Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Programmed crystallization via epitaxial growth and ligand replacement towards hybridizing porous coordination polymer crystals

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Contents

S1. Experimental section

Materials

$Zn(NO_3)_2$•$6H_2O$, *N*,*N*-dimethylformamide (DMF), methanol (MeOH) and idopropane were purchased from Wako Pure Chemical Industries. 5-nitroisophthalic acid (NO_2-H_2ip) were purchased from acid Sigma-Aldrich, Inc. 4,4'-bipyridyl (bpy) were purchased from Tokyo Chemical Industry. *N*,*N*'-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide (dpndi) was prepared according to the literature procedures.[S1]

Synthesis of single crystals of 1

The suspension of dpndi (42.0 mg, 0.10 mmol) in MeOH (2 mL) was slowly layered on the top of the solution of $Zn(NO_3)_2$•$6H_2O$ (29.7 mg, 0.10 mmol), NO_2-H_2ip (21.1 mg, 0.10 mmol) in DMF (2mL). The solution was heated at 70 °C for 1 day. After cooling, yellow crystals were harvested. Elemental analysis calcd. for $C_{36.5}H_{25.5}N_{6.5}O_{11.5}Zn$ {[Zn(NO_2-ip)(dpndi)]•$(DMF)_{1.5}(MeOH)_{1.5}$}$_n$: C, 54.49; H, 3.19; N, 11.31, Found: C, 53.43; H, 3.09; N, 10.98.

Synthesis of powder crystals of 1

The solution of $Zn(NO_3)_2$•$6H_2O$ (118.8 mg, 0.4 mmol), NO_2-H_2ip (84.4 mg, 0.4 mmol) and bpy (168 mg, 0.4 mmol) in 20 mL DMF was stirred for several hours. The dozens of well-dispersed single crystals of **1** were put into the solution. The solution was heated up to 393 K for 3 hours by microwave (Initiator, Biotage). After cooling, the powder crystals were harvested.

Synthesis of hybrid single crystal, S-1/2

The solution of $Zn(NO_3)_2$•$6H_2O$ (59.4 mg, 0.2 mmol), NO_2-H_2ip (42.2 mg, 0.2 mmol) and bpy (31.2 mg, 0.2 mmol) in 10 mL DMF was stirred for several hours. The dozens of well-dispersed single crystals of **1** were put into the solution. The solution was heated up to 353 K for several days. After cooling, the crystals were harvested.

Synthesis of hybrid powder crystals, C-1/2

The solution of bpy (15.6 mg, 0.1 mmol) in 100 mL DMF was stirred for several hours. The powder crystals of **1** (7.47 mg, 0.01 mmol) were put into the solution and the solution was stirred for 12 hours.

Accommodation of iodopropane

The as-synthesized powder crystals of **1**, **2** and **C-1/2** were evacuated at 150 °C under the vacuum condition. The crystals of degassed **1**, **2** and **C-1/2** were immersed in iodopropane. After the filtration and drying, the crystals were analyzed by SEM-EDX and TG.

Characterization methods

The compounds were characterized with X-ray diffraction (XRD), microscopic laser Raman spectroscopy, synchrotron XRD, thermogravimetry (TG), ^{1}H-NMR, elemental analysis and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). Powder X-Ray diffraction (XRD) studies were performed using a Rigaku diffractometer with Cu Kα radiation (λ = 1.5418 Å). The Raman spectra were measured by a LabRAM HR-800 spectrometer (Horiba Jobin Yvon Ltd.) with a semiconductor laser at 785 nm. TG measurements were carried out by Thermo plus EVO II. Elemental analysis was carried out on a Flash EA 1112 series, Thermo Finnigan instrument. Single crystal X-ray diffraction measurements were made on a Rigaku AFC10 diffractometer with Rigaku Saturn CCD system equipped with a rotating-anode X-ray generator producing multi-layer mirror monochromated MoKα radiation. SEM-EDX studies were performed using JEOL JSM 5600.

Structural determination of as-synthesized 1

X-ray data collection ($5^\circ < 2\theta < 55^\circ$) was conducted at 223K on Rigaku AFC10 diffractometer Mo-Kα radiation (λ = 0.7105 Å) with Rigaku Mercury CCD system. The structures were solved by a direct method (SIR92) and expanded using Fourier techniques. All calculations were performed using the CrystalStructure crystallographic software package 4.0 of Rigaku. The crystallizing solvents (DMF and MeOH molecules) were severely disordered and could not be satisfactorily localized. All non-hydrogen atoms except for those of disordered solvent molecules were refined anisotropically. Hydrogen atoms severely disordered and could not be satisfactorily localized. The pyridyl ring including C_{10} and C_{12} severely rotates, thus leading to the relatively high Ueq of C_{10} and C_{12}. The contributions from disordered solvent molecules were removed by the SQUEEZE (PLATON), and the outputs from the SQUEEZE calculations are attached to each CIF file. The elemental analysis and TGA suggest that 3 DMF and 3 MeOH are accommodated as guest molecules in a single unit cell of as-synthesized **1**. The number of electrons in 3 DMF and 3 MeOH are 315, which nearly corresponds to the result of SQUEEZE calculations (counted electrons: 282).

Crystal data for as-synthesized 1: $C_{64}H_{30}N_{10}O_{20}Zn_2$, *monoclinic*, space group *C2/c*, (no. 15), a = 31. 110 (9) Å, b = 10.192(3) Å, c = 22.095(6) Å, β = 93.938(4), V = 6990(4) Å^3, Z = 4, T = 223 K. ρ_{calcd} = 1.391 gcm^{-3}, μ(MoKα) = 0.769 cm^{-1}, 8009 reflections measured, 6499 observed ($I > 2.00\sigma(I)$ 433 parameters; R_1 = 0.0603, wR_2 = 0.1868, GOF = 1.101.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. (CCDC number: 924193)

Synchrotron X-ray measurement for film-structural analysis

The measurements were performed with a four-circle diffractometer having ϕ, χ, θ, and 2θ circles at beamline BL13XU for surface and interface structures, SPring-8. The hybridized crystal, **S-1/2**, was picked up just before the measurement, and then fixed on the glass substrate with the orientation where orange part of **S-1/2** was parallel to the glass substrate by double-faced adhesive. The measurement was carried out under Helium gas condition.

S2. Four-axis diffractometer of synchrotron surface XRD

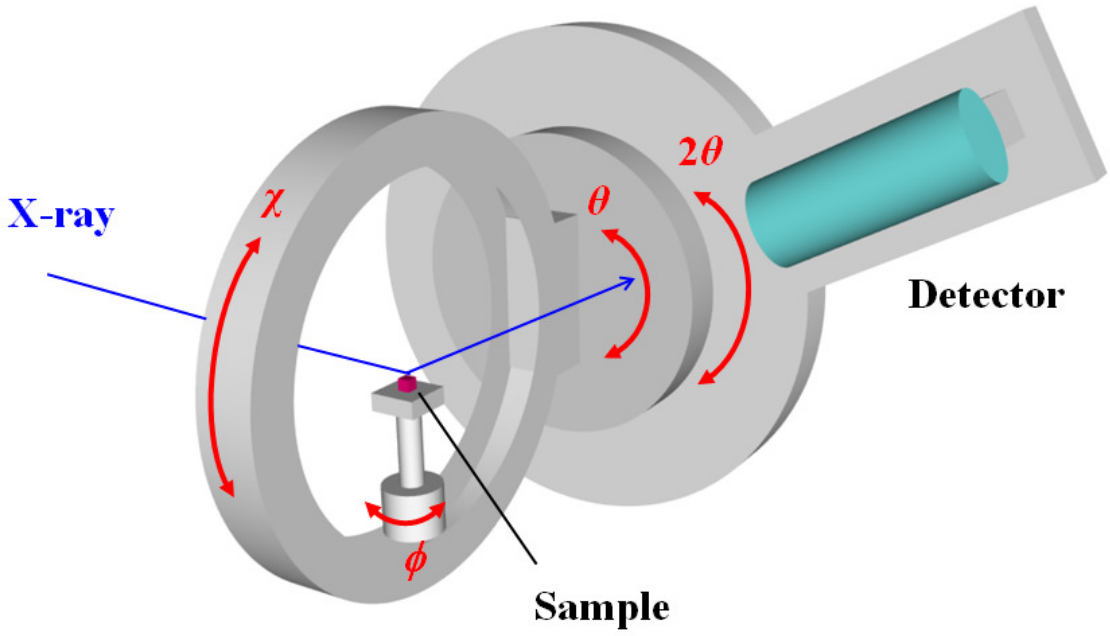

Fig. S1 The schematic drawing of the four-circle diffractometer at beamline BL13XU for surface and interface structures, SPring-8.

S3. Crystal structure of as-synthesized 1

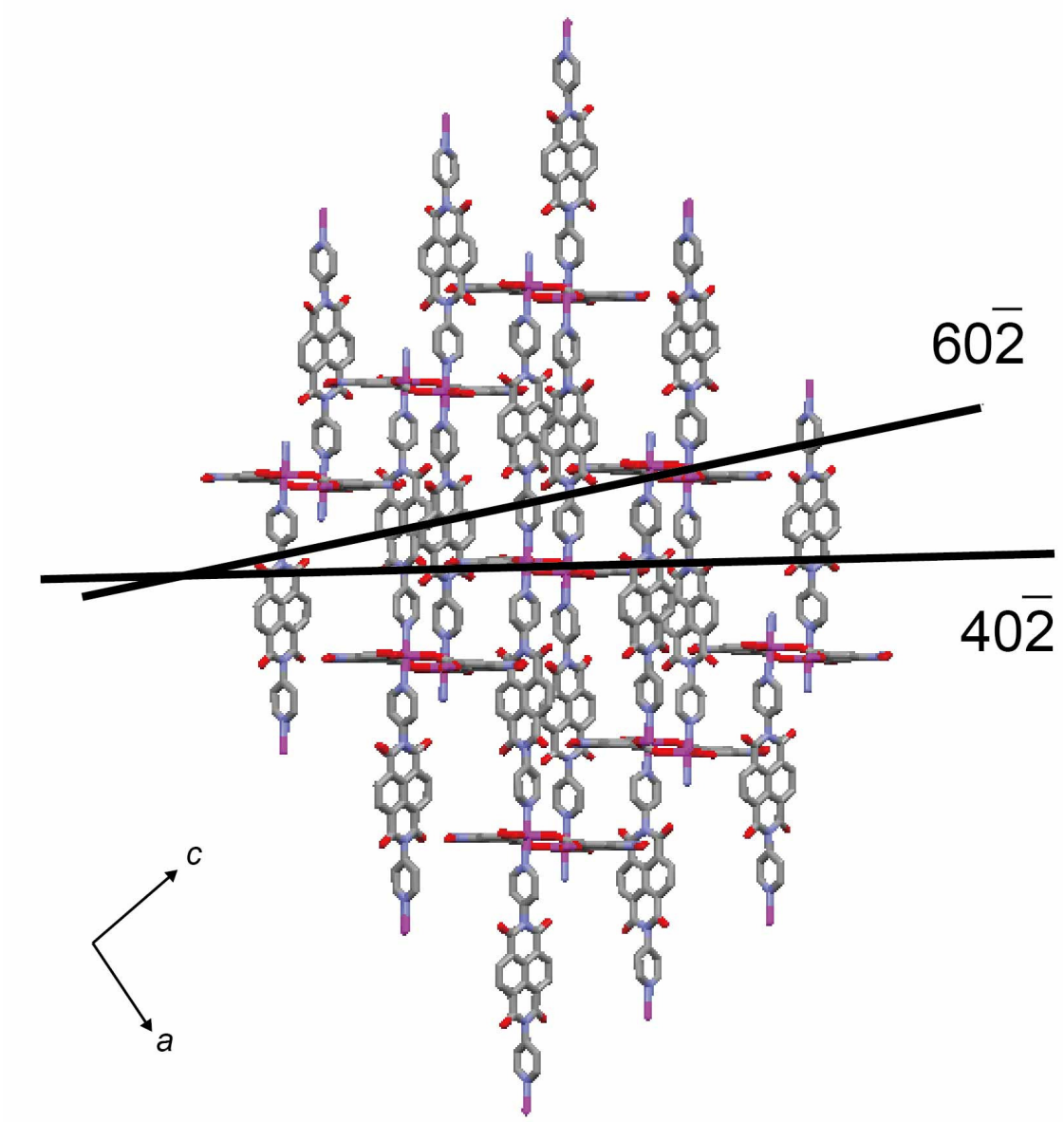

Fig. S2 The crystal structures of **1**. The diffraction plane of (40-2) is perpendicular and (60-2) is slightly inclined against the direction of dpndi.

S4. Crystal structure of as-synthesized 2

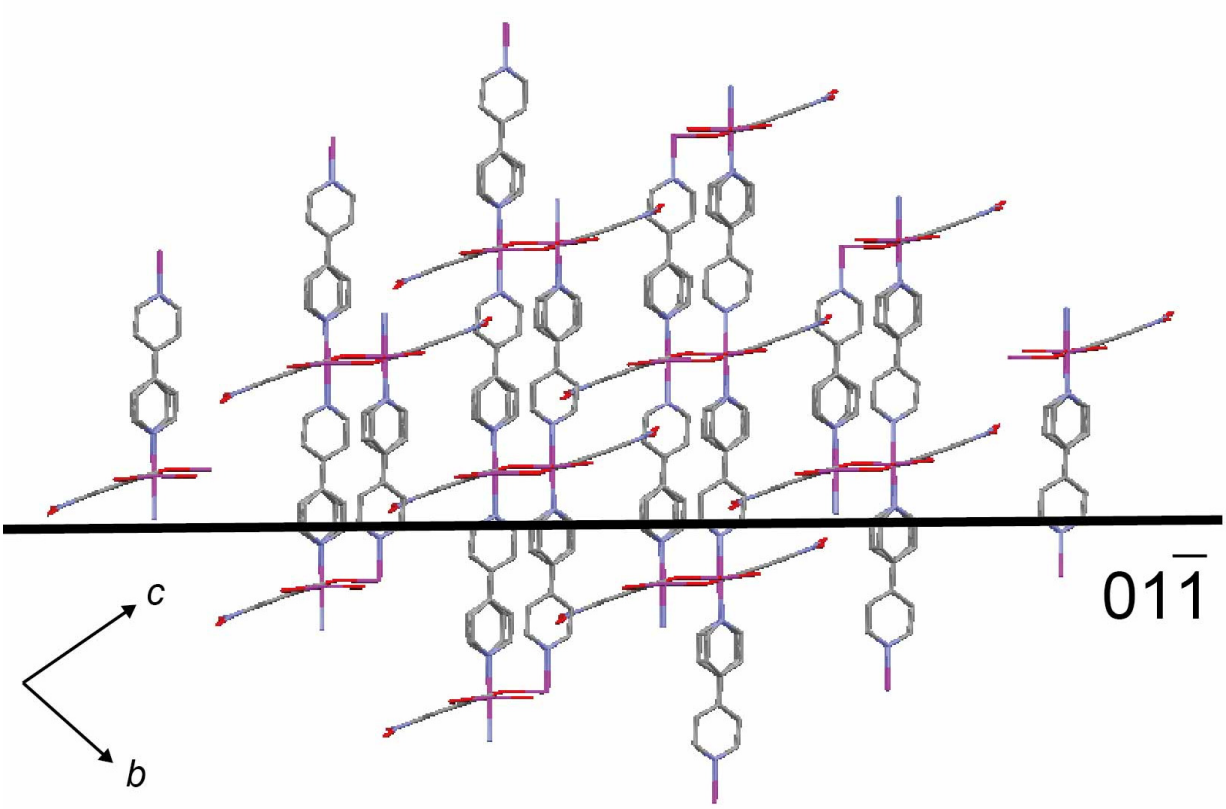

Fig. S3 The crystal structures of as-synthesized **2**. The diffraction plane of (01-1) is perpendicular to the direction of bpy.

S5. NMR

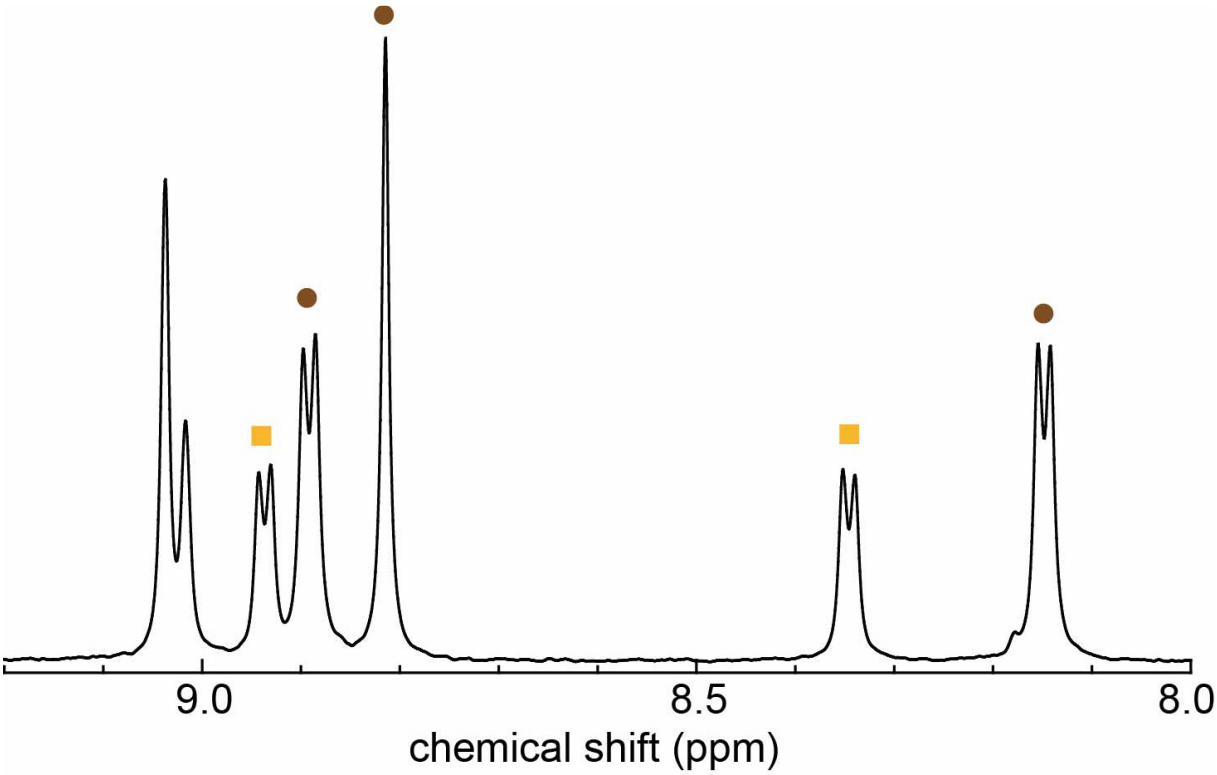

Fig. S4 ^{1}H-NMR spectra of **C-1/2**. Brown circles and yellow squares are assigned to dpndi and bpy, respectively. The molar ratio of dpndi and bpy is 0.65 : 0.35.

S6. TGA of 1

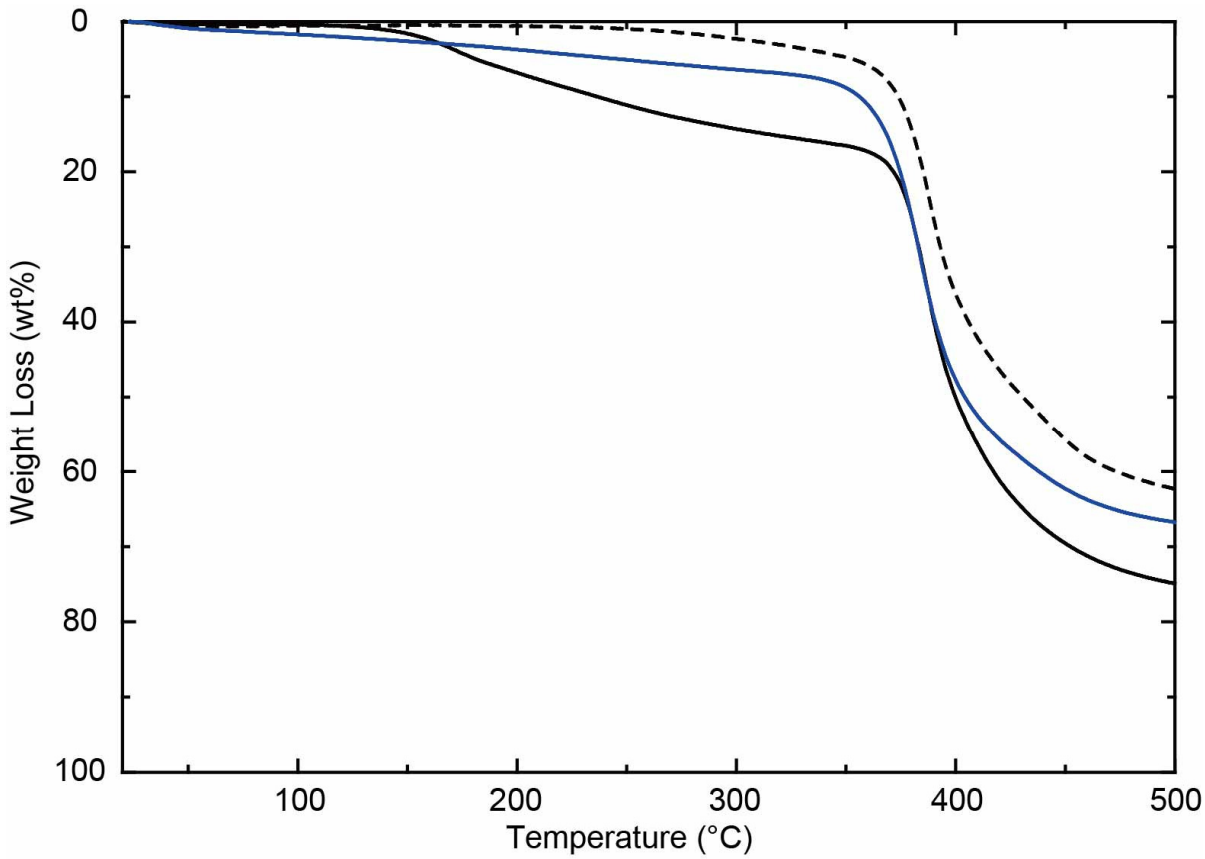

Fig. S5 TG analysis showing the weight loss in degassed **1**, as-synthesized **1** and **1** soaked in idopropane. Black dot line, black line and blue line are degassed **1**, as-synthesized **1** and **1** soaked in idopropane, respectively.

S7. TGA of 2

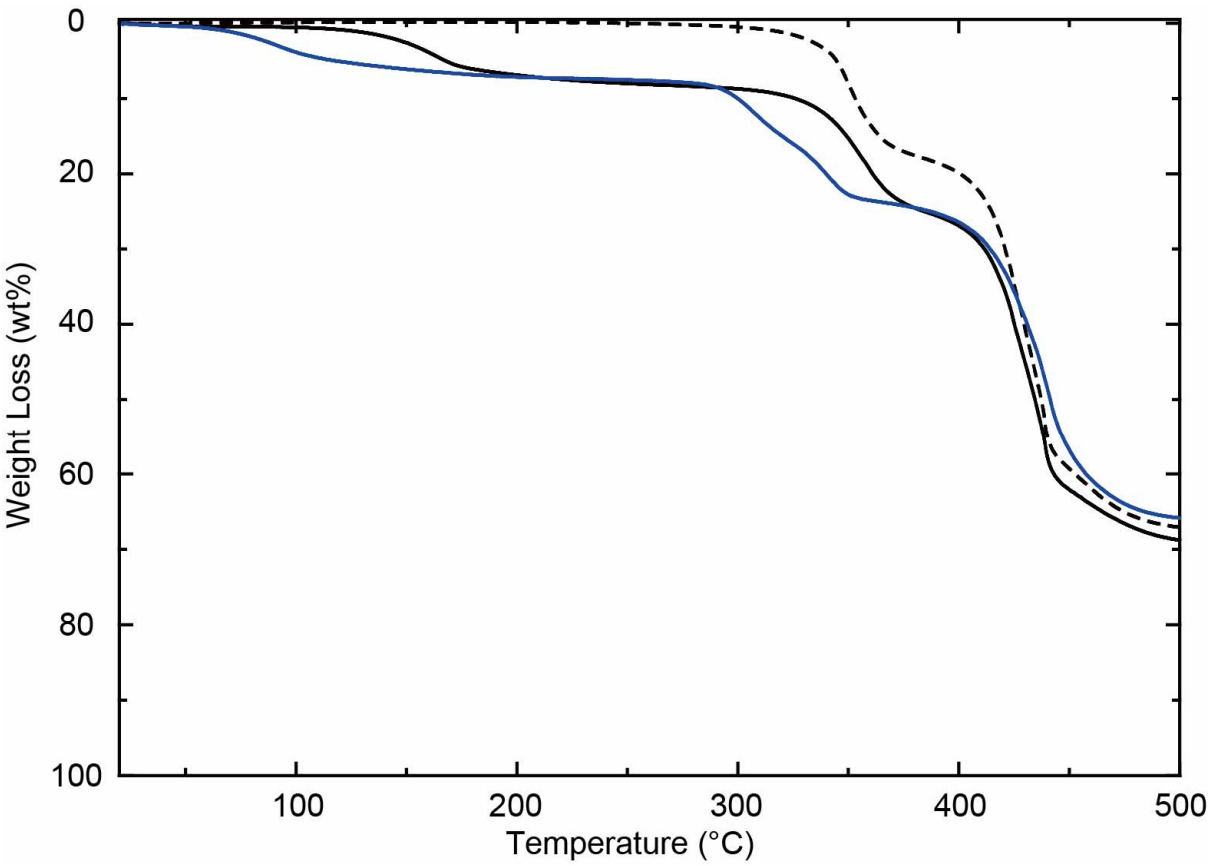

Fig. S6 TG analysis showing the weight loss in degassed **2**, as-synthesized **2** and **2** soaked in idopropane. Black dot line, black line and blue line are degassed **2**, as-synthesized **2** and **2** soaked in idopropane, respectively.

S8. TGA of C-1/2

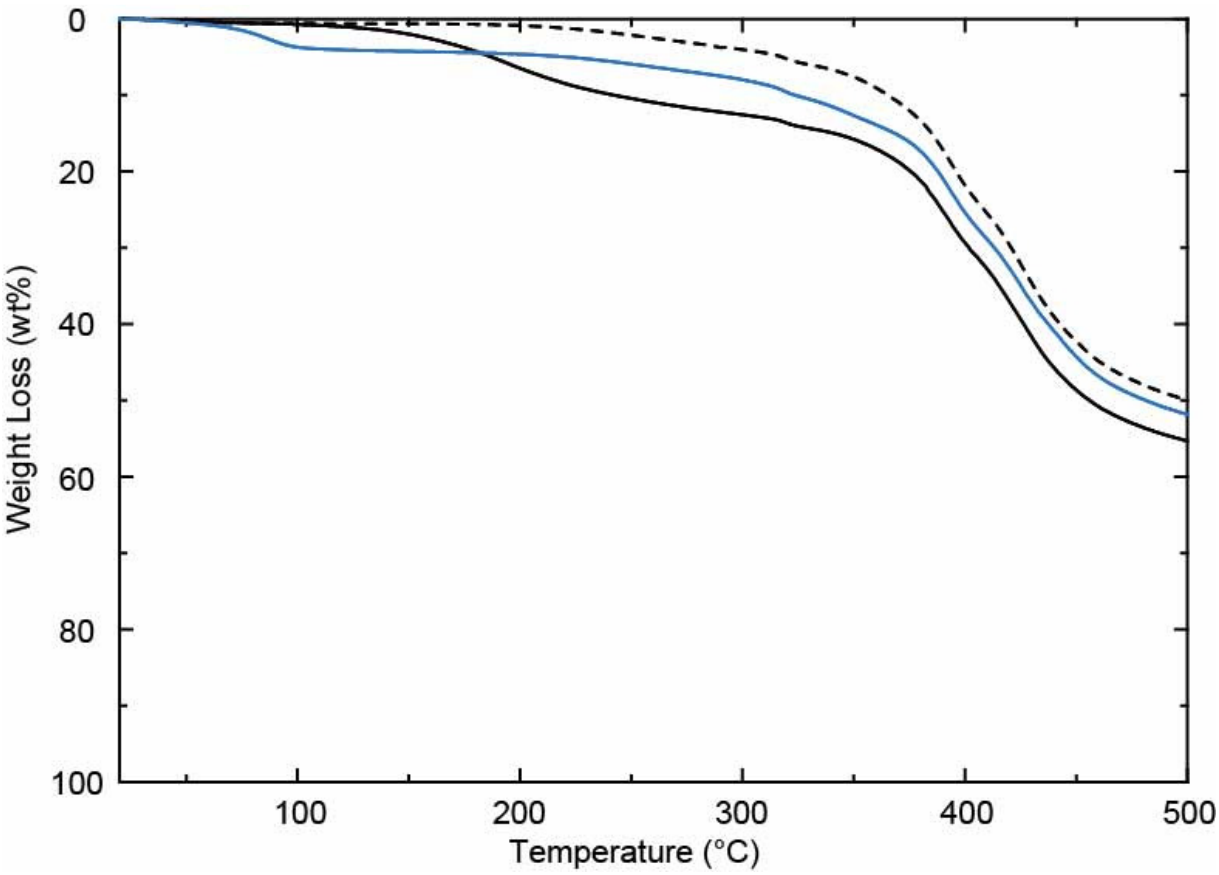

Fig. S7 TG analysis showing the weight loss in degassed **C-1/2**, as-synthesized **C-1/2** and **C-1/2** soaked in idopropane. Black dot line, black line and blue line are degassed **C-1/2**, as-synthesized **C-1/2** and **C-1/2** soaked in idopropane, respectively.

S9. SEM-EDX Spectrum of 1

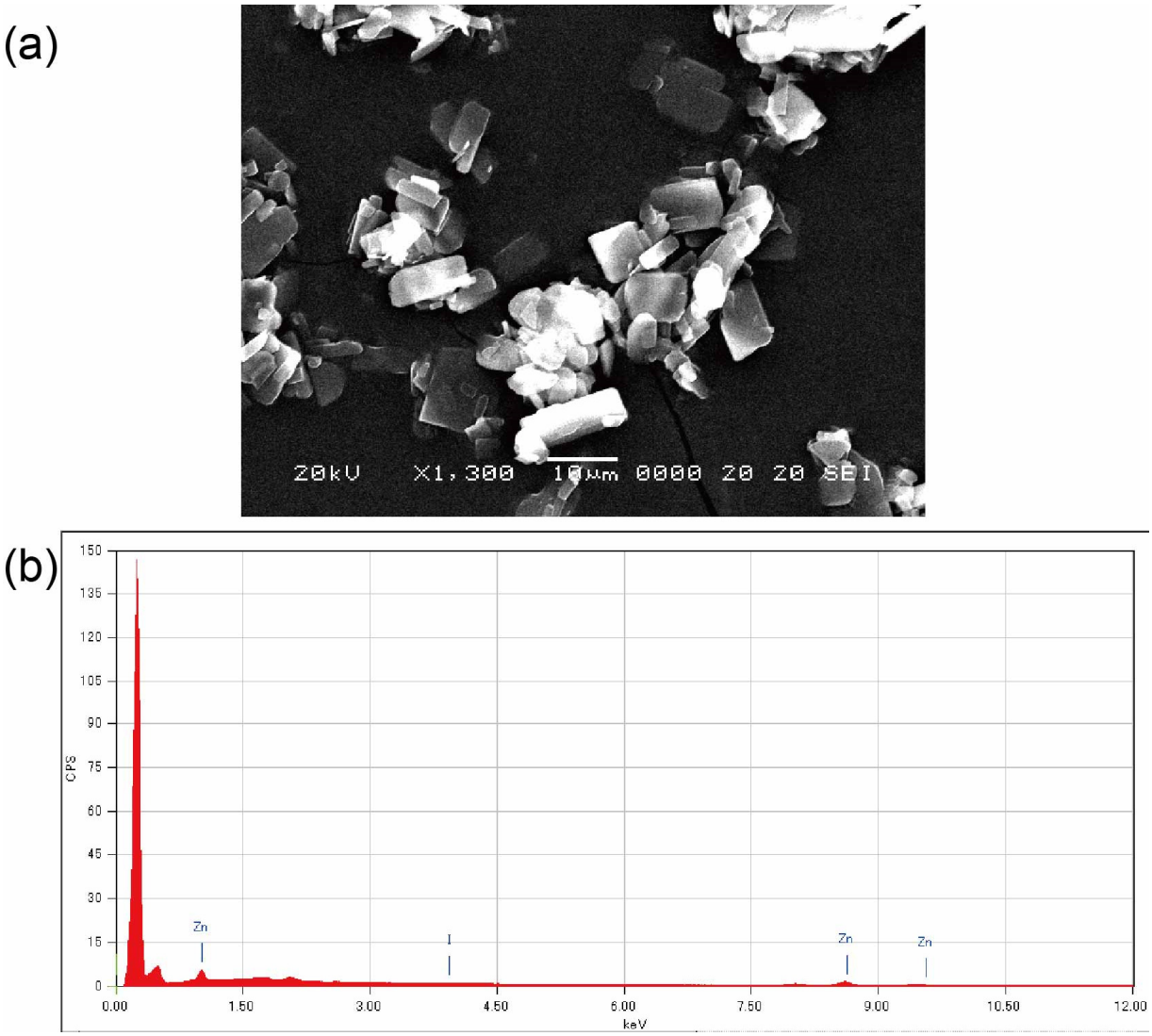

Fig. S8 (a) The SEM image of **1** soaked in iodopropane, and (b) EDX spectrum of **1** soaked in iodopropane. The iodine was not detected.

S10. SEM-EDX Spectrum of 2

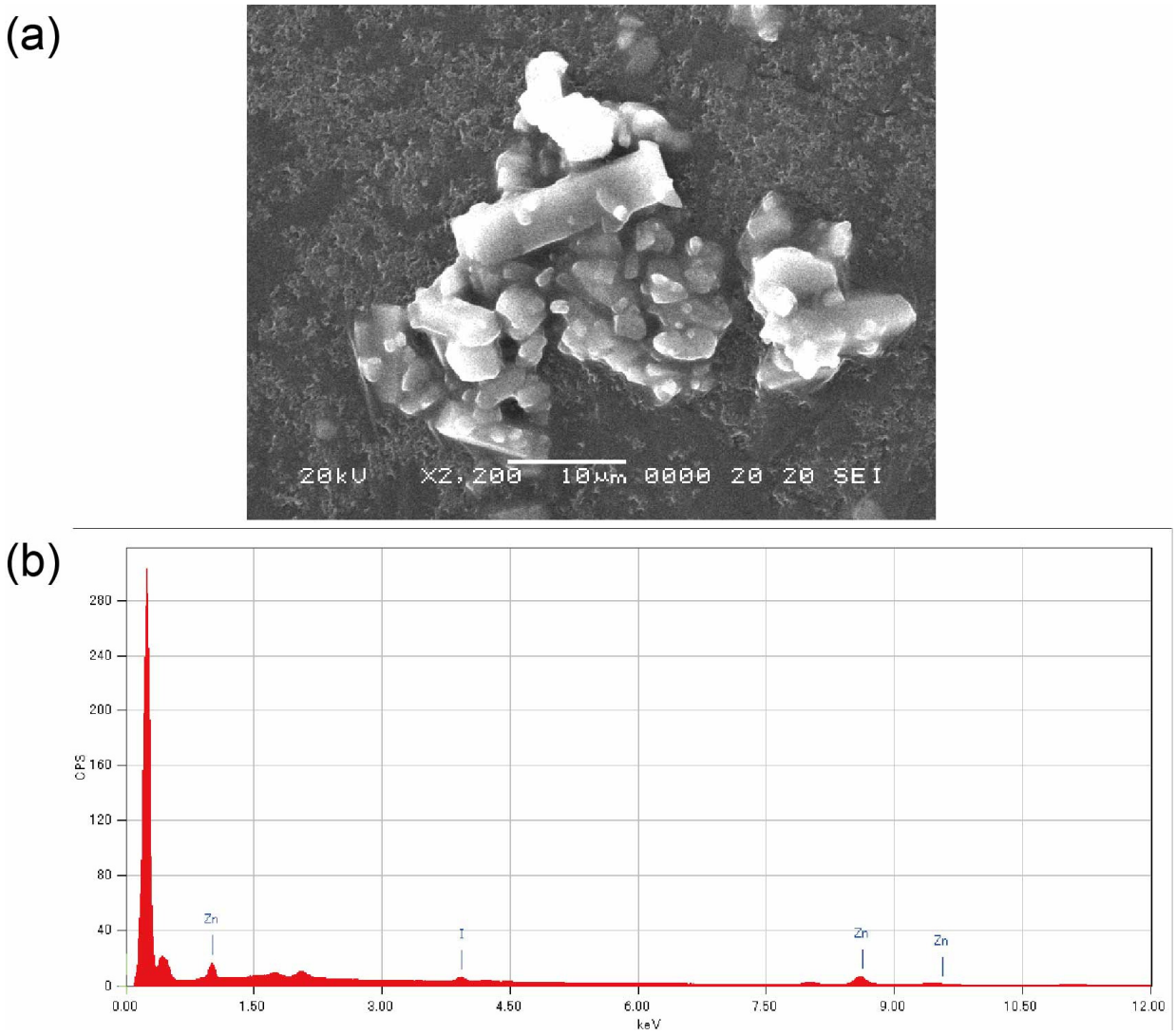

Fig. S9 (a) The SEM image of **2** soaked in iodopropane, and (b) EDX spectrum of **2** soaked in iodopropane. The iodine was detected around 4.00 keV.

S11. SEM-EDX of ioropropane accommodated 2

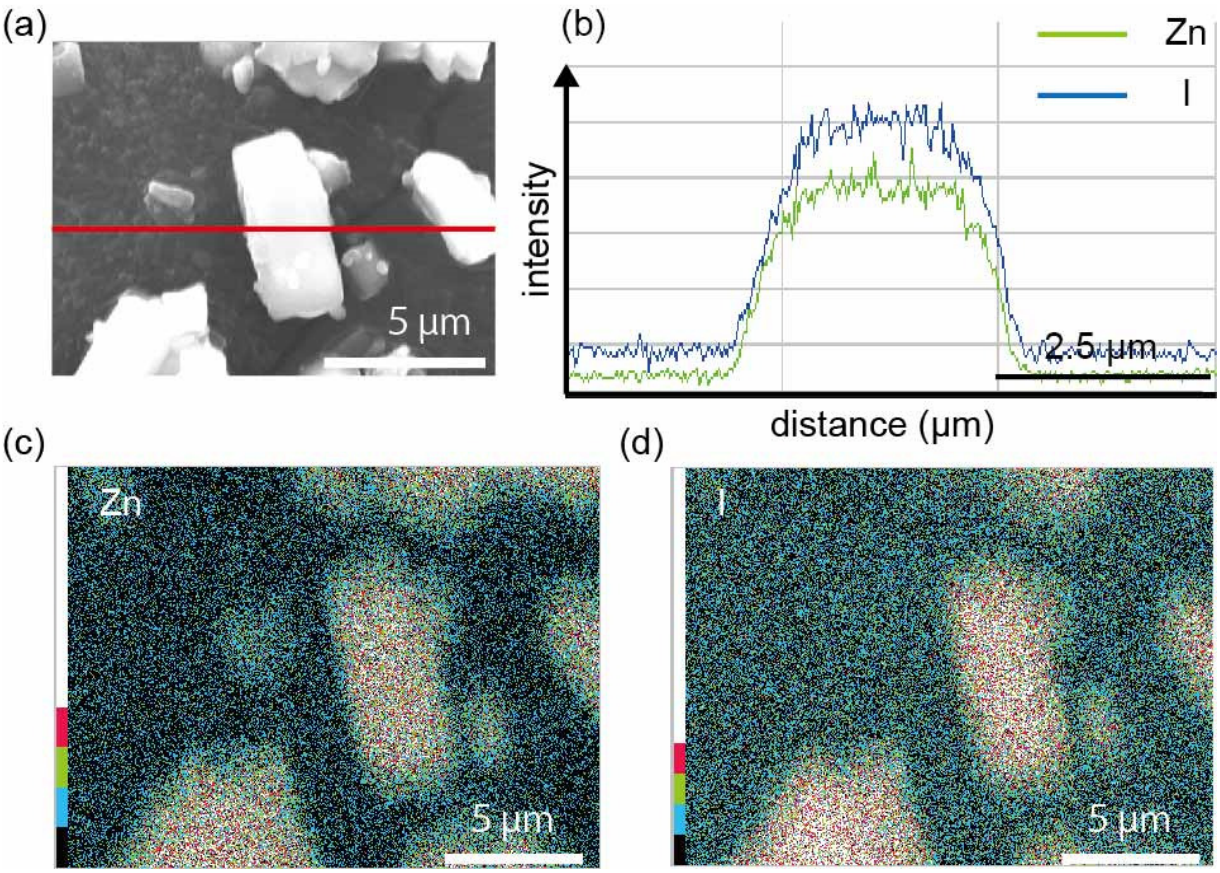

Fig. S10 (a) SEM image of crystals of CID-5 (**2**). The red line indicates the measurement line of EDX, (g) Line profile for intensity of Zn and I, (h) mapped intensity of Zn, and (i) I.

S12. Adsorption isotherms of 1

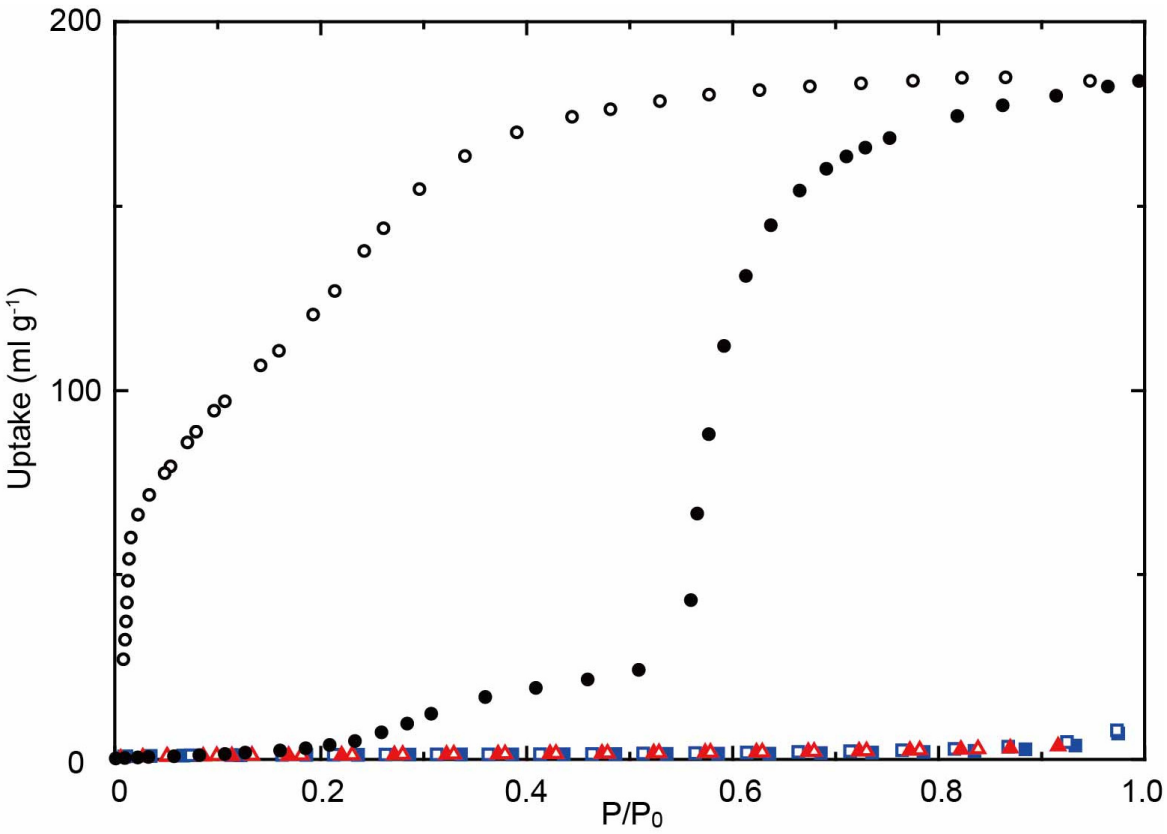

Fig. S11 Adsorption isotherms of gas molecules of CO_2 (black circle), N_2 (blue square) and O_2 (red triangle) for **1**. Closed and open symbols show adsorption and desorption, respectively.

S13. Adsorption isotherms of 2

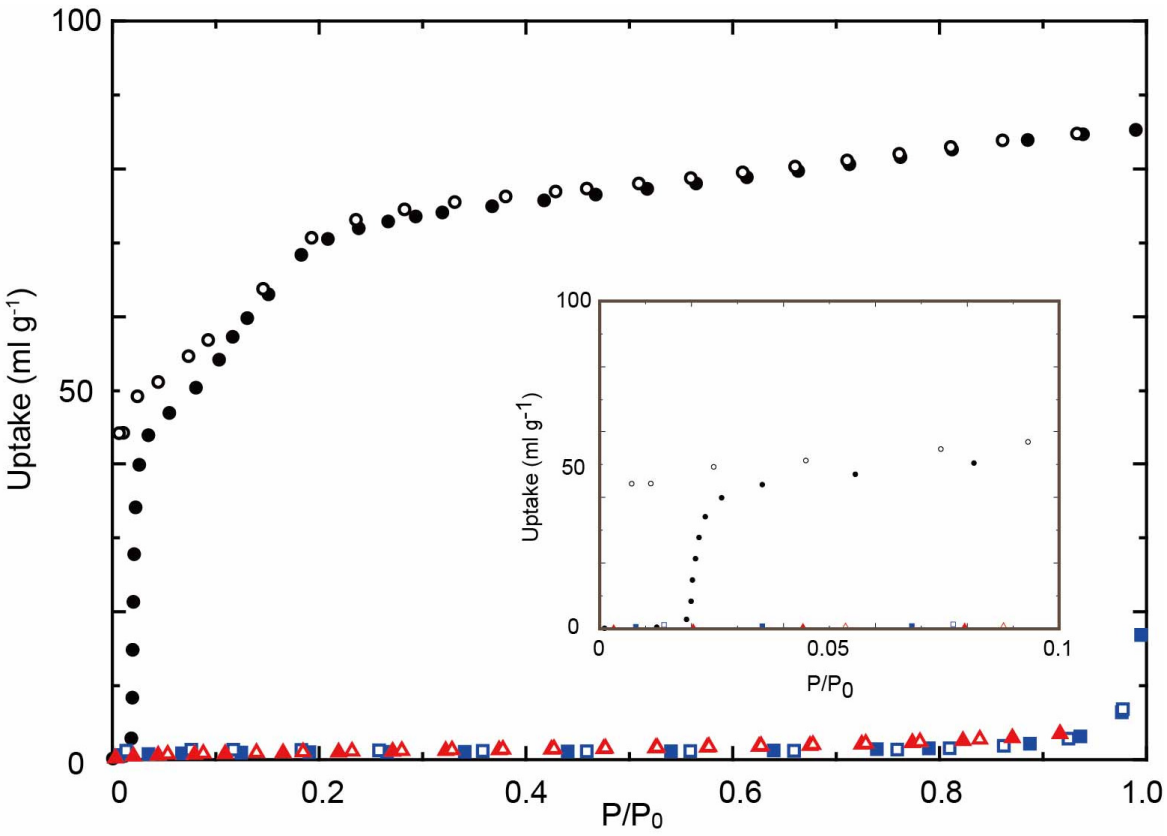

Fig. S12 Adsorption isotherms of gas molecules of CO_2 (black circle), N_2 (blue square) and O_2 (red triangle) for **2**. Closed and open symbols show adsorption and desorption, respectively. The inset graph is the closed-up of low pressure region ($P/P_0 \leq 0.1$)

S14. PXRD of 1, 2 and C-1/2

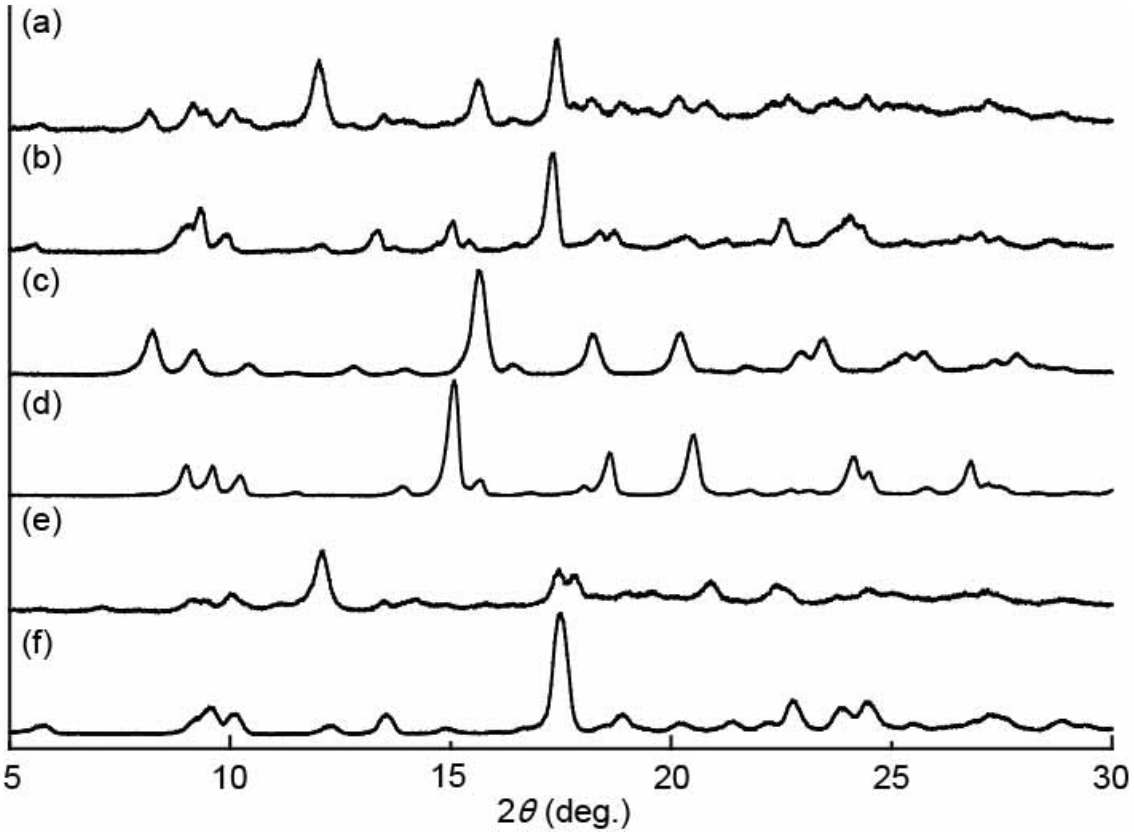

Fig. S13 Powder X-ray diffraction patterns of (a) degassed **C-1/2**, (b) as-synthesized **C-1/2**, (c) degassed **2**, (d) as-synthesized **2**, (e) degassed **1**, and (f) as-synthesized **1**.

S15. Reference

S1 P. H. Dinolfo, M. E. Williams, C. L. Stern, J. T. Hupp, *J. Am. Chem. Soc.*, 2004, **126**, 12989.