A Blue Photoluminescent 2-D Coordination Polymer Constructed by Dinuclear Zinc(II) Subunits $[Zn_2(oz)_2]$ [Hoz = 2-(2′-Hydroxyphenyl)-2-oxazoline] and Dicyanamide

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Keywords: Zinc / Photoluminescence / Dinuclear subunit / Polymer / Thermal stability

Substitution of the terminal oz group of the dinuclear $[Zn(oz)_2]_2$ complex (**1**) with dicyanamide [where Hoz = 2-(2′-Hydroxyphenyl)-2-oxazoline] results in the formation of a 2-D coordination polymer $[Zn(oz)N(CN)_2]_n$ (**2**) based on $[Zn_2(oz)_2]$ subunits. Both compounds exhibit strong blue photoluminescence but the coordination polymer **2** has greater thermal stability than the dinuclear complex **1**.

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Introduction

Blue luminescent compounds have received considerable attention in recent years because of their potential applications in electroluminescent (EL) devices or light-emitting diodes (LED).[1] Since the realization of blue electroluminescence using poly(9,9-dihexylfluorene)[3a][3b] and poly(*p*-phenylene),[3c] intensive research in this area has been reported.[3d] Most of the reported examples are aromatic organic molecules, conjugated organic polymers,[1,2] organometallic compounds or metal−chelate compounds of Al^{III}, B(III), Zn^{II} or Cd^{II} based on 8-hydroxyquinoline,[4] methylquinolin-8-ol,[5] azomethine,[6] azaindole,[7] oxadiazole[8] and bipyridyl[9] ligands, while cases of condensed coordination polymers exhibiting blue luminescence are still rare. With the advantages of high thermal stability, good mechanical properties, versatile structures and relatively high emitting intensity (with respect to pure organic materials), blue luminescent coordination polymers have recently attracted significant interest.[10] Inspired by the electroluminescence research on the mononuclear complex of bis[2-(2-hydroxyphenyl)benzothiazolate]zinc $[Zn(BTZ)_2]$,[8a] we started using the ligand 2-(2′-hydroxyphenyl)-2-oxazoline, (Hoz), and dicyanamide anions as structural motifs to develop new blue luminescent coordination-polymers. Hoz has a smaller conjugated system than 2-(2-hydroxyphenyl)benzothiazolate, which may shift the emission wavelength of complexes with such a ligand to blue luminescence since fluorescent emission is dominated by the coordinated ligand. We herein describe the preparation, structural characterization and preliminary luminescence study of a dinuclear zinc complex $[Zn(oz)_2]_2$ (**1**) and a 2-D coordination polymer $[Zn(oz)N(CN)_2]_n$ (**2**) with the dinuclear $[Zn_2(oz)_2]$ fragment as subunit. The two dimer-based compounds may provide a model for studying the influence of the polymerization process upon luminescence and thermal stability.

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Results and Discussion

Complex **1** was prepared by mixing $Zn(ClO_4)_2$, Hoz, and triethylamine in methanol in a 1:2:2 molar ratio. Colorless single crystals were obtained after the reaction solution was left to stand overnight at room temperature. Complex **2** was prepared by dissolving equimolar amounts of sodium dicyanamide, Hoz and triethylamine in methanol (20 mL) and then adding $Zn(ClO_4)_2$ in methanol (5 mL) to the solution. The reaction mixture was filtered and after one week colorless crystals appeared in the filtrate. The ORTEP drawing of **1** is shown in Figure 1. Complex **1** is dimeric with two discrete molecules per unit cell. The zinc atom is five-coordinate with three oxygen and two nitrogen atoms. One chelated terminal ligand provides one oxygen and one nitrogen atom, and the two bridging ligands provide a total of two oxygen and one nitrogen atom. The coordination sphere can be described as distorted trigonal-bipyramidal. The two zinc atoms in a discrete molecule are symmetrically related and connected by the O1 atoms of the bridging ligands. Compared with the previously reported mononuclear com-

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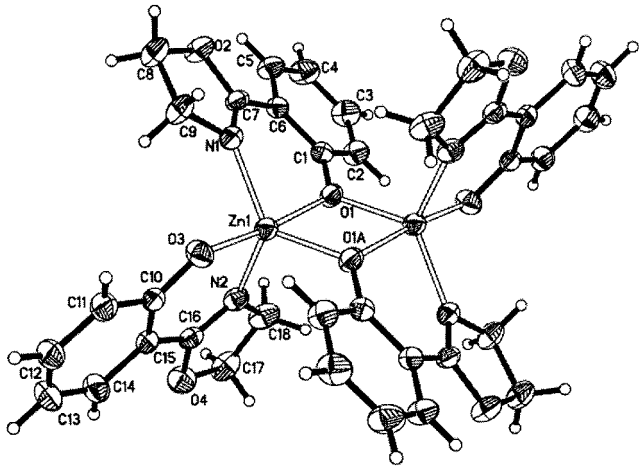

Figure 1. Perspective view of **1** (30% thermal ellipsoids except for hydrogen) and atom-numbering scheme; significant bond lengths (Å) and angles (°): Zn(1)−O(1) 2.118(2); Zn(1)−O(1A) 2.026(2); Zn(1)−O(3) 1.985(2); Zn(1)−N(1) 2.041(3); Zn(1)−N(2) 2.019(3); O(3)−Zn(1)−N(2) 90.14(11); O(3)−Zn(1)−O(1A) 102.50(10); N(2)−Zn(1)−O(1A) 106.12(11) O(3)−Zn(1)−N(1) 90.36(11); N(2)−Zn(1)−N(1) 125.00(12); O(1A)−Zn(1)−N(1) 127.28(11); O(3)−Zn(1)−O(1) 174.09(10); N(2)−Zn(1)−O(1) 95.31(11); O(1)−Zn(1)−O(1A) 78.22(10); N(1)−Zn(1)−O(1) 84.64(10)

plex $Zn(BTZ)_2$,[8a] the formation of the dinuclear motif in **1** may be caused by the smaller oz ligand and the existence of oxygen atoms acting as μ_2 bridges.

The zinc atoms in **2** display trigonal-bipyramidal geometry, as in **1**, with three nitrogen atoms, two of which are provided by terminal N atoms of different $[N(CN)_2]^-$ ligands and the other by the chelating oz ligand, and two oxygen atoms from two oz ligands. Hence, two oxygen atoms from two ligands bridging two symmetrically related zinc atoms form the dinuclear subunit. The ORTEP drawing of the dinuclear subunit is shown in Figure 2. Each subunit is further linked to four subunits through $\mu_{1,5}$ bridges of $[N(CN)_2]^-$ and each $[N(CN)_2]^-$ moiety acts as a bidentate spacer to coordinate to two zinc atoms with two nitrile nitrogen atoms. If the dinuclear units are viewed as connecting points, the structure can be simplified into a 2-D square-grid network (see **a** in Figure 3). Each square grid shares four $\mu_{1,5}$ $[N(CN)_2]^-$ groups as rhombic sides and four dimers as connecting nodes. The average distance between two parallel ligands from adjacent layers is 3.54 Å, indicating the existence of π−π stacking in the 3-D supramolecular architecture (see **b** in Figure 3).

The two complexes were further studied by thermogravimetric analysis, which showed that **1** began to lose weight at around 320 °C (see **a** in Figure 4) while **2** exhibited a higher decomposition temperature at 374 °C (see **b** in Figure 4).

The absorption spectrum of **1** in methanol at 298 K shows an intense low-energy band at λ_{max} = 337 nm, which is similar in energy to the absorption band (λ_{max} = 323 nm) of the deprotonated ligand oz^- in a KOH/MeOH solution (ca. 0.2 M; see Figure 5). Complex **1** is highly luminescent in methanol solution at 298 K and the emission maximum and quantum yield are 404 nm and 0.28 (quinine sulfate in

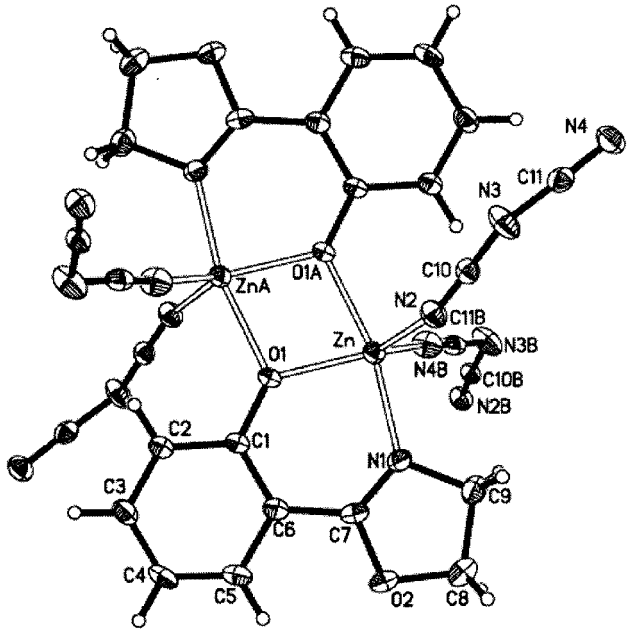

Figure 2. Perspective view of **2** (30% thermal ellipsoids except for hydrogen) and atom-numbering scheme: Zn−O(1) 1.9971(19); Zn−N(2) 2.029(2); Zn−N(1) 2.046(2); Zn−N(4B) 2.047(3); Zn−O(1A) 2.122(2); O(1)−Zn−N(2) 119.54(9); O(1)−Zn−N(1) 89.26(9); N(2)−Zn−N(1) 97.52(10); O(1)−Zn−N(4B) 127.02(10); N(2)−Zn−N(4B) 112.70(10); N(1)−Zn−N(4B) 92.35(11); O(1)−Zn−O(1A) 78.02(8); N(2)−Zn−O(1A) 92.26(9); N1−Zn−O(1A) 166.68(9); N(4B)−Zn−O(1A) 92.20(10)

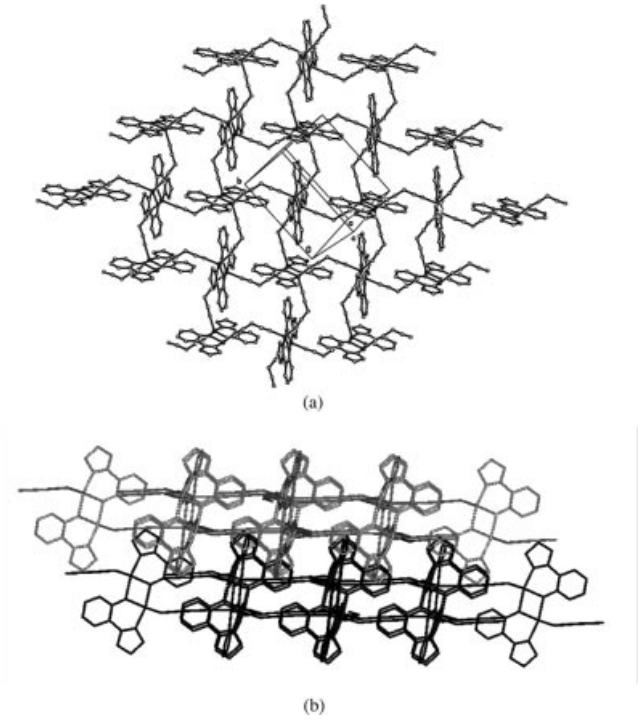

Figure 3. (a) 2-D square-grid network of **2**; (b) π-π stacking between adjacent layers

0.1 N sulfuric acid as reference), respectively. The lifetime for this emission is too short to be measured accurately by our instrument with a threshold of 100 ns. This emission is

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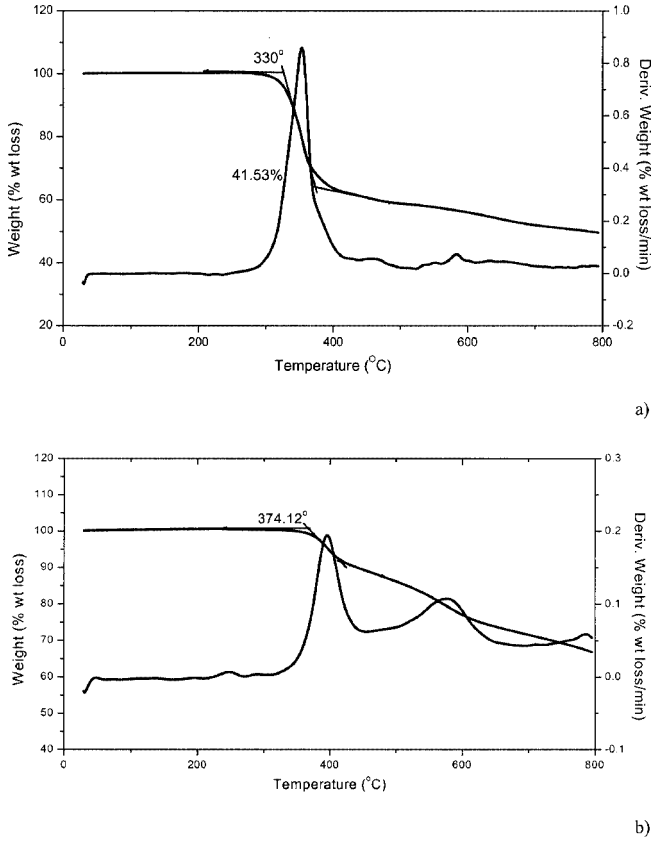

Figure 4. (a) TGA and DTGA curves of complex **1**; (b) TGA and DTGA curves of **2**

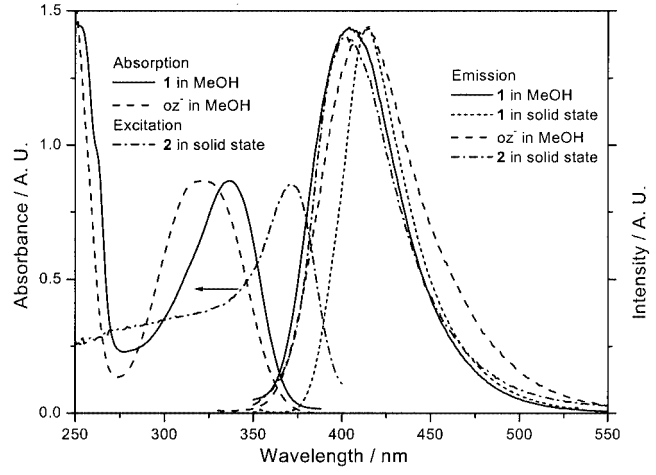

Figure 5. Absorption of the deprotonated oz^- ligand (λ_{ex} = 325 nm) and **1**, excitation of **2** (λ_{ex} = 430 nm) (left, the low-energy bands are normalized for comparison), and normalized emission (right) of the deprotonated oz^- ligand and **1** and **2** at 298 K (λ_{ex} = 325 nm)

similar in energy to that (emission maximum 415 nm, quantum yield 0.09) recorded for the deprotonated ligand oz^- in a KOH/MeOH solution (ca. 0.2 M; see Figure 5) but with a significantly higher quantum yield. These results indicate that the emission from complex **1** originates from the oz^- ligand and an intraligand charge-transfer excited-state is tentatively assigned. The emission enhancement from oz^- to complex **1** could be attributed to the coordination at the zinc atom, which presumably increases the structural rigidity and hence reduces the non-radiative decay-pathway for the excited state. The solid-state emission spectra of dimeric **1** and polymeric **2** (which is not soluble in common organic solvents) have also been recorded at 298 K and depicted in Figure 5. The emission energies (λ_{max} = 415 nm for **1** and 402 nm for **2**) are similar to that recorded for **1** in methanol solution at 298 K, suggesting that no new emissive species such as a $\pi-\pi^*$ excimer or exciplex are formed in the solid states.

Conclusion

Herein we reported the synthesis and photoluminescence study of a dinuclear zinc complex and a 2-D zinc coordination polymer containing dinuclear subunits. The two complexes exhibit similar ligand-centered fluorescence in the blue region. Incorporation of the dinuclear $[Zn_2(oz)_2]$ unit into a coordination polymer appears to improve the thermal stability while luminescence properties are not significantly modified.

Experimental Section

Synthesis of $[Zn(oz)_2]_2$ (1): $Zn(ClO_4)_2$ (0.5 mmol) was added to a methanol solution (20 mL) containing Hoz (1 mmol) and triethylamine (1 mmol). Colorless single crystals were obtained after the reaction solution was left to stand overnight at room temperature. $C_{36}H_{32}N_4O_8Zn_2$ (779.40): calcd. C 55.48, H 7.19, N 4.14; found C 55.24, H 7.25, N 4.17. IR (KBr): 2978(w), 2907(w), 1624(s), 1535(m), 1469(m), 1390(m), 1359(m), 1324(m), 1241(s), 1157(m), 1073(m), 951(m), 930(m), 847(m), 757(m), 689(m), 575(w), 535(w), 433(w) cm^{-1}.

Synthesis of $[Zn(oz)N(CN)_2]_n$ (2): Equimolar amounts of sodium dicyanamide, Hoz and triethylamine were dissolved in methanol (20 mL) and then $Zn(ClO_4)_2$ in methanol (5 mL) was added and the solution was filtered. After the filtrate was left at room temperature for one week, colorless crystals appeared. $C_{11}H_8N_4O_2Zn$ (293.58): calcd. C 45.00, H 2.75, N 19.08; found C 44.89, H 2.84, N 19.01. IR (KBr): 2977 (w), 2907 (w), 2339 (m), 2267 (m), 2198 (s), 1639 (s), 1555 (m), 1483 (s), 1384 (m), 1371 (m), 1323 (m), 1242 (s), 1159 (m), 1067 (m), 944 (m), 930 (m), 840 (m), 758 (m), 688 (m), 575 (w), 508 (w), 433 (w) cm^{-1}.

X-ray Crystallographic Determinations of 1 and 2: All the data collections were carried out on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation (0.71073 Å) at 293 K. Empirical absorption correction was applied to both cases. The structures were solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL 97 program. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed by calculation positions and refined isotropically (see Table 1).

CCDC-221016 (**1**) and CCDC-221015 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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

	1	**2**
Formula	$C_{36}H_{32}N_4O_8Zn_2$	$C_{11}H_8N_4O_2Zn$
M_R	779.400	293.58
λ (Å)	0.71073	0.71073
T (K)	293	293
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	8.9417(18)	9.5703(3)
b (Å)	9.851(2)	12.2372(4)
c (Å)	18.920(4)	9.7463(3)
α (°)	90	90
β (°)	96.181(3)	98.7230(10)
γ (°)	90	90
V (Å^3)	1656.8(6)	1128.22(6)
Z	2	4
ρ_{cacld} (Mg·m^{-3})	1.562	1.728
μ(Mo-K_α) (mm^{-1})	1.508	2.175
F(000)	800	592
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 12$, $-24 \le l \le 23$	$-12 \le h \le 12$, $-15 \le k \le 15$, $-12 \le l \le 12$
Reflections collected	25062	19938
Independent reflections	3763	2479
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Parameters	227	163
Goodness-of-fit	1.024	1.004
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.046$, $wR2 = 0.08$	$R1 = 0.036$, $wR2 = 0.068$
Largest diff. peak/hole (e·Å^{-3})	0.57/−0.44	0.49/−0.47

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