

Synthesis, Crystal Structure and Luminescent Property of A Novel Cd(II) Coordination Polymer with Bis-imidazole Ligand

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Research related to metal-organic coordination polymers has been a subject of great interest, not only from the view of potential applications, but also because of their intriguing architectures and framework topologies.¹⁻³ The key to the successful design of metal-organic coordination polymers is the judicious selection of organic ligand.⁴ Recently, polydentate aromatic nitrogen heterocyclic ligands with five-membered rings have been well-studied in the construction of supramolecular structure for their *N*-coordinated sites apt to coordinating to transition metals. Similar to six-membered *N*-heterocyclic ligands, the azole-based five-membered *N*-heterocyclic ligands, such as imidazoles, triazoles and tetrazoles have been extensively employed in the construction of various coordination polymers with diverse topologies and interesting properties.⁵⁻¹⁵ The bis(azole) ligands in which *N*-donor azole rings (imidazole, triazole, or tetrazole) are separated by alkyl, (CH₂)_n, spacers are good choices for flexible bridging ligands. The conformational flexibility of the spacers makes the ligands adaptable to various coordination networks with one-, two-, and three dimensional structures. There are an increasing number of recently characterized, interesting frameworks incorporating flexible bridging ligands and metal ions have been reported.^{16,17} Meanwhile, d¹⁰ metal ions present variable coordination numbers and geometries, and their metal-organic complexes generally exhibit luminescent properties.¹⁸⁻²⁰ It has been demonstrated that incorporation of fluorescent organic molecules into metal-organic frameworks has, in some cases, led to significant enhancements of fluorescent intensities compared to its free ligands.^{21,22} Furthermore, metal-organic frameworks can offer the advantages of higher thermal stability and solvent resistance compared to the all-organic materials.²³ Here we present the synthesis, structure and luminescent property of a 3D open framework of Cd(II), {[Cd(bbi)₃](NO₃)₂·(H₂O)₂]_n (**1**) (bbi=1,1'-(1,4-butanediyl)-bis(imidazole)), which shows enhancement and blue-shift fluorescent emission compared to bbi.

The framework {[Cd(bbi)₃](NO₃)₂·(H₂O)₂]_n (**1**) was synthesized by the reaction of Cd(NO₃)₂·4H₂O with bbi under hydrothermal condition. The crystal structure of **1** reveals a 3D coordination polymer composed of one Cd(II) ion, three bbi ligands, two NO₃⁻ and two water molecule in the asym-

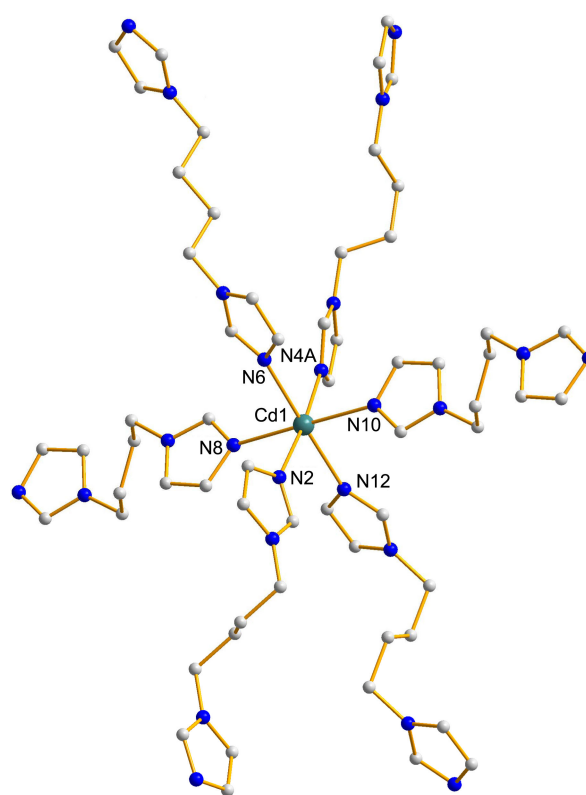


Figure 1. View of the coordination environment of Cd(II) ions in **1** (symmetry code: (A) x, y, z-1. hydrogen atoms and nitrate anion are omitted for clarity).

metric unit. Each Cd(II) is octahedrally coordinated by six imidazole nitrogen atoms, each of which is from a different bbi ligand (Figure 1). The Cd-N bond distances range from 2.346(4) to 2.380(4) Å, which are in the normal Cd-N bond length range for similar complexes reported.^{24,25} The bbi ligands adopt *trans* conformations as demonstrated by the torsion angle C1-N1-C7-C8 (-105.4(5)°), C4-N3-C10-C9 (100.6(6)°), C23-N9-C24-C25 (89.8(6)°) and C23E-N9E-C24E-C25E (89.8(6)°). The dihedral angles between the two imidazole rings are 0° and 6.2°, respectively (Figure 2). The bbi ligands link Cd(II) ions through the nitrogen atoms to give rise to zigzag chains. Consequently, each Cd(II) ions is linked to four neighboring ones through four bbi ligands to

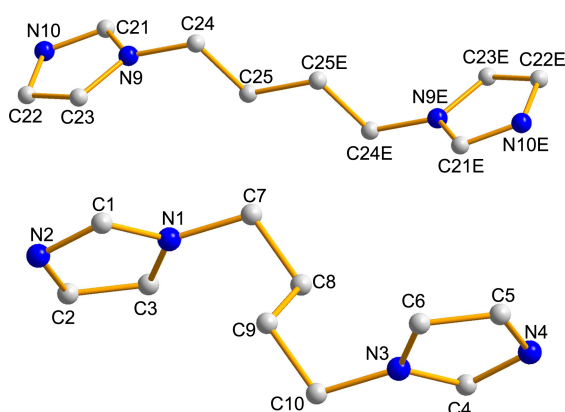


Figure 2. The conformation of bbi ligands (symmetry code: (E) $-x, -y+2, -z$).

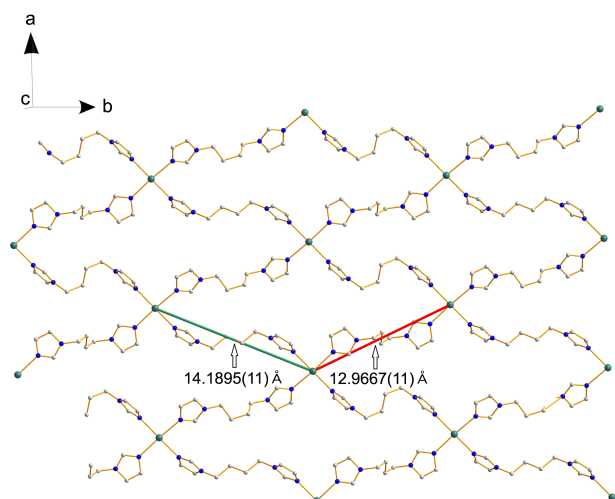


Figure 3. One layer of compound **1** viewed along the ab plane.

form a 2D layer extending along the ab plane, which contains $[\text{Cd}_4(\text{bbi})_4]$ squares (44-membered tetrametallacycles) with the Cd(II) ions as corners and the bbi ligands as edges (Figure 3). The Cd \cdots Cd distances spanned by the ligands are 12.9667(11) and 14.1895(11) Å, respectively. All the Cd(II) ions in each layer are strictly coplanar. Furthermore, the adjacent 2D layers are connected *via* an additional pair of bbi ligands along the c axis to form the resultant 3D supramolecular architectures with the inter-layer distance of 14.0271(15) Å (Figure 4). From the topological point of view, the 3D structure of **1** can be reduced to a (4, 4) grid net with a Schläfli symbol of $4^4 6^2$. There have been some reports on polymers based upon bbi. $[\text{Cd}(\text{bbi})_{1.5}(\text{H}_2\text{O})_2(\text{SO}_4)] \cdot 4(\text{H}_2\text{O})$ is composed of a (6, 3) network with the hexagonal smallest circuit containing six Cd^{2+} and six bbi (66-membered ring),²⁶ in which the sulfate ions coordinate to the central metal ions. However, the nitrate ions in **1** do not. These differences reveal that the anions play a crucial role in structural assembly. Polymers $\text{Mn}(\text{bbi})_3(\text{BF}_4)_2$, $\text{Mn}(\text{bbi})_3(\text{ClO}_4)_2$ and $\text{Mn}(\text{bbi})_3\text{I}_2$ have the similar compositions with **1**.^{27,28} The structures of these complexes comprise two equivalent, mutually interpenetrating three-dimensional networks,

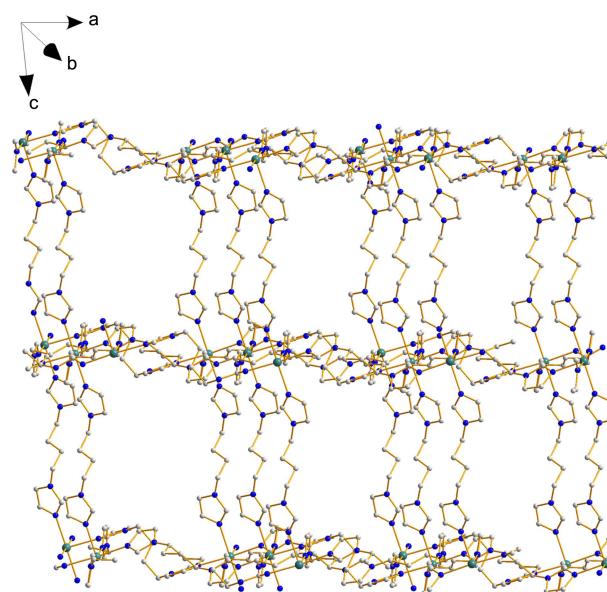


Figure 4. Packing of 2D layers to form 3D supramolecular structure by bbi bridge.

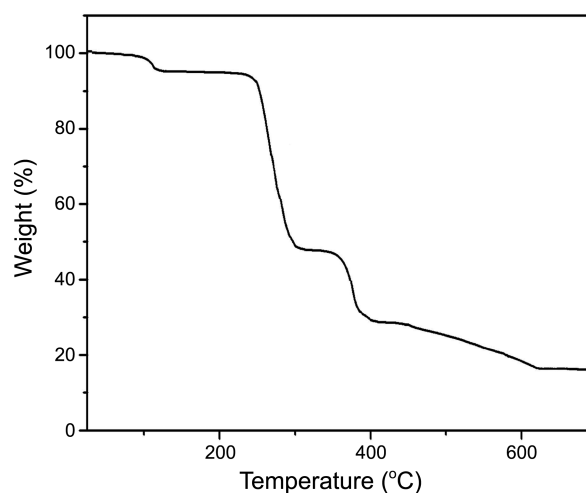


Figure 5. TG curve of complex **1**.

while polymer **1** forms an open, microporous structure.

To examine the thermal stability of complex **1**, thermal gravimetric analysis was performed on crystalline samples of the compound in the temperature range of 25–700 °C (Figure 5). The TG curve of **1** indicates the release of two lattice water molecules at the range of 100 to 121 °C (obsd 4.6%, calcd 4.3%). The weight loss from 235 to 303 °C is attributed to the decomposition of two bbi ligands (obsd 47.2%, calcd 45.1%). When **1** is completely decomposed, the residue, CdO, is 16.3% (calcd. 15.2%).

As mentioned earlier, luminescent complexes are currently of great interest because of their various applications in chemical sensors, photochemistry and electroluminescent display.²⁹ The luminescent properties of complex **1** and free bbi ligand have been investigated. In the solid state, free bbi ligand exhibits a broad fluorescent emission at 340 nm upon excitation at 300 nm. Relative to bbi, **1** exhibits a large blue-

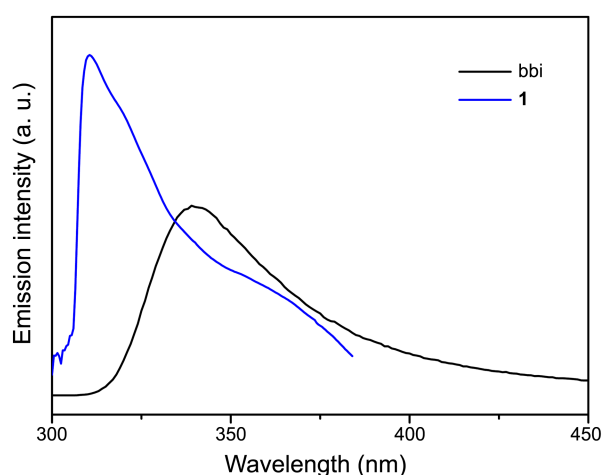


Figure 6. The emission spectra of **1** and bbi in the solid state at room temperature.

shift of emission with a main peak at 311 nm with larger intensity (Figure 6). Since Cd(II) ions with d^{10} configuration are difficult to be oxidized or reduced,³⁰ the fluorescent emission of **1** belongs to neither metal-to-ligand nor ligand-to-metal transfer. Therefore, the band is assigned to $(\pi^* - \pi)$ intra-ligand fluorescence. The strong emission at short wavelength of **1** may be due to the symmetry decrease and the conformational rigidity enhancement of the coordination polymer compared with the free bbi ligand, thereby reducing the loss of energy *via* non-radiative decay of the intra-ligand

Table 1. Crystallographic data for complex **1**

Formula	$C_{30}H_{46}N_{14}O_8Cd$
Formula weight	843.21
Crystal size (mm^3)	$0.50 \times 0.39 \times 0.26$
Temperature (K)	298(2)
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	
$a(\text{\AA})$	10.9960(1)
$b(\text{\AA})$	14.0189(1)
$c(\text{\AA})$	14.0271(1)
$\alpha(^{\circ})$	61.9000(1)
$\beta(^{\circ})$	80.5850(1)
$\gamma(^{\circ})$	85.441(2)
Volume/ \AA^3	1881.7(3)
Z	2
Density (calculated) (mg/mm^3)	1.488
Absorption coefficient (mm^{-1})	0.647
θ range for data collection/ $^{\circ}$	2.32 to 25.02
Reflections collected/unique	9485/6544 [$R(\text{int}) = 0.0360$]
$F(000)$	872
Limiting indices	$-9 \leq h \leq 13, -14 \leq k \leq 16, -15 \leq l \leq 16$
Data / restraints / parameters	6544 / 0 / 515
Goodness-of-fit on F^2	1.041
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0489, wR_2 = 0.1153$
Largest diff. peak and hole/ $(e^{-}\text{\AA}^{-3})$	0.841 and -0.875

excited states.³¹⁻³³ These results reveal that complex **1** may be excellent candidate for potential photoluminescent material.

Experimental

The bbi ligand was synthesized according to the literature method.³⁴ IR spectra were measured on a Nicolet 170SX FT-IR spectrophotometer with KBr pellets in the range of 4000–400 cm^{-1} . Elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. Thermogravimetric (TG) analyses were recorded with a NETZSCH STA 449C microanalyzer in air at a heating rate of 10 $^{\circ}C \cdot min^{-1}$. Solid state emission and excitation spectra of compounds were measured using a Cary Eclipse fluorescence spectrophotometer.

For the synthesis of compound **1**, a mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.118 g, 0.5 mmol), bbi (0.095 g, 0.5 mmol) and NaOH (0.01 g, 0.25 mmol) was dissolved in 10 mL of distilled water. Consequently, the resulting solution was transferred and sealed in a 25 mL Teflon-lined stainless steel vessel, which was heated at 140 $^{\circ}C$ for 72 h. The solution was then cooled to room temperature at a rate of 5 $^{\circ}C \cdot h^{-1}$, to yield a very fine yellow crystalline product of **1** in 60% yield. Elemental analysis (%) calcd for $C_{30}H_{46}N_{14}O_8Cd$: C, 42.69; H, 5.46; N, 23.24. Found: C, 42.72; H, 5.50; N, 23.20. IR (cm^{-1} , KBr pellets): 3119w, 2938w, 1575m, 1512m, 1384s, 1231s, 1116s, 1086m, 929m, 834w, 742s.

Data collection for compound **1** was carried out on a Bruker Smart Apex CCD area-detector diffractometer equipped with a graphite-monochromated Mo-K α radiation with radiation wavelength 0.71073 \AA at 298(2) K. The structure was solved by direct method and refined with the full-matrix least-squares technique using the SHELXS-97³⁵ and SHELXL-97³⁶ programs. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final agreement factor values are $R_1 = 0.0489$ and $wR_2 = 0.1153$. A summary of the crystallographic data is given in Table 1. Crystallographic data for the structure reported here has been deposited with CCDC (Deposition No. CCDC-895787). These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk.

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