

Synthesis and luminescence of red, fluorinated iridium (III) complexes containing alkenyl benzothiazole ligand

Guoyong Xiao^{a,*}, Peng Lei^a, Haijun Chi^a, Yunhua Lu^a, Yan Dong^a, Zhizhi Hu^{a,*}, Zhiqiang Zhang^a, Xiao Li^b

^a School of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, People's Republic of China

^b Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China

ARTICLE INFO

Article history:

Received 8 October 2008

Received in revised form 11 December 2008

Accepted 26 December 2008

Available online 29 January 2009

Keywords:

Iridium complex

Alkenyl benzothiazole

Red phosphorescence

OLED

ABSTRACT

Two novel iridium(III) complexes (2-FSBT)₂Ir(acac) and (4-FSBT)₂Ir(acac) (2-FSBT, (*E*)-2-(2-fluorostyryl)benzo[d]thiazole; 4-FSBT, (*E*)-2-(4-fluorostyryl)benzo[d]thiazole; acac, acetylacetonate) were synthesized and characterized by ¹H NMR and mass spectrometry. The organic light emitting diodes based on these complexes with the structure of ITO/m-MTDATA(10 nm)/NPB(20 nm)/CBP:Ir-complex(X %, 30 nm)/BCP(10 nm)/Alq₃(30 nm)/LiF(1 nm)/Al(100 nm) were fabricated. The device based on (2-FSBT)₂Ir(acac) exhibited a maximum efficiency of 9.32 cd/A, a luminance of 8800 cd/cm²; and the device based on (4-FSBT)₂Ir(acac) showed a maximum efficiency of 8.5 cd/A, a luminance of 6986 cd/cm². The Commission International de L'Eclairage (CIE) coordinates (1931) of these complexes were (0.619, 0.381) and (0.621, 0.378), respectively.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Since Baldo et al. reported the first example of electrophosphorescence at room temperature, phosphorescent materials have attracted much attention due to their high external quantum efficiencies in organic light emitting diodes (OLEDs) [1,2]. Extensive investigations of phosphorescent materials have focused on heavy metal complexes such as Os(II) [3], Ir(III) [4,5] and Pt(II) [6]. OLEDs based on those phosphorescent materials can significantly improve electroluminescent (EL) performances because both singlet and triplet excitons can be harvested for light emission by strong spin–orbit coupling. The internal quantum efficiency of phosphorescent emitters can theoretically approach 100%. Among these phosphorescent materials, the Ir(III) complexes employed as emitters in OLEDs are the most effective. Full-color display applications require red, green and blue emission with excellent color purity and high efficiencies. Although great success has been achieved in the development of a green emitter [7], the red emitter as an indispensable component of full-color displays or lighting remains unsatisfying in efficiency and color purity. In an effort to develop red phosphorescent materials, Cheng's group reported the first example of highly efficient red Ir(III) complexes containing alkenyl pyridine ligands [8]. Then their groups achieved red

electrophosphorescent devices based on (PEQ)₂Ir(acac) (PEQ, 2-((*E*)-2-phenyl-1-ethenyl)quinoline; acac, acetylacetonate) with a high current efficiency of 9.21 cd/A [9].

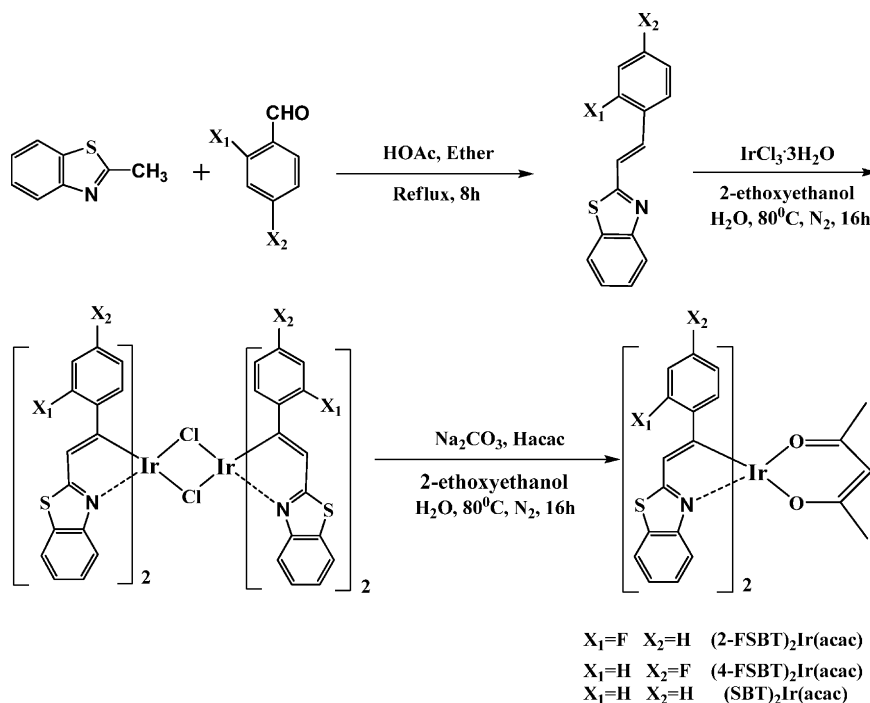
Hinted by Cheng's work, two fluorinated Ir(III) complexes containing alkenyl benzothiazole ligand, (2-FSBT)₂Ir(acac) and (4-FSBT)₂Ir(acac) (2-FSBT, (*E*)-2-(2-fluorostyryl)benzo[d]thiazole; 4-FSBT, (*E*)-2-(4-fluorostyryl)benzo[d]thiazole; acac, acetylacetonate) were designed, synthesized and used as efficient red phosphorescent dopants in OLEDs. Involvement of C–F bond instead of C–H bond probably presents the potential merits: to reduce the rate of radiationless deactivation and enhance the photoluminescence (PL) efficiency [10–12]; to reduce self-quenching of luminescence by altering the accumulation of molecules [11,13]; to make the complexes sublime better for thin film deposition and so on [14]. As a result, the devices based on the two red complexes exhibited very high efficiencies of 9.32 cd/A and 8.5 cd/A, respectively.

2. Experimental

Commercially available reagents were used for the synthesis of these Ir(III) complex. All reactions were carried out under a nitrogen atmosphere. Solvents were dried by standard procedures prior to use. ¹H NMR and mass spectroscopy (MS) were in agreement with the structure and were obtained on a Bruker AC 500 (TMS as internal standards) and Agilent 1100, respectively. UV–vis absorption spectra were recorded using a Perkin-Elmer Lambda-900 spec-

* Corresponding authors. Tel.: +86 412 5929881; fax: +86 412 5216902.

E-mail address: guoyong.xiao@yahoo.com.cn (G. Xiao).



Scheme 1. Synthesis of the complexes.

trophotometer. PL spectra were measured on a Perkin-Elmer LS-55 luminescence spectrophotometer.

2.1. The synthesis of Ir-complexes

For comparison, the unsubstituted complex, $(\text{SBT})_2\text{Ir}(\text{acac})$, $(\text{SBT}, (E)\text{-}2\text{-styrylbenzo}[d]\text{thiazole})$ is also prepared.

2.1.1. The synthesis of 2-FSBT [15]

The mixture of 2-fluorobenzaldehyde (24 mmol), 2-methylbenzothiazole (20 mmol), 3 mL glacial acetic acid and 6 mL acetic anhydride was heated to reflux for 8 h. After cooling to room temperature, treated with water, the resultant yellow precipitate was filtered off. The crude product was obtained. After recrystallized from methanol, the product was given with the yield of 81%. Mp 93–94 °C. ^1H NMR: (CDCl_3 , 500 MHz) δ (ppm): 7.12 (t, $J = 10.0$ Hz, 1H), 7.19 (t, $J = 7.5$ Hz, 1H), 7.31–7.34 (m, 1H), 7.39 (t, $J = 7.0$ Hz, 1H), 7.47–7.53 (m, 2H), 7.62–7.69 (m, 2H), 7.87 (d, $J = 8.0$ Hz, 1H), 8.0 (d, $J = 8.5$ Hz, 1H). MS (APCI): m/z 256.2 $[\text{M}+\text{H}^+]$.

2.1.2. The synthesis of 4-FSBT

This compound was prepared similarly from the reaction of 2-fluorobenzaldehyde with 2-methylbenzothiazole. Yield: 70%. Mp 160–161 °C. ^1H NMR: (CDCl_3 , 500 MHz) δ (ppm): 7.11 (t, $J = 8.5$ Hz, 2H), 7.34 (d, $J = 16.0$ Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.47–7.53 (m, 2H), 7.57–7.59 (m, 2H), 7.87 (d, $J = 8.0$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H). MS (APCI): m/z 256.2 $[\text{M}+\text{H}^+]$.

2.1.3. The synthesis of SBT

This compound was prepared similarly from the reaction of 2-fluorobenzaldehyde with 2-methylbenzothiazole. Yield: 78%. Mp 107–109 °C. ^1H NMR (CDCl_3 , 500 MHz) δ (ppm): 7.36–7.45 (m, 5H), 7.48 (t, 7.33 Hz, 1H), 7.55 (d, 16.23 Hz, 1H), 7.60 (d, 7.60 Hz, 2H), 7.87 (d, 7.98 Hz, 1H), 8.02 (d, 8.11 Hz, 1H). MS (APCI): m/z 238.4 $[\text{M}+\text{H}^+]$.

2.1.4. The synthesis of $(2\text{-FSBT})_2\text{Ir}(\text{acac})$ [8]

2-FSBT (2.2 mmol) was dissolved in 2-ethoxyethanol (10 mL) in 100 mL round-bottom flask. Iridium trichloride hydrate (1.0 mmol)

and 3.0 mL of water were then added to the flask. The mixture was stirred under nitrogen at 80 °C for 12 h and was cooled to room temperature. The precipitate was collected and dried in vacuum to give the corresponding chlorobridged dimer. Then in a 50-mL flask, the dimer complex, acetylacetonate (5.0 mmol) and Na_2CO_3 (10.0 mmol) were mixed with 2-ethoxyethanol (15 mL) and the mixture was refluxed at 80 °C under a nitrogen atmosphere for 12 h. After cooling to room temperature, the precipitate was filtered off and washed with water and ethanol. The crude product was purified on a silica gel column using acetic ether and n-hexane as eluent to give the desired red powder $(2\text{-FSBT})_2\text{Ir}(\text{acac})$. Yield: 35%. ^1H NMR: (CDCl_3 , 500 MHz) δ (ppm): 1.86 (s, 6H), 6.46 (t, $J = 7.5$ Hz, 2H), 6.57 (t, $J = 9.0$ Hz, 2H), 6.68–6.73 (m, 4H), 7.11 (s, 2H), 7.15–7.27 (m, 4H), 7.57 (t, $J = 9.5$ Hz, 4H). MS (APCI): m/z 801.1 $[\text{M}+\text{H}^+]$.

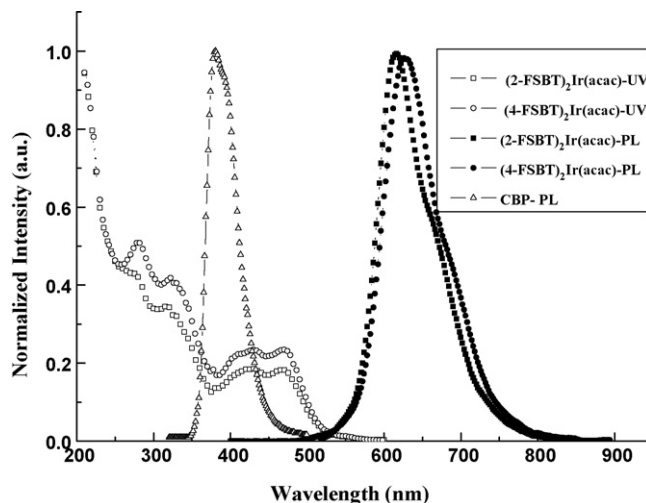


Fig. 1. UV-vis and PL spectra of two complexes in CH_2Cl_2 and PL spectrum of CBP film.

Table 1

EL device performances of Ir-complexes with different ratio.

Ir-complex	Ratio (%)	η_1^a	η_2^b	$L_{\max}^c$	$\lambda_{\max}^d$
(2-FSBT) ₂ Ir(acac)	6	7.13	4.95	6624	610
	8	9.32	6.8	8800	609
	10	8.22	6.1	8123	611
(4-FSBT) ₂ Ir(acac)	6	7.46	4.68	5270	611
	8	8.5	5.85	6986	610
	10	8.24	5.62	6237	612
(SBT) ₂ Ir(acac)	6	5.92	3.63	6309	614
	8	6.75	4.9	6648	613
	10	6.3	4.51	5850	614

^a Maximum current efficiency (cd/A).^b Current efficiency at 100 mA/cm².^c Maximum luminance (cd/m²).^d Peak emission wavelength (nm).

2.1.5. The synthesis of (4-FSBT)₂Ir(acac)

The compound was prepared similarly to the procedure described for the synthesis of (2-FSBT)₂Ir(acac). Yield: 42%. ¹H NMR: (CDCl₃, 500 MHz) δ (ppm): 1.71 (s, 6H), 6.41 (t, J = 8.5 Hz, 4H), 6.78 (t, J = 7.5 Hz, 4H), 7.00–7.08 (m, 6H), 7.31 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H). MS (APCI): m/z 800.9 [M+H⁺].

2.1.6. The synthesis of (SBT)₂Ir(acac)

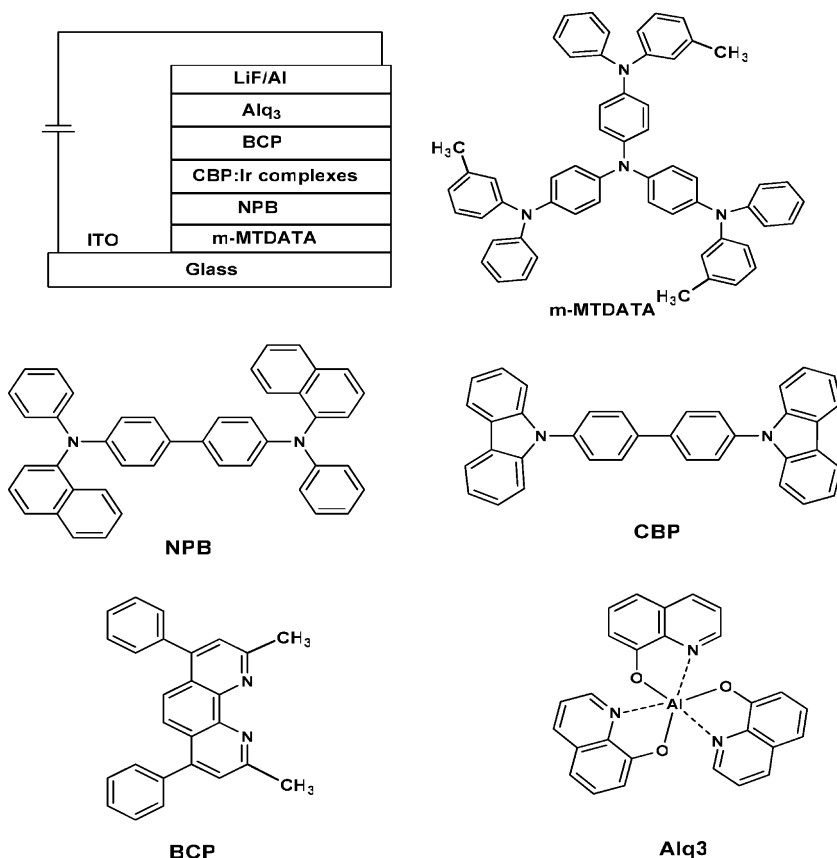
The compound was prepared similarly to the procedure described for the synthesis of (2-FSBT)₂Ir(acac). Yield: 45%. ¹H NMR (CDCl₃, 500 MHz) δ (ppm): 1.80 (s, 6H), 6.76–6.81 (m, 6H), 6.91–6.93 (m, 4H), 7.07–7.12 (m, 6H), 7.42 (dd, 7.3 Hz, 1.3 Hz, 2H), 7.57 (dd, 7.2 Hz, 1.4 Hz, 2H). MS (APCI): m/z 763.1 [M+H⁺].

2.2. EL measurements

In order to investigate EL properties of these Ir-complexes, devices using these complexes as dopant emitters were fabricated. The configuration of the devices was as follows: ITO/m-MTDATA(10 nm)/NPB(20 nm)/CBP: Ir-complex(X %, 30 nm)/BCP(10 nm)/Alq₃(30 nm)/LiF(1 nm)/Al(100 nm) in which ITO (indium tin oxide) was used as the anode, m-MTDATA(4,4',4''-tris[3-methylphenyl (phenyl)amino] triphenylamine) as the hole injection material, NPB (4, 4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl) as hole transporting layer, CBP (4,4'-N,N'-dicarbazole-biphenyl) as the host, BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) as electron blocking layer, Alq₃ (tris(8-hydroxyquinoline) aluminum) as electron transporting layer and LiF/Al as the cathode, respectively. The organic layers were sequentially deposited onto the pre-cleaned ITO glass substrates with a resistance of 20 Ω /sq. The pressure in the chamber was below 3×10^{-4} Pa. Deposition rates and thicknesses of the layers were monitored *in situ* using an oscillating quartz monitor. The evaporating rates were kept at 2–3 Å/s for organic layers and LiF layer and 10 Å/s for Al cathode, respectively. The luminance–current–voltage (L – I – V) characteristics of OLEDs were measured with a 3645 dc power supply combined with a 1980a spot photometer and recorded simultaneously with measurements.

3. Results and discussion

As shown in Scheme 1, the cyclometalated ligands 2-FSBT and 4-FSBT were conveniently prepared according to the literature procedures [15]. The synthesis of the bis-cyclometalated iridium complexes involved two steps. First, cyclometalated Ir(III)-chlorobridged dimers were synthesized by reacting IrCl₃· n H₂O and

**Fig. 2.** The general structure of the devices and the molecular structures of the compounds used in the devices.

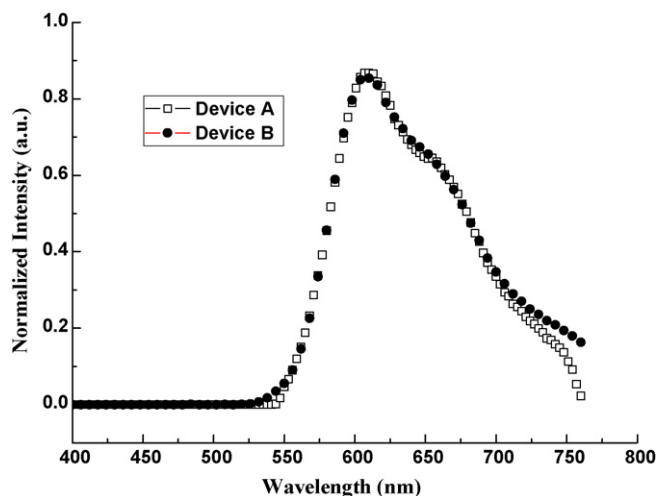


Fig. 3. The EL spectra of the devices.

two ligands. Then, the dimers were reacted with acetylacetone in 2-ethoxyethanol to afford target products in 35–45% yields.

Fig. 1 shows UV–vis absorption and PL spectra of (2-FSBT)₂Ir(acac) and (4-FSBT)₂Ir(acac) in dichloromethane solution at room temperature with the concentration of 1×10^{-5} M. And the PL spectrum of CBP film is also given in Fig. 1. The strong absorptions in the ultraviolet region between 275 nm and 350 nm with distinct vibronic features can be assigned to spin-allowed $^1\pi-\pi^*$ transitions from the cyclometalated ligand 2-FSBT and 4-FSBT. The absorption shapes of both complexes are similar. The low energy absorption bands extending into visible region around

400–500 nm are tentatively ascribed to spin-allowed metal-to-ligand charge transfer $^1\text{MLCT}$ and spin-forbidden $^3\text{MLCT}$ transition, just as observed in most Ir-complexes. On irradiation with 360 nm light, both (2-FSBT)₂Ir(acac) and (4-FSBT)₂Ir(acac) emit strong PL at 615 nm and 626 nm, respectively. Based on the observed optical properties and by comparison with those of known iridium complexes [16,17], it is clear that the observed emissions of these two iridium complexes are phosphorescent in nature. The quantum yields of (2-FSBT)₂Ir(acac) and (4-FSBT)₂Ir(acac), measured in dichloromethane, were 0.24 and 0.21 by using Ir(ppy)₃ as a reference which has a quantum yield of 0.40 [18], and the corresponding value of (SBT)₂Ir(acac) is only 0.19.

To understand the EL ability of these iridium complexes, the light emitting devices using these complexes as dopant emitters were fabricated. Table 1 summarized EL performances of the devices based on different concentrations of Ir-complexes. As shown in Table 1, all the 8% complexes doped devices exhibited the best performances. Moreover, the device properties based on two fluorinated complexes outperformed those based on (SBT)₂Ir(acac). Fig. 2 shows the general structure of the devices and molecular structures of the compounds used in these devices. For devices A and B, the emitting layers were doped with an optimized 8% (2-FSBT)₂Ir(acac) and (4-FSBT)₂Ir(acac), respectively. It is evident from Fig. 3 that both devices exhibited red ELs which originate from the doped Ir phosphors because of the similarity with the PL spectra of the two complexes molecules. Also, the emission peaks of NPB and the host which are located in the blue region around 400–480 nm are not present. Furthermore, there is a good overlap between PL spectrum of CBP and MLCT absorption bands of two complexes in Fig. 1. So, we surmise that the efficient Förster energy transfer based on the doped devices maybe occurs. Both devices emitted bright red colors, which were independent of the applied bias from 6 V to 18 V. The Commission International de L'Eclairage (CIE) coordinates (1931) are (0.619, 0.381) for device A and (0.621, 0.378) for device B and both values correspond to the red region of the CIE chromaticity diagram which are very close to the standard red required by the National Television Standards Committee (NTSC). Moreover, it is clearly seen that broader EL emissions with the full width of half maximum (FWHM) of about 107 nm than PL emissions with that of 86 nm are observed. The reasons for that are under investigating.

The I – V characteristics of the devices are displayed in Fig. 4. The current efficiency versus current density curves of the devices are also shown in inset of Fig. 4. In common with most phosphorescent devices, a pronounced reduction of efficiency was observed at high current densities for both devices, which has been attributed to a combination of triplet–triplet annihilation [19,20] and field-induced exciton dissociation [21,22]. The turn-on voltage (defined as a bias at a luminance of 1 cd/m²) is 4.5 V for device A and 5.0 V for device B. For device A, a maximum luminance of 8800 cd/m² at 17 V was achieved and a peak current efficiency was 9.32 cd/A at 2 mA/cm². The device B exhibited a maximum luminance of 6986 cd/m² at 18 V and a peak current efficiency of 8.5 cd/A at 1.5 mA/cm². These values are significantly higher compared to the previously reported results [23].

4. Conclusion

In summary, we designed and synthesized two novel red iridium complexes (2-FSBT)₂Ir(acac) and (4-FSBT)₂Ir(acac) containing a fluorinated alkenyl benzothiazole ligand for OLED applications. These two complexes show typical $^3\text{MLCT}$ emission characters. Highly efficient red phosphorescent devices employing these compounds have been demonstrated. These results represent the first example that the iridium complexes containing a fluorinated alkenyl benzothiazole ligand can serve as efficient emitters for red electrophosphorescence devices.

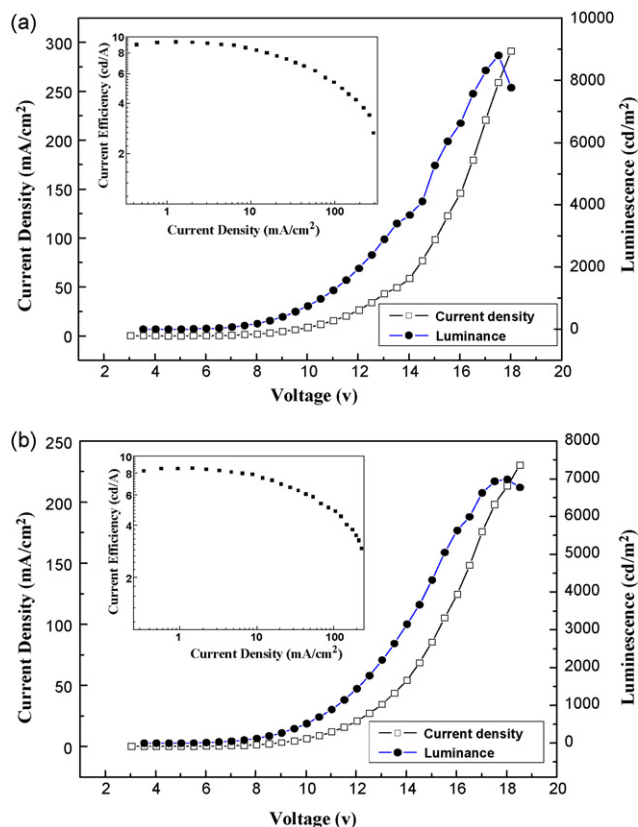


Fig. 4. I – V characteristics of device A (a) and device B (b). Inset: current efficiency versus current density curves of the devices.

Acknowledgements

This work was supported by Anshan Science and Technology Foundation (Granted No. 2007SF46). The authors would like to thank Professor Wenlian Li and Dr. Dongyu Zhang (Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences) for fabrication of OLEDs.

References

- [1] M.A. Baldo, D.F. O'Brian, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, *Nature* 395 (1998) 151.
- [2] M.A. Baldo, M.E. Thompson, S.R. Forrest, *Nature* 403 (2000) 750.
- [3] Y.-L. Tung, S.-W. Lee, Y. Chi, Y.-T. Tao, C.-H. Chien, Y.-M. Cheng, P.-T. Chou, S.-M. Peng, C.-S. Liu, *J. Mater. Chem.* 15 (2005) 460.
- [4] H.Z. Xie, M.W. Liu, O.Y. Wang, X.H. Zhang, C.S. Lee, L.S. Hung, S.T. Lee, P.F. Teng, H.L. Kwong, H. Zheng, C.M. Che, *Adv. Mater.* 13 (2001) 1245.
- [5] Y.M. You, C.-G. An, D.-S. Lee, J.-J. Kim, S.Y. Park, *J. Mater. Chem.* 16 (2006) 4706.
- [6] G.-J. Zhou, X.-Z. Wang, W.-Y. Wong, X.-M. Yu, H.-S. Kwok, Z.Y. Lin, *J. Organomet. Chem.* 692 (2007) 3461.
- [7] C. Adachi, M.A. Baldo, S.R. Forrest, M.E. Thompson, *Appl. Phys. Lett.* 77 (2000) 904.
- [8] B.M.J.S. Paulose, D.K. Rayabarapu, J.-P. Duan, C.-H. Cheng, *Adv. Mater.* 16 (2004) 2003.
- [9] D.K. Rayabarapu, B.M.J.S. Paulose, J.-P. Duan, C.-H. Cheng, *Adv. Mater.* 17 (2005) 349.
- [10] X. Zhang, J. Gao, C. Yang, L. Zhu, Z. Li, K. Zhang, J. Qin, H. You, D. Ma, J. Organomet. Chem. 691 (2006) 4312.
- [11] K.R. Justin Thomas, M. Velusamy, J.T. Lin, C.-H. Chien, Y.-T. Tao, Y.S. Wen, Y.-H. Hu, P.-T. Chou, *Inorg. Chem.* 44 (2005) 5677.
- [12] P.P. Sun, C.X. Li, Y. Pan, Y. Tao, *Synth. Met.* 156 (2006) 525.
- [13] V.V. Grushin, N. Herron, D.D. LeCloux, W.J. Marshall, V.A. Petrov, Y. Wang, *Chem. Commun.* (2001) 1494.
- [14] Y. Wang, N. Herron, V.V. Grushin, D. LeCloux, V. Petrov, *Appl. Phys. Lett.* 79 (2001) 449.
- [15] Z.-L. Huang, H. Lei, N. Li, Z.-R. Qiu, H.-Z. Wang, J.-D. Guo, Y. Luo, Z.-P. Zhong, X.-F. Liu, Z.-H. Zhou, *J. Mater. Chem.* 13 (2003) 708.
- [16] M.G. Colombo, T.C. Brunold, T. Riedener, H.U. Gudel, M. Fortsch, H.B. Burgi, *Inorg. Chem.* 33 (1994) 545.
- [17] M.G. Colombo, A. Hauser, H.U. Gudel, *Inorg. Chem.* 32 (1993) 3088.
- [18] K.A. King, P.J. Spellane, R.J. Watts, *J. Am. Chem. Soc.* 107 (1985) 1431.
- [19] M.A. Baldo, C. Adachi, S.R. Forrest, *Phys. Rev. B* 62 (2000) 10967.
- [20] C. Adachi, M.A. Baldo, S.R. Forrest, *J. Appl. Phys.* 87 (2000) 8049.
- [21] J. Kalinowski, W. Stampor, J. Mezyk, M. Cocchi, D. Virgili, V. Fattori, P. Di Marco, *Phys. Rev. B* 66 (2002) 235321.
- [22] M. Cocchi, V. Fattori, D. Virgili, C. Sabatini, P.D. Marco, M. Maestri, J. Kalinowski, *Appl. Phys. Lett.* 84 (2004) 1052.
- [23] Y. Ha, J.-H. Seo, Y.K. Kim, *Synth. Met.* 158 (2008) 548.