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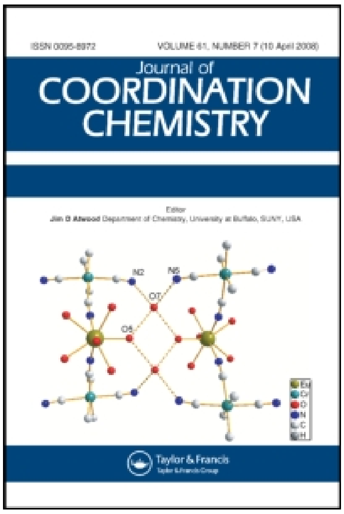

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In situ syntheses of two tetrazole coordination polymers

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In situ syntheses of two tetrazole coordination polymers

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Hydrothermal treatments of 2-(pyridin-2-yl)acetonitrile, NaN_3, and $Zn(NO_3)_2 \cdot 4H_2O$ (or $Cd(NO_3)_2 \cdot 4H_2O$) in the presence of water and ethanol afford *in situ* tetrazole coordination polymers, $C_{14}H_{12}N_{10}Zn$ (**1**) and $C_{14}H_{12}N_{10}Cd$ (**2**). Both compounds are characterized by single crystal X-ray diffraction and display 2-D structures, while their 3-D packing views show different packing types (ABA sequence and AAA sequence). Crystal data of **1**: *Pbcn*, $a = 9.096(8)$, $b = 8.681(7)$, $c = 18.801(16)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1485(2)$ Å^3, $Z = 4$, $R_1 = 0.0315$, $wR_2 = 0.0883$; Crystal data of **2**: $P2_1/c$, $a = 9.652(5)$, $b = 10.024(3)$, $c = 8.865(4)$ Å, $\beta = 116.33(2)°$, $V = 768.7(6)$ Å^3, $Z = 2$, $R_1 = 0.0198$, $wR_2 = 0.0712$. Both the compounds display similar fluorescence with emission peak at 390 nm, assigned to an intraligand fluorescent emission.

Keywords: 2-((1H-tetrazol-5-yl)methyl)pyridine; Hydrothermal synthesis; *In situ*; Tetrazole coordination compound; Fluorescence

1. Introduction

Organic–inorganic coordination compounds have potential applications such as reversible guest-exchange, shape selective, catalysis, gas storage, molecular recognition, photoluminescence, unusual magnetic, non-linear, semiconducting properties, chirality, and clathration [1–4]. Engineering of coordination frameworks with desired topologies and specific properties remains a challenge since a variety of factors influence self-assembly. Ligands as "building blocks" and coordination preferences of metal centers as "nodes" are important for the organic–inorganic coordination network. For example, many pyridyl-based bridging ligands, quinoline-based ligands, tetrazoles, imidazoles, and triazoles, were used in construction of metal–organic coordination networks [5].

Tetrazole has a wide range of applications in coordination chemistry, medicinal chemistry, and material science. Early routes to tetrazoles were highly toxic, volatile, and explosive; Sharpless and his co-workers explored a safe, convenient, and environmentally-friendly route to the preparation of 5-substituted 1*H*-tetrazoles

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in water with zinc salts as catalysts [6]. Enlightened by this work, we trapped and characterized a series of "intermediates" in this new preparation of 5-substituted 1*H*-tetrazole in water. Most display interesting topologies and physical properties including fluorescence, SHG, ferroelectric, and dielectric [7–14]. Herein, we report two 2-D tetrazole coordination compounds with the 2-(pyridin-2-yl)acetonitrile as starting material and their fluorescence. The coordination mode of 2-[(1H-tetrazol-5-yl)methyl] pyridine is different from that of 2-(1H-tetrazol-5-yl)pyridine whose *in situ* metal coordination compounds show monomers with nitrogens from pyridine and tetrazole chelating the metal.

2. Experimental

2-(Pyridin-2-yl)acetonitrile was commercially available; other chemicals and solvents were purchased from Aldrich and used as received. The FT-IR spectra were recorded in KBr from 4000–400 cm^{-1} on a Nicolet Inpact 170S FT-IR spectrometer. Elemental analyses (C, H, and N) and thermogravimetric analyses were carried out on a Perkin–Elmer 240C elemental analyzer or Rigaku thermo plus TG 8120 thermogravimetric analyzer at the Center of Material Analysis, Nanjing University.

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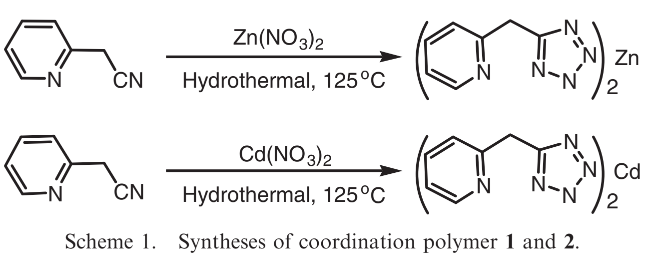
2.1. *Synthesis of the title complexes*

Complex **1** was prepared as shown in scheme 1. A heavy-walled Pyrex tube containing a mixture of 2-(pyridin-2-yl)acetonitrile (0.0236 g, 0.2 mmol), $Zn(NO_3)_2 \cdot 4H_2O$ (0.0498 g, 0.2 mmol), water (2.0 mL), and ethanol (0.5 mL) was frozen and sealed under vacuum, then placed inside an oven at 125°C. Colorless block-like crystals were obtained after 48 h of heating. Yield: 78% on the basis of 2-(pyridin-2-yl)acetonitrile. Elemental analysis (%) Calcd for $C_{14}H_{12}N_{10}Zn$: C, 43.59; H, 3.14; N, 36.31. Found: C, 44.01; H, 3.32; N, 36.52. IR (KBr, cm^{-1}) 607(w), 638(w), 671(w), 690(w), 762(m), 806(w), 839(w), 926(w), 993(w), 1015(m), 1065(w), 1105(w), 1153(w), 1217(w), 1242(w), 1242(w), 1292(w), 1333(w), 1385(w), 1422(m), 1443(s), 1481(m), 1570(w), 1603(m), 1670(w), 2912(w), 2937(w), 3034(w), 3064(w), 3111(w), 3210(wide, w), 3404(wide, w).

Complex **2** was prepared similarly. Yield: 78% on the basis of 2-(pyridin-2-yl)acetonitrile. Elemental analysis (%) Calcd for $C_{14}H_{12}N_{10}Cd$: C, 38.86; H, 2.79; N, 32.37. Found: C, 38.21; H, 2.98; N, 33.01. IR (KBr, cm^{-1}) 608(m), 685(m), 750(s), 843(w), 914 (w), 1015(m), 1061(m), 1157(w), 1225(w), 1296(m), 1333(m), 1410(s), 1439(s), 1477(s), 1570(m), 1599(s), 2072(w), 2897(w), 3395(wide, m).



Scheme 1. Syntheses of coordination polymer **1** and **2**.

2.2. *Single crystal structure determination*

X-ray diffraction data for **1** and **2** were collected at ambient temperature on Rigaku diffractometers (Mo-Kα X-radiation, $\lambda = 0.71069$ Å). Data were corrected for Lorentz and polarization effects, for extinction and for absorption [semi-empirical methods (ψ scans)]. The structures were solved by direct methods (SHELXL-97) [9] and refined (on F or F^2) by full-matrix least-squares techniques [10], with anisotropic thermal parameters for all non-hydrogen atoms giving residuals R and Rw (on F). Hydrogen atoms were either located by difference methods or included in respective refinements at calculated positions as riding models. Detailed information about the crystal data and structure determination for both compounds are summarized in table 1. Selected bond distances and angles are given in table 2.

3. Results and discussion

The *in situ* hydrothermal reactions between 2-(pyridin-2-yl)acetonitrile and $Zn(NO_3)_2$ (or $Cd(NO_3)_2$) offer colorless block crystalline coordination polymers, (2-((1H-tetrazol-5-yl)methyl)pyridine)$_2$Zn (**1**) and (2-((1H-tetrazol-5-yl)methyl) pyridine)$_2$Cd (**2**). IR spectra confirm the absence of a peak at about 2200 cm^{-1}, suggesting that cyano has changed to the tetrazole with several typical tetrazolyl group peaks at 1440, 1475, and 1333 cm^{-1}.

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Table 1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{14}H_{12}N_{10}Zn$	$C_{14}H_{12}N_{10}Cd$
F_w	385.71	432.74
T (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbcn*	$P2_1/c$
Unit of dimensions (Å, °)		
a	9.096(8)	9.652(5)
b	8.681(7)	10.024(3)
c	18.801(16)	8.865(4)
α	90	90
β	90	116.33(2)
γ	90	90
V (Å^3)	1485(2)	768.7(6)
Z	4	2
D_{Calcd} (g cm^{-3})	1.726	1.870
μ(Mo-Kα) (mm^{-1})	1.677	1.443
F(000)	784	428
θ range for data collection (°)	3.12–27.88	3.11–27.85
Reflections collected	14282	7663
Independent reflections	1776 [$R_{(int)} = 0.0287$]	1820 [$R_{(int)} = 0.0167$]
Refinement method	Full-matrix least-squares on $\lvert F\rvert^2$	Full-matrix least-squares on $\lvert F\rvert^2$
Data/restraints/parameters	1776/0/118	1820/0/115
Final R indices [$I > 2\sigma(I)$]	0.0315, 0.0883	0.0198, 0.0712
R indices (all data)	0.0339, 0.0906	0.0229, 0.0799
Largest difference peak and hole (e Å^{-3})	0.333, −0.569	0.520, −0.559

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

1		**2**	
Zn(1)–N(8)#1	2.0993(18)	Cd(1)–N(3)	2.3016(13)
Zn(1)–N(1)	2.1901(18)	Cd(1)–N(5)	2.3920(17)
Zn(1)–N(5)#1	2.289(2)	Cd(1)–N(4)#3	2.3830(13)
N(8)#1–Zn(1)–N(8)#2	88.40(10)	N(3)#1–Cd(1)–N(3)	180.0
N(8)#1–Zn(1)–N(1)#3	176.24(5)	N(3)#1–Cd(1)–N(5)	98.42(5)
N(8)#2–Zn(1)–N(1)#3	88.00(8)	N(3)–Cd(1)–N(5)	81.58(5)
N(1)#3–Zn(1)–N(1)	95.62(10)	N(5)–Cd(1)–N(5)#1	180.0
N(8)#1–Zn(1)–N(5)#1	84.69(7)	N(3)–Cd(1)–N(4)#2	85.67(5)
N(1)#3–Zn(1)–N(5)#1	96.44(7)	N(5)–Cd(1)–N(4)#2	88.00(5)
N(1)–Zn(1)–N(5)#1	87.88(7)	N(3)–Cd(1)–N(4)#3	94.33(5)
N(8)#1–Zn(1)–N(5)#2	90.70(7)	N(5)–Cd(1)–N(4)#3	92.00(5)
N(5)#1–Zn(1)–N(5)#2	173.58(8)	N(4)#2–Cd(1)–N(4)#3	180.00(3)

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

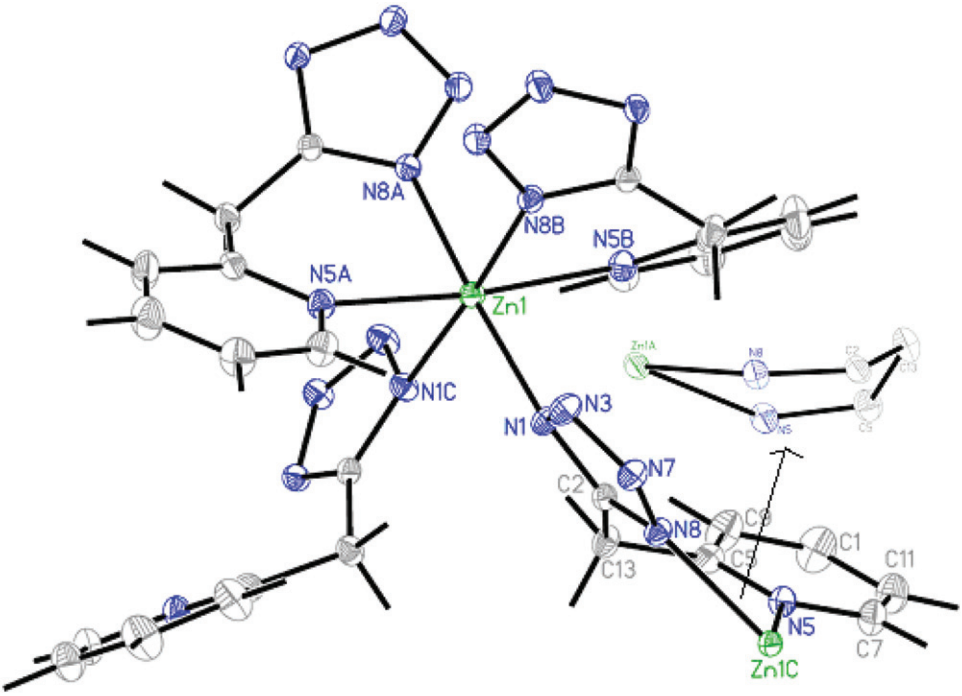

Figure 1. The molecular structure of **1**, showing the coordination geometry of zinc.

The 2-D structure of **1** was revealed by an X-ray single-crystal diffraction investigation. Crystallographic data of **1** (table 1) indicates that **1** is orthorhombic, space group *Pbcn*, and $Z=4$. The local coordination environment around zinc is a slightly distorted octahedron composed of six nitrogens from four tridentate 2-[(1H-tetrazol-5-yl)methyl]pyridine, as shown in figure 1. The coordination geometry of zinc has the tetragonal plane positions occupied by four nitrogens of four tetrazole rings

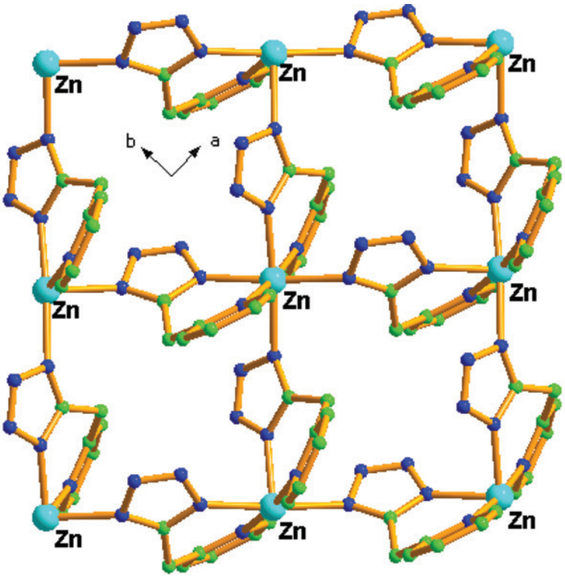

Figure 2. The 2-D structure of **1** displaying a (4, 4) net along *c* axis (Green ball: C; Blue ball: N).

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from four tetrazole ligands and two apical positions occupied by N atoms of pyridyl rings; N5B–Zn1–N5A is perpendicular to the plane completed by N8A, N8B, Zn1, N1C, and N1, as shown in figure 2. In **1**, the tetrazole is tridentate coordinating to neighboring zinc through 1 and 4 positions of the tetrazole ring and nitrogen of pyridine. One nitrogen of tetrazole and another from pyridine chelate a zinc to form a boat-like, six-membered ring (Zn1C–N5–C5–C13–C2–N8–Zn1C), as shown in figure 1, causing pyridine ring and tetrazole ring to have a dihedral angle of 41.19(10)°. Tetrazole ring, coordinates to neighboring zinc centers to form a 2-D plane with (4, 4) topology. Figure 3 shows the packing view of **1**, in which the distance between two neighboring zincs is 6.287 Å, while the angle of Zn–Zn–Zn is 92.675(6)° or 87.343°, which sums to 180.018°. All of these planes pack together by ABAB type along *c*-axis in 3-D.

Similar to the structure of **1**, in **2** the Cd center coordinates six nitrogens of four tridentate tetrazole ligands, with two nitrogens separately from tetrazole ring (1-position) and pyridine ring of the same tetrazole chelating one cadmium center (Cd1–N3–C1–C5–C7–N5–Cd1) and forming a boat-like, six-membered ring (figure 4). The 4-position nitrogen of tetrazole bonds to another Cd, with tridentate tetrazole coordinating to two cadmiums and forming a distorted (4, 4) net (figure 5). Different from **1**, in compound **2** of two tetrazole ligands chelate Cd in the tetragonal plane (the dihedral angle of pyridine ring and tetrazole ring is 41.33(8)°). The axial positions have two nitrogens of two tetrazole rings from two different tetrazole ligands (figure 4). The distance of neighboring cadmiums is about 6.691 Å and the (4, 4) topology extends on the *bc* plane. All of these planes pack together in AA sequence along an axis in 3-D space, as shown in figure 6.

Tetrazole coordination compounds and inorganic–organic hybrid coordination polymers have been investigated for fluorescence with potential use as fluorescent solid-state materials. The solid state luminescence spectra of **1** and **2** at room

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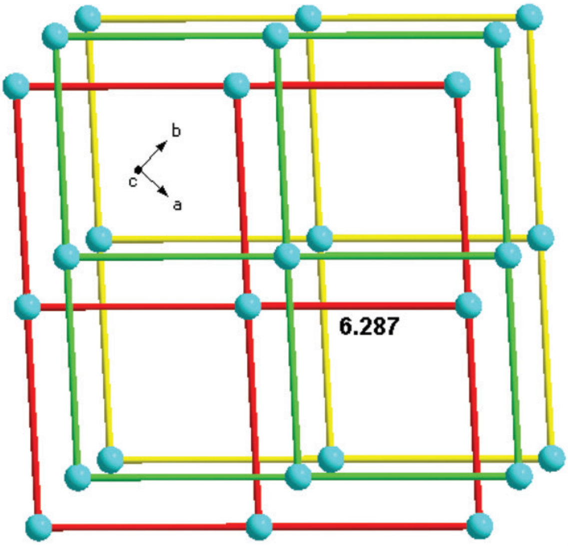

Figure 3. 3-D packing of **1** with ABA sequence; organic ligands were simplified with a long line and the distance between neighboring zinc centers is 6.287 Å.

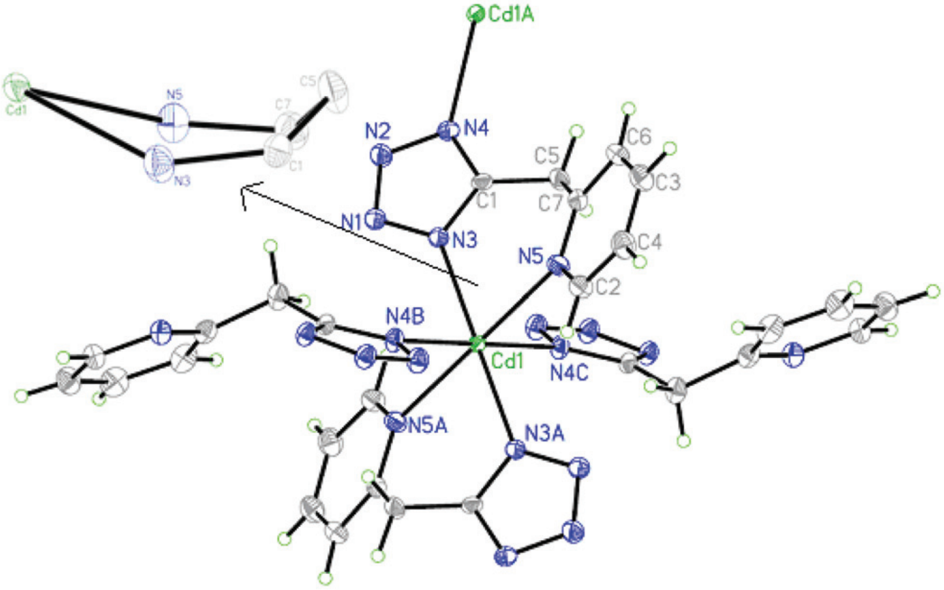

Figure 4. The molecular structure of **2**.

temperature are provided in "Supplementary material". When **1** and **2** are excited at 320 nm, they display similar fluorescence properties with emission at 390 nm, assigned to an intraligand fluorescent emission [15–23]. To study the thermal stability of the title compounds, thermogravimetric analysis (TGA) was performed on their polycrystalline samples (Supplementary material). Although coordination polymers **1**

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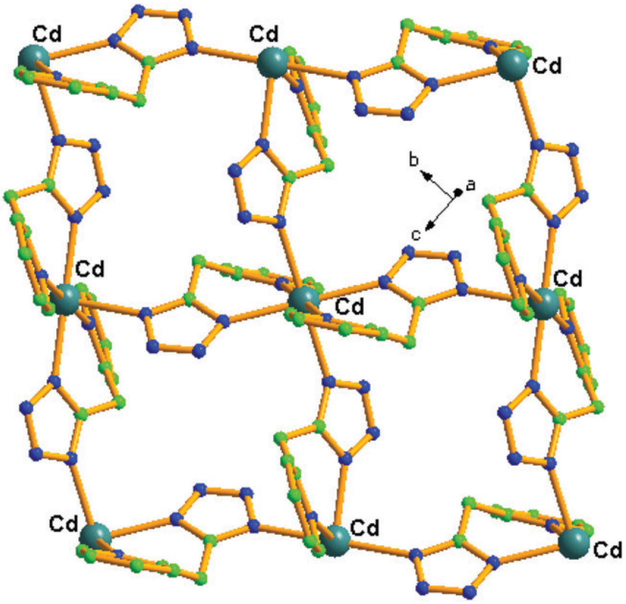

Figure 5. The 2-D structure of **2** with a (4, 4) net along a (Green ball: C; Blue ball: N).

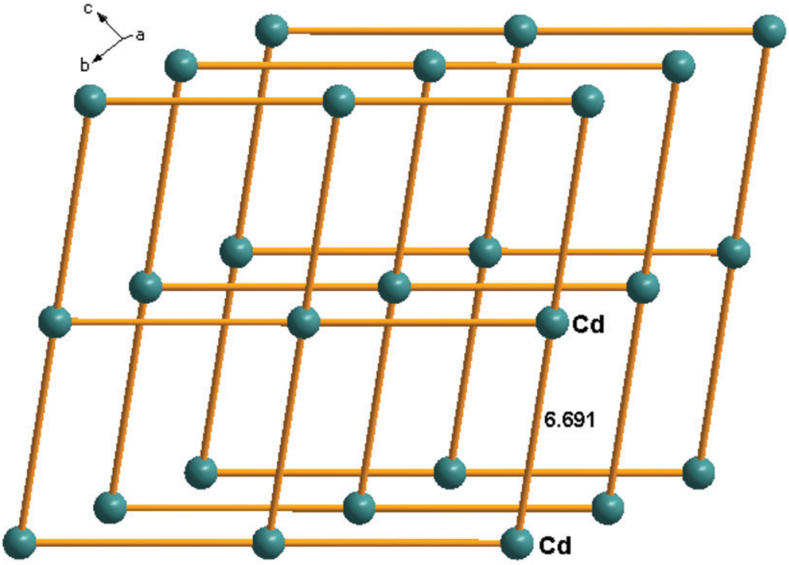

Figure 6. The 3-D packing of **2** with AA sequence; organic ligand is simplified with a long line and the distance between neighboring cadmiums is 6.691 Å.

and **2** show similar 2-D planar, their stabilities are different with **1** beginning decomposition at 120°C, while **2** begins decomposition at 180°C.

In conclusion, we have synthesized two *in situ* tetrazole coordination polymers based on 2-(pyridin-2-yl)acetonitrile under hydrothermal conditions. Although they display similar 2D (4, 4) net structures, the arrangements of 2D planes in 3D space are different. Solid state fluorescence measurements show both can be used as blue fluorescent materials.

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos 685658 for **1** and 685659 for **2**. Copies of this information may be obtained freely from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax (int. code) +44(1223)336-033 or Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). The solid state photoluminescent spectrum and thermogravimetric analysis curves of **1** and **2** have been shown in supplementary material.

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