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Supporting Information

Three-dimensional iron(II) porous coordination polymer exhibiting carbon dioxide-dependent spin crossover

Jong Won Shin, Ah Rim Jeong, Sungeun Jeoung, Hoi Ri Moon, Yuki Komatsumaru, Shinya Hayami, Dohyun Moon, and Kil Sik Min

Experimental Section

General: *N*,*N*,*N'*,*N'*-tetrakis(pyridin-4-yl)methanediamine (tpmd) was prepared according to literature method.¹ Synthesis involving Fe(II) species was carried out in deoxygenated solvent using a dry glove box with a nitrogen atmosphere. Infrared spectra were recorded with a Thermo Fisher Scientific IR200 spectrophotometer (±1 cm⁻¹) using KBr disk. Elemental analyses were carried out using a Fisons/Carlo Erba EA1108 instrument. Thermogravimetric analyses (TGA) were performed at a scan rate of 5 °C/min using a Seiko TG/DTA 320 & SSC 5200H Disk Station system.

X-ray powder diffraction (XRPD) analysis: Compound 1•4H₂O was ground and filled in the capillary (diameter, 0.5 mm; wall thickness, 0.01 mm). Diffraction data were collected at 100 K with 200 mm detector distance in 600 s exposure with synchrotron radiation ($\lambda = 1.00029$ Å) on an ADSC Quantum-210 detector at 2D SMC with a silicon(111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. The ADX program² was used for data collection, and the *Fit2D* program⁷ was used for conversion of a two-dimensional diffraction image to a one-dimensional diffraction pattern. Powder diffraction patterns of 1•4H₂O (298 K) were measured on a a Bruker AXS D2 Phaser X-ray Diffractometer with increments of degree and time step of 0.02° and 0.2 sec/step in 2 θ at room temperature. The XRPD pattern of 1•4H₂O is coincident with the simulated pattern derived from the X-ray single crystal data of 1•4H₂O, implying that the bulk sample is identical to the single crystal (Fig. S1).

Preparation of [Fe(tpmd)(NCBH₃)₂]•4H₂O (1•4H₂O): A solution of NaNCBH₃ (0.125 g, 2.0 mmol) in MeOH (3 mL) was added to FeSO₄·7H₂O (0.280 g, 1.0 mmol) in MeOH (8 mL). The mixture was stirred for 20 min and filtered. A solution of tpmd (0.090 g, 0.25 mmol) in MeOH (3 mL) was slowly added into filtered solution with stirring. From this solution a microcrystalline yellow precipitate formed within 1 h, which was collected by filtration, washed with MeOH and dried. Yield: 79 mg (56%). IR (KBr, cm⁻¹): 3437, 3095, 3066, 2978, 2340, 2187, 1592, 1503, 1367, 1219, 1118, 1011. Anal Calcd for $C_{23}H_{32}N_8B_2FeO_4$: C, 49.15; H, 5.74; N, 19.94. Found: C, 49.30; H, 5.39; N, 20.03. Solubility: H₂O (very slightly soluble); acetone, methanol, DMF and DMSO (insoluble).

Thermogravimetric analysis (TGA) of $1.4H_2O$ revealed a weight loss of 11.2% at 100 °C, which corresponds to the loss of four water molecules per unit formula; no chemical decomposition was observed up to 220 °C (Fig. S2).

Single Crystal X-ray Diffraction: Single crystal diffraction data of 1.4H₂O were collected with the same crystal at 100 and 298 K. The crystal data for 1•4H₂O at 298 K was obtained following the heating of a crystal of 1•4H₂O from 100 to 298 K at 100 K per hour. The crystal of $1.4H_2O$ was coated with paratone-N oil and the diffraction data measured at 100(2) and 298(2) K with synchrotron radiation ($\lambda = 0.65000$ and 0.80000 Å) on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea, respectively (Table S1). The ADSC Q210 ADX program² was used for data collection (detector distance is 63 mm, omega scan; $\Delta \omega = 1^{\circ}$, exposure time is 1 sec per frame) and HKL3000sm (Ver. 703r)³ was used for cell refinement, reduction and absorption correction. The crystal structures of 1.4H₂O at both temperatures were solved by direct methods,⁴ and refined by full-matrix least-squares refinement using the SHELXL-2013/2014 computer program.⁵ The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. However, due to the thermal disorder, boron atoms of the cyanoborohydride anions were refined isotropically. All hydrogen atoms were placed using a riding model, and their positions were constrained relative to their parent atoms using the appropriate HFIX command in SHELXL-2013/2014, except the hydrogen atoms of water molecules. Even though the guest solvent molecules were found in the structure, those could not be well refined because of severe disorder. The final refinement was performed with modification of the structure factors for contribution of the disordered solvent electron densities using the SQUEEZE option of PLATON program.⁶

In preparation for the gas adsorption in situ single crystal diffraction measurements, samples were mounted with 100 μ m grippers (Mitegen Company Inc.) with no oil to prevent the sample from moving upon evacuation and covered with 0.8 mm quartz capillaries. The capillary was fixed to a customized goniometer head with an attached gas line allowing connection to the pressure control equipment and turbo molecular pump. The carbon dioxide gas was extra-high purity quality (DAEHAN Gas Company, Korea, 99.999%). CO₂ gas was loaded in the capillary in small increments, and the pressure control was used under vacuum at 0 Torr and loaded CO₂ at 1 bar by using fine

adjustable needle valve. The temperature and pressure steps were selected on the basis of the CO_2 gas adsorption isotherm.

Single crystal diffraction data of 1 (298 K), 1•0.75CO₂ (298 K), 1•0.75CO₂ (273 K), and 1•2.50CO₂ (200 K) for in situ CO₂ gas adsorption were collected with the same crystal with synchrotron radiation ($\lambda = 0.70000$ Å, detector distance is 63 mm, omega scan; $\Delta \omega = 1^{\circ}$, exposure time is 1 sec per frame) on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea, respectively (Tables S1 and S2).

The crystal data for **1** were obtained following the evacuation with the turbo molecular pump at 298 K for 18 h until it did not reveal any significant residual electron density in the pores. The crystals data of $1\cdot0.75CO_2$ were measured from **1** with CO₂ gas at 1 bar at 298 K for 3 min. The crystal data of $1\cdot0.75CO_2$ were measured from **1** with CO₂ gas at 1 bar at 273 K. The crystal data for $1\cdot2.50CO_2$ were obtained from evacuated **1** with CO₂ gas at 1 bar for 3 min at 273 K. The crystal data for $1\cdot2.50CO_2$ were obtained from evacuated **1** with CO₂ gas at 1 bar for 3 min at 200 K.

The crystal structures of 1 (298 K), 1•0.75CO₂ (298 K), 1•0.75CO₂ (273 K), and 1•2.50CO₂ (200 K) were solved by direct methods,⁴ and refined by full-matrix least-squares refinement using the SHELXL-2014 computer program.⁵ The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. However, due to the disorder in 1 (298 K), 1•0.75CO₂ (298 K), 1•0.75CO₂ (273 K), and 1•2.50CO₂ (200 K), boron atoms of the cyanoborohydride anions were refined isotropically. The thermal factors of CO₂ molecules are not stable too high, performed isotropic refinement at CO₂ molecules and the C-O bond lengths were constrained from 1.13 to 1.16 Å in 1•0.75CO₂ (298 K), 1•0.75CO₂ (273 K), and 1•2.50CO₂ (200 K). All hydrogen atoms were placed using a riding model, and their positions were constrained relative to their parent atoms using the appropriate HFIX command in SHELXL-2014. The crystallographic data and the result of refinements of 1•4H₂O (100 K), 1•4H₂O (298 K), 1 (298 K), 1•0.75CO₂ (298 K), 1•0.75CO₂ (273 K), and 1•2.50CO₂ (200 K) are summarized in Tables S1 and S2.

Gas sorption study: The nitrogen adsorption-desorption isotherms were measured at 77 K on a BELsorp-MAX adsorption analyzer. Prior to adsorption measurement, the samples were evacuated at 100 °C under vacuum (p < 10010⁻⁵ mbar) for 12 h. The specific surface area was determined from the linear part of the BET equation, and the total pore volume was calculated from the amount adsorbed at a relative pressure of about 0.99. The carbon dioxide adsorption-desorption isotherms were measured at 196, 273, and 298 K on a BELsorp-MAX adsorption analyzer. The preparation for samples is same to the N_2 measurements. The detailed analysis of N_2 gas sorption experiment in 1 is as follows: Interestingly, the N_2 gas sorption isotherm at 77 K measured up to 1 bar exhibits two distinct steps (see Fig. S4). The first step at P = 0.00000285 - 0.0909 bar provides the surface area of 859 m² g⁻¹ as estimated by the Langmuir and Brunauer-Emmett-Teller (BET) methods, and the pore volume of 0.459 cm³ g⁻¹ as estimated by the Dubinin–Radushkevich (DR) equation. In the second step at P = 0.109-0.890 bar, the isotherm shows a sharp increase to reach the plateau, displaying a type I isotherm. The second step provides Langmuir and BET surface areas of 1569 and 888 m² g⁻¹, respectively, and pore volume of 0.492 cm³ g⁻¹. At 0.905 bar, the isotherm exhibits another sharp increase and then finally attains a saturation with the adsorbed N₂ amount of 483.30 cm³ g⁻¹ (60.3 wt%, 668 g L⁻¹) at 0.98 bar. In CO₂ sorption experiments, the isosteric heat of adsorption (Q_{st}) for CO₂ was calculated from the Clausius-Clapevron equation using adsorption data collected at 196, 273, and 298 K (Fig. S5). The zero coverage Q_{st} was estimated to be 35.2 kJ mol⁻¹ at low loading and remains nearly constant upon increasing CO₂ uptake (30-35 kJ mol⁻¹, Fig. S5).



Fig. S1 XRPD patterns for (a) the simulated pattern from the single crystal data of $1 \cdot 4H_2O$ and (b) $1 \cdot 4H_2O$ as prepared (powder).



Fig. S2 Thermogravimetric analysis (TGA) trace for 1•4H₂O.



Fig. S3 XRPD patterns for (a) the simulated pattern from the single crystal data of **1**, (b) **1** as prepared (powder), (c) dried **1** under vacuum at 100 °C for 4 h.



Fig. S4 N₂ gas sorption isotherm at 77 K for 1 (filled circles, sorption; open circles, desorption).



Fig. S5 Plot of the isosteric heat of adsorption of CO_2 in 1.



Fig. S6 Temperature dependence of $\chi_M T$ for 1•4H₂O (red; \blacktriangle (T \uparrow), \blacktriangledown (T \downarrow)), 1 (blue; \blacktriangle (T \uparrow), \blacktriangledown (T \downarrow)), and 1•*x*CO₂ (• (red, T \uparrow and blue, T \downarrow); under 1 bar CO₂).



Fig. S7 Temperature dependence of $\chi_M T$ for 1•4H₂O (blue) and 1•xN₂ (red; under 1 bar N₂).



Fig. S8 ORTEP view of $1 \cdot 0.75 \text{CO}_2$ at 298 K. The atoms are represented by 30% probable thermal ellipsoid. Hydrogen atoms are omitted for clarity. Symmetry code: N3' (-y, x, -z), N4' (1/2-y, 1/2-x, -z), N6' (-x, y, 1/2+z), O1' (-x, -y, z), O2' (1-x, -y, z).



Fig. S9 ORTEP view of $1 \cdot 0.75 \text{CO}_2$ at 273 K. The atoms are represented by 30% probable thermal ellipsoid. Hydrogen atoms are omitted for clarity. Symmetry code: N3' (-y, x, -z), N4' (1/2-y, 1/2-x, -z), N6' (-x, y, 1/2+z), O1' (-x, -y, z), O2' (1-x, -y, z).



Fig. S10 ORTEP view of $1 \cdot 2.50 \text{CO}_2$ at 200 K. The atoms are represented by 30% probable thermal ellipsoid. Hydrogen atoms are omitted for clarity. Symmetry code: N3' (-y, x, -z), N4' (1/2-y, 1/2-x, -z), N6' (-x, y, 1/2+z), and O1' (2-x, -y, z).



Fig. S11 CO_2 packed structures in 1•2.50 CO_2 at 200 K, showing molecular interactions between the absorbed CO_2 molecules. Four structures (a~d) represent in different axes.

Compound	1• 4H ₂ O	1• 4H ₂ O	1
Empirical formula	$C_{23}H_{32}B_2FeN_8O_4$	$C_{23}H_{32}B_2FeN_8O_4$	$C_{23}H_{24}B_2FeN_8$
Formula weight	562.03	562.03	489.97
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space group	<i>I</i> ⁴ <i>c</i> 2	$I^{\overline{4}}c^{2}$	$I^{\overline{4}}c^{2}$
Color	Red	Yellow	Yellow
Crystal size, mm ³	0.080×0.080×0.080	0.080×0.080×0.080	0.100×0.100×0.100
<i>a</i> , Å	21.432(3)	21.983(3)	22.018(3)
<i>b</i> , Å	21.432(3)	21.983(3)	22.018(3)
<i>c</i> , Å	28.249(6)	28.972(6)	29.028(6)
<i>V</i> , Å ³	12976(4)	14000(5)	14073(5)
Ζ	16	16	16
$d_{\rm calc}$, g cm ⁻³	1.151	1.067	0.925
λ, Å	0.65000	0.80000	0.70000
Т, К	100(2)	298(2)	298(2)
μ , mm ⁻¹	0.395	0.644	0.431
<i>F</i> (000)	4704	4704	4064
Reflections collected	91011	46255	72790
Independent reflections	15488	6913	10269
Reflections with $I > 2\sigma(I)$	10987	4773	9396
Goodness-of-fit on F^2	1.065	1.001	1.052
Final R indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0597$	$R_1 = 0.0792$	$R_1 = 0.0563$

Table S1 Crystallographic data and structure refinement for $1{\mathchar`4}{\rm H_2O}$ and 1

	$wR_2 = 0.1832$	$wR_2 = 0.2306$	$wR_2 = 0.1955$
Final R indices [all data] ^a	$R_1 = 0.0948$	$R_1 = 0.0987$	$R_1 = 0.0593$
	$wR_2 = 0.2013$	$wR_2 = 0.2490$	$wR_2 = 0.1995$

 $\overline{{}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|, wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2}/\Sigma w (F_{o}^{2})^{2}]^{1/2}}.$

Compound	1•0.75CO ₂	1•0.75CO ₂	1•2.50CO ₂
Empirical formula	$C_{23.75}H_{24}B_2FeN_8O_{1.50}$	$C_{23.75}H_{24}B_2FeN_8O_{1.50}$	$C_{25.50}H_{24}B_2FeN_8O_5$
Formula weight	522.98	522.98	600.00
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space group	$I^{\overline{4}}c^{2}$	$I^{\overline{4}}c^{2}$	$I^{\overline{4}}c^{2}$
Color	Yellow	Yellow	Yellow
Crystal size, mm ³	0.100×0.100×0.100	0.100×0.100×0.100	0.100×0.100×0.100
<i>a</i> , Å	22.012(3)	22.005(3)	22.056(3)
<i>b</i> , Å	22.012(3)	22.005(3)	22.056(3)
<i>c</i> , Å	28.983(6)	28.943(6)	29.005(6)
<i>V</i> , Å ³	14043(5)	14015(5)	14110(5)
Ζ	16	16	16
$d_{\rm calc}$, g cm ⁻³	0.989	0.991	1.130
λ, Å	0.70000	0.70000	0.70000
<i>Т</i> , К	298(2)	273(2)	200(2)
μ , mm ⁻¹	0.439	0.439	0.451
<i>F</i> (000)	4328	4328	4944
Reflections collected	72602	72505	49712
Independent reflections	10241	10217	7269
Reflections with $I > 2\sigma(I)$	9155	9184	3624
Goodness-of-fit on F ²	1.095	1.063	1.244

Table S2 Crystallographic data and structure refinement for $1 \cdot 0.75 \text{CO}_2$ and $1 \cdot 2.50 \text{CO}_2$

Final P indices [1-2-(1)]a	$R_1 = 0.0638$	$R_1 = 0.0695$	$R_1 = 0.1340$
Final R indices [all data] ^a	$wR_2 = 0.2201$	$wR_2 = 0.2317$	$wR_2 = 0.3456$
	$R_1 = 0.0679$	$R_1 = 0.0733$	$R_1 = 0.1987$
	$wR_2 = 0.2254$	$wR_2 = 0.2374$	$wR_2 = 0.3826$

 $\overline{a} R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|, wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{1/2}.$

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