

1,2,4-Triazole Controlled Cd^{II}/Mn^{II} Complexes with Discrete Mononuclear, Polymeric 1D Chain, and 2D Layer Motifs

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Abstract. Three Htrz-based metal complexes, [Cd(trz)(CH₃OH)(nb)]_n (**1**), [Cd(Htrz)(H₂O)(nb)₂]_n (**2**), and {[Mn(Htrz)₂(H₂O)₄·2nb]} (**3**) (Htrz = 1,2,4-triazole, Hnb = 4-nitrobenzoic acid), have been synthesized by diffusion or solvent evaporation method and structurally characterized by single crystal X-ray crystallography, elemental analysis, IR and fluorescence spectroscopy, and TG-DTA. Structural determinations revealed that complex **1** has a two-dimensional (2D) layer structure constructed by tridentate μ_{N1,N2,N4}-bridging trz anions and Cd^{II} ions. Complex **2** presents a 1D polymeric chain structure bridged by bidentate μ_{N1,N4}-bridging Htrz molecule and Cd^{II} ions, whereas com-

pound **3** is a supramolecular assembly containing a mononuclear [Mn(Htrz)₂(H₂O)₄]²⁺ dication and two free nb anions for charge compensation. Thus, the structural diversity of the three complexes is significantly governed by the coordination modes of the neutral/deprotonated Htrz ligand, rather than the terminal/lattice nb anion. Additionally, the thermal stability of the complexes is observed to be dependent on the polymeric or discrete structure nature. At room temperature, the three solid complexes show Htrz-based intraligand fluorescent emission.

Introduction

The 1,2,4-triazole (Htrz)-based coordination complexes have recently gained more and more interest due to their intriguing framework topologies and potential applications in magnetism, luminescence, and gas storage [1–13]. As one of the five-membered nitrogen containing heterocycles, the neutral Htrz molecule or its deprotonated anion has exhibited multiple coordination modes by far. For example, the neutral Htrz can act as a terminal ligand coordinating with the discrete metal atom in a μ_{N4}-monodentate fashion, probably resulted from the protonation behavior. And the anionic trz can potentially function as a bridge ligand to connect different metal ions in μ_{N1,N2}-, μ_{N1,N4}-, and μ_{N1,N2,N4}-modes. Obviously, the diverse coordination modes of Htrz in complexes are highly dependent on the synthetic conditions, the presence of coligands as well as on the nature of the metal ions, which critically determine the final coordination architectures of the target complexes. To the best of our knowledge, tridentate bridging mode of the trz is commonly observed in the reported complexes with mixed ligands especially those prepared by hydrothermal methods. Therefore, the selective tuning of the coordination fashion of Htrz is of significance for the detailed investigations on the binding behavior as well as the controllable construction of the well-designed complexes. Herein, by judicious selection of the

preparation methods and the metal ions, we successfully isolated and characterized three novel Htrz-based complex, [Cd(trz)(CH₃OH)(nb)]_n (**1**), [Cd(Htrz)(H₂O)(nb)₂]_n (**2**), and {[Mn(Htrz)₂(H₂O)₄·2nb]} (**3**) (Htrz = 1,2,4-triazole, Hnb = 4-nitrobenzoic acid). Interestingly, the complexes exhibit a polymeric 2D layer for **1**, 1D chain for **2** as well as a discrete mononuclear structure for **3**, which is significantly controlled by the binding modes of the Htrz. Additionally, their thermal stability and solid fluorescent emission were investigated and compared.

Experimental Section

Reagents and Instruments

Reagents were purchased commercially (Htrz and Hnb were from Acros and other analytical grade reagents were from Tianjin chemical reagent factory) and used without further purification. Doubly deionized water was used for the conventional synthesis. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a CE-440 (Lee-man-Labs) analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken with an AVATAR-370 (Nicolet) spectrometer in the range 4000–400 cm⁻¹. Thermogravimetric analysis (TGA) experiments were carried out with Shimadzu simultaneous DTG-60A thermal analysis instrument from room temperature to 800 °C under a nitrogen atmosphere (flow rate 10 mL·min⁻¹) at a heating rate of 5 °C·min⁻¹. Fluorescence spectra of the polycrystalline powder samples were performed with a Cary Eclipse fluorescence spectrophotometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature.

Synthesis of Complexes

[Cd(trz)(CH₃OH)(nb)]_n (**1**): Hnb (16.7 mg, 0.1 mmol) and Htrz (6.9 mg, 0.1 mmol) were dissolved in CH₃OH (5 mL) and the pH va-

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lue of the mixture was carefully adjusted to 7 by triethylamine. The mixture was then carefully layered onto an aqueous solution of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (26.6 mg, 0.1 mmol) in a straight test tube. Colorless block-shaped crystals appeared at the tube wall within two weeks at room temperature. Yield: 60 % based on Cd^{II} salts. $\text{C}_{10}\text{H}_{10}\text{CdN}_4\text{O}_5$: calcd. C 31.72; H 2.66; N 14.80 %, found: C 31.76; H 2.54; N 14.82 %. IR (KBr): $\tilde{\nu}$ = 3426 br, 3130 m, 1615 w, 1567 s, 1524 m, 1508 m, 1412 s, 1353 s, 1319 m, 1286 m, 1209 w, 1162 m, 1066 m, 1013 s, 984 m, 877 m, 845 s, 797 m, 722 s, 669 s, 524 cm^{-1} .

[Cd(Htrz)(H₂O)(nb)₂]_n (2): A mixture containing Hnb (16.7 mg, 0.1 mmol) and Htrz (6.9 mg, 0.1 mmol) in CH_3OH (5 mL) was carefully layered onto an aqueous solution of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (26.6 mg, 0.1 mmol) in a straight test tube. Pale yellow block-shaped crystals suitable X-ray diffractions were obtained at the tube wall within two weeks at room temperature. Yield: 60 % based on Cd^{II} salts. $\text{C}_{16}\text{H}_{13}\text{CdN}_5\text{O}_9$: calcd. C 36.14; H 2.46; N 13.17 %, found: C 36.22; H 2.44; N 13.21 %. IR (KBr): $\tilde{\nu}$ = 3440 br, 3127 w, 1619 m, 1567 s, 1523 w, 1508 w, 1411 s, 1351 s, 1319 w, 1283 m, 1159 m, 1106 m, 1066 m, 1013 m, 985 w, 878 m, 840 m, 799 s, 668 m, 523 cm^{-1} .

[Mn(Htrz)₂(H₂O)₄·2nb] (3): To an aqueous solution (5 mL) of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (36.2 mg, 0.1 mmol) was slowly added a methanol solution (10 mL) containing Htrz (13.8 mg, 0.2 mmol) and Hnb (16.7 mg, 0.1 mmol) with constant stirring. The pH value of the mixture was then adjusted to 7 by triethylamine, and the mixture was filtered. Colorless block-shaped crystals suitable for X-ray diffraction were obtained by slow evaporation of the filtrate at room temperature within two weeks. Yield: 78 % based on Htrz. $\text{C}_9\text{H}_{11}\text{MnO}_5\text{N}_4\text{O}_6$: calcd. C 36.19; H 3.71; N 18.76 %, found: C 36.22; H 3.74; N 18.79 %. IR (KBr): $\tilde{\nu}$ = 3349 br, 3141 w, 2940 w, 2894 w, 2751 w, 2677 m, 2491 w, 1614 w, 1582 s, 1347 s, 1319 w, 1288 w, 1150 w, 1088 m, 987 w, 863 m, 801 m, 720 m, 675 m, 632 m, 553 w, 512 cm^{-1} .

X-ray Crystallography

Diffraction intensities for complexes **1–3** were collected with a Bruker APEX-II CCD diffractometer equipped with graphite-monochromated $\text{Mo-K}\alpha$ radiation with radiation wavelength 0.71073 Å by using the φ - ω scan technique at ambient temperature. There was no evidence of crystal decay during data collection. Semiempirical absorption corrections were applied (SADABS) [14], and the program SAINT was used for integration of the diffraction profiles [15]. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [16]. The organic hydrogen atoms were generated geometrically; the hydrogen atoms of the water molecules were located from difference maps and refined with isotropic temperature factors. The crystallographic data and selected bond lengths and angles were listed in Table 1, Table 2, Table 3, and Table 4. Hydrogen bond arrangements were summarized in Table 5.

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

Cd(1)–N(1)#1	2.261(3)	Cd(1)–O(5)	2.405(2)
Cd(1)–N(3)	2.315(3)	Cd(1)–O(2)	2.515(2)
Cd(1)–N(2)#2	2.303(3)	Cd(1)–O(1)	2.299(2)
N(1) ^{#1} –Cd(1)–O(1)	108.80(9)	N(3)–Cd(1)–O(5)	167.58(9)
N(1) ^{#1} –Cd(1)–N(2)#2	106.51(9)	N(1) ^{#1} –Cd(1)–O(2)	160.25(9)
O(1)–Cd(1)–N(2)#2	142.69(9)	O(1)–Cd(1)–O(2)	54.04(8)
O(1) ^{#1} –Cd(1)–N(3)	94.68(9)	N(2) ^{#2} –Cd(1)–O(2)	88.97(8)
N(2) ^{#2} –Cd(1)–N(3)	89.31(1)	N(3)–Cd(1)–O(2)	89.93(9)
N(1) ^{#1} –Cd(1)–O(5)	89.30(9)	O(5)–Cd(1)–O(2)	80.38(8)
N(1) ^{#1} –Cd(1)–N(3)	102.18(1)	N(2) ^{#2} –Cd(1)–O(5)	82.82(9)
O(1)–Cd(1)–O(5)	85.93(9)		

Symmetry codes: #1 $x, -y + 5/2, z - 1/2$; #2 $-x + 1, y - 1/2, -z + 1/2$.

Table 1. Crystal data and structure refinement for compounds **1–3**.

Compound	1	2	3
Empirical formula	$\text{C}_{10}\text{H}_{10}\text{CdN}_4\text{O}_5$	$\text{C}_{16}\text{H}_{13}\text{CdN}_5\text{O}_9$	$\text{C}_9\text{H}_{11}\text{MnO}_5\text{N}_4\text{O}_6$
Fw / $\text{g}\cdot\text{mol}^{-1}$	378.62	531.71	298.69
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a /Å	14.8034(9)	7.8857(3)	6.4609(6)
b /Å	8.0917(5)	22.5795(1)	7.5898(7)
c /Å	10.5824(7)	10.4642(4)	12.6870(1)
α /°	90	90	97.9550(1)
β /°	93.3230(1)	96.5780(1)	92.8300(1)
γ /°	90	90	102.4460(1)
V /Å ³	1265.48(1)	1850.94(1)	599.64(1)
Z	4	4	2
$\rho_{\text{calcd.}}$ / $\text{g}\cdot\text{cm}^{-3}$	1.987	1.908	1.654
μ / mm^{-1}	1.752	1.245	0.632
Crystal size /mm	$0.34 \times 0.32 \times 0.29$	$0.32 \times 0.29 \times 0.28$	$0.28 \times 0.21 \times 0.20$
$F(000)$	744	1056	307
θ range	2.76–25.01	2.16–25.01	2.78–25.01
$h / k / l$	–17, 16 / –9, 9 / –10, 12	–9, 7 / –26, 26 / –12, 12	–7, 7 / –8, 9 / –14, 15
Reflections collected / unique	6499 / 2202	9966 / 3266	3266 / 2075
$R(\text{int})$	0.0117	0.0141	0.0124
GOF	1.048	1.043	1.054
R_1, wR_2 [$I > 2\sigma(I)$] ^{a)}	0.0246 / 0.0478	0.0190 / 0.0491	0.0261 / 0.0705
R_1, wR_2 (all data) ^{a)}	0.0268 / 0.0484	0.0214 / 0.0504	0.0280 / 0.0712
Max. and min. transmission	0.602 / 0.557	0.706 / 0.678	0.881 / 0.853
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ / $\text{e}\cdot\text{Å}^{-3}$	0.398 / –0.492	0.218 / –0.341	0.191 / –0.241

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

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

Cd(1)–O(2)	2.2974(2)	Cd(1)–N(2) ^{#1}	2.4083(2)
Cd(1)–O(6)	2.3376(2)	Cd(1)–O(5)	2.4693(2)
Cd(1)–N(3)	2.3537(2)	Cd(1)–O(1)	2.4973(2)
Cd(1)–O(9)	2.3719(2)	O(5)–Cd(1)–O(1)	130.17(5)
O(2)–Cd(1)–O(6)	130.29(5)	O(2)–Cd(1)–O(5)	76.56(6)
O(2)–Cd(1)–N(3)	93.37(6)	O(6)–Cd(1)–O(5)	53.82(5)
O(6)–Cd(1)–N(3)	92.09(6)	N(3)–Cd(1)–O(5)	99.51(7)
O(2)–Cd(1)–O(9)	136.48(5)	O(9)–Cd(1)–O(5)	146.91(5)
O(6)–Cd(1)–O(9)	93.10(5)	N(2) ^{#1} –Cd(1)–O(5)	98.73(6)
N(3)–Cd(1)–O(9)	79.98(6)	O(2)–Cd(1)–O(1)	54.24(5)
O(2)–Cd(1)–N(2) ^{#1}	96.97(6)	O(6)–Cd(1)–O(1)	173.99(5)
O(6)–Cd(1)–N(2) ^{#1}	93.58(6)	N(3)–Cd(1)–O(1)	91.49(5)
N(3)–Cd(1)–N(2) ^{#1}	160.69(7)	O(9)–Cd(1)–O(1)	82.77(5)
O(9)–Cd(1)–N(2) ^{#1}	81.29(6)	N(2) ^{#1} –Cd(1)–O(1)	81.51(5)

Symmetry code: #1 $x - 1/2, -y + 1/2, z + 1/2$.**Table 4.** Selected bond lengths /Å and angles /° for **3**.

Mn(1)–O(6)	2.1476(1)	Mn(1)–O(5)	2.2169(1)
Mn(1)–N(3)	2.2345(1)	N(3) ^{#1} –Mn(1)–N(3)	180.00
O(6)–Mn(1)–O(6) ^{#1}	180.00	O(5)–Mn(1)–N(3) ^{#1}	89.08(5)
O(6)–Mn(1)–O(5)	93.49(5)	O(6)–Mn(1)–N(3)	89.19(5)
O(5)–Mn(1)–O(5) ^{#1}	180.00	O(5)–Mn(1)–N(3)	90.92(5)

Symmetry code: #1 $-x, -y, -z + 1$.**Table 5.** Hydrogen-bonding parameters /Å,° for compounds **1–3**.

Donor–H...Acceptor	D–H	H...A	D...A	D–H...A
1				
O5–H5'...O2 ^{#1}	0.85	1.89	2.684(7)	156
C1–H1...O5 ^{#2}	0.93	2.48	3.406(4)	172
C2–H2...O4 ^{#3}	0.93	2.56	3.377(9)	147
2				
N1–H1A...O9 ^{#4}	0.86	2.62	3.094(4)	116
O9–H9B...O7 ^{#5}	0.85	2.44	3.222(0)	153
N1–H1A...O5 ^{#6}	0.86	2.02	2.823(8)	156
O9–H9A...O2 ^{#6}	0.85	1.89	2.700(8)	160
O9–H9B...O5 ^{#6}	0.85	2.58	3.040(6)	115
3				
O6–H6A...N2 ^{#7}	0.85	2.02	2.852(2)	168
O6–H6B...O1 ^{#8}	0.85	1.92	2.763(7)	173
O5–H5B...O2	0.85	1.82	2.660(5)	168
O5–H5A...O1 ^{#9}	0.85	2.06	2.911(4)	174
N1–H1...O1 ^{#10}	0.86	1.96	2.794(8)	162

Symmetry codes: #1 $x, 1/2 - y, 1/2 + z$; #2 $x, 1/2 - y, -1/2 + z$; #3 $-x, 1/2 + y, 1/2 - z$; #4 $1/2 + x, 1/2 - y, -1/2 + z$; #5 $3/2 - x, -1/2 + y, 1/2 - z$; #6 $1/2 + x, 1/2 - y, 1/2 + z$; #7 $-x, 1 - y, 1 - z$; #8 $-x, -y, 1 - z$; #9 $-1 + x, y, z$; #10 $1 - x, 1 - y, 1 - z$.

CCDC-709593, CCDC-709594, and CCDC-709595 for complexes **1–3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

Results and Discussion

Syntheses and FT-IR Spectra

Colorless crystals of **1** and pale yellow crystals of **2**, were obtained by the reaction of Htrz, Hnb with Cd(OAc)₂·2H₂O in a molar ratio of 1:1:1 under diffusion conditions. The sole difference for the preparation of the two complexes is the pH of the medium containing the mixed-ligand. Indeed, the slightly pH change significantly led to the deprotonation of Htrz ligand to some different extent. In contrast, colorless crystals of **3** with suitable crystal size were obtained by solvent evaporation in a satisfactory yield. Attempts to prepare **3** by diffusion method were tried but failed. Additionally, the ratio of the reactant mixture has also significantly decided the growth of the Mn^{II}-based complex. Complex **3** is prepared from the molar ratio of 1:2:1 (Mn^{II}:Htrz:Hnb). In contrast, the two Cd^{II}-based complexes are obtained in an equimolar reactant mixture. Therefore, it can be concluded that the preparation method, the ratio of the reactants and the pH value of the medium are all important factors for the growth of the three target complexes.

In their infrared spectra, the strong and broad absorption bands centered at 3426 cm^{−1} for **1**, 3440 cm^{−1} for **2**, and 3349 cm^{−1} for **3** are ascribed to ν(O–H) of methanol for **1** and water for both **2** and **3**, respectively [17]. Compared with the free Hnb, the absence of strong absorption band at 1694 cm^{−1} in the three complexes indicates the full deprotonation of carboxylic group. Correspondingly, the asymmetric stretching frequencies (ν_{as}) for carboxylate group occur at 1567 and 1508 cm^{−1} for **1** and **2**, and the symmetric carboxylate stretching frequencies (ν_s) appeared at 1412 and 1353 cm^{−1} for **1**, 1411 and 1351 cm^{−1} for **2**, respectively. Their small difference Δν (Δν = ν_{as} – ν_s < 200 cm^{−1}) indicates the chelating bidentate coordination modes of carboxylate group, which is also confirmed by single crystal structure analysis. The stretching vibration bands of the carboxylate group in **3** (1614, 1582, 1347, and 1319 cm^{−1}) are comparable to the corresponding values in sodium 4-nitrobenzoate (1617, 1585, 1351, and 1319 cm^{−1}), suggesting that the nb anion in **3** is isolated. Additionally, the bands in the range of 800–1400 cm^{−1} are associated with trz ligand vibrations [11b].

Structure Descriptions of Complexes **1–3**

[Cd(trz)(CH₃OH)(nb)]_n (**1**)

Single crystal X-ray analysis reveals that **1** presents an infinite two-dimensional (2D) network built from dinuclear [Cd₂(trz)₂]²⁺ subunits. As shown in Figure 1a, the asymmetric unit of **1** contains one crystallographically independent Cd^{II} atom, one deprotonated trz molecule, one nb anion and one coordinated methanol molecule. The hexacoordinated Cd1 atom is bound to three nitrogen atoms from three separate trz (N1B, N2A, and N3) anions, three oxygen atoms from one nb anion (O1, O2) and one methanol (O5) molecule, leading to a distorted octahedral arrangement. The bond lengths of Cd–N and Cd–O vary slightly from 2.261(3) to 2.515(2) Å (Table 2), and are similar to those previously reported values [8–11].

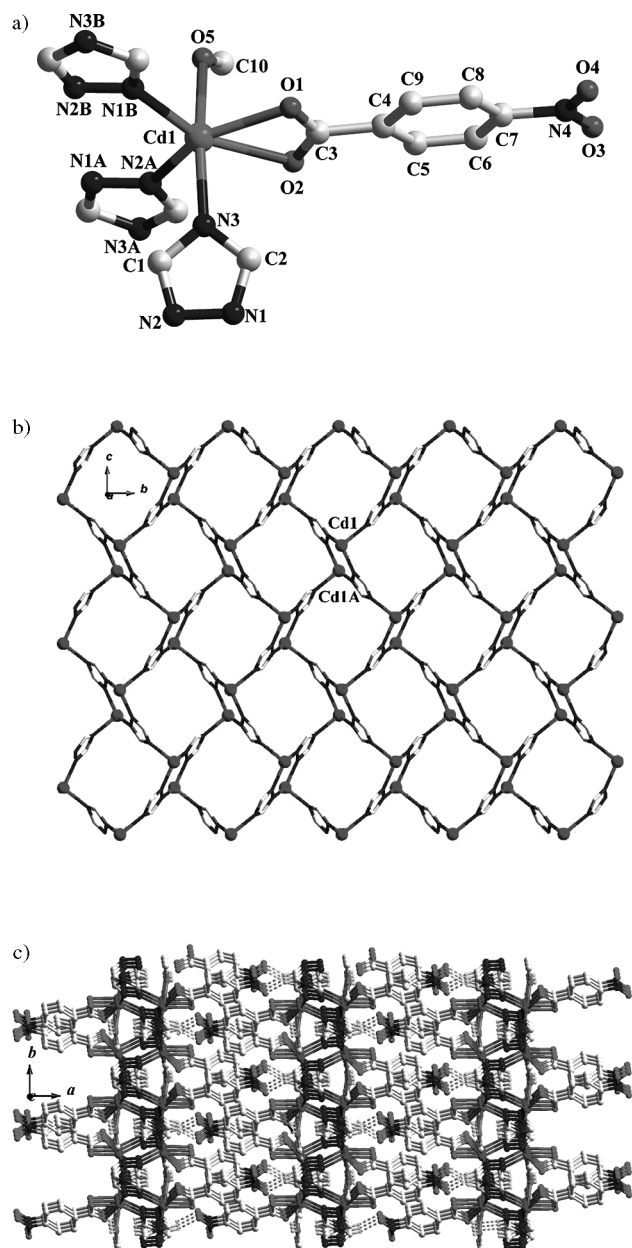


Figure 1. (a) Local coordination environments of Cd^{II} in **1** with atomic labels in the asymmetric unit. (Hydrogen atoms were omitted for clarity). (b) 2D layer of **1** formed by trz molecules and Cd^{II} atoms. (c) 3D hydrogen bonded network by weak interlayer $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond interactions.

Two symmetry-related Cd^{II} sites are doubly bridged by two trz anions in a $\mu_{\text{N1},\text{N2}}$ -bridging mode to generate a dinuclear $[\text{Cd}_2(\text{trz})_2]^{2+}$ subunit. The $\text{Cd}\cdots\text{Cd}$ separation within the dinuclear subunit is 4.1006(2) Å and the two trz rings are strictly coplanar. The dinuclear $[\text{Cd}_2(\text{trz})_2]^{2+}$ unit is connected with its four adjacent subunits through the coordination of Cd^{II} atoms with the remaining N4 position of the trz, generating an infinite 2D layer in the bc plane (Figure 1b). Thus, each trz ligand in **1** affords its three nitrogen atoms to link three Cd^{II} sites in a $\mu_{\text{N1},\text{N2},\text{N4}}$ -tridentate bridging mode. Viewed along the crystallographic a direction, the 2D layer contains 16-membered mac-

rocycles composed by four Cd^{II} sites and four trz ligands. Moreover, two hydrogen-bond interactions ($\text{O5}-\text{H5}'\cdots\text{O2}$ and $\text{C1}-\text{H1}\cdots\text{O5}$, see Table 5) were observed within the 2D layer. And the adjacent 2D layers were interlinked by weak $\text{C2}-\text{H2}\cdots\text{O4}$ (see Table 5) hydrogen-bonds interactions into a 3D supramolecular network (Figure 1c).

$[\text{Cd}(\text{Htrz})(\text{H}_2\text{O})(\text{nb})_2]_n$ (**2**)

Complex **2** crystallizes in the monoclinic $P2_1/n$ space group, exhibiting a 1D chain motif bridged by the neutral Htrz ligand. The asymmetric unit of **2** consists of one Cd^{II} atom, one neutral Htrz molecule, two nb anions, and one coordinated water molecule. Different from **1**, the sole Cd^{II} atom in **2** is heptacoordinated by two nitrogen atoms (N3, N2A) from a pair of symmetry-related Htrz ligands and five oxygen atoms from two nb

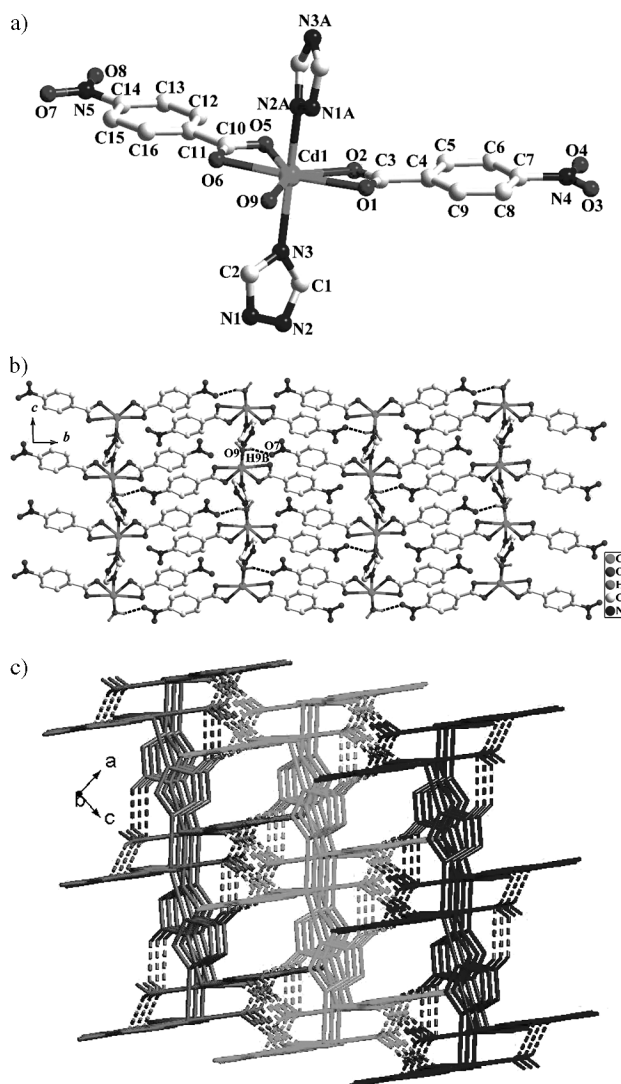
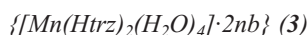


Figure 2. (a) Local coordination environments of Cd^{II} atom in **2** with atomic labels in the asymmetric unit (hydrogen atoms were omitted for clarity). (b) 1D chain and 2D layer of **2** constructed from interchain $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond interactions. (c) 3D supramolecular structure of **2** by hydrogen bond interactions.

anions (O1, O2, O5, and O6) and one coordinated water molecule (O9). The arrangement around each Cd^{II} atom can be described as a distorted pentagonal-bipyramidal polyhedron, in which the Cd^{II} atom deviates from the least-squares plane generated by O1–O2–O5–O6–O9 only about 0.0177 Å. The Cd–O and Cd–N bond lengths are in the range of 2.2974 Å to 2.4973(2) Å, and the bond angles around each Cd^{II} atom range from 53.82(5)° to 173.99(5)° (Table 3). Acting as a terminal ligand, the nb anion in complex **2** also affords its carboxylate group to connect to the Cd^{II} atom in a bidentate chelating fashion. The neutral Htrz ligand in **2** adopts a $\mu_{N1,N4}$ -bridging mode to connect the adjacent Cd^{II} atoms into a 1D linear chain along the *c* axis with a Cd...Cd separation of 6.9204(3) Å (Figure 2b). Such the linear chains are further stabilized by intra-chain N1–H1A...O9 hydrogen bond interactions between Htrz and coordinated water molecules (see Table 5)

Furthermore, these neighboring 1D chains were interlinked in an *anti*-parallel manner by O9–H9B...O7 hydrogen-bonds between coordinated water and the nitro group of nb, forming an interdigitated 2D supramolecular layer (Figure 2b). As shown in Figure 2c, these layers are further stacked together in a parallel manner though classic O9–H9A...O2 and N1–H1A...O5 hydrogen bonds to generate a supramolecular architecture (see Table 5).



X-ray crystal structural analysis points out that complex **3** is a supramolecular assembly containing a discrete mononuclear $[Mn_{0.5}(Htrz)(H_2O)_2]^+$ cation, and a free nb anion for charge compensation (Figure 3a). The Mn^{II} atom is surrounded in a distorted octahedral arrangement by two nitrogen atoms (N3, N3A) from a pair of symmetry-related Htrz molecules and four oxygen atoms (O5, O6, O5A, and O6A) from two pairs of water molecules. Interestingly, rather than adopting the $\mu_{N1,N2,N4}$ - and $\mu_{N1,N4}$ -bridging coordination modes, the neutral Htrz molecule in **3** only coordinates in a monodentate fashion through its N3 atom to the Mn^{II} atom. Acting as a typical hydrogen-bond donor, the four coordinated water molecules produce abundant hydrogen-bonds interactions with the neutral Htrz and anionic nb ligands (see Table 4 and Table 5), which connects the discrete mononuclear $[Mn_{0.5}(Htrz)(H_2O)_2]^+$ cations into a 1D infinite chain with the free nb anions attached on the both sides (Figure 3b). These adjacent chains are further extended into a 2D supramolecular layer by O5–H5A...O1 and N1–H1...O1 hydrogen-bond interactions. π – π -stacking interactions between the aromatic ring of the attached nb anions assemble these layers into a 3D supramolecular architecture. The centroid–centroid separations and dihedral angle of the benzene rings are 3.655 Å and 0.000(78)° respectively.

Thermal Stability of 1–3

To investigate the correlation between the complex structure and their thermal stability, thermogravimetric experiments of **1–3** were carried out (Figure 4). The TGA curve of complex **1** indicates that the coordinated CH₃OH molecule is released

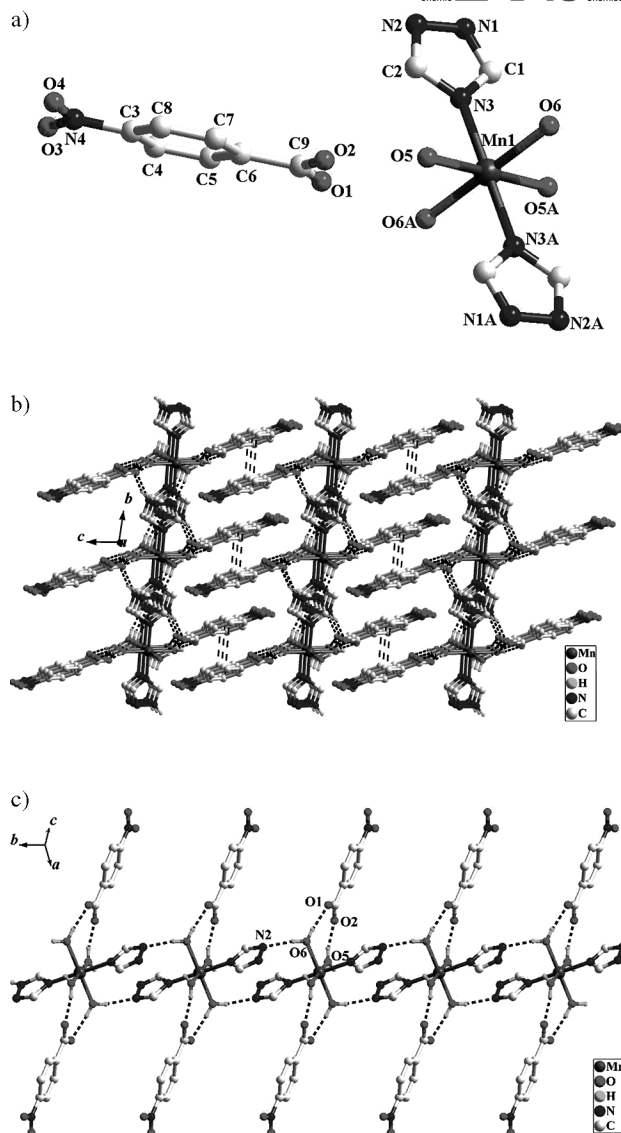


Figure 3. (a) Molecule structure of **3**. (b) 1D supramolecular chain of **3** by hydrogen bond interactions. (c) 3D supramolecular network of **3** by hydrogen bond and π – π stacking interactions.

between 98 °C and 146 °C (obsd.: 8.7 %, calcd.: 8.5 %). And the framework is stable up to 317 °C. Upon further heating, the organic mixed-ligands of **1** are observed to be decomposed progressively up to 446 °C, leaving CdO as the final product (obsd.: 34.7 %, calcd.: 33.9 %). Much different from **1**, complex **2** shows that the coordinated H₂O and Htrz molecules are released from 119 °C to 253 °C (obsd.: 17.1 %, calcd.: 16.4 %). The aromatic nb anions of **2** are removed from 340 °C to 504 °C. An amorphous powder, which is calculated to be CdO, is left as final product above 504 °C (obsd.: 23.8 %, calcd.: 24.1 %).

In contrast, complex **3** displays the thermal instability. When the temperature is above 70 °C, the slow weight-loss process of **3** occurs and ends at 528 °C, corresponding to the continuous release of the coordinated water molecules, lattice nb anions and neutral Htrz ligand. The final product is calculated

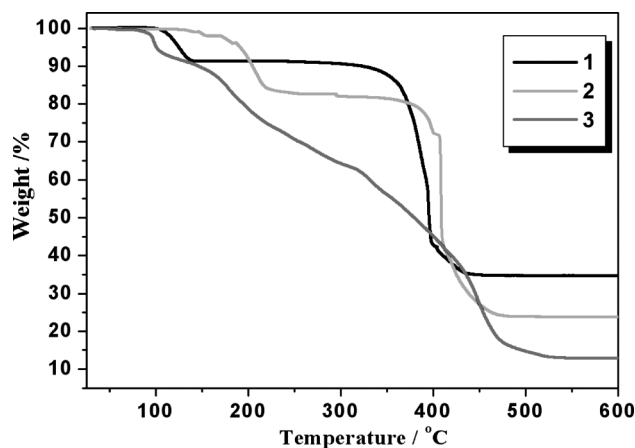


Figure 4. TG curves for 1–3.

to be MnO_2 (expt.: 13.7 %, calcd.: 14.6 %). Thus, the three complexes from discrete mononuclear to polymeric 2D structures show much different thermal stability, significantly influenced by polymeric nature.

Luminescent Properties

The solid state fluorescence spectra of 1–3 at room temperature are depicted in Figure 5. Upon excitation at 374 nm, the three complexes display similar emissions at 424 nm only with a slightly different intensity. In comparison, the free Htrz presents the relatively weak emission at 422 nm ($\lambda_{\text{ex}} = 374$ nm). Therefore, the fluorescent emission of the three complexes should be assigned to the Htrz-based charge transfer [11]. The slight difference between the complexes and free Htrz should be resulted from the ligand chelation to the metal center and the deprotonation of the trz ligands.

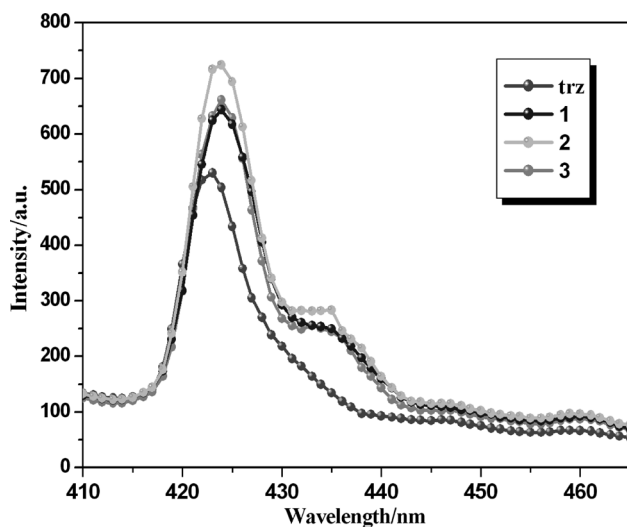


Figure 5. Solid state emission spectra of 1–3 and free Htrz ligand at room temperature.

Conclusions

In summary, three solid complexes with mixed Htrz and Hnb ligands were prepared by diffusion or solvent evaporation, which exhibit the structural diversity ranged from discrete mononuclear, polymeric 1D chain to infinite 2D layer significantly dominated by the coordination modes of Htrz ligand. A similar fluorescent emission based on intraligand charge transfer and different structure-dependent thermal stability, were also observed for the three complexes.

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References

- J.-G. Haasnoot, *Coord. Chem. Rev.* **2000**, *131*, 200, and references cited therein.
- J.-R. Li, Q. Yu, E. C. Sañudo, Y. K. Tao, X.-H. Bu, *Chem. Commun.* **2007**, 2602.
- a) J.-H. Zhou, R.-M. Cheng, Y. Song, Y.-Z. Li, Z. Yu, X.-T. Chen, Z.-L. Xue, X.-Z. You, *Inorg. Chem.* **2005**, *44*, 8011; b) S. Gorter, D. W. Engelfriet, *Acta Crystallogr., Sect. B* **1981**, *37*, 1214.
- J.-P. Zhang, Y.-Y. Lin, X.-C. Huang, X.-M. Chen, *J. Am. Chem. Soc.* **2005**, *127*, 5495.
- K. H. Sugiyarto, H. A. Goodwin, *Aust. J. Chem.* **1994**, *47*, 263.
- O. M. Yaghi, M. O. Keefe, N. W. Ockwig, H. K. Chae, M. Edaoudi, J. Kim, *Nature* **2003**, *423*, 705.
- B. Ding, L. Yi, P. Cheng, D.-Z. Liao, S.-P. Yan, *Inorg. Chem.* **2006**, *45*, 5799.
- a) W. Ouellette, B. S. Hudson, J. Zubieta, *Inorg. Chem.* **2007**, *46*, 4887; b) W. Ouellette, A. V. Prosvirin, V. Chieffo, K. R. Dunbar, B. S. Hudson, J. Zubieta, *Inorg. Chem.* **2006**, *45*, 9346; c) W. Ouellette, M. H. Yu, C. J. O'Connor, D. Hargman, J. Zubieta, *Angew. Chem. Int. Ed.* **2006**, *45*, 3497; d) W. Ouellette, J. R. Galán-Mascarós, K. R. Dunbar, J. Zubieta, *Inorg. Chem.* **2006**, *45*, 1909.
- a) Q.-G. Zhai, C.-Z. Lu, S.-M. Chen, X.-J. Xu, W.-B. Yang, *Cryst. Growth Des.* **2006**, *6*, 1393; b) Q.-G. Zhai, X.-Y. Wu, S.-M. Chen, C.-Z. Lu, W.-B. Yang, *Cryst. Growth Des.* **2006**, *6*, 2126; c) Q.-G. Zhai, X.-Y. Wu, S.-M. Chen, Z.-G. Zhao, C.-Z. Lu, *Inorg. Chem.* **2007**, *46*, 5046; d) Q.-G. Zhai, C.-Z. Lu, X.-Y. Wu, S. R. Batten, *Cryst. Growth Des.* **2007**, *7*, 2332.
- a) H. Park, D. M. Moureau, J. B. Parise, *Chem. Mater.* **2006**, *18*, 525; b) H. Park, J. F. Britten, U. Mueller, J. Y. Lee, J. Li, J. B. Parise, *Chem. Mater.* **2007**, *19*, 1302; c) H. Park, G. Krigsfeld, J. B. Parise, *Cryst. Growth Des.* **2007**, *7*, 736.
- a) E.-C. Yang, Q.-Q. Liang, X.-G. Wang, X.-J. Zhao, *Aust. J. Chem.* **2008**, *61*, 813; b) Z.-Y. Liu, X.-G. Wang, E.-C. Yang, X.-J. Zhao, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1807; c) E.-C. Yang, Z.-Y. Liu, X.-G. Wang, S. R. Batten, X.-J. Zhao, *CrystEngComm* **2008**, *10*, 1140; d) E.-C. Yang, Q.-Q. Liang, P. Wang, X.-J. Zhao, *Inorg. Chem. Commun.* **2009**, *12*, 211.
- Y.-C. Lu, X.-R. Li, Z.-H. Zhang, M. Du, *Chin. J. Struct. Chem.* **2007**, *26*, 15.
- a) D. Olea, U. García-Couceiro, O. Castillo, J. Gómez-Herrero, F. Zamora, *Inorg. Chim. Acta* **2007**, *360*, 48; b) O. Castillo, U. García-Couceiro, A. Luque, J. P. García-Terán, P. Román, *Acta Crystallogr., Sect. E* **2004**, *60*, m9.
- G. M. Sheldrick, *SADABS*, Siemens Area Detector Absorption Corrected Software, University of Göttingen, Germany, **1996**.
- Bruker AXS, *SAINT*, Software Reference Manual (Madison, WI), **1998**.

- [16] G. M. Sheldrick, *SHELXTL NT*, Version 5.1; Program for Solution and Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.
- [17] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, **1986**.

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