Soft 2-D layer porous coordination polymers with 1,2-di(4-dipyridyl)ethane

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Abstract

Porous coordination polymer compounds consist of Zn^{2+}, 1,2-di(4-dipyridyl)ethane and dicarboxylates were synthesized and their crystal structures were determined. These are doubly interpenetrated 2-D layer structures, and the flexibility of porous structures is dependent on the substituent group of dicarboxylate. From the gas adsorption studies, distinct adsorption isotherms were observed for CO_2, CH_4, C_2H_4 and C_2H_6 at 195 K and 273 K, respectively.

Introduction

Synthesis and characterization of porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) have been of significant interest due to their potential applications in gas storage, separation, magnetism, and catalysis.[1] To construct open frameworks, the combination of divalent metal cation, neutral dipyridyl ligand and anionic dicarboxylate is one of useful approaches.[2] The mixed ligand compounds could have the organic functionality in the pore, because one of the ligand constructs the stable porosity, and the other works on functional site. In terms of systematic synthesis

of frameworks with dipyridyl and dicarboxylate, there are still limited numbers of example.[3] To explorer the rational synthesis of PCP/MOFs, it is important to discover the new series of mixed-ligand type compounds. Herein, we demonstrated the syntheses of three two-dimensional (2-D) layer structures, $\{[Zn(5\text{-}R\text{-isophthalate})(dpa)](DMF)\}_n$ (**1⊃DMF** : *R* = H, **2⊃DMF** : *R* = MeO, **3⊃DMF** : *R* = Me, dpa = 1,2-di(4-pyridyl)ethane) comprised of Zn^{2+}, 5-substituted isophthalate and dpa, by using DMF as a template solvent.

Results and discussion

Single crystal X-ray structural analyses confirmed that **1⊃DMF**, **2⊃DMF** and **3⊃DMF** form structurally similar motif. These are two-fold interpenetrating two-dimensional coordination networks. Figure 1 shows the crystal structure of **1⊃DMF**. The asymmetric unit of the three compounds consist of each one Zn^{2+}, isophthalate, dpa and one DMF molecule. Zn^{2+} atom is in a tetrahedral geometry, and coordinated by two nitrogen atoms (N1 and N2) from two dpa and two carboxylates (O1 and O3). The Zn–N bond lengths are in the range of 2.024 – 2.053 Å, and the Zn–O bond lengths are 1.969 – 1.986 Å, respectively. All three compounds have a space group of Orthorhombic *Pbca*. The 2-D layer is **sql** topology (Figure 1a).[3] Two 2-D layers are interpenetrated each other, and run along the *b* axis. The interpenetrated layer structures are stacked with the plane of isophthalate ligands of adjacent layers (Figure 1b). 1-D channels are created with a cross section of about 3.0 × 4.5 $Å^2$. The channels are surrounded with aromatic rings of dpa and dicarboxylate, and hydrophobic pores are formed. One DMF molecule per unit cell is trapped as a guest molecule. Guest-accessible void volumes of **1⊃DMF**, **2⊃DMF**, **3⊃DMF** are 21.7, 23.6, and 23.0% (probe molecule radius = 1.4 Å) by using PLATON software.[4]

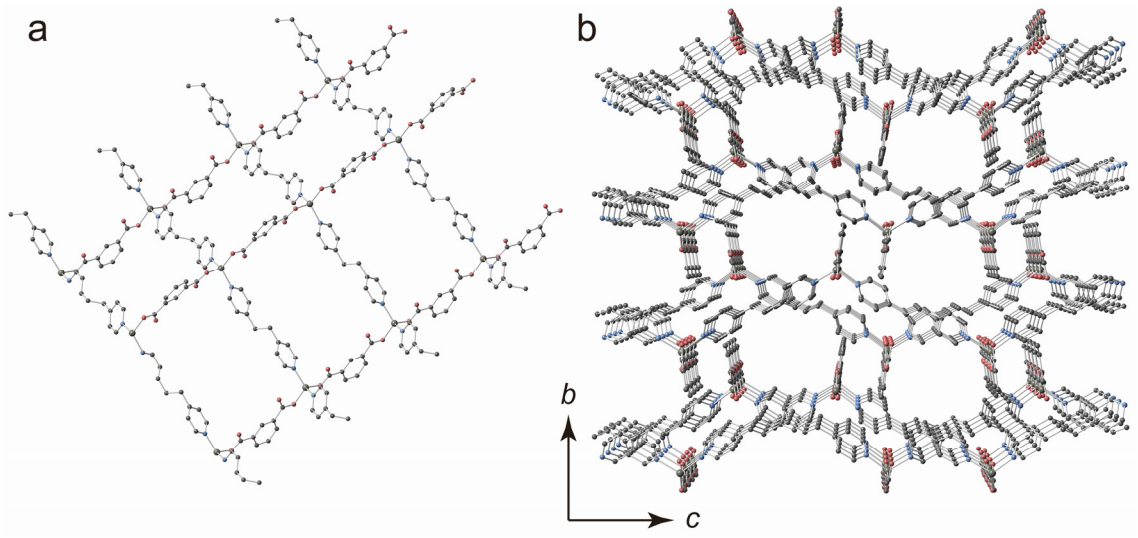

Figure 1. Crystal structures of (a) 2-D layer and (b) 3-D assembly along the *a* axis of **1⊃DMF**. Large and small gray are Zn, C. Blue and pink are N and O. DMF molecules are omitted for clarity.

1⊃DMF and **3⊃DMF** are the isomers of previously reported compounds [Zn(ip)(dpa)][5a,b] and [Zn(Meip)(dpa)].[5c] The crystal structures of the reported compounds are four-connected 3-D (6^5.8)-**dmp** topology with three-fold interpenetration or 2-D **sql** topology with multiply interpenetration. The 3-D assembled structures are different from **1⊃DMF** and **3⊃DMF**. The reported compounds are obtained by using water or alcohols as solvent, whereas the **1⊃DMF** and **3⊃DMF** are constructed by using DMF. The difference of the synthetic solvents provides the different crystal structures. On the other hand, one of the **sql** structures with dipyridyl ligand and dicarboxylate is synthesized from DMF; [Zn(MeOip)(dpe)] (dpe = 1,2-di(4-pyridyl)ethylene).[6] The compound has three-fold interpenetration of 2-D layers, and no porosity forms. The structural difference may be derived from the slightly smaller steric hindrance of dpe ligand than dpa, and also because of their different rigidity.

Thermogravimetric analysis (TGA) of **1⊃DMF**, **2⊃DMF** and **3⊃DMF** show weight loss at 220 °C (Figure 2). The weight loss is corresponding to the one DMF molecule. The accommodated DMF are removed by the evacuation procedure at 150 °C.

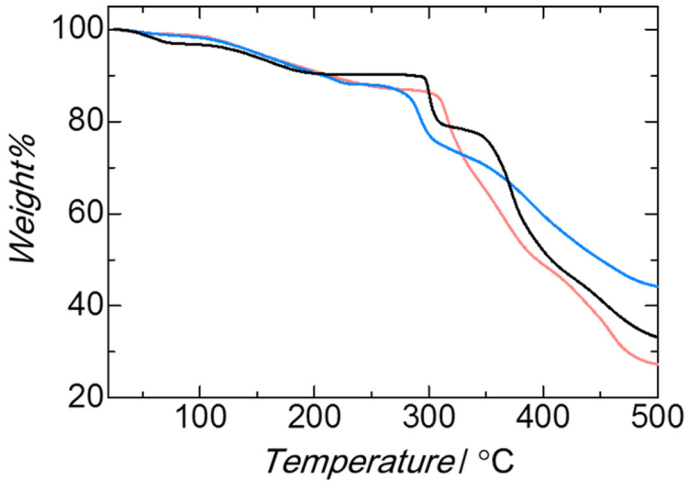

Figure 2. TGA curves of **1⊃DMF** (black), **2⊃DMF** (blue) and **3⊃DMF** (pink).

The structural expansion and contraction behaviors of 2-D layer PCP/MOFs via the gas adsorption have been reported. Figure 3 shows the observed powder X-ray diffraction (PXRD) patterns of **1⊃DMF**, **2⊃DMF**, **3⊃DMF**, and their degassed forms **1, 2**, **3** with simulated patterns from the single crystal structures. PXRD patterns of **1⊃DMF, 2⊃DMF** and **3⊃DMF** measured at room temperature are in good agreement with that of simulated pattern. The PXRD patterns of **1** and **2** are similar to those of **1⊃DMF** and **2⊃DMF**. This indicates that the structures of these two compounds are robust, and they do not have the structural rearrangement via DMF release. The PXRD patterns of **3⊃DMF** and **3** are slightly different. This suggests that **3** has structural flexibility. We confirmed that crystal structure of **3** after the soaking to DMF returned to the same structure of **3⊃DMF** by PXRD study. The structural rearrangement is reversible.

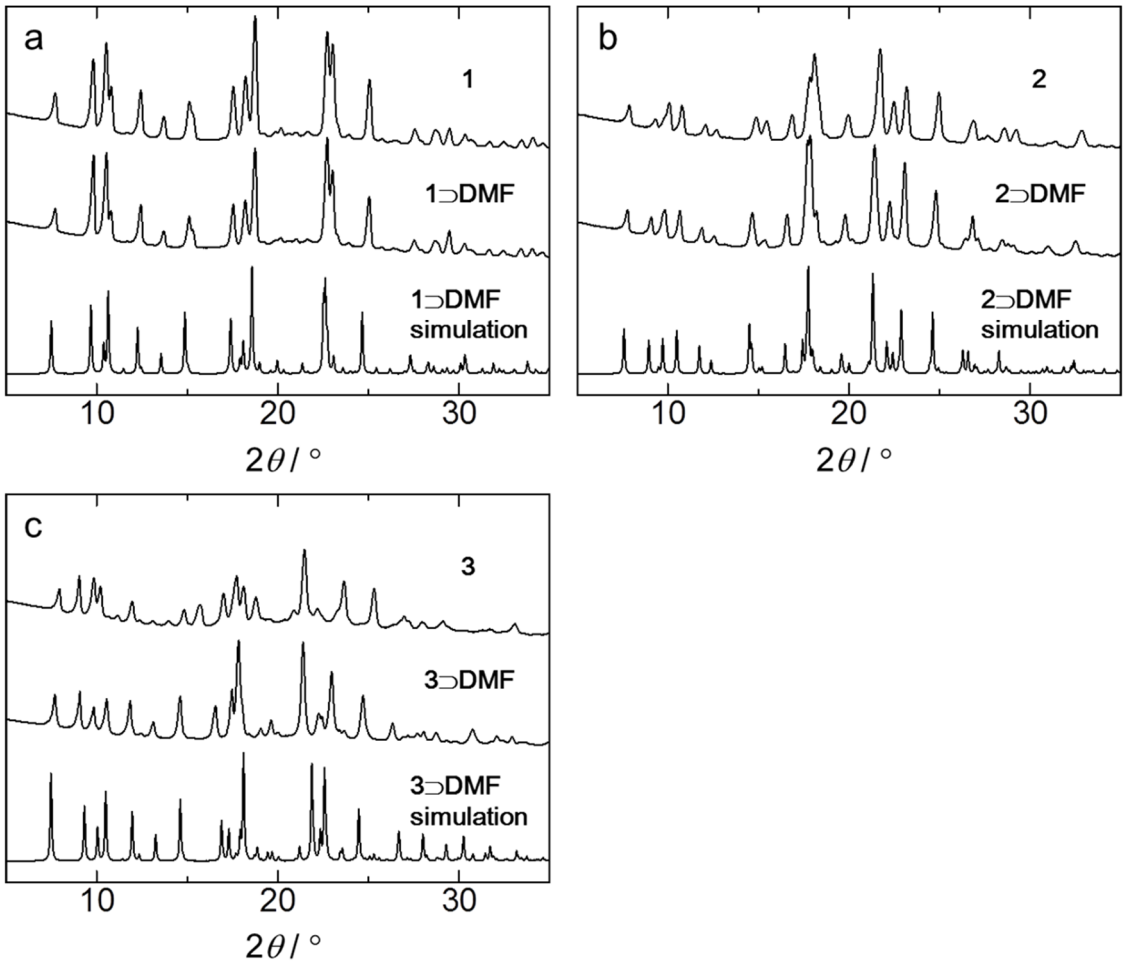

Figure 3. Powder X-ray diffraction patterns of (a) **1⊃DMF**, **1** (b) **2⊃DMF**, **2** (c) **3⊃DMF**, **3**, and their simulated patterns from single crystal X-ray structures.

We measured gas adsorption isotherms of N_2 (Figure 4). The N_2 adsorption isotherms measured for **1-3** at 77 K reveal low uptakes. CO_2 and C1-C2 hydrocarbon gases at 195K were conducted to evaluate their permanent porosity. The study on adsorption properties of these gases is significant for storage and separation.[7] All compounds show Type-I or "gate-opening" [8] type adsorption isotherms for these gases which indicates their microporosity. A similar molecular-sieving effect to N_2 has been observed in other PCP/MOFs or Zeolites,[9] and we consider the unusual behavior is because of the deficiency of the energy of N_2 diffusion into the small channels of **1-3**. BET surface area of **2** and **3** calculated from CO_2 adsorption are 289 and 343 $m^2 g^{-1}$. On the other hand, CO_2 adsorption isotherm of **1** shows a sudden jump at 80 kPa, and the total gas uptake reaches 100 mLg^{-1} at 100 kPa. The stepwise profile would be due to the structure transformation. Desorption of CO_2 in **1** occurs below 20 kPa, and we observe the large

hysteresis in the adsorption and desorption processes. We could consider the pore structure of **1** has high affinity for CO_2, and the condensation of CO_2 into **1** promotes the structure transformation to another phase. In case of CH_4 adsorption isotherms, **3** also shows "gate-opening" type behavior as is the case with **1** for CO_2. There is no CH_4 adsorption from 0 to 15 kPa, and it has a plateau near the uptake of one CH_4 molecules per formula unit at 30 kPa. In the desorption profile, we observe the hysteresis in the range of pressure of 0 to 30 kPa. For C2 hydrocarbons, all compounds show typical Type-I isotherms with a steep rise at the low-pressure region.[10] The total gas uptakes of **1**-**3** for C1 and C2 hydrocarbons reach about 50-55 ml g^{-1}, that are corresponding to the accommodation of one CH_4, C_2H_4 or C_2H_6 molecule per one Zn^{2+} in the structures. All compounds possess a bottle-and-neck type channel structure, and they provide the commensurate type adsorption of guest molecules.

Because of the 3-D assembled structures of these compounds are same, the observed different gas adsorption properties are caused by the different substituent groups of isophthalates in the structures. These compounds have higher affinity to CO_2 than the other gases at 195 K. **2** shows Type-I adsorption isotherms for all gases, and it represents the robustness of the porous structure. **1** and **3** have structural flexibility with gate-opening type sorption behaviors. We have reported that the structure flexibility depends on the substituent groups of isophthalate ligands in the 2-D interdigitated compounds.[11] We also observe the similar effects of the substituent group on the flexibility in the present compounds. The introduction of the substituent groups into the porous framework may affect both host-guest and host-host interaction, and it is hard to explain the origin of the gate-opening type sorption behaviors.

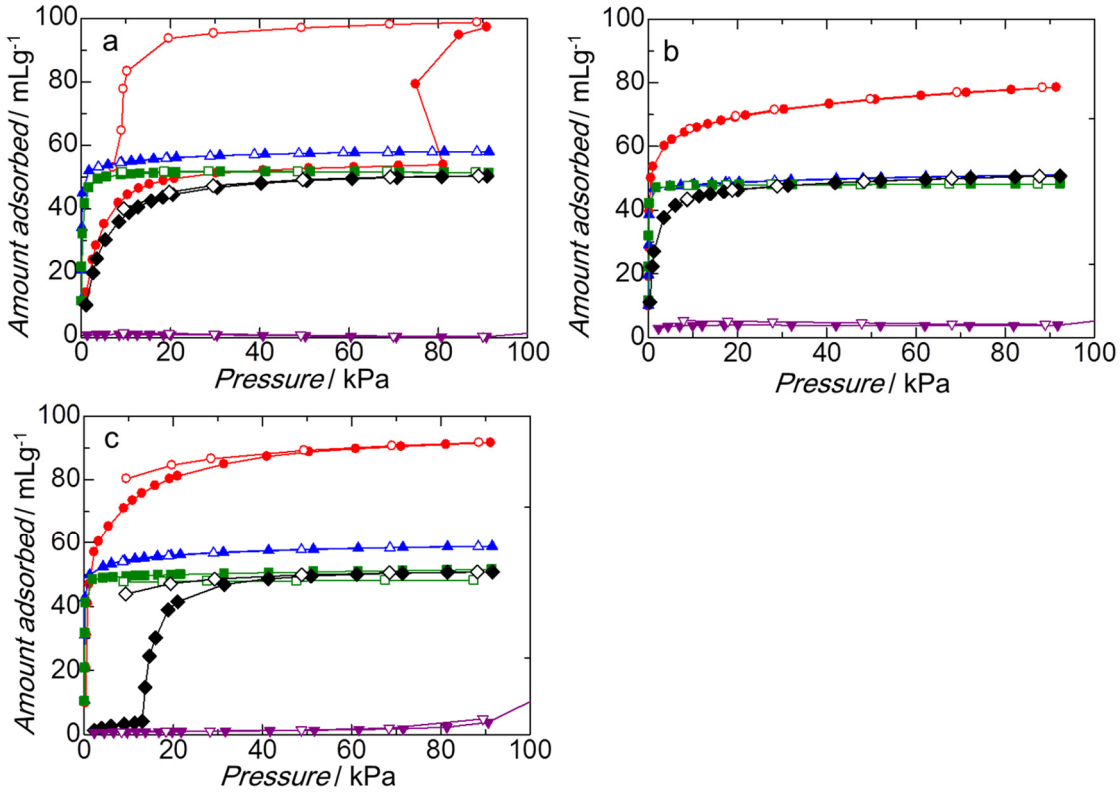

Figure 4. Gas adsorption and desorption isotherms of (a) **1**, (b) **2**, and (c) **3** at 77 K (purple: N_2) and 195 K (red: CO_2, black: CH_4, blue: C_2H_4, green: C_2H_6). Solid symbols are adsorption and open symbols are desorption, respectively.

We also studied the gas adsorption isotherms for these compounds at near room temperature and pressure range of 0 to 900 kPa (Figure 5). The gas adsorption isotherms are regarded as similar with those in the lower pressure region at 195 K. In case of **1**, we observed Type-I isotherms for CO_2, C_2H_4 and C_2H_6, whereas the gradual curve for CH_4 is observed because of the lower interaction with the framework. The studied pressure region (~900 kPa) is not enough to promote the consequent structure transformation. In case of **2**, all the gas isotherms are Type-I which is similar with **1**, and the isotherms of C_2H_4 and C_2H_6 have high steepness of uptake at lower pressure region. For **3**, we also observed stepwise isotherm of CH_4 and the second adsorption occurs at 150 kPa. The step at 195 K is more abrupt, and this is because the gas diffusion rate at the higher temperature (273 K) would be larger and it provides the gradual uptake until 150 kPa.

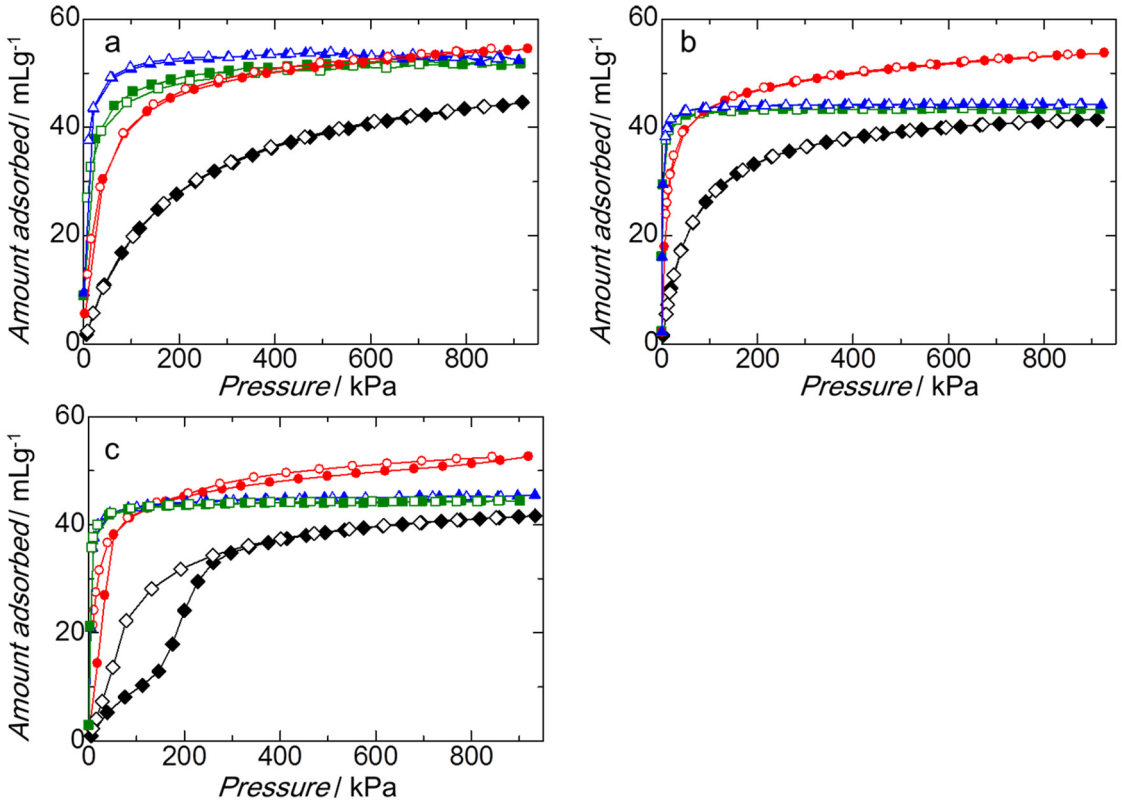

Figure 5. Gas adsorption and desorption isotherms of (a) **1** (b) **2** and (c) **3** at 273 K (Red: CO_2, black: CH_4, blue: C_2H_4, green: C_2H_6). Solid symbols are adsorption and opened symbols are desorption, respectively.

Conclusion

In this work, we synthesized three compounds of 2-D layer type PCP/MOFs consisting of Zn^{2+}, dpa (dipyridylethane), and 5-substituted isophthalate ligands. The structure of 2-D layer of these compounds is **sql** topology and each substituent group provides different pore structures and structure flexibilities. We observed the various gas adsorption profiles for CO_2, CH_4, C_2H_4, and C_2H_6 at 195 K and 273 K for these compounds. They show a preferable adsorption on CO_2 compared with other gases. For the synthesis from the combination of conventional metal ion and organic ligands, the synthetic solvent (DMF) is the key for constructions of the new types of 2-D layer structures. It demonstrates the promising approach to construct the PCP/MOFs by solvent optimization.

Acknowledgement

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Experimental section

All chemicals and solvents used in the syntheses were of reagent grade and used without further purification. $Zn(NO_3)_2{\cdot}6H_2O$ and *N*,*N*'-dimethylformamide (DMF) were purchased from Wako Pure Chemical Industries Inc. and isophthalic acid (H_2-ip), 5-methoxyisophthalic acid (H_2-5-MeOip), 5-methoxyisophthalic acid (H_2-5-Meip) and 1,2-di(4-pyridyl)ethane (dpa) were from Tokyo Chemical Industry Co..

Synthesis of {[Zn(ip)(dpa)](DMF)}$_n$ (1⊃DMF). $Zn(NO_3)_2{\cdot}6H_2O$ in DMF (0.1 M, 0.2 ml), isophthalic acid in DMF (0.1 M, 0.2 mmol), 1,2-di(4-pyridyl)ethane in DMF (0.1 M, 0.2 ml) and H_2O (0.5 ml) were reacted in a 1.5 mL vial for 72 hours at 80 °C. Colorless single crystals were obtained and one of these was used for X-ray crystallographic analysis. The bulk sample was obtained by the following procedure. $Zn(NO_3)_2{\cdot}6H_2O$ (0.600 g, 2.02 mmol), isophthalic acid (0.339 g, 2.04 mmol) and 1,2-di(4-pyridyl)ethane (0.393 mg, 2.13 mmol) were reacted with 60 mL of DMF and 50 ml of water in a 300 mL round flask and stirred for 16 hours at 80 °C under N_2 atmosphere. White microcrystalline precipitate was filtered, washed with DMF and methanol several times and dried under vacuum at room temperature (0.240 g, 26%).

Synthesis of {[Zn(MeOip)(dpa)](DMF)}$_n$ (2⊃DMF). $Zn(NO_3)_2{\cdot}6H_2O$ in DMF (0.1 M, 0.3 ml), 5-methoxyisophthalic acid in DMF (0.1 M, 0.3 mmol), 1,2-di(4-pyridyl)ethane

in DMF (0.1 M, 0.3 ml) and DMF (0.2 ml) were reacted in a 1.5 mL vial for 72 hours at 80 °C. Colorless single crystals were obtained and one of these was used for X-ray crystallographic analysis. The bulk sample was obtained by the following procedure. $Zn(NO_3)_2 \cdot 6H_2O$ (1.49 g, 5.00 mmol), 5-methoxyisophthalic acid (0.932 g, 4.75 mmol) and 1,2-di(4-pyridyl)ethane (0.924 mg, 5.02 mmol) were reacted with 100 mL of DMF in a 300 mL round flask and stirred for 16 hours at 120 °C under N_2 atmosphere. Light brown microcrystalline precipitate was filtered, washed with DMF and methanol several times and dried under vacuum at room temperature (1.19 g, 52%).

Synthesis of {[Zn(Meip)(dpa)](DMF)}$_n$ (3⊃DMF). $Zn(NO_3)_2 \cdot 6H_2O$ in DMF (0.1 M, 0.4 ml), 5-methylisophthalic acid in DMF (0.1 M, 0.4 mmol), 1,2-di(4-pyridyl)ethane in DMF (0.1 M, 0.2 ml) and DMF (0.1 ml) were reacted in a 1.5 mL vial for 72 hours at 80 °C. Colorless single crystals were obtained and one of these was used for X-ray crystallographic analysis. The bulk sample was obtained by the following procedure. $Zn(NO_3)_2 \cdot 6H_2O$ (1.50 g, 5.04 mmol), 5-methylisophthalic acid (0.901 g, 5.00 mmol) and 1,2-di(4-pyridyl)ethane (0.928 mg, 5.04 mmol) were reacted with 100 mL of DMF in a 300 mL round flask and stirred for 16 hours at 120 °C under N_2 atmosphere. Light brown microcrystalline precipitate was filtered, washed with DMF and methanol several times and dried under vacuum at room temperature (1.32 g, 56%).

Single crystal X-ray diffraction. The colorless single crystals of **1⊃DMF**, **2⊃DMF**, **3⊃DMF** were mounted on glass fibers with epoxy resin. X-ray data collection for the single crystal was carried out on a Bruker AXS SMART APEX II Ultra diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å) and a CCD two-dimensional detector at 223K (for **1⊃DMF**) or 100 K (for **2⊃DMF** and **3⊃DMF**) in a cold nitrogen stream. The condition of X-ray for **1⊃DMF** was 50 kV×100 mA. Absorption corrections were applied by using multi-scan program SADABS and the structures were solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions and refined using a riding model. The crystallographic data for compound **1⊃DMF**, **2⊃DMF**, **3⊃DMF** are listed in Tables 1. CCDC deposit numbers of **1⊃DMF**, **2⊃DMF**, **3⊃DMF** are 905315, 905316, 905317, respectively.

Table 1. Summary of the crystal data for compounds

Compound	**1⊃DMF[a)]**	**2⊃DMF**	**3⊃DMF**

Molecular formula	$C_{20}H_{16}N_2O_4Zn$	$C_{24}H_{25}N_3O_6Zn$	$C_{24}H_{25}N_3O_5Zn$
Molecular weight	413.74	516.84	500.84
Temperature [K]	223	100	100
Space group	*Pbca*	*Pbca*	*Pbca*
a [Å]	10.1459(11)	10.2480(12)	10.1606(13)
b [Å]	18.125(2)	18.957(2)	19.747(3)
c [Å]	23.509(3)	23.615(3)	23.294(3)
V [Å^3]	4323.2(9)	4673.7(10)	4587.8(9)
Z	8	8	8
D_c [g cm^{-3}]	1.271	1.469	1.436
μ [mm^{-1}]	1.160	1.096	1.111
GOF	1.761	1.009	1.078
R_1 [$I > 2\sigma(I)$]	0.0563	0.0256	0.0286
wR_2 [all data]	0.2150	0.0761	0.0773

a) We applied SQUEEZE program for 1⊃DMF because the accommodated DMF molecule is heavily disordered. The amount of DMF was confirmed by TGA analysis.

Other physical measurements. Thermogravimetric analysis (TGA) were performed using a Shimadzu DTG-60A apparatus in the temperature range between 298 and 723 K in a N_2 atmosphere and at a heating rate of 10 K min^{-1}. X-ray powder diffraction (XRPD) data were collected on a Rigaku Multiflex diffractometer with CuKα radiation. Adsorption isotherms at 273 K were measured with BEL-HP volumetric adsorption equipment from BEL Japan, Inc. Adsorption isotherms at 195 K were measured with BEL-mini instrument.