Dyes and Pigments 141 (2017) 217-224

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Bipolar host materials with carbazole and dipyridylamine groups showing high triplet energy for blue phosphorescent organic light emitting diodes

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ARTICLE INFO

Article history: Received 19 January 2017 Received in revised form 10 February 2017 Accepted 10 February 2017 Available online 14 February 2017

Keywords: Organic light emitting diodes Blue host materials Highly efficient blue PHOLED Carbazole based host materials

ABSTRACT

A series of new bipolar host materials with carbazole and different number of dipyridyl amine groups were synthesized for blue phosphorescent organic light-emitting diodes (PHOLEDs). Especially, we applied dipyridyl amine to control the polarity as well as electron transporting property of the carbazole based host materials for comparison with the properties of 1,3-di(9*H*-carbazol-9-yl)benzene (mCP). As a result, all the carbazole based host materials with dipyridyl amine moieties showed very high triplet energies (>2.9 eV) as well as wide band gap (>3.5 eV). Thus, the blue phosphorescent devices employing those materials with bis(4,6-difluorophenyl pyridinato-*N*,*C*2)picolinato-iridium (III) (FIrpic) as a dopant and we obtained moderately high external quantum efficiency (EQE) up to 21.6% with *N*-(3,5-di(9*H*-carbazol-9-yl)phenyl)-*N*-(pyridin-2-yl)pyridin-2-amine (**DCPPy**).

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1. Introduction

Organic light emitting diodes (OLEDs) have received considerable attention due to their superior device properties which are perfectly suitable for large area displays and solid-state lightings. However, OLEDs are still struggling against liquid crystal displays (LCDs) due to a short lifetime as well as a low efficiency of blue emitting materials. Hence, materials for blue phosphorescent organic light-emitting diodes (PHOLEDs) has become very important to overcome such critical issues [1-10]. Nevertheless, it is still being required to understand premise condition for materials design of blue phosphorescent emitters because there has been no great success to synthesize the materials showing moderately long lifetime behavior for last decade. Indeed many research groups are focusing on the development into a suitable host materials for blue PHOLEDs. Especially, they are trying their best to avoid side effects such as triplet-triplet annihilation (TTA), triplet-polaron annihilation (TPA), and many other types of self-quenching processes

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[11,12].

In principle, blue host materials are required to have a large band gap (E_g) above 3.5 eV as well as a large triplet energy (T_1) level greater than 2.9 eV to prevent the back energy transfer from dopant to host materials (T_1 of dopant > 2.7 eV) [13,14]. Besides, they should have moderate hole as well as electron charge transport behavior and thermal stability for stable device performance [15–20]. The most common approach is to use a carbazole core moiety and an electron accepting heteroaromatic ring moiety with limited conjugation length to increase the band gap as well as T₁ level for blue phosphorescent devices [21,22]. At the beginning, the most representative material with carbazole groups was 1.3-di(9Hcarbazol-9-yl)benzene (mCP) reported by Forrest [23]. Especially, a mCP was a very suitable host material for blue PHOLEDs because it has moderately high triplet energy and large band gap about 2.9 eV and 3.5 eV, respectively. Unfortunately, the devices prepared by using this material show very short lifetime presumably due to its low glass transition temperature (T_g) (about 60 °C) which may cause molecular aggregation or crystallization from joule heating of the devices [24]. To overcome such an issue, it is necessary to synthesize new host materials with increased Tg for blue phosphorescent devices.

In this paper, we report three different types of bipolar host





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materials with high triplet energy ($T_1 > 2.9 \text{ eV}$) by connecting carbazole and different number of dipyridyl amine groups to the core phenyl linker for improvement of their hole as well as electron transport properties. As a result, we obtained moderately high external quantum efficiency (EQE) up to 21.6% with *N*-(3,5-di(9*H*-carbazol-9-yl)phenyl)-*N*-(pyridin-2-yl)pyridin-2-amine (**DCPPy**) device.

2. Experimental

2.1. Synthesis of new host material

2.1.1. Instruments

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE 400FT-NMR(400 Hz). The absorption spectra were obtained by ultraviolet-visible (UV-vis) spectrophotometer (HEWspectrophotometer). LETT PACKARD 8453 UV-vis Photoluminescence (PL) spectra were collected by PERKIN ELMER LS 50B luminescence spectrometer. The differential scanning calorimetry (DSC) was performed on TA instruments and thermogravimetric analysis (TGA) using TA INSTRUMENT TA4100. High resolution mass spectra were recorded using a HR-ESI MS SYNAPU G2 (Waters, U.K.) HOMO (Highest Occupied Molecular Orbital) was measured with a photoelectron spectrometer (AC2, Hitachi High Tech).

2.1.2. Synthetic details

2.1.2.1. Synthesis of N-(3-(9H-carbazol-9-yl)phenyl)-N-(pyridin-2-yl) pyridin-2-amine (**mCPPy**). In a Schlenk flask, 9-(3-bromophenyl)-

9H-carbazole (5 g, 10.3 mmol), 2,2'-dipyridylamine (1.9 g, 11.3 mmol), copper(I) iodide (0.2 g, 1.0 mmol), 18-Crown-6 (0.09 g, 0.34 mmol), cesium carbonate (7.2 g, 20.5 mmol) was dissolved in 1,2-dichlorobenzene (72 ml). And 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) (0.25 mL) was put into reactor, then keep heating at 170 °C for 18 h under nitrogen. After cooling to room temperature, the mixture was poured into a cold hexane. The precipitate was filtered and washed with hexane. The solid was purified with column chromatography [n-Hexane: Ethylacetate = 1: 5 (vol.: vol.)] to give yellowish powder in 38% of yield. After primary purification, N-(3-(9H-carbazol-9-yl)phenyl)-*N*-(pyridin-2-yl)pyridin-2-amine (**mCPPy**) was obtained as a white powder by train sublimation. (m.p. = $132 \circ C$) ¹H NMR (400 MHz, CD_2Cl_2) δ (ppm) 8.35 (s, 2H) 8.10–8.12 (d, J = 8.0, 2H) 7.62–7.65 (t, J = 8.0, 2H 7.56–7.60 (t, J = 8.0, 1H 7.50–7.52 (d, J = 8.0, 2H) 7.39–7.43 (t, J = 8.0, 3H) 7.36 (s, 1H) 7.25–7.29 (t, J = 8.0, 2H) 7.21-7.23 (d, J = 8.0, 1H) 7.11-7.12 (d, J = 8.0, 2H) 7.00-7.02 (d, J = 8.0, 1H) 6.99–7.00 (d, J = 8.0, 1H) i¹³C NMR (400 MHz, CD₂Cl₂) 117.7, 119.1, 120.4, 120.5, 123.1, 123.7, 125.21, 125.25, 126.3, 130.8, 138.0, 138.8, 140.8, 147.1, 148.9, 158.3 ppm [M+H]⁺: *m*/*z* calcd for C₂₈ H₂₁ N4, 413.1766 found 413.1768.

2.1.2.2. Synthesis of 9,9'-(5-bromo-1,3-phenylene)bis(9H-carbazole) (1). In a flask a mixture of 1,3,5-tribromobenzene (10 g, 31.8 mmol), carbazole (10.7 g, 64.2 mmol), copper(I) iodide (2.4 g, 12.7 mmol), Cesium carbonate (16.8 g, 47.7 mmol) in Toluene (96 ml) was stirred. And trans-1,2-diaminocyclohexane (1.9 ml, 15.9 mmol) was put into reactor, then keep it heating at 80 °C under N₂ atmosphere for 24 h. The resulting mixture was cooled to room temperature and



Scheme 1. Synthesis of new blue host materials.



Fig. 1. Optimized molecular geometry of (a) mCPPy (b) CPDPy and (c) DCPPy molecules showing HOMO (left), LUMO (middle), and side view of molecules (right).

then filtered and washed CH₂Cl₂. After removal of the solvent by rotary evaporation, the residue was purified by silica gel column chromatography (n-hexane:CH₂Cl₂ 7:1, white powder, yield 28%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.14–8.16 (d, *J* = 8.0 Hz, 4H) 7.86–7.87 (s, 2H) 7.79–7.80 (s, 1H) 7.54–7.56 (d, *J* = 8.0, 4H) 7.44–7.48 (t, *J* = 8.0, 4H) 7.31–7.35 (t, *J* = 8.0, 4H).

2.1.2.3. Synthesis of 5-(9H-carbazol-9-yl)-N¹,N¹,N³,N³-tetra(pyridin-2-yl)benzene-1,3-diamine (CPDPy). In a schlenk flask Compound (1) (5 g, 12.5 mmol), 2,2'-dipyridylamine (4.9 g, 28.7 mmol), copper(I) iodide (0.95 g, 5.0 mmol), 18-Crown-6 (0.33 g, 1.3 mmol), cesium carbonate (15.4 g, 43.6 mmol) was dissolved in dimethylsulfoxide (52 ml). And DMPU (1.3 mL) was put into reactor, then keep it heating at 170 °C for 18 h under nitrogen. After cooling to room temperature, the mixture was pour cold hexane. The precipitate was filtered and washed hexane. The solid was purified with column chromatography [n-Hexane: Ethylacetate = 1:1 (vol.: vol.)] to give yellowish powder in 37% of yield. 5-(9H-carbazol-9yl)-*N*¹,*N*¹,*N*³,*N*³-tetra(pyridin-2-yl)benzene-1,3-diamine (CPDPv) was obtained as a white powder by train sublimation. $(m.p. = 263 \ ^{\circ}C)$ ¹H NMR (400 MHz, CD₂Cl₂) δ 8.33–8.35 (d, 4H) 8.06-8.08 (d, 2H) 7.59-7.63 (t, 4H) 7.55-7.58 (d, 2H) 7.37-7.41 (t, 2H) 7.22-7.26 (t, 2H) 7.13-7.15 (d, 3H) 7.13 (s, 3H) 6.96-7.00 (m, 5H) ppm ¹³C NMR (400 MHz, CD₂Cl₂) 117.9, 119.2, 120.4, 120.5, 122.2, 123.7, 126.2, 138.0, 139.2, 140.5, 147.4, 148.9, 158.0 ppm ESI-MS [M+H]⁺: *m*/*z* calcd for C₃₈ H₂₈ N₇, 582.2406; found 582.2414.

2.1.2.4. Synthesis of 9,9'-(5-bromo-1,3-phenylene)bis(9H-carbazole) (2). In a flask a mixture of 1,3,5-tribromobenzene (10 g, 31.8 mmol), carbazole (10.7 g, 64.2 mmol), copper(I) iodide (2.4 g, 12.7 mmol), Cesium carbonate (16.8 g, 47.7 mmol) in Toluene (96 ml) was stirred. And trans-1,2-diaminocyclohexane (1.9 ml, 15.9 mmol) was put into reactor, then keep it heating at 80 °C under N₂ atmosphere for 24 h. The resulting mixture was cooled to room temperature and then filtered and washed CH₂Cl₂. After removal of the solvent by rotary evaporation, the residue was purified by silica gel column chromatography [n-hexane: CH₂Cl₂ = 7: 1 (vol.: vol)], to give white

powder in 28% of yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.14–8.16 (d, J = 8.0 Hz, 4H) 7.86–7.87 (s, 2H) 7.79–7.80 (s, 1H) 7.54–7.56 (d, J = 8.0, 4H) 7.44–7.48 (t, J = 8.0, 4H) 7.31–7.35 (t, J = 8.0, 4H).

2.1.2.5. Synthesis of N-(3,5-di(9H-carbazol-9-yl)phenyl)-N-(pyridin-2-yl)pyridin-2-amine (DCPPy). In a schlenk flask Compound (2) (5 g, 10.3 mmol), 2,2'-dipyridylamine (1.9 g, 11.3 mmol), copper(I) iodide (0.2 g, 1.0 mmol), 18-Crown-6 (0.1 g, 0.4 mmol), cesium carbonate (7.4 g, 20.5 mmol) was dissolved in 1,2-dichlorobenzene. And DMPU (3 mL) was put into reactor, then keep it heating at 180 °C for 13 h under nitrogen. After cooling to room temperature, the mixture was pour cold hexane. The precipitate was filtered and washed hexane. The solid was purified with column chromatography [n-Hexane:Ethylacetate 7: 5 (vol.: vol)] to give yellowish powder in 41% of yield. N-(3,5-di(9H-carbazol-9-yl)phenyl)-N-(pyridin-2-yl)pyridin-2-amine (DCPPy) was obtained as a white powder by train sublimation. (m.p. = $263 \circ C$) ¹H NMR (400 MHz, CD_2Cl_2) δ (ppm) 8.45–8.47 (s, 2H) 8.12–8.13 (d, J = 8.0, 4H) 7.67–7.71 (t, J = 8.0, 2H) 7.64–7.66 (m, J = 4.0, 5H) 7.41–7.45 (t, I = 8.0, 6H 7.27–7.30 (t, I = 8.0, 4H 7.20–7.22 (d, 2H) 7.05–7.09 (t, I = 8.0, 2H) ¹³C NMR (400 MHz, CD₂Cl₂) 110.4, 118.2, 119.8, 122.4, 123.8, 126.4, 138.4, 139.8, 140.6, 148.1, 149.2, 157.9 ppm ESI-MS [M+H]⁺: *m*/*z* calcd for C₄₀ H₂₈ N₅, 578.2345; found 578.2345.

2.2. Fabrication of blue PHOLEDs

2.2.1. Materials

We purchased or synthesized the following materials. Poly(3,4ethylene dioxythiophene) (PEDOT) doped with poly(styrenesulfonate)anions (PSS) (PEDOT:PSS) (PEDOT:PSS) was purchased from Heraeus (Heraeus Clevios™ P VP CH 8000) as a hole injection layer (HIL). 1,1'-bis(di-4-tolylaminophenyl) cyclohexane (TAPC) and mCP were purchased from Lumtec Corp. and used as a hole transporting materials (HTL) as well as an exciton blocking layer (EBL), respectively. **mCPPy, CPDPy** and **DCPPy** were synthesized as aforementioned and utilized as host materials for emitting



Fig. 2. UV-visible absorption and photoluminescence spectra of (a) mCPPy (b) CPDPy and (c) DCPPy, respectively.

layer (EML). In addition, bis(4,6-difluorophenyl pyridinato-*N*,*C*2) picolinato-iridium (III) (FIrpic) was purchased from Lumtec Corp. and used as a phosphorescent blue dopant for EML. 1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB) as an electron transporting material (ETL), lithium fluoride (LiF) as the materials for an electron injection layer (EIL), and aluminum (Al) as a cathode were also purchased from the commercial suppliers and were used without purification.

2.2.2. Device fabrication

To fabricate OLED devices, a 150 nm thick patterned indium-tin



Fig. 3. (a) DSC and (b) TGA results of mCPPy, CPDPy and DCPPy, respectively.

oxide (ITO) glasses with an open emission area of 4 mm² were used. The ITO glasses were cleaned in acetone and isopropyl alcohol with sonication process and rinsed in deionized water. Then, ITO glass substrates were treated in UV-ozone to eliminate all the organic impurity remained during previous fabrication processes. PEDOT:PSS was spin-coated on ITO glass in ambient condition and annealed at 120 °C for 15min in nitrogen atmosphere. Subsequently, All the organic materials were deposited on PEDOT:PSS by the vacuum evaporation technique under a pressure of ~1 × 10⁻⁶ Torr. The deposition rate of organic layers was about 0.5 Å/s. LiF and Al were deposited with rates of 0.1 Å/s and 3 Å/s, respectively.

2.2.3. Measurements

The current density-voltage (J-V) and luminance-voltage (L-V)

Table 1

Summary of physical properties of blue host materials.

Compound	λ _{abs} a [nm]	λ _{pl} ^b [nm]		T ₁ [eV]	T ₁ ^c [eV]	HOMO ^d [eV]	LUMO [eV]	E _g [eV]	T _g [°C]	T _m [°C]	T _d [°C]
		Solution	Film	(Exp)	(Cal)	(AC2)					
mCPPy	294, 341	366	377	2.94	3.25	-5.86	-2.30	3.56	63	132	299
CPDPy	294	368	375	2.95	3.12	-5.78	-2.24	3.54	97	264	382
DCPPy	294, 340	362	372	2.94	3.22	-5.86	-2.30	3.57	108	263	383

^a λ_{abs} : peak wavelength observed from UV–visible absorption spectroscopy (at 297 K).

 b λ_{pl} : peak wavelength measured from photoluminescence (PL) spectra (at 297 K and 77 K).

^c T_1 was calculated from DMol3.

^d HOMO values were determined by photoelectron spectroscopy (AC2, RIKEN KEIKEI).



Fig. 4. Energy diagrams of (a) blue PHOLEDs (b) hole only devices, and (c) electron only devices in this study.

data of OLEDs were collected by Keithley SMU 2635A and Minolta CS-100A, respectively. The OLED area was 4 mm² for all the samples studied in this work. Electroluminescence (EL) spectra and the Commission Internationale De'Eclairage (CIE) coordinate were obtained using a Minolta CS-2000A spectroradiometer.

3. Results and discussion

3.1. Analysis of newly synthesized blue host materials

We prepared three different types of bipolar host materials by moderately simple procedure. Especially, we selected carbazole and dipyridyl amine moieties to obtain high triplet energy. Those moieties were selected to improve electron transport as well as hole transport ability. Especially, we used benzene ring as a central linker unit of host materials which could appropriately limit the π conjugation to increase in triplet energy due to a steric hindrance of substituents [25,26]. The detailed synthetic route for preparation of such materials are shown in Scheme 1.

Fig. 1 shows the molecular geometries of the ground state of new host materials obtained from the molecular simulation using simulation at Lee-Yang-Parr correlation (B3LYP) functional with the double numerical plus d-functions (DND) basis set in the DMol3 module of Materials Studio 2017. From this simulation, we found that the electron density in the HOMO was mostly located on the carbazole units, while that of lowest unoccupied molecular orbital (LUMO) was mostly localized over dipyridyl amine and benzene core moieties in **mCPPy**, **CPDPy** and **DCPPy** molecules. In other words, the hole carriers could be easily transported through the carbazole, while the electron carriers could be transported through the dipyridyl amine and benzene moieties after charge injection.

Fig. 2 shows the UV–vis absorption and PL spectra for **mCPPy**, **CPDPy** and **DCPPy** of Fig. 2(a), (b) and (c), respectively. The band gap determined from the band edge of UV–vis spectra were 3.56, 3.54, 3.57 eV for **mCPPy**, **CPDPy** and **DCPPy**, respectively. The HOMO energy level was measured by AC2 analyzer and LUMO energy level of materials were assigned from subtraction of band gap from those HOMO energy levels. All of those compounds showed featureless emission spectral patterns, while we could found some vibronic fine emission peaks from the emission spectra obtained at low temperature condition (77 K). Meanwhile, T₁ of those materials which were determined from such low temperature PL spectra were 2.94, 2.95, 2.94 eV for **mCPPy**, **CPDPy** and **DCPPy**, respectively. Hence, they are suitable for host materials which can be used in blue PHOLEDs. The representative results are also summarized in Table 1.

We investigated the thermal stability of the materials synthesized in this study because this is very critical for the materials with highly twisted geometry to result in high triplet energy as well as wide band gaps as shown in Fig. 3. From the measurement of DSC, we found that **CPDPy** and **DCPPy** showed higher T_g of 97 and 108 °C, respectively, than that of the **mCPPy** (63 °C) as shown in



Fig. 5. (a) *J-V-L*, (b) current efficiency -L, and (c) external quantum efficiency -L characteristics of blue PHOLEDs.

Fig. 3(a). Meanwhile, the T_g of **mCPPy** is very similar to that of mCP (60 °C), which might be due to an increased free volume compared to those of other materials having more substituents which may reduce the free volume inside of bulk film. However, compared with mCP with two carbarzole units on benzene core, Tg's of CPDPy and DCPPy were highly increased about 40 °C or more due to additional substituents such as dipyridyl amine or carbazole on the same core. Generally, the Tg values increase with increasing molecular weight and molecular size. Besides, the crystallization temperature (T_c) and melting points (T_m) of three host materials were not observed in DSC 2nd scans. It means that all synthesized materials is amorphous. Therefore, it is expected that it will prevent the decrease in the efficiency of the devices caused by the recrystallization in the fabrication and the driving of device [27]. In contrast, the thermal decomposition temperature (T_d) determined by TGA were pretty high up to 299, 382 and 383 °C for mCPPy, CPDPy and DCPPy, respectively, as shown in Fig. 3(b) although their Tg's were not that high. The representative results including Tm's are also summarized in Table 1.

Table 2

Summary of device characteristics of the blue PHOLEDs.

Device	V_{on}^{a}/V_{op}^{b} [V]	CE ^c /PE ^d /EQE ^e [co	CIE ^f (x,y)		
		Maximum	At 1000 cd m^{-2}		
Reference	4.0/6.2	36.3/27.2/18.3	33.6/16.1/17.0	(0.16, 0.31)	
Device A	4.0/6.3	31.9/22.3/16.3	26.0/12.3/13.4	(0.15, 0.30)	
Device B	4.0/6.3	37.9/26.5/18.9	33.9/16.4/17.2	(0.16, 0.31)	
Device C	4.1/6.5	43.3/24.4/21.6	43.2/19.4/21.6	(0.15, 0.32)	

^a V_{on} : turn-on voltage, measured at 1 cd m⁻².

^b V_{op} : operating voltage, measured at 1000 cd m⁻².

^c CE: current efficiency.

^d PE: power efficiency.

^e EQE: external quantum efficiency, the EQE was obtained from the calculation based on the assumption of a Lambertian distribution.

^f CIE: Commission International de L'Eclairage.

3.2. Device characteristics

To investigate the basic properties of those host materials in full devices, we prepared the blue PHOLEDs having following device configurations (see also Fig. 4(a)). We also fabricated the reference devices with common host materials (mCP) to compare the performance level of blue PHOLEDs applied new synthetic host materials.

Reference: ITO/PEDOT:PSS (55 nm)/TAPC (20 nm)/mCP (10 nm)/mCP: FIrpic (10%, 25 nm)/TmPyPB (35 nm)/LiF (1 nm)/Al (100 nm).

Device A: ITO/PEDOT:PSS (55 nm)/TAPC (20 nm)/mCP (10 nm)/ **mCPPy**: FIrpic (10%, 25 nm)/TmPyPB (35 nm)/LiF (1 nm)/Al (100 nm).



Fig. 6. *J-V* characteristics of (a) hole only devices (blue host: Flrpic 10%) and electron only devices (blue host: Flrpic 10%), (b) relative current density (J(hole)/J(electron)) with newly synthesized blue host materials in this study.



Fig. 7. Normalized EL spectra of fabricated blue PHOLEDs (at a brightness of 1000 cd/ $m^2).$

Device B: ITO/PEDOT:PSS (55 nm)/TAPC (20 nm)/mCP (10 nm)/ **CPDPy**: Flrpic (10%, 25 nm)/TmPyPB (35 nm)/LiF (1 nm)/Al (100 nm).

Device C: ITO/PEDOT:PSS (55 nm)/TAPC (20 nm)/mCP (10 nm)/ **DCPPy**: FIrpic (10%, 25 nm)/TmPyPB (35 nm)/LiF (1 nm)/AI (100 nm).

We used CH8000 (PEDOT:PSS) as a HIL to reduce the leakage current level of the devices. Meanwhile, we used TAPC and TmPyPB as a HTL and an ETL to suppress the exciton energy quenching of EML because they show higher triplet energy levels [T₁ (TAPC) = 2.9 eV; T₁ (TmPyPB) = 2.8 eV] than that of FIrpic (T₁ = 2.7 eV).

Fig. 5(a) shows the current density - voltage - luminance (I - V - V)L) characteristics of the devices fabricated in this study. At a given constant voltage of 5.0 V, current density values were recorded to 0.39, 0.49, 0.26, and 0.12 mA/cm² from **Reference**, **Device A**, **Device B** and **Device C**, respectively. The turn-on voltages (V_{on}) of 4.0, 4.0, 4.0, and 4.1 V were obtained from Reference, Device A, Device B and **Device C**, respectively. Meanwhile, the operation voltages (V_{op}) to reach 1000 cd/m^2 were 6.2, 6.3, 6.3, and 6.5 V for **Reference**, Device A, Device B, and Device C, respectively (see Table 2). At a given constant luminance of 1000 cd/m², the current and power efficiencies were 33.6 cd/A and 16.1 lm/W for Reference, 26.0 cd/A and 12.3 lm/W for Device A, 33.9 cd/A and 16.4 lm/W for Device B and 43.2 cd/A and 19.4 lm/W for Device C, respectively, as shown in Fig. 5(b) And, those are also summarized in Table 2. Those efficiency data correspond to 17.0, 13.4, 17.2 and 21.6% of EQEs for Reference and Device A, B, and C, respectively. Very interestingly, the EQE values increased the order of Device A < Reference < Device **B** < **Device C** at the given brightness of 1000 cd/m^2 as shown in Fig. 5(c) Likewise, the maximum current and power efficiencies were 36.3 cd/A and 27.2 lm/W for Reference, 31.9 cd/A and 22.3 lm/ W for Device A, 37.9 cd/A and 26.5 lm/W for Device B, 43.3 cd/A and 24.4 lm/W for **Device C**, respectively, as summarized in Table 2. In particular, maximum EQE values also increased in the order of **Device A** < **Reference** < **Device B** < **Device C** (e.g., **Reference**: 18.3%; Device A: 16.3%; Device B: 18.9%; Device C: 21.6%). As a result, we found that **Device C** (**DCPPy**) showed a better efficiency behavior than that of the other materials. Meanwhile, the device performance of **Device A** (mCPPy) and **Device B** (CPDPy) is very lower or similar to that of **Reference** (mCP).

To understand the reason of the difference in device performances, we fabricated hole only devices (HODs) as well as electron only devices (EODs) as follow (see also Fig. 4(b) and (c)):

HOD A: ITO/PEDOT:PSS (55 nm)/TAPC (20 nm)/mCP (10 nm)/ mCPPy: Flrpic (10%, 25 nm)/MoO₃ (10 nm)/Al (100 nm).

HOD B: ITO/PEDOT:PSS (55 nm)/TAPC (20 nm)/mCP (10 nm)/ CPDPy: FIrpic (10%, 25 nm) MoO₃ (10 nm)/Al (100 nm).

HOD C: ITO/PEDOT:PSS (55 nm)/TAPC (20 nm)/mCP (10 nm)/ DCPPy: Flrpic (10%, 25 nm)/MoO3 (10 nm)/Al (100 nm).

EOD A: ITO/TmPyPB (10 nm)/**mCPPy:** FIrpic (10%, 25 nm)/ TmPyPB (35 nm)/LiF (1 nm)/Al (100 nm).

EOD B: ITO/TmPyPB (10 nm)/**CPDPy:** FIrpic (10%, 25 nm)/ TmPyPB (35 nm)/LiF (1 nm)/Al (100 nm).

EOD C: ITO/TmPyPB (10 nm)/**DCPPy:** FIrpic (10%, 25 nm)/ TmPyPB (35 nm)/LiF (1 nm)/Al (100 nm).

Here, the purpose of molybdenum oxide (MoO₃) and TmPyPB in HOD and EOD devices is to block the injection of electron and hole carriers from the Al (~-4.30 eV) and ITO (~-2.90 eV) electrode, respectively. Actually, we used CH8000 (PEDOT:PSS) as a HIL to reduce the leakage current level mentioned above (see also Fig. 4(a). Commonly, CH8000 based devices exhibit maximum current efficiency at low current density, while the efficiency drops sharply at high current density which might be due to the seriously increased amount of PSS acting as an insulator [28,29]. As a result, exciton may be formed at the interface close to the anode side since the hole injection into the EML is pretty limited even at the high current density condition. Hence, it is very important to inject the electron carriers deeply into an anode side to increase the probability of charge recombination for outstanding device performances. To estimate the relative position for charge recombination, we prepared the half devices with EML doped by 10 wt% of FIrpic. Particularly, we plotted the relative current density of those devices by dividing the hole current density of HODs by the electron current density of the EODs [e.g., J(hole)/J(electron) where J: current density, mA/cm^2 as shown in Fig. 6(b), where the *I* - *V* characteristics shown in Fig. 6(a) were collected from the HODs and EODs, respectively. From this plot, we could expect that the DCPPy could give the most desirable device performance because the relative charge density value of the device fabricated with **DCPPy** showed fastest electron transporting behavior. Very interestingly, the devices fabricated with CPDPy also showed fast electron transporting behavior so that the full device also show relatively high efficiency values. In contrast, the devices containing EML with mCPPy showed poor electron transporting behavior which cannot gives high performances when it was applied to the full devices.

Fig. 7 shows the normalized EL spectra of **Reference** and **Device A-C** at the brightness of 1000 cd/m². All spectra have FIrpic emission with a peak wavelength (λ_{max}) at 472 nm for **Reference** and **Device A-C**, respectively.

4. Conclusions

In this study, we found that the introduction of carbazole moieties and dipyridyl amine moieties is very useful to prepare the host materials for highly efficient blue PHOLEDs. We could control the electron transporting properties by changing the numbers of dipyridyl amine moieties. New host materials showed moderate current efficiency as well as EQE values when it was applied to the blue PHOLEDs. Especially, we found that the selection of fast electron moving EML is profitable to prepare highly efficient blue PHOLEDs. In this study, **DCPPy** was selected as the best candidate for highly efficient blue PHOLEDs which could give high EQE up to 21.6%.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) funded by the Korea government (MSIP) (NRF-2014R1A2A2A01002417). And this research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2015R1D1A3A01020008) and this was supported by Korea National University of Transportation in 2016.

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