Supporting information

Flexible Two-Dimensional Layered Metal-Organic Framework Functionalized with (Trifluoromethyl)trifluoroborate: Synthesis, Crystal Structure, and Adsorption/Separation Properties

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Contents

Repetitive adsorption property

Carbon dioxide repetitive adsorption characteristics of ELM-13 were evaluated. Pre-treatment under reduced pressure at 110 °C was carried out only before the first, second, and 24th measurement. Other measurements (3rd to 23th) were carried out without pretreatment.

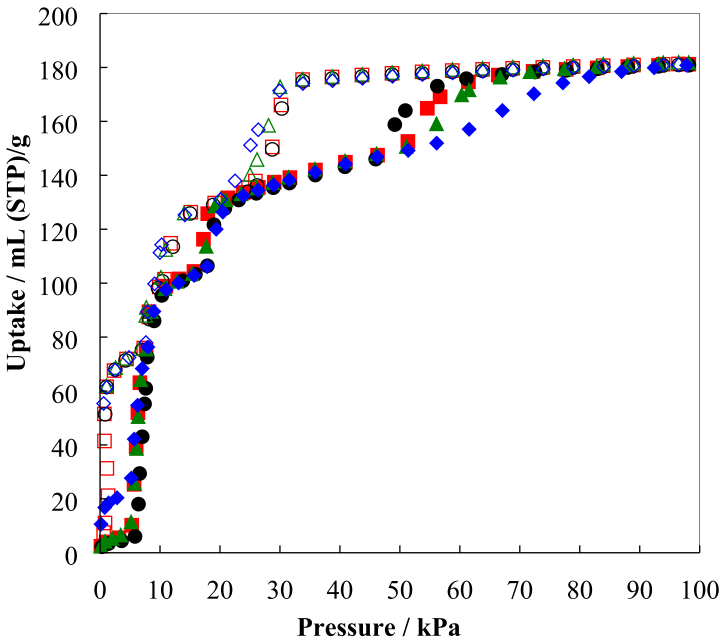

Figure 1S. Adsorption isotherms of CO_2 at 195 K: the first (black, circle), 2nd (red, square), 3rd (green, triangle), and 24th (diamond, blue). Open and solid symbol denotes adsorption and desorption, respectively.

Long-term preservability in synthetic mother liquid

The crystal of ELM-13 was kept in the synthetic mother liquor at room temperature. The crystal was filtered after 9 years, washed with water, air-dried and gas adsorption property was compared to freshly prepared ELM-13.

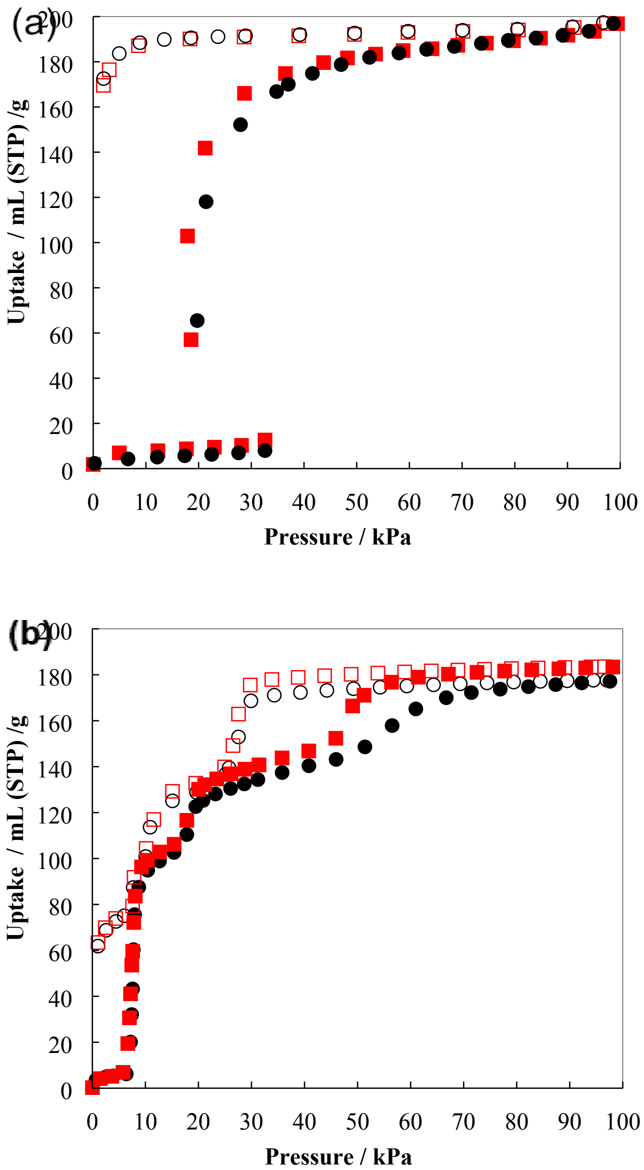

Figure 2S. Gas adsorptivity of freshly prepared ELM-13 (black, circle) and ELM-13 aged in mother liquid for 9 years (red, square). Open and solid symbol denotes adsorption and desorption, respectively: (a) N_2 at 77 K, (b) CO_2 at 195 K.

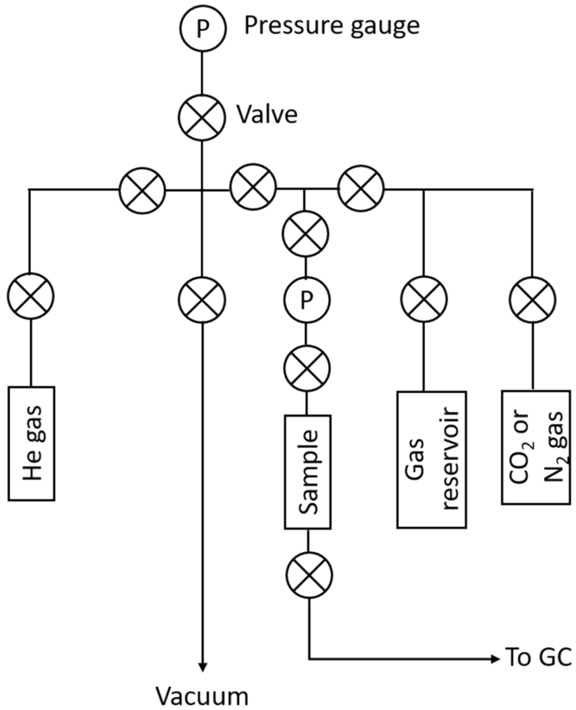

Figure 3S. Schematic representation of a hand-made vacuum/gas loading line for high-pressure mixed-gas separation experiments.

Experimental procedure of high-pressure CO_2/N_2 mixed-gas separation

High-pressure CO_2/N_2 mixed-gas separation experiments were performed with a hand-made line shown in Figure 3S. Several grams (ca. 2 g) of powder sample were placed in a stainless steel column with an inner diameter of 3.1 mm and connected to the line. Before the experiment, the column was heated at 373 K for 2 h under vacuum (P < 1 mPa) to activate the sample. Equimolar CO_2/N_2 mixed gas with a total pressure of 1.0 MPa was introduced into the column containing the sample at 273 K in an ice-water bath. After 30 min to reach adsorption equilibrium, the sample was heated at 353-333 K to desorb the adsorbed gases, and then the desorbed gases were collected in a gas baggage with He gas loading. The ratio of CO_2/N_2 obtained from a GC-9A gas chromatograph with a thermal conductivity detector (Shimadzu Co.) was used to calculate the ratio of the adsorbed gases on the sample.

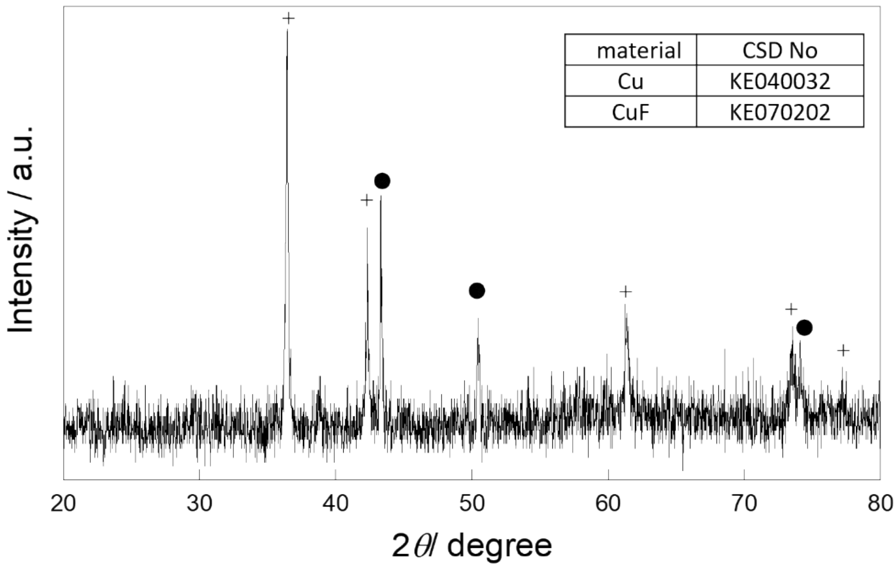

Figure 4S. XRD pattern (CuKα radiation, λ = 1.5418 Å) of the residue after TG measurement. Cross and circle symbol indicates diffraction peaks assigned to CuF (CSD No. KE070202) and Cu (CSD No. KE040032), respectively.

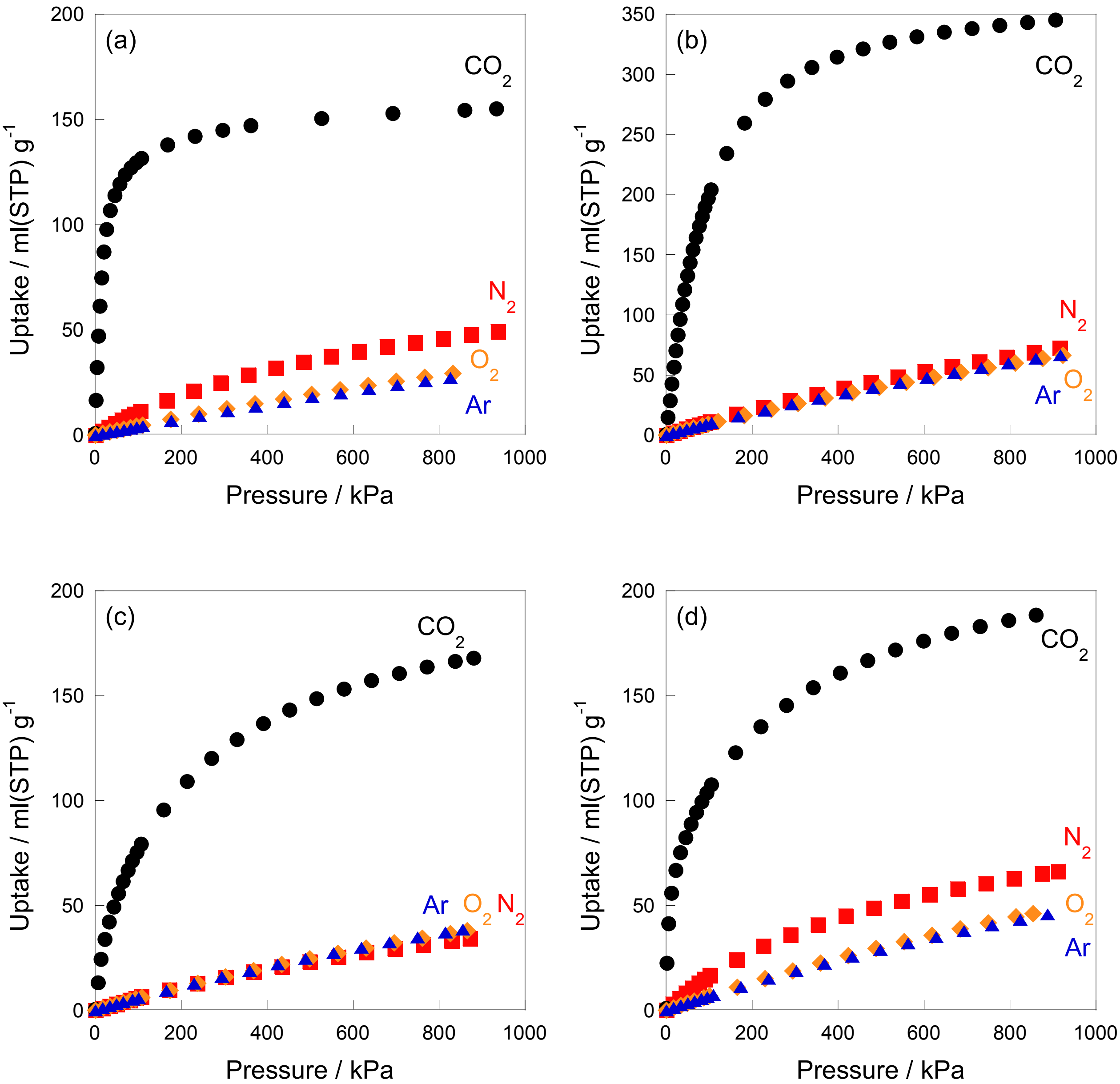

Figure 5S. High pressure adsorption isotherms on (a) zeolite 13X, (b) HKUST-1, (c) UiO-66, and (d) Mg-MOF-74 at 273 K. (CO_2, black; N_2, red; O_2, orange; Ar, blue).

Estimation of CO_2 selectivity

The ratio of adsorbed amount of CO_2 over that of N_2 ($N_{CO2/N2} = N_{CO2}/N_{N2}$) was calculated from single component gas adsorption isotherms by dividing the CO_2 adsorption amount by that of N_2 at each pressure points. The adsorbed amounts of CO_2 and N_2 at 273 K and 0.25 MPa and resultant value $N_{CO2/N2}$ on zeolite 13X, HKUST-1, UiO-66, Mg-MOF-74 and ELM-13 are summarized in table 1S. The CO_2 selectivities (K_{CO2}/K_{N2}) were also evaluated by using Henry coefficients estimated from the CO_2 and N_2 adsorption isotherms at low pressures except ELM-13. The value of the selectivity on Mg-MOF-74 was took from reference [1]. Pressure dependence of the ratio $N_{CO2/N2}$ on the microporous materials in the wide pressure range up to 850 kPa are also shown in Figure 6S.

Table 1S. Adsorption amount of CO_2 and N_2, ratio of adsorbed CO_2 over N_2 ($N_{CO2/N2}$) at 273 K and 0.25 MPa, and selectivity (S_{Henry}) evaluated from Henry coefficients on selected microporous materials.

	CO_2 / mmol g^{-1}	N_2 / mmol g^{-1}	$N_{CO2/N2}$	S_{Henry}
Zeolite 13X	6.5	0.95	6.8	45
HKUST-1	12.7	1.2	10.6	26
UiO-66	5.1	0.62	8.2	25
Mg-MOF-74	8.1	1.5	5.4	29*
This work	2.8	0.035	81	-

*The value was used from reference [1]

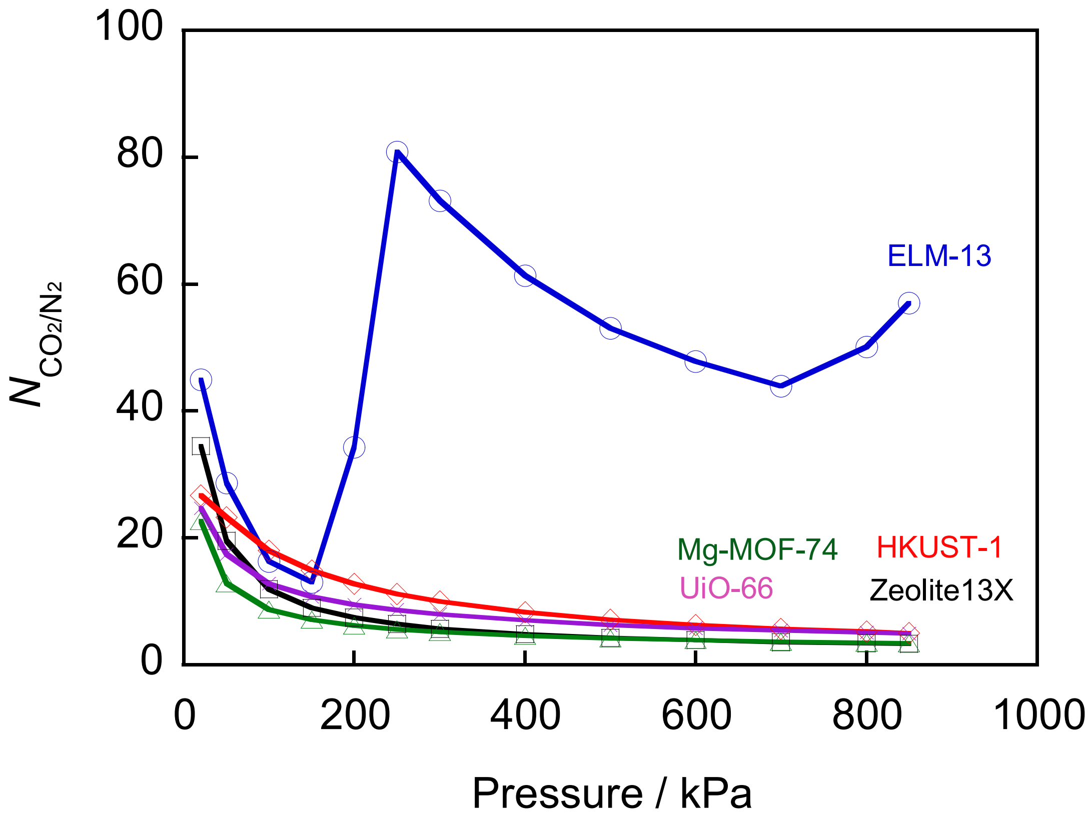

Figure 6S. Pressure dependence of the ratio of adsorbed CO_2 over N_2 at 273 K. (ELM-13, blue; zeolite 13X, black; HKUST-1, red; UiO-66, purple; Mg-MOF-74, green)

References

[1] A. N. Dickey, A. Ö. Yazaydin, R. R. Willis, R. Q. Snurr, *Can. J. Chem. Eng.*, **2012**, *90*, 825-832.