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# Cadmium(II) nano-dimensional square grid polymers based on bis(imidazol-1-yl-methyl)benzene: synthesis, characterization, and photoluminescence

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Two new nano-dimensional square grid metal–organic polymers, $\{[Cd(1,3\text{-bix})_2(H_2O)_2](NO_3)_2\}_n$ (**1**) and $[Cd(1,3\text{-bix})_2(NO_3)_2]_n$ (**2**) (1,3–bix = 1,3-bis(imidazol-1-yl-methyl)benzene), have been synthesized and structurally characterized by single-crystal X-ray crystallography and FT-IR spectroscopy. Polymers **1** and **2** are 2-D layer structures consisting of nano-dimensional square grid units. The photoluminescent properties of **1** and **2** were investigated.

*Keywords*: Nano-dimensional square grid; Cadmium(II); Coordination polymer

## 1. Introduction

Design of nano-dimensional metal–organic coordination polymers is one focus of crystal engineering [1–8]. These coordination polymers have fascinating architectures and applications in fields, such as molecular recognition, catalysis, ion exchange, and drug delivery [9]. The structure and properties of coordination polymers depend on the coordination and geometries of metal ions and ligands, as well as the influence of secondary interactions such as hydrogen-bonding [10–15]. Several factors, including coordination bonds and secondary interactions, the metal-to ligand molar ratio, the coordination of the ligands, the type of metal ions, and the presence of solvent should be taken into account in the process of the design and synthesis of metal-coordination polymers [16–20]. Progress has been made on the effect of flexible bridging ligands on framework formation of coordination polymers. 1,3-Bis(imidazol-1-yl-methyl)benzene, a highly flexible ligand with a multinitrogen heterocycle, is widely used owing to free rotation of the two imidazole planes, which can meet the requirement of coordination geometries of metal ions in the assembly process [21–28]. We have synthesized and

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characterized two cadmium(II) coordination polymers with 1,3-bis(imidazol-1-yl-methyl)benzene, $\{[Cd(1,3\text{-bix})_2(H_2O)_2](NO_3)_2\}_n$ (**1**) and $[Cd(1,3\text{-bix})_2(NO_3)_2]_n$ (**2**). Luminescent properties of **1** and **2** were also investigated.

## 2. Experimental

### 2.1. *Materials and methods*

Commercially available chemicals are of reagent grade and used without purification. 1,3-Bis(imidazol-1-yl-methyl)benzene is synthesized by following the procedures described previously [21]. FT-IR spectra were recorded from KBr pellets (4000–400 $cm^{-1}$) on an EQUINOX 55 Fourier transform infrared spectrometer. The solid-state emission/excitation spectra of **1** and **2** were recorded on an F-7000 FL spectrophotometer at room temperature.

### 2.2. *Syntheses of $\{[Cd(1,3\text{-bix})_2(H_2O)_2](NO_3)_2\}_n$ (1)*

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.0457 g, 0.148 mmol) and 1,3-bis(imidazol-1-yl-methyl)benzene (0.0232 g, 0.097 mmol) was dissolved in methanol (10 mL), then distilled water (20 mL) was added to the above solution. The colorless solution was allowed to stand at room temperature. Good quality colorless crystals were obtained seven weeks later. Anal. Calcd for $C_{28}H_{32}CdN_{10}O_8$ (%): C, 44.90; H, 4.31; N, 18.70. Found (%): C, 44.73; H, 4.25; N, 18.59. FT-IR (KBr pellet, $cm^{-1}$) selected bands: $\nu = 3436$m, 3109m, 2369w, 1061w, 1514m, 1382s, 1229m, 1079m, 1027w, 929w, 822w, 726 m, 656 m, 625w.

### 2.3. *Syntheses of $[Cd(1,3\text{-bix})_2(NO_3)_2]_n$ (2)*

$Cd(NO_3)_2 \cdot 4H_2O$ (0.0309 g, 0.10 mmol) and 1,3-bis(imidazol-1-yl-methyl)benzene (0.0240 g, 0.10 mmol) were dissolved in methanol (10 mL). The colorless solution was allowed to stand at room temperature. Good quality colorless crystals were obtained two weeks later. Anal. Calcd for $C_{28}H_{28}CdN_{10}O_6$ (%): C, 47.17; H, 3.96; N, 19.65. Found (%): C, 47.12; H, 3.82; N, 19.49. FT-IR (KBr pellet, $cm^{-1}$) selected bands: $\nu = 3424$m, 3112w, 1686w, 1599w, 1515m, 1380s, 1231m, 1082m, 1028w, 932w, 822w, 728m, 657m, 627w.

### 2.4. *X-ray crystallography*

Single-crystal analyses were performed with the Bruker SMART APEXII CCD diffractometer for **1** and **2** using graphite monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and orientation matrix for data collection were obtained from least-squares refinement. The structures are solved by direct methods and refined by full-matrix least-squares techniques on $F^2$. Crystal data and refinement parameters are given in table 1. Selected bond lengths and angles are given in tables 2 and 3.

Table 1. Crystallographic data for **1** and **2**.

| Identification code | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{28}H_{32}CdN_{10}O_8$ | $C_{28}H_{28}CdN_{10}O_6$ |
| Formula weight | 749.04 | 713.00 |
| Temperature (K) | 298(2) | 298(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ |
| Unit cell dimensions (Å, °) | | |
| $a$ | 17.830(4) | 8.4415(4) |
| $b$ | 8.2270(19) | 19.3716(9) |
| $c$ | 23.304(5) | 9.2108(4) |
| $\alpha$ | 90 | 90 |
| $\beta$ | 109.432(4) | 102.4820(10) |
| $\gamma$ | 90 | 90 |
| Volume (Å$^3$), $Z$ | 3223.7(12), 4 | 1470.60(12), 2 |
| Calculated density (g cm$^{-3}$) | 1.543 | 1.610 |
| $F(000)$ | 1528 | 724 |
| $R$(int) | 0.0409 | 0.0200 |
| Data/restraints/parameters | 5694/0/424 | 2711/30/214 |
| Goodness-of-fit on $F^2$ | 1.075 | 1.060 |
| $R_1{}^a$ $[I > 2\sigma(I)]$ | 0.0402 | 0.0258 |
| $WR_2{}^b$ $[I > 2\sigma(I)]$ | 0.1233 | 0.0836 |
| $R^a$ (all data) | 0.0580 | 0.0312 |
| w$R_2{}^b$ (all data) | 0.1537 | 0.0956 |
| Largest difference peak and hole (e Å$^{-3}$) | 1.241 and −0.602 | 0.669 and −0.427 |

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

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

| | | | |
|---|---|---|---|
| Cd(1)–N(4)#1 | 2.287(4) | Cd(1)–N(5) | 2.306(4) |
| Cd(1)–N(1) | 2.316(4) | Cd(1)–N(8)#2 | 2.324(4) |
| Cd(1)–O(8) | 2.376(3) | Cd(1)–O(7) | 2.395(3) |
| N(4)–Cd(1)#3 | 2.287(4) | N(8)–Cd(1)#4 | 2.324(4) |
| N(4)#1–Cd(1)–N(5) | 172.84(13) | N(4)#1–Cd(1)–N(1) | 92.57(14) |
| N(5)–Cd(1)–N(1) | 88.63(13) | N(4)#1–Cd(1)–N(8)#2 | 91.65(14) |
| N(5)–Cd(1)–N(8)#2 | 88.29(13) | N(1)–Cd(1)–N(8)#2 | 170.06(16) |
| N(4)#1–Cd(1)–O(8) | 91.14(13) | N(5)–Cd(1)–O(8) | 95.98(13) |
| N(1)–Cd(1)–O(8) | 86.34(15) | N(8)#2–Cd(1)–O(8) | 84.58(14) |
| N(4)#1–Cd(1)–O(7) | 88.46(13) | N(5)–Cd(1)–O(7) | 84.40(13) |
| N(1)–Cd(1)–O(7) | 95.60(16) | N(8)#2–Cd(1)–O(7) | 93.50(15) |
| O(8)–Cd(1)–O(7) | 178.04(13) | | |

Symmetry transformations used to generate equivalent atoms: #1: $x, -y + 5/2, z - 1/2$; #2: $x, -y + 1/2, z - 1/2$; #3: $x, -y + 5/2, z + 1/2$; #4: $x, -y + 1/2, z + 1/2$.

## 3. Results and discussion

Single-crystal structural determination reveal that **1** crystallizes in the monoclinic space group $P2_1/c$, and the structure unit consists of two 1,3-bix ligands, two coordinated water molecules, two free nitrates, and one Cd. As illustrated in figure 1, each Cd(II) is six-coordinate by four nitrogen atoms from 1,3-bix at the equatorial plane, and two coordinated water molecules in axial positions, forming a slightly distorted $[CdN_4O_2]$ octahedral geometry. All 1,3-bix ligands adopt V-shape conformation with two

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

| | | | |
|---|---|---|---|
| Cd(1)–N(4)#1 | 2.320(2) | Cd(1)–N(4)#2 | 2.320(2) |
| Cd(1)–N(1)#3 | 2.330(2) | Cd(1)–N(1) | 2.330(2) |
| Cd(1)–O(1)#3 | 2.374(2) | Cd(1)–O(1) | 2.374(2) |
| N(4)–Cd(1)#4 | 2.320(2) | | |
| N(4)#1–Cd(1)–N(4)#2 | 180.000(1) | N(4)#1–Cd(1)–N(1)#3 | 91.16(8) |
| N(4)#2–Cd(1)–N(1)#3 | 88.84(8) | N(4)#1–Cd(1)–N(1) | 88.84(8) |
| N(4)#2–Cd(1)–N(1) | 91.16(8) | N(1)#3–Cd(1)–N(1) | 180.000(1) |
| N(4)#1–Cd(1)–O(1)#3 | 99.38(8) | N(4)#2–Cd(1)–O(1)#3 | 80.62(8) |
| N(1)#3–Cd(1)–O(1)#3 | 87.06(9) | N(1)–Cd(1)–O(1)#3 | 92.94(9) |
| N(4)#1–Cd(1)–O(1) | 80.62(8) | N(4)#2–Cd(1)–O(1) | 99.38(8) |
| N(1)#3–Cd(1)–O(1) | 92.94(9) | N(1)–Cd(1)–O(1) | 87.06(9) |
| O(1)#3–Cd(1)–O(1) | 180.0 | N(5)–O(1)–Cd(1) | 131.1(2) |

Symmetry transformations used to generate equivalent atoms: #1: $x-1$, $-y+3/2$, $z+1/2$; #2: $-x+1$, $y-1/2$, $-z+3/2$; #3: $-x$, $-y+1$, $-z+2$; #4: $-x+1$, $y+1/2$, $-z+3/2$.

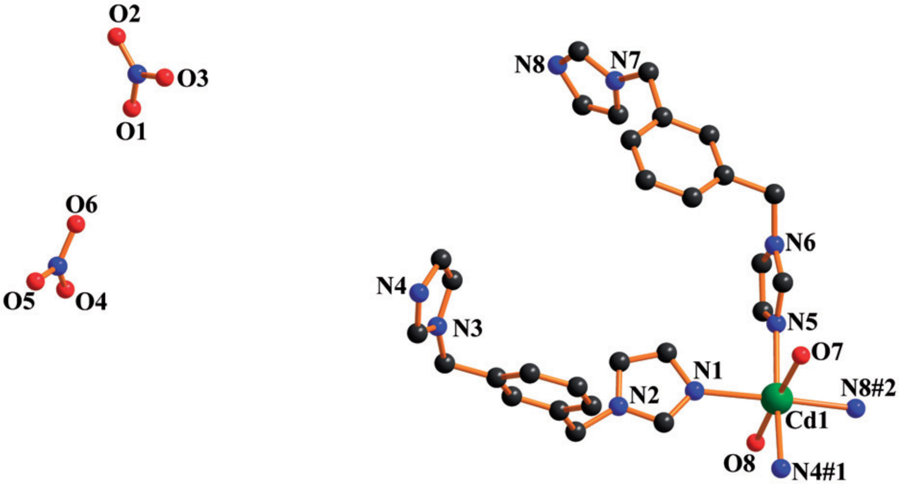

Figure 1. View of the coordination environment of Cd(II) in **1**. Hydrogen atoms have been omitted for clarity. Symmetry code for the generated atoms: #1: $x$, $5/2-y$, $-1/2+z$; #2: $x$, $1/2-y$, $-1/2+z$.

imidazoles located on the same side of the central benzene ring plane; dihedral angles between the phenyl and each imidazolyl ring are 80.96° and 84.87°. Each 1,3-bix binds two Cd(II) ions to form a 2-D layer structure consisting of nano-dimensional 2-D(4,4) square grid units (figure 2). The size of the formed square grids is $1.46 \times 1.46$ nm. The grid-like $Cd_4$(1,4-bix)$_4$ units can be viewed as basic building blocks of the structure. Grid layers are tightly stacked in a parallel way. There are O–H···O hydrogen bonds between coordinated water and free nitrates among the grid layers (figure 3), which play an important role in consolidating the architecture.

Compound **2** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit of **2** contains one Cd(II), two 1,3-bix ligands, and two coordinated nitrates. As illustrated in figure 4, Cd(II) is coordinated by four nitrogen atoms from four 1,3-bix ligands and two oxygen atoms from two axial nitrates, showing a $CdN_4O_2$ octahedral sphere with Cd–N lengths of 2.320(2)–2.374(3) Å and Cd–O length of 2.374 Å.

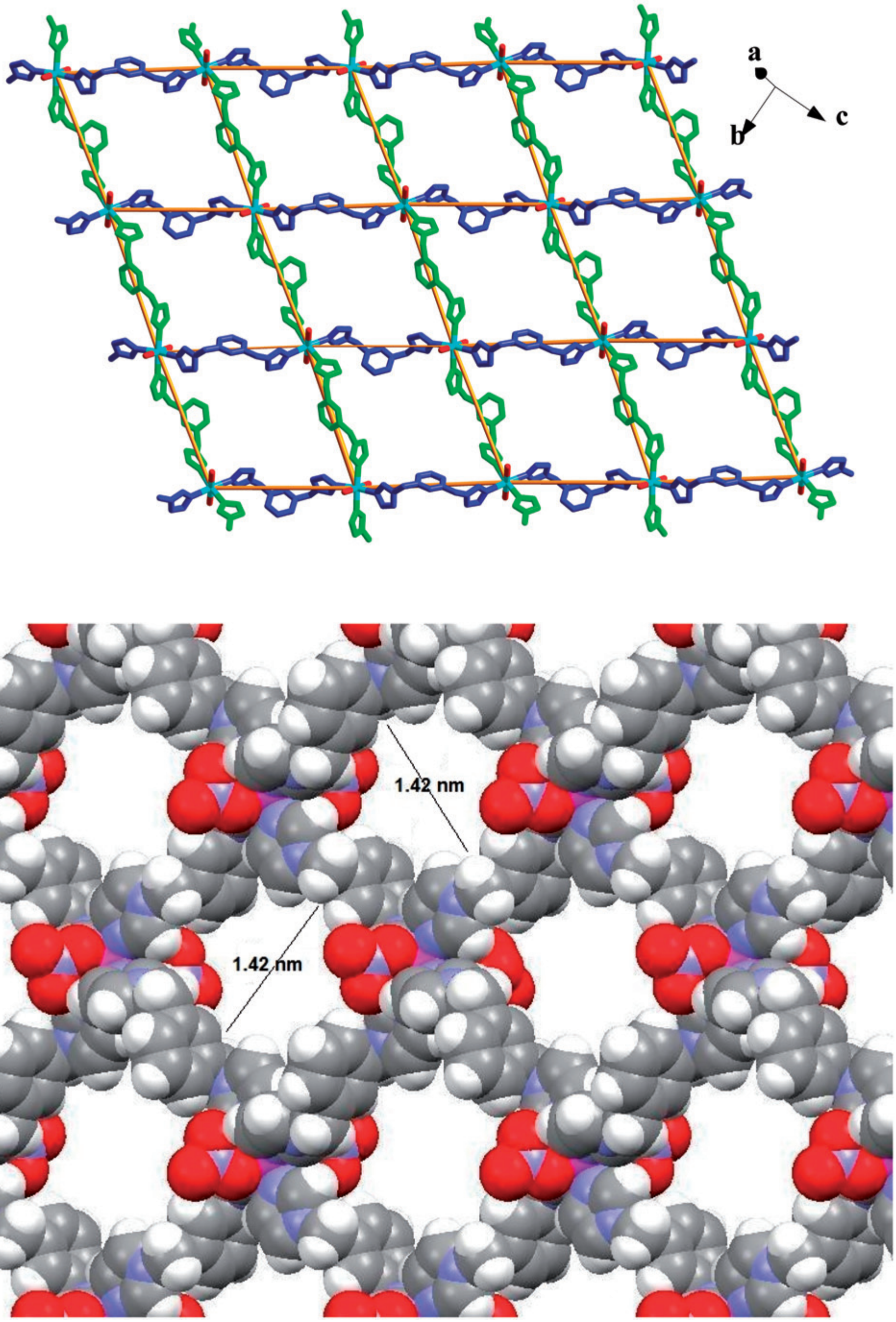

Figure 2. The 2-D layer structure consisting of large 2-D(4,4) square grid units in **1**.

However, 1,3-bix adopts Z-shape with two imidazoles locating on opposite side of the central benzene plane; dihedral angles between phenyl and each imidazolyl are 70.89° and 80.93°. As in **1**, each 1,3-bix connects two Cd(II) ions to generate a 2-D layer structure consisting of nano-dimensional 2-D(4,4) square grid units (figure 5).

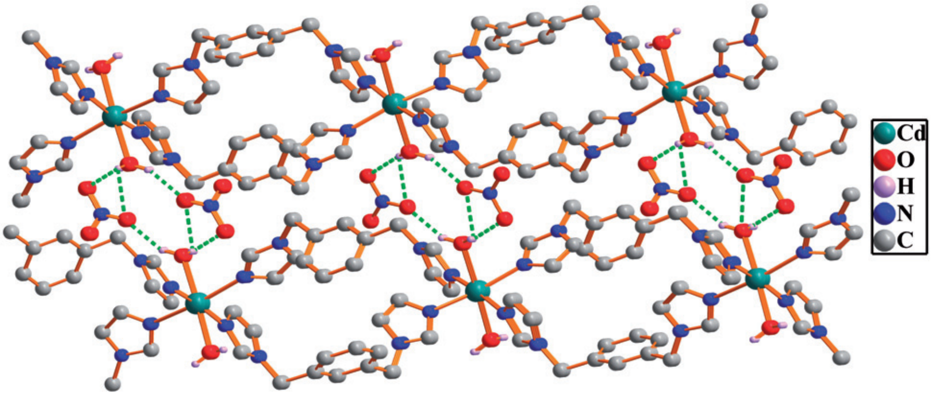

Figure 3. The 3-D hydrogen-bonding structure in **1**.

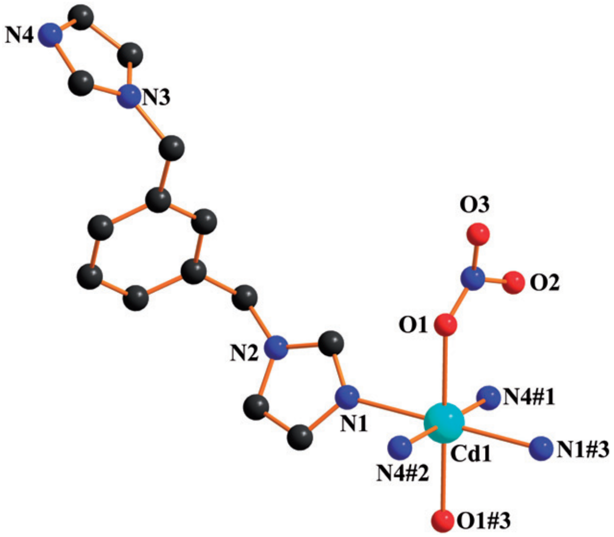

Figure 4. Perspective view of the coordination environment of Cd(II) in **2**. Hydrogen atoms were removed for clarity. Symmetry code for the generated atoms: #1: $1-x$, $-0.5+y$, $1.5-z$; #2: $-1+x$, $1.5-y$, $0.5+z$; #3: $-x$, $1-y$, $2-z$.

The grid-like $Cd_4(1,4\text{-bix})_4$ units have dimensions of $1.42 \times 1.42$ nm, with the layers being tightly stacked in a parallel way.

Photoluminescence experiments on **1** and **2** were performed at room temperature in the solid state. Intense broad emissions at 466 nm ($\lambda_{ex} = 399$) for **1** and 435 nm ($\lambda_{ex} = 409$ nm) for **2** are observed. Free 1,2-bix exhibits fluorescent emission at 396 nm ($\lambda_{ex} = 326$ nm) under the same experimental conditions (figure 6). Taking the emission bands of ligand into consideration, the emissions of **1** and **2** may also be assigned as ligand-to-metal charge transition. The coordination polymers may, thus, be candidates for optical materials.

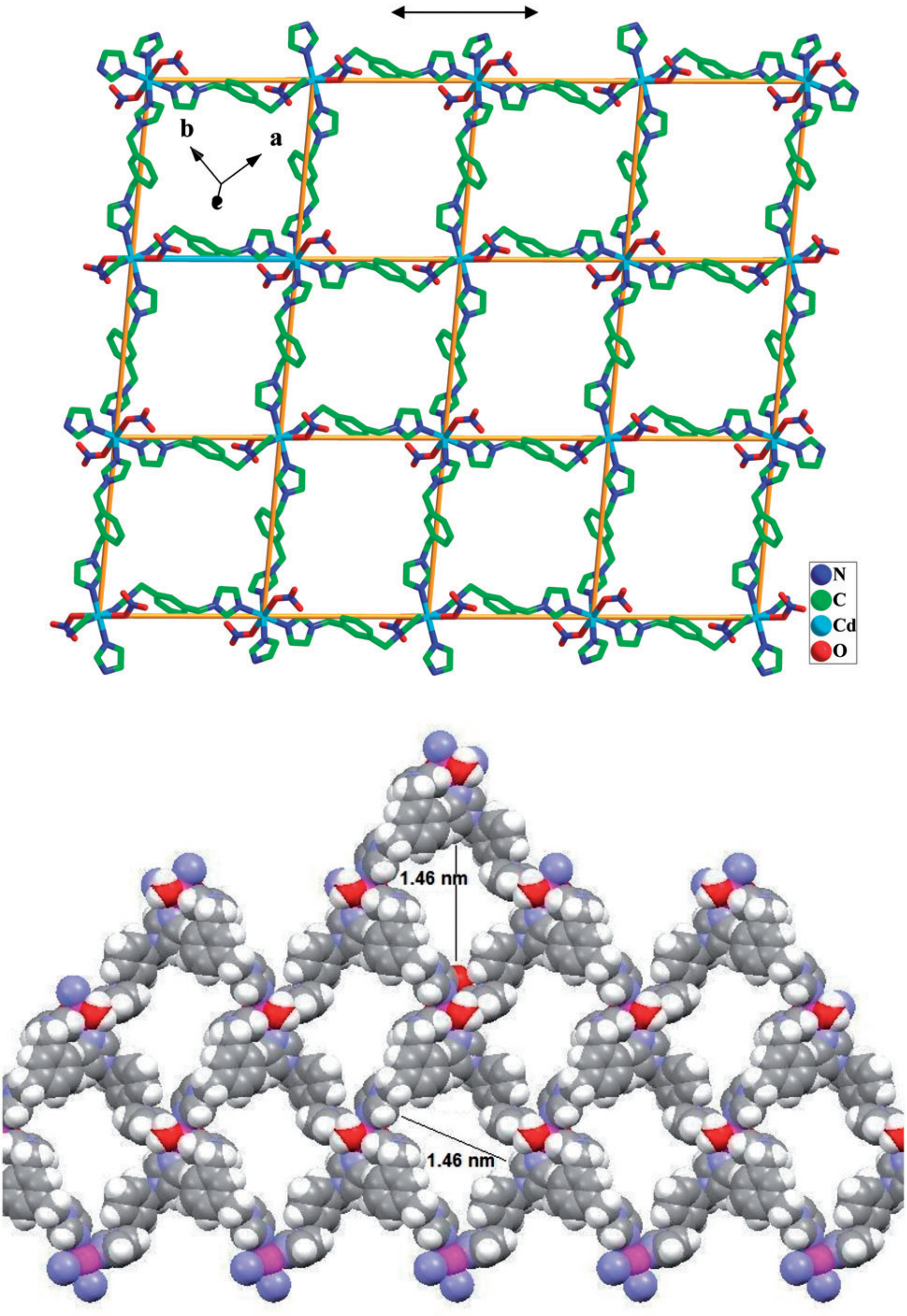

Figure 5. The 2-D layer structure consisting of nano-dimensional 2-D(4,4) square grid units in **2**.

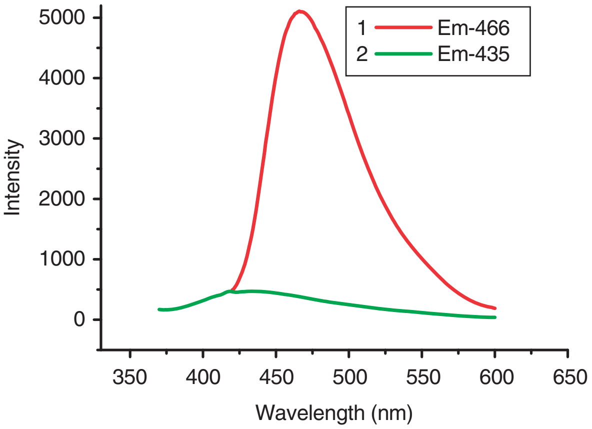

Figure 6. Solid-state photoluminescence spectra of **1** ($\lambda_{ex} = 399$ nm) and **2** ($\lambda_{ex} = 356$ nm) at room temperature.

## 4. Conclusion

Two cadmium(II) coordination polymers with bis(imidazol-1-yl-methyl)benzene have been synthesized, structurally characterized, and the photoluminescent properties investigated. The structures of **1** and **2** are 2-D layer structures consisting of nano-dimensional square grid units.

## Supplementary material

Crystallographic data for the structure reported in the article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos CCDC 863986 and 863987 for **1** and **2**, respectively. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44–1223/150 336033; E-mail: deposit@ccdc.cam.ac.uk].

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