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Yoon-Mi Lee^a, Soo-Kang Kim^a, Chang-Jun Lee^a,
Ji-Hoon Lee^b & Jong-Wook Park^a

^a Department of Chemistry/Display Research Center,
The Catholic University of Korea, Wonmi, Bucheon,
Korea

^b Department of Polymer Science and Engineering,
Chungju National University, Chungju, Korea

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Synthesis and Hole-Transporting Properties of Ethyl-Carbazolyl Derivatives

Yoon-Mi Lee¹, Soo-Kang Kim¹, Chang-Jun Lee¹,
Ji-Hoon Lee², and Jong-Wook Park¹

¹Department of Chemistry/Display Research Center, The Catholic University of Korea, Wonmi, Bucheon, Korea

²Department of Polymer Science and Engineering, Chungju National University, Chungju, Korea

We synthesized new hole-transporting material, N,N'-diethyl-3,3'-bicarbazolyl (E-Cvz-2), 9,9'-diethyl-6-(9-ethyl-carbazol-3-yl)-3,3'-bicarbazole (E-Cvz-3), 6-(9,9'-diethyl-3,3'-bicarbazol-6-yl)-9,9'-diethyl-3,3'-bicarbazole (E-Cvz-4A) and 9-ethyl-6-(9-ethyl-3,3'-bicarbazol-6-yl)-3,9'-bicarbazole (E-Cvz-4B).

EL luminance efficiencies of E-Cvz-2, E-Cvz-3, E-Cvz-4A and E-Cvz-4B devices were found to be 4.77, 5.68, 4.27 and 4.64 cd/A, respectively, when synthesized materials are using as a HTL material. The luminance efficiency of E-Cvz-3 is 25% higher than that of NPB, a commercialized HTL material used as a reference in this study.

Keywords: carbazole; electroluminescence; hole-transporting material; OLED; Suzuki reaction

INTRODUCTION

If a material with excellent luminous efficiency of OLED device is developed, it would allow operations at a very low voltage. Highly efficient OLED device is a critical issue in simultaneously solving such problems as low operation voltage, reduction of joule-heating, and the

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Address correspondence to Prof. Jong Wook Park, Department of Chemistry/Display Research Center, The Catholic University of Korea, 43-1, Yeoksok, Wonmi, Bucheon 420-743, Korea (ROK). E-mail: hahapark@catholic.ac.kr

device life-time [1–5]. Research to realize high-efficiency is divided into research of electron transporting layer for high-efficiency device and research of high-efficiency emitting materials; and, this paper is part of research on electron transporting layer for high-efficiency. While much research on emitting layer has been carried out with OLED, research to develop hole-transporting layer (HTL) is still very insufficient. One of the most important aspects in HTL development is to maintain the efficiency of OLED device and to improve one of the most serious issues of the existing commercial materials, 4,4-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (NPB) [6] – thermal stability. This is a critical issue that is directly related to life-time.

Our research group synthesized a new HTL material by using carbazole moiety. Even though carbazole which was used in synthesis is well-known for excellent hole mobility, most studies have dealt with carbazole as an emitting material, but few studies have focused on HTL.

Here in, we report the synthesis of the ethyl-carbazole derivatives as a new hole transporting materials. The synthesized material was N,N'-diethyl-3,3'-bicarbazyl (E-Cvz-2), 9,9'-diethyl-6-(9-ethyl-carbazol-3-yl)-3,3'-bicarbazole (E-Cvz-3), 6-(9,9'-diethyl-3,3'-bicarbazol-6-yl)-9,9'-diethyl-3,3'-bicarbazole (E-Cvz-4A) and 9-ethyl-6-(9-ethyl-3,9'-bicarbazol-6-yl)-3,9'-bicarbazole (E-Cvz-4B).

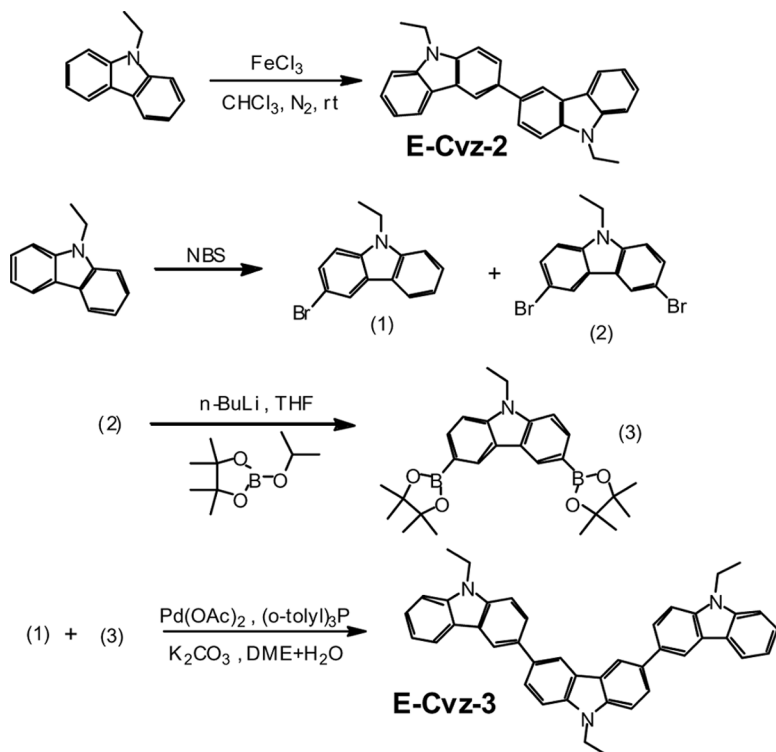
The electro-optical properties of these materials were characterized with cyclic voltammetry (CV), and UV-visible and photoluminescence (PL) spectroscopy. Moreover, multilayered EL devices were fabricated using these materials as a hole-transporting layer (HTL).

EXPERIMENTAL

Synthesis

Synthesis of N,N'-diethyl-3,3'-bicarbazyl (E-Cvz-2)

N,N'-Diethyl-3,3'-bicarbazyl (E-Cvz-2) was synthesized by the oxidative coupling reaction (see Scheme 1). To a 500 ml round flask were placed Iron(III) chloride (9.97 g, 61.5 mmol) and CHCl_3 (200 ml) under N_2 . To this mixture was very slowly added a solution of 9-ethyl-carbazole (3 g, 15.36 mmol) in chloroform (100 ml). The mixture was stirred at room temperature for 4hr. After 10% sodium hydroxide solution was added in the mixture, the aqueous solution was thoroughly extracted with chloroform. The crude product was dissolved in chloroform (10 ml) and reprecipitated slowly in methanol (200 ml). The product was collected by filtration and dried under vacuum at room



SCHEME 1 Synthetic routes of E-Cvz-2 and E-Cvz-3.

temperature. (2.5 g, 83%) (see Scheme 1). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.42(s, 2H), 8.19(d, 2H), 7.84(t, 2H), 7.51~7.41(m, 6H), 7.25(t, 2H), 4.41(q, 4H), 1.47(t, 6H); Fab^+ -Mass m/e : 388.

Synthesis of 3-bromo-9-ethyl-carbazole (1) and 3,6-dibromo-9-ethyl-carbazole (2)

9-Ethyl-carbazole (10 g, 51.2 mmol), NBS (12.35 g, 66.6 mmol) were added to 300 ml of CHCl_3 solution. The mixture was stirred at room temperature for 2 h. The product was isolated by silicagel column chromatography using EA:Hexane (1:20) as the eluent afford white solid (1) (9.3 g), and beige solid (2) (2.2 g).

Synthesis of 9-ethyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole (3)

3,6-Dibromo-9-ethyl-carbazole (2) (2 g, 5.68 mmol) was dissolved in 150 ml of dry THF solution and stirred at -78°C , then 1.6 M $n\text{-BuLi}$

14 ml was added. And then isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.6 ml, 11.63 mmol) was added to the reaction after 30 min. After the reaction finished, the reaction mixture was extracted with diethyl ether and water. The organic layer was dried by anhydrous MgSO_4 and filtered. The product was isolated by silicagel column chromatography using EA:Hexane (1:10) as the eluent afford beige solid (4) (1.28 g, 51%).

Synthesis of 9,9'-diethyl-6-(9-ethyl-carbazol-3-yl)-3,3'-bicarbazole (E-Cvz-3)

3-Bromo-9-ethyl-carbazole (1) (3.3 g, 5.9 mmol), 9-ethyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole (3) (1.2 g, 2.68 mmol), $\text{Pd}(\text{OAc})_2$ (0.18 g, 0.8 mmol) and $(\text{tris-o-tolyl})_3\text{P}$ (0.24 g, 0.8 mmol) were added to DME (300 ml) solution, then the prepared K_2CO_3 solution, which was dissolved in DME and H_2O (1:1, 100 ml) solvent, was added to reaction mixture. The mixture was heated to 100°C for 10 h under nitrogen. Reactant mixture was cooling down after 1 h and then the product was extracted by diethyl-ether. The organic layer was dried by anhydrous MgSO_4 and filtered. The solution was evaporated. The obtained solid was purified by column chromatography with CHCl_3 :Hexane (2:1) eluent to afford beige solid (E-Cvz-3) (0.55 g, 35%) $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 8.51(s, 2H), 8.45(s, 2H), 8.2(d, 2H), 7.88~7.85(m, 4H), 7.54~7.43(m, 8H), 7.25(t, 2H), 4.42(q, 6H), 1.47(t, 9H); Fab^+ -Mass m/e : 581.

Synthesis of 6,6'-dibromo-9,9'-diethyl-3,3'-bicarbazole (4)

E-Cvz-2 (4 g, 10.2 mmol), NBS (4.0 g, 22.4 mmol) were added to 200 ml of CHCl_3 solution. The mixture was stirred at room temperature for 5 h. The product was isolated by silicagel column chromatography using EA:Hexane (1:20) as the eluent afford white solid (1) (3.9 g, 70.5%).

Synthesis of 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole (5)

3-Bromo-9-ethyl-carbazole (1) (2.4 g, 8.79 mmol) was dissolved in 150 ml of dry THF solution and stirred at -78°C , then 1.6 M n-BuLi 11 ml was added. And then isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.6 ml, 17.6 mmol) was added to the reaction after 30 min. After the reaction finished, the reaction mixture was extracted with diethyl ether and water. The organic layer was dried by anhydrous MgSO_4 and filtered. The product was isolated by silicagel column chromatography using EA:Hexane (1:10) as the eluent afford beige solid (4) (2.0 g, 70%).

Synthesis of 6-(9,9'-diethyl-3,3'-bicarbazol-6-yl)-9,9'-diethyl-3,3'-bicarbazole (E-Cvz-4A)

6,6'-Dibromo-9,9'-diethyl-3,3'-bicarbazole (4) (1.5 g, 2.7 mmol), 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole (5) (2 g, 6.23 mmol), Pd(OAc)₂ (0.18 g, 0.8 mmol) and (tris-*o*-tolyl)₃P (0.24 g, 0.8 mmol) were added to DME (300 ml) solution, then the prepared K₂CO₃ solution, which was dissolved in DME and H₂O (1:1, 100 ml) solvent, was added to reaction mixture. The mixture was heated to 100°C for 10 h under nitrogen. Reactant mixture was cooling down after 1 h and then the product was extracted by diethyl-ether. The organic layer was dried by anhydrous MgSO₄ and filtered. The solution was evaporated. The obtained solid was purified by column chromatography with EA:Hexane (1:10) eluent to afford beige solid (E-Cvz-4A) (1.15 g, 55%) ¹H-NMR (500 MHz, CDCl₃) δ 8.53(d, 4H), 8.45(s, 2H), 8.2(d, 2H), 7.90~7.85(m, 6H), 7.54~7.42(m, 10H), 7.23(t, 2H), 4.42(q, 8H), 1.51(m, 12H); Fab⁺-Mass *m/e*: 774.

Synthesis of 9-ethyl-6-(9-ethyl-3,9'-bicarbazol-6-yl)-3,9'-bicarbazole (E-Cvz-4B)

6,6'-Dibromo-9,9'-diethyl-3,3'-bicarbazole (4) (1.0 g, 1.84 mmol), carbazole (0.68 g, 4.1 mmol), *t*-BuONa (1.06 g, 11 mmol), Pd₂(dba)₃ (0.1 g, 0.11 mmol) were added to dried toluene solvent (150 ml), then (*t*-Bu)₃P (22 mg, 0.11 mmol) were added into the reaction mixture. The mixture was heated to 110°C for 3 h under nitrogen. After the reaction mixture cooled, it was then acidified with 1N HCl solution, and extracted with CHCl₃. The organic layer was dried by anhydrous MgSO₄ and filtered. The solution was evaporated. The residue was dissolved in CHCl₃ and added to methanol. The precipitate was filtered and washed with methanol. The dark blue residue was purified by column chromatography with EA:Hexane (1:2) eluent to afford beige solid (E-Cvz-4B) (0.92 g, 70%) ¹H-NMR (500 MHz, CDCl₃) δ 8.36(s, 2H), 8.30(s, 2H), 8.17(d, 4H), 7.88(d, 2H), 7.62(s, 4H), 7.56(d, 2H), 7.42~7.38(m, 8H), 7.28~7.26(m, 4H), 4.50(q, 4H), 1.47(t, 6H); Fab⁺-Mass *m/e*: 718.

Characterization

¹H NMR spectra were recorded on Bruker Avance 500 spectrometers. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were obtained with a HP 8453 UV-VIS-NIR spectrometer. A Perkin Elmer luminescence spectrometer LS50 (xenon flash tube)

was used for photo- and electro-luminescence spectroscopy. The redox potentials of the compounds were determined with cyclic voltammetry (CV) using an EG&G 362 electrochemical workstation with a scanning rate of 50~200 mV/s. The synthesized materials were dissolved in N,N-dimethylformamide (DMF) with 0.1 M tetrabutylammonium tetrafluoroborate as the electrolyte. We used a platinum working electrode and a saturated Ag/AgNO₃ reference electrode. Ferrocene was used for potential calibration and for reversibility criteria.

Density functional theoretical calculations were performed using Spartan'04 (for Windows) [7]. The structures were drawn at the entry-level of input and minimized. Equilibrium geometry was obtained at the B3LYP level of DFT for each molecule at the ground state from its initial geometry subject to symmetry with a 6-31G* basis set [8]. Orbitals and energies, atomic charges, vibrational modes, and thermodynamic properties were chosen as output parameters. HOMO and LUMO orbital surfaces were then obtained from the output.

For the EL devices, all organic layers were deposited under 10⁻⁶ torr, with a rate of deposition of 1 Å/s to give an emitting area of 9 mm². The LiF and aluminum layers were continuously deposited under the same vacuum conditions.

The current-voltage (I-V) characteristics of the fabricated EL devices were obtained with a Keithley 2400 electrometer. Light intensity was obtained with a Minolta CS-100A.

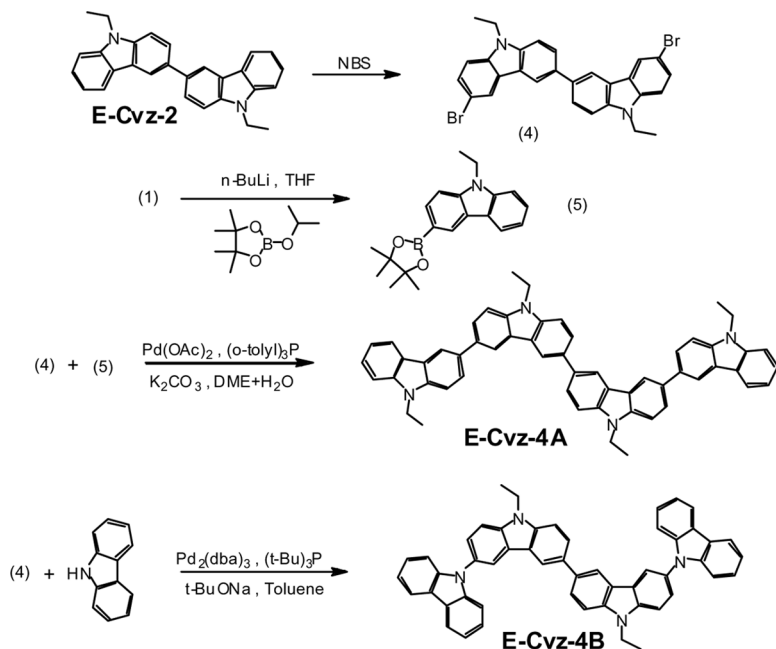
RESULTS AND DISCUSSION

Synthetic routes of four ethyl-carbazole derivatives are described in Schemes 1 and 2. All compounds were obtained by using the oxidative coupling reaction and Suzuki reaction.

Synthesized materials are placed on glass to make a film through vacuum deposition, and UV-Visible and PL spectra are measured. The data are summarized in Table 1.

UV_{onset} showed that E-Cvz-4A, which was expected to have the longest conjugation length, had the most blue-shifted value. This can be explained that: as ethyl-carbazole is substituted, steric effect between carbazoles increases and molecules are more twisted, affecting conjugation length.

The maximum absorbance of E-Cvz-2, E-Cvz-3, E-Cvz-4A and E-Cvz-4B appeared at around 311 nm, 311 nm, 308 nm and 311 nm, respectively. It was confirmed that E-Cvz-2 and E-Cvz-4B only showed shoulder in UV at (around) 350 nm. PL_{max} values of four compounds showed 433 nm (E-Cvz-2), 432 nm (E-Cvz-3), 434 nm (E-Cvz-4A) and



SCHEME 2 Synthetic routes of E-Cvz-4A and E-Cvz-4B.

432 nm (E-Cvz-4B) wavelength, which are blue colors. UV_{max} and PL_{max} values of the four materials were found to be similarly close to 310 nm and 433 nm. Based on these results, it is possible to assume that bi-ethylcarbazyl group provides a major optical property that determines UV_{max} and PL_{max} . Moreover, in terms of FWHM values, E-Cvz-2 has the sharpest peak with 43 nm, and as the number of carbazole moiety increased, FWHM value also increased. This is attributed to the inference that when molecular structure became more complex, the types of transition within molecule increased.

TABLE 1 Optical, Electrical and Thermal Properties of Synthetic Compounds

	UV_{onset} (nm)	UV_{max} (nm)	PL_{max} (nm)	FWHM (nm)	HOMO (eV)	LUMO (eV)	E_g (eV)
E-Cvz-2	392	311, 352	433	43	5.06	1.90	3.16
E-Cvz-3	383	311	432	62	4.96	1.73	3.23
E-Cvz-4A	365	308	434	62	4.91	1.62	3.39
E-Cvz-4B	384	311, 345	432	72	5.11	1.88	3.23

The ground-state structure and electron state of HOMO and LUMO were calculated by using B3LYP/6-31G* method of Spartan '04 program [7,8].

Dihedral angle between carbazole-carbazole group in carbazole derivatives was identified. E-Cvz-2, E-Cvz-3, and E-Cvz-4A with carbazole moiety increasing one by one had the dihedral angle values of 37.8 deg, 39.6 deg, and 42.5 deg, respectively. In other words, it was confirmed that molecules were twisted as carbazole was combined, which could be associated with UV_{onset} values. Dihedral angle of E-Cvz-4B was 36.2 deg, while dihedral angle between carbazole-carbazole combined with C-N was 63 deg showing a very twisted state.

Figures 1 and 2 show electron distribution of HOMO and LUMO in synthesized materials. HOMO electron density appeared to be densely distributed around the points where carbazole are combined in carbazole-carbazole bonding as shown in Figure 1. Thus, in the case of E-Cvz-3 or E-Cvz-4A, HOMO electrons were sparsely distributed at the side ends of molecules. E-Cvz-4B in which carbazoles are combined in the C-N state, electrons were evenly distributed.

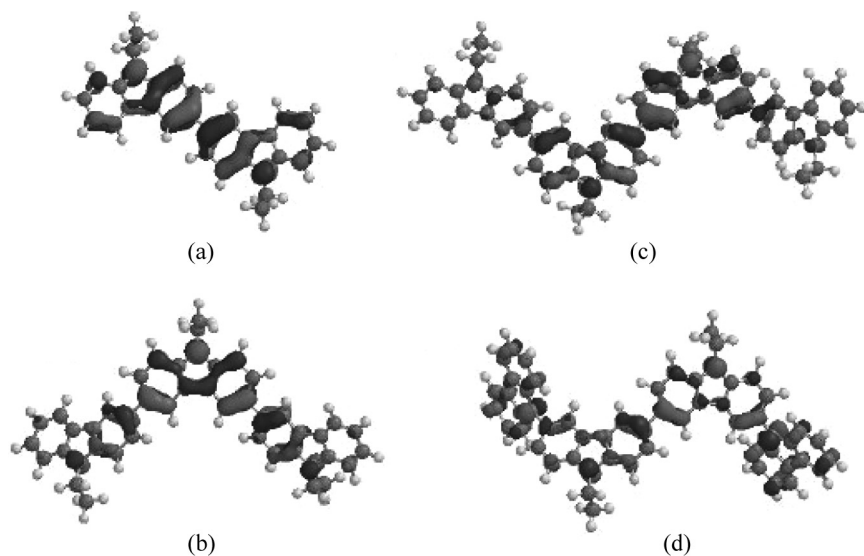


FIGURE 1 HOMO levels of (a) E-Cvz-2, (b) E-Cvz-3 (c) E-Cvz-4A and (d) E-Cvz-4B calculated at the B3LYP/6-31G* level of density functional theory with a 6-31G* basis set using Spartan '04.

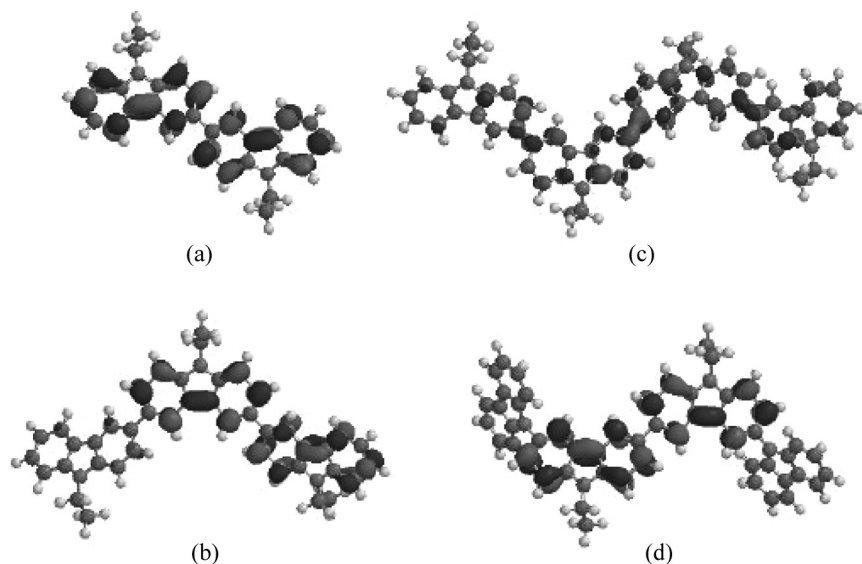


FIGURE 2 LUMO levels of (a) E-Cvz-2, (b) E-Cvz-3 (c) E-Cvz-4A and (d) E-Cvz-4B calculated at the B3LYP/6-31G* level of density functional theory with a 6-31G* basis set using Spartan '04.

LUMO electrons were also distributed overall over carbazole, E-Cvz-4B existed only in bi-carbazyl, showing a similar shape with that of E-Cvz-2.

CV was measured to identify HOMO values of synthesized materials. Even when cycles are scanned for more than 50 times or so, CV result appeared stable. This is led to a very stable hole transportation under device operation in consideration of the characteristics of HTL which continues to deliver holes in the state of radical cation.

By using band-gap identified with UV_{onset} and HOMO values measured through CV, LUMO was confirmed, which are summarized in Table 1. All four compounds are located between the CuPc HOMO value (4.7 eV) [9] and Alq₃ HOMO value (5.8 eV) [10]. This demonstrates that all synthesized materials have the proper electronic levels as a HTL. Especially the LUMO value is in 1.62~1.90 eV, higher than NPB (2.2 eV) [6] by more than 0.3 eV; it is expected to act as an EBL layer that blocks electrons transported from emitting layer under OLED device operation.

In order to identify electroluminescent property of synthesized materials, multi-layered OLED devices were fabricated. Device

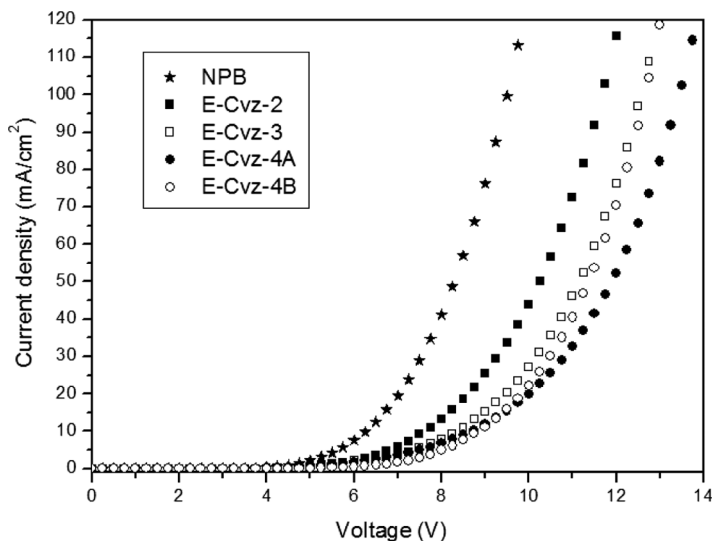


FIGURE 3 Current density-voltage characteristics of ITO/CuPc (20 nm)/synthesized material or NPB (50 nm)/Alq₃(60 nm)/LiF (1 nm)/Al devices.

structure is as follows: ITO/CuPc (20 nm)/synthesized materials (50 nm)/Alq₃ (60 nm)/LiF (1 nm)/Al (200 nm). For an objective comparison of electroluminescent properties of synthesized materials, a reference device was fabricated and NPB was used as a HTL material: ITO/CuPc (20 nm)/NPB (50 nm)/Alq₃ (60 nm)/LiF (1 nm)/Al (200 nm).

Figure 3 shows I-V curves of five types of fabricated devices. Of the synthesized materials, it was identified that E-Cvz-2 had low turn-on voltage. The device that used NPB as HTL has a curve showing relatively low turn-on.

Table 2 listed the efficiencies of new carbazole materials and NPB-based EL devices. All of these EL devices exhibited a green light emission at round 520 nm due to the Alq₃ emission. EL luminance efficiencies of E-Cvz-2, E-Cvz-3, E-Cvz-4A and E-Cvz-4B devices were found to be 4.77, 5.68, 4.27 and 4.64 cd/A, respectively. The luminance efficiency of E-Cvz-3 is 25% higher than that of NPB, a commercialized, superior HTL material used as a reference in this study.

However, power efficiency of E-Cvz-3 device is decreased 5% than NPB's because of increased operating voltage. These results mean that the carrier mobility of HTL also affects the efficiency of the EL device

TABLE 2 EL Performance of Multi-Layered Devices with the Structure: ITO/CuPc (20 nm)/Synthesized Material or NPB (50 nm)/Alq₃ (60 nm)/LiF (1 nm)/Al (200 nm)

	@ 10 mA/cm ²				@ 50 mA/cm ²			
	Voltage (V)	Brightness (cd/m ²)	Efficiency (cd/A)	Efficiency (lm/W)	Voltage (V)	Brightness (cd/m ²)	Efficiency (cd/A)	Efficiency (lm/W)
E-Cvz-2	7.6	477	4.77	1.97	10.2	2250	4.50	1.39
E-Cvz-3	8.6	598	5.68	2.07	11.5	3060	6.12	1.67
E-Cvz-4A	8.4	427	4.27	1.60	11.3	2260	4.52	1.26
E-Cvz-4B	9.1	464	4.64	1.60	11.3	2470	4.94	1.37
NPB	6.4	442	4.42	2.17	8.2	2360	4.72	1.81

in spite of the similar carrier injection. The mobility of these materials will be investigated more.

CONCLUSIONS

Ethyl-carbazole derivatives as a new hole transporting materials were synthesized. The synthesized materials were E-Cvz-2, E-Cvz-3, E-Cvz-4A and E-Cvz-4B. PL_{max} values of four compounds showed 433 nm (E-Cvz-2), 432 nm (E-Cvz-3), 434 nm (E-Cvz-4A) and 432 nm (E-Cvz-4B) wavelength, which are blue colors.

Multilayered EL devices were fabricated using these materials as a HTL. EL luminance efficiencies of E-Cvz-2, E-Cvz-3, E-Cvz-4A and E-Cvz-4B devices were found to be 4.77, 5.68, 4.27 and 4.64 cd/A, respectively. The luminance efficiency of E-Cvz-3 is 25% higher than that of NPB. However, power efficiency of E-Cvz-3 device is decreased 5% than NPB's because of increased operating voltage. These results mean that the carrier mobility of HTL also affects the efficiency of the EL device in spite of the similar carrier injection.

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