

A Novel Layer Cadmium Coordination Polymer Containing Tetranuclear $[\text{Cd}_4(\text{tpt})_2(\text{Cl})_4]^{4+}$ as a Secondary Building Unit (SBU) Bridged by Pyridine 2,4-Dicarboxylic Acid^①

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ABSTRACT A novel 2-D $\{[\text{Cd}_4(\text{tpt})_2(\text{Cl})_4(2,4\text{-pdc})_2]\cdot 4\text{H}_2\text{O}\}_n$ (**1**) has been synthesized from the hydrothermal reaction of 3,5,6-tris(2-pyridyl)-1,3,5-triazine (tpt), hydrated CdCl_2 , and 2,4-dicarboxylic acid (2,4- H_2pdc). Compound **1** crystallizes in triclinic, $P\bar{1}$ space group with $\alpha = 8.9434(5)$, $b = 9.5486(7)$, $c = 17.5772(8)$ Å, $a = 75.014(5)$, $\beta = 83.778(5)$, $\gamma = 68.304(6)^\circ$, $V = 1347.14(14)$ Å³, $\text{C}_{50}\text{H}_{38}\text{Cd}_4\text{Cl}_4\text{N}_{14}\text{O}_{12}$, $M_r = 1618.32$, $D_c = 1.990$ g/cm³, $S = 0.95$, $\mu(\text{MoK}\alpha) = 1.83$ mm⁻¹, $F(000) = 788$, $Z = 1$, $R = 0.039$ and $wR = 0.080$. The structure consists of tetranuclear $[\text{Cd}_4(\text{tpt})_2(\text{Cl})_4]^{4+}$ cores as the secondary building unit, which is further connected by the ligand pdc^{2-} to give a 2-D extended structure. Tpt entities are located on both sides of each 2-D framework and act as ‘side arms’ to form a corrugated layer and the adjacent layers are arranged in a tongue-and-groove interdigitating fashion. **1** was characterized by IR, TGA, PX1RD, and elemental analysis. The solid state luminescent properties were also investigated at room temperature.

Keywords: cadmium, cluster, luminescence, crystal structure, solvothermal synthesis

1 INTRODUCTION

Much interest has been directed toward the research of novel materials based on metal-organic frameworks (MOFs), which is driven not only by their fascinating topologies, but also by their potential applications as functional materials in many fields such as molecular magnet, catalysis, gas separation and storage, nonlinear optics, and photoluminescent materials^[1–5]. Rational design and synthesis of cluster-based MOFs is one of the most effective methods to get some fascinating functional materials, since metal clusters are much better than

single metal ions at constructing specific geometries and endowing physical properties to MOFs^[6]. Usually, polynuclear metal clusters with more coordination sites are effectively used as nodes for the construction of higher-connected topologies due to their large surface areas, which are beneficial to accommodate the steric demands of organic ligands. As is known, the most important factor in determining the resulting materials is the selected ligands. The polytopic ligand 3,5,6-tris(2-pyridyl)-1,3,5-triazine (tpt) is a ligand of current interest, because of its multiple coordination sites and large π system. The inherently rigid backbone and the

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extended aromatic system favor the formation of non-covalent cooperative forces such as π - π interactions and/or hydrogen bonds. Although the coordination chemistry of tpt has been investigated towards Ru(II), Re(II), Fe(II), Ag(I), Zn(II), Cd(II) and Mn(II)^[7-12], cluster-based MOFs on the basis of tpt have been seldom reported.

Polynuclear d^{10} metal compounds have been extensively studied for their fascinating photo-luminescent properties^[13]. Consequently, a series of d^{10} metal-organic framework with tetra, hexa, and even octanuclear clusters have been synthesized by the reaction of Cd(II)/Zn(II) salts and different organic ligands, where those compounds possess interesting supramolecular structures and emission properties. In this context, our synthetic strategy is to fabricate new topological frameworks by the self-assembly of tpt, pyridine 2,4-dicarboxylic acid (2,4-H₂pdc), and Cd^{II} ion, because many studies showed that the mixed ligands may play different roles in structural construction and functional properties of the resulting products^[14]. A novel 2-D layer complex $\{[\text{Cd}_4(\text{tpt})_2(\text{Cl})_4(2,4\text{-pdc})_2]\cdot 4\text{H}_2\text{O}\}_n$ (**1**) with a tetranuclear $[\text{Cd}_4(\text{tpt})_2(\text{Cl})_4]^{4+}$ core as a secondary building unit (SBU) was obtained. The compound was characterized by IR, TGA, PXRD, and elemental analysis. Its single-crystal structure was determined by X-ray crystallography and the solid-state luminescence properties of **1** were investigated at room temperature.

2 EXPERIMENTAL

2.1 Reagents and instruments

Materials and instruments: 3,5,6-tris(2-pyridyl)-1,3,5-triazine (tpt), 2,4-dicarboxylic acid (2,4-H₂pdc), and CdCl₂·5/2H₂O were purchased from Aldrich. Other chemicals were of reagent grade and used without further purification. All manipulations were performed without precaution to exclude air or moisture unless otherwise stated. IR spectrum was obtained in the 4000~400 cm⁻¹ range as KBr discs with a Nicolet 360 FTIR spectrophotometer. Ele-

mental analysis was performed with an Elementar Vario EL Analyzer. Thermogravimetric analysis experiments were carried out with a Perkin-Elmer TGA7 thermogravimetric analyzer with the heating rate of 10 °C·min⁻¹ from 30 to 600 °C in a nitrogen atmosphere. Fluorescence spectrum of **1** was recorded with an F-2500 FL Spectrophotometer analyzer.

2.2 Synthesis of 1

The mixture of 3,5,6-tris(2-pyridyl)-1,3,5-triazine (50.0 mg, 0.16 mmol), pyridine 2,4-dicarboxylic acid (53.5 mg, 0.32 mmol) and CdCl₂·5/2H₂O (80.0 mg, 0.35 mmol) in a mixed solvent of EtOH and H₂O (15 mL, v/v = 2:1) was heated in a 25 mL bomb at 433 K for 3 d, then cooled to room temperature at a rate of 6 K·h⁻¹. Colorless block crystals suitable for X-ray analysis were obtained in a yield of 55% based on the ligand 3,5,6-tris(2-pyridyl)-1,3,5-triazine. The product was washed with EtOH and H₂O, and then air-dried at ambient temperature. Elemental analysis for C₅₀H₃₄Cd₄Cl₄N₁₄O₁₂ found: C, 37.30; H, 2.22; N, 12.10%. Calcd.: C, 37.22; H, 2.12; N, 12.15%. Selected IR (KBr, cm⁻¹): 1627 (m), 1589 (m), 1574 (w), 1551 (s), 1531 (s), 1379 (s), 1355 (m), 1259 (w), 1008 (w), 772 (s), 729 (m), 687 (m).

2.3 Structure determination

A colorless single crystal of **1** with dimensions of 0.30mm × 0.20mm × 0.04mm was chosen for X-ray diffraction analysis performed on an Oxford CCD diffractometer using a graphite-monochromated MoK α radiation (λ = 0.71073 Å) at 298(2) K. Cell parameters were measured using the SMART software^[15]. Data were corrected for Lorentz and polarization effects using the program SAINT^[16]. Absorption corrections were applied with SADABS^[17]. A total of 8787 reflections were collected in the range of 2.45< θ <25.02° at room temperature. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms, except those of water molecules which were located from Fourier map directly, were treated using the riding mode. The final cycle of full-matrix least-squares refinement on F^2 was based on 4767 unique reflections and 379 variable parameters. All

calculations were carried out with SHELXL-97 programs^[18-19]. Selected bond distances and bond angles of **1** are summarized in Table 1.

Table 1. Selected Bond Parameters (Å, °) for **1**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Cd(1)–O(2) ⁱ	2.324(3)	Cd(1)–Cl(2) ⁱⁱⁱ	2.5940(15)	Cd(2)–N(2)	2.363(4)
Cd(1)–N(7) ⁱ	2.358(5)	Cd(1)–Cl(2)	2.6343(16)	Cd(2)–N(1)	2.437(4)
Cd(1)–O(4) ⁱⁱ	2.398(4)	Cd(2)–O(4) ⁱⁱ	2.248(4)	Cd(2)–N(5)	2.497(5)
Cd(1)–Cl(1)	2.5258(15)	Cd(2)–O(1)	2.291(4)	Cd(2)–Cl(1)	2.7061(15)
Angle	(°)	Angle	(°)	Angle	(°)
O(2) ⁱ –Cd(1)–N(7) ⁱ	71.05(15)	O(2) ⁱ –Cd(1)–Cl(2)	90.97(10)	N(2)–Cd(2)–N(1)	67.52(16)
O(2) ⁱ –Cd(1)–O(4) ⁱⁱ	95.61(13)	N(7) ⁱ –Cd(1)–Cl(2)	83.90(12)	O(4) ⁱⁱ –Cd(2)–N(5)	78.09(15)
N(7) ⁱ –Cd(1)–O(4) ⁱⁱ	96.56(15)	O(4) ⁱⁱ –Cd(1)–Cl(2)	173.19(10)	O(1)–Cd(2)–N(5)	94.67(15)
O(2) ⁱ –Cd(1)–Cl(1)	97.38(10)	Cl(1)–Cd(1)–Cl(2)	101.30(5)	N(2)–Cd(2)–N(5)	66.80(15)
N(7) ⁱ –Cd(1)–Cl(1)	167.55(12)	O(4) ⁱⁱ –Cd(2)–N(2)	114.51(16)	O(1)–Cd(2)–Cl(1)	87.34(10)
O(4) ⁱⁱ –Cd(1)–Cl(1)	79.63(10)	O(1)–Cd(2)–N(2)	90.06(15)	N(2)–Cd(2)–Cl(1)	155.04(11)
O(2) ⁱ –Cd(1)–Cl(2) ⁱⁱⁱ	159.39(10)	O(4) ⁱⁱ –Cd(2)–N(1)	116.52(15)	N(1)–Cd(2)–Cl(1)	87.70(12)
N(7) ⁱ –Cd(1)–Cl(2) ⁱⁱⁱ	88.49(12)	O(1)–Cd(2)–N(1)	91.10(15)	N(5)–Cd(2)–Cl(1)	138.15(10)

Symmetry codes: (i) $-x+2, -y+1, -z$; (ii) $x+1, y-1, z$; (iii) $-x+2, -y, -z$

3 RESULTS AND DISCUSSION

3.1 Synthesis and characterization of compound **1**

Solvothermal reaction of tpt, 2,4-H₂pdc and hydrated CdCl₂ in a molar ratio of 1:1:1.2 in a mixed solvent EtOH/H₂O (15 mL; v:v = 2:1) afforded the 2-D layer structure {[Cd₄(tpt)₂(Cl)₄(2,4-pdc)₂·4H₂O]₂ (**1**) with moderate yield. In the IR spectrum of **1**, the absorption bands resulting from skeletal vibrations of the aromatic ring are observed in the range of 1600~1400 cm⁻¹. The absence of the stretching bands round 1700 cm⁻¹ for the characteristic ν(C=O) bands of carboxylate group in **1** indicates the complete coordination and deprotonation of carboxylic acids of the ligand 2,4-H₂pdc. The IR also shows the presence of ν_{as}(COO) stretching bands at 1627 and 1589 cm⁻¹ and ν_s(COO) stretching band at 1379, 1355 cm⁻¹, respectively. The frequency separations (Δν) between the asymmetric (ν_{as}) and symmetric (ν_s) stretching modes of the carboxylic units also provide an indication of its coordination mode.

3.2 Structural description of compound **1**

The crystal structure of **1** was determined by X-ray crystallography, as shown in Fig. 1. **1** crystallizes in triclinic $P\bar{1}$ space group and its asymmetric unit includes two crystallographically independent cadmium atoms, one tpt, one 2,4-pdc²⁻ and two Cl⁻ ligands and four lattice water molecules. This structure is composed of a 2-D framework with an unprecedented [Cd₄(tpt)₂(Cl)₄]⁴⁺ core as SBU (Fig. 1). The extended structure may be described in terms of the interconnected [Cd₄(tpt)₂(Cl)₄]⁴⁺ subunits bridged by the 2,4-pdc²⁻ ligands (Fig. 2). Four Cd atoms are clustered by virtue of four Cl⁻ and two O donors from two symmetry-related 2,4-pdc²⁻ ligands. There is a crystallographically imposed inversion point on the mid-point of Cd(1) and Cd(1)ⁱ (symmetry code *i*: $-x+2, -y, -z$). Four Cd atoms, six 2,4-pdc²⁻ ligands, two tpt ligands, and four Cl⁻ are related to each other by this inversion point in the SBU. It is interesting to note that three four-membered rings in the SBU, namely Cd(2)–O(4)ⁱⁱ–Cd(1)–Cl(1), Cd(1)–Cl(2)–Cd(1)ⁱⁱⁱ–Cl(2)ⁱⁱⁱ, and Cd(1)ⁱⁱⁱ–Cl(1)ⁱⁱⁱ–Cd(2)^{iv}–O(4)^{iv}, are linearly arranged (symmetry codes: (i) $-x+2, -y+1, -z$; (ii) $x+1, y-1, z$; (iii) $-x+2, -y, -z$; (iv) $x, y-1, z$). The central

four-membered ring forms the dihedral angle with respect to two symmetry-related four-membered rings with the value of 77.3° . The tpt acts as a tridentate ligand that bonds to a Cd atom *via* three N donors. The tpt also forms H-bonding interaction with the lattice water molecules, which is indicated by shorter distances of 2.884 and 3.336 Å for $\text{N}(6)\cdots\text{O}(6)$ and $\text{N}(3)\cdots\text{O}(6)$ separations, respectively. The lattice water molecules also form strong

H-bonding with O atoms from carboxylate groups in the $2,4\text{-pdc}^{2-}$ ligands, which are indicated by the $\text{O}\cdots\text{O}$ separations in the range of $2.832\sim 3.123$ Å. Moreover, a strong H-bonding interaction between two lattice water molecules is found with the $\text{O}(5)\cdots\text{O}(5)^a$ separation with a value of 2.504 Å (symmetry code (a) $-x+1, -y+1, -z+1$). The detailed H-bonding parameters are summarized in Table 2. The four heterocycles in tpt are perfectly coplanar.

Table 2. Hydrogen Bond Lengths (Å) and Bond Angles ($^\circ$)

D–H $\cdots$ A	D–H	H $\cdots$ A	D $\cdots$ A	D–H $\cdots$ A
$\text{O}(5)\text{--H}(5\text{A})\cdots\text{O}(5)^a$	0.85	1.66	2.504(18)	176
$\text{O}(5)\text{--H}(5\text{D})\cdots\text{O}(6)$	0.85	2.28	3.123(11)	173
$\text{O}(6)\text{--H}(6\text{C})\cdots\text{N}(6)$	0.85	2.39	2.884(7)	118
$\text{O}(6)\text{--H}(6\text{C})\cdots\text{N}(3)$	0.85	2.60	3.336(6)	146
$\text{O}(6)\text{--H}(6\text{A})\cdots\text{O}(3)^a$	0.85	2.09	2.832(6)	145

Symmetry codes: (a) $-x+1, -y+1, -z+1$

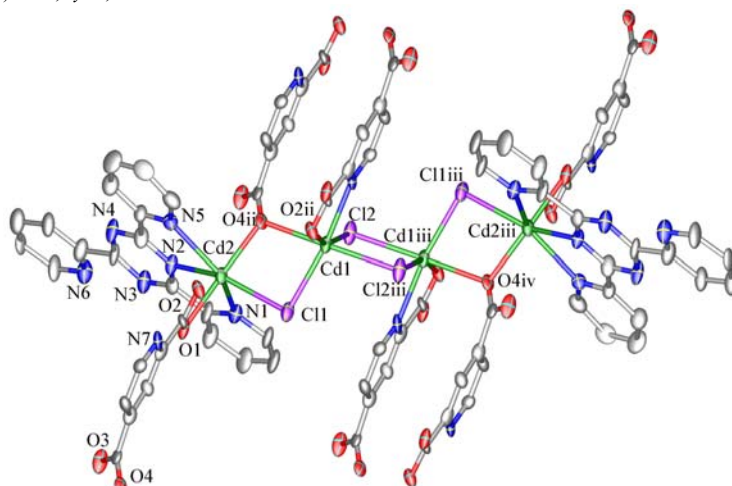


Fig. 1. Structural fragment of 1 showing the coordination environments of metal centres (Symmetry codes: (i) $-x+2, -y+1, -z$; (ii) $x+1, y-1, z$; (iii) $-x+2, -y, -z$; (iv) $x, y-1, z$)

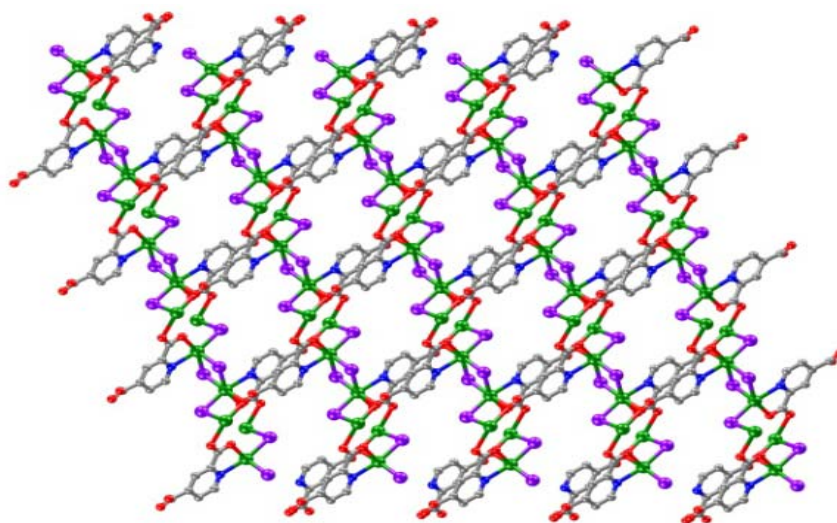


Fig. 2. Extended structure of 1 along the *ac* plane (tpt ligands were omitted for clarity)

The Cd(1) atom is octahedrally coordinated by one N and two O donors from two symmetry-related 2,4-pdc²⁻ ligands, and three Cl⁻ ligands. The Cd(2) atom is also octahedrally coordinated by three N donors from a tpt, two 2,4-pdc²⁻ ligands donating two carboxyl O donors, and one Cl⁻ ligand. The coordination geometry of Cd(2) is more distorted than that of Cd(1), due to the steric demand of tpt ligand. Thus, the structural unit is built up from four edge-sharing distorted octahedra as the repeating structural motif (Fig. 3). The *cis*-bond angles around the Cd(1) and Cd(2) metal centres in the ranges of 71.05 ~ 97.38° and 66.80 ~ 94.67°, respectively, while the *trans*-bond angles fall in the 101.30 ~ 173.19° and 114.54 ~ 155.04° ranges, respectively. The Cd–N bond distances vary from 2.358(5) to 2.497(5) Å and the Cd–O bond distances are in the range of 2.248(4) ~ 2.398(4) Å. The Cd–Cl bond distances change from 2.5258(15) to 2.7061(15) Å. These bond parameters are in accordance with the previously reported Cd(II) coordination compound^[20].

The Cd(1) and Cd(2) atoms are doubly bridged by a Cl⁻ and monoatomic O(2)ⁱⁱ atom from a carboxylate with a separation of 3.784 Å, while the Cd(1) and Cd(1)ⁱⁱⁱ are also doubly bridged by two Cl⁻ ligands with a separation of 3.721 Å. These Cd...Cd distances are close to the *ca.* 3.8 Å in the related

edge-sharing polymers^[21]. The Cd(1)–O(4)ⁱⁱ–Cd(2) bond angle is 109.1°, while the Cd(1)–Cl(1)–Cd(2) bond angle is 92.6°. The Cd(1)–Cl(2)ⁱⁱⁱ–Cd(1)ⁱⁱⁱ in the central four-membered ring is close to a right angle (90.7°). The two carboxylate groups in the 2,4-bpc²⁻ ligand have distinct bridging modes: the 2-position carboxylate group (O(1)–C(19)–O(2)) links two different Cd atoms *via* a $\mu_2\text{-}\eta^1\text{:}\eta^1$ syn-anti bridging mode, while the 4-position carboxylate group (O(3)–C(25)–O(4)) links two Cd atoms *via* a $\mu_2\text{-}\eta^2\text{:}\eta^0$ mode. Thus, the 2,4-bpc²⁻ ligand actually acts as a pentadentate bridging ligand linking four distinct Cd atoms. All the Cl⁻ ligands in the SBU act as the μ_2 -bridging ligand linking two Cd atoms. Each subunit is further connected to each other *via* six bridging 2,4-bpc²⁻ ligands. If the [Cd₄(tpt)₂(Cl)₄]⁴⁺ cores are taken as nodes and the 2,4-bpc²⁻ ligands are taken as linkers of a topological network, a 4⁴ grid-like topological architecture with a grid length of 8.94 Å is generated, as shown in Fig. 4. In each layer, extensive offset face-to-face π - π stacking interactions among pyridyl rings of 2,4-bpc²⁻ ligands have been observed, where the average centroid-to-centroid distance is 3.389 Å. The π - π stacking interactions also are found between the pyridyl rings of tpt ligand; however, the centroid-to-centroid distance is obviously longer with a value of 3.963 Å.

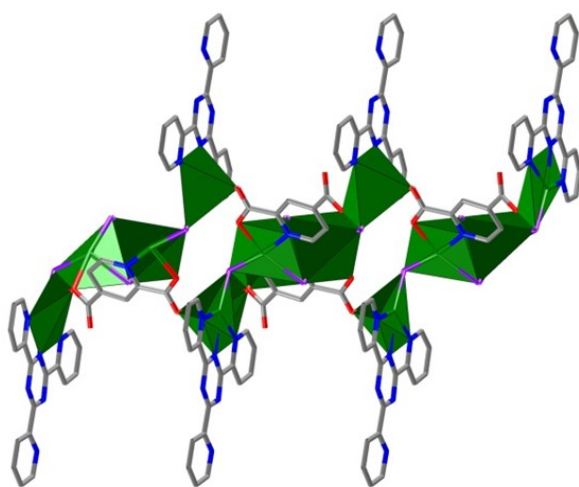


Fig. 3. Perspective view showing the edge-sharing octahedra

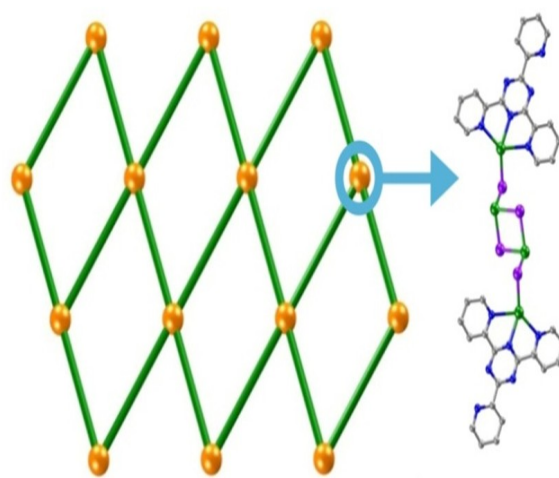


Fig. 4. Topological view of 2-D framework of 1 showing 4⁴ grid structure by the linkages of 2,4-pdc²⁻ ligands and [Cd₄(Cl)₄(tpt)₂]⁴⁺ clusters as nodes

A side view of the layer structure along the *bc* plane indicates that the tpt entities are located at both sides of each 2-D framework and act as ‘side arms’ to form a corrugated layer. As a consequence, such arrays exhibit the unique structural feature of 3-D stacking, which are alternately arranged in a tongue-and-groove interdigitating fashion (Fig. 5). The presence of significant interlayer aromatic stacking between the tpt ligands further stabilizes the whole

framework. The centroid-to-centroid separation of the neighbouring aromatic rings is *ca.* 3.509 Å, respectively. Such π - π stacking interactions lead to a fascinating supramolecular architecture^[22]. To our best knowledge, only a few cadmium-containing MOFs are constructed by high nuclearity clusters (more than four Cd^{2+} ions) as SBUs, while the MOFs containing tetranuclear SBU that was clustered by Cl⁻ ligands are seldom reported^[23].

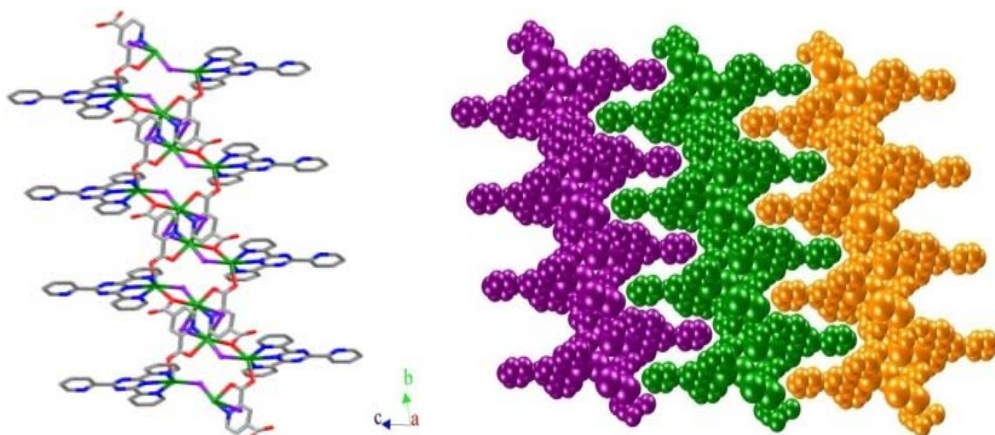


Fig. 5. Packing diagram showing the significant interlayer aromatic stacking between the tpt ligands

3.3 Thermal stability and PXRD of 1

The thermal behaviour of **1** was studied by thermogravimetric analysis (TGA) under a N_2 atmosphere with a heating rate of 10 °C/min (Fig. 6). Compound **1** loses its water molecules in the range of 90~265 °C with the weight loss of 4.41%, corresponding to the removal of its two lattice water molecules per formula unit (calcd. 4.45%). Then the compound decomposes rapidly from 325 °C. To

confirm whether the crystal structure is truly representative of the bulk materials tested in photochemical studies, PXRD experiment was carried out for compound **1**. The PXRD experimental and computer-simulated patterns of **1** show that the bulk synthesized materials and the measured single crystals of **1** are the same. The differences in intensity may be due to the preferred orientations of powder samples (Fig. S1).

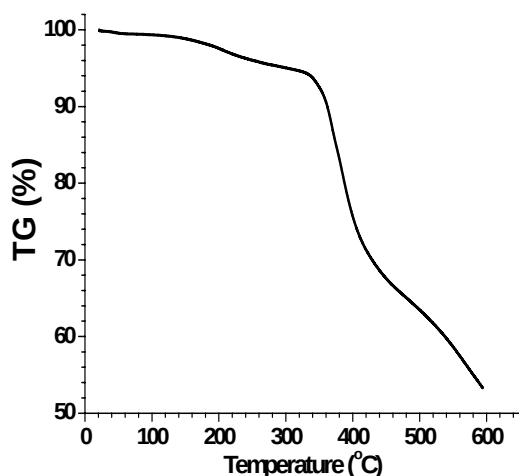


Fig. 6. TG curve of **1**

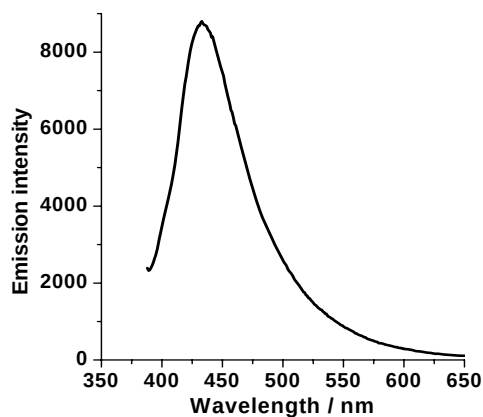


Fig. 7. Emission spectrum of **1** at room temperature

3.4 Luminescent properties of **1** at room temperature

The luminescent properties of complexes with d^{10} metal centres are of great interest for their potential applications in photochemistry, chemical sensors, and electroluminescent display^[13]. The luminescence properties of compound **1** were investigated in the solid state at room temperature. As shown in Fig 7, an intense emission band was observed at $\lambda_{\text{em}} = 432$ nm between blue and green emissions upon the excitation at $\lambda_{\text{ex}} = 379$ nm. Considering the emission spectrum of free tpt with $\lambda_{\text{em}} = 495$ nm^[24], the observed emission band of **1** may result from intra-ligand $\pi \rightarrow \pi^*$ transition between the π -bonding orbital (HOMO) and π^* -antibonding orbital (LUMO) of tpt ligand, rather than metal-to-ligand charge

transfer (MLCT) or ligand-to-metal charge transfer (LMCT) in nature^[25].

4 CONCLUSION

A cadmium(II) adduct containing the mixed ligands tpt and H_2pdc has been prepared and characterized and its crystal structure has been studied by X-ray single-crystal diffractions. A Cd_4Cl_4 cluster acts as the SBU. The tpt entities are located at both sides of each 2-D framework and act as 'side arms' to form a corrugated layer. The layers are stacked in arranged tongue-and-groove interdigitating fashion. The strong luminescence properties of **1** indicate that it is a good candidate for potential fluorescent materials.

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