

Syntheses, crystal structures and fluorescent properties of Cd(II), Hg(II) and Ag(I) coordination polymers constructed from 1H-1,2,4-triazole-1-acetic acid

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ABSTRACT

Three new d^{10} coordination polymers, namely $[\text{Cd}(\text{taa})\text{Cl}]_n$ **1**, $[\text{Hg}(\text{taa})\text{Cl}]_n$ **2**, and $[\text{Ag}_{1.5}(\text{taa})(\text{NO}_3)_{0.5}]_n$ **3** ($\text{taa} = 1\text{H-1,2,4-triazole-1-acetate anion}$) have been prepared and characterized by elemental analysis, IR, and single crystal X-ray diffraction. Compound **1** consists of two-dimensional layers constructed by carboxyl-linked helical chains, which are further linked through carboxyl group to generate a unique 3D open framework. Topological analysis reveals that the structure of **1** can be classified as an unprecedented (3,8)-connected network with the Schläfli symbol $(4.5^2)_2(4^2.5^8.6^{14}.7^3.8)$. Compound **2** manifests a doubly interpenetrated decorated α -polonium cubic network with the Schläfli symbol of $(4^{10}.6^2.8^3)$. Compound **3** consists of 2D puckered layers made up of Ag centers and taa^- bridges. In addition, all of these compounds are photoluminescent in the solid state with spectra that closely resemble those of the ligand precursor.

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1. Introduction

In past decades, the rational design and construction of metal-organic frameworks (MOFs) has attracted considerable attention in supramolecular and materials chemistry due to their enormous variety of interesting structural topologies as well as wide potential applications as functional materials [1–6]. Significant progress has been achieved in this field, however, the assembly of MOFs with predicted structures and properties is still a great challenge for chemists and material scientists because the resulting MOFs structures are determined by several factors, including the coordination nature of metal ions, the structural characteristics of the ligand, the counter anion, and so on. So, an effective approach to synthesize the desired MOFs is to choose appropriate ligands as “building block” and metal-connecting nodes. As a ligand with multiple coordination sites, 1,2,4-triazole has been shown to be good organic linker in generation of structurally versatile MOFs since it can bridge different metal centers to afford coordination polymers that exhibit extraordinary structural diversity and facile accessibility of functionalized new magnetic materials [7–10]. Furthermore, functional groups such as carboxylate, amino, and pyridyl, can be introduced in 1,2,4-triazole, which could make coordination chemistry of 1,2,4-triazole more abundant and complicated. Encouraged by all that

was mentioned above, we select a simple bifunctional ligand simultaneously containing 1,2,4-triazole and carboxylate groups, 1H-1,2,4-triazole-1-acetic acid monohydrochloride (Htaa), which is first used in the assembly of new MOFs, to study its coordination chemistry together with its potential application in material science. In this paper, we employ Htaa as the organic linker with luminescent d^{10} ions (Cd^{II} , Hg^{II} , and Ag^{I}) as metal centers to construct the new MOFs. Fortunately, our efforts lead to three novel compounds, namely $[\text{Cd}(\text{taa})\text{Cl}]_n$ **1**, $[\text{Hg}(\text{taa})\text{Cl}]_n$ **2**, and $[\text{Ag}_{1.5}(\text{taa})(\text{NO}_3)_{0.5}]_n$ **3**. All compounds are characterized by elemental analysis, IR spectrum and X-ray crystallography. The crystal structures as well as topological analysis of these compounds will be represented and discussed. In addition, the photoluminescence properties in the solid state are discussed in detail.

2. Experimental section

2.1. Materials and measurements

Htaa was prepared according to the literature [11]. All other starting materials were purchased as reagent-grade chemicals and used without further purification. Elemental analyses were performed on a Carlo-Erba 1160 elemental analyzer. The IR spectra were obtained as KBr disks on a Shimadzu IR 435 spectrometer. Thermogravimetric analyses were carried out on a NETZSCH STA409PC unit at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under an oxygen atmosphere. Luminescence spectra for the solid samples were recorded with a Hitachi 850 fluorescence spectrophotometer.

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2.2. Preparation of $[Cd(taa)Cl]_n$ **1**

A mixture of Htaa (0.50 mmol, 82 mg) and $CdAc_2 \cdot 2H_2O$ (0.50 mmol, 135 mg) in 10 mL of H_2O , was kept in a Teflon-lined autoclave at 175 °C for 72 h. After slowly cooling to room temperature, colorless prism crystals were obtained as a mono-phasic product. The crystals were manually selected and used for physical measurements. Yield: 92 mg (68% based on Cd). Anal. found (calcd.) for $C_4H_4N_3O_2ClCd$: C, 17.71 (17.52); H, 1.54 (1.46); N, 15.56 (15.33). IR (KBr, cm^{-1}): 3432(m), 3123(m), 2935(w), 1603(s), 1520(m), 1425(m), 1394(m), 1316(s), 1217(w), 1183(w), 1139(m), 1039(m), 989(w), 890(w), 794(m), 704(m), 665(m), 586(w).

2.3. Preparation of $[Hg(taa)Cl]_n$ **2**

An aqueous solution (6 mL) of Htaa (16.5 mg, 0.1 mmol) was dropwise added into an aqueous solution (1 mL) of $Hg(NO_3)_2 \cdot 1/2H_2O$ (334 mg, 0.1 mmol). The resulting reaction mixture was put at room temperature. Colorless needle-like crystals suitable for X-ray diffraction were obtained three days later. Yield: 28 mg (76% based on Hg). Anal. found (calcd.) for $C_4H_4N_3O_2ClHg$: C, 13.52 (13.26); H, 1.23 (1.11); N, 11.76 (11.60). IR (KBr, cm^{-1}): 3444(m), 3120(w), 2926(m), 2857(w), 1620(s), 1523(w), 1387(s), 1308(m), 1214(w), 1176(w), 1133(m), 1027(w), 882(w), 796(w), 671(m), 583(w).

2.4. Preparation of $[Ag_{1.5}(taa)(NO_3)_{0.5}]_n$ **3**

An aqueous solution (6 mL) of Htaa (16.5 mg, 0.1 mmol) was dropwise added into an aqueous solution (1 mL) of $AgNO_3$ (340 mg, 0.2 mmol). A white precipitate was immediately formed. The precipitate was filtered, and the filtrate was put at room temperature. Colorless needle-like crystals suitable for X-ray diffraction were obtained one day later. Yield: 27 mg (85% based on Htaa). Anal. found (calcd.) for $C_4H_4N_3O_3.5Ag_{1.5}$: C, 15.21 (15.05); H, 1.34 (1.26); N, 15.65 (15.37). IR (KBr, cm^{-1}): 3447(m), 3096(m), 1627(s), 1514(m), 1388(s), 1315(m), 1272(m), 1211(m), 1171(m), 1135(m), 1030(m), 961(m), 895(m), 798(m), 680(s), 582(w).

Table 1
Crystallographic data for compounds **1**, **2**, and **3**.

	1	2	3
Empirical	$C_4H_4N_3O_2ClCd$	$C_4H_4N_3O_2ClHg$	$C_4H_4N_3O_3.5Ag_{1.5}$
Mr	273.9	362.1	318.9
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
a (Å)	6.9552(14)	6.8780(12)	15.899(3)
b (Å)	12.592(3)	13.132(2)	7.2573(15)
c (Å)	7.9427(16)	8.1870(15)	13.543(3)
α (°)			
β (°)	108.81(3)	111.282(2)	111.32(3)
γ (°)			
V (Å ³)	658.5(2)	689.1(2)	1455.7(5)
Z	4	4	8
μ (mm ⁻¹)	3.663	2.669	4.051
D_c (g cm ⁻³)	2.763	3.491	2.910
F(000)	520	648	1208
Reflections	5617	3376	7972
Unique	1254	1214	1580
Goodness-of-fit	1.043	1.031	1.077
R_1 ($I > 2\sigma(I)$)	0.0382	0.0200	0.0339
wR ₂ (all data)	0.0874	0.0533	0.0769

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

Table 2
Selected bond lengths (Å) and angles (deg) for complex **1**, **2**, and **3**.

Compound 1 ^a			
Cd(1)–O(1)	2.472(4)	Cd(1)–Cl(1)	2.6497(16)
Cd(1)–N(3)#1	2.291(5)	Cd(1)–N(2)#2	2.395(5)
Cd(1)–O(1)#3	2.428(4)	Cd(1)–O(2)#3	2.567(5)
Cd(1)–Cl(1)#4	2.6481(17)		
N(3)#1–Cd(1)–N(2)#2	170.09(16)	N(3)#1–Cd(1)–O(1)#3	92.08(16)
N(2)#2–Cd(1)–O(1)#3	87.25(16)	N(3)#1–Cd(1)–O(1)	85.47(15)
N(2)#2–Cd(1)–O(1)	85.09(15)	O(1)#3–Cd(1)–O(1)	68.41(17)
N(3)#1–Cd(1)–O(2)#3	89.86(17)	N(2)#2–Cd(1)–O(2)#3	97.48(17)
O(1)#3–Cd(1)–O(2)#3	52.17(14)	O(1)–Cd(1)–O(2)#3	120.16(15)
N(3)#1–Cd(1)–Cl(1)#4	93.48(13)	N(2)#2–Cd(1)–Cl(1)#4	82.75(12)
O(1)#3–Cd(1)–Cl(1)#4	152.58(11)	O(1)–Cd(1)–Cl(1)#4	85.29(11)
O(2)#3–Cd(1)–Cl(1)#4	154.53(11)	N(3)#1–Cd(1)–Cl(1)	90.90(12)
N(2)#2–Cd(1)–Cl(1)	97.55(12)	O(1)#3–Cd(1)–Cl(1)	125.45(11)
O(1)–Cd(1)–Cl(1)	165.88(11)	O(2)#3–Cd(1)–Cl(1)	73.39(11)
Cl(1)#4–Cd(1)–Cl(1)	81.31(5)		
Compound 2 ^b			
Hg(1)–O(1)	2.591(3)	Hg(1)–O(1)#3	2.591(3)
Hg(1)–N(3)#1	2.117(4)	Hg(1)–N(3)#2	2.117(4)
Hg(2)–O(1)	2.615(3)	Hg(2)–Cl(1)	2.3333(13)
Hg(2)–O(1)#4	2.615(3)	Hg(2)–Cl(1)#4	2.3333(13)
N(3)#1–Hg(1)–N(3)#2	180.0(3)	N(3)#1–Hg(1)–O(1)#3	91.16(13)
N(3)#2–Hg(1)–O(1)#3	88.84(13)	N(3)#1–Hg(1)–O(1)	88.84(13)
N(3)#2–Hg(1)–O(1)	91.16(13)	O(1)#3–Hg(1)–O(1)	180.00(9)
Cl(1)#4–Hg(2)–Cl(1)	180.0	Cl(1)#4–Hg(2)–O(1)	85.06(8)
Cl(1)–Hg(2)–O(1)	94.94(8)	Cl(1)#4–Hg(2)–O(1)#4	94.94(8)
Cl(1)–Hg(2)–O(1)#4	85.06(8)	O(1)–Hg(2)–O(1)#4	180.0
Compound 3 ^c			
Ag(1)–O(1)#2	2.285(3)	Ag(1)–O(2)#3	2.331(3)
Ag(1)–N(2)	2.345(3)	Ag(1)–O(3)	2.532(3)
Ag(2)–N(3)#1	2.174(3)	Ag(2)–N(3)	2.174(3)
O(1)#2–Ag(1)–O(2)#3	138.00(12)	O(1)#2–Ag(1)–N(2)	107.50(12)
O(2)#3–Ag(1)–N(2)	92.29(10)	N(3)–Ag(2)–N(3)#1	179.999(1)

^a Symmetry transformations used to generate equivalent atoms in compound **1**: (#1) $-x+1, y-1/2, -z+1/2$; (#2) $x+1, y, z$; (#3) $-x+2, -y+1, -z+1$; (#4) $-x+2, -y+1, -z$.

^b Symmetry transformations used to generate equivalent atoms in compound **2**: (#1) $x-1, -y+1/2, z-1/2$; (#2) $-x+1, y-1/2, -z+1/2$; (#3) $-x, -y, -z$; (#4) $-x, -y, -z+1$.

^c Symmetry transformations used to generate equivalent atoms in compound **3**: (#1) $-x+2, -y, -z+2$; (#2) $-x+1, y, -z+3/2$; (#3) $x, -y, z+1/2$.

2.5. Single-crystal structure determination

The intensity data for **1–3** were collected at 291 K(2) on a Bruker Smart CCD diffractometer using graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.71073$ Å). All of the structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical constraints. Position disorder has been found for the oxygen atoms of NO_3^- anion for compound **3**. The final cycle of full-matrix least squares refinement was based on the observed reflections and variable parameters. All calculations were performed using the *SHELXL* crystallographic software package [12]. Table 1 shows crystallographic data of **1–3**. Selected bond distances and angles for compound **1–3** are listed in Table 2.

3. Results and discussion

3.1. Description of the crystal structures

3.1.1. Crystal structure of $[Cd(taa)Cl]_n$ **1**

Single-crystal X-ray structural analysis reveals that compound **1** crystallizes in the monoclinic space group $P2_1/c$, and consists of 1D helical chains. The asymmetric unit contains one Cd(II) ion,

one taa^- ligand, and one chlorine anion, in which each Cd(II) ion is seven-coordinated with a distorted $[\text{CdO}_3\text{N}_2\text{Cl}_2]$ pentagonal bipyramidal geometry. The coordination sphere around Cd(II) ion is composed of three oxygen atoms O1, O1#3, O2#3, two nitrogen atoms N2#2, N3#1 and two chlorine atoms Cl1 and Cl1#4 (Fig. 1). The equatorial plane is completed by O1, O1#3, O2#3 atoms from two equivalent taa^- ligands and two chlorine atoms (Cl1 and Cl1#4). The axial sites are occupied by two nitrogen atoms N2#2 and N3#1 provided by other two equivalent taa^- ligands. The Cd–O bond lengths vary from 2.428(4) to 2.567(5) Å. The Cd–Cl bond lengths are 2.6497(16) and 2.6481(17) Å, while the Cd–N bond lengths range between 2.291(5) and 2.395(5) Å. All lengths about Cd(II) ion are consistent with those reported in other Cd(II) complexes with distorted pentagonal bipyramidal geometry [13]. With its chelating-bridging carboxyl group and bridging triazole moiety, each taa^- ligand in compound **1** is bound to four Cd(II) centers acting as a tetradentate ligand. First, in the [010] direction adjacent Cd(II) ions are linked together by triazole N atoms (N2 and N3) to generate a single-chain helicate motif with a pitch of 12.592 Å (Fig. 2). Then the adjacent helical chains are fused through the coordination of the carboxyl oxygen atom (O1) from one chain to the Cd atom from the other, hence generating a 2D layer in the ab plane (Fig. 3). Therefore, the sheet can be considered as being constructed by carboxyl-linked helical chains. Within the layer, all carboxyl-linked helical chains display the same chirality. Eventually, the neighboring layers are pillared through the chelating-bridging junctions of O1 and O2 atoms from carboxyl group along the c -axis, leading to the formation of a 3D framework. Consequently, two contiguous Cd(II) ions are fused together by carboxyl group to give a bimetallic unit $[\text{Cd}_2(\text{CO}_2)_2]$ in the bc plane. In addition, chlorine atoms also participate in the inosculation acting as a bridging ligand (Fig. 4). In the whole framework, the adjacent layers display opposite chirality, so that compound **1** is racemic.

A better insight into the nature of this intricate framework can be achieved by the application of topological approach, reducing multidimensional structures to simple node and connection nets. As discussed above, if the $[\text{Cd}_2(\text{CO}_2)_2]$ unit is considered as a eight-connected node (connecting to six taa^- ligands and other two $[\text{Cd}_2(\text{CO}_2)_2]$ units), the taa^- ligand can be considered as a three-connected node (connecting to three bimetallic $[\text{Cd}_2(\text{CO}_2)_2]$ units), from the topological point of view, the structure of **1** can be classified as an unprecedented (3,8)-connected network with the Schläfli symbol $(4.5^2)_2(4^2.5^8.6^{14}.7^3.8)$ (Fig. 5).

3.1.2. Crystal structure of $[\text{Hg}(\text{taa})\text{Cl}]_n$ **2**

The structure analysis shows that compound **2** has a two fold interpenetrating 3D α -polonium cubic network. Compound **2** crystallizes in the monoclinic space group $P2_1/c$ and the asymmetric unit consists of two crystallographically distinct half-occupied mercury atoms, one taa^- ligand, and one chlorine atom. Both Hg1 and Hg2 atoms possess slightly distorted square

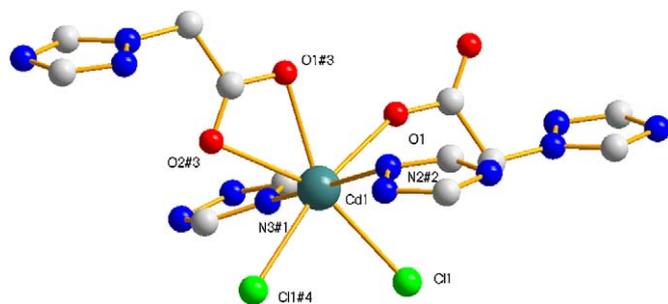


Fig. 1. The coordination environments around the Cd atom for **1**.

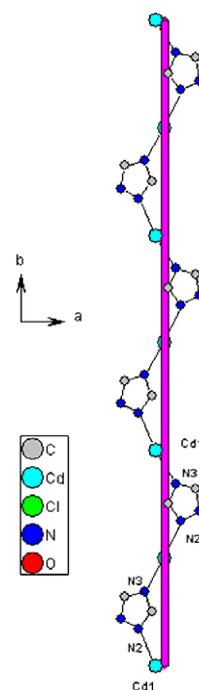


Fig. 2. Perspective view of the 1D helical chain of **1**.

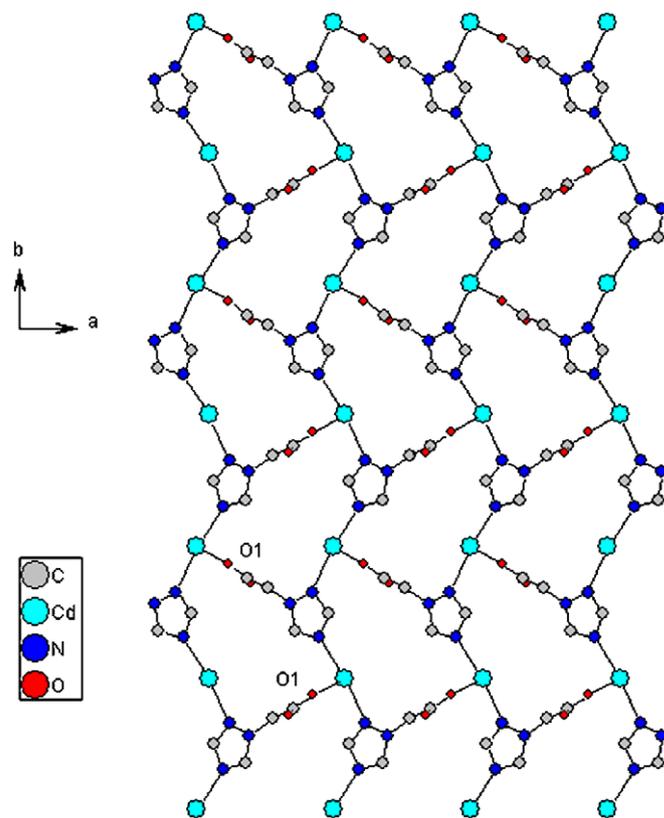


Fig. 3. View of 2D coordination layer in **1** along the crystallographic c -axis.

coordination geometries. Hg1 is coordinated to two oxygen atoms (O1 and O1#3) and two nitrogen atoms (N3#1 and N3#2) from four taa^- ligands with Hg1–O and Hg1–N bond lengths being 2.591(3) and 2.117(4) Å, respectively. The four coordination sites around Hg2 are provided by two oxygen atoms (O1 and O1#4) and two chlorine atoms (Cl1 and Cl1#4). The Hg2–O and Hg2–Cl bond

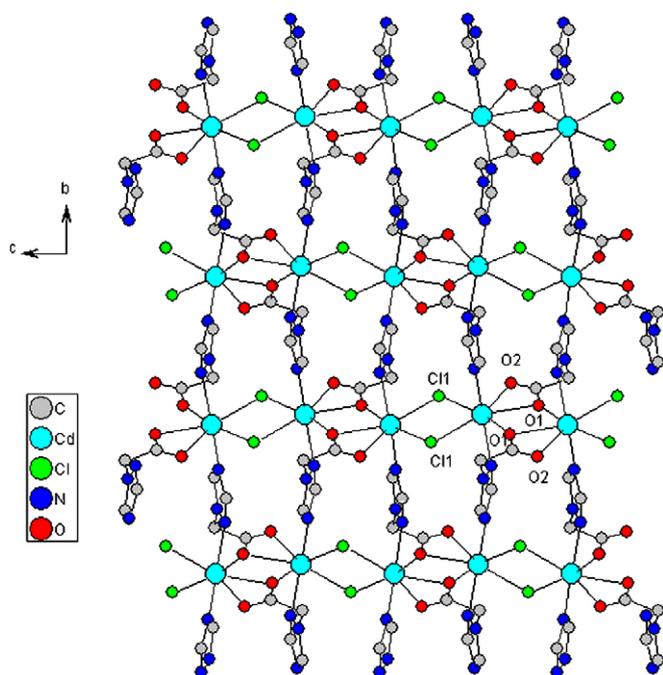


Fig. 4. Packing diagram of 1 viewed along the *a* axis.

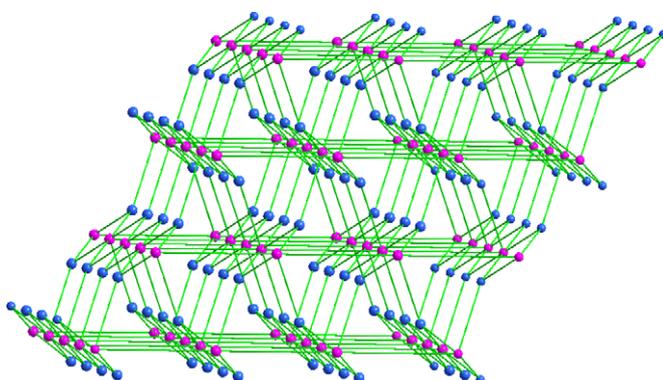


Fig. 5. View of the 3D (3,8)-connected network of $(4.5^2)_2(4^2.5^8.6^{14}.7^3.8)$ topology with purple nodes representing bimetallic $[Cd_2(CO_2)_2]$ units and blue ones representing the taa^- ligands.

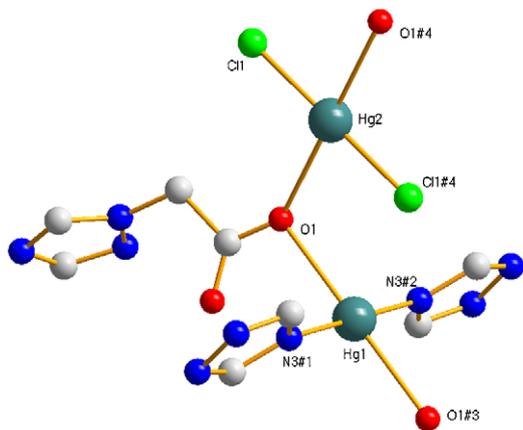


Fig. 6. The coordination environments around the Hg atom for 2.

lengths are 2.615(3) and 2.3333(13) Å, respectively (Fig. 6). Each taa^- ligand behaves as tridentate ligand, oxygen atom O1 connecting Hg1 and Hg2, and nitrogen atom N3 binding to Hg1.

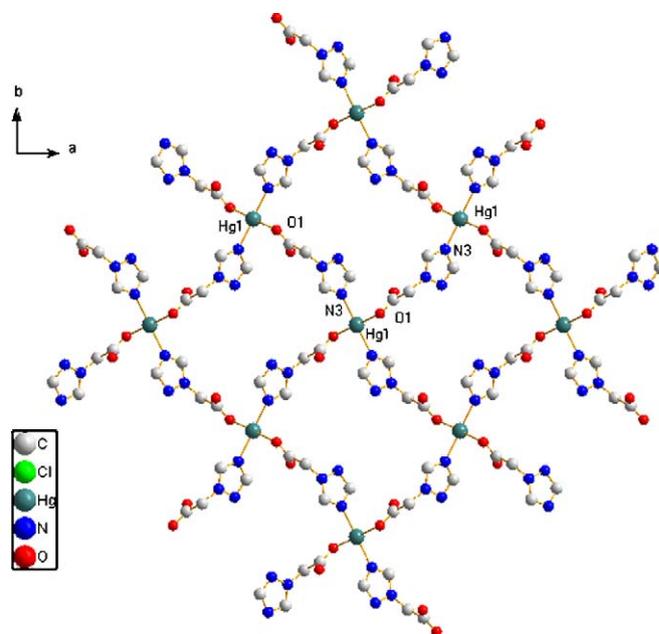


Fig. 7. View of 2D coordination layer in 2.

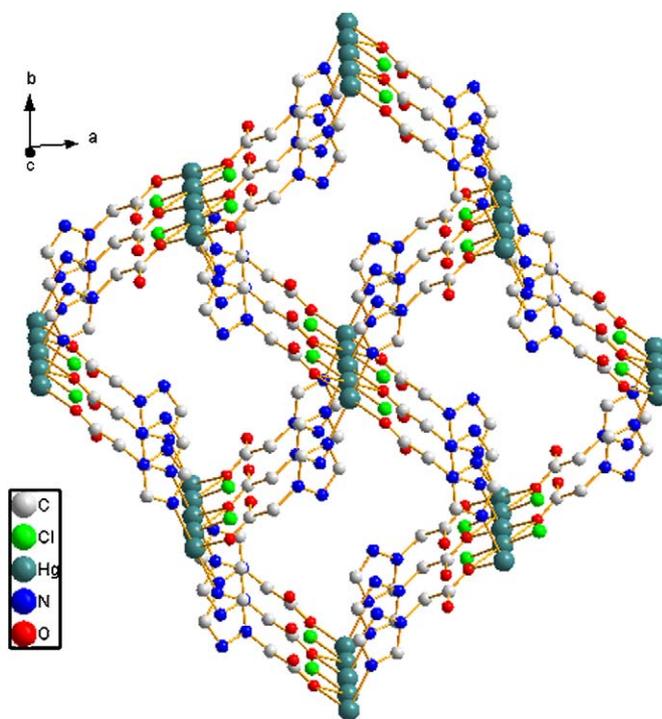


Fig. 8. View of the 3D α -polonium cubic network in 2. Hydrogen atoms are omitted for clarity.

As a result, each Hg1 center is linked to four adjacent Hg1 centers by four taa^- ligands resulting in a 2D dumbbell-like grid parallel to the [110] crystal planes with a $Hg \cdots Hg$ separation of 9.313 Å (Fig. 7). The O1 atom acts as a μ_3 -O and links Hg1 and Hg2 centers with the $Hg1 \cdots Hg2$ distance of 4.094 Å. On the basis of this connection mode, neighboring grids are further extended into a 3D coordination framework via the Hg2 atoms containing large cubic cages (Fig. 8). Because the single cubic network has spacious voids, it allows one more identical cubic network to interpenetrate giving rise to a two fold interpenetrating 3D α -polonium cubic network (Fig. 9).

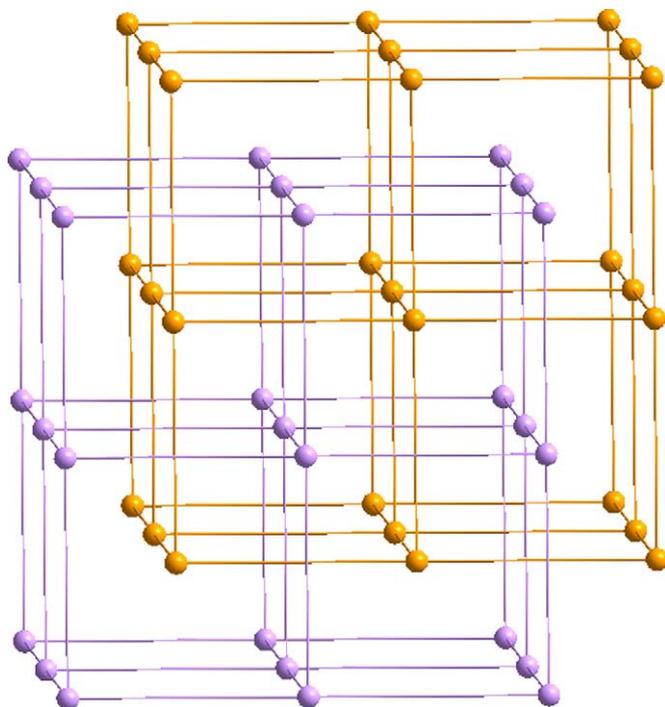


Fig. 9. Schematic diagram of the two fold interpenetrated α -polonium cubic network of **2**.

From a topological view, the formed 3D net of **2** can be best described as a doubly interpenetrated six-connected net with the Schläfli symbol of $(4^{10}.6^2.8^3)$, as depicted in Fig. 9, when the Hg1 centers are treated as six-connected nodes while taa^- ligands and Hg2 atoms as bridging linkers.

3.1.3. Crystal structure of $[\text{Ag}_{1.5}(\text{taa})(\text{NO}_3)_{0.5}]_n$ **3**

Single crystal structural analysis reveals that compound **3** crystallizes in the monoclinic space group $C2/c$, and consists of 2D puckered layers made up of Ag centers and taa^- bridges. As shown in Fig. 10, the asymmetric unit consists of one and a half crystallographically independent Ag(I) ions, one taa^- ligand, and half of NO_3^- anion, in which Ag(I) ions exhibit two types of coordination geometries. Two carboxyl oxygen atoms and one nitrogen atom from three equivalent taa^- ligands, and one oxygen atom from NO_3^- anion complete the four-coordinate environment of Ag1 atom, which conforms closely to a slightly distorted tetrahedron (Ag1–N2 2.345(3) Å; Ag1–O1#2 2.285(3) Å; Ag1–O2#3 2.331(3) Å; Ag1–O3 2.532(3) Å). Each Ag2 atom is coordinated in an exactly linear geometry by two triazole nitrogen atoms from two taa^- ligands (Ag2–N3 2.174(3) Å; N3–Ag2–N3#1 179.999(17)°). With its bridging carboxyl groups and triazole moieties, each taa^- ligand is bound to four Ag atoms. First, two adjacent Ag1 ions are joined together via O1 and O2 atoms from carboxyl group to generate a bimetallic unit $[\text{Ag}_2(\text{CO}_2)_2]$. In other words, each pair of adjacent Ag1 atoms, separated at 2.970 Å (Ag1–Ag1#4), is bridged by the bidentate carboxylate groups. The Ag...Ag interaction is proportional to the bite size of the carboxylate. It is noteworthy that such a distance is longer than the Ag...Ag separation of 2.88 Å in the metallic state [14,15], and is shorter than the sum of van der Waals radii of two silver atoms (3.44 Å) [14]. Then these bimetallic units are further connected through the N2 atoms from triazole moieties affording a 1D $\{\text{Ag}(\text{taa})\}_n$ chain propagating along the [001] direction. Eventually, the neighboring chains are fused through the coordination of Ag2 atoms to the N3 atoms along the a -axis,

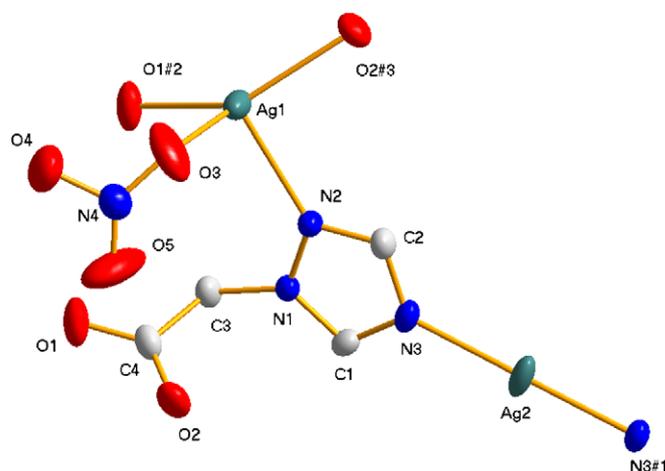


Fig. 10. The coordination environments of Ag atom in **3** with thermal ellipsoids drawn at 30% probability with the atomic labeling scheme. All hydrogen atoms are omitted for clarity.

hence resulting in a 2D puckered layers (Fig. 11). In addition, NO_3^- counter ions are located above and below the plane, neutralizing the charge of puckered layers. The 2D layer lies in the ac crystallographic plane and contains quadrate openings of a minimum 7.04×4.04 Å size as defined by the shortest transannular distance factoring van der Waals radii. The layers are noninterpenetrated despite the large cavity size. The adjacent layers are stacked offset with respect to each other in an ABAB fashion by van der Waals interactions into a 3D supramolecular network.

3.2. Thermogravimetric analysis and photoluminescent properties

TG data shows that compound **1** is thermally stable up to 270 °C. Subsequently, decomposition occurs in two steps with a total weight loss of 52.2% until 530 °C (Fig. 12). The first stage, which occurs from 270 to 290 °C, is attributed to the loss of the $\text{C}_2\text{H}_2\text{N}_3\text{-CH}_2\text{-CO}$ unit of the ligand. The observed weight loss (39.55%) is in agreement with the calculated value (40.15%). The second stage, occurring between 290 and 530 °C, corresponds to the loss of Cl^- anion. The residual percentage weight (observed 47.83%) is consistent with the formation of CdO (expected 46.87%).

The TG curve of **3** exhibits two well-separated weight loss stages (Fig. 10). The first, of 41.00% from 250 to 300 °C, corresponds to the loss of the total ligand (calcd: 41.38%). The second, of 8.85% from 390 to 480 °C, is equivalent to the loss of the NO_3^- counter ion (calcd: 9.72%). The remaining weight (50.15%) corresponds to a final product of Ag_2O (calcd: 50.79%).

It is well known that metal-organic polymers with a d^{10} closed-shell electronic configuration have been found to exhibit fluorescent properties. Here, the fluorescent properties of compounds **1–3** in solid state at room temperature are investigated (Figs. 13 and 14). Excitation at 380 nm leads to blue fluorescent emission band at 415 nm for the compounds **1,2**. The emission is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature since the Cd^{2+} , Hg^{2+} ions are difficult to oxidize or to reduce due to the d^{10} configuration. The emission can probably be assigned to the intraligand ($\pi\text{-}\pi^*$) fluorescent emission because the free ligand display fluorescent properties in solid state with the emission maximum being located at 410 nm. Compound **3** exhibits the photoluminescence with the emission maximum at 485 nm (excited at 405 nm), which means a red shift of ca. 75 nm relative to that of the free ligand. Considering that the structural difference between

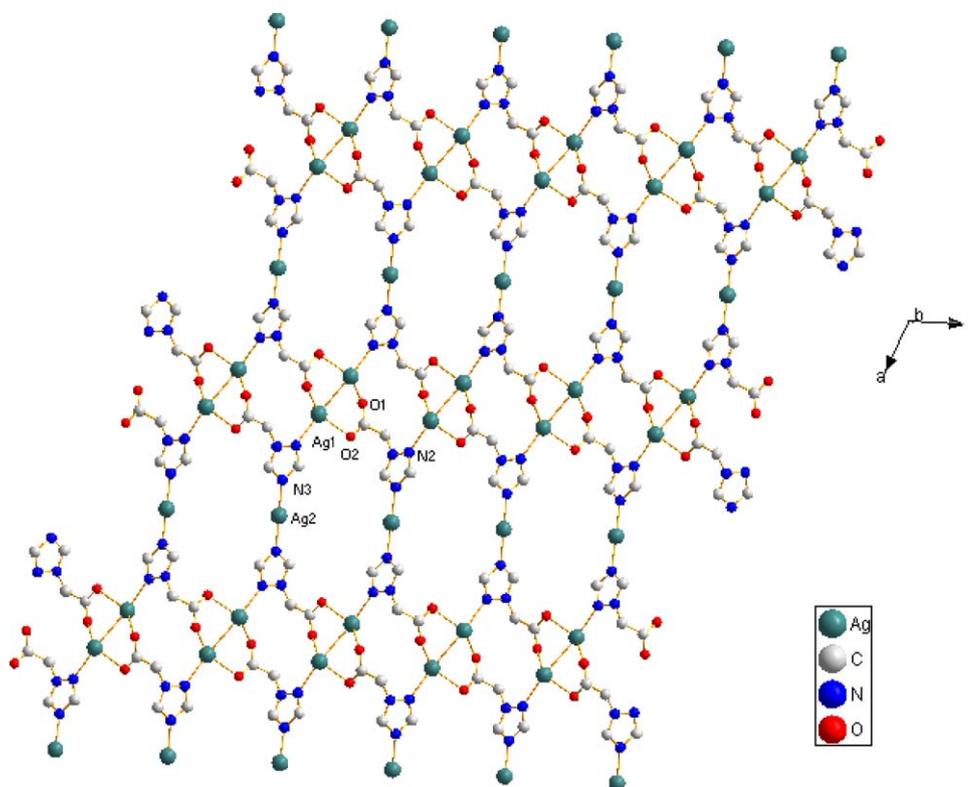


Fig. 11. 2D network structure of $[Ag_{1.5}(taa)(NO_3)_{0.5}]_n$ extended along the ac plane. H atoms and NO_3^- counter ions are omitted for clarity.

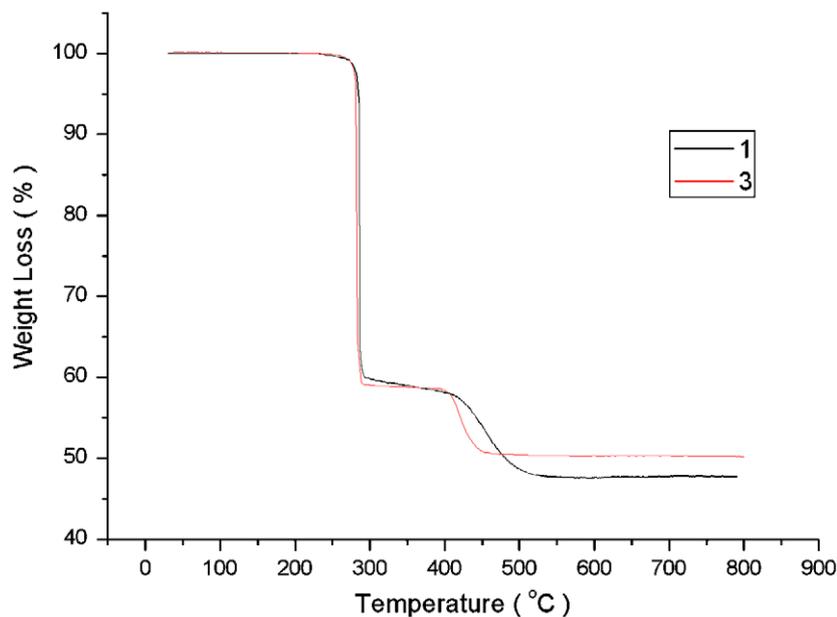


Fig. 12. TGA curves of compound 1 and 3.

compound 3 and compound 1,2, we believe that the short Ag...Ag interaction (2.970 \AA) is crucial contributing to the photoluminescent properties of compound 3.

4. Conclusions

In summary, we reported a set of coordination polymers based on different d^{10} ions (Cd^{2+} , Hg^{2+} , Ag^+), and 1H-1,2,4-triazole-1-

acetic acid that generate unusual networks with new topology. The crystal structure of 1 possesses an unprecedented 3D coordination framework of $(4.5^2)_2(4^2.5^8.6^{14}.7^3.8)$ topology containing carboxyl-linked helical chains. Compound 2 exhibits a doubly interpenetrated network with $(4^{10}.6^2.8^3)$ topology. Compound 3 consists of 2D puckered layers made up of Ag centers and taa^- bridges. All these compounds display luminescent properties and may be potential candidates for luminescent materials.

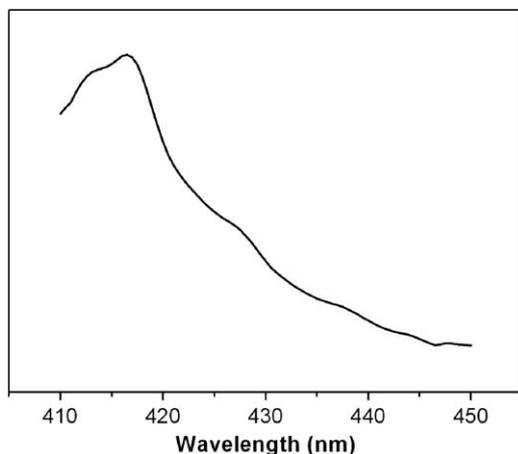


Fig. 13. Emission spectra of compound 1, 2 at 298 K in solid state.

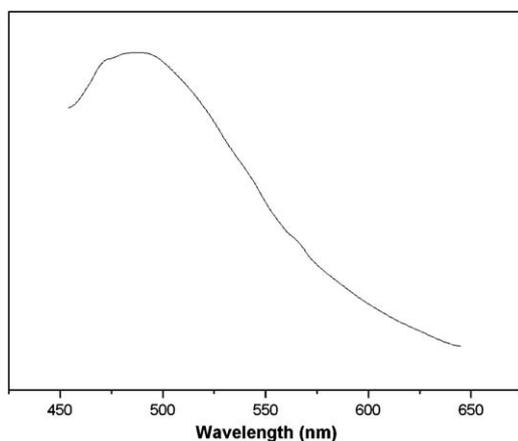


Fig. 14. Emission spectra of compound 3 at 298 K in solid state.

Supplementary information

Crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Centre with CCDC numbers

694121, 694122, and 694123 for compounds **1–3**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk; or <http://www.ccdc.cam.ac.uk>).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.02.026.

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