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Synthesis and electroluminescent properties of substituted benzoate bis (8-hydroxyquinaldine) gallium (III) complexes

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Since the original report of Tang [1, 2] on organic electroluminescence (EL) from the tris(8-quinolinolato) aluminum (Alq_3), the research of tris(8-quinolinolato) metal (III) chelates has attracted much attention [3, 4]. Many derivatives of Alq_3 have been investigated as emitter materials, such as Kido and Iizumi showed that aluminum tris(4-methyl-8-quinolinolato) exhibited larger EL efficiency than that of Alq_3 [5]. Sapochak and co-workers prepared the pentacoordinate bis(8-hydroxyquinaldine) gallium (III) complexes (q'$_2$GaX with $X =$ acetate, benzoate, dimethylpropionate, and chloro), it is proved that the q'$_2$Gaben OELD has higher EL quantum efficiency at low drive currents [6]. More recently, Elschner *et al.*, proved that the ternary bis(8-hydroxyquinaldine) gallium (III) complex (Gaq'$_2$OAc) has high fluorescence efficiency and brightness at low turn-on voltages [7]. Furthermore, a series of methyl substituted tris(8-quinolinolato) chelates of aluminum and gallium have been prepared by Sapochak and co-workers, the effect of methylation of aluminum and gallium tris(8-quinolinolato) chelates on the PL, EL, and thermal properties was discussed [8].

In this paper we synthesized a new series of pentacoordinate substituted *p*-benzoate bis(8-hydroxyquinaldine) gallium (III) complexes (q'$_2$GabenX, see Fig. 1). The structure of complexes was characterized by FT-IR, UV-Vis and element analysis. The effect of substituted group of second ligand on the PL and EL properties of q'$_2$GabenX Complexes was investigated.

The Bis(8-hydroxyquinaldine) gallium benzoate complex (q'$_2$Gaben) was prepared in accordance with the method proposed by Sapochak [6]. FT-IR(KBr): 1633, 1610, 1509, 1577, 1508, 1467, 1432, 1340, 1274, 1112, 839, 755, 728. UV-Vis: 260.2 nm, 364 nm. Anal. Calcd (%) for $C_{27}H_{21}GaN_2O_4$: C, 63.96; H, 4.19; N, 5.52; Found: C, 63.61; H, 3.99; N, 5.20.

Bis(8-hydroxyquinaldine) gallium *p*-methylbenzoate complex (q'$_2$GabenCH$_3$) was prepared by the following procedure. *P*-methyl benzoic acid (10 mmol) was added to 10 mL of water, sodium hydroxide (10%) was used to adjust pH to 7.0, then the above solution and 8-hydroxyquinaldine (2 mmol) in 30 ml of ethanol were added to a solution of $Ga(NO_3)_3 \cdot xH_2O$ (1 mmol) in 20 mL of water under stirring rapidly. The precipitation occurred immediately, and the reaction mixture was stirred an addition 4 h after all the reactants had been added. The precipitate was filtered, washed with water and ethanol, dried in a vacuum oven, and recrystallized from chloroform and methanol (1:2). FT-IR (KBr): 1640, 1608, 1508, 1576, 1507, 1431, 1385, 1339, 1273, 1174, 1111, 838, 753. UV-Vis: 260.6 nm, 364 nm. Anal. Calcd (%) for $C_{28}H_{23}GaN_2O_4$: C, 64.52; H, 4.45; N, 5.37; Found: C, 64.24; H, 4.21; N, 5.40.

Bis(8-hydroxyquinaldine) gallium *p*-nitryl benzoate complex (q'$_2$GabenNO$_2$) was synthesized by similar method of q'$_2$GabenCH$_3$. FT-IR (KBr): 1660, 1603, 1577, 1527, 1508, 1467, 1430, 1340, 1272, 1115, 834, 756, 724. UV-Vis: 261.0 nm, 369 nm. Anal. Calcd (%) for $C_{27}H_{20}GaN_3O_6$: C, 58.73; H, 3.65; N, 7.61; Found: C, 58.06; H, 3.57; N, 7.32.

Absorption spectra were recorded with a Shimadzu UV-265 UV-vis spectrophotometer for choroform solution of 10^{-5} M, and PL spectra were obtained with a Shimadzu RF-5301 PC spectrofluorimeter for both choroform solution and thin film samples on quartz.

Organic light-emitting device (OELD) was fabricated using one of the complexes (q'$_2$GabenCH$_3$) as the emissive layer. A hole transporting material, N,N′-diphenyl-N,N′-bis(1-naphthyl)-1,1′-biphenyl-4, 4′-diamine (NPB), was deposited on the ITO substrate by thermal evaporation. The device structure of ITO/NPB/q'$_2$GabenCH$_3$/Al was employed. The EL spectrum of the device was measured with a spectrometer. All measurements were carried out at room temperature in air.

Fig. 2 shows the excitation and emission spectra of three complexes in $CHCl_3$ solution (10^{-5} M). The maximal excitation wavelength of three complexes is at 411 nm, the complexes of q'$_2$Gaben and q'$_2$GabenCH$_3$ show strong emission peaks at 502 nm. But the q'$_2$GabenNO$_2$ complex exhibits only a weak emission peak. The PL spectra of the thin films of the complexes are shown in Fig. 3, the data of excitation and emission spectra are listed in Table I. The results indicate that the complexes of q'$_2$GabenCH$_3$ and q'$_2$Gaben, excitated with 274 nm, have strong broad peaks at 483 nm. Compared with the PL spectra of three complexes thin films, the maximum intensity emission is observed for q'$_2$GabenCH$_3$ complex, and the complex of q'$_2$GabenNO$_2$ show only a small peak at 469 nm. It can be concluded that electron-donating group (—CH$_3$) in the second ligand results in the enhancement of the fluorescent intensity and electron-withdrawing group

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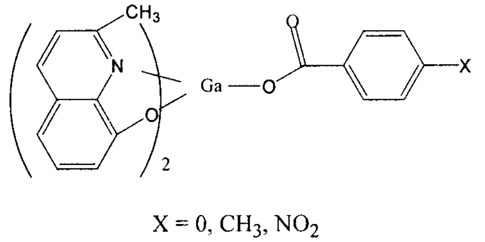

Figure 1 The structure of q'$_2$GabenX.

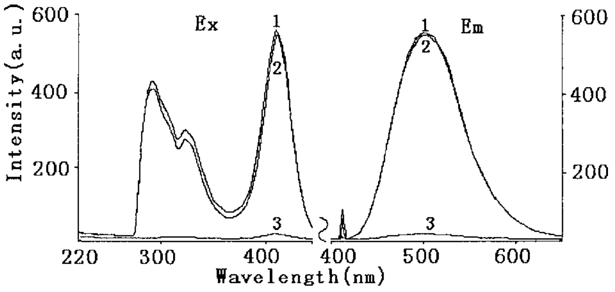

Figure 2 Excitation and emission spectra of three complexes in chloroform solution 1, q'$_2$GabenCH$_3$; 2, q'$_2$Gaben; 3, q'$_2$GabenNO$_2$.

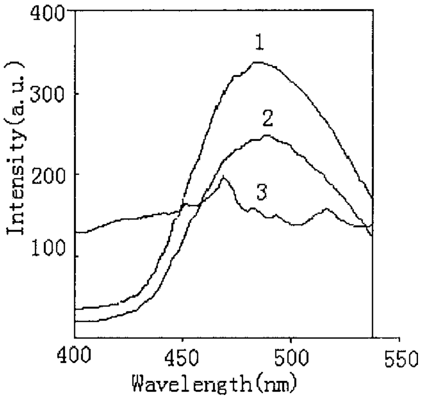

Figure 3 Emission spectra of the films of three complexes: 1, q'$_2$GabenCH$_3$; 2, q'$_2$Gaben; 3, q'$_2$GabenNO$_2$.

(—NO$_2$) in the second ligand decreases the fluorescent intensity. It is because the electron-donating groups in the second ligand increase the density of n-type electron, so the rate of $\pi^* - \pi$ transition increases and fluorescent intensity enhances. Whereas, electron-withdrawing groups in the second ligand reduce the difference in energy split between the singlet and triplet states, so the probability of intersystem-crossing becomes great which leads to the enhancement of phosphorescence and decreasing of fluorescent intensity.

TABLE I Excitation and emission spectra data of complexes thin film

Complexes	Ex (nm)	Em (nm)	Intensity (a.u.)
q'$_2$GabenCH$_3$	274	483	337
q'$_2$Gaben	274	483	245
q'$_2$GabenNO$_2$	356	469	197

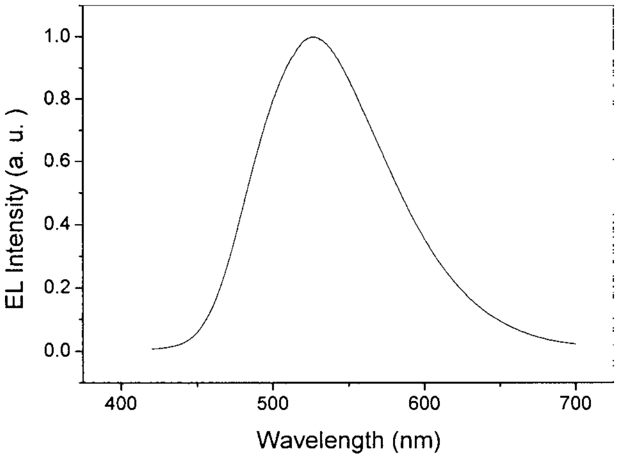

Figure 4 EL spectrum of ITO/NPB/ q'$_2$GabenCH$_3$/Al device.

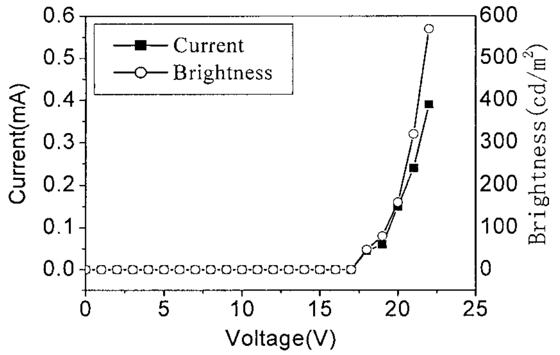

Figure 5 Current-voltage-brightness curves of ITO/NPB/ q'$_2$GabenCH$_3$/Al device.

The EL spectrum of ITO/NPB/ q'$_2$GabenCH$_3$/Al device is shown in Fig. 4, the peak of EL emission is at 560 nm, which is red-shifted 60 nm compared to the EL spectrum of q'$_2$Gaben complex [6]. Fig. 5 shows the current-voltage-brightness characteristic curves for an EL device with q'$_2$GabenCH$_3$, they indicate that the turn-on voltage of the device is 17 V, and the brightness is approximately proportional to the current. When the operation voltage is 22 V, its brightness (over 570 cd/m^2) can be observed in normal room light.

Acknowledgments

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