Three 1-(4-Hydroxyphenyl)-1H-1,2,4-triazole-based Cd(II) Coordination Polymers Directed by Aromatic Polycarboxylate Coligands

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The reactions of 1-(4-hydroxyphenyl)-1H-1,2,4-triazole (hptrz) and inorganic Cd(II) salts with different aromatic polycarboxylic acids in mixed-solvent led to the formation of three new crystalline coordination polymers, $\{[Cd(H_2O)_2(hptrz)(Hbtc)]_n \cdot CH_3OH \cdot H_2O\}$ **1**, $[Cd_2(H_2O)_2(hptrz)_2(tp)_2]_n$ **2**, and $\{[Cd(H_2O)_2(hptrz)-(OH-ip)]_n \cdot DMF \cdot H_2O\}$ **3** (H_3btc = 1,3,5-benzenetricarboxylic acid, H_2tp = terephthalic acid, and OH-H_2ip = 5-hydroxyisophthalic acid), which were fully characterized by elemental analysis, IR spectroscopy, single crystal X-ray crystallography, thermogravimertric analysis and luminescence spectra. Structure determination revealed that one-dimensional (1-D) polymeric chains for **1** and **3**, and 2-D layered structure for **2** are significantly directed by the coordination mode of the carboxylate groups from aromatic coligands. In contrast, the terminal hptrz ligand affords its uncoordinated phenolic OH group to form classical H-bond interactions with coordinated water and/or carboxylate groups, which are responsible for the formation of 3-D supramolecular networks. In addition, the three solid coordination polymers with considerable thermal stability present strong hptrz-based fluorescence emissions at room temperature.

Key Words : 1-(4-Hydroxyphenyl)-1H-1,2,4-triazole, Mixed-ligand, Coordination polymer

Introduction

During the past decades, 1,2,4-triazole (Htrz) and its diverse derivatives have already becoming one of the most promising ligands, and are widely applied upon the construction of various transitional metal complexes with luminescence, magnetic and ion precursor properties.[1-3] Bearing three nitrogen atoms in a five-membered heterocycle, the unsubstituted trz in the neutral and/or anion form has exhibited diverse coordination modes such as bidentate-, tridentate-bridging and terminal monodentate-coordination fashions, connecting the discrete metal atoms into polynuclear or extending structures.[4] However, the coordination behaviors of trz derivatives have been less investigated by far.[5] Recently, Kahn group has synthesized two linear trinuclear-iron (II) complexes with 4-(p-methoxyphenyl)-1,2,4-triazole (p-MeOptrz) and further investigated their magnetic properties.[6] They found that the central Fe(II) atom in the trinuclear complex was triply bridged to each of the external Fe(II) atoms by p-MeOptrz ligand through the nitrogen atoms in the 1,2-positions, which showed the spin crossover phenomenon associated with cooperative interactions between the Fe(II) centers.[6,7] Additionally, novel Cu(II)-polymers with m-phenol-1,2,4-triazole (m-ptr) or p-phenol-1,2,4-triazole (p-ptr) ligand were also isolated respectively,[8-10] exhibiting antiferromagnetic interactions between the Cu(II) ions. On the other hand, to explore the potential fluorescence properties of the trz derivatives, a series of Zn(II)/Hg(II) complexes bridged by bidentate m-ptr were successively prepared. As expected, these complexes displayed green and blue fluorescence emissions originated from the π-π* transition of the triazole rings as well as the

ligand-to-metal transfer (LMCT).[9,10] In addition to the bidentate-bridging mode presented by the derivatives of trz, new mononuclear complexes of Co(II), Ni(II) and Cu(II) with 1-(4-hydroxyphenyl)-1H-1,2,4-triazole (hptrz) were obtained, in which hptrz acted as a simple monodentate ligand.[11] Thus, the derivatives of trz coordinate to a metal ion in various modes (monodentate or bidentate-bridging), depending on the substituted position of the triazole ring.[12] To further explore the coordination behaviors of trz derivatives as well as their potential applications, in the present paper, three hptrz-based Cd(II) coordination polymers with aromatic polycarboxylate coligands, $\{[Cd(H_2O)_2(hptrz)-(Hbtc)]_n \cdot CH_3OH \cdot H_2O\}$ **1**, $[Cd_2(H_2O)_2(hptrz)_2(tp)_2]_n$ **2**, and $\{[Cd(H_2O)_2(hptrz)(OH-ip)]_n \cdot DMF \cdot H_2O\}$ **3** (H_3btc = 1,3,5-benzenetricarboxylic acid, H_2tp = terephthalic acid, OH-H_2ip = 5-hydroxyisophthalic acid), have been prepared and their crystal structures and fluorescence properties were fully characterized. X-ray diffractions reveal that the diverse structures of 1-D polymeric chain for **1** and **3** as well as the 2-D infinite layer for **2**, are significantly governed by the aromatic carboxylate groups and the neutral hptrz only acts as a terminal ligand to coordinate with Cd(II) atom in a μ_4-monodentate fashion.

Experimental Section

General Methods. Reagents were purchased commercially (hptrz, H_3btc, H_2tp and OH-H_2ip, were from Acros and other analytical-grade reagents were from Tianjin chemical reagent factory) and used without further purification. Doubly deionized water was employed for the conventional synthesis. Fourier transform (FT) IR spectra (KBr pellets) were

collected on a Nicolet IR-200 spectrometer in the range 4000-400 cm^{-1}. Elemental analyses for C, H and N were determined on a Perkin-Elmer 2400C elemental analyzer. Thermogravimetric analysis experiments were carried out on a Shimadzu simultaneous DTG-60A thermal analysis instrument from room temperature to 800 °C under a N$_2$ atmosphere (flow rate 10 mL·min^{-1}) at a heating rate of 8 °C·min^{-1}. Fluorescence spectra of the polycrystalline samples were performed on a Cary Eclipse fluorescence spectro-photometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature.

Synthesis of {[Cd(H$_2$O)$_2$(hptrz)(Hbtc)]$_n$·CH$_3$OH·H$_2$O} 1. To a methanol solution (5 mL) containing hptrz (0.05 mmol, 8.1 mg) and H$_3$btc (0.2 mmol, 42.0 mg) was slowly added an aqueous solution (5 mL) of Cd(NO$_3$)$_2$·4H$_2$O (0.2 mmol, 61.6 mg) with stirring. The mixture was filtered after further stirring for half an hour. Colorless block crystals suitable for X-ray diffraction were grown by slow evapo-ration of the filtrate within several days. Yield based on Cd: 56.7 mg, 50%. Elemental analysis for C$_{18}$H$_{21}$CdN$_3$O$_{11}$: Found (Calc.); C, 38.16 (38.08); H, 3.71 (3.73); N, 7.43 (7.40). IR data (in KBr, cm^{-1}): 3466 (s), 3348 (s), 3109 (w), 1687 (m), 1616 (vs), 1560 (m), 1528 (vs), 1436 (m), 1372 (s), 1324 (w), 1270 (vs), 1131 (w), 1107 (w), 1050 (w), 1008 (w), 982 (w), 828 (w), 753 (w), 693 (w), 525 (w).

Synthesis of [Cd$_2$(H$_2$O)$_2$(hptrz)$_2$(tp)$_2$]$_n$ 2. To a DMF

solution (5 mL) of hptrz (0.1 mmol, 16.1 mg) and H$_2$tp (0.1 mmol, 16.6 mg) was added slowly an aqueous solution (5 mL) of Cd(OAc)$_2$·2H$_2$O (0.1 mmol, 26.6 mg) with stirring and the pH value of the mixture was adjusted to 7 by tri-ethylamine. The mixture was then filtered after further stirring for half an hour. Colorless block crystals suitable for X-ray diffraction were obtained by slow evaporation of the filtrate at room temperature within a few days. Yield based on Cd: 16.0 mg, 35%. Elemental analysis for C$_{32}$H$_{26}$Cd$_2$N$_6$O$_{12}$, Found (Calc.); C, 42.32 (42.17); H, 2.82 (2.88); N, 9.19 (9.22). IR data (in KBr, cm^{-1}): 3437 (br, s), 3131 (m), 1637 (m), 1562 (s), 1526 (m), 1406 (m), 1270 (w), 1212 (w), 1131 (w), 981 (w), 828 (w), 744 (w), 512 (w).

Synthesis of {[Cd(H$_2$O)$_2$(hptrz)(OH-ip)]$_n$·DMF·H$_2$O} 3. To a mixed DMF-methanol (1:1 v/v) solution (5 mL) containing hptrz (0.1 mmol, 16.1 mg) and OH-H$_2$ip (0.1 mmol, 18.2 mg) was slowly added an aqueous solution (5 ml) of Cd(NO$_3$)$_2$·4H$_2$O (0.1 mmol, 30.8 mg) with stirring. The pH value of the mixture was adjusted to 7 by tri-ethylamine. The mixture was then filtered. Colorless sheet crystals suitable for X-ray diffraction were obtained by slow evaporation of the filtrate at room temperature within a few days. Yield based on Cd: 20.3 mg, 35%. Elemental analysis for C$_{19}$H$_{24}$CdN$_4$O$_{10}$, Found (Calc.): C, 39.46 (39.29); H, 4.29 (4.16); N, 9.83 (9.65). IR data (in KBr, cm^{-1}): 3346 (s), 3110 (m), 1657 (s), 1619 (s), 1562 (vs), 1527 (vs), 1473 (w), 1418

Table 1. Crystal data and structure refinements for **1-3**^{a}

	1	**2**	**3**
Empirical Formula	C$_{18}$H$_{21}$CdN$_3$O$_{11}$	C$_{32}$H$_{26}$Cd$_2$N$_6$O$_{12}$	C$_{19}$H$_{24}$CdN$_4$O$_{10}$
Color and Habit	colorless block	colorless block	colorless sheet
Crystal Size (mm)	0.30 × 0.28 × 0.16	0.24 × 0.23 × 0.18	0.24 × 0.23 × 0.12
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	C2/c	P–1	P–1
a (Å)	18.9284(5)	8.989(3)	10.1886(6)
b (Å)	10.3163(3)	9.929(3)	10.4330(6)
c (Å)	21.7021(6)	10.818(3)	12.2766(7)
β (°)	94.54	96.961(4)	96.8640(10)
V (Å^3)	4224.5(2)	818.7(4)	1137.18(11)
Z	8	1	2
Fw	567.78	911.39	580.82
D_{calcd} (Mgm^{-3})	1.785	1.848	1.696
μ (mm^{-1})	1.101	1.374	1.023
F (000)	2288	452	588
θ (°)	1.88 to 25.01	2.00 to 25.00	2.22 to 25.01
Reflections measured	10550	4438	6222
Index ranges of measured data	−22 ≤ h ≤ 22	−5 ≤ h ≤ 10	−12≤ h ≤ 10,
	−12 ≤ k ≤ 11	−11 ≤ k ≤ 11	−10 ≤ k ≤ 12,
	−20 ≤ l ≤ 25	−12 ≤ l ≤ 12	−14 ≤ l ≤ 14
Independent reflections	3720 (R_{int} = 0.0114)	2851 (R_{int} = 0.0133)	3965 (R_{int} = 0.0171)
Observed Reflection[I > 2σ(I)]	3490	2590	3636
Parameter / Restraints / Data(obs.)	302 / 0 / 3720	236 / 0 /2851	311 / 0 / 3965
Final $^aR_1$, $^bwR_2$[I > 2σ(I)]	0.0182, 0.0501	0.0219, 0.0572	0.0241, 0.0706
R_1, wR_2 indices(all)	0.0198 / 0.0515	0.0248 / 0.0579	0.0265/ 0.0724
S	1.049	1.041	1.040
$(\Delta/\sigma)_{max/min}$	0.000, 0.000	0.001, 0.000	0.001, 0.000
$(\Delta\rho)_{max/min}$ (eÅ^{-3})	0.317, −0.418	0.394, −0.490	0.553, −0.574

$^aR_1 = \Sigma(||F_0|-|F_c||)/\Sigma|F_0|$; $wR_2 = [\Sigma w(|F_0|^2-|F_c|^2)^2/\Sigma w(F_0^2)]^{1/2}$.
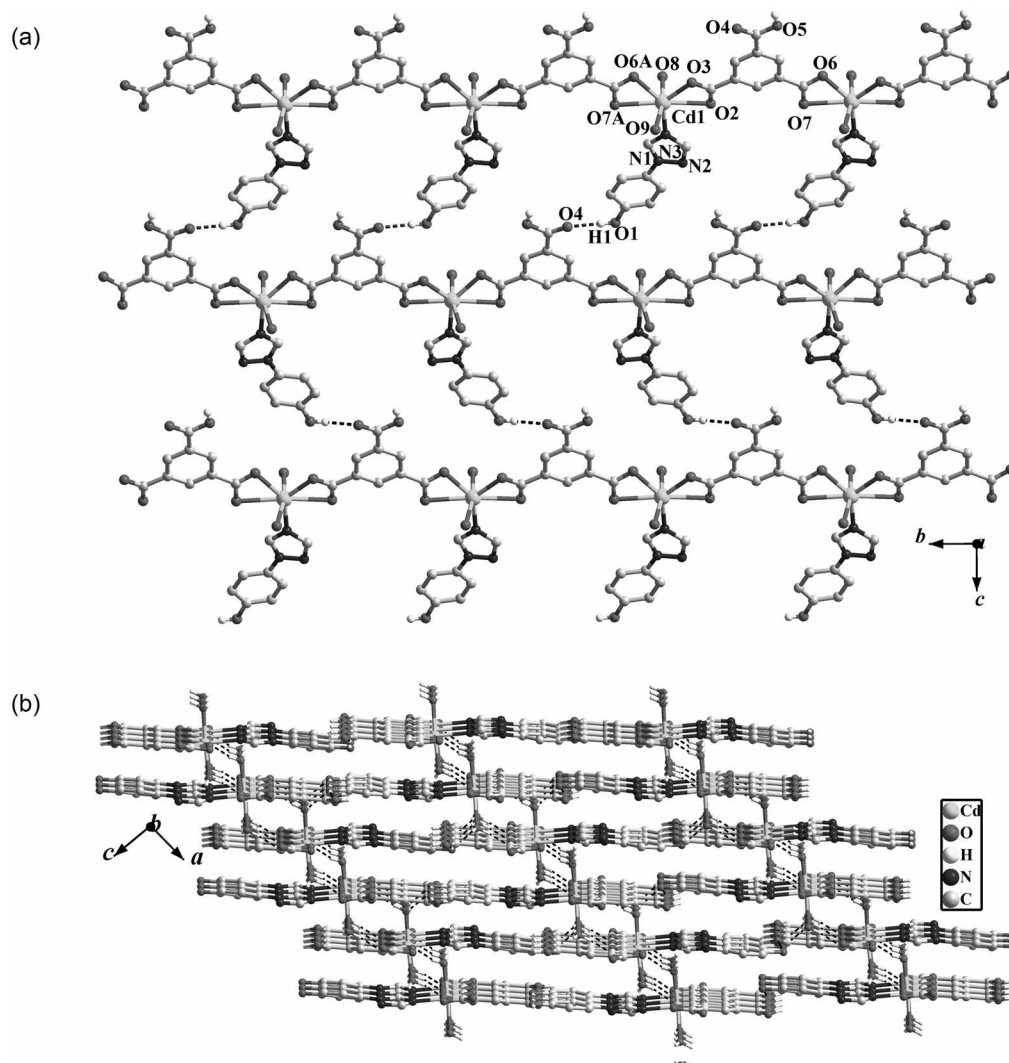
(s), 1387 (vs), 1273 (m), 1217 (w), 1130 (w), 1103 (w), 1051 (w), 829 (m), 731 (m), 668 (w), 627 (w), 569 (w), 527 (w).

X-ray Crystallography. Diffraction intensities for **1-3** were collected on a computer controlled Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Mo-*K*α radiation with radiation wavelength 0.71073 Å by using a ω-scan technique. The program SAINT was used for integration of the diffraction profiles.[13] Semi-empirical absorption corrections were applied using SADABS program.[14] The structures were solved by direct method and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs.[15] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically. The starting positions of H attached to oxygen atom were located in difference Fourier syntheses and then fixed geometrically as riding atoms. The crystallographic data and experimental details for structural analyses were summarized in Table 1. Selected bond distances and angles for **1-3** were listed in Tables 2-4, respectively. Hydrogen bond geometries were summarized in Table 5.

Results and Discussion

Synthesis and FT-IR Spectra. Single-crystals for the three compounds (**1-3**) were successfully obtained by careful control of the reaction media due to the considerable solubility of the hptrz. **1** was obtained in mixed methanol-water solution, which was different from the DMF-water medium for **2**. While **3** was obtained in ternary DMF-methanol-water medium. Additionally, the pH value of the medium also became a critical factor for the formation of the target complexes. **1** was grown in the weak acidic medium controlled by the molar ratio of mixed ligands (hptrz:H₃btc = 1:4). Both **2** and **3** were grown at neutral solution adjusted by triethylamine.

In their IR spectra, the broad and strong absorption bands appeared at 3466 and 3348 cm⁻¹ for **1**, 3437 cm⁻¹ for **2** and 3346 cm⁻¹ for **3** should be ascribed to the O-H stretching vibrations of water, hptrz and methanol, or OH-ip. The medium peak located at 1687 cm⁻¹ in **1** should be assigned to undeprotonated carboxylic group. In contrast, the absence of peaks between 1730 and 1690 cm⁻¹ in both **2** and **3**

Figure 1. (a) 2-D layer of **1** formed by interchain O-H⋯O H-bonds interactions with atomic labels in the asymmetric unit (only H-atoms involved in H-bond were included). (b) 3-D H-bonded network of **1**.

indicated the full deprotonation of H_2tp and $OH-H_2ip$,[16] which was consistent with the results of single crystal structure determinations. Additionally, 1 showed the characteristic bands of carboxylate groups at 1616 and 1560 cm^{-1} for asymmetric stretching and at 1528 and 1436 cm^{-1} for symmetric stretching, the smaller separation (< 200 cm^{-1}) between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ indicated the chelating bidentate coordination mode of carboxylate group. For 2, the asymmetric and symmetric stretching bands of carboxylate groups appeared at 1562, 1526 cm^{-1} and 1406 cm^{-1}. And their separations less than 200 cm^{-1} suggested the absence of the monodentate binding fashion of the carboxylate groups.[16] The asymmetric and symmetric stretching bands of carboxylate groups of 3 appear at 1657 and 1619 cm^{-1} and 1562, 1527, 1418 and 1387 cm^{-1}, suggesting the mixed coordination modes of the OH-ip dianion in the monodentate and chelating bidentate fashions respectively.[16] Additionally, the medium bands of the three complexes appeared at 1480-1520 cm^{-1} and 800-1400 cm^{-1} ranges should be associated with triazole ligand vibrations.[17] Thus, the results of IR spectra were well agreement with those of crystal structure determinations.

Solid Structures of 1-3. X-ray single crystal analyses reveal that 1 crystallizes in monoclinic *C2/c* space group, exhibiting a one-dimensional (1-D) polymeric chain bridged by partly deprotonated Hbtc. As shown in Figure 1a, the sole Cd(II) atom in the crystallographically asymmetric unit is seven-coordinated by one N donor from a neutral hptrz ligand and six O donors from two separate Hbtc anions and two water molecules, adopting a distorted pentagonal-bipyramidal geometry with two coordinated water molecules occupying the axial positions. The bond lengths of Cd-O and Cd-N are ranged from 2.2733(13) to 2.6369(15) Å (Table 2) and the central Cd(II) atoms deviates from the least-squares plane generated by O2-O3-O6A-O7A-N3 only *ca* 0.0352 Å.

The doubly deprotonated Hbtc anion affords its two deprotonated carboxylate groups to bridge the adjacent Cd(II) atoms in a bis-bidentate chelating fashion, resulting in the formation of 1-D linear chain along the *b*-direction (Figure 1a). And the nearest Cd⋯Cd distance across the same Hbtc anion is 10.3163(3) Å. Acting as a terminal ligand, the neutral hptrz coordinates with the Cd(II) atom in μ_4-monodentate fashion. Additionally, hptrz affords its uncoordinated phenolic OH group as H-bonds donor to produce interchain O(1)-H(1)⋯O(4) H-bonds interactions with the carboxylic group from the adjacent chain. Thus, these 1-D chains are assembled into 2-D supramolecular layer (Figure 1a). The H(1)⋯O(4) distance is 1.931 Å, and O(1)-H(1)⋯O(4) angle is 167.68° (see Table 5). These 2-D layers are further stacked together in *anti*-parallel manner by three-fold H-bonds interactions between coordinated water and carboxylate group of Hbtc or phenolic OH of hptrz (Figure 1b). H-bonds distances and angles are listed in Table 5. In addition, the lattice water and methanol molecules are further entrapped in the 3-D supramolecular network of 1 by classical O-H⋯O and O-H⋯N H-bonds interactions (see Table 5).

Different from 1, complex 2 shows a binuclear-based 2-D

Table 2. Selected bond distances (Å) and angles (°) for 1[a]

Cd(1)-O(3)	2.2733(13)	Cd(1)-O(8)	2.2811(15)
Cd(1)-N(3)	2.2901(16)	Cd(1)-O(6)#1	2.3095(13)
Cd(1)-O(9)	2.3271(14)	Cd(1)-O(2)	2.6283(14)
Cd(1)-O(7)#1	2.6369(15)		
O(3)-Cd(1)-O(8)	98.19(5)	O(3)-Cd(1)-N(3)	131.73(5)
O(8)-Cd(1)-N(3)	88.55(6)	O(3)-Cd(1)-O(6)#1	88.34(5)
O(8)-Cd(1)-O(6)#1	87.05(5)	N(3)-Cd(1)-O(6)#1	139.88(5)
O(3)-Cd(1)-O(9)	91.51(5)	O(8)-Cd(1)-O(9)	168.86(5)
N(3)-Cd(1)-O(9)	89.06(5)	O(6)#1-Cd(1)-O(9)	87.78(5)
O(3)-Cd(1)-O(2)	52.60(4)	O(8)-Cd(1)-O(2)	85.92(5)
N(3)-Cd(1)-O(2)	80.63(5)	O(6)#1-Cd(1)-O(2)	138.60(4)
O(9)-Cd(1)-O(2)	104.42(5)	O(3)-Cd(1)-O(7)#1	139.76(4)
O(8)-Cd(1)-O(7)#1	87.66(5)	N(3)-Cd(1)-O(7)#1	87.96(5)
O(6)#1-Cd(1)-O(7)#1	52.04(4)	O(9)-Cd(1)-O(7)#1	81.38(5)
O(2)-Cd(1)-O(7)#1	167.04(5)		

[a]Symmetry code: #1 = $x, y + 1, z$.

(4 4) layer motif extended by tp anions. As shown in Figure 2a, the fundamental structure subunit of 2 comprises two Cd(II) atoms, two coordinated H_2O molecules (O6 and O6A), two neutral hptrz ligands and two centro-symmetrical tp anions. Both Cd(II) atoms are seven-coordinated by one N donor from terminal hptrz ligand and six O donors from three tp anions and one water molecule, exhibiting a distorted pentagonal-bipyramidal coordination polyhedron (Table 3).

Two tp anions with symmetry center extend the binuclear subunits in the crystallographic *bc*-plane, leading to the formation of an infinite 2-D (4 4) layer (Figure 2b). The tp anions along *b*-direction adopt chelating and bridging bidentate coordination mode to strengthen four Cd(II) atoms from adjacent binuclear subunits. While the tp anions along *c*-axis is in a bis-bidentate chelating fashion to link the two Cd(II) atoms from the separate binuclear subunit. The adjacent 2-D planes are further linked together to form a 3-D network through the O-H⋯O H-bonds interactions between the deprotonated carboxylate group of tp ligand and the coordinated water or phenolic OH group of hptrz (Figure 2c). H-bonds distances and angles were listed in Table 5.

3 crystallizes in the triclinic *P*-1 space group, displaying a 1-D polymeric chain bridged by OH-ip dianions. The crystallographically asymmetric unit of 3 contains one Cd(II) atom, one hptrz ligand, one OH-ip anion, three H_2O molecules (two are coordinated and the third one is lattice water molecules), and a free DMF molecule respectively. The Cd(II) atom is six-coordinated by one N donor from one hptrz and five O donors from two OH-ip ligands and two water molecules, adopting a distorted octahedral coordination geometry (Figure 3a). The Cd-O and Cd-N distance are ranged from 2.252(2) to 2.4471(18) Å (Table 4), and are comparable to those Cd(II)-coordination polymers with mixed ligands containing N,O-donors.[18]

Notably, in addition to the chelating bidentate coordination fashion, one of the carboxylate groups from OH-ip anion also presents a monodentate binding mode, which alternately link the adjacent Cd (II) ions into an infinite 1-D
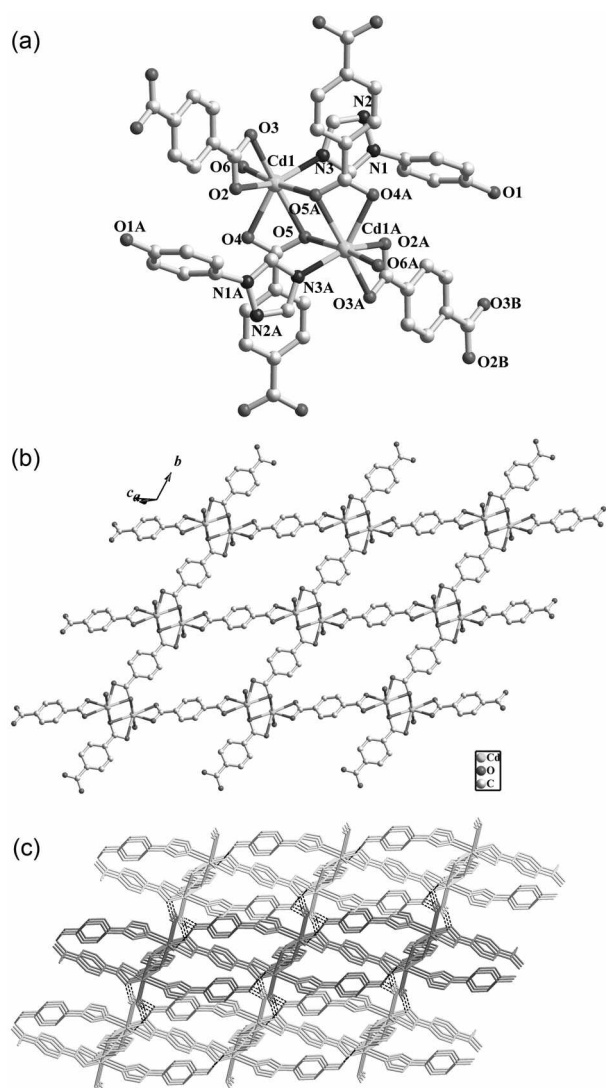
Figure 2. (a) Local coordination environment of Cd(II) in **2** (H atoms are omitted for clarity). (b) 2-D layer of **2** (hptrz ligands were omitted for clarity). (c) 3-D supramolecular network of **2** formed by H-bonds interactions.

Table 3. Selected bond distances (Å) and angles (°) for **2**[a]

Cd(1)–N(3)	2.289(2)	Cd(1)–O(6)	2.311(2)
Cd(1)–O(2)	2.312(2)	Cd(1)–O(3)	2.3917(19)
Cd(1)–O(4)	2.409(2)	Cd(1)–O(5)#1	2.471(2)
Cd(1)–O(5)	2.475(2)		
N(3)–Cd(1)–O(6)	90.35(8)	N(3)–Cd(1)–O(2)	147.94(8)
O(6)–Cd(1)–O(2)	105.48(8)	N(3)–Cd(1)–O(3)	98.16(8)
O(6)–Cd(1)–O(3)	88.71(7)	O(2)–Cd(1)–O(3)	55.56(7)
N(3)–Cd(1)–O(4)	131.05(8)	O(6)–Cd(1)–O(4)	78.51(7)
O(2)–Cd(1)–O(4)	80.13(7)	O(3)–Cd(1)–O(4)	128.56(7)
N(3)–Cd(1)–O(5)#1	82.45(8)	O(6)–Cd(1)–O(5)#1	172.57(6)
O(2)–Cd(1)–O(5)#1	80.06(7)	O(3)–Cd(1)–O(5)#1	90.51(7)
O(4)–Cd(1)–O(5)#1	107.63(7)	N(3)–Cd(1)–O(5)	84.98(8)
O(6)–Cd(1)–O(5)	104.45(7)	O(2)–Cd(1)–O(5)	116.49(7)
O(3)–Cd(1)–O(5)	166.50(6)	O(4)–Cd(1)–O(5)	53.38(6)
O(5)#1–Cd(1)–O(5)	76.84(7)		

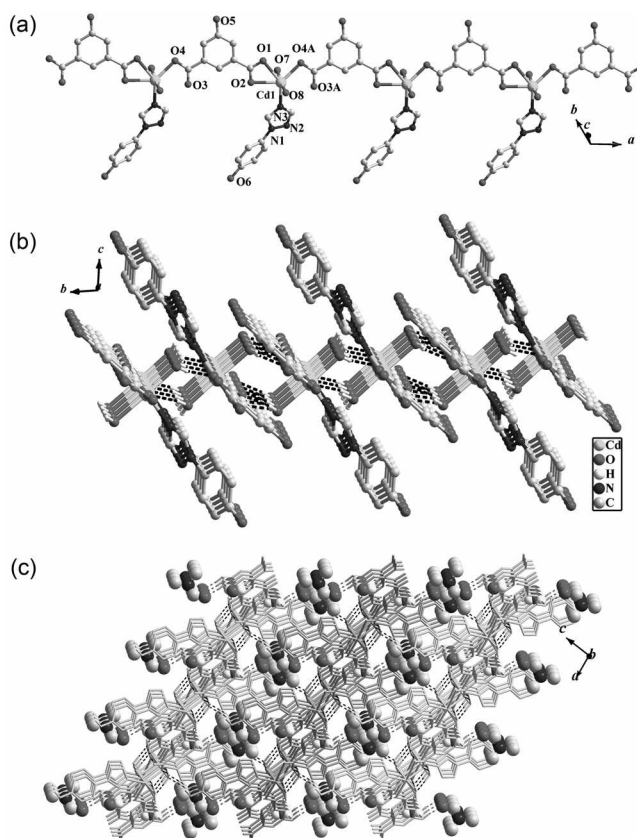[a]Symmetry code: #1 = −x + 1, −y + 1, −z + 1

Figure 3. (a) 1-D polymeric chain of **3** with atomic label in the asymmetric unit (H atoms are omitted for clarity). (b) 2-D layer of **3**. (c) 3-D supramolecular network of **3** formed by H-bonds interactions.

chain with the nearest Cd···Cd distance of being 10.1886(6) Å (Figure 3a). As shown in Figure 3b, the adjacent 1-D chains are further linked together to form a 2-D layer through H-bonds interactions between coordinated water and deprotonated carboxylate groups (O7-H7A···O1, O(7)-H(7B)···O(4) and O8-H8A···O3, Table 5). The adjacent layers are further assembled together into a 3-D supramolecular network by H-bonds interactions between phenolic OH of hptrz and coordinated water molecules. The lattice water and DMF molecules are entrapped within the 3-D network by extensive O-H···O interactions (Figure 3c and Table 5).

Coordination Modes of trz and Its Derivatives. It is well known that the binding preferences of a specific ligand towards metal ions depend essentially on the basicity of the N/O donor site, the steric hindrance of the substituent, the metal properties (main group or transition metal, charge, d-electron configuration, and the hard or softness) and, sometimes, the coligands that complete the metal coordination sphere.[19] Unsubstituted trz with less steric hindrance has exhibited four kinds of coordination modes (Scheme 1): $\mu_{1,4}$-bidentate bridging, μ_1- and μ_4-monodentate[20,21] mode in a neutral ligand and $\mu_{1,2,4}$-tridentate bridging manner in an anionic form,[1,12] which highly depend on the deprotonation ability. In contrast, the binding mode of the trz derivatives is considerably less diverse, and is close related to the position of the substituent. Hptrz, 1-substituted trz ligand, displays

**Table 4.** Selected bond distances (Å) and angles (°) for 3[a]

Cd(1)–O(8)	2.252(2)	Cd(1)–O(4)#1	2.2601(19)
Cd(1)–N(3)	2.268(2)	Cd(1)–O(1)	2.4213(19)
Cd(1)–O(2)	2.434(2)	Cd(1)–O(7)	2.4471(18)
O(8)–Cd(1)–O(4)#1	93.69(7)	O(8)–Cd(1)–N(3)	97.05(8)
O(4)#1–Cd(1)–N(3)	131.39(8)	O(8)–Cd(1)–O(1)	92.68(7)
O(4)#1–Cd(1)–O(1)	84.27(7)	N(3)–Cd(1)–O(1)	141.88(7)
O(8)–Cd(1)–O(2)	99.76(8)	O(4)#1–Cd(1)–O(2)	135.70(7)
N(3)–Cd(1)–O(2)	88.68(8)	O(1)–Cd(1)–O(2)	53.30(7)
O(8)–Cd(1)–O(7)	176.61(6)	O(4)#1–Cd(1)–O(7)	83.05(7)
N(3)–Cd(1)–O(7)	84.47(7)	O(1)–Cd(1)–O(7)	87.94(6)
O(2)–Cd(1)–O(7)	83.28(7)		

[a]Symmetry code: #1 = x + 1, y, z.

**Table 5.** Hydrogen-bonding parameters (Å, °) for 1-3[a]

Donor–H···Acceptor	D–H	H···A	D···A	D–H···A
1				
O1 – H1···O4#1	0.82	1.931	2.738(1)	167.68
O5 – H5···O11#2	0.82	1.844	2.663(1)	177.02
O8 – H8A···O2#3	0.85	1.874	2.711(1)	167.69
O8 – H8B···O10#4	0.85	1.920	2.754(1)	166.31
O9 – H9A···O6#5	0.85	1.858	2.705(1)	174.49
O9 – H9B···O1#6	0.85	2.258	3.002(4)	146.28
O10 – H10A···O7#7	0.85	1.863	2.711(0)	174.69
O10 – H10B···O4#8	0.85	2.222	2.990(5)	150.36
O11 – H11···N2#9	0.82	2.308	3.034(0)	147.89
2				
O1–H1···O4#1	0.82	1.832	2.648(0)	173.24
O6–H6A···O1#2	0.85	2.031	2.869(3)	168.47
O6–H6B···O3#3	0.85	1.850	2.693(4)	171.39
3				
O5 – H5··· O9#1	0.82	1.747	2.550(1)	165.61
O6 – H6···O7#2	0.82	2.011	2.776(1)	154.98
O7 – H7A···O1#3	0.85	2.021	2.720(1)	138.86
O7 – H7B···O4#4	0.85	1.921	2.701(3)	152.13
O8 – H8A···O3#5	0.85	1.897	2.730(0)	166.02
O8 – H8B···O10#5	0.85	1.889	2.723(1)	166.29
O10 – H10A···O2	0.85	1.896	2.742(4)	173.75
O10 – H10B···O5#4	0.85	2.016	2.837(4)	162.39

[a]Symmetry codes: For **1**: #1 = x – 1/2, –y + 1/2, z + 1/2; #2 = x, y –1, z – 1; #3 = – x, – y, – z; #4 = – x, – y + 1, – z; #5 = – x + 1/2, – y – 1/2, – z; #6 = – x, y, – z + 1/2; #7 = x, y + 1, z; #8 = – x + 1/2, – y + 1/2, – z; #9 = x + 1/2, – y + 1/2, z + 1/2. For **2**: #1 = x – 1, y – 1, z –1; #2 = – x + 1, – y + 1, – z; #3 = – x + 2, – y + 1, – z + 1. For **3**: #1 = x, y + 1, z + 1; #2 = – x + 1, – y + 1, – z; #3 = – x + 2, – y + 2, – z + 1; #4 = – x + 1, – y + 2, – z + 1; #5 = – x + 1, – y + 1, – z + 1.

two types of monodentate modes: μ_2- and μ_4-binding modes probably resulted from the steric hindrance of aromatic ring.[11] The corresponding 4-substituted trz ligands such as *p*-MeOptrz, *m*-ptr and *p*-ptr show μ_2-monodentate and $\mu_{1,2}$-bidentate bridging modes.[6,8-10] Obviously the binding behaviors of the reported trz derivatives herein are only dominated by the trz ring, rather than the substitute. Therefore, the design and exploration of the novel trz-based ligand with potentially multiple coordinate sites are important and necessary to fully investigate the complex structure and their applications.
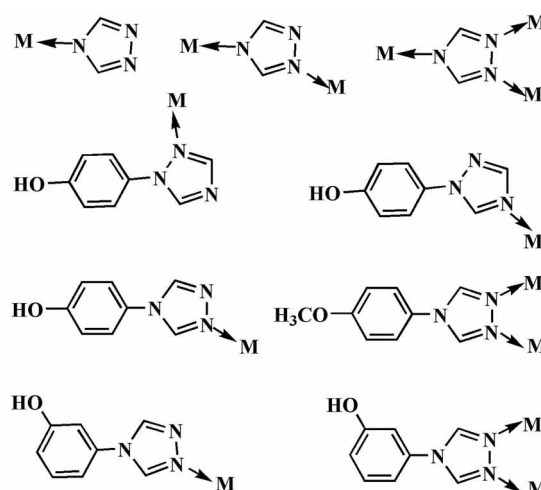
Scheme 1. Coordination modes of 1,2,4-triazole and its derivatives.

Thermal Stability. Owing to the analogous structure of **1** and **3**, in the present investigation, only **1** and **2** were selected as the representatives to explore the thermal stability of the hptrz-based mixed-ligand complexes. Both complexes presented two obvious weight-loss processes (Figure 4). For **1**, the first weight-loss began at 40 °C and ended at 142 °C, corresponding to the synchronous release of lattice/coordinated water and CH₃OH molecules (obs: 13.2%, calcd: 12.3%). Then, due to the consecutive decomposition of the mixed-ligand, the second weight-loss of **1** was ranged from 225 to 486 °C. And the final product was calculated to be CdO (obs: 21.7%, calcd: 22.6%). In contrast, coordination polymer **2** was thermally stable up to 184 °C. The first weight-loss occurred from 184 °C to 240 °C, due to the release of the two coordinated water molecules. The second weight-loss process between 307 °C and 473 °C was corresponding to the continuous decomposition of organic ligands (obsd: 72.3%, calcd: 71.8%). The weight of the residue above 473 °C (obsd: 27.7%) was assigned to CdO (calcd: 28.2%). Thus 2-D layered **2** displays considerable higher thermal stability than that of **1** with polymeric chain motif.
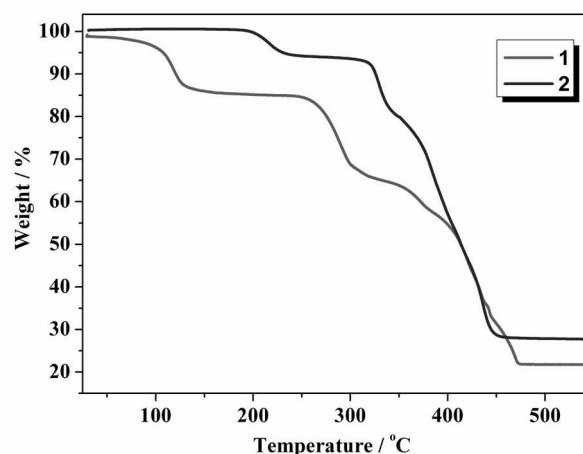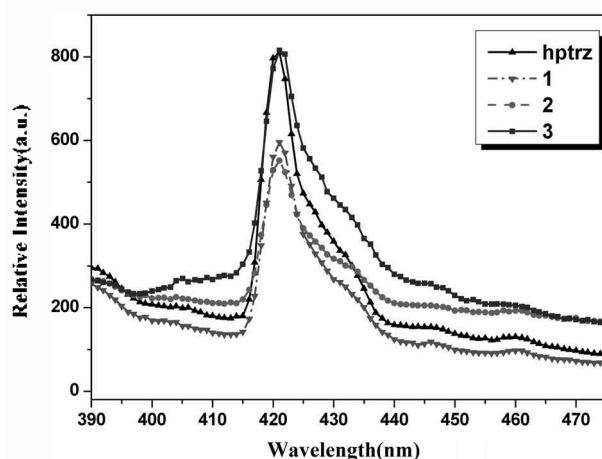

Figure 4. TG curves for 1 and 2.

Figure 5. Solid state fluorescence emission spectra of 1-3 and free hptrz ligand at room temperature.

Luminescent Properties. The solid-state fluorescent emission spectra of **1-3** were measured and presented in Figure 5. Upon excitation at 370 nm, the three solid samples displayed the maximum emissions at 421 nm but with variable intensity. In contrast, under the comparable experimental conditions, the similar emission behavior to the solid complexes was observed for the free hptrz ligand. Thus, the analogous emissions between hptrz and the solid complexes indicated that the emission were originate from π-π^* transition of the triazole rings.[18,22] The slightly shift of the emission peaks should be ascribed to both the deprotonation of the aromatic coligand as well as the chelating coordination action of the carboxylate and hptrz to Cd (II) ions.

Conclusion

Three hptrz-based Cd(II)-coordination polymers, infinite 1-D chains for **1** and **3** and 2-D layer for **2**, have been isolated by conventional evaporation method. Structure determinations confirm that the diversity structures of **1-3** are significantly directed by the aromatic polycarboxylate coligands not the terminal hptrz. Instead, their appreciable fluorescence emission behaviors mainly originate from the π-π^* electronic transfer of the core hptrz ligands.

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