Supplementary Information

Crystal Size-Dependent Framework Flexibility of a Prototypical Metal Organic Framework is Related to Metal Content: Zeolitic Imidazolate Framework-7

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1. Thermogravimetric analysis (TGA)

Data were collected on a TA Instruments SDT-Q600 using alumina pans (110 μL). Heating and cooling rates of 10 °C/min were used, and experiments were conducted under a flow of N_2 gas. All data analysis was performed using the TA Instruments Universal Analysis software package. TGA results of ZIF-7 solid (Figure S1) indicate that there is an initial weight reduction of approximately 20 % (20 wt%) as a result of temperature increase from ~30 °C to 300 °C, which can be attributed to the desorption of guest molecules (Dimethylformamide (DMF) and H_2O) from the framework, followed by no apparent weight change between ~300 °C and 500 °C, which is indicative of higher thermal stability (up to ca 500 °C) of the solid. At temperatures above ~500 °C, thermal degradation of the framework is observed. The TGA results are consistent with those previously published for ZIF-7 crystals.[1, 2]

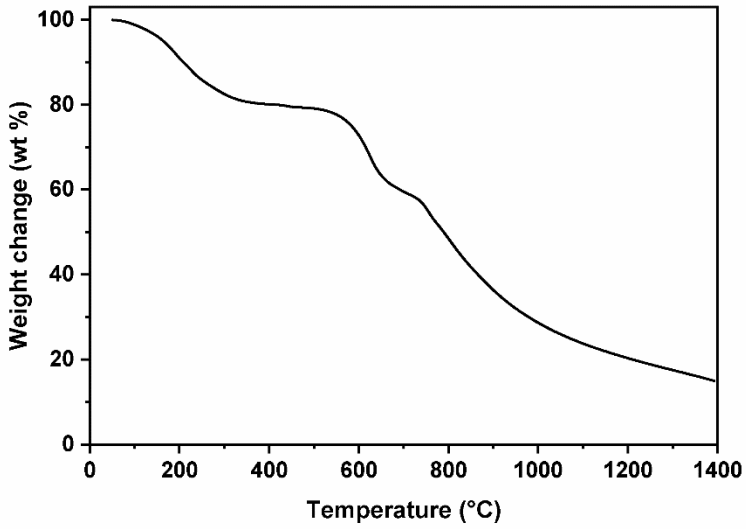

Figure S1. TGA results for ZIF-7 in N_2 atmosphere.

2. ^{1}H nuclear magnetic resonance (NMR) spectral data

For these measurements, 6 mg of ZIF-7 solid was dissolved in 0.6 mL of deuterated acetic acid-d4 in an NMR vial, yielding 10 mg/mL solution. Solution ^{1}H NMR spectrum of dissolved ZIF-7 was collected at ambient temperature using a Bruker AVANCE NEO 400 MHz NMR spectrometer (Figure S2). All NMR data were processed with Bruker TopSpin NMR Software and Origin Lab software. Protons attributed to benzimidazole were observed at (1) 9.13 ppm, (2) 7.84 ppm, and (3) 7.48 ppm. Protons attributed to dimethylformamide (DMF) were observed at (4) 8.11 ppm, (5) 3.06 ppm, and (6) 2.95 ppm. The presence of DMF likely due to DMF molecules trapped inside ZIF-7 pores during the synthesis. The NMR spectrum is in good agreement with previous reports on dissolved ZIF-7 samples, confirming the formation of ZIF-7 solid in the present work.[3]

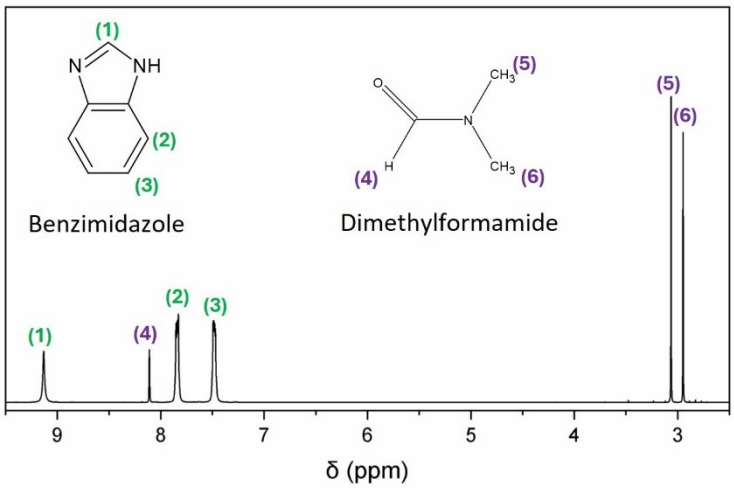

Figure S2. Solution ^{1}H-NMR spectrum of ZIF-7 solution in deuterated acetic acid-d4.

3. References

1. J. Kim and D. Lee, *Journal of Materials Chemistry A*, 2016, **4**, 5205-5215.
2. W. Cai, T. Lee, M. Lee, W. Cho, D. Y. Han, N. Choi, A. C. Yip and J. Choi, *J Am Chem Soc*, 2014, **136**, 7961-7971.
3. L. Gong, Z. Cai, Q. Wu, L. Liu, C. Wang, L. Shan, X. Meng, S. Luo, Z. Liu and S. Zhang, *Journal of Materials Chemistry A*, 2022, **10**, 24975-24984.