Strongly luminescent metal–organic compounds: spectroscopic properties and crystal structure of substituted 1,8-naphthyridine and its zinc(II) complex

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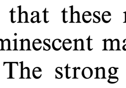
N,*N*′-Bisbenzyl-2,7-diamino-1,8-naphthyridine (L) and its zinc(II) complex, [Zn(L)$_2$(OAc)$_2$], are strongly luminescent materials with emission quantum yields in methanol being 0.38 and 0.59, respectively. The crystal structure of [Zn(L)$_2$(OAc)$_2$] features a one-dimensional chain structure through intermolecular π–π stacking interactions. A broad emission band ranging from 400 to 600 nm is observed from the [Zn(L)$_2$(OAc)$_2$] solid at room temperature.

Introduction

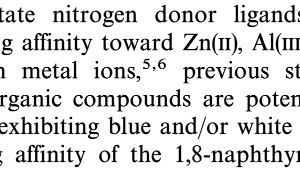
There is a current interest in strongly luminous materials due to their potential applications in light-emitting diode devices.[1–4] However, few metal–organic compounds showing intense fluorescence or phosphorescence at wavelengths <450 nm are reported in the literature. Notable examples are those containing either 8-hydroxyquinoline or 7-azaindolate (aza) ligands.[3,4] While polydentate nitrogen donor ligands are known to have high binding affinity toward Zn(II), Al(III) and some heavy non-transition metal ions,[5,6] previous studies suggest that these metal–organic compounds are potentially new luminescent materials exhibiting blue and/or white emissions.[6] The strong binding affinity of the 1,8-naphthyridine moiety toward metal ions is well documented in the literature.[7] Recent studies by various workers have demonstrated that aromatic amides can be effective chelating and/or bridging ligands in a variety of metal complexes as exemplified by those linear metal atoms arrays.[5,8] In this work, we prepared *N*,*N*′-bisbenzyl-2,7-diamino-1,8-naphthyridine (L) which combines the structural features of naphthyridine and aromatic amide ligands.

Results and discussion

L was synthesized by the reaction of 2,7-dichloro-1,8-naphthyridine[9] with benzylamine in toluene according to the reported procedure *i.e.* refluxing a methanolic solution of Zn(OAc)$_2 \cdot 2H_2O$ and L for 30 min, and a pale yellow crystalline solid was isolated by slow diffusion of diethyl ether into the resultant solution. The solid was subsequently identified by X-ray crystal analysis as [Zn(L)$_2$(OAc)$_2$].



1,8-naphthyridine



L

Fig. 1 depicts a perspective view of the [Zn(L)$_2$(OAc)$_2$] molecule. The Zn atom adopts a distorted tetrahedral coordination geometry; the measured Zn–N(3) and Zn–N(7) distances of 2.043(2) and 2.050(2) Å, respectively, are comparable to the related bond distance (2.055 Å) found for [Zn(dpa)(OAc)$_2$][5b] (dpa = 2,2′-dipyridylamine). In principle, L can exhibit a mondentate, bidentate or dinuclear bridging binding mode. As shown in the crystal packing diagram (Fig. 2), the molecules are self-organized through extensive π–π stacking interactions between the naphthyridyl rings. The interplanar separations are 3.489 Å, and the molecules are linked to generate a supramolecular one-dimensional chain structure. We cannot identify any significant π–π stacking interaction between the phenyl substituents as reflected by the rather large interplanar separation (>4.0 Å).

The photophysical properties of L and [Zn(L)$_2$(OAc)$_2$] are listed in Table 1. The zinc complex shows two intense absorptions at $\lambda_{max} = 236$ ($\varepsilon = 1.48 \times 10^5$) and 367 nm ($\varepsilon = 8.3 \times 10^4$ dm^3 cm^{-1} mol^{-1}), which are assigned to intraligand π–π*

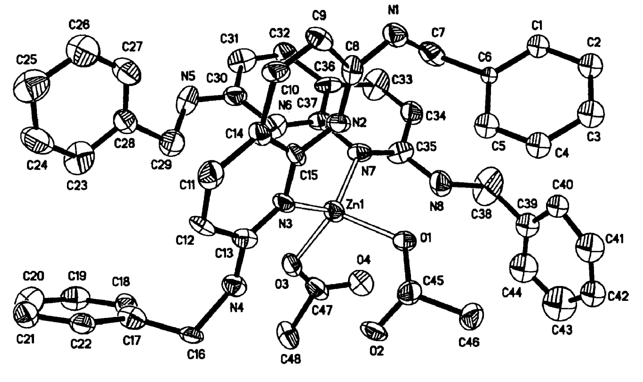


Fig. 1 Perspective view of [Zn(L)$_2$(OAc)$_2$] (50% thermal ellipsoids) and atom-numbering scheme. Significant bond distances (Å) and angles (°): Zn(1)–N(3) 2.043(2), Zn(1)–N(7) 2.050(2), Zn(1)–O(1) 1.937(2), Zn(1)–O(3) 1.965(2); N(3)–Zn(1)–N(7) 129.00(9), N(3)–Zn(1)–O(1) 107.21(10), N(3)–Zn(1)–O(3) 99.07(9), N(7)–Zn(1)–O(1) 99.58(9), N(7)–Zn(1)–O(3) 109.22(10); O(1)–Zn(1)–O(3) 113.08(9).

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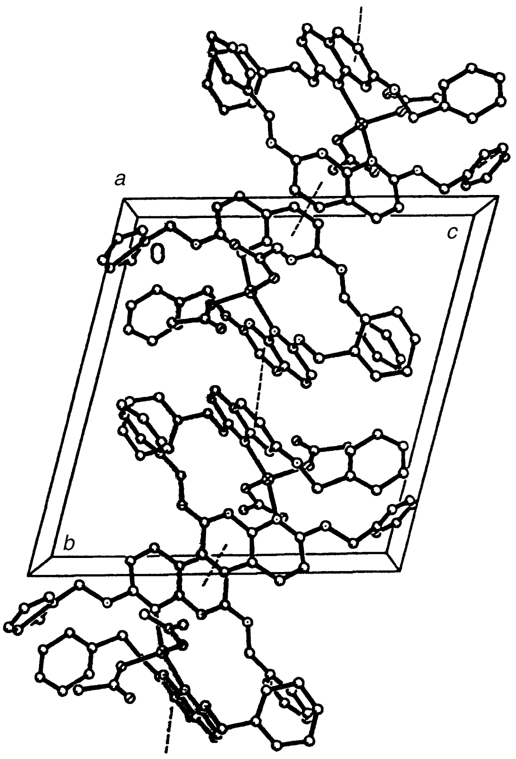

Fig. 2 $[Zn(L)_2(OAc)_2]$ molecules are self-assembled to form infinite one-dimensional chains by π–π stacking interactions.

transitions of L. At room temperature, the zinc complex shows an intense emission at $\lambda_{max} = 395$ nm ($\tau = 4.5$ ns) in degassed MeOH, the excitation spectrum of which is the same as the absorption spectrum. The emission is poorly vibronically-resolved with the vibrational spacing (*ca.* 1100 cm^{-1}) comparable to the skeletal vibrational frequency of the free ligand (Fig. 3). We assign the emission to an intraligand $^1(\pi\text{–}\pi^*)$ fluorescence. It is noteworthy that the $[Zn(L)_2(OAc)_2]$ complex has a higher emission quantum yield than L (0.59 *vs.* 0.38) in methanol solution at room temperature. Presumably, coordination of L to Zn(II) increases the ligand conformational rigidity, thereby reducing the non-radiative decay of the intraligand $^1(\pi\text{–}\pi^*)$ excited state. Similar enhancement of the intraligand fluorescence has also been reported for the $[Zn(terpyridine)_2]^{2+}$ system.[6] At room temperature, the crystalline $[Zn(L)_2(OAc)_2]$ solid shows a broad emission band (solid line in Fig. 3) ranging from 400 to 600 nm (peak maxima at 434 and 470 nm), which is significantly red-shifted from the solution emission spectrum. As revealed by the crystal packing diagram of the complex, the interplanar separation of 3.489 Å should allow excimeric interaction of the 1,8-naphthyridine moieties in the solid state, which may be responsible for the low energy solid state emission at wavelengths >450 nm.

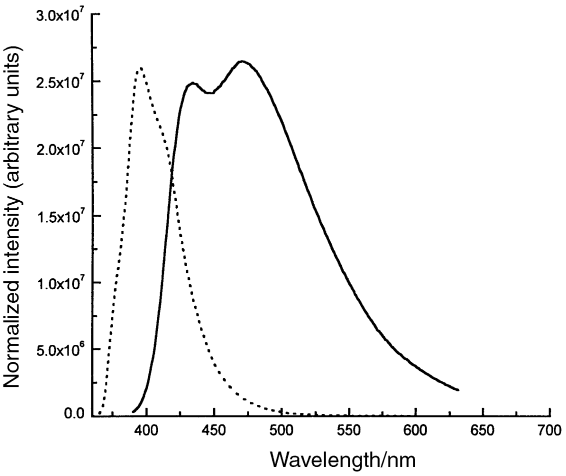

Fig. 3 Emission spectra of $[Zn(L)_2(OAc)_2]$ in degassed MeOH (···) and in the solid state (——) at room temperature. Excitation: 367 nm.

Conclusion

In conclusion, the naphthyridyl ligand and its zinc(II) complex exhibit a high energy blue emission in solution and a broad white emission in the solid form. Compared with $[Zn_4O(Aza)_6]^4$ ($\Phi = 0.17$), the $[Zn(L)_2(OAc)_2]$ molecules self-assemble through intermolecular π–π interactions to form a supramolecular structure. The high UV intraligand emission together with the visible emission arising from intermolecular ligand–ligand interactions suggest a future for supramolecular zinc(II) complexes as advanced materials in the design of white light emitters.[6]

Experimental

All the starting materials were used as received and solvents were purified according to standard methods. 2,7-Dichloro-1,8-naphthyridine was obtained commercially. The UV-vis spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer, emission spectra on a SPEX Fluorolog-2 Model F11 fluorescence spectrophotometer. Emission lifetimes of the compounds were measured with a Quanta Ray DCR-3 Nd-YAG laser as the excitation light source (pulse output 266 nm, 8 ns). The ^1H NMR spectra were recorded on a DPX-300 Bruker FT spectrometer with chemical shifts (in ppm) relative to tetramethylsilane. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences, Beijing.

Preparation of *N,N′*-bisbenzyl-2,7-diamino-1,8-naphthyridine (L)

A mixture of 2,7-dichloro-1,8-naphthyridine[7](0.5 g, 2.5 mmol) and benzylamine (30 ml) was refluxed at 150 °C for 8 h. After solvent evaporation, the residue was recrystallized from toluene (20 ml) to afford a yellow crystalline solid. Overall yield: 0.48 g, 56%. Found: C, 77.59; H, 5.95; N, 16.50%. Calc. for $C_{22}H_{20}N_4$: C, 77.62; H, 5.92; N, 16.46%. ^1H NMR (270

Table 1 Photophysical data for L and the zinc(II) complex

	UV-vis λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})^a	Solid emission maxima 298 K	Solid emission maxima 77 K	Methanol solution at 298 K λ_{max}/nm^b	Φ_{em}	τ/ns^c
L	236 (54 000) 367 (32 000)	418, 434 500(sh)	389, 410	396, 413(sh)	0.38	3.6
$[Zn(L)_2(OAc)_2]$	236 (148 000) 367 (83 000)	434, 470	407	395, 414(sh)	0.59	4.5

^{a} In MeOH at 298 K. ^{b} Excitation wavelength = 367 nm. ^{c} Excited at 266 nm picosecond pulses (300 K).

MHz, CD_3OD, TMS):δ 7.59 (d, 2H, $^3J = 8.7$), 7.38 (d, 4H, $^3J = 7.4$), 7.29 (t, 4H, $^3J = 7.1$), 7.27 (t, 2H, $^3J = 6.1$), 6.46 (d, 2H, $^3J = 8.64$ Hz), 4.68 (s, 4H). IR (KBr) v/cm^{-1}: 1600s, 1528s, 1342m, 1147m, 796w, 796w, 695w. EI-MS: m/z 340 $[M]^+$.

Preparation of $[Zn(L)_2(OAc)_2]$

A methanolic solution (20 ml) of L (0.34 g, 1 mmol) was added to a refluxing solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.11 g, 0.5 mmol) in MeOH (30 ml), and the mixture was refluxed for 3 h. After cooling to room temperature, the solvent was removed by rotary evaporation, and the white residue was recrystallized by slow diffusion of diethyl ether into a methanolic solution to afford colorless crystals. Overall yield: 0.3 g, 70%: Found: C, 66.45; H, 5.51; N, 12.84%. Calc. for $C_{48}H_{46}N_8O_4Zn$: C, 66.70; H, 5.37; N, 12.96%. ^{1}H NMR (270 MHz, CD_3OD, TMS):δ 7.62 (d, 2H, $^3J = 8.5$), 7.34 (m, 8H), 7.25 (m, 2H), 6.48 (d, 2H, $^3J = 8.6$), 4.60 (d, 4H, $^3J = 5.5$ Hz), 1.90 (s, 3H). FAB-MS: m/z 805 $[M^+ - OAc]$, 463 $[M^+ - L - OAc]$.

X-Ray crystallographic chracterisation of $[Zn(L)_2(OAc)_2]$

Crystals suitable for X-ray structure determinations were obtained by slow diffusion of diethyl ether into a methanol solution of the complex at room temperature. Data were collected on a Bruker CCD SMART system, the crystal data and structure refinement are: triclinic, space group $P\bar{1}$, $a = 9.612(9)$, $b = 15.884(15)$, $c = 15.884(15)$ Å, $\alpha = 105.35(2)$, $\beta = 92.65(3)$, $\gamma = 92.65(3)°$, $U = 2332(4)$ Å^3, $Z = 2$, $D_c = 1.231$ Mg m^{-3}, μ(Mo-Kα) = 0.577 mm^{-1}, $F(000) = 904$, $T = 294(2)$ K, 8311 independent reflections with $I > 2\sigma(I)$ were used in the refinement. The data were refined by full matrix least squares on F^2, and $R = 0.085$, $R_w = 0.21$ with a goodness-of-fit of 0.82 were obtained. Note that the C(1)–C(6) and C(39)–C(41) atoms are disordered and were refined by isotropic refinement.

CCDC reference number 440/222. See http://www.rsc.org/suppdata/nj/b0/b005644h/ for crystallographic files in .cif format.

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