Supporting Information

Step-by-Step Fabrication of a Highly Oriented Crystalline Three-Dimensional Pillared-Layer-Type Metal–Organic Framework Thin Film Confirmed by Synchrotron X-ray Diffraction

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1. Materials and Methods

General. All of the reagents were purchased from Wako Pure Chemical Industries Ltd., TCI Co., Ltd., Alfa Aesar Co, and Sigma-Aldrich Chemical Co., and used without further purification. The substrates for all the measurements were prepared by evaporating a 5 nm chromium buffer followed by 100 nm of gold onto polished silicon wafers (Au/Cr/Si, purchased from Nilaco Corp.). Typical substrate size was $20 \times 15 \times 0.5$ mm^3. Before thin-film preparation, H_2-annealing was performed on the substrate. Infrared reflection absorption spectra (IRRAS) were collected with a Thermo Nicolet NEXUS 670 FT-IR spectrometer and Thermo Scientific Spectra-Tech Collector diffuse reflectance accessory (incident angle = 80°). Raman spectra were recorded with a JASCO NRS-1000 using a microscope. A Showa Optronics JUNO 532-100S Nd:YAG laser provided the exciting line (532 nm). Synchrotron X-ray diffraction (XRD) measurements under constant He flow were performed using a multi-axis diffractometer (Kohzu-Seiki TDT-17) with a NaI scintillation detector installed on the BL13XU beamline of SPring-8, Japan. The incident X-ray was monochromatized to 8 keV (λ = 1.555 Å) with a Si111 double-crystal monochromator. In-plane and out-of-plane XRD patterns were obtained with a 0.1° step. Out-of-plane XRD measurement was performed in a typical θ–2θ scattering geometry. Rocking curve (θ-scan mode) and azimuthal-angle dependence (ϕ-scan mode) measurements were performed at the 001 peak position in the out-of-plane geometry (see insets of Figures 3 and S2) with 0.1° and 1° steps, respectively. In the case of in-plane XRD (grazing-incidence mode), strong diffraction can be observed on the condition that the X-ray incident angle (α) to the sample is below a critical angle. Thus, incident-angle dependence measurement at the 110 peak position was performed before the in-plane XRD measurement, and the diffraction pattern was collected at α = 0.1°. A Soller slit (Huber 3030-I, 0.4°) was placed between the sample substrate and the scintillation detector to improve the signal/noise ratio of the diffraction. XRD pattern fittings shown in Figure 3 were performed using Topas program.[S1] Simulated XRD patterns shown in Figure 3 were obtained using the Mercury software package.[S2] In the case of *in situ* XRD measurements, the benzene vapor pressure was controlled and constantly introduced into sample cell made of kapton using a BEL-Flow apparatus (BEL-Japan). Atomic force microscopy (AFM) images were obtained in tapping mode using NanoScope IIIa equipment (Veeco Instruments) with a Si cantilever.

Film Preparation. The starting material, $[(C_4H_9)_4N]_2Pt(CN)_4$, was prepared by the cation-exchange reaction of $K_2Pt(CN)_4$ using $[(C_4H_9)_4N]ClO_4$ in methanol. $Fe(BF_4)_2{\cdot}6H_2O$, and pyrazine (pz) were used as purchased. First, the Au/Cr/Si substrate was soaked in an ethanol (EtOH) solution of 4-mercaptopyridine for a day. Functionalization of the self-assembled monolayer (SAM) was monitored by using a quarts crystal microbalance (QCM). After this treatment, the substrate was washed with EtOH and dried by N_2 flow. Next, this substrate was alternately soaked in EtOH solutions of $Fe(BF_4)_2{\cdot}6H_2O$ (100 mM), $[(C_4H_9)_4N]_2Pt(CN)_4$ (100 mM), pz (100 mM) in this order for 1 min. at 212 K (using chloroform/liq. N_2 mixture) for a total of 30 cycles. To avoid contamination of the different pillar ligand, we did not use 4,4′-azopyridine even upon the first five cycles; this procedure is different from the previous report.[12] The substrate was washed with EtOH with respect to each soaking. A bulk powder sample of $Fe(pz)[Pt(CN)_4]$ for comparison with film sample was prepared according to the literature method.[11a]

2. Figures S1 to S3

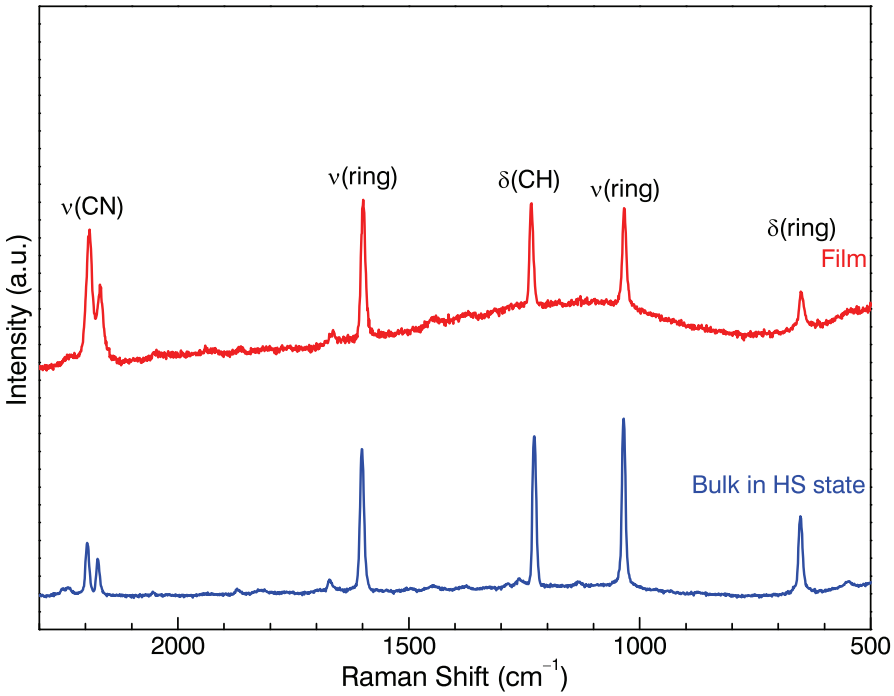

Figure S1. Raman spectra of thin film (red line) and bulk (blue line, HS state) samples of $Fe(pz)[Pt(CN)_4]$ at rt. Peak assignments are based on the previous report.[S3]

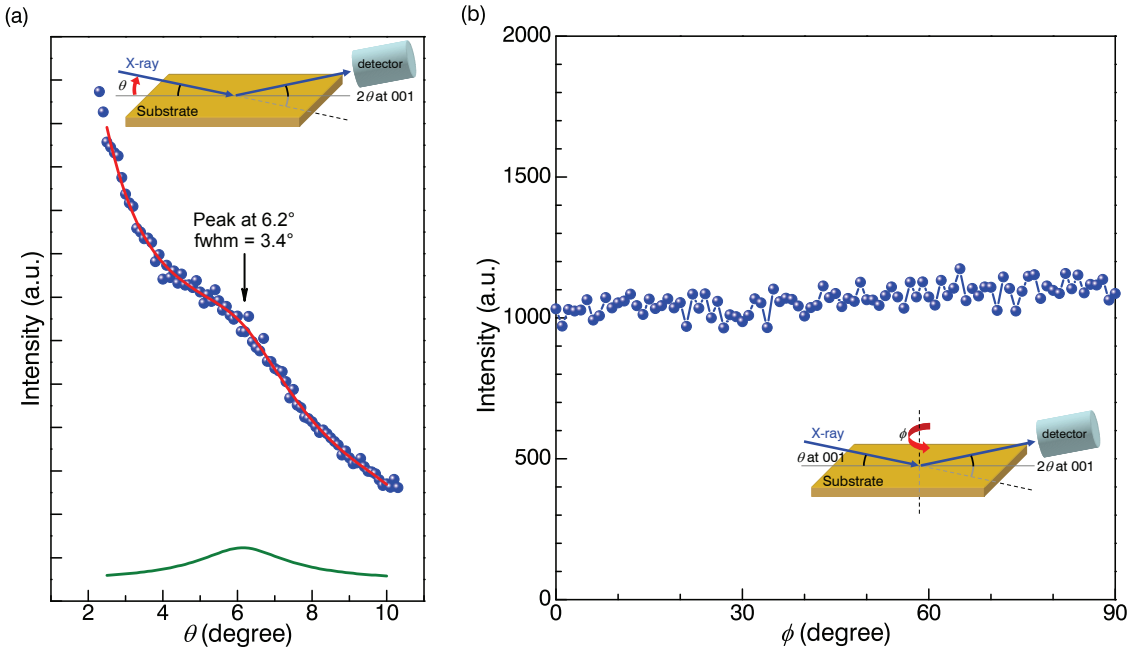

Figure S2. Rocking curve (a) and azimuthal-angle dependence (b) measurements at 001 position. Blue circles in each panel, and red and green lines in panel (a) denote experimental data, fitting result, and background subtracted fitting diffraction patterns, respectively. Inset figures in each panel show the scattering geometries of each XRD measurement.

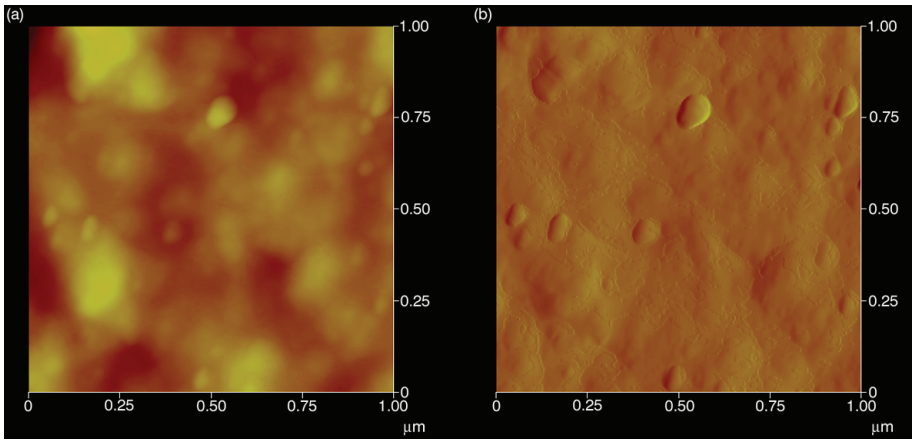

Figure S3. AFM images of thin-film sample of Fe(pz)[Pt(CN)$_4$] at rt. (a) Height image. (b) Amplitude image.

3. References

S1. Bruker AXS, *TOPAS V3*: General profile and structure analysis software for powder diffraction data, Bruker AXS, Karlsruhe, Germany, **2005**.

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