CrystEngComm

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/crystengcomm

Journal Name

RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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

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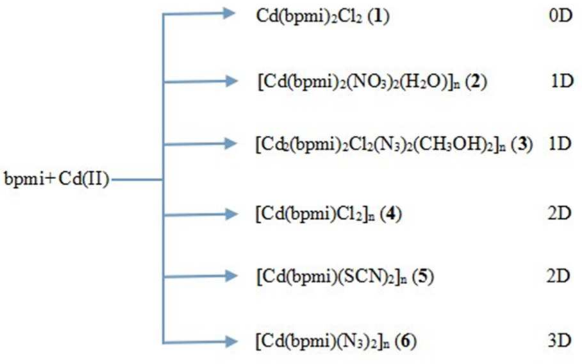
Six new Cd(II) complexes, $Cd(bpmi)_2Cl_2$ (**1**), $[Cd(bpmi)_2(NO_3)_2(CH_3OH)]_n$ (**2**), $[Cd_2(bpmi)_2Cl_2(N_3)_2(CH_3OH)_2]_n$ (**3**), $[Cd(bpmi)Cl_2]_n$ (**4**), $[Cd(bpmi)(SCN)_2]_n$ (**5**) and $[Cd(bpmi)(N_3)_2]_n$ (**6**) are synthesized by the reaction of Cd(II) salts with the asymmetric multi-dentate ligand 1-(benzotriazole-1-methyl)-2-propylimidazole (bpmi). X-ray single-crystal analyses reveal that these complexes show rich structural chemistry ranging from zero-dimensional (**1**), one-dimensional (**2** and **3**), two-dimensional (**4** and **5**) to three-dimensional (**6**) structures. These complexes share common features that all of them contain inorganic SBUs and have 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 fluorescent spectra.

Introduction

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

Anions, besides organic ligands and metal centers, are important components in a metal–organic coordination complex. Anions are 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, the anions are the excellent candidate as the auxiliary ligands to coordinate to the metal centers, which tune the coordination numbers and geometry of metal centers, hence manipulating the physical-chemical properties of those compounds. For example, Dunbar and co-workers recently reported an anion-directed assembly of Ni(II) and Zn(II) metallacyclophanes with ligand 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine as a bridging ligand; tetrahedral BF_4^- and ClO_4^- ions direct the formation of molecular squares, $[\{M_4(bptz)_4(CH_3CN)_8\}X][X]_7$ (M = Zn(II), Ni(II); X = BF_4^-, ClO_4^-), whereas octahedral SbF_6^- induces the formation of pentagonal $[\{Ni_5(bptz)_5(CH_3CN)_{10}\}SbF_6][SbF_6]_9$.[15] Richard A. Jones and co-workers reported that in heterotrinuclear and heterodinuclear Zn-Ln (Ln = Eu and Tb) Schiff-base complexes, anions ($CF_3SO_3^-$ versus NO_3^-) played dominant roles in inducing the structures by operating the stoichiometry and then significantly regulated the intense luminescence emission.[16] Meanwhile, our group have reported Cu(II) coordination complexes containing SO_4^{2-}, NO_3^-, Cl^-, ClO_4^-, N_3^- and 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 structure differences of these complexes. Generally, the inorganic counter anions tune the coordination complexes assemblies in two ways in the synthetic process. One way is in the system using a negative ligand (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.[17-18] Another way is in the system using neutral ligand (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,[19-22] it still remains a considerable challenge to systematic research the role of counter anions in guiding the coordination assemblies in 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 Cd(II) center in the presence of different counter anions with the strong coordination capacity, such as Cl^-, NO_3^-, SCN^-, N_3^-. Six novel complexes have been prepared successfully, $Cd(bpmi)_2Cl_2$ (**1**), $[Cd(bpmi)_2(NO_3)_2(CH_3OH)]_n$ (**2**), $[Cd_2(bpmi)_2Cl_2(N_3)_2(CH_3OH)_2]_n$ (**3**), $[Cd(bpmi)Cl_2]_n$ (**4**), $[Cd(bpmi)(SCN)_2]_n$ (**5**), $[Cd(bpmi)(N_3)_2]_n$ (**6**) (Scheme 1). It is noted that in the synthesis process of **1**, we use pure CH_3OH system. Considering the variation polarity of the solvent can influence the structures of coordination complexes, we replace pure CH_3OH system as CH_3OH/H_2O system in synthesis process of **2**-**6**. In other words, in synthesis process of **2**-**6**, all reaction factors such as the temperature, the solvent and ratio of starting materials are the same except the types of counter anions, in order to grasp the key role of the anion in the self-assembly process. These complexes display a common feature that all of them contain inorganic SBUs. Complex **1** is a mononuclear structure containing $[Cd(NO_3)_2]$. Complex **2** is a one dimensional (1D) sinusoidal chain composed of SBU $[Cd(NO_3)_2]$, and **3** is a 1D chain comprised of binuclear $[CdCl(CH_3OH)(N_3)]_2$. However, compared to the mononuclear inorganic SBU in **2** and dinuclear inorganic SBU in **3**, the inorganic SBUs in **4** and **5** are 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 counter anions on dominating the diverse structures of **1–6** has been illustrated and their thermal stabilities and fluorescence properties have also been investigated.



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

Experimental

General Details

All analytical grade chemicals and solvents were purchased commercially and 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^{-1} region. UV–Vis spectra were obtained using UV–2600 spectrophotometer, $BaSO_4$ powders were used as 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^{-1}. The luminescent 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 (λ = 1.54184 Å) and focusing multilayer mirror optics with a small pellets.

Caution! Sodium azide is potentially explosive and should be handled with great care.

Synthesis of $Cd(bpmi)_2Cl_2$ (**1**)

A mixture of bpmi (0.0039 g, 0.02 mmol), and $CdCl_2{\cdot}2.5H_2O$ (0.0046 g, 0.02 mmol) were 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. Crystals were collected by mechanical isolation and washed with MeOH (3×10 ml) then dried at 40 ºC (Yield: 57%). Calcd. For $C_{26}H_{30}CdCl_2N_{10}$: C, 46.90; H, 4.54; N, 21.03. Found: C, 46.87; H, 4.52; N, 21.01. IR (cm^{-1}, KBr): 3114 m, 2956 m, 1588 w, 967 w, 746 s, 428 w.

Synthesis of $[Cd(bpmi)_2(NO_3)_2(CH_3OH)]_n$ (**2**)

A mixture of bpmi (0.0039 g, 0.02 mmol), and $Cd(NO_3)_2{\cdot}4H_2O$ (0.0062 g, 0.02 mmol) were 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. Crystals were collected by mechanical isolation and washed with water (3×10 ml) and MeOH (3×10 ml), then dried at 40 ºC (Yield: 78%). Calcd. For $C_{27}H_{34}CdN_{12}O_7$: 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 (cm^{-1}, KBr): 3114 m, 2956 m, 2058 w, 1588 w, 1436 m, 935 w, 428 w.

Synthesis of $[Cd_2(bpmi)_2Cl_2(N_3)_2(CH_3OH)_2]_n$ (**3**)

A mixture of bpmi (0.0039 g, 0.02 mmol), $CdCl_2{\cdot}2.5H_2O$ (0.0046 g, 0.02 mmol), and NaN_3 (0.0013 g, 0.02 mmol) were 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. Crystals were collected by mechanical isolation and washed with MeOH (3×10 ml) then dried at 40 ºC (Yield: 74%). Calcd. For $C_{28}H_{38}Cd_2Cl_2N_{16}O_2$: 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 (cm^{-1}, KBr): 3114 m, 2964m, 2868 m, 2082s, 858 w, 546 w, 412 w.

Synthesis of [Cd(bpmi)Cl_2]$_n$ (**4**)

Complex **4** was prepared under conditions similar to those of **2** with $CdCl_2·2.5H_2O$ (0.0046 g, 0.02 mmol) instead of $Cd(NO_3)_2·4H_2O$. Colourless block crystals for X–ray diffraction were formed a few days later. Crystals were collected by mechanical isolation and washed with water (3×10 ml) and MeOH (3×10 ml), then dried at 40 ºC (Yield: 64%). Calcd. For $C_{13}H_{15}CdCl_2N_5$: C, 36.77; H, 3.56; N, 16.49. Found: C, 36.75; H, 3.54; N, 16.46. IR (cm^{-1}, KBr): 3106 m, 2956 m, 2058 w, 1596 w, 927 w, 658 w.

Synthesis of [Cd(bpmi)$(SCN)_2$]$_n$ (**5**)

Similar to the synthesis of complex **3**, KSCN (0.0019 g, 0.02 mmol) instead of NaN_3 gave colourless block crystals of **5**. Crystals were collected by mechanical isolation and washed with water (3×10 ml) and MeOH (3×10 ml), then dried at 40 ºC (Yield: 72%). Calcd. For $C_{15}H_{15}CdN_7S_2$: C, 38.34; H, 3.22; N, 20.87. Found: C, 38.33; H, 3.21; N, 20.89. IR (cm^{-1}, KBr): 3122 m, 2956 m, 2090 s, 1372 w, 850 w, 460 w.

Synthesis of [Cd(bpmi)$(N_3)_2$]$_n$ (**6**)

Complex **6** was prepared under conditions similar to those of **3** with $Cd(NO_3)_2·4H_2O$ (0.0062 g, 0.02 mmol) instead of $CdCl_2·2.5H_2O$. Pink block crystals for X–ray diffraction were formed a few days later. Crystals were collected by mechanical isolation and washed with water (3×10 ml) and MeOH (3×10 ml), then dried at 40 ºC (Yield: 67%). Calcd. For $C_{13}H_{15}CdN_{11}$: C, 35.67; H, 3.45; N, 35.20. Found: C, 35.66; H, 3.47; N, 35.23. IR (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-Kα, λ = 1.54184 Å for **1**, **3-6** and Mo-Kα, λ = 0.71073 Å for **2**) micro focus source and focusing multilayer mirror optics. The data were collected at a temperature of 293(2) K and processed using CrysAlis^{Pro}.[23] The structures were solved and refined using Full–matrix least–squares based on F^2 with program SHELXS–97 and SHELXL–97.[24] 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 bpmi ligand, which is observed in the terminal group of organic molecules. Specifically, C(25) and C(26) occupied over two positions in the bmpi molecule [C(25) and C(26) with SOF = 0.54, C(8A) and C(26A) with SOF = 0.46]. In order to maintain normalized internal bond distances and angles for bmpi 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 rations of the maximum and minimum displacement parameters for the solvent methanol in **2** and 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**

Table 1 Crystallographic data for **1-6**

Empirical formula	$C_{26}H_{30}CdCl_2N_{10}$ (**1**)	$C_{27}H_{34}CdN_{12}O_7$ (**2**)	$C_{28}H_{38}Cd_2Cl_2N_{16}O_2$ (**3**)	$C_{13}H_{15}CdCl_2N_5$ (**4**)	$C_{15}H_{15}CdN_7S_2$ (**5**)	$C_{13}H_{15}CdN_{11}$ (**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* -1	*C* 2/*c*	*P* 2_1/*c*	*P* 2_1/*c*	*P* -1	*P* -1
a / Å	9.5360(3)	26.5918(9)	12.4688(1)	9.3734(5)	9.4788(4)	9.5550(1)
b / Å	12.7918(5)	13.5595(5)	15.9995(1)	18.5736(5)	10.2419(5)	9.8491(1)
c / Å	13.7773(5)	18.1128(6)	19.4700(2)	9.2232(3)	10.5173(2)	9.8850(9)
α (°)	73.510(8)	90	90	90	95.716(3)	72.948(10)
β (°)	80.939(7)	94.582(3)	103.058(5)	107.887(5)	99.798(3)	68.962(9)
γ (°)	68.353(9)	90	90	90	109.484(4)	86.711(1)
V / Å^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_c / Mg cm^{-3}	1.480	1.533	1.626	1.846	1.669	1.754
μ /mm^{-1}	7.773	0.734	10.719	14.665	11.553	10.757
F(000)	676	3072	1856	840	468	436
Reflections collected	14574	5952	15797	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^{ab} indices [I>2σ(I)]	$R_1 = 0.0296$, $wR_2 = 0.0765$	$R_1 = 0.0483$, $wR_2 = 0.1063$	$R_1 = 0.0280$, $wR_2 = 0.0760$	$R_1 = 0.027$, $wR_2 = 0.0725$	$R_1 = 0.0351$, $wR_2 = 0.0959$	$R_1 = 0.0232$, $wR_2 = 0.0584$
R indices (all data)	$R_1 = 0.0334$, $wR_2 = 0.0793$	$R_1 = 0.0688$, $wR_2 = 0.1193$	$R_1 = 0.0305$, $wR_2 = 0.0783$	$R_1 = 0.0321$, $wR_2 = 0.0761$	$R_1 = 0.0364$, $wR_2 = 0.0977$	$R_1 = 0.0249$, $wR_2 = 0.0594$

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

Results and discussion

Synthesis

Recently, the control of topology and geometry of the complexes has become one of the research highlights in coordination chemistry. However, due to the complexity and difficult prediction of the resulting composition or structure, the influential principles in self-assembly systems are still less ascertained and not conclusive. For the neutral ligand, the different of 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 inorganic SBUs can be used as a structure-directing agent in such a reaction process and various dimensional (0D-3D) architectures. Therefore, in order to further investigate the role of inorganic anions on regulating the resultant coordination assemblies, we should design the reaction condition in which ligand, metal center and solvent etc. can be fixed successfully, namely all factors for the coordination structures are consistent except the counter anions.

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

We first selected metal salt $CdCl_2$ as the SBU, a discrete structure $Cd(bpmi)_2Cl_2$ (**1**) with Cl^- as charge compensation anions was obtained in pure CH_3OH solvent. The Cl^- anion coordinated to the metal centers in monodentate mode. Considering the variation polarity of the solvent can influence the structures of coordination complexes, we replace pure CH_3OH system as CH_3OH/H_2O system, which makes subsequent experiments can be conducted. Four kinds of counter anions with different size and coordination tendency are selected, Cl^-, NO_3^-, SCN^- and N_3^-, to observe their regulations on the assembly of complexes. The refined regulation of counter anions allowed the main ligand bpmi to bend and rotate when coordinated to metal centers. Hence, as we have expected, one–dimension $[Cd(bpmi)_2(NO_3)_2(CH_3OH)]_n$ (**2**) and $[Cd_2(bpmi)_2Cl_2(N_3)_2(CH_3OH)_2]_n$ (**3**), two–dimension $[Cd(bpmi)Cl_2]_n$ (**4**) and $[Cd(bpmi)(SCN)_2]_n$ (**5**) to three–dimensional structures of $[Cd(bpmi)(N_3)_2]_n$ (**6**) are obtained successfully. 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 synthetic process of coordination complexes.

Description of the structures

Structure of $Cd(bpmi)_2Cl_2$ (1)

Single crystal X–ray diffraction analysis reveals that complex **1** crystallizes in the triclinic space group *P*–1. The asymmetric unit contains one crystallographically unique Cd(II) ion, two bpmi ligands, and two Cl^- 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^- anions (Cl1 and Cl2). Among them, two Cl^- anions and one Cd(II) cation, namely $[CdCl_2]$, composes inorganic SBU. In the tetrahedron, the distances of Cd–N [2.2198(2) – 2.2320(3) Å] and Cd–Cl [2.3991(3) – 2.4303(2) Å] are in the normal ranges of those observed in reported Cd(II) complexes, and bond angels around in the central Cd(II) ion vary from 99.435(5)° to 119.744(6)°.[25-26] 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. (Fig. S1) As shown in Fig. 1b, one pair of the C–H···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 *c* axis. In the chain, the bridged Cd···Cd distance varies from 6.8977(6) Å to 7.0023(5) Å. 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) Å, which demonstrates weak π···π stacking interaction. Thus, 2D supramolecular sheet structure is formed *via* the π···π stacking interactions between the bmpi units from adjacent chains. Both hydrogen bonding (Table S2) and π···π stacking interactions (Fig. 1c) play important roles for stabilizing the 2D sheet structure.

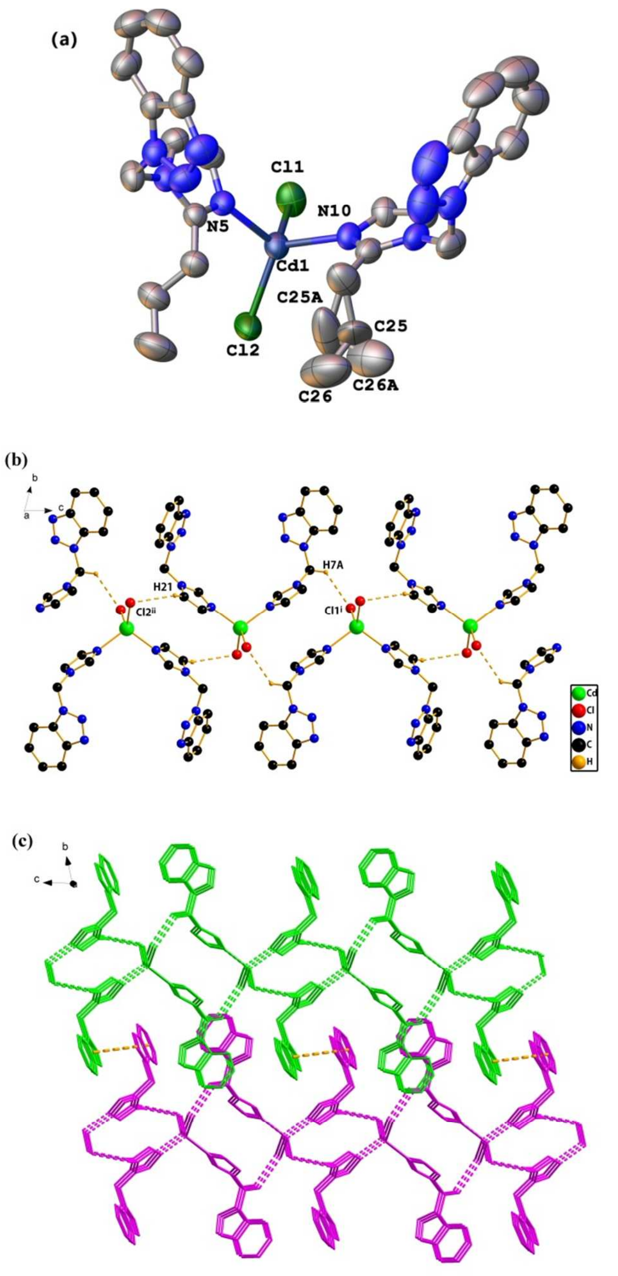
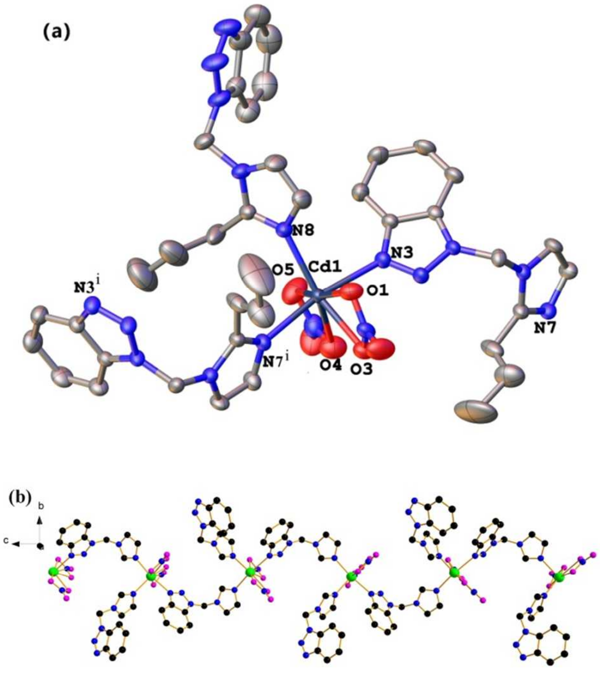


Fig. 1. (a) Perspective drawing of **1** showing the local coordination environment around Cd(II). (b) The 1D supramolecular chain along the *c* axis, consisting of SBUs [CdCl$_2$] in **1**. Symmetry codes: (i) 1–x, –y, –z; (ii) 1–x, –y, 1–z; (c) View down the *a* axis of the 2D supramolecular sheet built up through π···π interactions between the neighbor supramolecular chains. All hydrogen atoms and propyl groups are omitted for clarity.

Crystal structure of [Cd(bpmi)$_2$(NO$_3$)$_2$]$_n$(CH$_3$OH)$_n$ (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$_3^-$ anions and one solvent CH$_3$OH molecule. The central Cd(II) displays a distorted pentagonal bipyramidal geometry, defined by four oxygen atoms (O1, O3, O4, O5) from two NO$_3^-$ with chelating bidentate mode and one nitrogen atom (N8) from the bpmi ligand in the equatorial plane, and two nitrogen atoms [N3, N7$^{\mathrm{i}}$; 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 Cd atom.[27]

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 reported Cd(II) complexes.[28-32] In **2**, the bpmi presents bridge- and mono- coordination modes. A bmpi ligand bridges two inorganic SBU [Cd(NO$_3$)$_2$] with benzotriazole–N (N3) and imidazole–N (N7$^{\mathrm{i}}$), which lead to a 1D sinusoidal chain along *c* axis. Alternatively, one [Cd(NO$_3$)$_2$] connects the other one through a bpmi ligand to form a 1D chain (Fig. 2b). In the other hand, a bpmi ligand adopts monodentate coordination mode with imidazole–N as the decorations 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 π···π interactions with the shortest face to face distances of 3.36 Å to form a 2D supramolecular wave sheet on the *bc* plane (Fig. 2c).



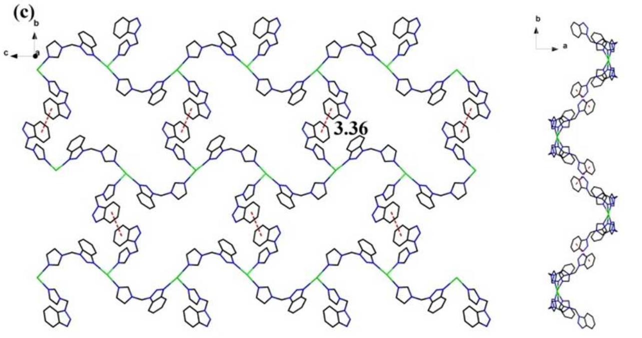


Fig. 2. (a) A view of the asymmetric unit and some symmetry–related atoms in **2**. (Symmetry codes: (i) x, 2–y, 0.5+z). (b) The 1D sinusoidal chain constructed from SBUs [Cd(NO_3)$_2$] and bpmi ligands in **2**. (c) The 2D supramolecular layer built up through π···π interactions between the neighbor sinusoidal chains on the *bc* plane in **2** and a view of the wave layer of **2** down the *c* direction. All hydrogen atoms and propyl groups are omitted for clarity.

Structure of [$Cd_2(bpmi)_2Cl_2(N_3)_2(CH_3OH)_2$]$_n$ (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 Cl^- anions, two N_3^- anions, and two CH_3OH 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^i, N14^i [Symmetry codes: (i) -1+x, y, z] from two N_3^- anions; for Cd2 octahedron, N1 and N10 from other two bpmi ligands and N11 and N14 from the same two 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)°, which are in agreement with other complexes containing Cd(II).[33-37] The {Cd(1)OClN$_4$} octahedron and {Cd(2)OClN$_4$} octahedron share two N atoms (N11 and N14) from two N_3^- anions to form a binuclear unit containing an inorganic SBU [CdCl(CH_3OH)(N_3)]$_2$, 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 *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 with neighboring three ones to form a 3D network structure *via* the C–H···Cl hydrogen bonds (Fig. 3c). In the hydrogen bonds, C7 atom of a bpmi ligand act as H–donors, and chlorine atoms in the adjacent chain act as H–acceptors. As listed in the **Table S2**, the distances between donors and acceptors range from 3.4438(0) to 3.4951(0) Å. And the related bond angles locate in the scope of 142.175(1)° and 166.141(0)°.

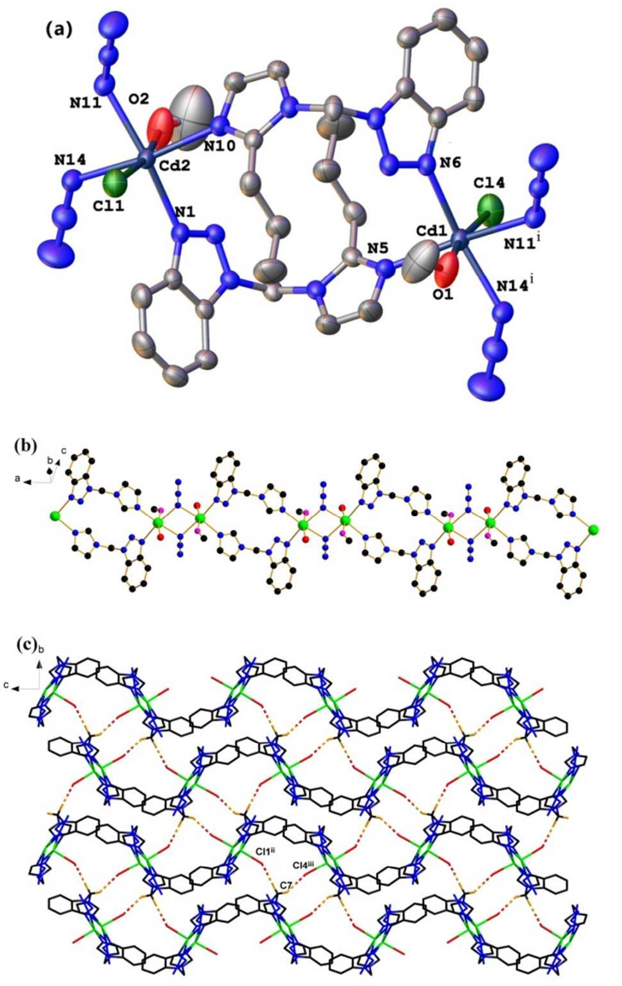
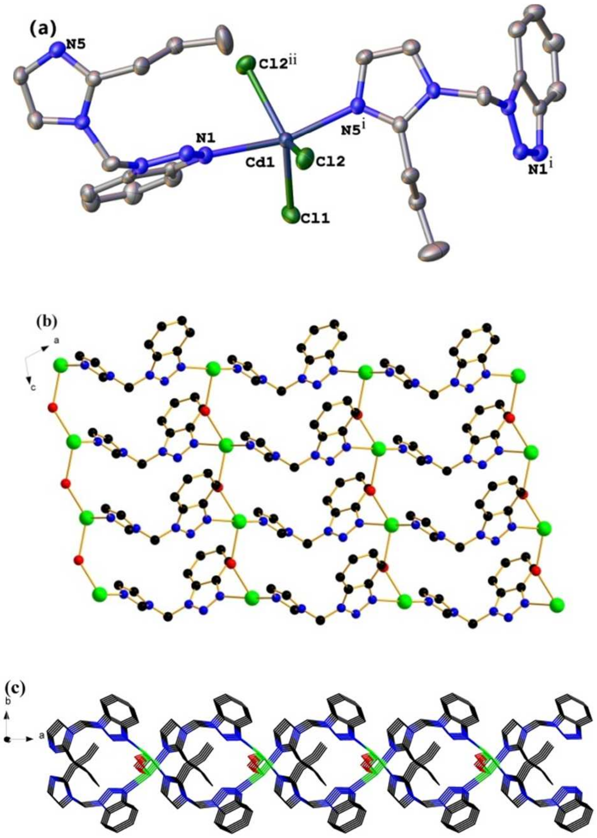


Fig. 3. (a) A view of the asymmetric unit and some symmetry–related atoms in **3** . Symmetry codes: (i) -1+x, y, z. (b) The 1D chain is composed of binuclear SBUs [Cd(N_3)Cl]$_2$ in **3**. (c) View down the *a* axis, showing the 3D supramolecular structure built up *via* C-H···Cl hydrogen bondings. All hydrogen atoms and propyl groups are omitted for clarity.

Structure of [$Cd(bpmi)Cl_2$]$_n$ (4)

Single crystal X–ray diffraction analysis reveals the 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 Cl^- anions. As shown in Fig. 4a, the Cd(II) ion is located in a slightly distorted CdN_2Cl_3 trigonal bipyramid coordination geometry completed by two N atoms from two bpmi ligands and three Cl^- anions, in which two N atoms (N1 and N5^i) locate on the apexes position and three Cl^- anions (Cl1, Cl2 and Cl2^{ii}) 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^{ii} 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 bond Cd–N5^i (**Table S1**). The apexes bond angle N1–Cd–N5^i is 164.951(1)°; and the bond angles in the bipyramid base lie in the range of 79.361(1)–128.796(1)°. There are two crystallographically independent Cl^- anions in the asymmetric unit of **4**. Cl2 atom serves as the bridge and connect the adjacent Cd atoms [Cd···Cd = 4.8031(2) Å] into 1D infinite inorganic chain [-Cl-Cd-Cl-] along the *c* axis, the Cl–Cd–Cl bond angle is 128.786(1)º (Fig. 4b). Cl1 atom is the second kind of Cl atom which acts as the monodentate ligand and decorates on the sides of 1D inorganic chain. The adjacent 1D inorganic chains as inorganic SBUs are bridged by bpmi ligands into 2D sheet in the *ac* plan with large rhombic void spaces with dimensions of 4.8031(2) × 9.1857(6) Å. In the 2D sheet, the bpmi ligands locate on both sides of the sheet and form a 1D channel filled by the propyl groups of bpmi ligands (Fig. 4c). From the topological point of view, each Cd(II) atom connects with four neighbor ones *via* two Cl atoms and two bpmi ligands to form a 2D 4–connected sheet structure with the Schläfli symbol $(4^4{\cdot}6^2)$.[38]

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



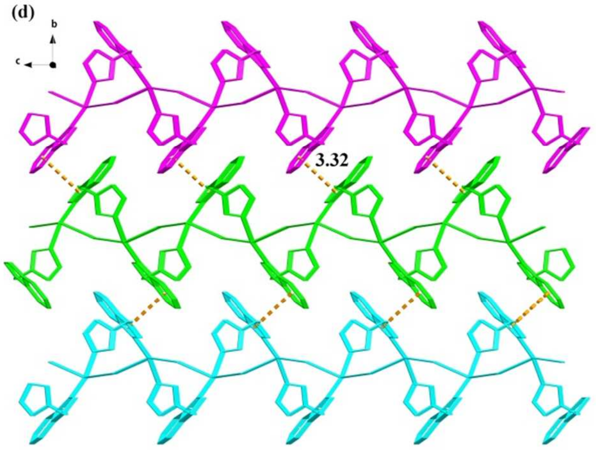


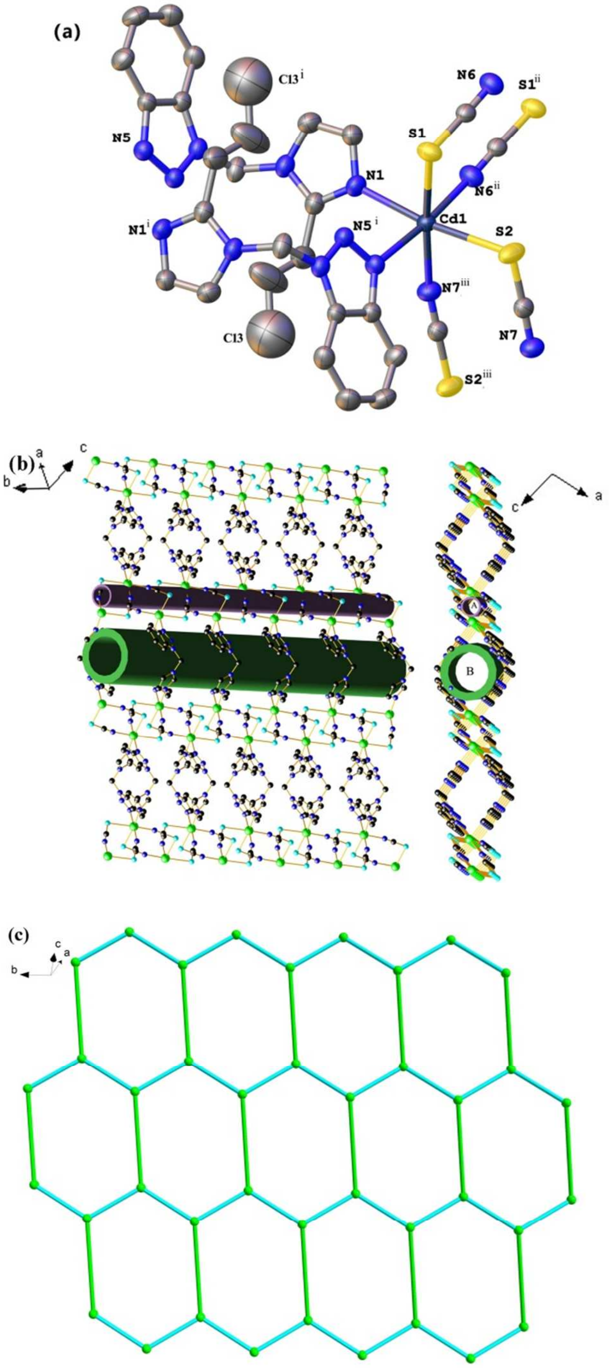
Fig. 4. (a) A view of the asymmetric unit and some symmetry–related atoms in **4.** [Symmetry codes: (i) 1+x, 1.5–y, 0.5+z; (ii) x, 1.5–y, –0.5+z.] (b) The 2D network containing SBUs [-Cl-Cd-Cl-] in the complex **4**. (c) A view of 1D channel in the 2D sheet. (d) The 3D supramolecular network built up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

Crystal structure of $[Cd(bpmi)(SCN)_2]_n$ (5)

The X–ray crystallographic analysis shows that complex **5** is a 6–connected 2D network with the Schläfli symbol of (6^3). It crystallizes in the triclinic system, *P*–1 space group. The asymmetric unit contains one crystallographically independent Cd(II) ion, one bpmi ligand and two $SCN^–$ anions. As shown in Fig. 5a, each Cd(II) ion is located in a distorted octahedral coordination 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···Cd = 5.8830(2) Å] are bridged together by two $SCN^–$ 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 coordinate to Cd(II) atom belonging to two neighbor inorganic chains and then extend the 1D inorganic chain into a 2D sheet structure on the (1 0 –1) plane with 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 $SCN^–$ anions with dimensions of ≈ 2.78 × 5.03 Å and is located inside the inorganic chain, however, tunnel B is located between two inorganic chains along the *b* axis and formed by two Cd(II) atoms and two bpmi ligands with dimensions of ≈ 5.89 × 5.89 Å (Fig. 5b). The second feature of **5** is that there are a hexagonal geometry built by six adjacent Cd(II) atoms, four bpmi ligands and eight $SCN^–$ anion in the 2D sheet. From the topological point of view, each Cd(II) center, being connected by four $SCN^–$ anions and two bpmi ligands, can be simplified as a six–connected node; each $SCN^–$ 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 neighbor sheets are almost parallel to each other with the shortest distance of 3.52 Å and 3.37Å, which indicate strong $\pi\cdots\pi$ stacking interactions. Therefore, the 2D sheets are arranged in interesting 3D supramolecular network *via* $\pi\cdots\pi$ stacking interactions.



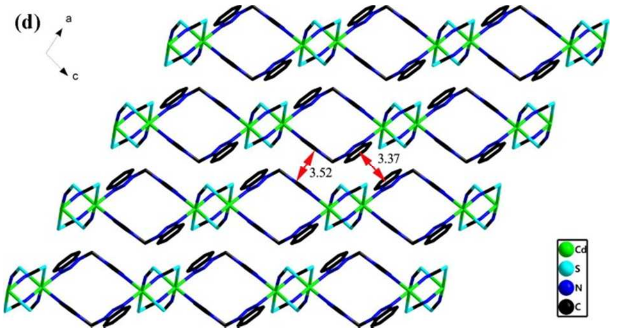
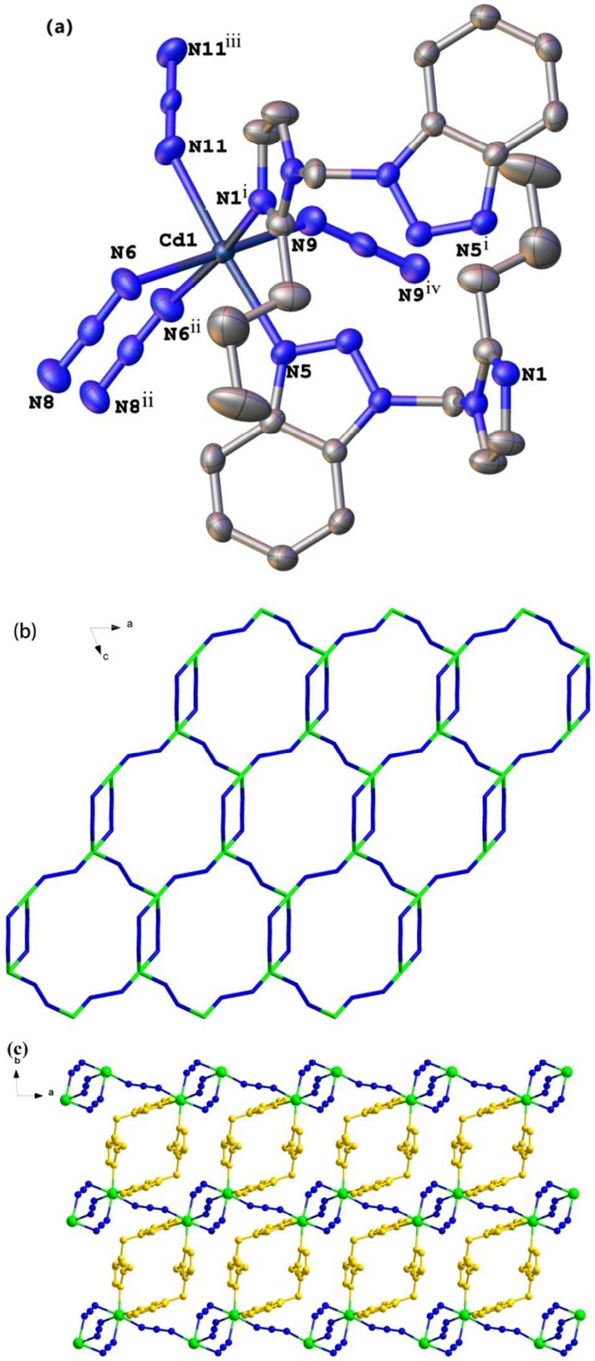


Fig. 5. (a) A view of the asymmetric unit and some symmetry–related atoms in **5.** [Symmetry codes: (i) 2–x, 1–y, 1–z; (ii) 1–x, 1–y, –z; (iii) 1–x, –y, –z.]. (b) A view of the 2D sheet containing inorganic SBUs [-SCN-Cd-SCN-] and A and B tunnels in the complex **5** from two directions. (c) Scheatic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

Structure of $[Cd(bpmi)(N_3)_2]_n$ (6)

The X–ray crystallographic study reveals that complex **6** crystallizes in the triclinic *P*–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 N_3^- anions and one complete N_3^- 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 ones from three distinct N_3^- molecules (N6, N9, N8^{ii}), and the apical sites are occupied by one nitrogen atom (N5) from bpmi molecule and one nitrogen atom (N11) from N_3^- molecule [Symmetry codes: (i) 1–x,1–y, 1–z; (ii) –x, –y, 2–z]. The Cd(II)–N bond distances range from 2.3175(3) to 2.3784(3) Å and bond angels around the central Cd(II) ion vary from 84.112(6) to 174.685(7)°. An unusual feature of complex **6** possesses a 2D inorganic sheet structure with honeycomb caves on *ac* plan which is built by the N_3^- anions adopting $\eta^{1,3}$ coordination mode to bridge the adjacent Cd(II) atoms (Fig. 6b). The 2D inorganic layers $[Cd_n(N_3)_{2n}]$ as SBUs are further connected by 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_3^- anions are linkers, this framework can be simplified into a four–connected diamond net with short and long Schläfli symbols 6^6 and $(6_2\cdot6_2\cdot6_2\cdot6_2\cdot6_2\cdot6_2)$ (Fig. 6c).



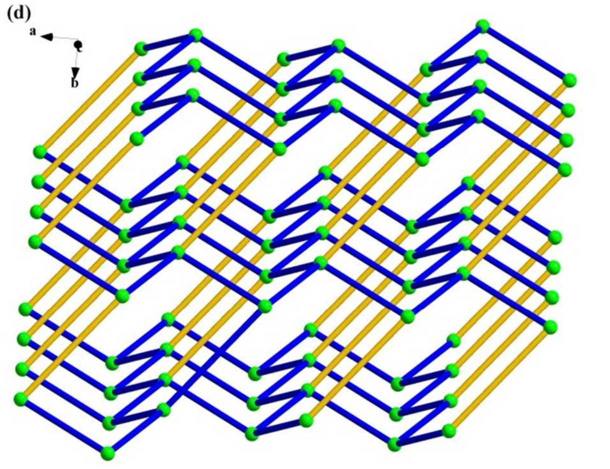


Fig. 6. (a) A view of the asymmetric unit and some symmetry–related atoms in **6**. [Symmetry codes: (i) 1–x, 1–y, 1–z; (ii) –x, –y, 2–z; (iii) –x, –y, 1–z; (iv) 1–x, –y, 1–z.]. (b) A view showing the 2D inorganic sheet structure with honeycomb caves in **6**. (c) The 3D network built up *via* bpmi ligands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

The role of counter anions

In this paper, complexes **2**-**6** have been prepared by the self-assembly of bpmi and different Cd(II) salt in the same reaction conditions, so the difference of resulting structures only depend on the effect of the counter anions. It is interesting that all these complexes are constructed by the combination of inorganic SBUs and bpmi ligand. The results confirm the feasibility of the foregoing idea using specially selected inorganic SBUs as structure-directing agents to tune the dimensionalities of the complexes. In **2**, inorganic SBU is composed of one center Cd(II) ion and two counter anions NO_3^-, namely $[Cd(NO_3)_2]$. Adjacent units are further linked each other by main ligand bpmi to form a 1D sinusoidal chain structure. Complex **3** is also a 1D chain, but the SBUs are comprised of binuclear $[CdCl(CH_3OH)(N_3)]_2$. 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 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 $[Cd(N_3)_2]_n$ of **6** is a 2D inorganic sheet structure with honeycomb caves on the *ac* plan which is built by the N_3^- anions adopting $\eta^{1,3}$ 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 Cd(II) center and the coordination mode of bpmi show obvious difference due to the selection of the counter anions with different nature, which directly result in the diverse structures of **2**-**6**.

Firstly, as mentioned ahead, center Cd(II) possesses diverse coordination geometries. When NO_3^- is used as counter anions in **2**, Cd(II) exhibits a distorted pentagonal bipyramidal geometry; the introduction of Cl^- and N_3^- in **3**, SCN^- in **5** and N_3^- in **6** lead to the distorted octahedral coordination geometries of Cd(II); while the use of Cl^- for its own results in a trigonal bipyramid coordination geometry of Cd(II) in **4**. We think that the difference in the coordination environment of central Cd(II) ions may depend on the size and coordination mode of counter anions. It is well-known that the introduction of linker adopting the chelating coordination mode is capable of "passivating" metal sites and may induce lower-dimensional complexes.[39] In complex **2**, the counter anion NO_3^- with larger steric hindrance adopts a chelating mode, which makes it extend in only one direction. So **2** reveals a structure of 1D chain, though Cd(II) has high coordination number. Compared with NO_3^-, Cl^-, SCN^- and N_3^- with small steric hindrance are more favor to adopt the bridging coordination mode. So these anions are favorable for forming the structures with higher dimension, 2-D **4** and **5** and 3-D **6**. Especially, the N_3^- anions adopting the $\eta^{1,3}$ mode show strong coordination ability to form a novel inorganic sheets $[Cd(N_3)_2]_n$ in **6**. Surprisingly, **3** containing N_3^- and Cl^- is a 1D chain structure. In **3**, the N_3^- is coordinated to Cd(II) ions in the mode of μ_2, and Cl^- is coordinated to Cd(II) ion as a monodentate. The formation of low dimensional structure **3** can be contributed to competition and compromise of two anions (N_3^- and Cl^-) in the system, though both of them have strong coordination ability.

Second, about the bpmi ligand, there are two coordination modes in **2**-**6**. For **2**, one bpmi as the monodentate is coordinated with a Cd(II) by 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 the bpmi ligands play a role of bidentate. The results can also be explained by the size and space steric of counter anions. Though both imidazole and benzotriazole groups have the strong bridging ability, the bigger benzotriazole group is hardly coordinated with Cd(II) due to the existence of chelate NO_3^- with 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 Cd(II) center and the coordination mode of ligand are surely dependent on the size and coordination tendency of 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 ligand bpmi 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 bpmi ligand, the absorbance of the complexes is weaker. The 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 intra-ligand π*→π transition. Obviously, there is no peak at 406 nm in complexes **1**–**6**. This phenomenon proves that coordination between metal ions and ligands changed the distribution of the electrons in the ligand molecules.

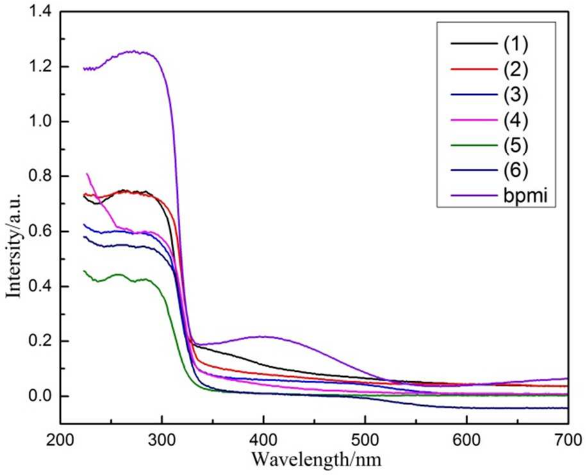


Fig. 7. The UV–Vis spectrums for complexes **1** - **6** and bpmi.

Thermogravimetric analyses of complexes

To characterize the complexes more fully in terms of thermal stability, their thermal behaviors were studied by the TGA (Fig. S2). Complex **1** starts to decompose from 225 °C in according with that no solvent molecules exist in the lattice. Complex **2** breaks down at lower temperature due to 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_3OH molecules (Calcd. 2.43%), which is followed by the decomposition of organic ligand and N_3^- anions. For complex **3**, an initial weight loss at 198 °C stand for the disintegration of coordinated CH_3OH. Then the organic ligand and inorganic anions part starts to eliminate until 624 °C. Complex **4** are stable up to 187 °C, and the collapse of the organic ligand and SCN^- anions is continuing 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 of 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 luminescent properties of complexes and free ligand have been investigated in the solid state at room temperature (Fig. 9). It can be seen that the emission band of free ligand is at 407 nm upon excitation of 350 nm. The complexes **1**, **2** and **4** exhibit the 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 intraligand π*→π transition. To complex **5**, except the characteristics band of intraligand π*→π transition at 402 nm, the band situated in 382 nm may be the result of charge–transfer LMCT. Differently, complex **3** and **6** don't exhibit any significant luminescent behavior. In addition, 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.

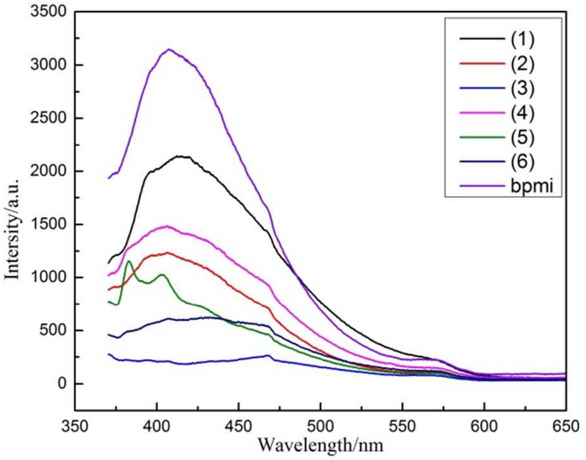


Fig. 9. The emission spectra for complexes and free bpmi ligand.

Powder XRD patterns of complexes

The results powder XRD patterns of 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 singlephase.

Conclusions

In summary, by the reactions of an asymmetric multidentate ligand bpmi and Cd(II) salts with different counter anions Cl^-, NO_3^-, SCN^- and N_3^-, 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 geometry 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.

Acknowledgements

We gratefully acknowledge the financial support by the National Natural Science Foundation of China (No. 51108122), Youth Foundation of Shanxi Province (No. 2010021022–1).

Notes and references

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† Electronic Supplementary Information (ESI) available:Additional figures and tables. CCDC reference numbers: 992031 (**1**), 992038 (**2**), 992035 (**3**), 992036 (**4**), 992034 (**5**), 992037 (**6**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

[1] S. Kitagawa, R. Kitaura, S.-i. Noro, *Angew. Chem. Int. Ed.,* 2004, **43**, 2334-2375.

[2] A. Hori, S. Takatani, T.K. Miyamoto, M. Hasegawa, *CrystEngComm*, 2009, **11**, 567-569.

[3] M. Du, C.-P. Li, C.-S. Liu, S.-M. Fang, *Coord. Chem. Rev.*, 2013, **257**, 1282-1305.

[4] D. Bradshaw, J.B. Claridge, E.J. Cussen, T.J. Prior, M.J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273-282.

[5] M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.*, 2005, **38**, 369-378.

[6] T. Osuga, T. Murase, K. Ono, Y. Yamauchi, M. Fujita, *J. Am. Chem. Soc.*, 2010, **132**, 15553-15555.

[7] X. Wang, X. Shen, Y.-J. Zhang, F. Su, G. Liu, Y. Xu, D.-R. Zhu, *Inorg. Chem. Commun.*, 2013, 35, 45-49.

[8] O.M. Yaghi, M. O'Keeffe, M. Kanatzidis, *J. Solid State Chem.*, 2000, **152**, 1-2.

[9] C.N.R. Rao, S. Natarajan, R. Vaidhyanathan, Angew. *Chem. Int. Ed.*, 2004, **43**, 1466-1496.

[10] X. Liu, H. Wang, B. Lavina, B. Tu, W. Wang, Z. Fu, *Inorg. Chem.*, 2014, **53**, 5986-5992.

[11] P. Thuery, *Eur. J. Inorg. Chem.*, 2013, **2013**, 4563-4573.

[12] P.P. Zhang, J. Peng, H.J. Pang, Y.A. Chen, M. Zhu, D.D. Wang, M.G. Liu, Y.H. Wang, *Solid State Sci.*, 2010, **12**, 1585-1592.

[13] Y.Z. Voloshin, A.S. Belov, Z.A. Starikova, A.V. Vologzhanina, *Russ. Chem. Bull.*, 2014, **62**, 1858-1865.

[14] A.J. Swarts, S.F. Mapolie, *Dalton Trans*., 2014, **43**, 9892-9900.

[15] C.S. Campos-Fernández, B.L. Schottel, H.T. Chifotides, J.K. Bera, J. Bacsa, J.M. Koomen, D.H. Russell, K.R. Dunbar, *J. Am. Chem. Soc.* , 2005, **127**, 12909-12923.

[16] X. Yang, D. Schipper, A. Liao, J.M. Stanley, R.A. Jones, B.J. Holliday, *Polyhedron*, 2013, **52**, 165-169.

[17] B. Hu, Q.-Q. Liu, T. Tao, K. Zhang, J. Geng, W. Huang, *Inorg. Chim. Acta* 2013, **394**, 576-582.

[18] C.-H. Jiang, Y.-M. Qi, Y. Sun, Q. Chi, Y.-M. Guo, *J. Mol. Struct.*, 2012, **1017**, 65-71.

[19] M.J. Hannon, C.L. Painting, E.A. Plummer, L.J. Childs, N.W. Alcock, *Chem.–Eur. J.*, 2002, **8**, 2225-2238.

[20] J.R. Price, Y.H. Lan, G.B. Jameson, S. Brooker, *Dalton Trans.*, 2006, 1491-1494.

[21] Z. Zheng, C.B. Knobler, M.F. Hawthorne, *J. Am. Chem. Soc.*, 1995, **117**, 5105-5113.

[22] A.R. Paital, M. Mikuriya, D. Ray, *Eur. J. Inorg. Chem.*, 2007, **2007**, 5360-5368.

[23] CrysAlis^{Pro} Version 1.171.35.19. Agilent Technologies Inc. Santa Clara, CA, USA (**2011**).

[24] Sheldrick, G. M. SHELXTL–97: Program for Refining Crystal Structure Refinement, University of Götingen, Germany (**1997**).

[25] B. Chand, U. Ray, G. Mostafa, T.-H. Lu, C. Sinha, *Polyhedron*, 2004, **23**, 1669-1676.

[26] S. Hu, P. Zhang, F.-Y. Yu, D.-R. Lin, M.-X. Chen, *J. Mol. Struct.*, 2013, **1051**, 72-77.

[27] X.-Y. Yu, X.-B. Cui, X. Zhang, L. Jin, Y.-N. Luo, J.-J. Yang, H. Zhang, X. Zhao, *Inorg. Chem. Commun.* , 2011, **14**, 848-851.

[28] B.-M. Kukovec, C.L. Oliver, *Polyhedron*, 2012, **34**, 46-55.

[29] S.K. Dey, S. Shit, R. Sankolli, T.N.G. Row, *J. Mol. Struct.*, 2013, **1048**, 6-10.

[30] H.-J. Cheng, R.-X. Yuan, C.-N. Lu, J.-P. Lang, *Inorg. Chem. Commun.*, 2014, **40**, 138-142.

[31] J.A. Wilson, P.E. Kraft, R.L. LaDuca, *Inorg. Chim. Acta*, 2013, **404**, 97-104.

[32] L.-F. Liu, B. Cai, C.-S. He, J.-Z. Wu, Q.-M. Wang, Y. Yu, *Inorg. Chem. Commun.*, 2013, **30**, 105-110.

[33] H.-W. Kuai, X.-C. Cheng, X.-H. Zhu, *Polyhedron*, 2013, **53**, 113-121.

[34] Y. Feng, D.-B. Wang, B. Wan, X.-H. Li, Q. Shi, *Inorg. Chim. Acta* 2014, **413**, 187-193.

[35] J. Xie, Z. Han, W. Pei, Y. Zou, X. Ren, *Inorg. Chem. Commun.*, 2011, **14**, 1266-1270.

[36] J.-C. Dai, X.-T. Wu, Z.-Y. Fu, C.-P. Cui, S.-M. Hu, W.-X. Du, L.-M. Wu, H.-H. Zhang, R.-Q. Sun, *Inorg. Chem.*, 2002, **41**, 1391-1396.

[37] C. Wang, T. Wang, L. Li, B. Guo, Y. Zhang, Z. Xiong, G. Li, *Dalton Trans.*, 2013, **42**, 1715-1725.

[38]V. A. Blatov, A. P. Shevchenko, TOPOS 4.0; Samara State University, Russia, 2008;

[39] J.-J. Jiang, S.-R. Zheng, Y. Liu, M. Pan, W. Wang, C.-Y. Su, *Inorg. Chem.*, 2008, **47**, 10692-10699.

Graphical contents entry

Anion–dependent assemblies of a series of Cd(II) coordination complexes based on an asymmetric multidentate ligand and inorganic SBUs: Syntheses, crystal structures, and fluorescent properties

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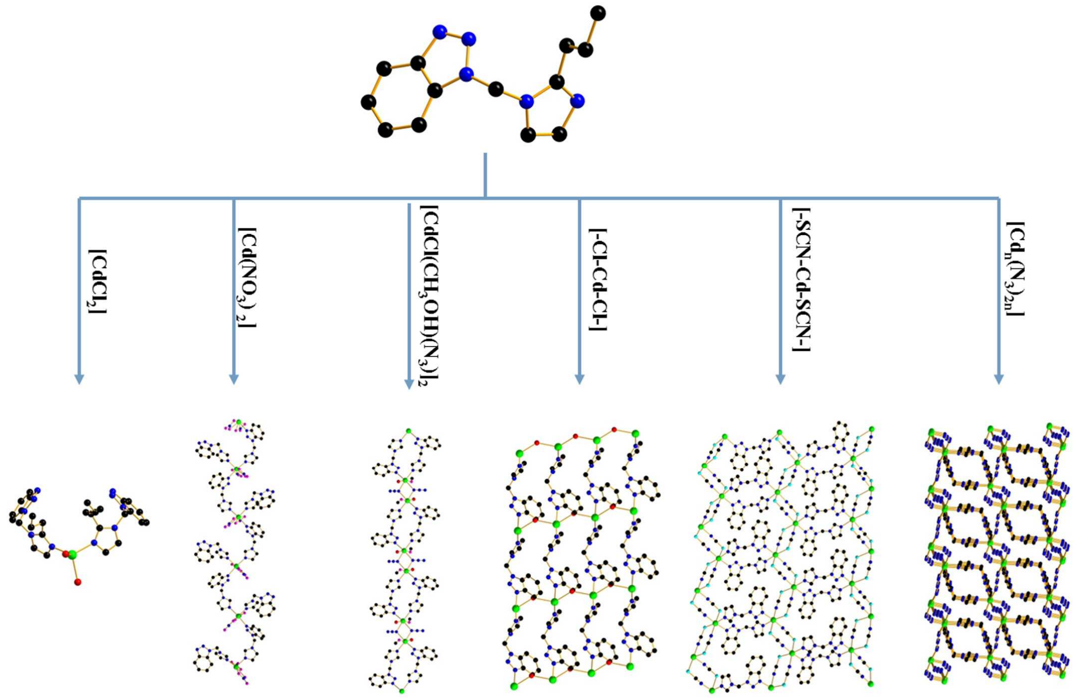

Six novel Cd(II) complexes, Cd(bpmi)$_2$Cl$_2$ (**1**), [Cd(bpmi)$_2$(NO$_3$)$_2$(H$_2$O)]$_n$ (**2**), [Cd$_2$(bpmi)$_2$Cl$_2$(N$_3$)$_2$(CH$_3$OH)$_2$]$_n$ (**3**), [Cd(bpmi)Cl$_2$]$_n$ (**4**), [Cd(bpmi)(SCN)$_2$]$_n$ (**5**) and [Cd(bpmi)(N$_3$)$_2$]$_n$ (**6**) are synthesized by the reaction of 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 that all of them contain inorganic SBUs and have 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 fluorescent spectra.