Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary information

Targeted functionalisation of a hierarchically-structured porous coordination polymer crystal enhances its entire function

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Contents

S1. Experimental section

Materials

$Zn(NO_3)_2•6H_2O$, 2-amino-1,4-benzenedicarboxylic acid (H_2abdc), 1,4-diaza[2.2.2]bicyclooctane (dabco), succinic anhydride, *N,N'*-dimethylformamide (DMF), methanol (MeOH), *N,N'*-dimethylaniline and benzene were purchased from Wako Pure Chemical Industries. 9,10-anthracene dicarboxylic acid (adc) was prepared according to the literature procedures.[S1]

Synthesis of 1

The solution of $Zn(NO_3)_2•6H_2O$ (125 mg, 0.420 mmol), H_2adc (110 mg, 0.414 mmol), and dabco (23.8 mg, 0.213 mmol) in 25 mL DMF/MeOH (DMF : MeOH = 1 : 1) was stirred for several hours. After the white tiny crystals were removed by filtration, the transparent solution was diluted four times with DMF/MeOH. The solution was heated up to 333 K for 2 days. After cooling, the crystals were harvested.

Synthesis of hybrid crystal, 1/2

The solution of $Zn(NO_3)_2•6H_2O$ (104 mg, 0.35 mmol), H_2abdc (73 mg, 0.40 mmol), and dabco (72 mg, 0.64 mmol) in 10 mL DMF was stirred for several hours. After the white precipitates were removed by filtration, the dozens of well-dispersed single crystals of **1** were put into the solution. The solution was heated up to 333 K for 4 days. After cooling, the crystals were harvested.

Post-synthetic modification of 1/2

Post-synthetic modification was performed according to the literature procedures.[S2] Dozens of the core/shell crystal (**1/2**) was put in a container with succnic anhydride dissolved in $CHCl_3$. After the sample was allowed to stand for two days, the crystals were washed with $CHCl_3$ then soaked in pure $CHCl_3$ for three days, with fresh $CHCl_3$ added every day. After the soaking, the crystals were stored in the last $CHCl_3$ solution until being analyzed.

Synthesis of single crystal of 2

The solution of dabco (0.56 mg, 0.005 mmol) dissolved in 2 mL toluene was slowly layered on the solution of $Zn(NO_3)_2•6H_2O$ (2.98 mg, 0.01 mmol) and H_2abdc (1.82 mg, 0.01 mmol) dissolved in 2 mL DMF, where a mixture of DMF/toluene (1:1) was placed between two layered solutions. The brown cuboid crystals suitable for single crystal X-ray analysis were obtained after three month. Elemental analysis calcd. for $C_{31}H_{47}N_7O_{11}Zn$ $\{[Zn(abdc)(dabco)]\cdot(DMF)_3\}_n$: C, 45.16; H, 5.746; N, 11.89, Found: C, 44.86; H, 5.47; N, 11.97.

Characterization methods

The compounds were characterized with X-ray diffraction (XRD), microscopic laser Raman spectroscopy, synchrotron XRD, thermogravimetry (TG) and elemental analysis. Powder X-Ray diffraction (XRD) studies were performed using a Rigaku diffractometer with Cu Kα radiation (λ = 1.5418 A°). 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.

Physical measurements

The fluorescence images and spectra were obtained by a FV1000 microscope (Olympus). The fluorescent images were obtained by a FV1000 microscope (Olympus) with a semiconductor laser at 405 nm and fluorescent emission was collected in the 500-550 nm range. Gas chromatography-mass spectrometry (GC-MS) was performed using a SHIMADZU QP2010. IR measurement was performed by Thermo Scientifi Nicolet iS5 FT-IR.

Structural determination of 2 ⊃solvent

X-ray data collection ($5^{o} < 2\theta < 55^{o}$) 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 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. Crystal data for **2⊃solvent**: $C_{31}H_{47}N_7O_{11}Zn$, tetragonal, space group *P4/mmm*, (no. 123), a = 10.9681(9) Å, c = 9.7190(10) Å, V = 1169.19(19) Å^3, Z = 1, T = 223 K. ρ_{calcd} = 0.854 gcm^{-3}, $\mu(MoK_{\alpha})$ = 1.054 cm^{-1}, 1147 reflections measured, 923 observed ($I > 2.00\sigma(I)$ 42 parameters; R_1 = 0.0815, wR_2 = 0.3022, GOF = 1.177. 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: 867374)

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/p2**, was picked up just before the measurement, and then fixed on the glass substrate with the orientation where orange part of **1/p2** was parallel to the glass substrate by double-faced adhesive. The measurement was carried out under Helium gas condition.

S2. Crystal structure of 2

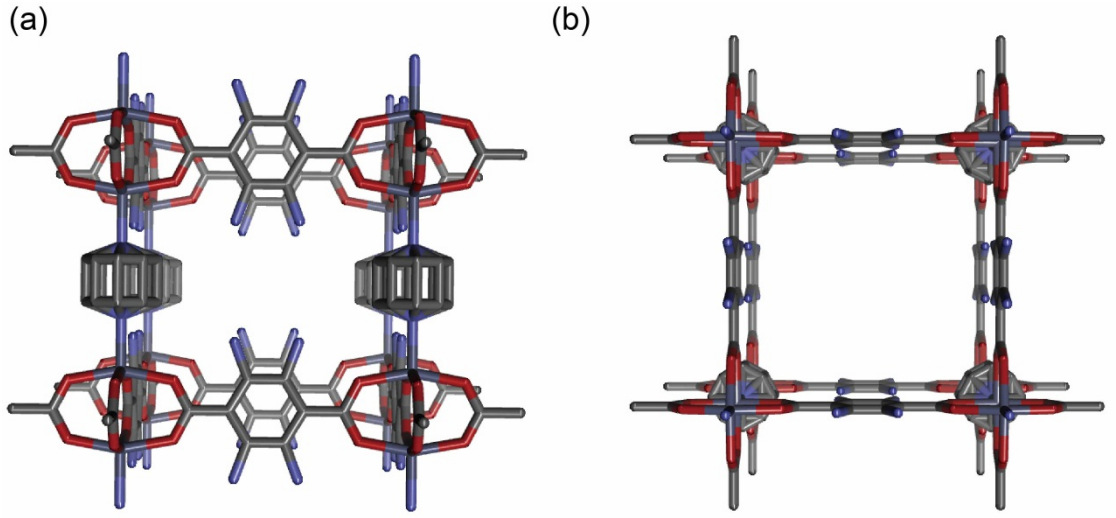

Fig. S1 a) A view from the [100] direction, b) from the [001] direction of **2**. The dabco and abdc were disordered due to the symmetry operation. The hydrogen atoms are omitted for the clarity.

S3. ^{1}H-NMR

The PSM-modified core-shell PCP crystals were dried under vacuum condition and digested in the mixture of DMSO-d_6 and HCl.

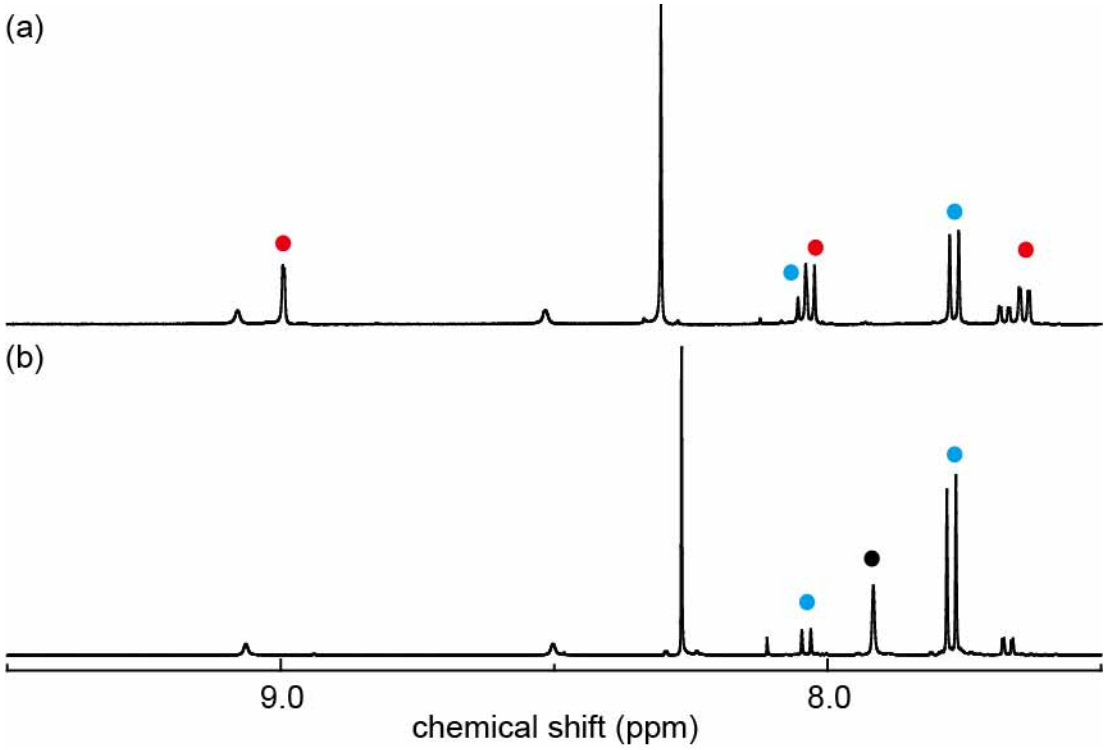

Fig. S2 ^{1}H-NMR spectra of a) **2** and b) **p2**. Red, blue and black circles are assigned to **p2**, **2** and DMF, respectively. The results suggest 52 % of NH_2-groups was reacted with succinic anhydride.

S4. Four-axis diffractometer

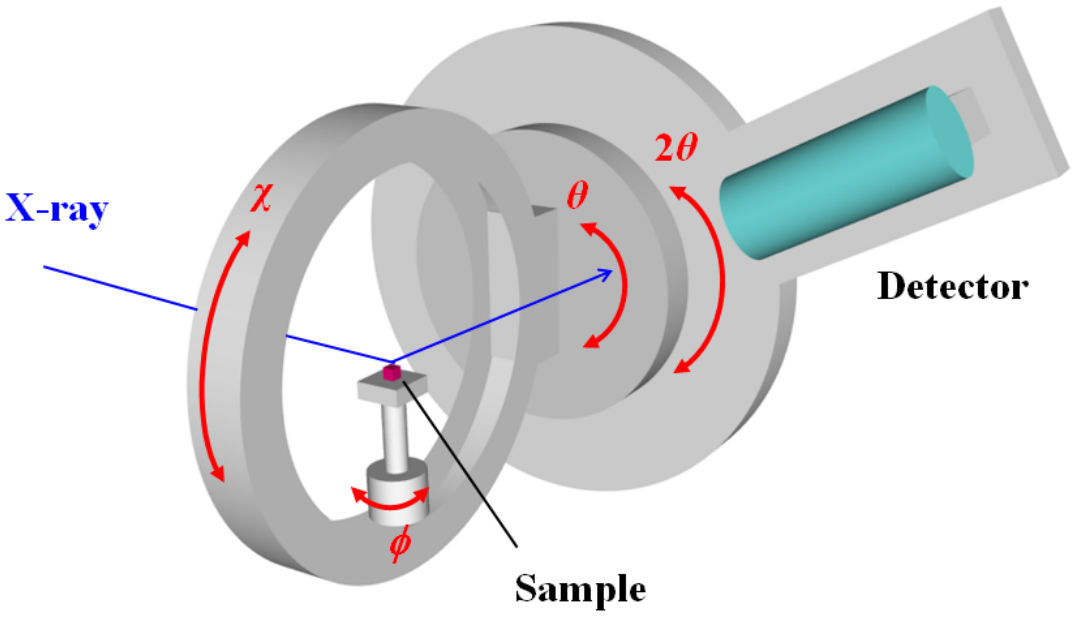

Fig. S3 The schematic drawing of the four-circle diffractometer at beamline BL13XU for surface and interface structures, SPring-8.

S5. Synchrotron surface XRD

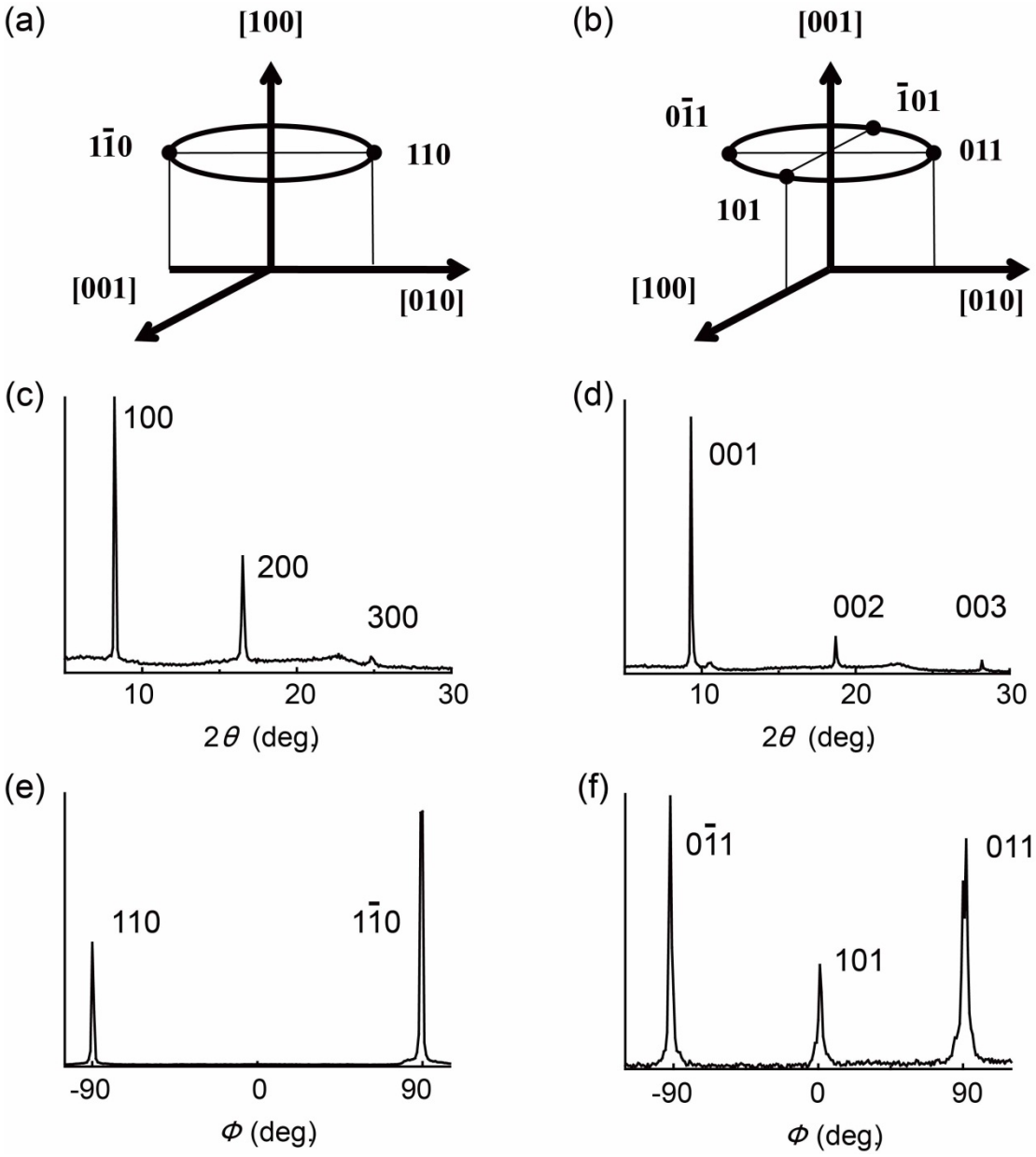

Fig. S4 The reciprocal lattice space corresponding to the rotational scan, a) around the [100] direction, and b) around the [001] direction. The θ-2θ scan of the core/shell crystal (**1**/**p2**) on the glass substrate at the initial position (χ = 90º), c) with the *a* axis orientation, and d) with the *c* axis orientation. The scan of the rotation angle, e) around the [100] direction (the ϕ scan), and f) around the [001] direction.

S6. ATR-IR

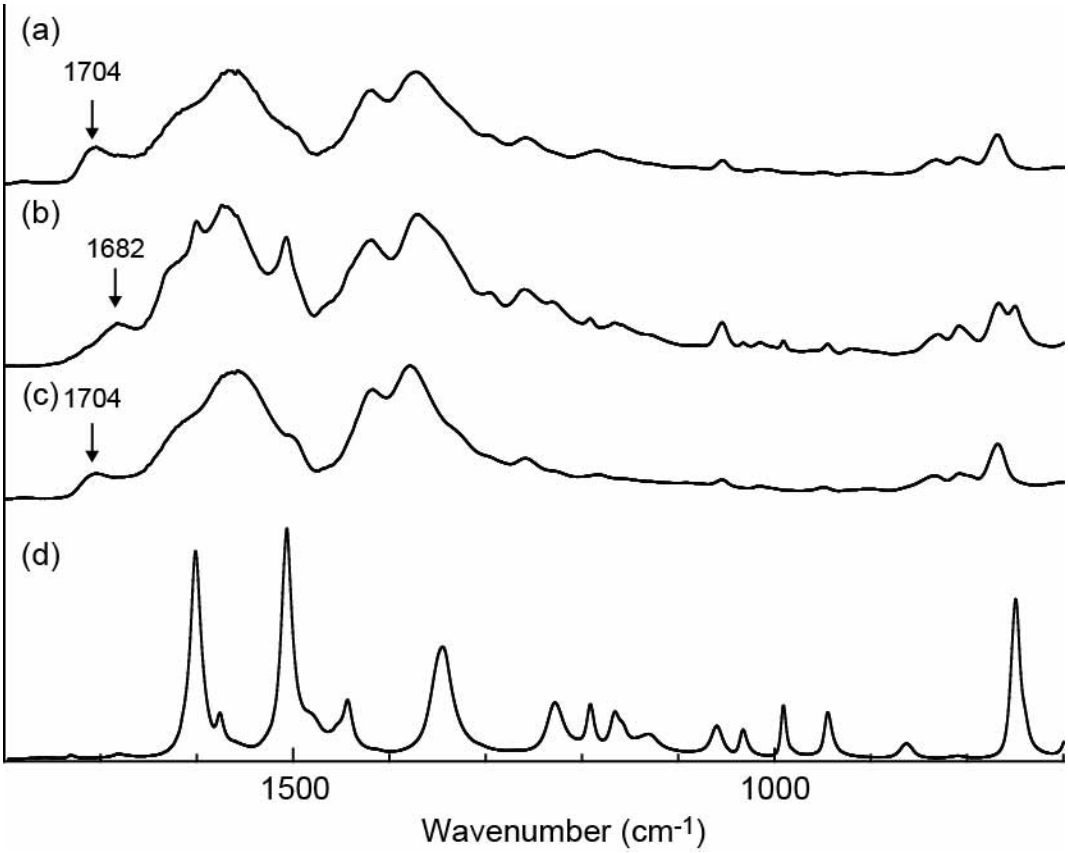

Fig. S5 (a) Attenuated total reflection IR spectra of **p2** with benzene, (b) with DMA, (c) degassed **p2**, (d) DMA. Blue shift of CO vibration in free COOH group was observed in **p2** with DMA.

S7. Microscopic laser Raman spectroscopy

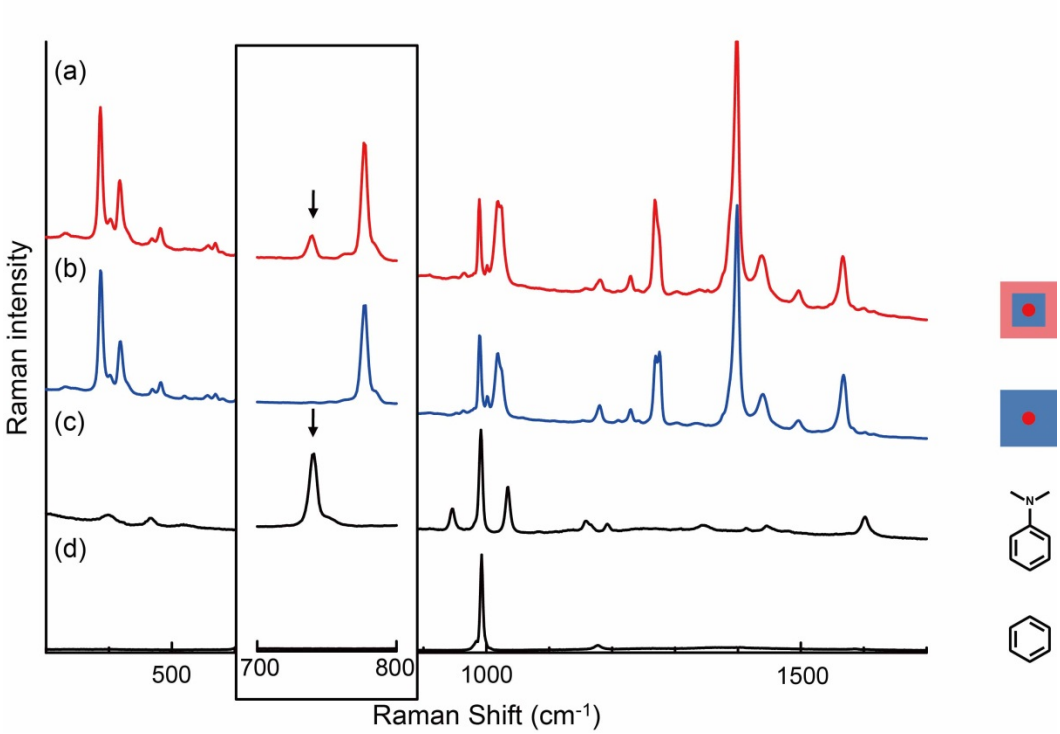

Fig. S6 The Raman spectra obtained from (a) the core part of **1/p2**, (b) **1** immersed in the mixture, (c) DMA and (d) benzene. The red points in the core/shell crystal of indicates the point at which the Raman laser is focused. The arrows indicate the characteristic Raman signal of DMA.

Reference

S1 S. Jones, C. J. Atherton, R. J. M. Elsegood and W. Clegg, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **2000**, *56*, 881.

S2 S. J. Garibay, Z. Wang, K. K. Tanabe and S. M. Cohen, *Inorg. Chem.*, **2009**, *48*, 7341.