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Charge Carrier Transport in Neat Thin Films of Phosphorescent Iridium Complexes

Noriyuki MATSUSUE, Yuichiro SUZUKI and Hiroyoshi NAITO

Department of Physics and Electronics, Osaka Prefecture University, Gakuen-cho, Sakai, Osaka 599-8531, Japan

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The charge carrier transport properties of neat thin films of red-, green- and blue-phosphorescence Ir complexes have been investigated in terms of time-of-flight transient photocurrent measurement. Bis(2-(2'-benzo[4,5-a]thienyl)pyridinato-*N,C*^{3'})iridium(acetylacetonate) (btp₂Ir(acac)) (red-phosphorescence emitter) and iridium(III) bis[(4,6-di-fluorophenyl)-pyridinato-*N,C*^{2'}]picolinate (Flrpic) (blue-phosphorescence emitter) thin films exhibit bipolar charge transport. In contrast, the electron and hole transit signals of *fac*-tris(2-phenylpyridine)iridium(III) (Ir(ppy)₃) (green-phosphorescence emitter) thin films are unobservable. The charge carrier transport properties of thin films of an Ir-complex-doped 4,4'-*N,N'*-dicarbazole-biphenyl (CBP) and the appropriateness of Flrpic as a triplet-exciton and hole blocking layer are shown.

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KEYWORDS: iridium complexes, charge carrier transport, phosphorescence, OLED

1. Introduction

Highly efficient organic light-emitting diodes (OLEDs) using an iridium-based electrophosphorescent material as a dopant have been demonstrated.^{1,2)} In iridium complexes such as *fac*-tris(2-phenylpyridine)iridium(III) (Ir(ppy)₃), the strong spin-orbit coupling of the heavy atom allows efficient intersystem crossing between singlet and triplet states, which leads to a high quantum yield.

Recently, it has been demonstrated that a high quantum efficiency can be achieved in phosphorescent OLEDs using a charge and triplet exciton blocking layer (BL) of the neat layer of Ir complexes.³⁾ Admovich *et al.* have obtained highly efficient green- and blue-phosphorescence OLEDs with a structure of indium-tin oxide (ITO)-precoated glass substrate/hole transport layer (HTL)/Ir-complex-doped 4,4'-*N,N'*-dicarbazole-biphenyl (CBP) emitting layer (EML)/iridium(III) bis[(4,6-di-fluorophenyl)-pyridinato-*N,C*^{2'}]picolinate (Flrpic) BL/electron transport layer (ETL)/cathode. In this structure, Flrpic acts as a hole and triplet-exciton BL, which blocks the injection of holes and triplet excitons in EML to ETL because Flrpic has a high triplet energy and deep highest occupied molecular orbital (HOMO) level. In addition, *fac*-tris(1-phenylpyrazolato-*N,C*^{2'})iridium(III) (Ir(ppz)₃) has been used as an efficient triplet-exciton and electron BL, which is inserted between HTL and EML.³⁻⁵⁾ Therefore, information concerning the charge carrier transport in BLs (neat thin films of Ir complexes) is important to gain insight into the charge carrier injection from a charge transport layer to EML. For instance, the observation of electron transport in Flrpic BL is required, for the electron injection from ETL to EML in the device structure mentioned above.

The driving voltage of the phosphorescent OLEDs decreases with increasing doping concentration of Ir complexes in charge transporting matrices.⁶⁻⁸⁾ The decrease in the driving voltage and the understanding of its origin are of practical importance. Therefore charge carrier transport measurements in neat thin films of Ir complexes as well as in Ir-complex-doped CBP thin films are necessary.

In this study, we report the charge carrier transport properties of btp₂Ir(acac), Ir(ppy)₃ and Flrpic neat thin films

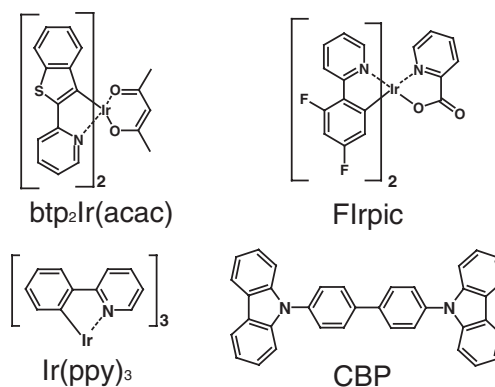


Fig. 1. Chemical structures of btp₂Ir(acac), Ir(ppy)₃, Flrpic and CBP.

studied by time-of-flight (TOF) transient photocurrent measurements. We also report the charge carrier transport properties of btp₂Ir(acac)-, Ir(ppy)₃- and Flrpic-doped CBP thin films.

2. Experiment

The chemical structures of three Ir complexes and CBP are shown in Fig. 1. For TOF measurements, neat phosphorescent thin films were prepared via thermal deposition at $\sim 1 \times 10^{-5}$ Pa onto ITO-precoated glass substrates. The thickness of the deposited Ir complex neat thin films was $\sim 1 \mu\text{m}$. Au semitransparent electrodes of 80 nm thickness were vapor-deposited through a shadow mask onto the film surfaces. The TOF samples, having a structure of ITO/Ir complex neat film/Au, were fabricated without breaking vacuum. Subsequently, the samples were encapsulated using a glass lid and ultraviolet-light-cured epoxy in a N₂-filled glovebox. Thin-film samples of Ir-complex-doped CBP prepared by codeposition⁹⁾ were fabricated in the same manner. In the TOF measurements,¹⁰⁾ the photoexcitation was carried out through a semitransparent Au electrode using a nitrogen pulse laser ($\lambda_{\text{ex}} = 337 \text{ nm}$). By choosing the polarity of the electric field applied to the samples, electron and hole transports can be studied separately. The current passing through the samples was monitored with a digital oscilloscope. At the excitation wavelength, the absorption

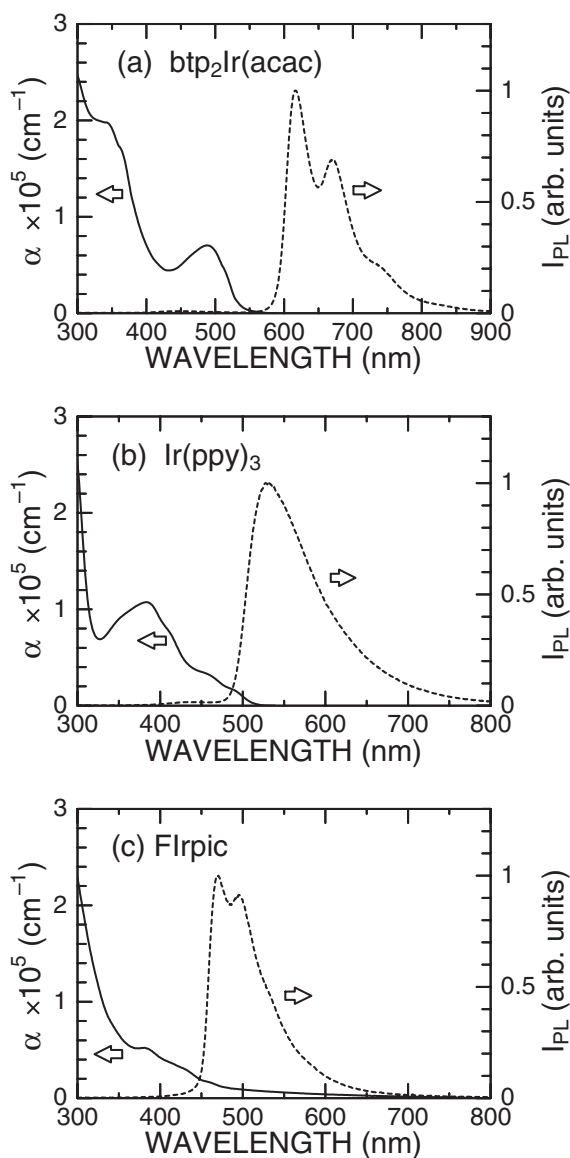


Fig. 2. Optical absorption and photoluminescence (I_{PL}) spectra of $\text{btp}_2\text{Ir(acac)}$ (a), Ir(ppy)_3 (b) and Flrpic (c) neat thin films at 300 K.

coefficients, α , of $\text{btp}_2\text{Ir(acac)}$, Ir(ppy)_3 and Flrpic thin films are 2.0×10^5 , 0.76×10^5 and $0.84 \times 10^5 \text{ cm}^{-1}$, respectively, as seen in Fig. 2, which result in the shallow penetration depth of the excitation light and hence the thin sheet of charge carriers in the TOF experiment was generated beneath the illuminated electrode.¹¹⁾ In Fig. 2, the photoluminescence spectra of the red-, green- and blue-phosphorescence Ir complexes are also shown.

3. Results and Discussion

Figures 3 and 4 show the hole and electron TOF transients of $\text{btp}_2\text{Ir(acac)}$, Ir(ppy)_3 and Flrpic neat thin films at $E = 2.8 \times 10^5 \text{ V/cm}$ and 300 K. The shapes of the TOF transient photocurrents of $\text{btp}_2\text{Ir(acac)}$ and Flrpic neat thin films show dispersive transport. A distinct change in slopes is found in the double logarithmic plot of both hole and electron TOF transients of $\text{btp}_2\text{Ir(acac)}$ as shown in Figs. 3(a) and 4(a), respectively. This indicates that $\text{btp}_2\text{Ir(acac)}$ is a bipolar transport material. The transit time of charge carriers is identified as the inflection point in the

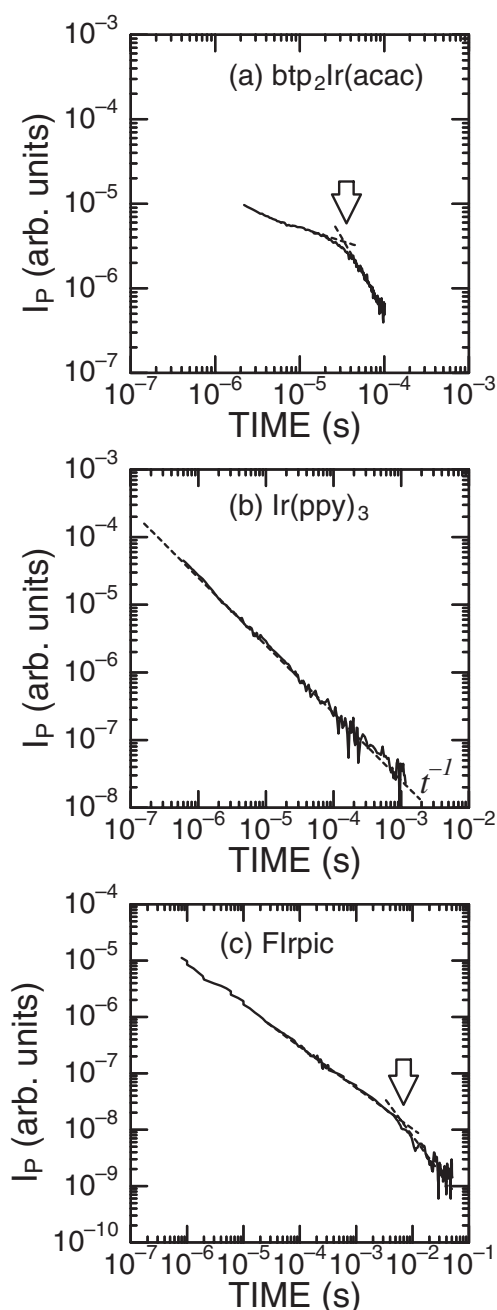


Fig. 3. Double logarithmic plots of hole TOF transients in $\text{btp}_2\text{Ir(acac)}$ (a), Ir(ppy)_3 (b) and Flrpic (c) neat thin films at $2.8 \times 10^5 \text{ V/cm}$ and 300 K. The transit times are marked by the arrows.

double logarithmic plots of the TOF transients (the transit times are marked by arrows). The drift mobility is calculated as $\mu = L/t_r E$, where μ is the drift mobility, L is the film thickness, E is the external electric field, and t_r is the transit time of carriers. The hole and electron drift mobilities of $\text{btp}_2\text{Ir(acac)}$ are 2.9×10^{-4} and $2.4 \times 10^{-5} \text{ cm}^2/\text{V s}$, respectively, at $2.8 \times 10^5 \text{ V/cm}$ and 300 K.

The hole and electron TOF signals of Flrpic neat thin films are more dispersive than those of $\text{btp}_2\text{Ir(acac)}$, but the transit times can be determined from the double logarithmic plots of photocurrent vs time. On the other hand, in Ir(ppy)_3 neat thin films, the TOF transit time cannot be identified. Both hole and electron TOF photocurrents of Ir(ppy)_3 neat thin films decay as t^{-1} and their magnitude are almost the same [Figs. 3(b) and 4(b)]. Thus, the photocurrent decay in

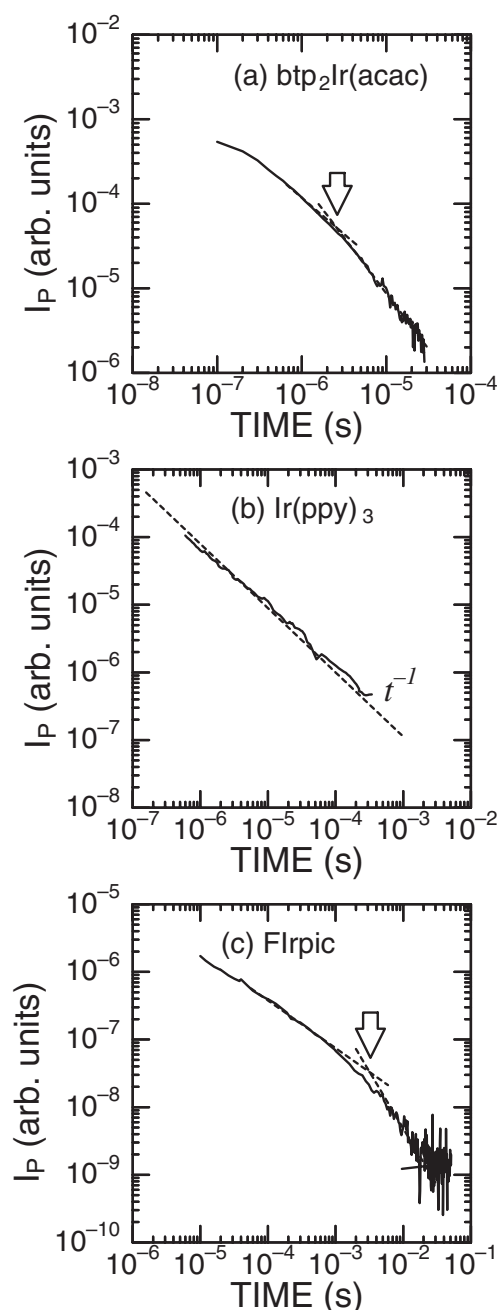


Fig. 4. Double logarithmic plots of electron TOF transients in $\text{btp}_2\text{Ir}(\text{acac})$ (a), $\text{Ir}(\text{ppy})_3$ (b) and FIrpic (c) neat thin films at $2.8 \times 10^5 \text{ V/cm}$ and 300 K. The transit times are marked by the arrows.

Figs. 3(b) and 4(b) of $\text{Ir}(\text{ppy})_3$ neat thin films is likely to be due to the bimolecular recombination within the photo-generation zone beneath the illuminated electrode because both electrons and holes in $\text{Ir}(\text{ppy})_3$ are almost immobile. These results are consistent with those reported in the literature; the low value of the incident photon-to-current efficiency in $\text{Ir}(\text{ppy})_3$ single-layer photovoltaic devices, due to the low mobility of $\text{Ir}(\text{ppy})_3$, has been reported.¹²⁾

The electric-field dependences of the hole and electron drift mobilities of CBP, $\text{btp}_2\text{Ir}(\text{acac})$ and FIrpic are plotted in Fig. 5. All the materials exhibit bipolar transport. The electron drift mobility of FIrpic neat thin films is on the order of $10^{-6} \text{ cm}^2/\text{Vs}$, which is almost the same as that of tris(8-hydroxy-quinoline)aluminum (Alq_3) (Alq_3 is a well known electron transport material^{13–15)}). In addition, elec-

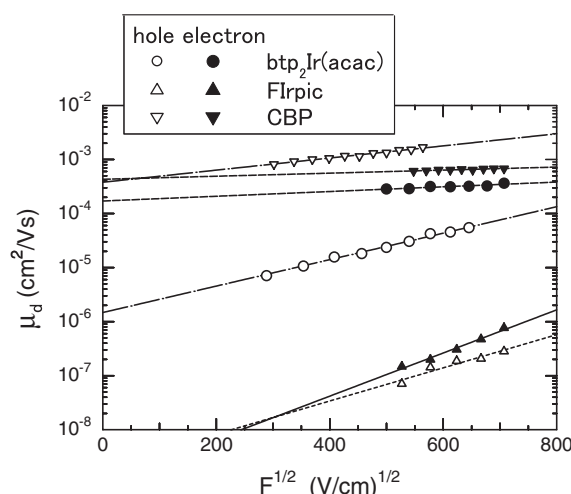


Fig. 5. Dependence of the hole and electron drift mobilities of CBP, FIrpic and $\text{btp}_2\text{Ir}(\text{acac})$ neat thin films on the square root of electric field at 300 K.

trons can be injected from ETL to EML, where FIrpic BL is inserted between ETL and EML because the difference in the energy level of lowest unoccupied molecular orbitals (LUMOs) between FIrpic (2.9 eV) and Alq_3 (3.0 eV),³⁾ a representative material for ETL, is relatively small. Hence, we conclude that FIrpic thin films are suitable for a triplet-exciton and hole BL.

The electron drift mobilities of $\text{btp}_2\text{Ir}(\text{acac})$ show weak field dependence and are on the order of $10^{-4} \text{ cm}^2/\text{Vs}$ in the range of 2.8×10^5 to $5.0 \times 10^5 \text{ V/cm}$ at 300 K (the electron drift mobilities of $\text{btp}_2\text{Ir}(\text{acac})$ are approximately two orders of magnitude higher than those of FIrpic). The drift mobilities of electron transporting materials such as oxadiazole derivatives,¹⁶⁾ starburst phenylquinoxalines,¹⁷⁾ and phenanthroline derivatives,¹⁸⁾ range from 10^{-5} to $10^{-4} \text{ cm}^2/\text{Vs}$. In comparison with these materials, $\text{btp}_2\text{Ir}(\text{acac})$ has a relatively high electron drift mobility.

The concentration dependences of the electron and hole drift mobilities of Ir-complex-doped CBP thin films are shown in Fig. 6 (the hole transport in $\text{btp}_2\text{Ir}(\text{acac})$ -doped CBP and in $\text{Ir}(\text{ppy})_3$ -doped CBP thin films and the electron transport in FIrpic -doped CBP thin films have not been observed). As shown in Fig. 6, the three Ir complex-doped CBP thin films exhibit unipolar transport. This can be understood from the difference in HOMO or LUMO level between an Ir complex and CBP. For instance, in $\text{Ir}(\text{ppy})_3$ -doped CBP thin films, electrons generated on $\text{Ir}(\text{ppy})_3$ sites can be injected to the LUMO level of CBP because the difference in LUMO level between $\text{Ir}(\text{ppy})_3$ (3.0 eV) and CBP (2.9 eV) is relatively small.⁹⁾ On the other hand, holes on $\text{Ir}(\text{ppy})_3$ sites cannot be injected into the HOMO level of CBP because of the large energy difference in HOMO level between $\text{Ir}(\text{ppy})_3$ (5.4 eV) and CBP (6.0 eV).⁹⁾ A similar interpretation is applicable to the understanding of the unipolar transport in FIrpic -doped CBP and in $\text{btp}_2\text{Ir}(\text{acac})$ -doped CBP thin films [FIrpic (LUMO: 3.3 eV, HOMO: 6.0 eV), $\text{btp}_2\text{Ir}(\text{acac})$ (LUMO: 3.2 eV, HOMO: 5.1 eV)].

The photocurrent transients of the three Ir complex-doped CBP thin films whose drift mobilities are shown in Fig. 6 are dispersive, and become more dispersive with increasing Ir

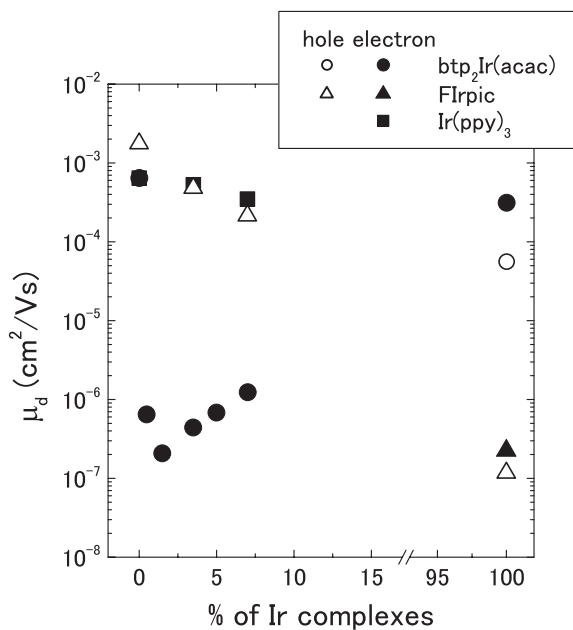


Fig. 6. Btp₂Ir(acac), Ir(ppy)₃ and Flrpic concentration dependences of electron (open symbols) and hole (solid symbols) mobilities in a CBP host matrix at 3.6×10^5 V/cm and 300 K. The electron and hole mobilities of neat thin films of btp₂Ir(acac) and Flrpic are also shown.

complex concentration. In Flrpic- or Ir(ppy)₃-doped CBP thin films, the charge carrier mobilities are slightly decreased with increasing concentration of Ir complex.⁹⁾ The concentration dependences of the drift mobility and the dispersion are caused by the increase in the extent of energetic disorder, which is attributable to dipolar disorder due to the interaction between charge carriers and randomly oriented permanent dipoles of the dopants.^{9,19)} In contrast, the addition of btp₂Ir(acac) (< 1.5% btp₂Ir(acac)) rapidly decreases the electron drift mobility by approximately three orders of magnitude. The rapid decrease has the same origin as the decrease in the drift mobilities of Ir(ppy)₃ and Flrpic, and we speculate that the rapid decrease is due to the permanent dipole of btp₂Ir(acac) being larger than those of Ir(ppy)₃ and Flrpic. The further addition of btp₂Ir(acac) (> 1.5%) causes an increase in the electron drift mobility in btp₂Ir(acac)-doped CBP thin films. This is due to the electron hopping transport between btp₂Ir(acac) molecules because of the relatively high electron drift mobilities of btp₂Ir(acac) neat thin films, which are close to those of CBP thin films, as shown in Fig. 5.

4. Conclusions

We have studied the charge carrier mobilities of neat thin films of Ir complexes (btp₂Ir(acac), Ir(ppy)₃ and Flrpic), which are widely used as red-, green- and blue-phosphorescence dopants in OLEDs by TOF transient photocurrent measurements. We find that the hole and electron drift

mobilities of btp₂Ir(acac) are 3.2×10^{-4} and 5.5×10^{-5} cm²/V s, respectively, at 4.2×10^5 V/cm and 300 K. In btp₂Ir(acac)-doped CBP thin films, the electron drift mobility rapidly decreases with doping concentration of < 1.5% and increases by further addition of btp₂Ir(acac) to CBP. The increase in electron drift mobility is due to the electron hopping between btp₂Ir(acac) molecules. We observe the bipolar charge carrier transport of Flrpic thin films as well. The electron drift mobility of Flrpic neat thin films is in the order of 10^{-6} cm²/V s, which is almost the same as that of Alq₃. Because of the relatively high electron drift mobility and low injection barrier of electrons from ETL, Flrpic is appropriate for a triplet-exciton and hole BL. On the other hand, the electron and hole transit signals of Ir(ppy)₃ thin films are unobservable. Unlike btp₂Ir(acac), the additions of Flrpic and Ir(ppy)₃ to CBP slightly and continuously decrease hole and electron drift mobilities, respectively.

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