Supplementary Information

A block PCP crystal: anisotropic hybridization of porous coordination polymers by face-selective epitaxial growth

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1. Experimental Section

**Materials and Reagents.** All the syntheses were performed at ambient condition. Dehydrated DMF, 1,4-naphthalene dicarboxylic acid (ndc), and Zn(NO$_3$)$_2$·6H$_2$O were purchased from Wako Pure Chemical Industries. 1,4-diazabicyclo[2,2,2]octane (dabco) was purchased from TCI. All chemicals were used without further purification. The syntheses of $N,N'$-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide (dpndi)$_2$ and [Zn$_2$(ndc)$_2$(dabco)] (1)$_2$ were prepared according to literature procedures.

**Synthesis of 2 ⊃ Solvents.** The solution of Zn(NO$_3$)$_2$·6H$_2$O (6.1 mg, 0.020 mmol), ndc (4.4 mg, 0.020 mmol), and dpndi (4.2 mg, 0.010 mmol) in 4 mL DMF were heated up to 373 K for 2 days. After cooling, the reaction solution was left at room temperature for a few days. The orange crystals were harvested. Elemental analysis calc'd. for C$_{73.5}$H$_{83.5}$N$_{12.5}$O$_{20.5}$Zn$_2${[Zn$_2$(ndc)$_2$(dpndi)]·8.5DMF}$_n$: C, 55.15; H, 5.26; N, 10.99, Found: C, 54.95; H, 5.25; N, 11.15.

**Synthesis of hybridized crystal, 1/2.** Dozens of the core crystals (the size about $200 \times 300 \times 300$ mm$^3$) of 1, were put into 4 mL of the reaction solution for 2 as Zn(NO$_3$)$_2$·6H$_2$O (6.1 mg, 0.020 mmol), ndc (4.4 mg, 0.020 mmol), and ndi (4.2 mg, 0.010 mmol) in 4 mL DMF, then, the reaction mixture was heated up to 353 K for 2 days. After cooling, the reaction solution was left at room temperature. The two-color (colorless and orange) hybridized crystals (1/2) were obtained.

**Physical Measurements.** Infrared spectra were measured by a FT/IR 6100 with an infrared microscope IRT-5000 (JASCO). The attenuated total reflection attachment (ATR) was used for the measurement. Elemental analysis was carried out with a Thermo Finnigan EA1112.

**Single crystal X-ray crystallographic analysis.** The single crystal of 2 ⊃ DMF was mounted in glass capillary. X-ray data collection ($6.4 < 2\theta < 55^\circ$) was conducted at 223K on Rigaku AFC10 diffractometer Mo–Kα radiation ($\lambda = 0.7105$ Å) with Rigaku Saturn CCD system. The structures were solved by a direct method (SHELXL) and expanded using Fourier techniques. All calculations were performed using the crystal clear crystallographic
software package 3.8 of Rigaku. The crystallizing solvents (DMF 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 of ndc severely disordered and could not be satisfactorily localized. Hydrogen atoms except for those of ndc, were added at their geometrically ideal positions and refined isotropically. Crystal data for 2·8.5DMF: C₄₈H₂₄N₄O₁₂Zn₂, tetragonal, space group P4/mmm, (no. 123), a = 10.906 (2) Å, c = 22.456 (4) Å, V = 2670.8 (9) Å³, Z = 1, T = 223 K. ρ(calc) = 0.609 gcm⁻³, μ(MoKα) = 0.478 cm⁻¹, 1839 reflections measured, 1325 observed (I > 2.00σ(I)) 99 parameters; R₁ = 0.0916, wR₂ = 0.0748, GOF = 0.912.

**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, 1/2, was picked up just before the measurement, and then fixed on the glass substrate with the orientation where orange part of 1/2 was parallel to the glass substrate by double-faced adhesive. The measurement was carried out under Helium gas condition. In this condition, guest DMF molecules were most likely accommodated in pores of the PCP crystal.

The θ-2θ scan at the initial position (χ = 90⁰) was carried out to determine the orientation of hybridized crystals. Only 00l Bragg peaks of from both 1 and 2 were observed. The 00l Bragg peaks simultaneously observed from 1 and 2 in the same scan suggest that the epitaxial growth of 2 occurs at (001) surfaces of 1. The angles of φ, χ, θ and 2θ were moved to a desired Bragg position where diffractions were recorded. A scan of the rotation angle around the [001] direction (the φ scan) at the 101 and 011 Bragg position from 1 gave two sharp peaks assigned to the 110 and 110 Bragg peaks. In the same way, two peaks at the same φ angles as 1 were observed, and assigned to the 101 and 110 Bragg position of 2. This result indicates that the (001) surface of 2 perfectly matches to the (001) surfaces of 1 at the crystal-crystal interfaces.
2. Crystal Structure of 2 ⊃ DMF

Whereas four surfaces of rectangular prism crystals of 2 ⊃ DMF denoted as the (100) surface have a rectangular lattice composed of ndc and dpndi, the (001) surface with a square lattice based on only ndc appeared on the remaining two surfaces.

Fig. S1. a) A view from the [001] direction and b) from the [100] direction of 2. The naphthalene moieties of ndc, and dpndi itself were disordered due to the symmetry operation.
3. Thermogravimetric data of 2 ⊃ DMF

Thermogravimetric (TG) analysis were performed using a Rigaku Thermo plus TG 8120 apparatus in the temperature range between 298 and 773 K in a N\textsubscript{2} atmosphere and at a heating rate of 10 Kmin\textsuperscript{-1}. The first weight loss corresponded to the loss of 8.5 DMF molecules from the 2 ⊃ DMF.

Fig. S2 TG analysis showing the weight loss in 2 ⊃ DMF. The observed weight loss (39.7\%) corresponds to the weight of 8.5 DMF molecules (calcd: 38.8\%).

Reference: