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Cite this: DOI: 10.1039/c0xx00000x

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A preferable molecular crystal membrane for H₂ gas separationYuichi Takasaki^a and Satoshi Takamizawa^{*a}

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

5 A novel molecular crystal membrane [Cu(II)₂(9-AC)₄(pyz)]_n (9-AC: 9-anthracenecarboxylate, pyz: pyrazine) shows high permselectivity for H₂/CO (79.0), H₂/CH₄ (137), and H₂/CO₂ (12.1) due to high rate of H₂ permeation (3820 Barrer) while inhibiting the permeation of such large gas even in its wider channel than the Lennard-Jones diameter of each gas.

Membrane gas separation is considered to be one of the most effective techniques for gas purification due to its low energy cost and ease of operation.^{1,2} In industry, hydrogen is regarded as the most important gas species in petroleum refining, semiconductor manufacturing, and fuel cell activation.^{3,4} The purification of H₂ gas from gas mixtures including H₂ has the potential of improving efficiency and/or reducing costs in the above processes. Generally, trade-off relationships⁵ between permselectivity and diffusivity hamper the improvement of efficiency in the gas separation process but, for general gas separation membranes such as polymeric membranes^{6,7} or inorganic polycrystalline membranes,^{8,9} which have superior durability and formability, precise observation between pore structure and gas permeation properties is difficult due to pore disarray and structural defects in the membranes. Due to the high regularity and homogeneity of their pores with few structural defects, single-crystal membranes are attractive materials for investigating the mechanism of gas permeation or separation. In this study, we synthesized a novel molecular crystal of a metal complex [Cu(II)₂(9-AC)₄(pyz)]_n (**1**),¹⁰ which is a derivative of [Cu(II)₂(bza)₄(pyz)]_n (**2**) (bza: benzoate),¹¹ and investigated its gas permeation properties. Although we demonstrated anisotropic gas permeation along the channel running layer of **2** with higher permeability compared with that of a conventional zeolite single-crystal membrane,^{12,13} the improved gas selectivity with an increase in permeability through the single-crystal membrane and clarification of the mechanism were of great interest. This study introduces preferable H₂ permselectivity due to the high H₂ permeability through the single-crystal membrane of **1** with the inhibition of gas permeation for larger gases such as CO, CH₄, and N₂, which must be removed in the process of H₂ purification. The crystal structure of **1** (Tetragonal, *P4/nnc*)¹⁴ is formed by 1D chains in which the paddle-wheel units (binuclear Cu₂ center with four 9-AC) are bridged by pyz. The packing structure of **1** was formed through π - π interaction between the anthracene moiety of neighboring 1D chains with a mean distance of 3.398 Å to generate a straight cylindrical 1D channel running along the *c* axis, which is parallel to the direction of the 1D chain. The void

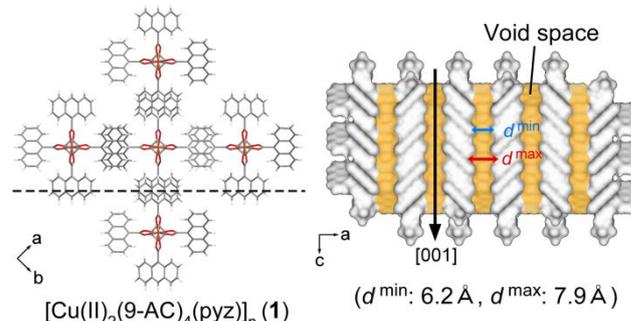


Fig. 1 Packing structure of **1** at 90 K. The right figure as a solvent accessible surface model is a cross section structure cut along the dotted lines shown in the packing structure. Yellow areas indicate void spaces.

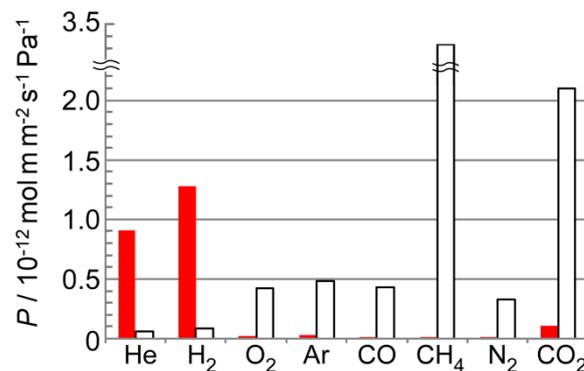


Fig. 2 Observed permeability (*P*) of **1** (red) along [001] compared with values estimated by the Knudsen diffusion model (white) at 293 K and 150 kPa. The differential concentration (ΔC_0), which appears in the Knudsen diffusion model, was substituted by the adsorption amounts at 150 kPa in each gas adsorption isotherm at 293 K. (Table S2)

volume calculated by PLATON was 342.1 Å³ with a porosity of 13.0%, which was near the value of a single crystal of **2**. (465.5 Å³, 14.3%)¹¹ The widest channel diameter (d_1^{\max}) and the narrowest channel diameter (d_1^{\min}), which were measured between the van der Waals surface of the channel walls constructed by the anthracene moiety, were 7.9 Å and 6.2 Å, respectively; the differential value between these diameters (Δd_1 : 1.7 Å) was smaller than that of **2**. (Δd_2 : 2.7 Å for d_2^{\max} : 8.2 Å and d_2^{\min} : 5.5 Å) This means that the channel of **1** has a flatter cylindrical shape than that of **2**. This is thought to permit smooth permeation for all gas species because the Lennard-Jones diameter¹⁵ of gas molecules used in this study were obviously smaller than the d^{\min} of **1**.

Table 1 Gas permeability for **1** at 293 K and 150 kPa with diameter of gas molecules and the ideal selectivity^{8,18} ($F\alpha$) of H₂ versus the other gases for **1**.

Gas	$\sigma_{LJ}^a / \text{\AA}$	Permeability		$F\alpha$ (H ₂ /gas)
		/ mol m m ⁻² s ⁻¹ Pa ⁻¹	/ Barrer ^b	
He	2.551	9.10×10^{-13}	2720	1.41
H ₂	2.827	1.28×10^{-12}	3820	-
O ₂	3.467	2.13×10^{-14}	63.6	60.1
Ar	3.542	2.70×10^{-14}	80.6	47.4
CO	3.690	1.62×10^{-14}	48.4	79.0
CH ₄	3.758	9.34×10^{-15}	27.9	137
N ₂	3.798	1.14×10^{-14}	34.0	112
CO ₂	3.941	1.06×10^{-13}	316	12.1

^a σ_{LJ} : Lennard-Jones diameter.¹⁵

^b 1 Barrer = 3.35×10^{-16} mol m m⁻² s⁻¹ Pa⁻¹.

The gas permeability of **1** for He and H₂ were high, at 9.10×10^{-13} mol m m⁻² s⁻¹ Pa⁻¹ and 1.28×10^{-12} mol m m⁻² s⁻¹ Pa⁻¹ at 293 K and differential pressure of 150 kPa, which are near the values of **2**¹³ for He and H₂ at 4.24×10^{-13} mol m m⁻² s⁻¹ Pa⁻¹ and 1.11×10^{-12} mol m m⁻² s⁻¹ Pa⁻¹, respectively. But the values for the others (O₂, Ar, CO, CH₄, N₂, and CO₂) were in the range of 10^{-14} ~ 10^{-13} mol m m⁻² s⁻¹ Pa⁻¹, which are about 10 times lower than those of **2**.³ Especially, permeability of CO₂ in **1** was significantly smaller than that of **2**, although the gas adsorption amount of CO₂ for **1** (16.1 Ncc g⁻¹) was similar to that of **2** (19.0 Ncc g⁻¹) at 293 K and 150 kPa.¹⁷ (Table S2) This result indicated that the small permeability of CO₂ would be affected by the lower diffusivity of CO₂ gas in **1** compared with that of **2**.

The ideal selectivity^{8,18} ($F\alpha$) for H₂ versus the other gas species calculated as the ratios of each gas permeability value were remarkably high, and the largest improvement from that value of **2** was observed especially for $F\alpha$ of H₂/CO₂ (12.1 for **1** and 0.775 for **2**). In addition, $F\alpha$ of **1** for H₂/CO (79.0), H₂/CH₄ (137), and H₂/N₂ (112), which are considered as important factors for H₂ gas purification in industry,^{3,4} were considerable compared with the values of polymeric membranes known as 71 for H₂/CO through polyimide,¹⁹ 53.1 for H₂/CH₄ through polysulfone,²⁰ and 14.8 for H₂/N₂ through PIM-EA-TB,²¹ for example. Although extremely high values of $F\alpha$ for H₂ against CO or CH₄ in several membranes such as molecular sieve carbon membranes (H₂/CO: 5900)²² and defect-free silica membrane (H₂/CH₄: 561)⁸ were reported, the single-crystal membrane of **1**

is superior to those membranes because of its high H₂ permeability, as shown in Figure 3 whose upper right-hand corner indicates high efficiency of H₂ separation. For the metal organic frameworks (MOFs) such as HKUST-1, gas permeability can be improved by the specific type of membrane used,²³⁻²⁵ but in terms of $F\alpha$, the single-crystal membrane of **1** showed an obviously higher value than the membranes including those polycrystalline MOFs, although the comparisons of permselectivity and permeability are not simple in such heterogeneous membranes because of the defects or crystal boundaries in those membranes.

Conclusions

We synthesized a novel molecular crystal [Cu(II)₂(9-AC)₄(pyz)]_n, which has a straight 1D channel parallel to the 1D chain. Selective He and H₂ gas permeation with high permeability were observed by using the single-crystal membrane of **1** but the permeability values of O₂, Ar, CO, CH₄, N₂, and CO₂ were about 10–100 times lower than were those of He and H₂. Although the observed permeabilities for He and H₂ were higher than the estimated permeabilities based on the Knudsen diffusion model with the channel diameter determined by X-ray structural analysis, those for other gases were 20-350 times lower than the estimated values, and inhibition for permeation of these gases other than He and H₂ was observed. Accordingly, the ideal selectivity ($F\alpha$) for H₂/CO, H₂/CH₄, H₂/N₂, and H₂/CO₂ showed high values with smooth H₂ permeation at 293 K and 150 kPa, compared with those values of the above gas separation membranes such as polymeric membranes,¹⁹⁻²¹ molecular sieve carbon membranes,²² and defect-free silica membranes,⁸ which are used for practical applications as well as scientific research. Further research into the mechanism of selective permeation of small gas molecules would provide a novel principle for designing a molecule for efficient gas separation.

This work was partially supported by a Grant-in-aid for Fundamental Scientific Research (B) (Grant No. 23350028 for S.T.) and a Grant-in-Aid for JSPS fellows (No.24-10567 for Y.T.)

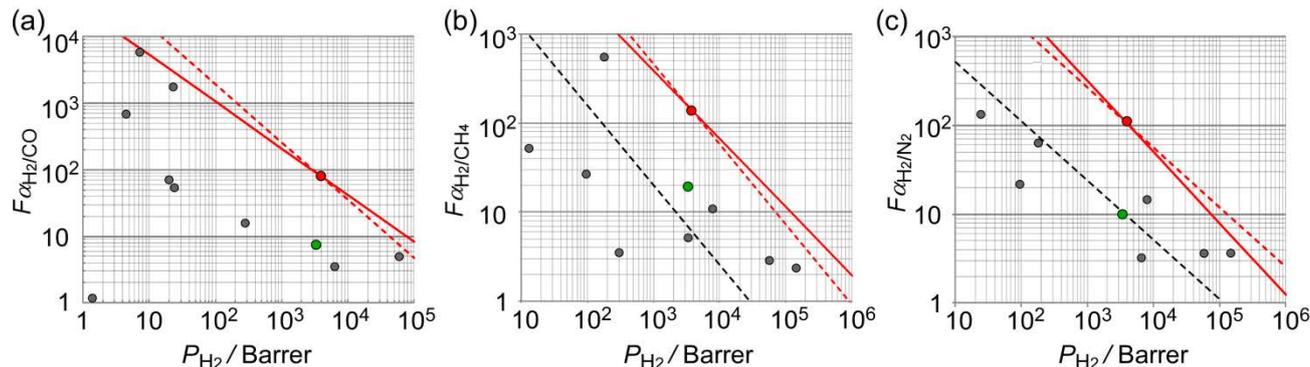


Fig. 3 H₂ gas permeability (1 Barrer = 3.35×10^{-16} mol m m⁻² s⁻¹ Pa⁻¹) versus ideal selectivity ($F\alpha$) of H₂ against CO (a), CH₄ (b), and N₂ (c) of **1** (red plots) compared with those values of other reported membranes (gray plots).^{8,19-33} (Table S4) The green plots are the values of **2**.¹³ Each red line is calculated based on the slope of upper bound ($-\lambda$),⁵ which relates to the empirical correlation of $\lambda = x - \sigma_{H_2}$, where x is the Lennard-Jones diameter (solid line) or kinetic diameter³⁴ (dotted line) of CO, CH₄, and N₂. The black dotted lines are latter Robeson upper bound.⁵

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and crystallographic data. See DOI: 10.1039/b000000x/

‡ The estimated permeability was calculated based on the Knudsen diffusion model,¹⁶ as below.

$$P = \frac{1}{3} \frac{\varepsilon}{\tau} d \left(\frac{8RT}{\pi M} \right)^{\frac{1}{2}} \frac{\Delta C_0}{\Delta p} \quad (1)$$

, where ε is porosity (0.130), τ is tortuosity (1) (l_d/l_s : ratio of pathway length, l_d , versus membrane thickness, l_s), d is channel diameter (d^{\min} , in this estimation), R is gas constant, T is absolute temperature (293 K), M is molecular weight, ΔC_0 is differential gas concentration between top and back of membrane under a static state, and Δp is differential pressure (150 kPa). The observed permeabilities of **1** for He and H₂ were higher than the estimated permeability based on the Knudsen diffusion model with the channel diameter and geometry determined by X-ray structural analysis, but those for the other gases were 20-350 times lower than the estimated values even though the estimated values of **2** showed preferable agreement with the observed values.¹³ (Fig. 2)

§ Ideal selectivity: parameter defined as the ratio of the permeability coefficient of component A to that of component B and equal to the “separation factor” where a perfect vacuum exist at the downstream membrane face for gas and vapor permeation systems.^{18(a)}

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10 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.

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14 Single-crystal X-ray structural analysis of **1** was performed at 90 K on a Bruker Smart APEX CCD area diffractometer (Bruker AXS) with a nitrogen-flow temperature. Crystal data for **1** at 90K: Tetragonal, $P4/nnc$, $a = 16.589(2)$ Å, $b = 16.589(2)$ Å, $c = 9.584(2)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 2637.5(8)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.375$ Mg m⁻³, $R_1 = 0.0519$ (0.0806), $wR_2 = 0.1400$ (0.1493) for 755 reflections with $I > 2\sigma(I)$ (for 1178 reflections (13444 total measured)), goodness-of-fit on $F^2 = 0.958$, largest diff. peak (hole) = 1.046 (-1.207) e Å⁻³. CCDC-988619 contain the supplementary crystallographic data for this paper.

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