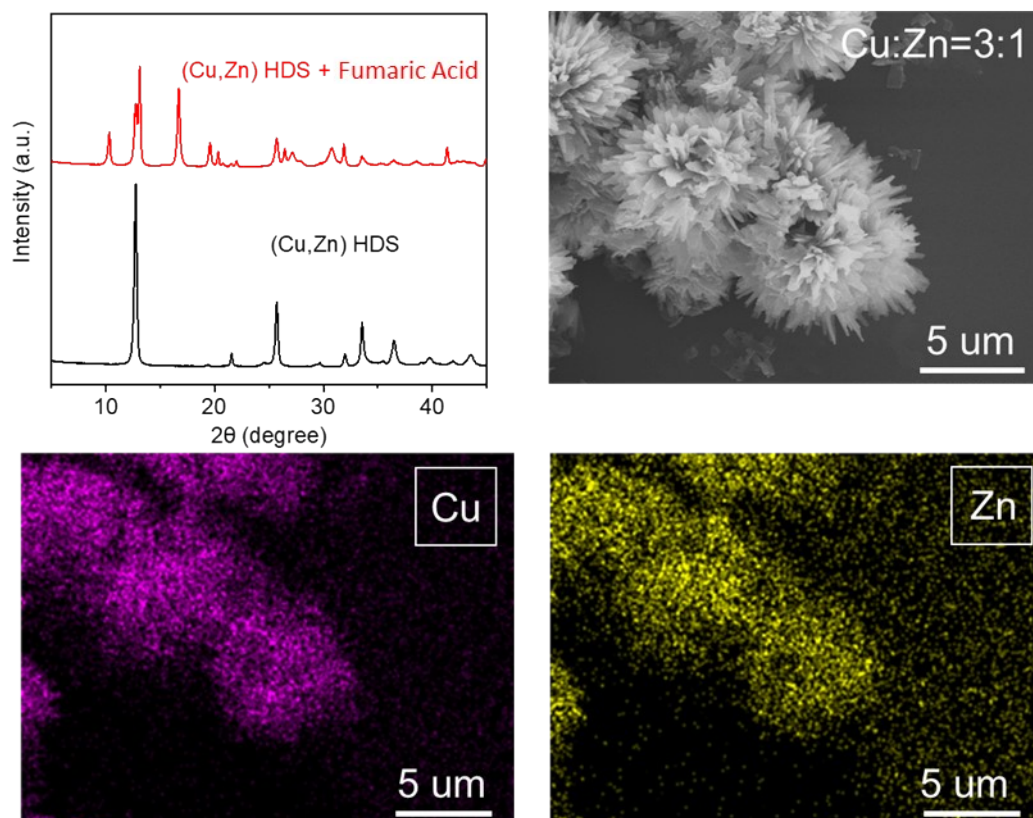
**Figure S4.** SEM images of the (Zn, Co) HDS and the mmZIF-7 converted from HDS templates with different metal ratios.



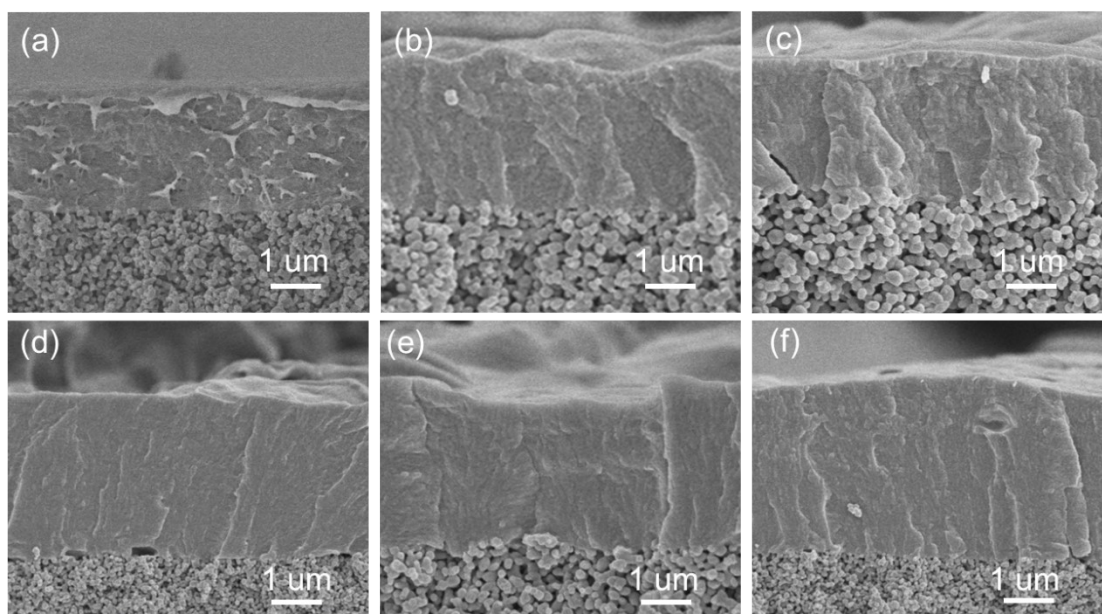
**Figure S5.** SEM images and EDX mapping images of the mixed-metal ZIF-8 series converted from HDS templates with different metal combinations.



**Figure S6.** Powder XRD patterns of the mixed-metal ZIF-8 series converted from HDS templates with different metal combinations.



**Figure S7.** Powder XRD patterns, SEM images and EDX mapping images of the fumarate MOF converted from (Cu, Zn) HDS (Cu:Zn=3:1).



**Figure S8.** Cross-sectional SEM image of the membranes supported on porous alumina substrates: (a) pure Pebax-2533 (thickness =  $2.50 \pm 0.06 \mu\text{m}$ ), (b) ZIF-7(Zn)@Pebax-2533 (thickness =  $3.03 \pm 0.23 \mu\text{m}$ ), (c) ZIF-9(Co)@Pebax-2533 (thickness =  $2.97 \pm 0.16 \mu\text{m}$ ), (d) mmZIF-7 (Co:Zn=3:1)@Pebax-2533 (thickness =  $3.35 \pm 0.10 \mu\text{m}$ ), (e) mmZIF-7 (Co:Zn=1:1)@Pebax-2533 (thickness =  $3.27 \pm 0.25 \mu\text{m}$ ), (f) mmZIF-7 (Co:Zn=1:3)@Pebax-2533 (thickness =  $3.44 \pm 0.15 \mu\text{m}$ ).

- 1 C. Machingauta, PhD Dissertation, Marquette University, 2013.
- 2 M. Tu, C. Wiktor, C. Rösler and R. A. Fischer, *Chem Commun*, 2014, **50**, 13258–13260.
- 3 S. Yan, S. Ouyang, H. Xu, M. Zhao, X. Zhang and J. Ye, *J. Mater. Chem. A*, 2016, **4**, 15126–15133.