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## Anion-dependent assemblies of a series of Cd(II) coordination complexes based on an asymmetric multi-dentate ligand and inorganic SBUs: syntheses, crystal structures, and fluorescent properties<sup>†</sup>

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Six novel Cd(II) complexes,  $\text{Cd}(\text{bpmi})_2\text{Cl}_2$  (**1**),  $[\text{Cd}(\text{bpmi})_2(\text{NO}_3)_2(\text{H}_2\text{O})]_n$  (**2**),  $[\text{Cd}_2(\text{bpmi})_2\text{Cl}_2(\text{N}_3)_2(\text{CH}_3\text{OH})_2]_n$  (**3**),  $[\text{Cd}(\text{bpmi})\text{Cl}_2]_n$  (**4**),  $[\text{Cd}(\text{bpmi})(\text{SCN})_2]_n$  (**5**) and  $[\text{Cd}(\text{bpmi})(\text{N}_3)_2]_n$  (**6**), are synthesized by the reaction of different Cd(II) salts with an asymmetric multidentate ligand 1-(benzotriazole-1-methyl)-2-propylimidazole (bpmi). X-ray single-crystal analyses reveal that these complexes show rich structural chemistry ranging from mononuclear (**1**), one-dimensional (**2** and **3**), two-dimensional (**4** and **5**) to three-dimensional (**6**) structures. These complexes share common features such as they all contain inorganic SBUs and have a high degree of dependence on the corresponding counter anions. In this paper, the fine regulation of counter anions has been discussed in detail. Furthermore, these complexes have been investigated by solid-state UV-vis spectra, thermogravimetric analyses and fluorescence spectra.

## Introduction

The design and preparation of metal-organic coordination complexes have attracted widespread interest for decades, not only due to their fascinating structures, such as molecular cage, honeycomb, grid, ladder, rotaxane and catenane structures, but also their promising applications in gas adsorption, magnetism, ion-exchange, catalysis, and luminescence.<sup>1–8</sup> Since rapid expansion in this field has occurred in recent years, growing interest has focused on the controlled-synthesis of crystalline materials with the desired fascinating structures and related versatile properties.<sup>9,10</sup> The components of a compound receive great attention from the research community. Organic ligands have proved their roles as structure directing templates<sup>11,12</sup> through their various coordination modes to the metal centers. Metal centers control the special properties of a compound and choose their coordination preferences.<sup>13,14</sup>

Anions, besides organic ligands and metal centers, are important components in a metal-organic coordination complex. Anions not only act as the guests and/or counter ion to template the construction of host frameworks, but also act as the hydrogen-bonded donor or acceptor to extend the molecular units into high-dimension networks. On the other hand, anions are excellent candidates for the auxiliary ligands to coordinate to the metal centers, which tune the coordination numbers and geometry of the metal centers, hence manipulating the physical-chemical properties of these compounds. For example, Dunbar and co-workers recently reported the anion-directed assembly of Ni(II) and Zn(II) metallacyclophanes with a 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine ligand as a bridging ligand; tetrahedral  $\text{BF}_4^-$  and  $\text{ClO}_4^-$  ions direct the formation of molecular squares,  $[\{\text{M}_4(\text{bptz})_4(\text{CH}_3\text{CN})_8\}\text{X}]_n$  ( $\text{M} = \text{Zn(II)}, \text{Ni(II)}$ ;  $\text{X} = \text{BF}_4^-, \text{ClO}_4^-$ ), whereas octahedral  $\text{SbF}_6^-$  induces the formation of pentagonal  $[\{\text{Ni}_5(\text{bptz})_5(\text{CH}_3\text{CN})_{10}\}\text{SbF}_6]_n$ .<sup>15</sup> Richard A. Jones and co-workers reported that in heterotrinuclear and heterodinuclear Zn-Ln ( $\text{Ln} = \text{Eu}$  and  $\text{Tb}$ ) Schiff-base complexes, anions ( $\text{CF}_3\text{SO}_3^-$  versus  $\text{NO}_3^-$ ) played a dominant role in inducing the structure by controlling the stoichiometry and then significantly regulating the intense luminescence emission.<sup>16</sup> Meanwhile, our group have reported Cu(II) coordination complexes containing  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ ,  $\text{N}_3^-$  and  $\text{SCN}^-$ , respectively. In these complexes, counter anions show different coordination modes and capabilities, and the nature of the counter anions is the underlying reason for the structural differences of these complexes. Generally, during

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the synthetic process, inorganic counter anions tune the coordination complexes assemblies in two ways. One way, is using a negative ligand in the system (metal–negative ligand system), the anions acting as the template in the crystal lattice do not often participate in the framework structures of the coordination complexes because the charges are balanced by the negative organic ligand. In these cases, the anions can significantly influence the physical-chemical properties and the final structures through hydrogen bonds and/or altering the lattice phonon distribution that affects crystal packing modes and intermolecular interactions.<sup>17,18</sup> Another way, is using a neutral ligand in the system (metal–neutral ligand system), the inorganic counter anions acting as the auxiliary ligands have the capability of constructing inorganic secondary building units (SBUs) which are further connected by organic links during the synthesis of coordination complexes. In this regard, introducing anions with different sizes, charges, and coordination tendency into the same self-assembly processes can lead to diverse structures. Though the role of the counter anions in a self-assembly process has emerged as an increasingly active topic in recent literature,<sup>19–22</sup> it still remains a considerable challenge to systematically research the role of counter anions in controlling the coordination assemblies during the synthesis process.

As a continuous work, we selected a derivative of benzotriazole, 1-(benzotriazole-1-methyl)-2-propylimidazole (bpmi), an asymmetric multidentate ligand, to assemble with a Cd(II) center in the presence of different counter anions with strong coordination capacity, such as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>, and N<sub>3</sub><sup>-</sup>. Six novel complexes have been prepared successfully, Cd(bpmi)<sub>2</sub>Cl<sub>2</sub> (**1**), [Cd(bpmi)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>OH)]<sub>n</sub> (**2**), [Cd<sub>2</sub>(bpmi)<sub>2</sub>Cl<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>OH)]<sub>n</sub> (**3**), [Cd(bpmi)Cl<sub>2</sub>]<sub>n</sub> (**4**), [Cd(bpmi)(SCN)]<sub>n</sub> (**5**), and [Cd(bpmi)(N<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (**6**) (Scheme 1). It is noted that in the synthesis of **1**, we use a pure CH<sub>3</sub>OH system. Considering the variation in the polarity, the solvent can influence the structures of coordination complexes, we therefore replaced the pure CH<sub>3</sub>OH system with a CH<sub>3</sub>OH–H<sub>2</sub>O system in synthesis of **2–6**. In other words, in the synthesis of **2–6**, all of the reaction factors such as the temperature, the solvent and ratio of starting materials are the same except the types of counter anions that were used, in order to grasp

the key role of the anion in the self-assembly process. These complexes display a common feature, they all contain inorganic SBUs. Complex **1** is a mononuclear structure containing [Cd(NO<sub>3</sub>)<sub>2</sub>]. Complex **2** is a one dimensional (1D) sinusoidal chain composed of an SBU [Cd(NO<sub>3</sub>)<sub>2</sub>], and **3** is a 1D chain comprised of binuclear [CdCl(CH<sub>3</sub>OH)(N<sub>3</sub>)]<sub>2</sub>. However, compared to the mononuclear inorganic SBU in **2** and dinuclear inorganic SBU in **3**, the inorganic SBUs in **4** and **5** are a 1D chain [-Cl–Cd–Cl-] for **4** and [-SCN–Cd–SCN-] for **5**. As the most characteristic 3D structure, the inorganic SBU of **6** is a 2D inorganic sheet structure with honeycomb caves. The influence of the counter anions on dominating the diverse structures of **1–6** has been illustrated and their thermal stabilities and fluorescence properties have also been investigated.

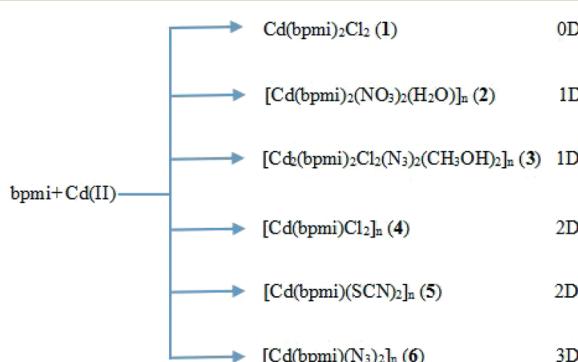
## Experimental

### General details

All of the analytical grade chemicals and solvents were purchased commercially and were used without further purification. Elemental analyses (C, H and N) were carried out on a FLASH EA 1112 elemental analyzer. IR data were recorded on a Fourier translation infrared spectrum (FTIR-8400S) spectrophotometer with KBr pellets in the 400–4000 cm<sup>-1</sup> region. UV-Vis spectra were obtained using a UV-2600 spectrophotometer, BaSO<sub>4</sub> powders were used as the substrate. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TAG-7 instrument from room temperature to 800 °C with a heating rate of 10 °C min<sup>-1</sup>. The luminescence measurements for the solid samples were performed at room temperature using a HITACHI F-4500 fluorescence spectrophotometer. The excitation slit, as well as the emission slit was 2 nm. Powder X-ray diffraction patterns were recorded on an Agilent Technology SuperNova Eos Dual system with a (Cu) micro focus source ( $\lambda = 1.54184 \text{ \AA}$ ) and focusing multi-layer mirror optics with small pellets.

**Synthesis of Cd(bpmi)<sub>2</sub>Cl<sub>2</sub> (**1**)**. A mixture of bpmi (0.0039 g, 0.02 mmol), and CdCl<sub>2</sub>·2.5H<sub>2</sub>O (0.0046 g, 0.02 mmol) was thoroughly dissolved in 5 mL of MeOH. The mixture was stirred at 80 °C for 1 h and was subsequently filtered. After, 5 mL of MeOH was added into the filtrate, colourless block crystals for X-ray diffraction were formed a few days later. The crystals were collected by mechanical isolation and washed with MeOH (3 × 10 ml) then dried at 40 °C (yield: 57%). Calcd. For C<sub>26</sub>H<sub>30</sub>CdCl<sub>2</sub>N<sub>10</sub>: C, 46.90; H, 4.54; N, 21.03. Found: C, 46.87; H, 4.52; N, 21.01. IR (cm<sup>-1</sup>, KBr): 3114 m, 2956 m, 1588 w, 967 w, 746 s, 428 w.

**Synthesis of [Cd(bpmi)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>OH)]<sub>n</sub> (**2**)**. A mixture of bpmi (0.0039 g, 0.02 mmol), and Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.0062 g, 0.02 mmol) was thoroughly dissolved in 5 mL of MeOH. The mixture was stirred at 80 °C for 1 h and was subsequently filtered. After, 5 mL of water was added into the filtrate, colourless block crystals for X-ray diffraction were formed a few weeks later. The crystals were collected by mechanical isolation and washed with water (3 × 10 ml) and MeOH (3 × 10 ml), then dried at 40 °C (yield: 78%). Calcd. For



Scheme 1 Experimental routes for complexes **1–6**.

$C_{27}H_{34}CdN_{12}O_7$ : C, 42.14; H, 4.53; N, 22.37; O, 14.91. Found: C, 42.13; H, 4.55; N, 22.36; O, 14.92. IR ( $\text{cm}^{-1}$ , KBr): 3114 m, 2956 m, 2058 w, 1588 w, 1436 m, 935 w, 428 w.

**Synthesis of  $[\text{Cd}_2(\text{bpymi})_2\text{Cl}_2(\text{N}_3)_2(\text{CH}_3\text{OH})_2]_n$  (3).** A mixture of bpymi (0.0039 g, 0.02 mmol),  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  (0.0046 g, 0.02 mmol), and  $\text{NaN}_3$  (0.0013 g, 0.02 mmol) was thoroughly dissolved in 5 mL of MeOH. The mixture was stirred at 80 °C for 1 h and was subsequently filtered. After, 5 mL of water was added into the filtrate, colourless block crystals for X-ray diffraction were formed a few days later. The crystals were collected by mechanical isolation and washed with MeOH (3 × 10 ml) then dried at 40 °C (yield: 74%). Calcd. For  $C_{28}H_{38}Cd_2\text{Cl}_2\text{N}_{16}\text{O}_2$ : C, 36.30; H, 4.13; N, 24.19; O, 3.45. Found: C, 36.27; H, 4.12; N, 24.19; O, 3.47. IR ( $\text{cm}^{-1}$ , KBr): 3114 m, 2964 m, 2868 m, 2082 s, 858 w, 546 w, 412 w.

**Synthesis of  $[\text{Cd}(\text{bpymi})\text{Cl}_2]_n$  (4).** The complex 4 was prepared under conditions similar to those of 2 with  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  (0.0046 g, 0.02 mmol) used instead of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . Colourless block crystals for X-ray diffraction were formed a few days later. The crystals were collected by mechanical isolation and washed with water (3 × 10 ml) and MeOH (3 × 10 ml), then dried at 40 °C (yield: 64%). Calcd. For  $C_{13}H_{15}\text{CdCl}_2\text{N}_5$ : C, 36.77; H, 3.56; N, 16.49. Found: C, 36.75; H, 3.54; N, 16.46. IR ( $\text{cm}^{-1}$ , KBr): 3106 m, 2956 m, 2058 w, 1596 w, 927 w, 658 w.

**Synthesis of  $[\text{Cd}(\text{bpymi})(\text{SCN})_2]_n$  (5).** The synthesis process of 5 was similar to the synthesis of complex 3, with  $\text{KSCN}$  (0.0019 g, 0.02 mmol) used instead of  $\text{NaN}_3$ , which gave colourless block crystals of 5. The crystals were collected by mechanical isolation and washed with water (3 × 10 ml) and MeOH (3 × 10 ml), then dried at 40 °C (yield: 72%). Calcd. For  $C_{15}H_{15}\text{CdN}_7\text{S}_2$ : C, 38.34; H, 3.22; N, 20.87. Found: C, 38.33; H, 3.21; N, 20.89. IR ( $\text{cm}^{-1}$ , KBr): 3122 m, 2956 m, 2090 s, 1372 w, 850 w, 460 w.

**Synthesis of  $[\text{Cd}(\text{bpymi})(\text{N}_3)_2]_n$  (6).** Complex 6 was prepared under conditions similar to those of 3 with  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.0062 g, 0.02 mmol) instead of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ . Pink block crystals for X-ray diffraction were formed a few days later. The crystals were collected by mechanical isolation and washed with water (3 × 10 ml) and MeOH (3 × 10 ml), then dried at 40 °C (yield: 67%). Calcd. For  $C_{13}H_{15}\text{CdN}_{11}$ : C, 35.67; H, 3.45; N, 35.20. Found: C, 35.66; H, 3.47; N, 35.23. IR ( $\text{cm}^{-1}$ , KBr): 3415 m, 3122 m, 2973 m, 2098 s, 1580 w, 1380 m, 967 w, 522 w.

## X-ray crystallography

All data were collected on an Agilent Technology SuperNova Eos Dual system with a (Cu-K $\alpha$ ,  $\lambda = 1.54184 \text{ \AA}$  for 1, and 3–6, and Mo-K $\alpha$ ,  $\lambda = 0.71073 \text{ \AA}$  for 2) micro focus source and focusing multilayer mirror optics. The data were collected at a temperature of 293 K and processed using CrysAlis<sup>Pro</sup>.<sup>23</sup> The structures were solved and refined using full-matrix least-squares based on  $F^2$  with program SHELXS-97 and SHELXL-97.<sup>24</sup> All non-hydrogen atoms were refined anisotropically, the hydrogen atoms of the ligands were localized

in their calculated positions and refined using a riding model. Complex 1 exhibits some disorder in the bpymi ligand, which is observed in the terminal group of the organic molecules. Specifically, C(25) and C(26) occupied over two positions in the bpymi molecule [C(25) and C(26) with SOF = 0.54, C(8A) and C(26A) with SOF = 0.46]. In order to maintain the normalized internal bond distances and angles for bpymi ligand, C(24)–C(25), C(24)–C(25A), C(25)–C(26) and C(25A)–C(26A) bond distances were restrained to 1.50(2) Å. The ratios of the maximum and minimum displacement parameters for the methanol solvent in 2 and the C13 atom in 5 were larger than 2, and were restrained. Further details of the X-ray structural analyses are given in Table 1. Selected bond lengths and bond angles of the complex are listed in Table S1.†

## Results and discussion

### Synthesis

Recently, control of the topology and geometry of complexes has become one of the research highlights in coordination chemistry. However, due to the complexity and difficulty in predicting the resulting composition or structure, the influential principles in self-assembly systems are not ascertained nor conclusive. For neutral ligands, the difference in the resulting structures are primarily dependent upon the connective and regulative ability of the inorganic anions if the systems contain the same ligand and the same metal ions. On the condition that the ligand and the metal center were assembled, the spacer containing the inorganic SBUs can be used as a structure-directing agent in the reaction process and in various dimensional (0–3D) architectures. Therefore, in order to further investigate the role of inorganic anions on regulating the resultant coordination assemblies, we should design the reaction conditions in which the ligand, metal center and solvent *etc.* can be fixed successfully, *i.e.* all factors controlling the coordination structures are consistent except the counter anions.

Based on the above consideration, we select an asymmetric multidentate neutral ligand, bpymi, as the main spacer. This ligand contains both benzotriazole and imidazole groups, so it has a great ability to adopt different coordination modes and satisfy many metal coordination preferences. Meanwhile, the Cd(II) ion, possessing diverse coordination geometries (five, six, seven-coordinated, *etc.*), can be used as the metal center for the construction of various coordinations. The combination of the Cd(II) ion and bpymi should be able to bring the advantage of both sides. And then choosing counter anions with different sizes and coordination tendencies, complexes with abundant structural diversity could be constructed.

We first selected the metal salt,  $\text{CdCl}_2$ , as the SBU, a discrete structure  $[\text{Cd}(\text{bpymi})_2\text{Cl}_2]$  (1) with  $\text{Cl}^-$  as the charge compensation anion was obtained in pure  $\text{CH}_3\text{OH}$  solvent. The  $\text{Cl}^-$  anion coordinated to the metal center in the monodentate mode. Considering the variation of the polarity, the solvent can influence the structures of coordination

**Table 1** Crystallographic data for **1–6**

Empirical formula	C <sub>26</sub> H <sub>30</sub> CdCl <sub>2</sub> N <sub>10</sub> (1)	C <sub>27</sub> H <sub>34</sub> CdN <sub>12</sub> O <sub>7</sub> (2)	C <sub>28</sub> H <sub>38</sub> Cd <sub>2</sub> Cl <sub>2</sub> N <sub>16</sub> O <sub>2</sub> (3)	C <sub>13</sub> H <sub>15</sub> CdCl <sub>2</sub> N <sub>5</sub> (4)	C <sub>15</sub> H <sub>15</sub> CdN <sub>7</sub> S <sub>2</sub> (5)	C <sub>13</sub> H <sub>15</sub> CdN <sub>11</sub> (6)
Formula weight	665.90	751.06	926.44	424.60	469.86	437.76
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P $\bar{1}$	C $2/c$	P $2_1/c$	P $2_1/c$	P $\bar{1}$	P $\bar{1}$
a/ $\text{\AA}$	9.5360(3)	26.5918(9)	12.4688(1)	9.3734(5)	9.4788(4)	9.5550(1)
b/ $\text{\AA}$	12.7918(5)	13.5595(5)	15.9995(1)	18.5736(5)	10.2419(5)	9.8491(1)
c/ $\text{\AA}$	13.7773(5)	18.1128(6)	19.4700(2)	9.2232(3)	10.5173(2)	9.8850(9)
$\alpha$ ( $^\circ$ )	73.510(8)	90	90	90	95.716(3)	72.948(10)
$\beta$ ( $^\circ$ )	80.939(7)	94.582(3)	103.058(5)	107.887(5)	99.798(3)	68.962(9)
$\gamma$ ( $^\circ$ )	68.353(9)	90	90	90	109.484(4)	86.711(1)
V/ $\text{\AA}^3$	1494.12(10)	6510.1(4)	3783.70(6)	1528.12(11)	935.00(7)	828.89(17)
Z	2	8	4	4	2	2
D <sub>c</sub> /Mg cm <sup>-3</sup>	1.480	1.533	1.626	1.846	1.669	1.754
$\mu/\text{mm}^{-1}$	7.773	0.734	10.719	14.665	11.553	10.757
F(000)	676	3072	1856	840	468	436
Reflections collected	14 574	5952	15 797	5777	6942	6036
Independent reflections	5063	4510	7210	2892	3505	2949
Goodness-of-fit on $F^2$	0.988	1.050	1.045	1.042	1.039	1.053
Final $R^{a,b}$ indices	$R_1 = 0.0296$ ,	$R_1 = 0.0483$ ,	$R_1 = 0.0280$ ,	$R_1 = 0.027$ ,	$R_1 = 0.0351$ ,	$R_1 = 0.0232$ ,
[ $I > 2\sigma(I)$ ]	wR <sub>2</sub> = 0.0765	wR <sub>2</sub> = 0.1063	wR <sub>2</sub> = 0.0760	wR <sub>2</sub> = 0.0725	wR <sub>2</sub> = 0.0959	wR <sub>2</sub> = 0.0584
R indices (all data)	$R_1 = 0.0334$ ,	$R_1 = 0.0688$ ,	$R_1 = 0.0305$ ,	$R_1 = 0.0321$ ,	$R_1 = 0.0364$ ,	$R_1 = 0.0249$ ,
	wR <sub>2</sub> = 0.0793	wR <sub>2</sub> = 0.1193	wR <sub>2</sub> = 0.0783	wR <sub>2</sub> = 0.0761	wR <sub>2</sub> = 0.0977	wR <sub>2</sub> = 0.0594

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup> wR<sup>2</sup> =  $[\sum w(|F_o|^2 - |F_c|^2)^2 / \sum |w(F_o^2)|^2]^{1/2}$ .

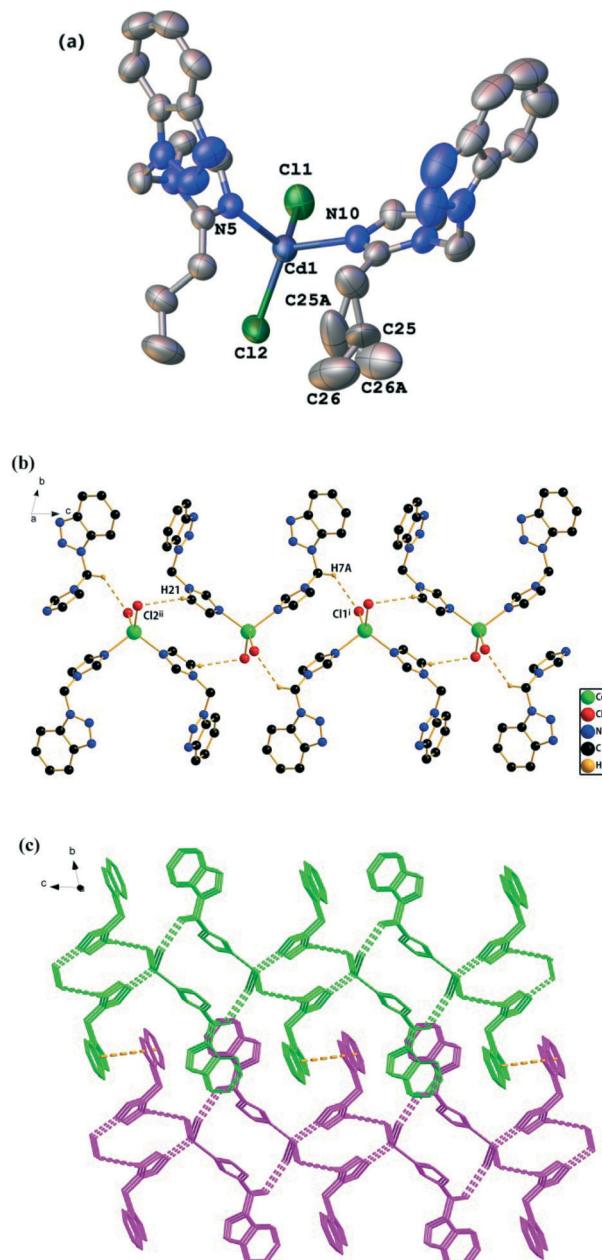
complexes, we therefore replaced pure the CH<sub>3</sub>OH system with a CH<sub>3</sub>OH–H<sub>2</sub>O system, which allows subsequent experiments to be conducted. Four kinds of counter anions with different sizes and coordination tendencies are selected, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SCN<sup>-</sup> and N<sub>3</sub><sup>-</sup>, to observe their control on the assembly of complexes. The refined regulation of the counter anions allowed the main ligand, bpmi, to bend and rotate when coordinated to metal centers. Hence, as we have expected, one-dimensional [Cd(bpmi)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>OH)]<sub>n</sub> (2) and [Cd<sub>2</sub>(bpmi)<sub>2</sub>Cl<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>OH)]<sub>n</sub> (3), two-dimensional [Cd(bpmi)Cl<sub>2</sub>]<sub>n</sub> (4) and [Cd(bpmi)(SCN)<sub>2</sub>]<sub>n</sub> (5) and three-dimensional structures of [Cd(bpmi)(N<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (6), are successfully obtained. These complexes are air stable and almost insoluble in common organic solvents, except DMF in which all complexes have low solubility. Especially, in the syntheses of complexes **1** and **4**, all factors are consistent except the solvent. The difference in their structures confirms the importance of the solvent in the synthesis of coordination complexes.

### Description of the structures

**Structure of Cd(bpmi)<sub>2</sub>Cl<sub>2</sub> (1).** Single crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the triclinic space group P $\bar{1}$ . The asymmetric unit contains one crystallographically unique Cd(II) ion, two bpmi ligands, and two Cl<sup>-</sup> anions (Fig. 1a). The central Cd(II) ion, exhibiting a distorted tetrahedron geometry, is four-coordinated by two nitrogen atoms, N5 and N10, from two different bpmi ligands, and two Cl<sup>-</sup> anions (Cl1 and Cl2). Among them, two Cl<sup>-</sup> anions and one Cd(II) cation, namely [CdCl<sub>2</sub>], composes the inorganic SBU. In the tetrahedron, the distances of Cd–N

[2.2198(2)–2.2320(3)  $\text{\AA}$ ] and Cd–Cl [2.3991(3)–2.4303(2)  $\text{\AA}$ ] are in the normal ranges of those observed in reported Cd(II) complexes, and bond angles around the central Cd(II) ion vary from 99.435(5) $^\circ$  to 119.744(6) $^\circ$ .<sup>25,26</sup> In the bpmi ligand, the C25 and C26 atoms in the propyl group are crystallographically disordered and split into two parts with the occupancies of 0.54 and 0.46 for C25, C26 and C25A, C26A, respectively. (Fig. S1†) As shown in Fig. 1b, one pair of the C–H $\cdots$ Cl hydrogen bonds between C (C7 and C21) atoms from the different bpmi ligands as hydrogen donors and Cl [symmetry codes: (i) 1 – x, –y, –z; (ii) 1 – x, –y, 1 – z;] atoms from two different adjacent molecules as H-acceptors, form a 1D straight chain along the c axis. In the chain, the bridged Cd $\cdots$ Cd distance varies from 6.8977(6)  $\text{\AA}$  to 7.0023(5)  $\text{\AA}$ . At the same time, two benzotriazole rings from two adjacent supramolecular chains are almost parallel to each other with a distance of 3.9538(2)  $\text{\AA}$ , which demonstrates a weak  $\pi\cdots\pi$  stacking interaction. Thus, a 2D supramolecular sheet structure is formed via the  $\pi\cdots\pi$  stacking interactions between the bpmi units from adjacent chains. Both hydrogen bonding (Table S2†) and  $\pi\cdots\pi$  stacking interactions (Fig. 1c) play important roles in stabilizing the 2D sheet structure.

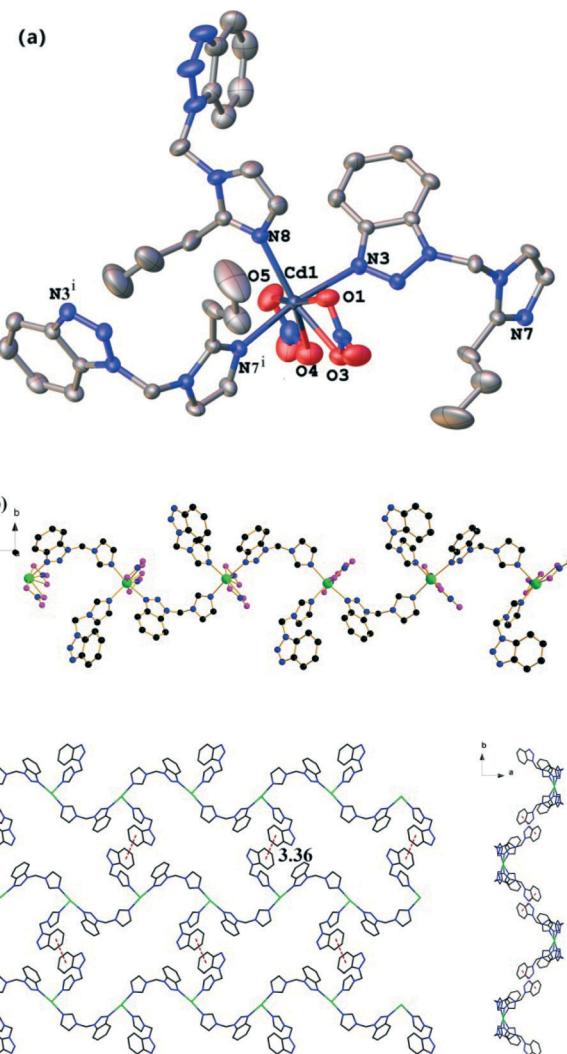
**Crystal structure of [Cd(bpmi)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub>(CH<sub>3</sub>OH)<sub>n</sub> (2).** Single crystal X-ray diffraction analysis reveals that **2** crystallizes in the monoclinic C $2/c$  space group, displaying a sinusoidal chain structure. As shown in Fig. 2a, the asymmetric unit of **2** contains one crystallographically unique Cd(II) ion, two bpmi ligands, two NO<sub>3</sub><sup>-</sup> anions and one solvent CH<sub>3</sub>OH molecule. The central Cd(II) displays a distorted pentagonal bipyramidal geometry, defined by four oxygen atoms (O1, O3, O4, O5) from two NO<sub>3</sub><sup>-</sup> with a chelating bidentate mode and one nitrogen atom (N8) from the bpmi ligand in the



**Fig. 1** (a) Perspective drawing of **1** showing the local coordination environment around Cd(II). (b) The 1D supramolecular chain along the *c* axis, consisting of SBUs [CdCl<sub>2</sub>] in **1**. Symmetry codes: (i) 1 - *x*, -*y*, -*z*; (ii) 1 - *x*, -*y*, 1 - *z*; (c) view down the *a* axis of the 2D supramolecular sheet built up through  $\pi\cdots\pi$  interactions between the neighboring supramolecular chains. All of the hydrogen atoms and propyl groups are omitted for clarity.

equatorial plane, and two nitrogen atoms [N<sub>3</sub>, N<sub>7</sub><sup>i</sup>; symmetry codes: (i) *x*, 2 - *y*, 0.5 + *z*] from two bridged bpmi ligands in the axial sites. To the best of our knowledge, such a feature of pentagonal bipyramidal geometry is rare in complexes containing a Cd atom.<sup>27</sup>

For the pentagonal bipyramidal geometry, the average Cd-N distance and Cd-O distance are 2.3 Å and 2.4 Å, respectively, which are in the normal ranges of those observed in



**Fig. 2** (a) A view of the asymmetric unit and some symmetry-related atoms in **2**. (b) The 1D sinusoidal chain constructed from SBUs [Cd(NO<sub>3</sub>)<sub>2</sub>] and bpmi ligands in **2**. (c) The 2D supramolecular layer built up through  $\pi\cdots\pi$  interactions between the neighboring sinusoidal chains on the *bc* plane in **2** and a view of the wave layer of **2** down the *c* direction. All of the hydrogen atoms and propyl groups are omitted for clarity.

reported Cd(II) complexes.<sup>28–32</sup> In **2**, the bpmi presents bridge- and mono-coordination modes. A bpmi ligand bridges two inorganic SBUs [Cd(NO<sub>3</sub>)<sub>2</sub>] with benzotriazole-N (N<sub>3</sub>) and imidazole-N (N<sub>7</sub><sup>i</sup>), which lead to a 1D sinusoidal chain along the *c* axis. Alternatively, one [Cd(NO<sub>3</sub>)<sub>2</sub>] connects the other one through a bpmi ligand to form a 1D chain (Fig. 2b). On the other hand, a bpmi ligand adopts a monodentate coordination mode with imidazole-N as the decoration of the 1D chain. In the chain, all Cd(II) ions are coplanar. The bridged Cd···Cd distance is about 9.07 Å. Adjacent chains stack together through  $\pi\cdots\pi$  interactions with shortest face to face distances of 3.36 Å to form a 2D supramolecular wave sheet on the *bc* plane (Fig. 2c).

**Structure of [Cd<sub>2</sub>(bpmi)<sub>2</sub>Cl<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]<sub>n</sub> (3).** Single crystal X-ray diffraction analysis reveals that **3** crystallizes in

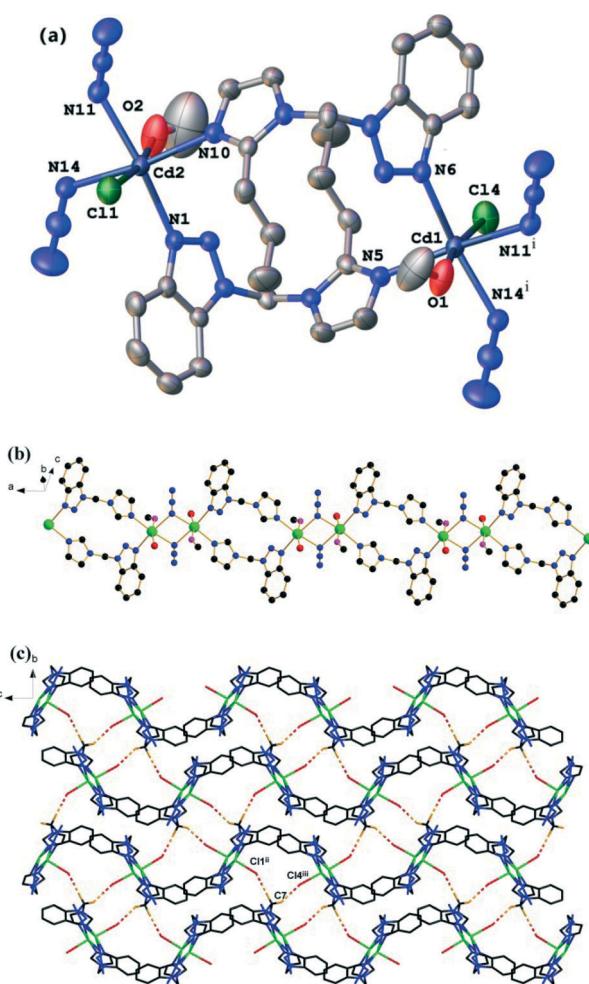
the monoclinic  $P2_1/c$  space group and displays a 1D chain structure. As shown in Fig. 3a, the asymmetric unit of 3 contains two crystallographically independent Cd(II) ions, two bpmi ligands, two  $\text{Cl}^-$  anions, two  $\text{N}_3^-$  anions, and two  $\text{CH}_3\text{OH}$  molecules. Both Cd1 and Cd2 atoms are in a slightly distorted octahedral coordination geometry, in which the equatorial plane is defined by four nitrogen atoms, {for Cd1 octahedron, N5, N6 from two bpmi ligands, and N11<sup>i</sup>, N14<sup>i</sup> [symmetry codes: (i)  $-1 + x, y, z$ ] from two  $\text{N}_3^-$  anions; for Cd2 octahedron, N1 and N10 from other two bpmi ligands and N11 and N14 from the same two  $\text{N}_3^-$  anions}. The apical sites are occupied by one chlorine atom (Cl4 for Cd1, Cl1 for Cd2) and one oxygen atom (O1 for Cd1, O2 for Cd2). The bond distances range: Cd(II)-N, from 2.2636(0) to 2.3933(0) Å; Cd(II)-O, from 2.4281(0) to 2.4607(0) Å and Cd(II)-Cl, from 2.5112(0) to 2.5586(0) Å. And bond angles around the central Cd(II) ion vary from 78.791(0) to 168.987(0) $^\circ$ , which are in agreement with other complexes containing Cd(II).<sup>33–37</sup> The

{Cd(1)OCIN<sub>4</sub>} octahedron and {Cd(2)OCIN<sub>4</sub>} octahedron share two N atoms (N11 and N14) from two  $\text{N}_3^-$  anions to form a binuclear unit containing an inorganic SBU [ $\text{CdCl}(\text{CH}_3\text{OH})(\text{N}_3^-)$ ]<sub>2</sub>, in which the Cd···Cd distance is 3.6381(0) Å. The adjacent inorganic SBUs are bridged by double bpmi ligands *via* head-to-tail interactions to form a 1D straight chain along the  $a$  axis. The Cd···Cd distance linked by bpmi ligands is 8.95931(1) Å (Fig. 3b).

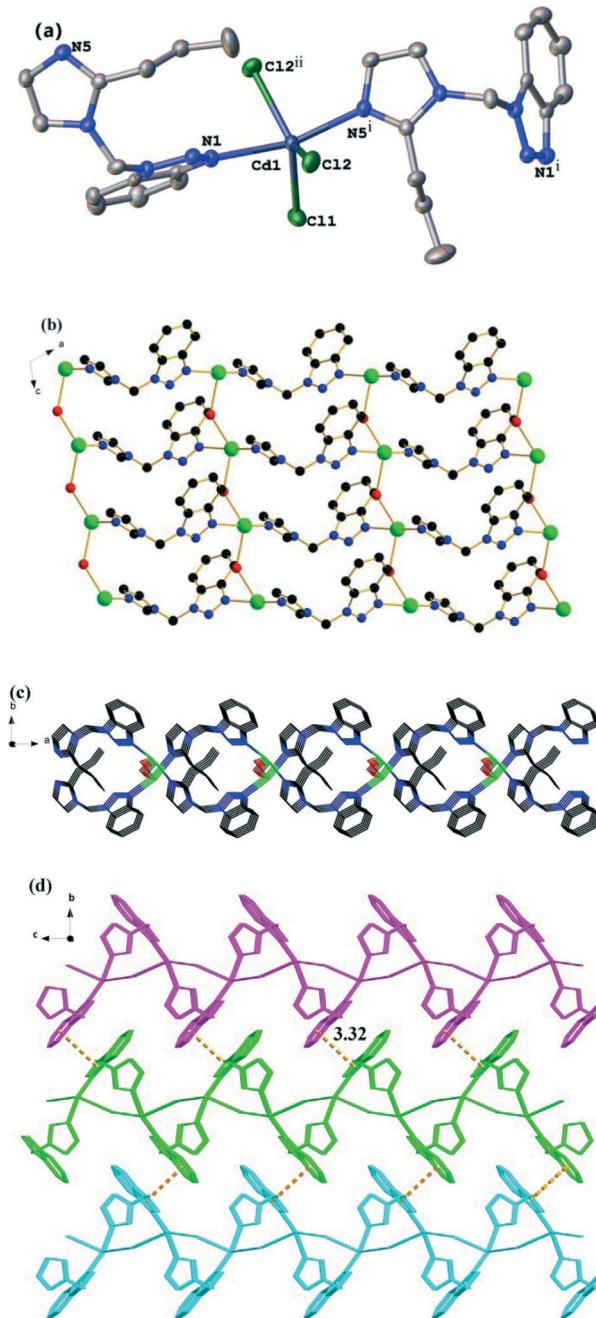
It is noteworthy that each 1D chain connects to three neighboring chains to form a 3D network structure *via* the C-H···Cl hydrogen bonds (Fig. 3c). In the hydrogen bonds, the C7 atoms of a bpmi ligands act as H-donors, and the chlorine atoms in the adjacent chain act as H-acceptors. As listed in Table S2,<sup>†</sup> the distances between donors and acceptors range from 3.4438(0) to 3.4951(0) Å. And the related bond angels are in the range of 142.175(1) $^\circ$  and 166.141(0) $^\circ$ .

**Structure of  $[\text{Cd}(\text{bpmi})\text{Cl}_2]_n$  (4).** Single crystal X-ray diffraction analysis reveals that complex 4 crystallizes in the monoclinic  $P2_1/c$  space group. The asymmetric unit of 4 contains one crystallographically unique Cd(II) ion, one bpmi ligand and two  $\text{Cl}^-$  anions. As shown in Fig. 4a, the Cd(II) ion is located in a slightly distorted  $\text{CdN}_2\text{Cl}_3$  trigonal bipyramidal coordination geometry completed by two N atoms from two bpmi ligands and three  $\text{Cl}^-$  anions, in which two N atoms (N1 and N5<sup>i</sup>) are located on the apexes position and three  $\text{Cl}^-$  anions (Cl1, Cl2 and Cl2<sup>ii</sup>) define the equatorial plane [symmetry codes: (i)  $1 + x, 1.5 - y, 0.5 + z$ ; (ii)  $x, 1.5 - y, -0.5 + z$ ]. The Cd-Cl2 and Cd-Cl2<sup>ii</sup> bonds are [2.5711(1) and 2.6146(1) Å, respectively] longer than the Cd-Cl1 bond (2.4751(1) Å). The Cd-N1 bond is 0.096 Å elongated in comparison with the Cd-N5<sup>i</sup> bond (Table S1<sup>†</sup>). The apexes bond angle N1-Cd-N5<sup>i</sup> is 164.951(1) $^\circ$ ; and the bond angles in the bipyramidal base lie in the range of 79.361(1)–128.796(1) $^\circ$ . There are two crystallographically independent  $\text{Cl}^-$  anions in the asymmetric unit of 4. The Cl2 atom serves as the bridge and connects the adjacent Cd atoms [Cd···Cd = 4.8031(2) Å] into a 1D infinite inorganic chain [-Cl-Cd-Cl-] along the  $c$  axis, the Cl-Cd-Cl bond angle is 128.786(1) $^\circ$  (Fig. 4b). The Cl1 atom is the second kind of Cl atom which acts as the monodentate ligand and decorates the sides of the 1D inorganic chain. The adjacent 1D inorganic chains as inorganic SBUs are bridged by bpmi ligands into a 2D sheet in the  $ac$  plane with large rhombic void spaces with dimensions of 4.8031(2)  $\times$  9.1857(6) Å. In the 2D sheet, the bpmi ligands are located on both sides of the sheet and form a 1D channel filled by the propyl groups of the bpmi ligands (Fig. 4c). From the topological point of view, each Cd(II) atom connects with four neighboring ones *via* two Cl atoms and two bpmi ligands to form a 2D 4-connected sheet structure with the Schläfli symbol (4<sup>4</sup>.6<sup>2</sup>).<sup>38</sup>

It is noteworthy that the planar benzotriazole rings of the bpmi ligands from neighboring sheets are almost parallel to each other, and the shortest distance between adjacent benzotriazole rings is 3.32 Å, indicating strong  $\pi \cdots \pi$  stacking interactions (Fig. 4d). Therefore, the 2D supramolecular sheets are arranged in an interesting 3D supramolecular network *via*  $\pi \cdots \pi$  stacking interactions.

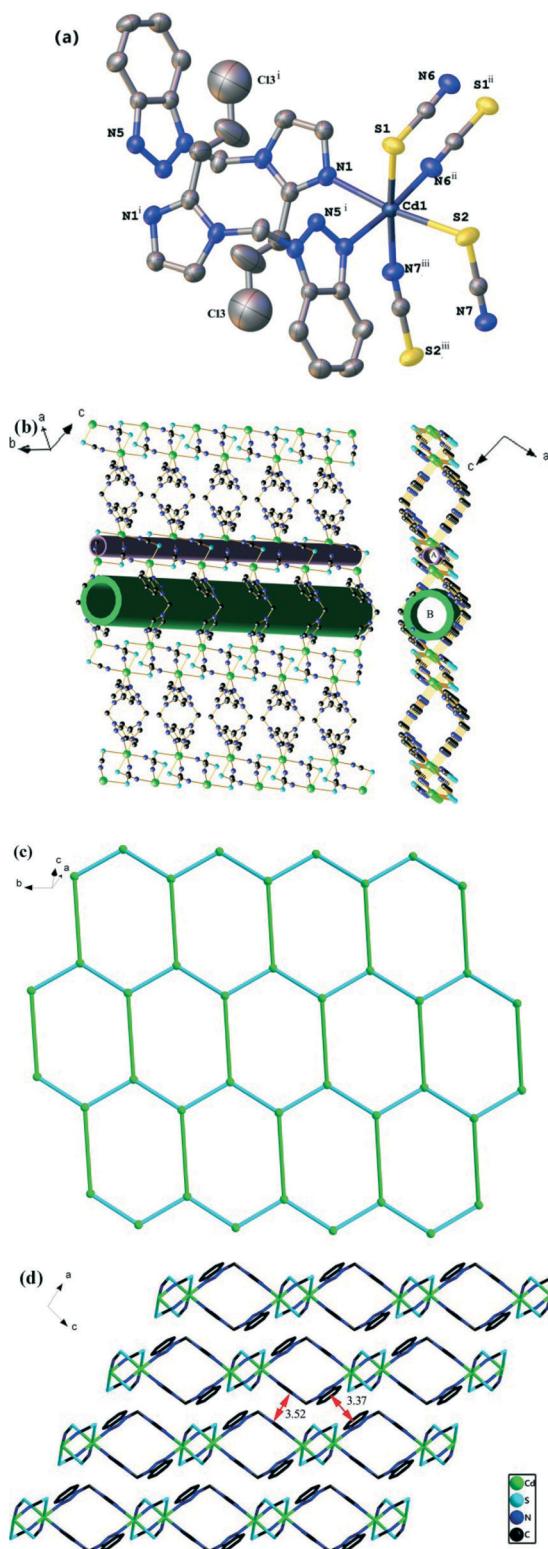


**Fig. 3** (a) A view of the asymmetric unit and some symmetry-related atoms in 3. Symmetry codes: (i)  $-1 + x, y, z$ . (b) The 1D chain is composed of binuclear SBUs  $[\text{Cd}(\text{N}_3^-)\text{Cl}_2]_2$  in 3. (c) View down the  $a$  axis, showing the 3D supramolecular structure built up *via* C-H···Cl hydrogen bondings. All of the hydrogen atoms and propyl groups are omitted for clarity.



**Fig. 4** (a) A view of the asymmetric unit and some symmetry-related atoms in **4**. [Symmetry codes: (i)  $1 + x$ ,  $1.5 - y$ ,  $0.5 + z$ ; (ii)  $x$ ,  $1.5 - y$ ,  $-0.5 + z$ .] (b) The 2D network containing SBUs  $[-\text{Cl}-\text{Cd}-\text{Cl}-]$  in the complex **4**. (c) A view of the 1D channel in the 2D sheet. (d) The 3D supramolecular network built up via  $\pi \cdots \pi$  stacking interactions of the benzotriazole rings. All of the hydrogen atoms and propyl groups and some of the chlorine atoms are omitted for clarity.

**Crystal structure of  $[\text{Cd}(\text{bpmi})(\text{SCN})_2]_n$  (5).** The X-ray crystallographic analysis shows that complex **5** is a 6-connected 2D network with a Schläfli symbol of  $(6^3)$ . It crystallizes in the triclinic system,  $P\bar{1}$  space group. The asymmetric unit contains one crystallographically independent  $\text{Cd}^{(II)}$  ion, one  $\text{bpmi}$  ligand and two  $\text{SCN}^-$  anions. As shown in Fig. 5a, each  $\text{Cd}^{(II)}$  ion is located in a distorted octahedral coordination

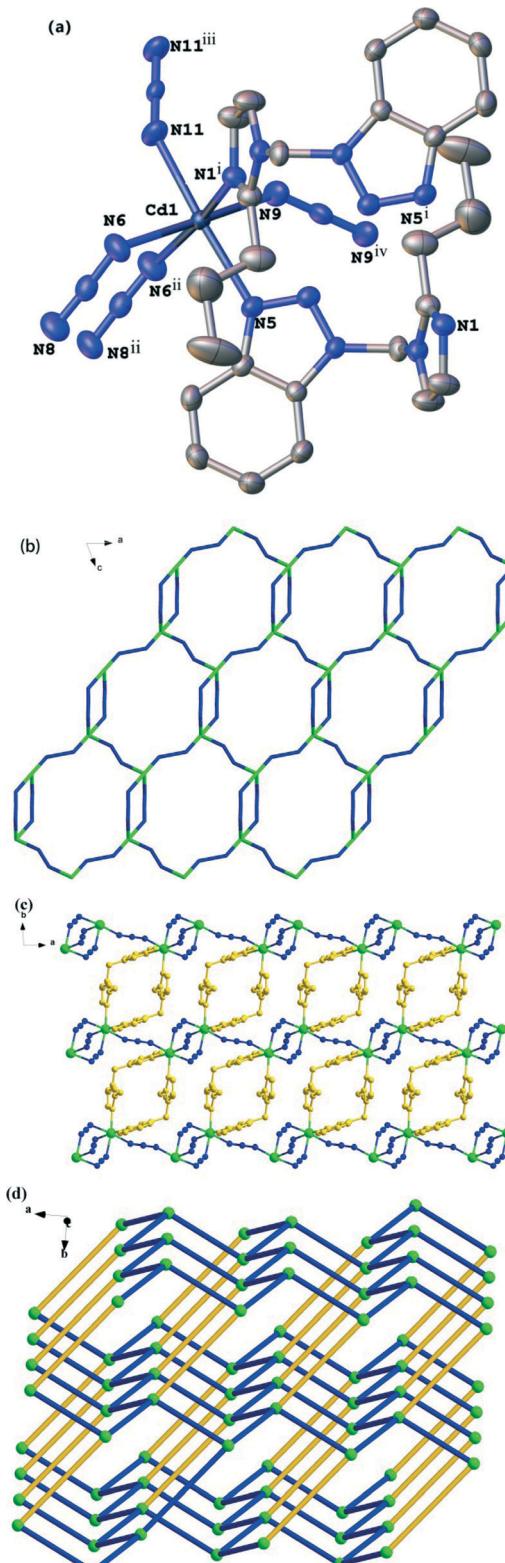


**Fig. 5** (a) A view of the asymmetric unit and some symmetry-related atoms in **5**. [Symmetry codes: (i)  $2 - x$ ,  $1 - y$ ,  $1 - z$ ; (ii)  $1 - x$ ,  $1 - y$ ,  $-z$ ; (iii)  $1 - x$ ,  $-y$ ,  $-z$ .] (b) A view of the 2D sheet containing inorganic SBUs  $[-\text{SCN}-\text{Cd}-\text{SCN}-]$  and A and B tunnels in complex **5** from two directions. (c) Schematic representation of the 6-connected 2D network with the Schläfli symbol of  $(6^3)$  of **5**. (d) The 3D supramolecular network built up via  $\pi \cdots \pi$  stacking interactions of imidazole rings and benzotriazole rings form neighboring sheets. All of the hydrogen atoms and propyl groups and some of the chlorine atoms are omitted for clarity.

environment, in which the equatorial plane is defined by three nitrogen atoms ( $N5^i$ ,  $N6^{ii}$ ,  $N7^{iii}$ ) and one sulfur atom (S1), and the axial sites are occupied by N1 and S2 [symmetry codes: (i)  $2 - x, 1 - y, 1 - z$ ; (ii)  $1 - x, 1 - y, -z$ ; (iii)  $1 - x, -y, -z$ ]. The Cd–N and Cd–S distances are located in the range of  $2.2804(1)$ – $2.3761(1)$  Å,  $2.7174(1)$ – $2.7863(1)$  Å, respectively. The adjacent Cd(II) atoms [ $Cd \cdots Cd = 5.8830(2)$  Å] are bridged together by two SCN<sup>−</sup> anions *via* head-to-tail interactions to form a 1D folding inorganic chain  $[-SCN-Cd-SCN-]$  along the *b* axis. Two bpmi ligands adopting bi-monodentate bridging mode coordinated to the Cd(II) atom belong to two neighboring inorganic chains and then extend the 1D inorganic chain into a 2D sheet structure on the  $(1\ 0\ -1)$  plane with a Cd–Cd distance of  $5.8830(2)$  Å. A feature of 5 is that there are two types of tunnels in 5. Tunnel A is formed by two Cd(II) atoms and two SCN<sup>−</sup> anions with dimensions of  $\approx 2.78 \times 5.03$  Å and is located inside the inorganic chain, however, tunnel B is located between two inorganic chains along the *b* axis and is formed by two Cd(II) atoms and two bpmi ligands with dimensions of  $\approx 5.89 \times 5.89$  Å (Fig. 5b). The second feature of 5 is that there is a hexagonal geometry built by six adjacent Cd(II) atoms, four bpmi ligands and eight SCN<sup>−</sup> anion in the 2D sheet. From the topological point of view, each Cd(II) center, being connected by four SCN<sup>−</sup> anions and two bpmi ligands, can be simplified as a six-connected node; each SCN<sup>−</sup> anion and bpmi ligand is simplified by a linear linker. Accordingly, the whole network can be extended to a 2D 6-connected sheet structure with the Schläfli symbol  $(6^3)$  (Fig. 5c).

As shown in Fig. 5d, those planar imidazole rings and benzotriazole rings of bpmi ligands from neighboring sheets are almost parallel to each other with a shortest distance of 3.52 Å and 3.37 Å, which indicate strong  $\pi \cdots \pi$  stacking interactions. Therefore, the 2D sheets are arranged in an interesting 3D supramolecular network *via*  $\pi \cdots \pi$  stacking interactions.

**Structure of  $[Cd(bpmi)(N_3)_2]_n$  (6).** The X-ray crystallographic study reveals that complex 6 crystallizes in the triclinic  $P\bar{1}$  space group and possesses 3D pillared frameworks with a diamond 3D topology. The asymmetric unit of 6 consists of one crystallographically independent Cd(II) ion, one bpmi ligand, two halves of the N<sub>3</sub><sup>−</sup> anions and one complete N<sub>3</sub><sup>−</sup> anion. As shown in Fig. 6a, the Cd1 is coordinated by six nitrogen atoms to form a distorted octahedral geometry, in which the equatorial plane comprises one nitrogen atom from bpmi ( $N1^i$ ) and three nitrogen atoms from three distinct N<sub>3</sub><sup>−</sup> molecules ( $N6$ ,  $N9$ ,  $N8^{ii}$ ). The apical sites are occupied by one nitrogen atom ( $N5$ ) from a bpmi molecule and one nitrogen atom ( $N11$ ) from a N<sub>3</sub><sup>−</sup> molecule [symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $-x, -y, 2 - z$ ; (iii)  $-x, -y, 1 - z$ ; (iv)  $1 - x, -y, 1 - z$ ]. The Cd(II)–N bond distances range from  $2.3175(3)$  to  $2.3784(3)$  Å and bond angles around the central Cd(II) ion vary from  $84.112(6)$  to  $174.685(7)$ °. Complex 6 possesses an unusual feature in the form of a 2D inorganic sheet structure with honeycomb caves on the *ac* plane which is built by the N<sub>3</sub><sup>−</sup> anions adopting a  $\eta^{1,3}$  coordination mode to bridge the adjacent Cd(II) atoms (Fig. 6b). The 2D inorganic layers  $[Cd_n(N_3)_2]_n$  as SBUs are further connected by



**Fig. 6** (a) A view of the asymmetric unit and some symmetry-related atoms in 6. [Symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $-x, -y, 2 - z$ ; (iii)  $-x, -y, 1 - z$ ; (iv)  $1 - x, -y, 1 - z$ .] (b) A view showing the 2D inorganic sheet structure with honeycomb caves in 6. (c) The 3D network built up *via* bpmi ligands double-pillaring the 2D inorganic sheet in 6. (d) Topological representation of the four-connected diamond net with the Schläfli symbol  $(6^3)$  of 6. All of the hydrogen atoms and propyl groups and some of the chlorine atoms are omitted for clarity.

a double-pillared bpmi ligand along the *b* axis to generate 3D porous frameworks. From the topological point of view, if each Cd(*II*) ion is considered as a four-connected node and bpmi ligands and N<sub>3</sub><sup>-</sup> anions are linkers, this framework can be simplified into a four-connected diamond net with short and long Schläfli symbols (6<sup>6</sup>) and (6<sub>2</sub>·6<sub>2</sub>·6<sub>2</sub>·6<sub>2</sub>·6<sub>2</sub>) (Fig. 6c).

### The role of counter anions

In this paper, complexes 2–6 have been prepared by the self-assembly of bpmi and a different Cd(*II*) salt in the same reaction conditions, so the difference in the resulting structures only depends on the effect of the counter anions. It is interesting that all of these complexes are constructed by the combination of inorganic SBUs and bpmi ligands. The results confirm the feasibility of the foregoing idea that using specially selected inorganic SBUs as structure-directing agents, the dimensionalities of the complexes can be tuned. In 2, the inorganic SBU is composed of one central Cd(*II*) ion and two counter anions NO<sub>3</sub><sup>-</sup>, namely [Cd(NO<sub>3</sub>)<sub>2</sub>]. Adjacent units are further linked to each other by bpmi to form a 1D sinusoidal chain structure. Complex 3 is also a 1D chain, but the SBUs are comprised of binuclear [CdCl(CH<sub>3</sub>OH)(N<sub>3</sub>)]<sub>2</sub>. The adjacent SBUs are bridged by two bpmi ligands *via* head-to-tail interactions to form a 1D straight chain along the *a* axis. In terms of the 2D sheet structures 4 and 5, the inorganic SBUs are no longer simple small molecules, but one-dimensional chain, [-Cl-Cd-Cl-] for 4 and [-SCN-Cd-SCN-] for 5. Then the bpmi ligands serve as bis-monodentate ligands and bridge adjacent 1D inorganic chains into 2D sheet structures. As the most characteristic 3D structure, the inorganic SBU [Cd(N<sub>3</sub>)<sub>2</sub>]<sub>n</sub> of 6 is a 2D inorganic sheet structure with honeycomb caves on the *ac* plane which is built by the N<sub>3</sub><sup>-</sup> anions adopting a η<sup>1,3</sup> coordination mode to bridge the adjacent Cd(*II*) atoms. The 2D inorganic layers are further connected by double-pillared bpmi ligand along the *b* axis to generate 3D porous frameworks. Though it is difficult to predict or rationalize the formation of each structure, some rules about the structures can be determined from the results of the present study. It can be observed that the coordination environment of the Cd(*II*) center and the coordination mode of bpmi differ depending on the selection of counter ions of different natures, which directly result in the diverse structures of 2–6.

Firstly, as mentioned above, the central Cd(*II*) ion possesses diverse coordination geometries. When NO<sub>3</sub><sup>-</sup> is used as the counter anion in 2, Cd(*II*) exhibits a distorted pentagonal bipyramidal geometry; the introduction of Cl<sup>-</sup> and N<sub>3</sub><sup>-</sup> in 3, SCN<sup>-</sup> in 5 and N<sub>3</sub><sup>-</sup> in 6 lead to distorted octahedral coordination geometries of Cd(*II*); while the use of Cl<sup>-</sup> for its own results in a trigonal bipyramidal coordination geometry of Cd(*II*) in 4. We think that the difference in the coordination environment of the central Cd(*II*) ions may depend on the size and coordination mode of the counter anions. It is well-known that the introduction of a linker adopting the chelating coordination mode is capable of “passivating” metal sites and may induce lower-dimensional complexes.<sup>39</sup> In complex 2,

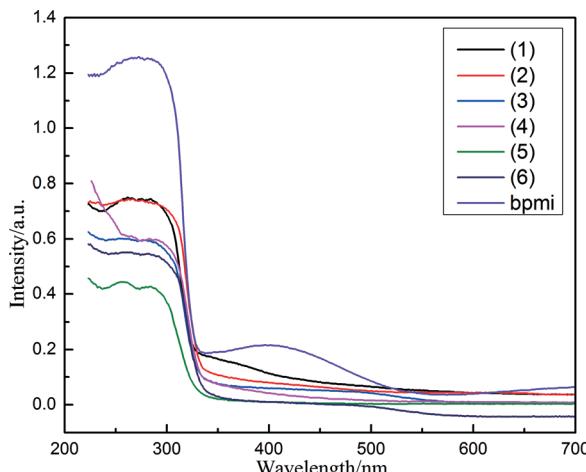
the counter anion NO<sub>3</sub><sup>-</sup> with larger steric hindrance adopts a chelating mode, which makes it extend in only one direction. So 2 reveals a 1D chain structure, though Cd(*II*) has a high coordination number. Compared with NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SCN<sup>-</sup>, and N<sub>3</sub><sup>-</sup> with a small steric hindrance are more likely to adopt the bridging coordination mode. So these anions are favorable for forming structures with a higher dimension, 2-D for 4 and 5 and 3-D for 6. Especially, the N<sub>3</sub><sup>-</sup> anions adopting the η<sup>1,3</sup> mode show a strong coordination ability to form novel inorganic sheets [Cd(N<sub>3</sub>)<sub>2</sub>]<sub>n</sub> in 6. Surprisingly, 3 containing N<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>, is a 1D chain structure. In 3, the N<sub>3</sub><sup>-</sup> is coordinated to Cd(*II*) ions in the μ<sub>2</sub> mode, and Cl<sup>-</sup> is coordinated to the Cd(*II*) ion as a monodentate ligand. The formation of the low dimensional structure of 3 can be contributed to the competition and compromise between the two anions (N<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>) in the system, though both of them have a strong coordination ability.

Second, with regard to the bpmi ligand, there are two coordination modes in 2–6. For 2, one bpmi acting as the monodentate is coordinated with a Cd(*II*) by the *N*-imidazole group, the other bpmi as the bidentate bridges the two Cd(*II*) *via* the *N*-imidazole and *N*-benzotriazole groups. But in the other four complexes 3–6, all of the bpmi ligands play a bidentate role. The results can also be explained by the size and space steric of the counter anions. Though both imidazole and benzotriazole groups have a strong bridging ability, the bigger benzotriazole group is hardly coordinated with Cd(*II*) due to the existence of a NO<sub>3</sub><sup>-</sup> chelate with a larger steric hindrance in 2. *Vice versa*, if the smaller counter anions with strong coordination ability exist in the system, the bpmi ligand will be a bidentate ligand, which further extends the simple structure to a higher dimensional network.

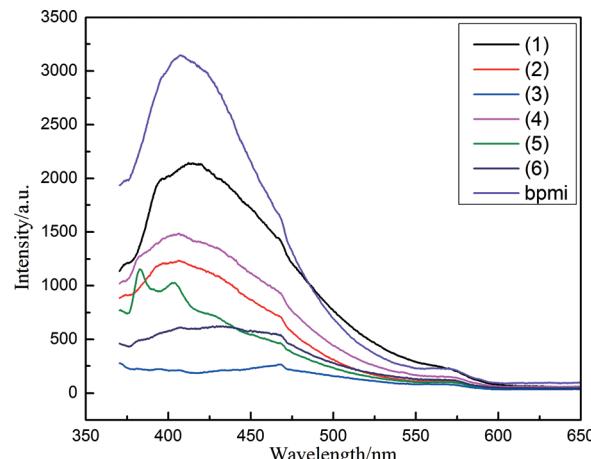
To sum up, the coordination environment of the Cd(*II*) center and the coordination mode of the ligand are surely dependent on the size and coordination tendency of the counter anions, which lead to complexes of diverse dimension and complexity.

### UV-Vis spectrums of bpmi and complexes

The UV-vis spectra of complexes 1–6 are shown in Fig. 7. The bpmi ligand exhibits two absorption bands in the UV region of the spectrum. The peak located in 274 nm is attributed to electron transitions of intra-ligand π-π\*. Then the weak peak at 406 nm is the result of intra-ligand n-π\* charge-transfer. Compared with the bpmi ligand, the absorbance of the complexes is weaker. Complexes 1–6 show the main absorption band around 277 nm, at 277 nm, 284 nm, 261 nm, 260 nm, 252 nm and 268 nm, respectively. These absorption bands, may be ascribed to the intra-ligand π\* → π transition. Obviously, there is no peak at 406 nm in complexes 1–6. This phenomenon proves that coordination between the metal ions and ligands changed the distribution of the electrons in the ligand molecules.



**Fig. 7** The UV-vis spectra for complexes 1–6 and bpmi.



**Fig. 8** The emission spectra for the complexes and free bpmi ligand.

## Thermogravimetric analyses of complexes

To characterize the complexes more fully in terms of thermal stability, their thermal behaviors were studied by TGA (Fig. S2†). Complex 1 starts to decompose from 225 °C as no solvent molecules exist in the lattice. Complex 2 breaks down at a lower temperature due to the existence of guest molecules. In the TGA curve of 2, the first step weight loss of 2.42% from 134 to 146 °C, corresponds to the loss of uncoordinated CH<sub>3</sub>OH molecules (calcd. 2.43%), which is followed by the decomposition of the organic ligand and N<sub>3</sub><sup>−</sup> anions. For complex 3, an initial weight loss at 198 °C corresponds to the disintegration of coordinated CH<sub>3</sub>OH. Then the organic ligand and inorganic anions start to decompose until 624 °C. Complex 4 is stable up to 187 °C, and the collapse of the organic ligand and SCN<sup>−</sup> anions continues from 187 to 646 °C. Complex 5 and complex 6 break down almost at the same time, 188 °C and 189 °C, respectively. For all six complexes, the remaining weight corresponds to the percentage of the Cd and O components, indicating that the final product is CdO. (Obsd. 19.26%, calcd. 19.28% for 1; obsd. 17.38%, calcd. 17.39% for 2; obsd. 27.70%, calcd. 27.72% for 3; obsd. 30.22%, calcd. 30.24% for 4; obsd. 27.31%, calcd. 27.33% for 5; obsd. 29.42%, calcd. 29.43% for 6).

## Photoluminescent properties of complexes

The luminescence properties of the complexes and free ligand have been investigated in the solid state at room temperature (Fig. 8). It can be seen that the emission band of the free ligand is at 407 nm upon excitation of 350 nm. The complexes 1, 2 and 4 exhibit a similar main emission band at 415 nm, 405 nm and 406 nm with the appropriate excitation wavelength, respectively. These emission bands, the same shape of spectrum as free ligand, may originate from intra-

ligand π\* → π transition. For complex 5, except the characteristic band of intra-ligand π\* → π transition at 402 nm, the band situated at 382 nm may be the result of charge-transfer LMCT. Differently, complex 3 and 6 don't exhibit any significant luminescence behavior. In addition, the fluorescence intensity of the six complexes are weaker than the free ligand, this may be due to the different coordination modes and different strength of force.

## Powder XRD patterns of complexes

The results of the powder XRD patterns of the complexes have been investigated in the solid state at room temperature (Fig. S3†). The simulative powder diffraction pattern was based on crystal structure analysis. The peak positions simulated from the single-crystal X-ray data of complexes are in good agreement with those observed. A comparison of the experimental and simulated powder diffraction patterns confirms that the complex structures are solved accurately and the products are single phase.

## Conclusions

In summary, by the reactions of an asymmetric multidentate ligand bpmi and Cd(II) salts with different counter anions Cl<sup>−</sup>, NO<sub>3</sub><sup>−</sup>, SCN<sup>−</sup> and N<sub>3</sub><sup>−</sup>, six novel complexes are successfully obtained. All these complexes not only contain discrete or infinite inorganic secondary building units (SBUs), but also indicate rich structural chemistry ranging from discrete 0D molecular architectures to infinite 1D, 2D, and 3D. The resulting structures prove that the counter anions can orient themselves in different geometries to facilitate the formation of distinctly different structures. Therefore, the counter anions can be used as structure-directing agents to control and tune the dimensionalities of the resulting frameworks.

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