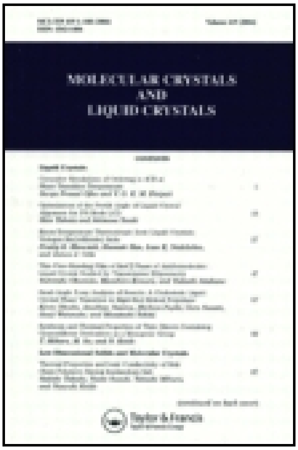

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CHARGE CARRIER MOBILITY IN VACUUM-SUBLIMED DYE FILMS FOR LIGHT-EMITTING DIODES STUDIED BY THE TIME-OF-FLIGHT TECHNIQUE

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CHARGE CARRIER MOBILITY IN VACUUM-SUBLIMED DYE FILMS FOR LIGHT-EMITTING DIODES STUDIED BY THE TIME-OF-FLIGHT TECHNIQUE

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The Charge carrier mobility has been examined for a representative organic hole transport material TPD and a host material CBP, doped with a fluorescent dye, rubrene and Ir(ppy)$_3$, by time-of-flight (TOF) technique. Decreasing of hole mobilities of the dye-doped films can be explained by a carrier-trapping model and the ionization potential difference of TPD and CBP. We successfully measured an electron mobility of the rubrene-doped TPD films, and Ir(ppy)$_3$-doped CBP films, while the mobility could not measured non-doped TPD and CBP films. The EL process of the dye-doped systems is discussed in terms of the electron transfer properties of emission layer.

Keywords: Ir(ppy)$_3$-doped CBP film; rubrene-doped TPD film; time-of-flight (TOF)

INTRODUCTION

Organic light-emitting devices (OLED) have attracted much interest due to potential application for high-performance flat-panel displays. The recent development of organic light-emitting diodes (OLED) has revealed that organic semiconductors have high potential for use as light emitting devices because of their high emission efficiency and various emission colors. One of the most significant improvements in OLED performances resulted from the doping of highly fluorescent molecules into emitter layers at a concentration of typically $1 \sim 5$ mol%. The addition of a small amount of dopant molecules such as quinacridone derivatives, rubrene, and perylene was shown to improve device performance markedly. In particular, rubrene

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*Corresponding author. Tel.: +81-92-583-7531, Fax: +81-92-575-2318, E-mail: tsuigz@mbox.nc.kyushu-u.ac.jp has been proved to be extremely stable in reduction and oxidation process in a cyclic voltammetry measurement [1]. This property directly assures that the radical species are stable in carrier transport process, both hole and electron transport, and contributes to the enhancement of the device stability. Recently, a very high quantum efficiency of electroluminescence (EL) in organic light-emitting devices using a triplet-emitter material tris(2-phenylpyridine) iridium [Ir(ppy)$_3$] has been reported [2,3]. It was revealed that the doping of the emitter layers with fluorescent molecules not only enhanced the electroluminescence (EL) quantum efficiency (ϕ_{EL}), but also considerably enhanced device durability, even though detailed underlying mechanism is still not clear.

Among many factors affecting EL device performance, charge carrier mobility is the most dominant factors relating to charge carrier balance of electron and holes within carrier recombination zone [4]. Thus carrier mobilities of organic materials are of keen interest for understanding the operating mechanism of organic electroluminescent (EL) devices [5]. In particular, we are interested in charge carrier mobility at the recombination zone consisted of host and guest molecules. In this study, we tried direct determination of hole and electron mobility for model systems for emission layers, rubrene-doped TPD, CBP films and Ir(ppy)$_3$-doped CBP films, using a conventional time-of-flight (TOF) technique.

EXPERIMENTAL

Figure 1 shows chemical structure of the compounds, a representative organic hole transport material, N,N′-diphenyl-N,N′-(3-methylphenyl)-(1,1′-biphenyl-4,4′-diamine) [TPD] and a host material for emissive layer, 4,4′-N,N′-dicarbazole-diphenyl [CBP], a fluorescent dopant, rubrene and phosphorescent dopant, *fac*-tris(2-phenylpyridine)iridium [Ir(ppy)$_3$]. CBP was synthesized by Copper-Catalyzed Ullmann reaction [6]. Rubrene was purchased from TCI Corp. The phosphorescent dopant, Ir(ppy)$_3$ was synthesized according to the literature [7].

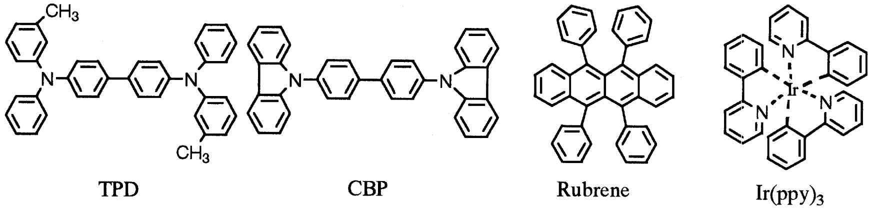

FIGURE 1 Chemical structure of the compounds discussed in this paper.

The mobility measurement were carried out by conventional time-of-flight technique using a nitrogen laser pulse ($\lambda = 337$ nm, 3 ns pulse width) [8]. Dye doped films were prepared by vapor co-deposition onto a glass substrate precoated with semitransparent aluminum (20 nm). The upper aluminum electrode (40 nm) was deposited on dye-doped films. Thickness of the dye-doped films were at the range of $3 \sim 5\,\mu$m, measured by a surface profiler Sloan Dektak3, and a sample area was $2 \times 2\,\text{mm}^2$. All measurements were performed at room temperature.

RESULTS AND DISCUSSION

A transient photocurrent for both 4 wt.% rubrene-doped TPD film of hole transport and 8 wt.% rubrene-doped TPD film for electron transport (inset) are shown in Figure 2. The photocurrent shapes of hole carrier transport showed a non-dispersive behavior with a clear plateau and subsequent drop. However, a cusp is observed in the electron transient (Fig. 2 inset). The cusp developed only in the case of electron transient independent of the amounts of transported charges. A very few examples of electron drift mobilities in bulk molecular films have been reported, mainly due to technical difficulties in measurement electron drift currents [9]. We successfully measured an electron mobility of the rubrene-doped TPD films, though a non-doped TPD film showed no feature of electron transport signal. Rubrene has been proved to be extremely stable in both reduction and oxidation processes in cyclic voltammetry measurements. High stability of radical anions of rubrene may be related with easy detection of the

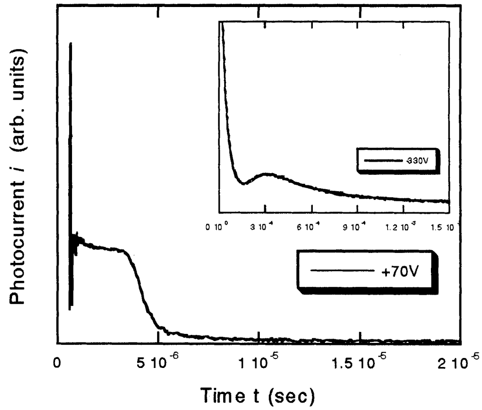

FIGURE 2 Typical transient photocurrent observed for 4 wt.% rubrene-doped (hole) and 8 wt.% rubrene-doped TPD film (electron, inset).

electron transit signals. Anyway our carrier mobility results gave a proof that rubrene have electron transport property.

In some cases typically depicted in (Figure 2), transit times were able to determined from linear plots of transient profiles, but in other cases, transit profiles were featureless. Thus, the transit times were determined from the log*i* vs. log*t* plots based on the Scher–Montroll theory [10]. The carrier mobility was calculated from the transit times, according to the expression $\mu = L^2/t_T V$, where L is the sample thickness and V is applied voltage.

Figure 3 shows the electron field dependences of hole and electron drift mobilities in vacuum-sublimed rubrene-doped TPD films for different rubrene concentrations. Hole mobility decreased with the increase of the rubrene concentration, indicating that rubrene molecules are behaving as trapping sites for hole transport. Appearance of electron transport feature in rubrene-doped TPD films indicates that electron can move via hopping on rubrene dopant, even though the average distance between rubrene molecules is rather large. Two rather peculiar observations related with electron transport behaviors in (Figure 3), the decrease of electron mobility with the increase of the dopant concentration and negative field dependency of electron mobility, may suggest invalidity of the assumption for random distribution of dopant molecules.

On the other hand, in electron carrier transport, the transient photocurrent showed highly dispersive behavior and transient time could not be determined even when double logarithmic plots of photocurrent versus time were used (not shown). The electric field dependence of the hole mobility for rubrene-doped CBP films is depicted in (Figure 4). Only 5 wt.%

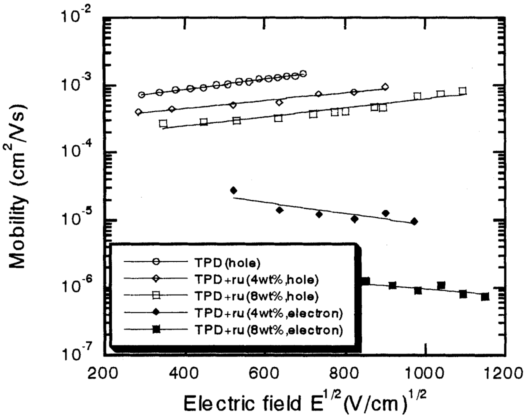

FIGURE 3 Field dependencies of the mobility in a rubrene-doped TPD films at room temperature.

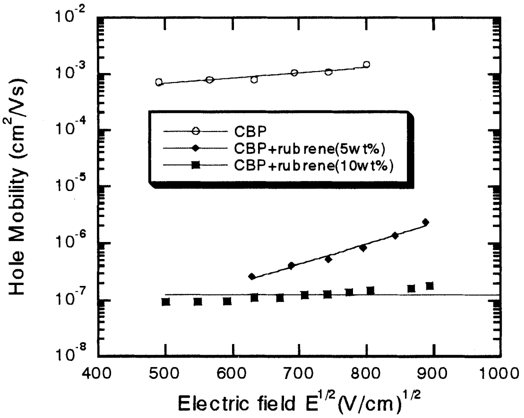

FIGURE 4 Field dependencies of the mobility in a rubrene-doped CBP films at room temperature.

addition of rubrene brought about nearly four orders of magnitude decrease in hole mobility. Decrease of hole mobility with rubrene doping in CBP films is much larger than the case of rubrene doping in TPD. This observation can be explained from the difference in trapping effect due to the difference of ionization potential between TPD and CBP. The ionization potential of the TPD (−5.37 eV) is close to that of rubrene (−5.36 eV), and traps due to rubrene are very shallow. In contrast, CBP has large ionization potential around −6.3 eV, located far below the level of rubrene.

Figure 5 shows typical photocurrent transients for the sample of 8 wt.% $Ir(ppy)_3$-doped CBP film for hole transport. A sample thickness is 3.6 μm. The transient signals for holes are similar with the rubrene-doped CBP films. The current follow a plateau region and tails off slowly after the inflection point, which indicates the transit time of the carrier. The broad dispersion from inflection point results from a broad distribution of hopping sites and deep carrier traps. However, in electron transport, the transient photocurrent showed dispersive behavior and transient times were able to be determined from the double logarithmic plot of photocurrent versus time. Figure 6 shows the electron field dependences of the hole and electron drift mobilities for the 8 wt.% $Ir(ppy)_3$-doped CBP films. The hole mobility of the 8 wt.% $Ir(ppy)_3$-doped CBP films was nearly four orders of magnitude lower than that for a non-doped CBP film. Deep trapping due to $Ir(ppy)_3$-dopants, which is quite similar to the case of rubrene doping was observed. We are successful in observing electron transport in the 8 wt.% $Ir(ppy)_3$-doped CBP film, although electron mobility is the order of 10^{-8} cm²/Vs. Therefore, it is assumed that ambipolar transport of holes and electrons is possible in $Ir(ppy)_3$-doped CBP films, even though absolute

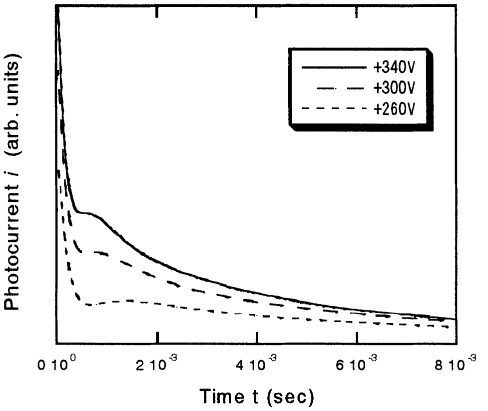

FIGURE 5 Typical transient photocurrent observed for 8 wt.% Ir(ppy)$_3$-doped CBP film (hole).

mobility values for holes and electrons are very low. Ambipolar characteristics of the Ir(ppy)$_3$-doped layer have been discussed from the analysis of triplet-triplet annihilation, exciton formation and luminance-current-voltage characteristics [11].

Mechanism for carrier recombination and emission in OLED with doped emission layers have been discussed in terms of the energy transfer from excitons formed in the host by the carrier recombination or direct carrier recombination at the fluorescent emissive centers. The direct observation

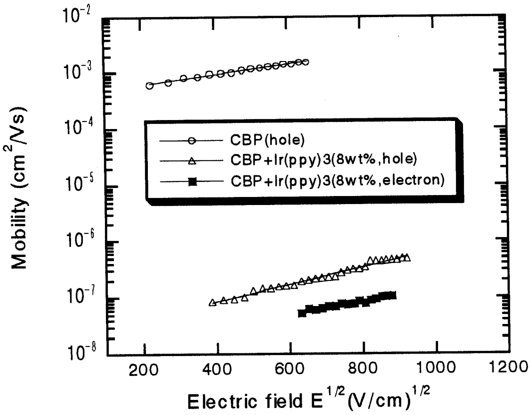

FIGURE 6 Field dependencies of the mobility in a Ir(ppy)$_3$-doped CBP films at room temperature.

of hole and electron transport in the rubrene-doped TPD films suggests that major emission mechanism of the rubrene-doped OLEDs is direct carrier recombination at the dopant centers [12,13]. The ambipolar mobility of the Ir(ppy)$_3$-doped CBP films may indicate that emission of the Ir(ppy)$_3$-doped OLEDs occurs via direct carrier recombination at the dopant centers [2,3].

In conclusion, we successfully measured an electron mobility of rubrene-doped TPD films, and Ir(ppy)$_3$-doped CBP films, while no feature of electron transport could be observed in non-doped TPD and CBP films. The electron mobility of rubrene-doped TPD and Ir(ppy)$_3$-doped CBP films suggest that emission occurs via direct recombination of holes and electrons at the dopant molecules.

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