

Tuning of Gate Adsorption : Modification of a Flexible Metal-Organic Framework by Secondary Organic Ligands

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Materials

All chemicals were used as received without further purification. The ligand, 4,4'-bipyridine (bpy) was purchased from Tokyo Chemical Industry Co., Ltd and picoline and 4-tertiary-butylpyridine were purchased from Wako Pure Chemical Industries, Ltd. Metal salt $\text{Cu}(\text{BF}_4)_2 \cdot 6(\text{H}_2\text{O})$ was purchased from Wako Pure Chemical Industries, Ltd. Ethanol solvent was purchased from Kanto Chemical Co., Inc. Milli-Q filtered water with resistivity $> 18 \text{ M}\Omega \cdot \text{cm}$ was used throughout the experiments.

Preparation of samples

CuMOF was prepared according to the reported procedure with slight modification.^[1,2] Ethanol solution of bpy (1.0 mmol in 12 ml) was dropped into aqueous solution of $\text{Cu}(\text{BF}_4)_2$ (0.5 mmol, 12 ml) under stirring at 343 K and the mixture was reacted for 2 hours at 343 K. After the reaction, the reaction solution was cooled to room temperature and stood for one day for aging. The blue powder crystals were obtained after filtration, washing with distilled water and ethanol, and drying in air. Modified MOFs (CuMOF-PI and CuMOF-TBP) were synthesized in a similar manner to CuMOF. Ethanol solution (12 ml) of bpy (1.0 mmol) and the secondary organic ligands (picoline : PI or 4-tertiary-butylpyridine : TBP, x mmol) was dropped into aqueous solution of $\text{Cu}(\text{BF}_4)_2$ (0.5 mmol, 12 ml) under stirring at 343 K and the mixture was reacted for 2 hours at 343 K. The molar ratio of the mixture is Cu : bpy : secondary ligand = 1 : 2 : x in the mixture, where The value x is 0.15 (standard) or 0.25. After the reaction, the reaction solution was cooled to room temperature and stood for a few days for aging. The blue powder crystals were obtained after filtration, washing with distilled water and ethanol, and drying in air.

Extraction of organic ligands for NMR experiment

Organic ligands bpy, PI and TBP were extracted by the following procedure. The modified CuMOFs were dissolved in DMSO and concentrated HCl solution (36wt%) was added to decompose the MOF completely and Cu ions were removed as a sediment of Cu(OH)₂ with controlling pH by NaOH solution. Extraction of the organic ligands into diethyl ether was repeated three times and final residual was dissolved in DMSO-*d*₆ which was used for ¹H-NMR measurements.

Physical Measurements

CHN elemental analysis was carried out using a Perkin-Elmer Series II CHNS/O analyzer 2400. Fourier transform infrared (FT-IR) of the MOFs was recorded on a JASCO FT-IR 4200 type A over the range 4000-600 cm⁻¹ by 1024 accumulations at a resolution of 2 cm⁻¹. Thermogravimetric analysis (TGA) was carried out using a Thermo Plus 2 (Rigaku) under a nitrogen atmosphere (flow rate of 120 mL/min.) from a room temperature to 773 K with a heating rate of 10 K/min. ¹H-NMR spectra were recorded on JEOL JNM EX-400 with an operating frequency of 400MHz. Powder X-ray diffraction (PXRD) patterns except the synchrotron data and the data related to DMB removal were measured on a RINT-2100S (Rigaku) using monochromated Cu-K α radiation. The XRD patterns on the materials from which DMB was removed by vacuum heating treatment (383 K, 2h) were collected on a Rad-C (Rigaku) using monochromated Cu-K α radiation. Synchrotron X-ray diffraction data was obtained on the large Debye-Scherrer camera with an imaging plate as a detector at beamline BL02B2 SPring-8.^[3] The wavelength of the incident X-ray is 0.99749 Å for thermal expansion experiment of CuMOF and 0.79819 Å for other experiments. Before the data collections, the powder sample was put in a glass capillary with the diameter of 0.5 mm

and outgassed under vacuum at 383 K for more than 2 h.

Gas adsorption measurements

The CO₂ and 2,2-dimethylbutane adsorption measurements were performed at 273 K by using automatic volumetric adsorption apparatuses (BELSORP18; BEL Japan inc.). A known weight (*ca.* 50 mg) of samples was placed in the sample cell and all the samples were degassed at 383 K under vacuum ($P < 10^{-1}$ Pa) for 2 h before gas adsorption measurements.

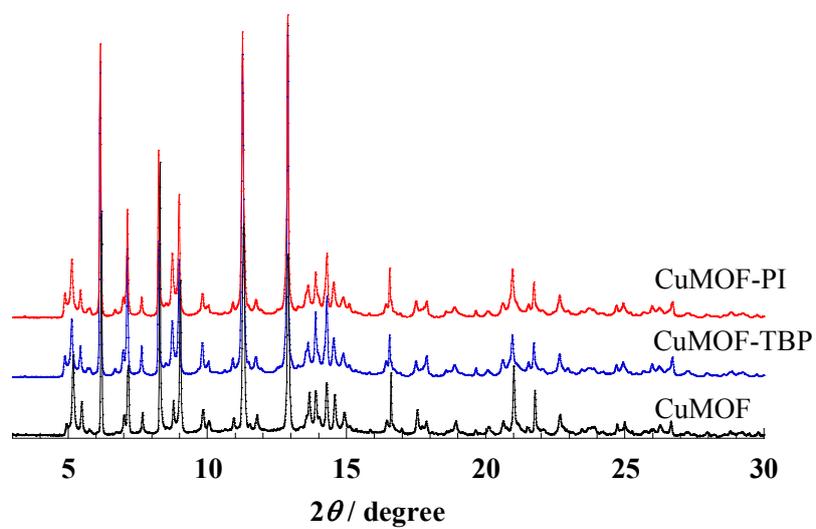
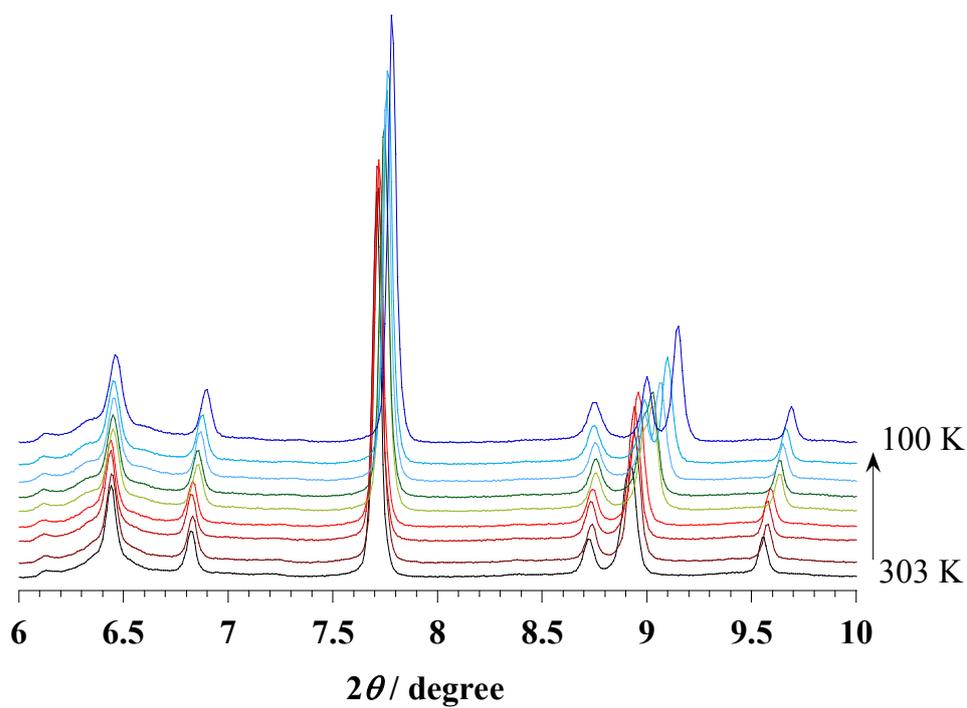


Figure S1. Synchrotron XRD patterns of CuMOF, CuMOF-TBP, and CuMOF-PI (from bottom to top). The wavelength is 0.79819 Å.

(a)



(b)

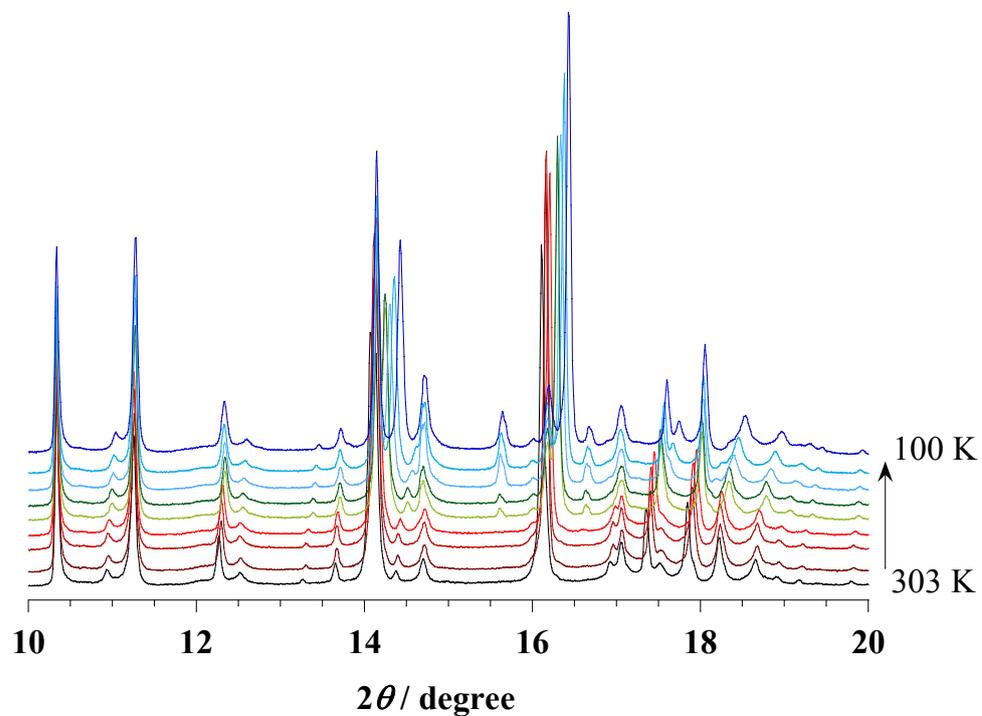


Figure S2. Temperature dependence of XRD patterns of CuMOF at 100–303 K in the range of (a) 6–10 degree and (b) 10–20 degree. The wavelength is 0.99749 Å.

Table S1. Results of CHN elemental analysis on CuMOF-PI and CuMOF-TBP.

	C / wt%	H / wt%	N / wt%
CuMOF (calcd.)	41.0	3.30	9.55
CuMOF-PI	40.9	3.2	9.5
CuMOF-TBP	40.8	3.3	9.5

The weight percentages on CuMOF are the reported values by Blake *et al.*^[4]

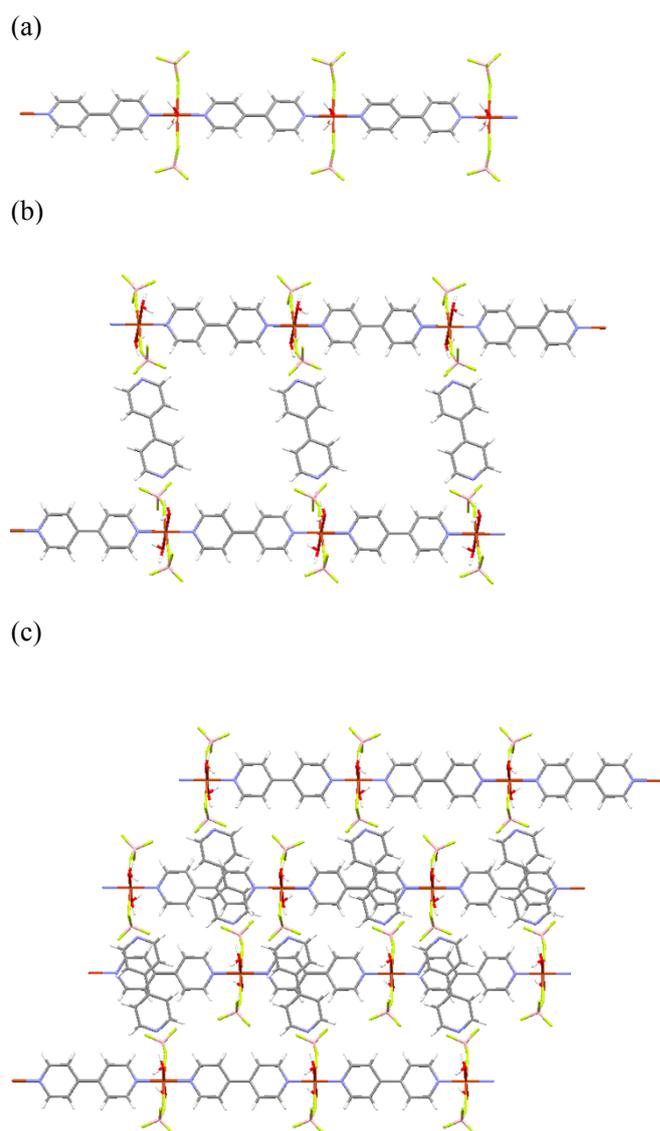


Figure S3. Schematic representations of CuMOF. (a) 1D chain structure, (b) quasi-2D structure via hydrogen bondings, and (c) 3D accumulation structure.

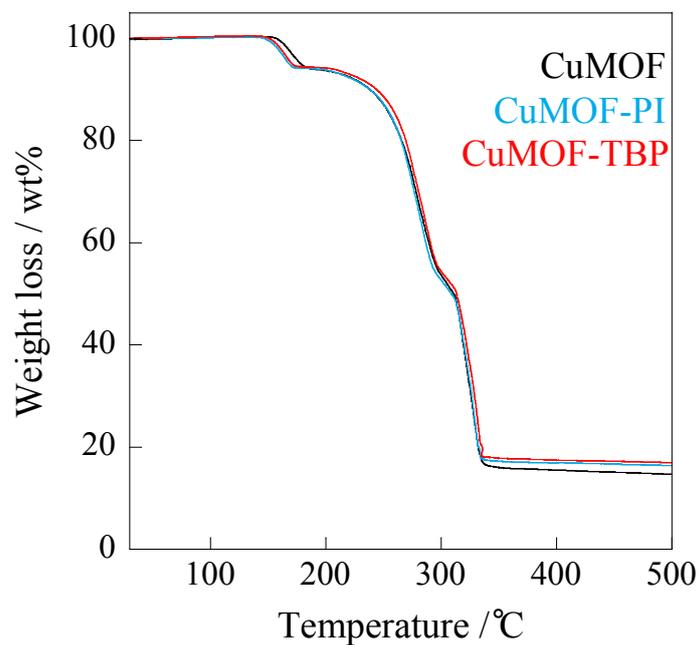


Figure S4. TG curve of CuMOF, CuMOF-PI, and CuMOF-TBP in the range of r.t. to 500 °C under N₂ flow (120 ml/min).

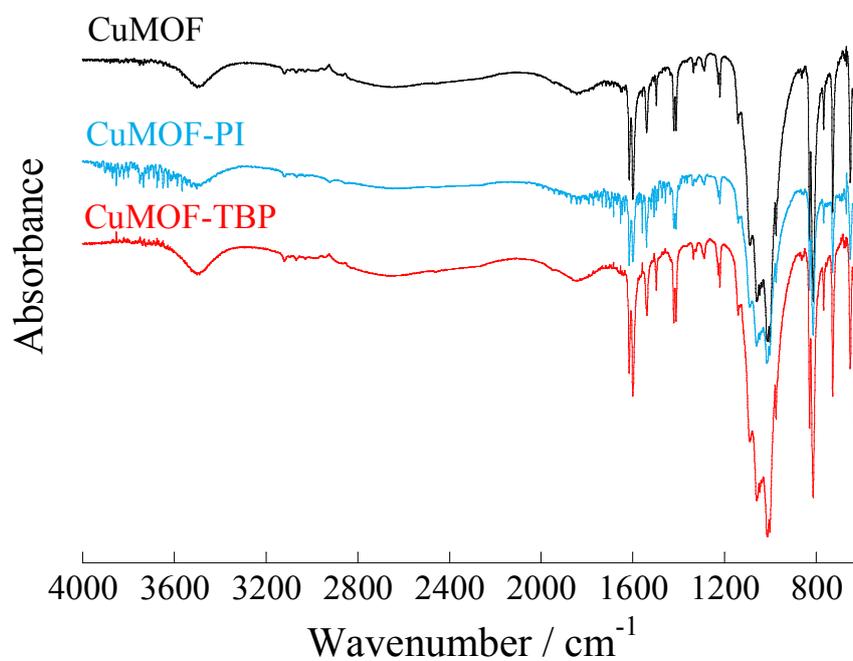
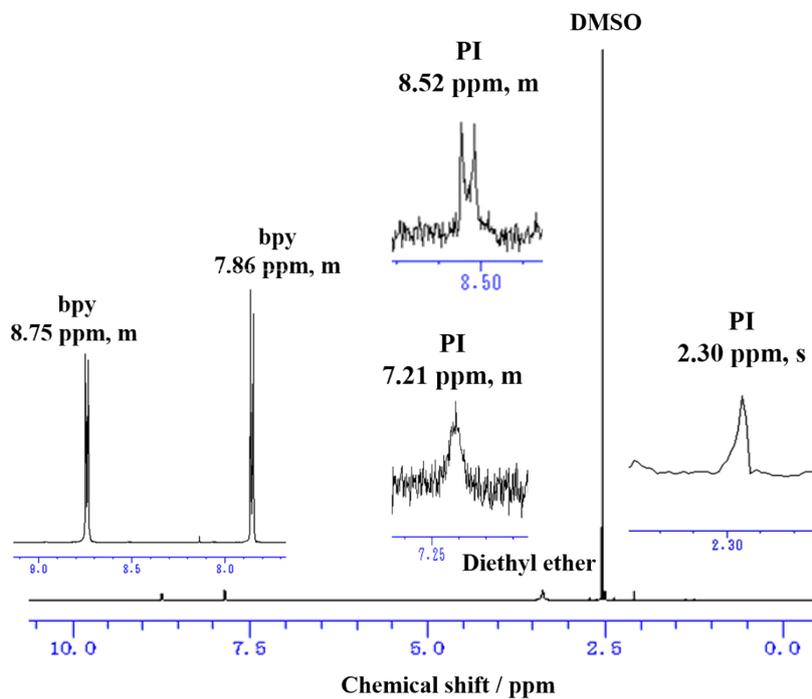


Figure S5. IR spectra of CuMOF, CuMOF-PI, and CuMOF-TBP in the range of 600–4000 cm⁻¹.

(a)



(b)

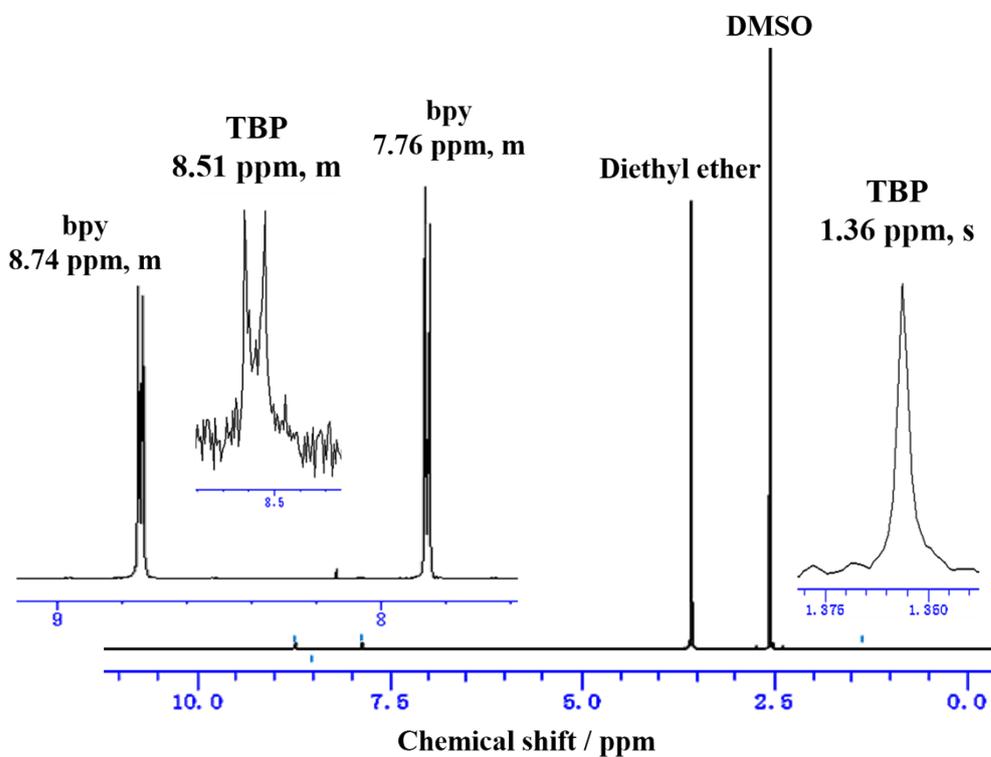
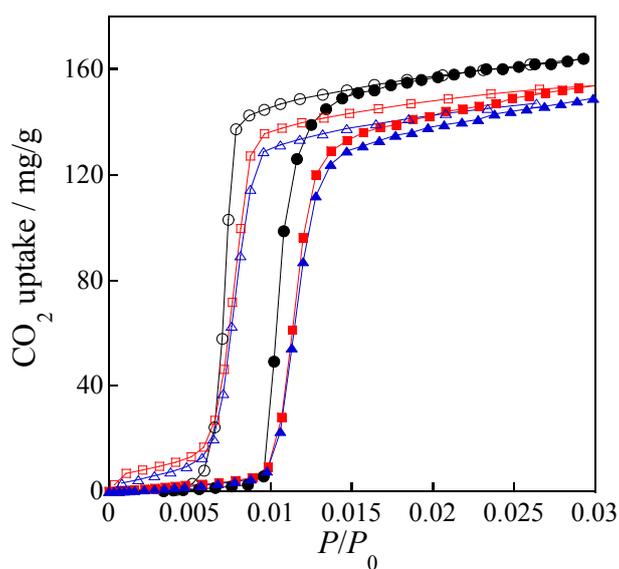


Figure S6. ¹H-NMR spectra of organic molecules extracted from (a) CuMOF-PI and (b) CuMOF-TBP

Table S2. NMR results of CuMOF-PI and CuMOF-TBP

	Assignment	Mult	Chemical shift / ppm
CuMOF-PI	PI (-CH ₃)	s	2.3
	PI (α -H)	m	8.5
	PI(β -H)	m	7.2
	bpy (α -H)	m	8.8
	bpy (β -H)	m	7.9
CuMOF-TBP	TBP (-C(CH ₃) ₃)	s	2.3
	TBP (α -H)	m	8.5
	bpy (α -H)	m	8.7
	bpy (β -H)	m	7.8

**Figure S7.** Carbon dioxide adsorption isotherms at 273 K on CuMOF (black), CuMOF-PI (red), and CuMOF-TBP (blue). Open and filled symbol represent adsorption and desorption, respectively.

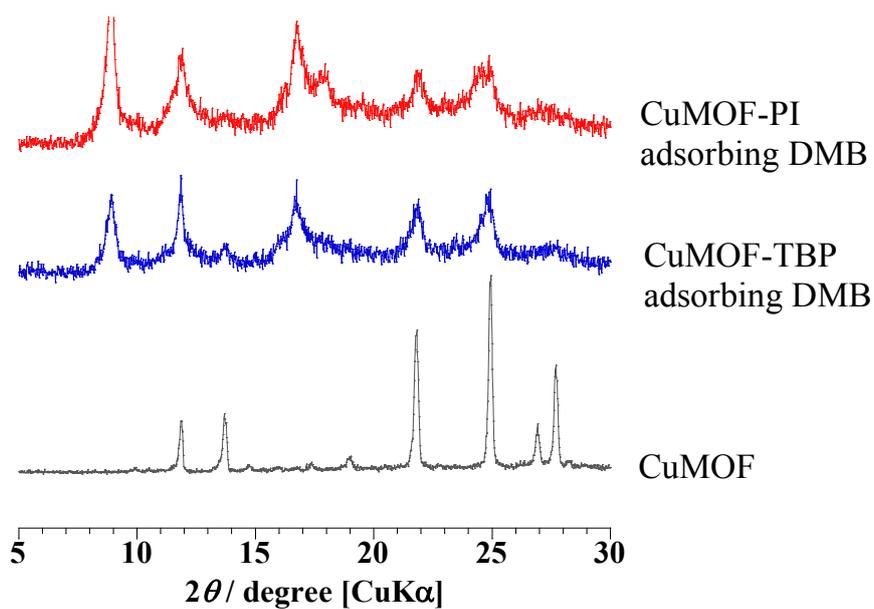


Figure S8. XRD patterns of CuMOF, CuMOF-TBP adsorbing DMB, and CuMOF-PI adsorbing DMB (from bottom to top).

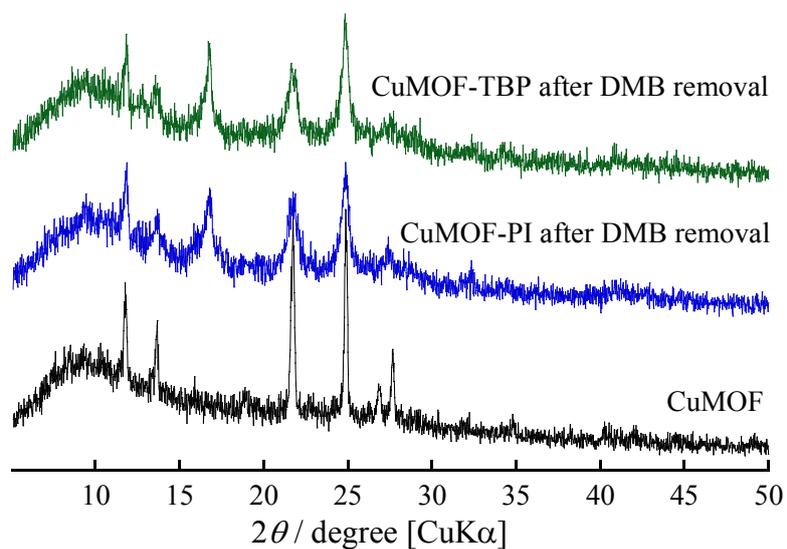


Figure S9. XRD patterns of CuMOF, CuMOF-PI after DMB removal, and CuMOF-TBP after DMB removal.

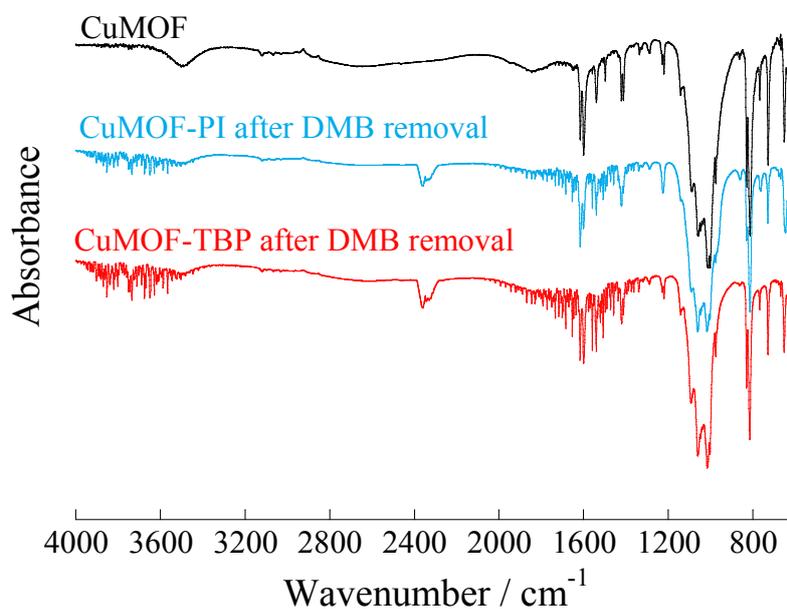


Figure S10. FT-IR spectra of CuMOF, CuMOF-PI after removal of DMB removal, and CuMOF-TBP after DMB removal.

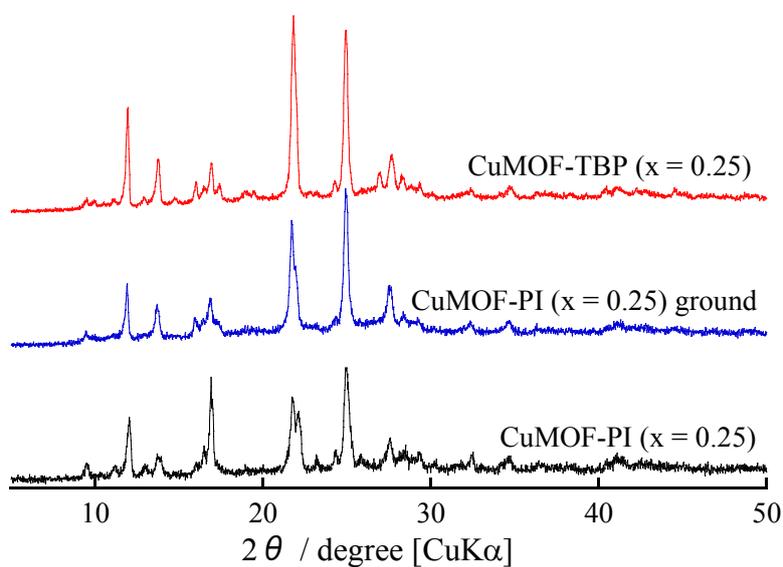


Figure S11. XRD patterns of CuMOF-PI (x = 0.25), CuMOF-PI (x = 0.25) ground, and CuMOF-TBP (x = 0.25).

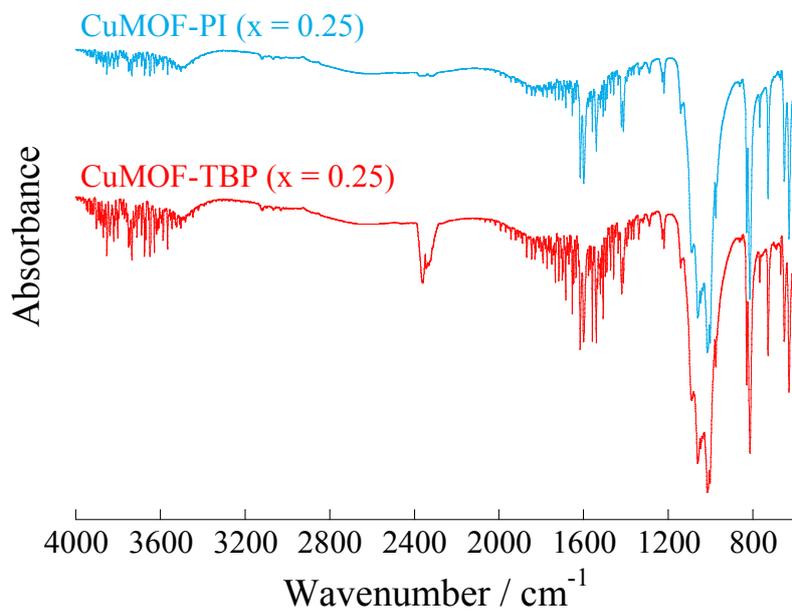


Figure S12. FT-IR spectra of CuMOF-PI (x = 0.25) and CuMOF-TBP (x = 0.25).

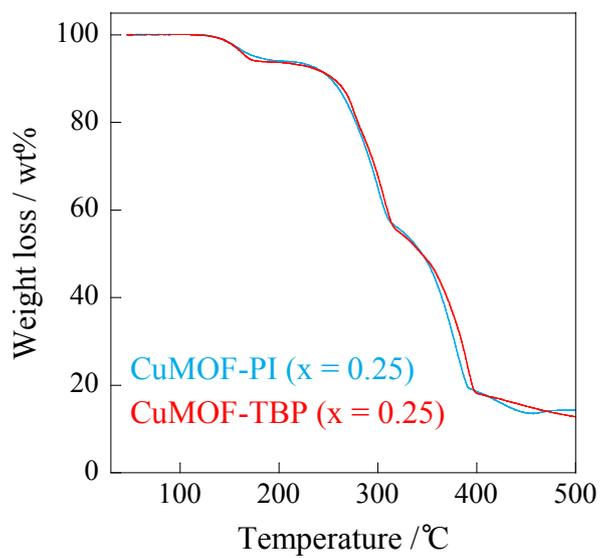


Figure S13. TG curves of CuMOF-PI (x = 0.25) and CuMOF-TBP (x = 0.25).

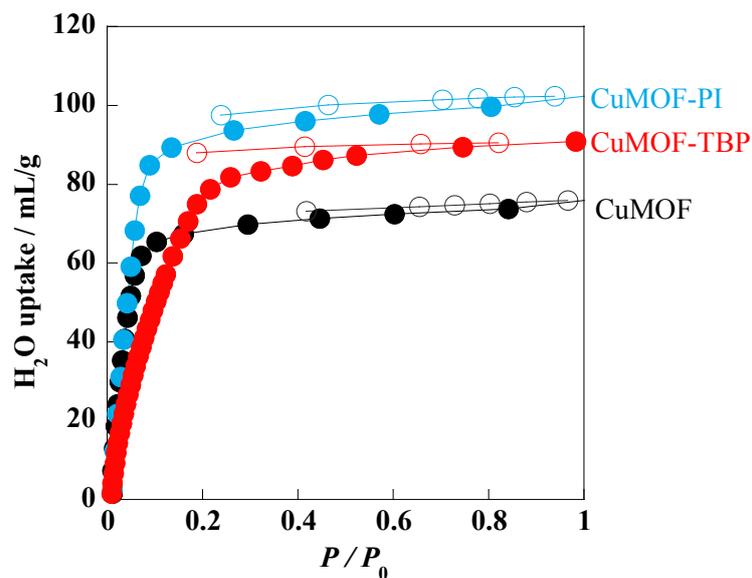


Figure S14. Water adsorption isotherms on CuMOF, CuMOF-TBP, and CuMOF-PI at 303 K.

References

- [1] A. J. Blake, S. J. Hill, P. Hubberstey, W.-S. Li, *Dalton Trans.*, **1997**, 913-914.
- [2] D. Jiang, T. Mallat, F. Krumeich, A. Baiker, *J. Catalysis*, **2008**, 257, 380-395.
- [3] E. Nishibori, M. Takata, K. Kato, M. Sakata, Y. Kubota, S. Aoyagi, Y. Kuroiwa, M. Yamakata and N. Ikeda, *Nucl. Instr. Meth. Phys. Res. A*, **2001**, 467-468, 1045-1048.
- [4] A. J. Blake, S. J. Hill, P. Hubberstey, W.-S. Li, *Dalton Trans.*, **1997**, 913-914.