

Supporting Information for

Modification of Flexible Part in Cu²⁺ Interdigitated Framework for CH₄/CO₂ Separation

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Experimental

Preparation of 4,4'-dihydroxybiphenyl-3-carboxylic acid (H₃dhbpc).

Pd(II) acetate (55 mg; 0.23 mmol) was added under argon to a mixture of 5-bromosalicylic acid (5.4 g; 22.4 mmol), sodium carbonate (7.2 g; 68.1 mmol) and 4-methoxyboronic acid (3.8 g; 25 mmol) in water (125 mL). The reaction mixture was stirred at room temperature for 1 h. The resulting slurry was dissolved in hot water (1.3 L) and filtered to give a filtrate and precipitate. The filtrate was acidified with hydrochloric acid. The precipitate was washed with water and dried in vacuo to give 5.3 g (95%) of 4-hydroxy-4'-methoxy-3-biphenylcarboxylic acid.

A solution of 4-hydroxy-4'-methoxy-3-biphenylcarboxylic acid (5.3 g; 21.6 mmol), tetrabutylphosphonium bromide (0.8 g; 2.3 mmol), acetic acid (35 mL) and hydrobromic acid (35 mL of a 48% solution) was heated at reflux for 6 h. The reaction mixture was cooled and poured into water (400 mL). The resulting precipitate was isolated and recrystallised from ethyl acetate to give 2.4 g (47%) of 4,4'-dihydroxybiphenyl-3-carboxylic acid.

Preparation of [Cu(dhbpc)₂(4,4'-bpy)]·2Acetone (2⊃Acetone).

A water solution (20 mL) of Cu(NO₃)₂·3H₂O (0.24 g) was added to a acetone solution (20 mL) of 4,4'-dihydroxybiphenyl-3-carboxylic acid (H₃dhbpc) (0.74 g) and 4,4'-bipyridyl (0.13 g). After the mixture was allowed to stand for several days at 298 K, a green precipitate was collected, washed with acetone, and dried at 373 K under a vacuum. Elemental analysis for **2**; calc (%): C 63.8; H 3.9; N, 4.1; O 18.9; Cu 9.4. Found (%): C 62.9; H 3.5; N 4.3; O 20.2; Cu 9.2.

Single Crystal X-ray Diffraction.

Single crystal X-ray diffraction data collection for **1** was carried out on a Rigaku Saturn diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.71075 \text{ \AA}$) and a CCD two-dimensional detector. Single crystal X-ray diffraction data collection for **2⊃Acetone** was carried

out on a Rigaku Mercury diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.71070$ Å) and a CCD two-dimensional detector. The crystal structure was solved by a direct method (SIR-97 for **1** and SIR-2004 for **2**→Acetone) and refined by full matrix least squares refinement using the SHELXL-97. The hydrogen atoms were positioned geometry and refined using a riding model.

Crystal data of **1** and **2**→Acetone.

Crystal data for **1**. C₂₄H₁₈CuN₂O₈, $M = 525.96$, triclinic, $a = 6.6917(17)$, $b = 8.125(2)$, $c = 11.044(3)$, $\alpha = 84.075(17)$, $\beta = 75.581(14)$, $\gamma = 77.251(18)$, $U = 556.5(3)$, $T = 93(1)$ K, space group $P-1$ (no. 2), $Z = 1$, 8289 reflections measured, 2058 unique ($R_{\text{int}} = 0.038$) which were used in all calculations. The final $R_1(\text{obs})$ was 0.0393 and $wR(F_2)$ was 0.096 (all data).

Crystal data for **2**→Acetone. C₄₂H₃₄CuN₂O₁₀, $M = 790.25$, monoclinic, $a = 23.078(9)$, $b = 11.080(4)$, $c = 15.594(6)$, $\beta = 106.481(4)$, $U = 3824(2)$, $T = 223(2)$ K, space group $P2/c$ (no. 13), $Z = 4$, 55430 reflections measured, 8750 unique ($R_{\text{int}} = 0.0463$) which were used in all calculations. The final $R_1(\text{obs})$ was 0.0655 and $wR(F_2)$ was 0.193 (all data).

Physical Measurements.

All chemicals and solvents used in the syntheses were of reagent grade and used without further purification. Thermogravimetric analysis (TGA) were performed using a Rigaku Thermo plus TG 8120 apparatus in the temperature range between 298 and 773 K in a N₂ atmosphere and at a heating rate of 10 Kmin⁻¹. Elemental analysis was examined using PerkinElmer 2400II for C, H, N. Cu was determined by ICP instrument (Thermo Scientific IRIS-AP). X-ray powder diffraction (XRPD) data were collected on a Rigaku RINT-2200HF (Ultima) diffractometer with CuK α radiation. The adsorption isotherms for CO₂ and CH₄ at 273 K were measured with BELSORP-HP and adsorption isotherms for H₂O at 298 K were measured with BELSORP-aqua3 volumetric adsorption equipment from BEL JAPAN, INC. The powder pattern of **2** was measured at BL19B2 Synchrotron line of SPring-8 (Super Photon ring-8 GeV), Hyogo, Japan and indexed by using the indexing program DICVOL91 and unit cell refinement was obtained by using the Le Bail fitting method. Obtained parameters are : $a = 11.861(1)$ Å, $b = 11.274(1)$ Å, $c = 6.9254(2)$ Å, $\alpha = 69.602(2)^\circ$, $\beta = 102.000(3)^\circ$, $\gamma = 113.000(3)^\circ$, $V = 796(1)$ Å³, $R_p = 2.32\%$, $R_{wp} = 3.22\%$, $\chi^2 = 1.52$ (see Figure S4).

Selective CO₂ adsorption experiment from CH₄/CO₂ mixture.

10 mL of round bottom two-neck flask containing powder sample (0.10 g) of whose one neck was closed with septum and syringe with 100 mL of mixed gas (50 mL of CO₂ and CH₄) and vacuum

pump are connected. The sample was activated by evacuation for three hours at 373 K and set the system in vacuo, and the 100 mL of mixed gas was introduced to the sample until the system reaches 1 atm at 273 K. After three hours the residual gas (1 mL) was picked up from septum and characterized the composition by gas chromatography (Shimazu GC-14B).

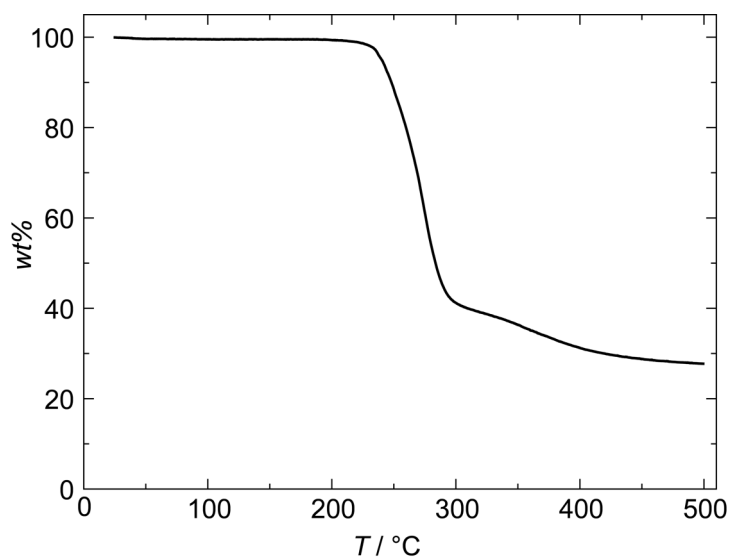


Figure S1 TGA curve of **2** over the temperature range from 25-500 °C at a heating rate of 5 °C min⁻¹ under the N₂ atmosphere.

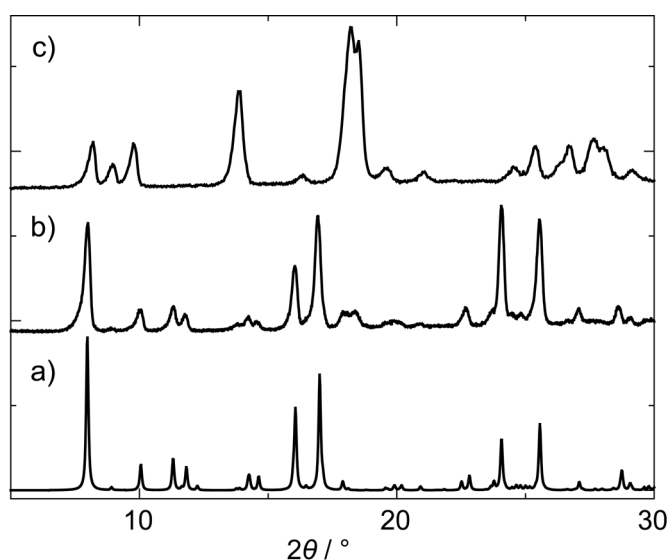


Figure S3. Powder X-ray diffractions of (a) simulated pattern of **2**-Acetone from single crystal structure and experimental patterns of (b) **2**-Acetone and (c) **2** (degassed phase).

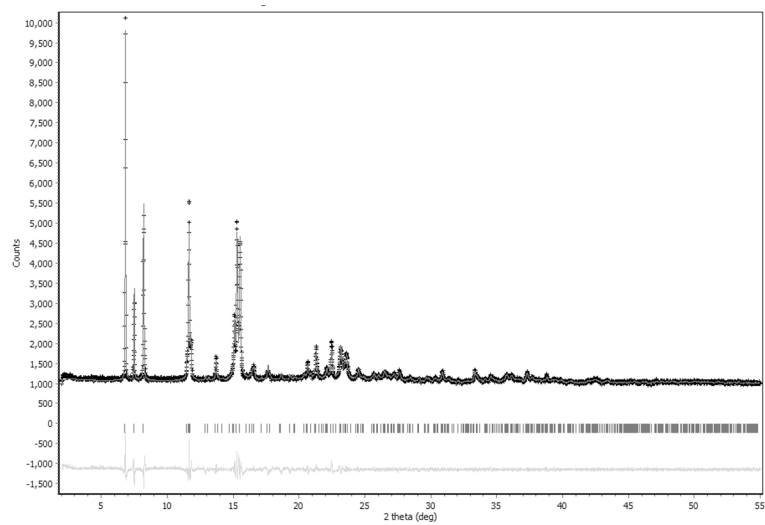


Figure S4. Result on the LeBail fitting of **2**.

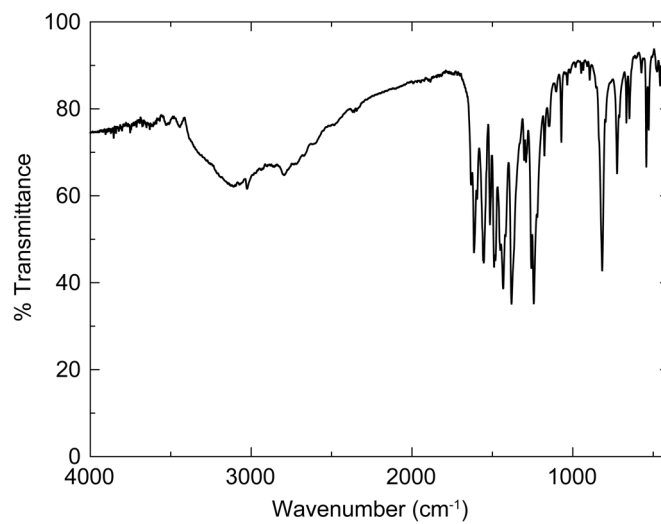


Figure S5. IR spectrum of **2**.

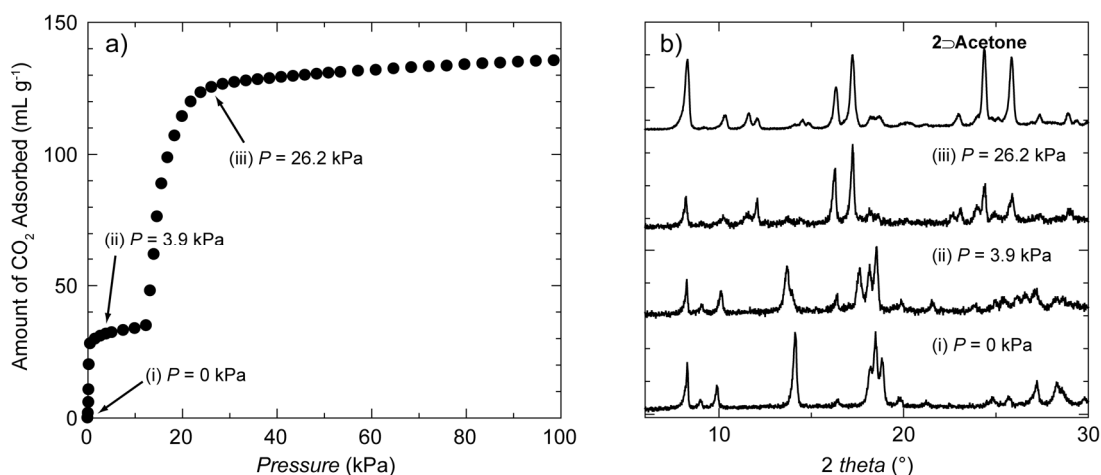


Figure S6. Simultaneous measurements of (a) CO₂ adsorption and (b) powder X-ray diffraction for **2** at 195 K. The each pressure point ((i)~(iii)) is corresponding to the powder X-ray diffraction in (b).

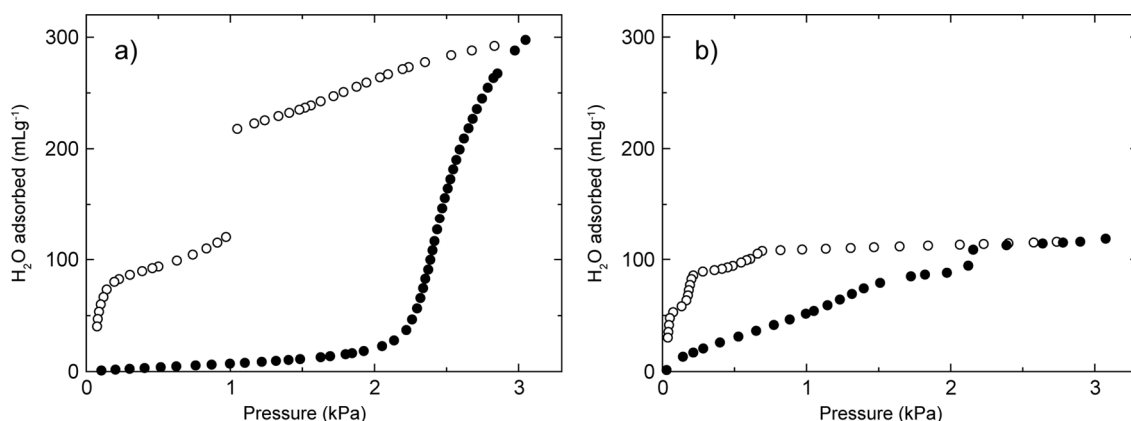


Figure S7. Adsorption (closed circle) and desorption (open circle) isotherms of H₂O for (a) **1** and (b) **2** at 298 K. Abrupt drop at $P = 1$ kPa in desorption profile in (a) is attributed by structural transformation as guests release.

Table S1. Selected lists of reported compounds about adsorption results on CO₂ and CH₄ from single gas component measurement. Note some of values here were obtained from figures of adsorption isotherms in the references.

Compounds	Adsorption amounts of CO ₂ and CH ₄ (mLg ⁻¹)	Measurement conditions (temperature and pressure)	References
CUK-1	87 (CO ₂)	298 K, 1 atm	<i>Adv. Mater.</i>

	8 (CH ₄)		2007, 19, 1830–1834.
SAPO-34	80 (CO ₂) 4.5 (CH ₄)	295 K, 1 atm	<i>Microporous and Mesoporous Materials</i> 2008, 110, 310–317.
[Zn ₃ (OH)(<i>p</i> -CDC) _{2.5}] ¹	67 (CO ₂) 27 (CH ₄)	298 K, 1 MPa	<i>Chem. Commun.</i> 2008, 4135–4137.
Nitrogen doped carbon nanotubes (CN-3)	85 (CO ₂) 29 (CH ₄)	273 K, 1 MPa	<i>Chem. Commun.</i> 2010, 46, 1308–1310.
MIL-53	18 (CO ₂) trace (CH ₄)	304 K, 1 MPa	<i>Angew. Chem. Int. Ed.</i> 45, 2006, 7751–7754.
MIL-120	94 (CO ₂) 40 (CH ₄)	303 K, 1 MPa	<i>Chem. Mater.</i> 2009, 21, 5783–5791.
ZIF-8	48 (CO ₂) 3.3 (CH ₄)	Room temperature, 1 atm	<i>J. Am. Chem. Soc.</i> 2010, 132, 76–78.
NaY zeolite	95 (CO ₂) 28 (CH ₄)	303 K, 1 MPa	<i>Microporous and Mesoporous Materials</i> , 2009, 119, 117–128.
2	115 (CO ₂) 4.6 (CH ₄)	273 K, 0.95 MPa	This work

¹ *p*-CDC²⁻ = deprotonated form of 1,12-dihydroxydicarbonyl-1,12-dicarba-*closo*-dodecaborane