

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

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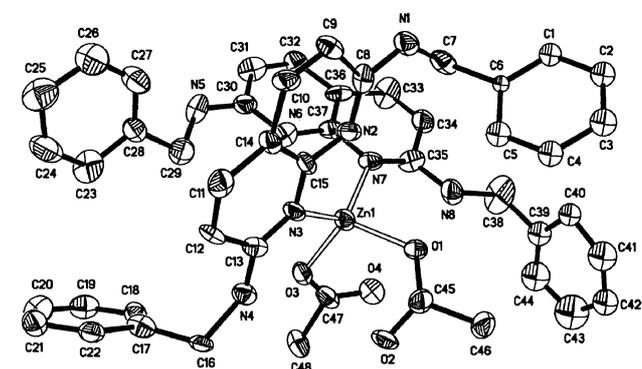
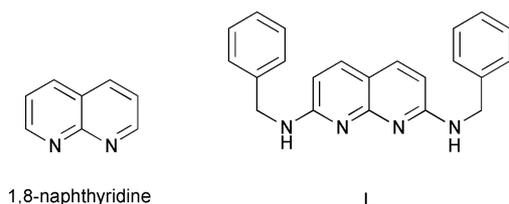
*N,N'*-Bisbenzyl-2,7-diamino-1,8-naphthyridine (L) and its zinc(II) complex,  $[\text{Zn}(\text{L})_2(\text{OAc})_2]$ , are strongly luminescent materials with emission quantum yields in methanol being 0.38 and 0.59, respectively. The crystal structure of  $[\text{Zn}(\text{L})_2(\text{OAc})_2]$  features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

## Introduction

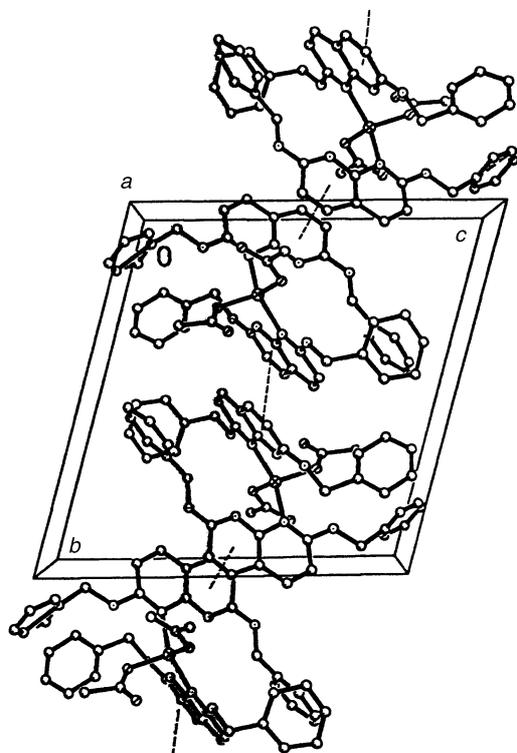
There is a current interest in strongly luminous materials due to their potential applications in light-emitting diode devices.<sup>1–4</sup> However, few metal–organic compounds showing intense fluorescence or phosphorescence at wavelengths < 450 nm are reported in the literature. Notable examples are those containing either 8-hydroxyquinoline or 7-azaindolate (aza) ligands.<sup>3,4</sup> While polydentate nitrogen donor ligands are known to have high binding affinity toward Zn(II), Al(III) and some heavy non-transition metal ions,<sup>5,6</sup> previous studies suggest that these metal–organic compounds are potentially new luminescent materials exhibiting blue and/or white emissions.<sup>6</sup> The strong binding affinity of the 1,8-naphthyridine moiety toward metal ions is well documented in the literature.<sup>7</sup> 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.<sup>5,8</sup> 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<sup>9</sup> with benzylamine in toluene according to the reported procedure *i.e.* refluxing a methanolic solution of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  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  $[\text{Zn}(\text{L})_2(\text{OAc})_2]$ .

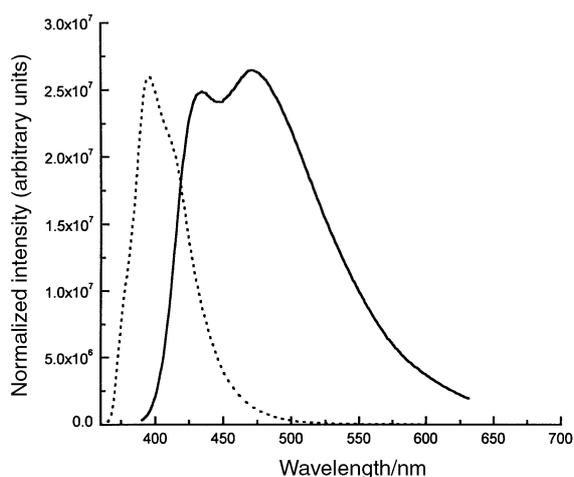


**Fig. 1** Perspective view of  $[\text{Zn}(\text{L})_2(\text{OAc})_2]$  (50% thermal ellipsoids) and atom-numbering scheme. Significant bond distances (Å) and angles (°): Zn(1)–N(3) 2.043(2), Zn(1)–N(7) 2.050(2), Zn(1)–O(1) 1.937(2), Zn(1)–O(3) 1.965(2); N(3)–Zn(1)–N(7) 129.00(9), N(3)–Zn(1)–O(1) 107.21(10),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



**Fig. 2**  $[\text{Zn}(\text{L})_2(\text{OAc})_2]$  molecules are self-assembled to form infinite one-dimensional chains by  $\pi$ - $\pi$  stacking interactions.

transitions of L. At room temperature, the zinc complex shows an intense emission at  $\lambda_{\text{max}} = 395 \text{ nm}$  ( $\tau = 4.5 \text{ ns}$ ) 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



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

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

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

<sup>a</sup> In MeOH at 298 K. <sup>b</sup> Excitation wavelength = 367 nm. <sup>c</sup> Excited at 266 nm picosecond pulses (300 K).

$\text{cm}^{-1}$ ) comparable to the skeletal vibrational frequency of the free ligand (Fig. 3). We assign the emission to an intraligand  $^1(\pi-\pi^*)$  fluorescence. It is noteworthy that the  $[\text{Zn}(\text{L})_2(\text{OAc})_2]$  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  $^1(\pi-\pi^*)$  excited state. Similar enhancement of the intraligand fluorescence has also been reported for the  $[\text{Zn}(\text{terpyridine})_2]^{2+}$  system.<sup>6</sup> At room temperature, the crystalline  $[\text{Zn}(\text{L})_2(\text{OAc})_2]$  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  $>450 \text{ nm}$ .

## 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  $[\text{Zn}_4\text{O}(\text{Aza})_6]^{4+}$  ( $\Phi = 0.17$ ), the  $[\text{Zn}(\text{L})_2(\text{OAc})_2]$  molecules self-assemble through intermolecular  $\pi$ - $\pi$  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.<sup>6</sup>

## 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  $^1\text{H}$  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<sup>7</sup> (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  $\text{C}_{22}\text{H}_{20}\text{N}_4$ : C, 77.62; H, 5.92; N, 16.46%.  $^1\text{H}$  NMR (270

MHz, CD<sub>3</sub>OD, TMS):  $\delta$  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)  $\nu/\text{cm}^{-1}$ : 1600s, 1528s, 1342m, 1147m, 796w, 796w, 695w. EI-MS:  $m/z$  340 [M]<sup>+</sup>.

### Preparation of [Zn(L)<sub>2</sub>(OAc)<sub>2</sub>]

A methanolic solution (20 ml) of L (0.34 g, 1 mmol) was added to a refluxing solution of Zn(OAc)<sub>2</sub> · 2H<sub>2</sub>O (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<sub>48</sub>H<sub>46</sub>N<sub>8</sub>O<sub>4</sub>Zn: C, 66.70; H, 5.37; N, 12.96%. <sup>1</sup>H NMR (270 MHz, CD<sub>3</sub>OD, TMS):  $\delta$  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<sup>+</sup> – OAc], 463 [M<sup>+</sup> – L – OAc].

### X-Ray crystallographic characterisation of [Zn(L)<sub>2</sub>(OAc)<sub>2</sub>]

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*1̄,  $a = 9.612(9)$ ,  $b = 15.884(15)$ ,  $c = 15.884(15)$  Å,  $\alpha = 105.35(2)$ ,  $\beta = 92.65(3)$ ,  $\gamma = 92.65(3)^\circ$ ,  $U = 2332(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.231$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.577$  mm<sup>-1</sup>,  $F(000) = 904$ ,  $T = 294(2)$  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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