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# Structure and Topology Versatility of Metal–Organic Frameworks Based on Tetradentate Ligands Isolated from Hydrothermal Metal/Ligand Reactions

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**ABSTRACT:** The use of the planar tetradentate ligands 1,2,4,5-tetra(4-pyridyl)benzene (bztpy) and 1*a*,4*a*-dihydroxy-1*e*,2*e*,4*e*,5*e*-tetra(4-pyridyl)cyclohexane (chtpy) obtained by hydrothermal in situ metal/ligand reactions enabled the isolation of three metal–organic frameworks (MOFs) related to ligand-influencing factors with the formulas  $\alpha$ -[CdCl<sub>2</sub>(bztpy)]·H<sub>2</sub>O (**1**),  $\beta$ -[CdCl<sub>2</sub>(bztpy)]·H<sub>2</sub>O (**2**), and [Cd<sub>4</sub>(O<sub>2</sub>CPh)<sub>2</sub>Cl<sub>2</sub>(OH)(chtpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>·4.5H<sub>2</sub>O (**3**). **1** and **2** are two supramolecular isomers featuring a two-dimensional (2D) (4,4) net and three-dimensional (3D) NbO net that result from the conformational freedom of the bztpy ligands. **3** has a novel 3D MOF structure based on cuboidal {Cd<sub>4</sub>} clusters. The high-connected {Cd<sub>4</sub>} clusters connected to each other through planar tetradentate ligands in **3** ensured its uncommon (4,8)-connected *scu* topology. A discussion of the crystal structures, as well as the coordination behavior of the special tetradentate ligands upon differences geometries of the central connector, is provided.

## Introduction

The rapidly expanding field of crystal engineering of multi-dimensional metal–organic frameworks (MOFs) is of great current interest for both structural and topological diversity as well as for their potential application as functional materials.<sup>1</sup> Crystal engineering principles provide a facile approach to the controlled assembly of one- to three-dimensional (1–3D) extended networks,<sup>2</sup> which has recently become marvelously state-of-the-art. Recent elaboration has demonstrated the dramatic influence of the building-block approach on the framework of inorganic materials, and much effort has been made toward the connecting of suitable predetermined building blocks into networks in order to obtain the desired materials.<sup>3</sup> A potentially efficient way to synthesize high dimensional MOFs should be to focus on the organic ligands with specific structural features. In this regard, development of new multitopic building blocks is one of the central tasks.

As a nonconventional method, hydrothermal in situ metal/ligand reactions provide not only novel functional MOFs, but also unusual organic ligands that are inaccessible or not easily obtainable by conventional methods.<sup>4</sup> We have been recently investigating a novel in situ metal/organic reaction of an unprecedented dehydrogenative coupling and hydroxylation of 1,3-bis(4-pyridyl)propane (bpp) into a dihydroxycyclohexane ligand *a,a*-1,4-dihydroxy-*e,e,e,e*-1,2,4,5-tetra(4-pyridyl)cyclohexane (chtpy) in its Cu<sup>I</sup> coordination polymers, which could be isolated by demetallization with Na<sub>2</sub>(H<sub>2</sub>edta). Fortunately, the 1,2,4,5-tetra(4-pyridyl)benzene (bztpy) has also been successfully isolated from the powder product of the above hydrothermal systems, which can be applied to construct a series of novel 2D and 3D MOFs.<sup>5a,b</sup>

Tetradentate nitrogen-containing ligands with novel structural features offer the possibility to realize MOFs with specific topologies.<sup>6</sup> In our previous investigation, we prepared and characterized a (4,4) net, a rare moganite net, a PtS net, and a (3,4)-connected net with tetrahedral Cu<sup>I</sup> atoms and the planar tetratopic ligands chtpy generated in situ.<sup>5a</sup> Generally, employing a planar tetratopic bridging ligand promotes the formation of 2–3D MOFs. However, the topological tunable properties of MOFs are also influenced by factors of the coordination nature of the central connector of metal ion or cluster subunit.<sup>7</sup> As part of our ongoing efforts in the extension of these functional four-connected ligands to other metal salts or polynuclear metal cluster blocks, we report herein three new MOFs, namely,  $\alpha$ -[CdCl<sub>2</sub>(bztpy)]·H<sub>2</sub>O (**1**),  $\beta$ -[CdCl<sub>2</sub>(bztpy)]·H<sub>2</sub>O (**2**), and [Cd<sub>4</sub>(O<sub>2</sub>CPh)<sub>2</sub>Cl<sub>2</sub>(OH)(chtpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>·4.5H<sub>2</sub>O (**3**). Two supramolecular isomers **1** and **2** were obtained by adjusting the template and reaction temperature, displaying (4,4) and NbO net topologies, respectively. **3** is a rare, bcu-type framework, assembled from chtpy as a bridging ligands and an eight-connecting tetracadmium cluster as a building block. **3** is a good candidate for the MOFs constructed from a high-connected polynuclear metal cluster unit and a predesigned polydentate ligand.

## Experimental Section

**Materials and Methods.** The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm<sup>−1</sup> on a Bio-Rad FTS-7 spectrometer. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/M-2200T automated diffractometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in (CD<sub>3</sub>)<sub>2</sub>SO on Mercury-Plus 300 spectrometers. ESI-MS were recorded using an LCMS-2010A mass spectrometer.

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Table 1. Crystal Data and Structure Refinements for bztpy·EtOH, bztpy·2H<sub>2</sub>O, and 1–3

	bztpy·EtOH (123 K)	bztpy·2H <sub>2</sub> O (293 K)	1 (293 K)	2 (123 K)	3 (123 K)
empirical formula	C <sub>28</sub> H <sub>24</sub> N <sub>4</sub> O	C <sub>26</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>26</sub> H <sub>20</sub> CdCl <sub>2</sub> N <sub>4</sub> O	C <sub>26</sub> H <sub>20</sub> CdCl <sub>2</sub> N <sub>4</sub> O	C <sub>66</sub> H <sub>72</sub> Cd <sub>4</sub> Cl <sub>2</sub> N <sub>11</sub> O <sub>24.5</sub>
<i>M</i>	432.51	422.48	587.76	587.76	1931.85
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	trigonal	orthorhombic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 13)	<i>R</i> 3 <i>m</i> (No. 166)	<i>Cmcm</i> (No. 63)
<i>a</i> /Å	13.8997(18)	12.5739(17)	10.2936(12)	26.9517(14)	27.9319(6)
<i>b</i> /Å	14.854(2)	6.2862(8)	9.8758(12)	26.9517(14)	14.3167(9)
<i>c</i> /Å	11.1887(14)	15.712(2)	12.7191(15)	13.2369(14)	21.4476(6)
$\alpha$ /°	90	90	90	90	90
$\beta$ /°	102.556(3)	113.038(3)	105.893(2)	90	90
$\gamma$ /°	90	90	90	120.00	90
<i>V</i> /Å <sup>3</sup>	2254.8(5)	1142.9(3)	1243.6(3)	8327.0(11)	8576.7(6)
<i>Z</i>	4	2	2	12	4
$\rho_{\text{calcd}}/\text{g cm}^{-3}$	1.274	1.228	1.570	1.407	1.496
$\mu/\text{mm}^{-1}$	0.079	0.080	1.119	1.003	9.039
reflins collected	7742	5485	4185	11587	33269
unique reflins	4199	2233	2326	1936	3569
<i>R</i> <sub>int</sub>	0.0266	0.0226	0.0202	0.0388	0.0641
<i>S</i>	1.036	1.079	1.057	1.155	0.951
<i>R</i> <sub>1</sub> <sup>a</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0524	0.0535	0.0347	0.0492	0.0578
<i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.1370	0.1326	0.0857	0.1570	0.1792

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

**Isolation of bztpy.** Solution of (NH<sub>4</sub>)<sub>2</sub>S (0.681 g, 10 mmol) was dropwise added to a stirred suspension of the powder and crystal products (1.250 g), which were obtained from the hydrothermal treatment of in situ synthesized fresh Cu(OH)<sub>2</sub> (from Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and NaOH) with 1,3-bis(4-pyridyl)propane (bpp) and 1,4-cyclohexanedicarboxylic acid,<sup>5a</sup> in chloroform (120 mL) and water (40 mL) at room temperature. The reaction suspension was warmed to 60 °C, stirred and refluxed at this temperature for 4 h, and cooled to room temperature, and the organic phase was separated. The aqueous layers were extracted with chloroform (3 × 100 mL), and the combined organic layers were concentrated in rotatory evaporator. The residue was dissolved in dichloromethane and then purified by column chromatography (3% ether in petrol) to give chtpy (0.212 g) as a pale-yellow powder at first (data have been reported previously).<sup>5a</sup> Further elution yielded bztpy (0.120 g) as a faint yellow powder. (ESI-MS): *m/z* = 387; <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 500 MHz): δ = 7.27 [dd, *J*<sub>H–H</sub> = 4.4, 1.6 Hz, 8H, C2–H2, C4–H4, C10–H10, C13–H13], δ = 7.64 [m, 2H, C7–H7], δ = 8.51 ppm [dd, *J*<sub>H–H</sub> = 4.5, 1.5 Hz, 8H, C1–H1, C5–H5, C11–H11, C12–H12], <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 75 MHz): 124.5 (C-2), 132.4 (C-7), 137.9 (C-6), 146.7 (C-3), 149.5 ppm (C-1). Colorless crystals of bztpy·EtOH and bztpy·2H<sub>2</sub>O were obtained by dissolution of the powder in ethanol and in acetonitrile, respectively, at ambient temperature in air. Elemental analysis calcd for bztpy·EtOH: C, 77.75; H, 5.59; N, 12.95. Found: C, 77.79; H, 5.61; N, 12.91. IR (KBr, cm<sup>−1</sup>): 2956 (m), 2918 (vs), 2850 (s), 1466 (m), 723 (w).

**Preparation of α-[CdCl<sub>2</sub>(bztpy)]·H<sub>2</sub>O (1).** A mixture of CdCl<sub>2</sub>·4H<sub>2</sub>O (0.5 mmol), bztpy (0.1 mmol), and water (10 mL) was stirred for 2 min in air, then transferred and sealed in a 23-mL Teflon reactor. The resultant mixture was heated in a stainless steel reactor with a Teflon liner at 160 °C for 72 h. After a period of approximately 14 h of cooling to room temperature, colorless crystals of **1** were obtained (yield: 20%). Elemental analysis calcd (%) for **1**: C, 53.13; H, 3.43; N, 9.53. Found: C, 53.18; H, 3.44; N, 9.51. IR (KBr, cm<sup>−1</sup>): 3061 (w), 3027 (w), 1066 (s), 1548 (w), 1501 (w), 1477 (m), 1380 (w), 1336 (w), 1220 (s), 1071 (w), 1004 (m), 912 (w), 890 (w), 825 (s), 740 (s), 687 (m), 560 (w), 542 (m), 480 (w).

**Preparation of β-[CdCl<sub>2</sub>(bztpy)]·H<sub>2</sub>O (2).** A mixture of CdCl<sub>2</sub>·4H<sub>2</sub>O (0.5 mmol), bztpy (0.05 mmol), dpS<sub>2</sub> (1,2-diphenyldisulfane, 0.25 mmol), and water (9 mL) in a 23 mL Teflon reactor, which was heated at 185 °C for 96 h and then cooled to room temperature at a rate of 5 °C/h. Pale brown crystals were obtained (yield: 12%). Elemental analysis calcd (%) for **2**: C, 53.13; H, 3.43; N, 9.53. Found: C, 53.15; H, 3.42; N, 9.48. IR (KBr, cm<sup>−1</sup>): 3057 (w), 3029 (w), 1064 (s), 1547 (w), 1499 (w), 1476 (m), 1379 (w), 1334 (w), 1222 (s), 1070 (w), 1005 (m), 913 (w), 888 (w), 827 (s), 738 (s), 687 (m), 559 (w), 542 (m), 479 (w).

**Preparation of [Cd<sub>4</sub>(O<sub>2</sub>CPh)<sub>2</sub>Cl<sub>2</sub>(OH)(chtpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>·4.5H<sub>2</sub>O (3).** A mixture of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.5 mmol), chtpy (0.05 mmol), sodium benzoate (0.5 mmol), HCl (0.1 mmol), water (5 mL), and methanol (5 mL) in a 23 mL Teflon reactor, which was heated at 160 °C for 88 h and then cooled to room temperature at a rate of 5 °C/h. Colorless crystals were obtained (yield: 35%). Elemental analysis calcd (%) for **3**: C, 41.03; H, 3.76; N, 7.98. Found: C, 41.09; H, 3.72; N, 7.95. IR (KBr, cm<sup>−1</sup>): 3407 (m), 3078 (w), 2915 (w), 1612 (s), 1548 (m), 1499 (w), 1384 (s), 1302 (m), 1227 (w), 1070 (w), 1018 (w), 822 (w), 722 (w), 679 (w), 556 (m).

**X-ray Crystallography.** The diffraction data for compounds bztpy·EtOH, bztpy·2H<sub>2</sub>O, and **1–3** were recorded on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo–Kα radiation (λ = 0.71073 Å) at 123 K (for bztpy·EtOH, **2** and **3**) and 293 K (for bztpy·2H<sub>2</sub>O and **1**). Processing data was accomplished with use of the program *SAINT*; an absorption correction based on symmetry equivalent reflections was applied using the *SADABS* program.<sup>8</sup> The structures were solved by direct methods and refined by the full-matrix least-squares method on *F*<sup>2</sup> with SHELXTL program package.<sup>9</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters except for the disordered groups. The disordered guest molecules were subjected to geometric restraints during the refinements. The crystallographic details and selected bond lengths and bond angles are provided in Tables 1 and 2, respectively.

## Results and Discussion

**Synthesis and Characterization.** As the ligand was isolated from a copper coordination polymer, we found that bztpy has many desirable characteristics, including two stereoisomers (staggered and eclipsed conformations in bztpy·EtOH and bztpy·2H<sub>2</sub>O, respectively, see Scheme 1). The two kinds of conformation isomers, in which four pyridyl rings oriented as left- and right-handed propellers around the central phenyl rings differ. The energy barrier for the inversion of a propeller should be low enough that bztpy can exist in two forms at room temperature. Therefore, in a coordination network, there is a chance that one of the two supramolecular isomers will be favored over the other at a certain temperature.<sup>10</sup> This speculation did lead to the isolation of two supramolecular isomers **1** and **2**. Reaction of CdCl<sub>2</sub>·4H<sub>2</sub>O, bztpy, and water at 160 °C for 72 h yielded colorless needle crystals of **1** in a single phase. Interestingly, pale

Table 2. Selected Bond Lengths (Å) and Angles (°) for 1–3<sup>a</sup>

Compound 1			
Cd(1)–N(1)	2.389(3)	Cd(1)–Cl(1)	2.5624(9)
Cd(1)–N(2b)	2.396(3)		
N(1a)–Cd(1)–N(1)	92.34(13)	N(2b)–Cd(1)–Cl(1a)	87.73(7)
N(1)–Cd(1)–N(2b)	88.58(9)	N(1)–Cd(1)–Cl(1)	89.72(7)
N(1)–Cd(1)–N(2c)	177.28(10)	N(2b)–Cd(1)–Cl(1)	93.12(7)
N(2b)–Cd(1)–N(2c)	90.61(13)	Cl(1a)–Cd(1)–Cl(1)	178.79(4)
N(1)–Cd(1)–Cl(1a)	89.44(7)		
Compound 2			
Cd(1)–N(1)	2.418(4)	Cd(1)–Cl(1)	2.5615(13)
N(1)–Cd(1)–N(1b)	100.72(19)	N(1)–Cd(1)–Cl(1)	90.68(9)
N(1)–Cd(1)–N(1c)	79.28(19)	N(1)–Cd(1)–Cl(1a)	89.32(9)
Compound 3			
Cd(1)–N(2a)	2.306(6)	Cd(2)–O(3)	2.274(9)
Cd(2)–N(1)	2.319(7)	Cd(2)–Cl(1d)/O(1d)	2.573(4)
Cd(1)–O(2)	2.348(5)	Cd(2)–O(1)	2.573(4)
Cd(1)–O(1w)	2.397(12)	Cd(2)–Cl(2)	2.686(4)
Cd(1)–O(1)/Cl(1)	2.432(6)	Cd(2)···Cd(2c)	3.3291(14)
N(2a)–Cd(1)–N(2b)	109.7(3)	N(1d)–Cd(2)–Cl(1d)	175.5(2)
N(2a)–Cd(1)–O(2c)	162.5(3)	N(1)–Cd(2)–Cl(1d)	91.7(2)
N(2a)–Cd(1)–O(2)	85.0(2)	O(3)–Cd(2)–O(1d)	97.0(2)
N(2b)–Cd(1)–O(2)	162.5(3)	N(1)–Cd(2)–O(1d)	91.7(2)
O(2c)–Cd(1)–O(2)	79.1(3)	O(3)–Cd(2)–O(1)	97.0(2)
N(2a)–Cd(1)–O(1w)	89.8(3)	N(1d)–Cd(2)–O(1)	91.7(2)
O(2)–Cd(1)–O(1w)	80.5(3)	N(1)–Cd(2)–O(1)	175.5(2)
N(2a)–Cd(1)–O(1)	94.7(2)	Cl(1d)–Cd(2)–O(1)	86.8(2)
O(2)–Cd(1)–O(1)	93.5(2)	O(1d)–Cd(2)–O(1)	86.8(2)
O(1w)–Cd(1)–O(1)	172.2(3)	O(3)–Cd(2)–Cl(2)	178.5(2)
O(3)–Cd(2)–N(1)	87.3(3)	N(1)–Cd(2)–Cl(2)	93.7(2)
N(1d)–Cd(2)–N(1)	89.6(4)	Cl(1d)–Cd(2)–Cl(2)	81.90(12)
N(1d)–Cd(2)–O(1d)	175.5(2)	O(1)–Cd(2)–Cl(2)	81.90(12)
O(3)–Cd(2)–Cl(1d)	97.0(2)		

<sup>a</sup> Symmetry codes: (a)  $-x + \frac{1}{2}, y, -z + \frac{1}{2}$ ; (b)  $x, y - 1, z$ ; (c)  $-x + \frac{1}{2}, y - 1, -z + \frac{1}{2}$  for **1**; (a)  $-x + 1, -y, -z + 2$ ; (b)  $-x + y + 1, y, z$ ; (c)  $x - y, -y, -z + 2$  for **2**; (a)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (b)  $x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (c)  $-x, y, z$ ; (d)  $x, y, -z + \frac{1}{2}$  for **3**.

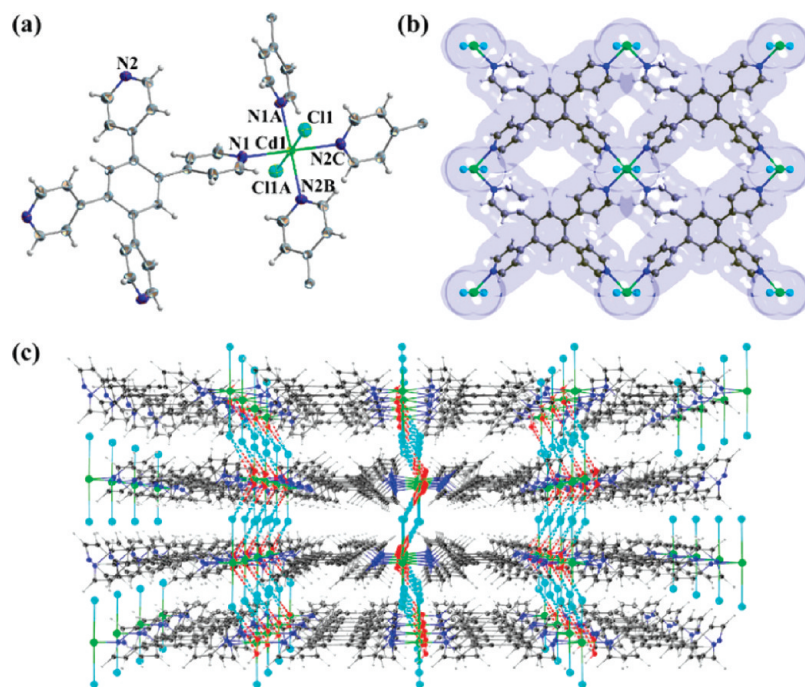
brown rhombic crystals of **2** was obtained by templating with 1,2-diphenyldisulfane when the analogous reaction was carried out at 185 °C for 96 h. **1** and **2** encompass the same CdCl<sub>2</sub> building unit connected with the bztpy ligand, but the orientation of bztpy differs, which induces the topology connectivity to change from (4,4) net to NbO net. An appropriate auxiliary small ligand is an important consideration to fulfill its geometric limitation in the construction of metal cluster SBU.<sup>11</sup> As an addition of terminal benzoic acid to the CdCl<sub>2</sub> and tetradentate ligand reaction system results in the formation of a high-connected cluster-based coordination polymer **3**, a cooperative assembly process different from the single metal species is indicated. Phase purity of the bulk materials was confirmed by comparison of its powder diffraction pattern with that calculated from the single crystal study (Figures S1–S3 in Supporting Information).

**Crystal Structures.** X-ray structural analysis shows that **1** crystallized in the monoclinic space group of *P2<sub>1</sub>/n*. The asymmetric unit contains one half of a formula unit, that is, half of a crystallographically unique Cd<sup>II</sup> atom, half of the bztpy ligand, one coordinated Cl<sup>−</sup> counterion and half of the lattice water molecule. The metal ion and the organic ligand are situated on a 2-fold rotation axis. The cadmium adapts an octahedral geometry with four bztpy units on the equatorial plane and accordingly, along with the four-bridging

ligands, form a two-dimensional (4,4) coordination layer. A perspective view of the coordination environment of the Cd<sup>II</sup> atom and the bridging planar 4-connected bztpy ligand is given in Figure 1a. The vertices are octahedral Cd atoms with equatorial planes filled by pyridyl nitrogen atoms from four different bztpy ligands (Cd–N = 2.389(3)–2.396(3) Å). The axial sites are filled by two symmetry-related Cl atoms (Cd–Cl = 2.562(1) Å). It is worth noting that bztpy ligand in **1** adopts a staggered conformation, the same as the original conformation in bztpy·EtOH that crystallized in ethanol; the dihedral angles between the centered benzene ring and pyridyl rings are 45.27 and 53.76°, respectively, and the dihedral angle of two opposite pyridyl rings is 81.00°. Each bztpy ligand acts as a tetradentate bridge to connect the CdCl<sub>2</sub> motifs into a 2D (4,4) net, which lies in the *bc* crystallographic plane and contains two square openings of ca. 4.06 × 4.06 and 3.03 × 3.03 Å as defined by the shortest transannular distance factoring van der Waals radii, respectively (Figure 1b). The adjacent grids are stacked offset with respect to each other in an ABAB fashion. The most interesting structural feature is the alternating layers are connected by O–H···Cl hydrogen-bonds (O<sub>water</sub>···Cl = 3.112–3.287 Å) between coordinated Cl atoms and the disorder guest water molecules clathrated in the grids, thereby generating two identical interpenetrated 3D hydrogen-bonded supramolecular frameworks (Figure 1c).

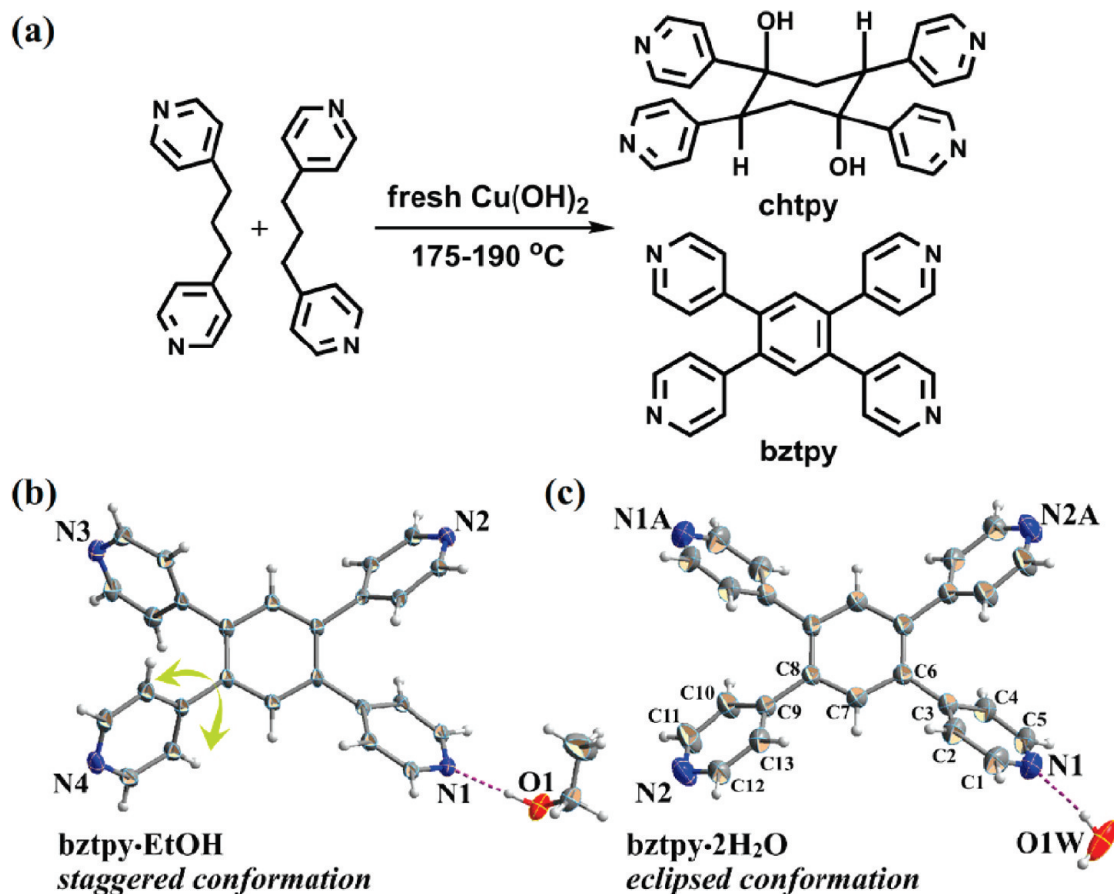
In contrast to **1**, it is interesting that the assembly of the same [CdCl<sub>2</sub>] building fragments and planar tetratopic bztpy linkers forms an extended 3D non-interpenetrated framework **2**. Owing to the conformation freedom in the geometry, the dihedral angles between the pyridyl rings and centered benzene ring are all distorted to 46.91°, the two opposite pyridyl rings are completely eclipsed in **2**, and the symmetry of the crystal system is higher from monoclinic to trigonal. A perspective view of the asymmetric unit of **2** with an atom numbering scheme is given in Figure 2a. In **2**, the asymmetric unit contains a quarter of the formula unit and there is one octahedral Cd<sup>II</sup> atom, which lies in a special position (SOF = 0.25), one quarter of the bztpy ligand lying on a special position, and one-half of Cl<sup>−</sup> atom and one-quarter of guest water molecule. The two symmetry-related terminal Cl<sup>−</sup> atoms coordinate axially to the Cd<sup>II</sup> atom (Cd–Cl = 2.561(1) Å), the pyridyl rings of four distinct bztpy ligands are found to occupy the equatorial positions about the metal center; the four Cd–N bond lengths are 2.418(4) Å. From the point of view of structural description of the coordination polymer, the Cd<sup>II</sup> atom may be considered equivalent to a 4-connecting square-planar node, as the Cl<sup>−</sup> atoms merely serve to fill the coordination sphere. Thus, the coordination polymer built up of 4-connecting *D*<sub>4h</sub>-symmetric metal ions and square-planar tetratopic bztpy ligands in the ratio 1:1 is precisely equivalent to the NbO network<sup>12</sup> (Figure 2d). Such a net structure can be characterized by a short vertex symbol of 6<sup>4</sup>.8<sup>2</sup>. The long Schläfli symbol is 6<sub>2</sub>.6<sub>2</sub>.6<sub>2</sub>.6<sub>2</sub>.8<sub>2</sub>.8<sub>2</sub>. However, because of the large twist (open angle: 69.5 and 110.4°) between the pyridyl rings in ortho and meta position in the bztpy link the neighboring Cd square units are not strict perpendicular, which leads to an oblique NbO-like extended network (Figure 2b). The 3D propagation of these adamantanoid units relative to their 3-fold screw axis (pitch: 6.6 Å) leads to the large left- and right-handed alternate hexagonal channels along the *c*-axis (Figure 2c); when the van der Waals radii are





**Figure 1.** The coordination environment of Cd atom in **1** (some equivalent atoms have been generated to complete the Cd coordination) (a), and a 2D (4,4) net in **1** (b), and the AB molecular packing of 2D layers showing hydrogen bonding interactions (c).

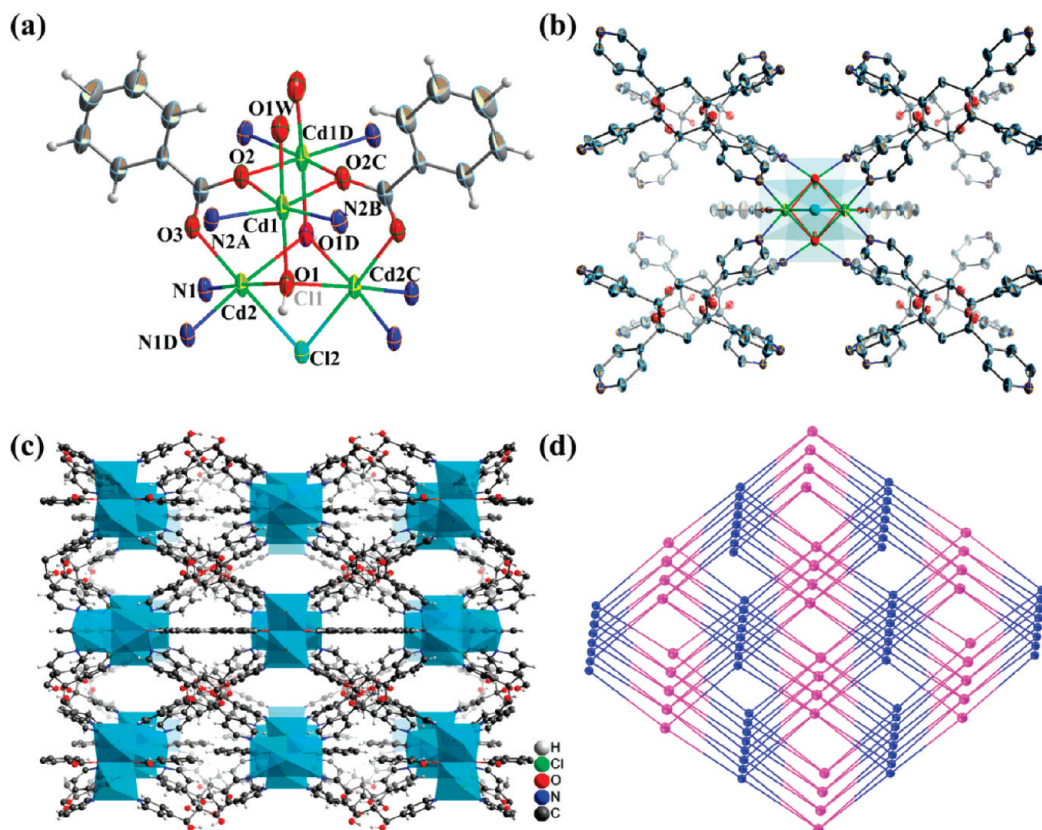
**Scheme 1. Hydrothermal in Situ Metal/Ligand Reactions in Our Previous Work<sup>a</sup>**



<sup>a</sup>Two novel tetradentate ligands **chtpy** and **bztpy** were isolated by demetallization with different precipitating agents (a). The staggered (b) and eclipsed conformations (c) of **bztpy** are found when **bztpy** molecules cocrystallized with two different solvents. These two different morphologies are also found in compounds **1** and **2** in the present work which is forthcoming.

The novel binodal high-connected topology can be simplified by considering just the tetradentate ligands (represented by a square-planar node) and the  $\{\text{Cd}_4\}$  clusters (represented by a cubic node). The resulting net is shown in Figure 3d, which is a rare (4,8)-connected net with square-planar nodes and cubic nodes in the ratio 2:1. A topological analysis of this net was performed with OLEX.<sup>15</sup> The long topological vertex symbol (O’Keeffe) is  $4.4_4.3_4.3_{8,18}.8_{18}$  for the chtpy node, and  $4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.8_9.8_9.8_9.8_9.8_9.8_9.8_9$  for the  $\text{Cd}_4$  node, which gives the short vertex symbol  $(4^4.6^2)_2$ - $(4^{16}.6^{12})$ . Thanks to the novel square-planar tetratopic chtpy ligand, compound **3** is a rare example of MOFs having (4,8)-connected  $scu^{16}$  topology consisting of square-planar and cubic





**Figure 3.** Perspective views showing local geometry of  $\{Cd_4\}$  core in the structure of **3** (only the pyridyl N atoms of the chtpy ligands are shown for clarity) (a), cubic connectivity of the eight-connected  $\{Cd_4\}$  node (b), the 3D noninterpenetrating framework with channels in the structure of **3** (c) and the 3D (4,8)-connected topological net (d). The violet red and blue spheres represent  $\{Cd_4\}$  and tetradentate ligands, respectively.

nodes. Of the important (4,8)-connected topological nets, there is another possible topology that is based upon tetrahedral and cubic nodes, the 3D networks of fluorite ( $CaF_2$  or flu) ( $4^6)(4^{12}.6^{12}.8^4)$ , which also have been seldom observed.<sup>17</sup>

### Conclusions

In summary, we successfully synthesized and characterized three new MOFs based on two novel tetradentate ligands isolated from our previously hydrothermal in situ metal/ligand reactions. Ligand oriented effects are exhibited in two supramolecular isomers **1** and **2** which possess a 2D (4,4) net and 3D NbO net, respectively. An even more important aspect is the high possibility to use these bulky tetradentate ligand skeletons for construction of more complicated 3D MOF structures with defined connectivity. **3** is a rare microporous, (4,8)-connected *scu*-type structure that contains an eight-connected polynuclear cluster unit and a planar tetradentate ligand. These results confirm the potential for synthesizing new MOF structures of functional materials using the uncommon planar tetradentate ligands isolated from an ingenious hydrothermal in situ metal/ligand reaction. Further research is currently in progress.

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**Supporting Information Available:** X-ray crystallographic files of **bztpy**·EtOH, **bztpy**·2H<sub>2</sub>O, and **1–3** (CIF), simulated and experimental XRPD data of **1–3**, and the TG and DTG curves for **2** and **3**.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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