

Electronic Supplementary Information

Boron-imidazolate coordination networks with 3d transition metals for enhanced CO₂ adsorption capability

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Supporting Figures

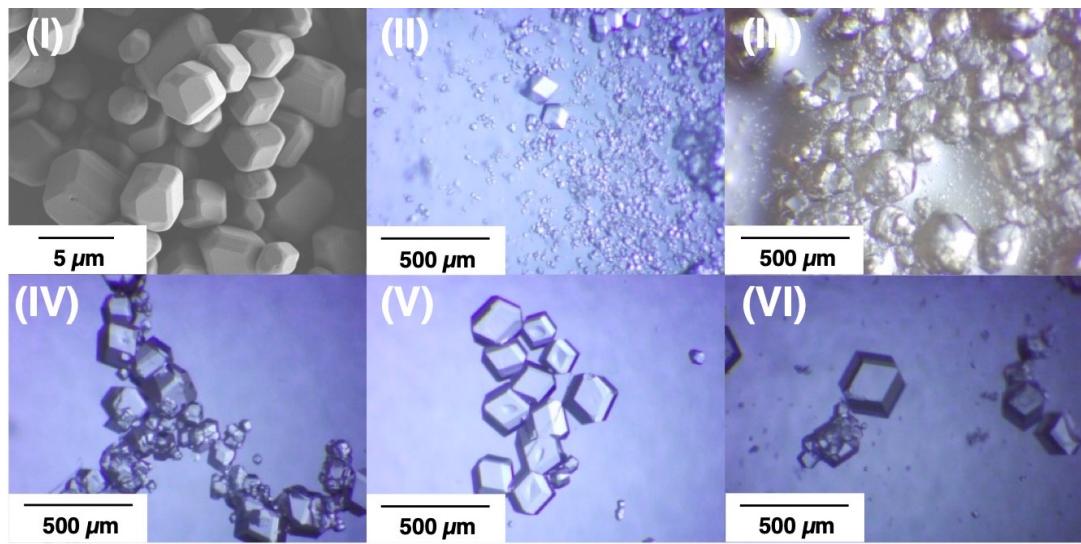


Figure S1. SEM and optical microscope images of the obtained BIF-3-Cu crystals prepared by (I): previously reported BIF-3-Cu synthesis method in Ref. 4, (II): using 2-amino-1-butanol as a reaction solvent at 100 °C for 4 days, (III): using CuCl as a metal salt, (IV): heating for 2 days, (V): heating 24 hours and (VI): heating 24 hours with adding NaI.

Table S1. Crystallographic data and structure refinement details of BIF-3-Cu

	Previous study ^{S1}	This study
Formula	C ₁₆ H ₂₀ BCuN ₈	C ₁₆ H ₂₀ BCuN ₈
Formula weight	398.75	398.75
<i>T</i> (K)	293	93.15
Crystal system	cubic	cubic
Space group	P-43n	P-43n
<i>a</i> (Å)	16.0184(2)	15.9474(4)
<i>b</i> (Å)	16.0184(2)	15.9474(4)
<i>c</i> (Å)	16.0184(2)	15.9474(4)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
<i>V</i> (Å ³)	4110.15	4055.7(3)
<i>Z</i>	6	6
<i>D</i> _{cal} (g cm ⁻³)	0.967	0.980
μ (mm ⁻¹)	0.809	0.820
<i>F</i> (000)	1236	1236.0
crystal size (mm)	N/A	0.156 × 0.111 × 0.072
2 <i>θ</i> range (deg)	3.60–50.08	5.108–52.718
reflns collected	14833	5449
indep reflns/ <i>R</i> _{int}	1222 / 0.1167	1329 / 0.0317
GOF on <i>F</i> ²	1.159	1.151
<i>R</i> ₁ , w <i>R</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.0605, 0.1537	0.0426, 0.1289
<i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.1001, 0.1755	0.0449, 0.1316

Table S2. Comparison of specific surface area of BIF-3-Cu

	Specific surface area (m^2/g)	Pore volume (cm^3/g)
This study	1000	0.60
Solvothermal synthesis ^{S1}	182.3	N/A
Mechanochemical synthesis ^{S2}	935	N/A

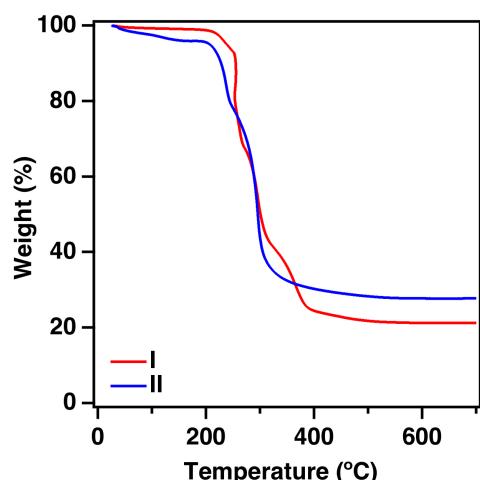


Figure S2. TG curves of the prepared BIF-3-Cu crystals, (I): using 2-amino-1-butanol as the reaction solvent at 100 °C for 4 days and (II): with triethylamine addition and at 50/50 (= MeOH/MeCN, v/v).

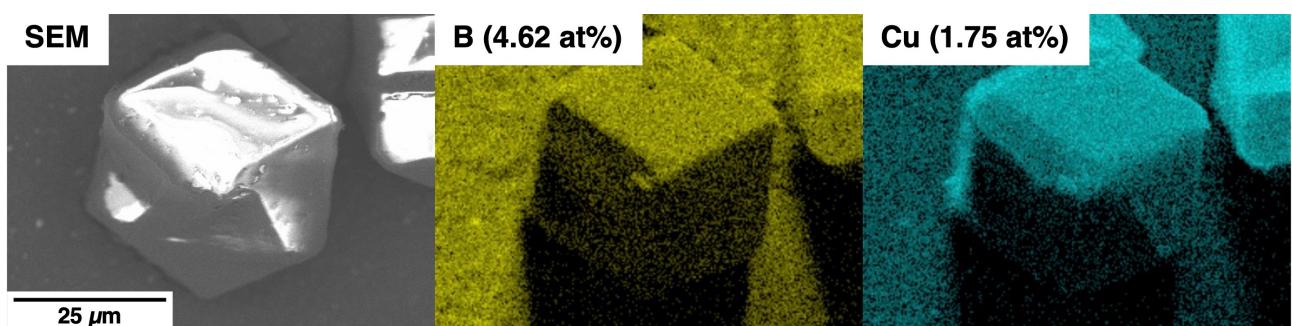


Figure S3. SEM/EDX mapping images of BIF-3-Cu.



Figure S4. Photograph of the obtained BIF-3-Cu.

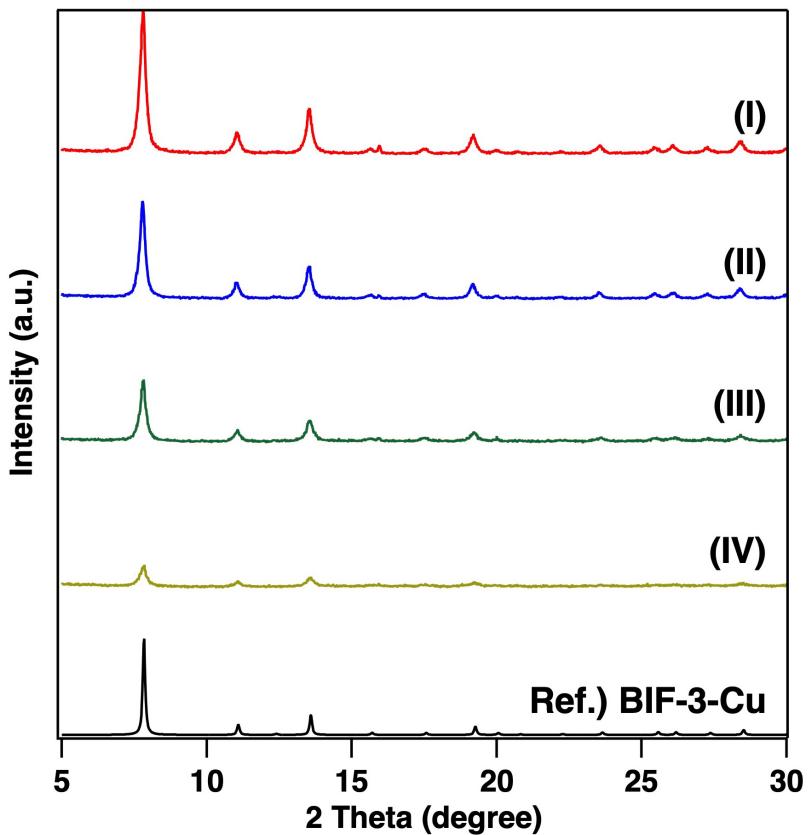


Figure S5. PXRD patterns of BIF-3-Cu crystals before and after soaking in the acetonitrile solution of tetracyanoethylene (TCNE) for 24 hours. (I): as-prepared sample (before soaking) and after soaking in (II): 5 mmol L⁻¹, (III): 25 mmol L⁻¹, (VI): 50 mmol L⁻¹ TCNE solution.

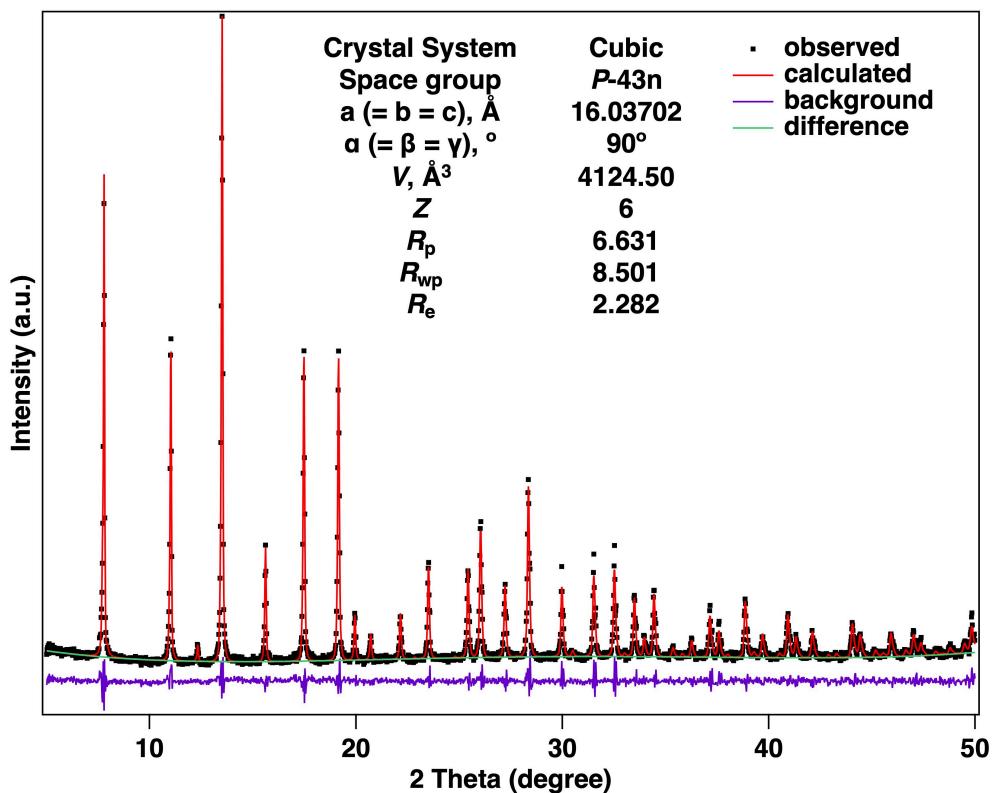


Figure S6. Rietveld refinement of BIF-3-Zn.

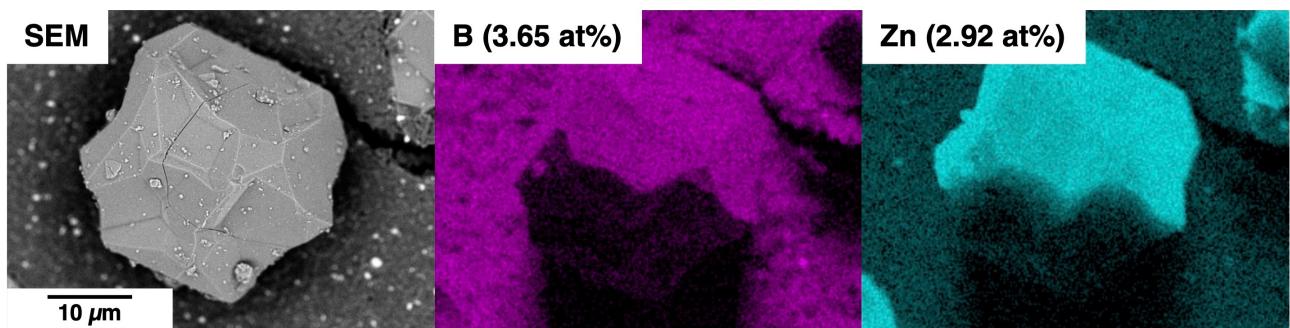


Figure S7. SEM/EDX mapping images of BIF-3-Zn.

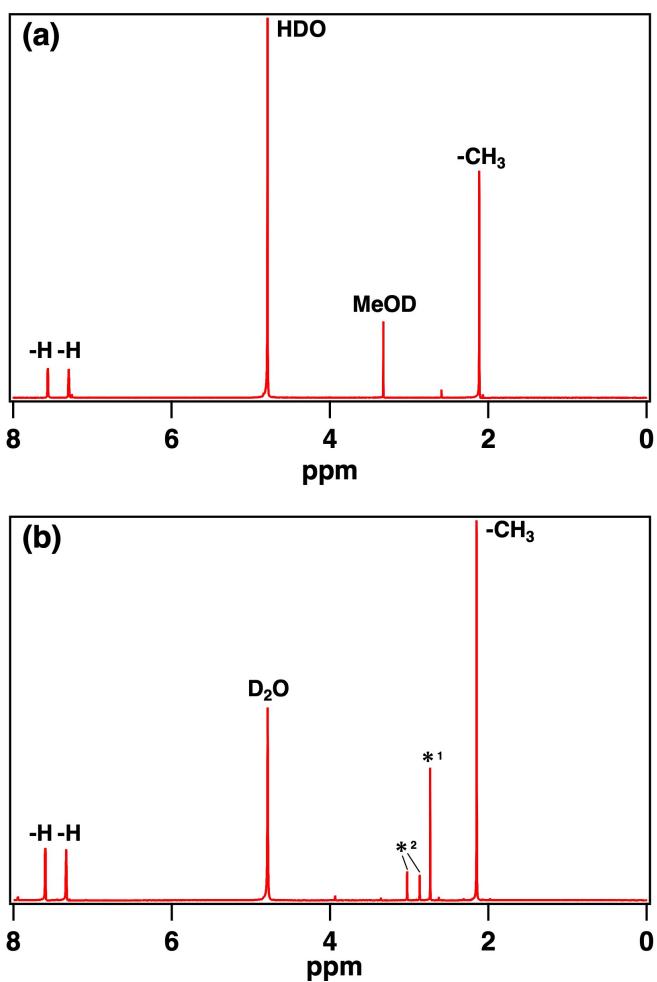


Figure S8. ^1H -NMR spectra of (a) $\text{H}[\text{B}(2\text{-MIm})_4]$ and (b) recovered ligand from prepared BIF-3-Zn crystal decomposed by $d\text{-HCl D}_2\text{O}$ solution. *1 indicates an internal standard (DMSO) and *2 indicates the reaction solvent.

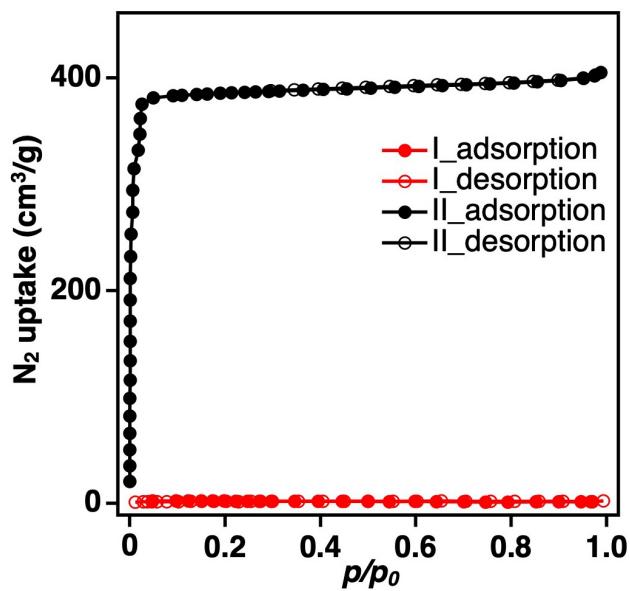


Figure S9. N_2 adsorption measurements (77 K) of (I): BIF-3-Zn and (II): ZIF-8.

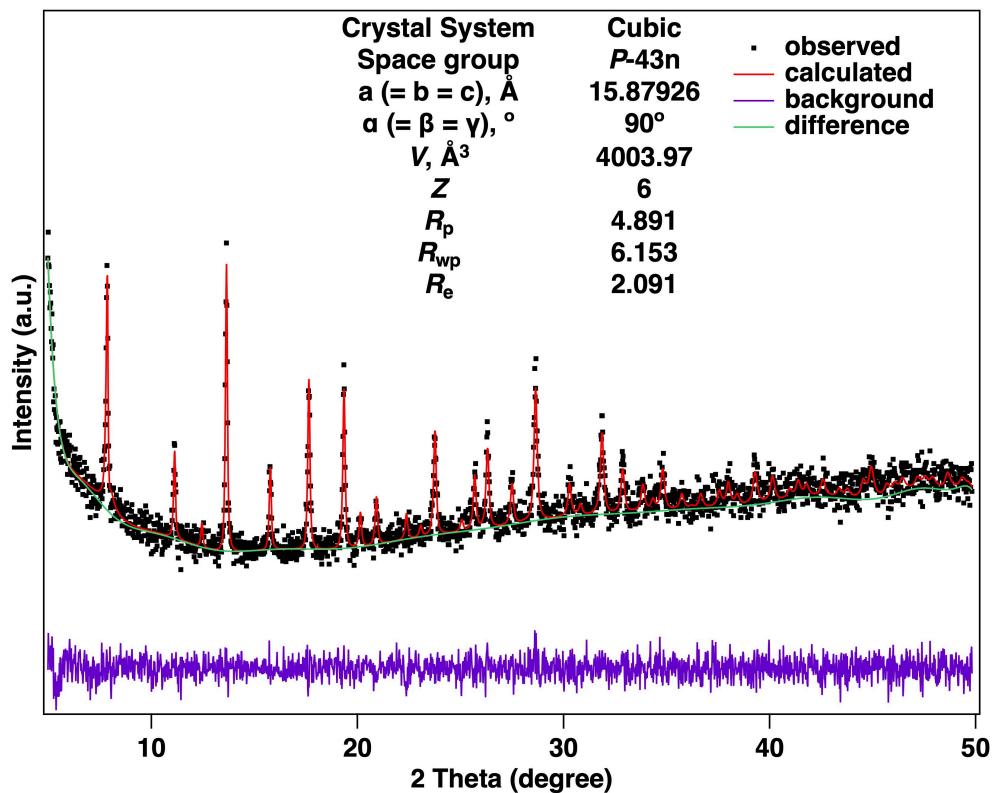


Figure S10. Rietveld refinement of BIF-3-Co.

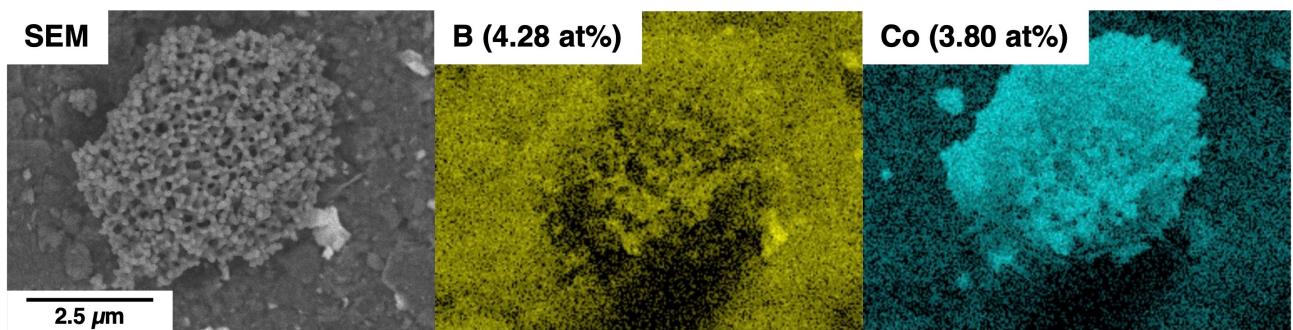


Figure S11. SEM/EDX mapping images of BIF-3-Co.

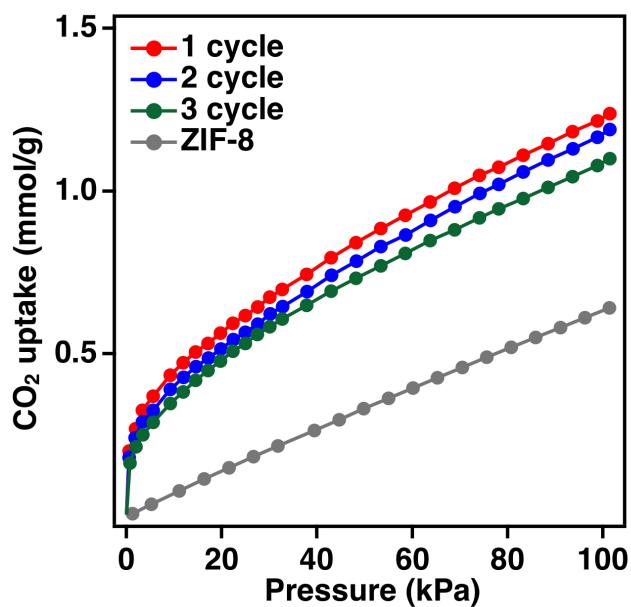


Figure S12. CO₂ adsorption cycle test of BIF-3-Zn (red: 1st cycle, blue: 2nd cycle, green: 3rd cycle).

Supporting Reference

- S1. J. Zhang, T. Wu, C. Zhou, S. Chen, P. Feng and X. Bu, *Angew. Chem. Int. Ed.*, 2009, **48**, 2542–2545.
- S2. C. B. Lennox, J. L. Do, M. Arhangelskis, H. M. Titi, O. K. Farha and T. Friscic, *Chem. Sci.*, 2021, **12**, 14499-14506.