

高效磷光铱配合物的合成及电致发光性能研究

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摘要: 合成了一种含苯并咪唑结构配体的环金属化铱配合物(ffbi)₂Ir(acac), (其中 ffbi 为 1-(4-氟苄基)-2-(4-氟苯基)苯并咪唑, acac 为乙酰丙酮), 并以其作为发光体, 制备了有机电致发光器件。结果表明该配合物具有强磷光发光特性, 器件发绿色光。其中结构为 TCTA(40 nm)/CBP:Ir(6.3%, 30 nm)/BCP(10 nm)/Alq(40 nm)的电致发光器件在 12 V 电压下最大发光亮度达 41 499 $\text{cd}\cdot\text{m}^{-2}$, 在 8 V 电压下, 最大外量子效率达 5.7%。

关键词: 铱配合物; 合成; 磷光材料; 有机电致发光二极管

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Highly Phosphorescent Iridium Complex for Organic Light Emitting Diodes

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Abstract: A bis-cyclometalated iridium complex (ffbi)₂Ir(acac) (ffbi =1-(4-fluorobenzyl)-2-(4-fluorophenyl)benzimidazole, acac =acetylacetone) containing benzimidazole-based ligand has been synthesized and used as an emitter in organic light emitting diodes (OLEDs). The results showed that this complex had a strong phosphorescent character and the EL devices based on this complex emitted green light. For the device with the structure of TCTA(40 nm)/CBP:Ir(6.3%, 30 nm)/BCP(10 nm)/Alq(40 nm), the maximum brightness reached 41 499 $\text{cd}\cdot\text{m}^{-2}$ at a voltage of 12 V and the maximum external efficiency reached 5.7% at a voltage of 8 V.

Key words: iridium complex; synthesis; phosphorescent material; organic light emitting diode

0 Introduction

Light-emitting diodes (LEDs) using small organic molecules are intensively studied after the initial work by Tang and VanSlyke^[1] due to the potential application of these devices as low-cost alternatives in flat panel displays. Among numerous devices, highly efficient organic light emitting diodes (OLEDs) using

phosphorescent dyes such as PtOEP, Ir(ppy)₃, (ppy)₂Ir(acac), etc. and their derivatives have aroused great interest, and much attention has been paid for this area in recent years^[2-8]. By employing triplet-based phosphorescent compound in OLEDs, where both singlet and triplet excited states participate, therefore the internal efficiency can reach 100%, and the external quantum efficiency can approach 20%^[9,10].

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Most of the previous investigations on phosphorescent materials have been focused on the iridium complexes because of their high efficiency and stability^[11]. Prototype heterocyclic ligands used include 2-phenylpyridine, benzoquinoline and 2-phenylbenzothiazole etc which coordinate to the metal center via the formation of Ir-N and Ir-C bonds^[4]. In these cases, devices were prepared by vacuum vapor deposition techniques. These works have shown that it is possible to tune the wavelength of emission of the complex by modifying the ligands. Additional efforts showed that it was possible to reduce self-quenching by the introduction of substitutional groups on the appropriate position of ligand^[12-14]. And also, fluorinated substituents in the aromatic ligand could result in markedly reduced concentration-quenching of luminescence and excellent volatility, hence helpful for device processing^[15,16].

Now we report in this paper a new iridium complex for organic light emitting diodes. The main ligand is a derivative of benzimidazole with substitution on its 1- and 2-positions by 4-fluorobenzyl and 4-fluorophenyl groups. The results show that the complex has a phosphorescent property, and the device based on this complex give a high brightness and quantum efficiency.

1 Experimental

1.1 Reagents and instruments

Reagents were used as purchased without further purification. Melting points were measured on a MP-2D melting point apparatus and were uncorrected. ¹H NMR spectra were recorded with a Bruker ARX-300 spectrometer; elemental analyses were performed on a Perkin-Elmer 240C instrument; mass spectra were obtained on a VG-ZAB-HS instrument; UV-Vis spectra were recorded on a Hitachi U-3300 model while PL spectra were taken using a Hitachi F-4500 fluorescence spectrophotometer. Current, voltage, and light-intensity measurements were made simultaneously using a Keithley 2400 source meter and a Newport 1835-C optical meter equipped with a Newport 818-ST silicon photodiode.

1.2 Synthesis of materials

1.2.1 Synthesis of 1-(4-fluorobenzyl)-2-(4-fluorophenyl)benzimidazole

Iodine (0.06 mmol) was dissolved in 10 mL THF-H₂O (1:1, V/V). To this solution was added 1,2-phenylenediamine (3.0 mmol) and p-florobenzaldehyde (6.0 mmol). The resulting mixture was stirred at room temperature for 3 h (monitored by TLC) then extracted with CH₂Cl₂ and purified by column chromatography on silica gel with hexane/ethyl acetate (5:1, V/V) as eluent to yield the product. Yield: 80%. m.p. 88~90 °C; ¹H NMR (CDCl₃): δ 8.15 (m, 1H), 7.88 (d, *J*=7.4 Hz, 1H), 7.65 (m, 2H), 7.30 (m, 3H), 7.15 (m, 2H), 7.07 (m, 3H), 5.43 (s, 2H); IR (KBr): 3 045, 3 067, 2 934, 2 846, 1 435, 1 096 cm⁻¹; MS: (EI) *m/z*: 320.1 (51.9, M⁺), 228.9 (7.7), 210.9 (7.3), 108.9 (100), 82.9 (19.8). Elemental analysis for C₂₀H₁₄N₂F₂: Calcd.: C, 74.99; H, 4.41; N, 8.75%; Found: C, 74.89; H, 4.45; N 8.71%.

1.2.2 Synthesis of Ir complex [(ffbi)₂Ir(acac)]

1-(4-Florophenylmethyl)-2-(4-florophenyl)benzimidazole (2.5 mmol) was dissolved in 10 mL 2-ethoxyethanol, then iridium trichloride hydrate (1 mmol) and 3 mL water were added. The mixture was stirred in an inert atmosphere at 120 °C for 24 h, and cooled to room temperature. The precipitate was collected and washed with ethanol, acetone, and then dried in vacuum. It gave a cyclometalated Ir (III) μ -chloro-bridged dimer. 2 mmol acetyl acetone, 5 mmol Na₂CO₃ and the dimer complex were dissolved in 15 mL 2-ethoxyethanol and refluxed in an inert atmosphere for 10~12 h. After cooling to room temperature, the precipitate was filtered off and washed with water, ethanol, and ether. The crude product was then sublimated at 300~320 °C and 4 × 10⁻³ Pa to give the pure complex. Yield: 68%. ¹H NMR (CDCl₃): δ 7.71 (d, *J*=7.5 Hz, 2H), 7.04~7.38 (m, 16H), 6.35 (t, *J*=9.3 Hz, 2H), 6.03 (d, *J*=9.0 Hz, 2H), 5.68~5.86 (m, 4H), 5.31 (s, 1H), 1.85 (s, 6H); MS (ESI) *m/z*: 929.7 (M⁺); Elemental analysis for C₄₅H₃₃F₄IrN₄O₂: Calcd.: C 58.12, H 3.58, N 6.02%; found: C 58.35, H 3.45, N 6.10%.

1.3 OLED fabrication and measurement

For studying the electroluminescent properties of

this iridium complex, several devices using this complex as dopant emitter were fabricated by vacuum deposition of the materials at 1.3×10^{-4} Pa onto a clean glass pre-coated with a layer of indium tin oxide with a sheet resistance of $25 \Omega \cdot \text{square}^{-1}$. The deposition rate for the organic compounds was $0.1 \sim 0.2 \text{ nm} \cdot \text{s}^{-1}$. The cathode of Mg/Ag alloy (10:1) was deposited by the co-evaporation of magnesium and silver metals, with deposition rates of 0.5 and $0.05 \text{ nm} \cdot \text{s}^{-1}$, respectively. The cathode was then capped with silver metal (100 nm) by evaporation silver at a rate of $0.3 \text{ nm} \cdot \text{s}^{-1}$.

2 Results and discussion

The ligand 1-(4-fluorobenzyl)-2-(4-fluorophenyl)

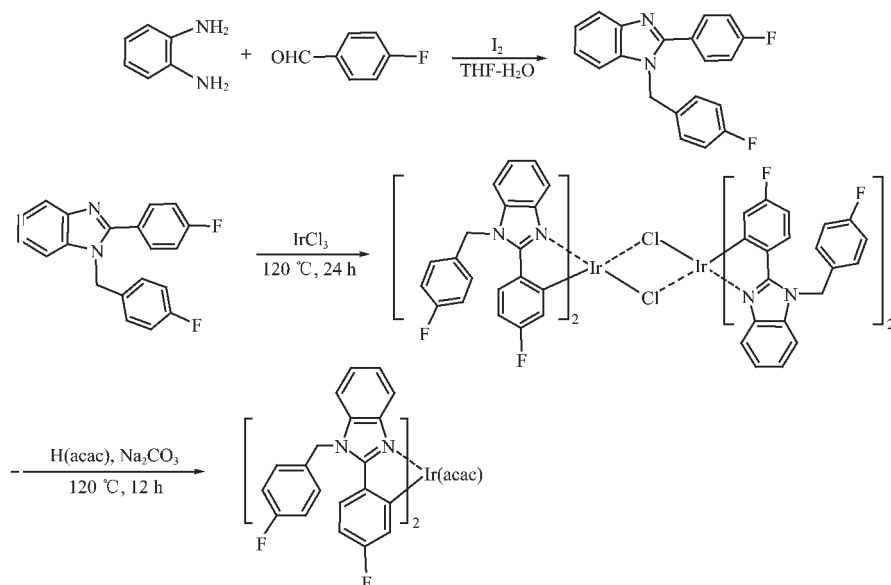


Fig.1 Synthesis of Ir complex

The absorption and photoluminescence spectra of the complex in dichloromethane are in Fig.2. In the UV-Vis spectrum, the strongest absorption band lying at 298 nm is assigned to ligand-centred (LC) $\pi-\pi^*$ transition, which closely resembles the absorption spectrum of the free ligand. It also shows a vibration absorption peak at 310 nm. The absorption band 400 and 425 nm can be assigned to singlet $^1\text{MLCT}^*$ and $^3\text{MLCT}^*$ states, based on the previously reported cyclometalated iridium complex and the calculations of Hay^[18]. Each of them is broad and featureless. The comparable intensities of $^1\text{MLCT}$ and $^3\text{MLCT}$ imply the presence of significant singlet-triplet coupling due

to spin-orbital coupling. benzimidazole was synthesized by an iodine catalyzed condensation of 1,2-phenylenediamine with 2 equivalent of aldehyde at room temperature in air^[17]. THF-H₂O (1:1, V/V) was used as solvent. It showed that I₂ exhibited a powerful catalytic activity to this reaction in an amount as low as 2mol%, which was enough to complete the reaction within 3 hours with a high yield. The iridium complex was then synthesized via the “bridge-splitting” method utilizing the Ir-chloride-bridged dimer formed by the ligand with iridium trichloride. The dimer reacted with acetylacetonate in the presence of Na₂CO₃ in ethoxyethanol afforded the corresponding complex with moderate yield. The synthetic route is shown in Fig.1.

to spin-orbital coupling.

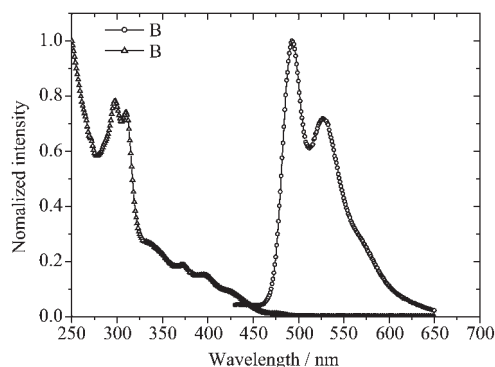


Fig.2 Absorption and photoluminescence spectra of the complex

On irradiation with 400 nm light, the complex

shows strong photoluminescence characteristics in dichloromethane at 493 and 527 nm with a green color. Both $^3\text{MLCT}$ and ligand-based $^3\pi-\pi^*$ transitions can contribute to the phosphorescence emission in the complex. Strong spin-orbit coupling in the complex leads to efficient phosphorescence. It exhibits a high

solution phosphorescence quantum yield of 0.43 at room temperature determined using $\text{Ir}(\text{ppy})_2(\text{acac})$ as a reference with a value of 0.34^[4].

Fig.3 shows the configurations of the devices and the molecular structures of the compounds used in the devices.

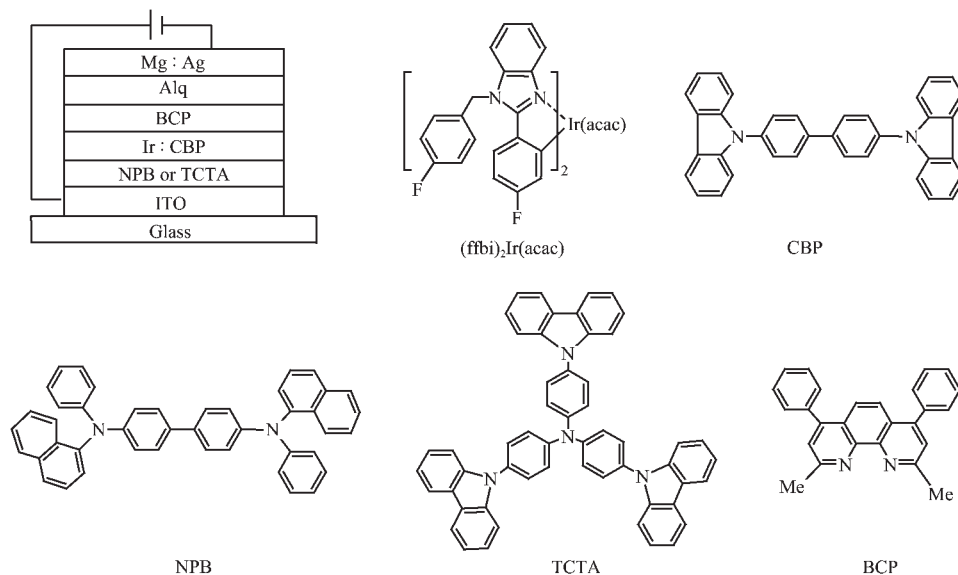


Fig.3 Structure of the device and the molecular structures of the compounds used in the device

A layer (40 nm) of 4,4'-bis{*N*-(1-naphthyl)-*N*-phenylamino}biphenyl (NPB) (device I) or tris[4-(9H-carbazol-9-yl)phenyl]amine (TCTA) (device II) for hole transport, a layer (30 nm) of 4,4'-*N,N'*-dicarbazolebiphenyl (CBP) doped with 6.3% of (ffbi)₂Ir(acac) as the emitter, a thin layer (10 nm) of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) for hole and exciton blocking (HBL), and a layer (40 nm) of tris (8-hydroxyquinoline) aluminum (Alq) for electron transport.

Both devices exhibit low turn-on voltages: 3.5 V for device I and 3.4 V for device II. The devices emit light characteristic of (ffbi)₂Ir(acac). The EL spectra of device II at different voltages are shown in Fig.4. It was found that the spectrum did almost not change when the voltage changed. That is, the EL spectrum of the device was independent of the applied voltage (6~15 V).

The current-voltage-luminance characteristics of the devices are shown in Fig.5. And the important device performance characteristics are collected in

Table 1. The maximum brightness of the device based on this complex reached 41 499 $\text{cd}\cdot\text{m}^{-2}$ at a voltage of 12 V and the maximum external efficiency reached 5.7% at a voltage of 8 V. The CIE (Commission Internationale de l'Eclairage) coordinates of the devices show the green emitting character.

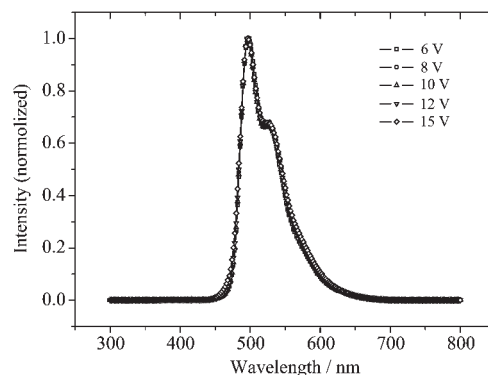


Fig.4 Electroluminescence spectra of device II at various applied voltages

It is worthy of noting that the device II has much higher efficiencies and brightness than the device I. Compared to NPB, TCTA has a greater conjugation, it provides a more appropriate HOMO

Table 1 Structure and performance data of Ir complexes-based OLEDs^a

Device	Device structure	Turn-on voltage / V	$\eta_{\text{ext}} / \%$	$L / (\text{cd} \cdot \text{m}^{-2})$	$\eta_c / (\text{cd} \cdot \text{A}^{-1})$	$\eta_p / (\text{lm} \cdot \text{W}^{-1})$	CIE, 8 V (x, y)
I	NPB(40 nm)/CBP:Ir(6.3% 30 nm)/ BCP(10 nm)/Alq(40 nm)	3.5	3.85 (6 V)	23 908 (13 V)	12.12 (6 V)	6.63 (5.5 V)	(0.21, 0.56)
II	TCTA(40 nm)/CBP:Ir(6.3% 30 nm)/ BCP(10 nm)/Alq(40 nm)	3.4	5.70 (8 V)	41 499 (12 V)	18.61 (8 V)	7.63 (7.5 V)	(0.23, 0.58)

^a The data for external quantum efficiency (η_{ext}), brightness (L), current efficiency (η_c), and power efficiency (η_p) are the maximum values of the device.

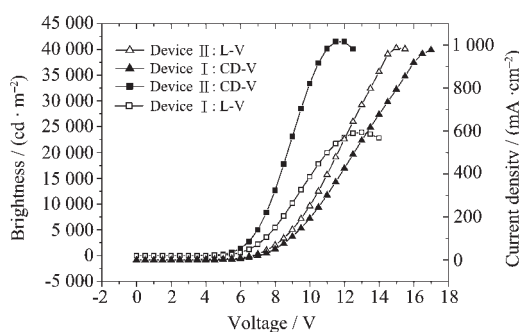


Fig.5 Luminance-voltage-current characters of devices I and II

energy level matching CBP^[19], so TCTA is found to be more efficient for hole transporting in the device based on this complex.

3 Conclusion

In summary, we have synthesized a bis-cyclometalated iridium complex containing benzimidazole-based ligand. This complex has strong phosphorescent properties. Green-emitting devices based on this complex were also fabricated with high brightness and efficiencies.

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