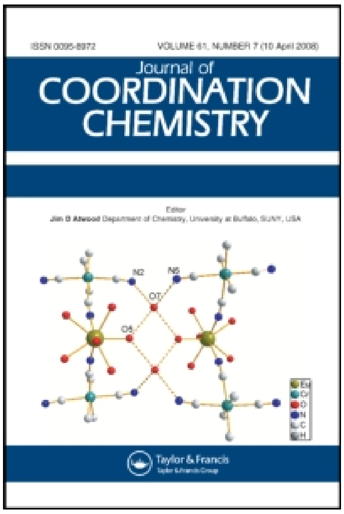

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Synthesis, structure and luminescent properties of zinc(II) and Hg(II) complexes with substituted 1,10-phenanthroline

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Synthesis, structure and luminescent properties of zinc(II) and Hg(II) complexes with substituted 1,10-phenanthroline

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Two d^{10} group 12 metal complexes, 2-(2-methoxyphenyl)-1,10-phenanthroline zinc dichloride (**2a**) and 2-(2-methoxyphenyl)-1,10-phenanthroline mercury dichloride (**2b**) were synthesized and characterized by IR, ^{1}H and ^{13}C NMR as well as elemental analysis. Structure of **2b** in the solid state was determined by single-crystal X-ray crystallography, revealing that **2b** is four-coordinate in a distorted tetrahedral geometry with the methoxy group uncoordinated. Luminescent properties of **2a** and **2b** in solution and the solid state were studied.

Keywords: Mercury complex; Zinc complex; 1,10-Phenanthroline; Luminescence

1. Introduction

Luminescent complexes are an active research field because of their potential application in optoelectronic devices and chemical sensors [1]. One of the most important considerations in organic light-emitting diodes (OLEDs) is the design and synthesis of molecules capable of tuning luminescent properties through modification of ligands [2, 3]. Organic compounds with aromatic nitrogen-containing heterocycles have been extensively studied because of their coordination ability and luminescence. A large number of complexes with 8-hydroxyquinoline, pyridyl-phenol, 7-azaindole and phenyl-pyridine have been investigated [3–5], and luminescent complexes of Re(I) [6], Ru(II) [7], Os(II) [8] containing bipyridine type ligands have attracted much attention due to their high luminescence efficiency. However, low yields and high costs of these complexes are disadvantages for their application as optoelectronic materials. Luminescent group 12 d^{10} metal complexes with nitrogen-containing ligands are of interest because of their low cost [9–12]. To develop new complexes of this type with improved luminescent performance, we have synthesized a new modified 1,10-phenanthroline ligand and its zinc(II) and mercury(II) complexes. The ligand was selected considering that larger conjugating system could give better luminescence properties. Herein we report the synthesis, structural characterization and

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photoluminescence of 2-(2-methoxyphenyl)-1,10-phenanthroline and its zinc(II) and mercury(II) complexes.

2. Experimental

2.1. *General procedures*

All experiments involving air and moisture sensitive compounds were performed using standard Schlenk techniques in an atmosphere of high purity nitrogen or using glove-box techniques. Toluene and diethyl ether were dried by refluxing over sodium and benzophenone and distilled under nitrogen prior to use. $ZnCl_2$, $HgCl_2$ and ^{n}BuLi were purchased from Aldrich and used as received. NMR spectra were measured on Varian Mercury-300 and Bruker AVANCE-500 NMR spectrometers. Elemental analyses were performed on a Perkin-Elmer 2400 analyzer. UV–Vis absorption spectra were recorded on an UV-3100 spectrophotometer, and fluorescence measurements were carried out on a RF-5301PC spectrophotometer.

2.2. *Preparation*

2.2.1. 2-(2-methoxyphenyl)-1,10-phenanthroline (1). A solution of ^{n}BuLi (30.3 mL, 48.5 mmol) in hexanes was added to a solution of 2-bromoanisole (9.071 g, 48.5 mmol) in Et_2O (30 mL) under a nitrogen atmosphere at −78°C. The mixture was allowed to warm to room temperature and stirred overnight. The resulting mixture was added dropwise to an ice-cooled solution of 1,10-phenanthroline (8.740 g, 48.5 mmol) in Et_2O (30 mL), and a wine red solution was obtained. The resulting mixture was refluxed for 12 h, cooled in an ice bath and quenched with water (30 mL). The organic phase was separated and stirred over MnO_2 for 24 h, then filtered and dried with anhydrous $MgSO_4$. Concentration of the solution gave the crude product that was further purified by column chromatography on silica gel with dichloromethane as eluent. Pure product (6.249 g, 45%) was obtained as a yellow oil. Anal. Calcd for $C_{19}H_{14}N_2O$ (%): C, 79.71; H, 4.93; N, 9.78. Found: C, 79.52; H, 4.86; N, 9.85. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ 3.89 (s, 3H, methoxy), 7.03 (d, $J = 8.0$ Hz, 1H, phenyl), 7.15 (t, $J = 7.5$ Hz, 1H, phenyl), 7.43 (t, $J = 7.5$ Hz, 1H, phenyl), 7.69 (t, $J = 6.5$ Hz, 1H, phen), 7.82 (d, $J = 8.5$ Hz, 1H, phen), 7.87 (d, $J = 7.5$ Hz, 1H, phen), 8.17 (d, $J = 7.5$ Hz, 1H, phen), 8.22 (d, $J = 8.5$ Hz, 1H, phen), 8.28 (d, $J = 8.5$, Hz, 1H, phenyl), 8.35 (d, $J = 8.0$ Hz, 1H, phen), 9.27 (d, $J = 4.0$ Hz, 1H, phen) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 293 K): δ, ppm 55.6 (OCH_3), 111.2, 121.3, 122.7, 125.4, 125.9, 126.6, 127.3, 128.8, 129.3, 130.3, 132.2, 135.3, 136.7, 145.3, 145.5, 149.6, 156.9, 157.2.

2.2.2. 2-(2-methoxyphenyl)-1,10-phenanthrolinezinc dichloride (2a). To a solution of $ZnCl_2$ (0.105 g, 0.77 mmol) in methanol (10 mL) was added a methanol solution (10 mL) of **1** (0.218 g, 0.76 mmol). The reaction mixture was stirred for 4 h at room temperature, and the crude product was collected on a frit as a light yellow solid and washed with cold methanol. Pure product (0.264 g, 82%) was obtained by recrystallization from CH_3CN/CH_2Cl_2. Anal. Calcd for $C_{19}H_{14}ON_2ZnCl_2$ (%): C, 54.39; H, 3.36; N, 6.68. Found: C, 54.50; H, 3.47; N, 6.55. ^{1}H NMR (300 MHz, DMSO-d_6, 293 K): δ 3.70

(s, 3H, methoxy), 6.80 (d, $J = 8.0$ Hz, 1H, phenyl), 6.91 (t, $J = 7.5$ Hz, 1H, phenyl), 7.23 (t, $J = 7.6$ Hz, 1H, phenyl), 7.55 (d, $J = 6.5$ Hz, 1H, phen), 8.13–8.16 (m, 2H), 8.20–8.26 (m, 2H), 8.74 (d, $J = 8.4$ Hz, 1H, phenyl), 8.86 (d, $J = 8.0$ Hz, 1H, phen), 9.31 (d, $J = 4.0$ Hz, 1H, phen) ppm. ^{13}C NMR (75 MHz, DMSO-d_6, 293 K): δ, ppm 55.5 (OCH_3), 110.9, 120.6, 120.7, 125.2, 126.7, 127.1, 127.3, 127.4, 127.6, 129.4, 130.4, 131.0, 138.2, 139.7, 150.1, 156.2, 156.5. IR (KBr, cm^{-1}) data: 3066 w, 2941 w, 2828 w, 1601 m, 1565 m, 1512 m, 1496 s, 1458 s, 1438 m, 1389 m, 1301 m, 1266 s, 1248 m, 1158 m, 1120 m, 1020 s, 892 w, 863 s, 769 s, 752 m, 652 w, 559 w.

2.2.3. 2-(2-methoxyphenyl)-1,10-phenanthrolinemercury dichloride (2b). To a solution of $HgCl_2$ (0.200 g, 0.74 mmol) in methanol (15 mL) was added a methanol solution (10 mL) of **1** (0.210 g, 0.73 mmol). The reaction mixture was stirred for 4 h at room temperature, and the crude product was collected on a frit as a light yellow solid and washed with cold methanol. Pure product (0.350 g, 86%) was obtained by recrystallization from CH_3CN/CH_2Cl_2. Anal. Calcd for $C_{19}H_{14}ON_2HgCl_2$ (%): C, 40.91; H, 2.53; N, 5.05. Found: C, 40.78; H, 2.60; N, 5.19. ^{1}H NMR (300 MHz, DMSO-d_6, 293 K): δ 3.70 (s, 3H, methoxy), 6.82 (d, $J = 8.0$ Hz, 1H, phenyl), 6.92 (t, $J = 7.6$ Hz, 1H, phenyl), 7.23 (t, $J = 7.5$ Hz, 1H, phenyl), 7.60 (t, $J = 6.6$ Hz, 1H, phen), 8.13–8.15 (m, 2H), 8.20–8.25 (m, 2H), 8.77 (d, $J = 8.4$ Hz, 1H, phenyl), 8.85 (d, $J = 8.0$ Hz, 1H, phen), 9.32 (d, $J = 3.9$ Hz, 1H, phen) ppm. ^{13}C NMR (75 MHz, DMSO-d_6, 293 K): δ 55.5 (OCH_3), 111.0, 120.6, 120.8, 125.2, 126.9, 127.3, 127.4, 127.5, 127.8, 129.5, 130.5, 131.1, 138.2, 139.9, 150.3, 156.3, 156.7. IR (KBr cm^{-1}) data: 3436 s, 3068 w, 3001 w, 2925 m, 2851 w, 1666 m, 1602 s, 1490 s, 1446 s, 1414 m, 1386 s, 1302 w, 1258 s, 1150 m, 1118 m, 1018 m, 858 m, 762 w, 565 w.

2.3. *X-ray crystallography*

Single crystals of **2b** suitable for X-ray structural analysis were obtained from CH_2Cl_2. Diffraction data were collected at 293 K on a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Details of the crystal data, data collection, and structure refinement are summarized in table 1. The structure was solved by direct methods [13] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in idealized positions. All calculations were performed using the SHELXTL [14] crystallographic software package.

3. Results and discussion

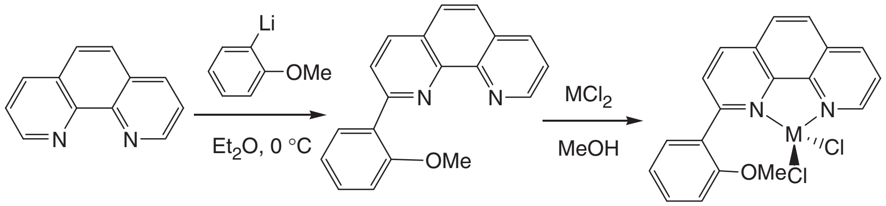
3.1. *Synthesis and characterization of compounds*

Ligand **1** was synthesized by reaction of 1,10-phenanthroline with 2-methoxyphenyllithium, obtained by treatment of 2-bromoanisole with *n*-BuLi, in a moderate yield after oxidative rearomatization (figure 1) [15]. Compound **1** was characterized by ^{1}H NMR spectroscopy along with elemental analysis. The appearance of the resonance at $\delta = 3.89$ ppm for CH_3 protons in the ^{1}H NMR spectrum is indicative of the formation of

Table 1. Crystal data and structural refinement details for **2b**.

Empirical formula	$C_{19}H_{14}N_2OCl_2Hg$
Molecular mass	557.81
T (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/n$
Unit cell dimensions (Å, °)	
a	8.6350(17)
b	14.628(3)
c	14.370(3)
α	90
β	90.05(3)
γ	90
V (Å^3)	1815.1(6)
Z	4
D_{Calcd} (g cm^{-3})	2.041
$F(000)$	1056
Crystal size (mm^3)	$0.34 \times 0.25 \times 0.05$
θ-range (°)	3.08 to 27.48
Limiting indices	$-11 \le h \le 11$, $-18 \le k \le 18$, $-21 \le l \le 21$
Data/restraints/parameters	4134/0/227
Goodness-of-fit on F^2	1.053
Final R indices ($I > 2\sigma(I)$)	$R_1{}^a = 0.0352$, $wR_2{}^b = 0.0651$
R indices (all data)	$R_1{}^a = 0.0545$, $wR_2{}^b = 0.0705$
Largest diff. peak/hole (e Å^{-3})	1.048, −0.761

[a] $R_1 = \|F_o| - |F_c\|/|F_o|$, [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.



1

2a M = Zn (82 %)
2b M = Hg (86 %)

Figure 1. Synthetic procedure of ligand **1** and complexes **2a** and **2b**.

1. Compound **1** is soluble in most organic solvents. Treatment of $ZnCl_2$ or $HgCl_2$ with one equivalent of **1** in methanol at ambient temperature afforded the corresponding d^{10} metal complexes **2a** and **2b** in good yields (>80%) as light yellow crystalline solids (figure 1). Complexes **2a** and **2b** were characterized by elemental analyses, IR spectroscopy, ^1H and ^{13}C NMR spectroscopy, and satisfactory analytical results were obtained on both compounds. In ^{13}C NMR spectra of the complexes, the resonance at ~55 ppm could be assigned to the carbon atom of the methoxy, and the resonances for the carbons of the phenanthroline shift to higher field in comparison with the corresponding signals of the free ligand. Both complexes are moderately soluble in DMSO and slightly soluble in dichloromethane, methanol, DMF and THF, and insoluble in saturated hydrocarbon solvents.

Table 2. Selected bond lengths (Å) and angles (°) for **2b**.

Hg–N(1)	2.362(4)	N(1)–Hg–Cl(2)	106.37(12)
Hg–N(2)	2.382(4)	Cl(2)–Hg–N(2)	119.34(10)
Hg–Cl(1)	2.3720(15)	Cl(1)–Hg–N(2)	108.82(10)
Hg–Cl(2)	2.3710(17)	C(1)–N(1)–Hg	124.8(4)
C(5)–N(1)	1.354(6)	C(5)–N(1)–Hg	115.9(3)
C(9)–N(2)	1.351(6)	C(12)–N(2)–Hg	124.2(3)
N(1)–Hg–N(2)	70.92(13)	C(9)–N(2)–Hg	114.6(3)
N(1)–Hg–Cl(1)	108.62(11)	Cl(2)–Hg–Cl(1)	127.24(6)

3.2. *Structure of 2b*

The molecular structure of **2b** was determined by X-ray crystallographic analysis. Single crystals of **2b** suitable for X-ray structure determination were grown from dichloromethane at room temperature. The ORTEP drawing of the molecular structure of **2b** is shown in the top of figure 2. Selected bond lengths and angles for the complex are given in table 2. The X-ray analysis reveals that **2b** adopts a distorted tetrahedral geometry with the metal center chelated by two nitrogens of the 1,10-phenanthroline moiety, while the oxygen does not coordinate, probably due to the weak donating ability of the –OMe group. In **2b**, the two Hg–N bond lengths are slightly different [2.362(4) Å for Hg–N(1) and 2.382(4) Å for Hg–N(2)] and the average bond distance is slightly longer than that of 6-(2-methoxyphenyl)-2,2′-bipyridine mercury analogue (2.359 Å) [12]. The values of the Hg–N bond length are consistent with those found in other four-coordinate Hg(II) complexes with similar ligands [16]. The N–Hg–N bite angle in **2b** [70.9(1)] is larger than the one [70.0(1)°] in its 6-(2-methoxyphenyl)-2,2′-bipyridine mercury analogue. The angle between the aromatic ring and the phenanthroline plane is 49.8° for **2b**, close to that in 6-(2-methoxyphenyl)-2,2′-bipyridine mercury (50.7°) [12]. In addition, there are π–π stacking interactions between the phenanthroline planes of neighboring molecules for **2b** in the solid state. A π–π stacking supramolecular structure is shown in the bottom of figure 2. The distances between the stacked aromatic planes, calculated according to a literature method [17], are 3.48 and 3.58 Å, alternately. Similar π–π stacking column structures for Hg(II) complexes have been reported [16c].

3.3. *Luminescence properties*

The UV–Vis and fluorescent properties of **1**, **2a** and **2b** determined in solution and the solid state are summarized in table 3. The normalized optical absorption spectra of these compounds in dilute dichloromethane are given in figure 3. The free ligand shows an absorption at 278 nm, while **2a** and **2b** exhibit a strong absorption (280 nm for **2a** and 286 nm for **2b**) and a weak absorption (357 nm for **2a** and 351 nm for **2b**). In CH_2Cl_2 solution, **1** gives an emission band at $\lambda_{max} = 382$ nm with a shoulder at 361 nm. In comparison with **1**, complexes **2a** and **2b** in CH_2Cl_2 solution show broader emission bands (bandwidth at half-height = 80–90 nm) with $\lambda_{max} = 440$ and 432 nm, respectively, as shown in figure 4. The emission maxima of the two complexes are red-shifted by 50–60 nm compared to the free ligand, normal for metal complexes with a chelating ligand. The luminescence of metal complexes is usually from the $\pi^* \rightarrow \pi$ transition of the ligand. Chelation of the ligand to the metal restricts the vibration and rotation

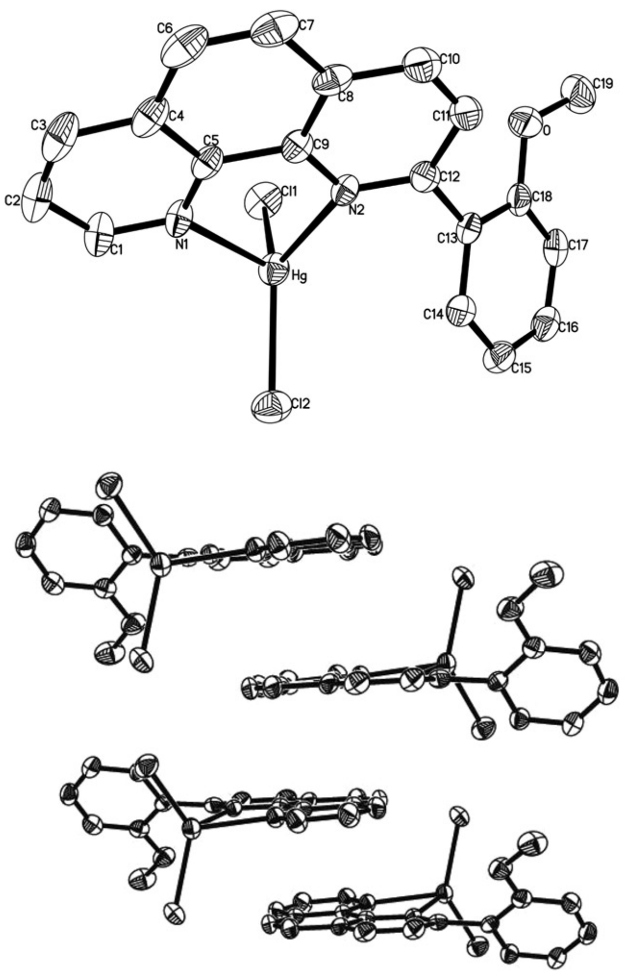


Figure 2. Top: molecular structure of **2b**; bottom: the π–π stacking column structure of **2b**. (Thermal ellipsoids are drawn at the 30% probability level.)

Table 3. Photoluminescent data for **1**, **2a** and **2b**.

Compound	Abs λ (nm) ε ($M^{-1} cm^{-1}$)	Em λ (nm)	Quantum yields[a]	Conditions
1	278(31000)	361, 382	0.064	CH_2Cl_2, 298K
		361, 464		solid, 298k
2a	286(22536), 357(4702)	440	0.101	CH_2Cl_2, 298K
		430		solid, 298k
2b	280(19750), 351(2912)	407, 432	0.031	CH_2Cl_2, 298K
		390		solid, 298k

[a] Determined using quinine sulfate in 0.1 M sulphuric acid as a standard.

increasing its conjugation and reducing the energy of the $\pi^* \rightarrow \pi$ transition [18]. The quantum yields of all three compounds have been determined in solution. The quantum yield of **2a** is higher than **1**, while the quantum yield of **2b** is lower than that of the free ligand. For **2a**, the rigid chelating ligand reduces energy loss via vibration and rotation,

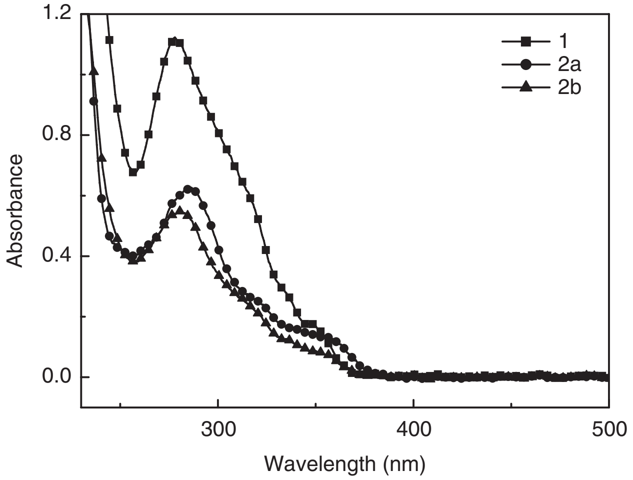


Figure 3. UV–Vis absorption spectra of **1**, **2a** and **2b** in CH_2Cl_2 ($\sim 1 \times 10^{-5}$ M).

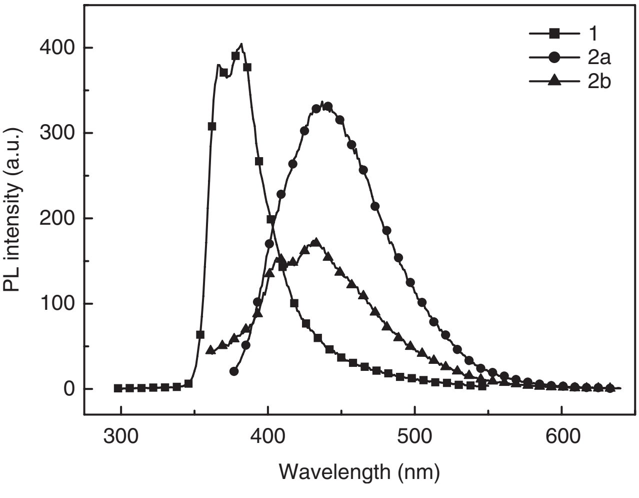


Figure 4. Emission spectra of **1**, **2a** and **2b** in CH_2Cl_2 ($\sim 1 \times 10^{-5}$ M).

and therefore increases the emission efficiency. It is well known that Hg(II) can quench fluorescence emission due to the heavy atom effect of Hg [19]. No phosphorescence was detected from **2b**; similar results for other Hg(II) complexes have been previously reported [16c]. The emission spectra of **1**, **2a** and **2b** in the solid state, shown in figure 5, emit bright fluorescence when irradiated with a proper exciting light. Compound **1** shows two emission peaks at 361 and 462 nm, respectively. The lower energy emission peak is probably from the excimer of **1**. PMMA films doped with ligand in different concentrations were made and fluorescence spectra of these films (figure 6) show low energy emission of the ligand in the films is enhanced with increase in doped concentration, which is indicative of the formation of the excimer [20]. The emission maxima of **2a** and **2b** (430 and 390 nm, respectively) in the solid state are blue shifted compared to their corresponding emission maxima in solution, presumably from

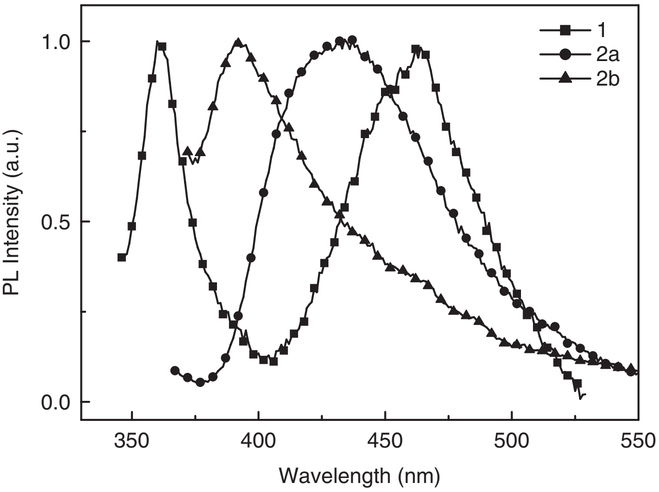


Figure 5. Emission spectra of **1**, **2a** and **2b** in the solid state.

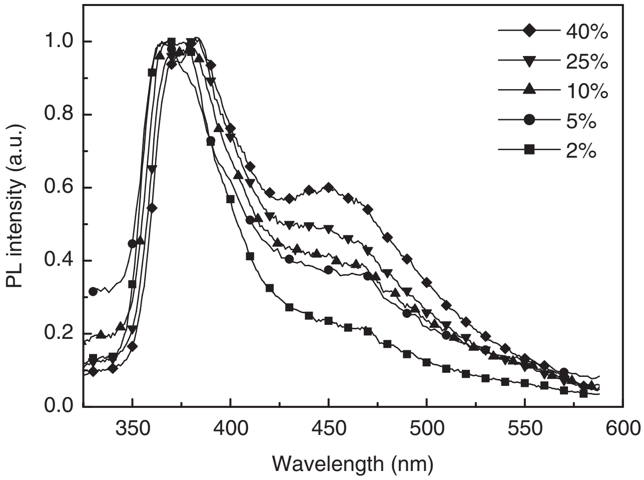


Figure 6. Fluorescence spectra of ligand in PMMA excited at 300 nm. The ligand concentration was varied from 2 to 40 wt%.

reduced conjugation of the two complexes in the solid state since free rotation of the aryl rings is blocked in the solid state [21].

4. Conclusion

A 2-position substituted 1,10-phenanthroline ligand and its Zn(II) and Hg(II) complexes have been synthesized and characterized by IR, ^{1}H and ^{13}C NMR as well as elemental analysis. Crystal structure analysis reveals that **2b** adopts a distorted tetrahedral geometry, forming a column supramolecular structure through π–π stacking interaction between the phenanthroline planes of neighboring molecules. Both **2a** and **2b** produce blue fluorescent emission in solution and the solid state.

Supplementary data

CCDC 655225 contains the supplementary crystallographic data for **2b**. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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References

[1] (a) C.W. Tang, S.A. Vanslyke. *Appl. Phys. Lett.*, **51**, 913 (1987); (b) S.N. Wang. *Coord. Chem. Rev.*, **215**, 79 (2001); (c) C.H. Chen, J. Shi. *Coord. Chem. Rev.*, **171**, 161 (1998); (d) F. Li, M. Zhang, G. Cheng, J. Feng, Y. Zhao, Y.G. Ma, S.Y. Liu, J.C. Shen. *Appl. Phys. Lett.*, **84**, 148 (2004); (e) Q.S. Zhang, Q.G. Zhou, Y.X. Cheng, L.X. Wang, D.G. Ma, X.B. Jing, F.S. Wang. *Adv. Mater.*, **16**, 432 (2004).

[2] (a) T.H. Kwon, H.S. Cho, M.K. Kim, J.W. Kim, J.J. Kim, K.H. Lee, S.J. Park, I.S. Shin, H. Kim, D.M. Shin, Y.K. Chung, J.I. Hong. *Organometallics*, **24**, 1578 (2005); (b) J. Li, P.I. Djurovuch, B.D. Alleyne, M. Yousufuddin, N.N. Ho, J.C. Thomas, J.C. Peters, R. Bau, M.E. Thompson. *Inorg. Chem.*, **44**, 1713 (2005).

[3] (a) V.A. Montes, G. Li, R. Pohl, J. Shinar, P. Anzenbacher, Jr. *Adv. Mater.*, **16**, 2001 (2004); (b) R. Pohl, V.A. Montes, J. Shinar, P. Anzenbacher Jr. *J. Org. Chem.*, **69**, 1723 (2004).

[4] (a) Q.G. Wu, J.A. Lavigne, Y. Tao, M. D'Iorio, S.N. Wang. *Inorg. Chem.*, **39**, 5248 (2000); (b) Q.G. Wu, A. Hook, S.N. Wang. *Angew. Chem. Int. Ed.*, **39**, 3933 (2000); (c) D.T. Song, S.N. Wang. *Eur. J. Inorg. Chem.*, 3774 (2003).

[5] (a) Y. Liu, J.H. Guo, H.D. Zhang, Y. Wang. *Angew. Chem. Int. Ed.*, **41**, 182 (2002); (b) Y.Q. Li, Y. Liu, W.M. Bu, J.H. Guo, Y. Wang. *Chem. Commun.*, 1551 (2000).

[6] (a) Z.J. Si, J. Li, B. Li, F.F. Zhao, S.Y. Liu, W.L. Li. *Inorg. Chem.*, **46**, 6155 (2007); (b) S. Ranjan, S.Y. Lin, K.C. Hwang, Y. Chi, W.L. Ching, C.S. Liu, Y.T. Tao, C.H. Chien, S.M. Peng, G.H. Lee. *Inorg. Chem.*, **42**, 1248 (2003).

[7] (a) Y.L. Tung, S.W. Lee, Y. Chi, L.S. Chen, C.F. Shu, F.I. Wu, A.J. Carty, P.T. Chou, S.M. Peng, G.H. Lee. *Adv. Mater.*, **17**, 1059 (2005); (b) H. Xia, C. Zhang, X. Liu, S. Qiu, P. Lu, F. Shen, J. Zhang, Y. Ma. *J. Phys. Chem. B*, **108**, 3185 (2004).

[8] (a) Y.L. Chen, S.W. Lee, Y. Chi, K.C. Hwang, S.B. Kumar, Y.H. Hu, Y.M. Cheng, P.T. Chou, S.M. Peng, G.H. Lee, S.J. Yeh, C.T. Chen. *Inorg. Chem.*, **44**, 4287 (2005); (b) Y.L. Tung, P.C. Wu, C.S. Liu, Y. Chi, J.K. Yu, Y.H. Hu, P.T. Chou, S.M. Peng, G.H. Lee, Y. Tao, J.C. Arthur, C.F. Shu, F.I. Wu. *Organometallics*, **23**, 3745 (2004).

[9] (a) X.M. Zhang, M.L. Tong, M.L. Gong, H.K. Lee, L. Luo, K.F. Li, Y.X. Tong, X.M. Chen. *Chem. Eur. J.*, **8**, 3187 (2002); (b) G. Yu, S.W. Yin, Y.Q. Liu, Z.G. Shuai, D.B. Zhu. *J. Am. Chem. Soc.*, **125**, 14816 (2003).

[10] (a) W.K. Lo, W.K. Wong, W.Y. Wong, J.P. Guo. *Eur. J. Inorg. Chem.*, 3950 (2005); (b) M.R. Haneline, M. Tsunoda, F.P. Gabbaï. *J. Am. Chem. Soc.*, **124**, 3737 (2002); (c) R.Q. Fan, D.S. Zhu, Y. Mu, G.H. Li, Y.L. Yang, Q. Su. *Eur. J. Inorg. Chem.*, 4891 (2004).

[11] (a) V.W.W. Yam, K.K.W. Lo, W.K.M. Fung, C.R. Wang. *Coord. Chem. Rev.*, **171**, 17 (1998); (b) H.H. Patterson, S.M. Kanan, M.A. Omary. *Coord. Chem. Rev.*, **208**, 227 (2000).
[12] X.M. Liu, X.Y. Mu, H. Xia, L. Ye, W. Gao, H.Y. Wang, Y. Mu. *Eur. J. Inorg. Chem.*, 4317 (2006).
[13] G.M. Sheldrick. *SHELXTL, PC Siemens Analytical X-ray Instruments: Madison*, WI (1993).
[14] G.M. Sheldrick. *SHELXTL Structure Determination Programs, Version 5.0, PC Siemens Analytical Systems: Madison*, WI (1994).
[15] C.C. Kwok, H.M.Y. Ngai, S.C. Chan, I.H.T. Sham, C.M. Che, N.Y. Zhu. *Inorg. Chem.*, **44**, 4442 (2005).
[16] (a) S.M. Berry, D.C. Bebout, R.J. Butcher. *Inorg. Chem.*, **44**, 27 (2005); (b) S.L. Zheng, J.P. Zhang, X.M. Chen, Z.L. Huang, Z.Y. Lin, W.T. Wong. *Chem. Eur. J.*, **9**, 3888 (2003); (c) Q.D. Liu, R.Y. Wang, S.N. Wang. *J. Chem. Soc., Dalton Trans.*, 2073 (2004).
[17] C. Janiak. *J. Chem. Soc., Dalton Trans.*, 3885 (2000).
[18] (a) D. Rendell (Ed). *Fluorescence and Phosphorescence*, Wiley, New York (1987); (b) H. Yersin, A.Vogler (Eds). *Photochemistry and Photophysics of Coordination Compounds*, Springer-Verlag, Berlin (1987).
[19] J.R. Lakowick. *Principles of Fluorescence Spectroscopy*, Academic/Plenum Publishers, New York (1999).
[20] C. Spies, R. Gehrke. *J. Phys. Chem. A*, **106**, 5348 (2002).
[21] X.M. Liu, W. Gao, Y. Mu, G.H. Li, L. Ye, H. Xia, Y. Ren, S.H. Feng. *Organometallics*, **24**, 1614 (2005).