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Full Paper

Soft 2D Layer Porous Coordination Polymers with 1,2-Di(4-pyridyl)ethane

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Porous coordination polymer compounds consisting of Zn^{2+}, 1,2-di(4-pyridyl)ethane, and dicarboxylates were synthesised and their crystal structures were determined. These are doubly interpenetrated 2D layer structures, and the flexibility of porous structures is dependent on the substituent group of the dicarboxylate. From 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.

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Introduction

Synthesis and characterisation of porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) have been of significant interest due to their potential applications for gas storage, separation, magnetism, and catalysis.[1] To construct open frameworks, a combination of a divalent metal cation, neutral dipyridyl ligand, and an anionic dicarboxylate is a useful approach.[2] Mixed ligand compounds have potential for organic functionality in the pore, because one of the ligands enables stable porosity, and the other provides a functional site. For frameworks with dipyridyl and dicarboxylate, only a limited number of examples have been reported.[3] To explore the rational synthesis of PCP/MOFs, it is important to discover a new series of mixed-ligand type compounds. Herein, we demonstrate the syntheses of three two-dimensional (2D) layer structures, $\{[\mathrm{Zn}(5\text{-R-isophthalate})(\mathrm{dpa})](\mathrm{DMF})\}_n$ (**1⊃DMF**: R = H, **2⊃DMF**: R = OMe, **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 motifs. These are two-fold interpenetrating 2D coordination networks. Fig. 1 shows the crystal structure of **1⊃DMF**. The asymmetric unit of the three compounds consist of one each of Zn^{2+}, isophthalate, dpa, and one DMF molecule. The Zn^{2+} ion is in a tetrahedral geometry, and coordinated by two nitrogen atoms (N1 and N2) from two dpa molecules 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 2D layer is **sql** topology (Fig. 1a).[3] Two 2D layers are interpenetrated into each other, and run along the *b* axis. The interpenetrated layer structures are stacked with the plane of isophthalate ligands of adjacent layers (Fig. 1b). 1D channels are created with a cross-section of $\sim 3.0 \times 4.5$ 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 calculated to be 21.7, 23.6, and 23.0 % (probe molecule radius = 1.4 Å) using PLATON software.[4]

1⊃DMF and **3⊃DMF** are the isomers of previously reported compounds [Zn(ip)(dpa)][5a,b] and [Zn(5-Meip)(dpa), where ip = isophthalate].[5c] The crystal structures of the reported compounds are four-connected 3D (6^5.8)-**dmp** topology with three-fold interpenetration or 2D **sql** topology with multiple interpenetration. The 3D assembled structures are different from **1⊃DMF** and **3⊃DMF**. The reported compounds are obtained using water or alcohols as solvent, whereas **1⊃DMF** and **3⊃DMF** are constructed with DMF. The difference of solvent provides the different crystal structures. On the other hand, one

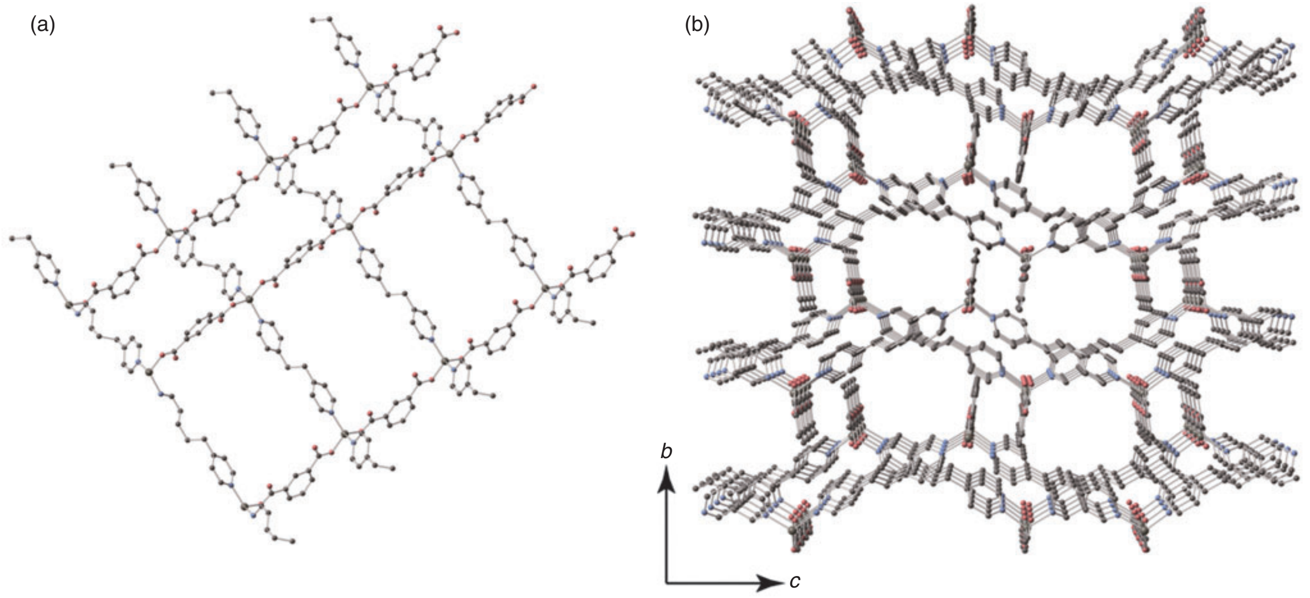

Fig. 1. Crystal structures of (a) 2D layer and (b) 3D assembly along the *a* axis of **1⊃DMF**. Large and small grey spheres are Zn and C. Blue and pink spheres are N and O. DMF molecules are omitted for clarity.

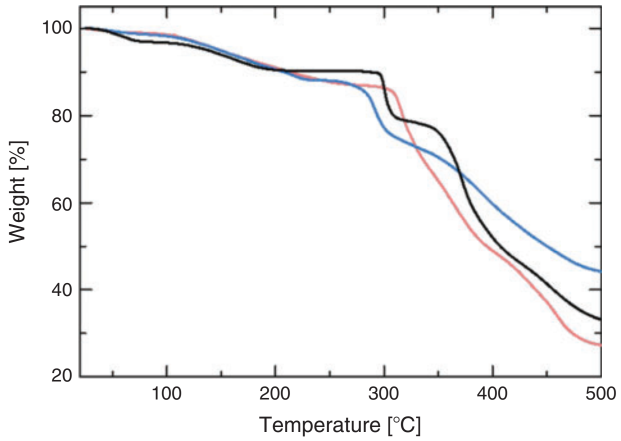

Fig. 2. TGA curves of **1⊃DMF** (black), **2⊃DMF** (blue) and **3⊃DMF** (pink).

of the **sql** structures with dipyridyl ligand and dicarboxylate is synthesised from DMF; [Zn(5-MeOip)(dpe)] (dpe = 1,2-di(4-pyridyl)ethylene).[6] The compound has three-fold interpenetration of 2D layers, and no porosity forms. The structural difference may be derived from the slightly smaller steric hindrance of the 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 (Fig. 2). The weight loss corresponds to the loss of DMF. The accommodated DMF are removed by the evacuation procedure at 150°C.

The structural expansion and contraction behaviour of 2D layer PCP/MOFs via gas adsorption have been reported. Fig. 3 shows the observed powder X-ray diffraction (PXRD) patterns of **1⊃DMF**, **2⊃DMF**, and **3⊃DMF**, and their degassed forms **1**, **2**, and **3** with simulated patterns of 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 the simulated patterns. 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 show much structural rearrangement upon DMF release. The PXRD patterns of **3⊃DMF** and **3** are slightly different. This suggests that **3** has structural flexibility. We confirmed that the crystal structure of **3**, after soaking with DMF, returned to the same structure of **3⊃DMF** by PXRD study; thus the structural rearrangement is reversible.

We then measured gas adsorption isotherms of N_2 (Fig. 4). The N_2 adsorption isotherms measured for **1**–**3** at 77 K reveal low uptakes. Adsorption of 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 towards N_2 has been observed in other PCP/MOFs or zeolites,[9] and we consider this unusual behaviour is due to the deficiency of the energy of N_2 diffusion into the small channels of **1**–**3**. The Brunauer–Emmer–Teller (BET) surface area of **2** and **3**, calculated from CO_2 adsorption, are 289 and 343 $m^2\ g^{-1}$. On the other hand, the CO_2 adsorption isotherm of **1** shows a sudden jump at 80 kPa, and the total gas uptake reaches 100 $mL\ g^{-1}$ at 100 kPa. This stepwise profile would be due to the structural transformation. Desorption of CO_2 in **1** occurs below 20 kPa, and we observe a 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 a structural transformation to another phase. In the case of CH_4 adsorption isotherms, **3** also shows 'gate-opening' type behaviour 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 molecule 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

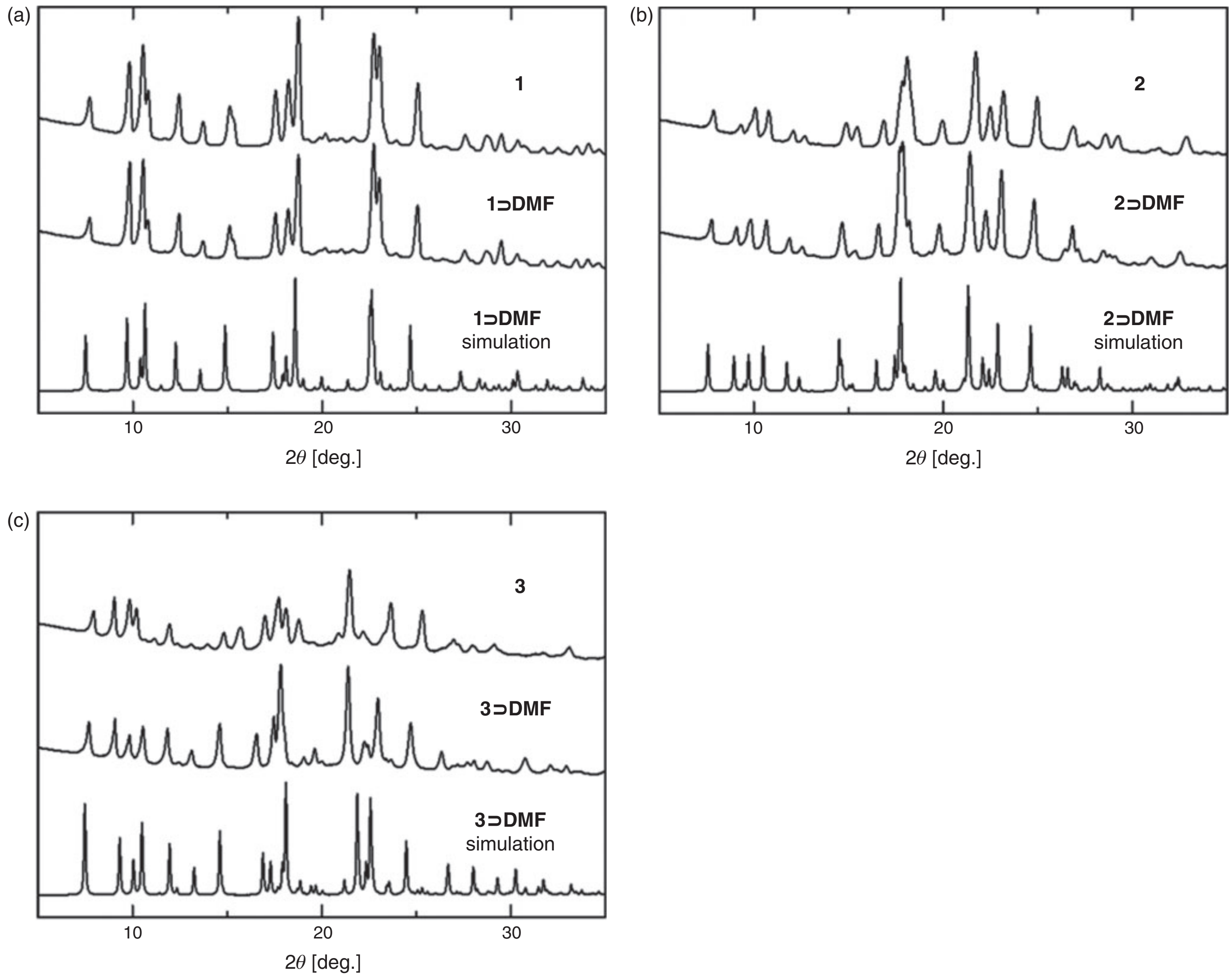

Fig. 3. Powder X-ray diffraction patterns of (a) **1⊃DMF**, **1**; (b) **2⊃DMF**, **2**; (c) **3⊃DMF**, **3**; and their simulated patterns from single crystal X-ray structures.

C1 and C2 hydrocarbons reach ~50–55 mL g^{-1}, which correspond to the accommodation of one CH_4, C_2H_4, or C_2H_6 molecule per Zn^{2+} ion in the structures. All compounds possess a bottle-and-neck type channel structure, and they provide the commensurate type adsorption of guest molecules.

Because the 3D assembled structures of these compounds are the same, the observed different gas adsorption properties must be caused by the different substituent groups on the 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 behaviours. We have previously reported that the structural flexibility depends on the substituent groups of isophthalate ligands in the 2D 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 behaviours.

We also studied the gas adsorption isotherms for these compounds at near room temperature and at pressure ranges of 0 to 900 kPa (Fig. 5). The gas adsorption isotherms are regarded as similar with those in the lower pressure region at 195 K. In the case of **1**, we observed Type-I isotherms for CO_2, C_2H_4, and C_2H_6, whereas a gradual curve for CH_4 is observed because of the lower interaction with the framework. The pressure region studied (~900 kPa) is not enough to promote the consequent structure transformation. In the 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 regions. For **3**, we also observed a stepwise isotherm of CH_4 and a 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, which provides the gradual uptake until 150 kPa.

Conclusion

In this work, we synthesised three compounds of 2D layer type PCP/MOFs consisting of Zn^{2+}, dpa (dipyridylethane), and 5-substituted isophthalate ligands. The structure of the 2D layer of these compounds is **sql** topology and each substituent group provides different pore structures and structure flexibilities. We measured 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 of CO_2 compared with other gases. For the synthesis of these frameworks, the synthetic solvent (DMF) is

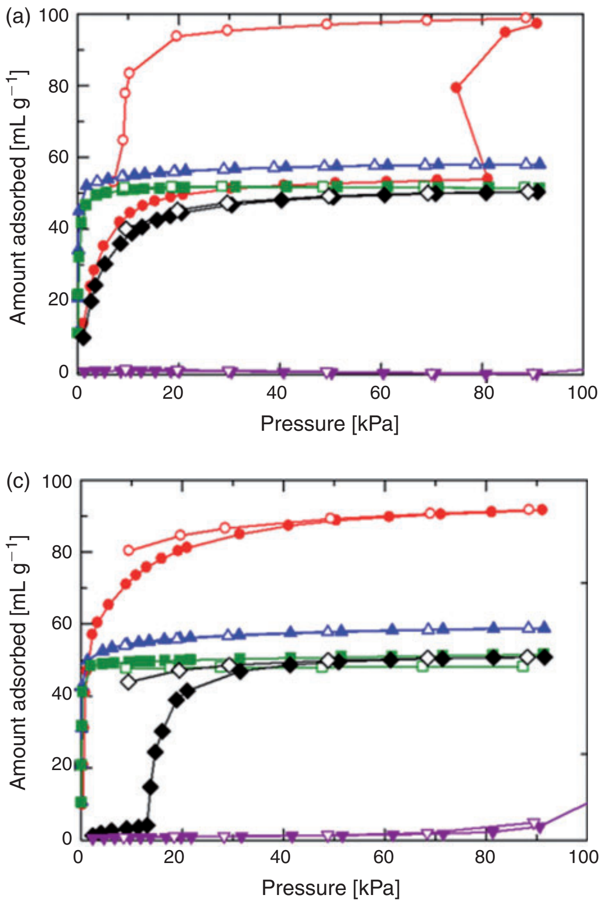

Fig. 4. Gas adsorption and desorption isotherms of (a) **1**, (b) **2**, and (c) **3** at 77 K (purple: N_2) and 195 K (red: CO_2, black: CH_4, blue: C_2H_4, green: C_2H_6). Solid symbols are adsorption and open symbols are desorption, respectively.

key for construction of these new types of 2D layer structures. We have demonstrated a promising approach to construct PCP/MOFs by solvent optimisation.

Experimental

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-methylisophthalic 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$\supset$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 h at 80°C. Colourless 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 bottomed flask and stirred for 16 h at 80°C under N_2 atmosphere. The 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(5-MeOip)(dpa)](DMF)}$_n$ ***(2$\supset$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 h at 80°C. Colourless 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 bottomed flask and stirred for 16 h at 120°C under N_2 atmosphere. A 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(5-Meip)(dpa)](DMF)}$_n$ ***(3$\supset$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 h at 80°C. Colourless 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 bottomed flask and stirred

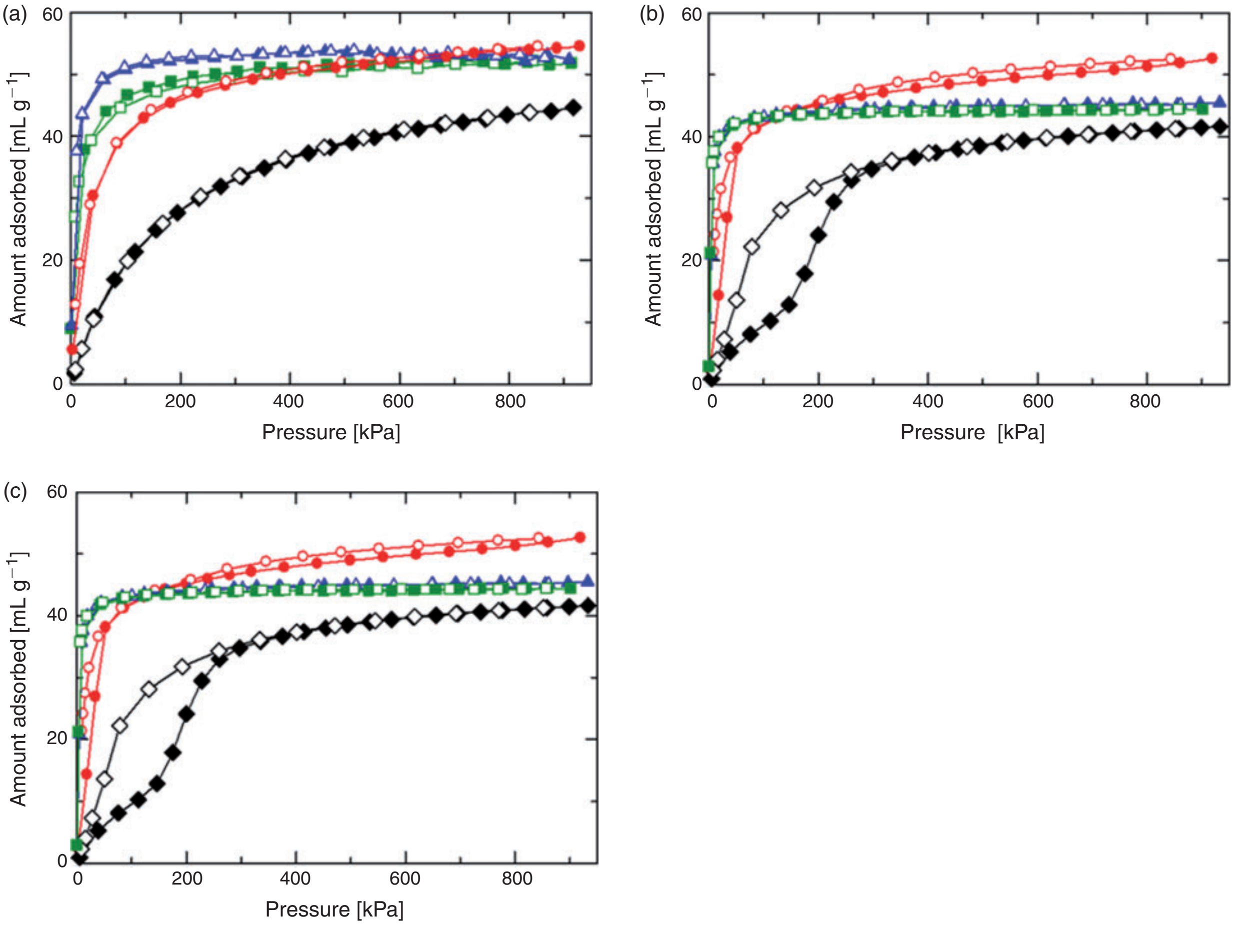

Fig. 5. Gas adsorption and desorption isotherms of (a) **1**, (b) **2**, and (c) **3** at 273 K (red: CO_2, black: CH_4, blue: C_2H_4, green: C_2H_6). Solid symbols are adsorption and opened symbols are desorption, respectively.

for 16 h at 120°C under N_2 atmosphere. A 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 colourless single crystals of **1⊃DMF**, **2⊃DMF**, and **3⊃DMF** were mounted on glass fibres with epoxy resin. X-ray data collection for the single crystals was carried out on a Bruker AXS SMART APEX II Ultra diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) and a CCD 2D detector at 223K (for **1⊃DMF**) or 100 K (for **2⊃DMF** and **3⊃DMF**) in a cold nitrogen stream. The conditions for X-ray of **1⊃DMF** were 50 kV × 100 mA. Absorption corrections were applied by using the 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**, and **3⊃DMF** are listed in Table 1. CCDC deposit numbers of **1⊃DMF**, **2⊃DMF**, **3⊃DMF** are 905315, 905316, and 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 used the *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 analyses (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}. Powder X-ray diffraction (PXRD) 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.

Acknowledgements

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References

[1] (a) O. M. Yaghi, H. L. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474. doi:10.1021/AR970151F

(b) S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1460. doi:10.1002/(SICI)1521-3773(19980619)37:11<1460::AID-ANIE1460>3.0.CO;2-Z

(c) G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* **2002**, *298*, 1762. doi:10.1126/SCIENCE.1075948

(d) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334. doi:10.1002/ANIE.200300610

(e) G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191. doi:10.1039/B618320B

(f) R. E. Morris, P. S. Wheatley, *Angew. Chem. Int. Ed.* **2008**, *47*, 4966. doi:10.1002/ANIE.200703934

(g) J. R. Li, R. J. Kuppler, H. C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477. doi:10.1039/B802426J

(h) G. K. H. Shimizu, R. Vaidhyanathan, J. M. Taylor, *Chem. Soc. Rev.* **2009**, *38*, 1430. doi:10.1039/B802423P

(i) D. M. D'Alessandro, B. Smit, J. R. Long, *Angew. Chem. Int. Ed.* **2010**, *49*, 6058. doi:10.1002/ANIE.201000431

(j) O. K. Farha, J. T. Hupp, *Acc. Chem. Res.* **2010**, *43*, 1166. doi:10.1021/AR1000617

(k) M. P. Suh, H. J. Park, T. K. Prasad, D. W. Lim, *Chem. Rev.* **2012**, *112*, 782. doi:10.1021/CR200274S

(l) N. Stock, S. Biswas, *Chem. Rev.* **2012**, *112*, 933. doi:10.1021/CR200304E

[2] (a) M. Kondo, T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, K. Seki, *Angew. Chem. Int. Ed.* **1999**, *38*, 140. doi:10.1002/(SICI)1521-3773(19990115)38:1/2<140::AID-ANIE140>3.0.CO;2-9

(b) H. Chun, D. N. Dybtsev, H. Kim, K. Kim, *Chem. – Eur. J.* **2005**, *11*, 3521. doi:10.1002/CHEM.200401201

(c) Y. Hijikata, S. Horike, M. Sugimoto, H. Sato, R. Matsuda, S. Kitagawa, *Chem. – Eur. J.* **2011**, *17*, 5138. doi:10.1002/CHEM.201003734

(d) K. Kishida, S. Horike, K. Nakagawa, S. Kitagawa, *Chem. Lett.* **2012**, *41*, 425. doi:10.1246/CL.2012.425

[3] M. O'Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi, *Acc. Chem. Res.* **2008**, *41*, 1782. doi:10.1021/AR800124U

[4] A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7. doi:10.1107/S0021889802022112

[5] (a) S. A. Bourne, J. J. Lu, B. Moulton, M. J. Zaworotko, *Chem. Commun.* **2001**, 861.

(b) Z. Hulvey, J. D. Furman, S. A. Turner, M. Tang, A. K. Cheetham, *Cryst. Growth Des.* **2010**, *10*, 2041. doi:10.1021/CG100121N

(c) L. F. Ma, L. Y. Wang, J. L. Hu, Y. Y. Wang, G. P. Yang, *Cryst. Growth Des.* **2009**, *9*, 5334. doi:10.1021/CG900825Y

[6] L. F. Ma, B. Li, X. Y. Sun, L. Y. Wang, Y. T. Fan, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1606. doi:10.1002/ZAAC.200900516

[7] S. Horike, K. Kishida, Y. Watanabe, Y. Inubushi, D. Umeyama, M. Sugimoto, T. Fukushima, M. Inukai, S. Kitagawa, *J. Am. Chem. Soc.* **2012**, *134*, 9852. doi:10.1021/JA302043U

[8] (a) R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa, *Angew. Chem. Int. Ed.* **2003**, *42*, 428. doi:10.1002/ANIE.200390130

(b) S. Horike, S. Shimomura, S. Kitagawa, *Nat. Chem.* **2009**, *1*, 695. doi:10.1038/NCHEM.444

(c) A. Kondo, H. Kajiro, H. Noguchi, L. Carlucci, D. M. Proserpio, G. Ciani, K. Kato, M. Takata, H. Seki, M. Sakamoto, Y. Hattori, F. Okino, K. Maeda, T. Ohba, K. Kaneko, H. Kanoh, *J. Am. Chem. Soc.* **2011**, *133*, 10512. doi:10.1021/JA201170C

[9] (a) M. Dinca, J. R. Long, *J. Am. Chem. Soc.* **2005**, *127*, 9376. doi:10.1021/JA0523082

(b) D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim, K. Kim, *J. Am. Chem. Soc.* **2004**, *126*, 32. doi:10.1021/JA038678C

(c) D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed, T. L. Thomas, *J. Am. Chem. Soc.* **1956**, *78*, 5963. doi:10.1021/JA01604A001

[10] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Appl. Chem.* **1985**, *57*, 603. doi:10.1351/PAC198557040603

[11] T. Fukushima, S. Horike, Y. Inubushi, K. Nakagawa, Y. Kubota, M. Takata, S. Kitagawa, *Angew. Chem. Int. Ed.* **2010**, *49*, 4820. doi:10.1002/ANIE.201000989