

Supporting Information

Guest-Specific Function of a Flexible Undulating Channel in a TCNQ Dimer-based Porous Coordination Polymer

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Experimental Section

Materials. 7,7,8,8-tetracyano-p-quinodimethane and 4,4'-Bipyridine were obtained from Tokyo Kasei Industrial and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were obtained from Wako and used without further purification. LiTCNQ was prepared by the literature method.

Synthesis of Porous Coordination Polymer $\{[\text{Zn}(\text{TCNQ-TCNQ})\text{bpy}] \cdot 1.5\text{benzene}\}_n$ (1**⊃benzene).** Single crystal of **1** was prepared by the following procedure. All procedure were carried out under N_2 atmosphere using Schlenk technique. A solution of LiTCNQ (0.1 mmol, 21 mg) and bpy (0.1 mmol, 16 mg) in MeOH/benzene mixture (20 ml) was carefully layered on the top of a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol, 30 mg) in MeOH/benzene mixture (20 ml). Green crystals began to form in a few days. The bulk product was obtained by the following procedure. Slow addition of a solution of LiTCNQ (2 mmol, 422 mg) and bpy (1 mmol, 156 mg) in MeOH/benzene mixture (100 ml) to a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 297 mg) in MeOH/benzene mixture (100 ml) at 293 K under N_2 atmosphere. The green powder obtained was collected by filtration. (yield 93%) Elemental analysis calcd. for $\text{C}_{43}\text{H}_{25}\text{N}_{10}\text{Zn}$: C, 69.17; H, 3.37; N, 18.75, Found: C, 68.48; H, 3.58; N, 18.65.

X-ray Crystal Analysis. Single crystal X-ray diffraction data collection was carried out

on a Rigaku mercury diffractometer with a graphite monochromated MoK α radiation ($\gamma = 0.71069 \text{ \AA}$) and a CCD detector. The crystal structure was solved by a direct method (SIR2002) and refined by full-matrix least-squares refinement using the CRYSTALS computer program. The positions of non-hydrogen atoms were refined with anisotropic displacement factors, except for the guest molecules. The hydrogen atoms were positioned geometrically and refined using a riding model.

Physical Measurements. The elemental analysis was carried out on a Flash EA 1112 series, Thermo Finnigan instrument. Thermal gravimetry analysis (TGA) was carried out with a Rigaku Instrument TG8120 in a nitrogen atmosphere. X-ray powder diffraction (XRPD) data were collected on a Rigaku RINT-2200HF (Ultima) diffractometer with Cu-K α radiation. The adsorption isotherms of CO₂ (195 K), acetone and benzene (298K) were measured in the gaseous state by using BELSORP18-Plus volumetric adsorption equipment from BEL Japan, Inc. VT ¹H NMR spectra were recorded on a JEOL A-500 spectrometer and referenced to residual protons of DMSO-*d*₆ solvent.

Guest arraignment of 1 \supset benzene. Only one benzene molecule per Zn^{II} ion was determined by crystallography to be in the cage of the undulating channel, and this is tightly fixed by the H- π interaction. The absence of other guest molecules in the channel of 1 \supset benzene was attributed to the disorder of included guest molecules.

The break of the benzene isotherm. In the measurement by BELSORP-18 Plus, measurer decides recorded points with an introduction pressure (P_i) of an adsorptive. P_i of an adsorptive is introduced into the cell and then it will achieve an equilibrium pressure (P_e). Then, the adsorption amount (A) are calculated and P_e and A are recorded. In this one cycle, there is no additional vapor-dosing of an adsorptive into the cell. This vapor dosing procedure is useful for the transition and kinetics evaluation of gas adsorption. This compound transforms from non porous (phase 2) to porous structure (phase 3) across the point A and suddenly starts to adsorb the benzene. Because adsorption isotherms of phase 2 and 3 are completely different, the pressure decreases to an equilibrium pressure (point B) and (rapid or sudden) uptake is observed. In the results, we get the isotherm with the break like Figure 2. Figure S3 shows the benzene isotherm and time dependent pressure change of this compound.

Table S1. Crystal data and Structure Solution and Refinement of **1**⊃benzene.

Empirical Formula	C ₄₀ H ₂₂ N ₁₀ Zn
Formula Weight	708.06
Crystal System	monoclinic
Lattice Parameters	a = 11.361(5) Å b = 12.645(6) Å c = 14.775(7) Å V = 2122.4(18) Å ³
Space Group	Pccm (#49)
Z value	2
D _{calc}	1.108 g/cm ³
F ₀₀₀	724.00
μ (MoKα)	6.155 cm ⁻¹
Radiation	MoKα (λ = 0.71070 Å) graphite monochromated
2θ _{max}	54.9°
No. of Reflections Measured	Total: 15080 Unique: 2521 (R _{int} = 0.041)
Completeness	99.8%
Refinement	Full-matrix least-squares on F ²
2θ _{max} cutoff	0.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I > 2.50σ(I))	2210
No. Variables	206
Reflection/Parameter Ratio	10.73
Residuals: R ₁ (I > 2.00σ(I))	0.0586
Residuals: R (All reflections)	0.0660
Residuals: wR ₂ (All reflections)	0.0591
Goodness of Fit Indicator	1.082
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.12 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.41 e ⁻ /Å ³

Supporting figures

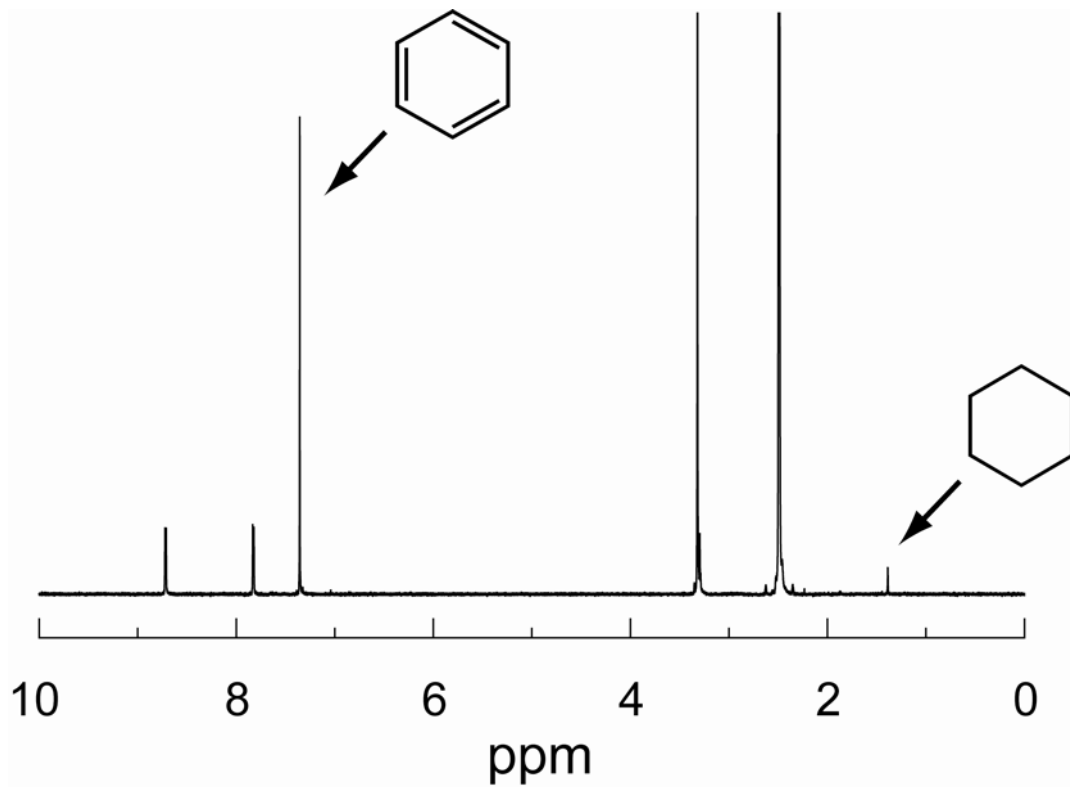


Figure S1. ¹H-NMR spectra of degassed [Zn(μ₄-TCNQ-TCNQ)bpy] (**2**) exposed to a vapor of a benzene/cyclohexane mixture (1:1) for 5 hours. The ratio of benzene and cyclohexane in this compound is 96:4

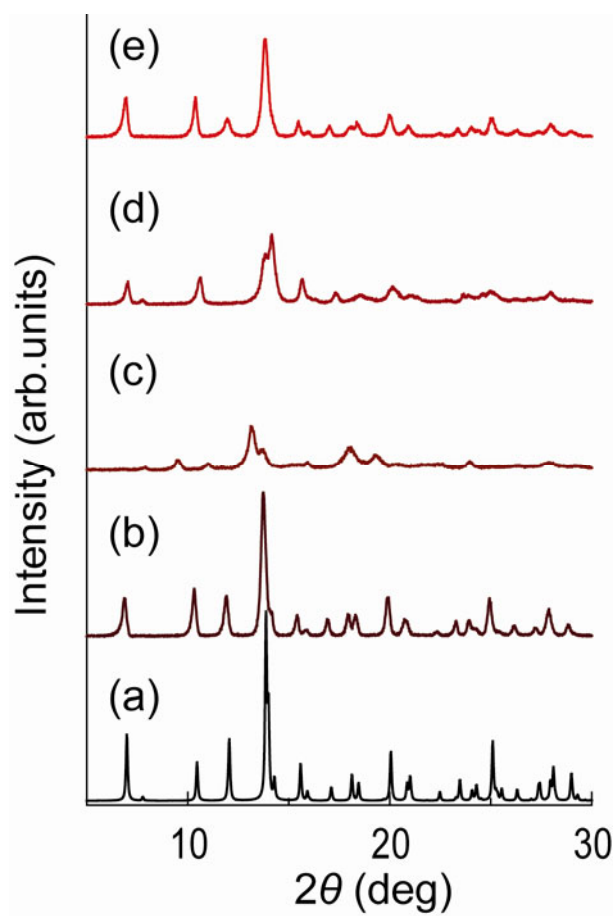


Figure S2. XRPD pattern of (a) simulation (**1D**-benzene), (b) as synthesized state (**1D**-benzene), (c) degassed state (**2**), (d) exposed to a vapor of benzene (**3D**-benzene), (e) exposed to a vapor of benzene/MeOH mixture (**1D**-benzene).

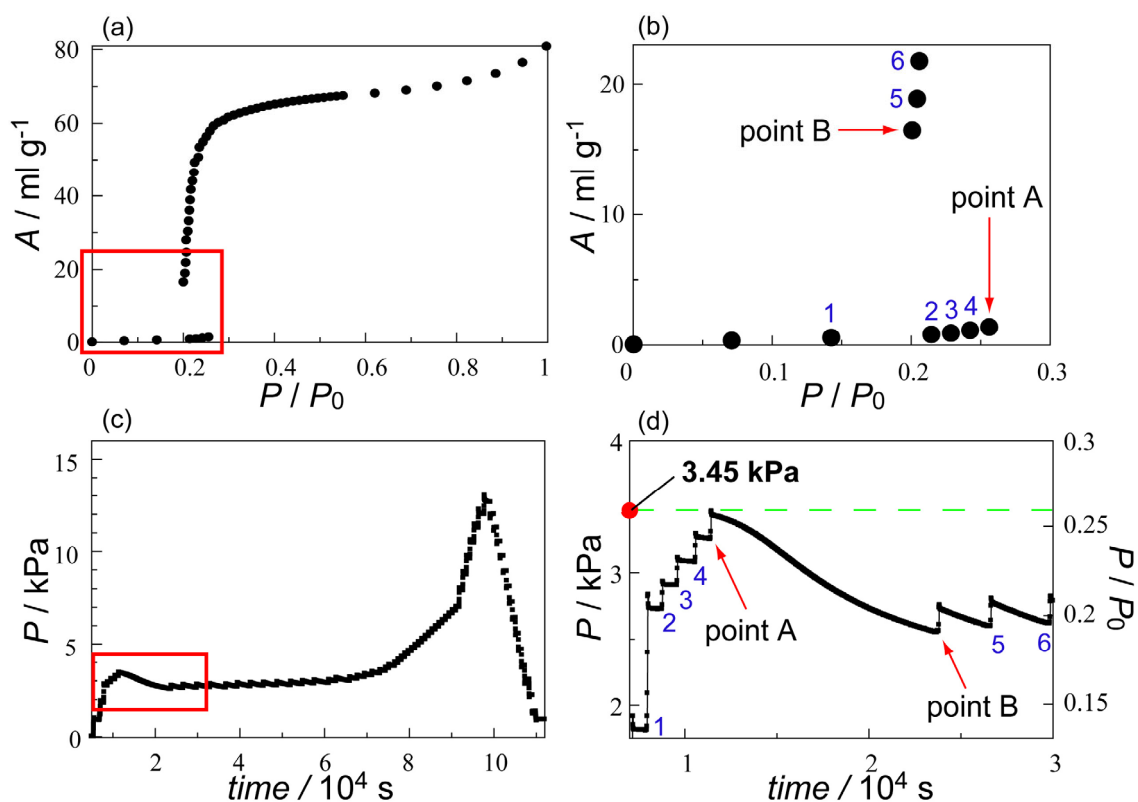


Figure S3. (a)(b) The benzene adsorption isotherm and the detail around the break. (c)(d) The time dependent pressure change in this measurement and the detail around the break. The labeled numbers of each point in (b) are directly corresponded to in (d). From (d), the adsorption starts above the pressure 3.45 kPa.

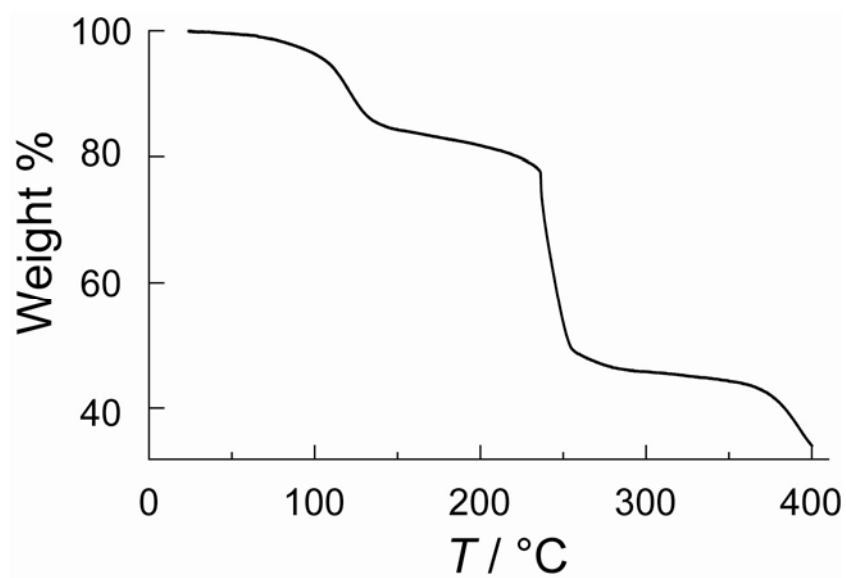


Figure S4. TG analysis of **1** in benzene over the temperature range from 25-400°C at a heating rate of $\beta = 5$ °C / min under the N₂ atmosphere.