

Aqueous Room Temperature Synthesis of Cobalt and Zinc Sodalite Zeolitic Imidizolate Frameworks

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Electronic Supplementary Information

Experimental details: Synthesis

Materials: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Aldrich), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Aldrich), 2-methylimidazole (HMe-Im, 97%, Alfa Aesar), and triethylamine (TEA, 99.5%, Aldrich) were used as received. Deionized water was supplied by an in-house system.

Synthesis of ZIF-67 with a 1:8:8 metal:ligand:TEA ratio: 0.717 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.46 mmol) was dissolved in 50 mL DI water. A second solution of 1.622 g HMe-Im (19.75 mmol) and 2.00 g TEA (19.76 mmol) in 50 mL DI water was stirred until dissolved. The Co solution was added to the stirred HMe-Im/TEA solution, the liquid immediately turned opaque purple, and the suspension was stirred for 10 minutes. The synthesis mixture was separated through centrifugation, the supernatant was decanted, and the solid was re-suspended in DI water. The ZIF remained in water for 12 hours, was separated through centrifugation, and re-suspended in DI water again. After another 12 hours the ZIF suspension was centrifuged and then the solid

was collected and dried in air in a 110 °C oven. Lastly, the sample was dried under vacuum at 150 °C for 1 hour.

1:4:4 and 1:16:16 metal:ligand:TEA ratio samples were synthesized by halving or doubling, respectively, the masses of ligand and TEA. The yield of the 1:4:4 synthesis was 93% with respect to Co, the yield of the 1:8:8 synthesis was 88% with respect to Co, and the yield of the 1:16:16 synthesis was 111% with respect to Co. The greater than stoichiometric yield for the 1:16:16 synthesis may have resulted from incomplete removal of excess HMe-Im from the pores of ZIF-67.

Synthesis of ZIF-8 with a 1:8:8 metal:ligand:TEA ratio: 0.733 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.46 mmol) was dissolved in 50 mL DI water. A second solution of 1.622 g HMe-Im (19.75 mmol) and 2.00 g TEA (19.76 mmol) in 50 mL DI water was stirred until dissolved. The Zn solution was added to the stirred HMe-Im/TEA solution, the liquid immediately turned opaque white, and the suspension was stirred for 10 minutes. The synthesis mixture was separated through centrifugation, the supernatant was decanted, and the solid was re-suspended in DI water. The ZIF remained in water for 12 hours, was separated through centrifugation, and re-suspended in DI water again. After another 12 hours the ZIF suspension was centrifuged and then the solid was collected and dried in air in a 110 °C oven. Lastly, the sample was dried under vacuum at 150 °C for 1 hour.

1:4:4 and 1:16:16 metal:ligand:TEA ratio samples were synthesized by halving or doubling, respectively, the masses of ligand and TEA. The yield of the 1:4:4 synthesis was 68% with respect to zinc, the yield of the 1:8:8 synthesis was 95% with respect to zinc, and the yield of the 1:16:16 synthesis was 101% with respect to zinc.

Experimental details: Analysis

X-ray diffraction (XRD) analyses were conducted on samples in glass capillary tubes using a Philips PW3040/60 X'Pert Pro diffractometer. Sample pore size, surface area, and pore volumes were characterized with N₂ absorption at Micromeritics Analytical Services (Norcross, GA). Data were analyzed using the Brunner-Emmett-Teller (BET) method. Thermogravimetric analysis (TGA) was performed using a TGA Q500 (TA Instruments). Samples were heated at a ramp rate of 10 °C/min to 800 °C in dry air. STEM and SEM images, of samples that were dispersed in isopropanol and deposited on TEM grids, were acquired on a Hitachi S-4800. Elemental analysis of 1:16:16 samples was performed by Columbia Analytical Services (Tucson, AZ).

The 1:16:16 Co:HMe-Im:TEA molar synthesis ratio ZIF-67 sample was 21.86 wt% Co, 46.28 wt% C, 6.36 wt% H, and 22.38 wt% N. This corresponds to a Co:C:H:N molar ratio of 1:10.40:17.15:4.31. Pure Co(Me-Im)₂ will have a Co:C:H:N molar ratio of 1:8:10:4. Thus there is extra C,H,N in the sample in this paper. This is likely extra methyl imidazole ligand in the pores that results in lower surface areas as compared to ideal ZIF-67.

The 1:16:16 Zn:HMe-Im:TEA molar synthesis ratio ZIF-8 sample was 22.10 wt% Zn, 47.35 wt% C, 6.73 wt% H, and 22.53 wt% N. This corresponds to a Zn:C:H:N molar ratio of 1:11.63:19.93:4.76. Pure Zn(Me-Im)₂ will have a Zn:C:H:N molar ratio of 1:8:10:4. Thus there is extra C,H,N in the sample in this paper. This is likely extra methyl imidazole ligand in the pores that results in lower surface areas as compared to ideal ZIF-8.

Supplementary Tables

Table S1 Predicted versus actual XRD peak positions for ZIF-67

h	k	l	d (nm)	Predicted 2 θ (deg)	1:16:16 ZIF-67 2 θ (deg)
0	1	1	1.199	7.37	7.31
0	0	2	0.848	10.43	10.36
1	1	2	0.692	12.79	12.72
0	2	2	0.600	14.77	14.40
0	1	3	0.536	16.53	16.45
2	2	2	0.490	18.12	18.04
1	1	4	0.400	22.24	22.15
2	3	3	0.362	24.62	24.53
2	2	4	0.346	25.73	25.62
1	3	4	0.333	26.80	26.70
0	4	4	0.300	29.80	29.67
3	3	4	0.291	30.74	30.62
2	4	4	0.283	31.65	31.55
2	3	5	0.275	32.55	32.43

Peak positions were predicted from the single crystal structure of ZIF-67 from R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O’Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939. The predicted and actual peak positions show excellent agreement, further reinforcing that the synthesized sample is ZIF-67. Any offset between the predicted and actual positions is likely due to collecting the single crystal structure at 153 K and collecting the data from this work at 300 K.

Table S2 Predicted versus actual XRD peak positions for ZIF-8

h	k	l	d (nm)	Predicted 2 θ (deg)	1:16:16 ZIF-8 2 θ (deg)
0	1	1	1.201	7.36	7.34
0	0	2	0.850	10.41	10.40
1	1	2	0.694	12.76	12.76
0	2	2	0.601	14.75	14.74
0	1	3	0.537	16.50	16.49
2	2	2	0.490	18.09	18.08
1	1	4	0.400	22.20	22.19
2	3	3	0.362	24.57	24.58
2	2	4	0.347	25.69	25.72
1	3	4	0.333	26.75	26.77
0	4	4	0.300	29.74	29.74
3	3	4	0.291	30.68	30.69
2	4	4	0.283	31.59	31.59
2	3	5	0.276	32.48	32.50

Peak positions were predicted from the single crystal structure of ZIF-8 from K. S. Park, Z. Ni, A. P. Cote, J. Y Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O’Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U.S.A.*, 2006, **103**, 10186. The predicted and actual peak positions show excellent agreement, further reinforcing that the synthesized sample is ZIF-8. Very minor offsets between the predicted and actual positions are likely due to collecting the single crystal structure at 258 K and collecting the data from this work at 300 K.

Supplementary Figures

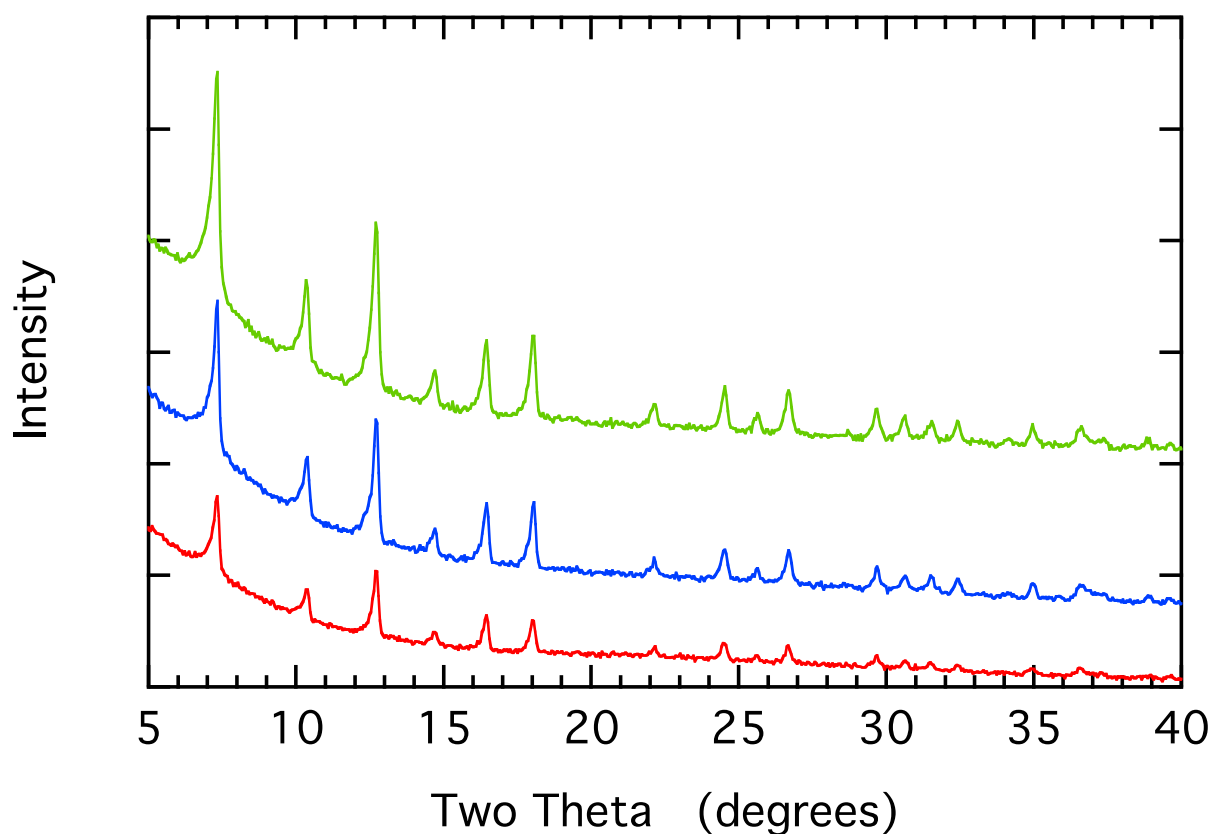


Fig. S1 XRD patterns of ZIF-67 samples with 1:16:16 (top/green), 1:8:8 (middle/blue), and 1:4:4 (bottom/red) metal:ligand:TEA molar ratios. Peak positions match the single crystal structure for ZIF-67 in Table S1. There is a 3x increase in peak intensity and thus crystallinity of samples as the metal:ligand:TEA ratio increases from 1:4:4 to 1:16:16.

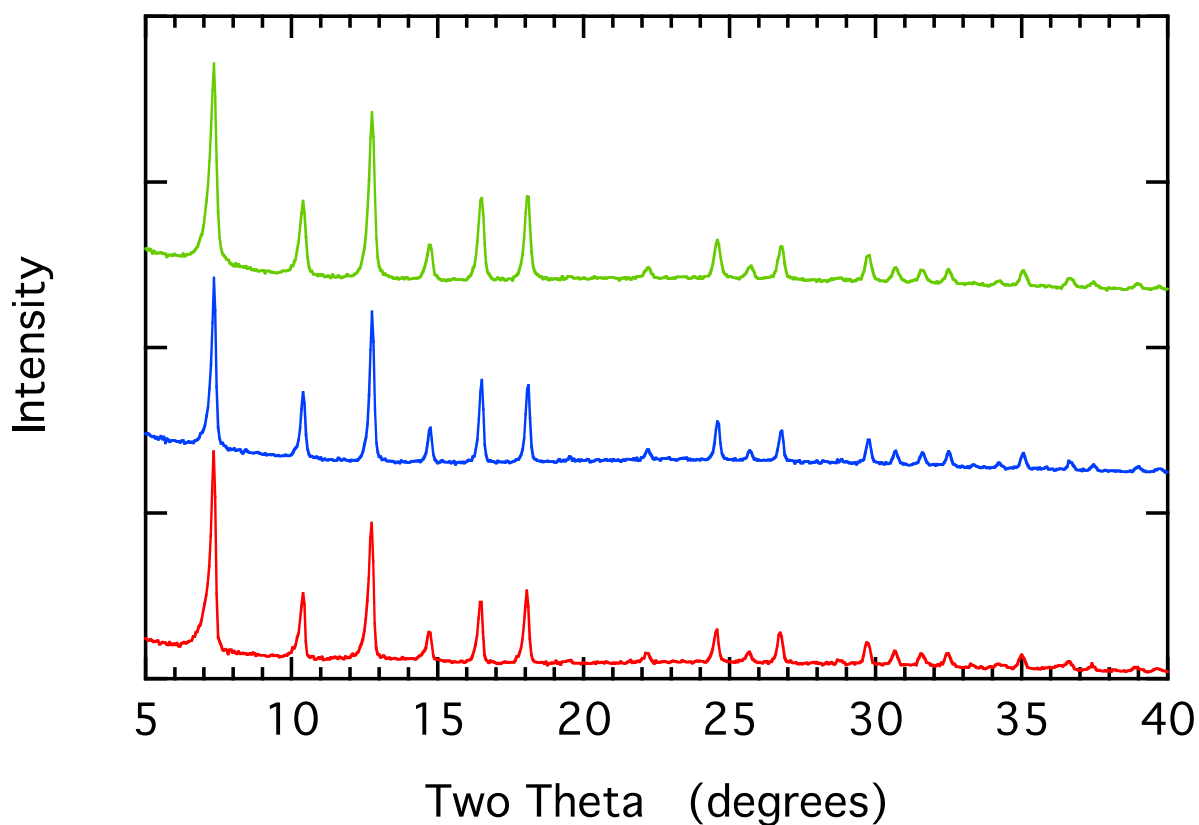


Fig. S2 XRD patterns of ZIF-8 samples with 1:16:16 (top/green), 1:8:8 (middle/blue), and 1:4:4 (bottom/red) metal:ligand:TEA molar ratios. Peak positions match the single crystal structure for ZIF-8 in Table S2. There is a small increase in peak intensity and thus crystallinity of samples as the metal:ligand:TEA ratio increases from 1:4:4 to 1:16:16.

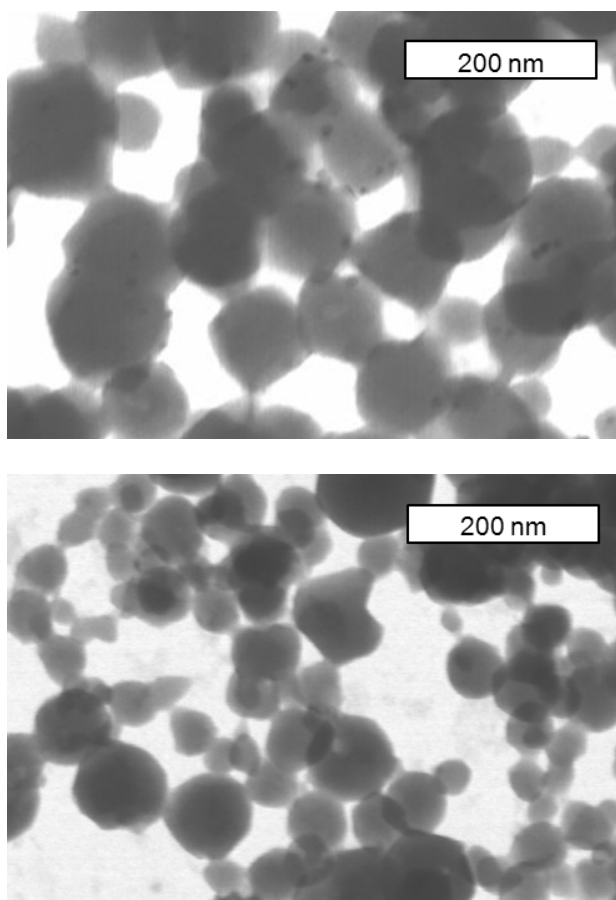


Fig. S3 STEM images of ZIF-67 (top) and ZIF-8 (bottom) nanoparticles. The particles appear distinct in both images. ZIF-67 and ZIF-8 nanoparticles have similar dimensions in both STEM images as well as SEM images (Figure 2).

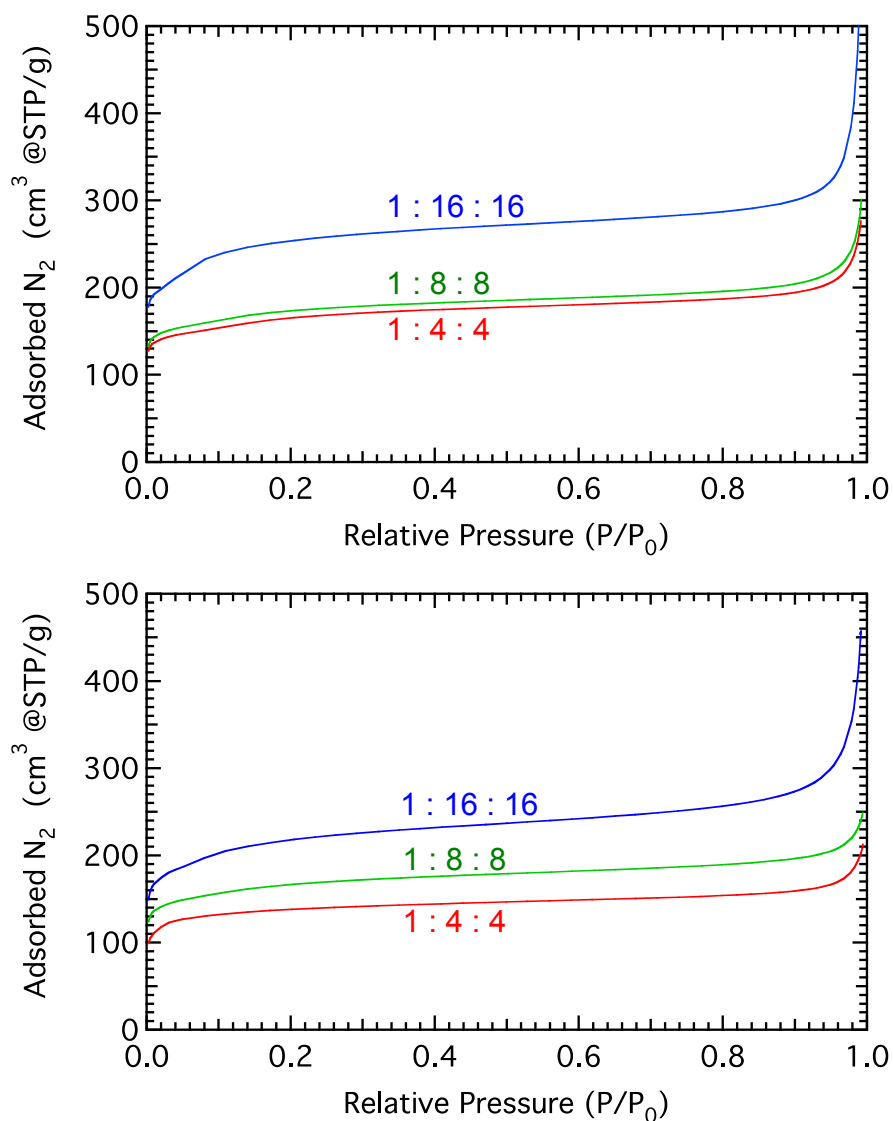


Fig. S4 N₂ adsorption isotherms from ZIF-67 (top) and ZIF-8 (bottom). All isotherms are labeled with the metal:ligand:TEA molar ratios. The isotherms show an initial sharp rise in N₂ adsorption from micropores and a second rise at higher pressure from mesoporosity between packed nanoparticles.

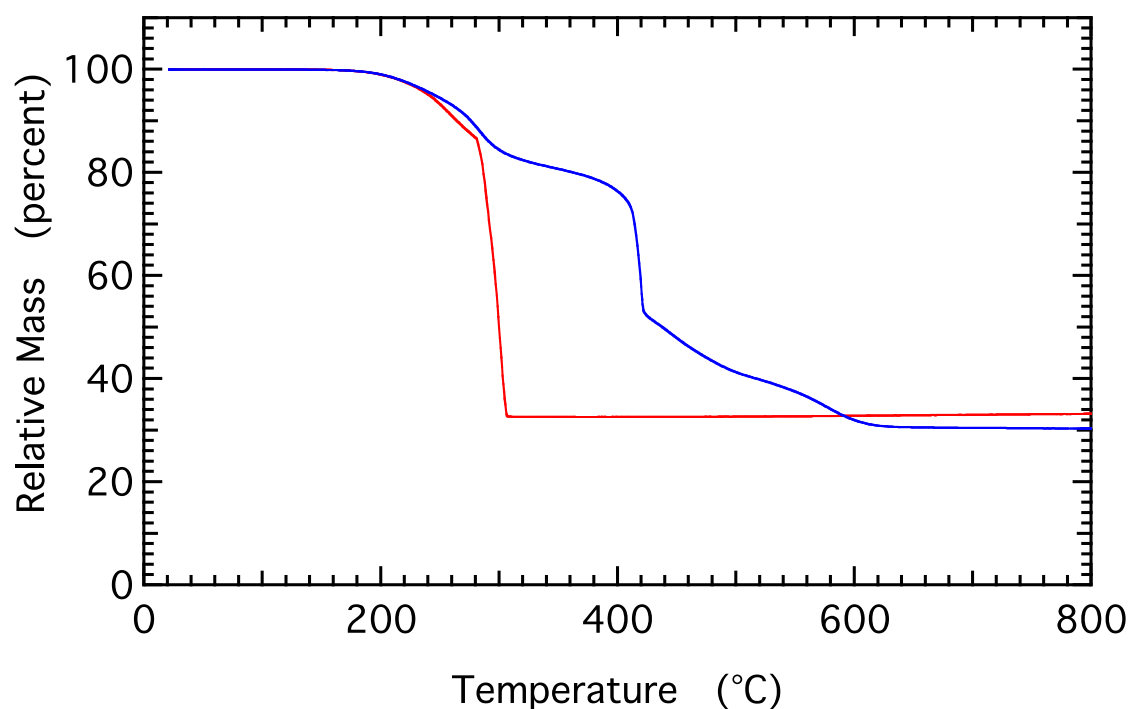


Fig. S5 TGA data on ZIF-67 (red) and ZIF-8 (blue). The ZIF-67 sample begins to lose mass above 200 °C, which probably corresponds to loss of guest molecules, and shows a sharp drop in mass at 300 °C due to structural degradation. The 33% residual mass is less than the predicted 36% residual mass of Co_3O_4 , indicating some residual organic material in the pores. Loss of guest molecules is observed below 350 °C for ZIF-8, while the 37% residual mass resulting from heating from 350 °C to 700 °C agrees with the expected 36% residual mass of ZnO from ZIF-8. Co_3O_4 and ZnO products were verified with XRD.

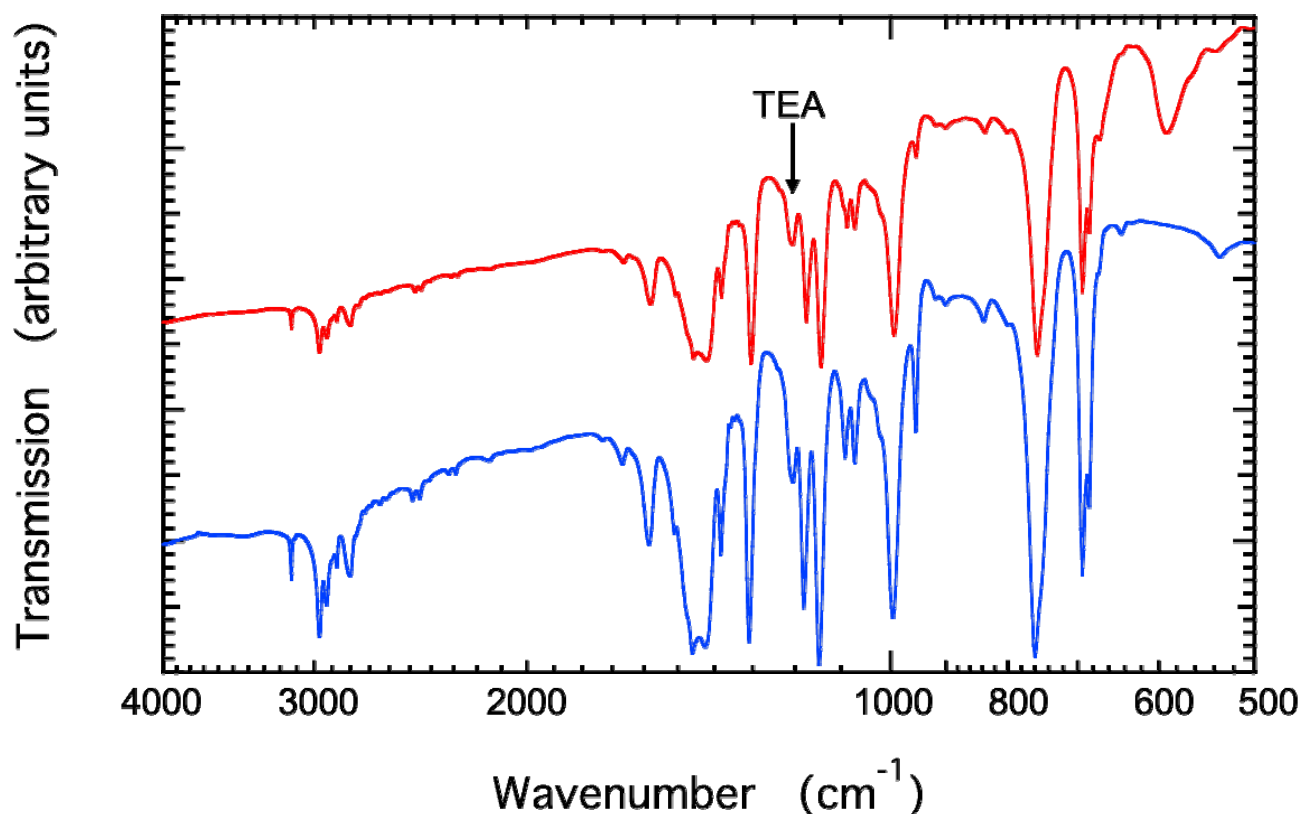


Fig. S6 FTIR transmission spectra of ZIF-67 (red) and ZIF-8 (blue) made with 1:16:16 metal:ligand:TEA molar ratios. The spectra match the known transmission spectrum of 2-methylimidazole from the Aldrich FT-IR Collection Edition II. There is a small amount of triethylamine in both samples indicated by the TEA C-N stretch at 1210 cm^{-1} , which is the strongest adsorbing peak in the TEA spectrum, where there is no Me-Im or HMe-Im adsorption (indicated on graph). TEA overlaps with most other Me-Im, peaks due to similar chemical bonds. The adsorptions from 3200 cm^{-1} to 2700 cm^{-1} are indicative of both protonated Me-Im (HMe-Im) and TEA. HMe-Im and TEA in the pores of these samples result in reduced surface areas and pore volumes. Note that the spectra are offset and the x-axis is plotted on a logarithmic scale for clarity.

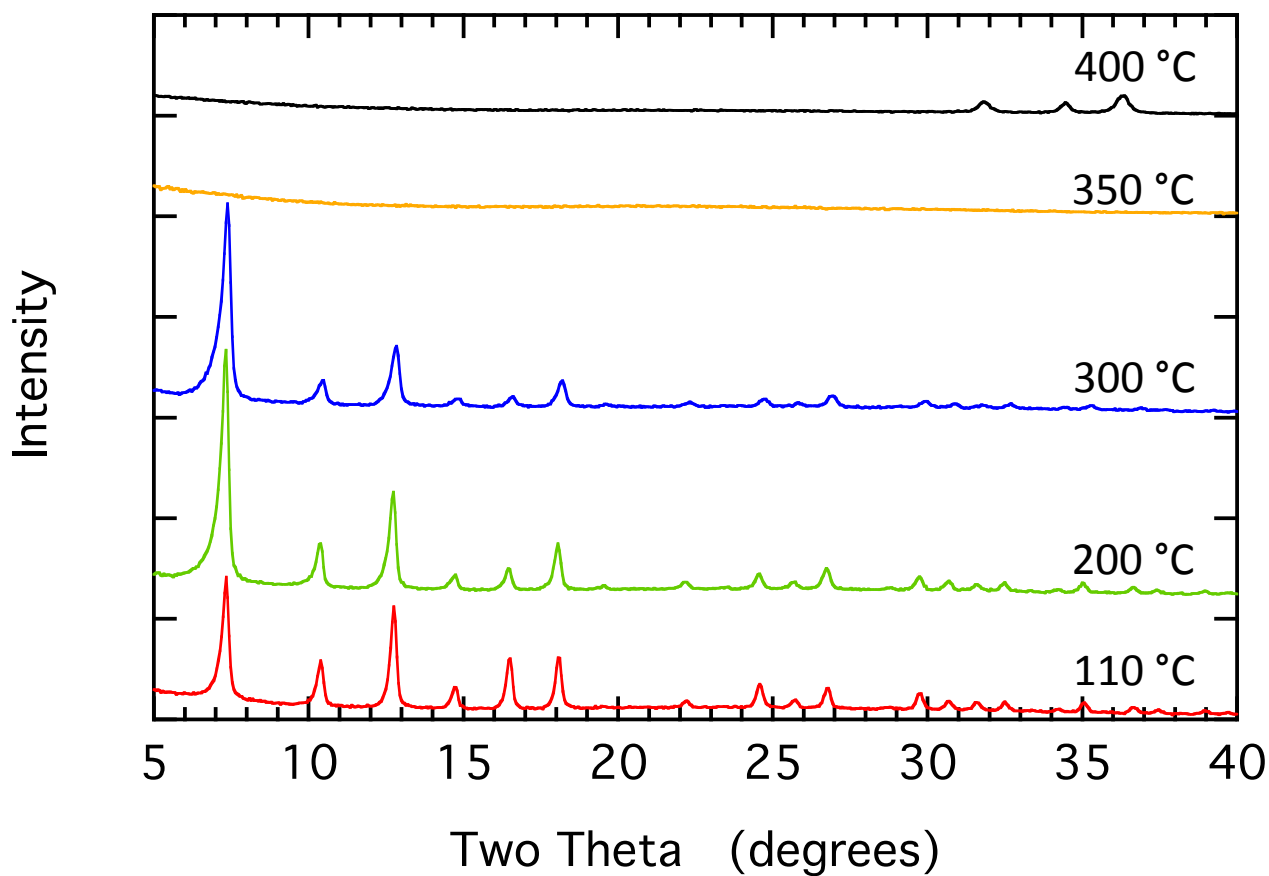


Fig. S7 XRD patterns of 1:16:16 metal:ligand:TEA molar ratio ZIF-8 samples heated in air. The samples were heated for one hour at the temperatures labeled on the XRD patterns. XRD patterns show no change up to 300 °C, a loss of structure at 350 °C, and formation of ZnO at 400 °C.