

Supplementary Information
Photochemical cycloaddition on the
pore surface of a porous coordination
polymer impacts on the sorption
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Supplementary Information for

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Materials:

Reagents and solvents were used as received from Tokyo Kasei Co. [5-methoxyisophthalic acid (H₂moip) (98%) and 1,2-bis(4-pyridyl)ethene (bpe) (98%)], Wako Pure Chemical Industries Ltd. [methanol (99.8%)], and Nacalai Tesque [zinc nitrate hexahydrate (99%), *N,N*-dimethylformamide (99.5%)].

Measurements:

¹H NMR spectra were recorded on a JEOL model JNM-ECS 400 spectrometer, operating at 399.8 MHz, using tetramethylsilane as an internal reference. The samples for ¹H NMR spectral measurements were digested in DMSO-*d*₆ containing a drop of conc. HCl. Thermogravimetric analyses were recorded on a Rigaku Thermo plus TG-8120 apparatus in the temperature range between 25 °C and 500 °C under a nitrogen atmosphere at a heating rate of 5 °C min⁻¹. Powder X-ray diffraction data were collected with a Bruker D8 Discovery with GADDS equipped with a sealed tube X-ray generator producing CuK_α radiation.

Gas adsorption measurement:

The sorption isotherm measurements for CO₂ were performed using an automatic volumetric adsorption apparatus (BELSORP-18PLUS; Bel Japan, Inc.) connected to a cryostat system. A known weight (~100 mg) of the as-synthesized PCP was placed on a copper plate, then, the sample was dried under high vacuum (below 10⁻² Pa) at 120 °C for 12 h to remove the solvated DMF molecules. The adsorbate was set on a cryostat system and heated under high vacuum (below 10⁻³ Pa) at 120 °C for 2 h prior to the measurements, then the temperature was set in the measurement temperature. The change of the pressure

was monitored and the degree of adsorption was determined by the decrease of the pressure at the equilibrium state.

Synthesis of PCP 1 in a 100 mg-scale:

The crystalline powder of **1** for the sorption measurements was synthesized using a microwave-assisted method in ~100 mg-scale as follows. A glass vial containing a methanol solution (20 mL) of H₂moip (1 mmol), bpe (1 mmol), and Zn(NO₃)₂·6H₂O (1 mmol) was subjected to a microwave synthesizer (Initiator; Biotage), and the solution was stirred at 120 °C for 1 h. After cooling to room temperature, the obtained suspension was centrifuged and the solid was washed with DMF third, then dried in a reduced pressure to give **1** as pale yellow powder. [Elemental analysis calcd. for C₂₄H₂₃N₃O₆Zn (**1**): C, 55.99; H, 4.50; N, 8.16; Found C, 54.92; H, 4.45; N, 7.88]

Synthesis of PCP 2 in a 100 mg-scale:

The crystalline powder of **2** for the sorption measurements was synthesized using a photochemical reactor (LZC-4; Luzchem) with a UV-lamp (LZC-UVA; Luzchem). The powder of **1** sandwiched between glass plates was irradiated for 24 h and the sample was agitated every 6 hours, leaving **2** as cream powder. [Elemental analysis calcd. for C₂₄H₂₃N₃O₆Zn (**2**): C, 55.99; H, 4.50; N, 8.16; Found C, 54.66; H, 4.28; N, 8.02]

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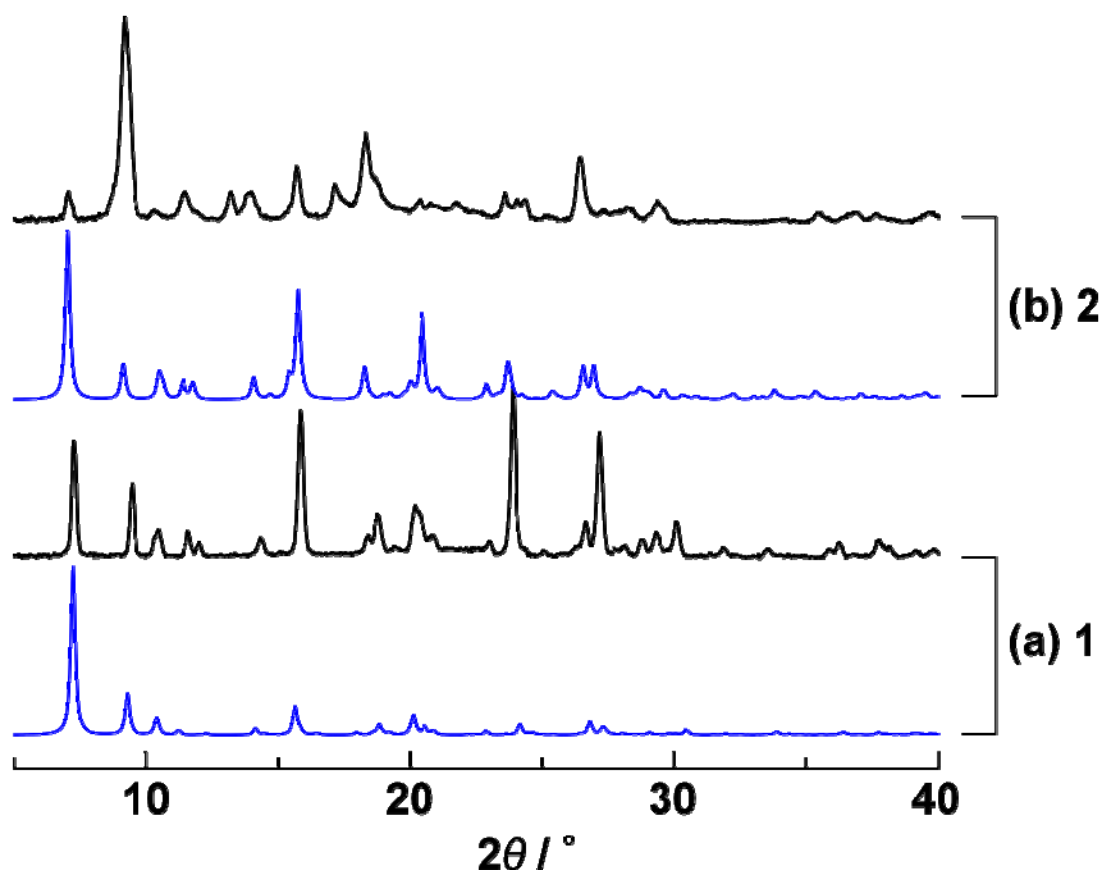


Fig. S1 Simulated (blue) and experimental (black) PXRD patterns of PCP (a) **1** and (b) **2**.

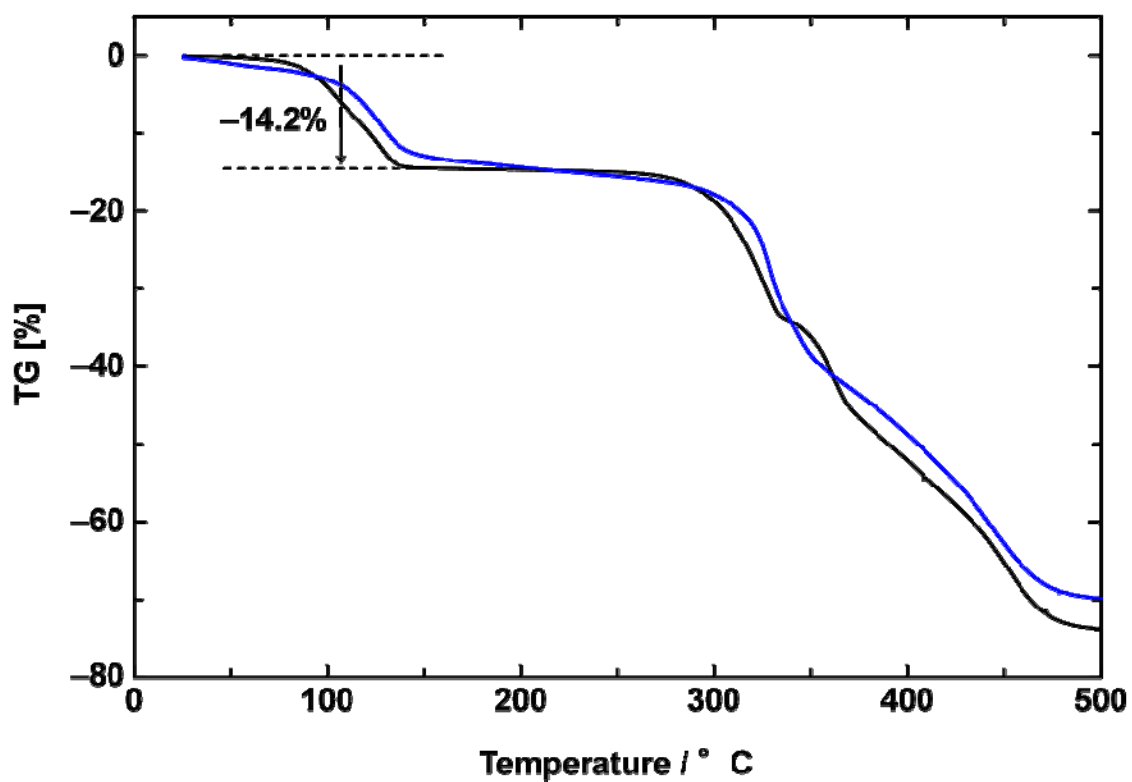


Fig. S2 TG analysis of PCP 1 (black) and 2 (blue). 14.2 wt% loss observed below 200 °C is due to a release of the included DMF (calcd. for $[\text{Zn}(\text{moip})(\text{bpe})(\text{DMF})]_n$: 14.2 wt%).

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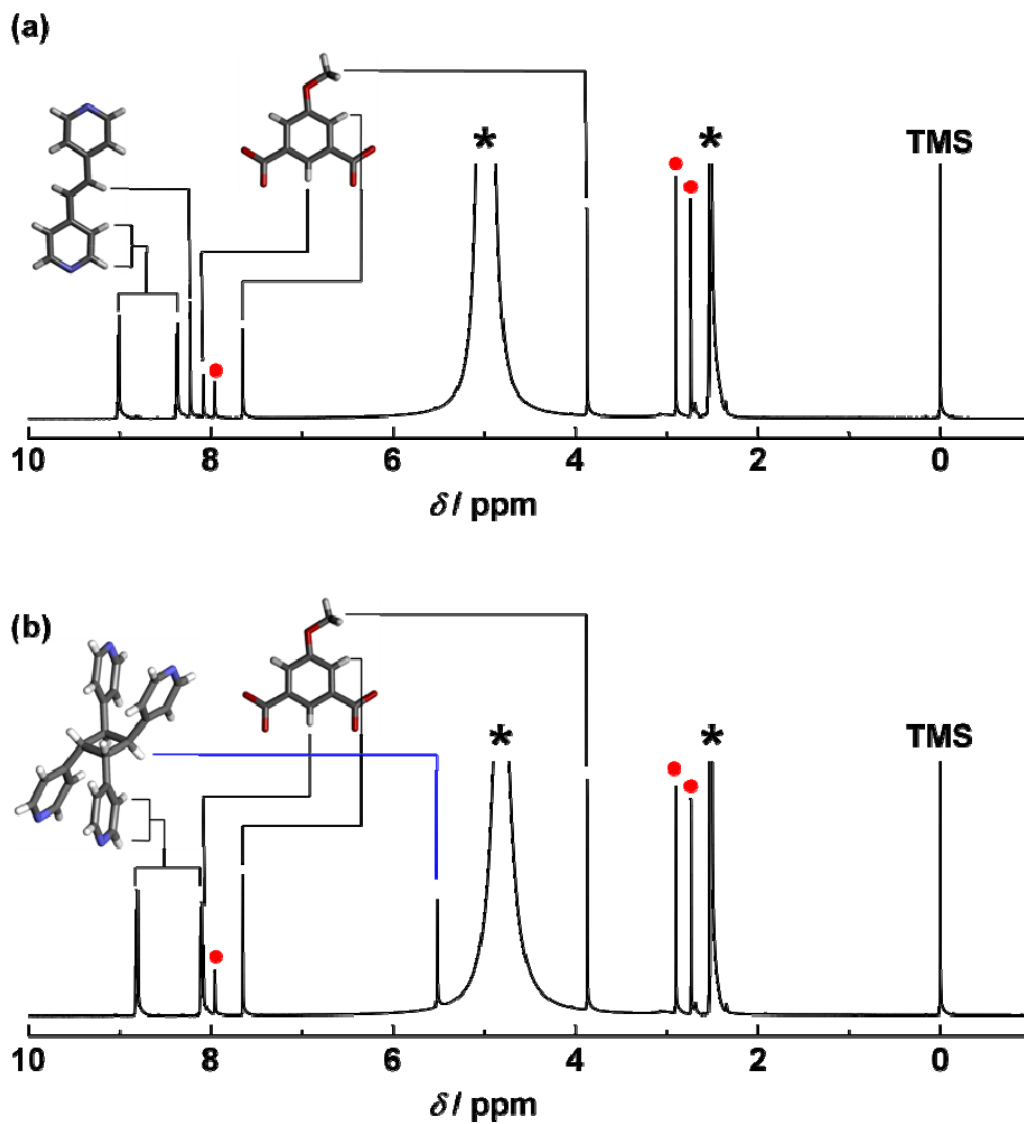


Fig. S3 ¹H NMR spectra of (a) **1** and (b) **2** digested in DMSO-*d*₆/aq.HCl at 298 K. Three singlet signals (●) at δ 7.96, 2.90, and 2.74 ppm are due to DMF molecules and the asterisks are the signals of the solvents (DMSO and H₃O⁺). After [2+2] reaction, the protons of the cyclobutane ring were observed at δ 5.52 ppm as a singlet signal. Integral ratios between the signals of DMF and those of organic ligands clearly indicated one molecule of DMF per Zn²⁺ is accommodated in **1** and **2**.

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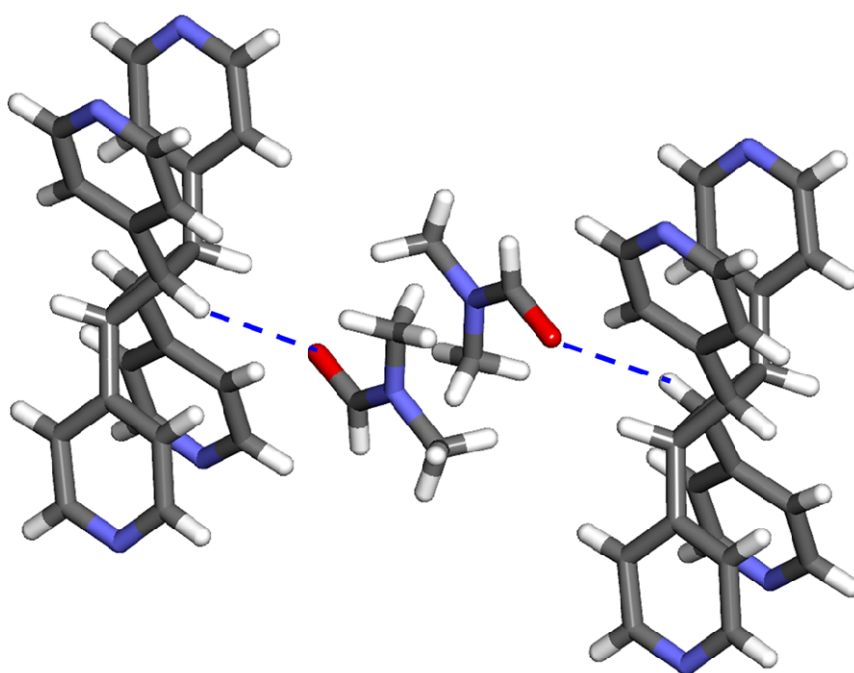


Fig. S4 Interactions between the accommodated DMF molecules and the framework of PCP 2. DMF molecules are trapped in the channel through the interactions (indicated by blue broken lines) between the hydrogen atoms of *rctt*-tpcb ligands the oxygen atoms of the carbonyl groups.

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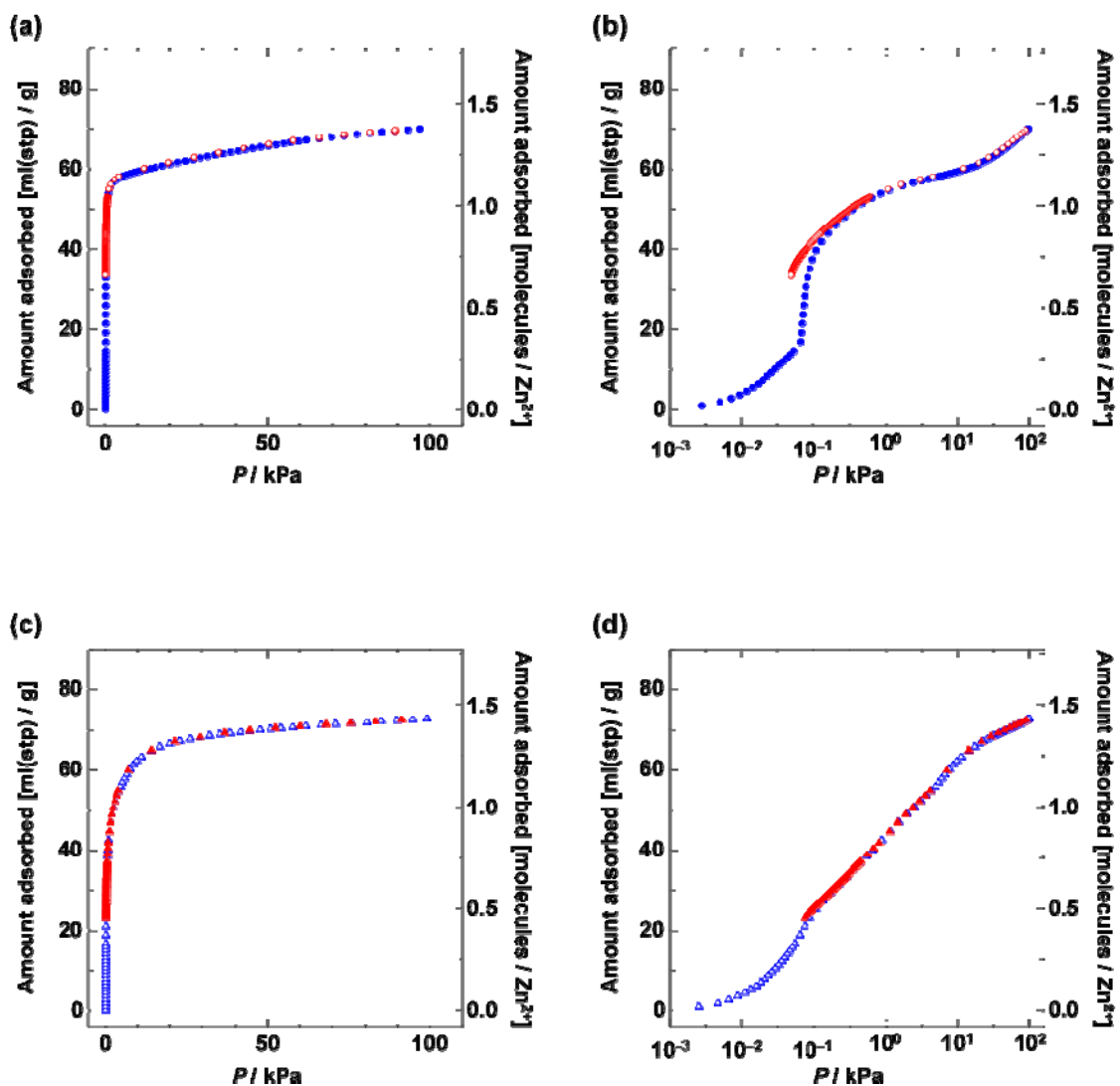


Fig. S5 CO₂ adsorption (blue) and desorption (red) isotherms of PCP (a and b) 1' and (c and d) 2' at 195 K. The pressures are shown in logarithmic scales in (b) and (d).

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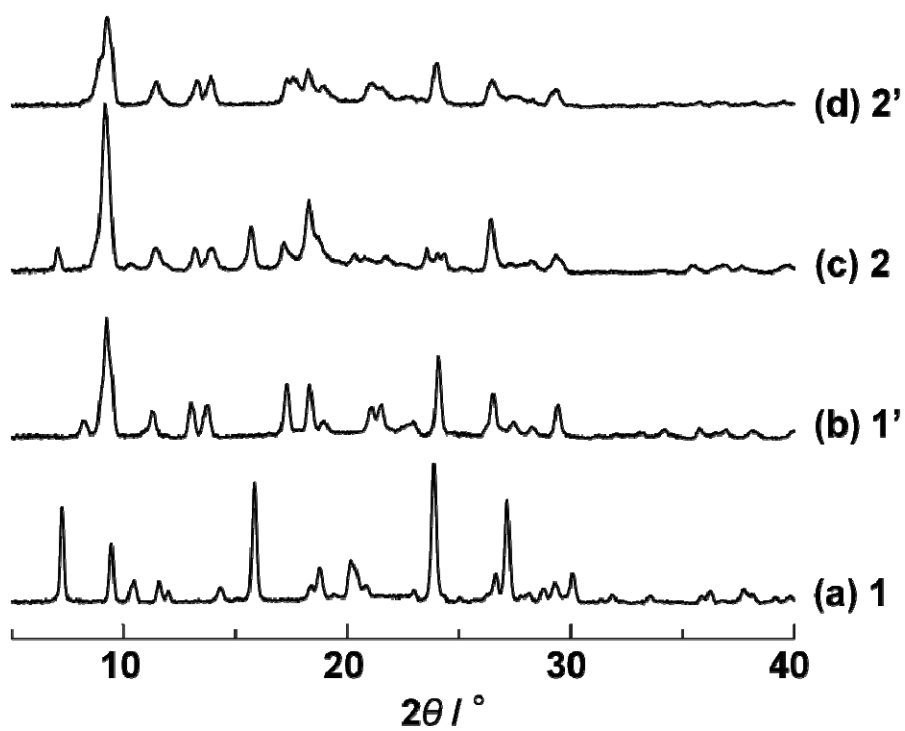


Fig. S6 XRD patterns of PCP (a) **1**, (b) **1'**, (c) **2**, and (d) **2'**.