

一种含载流子传输基的铱配合物:合成及深黄色电致磷光器件

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摘要: 合成了一种含有载流子传输基新的铱配合物 (BPPBI)₂Ir(ECTFBD) [HBPPBI: 1-苯基-2-(4-联苯基)苯并咪唑, HECTFBD: 1-(9-乙基-3-咪唑基)-4,4,4-三氟-1,3-丁二酮], 其结构和组成经核磁共振氢谱和元素分析所证实。研究了这种铱配合物二氯甲烷溶液的光物理和电化学性质。制作了基于这种铱配合物的电致磷光器件。器件结构是 ITO/MoO₃(10 nm)/NPB(80 nm)/CBP: *x*% (BPPBI)₂Ir(ECTFBD)(20 nm)/TPBi(45 nm)/LiF/Al [*x*%: 质量百分比为 4% 和 7% 的掺杂浓度; NPB: *N*⁴, *N*^{4'}-二(1-萘基)-*N*⁴, *N*^{4'}-二苯基-4,4'-联苯二胺, CBP: 4,4'-二(9-咪唑基)联苯, TPBi: 1,3,5-三(2-(1-苯基)苯并咪唑基)苯]。这些器件显示出深黄色的发射。对于 7% 掺杂浓度器件, 最大的电流效率和最大发光亮度分别是 5.2 cd·A⁻¹ 和 8 690 cd·m⁻²。

关键词: 铱配合物; 电致磷光; 有机电致发光二极管

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Iridium Complex Containing Carrier Transport Moieties: Synthesis and Deep Yellow Electrophosphorescence Devices

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Abstract: A novel Ir-complex (BPPBI)₂Ir(ECTFBD) (HBPPBI=2-(biphenyl-4-yl)-1-phenyl-1*H*-benzo[d]imidazole, HECTFBD=1-(9-ethyl-9*H*-carbazol-3-yl)-4,4,4-trifluorobutane-1,3-dione) containing carrier transport moieties was synthesized and characterized by ¹H NMR and elemental analysis. The photophysical and electrochemical properties of (BPPBI)₂Ir(ECTFBD) in dichloromethane were investigated. The Ir-complex-based electroluminescent devices were fabricated. The structure of devices was ITO/MoO₃ (10 nm)/NPB (80 nm)/CBP: *x*% (BPPBI)₂Ir(ECTFBD) (20 nm)/TPBi (45 nm)/LiF/Al [*x*%: 4% and 7% doping concentration by weight; NPB=*N*⁴, *N*^{4'}-di(naphthalen-1-yl)-*N*⁴, *N*^{4'}-diphenylbiphenyl-4,4'-diamine, CBP=4,4'-di(9*H*-carbazol-9-yl)biphenyl, TPBi=1,3,5-tris(1-phenyl-1*H*-benzo[d]imidazol-2-yl)benzene]. Deep yellow emission from the emissive layer was obtained. For the device at 7 wt% doping concentration, the maximum current efficiency and the maximum brightness were 5.2 cd·A⁻¹ and 8 690 cd·m⁻², respectively.

Key words: iridium complex; electrophosphorescence; organic light-emitting diode

Organic light-emitting diodes (OLEDs) exhibit high brightness, high light-emitting efficiency, relatively low drive voltages, full color display as well as low

cost of simple fabrication. Therefore, it has been attracted increasing interest for the application in many display fields such as personal computer, mobile phone

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and a variety of display screens during the past decade. Excellent OLEDs should possess such features as long lifetimes, high light-emitting efficiencies and good color purities. Heavy metal complexes as Pt-, Ir-, Ru-, Os-complexes can fully harvest both singlet and triplet excitons in the process of electroluminescence due to the strong spin-orbital coupling caused by heavy metal ions in the complexes. 100% phosphorescence quantum efficiency of Ir-complexes has been reported^[1]. Light-emitting efficiency of OLEDs predominately depends on structure and the materials used in the devices. In order to improve light-emitting efficiency, lots of electrophosphorescent materials were designed and synthesized^[2-3]. Generally, they were grafted by some carrier transport moieties such as carbazole, triarylamine, 1,3,4-oxadiazole^[4-9]. Zhu et al.^[10] reported a highly efficient electrophosphorescent device with external quantum efficiency of 10.4% due to the introduction of triarylamine unit. Fang et al.^[11] employed a tris-cyclometalated iridium complex containing carbazole unit as emissive layer to fabricate highly efficient red device. The carrier transport moieties in Ir-complexes are beneficial to improve the device efficiencies. In this paper, a novel Ir-complex with two BPPBI ligands (HBPPBI = 2-

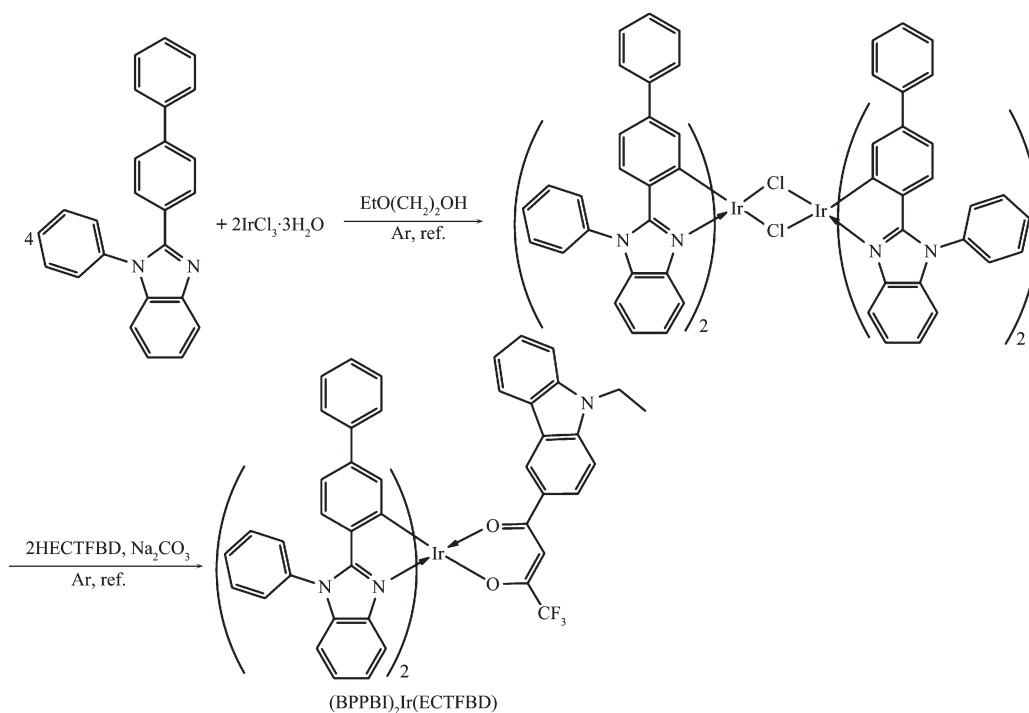
(biphenyl-4-yl)-1-phenyl-1*H*-benzo[d]imidazole), analogous to excellent electron transport material TPBi (TPBi = 1,3,5-tris (1-phenyl-1*H*-benzo[d]imidazol-2-yl) benzene, Fig.1) structurally, and ECTFBD β -diketone ligand (HCTFBD = 1-(9-ethyl-9*H*-carbazol-3-yl)-4,4,4-trifluorobutane-1,3-dione), linked by carbazole group, was synthesized and characterized. The devices based on this complex were fabricated.

1 Experimental

1.1 Synthesis of materials

The synthetic route for (BPPBI)₂Ir (ECTFBD) is shown in Scheme 1. HBPPBI and HECTFBD were prepared according to published literatures^[12-13].

(BPPBI)₂Ir (ECTFBD) was synthesized via the following procedures: 260 mg of IrCl₃ · 3H₂O (0.82 mmol, Sigma-Aldrich) and 1.14 g of HBPPBI (3.28 mmol) were added to a solution of 15 mL of 2-ethoxyethanol and 8 mL of H₂O in a 50 mL of three neck-flask. The reaction mixture was stirred and refluxed for 20 h under argon atmosphere. After cooling down to room temperature, a yellow precipitate was obtained, filtered and washed with water and ethanol for several times. The chloride-bridged diiridium complex



Scheme 1 Synthetic route for (BPPBI)₂Ir(ECTFBD)

(457 mg) was obtained in a yield of 60%.

380 mg (0.21 mmol) of the dimer, 182 mg (0.546 mmol) of HECTFBD and 35.0 mg of sodium carbonate were added to 20 mL of 2-ethoxyethanol in a three-neck flask. The mixture was refluxed under argon atmosphere for 13 h, then cooled down to ambient temperature, and a red precipitate was obtained. After filtered and washed with water and methanol, the precipitate was purified by column chromatography (silica gel as stationary phase, freshly-distilled toluene as eluant) to get a red solid product with a 78.3% yield (400 mg). ^1H NMR (300 MHz, CDCl_3 , ppm): δ =8.64 (1H, d, J =1.4 Hz), 8.09~8.05(2H, m), 7.92(1H, d, J =7.9 Hz), 7.69~7.60 (12H, m), 7.47~7.01 (14H, m), 6.91~6.51(11H, m), 4.35(1H, s), 3.70(2H, dd, J =7.0), 1.25 (3H, t, J =7.0). Elemental analysis of $\text{C}_{68}\text{H}_{47}\text{F}_3\text{IrN}_5\text{O}_2$, found (Calcd.): C, 67.92% (C, 67.20%); H, 4.17% (H, 3.90%); N, 5.57% (N, 5.76%).

1.2 Characterization

Elemental analysis was performed on Harrios Elemental Analysis Instrument. UV-Vis spectrum was recorded using an HP 8453 diode-array spectrophotometer. Photoluminescence (PL) spectrum was obtained on a Hitachi F-4500 luminescence spectrometer.

1.3 Measurement of cyclic voltammetry

Cyclic voltammetry was performed using CHI760

electrochemical workstation. $(\text{BPPBI})_2\text{Ir}(\text{ECTFBD})$ was dissolved in chromatography grade CH_2Cl_2 at a concentration level of $1.00 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$. Glassy carbon was used as the working electrode, Pt plate as the auxiliary electrode, saturation calomel electrode as the reference electrode and $n\text{-C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$ of $0.1 \text{ mol} \cdot \text{L}^{-1}$ as the supporting electrolyte. Prior to the measurement, the cell for cyclic voltammetry testing was purged by N_2 for 5 min. The cyclic voltammogram data were recorded at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$.

1.4 Fabrication and performance testing of devices

The structure of devices is depicted as ITO/ MoO_3 (10 nm)/NPB (80 nm)/CBP: $x\%$ $(\text{BPPBI})_2\text{Ir}(\text{ECTFBD})$ (20 nm)/TPBi (45 nm)/LiF (1 nm)/Al (60 nm). The Ir-complex (guest material) was doped in CBP (4,4'-di(9H-carbazol-9-yl) biphenyl, host material) as light-emitting layer at doping level of 4% or 7% by weight. MoO_3 and LiF served as hole- and electron-injecting layers, respectively. NPB ($N^4, N^{4'}$ -di(naphthalen-1-yl)- $N^4, N^{4'}$ -diphenylbiphenyl-4,4'-diamine) served as hole-transporting layer, and TPBi 1,3,5-tris(1-phenyl-1H-benzo[d]imidazol-2-yl)benzene) was used as electron-transporting and hole-blocking material. The molecular structures and device configuration are given in Fig.1.

Devices were fabricated by the procedures as

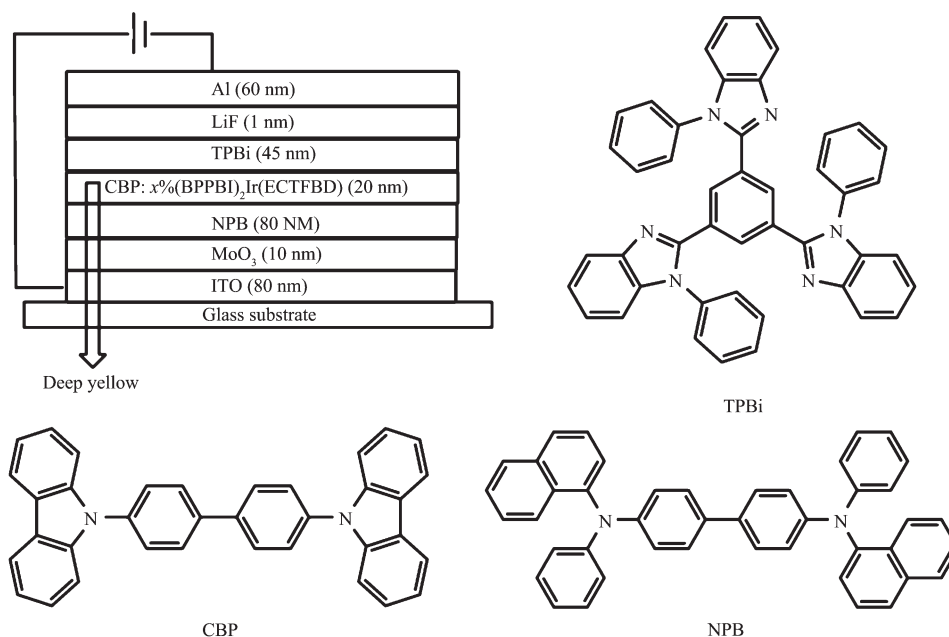


Fig.1 Device configuration and molecular structures of the materials used in the devices

follows: before the fabrication, the ITO glass substrate was pre-cleaned carefully and treated by oxygen plasma for 2 min. Then, all the materials were deposited to the ITO glass substrate by thermal sublimation under high vacuum of 10^{-4} Pa. At first, MoO_3 (10 nm) was deposited on the ITO substrate, followed by NBP, the emissive layer of $(\text{BPPBI})_2\text{Ir}(\text{ECTFBD})$ -doped CBP, TPBi and a cathode composed of lithium fluoride and aluminum. The active device area was 0.15 cm^2 . Resistance of the sheet ITO substrate was $10 \Omega \cdot \square^{-1}$. The current density or brightness vs voltage of the electroluminescent devices was obtained with a Keithley 2400 Source meter and a Keithley 2000 Source multi-meter equipped with a calibrated silicon photodiode. The electroluminescence (EL) spectra were measured with a JY SPEX CCD3000 spectrometer. All measurements were carried out under the ambient conditions.

2 Results and discussion

2.1 UV-Vis and photoluminescence spectra

Fig.2 shows the UV-Vis spectrum and photoluminescence (PL) properties of $(\text{BPPBI})_2\text{Ir}(\text{ECTFBD})$ dissolved in CH_2Cl_2 at about $1 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ concentration. The intense absorptions at 234, 284 and 313 nm origin from $\pi\text{-}\pi^*$ absorption of ligand-central (L-C) of benzene, benzimidazole and N-ethyl carbazole segments. A weak peak at 367 nm and a hardly distinguishing weak peak at 459 nm are assigned to spin-allowing singlet state $^1\text{MLCT}$ (metal-ligand charge transfer) absorption and spin-forbidding triplet state $^3\text{MLCT}$ absorption, respectively. The absorptions of $^1\text{MLCT}$ and $^3\text{MLCT}$ are necessary for obtaining high light-emitting

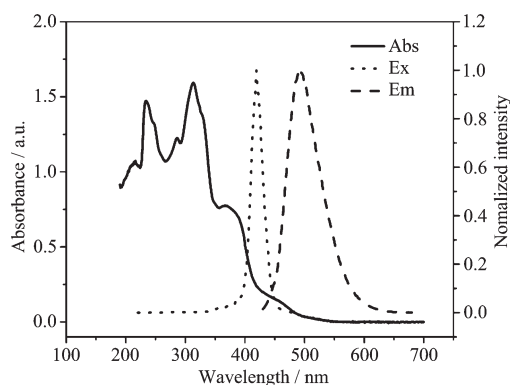


Fig.2 UV-Vis absorption and photoluminescence spectra of $(\text{BPPBI})_2\text{Ir}(\text{ECTFBD})$ in CH_2Cl_2

efficiency OLEDs (organic light emitting diodes) because the singlet and triplet states in the complex can be fully used in the processes of electroluminescence. From the PL spectrum, an intense emission at 492 nm could be observed, when the complex was excited by 419 nm light. The intense PL emission corresponds to the $^3\text{MLCT}$ transition^[14]. Compared to its absorption spectrum, PL emission has a Stoke's shift of 33 nm.

2.2 Electrochemical properties and energy level of materials

Fig.3a shows CV and UV-Vis absorption band gap edge. The complex has two reversible anodic waves at 0.92 and 0.77 V corresponding to the oxidation and reduction potentials of Ir metal cationic site ($\text{Ir}^{\text{III}} \rightarrow \text{Ir}^{\text{IV}}$)^[15], respectively. No clear reduction peak can be observed. In order to compare energy levels of HOMO and LUMO at the same level, the potential utilized for HOMO calculation is determined from the intersection (marked in Fig.3a)^[16] of the tangents of the rising oxidation current and background current in the cyclic voltammogram. Based on the intersection, the oxidation potential of $(\text{BPPBI})_2\text{Ir}(\text{ECTFBD})$ is 0.70 V, so energy level of HOMO is -5.10 eV [$-(0.70+4.40)=-5.10$]. The band gap between LUMO and HOMO, determined by UV-Vis absorption band gap edge, reveals as 3.00 eV (Fig.3a), so LUMO energy level of the Ir-complex is -2.10 eV . However, the higher LUMO energy level of -2.10 eV is disadvantage for electron transportation in the device. Fig.3b gives schematically estimated energy levels for the materials^[17-18] used in the OLEDs. The LUMO energy level of this Ir-complex is higher than that of CBP host material, so electron transportation is blocked in the Ir-complex region, resulting in a less electron-hole recombination on this Ir-complex. In contrast, more electron-hole recombination occurs on the CBP host material due to its lower LUMO energy level compared with $(\text{BPPBI})_2\text{Ir}(\text{ECTFBD})$. The required energy for the complex electroluminescence comes from the direct trapping of electron-hole on itself and CBP host material via Frster energy transfer. The electron-hole recombination is poor on the Ir-complex and the energy transferred from CBP to the Ir-complex is not efficient (Fig.4), therefore, light-emitting efficiency of

this Ir-complex-based device is moderate compared with some other iridium complex-based electroluminescent devices. The peak values of current and power efficiency for the devices are $5.2 \text{ cd} \cdot \text{A}^{-1}$ and $4.0 \text{ lm} \cdot \text{W}^{-1}$, respectively. *N*-ethyl carbazole moiety incorporated into the β -diketone ligand indeed causes a higher HOMO energy level of -5.1 eV , which is beneficial to hole transportation.

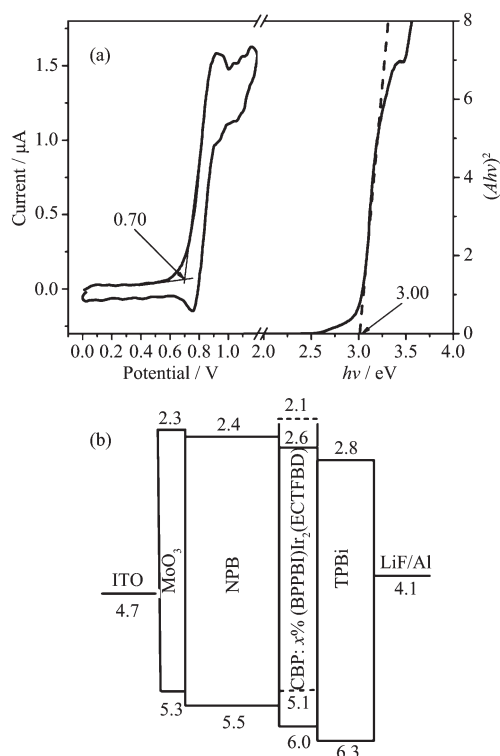


Fig.3 (a) Cyclic voltammogram and UV-Vis absorption band gap edge of $(\text{BPPBI})_2\text{Ir}(\text{ECTFBD})$ in CH_2Cl_2 , (b) An estimated energy level diagram for the materials used in the devices

2.3 Performance of devices

2.3.1 Electroluminescence spectra

Using bias voltage from 1 to 11 V towards the electroluminescent devices, intense electroluminescence (EL) can be observed at approximately 595 nm (Fig.4) from the iridium complex-doped CBP emissive layers at two doping levels of 4% and 7% by weight which corresponds to the transition of $^3\text{MLCT}^{[14]}$. Compared to PL spectrum of the Ir-complex dissolved in dichloromethane, EL spectra of thin solid film show a large red-shift of 103 nm with respect to the two most intense peaks. This is due to the stacking of $(\text{BPPBI})_2\text{Ir}$

(ECTFBD) molecules in the solid state leading to a closer distance among the molecules than those dissolved in CH_2Cl_2 , so $^3\pi-\pi^*$ energy level is lowered in the solid film. In addition, these Ir-complex molecules probably adopted a H aggregation mode, which leads to a red-shift for EL spectra comparing with the PL spectrum of this Ir-complex in $\text{CH}_2\text{Cl}_2^{[19]}$. Some shoulder peaks appear at about 555 nm in the left of the intense peaks from the transition of $^3\text{MLCT}$, which is generated by the perturbing of the $^3\pi-\pi^*$ excited state^[20]. In addition, there are some obvious emissions at 450 nm, which are the electroluminescence of CBP host material, and the emission intensity increases with voltage increasing, which clearly indicates that energy transferred from CBP to the complex is not sufficient. Therefore, the light-emitting efficiencies of the devices are not high. Characteristics of EL spectra for these devices at the two doping concentration levels are almost identical. The Commission Internationale de L'Eclairage (CIE) coordinate is (0.56, 0.38) at a bias voltage of 8 V at doping concentration of 7wt% by cutting the emission from the host material, which corresponds to deep yellow color.

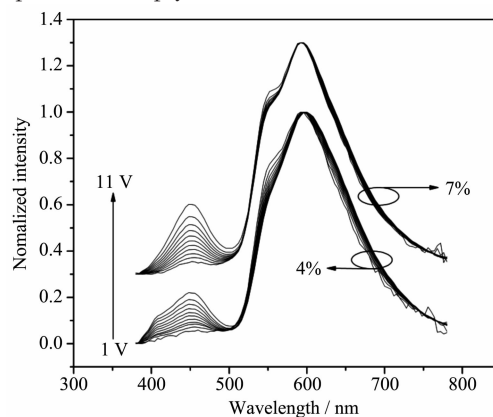


Fig.4 Electroluminescence spectra for $(\text{BPPBI})_2\text{Ir}(\text{ECTFBD})$ -doped CBP light-emitting layers at 4 and 7wt% doping concentration. Bias voltage from 1 to 11 V

2.3.2 Light-emitting efficiency and brightness

Fig.5a presents the curves of current efficiency and power efficiency vs current density of $(\text{BPPBI})_2\text{Ir}(\text{ECTFBD})$ -doped OLEDs at 4wt% and 7wt% doping concentration. The device at 7wt% doping concentration gives a maximum current efficiency of $5.2 \text{ cd} \cdot \text{A}^{-1}$

corresponding to a power efficiency of $4.0 \text{ lm} \cdot \text{W}^{-1}$ at a current density of $0.02 \text{ mA} \cdot \text{cm}^{-2}$. When the current density increases to $10.0 \text{ mA} \cdot \text{cm}^{-2}$, current efficiency decreases to $3.2 \text{ cd} \cdot \text{A}^{-1}$ with a loss of 38.5% attributed to the increasing triplet-triplet annihilation of the phosphorescence-related excitons and field-induced quenching effect^[21-22]. When the doping concentration reduces to 4wt%, the maximum current efficiency and power efficiency became lower correspondingly. With the decrease of doping concentration, the device performance decreases simultaneously, this suggests that the energy transfer mechanism from the host material to the guest material is predominately Förster energy transfer because the Ir-complex obtains energy from CBP. The device at 4wt% doping concentration demonstrates a maximum current efficiency of $4.1 \text{ cd} \cdot \text{A}^{-1}$ corresponding to a power efficiency of $3.0 \text{ lm} \cdot \text{W}^{-1}$ at a current density of $0.03 \text{ mA} \cdot \text{cm}^{-2}$. Fig.5b shows the current density and brightness vs voltage characteristics for the (BPPBI)₂Ir (ECTFBD)-doped CBP devices at 4wt% and 7wt% doping concentration. A maximum brightness of $8\,690 \text{ cd} \cdot \text{m}^{-2}$ is achieved at a bias voltage

of 17.1 V for the device of 7wt% doping concentration, corresponding to a current efficiency of $1.6 \text{ cd} \cdot \text{A}^{-1}$. The turn-on voltage is 4.3 V for the device with 7wt% doping concentration. The device with 4wt% doping concentration displays a maximum luminance of $6\,131 \text{ cd} \cdot \text{m}^{-2}$ at a voltage of 16.7 V. In order to improve emissive efficiencies, further optimization of device by utilizing new host material is in progress.

3 Conclusions

In summary, a novel Ir-complex containing carrier transport moieties was synthesized. (BPPBI)₂Ir (ECTFBD)-based devices exhibit a deep yellow emission. For the device based on (BPPBI)₂Ir(ECTFBD)-doped CBP as light-emitting layer at 7wt% doping level, a maximum current efficiency of $5.2 \text{ cd} \cdot \text{A}^{-1}$ and a maximum luminance of $8\,690 \text{ cd} \cdot \text{m}^{-2}$ were achieved. The moderate light-emitting efficiencies of the devices are attributed to the inadequate energy transfer from host material to guest material and the higher LUMO energy level of Ir-complex.

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References:

- [1] Baldo M A, Lamansky S, Burrows P E, et al. *Appl. Phys. Lett.*, **1999**,**75**(1):4-6
- [2] LI Chun-Xiang (李春香), HU Jia-Wei(胡嘉伟), SUN Pei-Pei (孙培培), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2007**,**23**(3):392-396
- [3] MEI Qun-Bo (梅群波), ZHANG Qian-Feng(张千峰), TONG Bi-Hai (童碧海). *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2009**,**25**(2):264-270
- [4] Yu X M, Kwok H S, Wong W Y, et al. *Chem. Mater.*, **2006**,**18**(21):5097-5103
- [5] He Z, Wong W Y, Yu X M, et al. *Inorg. Chem.*, **2006**,**45**(26): 10922-10937
- [6] Li Y Q, Rizzo A, Salerno M, et al. *Appl. Phys. Lett.*, **2006**,**89**(6):61125-61127
- [7] Fang Y, Hu S J, Meng Y Z, et al. *Inorg. Chim. Acta*, **2009**,**362**(14):4985-4990

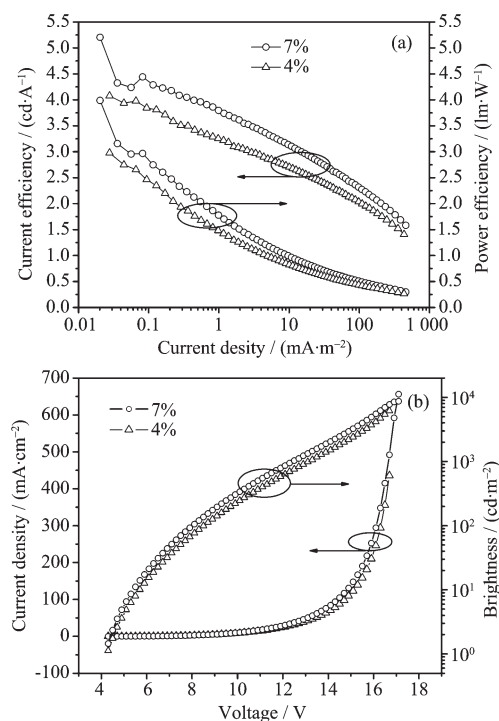


Fig.5 (a) Current efficiency and power efficiency vs current density, (b) Current density and brightness vs voltage based on the devices at 4 and 7wt% doping concentrations

- [8] ZHANG Chun-Lin(张春林), ZHANG Yu-Xiang(张玉祥), HU Ling-Feng(胡灵峰), et al. *Chinese J. Org. Chem. (Youji Huaxue)*, 2010, 30(9):1354-1357
- [9] WU Zhong-Lian(吴忠联), LUO Cui-Ping(罗翠萍), HU Zheng-Yong(胡峥勇), et al. *Chin. Phys. Lett. (Zhongguo Wuli Kuaibao)*, **2006**, **23**(11):3091-3093
- [10] ZHU Mei-Xiang(朱美香), WU Zhong-Lian(吴忠联), JIANG Chang-Yun(蒋昌云), et al. *Chin. Phys. Lett. (Zhongguo Wuli Kuaibao)*, **2005**, **22**(7):1793-1796
- [11] Fang Y, Tong B H, Hu S J, et al. *Org. Electr.*, **2009**, **10**(4): 618-622
- [12] Wang H H, He P, Liu S G, et al. *Inorg. Chem. Commun.*, **2010**, **13**(1):145-148
- [13] He P, Wang H H, Liu S G, et al. *J. Electr. Soc.*, **2009**, **156**(2): E46-E49
- [14] Xie H Z, Liu M W, Wang O Y. et al. *Adv. Mater.*, **2001**, **13**(16):1245-1248
- [15] Nazeeruddin M K, Weh R T, Zhou Z, et al. *Inorg. Chem.*, **2006**, **45**(23):9245-9250
- [16] Li Y F, Cao Y, Gao J, et al. *Synth. Met.*, **1999**, **99**(3):243-248
- [17] Tao Y T, Wang Q, Yang C L, et al. *Adv. Funct. Mater.*, **2010**, **20**:2923-2929
- [18] Cocchi M, Virgili D, Fattori V. *Appl. Phys. Lett.*, **2007**, **90**(2): 023506
- [19] HAN Kui(韩奎), LI Hai-Peng(李海鹏), WU Yu-Xi(吴玉喜), et al. *Acta Phys. Sin. (Wuli Xuebao)*, **2005**, **54**(12):5778-5783
- [20] Liu J, Yang C J, Cao Q Y, et al. *Inorg. Chim. Acta*, **2009**, **362**(2):575-579
- [21] Baldo M A, Adachi C, Forrest S R. *Phys. Rev. B*, **2000**, **62**(16):10967-10977
- [22] Kalinowski J, Stampor W, Mezyk J, et al. *Phys. Rev. B*, **2002**, **66**(23):235321-235336