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# Cadmium Metal-Directed Three-Dimensional Coordination Polymers: In Situ Tetrazole Ligand Synthesis, Structures, and Luminescent Properties

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**ABSTRACT:** Seven three-dimensional (3D) cadmium coordination frameworks,  $\{[\text{Cd}(\text{5MT})_2] \text{ (1a)}; [\text{Cd}_5(\text{N}_3)(\text{5MT})_9 \cdot 0.12\text{H}_2\text{O}] \text{ (1b)}; [\text{Cd}_3(\text{OH})\text{Cl}_{1.39}(\text{N}_3)_{0.61}(\text{5MT})_3] \text{ (1c)}, \text{5MT} = 5\text{-methyl-tetrazole}\}; \{[\text{Cd}_3(\text{OH})\text{Cl}(\text{N}_3)(\text{5AT})_3] \text{ (2a)}; [\text{Cd}_2(\text{OH})\text{Br}(\text{5AT})_2] \text{ (2b)}, \text{5AT} = 5\text{-amino-tetrazole}\}; \{[\text{Cd}_7\text{Cl}_2(\text{5BT})_{12}(\text{H}_2\text{O})_2] \text{ (3a)}; \text{ and } [\text{Cd}_7\text{Br}_2(\text{5BT})_{12}(\text{H}_2\text{O})_2] \text{ (3b)}, \text{5BT} = 5\text{-butyl-tetrazole}\}$ , were obtained through in situ tetrazole synthesis and have been structurally characterized by elemental analyses, Fourier transform infrared spectroscopy, thermal studies, and single crystal and powder X-ray diffraction. Compounds **1a** and **1b** were constructed by the interconnection of 5MT and cadmium metal ions, and both exhibited distinct topological nets: **1a** has a diamond-like framework, while **1b** has the **acs** topological net. Compounds **1c** and **2a** represented similar structural network motifs; both were intricate coordination polymers constructed from interconnected  $\{\text{ClCd}_3\text{O}\}$  subnets through tetrazole anions. Compound **2b** was constructed from two-dimensional (2D) wavelike  $\{\text{BrCd}_3\text{O}\}$  layers bridged by 5AT anions. Compounds **3a** and **3b** were structural isomorphs, constructed from 2D Cd-5BT wheel layers and halogen linkers. Furthermore, the luminescent properties of these complexes were investigated.

## Introduction

Metal–organic hybrid compounds are studied because of their intriguing structural architectures and topologies, as well as their potential applications as functional materials in the fields of molecular recognition, ion exchange, adsorption, fluorescence, catalysis, and magnetism.<sup>1–4</sup> Assembly processes directed by metal–ligand ligation have been extensively utilized to construct metal–organic frameworks (MOFs), which has witnessed a rapid progress in previous years. So far, considerable efforts have been devoted to the synthesis of unusual coordination polymers based on carboxylate and/or pyridine-based ligands,<sup>5</sup> while there are also many examples of synthetic materials derived from polydentate aromatic nitrogen heterocyclic ligands, such as pyrazoles, imidazoles, and triazoles.<sup>6</sup>

Over the past two decades, the tetrazole functional groups have been extensively utilized in coordination chemistry, medicinal chemistry, and materials science.<sup>7</sup> One of the main synthetic routes for the formation of tetrazole rings is the  $[2 + 3]$  cycloaddition between nitriles and organic azides, for instance, RCN and silyl, aliphatic, or aromatic azides  $\text{RN}_3$ .<sup>8</sup> However, these traditional cycloaddition reactions have many disadvantages which involve expensive and toxic metal–organic azide complexes, or a need for severe reaction conditions. Recently, tetrazole-based coordination networks entered the scene in larger numbers after the breakthrough by Demko and Sharpless, who developed a simple approach for the preparation of 5-substituted tetrazole groups using a

safe, convenient, and environmentally benign synthetic route through  $[3 + 2]$  cycloaddition reaction of azide anions with nitriles in water with Zn(II) salt as catalysts.<sup>9</sup> Later, Xiong and co-workers developed Sharpless' methods using Zn(II) to catalyze cycloaddition reactions of nitriles and azide to form zinc tetrazole coordination polymers via in situ hydrothermal synthesis.<sup>10</sup> Since then, tetrazole-based coordination polymers have been extensively investigated, and the examples reported so far exhibit various coordination networks with diverse topologies and interesting functional properties.<sup>11</sup> Tetrazole-based ligands have for example been shown to be capable of interconnecting metal centers to generate coordination compounds that incorporate polynuclear clusters.<sup>12,13</sup> For example, Long et al. prepared a series of MOFs mostly involving  $\text{M}_4\text{X}$  ( $\text{M} = \text{Mn}, \text{Mg}, \text{ or } \text{Cu}$ ;  $\text{X} = \text{Cl or O}$ ) clusters as building blocks;<sup>12</sup> Bu et al. synthesized a pcu-type topological network constructed from  $\text{DTA}^{2-}$  ( $\text{DTA}^{2-} = 9,10\text{-ditetrazolateanthracene}$ ) bridging rare heptanuclear  $[\text{Zn}_7(\text{OH})_8]^{6+}$  clusters as secondary building units (SBUs).<sup>13a</sup> Most recently, our group reported two highly symmetric cadmium organic frameworks incorporating trinuclear  $\text{Cd}_3(\text{OH})$  clusters or 48-membered tetraicosanuclear  $\text{Cd}_{24}\text{Cl}_{24}$  macrocycles based on in situ ligand synthesis.<sup>13b,c</sup>

In our continuing work in this field, we chose herein acetonitrile, butyronitrile, cyanoacetic acid and aminoacetonitrile, sodium azide with different Cd(II) salts as catalysts to synthesize novel metal–organic coordination frameworks, based on several considerations: (i) The  $d^{10}$  cadmium metal ion not only is able to tolerate various coordination numbers and geometries, but it also exhibits luminescent properties when bound to functional ligands;<sup>14</sup> (ii) in situ synthesis of the 5-substituted tetrazole group with its multifunctional four

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Table 1. Crystallographic Data and Structure Refinement Summary for Complexes 1–3

	1a	1b	1c	2a	2b	3a	3b
formula	C <sub>4</sub> H <sub>6</sub> CdN <sub>8</sub>	C <sub>18</sub> H <sub>27.24</sub> <sup>a</sup> Cd <sub>5</sub> N <sub>39</sub> O <sub>0.12</sub>	C <sub>6</sub> H <sub>10</sub> Cd <sub>3</sub> - Cl <sub>1.31</sub> N <sub>14.1</sub> O	C <sub>3</sub> H <sub>7</sub> Cd <sub>3</sub> - ClN <sub>18</sub> O	C <sub>2</sub> H <sub>5</sub> Br- Cd <sub>2</sub> N <sub>10</sub> O	C <sub>48</sub> H <sub>88</sub> Cd <sub>7</sub> - Cl <sub>2</sub> N <sub>48</sub> O <sub>2</sub>	C <sub>48</sub> H <sub>88</sub> Cd <sub>7</sub> - Br <sub>2</sub> N <sub>48</sub> O <sub>2</sub>
<i>M<sub>r</sub></i>	278.58	1353.95	679.32	682.91	489.87	2227.36	2316.28
crystal system	cubic	hexagonal	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	<i>Fd3m</i>	<i>P6<sub>3</sub>/mmc</i>	<i>Pnma</i>	<i>Pnma</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> (Å)	18.6197(1)	13.1406(2)	13.4656(2)	13.2682(3)	11.3146(4)	16.1695(3)	16.2507(2)
<i>b</i> (Å)	18.6197(1)	13.1406(2)	6.8717(1)	6.8889(2)	13.4518(4)	19.5139(3)	19.5860(2)
<i>c</i> (Å)	18.6197(1)	13.6199(3)	17.2726(3)	16.7812(4)	7.0149(2)	13.1046(2)	13.1491(1)
$\alpha$ (°)	90.00	90.00	90.00	90.00	90.00	90.00	90.00
$\beta$ (°)	90.00	90.00	90.00	90.00	105.790(2)	97.6200(10)	98.188(1)
$\gamma$ (°)	90.00	120.00	90.00	90.00	90.00	90.00	90.00
<i>V</i> (Å <sup>3</sup> )	6455.32(6)	2036.74(6)	1598.26(4)	1533.86(7)	1027.39(6)	4098.38(12)	4142.51(7)
<i>Z</i>	24	2	4	4	4	2	2
<i>D<sub>c</sub></i> (g/cm <sup>3</sup> )	1.720	2.208	2.823	2.962	3.167	1.805	1.857
$\mu$ (mm <sup>-1</sup> )	2.003	2.641	4.208	4.340	8.026	1.914	2.794
<i>F</i> (000)	3216	1298	1276	1280	904	2196	2268
parameters	37	72	179	172	146	552	552
goodness-of-fit	1.159	1.078	1.196	1.245	1.026	1.166	1.085
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0549	0.0324	0.0432	0.0608	0.0466	0.0468	0.0397
<i>wR</i> <sub>2</sub> (all data) <sup>b</sup>	0.1569	0.1045	0.0863	0.2082	0.1301	0.1110	0.0987

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

nitrogen atoms permits a range of versatile bridging modes; (iii) the counteranions and 5-substituted groups play important roles in the growth of crystalline materials, and their variation allows influence of the structural topologies of the resultant coordination frameworks.<sup>15</sup> In this context, we report seven metal-directed three-dimensional (3D) tetrazole coordination frameworks through in situ ligand synthesis. All synthetic crystalline materials are potential candidates for applications as photoactive materials.

## Experimental Section

**General Remarks.** All materials and reagents were obtained commercially and were used without further purification. Elemental (C, H, N) analyses were performed on a Perkin–Elmer 2400 element analyzer. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 4000–400 cm<sup>-1</sup> range using a Nicolet Avatar 360 Fourier transform infrared (FT-IR) spectrophotometer. Thermogravimetric analysis (TGA) experiments were performed on a NETZSCH TG 209 instrument with a heating rate of 10 °C min<sup>-1</sup>. Fluorescence spectra were recorded with an F-2500 FL spectrophotometer analyzer.

**Preparation of Compounds 1–3.** A mixture of [CH<sub>3</sub>CN (5 mL), Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.154 g; 0.5 mmol) for **1a**]; [HOOCCH<sub>2</sub>CN (0.09 g, 1 mmol), Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.154 g; 0.5 mmol) for **1b**], [HOOCCH<sub>2</sub>CN (0.09 g, 1 mmol), CdCl<sub>2</sub>·4H<sub>2</sub>O (0.127 g; 0.5 mmol) for **1c**], [H<sub>2</sub>NCN (5 mL), CdCl<sub>2</sub>·4H<sub>2</sub>O (0.127 g; 0.5 mmol) for **2a**], [H<sub>2</sub>NCN (5 mL), CdBr<sub>2</sub>·4H<sub>2</sub>O (0.172 g; 0.5 mmol) for **2b**], [CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CN (3 mL), CdCl<sub>2</sub>·4H<sub>2</sub>O (0.127 g; 0.5 mmol) for **3a**], [CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CN (3 mL), CdBr<sub>2</sub>·4H<sub>2</sub>O (0.172 g; 0.5 mmol) for **3b**], pyridine-3-sulfonic acid (0.080 g; 0.5 mmol), and H<sub>2</sub>O (8 mL) was sealed in a 23 mL Teflon reactor and kept under autogenous pressure at 170 °C for 3 days. The mixtures were cooled to room temperature at a rate of 5 °C h<sup>-1</sup> to obtain colorless crystals. **1a** [Cd(5MT)<sub>2</sub>, 5MT = 5-methyl-tetrazole], C<sub>4</sub>H<sub>6</sub>CdN<sub>8</sub> (278.58): calcd.: C 17.25, H 2.17, N 40.23; found: C 17.30, H 2.15, N 40.20; IR (KBr, cm<sup>-1</sup>): 3445, 3100, 2924, 1625, 1492, 1375, 1260, 1171, 1059, 695; **1b** [Cd<sub>5</sub>(N<sub>3</sub>)(5MT)<sub>9</sub>·0.12H<sub>2</sub>O, 5MT = 5-methyl-tetrazole], C<sub>18</sub>H<sub>27.24</sub>Cd<sub>5</sub>N<sub>39</sub>O<sub>0.12</sub> (1353.95): calcd.: C 15.59, H 2.03, N 40.35; found: C 15.65, H 2.10, N 40.41; IR (KBr, cm<sup>-1</sup>): 3423, 2041, 1621, 1498, 1376, 1256, 1170, 1055, 698; **1c** [Cd<sub>3</sub>(OH)Cl<sub>1.39</sub>(N<sub>3</sub>)<sub>0.61</sub>(5MT)<sub>3</sub>, 5MT = 5-methyl-tetrazole], C<sub>6</sub>H<sub>9</sub>Cd<sub>3</sub>Cl<sub>1.39</sub>N<sub>13.84</sub>O (677.39): calcd.: C 10.64, H 1.34, N 28.61; found: C 10.60, H 1.39, N 28.68; IR (KBr, cm<sup>-1</sup>): 3441, 3100, 2930, 2075, 1620, 1495, 1370, 1251, 1171, 1054, 700; **2a** [Cd<sub>3</sub>(OH)Cl(N<sub>3</sub>)(5AT)<sub>3</sub>, AT = 5-amino-tetrazole], C<sub>3</sub>H<sub>6</sub>-Cd<sub>3</sub>ClN<sub>18</sub>O (682.91): calcd.: C 5.28, H 0.89, N 36.92; found: C 5.25, H 0.85, N 36.98; IR (KBr, cm<sup>-1</sup>): 3395, 3325, 3220, 3102, 2074, 1617, 1497, 1373, 1250, 1175, 1051, 695; **2b** [Cd<sub>2</sub>(OH)Br(5AT)<sub>2</sub>, 5AT = 5-amino-tetrazole], C<sub>2</sub>H<sub>5</sub>BrCd<sub>2</sub>N<sub>10</sub>O (489.87): calcd.: C 4.90, H 1.03, N

28.59; found: C 5.94, H 1.09, N 28.65; IR (KBr, cm<sup>-1</sup>): 3392, 3321, 3218, 3100, 1625, 1498, 1371, 1250, 1175, 1051, 700; **3a** [Cd<sub>7</sub>Cl<sub>2</sub>(5BT)<sub>12</sub>·(H<sub>2</sub>O)<sub>2</sub>, 5BT = 5-butyl-tetrazole], C<sub>48</sub>H<sub>88</sub>Cl<sub>2</sub>Cd<sub>7</sub>N<sub>48</sub>O<sub>2</sub> (2227.36): calcd.: C 25.88, H 3.98, N 30.19; found: C 25.94, H 3.99, N 30.15; IR (KBr, cm<sup>-1</sup>): 3491, 3121, 2958, 2879, 1630, 1495, 1372, 1251, 1176, 1050, 698; **3b** [Cd<sub>7</sub>Br<sub>2</sub>(5BT)<sub>12</sub>·(H<sub>2</sub>O)<sub>2</sub>, 5BT = 5-butyl-tetrazole], C<sub>48</sub>H<sub>88</sub>-Br<sub>2</sub>Cd<sub>7</sub>N<sub>48</sub>O<sub>2</sub> (2316.28): calcd.: C 24.89, H 3.83, N 29.03; found: C 24.92, H 3.89, N 29.10; IR (KBr, cm<sup>-1</sup>): 3495, 3125, 2959, 2880, 1631, 1495, 1373, 1250, 1175, 1051, 698.

**Crystal Structure Determination.** Single crystal X-ray diffraction data collections of **1–3** were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Data collection and reduction were performed using the APEX II software.<sup>16</sup> Multiscan absorption corrections were applied for all the data sets using the APEX II program.<sup>16</sup> All structures were solved by direct methods and refined by full-matrix least-squares on *F*<sup>2</sup> using the SHELXTL program package.<sup>16</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Hydrogen atoms on water molecules and amino groups were located from difference Fourier maps and were refined using riding model. Compounds **1a** and **1b** exhibit the disorders of the 5-methyl-tetrazole units, which were created by a crystallographic mirror plane or a 2-fold axis. These disordered 5-methyl-tetrazole anions were restrained to be flat within a standard deviation of 0.1 Å<sup>2</sup>. Compound **2a** exhibits 1:1 disorder of both one of cadmium atoms (Cd1) and a tetrazole unit bonded to it as well as one the azide ligands bonded to neighboring Cd ion (Cd2). The disorder is created by the presence of a crystallographic mirror plane perpendicular to the *b*-axis, and the second Cd-tetrazole and azide units are created from the first by this mirror plane. The disordered tetrazole anion (including the amino H atoms) was restrained to be flat within a standard deviation of 0.1 Å<sup>2</sup>, and the amino hydrogen atoms were restrained to have N–H bond distances of 0.86(2) Å and to be 1.49(2) Å apart from each other. Compound **1c**, the methyl derivative of **2a**, is mostly isostructural to compound **2a** and exhibits the same disorder as observed in **2a**, but the site of the disordered azide is occupied by a mixture of azide and chloride in a ratio of 0.69(4)–0.31(4) in favor of the azide anion. The tetrazole ring for **1c** was also restrained to be flat within a standard deviation of 0.1 Å<sup>2</sup>. In both structures, the disorder also extends to the hydroxyl anion. It itself is located exactly on the mirror plane, but the acidic hydrogen atom is disordered over two alternative positions depending on the absence or presence of Cd1. The crystallographic data for all structures are listed in Tables 1, and the selected bond lengths and bond angles of the two compounds are listed in Table 2. CCDC Nos. 747759–747763 and 749208–749209 for all structures are contained in the supplementary crystallographic data for this paper.

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

compound 1a <sup>b</sup>					
Cd(1)–N(2)	2.352(7)	Cd(2)–N(1)	2.356(10)	N(2) <sup>#2</sup> –Cd(1)–N(2) <sup>#4</sup>	180.00(18)
N(2) <sup>#1</sup> –Cd(1)–N(2) <sup>#2</sup>	90.0(2)	N(2)–Cd(1)–N(2) <sup>#3</sup>	180.000(1)	N(2)–Cd(1)–N(2) <sup>#4</sup>	90.0(2)
compound 1b <sup>c</sup>					
Cd(1)–N(2)	2.382(6)	Cd(1)–N(4)	2.395(5)	N(1) <sup>#1</sup> –Cd(2)–N(1)	88.5(2)
N(2) <sup>#2</sup> –Cd(1)–N(2)	90.0(2)	N(2)–Cd(1)–N(5)	89.8(2)	N(1)–Cd(2)–N(6)	91.1(2)
compound 1c <sup>d</sup>					
Cd(1)–O(1)	2.323(6)	Cd(1)–N(8) <sup>#1</sup>	2.351(5)	Cd(1)–N(8)	2.351(5)
Cd(1)–N(4) <sup>#2</sup>	2.364(8)	Cd(1)–N(2)	2.535(9)	Cd(1)–Cl(1)	2.574(2)
Cd(2)–Cl(1)	2.643(3)	Cd(2)–O(1) <sup>#3</sup>	2.301(6)	Cd(2)–N(6) <sup>#1</sup>	2.362(6)
Cd(2)–N(6)	2.362(6)	Cd(2)–N(3)	2.405(8)	Cd(2)–Cl(2)	2.601(8)
Cd(3)–N(1)	2.380(10)	Cd(3)–N(5) <sup>#4</sup>	2.279(7)	Cd(3)–N(10) <sup>#4</sup>	2.35(3)
Cd(3)–N(7)	2.365(6)	Cd(3)–O(1)	2.167(5)	Cd(3)–Cl(2) <sup>#4</sup>	2.543(5)
O(1)–Cd(1)–N(8)	84.26(14)	N(8) <sup>#1</sup> –Cd(1)–N(8)	168.5(3)	O(1)–Cd(1)–N(4) <sup>#2</sup>	91.7(2)
N(8)–Cd(1)–N(4) <sup>#2</sup>	89.65(15)	N(8)–Cd(1)–N(2) <sup>#1</sup>	95.9(2)	N(8)–Cd(1)–N(2)	83.5(2)
N(12)–Cd(2)–N(6)	66.1(13)	N(12)–Cd(2)–O(1) <sup>#3</sup>	93.7(10)	N(12)–Cd(2)–N(3)	161.2(13)
O(1) <sup>#3</sup> –Cd(2)–N(3)	89.6(2)	N(6) <sup>#1</sup> –Cd(2)–N(3)	96.02(15)	O(1) <sup>#3</sup> –Cd(2)–Cl(2)	100.4(2)
O(1)–Cd(3)–N(7)	82.76(18)	O(1)–Cd(3)–N(1)	84.1(3)	O(1)–Cd(3)–Cl(2) <sup>#4</sup>	164.8(2)
N(1)–Cd(3)–Cl(2) <sup>#4</sup>	89.9(3)	N(5) <sup>#4</sup> –Cd(3)–N(1)	98.1(3)	N(10) <sup>#4</sup> –Cd(3)–N(1)	69.6(7)
compound 2a <sup>e</sup>					
Cd(1)–O(1)	2.213(6)	Cd(1)–N(9)	2.299(8)	Cd(1)–N(6)	2.313(8)
Cd(1)–N(9) <sup>#3</sup>	2.627(9)	Cd(1)–N(1)	2.378(14)	Cd(1)–N(12) <sup>#3</sup>	2.388(8)
Cd(2)–O(1)	2.289(9)	Cd(2)–N(12)	2.298(11)	Cd(2)–N(10) <sup>#4</sup>	2.357(8)
Cd(2)–N(3) <sup>#5</sup>	2.382(11)	Cd(2)–Cl(1)	2.671(4)	Cd(3)–O(1)	2.307(9)
Cd(3)–N(4) <sup>#5</sup>	2.327(11)	Cd(3)–N(7)	2.356(9)	Cd(3)–N(2)	2.527(14)
O(1)–Cd(1)–N(9)	104.3(3)	O(1)–Cd(1)–N(1)	84.4(4)	O(1)–Cd(2)–N(12)	92.5(4)
N(6)–Cd(1)–N(1)	84.9(4)	O(1)–Cd(2)–N(10) <sup>#3</sup>	83.51(19)	O(1)–Cd(2)–N(3) <sup>#5</sup>	90.5(4)
O(1)–Cd(1)–N(6)	84.3(3)	O(1)–Cd(2)–Cl(1)	179.3(2)	N(12)–Cd(2)–Cl(1)	88.1(3)
N(6)–Cd(1)–N(9) <sup>#3</sup>	78.9(3)	O(1)–Cd(3)–N(7)	86.2(2)	N(7) <sup>#1</sup> –Cd(3)–N(7)	172.4(4)
O(1)–Cd(3)–N(2)	81.3(4)	N(7)–Cd(3)–N(2)	82.6(3)	N(7)–Cd(3)–Cl(1) <sup>#2</sup>	93.8(2)
compound 2b <sup>f</sup>					
Cd(1)–O(1)	2.304(5)	Cd(1)–N(1)	2.346(6)	Cd(1)–N(9)	2.379(6)
Cd(1)–N(6)	2.437(7)	Cd(1)–Br(1) <sup>#1</sup>	2.7205(9)	Cd(1)–Br(1)	2.7890(9)
Cd(2)–O(1) <sup>#2</sup>	2.230(5)	Cd(2)–O(1)	2.235(5)	Cd(2)–N(4) <sup>#3</sup>	2.306(6)
Cd(2)–N(8) <sup>#4</sup>	2.341(6)	Cd(2)–N(7)	2.411(6)	Cd(2)–N(3) <sup>#5</sup>	2.499(7)
O(1)–Cd(1)–N(1)	82.4(2)	O(1)–Cd(1)–N(9)	86.86(19)	N(9)–Cd(1)–N(6)	166.6(2)
O(1)–Cd(1)–Br(1)	94.00(13)	N(1)–Cd(1)–Br(1)	176.34(16)	N(6)–Cd(1)–Br(1) <sup>#1</sup>	93.25(15)
O(1)–Cd(2)–N(8) <sup>#4</sup>	92.1(2)	N(8) <sup>#4</sup> –Cd(2)–N(7)	111.0(2)	N(7)–Cd(2)–N(3) <sup>#5</sup>	164.1(2)
O(1)–Cd(2)–N(7)	83.80(19)	N(4) <sup>#3</sup> –Cd(2)–N(7)	83.8(2)	O(1)–Cd(2)–N(4) <sup>#3</sup>	93.1(2)
compound 3a <sup>g</sup>					
Cd(1)–N(6)	2.327(5)	Cd(1)–N(22)	2.314(5)	Cd(1)–N(14)	2.334(5)
Cd(1)–N(18)	2.343(5)	Cd(1)–N(2)	2.376(5)	Cd(1)–N(11) <sup>#2</sup>	2.382(5)
Cd(2)–N(1)	2.322(5)	Cd(2)–N(5)	2.335(5)	Cd(2)–N(10)	2.343(5)
Cd(2)–N(21)	2.343(5)	Cd(2)–N(23) <sup>#3</sup>	2.354(5)	Cd(2)–N(15) <sup>#3</sup>	2.398(5)
Cd(3)–N(12)	2.314(5)	Cd(4)–Cl(1) <sup>#1</sup>	2.530(3)	Cd(3)–N(17) <sup>#3</sup>	2.351(6)
Cd(3)–N(7) <sup>#3</sup>	2.387(6)	Cd(4)–N(13)	2.325(5)	Cd(4)–O(1w)	2.344(5)
Cd(4)–N(3)	2.350(5)	Cd(4)–N(19)	2.364(6)		
N(22)–Cd(1)–N(6)	90.72(18)	N(1)–Cd(2)–N(5)	90.25(19)	N(12) <sup>#4</sup> –Cd(3)–N(12)	180.000(1)
N(6)–Cd(1)–N(14)	178.64(19)	N(1)–Cd(2)–N(10)	175.41(18)	N(12)–Cd(3)–N(17) <sup>#3</sup>	91.6(2)
N(6)–Cd(1)–N(2)	88.56(18)	N(1)–Cd(2)–N(21)	94.99(18)	N(12)–Cd(3)–N(17) <sup>#5</sup>	88.4(2)
N(18)–Cd(1)–N(2)	90.60(19)	N(5)–Cd(2)–N(21)	93.94(18)	N(12)–Cd(3)–N(7) <sup>#3</sup>	90.45(19)
N(13)–Cd(4)–N(3)	91.79(19)	O(1w)–Cd(4)–N(3)	170.0(2)	N(13)–Cd(4)–Cl(1) <sup>#1</sup>	94.99(15)
compound 3b <sup>h</sup>					
Cd(1)–N(22)	2.322(4)	Cd(1)–N(6)	2.334(4)	Cd(1)–N(14)	2.345(4)
Cd(1)–N(18)	2.349(4)	Cd(1)–N(2)	2.369(4)	Cd(1)–N(11) <sup>#2</sup>	2.386(4)
Cd(2)–N(1)	2.323(4)	Cd(2)–N(5)	2.335(4)	Cd(2)–N(10)	2.349(4)
Cd(2)–N(21)	2.356(4)	Cd(2)–N(23) <sup>#3</sup>	2.365(4)	Cd(2)–N(15) <sup>#3</sup>	2.387(4)
Cd(3)–N(12)	2.321(4)	Cd(3)–N(17) <sup>#3</sup>	2.361(5)	Cd(3)–N(7) <sup>#3</sup>	2.384(4)
Cd(4)–N(3)	2.332(4)	Cd(4)–N(13)	2.337(4)	Cd(4)–O(1w)	2.341(4)
Cd(4)–N(19)	2.370(5)	Cd(4)–Br(1) <sup>#1</sup>	2.6557(8)	N(12)–Cd(3)–N(7) <sup>#5</sup>	89.85(15)
N(6)–Cd(1)–N(2)	88.58(14)	N(1)–Cd(2)–N(5)	90.28(15)	N(12)–Cd(3)–N(7) <sup>#3</sup>	90.15(15)
N(6)–Cd(1)–N(18)	91.62(14)	N(1)–Cd(2)–N(10)	174.75(14)	N(17) <sup>#3</sup> –Cd(3)–N(7) <sup>#3</sup>	92.01(16)

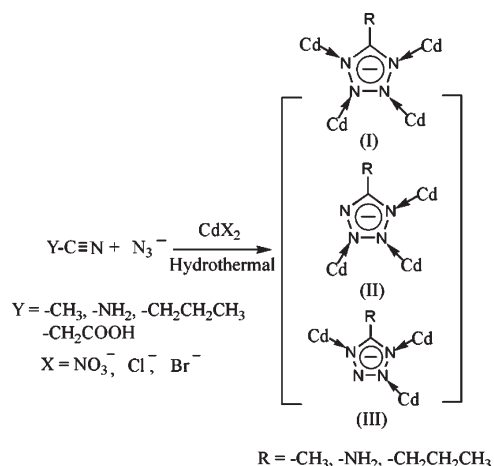


Table 2. Continued

compound <b>3b</b> <sup>a</sup>					
N(22)–Cd(1)–N(6)	90.95(14)	N(1)–Cd(2)–N(21)	95.01(14)	N(7) <sup>#5</sup> –Cd(3)–N(7) <sup>#3</sup>	180.0(1)
N(6)–Cd(1)–N(14)	178.25(14)	N(21)–Cd(2)–N(15) <sup>#3</sup>	85.27(14)	N(3)–Cd(4)–N(13)	92.42(15)
N(3)–Cd(4)–Br(1) <sup>#1</sup>	96.41(11)	N(19)–Cd(4)–Br(1) <sup>#1</sup>	173.26(11)	O(1w)–Cd(4)–Br(1)	84.40(10)

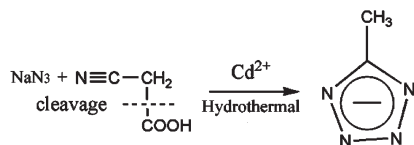
<sup>a</sup> Symmetry transformations used to generate equivalent atoms are given as footnotes. <sup>b</sup> #1  $-y + 1/2, -z + 1/2, -x$ ; #2  $-z, -x + 1/2, -y + 1/2$ ; #3  $-x, -y + 1, -z$ ; #4  $z, x + 1/2, y - 1/2$ . <sup>c</sup> #1  $-x, -x + y, -z$ ; #2  $-x + y, -x + 1, z$ . <sup>d</sup> #1  $x, -y + 5/2, z$ ; #2  $x - 1/2, y, -z + 3/2$ ; #3  $x + 1/2, y, -z + 3/2$ ; #4  $-x + 3/2, -y + 2, z + 1/2$ . <sup>e</sup> #1  $x, -y + 3/2, z$ ; #2  $x - 1/2, y, -z + 1/2$ ; #3  $-x + 2, -y + 2, -z$ ; #4  $-x + 2, y - 1/2, -z$ ; #5  $x + 1/2, y, -z + 1/2$ . <sup>f</sup> #1  $-x + 1, -y + 2, -z + 1$ ; #2  $x, -y + 3/2, z + 1/2$ ; #3  $-x, -y + 2, -z + 1$ ; #4  $x, -y + 3/2, z - 1/2$ ; #5  $-x, y - 1/2, -z + 1/2$ . <sup>g</sup> #1  $-x + 1, -y + 1, -z + 2$ ; #2  $x, -y + 1/2, z + 1/2$ ; #3  $x, -y + 1/2, z - 1/2$ ; #4  $-x, -y, -z + 1$ ; #5  $-x, y - 1/2, -z + 3/2$ . <sup>h</sup> #1  $-x + 1, -y + 1, -z + 2$ ; #2  $x, -y + 1/2, z + 1/2$ ; #3  $x, -y + 1/2, z - 1/2$ ; #4  $-x, -y, -z + 1$ ; #5  $-x, y - 1/2, -z + 3/2$ .

### Scheme 1. In Situ Hydrothermal Syntheses of Compounds and Their Coordination Modes<sup>a</sup>



<sup>a</sup> (I) observed in complexes (**1b**, **1c**, **2a**, **2b**); (II) observed in complexes (**1a**, **1b**, **2a**, **3a**, **3b**); (III) observed in complex (**2b**).

### Scheme 2. In Situ Decarboxylation Reaction



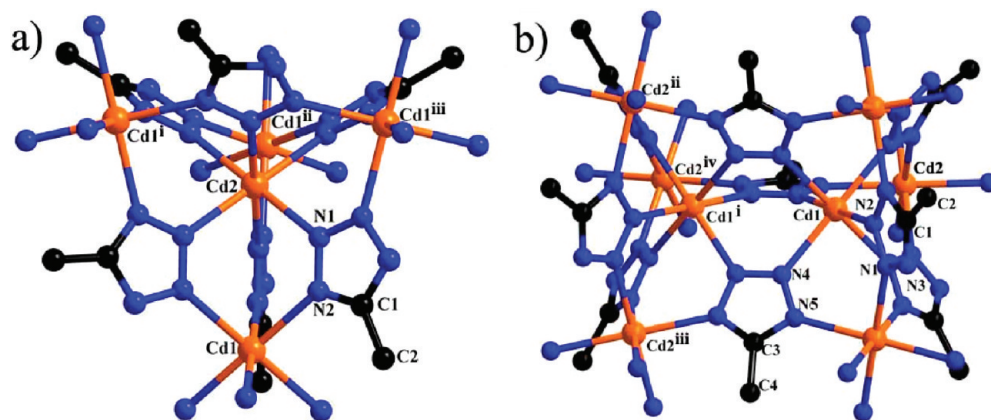
## Results and Discussion

**Synthesis.** Hydrothermal treatment of nitriles (R-CN) and sodium azide with the aid of different cadmium salts results in the formation of Cd-tetrazole coordination compounds (Scheme 1). (I) coordination modes observed in complexes (**1b**, **1c**, **2a**, **2b**); (II) coordination modes observed in complexes (**1a**, **1b**, **2a**, **3a**, **3b**); (III) coordination modes observed in complexes (**2b**). In the FT-IR spectra of the synthetic products, the strong bands appeared around  $3400\text{ cm}^{-1}$  should be ascribed to the stretching vibrations of O–H, suggesting the presence of free and/or coordinated water molecule. While the peaks indicative of nitriles or azides around  $2200\text{ cm}^{-1}$  were absent, the emergence of the peaks in the  $1400\text{--}1500\text{ cm}^{-1}$  region clearly confirmed the formation of the tetrazole groups. The peak at  $2041\text{ cm}^{-1}$  for the asymmetric stretching of  $\text{N}_3^-$  for **1b** confirms the existence of the azide anion in the compound. In our synthesis, the cyanoacetic acid failed to react to get the tetrazole-5-acetate but was instead in situ reduced to 5MT (Scheme 2). In situ hydrothermal decarboxylation reactions were also observed in other reports.<sup>17</sup> However, it is difficult to explain the exact reaction mechanism of in situ ligand synthesis due to the

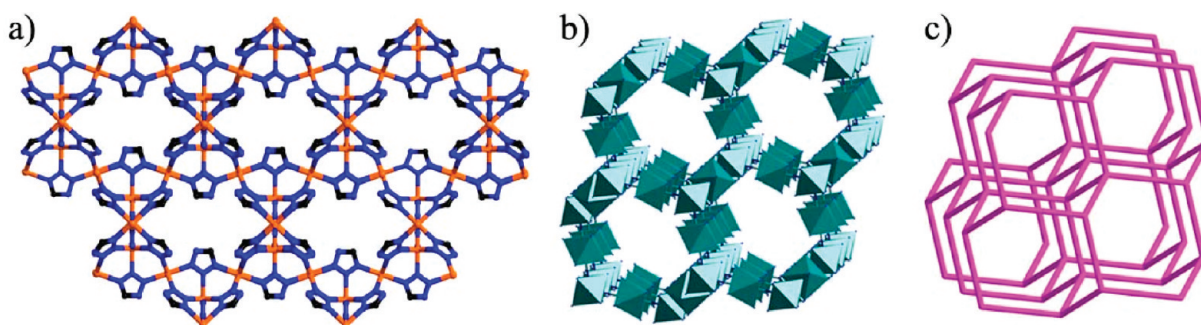
complexity at high temperature and pressure.<sup>18</sup> To further tune the assembly of the flexible cadmium metal ions and in situ synthesis of tetrazole ligands, we also varied the counter-anions leading to the formation of structural varieties of the compounds.

**Structures of **1a** and **1b**.** The two complexes are constructed from the interconnection of numerous Cd-5MT bridges. **1a** belongs to the cubic system space group  $Fd\bar{3}m$ , while **1b** is hexagonal with the space group  $P6_3/mmc$ . As depicted in Figure 1a, in the asymmetric unit of **1a** there are two crystallographically independent Cd(II) ions, Cd1 and Cd2, which are both coordinated to six nitrogen atoms from six 5MT ligands and display octahedral coordination geometries. The Cd–N bond distances fall between 2.352(7) and 2.356(10) Å. The structure of **1a** can be described as a 3D Cd-5MT network, in which each disordered 5MT ligands connects to three cadmium centers. The Cd2 atom in the middle is surrounded by this type of six 5MT ligands, such that there are four Cd1 atoms bridged on its four equivalent sides to create a  $\text{Cd}_4\text{Cd}_2(\text{5MT})_6$  subunit. Each subunit connects to four others to give an overall 3D network. A consequence of this packing arrangement is that small cavities are formed between these linkers into which the terminal  $-\text{CH}_3$  groups are pointing (Figure 2a). The 3D network may be viewed as a series of highly ordered arrays of numerous cadmium octahedrons assembled by 5MT anions (Figure 2b). To better understand the nature of the complicated framework, a topological approach to simplification of 3D structures can be accomplished by reducing them to simple nodes and links. Therefore, if the interconnections of cadmium octahedrons by 5MT bridges are regarded as nodes or links of a topological network, the 3D network can then be seen in a simplified way as a diamond-like net with Schläfli symbol “(6<sup>6</sup>)” (Figure 2c).

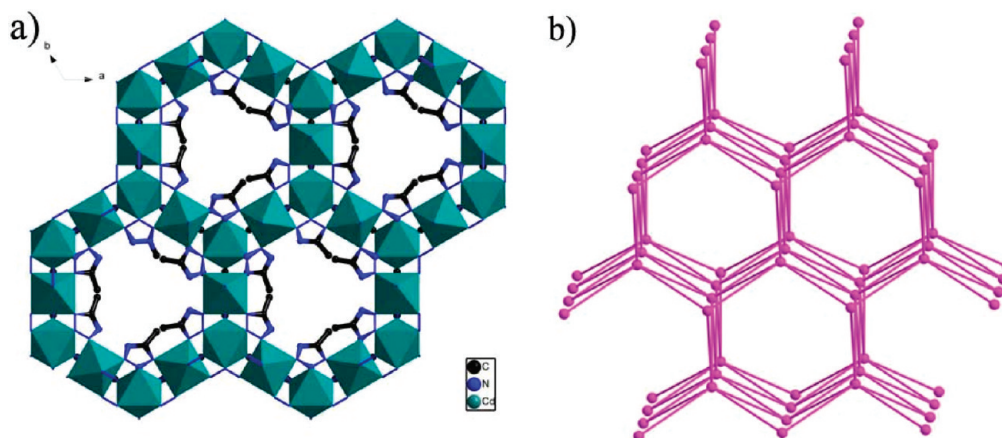
As described in Figure 1b, the asymmetric unit of **1b** consists of two unique Cd(II) ions, one disordered OH anions, and two kinds of 5MT ligands: one is 1:1 disordered across a 2-fold axis and coordinates to three metal atoms, while the other coordinates to four metal atoms. Both the Cd1 and Cd2 atoms are coordinated by six nitrogen donors of six different 5MT ligands with an octahedral coordination environment. The bond lengths range from 2.358(4) to 2.399(5) Å. In the structure of **1b**, three symmetry-related Cd2 ions are bridged to each other by three tridentate 5MT ligands, while Cd1 ion is coordinated to the three ligands, resulting in a  $\text{Cd}_1\text{Cd}_2(\text{5MT})_3$  “strut”. Two pairs of “struts” are bridged to each other by another three tetradentate 5MT ligands to create a  $\text{Cd}_2\text{Cd}_6(\text{5MT})_9$  subunit. A 3-fold axis thus passes through the center of one pair of symmetry-related Cd1 atoms. Each subunit connects to six others to generate a 3D network with small channels running



**Figure 1.** View of the asymmetric unit of structures **1a** (a) and **1b**. (b) All H atoms were omitted for clarity. N atoms are represented as blue, C as black, and Cd as yellow spheres. Symmetry codes: [**1a**] (i)  $0.5 - y, 0.75 + x, 0.25 + z$ ; (ii)  $0.25 - x, 1.25 - y, z$ ; (iii)  $-0.25 + y, 0.5 - x, 0.25 + z$ . [**1b**] (i)  $1 - y, 1 - x, 0.5 - z$ ; (ii)  $1 + x - y, 1 + x, 0.5 + z$ ; (iii)  $y, -x + y, 0.5 + z$ ; (iv)  $-x, 1 - y, 0.5 + z$ .



**Figure 2.** (a) View of the 3D network of **1a** in the  $[1/2, 1/2, 0]$  direction (All  $\text{CH}_3$  groups were omitted for clarity; N atoms are represented as blue, C as black and Cd as yellow spheres.) (b) View of the network of cadmium octahedrons assembled by the 5MT anions. (c) View of the diamond-like net generated by the interconnection of the cadmium octahedrons.

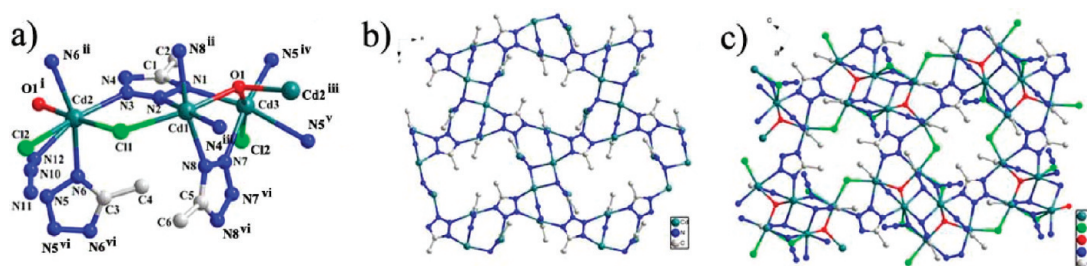


**Figure 3.** (a) View of the 3D network of **1b** in the  $[001]$  direction (All H atoms were omitted for clarity; N atoms were represented as blue, C as black and Cd as cyan spheres). (b) View of the **acs** net when each subunit drawn in Figure 1b is taken as a node.

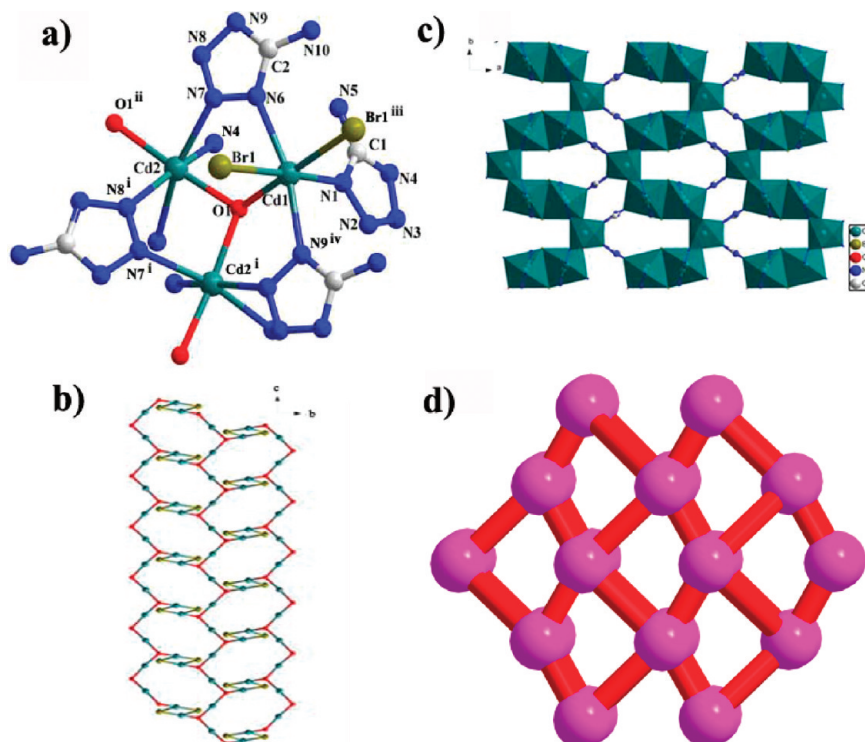
along the  $c$ -axis (Figure 3a). Disordered azide anions and water molecules are encapsulated into these channels. The different connectivity of the network in **1b**, compared with that of **1**, is highlighted by its simple net formed from this geometry with the **acs** net ( $4^9.6^6$ ) (Figure 3b).<sup>19</sup> In the complicated structure, each subunit drawn in Figure 1b is taken as a node (see Figure 3b). This highlights the significance of considering each 5MT ligand separately to distinguish between the different topologies of the systems.

**Structures of 1c and 2a.** The two complexes have very similar structural networks, except for the difference of the

substituting groups at the 5-position of the tetrazole, which is methyl for **1c** and amino for **2a**. Therefore, only compound **1c** is selected and described here in detail. Both compounds exhibit disorder of parts of the frameworks across a crystallographic mirror plane (see Crystal Structure Determination section for details), but in **1c** the site of the disordered azide is occupied by a mixture of azide and chloride in a ratio of 0.69(4) to 0.31(4) in favor of the azide anion. **1c** and **2a** crystallize in the orthorhombic group  $Pnma$ , and their structures are constructed from interconnected  $\{\text{ClCd}_3\text{O}\}$  subnets through tetradentate 5MT ligands. As shown in



**Figure 4.** (a) View of the asymmetric unit of **1c**. (b) View of the Cd-5AT network of **1c**. (c) View of the overall 3D network in the *b*-axis direction (All H atoms were omitted for clarity). Symmetry codes: (i)  $0.5 + x, 2.5 - y, 1.5 - z$ ; (ii)  $x, 2.5 - y, z$ ; (iii)  $-0.5 + x, 2.5 - y, 1.5 - z$ ; (iv)  $1.5 - x, 2 - y, 0.5 + z$ ; (v)  $-0.5 + x, y, 1.5 - z$ ; (vi)  $x, 1.5 - y, z$ .



**Figure 5.** (a) View of the asymmetric unit of **2b**. (b) View of the  $\{\text{BrCd}_3\text{O}\}$  layered network of **2b**. (c) View of the overall 3D network in the *c*-axis direction (All H atoms were omitted for clarity). (d) A quasi-*pecu* type rod packing topological net when the  $\{\text{Cd}_3\text{O}\}$  chains are regarded as finite “nodes”. Symmetry codes: (i)  $x, 1.5 - y, -0.5 + z$ ; (ii)  $x, 1.5 - y, 0.5 + z$ ; (iii)  $1 - x, 2 - y, 1 - z$ ; (iv)  $x, y, 1 + z$ .

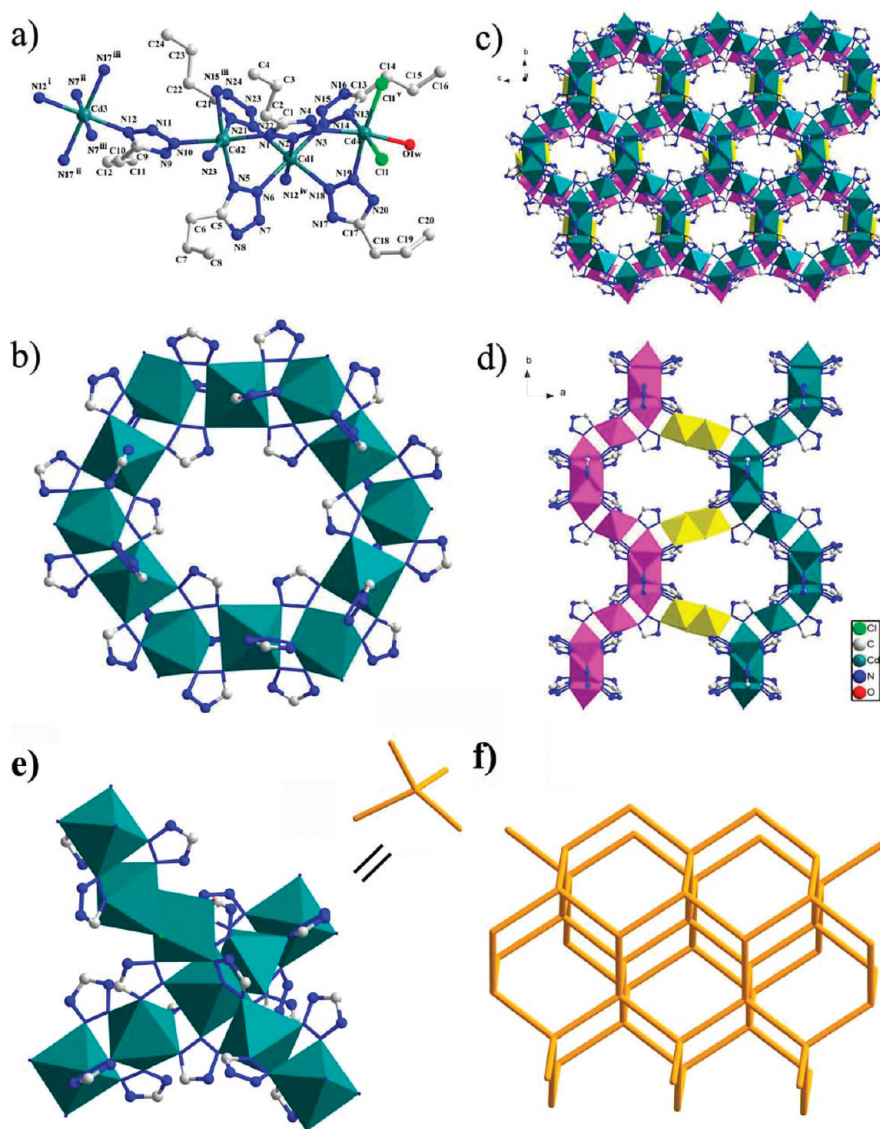
Figure 3a, the asymmetric unit of **1c** contains three crystallographically independent Cd(II) ions, three 5MT ligands, one  $\mu_2$ -Cl ligand, one  $\mu_3$ -OH anion, and the anionic site occupied by a mixture of chloride and azide in the ratio of about 0.3:0.7. All cadmium ions are six-coordinated and have a slightly distorted octahedral coordination environment: the Cd1 and Cd3 ions are both coordinated by four nitrogen atoms from four different 5MT ligands, one  $\mu_3$ -OH anion and one  $\mu_2$ -Cl ligand; the Cd2 ion coordination is defined by two nitrogen atoms from two different 5MT ligands, one  $\mu_3$ -OH anion, one  $\mu_2$ -Cl ligand, and by the disordered Cl/N<sub>3</sub> ligand. All coordination bond lengths fall in the normal range.<sup>13b,c</sup>

In the structure of **1c**, all 5MT ligands act in a tetradentate coordination mode to connect to four cadmium ions, with each OH anion coordinated to three cadmium ions. The Cl anion coordinate to two cadmium ions, while the Cl/N<sub>3</sub> anion coordinates to three cadmium ions. The 5MT bridges interconnect the cadmium metal ions to generate a 3D network (Figure 4b). An intriguing feature in the structure is that the 3D

$\{\text{ClCd}_3\text{O}\}$  cadmium cluster network forms a subnet, which is created by assembly of the Cd metal ions with the Cl and/or N<sub>3</sub> ions (see Supporting Information, Figure S1). These bridges play an important role in the help of supporting the 3D complicated network structure (Figure 4c).

**Structure of 2b.** The compound crystallizes in the monoclinic space group  $P2_1/c$  as a 3D coordination polymer constructed from two-dimensional (2D) wavelike  $[\text{BrCd}_3\text{O}]$  layers and 5-amino-tetrazole (5AT) linkers. As shown in Figure 5a, the asymmetric unit of **2b** contains two crystallographically independent Cd(II) ions, two types of 5AT ligands, one  $\mu_3$ -OH anion, and one Br atom. The two unique cadmium ions, Cd1 and Cd2, both have a distorted octahedral coordination geometry: Cd1 ion is coordinated by three nitrogen atoms from three different 5AT ligands, one  $\mu_3$ -OH anion and two Br atoms; Cd2 ion is surrounded by four nitrogen donors of four different 5AT ligands and two  $\mu_3$ -OH anions. The Cd–N and Cd–O bond lengths range from 2.230(5) to 2.499(7) Å, and the Cd–Br bond lengths are 2.7205(9) and 2.7890(9) Å.





**Figure 6.** (a) View of the asymmetric unit of **3a**. (b) View of the nanosized cadmium wheel with the 12-membered ring. (c) View of the 3D network constructed from the assembly of 2D wheel layers through Cd–Cl coordination bonds drawn by yellow octahedrons in the *bc*-plane and (d) in the *ab*-plane. (All butyl groups and H atoms were omitted for clarity; N atoms were represented as blue, C as white, Cd as cyan, O as red, and Cl as green spheres.) (e) View of a unit of **3a** and (f) a diamond-like topological net simplified by the interconnection of these units. Symmetry codes: (i)  $-x, -y, 1 - z$ ; (ii)  $-x, 0.5 + y, 1.5 - z$ ; (iii)  $x, 0.5 - y, -0.5 + z$ ; (iv)  $x, 0.5 - y, 0.5 + z$ ; (v)  $1 - x, 1 - y, 2 - z$ .

It should be noted that the structure of **2b** contains infinite  $[\text{Cd}_3\text{O}]$  chains is constructed through interconnection of Cd metal ions by  $\mu_3\text{-OH}$  anions. The three Cd metal ions are located at the corners of an almost equilateral triangle; the  $\mu_3\text{-OH}$  anion lies in the middle of this triangle about 0.55 Å above the plane of the three metal atoms and connects them with each other. A search of the database of the Cambridge Crystallographic Data Centre for  $\{\text{Cd}_3\text{O}\}$  chains revealed only two structures with similar  $\{\text{Cd}_3\text{O}\}$  chains.<sup>20</sup> The chains in the structure of **2b** extend along the *b*-axis and are further assembled through  $\mu_2\text{-Br}$  anions into a wavelike layered network in the *bc*-plane. As far as we can tell, this novel arrangement is not yet observed in crystal engineering and coordination chemistry. Each cavity within the layer is occupied by two 5AT ligands, where the two 5AT ligands act in a tetradentate coordination mode to connect four Cd metal ions, and both are antiorientated parallel to each other (Figure 5b). Another type of 5AT ligands acts in a tridentate coordination mode to connect to three Cd metal ions on the

top and bottom sides of the layers, resulting in the formation of a 3D coordination framework (Figure 5c). To assign a topological network to this structure is difficult. Since a series of metal carboxylate coordination polymers in terms of the packing and interconnection of 1D rods are proposed by Yaghi and O’Keeffe,<sup>21</sup> **2b** has a quasi-*pcu* type rod packing net when the  $\{\text{Cd}_3\text{O}\}$  chains are regarded as finite “nodes” (Figure 5d).

**Structures of 3a and 3b.** The two complexes have similar structural network motifs that differ only in the nature of the bridging halogen anions. Therefore, only compound **3a** is described here in detail. Complex **3a** exhibits the monoclinic space group  $P2_1/c$  and has an intricate 3D coordination framework that is constructed from the assembly of 2D Cd-5BT wheel layers (5BT = 5-butyltetrazole) and Cl linkers. As shown in Figure 6a, the asymmetric unit of **3a** contains four crystallographically independent Cd(II) ions, six 5BT ligands, one  $\mu_2\text{-Cl}$  atom, and one coordinated water molecule. Among the four unique Cd(II) metal ions, the Cd1, Cd2, and



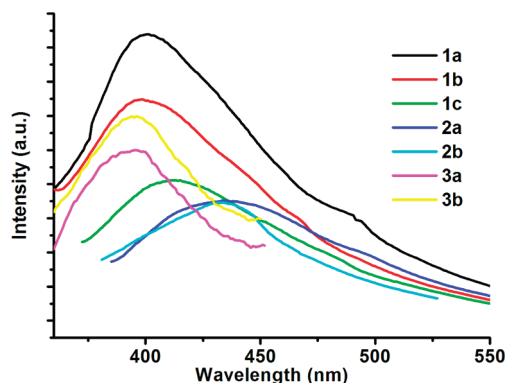
Cd3 ions adopt octahedral coordination environments that are formed by six nitrogen atoms from six different 5BT ligands, while the Cd4 center has a slightly distorted octahedral coordination environment that is defined by three nitrogen donors of three different 5BT anions, two  $\mu_2$ -Cl anions, and one water molecule. The Cd–N and Cd–O bond lengths range from 2.314(5) to 2.398(5) Å, and the Cd–Cl bond lengths are 2.530(3) and 2.611(2) Å.

On the basis of the connectivity of the multifunctional 5BT ligands, a nanosized cadmium wheel with a 12-membered ring is generated where each set of two Cd(II) octahedrons is linked by three tridentate 5BT ligands (Figure 6b). The diameter of the wheel is approximately 20 Å. The butyl groups of the 5BT anions thus point into the center of the 12-membered ring. Each wheel is further linked to adjacent wheels by sharing three Cd(II) octahedrons, resulting in a highly ordered wavelike layered wheel network running in the *bc*-plane (Figure 6c). Two pairs of  $\mu_2$ -Cl anions interconnect the adjacent layered wheel network via Cd–Cl coordination bonds to form a 3D coordination framework (Figure 6d). The 3D network can also be described as a diamond-like topological net with Schläfli symbol “(6<sup>6</sup>)”, if the crossed sites of Cd(II) octahedrons are simplified as nodes and other interconnected Cd(II) octahedrons to them are considered as links (Figure 6e,f).

#### Thermal Stability and Powder X-ray Diffraction (PXRD).

To examine the thermal stabilities of all seven compounds, thermogravimetric analyses were carried out at a heating rate of 10 °C min<sup>−1</sup> under a nitrogen atmosphere. As shown in the Supporting Information, Figure S4, the TGA curves of all compounds indicate that they are stable up to approximately 380 °C, while beyond these temperatures, their frameworks begin to disintegrate. A first weight loss for some complexes occurs between room temperature and 380 °C, corresponding to the loss of interstitial or coordinated water molecules. Simulated and experimental powder X-ray diffraction (PXRD) patterns of **1a**, **1b**, **2a**, **2b**, and **3a** are shown in Figure S5, Supporting Information. They are in fairly good agreement with the experimental patterns, which clearly confirms the phase purity of the as-prepared products.

**Luminescence Properties.** Owing to the excellent luminescent properties of d<sup>10</sup> Cd(II) complexes, the photoluminescence of all complexes in the solid state were investigated at room temperature. The emission spectra have broad peaks with maxima at 406, 405, 412, 422, 421, 394, and 395 nm for compounds **1–3**, respectively, with an excitation upon 350 nm for 5BT based complexes, 366 nm for 5AT based complexes, 331 nm for 5BT based complexes (Figure 7). The lifetimes for compounds **1–3** are 6.52, 6.19, 9.56, 10.23, 11.29, 2.34, and 2.56 ns, respectively. From reported literatures, the free tetrazole ligand presents a very weak photoluminescence emission centered at 325 nm at room temperature.<sup>22</sup> Therefore, the strong fluorescence emission and distinct red-shift may be ascribed to the cooperative effects of intraligand emission and ligand-to-metal charge transfer (LMCT).<sup>13,22</sup> When compared with the emission of compounds, the emission maxima for **3** (394, 395 nm) are blue-shifted compared to those of **1** and **2** (405–422 nm). Moreover, the lifetime of **3** is much shorter than those of **1** and **2**, which may be due to the long flexible butyl chains with stronger vibrations of the frameworks, and thus resulting in more radiationless decay of the energy. The variations of photoluminescence and their lifetimes of these compounds may be attributed to the difference in the substituting groups at the 5-position of



**Figure 7.** Solid-state emission spectra of all complexes at room temperature.

the tetrazole ligands to cadmium metal ions and/or their local coordination environments. In other words, the emissions can be tuned upon different ligands to same metal coordination environments (see **1c** and **2a**), as well as the cluster-based metal ions.<sup>23</sup> These emission bands in the blue region suggest that these complexes may be potential candidates as blue-light emitting materials.

#### Conclusion

Seven Cd-tetrazole coordination frameworks were synthesized by in situ ligand synthesis using hydrothermal methods. All complexes **1–3** exhibit intriguing three-dimensional (3D) frameworks constructed from cadmium octahedrons and tetrazole linkers. In particular, some of these 3D frameworks are also supported by diverse cadmium clusters, chains, or layers. These compounds not only have high thermal stabilities, but they also exhibit relative strong solid luminescent intensities and are thus potential candidates for applications as photoactive materials.

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**Supporting Information Available:** View of the 3D {ClCd<sub>3</sub>O} network of **2b** in the *ac*-plane (Figure S1); view of the disordered units of compound **1c** (Figure S2) and **2a** (Figure S3); TGA curves; powder XRD patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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