

Hole mobility and conductance of iridium complex doped NPB emission layers for organic light-emitting diodes

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ABSTRACT

Iridium complexes are widely used in dye phosphorescent guest-host systems which usually as emission layer of efficient organic light-emitting diodes. Phosphorescent organic light-emitting diodes (OLEDs) with tris(2-phenylpyridine) iridium [Ir(ppy)₃] as emissive dopant exhibited high internal quantum efficiency. N, N-diphenyl-N, N-bis(1-naphthylphenyl)-1,1-biphenyl-4,4-diamine (NPB) is a good candidate of host for guest–host system in OLEDs. It is significant that understanding and engineering of charge transport in Ir(ppy)₃ doped NPB films to design and optimize OLEDs, even organic lasers. In this paper, hole mobility and conductance of Ir(ppy)₃ doped NPB films were investigated by admittance spectroscopy. The results show that for a given applied voltage, with the doping concentration increasing, the conductance first increase reaching a maximum then decrease, which indicate that light doping of NPB with Ir(ppy)₃ weakly improves, while heavy doping deteriorates the conductivity. We found that light doping of NPB with Ir(ppy)₃ almost do not alter the hole mobility, which coincides with the previous theory. It is concluded that for films thinner than 300 nm, the electric field dependence of hole mobility is negative, that is, the mobility decrease, rather than increase, near exponentially with the square root of the electric field.

1. Introduction

Phosphorescent dye based guest-host systems are widely used for the emission layer of efficient organic light-emitting diodes [1–3] and organic laser diodes [4,5]. Due to strong spin-orbital coupling, iridium complexes have excellent phosphorescent properties. Phosphorescent OLEDs with tris(2-phenylpyridine)iridium [Ir(ppy)₃] as emissive dopant exhibit internal quantum efficiency as large as 100% [6]. Abundant research results for Ir(ppy)₃ are reported [7–15]. As a wide band gap high mobility hole transport organic semiconductor, except serving as hole transport layer, N,N-diphenyl-N,N-bis(1-naphthylphenyl)-1,1-biphenyl-4,4-diamine (NPB) is also a good candidate of host for guest–host emitting layers in OLEDs [16,17]. In the fact, OLEDs with NPB as the host and perylene [18], Eu complex [19], bis(1-phenylisoquinolinato-N,C2') iridium(acetylacetonate) [Ir(piq)₂(acac)] [20] and rubrene [21] as the dopant have been reported.

Realizing balanced electron and hole transport is the key for achieving high performance for OLEDs. The typical structure of OLEDs consists of hole transport layer (HTL), emission layer (EML) and

electron transport layer (ETL). For designing a high performance OLED, it is desired that the transport properties of all the function layers are ready for use. As the properties of commonly used HTL and ETL materials are well studied, therefore, thorough investigation of the transport properties of doped EML is of great important. As NPB: Ir(ppy)₃ thin film is expected to be p-type, therefore hole transport plays a more important role than that of electron. For measurement of carrier mobility, a variety of methods have been developed, such as time of flight (TOF), space-charge limited current conduction [22,23], and admittance spectroscopy (AS). Among the diverse methods, AS method has demonstrated to be suitable for both thick and thin films. As most organic films in the devices nowadays are in nanometer scale, so the AS method becomes a powerful tool for studying transport properties of organic thin films. Form the measured Capacitance-frequency(C-f) data, the negative differential susceptance, $-\Delta B = -\omega(C - C_{geo})$, is calculated. C_{geo} is the geometric capacitance calculated from $C_{geo} = \epsilon_0 \epsilon_r A/d$, where ϵ_0 and ϵ_r are the absolute dielectric constant of vacuum and the relative dielectric constant of NPB, respectively, A is the area of the electrode, and d is the thickness of the organic film. $-\Delta B \sim f$ curve generally yields

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a maximum at a distinct frequency f_r , which is called characteristic frequency. The mobility can be calculated directly by determining f_r from $-\Delta B$ vs. f plot: [24,25].

$$\mu = \frac{d^2}{0.56(V - V_{bi})f_r} \quad (1)$$

where d is the thickness of organic layer. A verity of theoretical works was conducted in order that AS method can be applicable for devices with large contact resistance [26]. Ir(ppy)₃ doped NPB film are frequently used as emitting layer in green and white light OLEDs. In this paper, we investigate on the hole transport properties of Ir(ppy)₃ doped NPB films by using AS method.

2. Experimental

The organic semiconductor materials in powder were purchased from Nichem. The hole-only devices samples for AS measurements have the structure of “ITO/MoO₃/NPB: Ir(ppy)₃/MoO₃/Al”. The bottom MoO₃ layer acts as the hole-injecting layer, which makes the contact of ITO/MoO₃/NPB: x wt.% Ir(ppy)₃ to be ohmic for holes to meet the requirement of AS measurements [27]. The top MoO₃ layer acts as the electron-blocking layer at positive bias to insure hole only transport in the device. For device fabrication, ITO-coated glass substrates with the sheet resistance of 10 Ω /sq were etched into strips of 4 mm wide and cleaned thoroughly using acetone, isopropyl alcohol, and de-ionized water in an ultrasonic bath followed by drying with nitrogen gas. Thereafter 5 nm MoO₃, and 100 nm NPB: Ir(ppy)₃ were thermally deposited sequentially under a vacuum of 5×10^{-4} Pa. The device was completed by thermal deposition of 120 nm Al layer using a shadow mask that define 4 mm wide strips that are perpendicular to the bottom ITO strips. The doping of Ir(ppy)₃ into NPB was carried out by co-evaporation. HP4192A LF Impedance Analyzer, Keithley 2400 Source Meter were used for the AS or current–voltage (IV) measurements.

3. Results and discussions

3.1. Conductance properties of green phosphorescent dye Ir(ppy)₃ doped NPB films

Fig. 1 shows the typical conductance–frequency dependencies for different voltage biases. It is interesting to note that the conductance–frequency curve has a plateau with a low frequency limit (LFL) conductance, G_{LFL} , at frequencies lower than a certain frequency f_{on} (inset of Fig. 1a), and both the length of the plateau, or f_{on} and G increase with the bias voltage. It is assumed that p-type doping give rise to charge transfer of electrons from the HOMO of the host to that of the dopant by thermal excitation, resulting in the formation of free holes [28,29]. The rapid increase of G_{LFL} with bias voltage implies that this kind of charge transfer may be also strongly electric field activated and contribute a lot

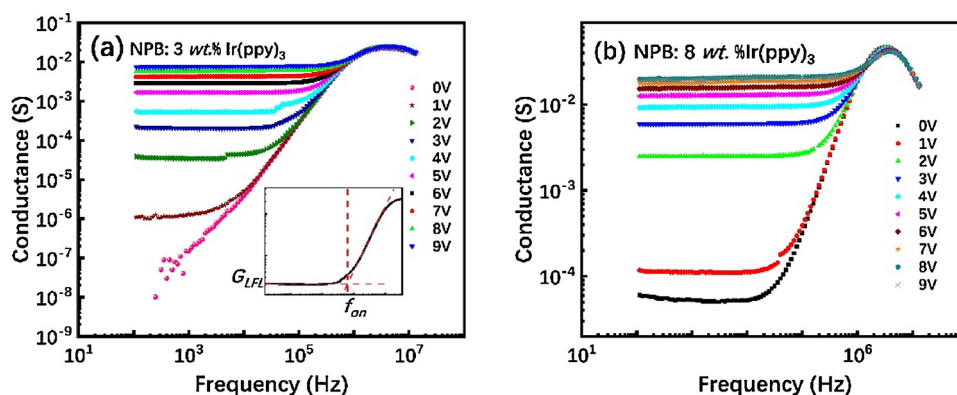


Fig. 1. Frequency dependent conductance for different bias voltages at doping concentration of 3.0 wt.% (a), and 8.0 wt.% (b).

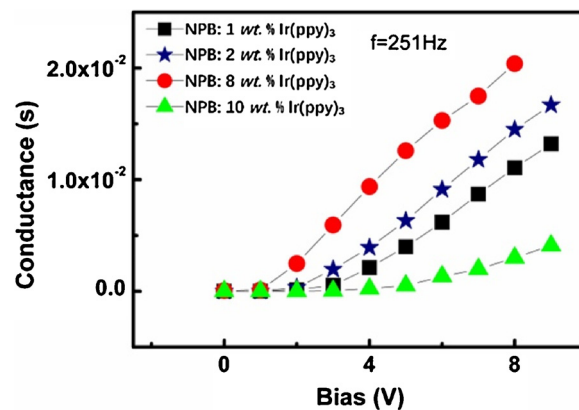


Fig. 2. The dependence of the conductance on the bias voltage for different doping concentrations at a low frequency of 251 Hz.

for free hole density increment in addition to the injection from the anode, especially in the case of light doping. A comparison of Fig. 1a and b reveals that the conductivity G_{LFL} at low voltage bias increases rapidly with doping concentration. At zero bias voltage, the conductivity of 3.0 wt.% doped sample is only $\sim 5 \times 10^{-8}$ S, while it is over 5×10^{-5} S in 8.0 wt.% doped sample, which is an increase of 3 order of magnitude. The appearance of f_{on} is the evidence that there exists a saturation velocity of charge carriers in the organic film, above f_{on} , the proportion of charge carriers that can catch up the change of alternating electric field decreases and finally becomes zero, which results in a constant capacitance and the decrease of the capacitance, and the increase of conductance.

Fig. 2 shows the typical voltage bias dependence of conductance at a low frequency of 251 Hz, for different doping concentrations. For doping concentration smaller than or equal to 8.0 wt.%, the conductance increases near linearly with the voltage bias above the turn-on voltage.

Fig. 3 shows the dependence of the conductance on the doping concentration for different bias voltages. It is seen that with doping concentration increasing, the conductance first increase, reaching a maximum at 8.0 wt.%, then decrease, which indicate that light doping of NPB with Ir(ppy)₃ weakly increases the conductivity, while heavy doping decreases the conductivity which may be due to increased trapping and scattering for hole transport [24]. The relations at other bias voltages are similar.

3.2. Capacitance-voltage-frequency characteristics

The C-V characteristics at low and high frequency are quite different for both cases of heavy and light doping. We pay attention at first for the case of heavy doping (10 wt.%) at low frequency (316 Hz). As

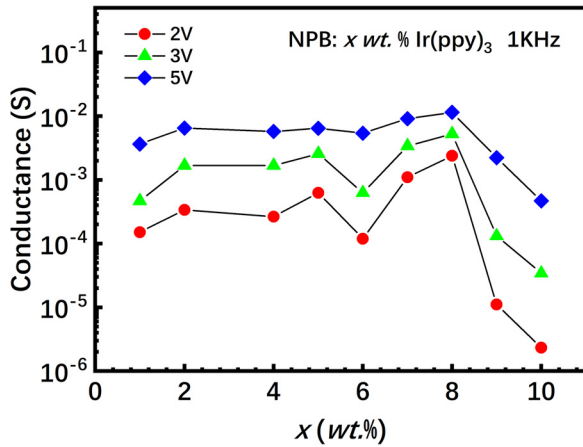


Fig. 3. The dependences of conductance on the doping concentration at bias voltages of 2 V, 3 V and 5 V.

shown in Fig. 4a, the C-V curve for this case can be divided into three regions, the neutral region ($V < V_0$), hole injection region ($V_0 < V < V_{max}$) and dual injection region ($V > V_{max}$). In the neutral region, the organic film is almost electrical neutral, there exists only small amount of charges near the anode/organic interface, and the capacitance is therefore low. In the hole injection region, large number of holes are injected into the organic from the anode, results in rapid increase of the capacitance; while when the voltage falls into the dual carrier injection region, large number of electrons are injected into the organic from the cathode, which recombine with holes, leading to the depletion of charges in the organic, which results in rapid decrease of the capacitance. However, at high frequencies the injected holes from the anode cannot catch up with the alternating electric field due to their low mobilities, therefore they do not contribute to the capacitance, which results in the decrease of capacitance with increasing voltage.

For the case of low doping concentrations, at high frequencies, the variation trend of the capacitance with the voltage bias is similar to that at high doping concentrations while it is quite different at low frequency (316 Hz). As shown in Fig. 5, with a light doping ratio of 2.0 wt. % and at low frequency of 316 Hz, the capacitance increases rapidly in the whole voltage range measured.

3.3. Hole mobility in Ir(ppy)₃ doped NPB film

For the determination of hole mobility, the negative differential susceptance spectrum $-\Delta B = -\omega(C - C_{geo})$ were obtained from the measured capacitance-frequency dependence, and the maximum position f_r was identified, from which the mobility was calculated according to Eq. (1). Fig. 6 shows the dependences of the hole mobility on the square root of the electric field. In contrary to the established experience, the

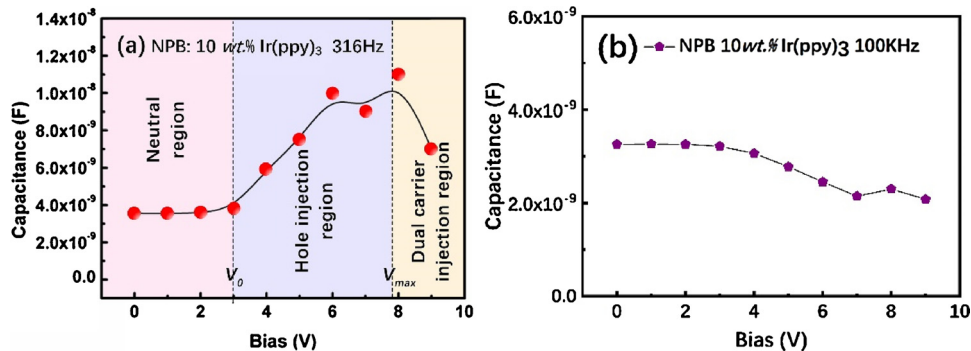


Fig. 4. Capacitance-voltage characteristic of NPB:Ir(ppy)₃ hole only device with a high doping concentration of 10 wt. % at a low frequency of 316 Hz (a) and a high frequency of 100 kHz (b).

mobility decrease, instead of increase, near exponentially with the square root of the electric field, which is similar to that observed in bis [2-(9,9-diethyl-9 H-fluoren-2-yl)-1-phenyl-1 Hbenzoimidazol-N,C3] iridium(acetylacetonate) [(fbi)₂Ir(acac)] doped thin NPB films [30]. For the doping concentrations in the range of 2.0~9.0 wt.%, the hole mobility decreased from around 10^{-4} to 10^{-5} cm²/Vs with the electric field increasing from 10^5 to 10^6 V/cm. Similar results were observed in pentacene doped distyrylbenzene (DSB) single crystal [23].

Arkhipov et al. studied the dependence of charge carrier mobility on doping concentration theoretically [31], their results showed that the mobility decreases at low electric fields, and increases at high electric fields with doping concentration. While at medium electric fields, the effect of doping on the mobility is small. Fig. 7 shows the typical dependence of hole mobility on doping concentration. It is seen that at doping concentrations less than 8.0 wt.%, the change of mobility with doping concentration is small, which coincide with the theory of Arkhipov et al. for the case of medium electric fields [31].

We have tried to determine the hole mobility of NPB:Ir(ppy)₃ thin film by using the well-known space charge limited (SCL) current method. The typical J-V curve for the device is presented in Fig. 8. The space charge limited current in organic thin film is generally described by following equation:

$$j_{SCL} = \frac{9}{8} \mu \epsilon_0 \epsilon_r \frac{V^2}{d^3} \quad (2)$$

where μ is the mobility of the carrier, ϵ_r is the relative dielectric constant and ϵ_0 is the vacuum dielectric constant. Using this equation, the mobility could be determined from measured J-V curve for the case that the mobility is electric field independent. However, for most organic films, the mobility is generally electric field (F) dependent, and is described by the equation $\mu = \mu_0 \exp(\beta \sqrt{F})$. Here μ_0 is the zero-field mobility, and β is a parameter for the electric field-dependence of mobility. In this case, Eq. (2) is replaced by Eq. (3) [32]:

$$j_{SCL} = \frac{9}{8} \mu_0 \epsilon_0 \epsilon_r e^{0.89\beta \sqrt{V/d}} \frac{V^2}{d^3} \quad (3)$$

In order to extract the parameter β of the field-dependent mobility, the measured J-V curve was fitted with Eq. (3). As shown in Fig. 8, the value of μ_0 and β were determined to be 4.0×10^{-3} cm²/Vs and -1.0×10^{-4} (V/cm)^{-1/2}, respectively. What important is that the value of β is negative, which is in reasonable good agreement with that measured with AS method.

4. Conclusion

In conclusion, hole mobility and conductance of Ir(ppy)₃ doped NPB films were systematically studied using AS method. At a given doping concentration, as the frequency increases, the conductance is kept unchanged at first, and then increases after reaching a turn-on frequency, and the turn-on frequency increases with the applied bias voltage. For

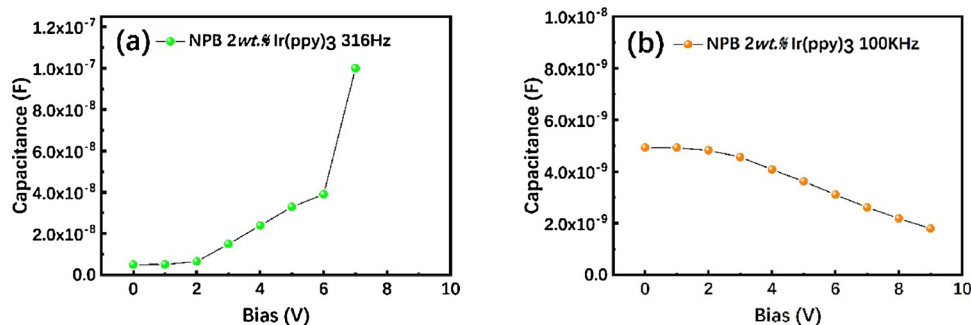


Fig. 5. Capacitance-voltage characteristic of NPB:Ir(ppy)₃ hole only device with a light doping concentration of 2.0 wt.% at a low frequency of 316 Hz (a) and a high frequency of 100 kHz (b).

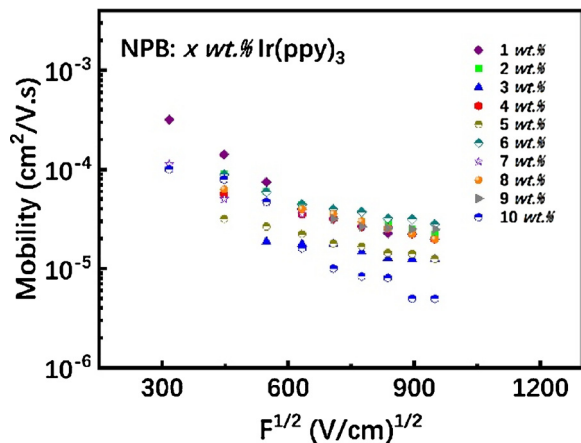


Fig. 6. Electric field dependence of hole mobility in NPB:Ir(ppy)₃ thin film for different doping concentrations.

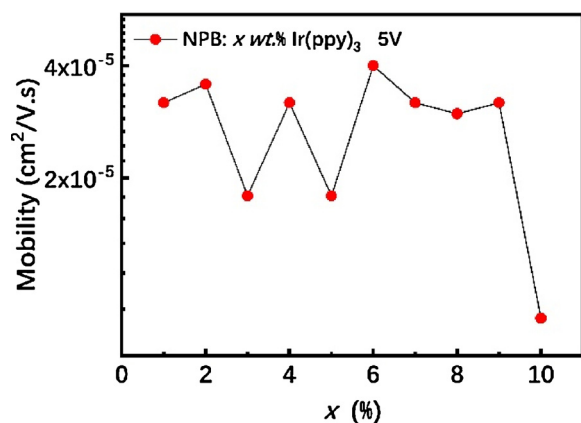


Fig. 7. The dependence of hole mobility on doping concentration in NPB:Ir(ppy)₃ thin film at bias voltage of 5 V.

doping concentration smaller than or equal to 8.0 wt.%, the conductance increase nearly linearly with the voltage bias above the turn-on voltage. For a given applied voltage, the conductance first increase, reaching a maximum at 8.0 wt.%, then decrease, which indicates that light doping of NPB with Ir(ppy)₃ weakly increases the conductivity, while heavy doping decreases the conductivity. Light doping of NPB with Ir(ppy)₃ almost do not alter the hole mobility, which coincides with the theory of Arkhipov et al. for the case of medium electric fields [31]. More importantly, we found that the electric field dependence of mobility is negative, that is, the mobility decrease, instead of increase, near exponentially with the square root of the electric field. For the doping concentrations in the range of 2.0–9.0 wt.%, the hole mobility

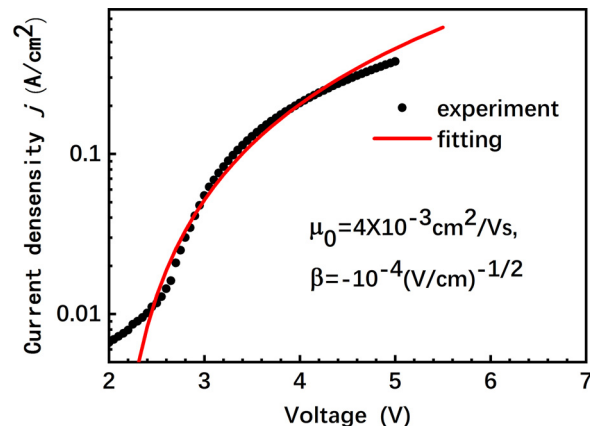


Fig. 8. Measured current-voltage characteristics of the device with a doping concentration of 8.0 wt.% (filled symbols) and the fitting with Eq. (3) (the solid line).

decreased from around 10^{-4} to $10^{-5} \text{ cm}^2/\text{Vs}$ with the electric field increasing from 10^5 to 10^6 V/cm . The mechanism underline the observed experimental dependences were analyzed.

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