

A Microporous Metal–Organic Framework Based on [2 + 2] Parallel and Inclined Interpenetrated 2D Sheets Interconnected by an Auxiliary Linker

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ABSTRACT: A microporous metal–organic framework (MOF), [Zn₂L₂(dabco)], was prepared using a long and rigid dicarboxylic acid, 1,4-bis(3-carboxyphenylethynyl)benzene (H₂L), with some rotational flexibility, and an auxiliary bridging diamine linker, 1,4-diazabicyclo[2.2.2]octane (dabco). The MOF, based on a Zn paddle-wheel secondary building unit, has [2 + 2] parallel and inclined interpenetrating 2D sheets interconnected by dabco to form a 3D network with 1D helical channels.

Introduction

Entanglement in catenanes, rotaxanes, and molecular knots is one of the major themes of supramolecular chemistry.¹ Metal–organic frameworks (MOFs) with ordered and periodic entanglements, interpenetrating MOFs,² are attractive to researchers owing to their potential applications as new functional materials³ and their intriguing topological structures.⁴

Interpenetrating MOFs can be classified as 1D,⁵ 2D,^{6,7} and 3D⁸ networks depending on the topology of their single networks. 2D interpenetrating networks can be further classified into two different types: inclined interpenetration and parallel interpenetration. To form a MOF of a parallel interpenetration, a single 2D net must be corrugated or have some appropriate element of undulation.⁶ To form a MOF of inclined interpenetration, the circuits in a single 2D net just need to be large enough to allow the other 2D net to pass through the circuits in an inclined fashion, and two nets in the inclined interpenetration are often approximately perpendicular to each other.⁷ Although there are numerous 2D interpenetrating MOFs of a single mode of two different types of interpenetrations, it is still quite rare to observe an MOF having both types of interpenetration modes simultaneously in a single MOF,⁹ probably because of the difficulties associated with generating a 2D net with both the undulation of the 2D net for parallel interpenetration and large enough circuits for simultaneous inclined interpenetration.

Here, we report on the preparation and characterization of a microporous MOF having [2 + 2] parallel and inclined interpenetrating 2D sheets interconnected by 1,4-diazabicyclo[2.2.2]octane (dabco) as an auxiliary ditopic linker, where the sheets are built based on a Zn-paddle-wheel secondary building unit (SBU) by using Zn(II) ion as a metal source and a new long dicarboxylic acid, 1,4-bis(3-carboxyphenylethynyl)benzene (H₂L), as a rigid dicarboxylate ligand. The MOF has undulated 2D sheets with a large rhombic circuit, which allow parallel and inclined interpenetration simultaneously.

Table 1. Crystal Data and Structure Refinement for **1**

1	
empirical formula	C ₂₇ H ₁₈ NO ₄ Zn
formula weight	485.79
temp/K	173(2)
crystal system	orthorhombic
space group	<i>Fddd</i>
<i>a</i> /Å	10.7448(17)
<i>b</i> /Å	36.868(6)
<i>c</i> /Å	60.435(10)
<i>V</i> (Å ³)	23941(7)
<i>Z</i>	32
<i>D_c</i> (g cm ^{−3})	1.078
<i>F</i> (000)	7968
<i>μ</i> /mm ^{−1}	0.846
<i>θ</i> range/deg	1.35–28.40
reflns collected	35706
independent reflns	7286
<i>R</i> _{int}	0.0985
goodness-of-fit	1.002
<i>R</i> ^a / <i>wR</i> ^b (<i>I</i> > 2σ(<i>I</i>))	0.0861/0.2229

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR = [\sum w(|F_o|^2 - |F_c|^2) / \sum w(F_o)^2]^{1/2}.$$

Experimental Section

General Procedures. All other reagents were purchased from commercial sources and were used without further purification. Elemental analyses were conducted at the Elemental Analysis Laboratory of the Korean Basic Science Institute, Korea. Mass spectral data were obtained on a Jeol JMS 700 high resolution mass spectrometer at the Korea Basic Science Institute (Daegu). FT-IR spectra were recorded as KBr pellets with a Varian 1000 FT-IR spectrophotometer (4000–400 cm^{−1}). Powder X-ray diffraction (PXRD) data was recorded using a Rigaku D/M 2200T automated diffractometer at room temperature with a step size of 0.02° in the 2 θ angle. Simulated PXRD patterns were calculated with the Material Studio program¹⁰ using the single crystal data.

Low-Pressure Gas Sorption Measurements. The nitrogen sorption isotherms were measured with a BELSORP-mini II (BEL Japan, Inc.) in a standard volumetric technique, at 77 K. The sorption of hydrogen was measured using liquid nitrogen (77 K) or liquid argon (87 K) as coolant. The gases used were of extrapure quality (N50 for nitrogen and N60 for hydrogen). A part of the N₂ sorption isotherms in the *P*/*P*₀ range 0.006–0.07 (for **1a**) was fitted to the Brunauer–Emmett–Teller (BET) equation to determine the BET surface areas. For the Langmuir surface areas, data from the whole adsorption isotherm were used.

Synthesis of 1,4-Bis(3-carboxyphenylethynyl)benzene Methyl Ester. A solution of 1,4-diethynylbenzene (0.630 g, 4.99 mmol) in

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diethylamine (DEA) (20 mL) was slowly added to a mixture of methyl-3-iodobenzoate (2.900 g, 11.07 mmol), dichlorobis(triphenylphosphino) palladium(II) (0.175 g, 0.249 mmol), and copper(I) iodide (0.145 g, 0.761 mmol) in DEA (80 mL) over 20 min under a N_2 atmosphere. The mixture was stirred for an additional 16 h at room temperature. A pale yellow precipitate was collected by filtration and dissolved in dichloromethane (50 mL). The solution was washed with water (3×100 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation under reduced pressure, and the solid residue was freeze-dried to afford the product, which was employed in the next step without further purification. Yield = 1.91 g, 97.0%. 1H NMR (300 MHz, $CDCl_3$, ppm): δ 8.23 (s, 2H, Ar-H), 8.03 (d, 2H, Ar-H), 7.72 (d, 2H, Ar-H), 7.54 (s, 4H, Ar-H), 7.46 (t, 2H, Ar-H), 3.96 (s, 6H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 165.9, 136.4, 133.2, 131.8, 129.4, 129.3, 128.3, 122.7, 122.3, 93.5, 89.6, 51.7. IR (KBr, cm^{-1}): 3449 (m), 3080 (m), 2996 (m), 1682 (vs), 1602 (m), 1578 (m), 1489 (w), 1447 (m), 1409 (m), 1319 (m), 1216 (s), 1147 (s), 913 (w), 826 (w), 754 (w), 679 (w), 531 (m).

Synthesis of 1,4-Bis(3-carboxyphenylethynyl)benzene (H_2L). Potassium hydroxide (5.611 g, 100.0 mmol) was dissolved in methanol (130 mL), and 1,4-bis(3-carboxyphenylethynyl)benzene methyl ester (1.900 g, 4.817 mmol) was added. The mixture was stirred overnight at 80 $^{\circ}C$. The solvent was then removed by evaporation under reduced

pressure. The residue was dissolved in hot water (500 mL), and the resulting solution was filtered. The filtrate was acidified to pH ~ 2 with 38% HCl. The product was collected as a gray powder. Yield = 1.60 g, 90.7%. HRMS (FAB) m/z calcd for $C_{24}H_{14}O_4$ ($[M]^+$) 366.0892; found 366.0896. 1H NMR (300 MHz, $DMSO-d_6$, ppm): δ 13.19 (s,

Scheme 1. Long and Rigid Dicarboxylic Acid Ligand (H_2L) with the Two *meta*-Carboxylic Groups

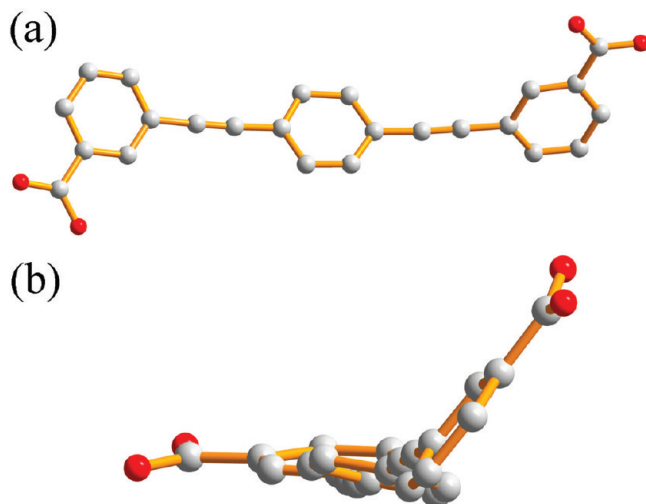
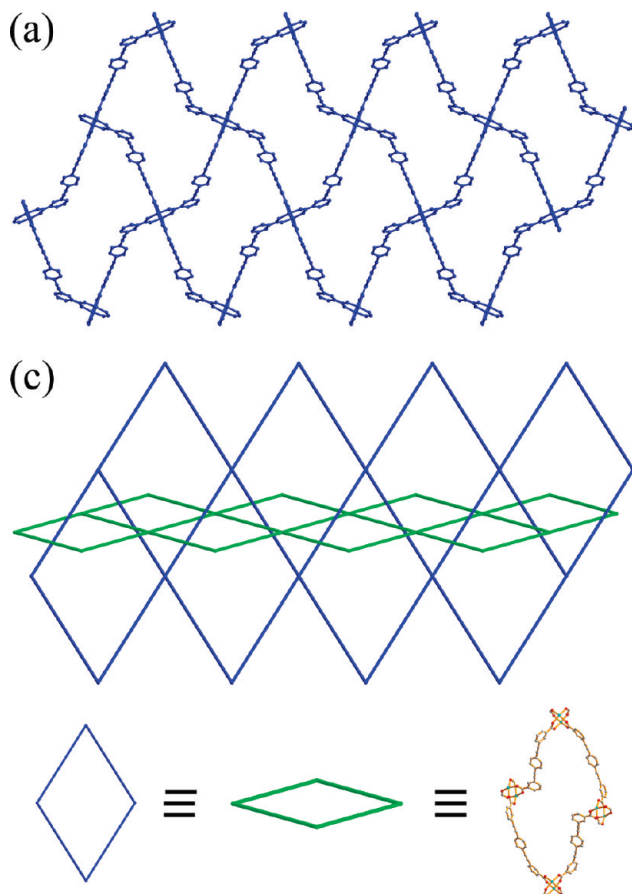
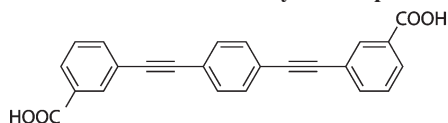


Figure 2. Ligand conformation observed in the crystal structure of 1: (a) top view that shows the two carboxylate groups in an approximate *trans*-conformation; (b) side view that shows a $\sim 120^{\circ}$ dihedral angle between the carboxylate groups.

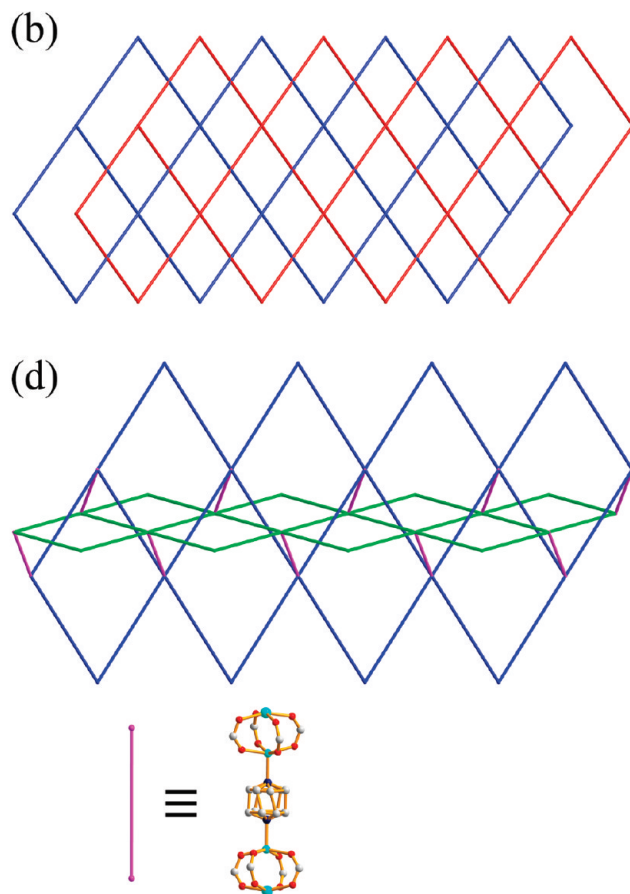


Figure 1. Interpenetration modes of the 2D sheets in the crystal structure of $[Zn_2L_2(dabco)]$ (1). (a) Undulated 2D network of (4, 4) net topology built based on Zn paddle-wheel SBUs. (b) Schematic view of two 2D parallel interpenetrating networks viewed along the crystallographic b -axis. (c) Schematic view of two 2D networks in an inclined interpenetration mode. (d) Schematic view of two 2D inclined interpenetrating networks interconnected by an auxiliary dabco linker to form a single 3D network.

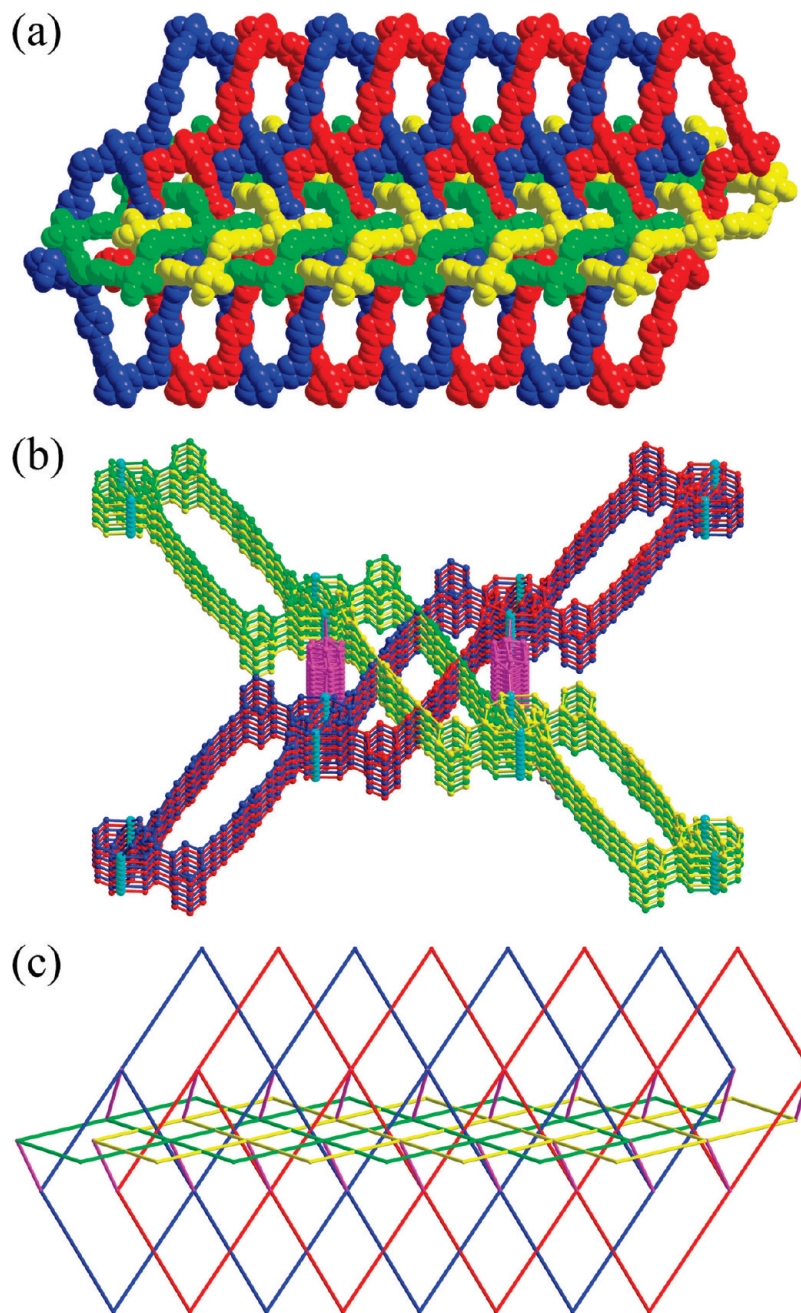


Figure 3. (a) Space-filling diagram of [2 + 2] parallel and inclined interpenetrating networks of **1** viewed along the crystallographic *b*-axis. (b) Ball-and-stick diagram of [2 + 2] parallel and inclined interpenetrating networks further interconnected by the dabco ligand (pink) to a 3D MOF viewed along the crystallographic *a*-axis. (c) Schematic view of part b.

2H, $-\text{COOH}$), 8.08 (s, 2H, Ar-H), 7.98 (d, 2H, Ar-H), 7.81 (d, 2H, Ar-H), 7.65 (s, 4H, Ar-H), 7.58 (t, 2H, Ar-H). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$, ppm): δ 166.6, 135.4, 132.2, 131.8, 131.6, 129.7, 129.3, 122.4, 90.5, 89.6. IR (KBr, cm^{-1}): 3449 (m), 3080 (m), 2996 (m), 1682 (vs), 1602 (m), 1578 (m), 1489 (w), 1447 (m), 1409 (m), 1319 (m), 1216 (s), 1147 (s), 913 (w), 826 (w), 754 (w), 679 (w), 531 (m).

Synthesis of $[\text{Zn}_2\text{L}_2(\text{dabco})]\cdot 2\text{H}_2\text{O}$ (1a**).** $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.062 g, 0.21 mmol) and H_2L (0.073 g, 0.20 mmol) were dissolved in dimethylformamide (DMF) (4 mL). 1,4-Diazabicyclo[2.2.2]octane (dabco) (0.012 g, 0.11 mmol) was added, and the mixture was stirred at room temperature for 1 h. The product was centrifuged and filtered. The resulting solution was divided into four equal portions, each of which was charged into a Pyrex tube. After tightly sealing the tubes, they were heated to 120 °C for 2 days. Pale yellow block-shaped crystals, **1**, were collected. The activated sample, **1a**, was prepared by soaking **1** in fresh DMF and then in MeOH for several

days, respectively, before drying under a dynamic vacuum overnight at 200 °C, and then by exposing to air (yield: 0.051 g, 51%). IR (KBr, cm^{-1}): 3434 (m), 3065 (m), 3037 (m), 2933 (m), 2891 (m), 1673 (vs), 1643 (m), 1621 (m), 1590 (m), 1570 (m), 1510 (w), 1428 (m), 1396 (vs), 1322 (m), 1258 (s), 1168 (s), 1094 (s), 1015 (s), 920 (w), 837 (w), 807 (w), 767 (w), 688 (w), 544 (m). EA. Calcd for $[\text{Zn}_2(\text{C}_{24}\text{H}_{12}\text{O}_4)_2(\text{C}_6\text{H}_{12}\text{N}_2)]\cdot 2\text{H}_2\text{O}$, **1a**: C, 64.37; H, 4.00; N, 2.78. Found: C, 64.05; H, 3.88; N, 2.24.

Crystallographic Data Collection and Refinement of the Structure. A crystal freshly harvested from the mother liquor was coated with paratone oil and the diffraction data collected at 173 K on a Bruker Smart CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) using the SMART and SAINT software packages.¹¹ Empirical absorption corrections were applied by use of the SADABS program based upon Laue symmetry using equivalent reflections.¹²

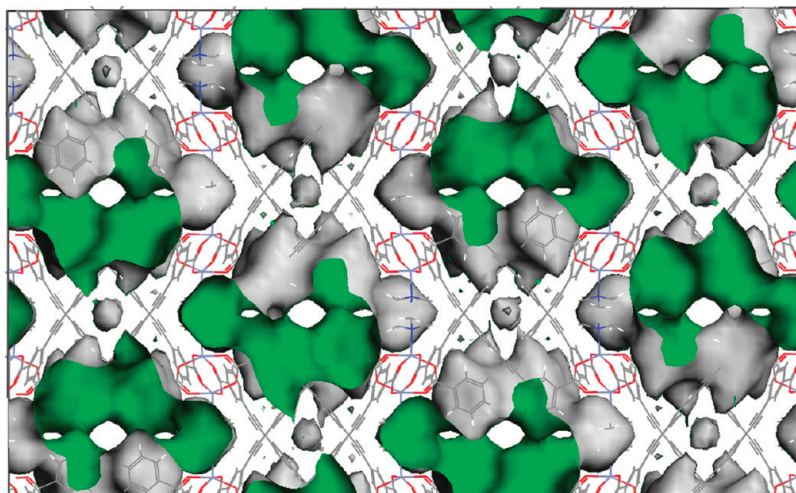


Figure 4. 1D helical channels of **1** along the crystallographic *a*-axis. The green represents the inside of the channels, and the gray represents the framework.

Crystal Structure Determination for 1. The crystal structure of **1** was solved by a direct method and refined by a full-matrix least-squares calculation with the SHELXTL-Plus (version 5.1) software package.¹³ One zinc atom, one dicarboxylate ligand, and a dabco on the crystallographic 2-fold axis were identified as an asymmetric unit in the crystal structure. The central phenyl residue of the dicarboxylate ligand and the dabco linker were statistically disordered. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were assigned isotropic displacement coefficients $U(\text{H}) = 1.2$ (Å²), and their coordinates were allowed to ride on their respective atoms. Although several lattice solvent sites were partially identified, they could not be appropriately modeled because of severe disordering. The refinement of the model with no lattice solvents converged to $R1 = 0.1321$ and $wR2 = 0.3252$ for 4068 reflections of $I > 2\sigma(I)$. Structure refinement after modification of the data for the lattice solvent sites with the SQUEEZE routine of PLATON (8110 Å³, 33.9% of the crystal volume, 1173 solvent electrons [~27 DMF molecules] per unit cell)¹⁴ led to better refinement and data convergence. Refinement converged at a final $R1 = 0.0861$ and $wR2 = 0.2229$ for 4097 reflections with $I > 2\sigma(I)$. A summary of the crystal and intensity data is given in Table 1. CCDC-732291 contains the supplementary crystallographic data.

Results and Discussion

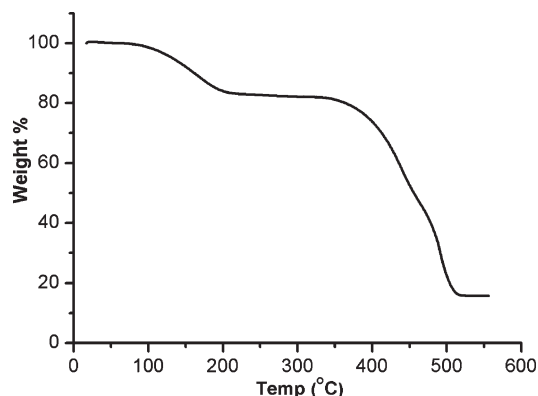
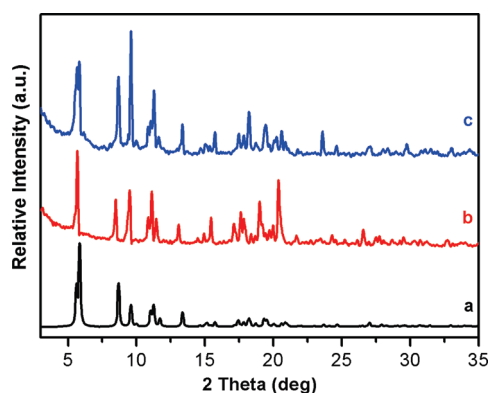
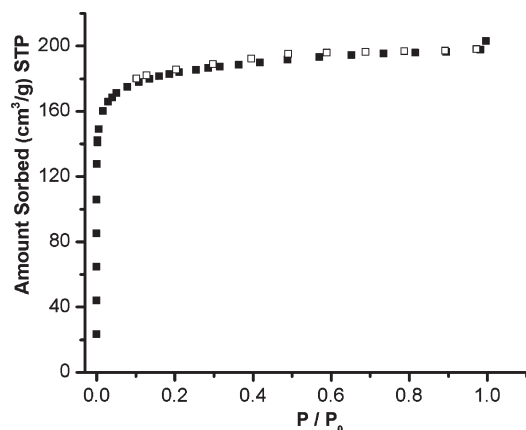
We designed a new long dicarboxylate ligand, H₂L, which is rigid but has some degree of rotational flexibility owing to the two C–C triple bonds (Scheme 1). Even though the ligand has a long, rigid, and linear linking moiety between the benzoic acid groups, it is not a linear dicarboxylic acid ligand but a bent one, because of the meta-positioning of the carboxylic acid groups. It is well-known that the Zn(II) ion has the tendency to form a Zn paddle-wheel SBU with carboxylate ligands in the presence of bridging diamine linkers such as bipyridine, pyrazine, and dabco.¹⁵ The meta-positioned two carboxylic acid groups with the rigid and long linking moiety in the ligand might allow the generation of an undulated 2D net with large circuits for a parallel interpenetrating MOF and yet still leave a large enough space for another type of interpenetration—an inclined interpenetration.

A solvothermal reaction of H₂L with Zn(NO₃)₂·6H₂O in the presence of dabco in DMF at 120 °C for 2 days afforded pale yellow, block-shaped crystals, [Zn₂L₂(dabco)] (**1**). The structure of **1** was determined by single-crystal X-ray diffraction.¹⁶ **1** is a 3D MOF in [2 + 2] parallel and inclined interpenetration mode of 2D nets built based on Zn paddle-wheel

SBUs, interconnected by a rigid and long moiety of the ligand (Figure 1), where the two carboxylates in the ligand are in the *trans*-conformation (a ~120° dihedral angle between the carboxylates; see Figure 2) to form an undulated 2D net of (4, 4) network topology with a large rhombic circuit, with the dimensions of 21.5 Å and 35.4 Å in diagonal distances (Figure 1a).

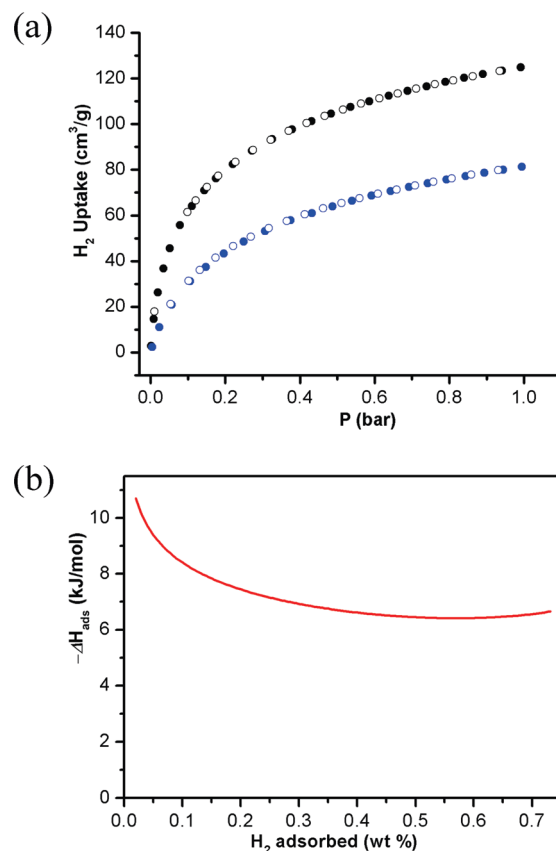
The undulated 2D net with a large rhombic circuit allowed 2-fold parallel interpenetration (Figure 1b). Owing to the rigid and long length of the ligand, the remaining inner space of the circuits in the parallel interpenetrating nets is still large enough to permit further 2-fold interpenetration of other parallel interpenetrating nets in an inclined fashion (Figure 1c), which resulted in a MOF in [2 + 2] parallel and inclined interpenetration mode (Figure 3a). In **1**, the nets in an inclined fashion are interconnected with each other through the axial sites of the Zn paddle-wheel SBUs by ditopic dabco linkers to form a single 3D net (Figure 1d). Figure 3a shows the simultaneous [2 + 2] parallel and inclined interpenetration in the framework, and these interpenetrated nets are further interconnected by the auxiliary dabco linkers to form a single 6-connected self-penetrating 3D network of the network topology with the Schläfli symbol 4⁸·6⁶·8 and the extended point symbol 4·4·4·4·4·4·4·4·6₂·6₂·6₃·6₃·6₃·6₃·8₄₂ (Figure 3b and c).¹⁷ Even though **1** is a 4-fold interpenetrating net, it still has quite a large solvent pore volume (8110 Å³, 33.9% of the crystal volume), because of the long and rigid nature of the ligand. The packing diagram of **1** indicates that the pore comprised 1D helical channels along the crystallographic *a*-axis, with a smallest aperture diameter of ~5 Å (Figure 4). When this channel is idealized as a straight cylindrical shape, the average diameter of the channel corresponds to ~10 Å.

Thermogravimetric analysis (TGA) indicated that all lattice solvent molecules of **1** could be removed from the framework up to about 200 °C and framework decomposition occurred above 350 °C (Figure 5). The bulk identity of **1** was confirmed by comparison of a simulated powder X-ray diffraction (PXRD) pattern from the single crystal structure with that of the bulk crystals (Figure 6). The PXRD pattern of the activated sample **1a**, prepared by repeatedly soaking and desolvating **1** in fresh DMF and vacuum-drying at 200 °C overnight, is in good agreement with the simulated pattern.

Figure 5. TGA of **1**.Figure 6. (a) Simulated PXRD pattern of the single crystal structure of **1** (black), (b) as-synthesized **1** (red), and (c) activated **1a** (cyan).Figure 7. Gas sorption isotherm of **1a** for N₂ at 77 K (solid and open shapes represent adsorption and desorption, respectively).

This high thermal stability of **1** might be due to the enhanced rigidity imposed by the ditopic dabco linker interconnecting the 4-fold interpenetrating 2D networks.

The type I N₂ sorption isotherm of **1a** indicates that **1a** has micropores, which is expected from the single crystal structure of **1** (Figure 7). The Brunauer–Emmett–Teller (BET) and Langmuir surface areas of **1a** are 710 m² g^{−1} and 850 m² g^{−1}, respectively. The measured pore volume from the N₂ sorption, 0.310 cm³ g^{−1}, is almost the same as that estimated from the single crystal structure, 0.315 cm³ g^{−1}.

Figure 8. (a) H₂ sorption isotherms on **1a** at 77 K (black) and 87 K (cyan) (solid and open shapes represent adsorption and desorption, respectively). (b) H₂ adsorption enthalpy on **1a**.

The H₂ sorption on **1a** was measured at 77 and 87 K. The hydrogen uptakes at 1 atm were 120 cm³ g^{−1} (1.1 wt %) and 81 cm³ g^{−1} (0.72 wt %), respectively (Figure 8a). The H₂ storage capacity was in the range expected from the BET or Langmuir surface area.¹⁸ The adsorption enthalpies have been estimated using the modified version of the Clausius–Clapeyron equation depending on the degree of H₂ loading;¹⁹ they ranged from 10.7 to 6.4 kJ mol^{−1} (Figure 8b). These values are much higher than the H₂ adsorption enthalpies reported for MOFs with no exposed metal centers.²⁰ The optimal pore size of the 1D channel might be responsible for such high H₂ adsorption enthalpies of **1a**, even with no exposed metal sites.^{18,20}

Conclusions

In conclusion, we successfully synthesized a Zn-based microporous MOF (**1**), using the long and rigid dicarboxylic ligand, 1,4-bis(3-carboxyphenylethynyl)benzene, with some degree of rotational flexibility. When the Zn(II) ions were self-assembled with the ligand in the presence of an auxiliary ditopic linker, dabco, a rare [2 + 2] parallel and inclined interpenetrating MOF based on a zinc paddle-wheel SBU could be prepared. The two meta-positioned carboxylate groups of the ligand, with the rigid and long linking moiety, might allow for an undulated 2D sheet with large enough circuit space for 4-fold interpenetration in [2 + 2] parallel and inclined interpenetration mode. The networks in the inclined interpenetration relation are further interconnected by dabco, which results in **1** having a framework of a single 3D network topology, enhancing the structural rigidity. Even though **1** is

4-fold interpenetrated, it still has 1D helical channels of ~ 10 Å average diameters, and this pore size might be responsible for the high H_2 adsorption enthalpies of the MOF.

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Supporting Information Available: Crystallographic details and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Frisch, H. L.; Wasserman, E. *J. Am. Chem. Soc.* **1961**, *83*, 3789. (b) *Molecular Catenanes, Rotaxanes and Knots, A Journey Through the World of Molecular Topology*; Sauvage, J.-P.; Dietrich-Buchecker, C., Eds.; Wiley-VCH: Weinheim, Germany, 1999. (c) Schill, G. In *Catenanes, Rotaxanes, and Knots*; Academic Press: New York, 1971. (d) Siegel, J. S. *Science* **2004**, *304*, 1256. (e) Lukin, O.; Vögtle, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 1456.
- (2) (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (b) Batten, S. R. *CrystEngComm* **2001**, *1*, 67.
- (3) (a) Miller, J. S. *Adv. Mater.* **2001**, *13*, 525. (b) Zeng, M. H.; Zhang, W. X.; Sun, X. Z.; Chen, X. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3079. (c) Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 428. (d) Chen, B.; Ma, S.; Zapata, F.; Fronczek, F. R.; Lobkovsky, E. B.; Zhou, H.-C. *Inorg. Chem.* **2007**, *46*, 1233. (e) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670.
- (4) (a) Yang, J.; Ma, J. F.; Batten, S. R.; Su, Z. M. *Chem. Commun.* **2008**, 2233. (b) Hou, L.; Zhang, J.-P.; Chen, X.-M. *Cryst. Growth Des.* **2009**, *9*, 2415. (c) Wang, X. L.; Qin, C.; Wang, E. B.; Su, Z. M.; Xu, L.; Batten, S. R. *Chem. Commun.* **2005**, 4789. (d) Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *CrystEngComm* **2004**, *4*, 378.
- (5) (a) Peedikakkal, A. M. P.; Vittal, J. J. *Cryst. Growth Des.* **2008**, *8*, 375. (b) Fraser, C. S. A.; Jennings, M. C.; Puddephatt, R. J. *Chem. Commun.* **2001**, 1310. (c) Arora, K. K.; Pedireddi, V. R. *Cryst. Growth Des.* **2005**, *5*, 1309. (d) Hoskins, B. F.; Robson, R.; Slizys, D. A. *J. Am. Chem. Soc.* **1997**, *119*, 2952. (e) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287.
- (6) (a) Batten, S. R.; Hoskins, B. F.; Robson, R. *Chem.—Eur. J.* **2000**, *1*, 156. (b) Son, S. U.; Kim, B. Y.; Choi, C. H.; Lee, S. W.; Kim, Y. S.; Chung, Y. K. *Chem. Commun.* **2003**, 2528. (c) Sarkar, M.; Biradha, K. *Chem. Commun.* **2005**, 2229. (d) Suh, M. P.; Choi, H. J.; So, S. M.; Kim, B. M. *Inorg. Chem.* **2003**, *42*, 676. (e) Ryan, P. E.; Lescop, C.; Laliberte, D.; Hamilton, T.; Maris, T.; Wuest, J. D. *Inorg. Chem.* **2009**, *48*, 2793. (f) Song, L.; Du, S.-W.; Lin, J.-D.; Zhou, H.; Li, T. *Cryst. Growth Des.* **2007**, *7*, 2268.
- (7) (a) Tong, M.-L.; Hu, S.; Wang, B.; Batten, S. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 5471. (b) Basavoju, S.; Aitipamula, S.; Desiraju, G. R. *CrystEngComm* **2004**, *4*, 120. (c) Marin, G.; Tudor, V.; Kravtsov, V. C.; Schmidtman, M.; Simonov, Y. A.; Muller, A.; Andruh, M. *Cryst. Growth Des.* **2005**, *5*, 279. (d) Wu, C.-De; Ma, L. Q.; Lin, W. B. *Inorg. Chem.* **2008**, *47*, 11446.
- (8) (a) Chun, H.; Dybste, D. N.; Kim, H.; Kim, K. *Chem.—Eur. J.* **2005**, *11*, 3521. (b) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469. (c) Dai, J.-C.; Wu, X.-T.; Fu, Z.-Y.; Hu, S.-M.; Du, W.-X.; Cui, C.-P.; Wu, L.-M.; Zhang, H.-H.; Sun, R.-Q. *Chem. Commun.* **2002**, 12.
- (9) Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Chem. Commun.* **1998**, 13.
- (10) *Materials Studio program*, version 4.3; Accelrys: San Diego, CA, 2008.
- (11) SMART and SAINT, Area Detector Software Package and SAX Area detector Integration Program; Bruker Analytical X-ray: Madison, WI, 1997.
- (12) SADABS, Area Detector Absorption Correction Program; Bruker Analytical X-ray: Madison, WI, 1997.
- (13) Sheldrick, G. M. *SHELXTL—PLUS*, Crystal Structure Analysis Package; Bruker Analytical X-ray: Madison, WI, 1997.
- (14) Platon program: Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194.
- (15) (a) Kim, J.; Chen, B.; Reineke, T. M.; Li, H.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 8239. (b) Bourne, S. A.; Lu, J.; Mondal, A.; Moulton, B.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2111. (c) Dybste, D. N.; Chun, H.; Kim, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5033. (d) Chun, H. *J. Am. Chem. Soc.* **2008**, *130*, 800. (e) Chun, H.; Moon, J. *Inorg. Chem.* **2007**, *46*, 4371.
- (16) Zhao, D.; Yuan, D.; Zhou, H.-C. *Energy Environ. Sci.* **2008**, *1*, 222.
- (17) Blatov, V. A. *IUCr Compcomm. Newsl.* **2006**, *7*, 4, <http://www.topos.ssu.samara.ru>.
- (18) Dincă, M.; Long, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 9376.
- (19) (a) Lee, J. Y.; Pan, L.; Kelly, S. P.; Jagiello, J.; Emge, T. J.; Li, J. *Adv. Mater.* **2005**, *17*, 2703. (b) Rowsell, J. L. C.; Millward, A. R.; Park, K. S.; Yaghi, O. M. *J. Am. Chem. Soc.* **2004**, *126*, 5666.
- (20) Wang, Q.; Johnson, J. K. *J. Chem. Phys.* **1999**, *110*, 577.