Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

A preferable molecular crystal membrane for H_2 gas separation

*Yuichi Takasaki, Satoshi Takamizawa**

†Department of Nanosystem Science; Graduate School of Nanobioscience; Yokohama City University; 22-2 Seto; Kanazawa-ku, Yokohama, Kanagawa 236-0027; Japan

staka@yokohama-cu.ac.jp

(a) Experimental information

(Preparation of crystal)

Introducing pyrazine vapor (0.20 g, 2.5 mmol) into the methanol solution (200 mL) of copper(II) acetate monohydrate (0.208 g, 1.04 mmol) and 9-anthracenecarboxylic acid (0.449 g, 2.02 mmol) gave dark red, rod-like single crystals of **1** with a size of 100-500 μm in 16.4% yield (90.3 mg). Well-formed single crystals were used for experiments after being vacuum dried at 298 K.

(Preparation of single-crystal membrane)

A single crystal of **1** was set in a hole of an aluminum sheet and the gap between the oriented crystal and the aluminum plate was sealed with epoxy resin. The single crystal was used as a membrane with the area of the crystal surface as 7.65×10^{-3} mm^2 for (001) and a crystal thickness of 0.115 mm along [001]. For the crystal membrane, the single crystals were cut to a suitable size along each crystal face.

(X-ray single crystal diffraction analysis)

Single-crystal X-ray structural analysis of **1** was performed at 90 K on a Bruker Smart APEX CCD area diffractometer (Bruker AXS K.K.) with a nitrogen-flow temperature controller using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Empirical absorption corrections were applied using the SADABS program. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) using the SHELX-TL program package. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed at calculated positions by riding model approximation.

(Gas adsorption measurement)

Gas adsorption measurements were performed at 293 K on a Belsorp-HP Measurement System (BEL JAPAN, Inc.) after drying the microcrystalline sample of **1** (412.7 mg) at 353 K for 2 hours. (Adsorbate gases: H_2, N_2, Ar, O_2, CO, CH_4, and CO_2)

(Gas permeation measurement)

Gas permeation was performed along the direction of [001] by using the single-crystal membrane on GTR-20XAYU Analyzer (GTR Tech Corporation) by the differential pressure method at 293 K and a differential pressure of 150 kPa. Gas permeation was monitored by gas chromatography with a thermal conductivity detector (TCD) on a GC-2014 Gas Chromatograph (Shimadzu Corporation).

(b) Crystallographic data and ortep drawing of **1**

Table S1. Crystallographic data of **1**.

Dimension / mm^3	0.48 × 0.12 × 0.09
Empirical formula	$C_{64}H_{40}Cu_2N_2O_8$
M / g mol^{-1}	1092.06
Crystal system	Tetragonal
Space group	*P*4/*nnc*
T / K	90
a / Å	16.589(2)
b / Å	16.589 (2)
c / Å	9.584(2)
α / °	90
β / °	90
γ / °	90
V / $Å^3$	2637.5(8)
Z	2
D_{calcd} / Mg m^{-3}	1.375
μ (Mo $K\alpha$) / mm^{-1}	0.866
Independent reflections (R_{int})	1178 (0.1282)
Goodness-of-fit on F^2	0.958
R_1 ($I > 2\sigma$(all data))	0.0519 (0.0806)
${}_wR_2$ ($I > 2\sigma$(all data))	0.1400 (0.1493)
Largest diff. peak (hole) / e $Å^{-3}$	1.046 (-1.207)

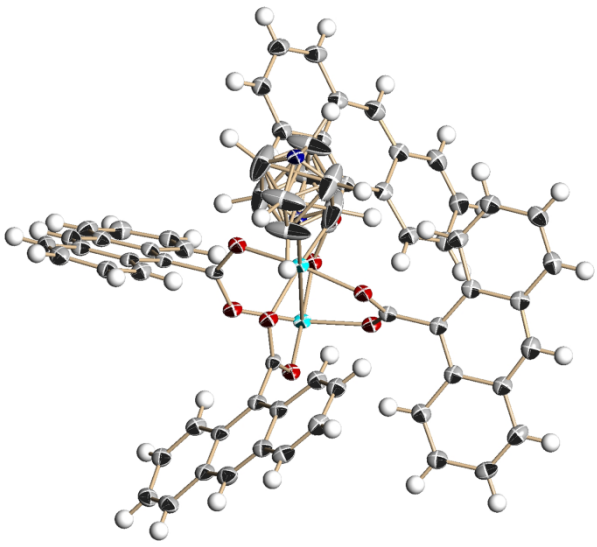

Figure S1. Molecular structure of **1** as an ortep view at 50% probability level for the ellipsoid.

(c) Gas adsorption properties of **1** at room temperature

In gas adsorption measurement, the linear isotherm only for H_2 and normal type I isotherms for other gases (O_2, Ar, N_2, CH_4, and CO_2) were obtained at 293 K. The specific surface area calculated from N_2 gas isotherm is 343.07 $m^2 g^{-1}$ which is near the value of **2** (211.8 $m^2 g^{-1}$). These adsorption isotherms indicate that the all gas species other than H_2 were sufficiently adsorbed in the channel of **1** at 293K and 150 kPa.

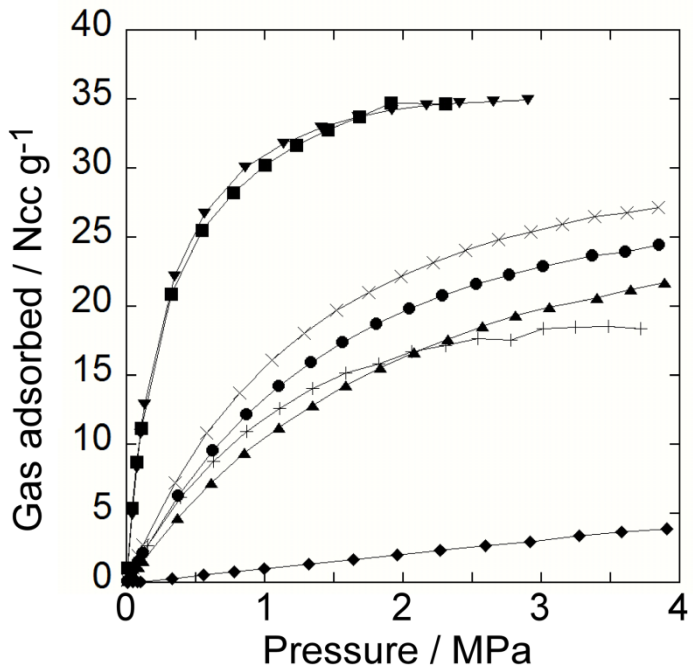

Figure S2. Gas adsorption isotherm of **1** for H_2 (diamond), O_2 (circle), Ar (x), CO (plus), CH_4 (inverted triangle), N_2 (triangle), and CO_2 (square) at 293 K.

Table S2. Gas adsorption amount (*A*) and gas concentration (*C*) in the channel at 293 K and 150 kPa calculated from the adsorption amount at a crystal density (90 K) of 1.375 g cm^{-3} for **1**. Gas concentration for helium was substituted with that for hydrogen because the adsorption measurement for helium gas was not performed.

Gas	*A* / Ncc g^{-1}	*C* / mol m^{-3}
H_2	0.114	8.83
O_2	2.76	170
Ar	3.53	217
CO	2.62	161
CH_4	15.3	941
N_2	2.02	124
CO_2	16.1	987

(d) Estimation of permeability based on Knudsen diffusion model

Table S3. Estimated permeability for **1** at 293 K and 150 kPa based on Knudsen diffusion model. P_{dmin} and P_{dmax} are the estimated permeability based on the values of d_{min} (= 6.2 Å) and d_{max} (= 7.9 Å) in Knudsen diffusion model, respectively.

Gas	P_{dmin} / mol m m^{-2} s^{-1} Pa^{-1}	P_{dmin} / Barrer	P_{dmax} / mol m m^{-2} s^{-1} Pa^{-1}	P_{dmax} / Barrer
He	6.23×10^{-14}	186	7.53×10^{-14}	225
H_2	8.81×10^{-14}	263	1.07×10^{-13}	318
O_2	4.24×10^{-13}	1270	5.13×10^{-13}	1530
Ar	4.84×10^{-13}	1440	5.85×10^{-13}	1750
CO	4.28×10^{-13}	1280	5.18×10^{-13}	1550
CH_4	3.32×10^{-12}	9900	4.01×10^{-12}	12000
N_2	3.30×10^{-13}	987	4.00×10^{-13}	1190
CO_2	2.10×10^{-12}	6260	2.54×10^{-12}	7580

(1 Barrer = 3.35×10^{-16} mol m m^{-2} s^{-1} Pa^{-1})

(e) Comparison of H_2 selectivity and permeability

Table S4. Ideal selectivity ($F\alpha$ (ratio of permeability)) of H_2 versus other gas species and H_2 permeability (P_{H2}) for reported membranes which were shown in Fig. 3(a-c).

Membrane	Gas	$F\alpha$	P_{H2} / Barrer	Reference
1	CO	79.0	3820	This work
	CH_4	137		
	N_2	112		
$[Cu_2(bza)_4(pyz)]_n$	CO	7.45	3310	S1
	CH_4	19.0		
	N_2	10		
Polyethylene	CO	1.2	1.4	S2
Cobalt doped silica	CO	700	4.5	S3
Molecular sieve carbon	CO	5900	7.2	S4
	CO	1770	23.5	
Polyimide (PI-2080)	CO	71	19.9	S5
Polyimide Matrimid 5218	CO	54.8	24.1	S6
	N_2	134		
Molecular sieve silica	CO	16	287	S7
Titania	CO	3.57	6390	S8
	N_2	3.24		
MFI-Type Zeolite	CO	5	59700	S9
Polysulfone	CH_4	53.1	13.1	S10
Defect free silica	CH_4	561	178	S11
	N_2	64		
Poly(tert-butyl acrylate)	CH_4	3.52	300	S12
PIM-EA-TB	CH_4	11.1	7760	S13
	N_2	14.8		
Teflon	CH_4	5.24	3300	S14
HKUST-1 (Cu-BTC)	CH_4	27	95	S15
	N_2	22		
	CH_4	2.4	142000	S16
	N_2	3.7		
	CH_4	2.9	55800	S17
	N_2	3.7		

(1 Barrer = 3.35×10^{-16} mol m m^{-2} s^{-1} Pa^{-1})

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