DOI: 10.1002/zaac.200800175

Two 1,2,4-Triazole-based Zinc(II) Complexes with Aromatic Acid as Coligand: Synthesis, Structure and Fluorescence Properties

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Received January 21st, 2008; accepted April 28th, 2008.

Abstract. Two two-dimensional (2-D) trz-based coordination polymers, $\{[Zn(trz)(mb)]\cdot H_2O\}_n$ (**1**) and $\{[Zn(trz)(ca)]\cdot H_2O\}_n$ (**2**) (Htrz = 1,2,4-triazole, Hmb = 4-methylbenzoic acid, and Hca = *trans*-cinnamic acid), have been synthesized by diffusion method and fully structural characterized by elemental analysis, FT-IR, single-crystal X-ray crystallography, TG and fluorescence spectra. Structural analysis reveals that both complexes exhibit the analogous 2-D Zn^{II}-trz layer motif with hydrophobic aromatic rings attached on both sides despite their different crystal system and space group (orthorhombic, *Pbca* for **1** and monoclinic, $P2_1/c$ for **2**). Interestingly, the discrete water-dimer and infinite 1-D water-chain were observed to be entrapped in the 2-D layer of **1** and **2**, respectively, resulted from the different orientation of lattice water molecules as well as the patterns of hydrogen bonds involved. In addition, their similiar thermal behaviors and fluorescence emissions originated from intraligand electronic transfer were also investigated and compared.

Keywords: Zinc; Cordination polymers; 1,2,4-Triazole; Aromatic acids; Mixed-ligands

Introduction

During the past decades, extensive interest has been focused on the design and construction of coordination polymers due to their potential applications in gas storage, separation, magnetism, nonlinear optics, luminescence, and catalysis as well as their rational design principles to construct intriguing structures and topologies [1]. Undoubtedly, the choice of functional organic ligand with different tether lengths, different charge balance requirements and alternative functional group orientations may play more important roles for the overall structure and functions of the target coordination polymers among variously possible factors including the ligand, inorganic counterion, solvent system and so on. In this aspect, unsubstituted 1,2,4-triazole (Htrz), as one of small and simple five-membered heterocycles, can not only function as a neutral bridging ligand to two metal sites or in the anionic form as a bridge to the three metal centers in $\mu_{1,2}$, $\mu_{2,4}$, and $\mu_{1,2,4}$ modes, but also be potentially applied in the fields of luminescence, magnetic materials and gas sorption [2, 3]. Recently, *Zubieta* and his coworkers [3] have thoroughly investigated the structure and properties of a series of binary metal/ triazolate and ternary metal/ trz/ X^{n-} complexes (X^{n-} = F^-, Cl^-, Br^-, I^-, OH^-, NO_3^- SCN^- and SO_4^{2-}), indicating that anionic componets X^{n-} can participate in the framework connectivity as bridging ligands and are responsible for the formation of diversity substructural components together with trz and metal ions. Such the substructure contains trinuclear and tetranuclear clusters, adamantoid cages, chains, and layers. More recently, aromatic/fatty acids, as one of the functional ligands displayed by various coordination modes of carboxylate group, are introduced into trz-based metal-complexes as coligands by hydrothermal method and have unexpectedly produced a series of novel 3-D topological framework with unusual polynuclear cluster (linear trinuclear, pentanuclear up to heptanuclear) as secondary building units [4]. It has been pointed out that the presence of aromatic polycarboxylate coligand plays a significant role in tuning the nuclearity of metal-trz clusters and the connectivity of a specific network [4]. However, despite the exciting preceding results, only limited trz-based complexes with aromatic acid as coligand have been reported to date probably resulted from the insoluble and intractable polycrystalline powders during the preparation [5, 2c]. Therefore, it is much necessary and significant to continue to systematically explore the coordination behavior involved in aromatic acid/ trz/ metal system. Thus, in the present paper, two novel trz-based complexes, $\{[Zn(trz)(mb)]\cdot H_2O\}_n$ (**1**) and $\{[Zn(trz)(ca)]\cdot H_2O\}_n$ (**2**), are successfully isolated by incorporating the aromatic acid (Hmb = 4-methylbenzoic acid, and Hca = *trans*-cinnamic acid) as coligand under diffusion method. The two complexes were fully structural characterized; their thermal stability and luminescence properties were further investigated and compared in more detail. The structure determinations suggest that the variation of coligand from Hmb to Hca can't significant affect

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their overall structure, although they belong to different crystal system and space group. Interestingly, the orientation of the lattice water molecules and their related hydrogen bonds arrangement lead to the presence of separate water-dimer in **1** and infinite one-dimensional (1-D) water-chain in **2**.

Experimental Section

Reagents and instruments

All reagents were purchased commercially 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 (Leeman-Labs) analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken on an AVATAR-370 (Nicolet) spectrometer in the range 4000 − 400 cm^{-1} region. Thermogravimetric analysis (TGA) experiments were carried out on Shimadzu simultaneous DTG-60A compositional analysis instrument from room temperature to 800 °C under N_2 atmosphere at a heating rate of 5 °C/min. Fluorescence spectra of the polycrystalline powder samples were performed on a Cary Eclipse fluorescence spectrophotometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature.

Synthesis of Complexes

$\{[Zn(trz)(mb)]\cdot H_2O\}_n$ (1). A solution containing Hmb (6.8 mg, 0.05 mmol) and Htrz (7.2 mg, 0.1 mmol) in CH_3OH (5 mL) was carefully layered onto a buffer layer of ethyl acetate (2 mL) in a straight glass tube, below which an aqueous solution of $Zn(OAc)_2\cdot 2H_2O$ (22 mg, 0.1 mmol) was placed. Upon slow evaporation of the mixture at room temperature, colorless block crystals appeared on the wall of the tube within two weeks, washed with ethanol and water and dried in air. Yield: 60 % based on Zn. Anal. Calcd. for $C_{10}H_{11}ZnN_3O_3$: C, 41.91; H, 3.87; N, 14.66 %. Found: C, 42,01; H, 4.01; N, 14.89 %. IR (KBr, cm^{-1}): 3467vs, 3127w, 2364w, 1609ms, 1543ms, 1514ms, 1412ms, 1392ms, 1293m, 1200w, 1169m, 1091ms, 1039w, 1002m, 860w, 790w, 768ms, 692w, 666ms, 635m, 433w.

$\{[Zn(trz)(ca)]\cdot H_2O\}_n$ (2). The colorless block single crystals of **2** suitable for X-ray analysis were obtained by adopting the similar procedures to **1** only with Hca instead of Hmb. Yield: 52 % based on Zn. Anal. Calcd for $C_{11}H_{11}ZnN_3O_3$: C, 44.25; H, 3.71; N, 14.07 %. Found: C, 44.23; H, 3.80; N, 14.14 %. IR (KBr, cm^{-1}): 3454vs, 1641ms, 1555ms, 1392ms, 1296m, 1241w, 1172w, 1095m, 1004w, 975w, 876w, 774w, 724w, 664m, 604w, 486w.

X-ray crystallography

Diffraction intensities for **1** − **2** were collected on Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation with radiation wavelength 0.71073 Å by using the φ-ω scan technique at 296(2) K. There was no evidence of crystal decay during data collection. Semiempirical absorption corrections were applied (SADABS), and the program SAINT was used for integration of the diffraction profiles [6]. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [7]. 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 are summarized in Table 1. Selected bond distances and angles for **1** and **2** are listed in Tables 2. Hydrogen bond geometries are summarized in Table 3. CCDC−674930 **1** and CCDC−674931 **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via **www.ccdc.can.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**).

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

	1	**2**
Empirical formula	$C_{10}H_{11}N_3O_3Zn$	$C_{11}H_{11}N_3O_3Zn$
Formula weight	286.59	298.60
Crystal size /mm	0.25 × 0.23 × 0.20	0.25 × 0.23 × 0.22
Temperature /K	296(2)	296(2)
Wavelength /Å	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	$P2_1/c$
Absorption coefficient (Mo$K\alpha$) /mm^{-1}	1.871	1.815
D_c /(g/cm^3)	1.451	1.463
a /Å	27.770(5)	14.6438(12)
b /Å	9.7213(17)	9.6060(8)
c /Å	9.7213(17)	9.6475(8)
β /°	90	92.7480(10)
V /Å^3	2624.4(8)	1355.54(19)
Z	8	4
h/ k/ l	−33, 24 / −11, 8 / −11, 11	−11, 17 / −11, 11 / −9, 11
F(000)	1168	608
Reflections collected / unique	11995 / 2299	6708 / 2397
R_{int}	0.0298	0.0157
Completeness to theta = 25.01	99.4 %	99.8 %
Data / restraints / parameters	2299 / 18 / 164	2397 / 36 / 173
R_1, $wR_2[I > 2\sigma(I)]$ [a)]	0.0624 / 0.1664	0.0320 / 0.0900
R_1, wR_2(all data) [a)]	0.0690 / 0.1707	0.0393 / 0.0953
Max. and min. transmission	0.740 / 0.673	1.000000 / 0.772582
GOF on F^2	1.043	1.019
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e·Å^{-3})	0.706 / −0.586	0.552 / −0.357

[a)] $R_1 = \Sigma(\|F_0|-|F_C\|)/\Sigma|F_0|$; $wR_2 = [\Sigma w(|F_0|^2-|F_C|^2)^2/\Sigma w(F_0^2)]^{1/2}$.

Results and Discussion

Syntheses and FT-IR spectra

Due to the insoluble precipitate immediately produced by the mixing of the reactants, **1** − **2** were finally obtained as crystalline phases by diffusion method. It should be noted that the preparation of the two complexes were also carried out by hydrothermal techniques, since it is also a good alternation for the crystallization and growth of compounds with limited solubility. Unfortunately, the obtained results reveals that the presence of disorder mb and ca in the corresponding crystal structure. Attempts to synthesize **1** − **2** in organic medium were failed by conventional evaporation method. Therefore, it can be concluded that the preparation methods greatly affect the crystallization and the growth of the target complexes.

In their IR spectra, the strong and broad adsorption bands centered at *ca*. 3467 cm^{-1} for **1** and 3454 cm^{-1} for **2** are the characteristic vibration of OH group in H_2O, further confirming the existence of lattice water molecules. The absence of the band at ca. 1700 cm^{-1} suggests the deprotonation of aromatic acids in **1** and **2**. And the asymmetric (ν_{as}) and symmetric vibrations (ν_s) of the carboxylate group are located at 1609 and 1392 cm^{-1} for **1**, and 1641 and 1392 for **2**, respectively. Their differences (217 nm for **1** and 249 nm for **2**) between ν_{as} and ν_s, which is larger than 200 cm^{-1}, indicates the unidentate coordination mode of carboxylate group [8] and are agreement with the crystal structure determinations. In addition, the medium bands appeared at 1480−1520 cm^{-1} should be associated with $\nu_{C=N}$ of the triazole. And the bands in the 800 − 1400 cm^{-1} range are also associated with triazole ligand vibrations [9].

Structure descriptions of complexes 1 − 2

{[Zn(trz)(mb)]·2H$_2$O}$_n$ (1). Crystal structural determination reveals that **1** is an infinite 2-D layer constructed from binuclear $[Zn_2(trz)_2]$ subunit. The asymmetric unit contains one Zinc(II) atom, one deprotonated trz, one mb anion and two lattice water molecules with 50 % occupancy for each oxygen atom. As shown in Figure 1a, the sole Zn^{II} atom is coordinated with three nitrogen atoms from three different trz and one carboxylate oxygen atom from mb anion, completing a distorted tetrahedral geometry. The bond lengths of Zn−N and Zn−O are slightly varied from 1.967(5) to 2.042(5) Å, which are comparable to the previously reported values [4, 5]. In the binuclear $[Zn_2(trz)_2]$ subunit, two symmetry-related Zn^{II} sites are bridged by two trz anions in the N1, N2-bridging mode, forming a $\{Zn_2N_4\}$ heterocycle, in which the Zn···Zn separation is 3.777 Å and the two trz rings are strictly coplanar. Then, the $\{Zn_2N_4\}$ heterocycle is connected with four adjacent subunits through the coordination bonds of Zn^{II} atoms with the remaining N4 position of an exocyclic trz, generating an infinite 2-D layer in *bc*-plane (Figure 1b). Thus, each trz ligand affords its three nitrogen atoms to link three Zinc sites together in $\mu_{1,2,4}$-tridentate mode. Viewed along the crystallographically *a*-direction, the 2-D layer contains 16-membered macrocycles composed by four Zinc sites and four trz ligands. Topologically, this connectivity pattern generates a 2-D 4, 8^2−net sheet, when both Zn1 and trz are treated as three connected nodes. In addition, on both sides of the wave-like layer, mb anions were further attached by coordination of carboxy O with Zinc sites and complete the layer motif with hydrophobic aromatic ring as exterior (Figure 1c). Unexpectedly, the presence of mb anions can't lead to the significant π···π interactions between aromatic rings within intra- and interlayer. Therefore, the adjacent layers are interdigitatedly stacked together with no obvious interactions and the interlayer Zn···Zn distance is 18.412 Å (Figure 1c). Interestingly, the separate water-dimer were entrapped within 2-D layer by O-H···O hydrogen bonds interactions between carboxylate O atom of mb and lattice water molecules (see Table 3 and Figure 1c). Specially, due to the specific orientations of the two lattices water molecules, double hydrogen bonds interactions are observed, resulting in the presence of water-dimer.

Table 2 Selected bond lengths/Å and angles/° for complex **1−2** $^{a)}$

1			
Zn(1)−O(1)	1.967(5)	Zn(1)−N(3) $^{b)}$	2.006(5)
Zn(1)−N(2) $^{a)}$	2.005(5)	Zn(1)−N(1)	2.042(5)
O(1)−Zn(1)−N(2) $^{a)}$	117.2(2)	O(1)−Zn(1)−N(1)	101.0(2)
O(1)−Zn(1)−N(3) $^{b)}$	114.8(2)	N(2)^a−Zn(1)−N(1)	107.11(19)
N(2)^a−Zn(1)−N(3) $^{b)}$	112.9(2)	N(3)^b−Zn(1)−N(1)	101.35(19)
2			
Zn(1)−O(1)	1.943(3)	Zn(1)−N(3) $^{a)}$	2.004(3)
Zn(1)−N(1)	1.994(3)	Zn(1)−N(2) $^{b)}$	2.031(2)
O(1)−Zn(1)−N(1)	119.44(12)	O(1)−Zn(1)−N(2) $^{b)}$	101.20(12)
O(1)−Zn(1)−N(3) $^{a)}$	113.57(12)	N(1)−Zn(1)−N(2) $^{b)}$	107.13(10)
N(1)−Zn(1)−N(3) $^{a)}$	111.49(11)	N(3)^a−Zn(1)−N(2) ^{b}	101.54(10)

$^{a)}$ Symmetry Codes: for **1** ^{a} $-x, -y + 1, -z$, ^{b} $x, -y + 3/2, z + 1/2$; for **2** ^{a} $-x + 1, y - 1/2, -z + 1/2$, $^{b)}$ $-x + 1, -y, -z + 1$.

Table 3 Selected hydrogen bond lengths/Å and bond angles/° $^{a)}$

D − H···A	*d* (D − H)	*d* (H···A)	*d* (D···A)	∠DHA
1				
O3 − H3A···O4$^{a)}$	0.850	2.564	2.920	106.41
O4 − H4B···O3$^{b)}$	0.850	2.397	2.921	120.38
O3 − H3B···O2	0.851	2.518	3.023	118.90
O4 − H4A···O2	0.857	2.506	2.770	98.88
2				
O3 − H3A···O4$^{a)}$	0.850	2.611	2.907	101.92
O3 − H3B···O4$^{a)}$	0.850	2.614	3.310	140.01
O4 − H4B···O2$^{b)}$	0.850	2.277	2.804	120.34
O3 − H3A···O2	0.850	2.503	3.025	120.60

$^{a)}$ Symmetry Codes: for **1** ^{a} $x, -y + 1/2, z - 1/2$, $^{b)}$ $x, -y + 1/2, z + 1/2$; for **2** ^{a} $x, y, z - 1$, ^{b} $x, y, z + 1$.

{[Zn(trz)(ca)]·H$_2$O}$_n$ (2). Different from **1** belonging to *Pbca* space group in orthorhombic crystal system, **2** crystallizes in the *P2$_1$/c* space group of monoclinic crystal system. However, the overall structure of **2** is much similar to those of **1**. All bond lengths around four-coordinated Zn^{II} site in **2** are slightly longer than those of **1** (see Table 2), suggesting that the potentially stronger coordination ability. Additionally, although relatively larger coligand (ca vs. mb) was introduced in **2**, the interlayer distance was shortened 3.768 Å obviously resulted from the much deeper interlude between the adjacent 2-D layers. Another striking difference between the two complexes is the orientation of lattice water molecules, which were arranged into infinite 1-D water-chain along the crystallographically *c* axis, as shown in Figure 2b. Within 1-D water-chain, O3 solely served as the donor of hydrogen bonds while O4 is only acts as the acceptor. Thus, 1-D water-chain not water-dimer of **1** was observed in **2**.

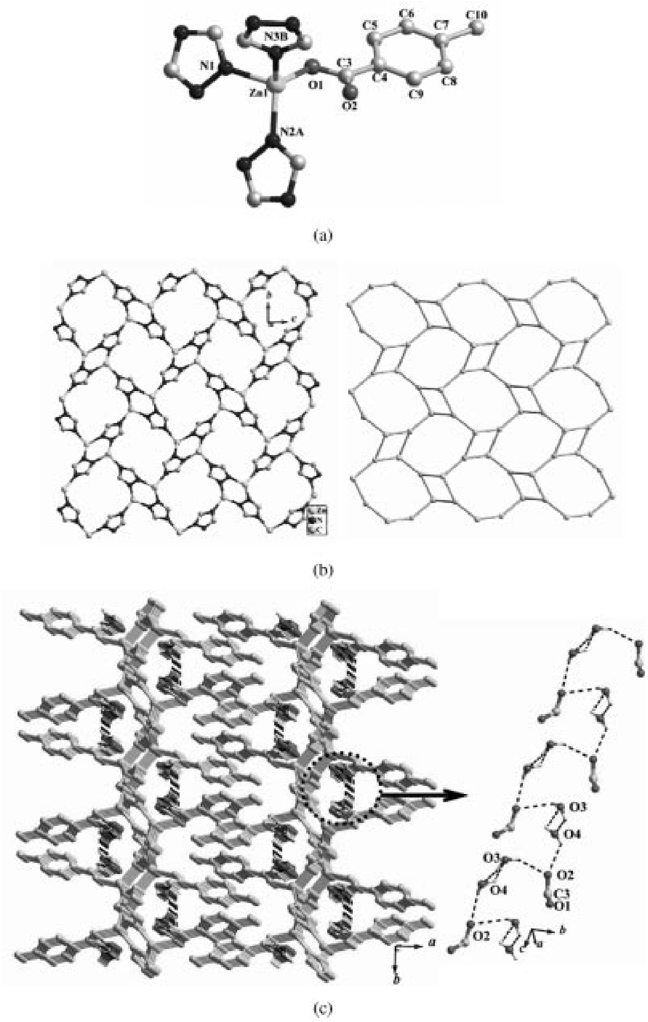

Figure 1 (a) Coordination environment of the Zinc(II) atom in **1**; (b) View of the Zn-trz layer along (100) direction and the $4,8^2$-net sheet; (c) 2-D interdigitated layers of **1** with water-dimer being trapped by H-bonds interaction.

Thermal Stability

Thermogravimetric experiments were conducted to compare the thermal stability of the two analogoue complexes. As shown in Figure 3, the two complexes display much similar thermal behavior. The lattice water molecules in **1** are lost between 30 °C and 95 °C (expt. 5.52 % calcd. 6.28 %). Then a region of plateau was appeared between 95 °C and 330 °C. Upon further heating, the framework starts to collapse, accompanying the decomposition of the mixed organic ligands (expt. 63.51 % calcd. 65.40 %), and leave amorphous grey powder as the final products (expt. 29.18 % calcd. 28.30 %), which is calculated to be ZnO. Compared with **1**, the total release of water molecules entrapped in **2** was slightly quickly (expt. 5.47 % calcd. 6.02 %). And the temperature is lowered 30 °C than that of **1**. In contrast, the decomposition of the 2-D layer of **2** is slow, which began at 285 °C and ended at 580 °C (expt. 66.18 % calcd. 66.69 %). The final product is also ZnO (expt. 29.51 % calcd. 27.13 %). Thus, the thermal behavior of the two complexes suggests their minor difference in thermal stability.

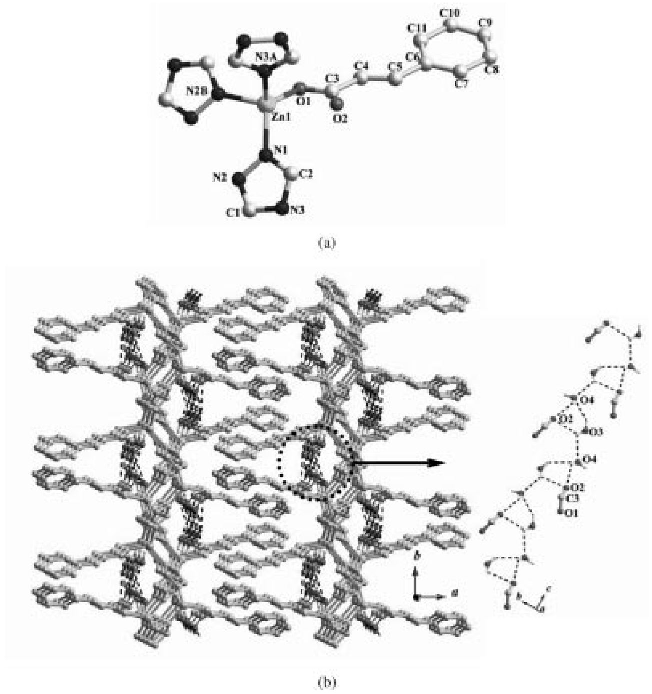

Figure 2 (a) Coordination environment of the Zinc(II) in **2**; (b) 2-D interdigitated layer of **2** with 1-D water-chain being trapped by H-bonds interaction.

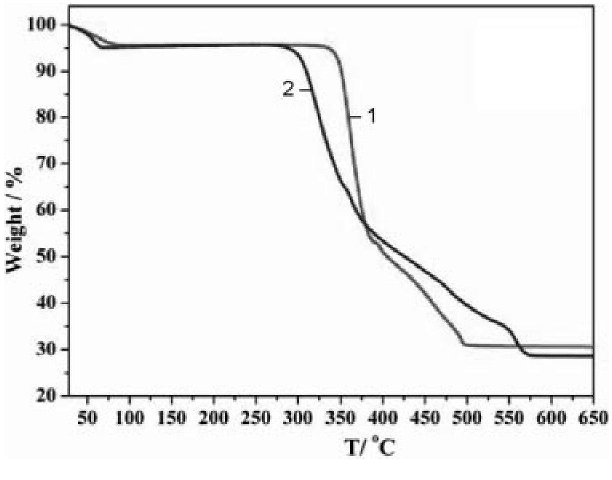

Figure 3 Thermogravimetric profiles for **1** − **2**.

Luminescent properties

The solid-state fluorescence spectra of **1** − **2** at room temperature are depicted in Figure 4 to examine the luminescent properties of the d^{10} metal complexes. Both complexes present much similar strong emission at ca. 422 nm and weak peaks at 510 nm upon excitation at 374 nm. To understand the nature of the emission spectra, the luminescence properties of the free trz ligand under the same conditions were also recorded for comparison. And the trz ligand exhibit emission bands at 422 nm upon excitation at 374 nm. Therefore, the emissions of **1** − **2** may be assigned to intraligand fluorescent emission [3, 4d]. The slight difference between the two complexes and free Htrz should be resulted from the ligand chelation to the metal center, and the deprotonation of the two ligands [10].

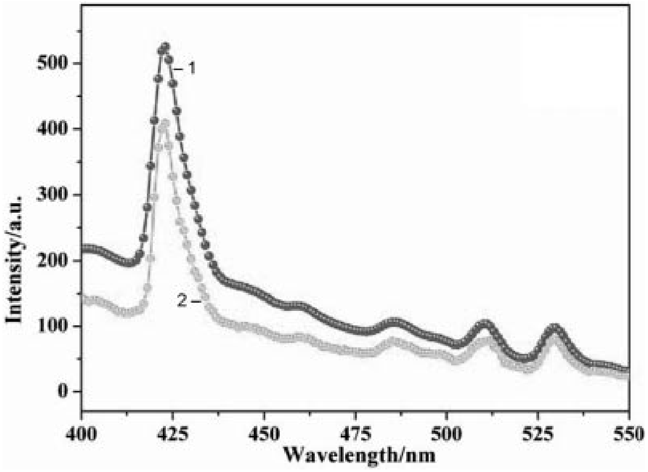

Figure 4 Solid-state emission spectra of **1** − **2** at room temperature.

Conclusion

Two ternary trz-based Zn(II) complexes with aromatic acid as coligand were isolated by room temperature diffusion method, which display similar Zn-trz layer motif with aromatic ring appending on both sides. The appearance of the independent water-dimer in **1** and infinite 1-D water-chain in **2** dominates their difference in structure. Additionally, their similar thermal behaviors and fluoresce properties were observed resulted from the analogous overall structure.

Acknowledgments. This present work was supported by the National Natural Science Foundation of China (20571056, 20703030), the National Key Fundamental Research Project of China (2005CCA01200), Natural Science Foundation of Tianjin (06YFJMJC03900, 07QTPTJC29800) and Tianjin Educational Committee (20060501, 2006ZD07).

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