Supplementary Information

Central metal dependent modulation of induced-fit gas uptake in molecular porphyrin solids

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Experimental

Sample preparation

1b and **2b** were synthesized by the method reported elsewhere²⁻⁴. To prepare guest-free forms of them, easilyremovable chloroform was used as the final solvent for their synthesis. In this case, the solvent (guest) can be completely removed by heating the sample at 373 K under vacuum. Absence of guest molecules was confirmed by ¹H-NMR. When **1b** and **2b** are exposed to vapour of aromatic compounds such as o-dichlorobenzene and toluene, they adsorb the aromatic compounds very strongly. To completely remove such aromatic compounds, a heat treatment at higher temperature is necessary. However, too high temperature depredates **1b** and **2b**. Thus, we have found out the optimum conditions of heat treatment under vacuum as follows: 433 K for 6 h for **1b** and 493 K for 3 h for **2b**.

Characterization

To confirm the presence of the remaining guest molecules in **1b** and **2b**, the sample was dissolved in CDCl₃ and analysed by ¹H NMR (Bruker Avance III 600). Moreover, porphyrin TG curves were measured by a Shimadzu TGA-51 thermogravimetric analyser (N₂ flow) to check any weight loss due to the presence of the remaining guest molecules.

Adsorption-desorption measurements were performed on an automatic gas/vapour sorption analyser (MicrotracBEL Corp. BELMAX), to examine the gas uptake behaviour on a variety of gases: N₂ at 77 K, Ar at 87 K, CO₂ at 195 K and 298 K, H₂O vapour at 298 K, methanol vapour at 298 K, and ethanol vapour at 298 K. The sample was evacuated at 373 K for 10 h prior to each measurement. Note that we have confirmed that there is no change in the powder X-ray diffraction (PXRD) patterns of **1b** and **2b** before and after the pre-treatment. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method in the pressure range within $P/P_0 = 0.05-0.35$. The range was selected so that the BET plot becomes straight and the BET constant, c, becomes positive. The total pore volume was calculated at $P/P_0 = 0.96$ for N2 (77 K), Ar (87 K), and CO₂ (195 K), while $P/P_0 = 0.94$ for H₂O, methanol, and ethanol.

The PXRD patterns of **1b** and **2b** were measured by a Rigaku SmartLab diffractometer (Cu K α 1 radiation, 45 kV, 200 mA, 1.540593 Å) monochromatized by a Ge(111) Johansson-type crystal monochromator. The transmission method was applied (glass capillary diameter = 0.5 mm). Powder diffraction data were collected between 2–75° (2 θ) with a 0.007° step for **1b** and 2–60° with a 0.01° step for **2b**.

In situ PXRD measurement during adsorption-isotherm measurement was carried out with a Rigaku SmartLab (PXRD analyzer) with Cu K α radiation. A sample is placed in a closed chamber of the PXRD analyzer, and the chamber is connected to a BEL Japan BELSORP 18 (gas sorption analyzer). These two apparatuses automatically communicate each other. When the gas sorption analyzer records a datum at an equilibrium point, subsequently the PXRD analyzer begins a measurement. Thus, PXRD patterns at each of adsorption data can be taken.

Accordingly, we can directly compare the in situ XRPD data and the adsorption/desorption isotherm data obtained by the BELSORP MAX apparatus, though they were obtained separately. It is also noteworthy that the specific 'opengate' behavior of H_4 -CPD_{py} is completely reproducible in Fig. S5. This means that the structure change shown in Fig. 2b upon CO₂ adsorption is reversible.

Analysis of remaining solvent in 1b and 2b Fig. S1 shows 1H-NMR spectra of 1b and 2b. There is no peak of toluene or *o*-dichlorobenzene.



Fig. S1 1 H-NMR of (a) **1b** and (b) **2b**.

We have further examined the absence of any solvent in **1b** and **2b** by thermogravimetry (TG) as shown in Fig. S2. There is no apparent weight loss up to 698 K, clearly showing the absence of any remaining solvent both in **1b** and **2b**.



Fig. S2 TG curves of $\boldsymbol{1b}$ and $\boldsymbol{2b}$ measured in N_2 flow.



Fig. S3 PXRD patterns of (a) 1a and 1b, and (b) 2a and 2b. For 1a and 2a, simulated patterns are shown.

Adsorption-desorption isotherms



Fig. S4 Adsorption-desorption isotherms shown with non-logarithmic plot. (a), (b), and (c) corresponds to Fig. 2a, 2b, and 2c, respectively.

CO2 adsorption-desorption amounts at 195 K based on the amount of substance

Fig. S5 shows adsorption-desorption isotherms (195 K) of **1b** and **2b**. The adsorption amount is expressed by the unit of mol-CO₂ mol⁻¹-CPD.



Fig. S5 CO₂ adsorption-desorption isotherms (195 K) on **1b** and **2b**. The adsorption amount is expressed by the unit of mol-CO₂ mol⁻¹-CPD. Adsorption and desorption data are shown by solid and blank markers, respectively. For **1b**, the adsorption isotherm measured for *in situ* PXRD is shown by solid diamond. The PXRD patterns at the arrowed data points are shown in Fig. 3a.

GCMC simulation of the CO₂ adsorption isotherm on a hypothetical guest-free framework of 1a

A hypothetical guest-free framework of **1a** was prepared simply by removing *o*-dichlorobenzene from the crystal structure of 1a in a structure editing software (CrystalMaker 1.3). CO₂ adsorption isotherm was calculated by the grand canonical Monte Carlo (GCMC) method. In the GCMC simulations, the framework atoms were immobilized and four trial moves for CO₂ (displacement, rotation, creation, and deletion) were made with the same probabilities. The system was equilibrated for 5×10^6 Monte Carlo steps, after which data were collected for another 5×10^6 MC steps. The interaction potential between CO_2 and the host framework of **1a** was assumed to be the sum of the Coulombic and Lennard-Jones (LJ) potentials. Periodic boundary conditions were applied in three directions and the Ewald summation method was used to correct the long-range Coulombic interactions with a charge screening constant of 4.0 nm⁻¹ and the reciprocal space sum for \mathbf{k} vectors of $L_a/2\pi |\mathbf{k}|$, $L_b/2\pi |\mathbf{k}|$, and $L_c/2\pi |\mathbf{k}| \le 10$ (where L_a , L_b , and L_c are the lengths of a parallelepiped-shaped cell of **1a** ($3 \times 3 \times 3$ unit cells): $L_a = 4.4685$ nm, $L_b = 4.47519$ nm, and $L_c = 4.67985$ nm). The short range interactions were calculated using a cut-off of 1.5055 nm. Periodic density functional theory calculations at the GGA-PBE/DNP level were performed using the DMol³ package,^{5,6} and the atomic charges in the host framework were obtained by Mulliken population analysis. The universal force field (UFF)⁷ was applied to the framework atoms to calculate the LJ interaction term. All the solid-fluid LJ cross interaction parameters were obtained by using the Lorentz-Berthelot mixing rules. The interaction parameters for the CO_2 - CO_2 interaction are as follows: $\sigma_{ff, O} = 0.3011$ nm, $\varepsilon_{\rm ff, 0}/k = 82.96$ K, $\sigma_{\rm ff, C} = 0.2789$ nm, $\varepsilon_{\rm ff, C}/k = 29.66$ K, bond length $l_{\rm C-O} = 1.18$ Å, and the partial point charges were located at the three LJ centers: $q_0 = -0.288e$ and $q_c = 0.576e$.

Fig. S6a compares the simulation and the experimental results. A snap shot at 101.3 kPa in the GCMC simulation is shown in Fig. S6b. It is found that the nanospace of the guest-free **1a** structure can be fully filled with CO_2 molecules at this pressure. It is found that the adsorption amount in **1b** is almost the half of that in the guest-free **1a**. Thus, the new crystalline phase formed by the CO_2 inclusion at 195 K is less porous than the framework of **1a**.



Fig. S6 (a) The simulated CO₂ adsorption isotherm (195 K) on the hypothetical guest-free **1a**, together with the experimental result on **1b**. (b) A snap shot at 101.3 kPa of CO₂ pressure in the GCMC simulation. Each atom of CO₂ is modeled by a sphere with the element's van der Waals radius.

Porosity data

Table S1 BET surface areas (S_{BET}) and total pore volumes (V_{total}) of CPDs, calculated from a variety of gas adsorption isotherms: N₂ (77 K), Ar (87 K), CO₂ (195 K), H₂O (298 K), MeOH (298 K), and EtOH (298 K).

Sample	$S_{\rm BET}$ (m ² g ⁻¹) ^{<i>a</i>}			$V_{\text{total}} (\text{cm}^3 \text{g}^{-1})^{b}$					
	N ₂	Ar	CO ₂	N ₂	Ar	CO ₂	H ₂ O	МеОН	EtOH
1a ^c			1689			0.67			
1b	495	558	696	0.24	0.24	0.34	0.07	0.32	0.31
2b	32	45	383	0.05	0.07	0.19	0.08	0.26	0.31

^a The range of BET plot for the calculation of BET surface area (S_{BET}) was selected by the following two criteria in the pressure range of $P/P_0 = 0.05 \cdot 0.35$: (1) BET plot becomes linear as much as possible and (2) *C* value in the BET equation becomes positive. Note that the present gas uptake is different from multi-layer adsorption which is covered by the BET theory, and the BET surface area cannot correctly describe the actual surface area. Here we show the values just as supporting information. ^b Total pore volume, V_{total} , was calculated at $P/P_0 = 0.96$ for N₂, Ar, and CO₂, while $P/P_0 = 0.94$ for H₂O, MeOH, and EtOH, to avoid the estimation from the pressure at which rapid uptake occurs. The total pore volume was calculated by assuming that the adsorbed species has the corresponding liquid density. If the actual density is different from the liquid density, V_{total} does not express the correct total pore volume. Thus, V_{total} is shown just as supporting information. ^c S_{BET} and V_{total} were calculated from the simulated isotherm shown in Fig. S6a on the imaginary guest-free structure of **1a**.

Examination of a variety of gas uptake by QCM

Gas uptake amounts of cyclohexane, toluene, acetic acid, pyridine, and NH₃ were roughly estimated on **1b** by using a quartz crystal microbalance (QCM; UQ-200-BK2, U.S.I Corp.). The QCM was placed in a closed box, and the weight change of a QCM gold electrode which was oscillated can be detected by the change of the resonance frequency. The resonance frequency was 9 MHz. The frequency decreased $(-\Delta F)$ is proportional to the increase in mass (Δm) based on the Sauerbrey equation.⁸ According to the intrinsic parameters for an AT cut quartz plate and electrode area, the relationship between $-\Delta F$ [ng] and Δm [Hz]can be simplified as follows:

$$\Delta m = 0.95 \times (-\Delta F) \tag{1}$$

The QCM frequency in air was stable within ± 2 Hz during 1 h. All experiments were carried out in an airconditioned room at 26 °C. Prior to the experiment, a chloroform solution of **1b** was dropped on a polished QCM gold electrode and dried under vacuum. By measuring the weight change of the electrode before and after the sample loading, the amount of 1b was determined by QCM (ca. 2 µg). Several QCM electrodes were prepared by the same manner. Then, the QCM electrode was set to the instrument and the weight was measured. When the weight became constant, a liquid of adsorbate was placed inside the closed box and the weight increase of **1b** was recorded. Depending on the gases, the uptake amount greatly varies. This is derived from the affinity of guest molecules and the **1b** chemical structure. Such affinity can be modulated by the chemical structure of CPD. In this work, we have demonstrated that just by the replacement of the chelate cation, it is possible to modulate the gas uptake behavior (Fig. 2). Thus, there is a great possibility to tune the selectivity of gases by chemical structure in porphyrin-based SVSs.



Fig. S7 Uptake amounts of a variety of gases on 1b measured by QCM.

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