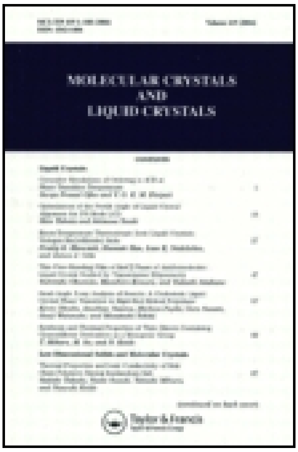

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High Mobility Electron Transport Material with Pyrene Moiety for Organic Light-Emitting Diodes (OLEDs)

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High Mobility Electron Transport Material with Pyrene Moiety for Organic Light-Emitting Diodes (OLEDs)

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We report a new electron transport material, 1,6-di(pyridin-3-yl)-3,8-di(phenyl)pyrene (PPP). It has a very good electron mobility of 4.1 $\times$ *10*$^{-3}$ *cm*^{2}*/Vs at the 0.1 MV/cm. This PPP is evaluated along with other electron transport materials such as* Alq_3 *(tris-(8-hydroxyquinoline)aluminum) and Bphen (4,7-diphenyl-1,10-phenanthroline) in green phosphorescent organic light-emitting diodes. The maximum external quantum efficiency is increased by 43.5% compared with a reference* Alq_3 *device. Operating voltage to reach 1000cd/m*^{2} *also is reduced to 1.2 V. Such high efficiency and low driving voltage are mainly attributed to the fast electron mobility and good LUMO (lowest unoccupied molecular orbital) level of the PPP material.*

Keywords organic light emitting diode; electron transport materials; pyrene; mobility; phosphorescent

Introduction

Organic light-emitting diodes (OLEDs) have become a main technology after the production of active matrix OLEDs for mobile phones and TV applications in flat panel displays. High power efficiency and long lifetime are very important factors for good commercial product specifications. In recent years, phosphorescent OLEDs (PHOLEDs) are gaining dominant position in the field of OLED devices owing to their superior efficiency, making them suitable for high-performance and high-brightness displays [1–3]. The upper limit in achieving the external quantum efficiency of 5% was observed in the fluorescent small molecule organic devices [4], which now has overcome by PHOLEDs because both the singlet and the triplet excitons can give the photon emission [5]. The iridium (III) and platinum (II) complexes are well-known phosphorescent emitters. The iridium (III) complexes are considered as the most efficient triplet dopants for high efficiency OLEDs [3,6]. To produce high efficiency in PH OLEDs, the excited energy of the phosphorescent emitter has to be confined within the emitter among the surrounding host and the carrier transporting materials [7,8]. Also, the device efficiency is affected by the hole-electron balance in the emitting layer [9]. In addition, a low driving voltage characteristic is very important

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to achieve the high power efficiency. The use of high carrier mobility materials with good ohmic contact at the metal interface is the most desirable approach for improving driving voltage of the devices. In general, hole mobility is faster than electron mobility in the most organic materials. As the result, hole carriers are accumulated at the interface of electron transporting layer or the dopant molecules in the emissive layer [10,11]. Therefore, good electron transport materials are necessary to achieve high efficiency OLEDs. The function of the electron transport material (ETM) is not only to reduce the energy barrier between the cathode and the emitter, but also to facilitate electron transportation to the emitter. The LUMO (lowest unoccupied molecular orbital) levels of ETMs should be close to the work function level of the cathode material so as to get low charge injection barriers. Also, faster electron transport mobility ($\geq 10^{-5}$ cm^2/Vs) is required to achieve the low driving voltage and high efficiency in OLEDs. On the basis of these criteria, chemical structures of usable ETMs are (1) metal chelates: Alq$_3$ (tris-(8-hydroxyquinoline)aluminum) and Bebq$_2$ (bis(10-hydroxyben-zo[h]quinolinato)beryllium), (2) N-atom containing aromatic compounds: Bphen (4,7-diphenyl-1,10phenanthroline), TPBI (2,2,2-(1,3,5-benzenetriyl)tris-[1-phenyl-1H-benzimidazole]), and TAZ (3-phenyl-4-(1′-naphthyl) -5-phenyl-1,2,4-triazole), (3) Oxadiazole compounds: PBD (2-(4-biphenyllyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole), (4) silole compound: PyPySPyPy (2,5-bis(2’,2”-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenylsilacyclopentadiene) [12], and (5) other compounds. Recently aromatic ring substituted pyrene moiety have been also reported as the ETM for blue fluorescent OLED [13].

In this study, we report a new electron transport material, PPP (1,6-di(pyridin-3-yl)-3,8-di[(3,5-diphenyl)-phenyl]pyrene) based on the pyrene moiety concept. In the PPP material, two 3,5-diphenyl-phenyl groups and two pyridine groups are attached to a pyrene moiety. This material has the faster electron mobility with a good LUMO level of 2.88 eV. The PPP as an ETM was investigated in green PHOLEDs and its performance was compared with the other known electron transport materials such as Alq$_3$ and Bphen.

Experimental

Synthesis of 1,6-di(pyridin-3-yl)-3,8-di[(3,5-diphenyl)-phenyl]pyrene

The PPP was synthesized by reacting 3,5-diphenyl-phenylboronic acid and 1,6-di(pyridin-3-yl)-3,8-dibromopyrene using the reported method [13] with same reaction scale (light yellow powder 73%). Its synthetic process was shown in Figure 1. A glass transition temperature (T_g) and a melting temperature (T_m) of the compound are 183 and 372°C, respectively, where T_g was obtained from the second heating scan of the glassy sample cooled after the first heating up to melting temperature (T_m). The heating rate was 10°C/min. The molecular structure was confirmed by ^{1}H NMR, mass spectrometry, and elemental analysis.

δ_H (500 MHz; CDCl$_3$; Me$_4$Si) 8.96 (2 H, d, *J* 2.1), 8.73 (2 H, d, *J* 4.9), 8.39 (2 H, d, *J* 9.5), 8.16 (2 H, d, *J* 9.5), 8.13 (2 H, s), 8.03 (2 H, d, *J* 7.7), 7.94 (2 H, t, *J* 1.5), 7.89 (4 H, s), 7.76 (8 H, d, *J* 8.4), 7.51 (10H, m), 7.41 (4 H, t, *J* 7.3) Elemental analysis: Found: C, 91.62; H, 4.94; N, 3.46%; Calc. for $C_{62}H_{40}N_2$: C, 91.60; H, 4.96; N, 3.45%. M/S (m/z, M$^+$): Found: 813.3273, Calc. for $C_{62}H_{41}N_2$: 813.3270.

Fabrication and Evaluation of Green PHOLEDs

To fabricate OLED devices, a glass substrate with a 150 nm ITO layer (a sheet resistance of 10 ∼ 12 Ω/square) was used as an anode. The glass substrate was cleaned by sonification in

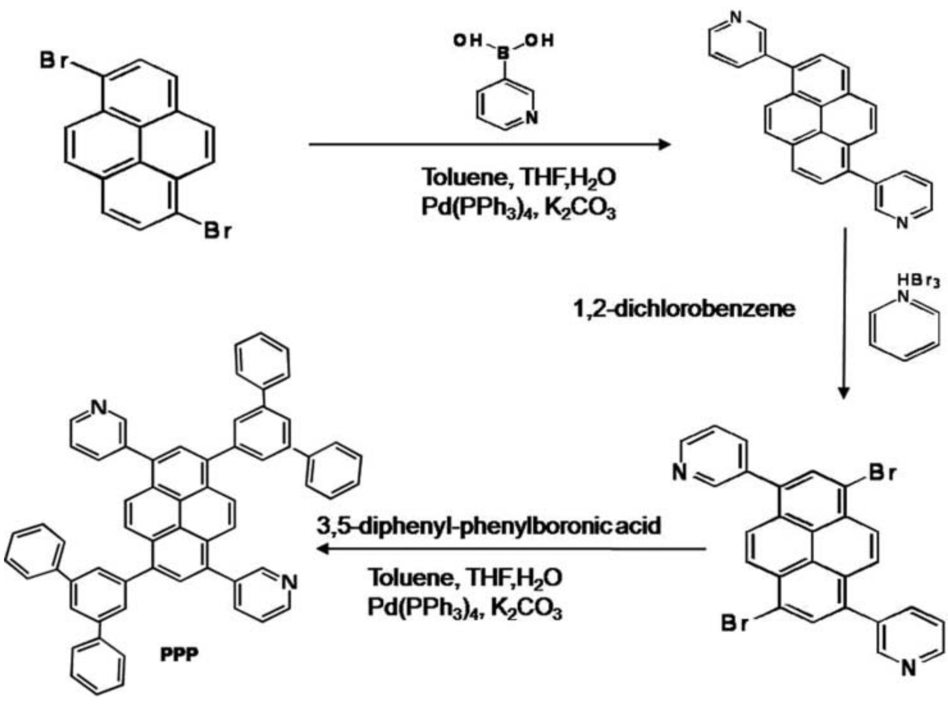

Figure 1. The synthetic process of PPP.

an isopropyl alcohol and rinsed in deionized water. It was finally irradiated in a UV-ozone chamber before organic layer deposition. All the organic materials were deposited by the vacuum evaporation technique under a pressure of $\sim 3.0 \times 10^{-7}$ Torr. Doping is carried out by co-evaporation from the independent sources and effusion rates were monitored using a quartz crystal microbalance (QCM). Subsequently the Al cathode was deposited with a deposition rate of $\sim$ 5 Å/s without breaking the vacuum.

Measurements

Cyclic voltammetry measurements were performed on BASi, Bioanalytical Systems Inc., analysis equipment (C-3 standard). The platinum wire electrode and 150-nm ITO film on glass were used as the counter and working electrodes respectively. Also, Ag (in 0.1M $AgNO_3$) was used as a reference electrode. An electrolyte solution of 0.1M Bu_4NClO_4 (tetrabutylammonium perchlorate) in acetonitrile was used in all experiments. In order to confirm our measurement accuracy, Alq_3 was also measured and compared with the reported results [14]. Alq_3 shows oxidation potential of 5.54 eV in our system. Solid-state electrochemistry was performed at a scan rate of 150 mV/s. UV-Vis and PL spectra of the used compounds were measured using SCINCO S-4100 and Jasco FP-6000 spectrometer, respectively. The current density-voltage (J-V) and luminance-voltage (L-V) data of PHOLEDs were measured using a Keithley 2635A and Minolta CS-100A, respectively. Electroluminescence (EL) spectra and CIE color co-ordinates were obtained using a Minolta CS-1000 spectroradiometer.

Results and Discussion

Figure 2(a) shows the absorption and photoluminescent (PL) spectra of a compound PPP in the toluene. The absorption spectrum of PPP exhibits a peak at 381 nm which can be attributed to π-π^* transition. From the absorption edge, optical energy band gap is estimated to be 2.85 eV. The PL spectra exhibit a peak at 426 nm. Cyclic voltammetry experiment was done to know the HOMO (highest occupied molecular orbital) value and the electrochemical properties of PPP. The cyclic voltammograms of PPP and Alq_3 are shown in Figure 2(b). The HOMO energy level was calculated as 5.73 eV by the on-set voltage of cyclic voltammogram. The LUMO level was decided to be 2.88 eV by taking the

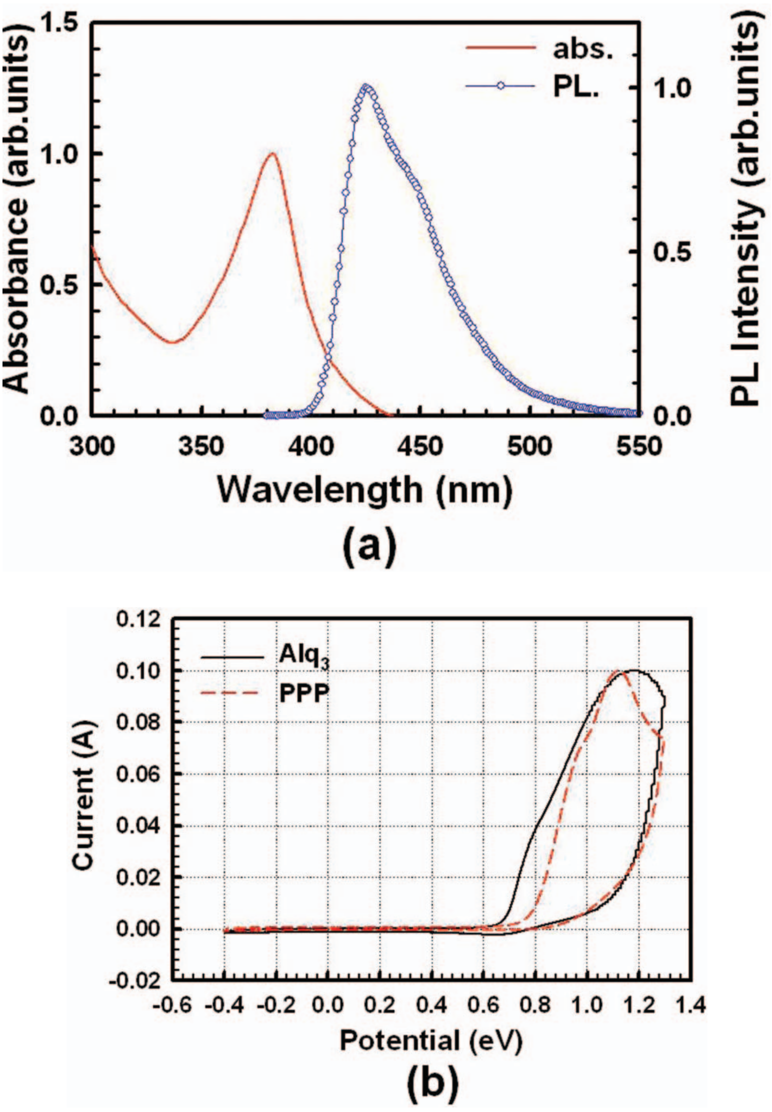

Figure 2. (a) UV-Vis and PL spectra of PPP in toluene, (b) Cyclic voltammetry characteristics of PPP.

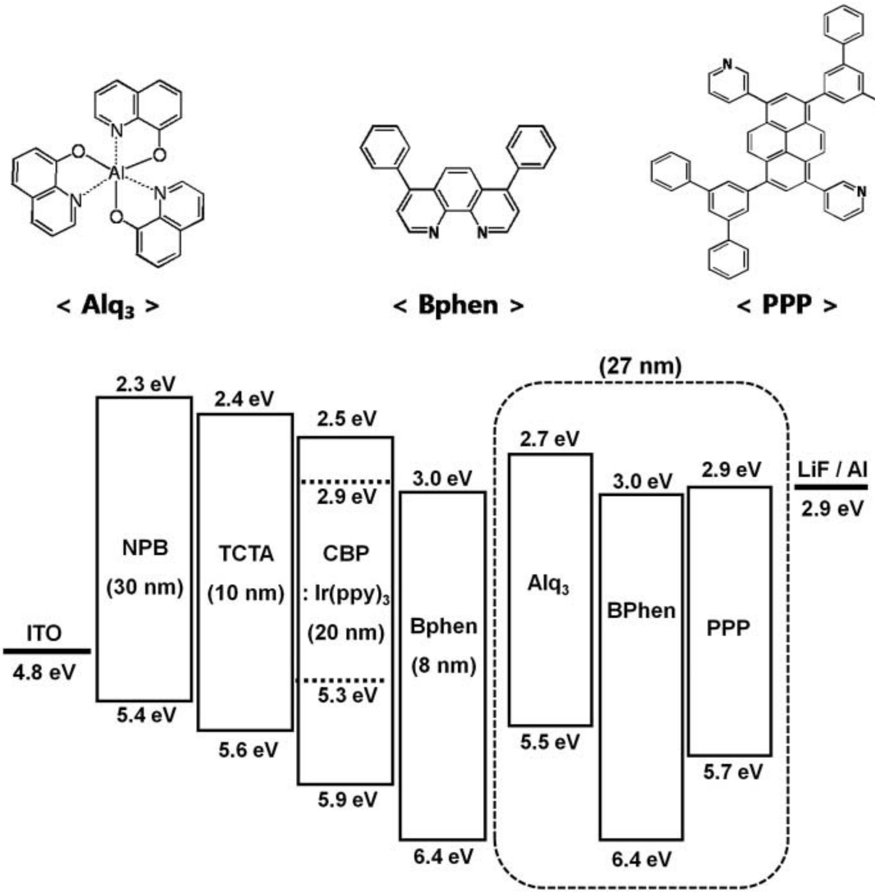

Figure 3. Chemical structure and energy level diagram of used materials.

difference of HOMO level and optical band gap. Figure 3 shows the energy level diagram of the used materials with PPP.

To investigate the effects of electron transporting layer (ETL), following three devices were designed and fabricated with the different ETMs;

Device A: ITO/NPB (30 nm)/TCTA (10 nm)/CBP: Ir(ppy)$_3$ 5% (20 nm)/Bphen (8 nm)/Alq$_3$ (27 nm)/LiF/Al,
Device B: ITO/NPB (30 nm)/TCTA (10 nm)/CBP: Ir(ppy)$_3$ 5% (20 nm)/Bphen (35 nm)/LiF/Al,
Device C: ITO/NPB (30 nm)/TCTA (10 nm)/CBP: Ir(ppy)$_3$ 5% (20 nm)/Bphen (8 nm)/PPP (27 nm)/LiF/Al.

In the above mentioned devices, TCTA and Bphen were used as a hole transporting and electron transporting layer, respectively. Both carrier transporting layers act as an exciton blocking layer because their triplet energies (2.7 eV for TCTA and 2.5 eV for Bphen) are higher than that of Ir(ppy)$_3$ (2.4 eV) dopant. Therefore, this device structure can confine triplet excitons in the EML. Chemical structures and energy level diagrams for the materials

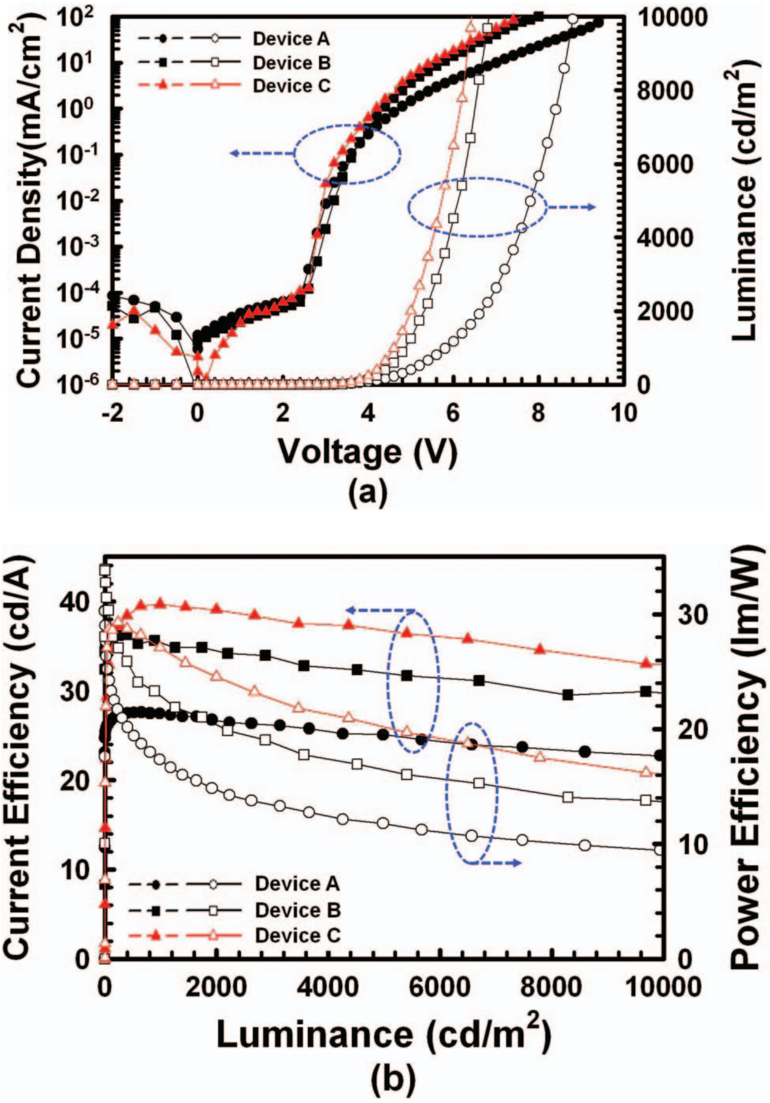

Figure 4. (a) J-V-L characteristics, (b) Luminance vs. current efficiency and power efficiency characteristics of green PHOLEDs.

used in this study were shown in Figure 3. The dopant concentration was fixed at 5% to evaluate only the material performances.

The three ETMs studied here are Alq_3 (device A), Bphen (device B), and PPP (device C). Figure. 4(a) shows the current density–voltage–luminance (J–V–L) characteristics of green PHOLEDs with different ETLs. The turn-on voltages to provide 1 cd/m^2 luminance were 3.0 V for device A, 3.0 V for device B, and 2.8 V for device C, respectively. The driving voltages for the devices A, B, and C were 5.8 V, 4.9 V, and 4.6 V at the 1,000 cd/m^2 respectively. This indicates that driving voltage of PPP ETM device (device C) was decreased by 1.2 V and 0.3 V compared with those of Alq_3 and Bphen devices. Device C with PPP ETM exhibits lower turn-on and operating voltage characteristics. The current

Table 1. The device performances of green PHOLEDs

	Device A (Alq_3)	Device B (Bphen)	Device C (PPP)
Turn-on voltage (at 1 cd/m^2)	3.0 V	3.0 V	2.8 V
Operating voltage (1000 cd/m^2)	5.8 V	4.9 V	4.6 V
Efficiency (1000 cd/m^2)	27.4 cd/A 14.9 lm/W	35.6 cd/A 23.3 lm/W	39.7 cd/A 27.1 lm/W
Efficiency (Maximum)	27.6 cd/A 26.0 lm/W	36.7 cd/A 33.9 lm/W	39.7 cd/A 28.7 lm/W
CIE (x,y) (1000 cd/m^2)	(0.31, 0.62)	(0.31, 0.62)	(0.31, 0.62)
EQE (%)	10.1	13.4	14.5

and power efficiency characteristics of the fabricated devices are shown in Figure 4(b). The maximum current and power efficiencies were 27.6 cd/A and 26.0 lm/W for device A, 36.7 cd/A and 33.9 lm/W for device B, 39.7 cd/A and 28.7 lm/W for device C, respectively. At a given constant luminance of 1000 cd/m^2, the current and power efficiencies were 27.4 cd/A and 14.9 lm/W for device A, 35.6 cd/A and 23.3 lm/W for device B, 39.7 cd/A and 27.1 lm/W for device C, respectively. These external quantum efficiencies (EQEs) data correspond to 10.1%, 13.4%, and 14.5% for the devices A, B, and C, respectively. The device C exhibits the higher efficiency than the others devices. The Commission Internationale de l'Eclairage (CIE) co-ordinates of device A, B and device C for green PHOLEDs show the same value as CIE (0.31, 0.62) at a brightness of 1000 cd/m^2. The electroluminescence spectra of all three devices using $Ir(ppy)_3$ dopant exhibit the same emission at 514 nm.(not shown here) These results clearly indicate that the designed device structure can confine all the excitons within the EML effectively. The performances of all the devices are summarized in Table 1.

All three devices have the same device structure except different ETMs. Their hole-carrier transport characteristics in the EML are same in all devices. As the hole carriers reach to the EML at the same time, electron injection and transport characteristics can affect to operating voltage and device efficiency in the devices. We measured the electron carrier mobility of each ETM to analyze the effect of PPP clearly. The SCLC (space charge limited current) method for electron mobility measurement for each ETM was applied [15]. The electron only devices of Al(100 nm)/ Cs_2CO_3 (1 nm)/ ETM (100 nm)/ Cs_2CO_3 (1 nm) /Al (100 nm) were fabricated using different ETMs. The thin Cs_2CO_3 layer on the electrode was inserted to make Ohmic contact so that SCLC region can be investigated clearly in the devices [16]. In all devices, carrier mobility depending on electric field was plotted as shown in Figure 5. The electron mobility of PPP was evaluated as $\sim 4.1\times10^{-3}$ cm^2/Vs at the 0.1 MV/cm. Both Alq_3 and Bphen show lower electron mobilities of 4.6×10^{-6} cm^2/Vs and 2.4×10^{-4} cm^2/Vs at the 0.1 MV/cm respectively. These Alq_3 and Bphen mobility values are very similar to previously reported ones [17,18]. It indicates that our calculation and measurement method is very accurate.

The device C exhibits lower operating voltage and higher efficiency compare with those of the device A and B. The operating voltage mainly depends on carrier injection and carrier transport characteristics. The LUMO level of PPP is 2.88 eV which lies close to the work function level of LiF/Al cathode. Electrons injected from the cathode can move freely

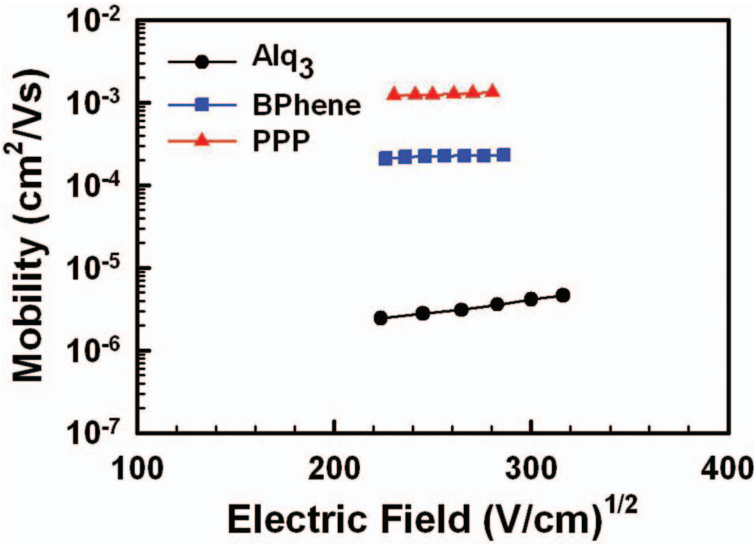

Figure 5. Carrier mobility curves of each ETM with electrical field measured by the SCLC method.

into the EML when PPP ETM is used. In addition, our PPP ETM has a very good mobility. These PPP material characteristics result in the decrease of operating voltage in the device. In our green PHOLEDs, most of hole carriers are trapped by Ir(ppy)$_3$ dopants in the EML and accumulate at the hole blocking BPhen layer. The recombination mainly depends on the electron transporting performance of ETMs of the device. The high electron mobility of PPP could help broad recombination region in the devices, resulting in increased device efficiency in the green color PHOLEDs.

Conclusions

We report a new ETM, PPP with pyrene moiety concept. This ETM exhibits a very high electron mobility of 4.1 $\times 10^{-3}$ cm^2/Vs and a good LUMO level of 2.88 eV. When this PPP is replaced to Alq$_3$ in the green PHOLED, the maximum external quantum efficiency is increased upto 43.5% and operating voltage to reach 1000cd/m^2 is reduced to 1.2 V. This ETM material can be applicable to many other OLED applications.

Acknowledgment

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