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Bifluorene compounds containing carbazole and/or diphenylamine groups and their bipolar charge transport properties in organic light emitting devices

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ABSTRACT

Novel bipolar bifluorene compounds containing carbazole and/or diphenylamine groups were synthesized by C–C and C–N coupling using a palladium catalyst. The ionization potentials of the compounds reflected the electron withdrawing or donating nature of the substituents. The charge transport properties of these compounds were evaluated from time-of-flight transient photocurrent measurements. Large transient currents (10^{-4}–10^{-3} cm^2/Vs) based on holes and electrons were observed. Hole or electron-only devices containing these compounds with *p*-type doping with MoO_3 and *n*-type with Cs showed Ohmic current density–voltage characteristics. Organic light emitting devices with homo-junction structures containing the bifluorene compounds (ITO/bifluorene:MoO_3 (50 mol%, 20 nm)/bifluorene (10 nm)/bifluorene:rubrene (60 nm)/bifluorene (10 nm)/bifluorene:Cs (30 wt.%, 20 nm)/Al) exhibited external quantum efficiencies of 1.5–2.0%.

1. Introduction

There has been a growing interest in organic light emitting devices (OLEDs) because they are expected to be the next generation in energy efficient flat panel displays and illumination light sources [1,2]. The charge balance of holes to electrons in the emitting layer is one of the important factors determining device efficiency. To ensure a well-balanced charge ratio, the host material in an emitting layer has to be bipolar, possessing both hole and electron transporting ability. The charge mobilities need to be as high as possible to reduce the driving voltage of the device. Recently host materials showing bipolar charge transport properties have been reported by several groups [3–10]. In this paper, we report the synthesis of novel bifluorene compounds incorporating carbazole and/or diphenylamine, 7,7′-bis-(*N*,*N*′-carbazolyl)-9,9,9′,9′-tetraethyl-2,2′-bifluorene (BCzBF), 7,7′-bis-(*N*,*N*′-diphenylamino)-9,9, 9′,9′-tetraethyl-2,2′-bifluorene (BDABF) and 7-(*N*-carbazole)-7′-(*N*-diphenylamine)-9,9,9′,9′-tetraethyl-2,2′-bifluorene (CzDABF). The charge mobilities of these compounds were assessed using time-of-flight (TOF) techniques. Carbazole groups are expected to endow the compounds with bipolar properties. However, the ionization potential (I_p) of a carbazole derivative should be large, like that of 4,4′,*N*,*N*′-diphenylcarbazole (CBP) (6.1 eV) [9]. This will cause a large energy barrier to hole injection from the anode which increases the driving voltage. CzDABF and BDABF which contain diphenylamine as an electron donating group were designed to decrease I_p. These bipolar materials were incorporated in OLEDs with a homo-junction structure [10,11] using *p*-type and *n*-type chemical doping [12–14]. The homo-junction device structure is effective at reducing the number of organic/organic interfaces, increasing the driving voltage and side reactions through accumulated charges [11].

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2. Experimental

2.1. Syntheses and characterization of compounds

Unless otherwise noted, all chemicals were obtained from commercial suppliers and used without further purification. ^{1}H NMR spectra were measured in deuterated solvents on a JEOL ECX 400 MHz spectrometer. Elemental analyses were carried out by the Elemental Analysis Service, Yamagata University, Japan. Thermal gravimetric analysis (TGA) was performed on Seiko SII EXSTAR 6000 and TGA/DTA 6200 analyzers. Differential Scanning Calorimetry (DSC) was performed on a Perkin–Elmer Diamond DSC calorimeter. Ionization potentials were measured with a photoelectron spectrometer surface analyzer (RIKEN KEIKI AC-3). UV–visible absorption spectra were recorded of solutions in chloroform or films on quartz with a Shimadzu UV-3150 spectrometer. PL spectra were recorded on a Jobin Yvon Fluoromax-2 fluorometer. PL quantum efficiencies were measured on a Hamamatsu C9920-01 integral sphere system under nitrogen.

Compound **2**: A mixture of 2,7-dibromo-9,9-diethylfluorene (**1**) (22.8 g, 60.0 mmol), carbazole (5.01 g, 30.0 mmol), copper (11.4 g, 180 mmol) and potassium carbonate (25.2 g, 180 mmol) in *o*-dichlorobenzene (200 ml) was stirred under reflux for 24 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water and then extracted with toluene. The combined organic phases were washed with brine and dried over $MgSO_4$. The crude mixture was purified by column chromatography on silica gel (chloroform/hexane = 1/3) affording **2** (8.61 g, 61.6%) as a white solid. ^{1}H NMR (400 Mz, $CDCl_3$, ppm) δ 0.44 (6H, t, J = 7.4 Hz), 2.02–2.07 (4H, m), 7.26–7.32 (2H, m), 7.39–7.45 (4H, m), 7.49–7.55 (4H, m), 7.64 (1H, d, J = 8.8 Hz), 7.89 (1H, d, J = 8.8 Hz), 8.16 (1H, d, J = 7.8 Hz).

BCzBF: A mixture of **2** (4.20 g, 9.00 mmol), bis(pinacolato)diboron (2.00 g, 15.0 mmol), $PdCl_2$(dppf) (0.183 g, 0.225 mmol), and potassium acetate (2.21 g, 22.5 mmol) in DMSO (350 ml) was stirred at 80 °C for 8 h under a nitrogen atmosphere. After cooling the solution to room temperature, **2** (3.80 g, 6.00 mmol), $PdCl_2$(dppf) (0.183 g, 0.225 mmol) and 2 M aqueous potassium carbonate (10 ml, 5.0 eq) were added and the mixture was stirred at 80 °C under nitrogen overnight. The mixture was cooled to room temperature and then the product was extracted with chloroform and washed with water, brine and dried over $MgSO_4$. The crude mixture was purified by column chromatography on silica gel (chloroform/hexane = 1/2), giving BCzBF as a yellow solid. The product was further purified by train sublimation. Yield: 2.08 g, 35.4%. ^{1}H NMR (400 Mz, $CDCl_3$, ppm) δ 0.53 (12H, t, J = 7.4 Hz), 2.08–2.23 (8H, m), 7.30–7.34 (6H, m), 7.42–7.46 (6H, m), 7.53–7.59 (4H, m), 7.69 (2H, s), 7.75 (2H, d, J = 7.4 Hz), 7.75 (2H, d, J = 8.1 Hz), 7.96 (2H, d, J = 7.5 Hz), 8.18 (4H, d, J = 8.0 Hz). Elemental Anal. Calcd for $C_{58}H_{48}N_2$: C, 90.12; H, 6.26; N, 3.62. Found C, 89.93; H, 6.26; N, 3.56%.

Compound **3**: A mixture of **1** (5.89 g, 15.5 mmol), diphenylamine (1.31 g, 7.75 mmol), $Pd(OAc)_2$ (34.8 mg, 0.155 mmol), 1,1′-bis(diphenylphosphino)ferrocene (0.687 g, 1.24 mmol) and sodium *tert*-butoxide (1.49 g, 23.4 mmol) in toluene (60 ml) was stirred under reflux for 24 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water and then extracted with toluene. The combined organic phases were washed with brine and dried over $MgSO_4$. The product was purified by column chromatography on silica gel (chloroform/hexane = 1/3), affording **3** (2.09 g, 57.6%) as a white solid. ^{1}H NMR (400 Mz, $CDCl_3$, ppm) δ 0.35 (6H, t, J = 6.5 Hz), 1.9 (4H, t, J = 7.8 Hz), 7.00 (3H, t, J = 7.3 Hz), 7.06 (1H, s), 7.10 (4H, d, J = 7.3 Hz), 7.21–7.27 (4H, m), 7.39–7.47 (3H, m), 7.52 (1H, d, J = 8.2 Hz).

BDABF: A mixture of **3** (1.20 g, 2.56 mmol), bis(pinacolato)diboron (0.541 g, 2.13 mmol), $PdCl_2$(dppf) (60.0 mg, 0.0768 mmol) and potassium acetate (0.627 g, 6.39 mmol) in DMSO (60 ml) was stirred at 80 °C for 5 h under a nitrogen atmosphere. After cooling the solution to room temperature, **3** (0.80 g, 1.70 mmol), $PdCl_2$(dppf) (0.04 g, 0.0510 mmol) and 2 M aqueous potassium carbonate (5.5 ml, 5.0 eq) were added and the mixture was stirred at 80 °C under nitrogen overnight. The mixture was cooled to room temperature and then the product was extracted with chloroform and washed with water, brine and dried over $MgSO_4$. The product was purified by column chromatography on silica gel (chloroform/hexane = 1/2), giving BDABF (0.880 g, 53.2%) as a yellow solid. The product was further purified by train sublimation. Yield: 0.801 g, 47.9%. ^{1}H NMR (400 Mz, $CDCl_3$, ppm) δ 0.42 (12H, t, J = 7.32 Hz), 1.9–2.1 (8H, m), 7.00–7.07 (6H, m), 7.13 (10H, d, J = 8.1 Hz), 7.23–7.28 (8H, m), 7.55–7.69 (8H, m). Elemental Anal. Calcd for $C_{58}H_{52}N_2$: C, 89.65; H, 6.75; N, 3.61. Found C, 89.65; H, 6.82; N, 3.48%.

Compound **4**: *n*-Butyl lithium (1.6 M, 49.3 ml, 78.9 mmol) was added to a stirred solution of **1** (30.0 g, 78.9 mmol) in dry THF (500 ml) under a nitrogen atmosphere at −78 °C. After stirring for 0.5 h, trimethylchlorosilane (11.1 ml, 94.7 mmol) was added. The mixture was warmed to room temperature, then the product was extracted with chloroform and washed with water, brine and dried over $MgSO_4$. The crude mixture was purified by column chromatography on silica gel (hexane) to give **4** (27.6 g, 93.7%) as a colorless oil. ^{1}H NMR (400 Mz, $CDCl_3$, ppm) δ 0.28–0.35 (15H, m), 1.95–2.06 (4H, m), 7.41–7.46 (4H, m), 7.48 (1H, d, J = 7.5 Hz), 7.56 (1H, d, J = 8.7 Hz), 7.65 (1H, d, J = 7.3 Hz).

Compound **5**: *n*-Butyl lithium (1.6 M, 55.3 ml, 88.7 mmol) was added to a stirred solution of **1** (27.5 g, 73.8 mmol) in dry THF (500 ml) under a nitrogen atmosphere at −78 °C. After stirring for 0.5 h, trimethylchlorosilane (27.2 ml, 133 mmol) was added. The mixture was cooled to room temperature, then the product was extracted with chloroform and washed with water, brine and dried over $MgSO_4$. The crude mixture was purified by column chromatography on silica gel (hexane) followed by recrystallization from toluene/ethanol = 1/4 to give **5** (21.9 g, 52.0 mmol) as a white solid. ^{1}H NMR (400 Mz, $CDCl_3$, ppm) δ 0.26–0.32 (15H, m), 1.4 (12H, s), 2.0–2.1 (4H, m), 7.45 (1H, s), 7.49 (1H, d, J = 7.3 Hz), 7.70 (2H, d, J = 7.3 Hz), 7.75 (4H, s), 7.8 (1H, d, *J = 7.3 Hz).*

Compound **6**: A mixture of **2** (5.68 g, 12.2 mmol), **5** (6.14 g, 14.6 mmol), $Pd(PPh_3)_4$ (0.28 g, 0.244 mmol) and 2 M aqueous potassium carbonate (5.00 g, 36.6 mmol) in toluene (60 ml) and ethanol (30 ml) was stirred under reflux for 24 h under nitrogen. After cooling to room temperature, the mixture was poured into water and then extracted with toluene. The combined organic phases were washed with brine and dried over $MgSO_4$. The crude mixture was purified by column chromatography on silica gel (chloroform/hexane = 2/3), affording **6** (6.32 g, 76.1%) as a white solid. ^1H NMR (400 Mz, $CDCl_3$, ppm) δ 0.33 (9H, s), 0.42 (6H, t, $J = 7.3$ Hz), 0.51 (6H, t, $J = 7.4$ Hz), 2.0–2.2 (8H, m), 7.28–7.35 (2H, m), 7.44–7.56 (8H, m), 7.63–7.74 (5H, m), 7.80 (1H, d, $J = 7.8$ Hz), 7.86 (1H, d, $J = 8.2$ Hz), 7.95 (1H, d, $J = 7.8$ Hz), 8.19 (2H, d, $J = 7.8$ Hz).

Compound **7**: A mixture of **6** (6.50 g, 9.55 mmol) and iodine monochloride (1 M in CH_2Cl_2, 10.5 ml, 10.5 mmol) in CH_2Cl_2 (80 ml) was stirred at 0 °C for 1 h under nitrogen. After cooling to room temperature, the mixture was poured into water and then extracted with toluene. The combined organic phases were washed with brine and dried over $MgSO_4$. The crude mixture was purified by column chromatography on silica gel (chloroform/hexane = 1/3), affording **7** (4.60 g, 65.6%) as a white solid. ^1H NMR (400 Mz, $CDCl_3$, ppm) δ 0.40 (6H, t, $J = 7.8$ Hz), 0.51 (6H, t, $J = 7.8$ Hz), 2.0–2.2 (8H, m), 7.28–7.35 (2H, m), 7.44 (4H, d, $J = 4.2$ Hz), 7.50 (1H, d, $J = 3.2$ Hz), 7.53–7.71 (8H, m), 7.76 (1H, d, $J = 7.8$ Hz), 7.77 (1H, d, $J = 7.8$ Hz), 7.85 (1H, d, $J = 7.8$ Hz), 7.95 (2H, d, $J = 7.8$ Hz).

CzDABF: A mixture of **7** (3.50 g, 4.77 mmol), diphenylamine (1.21 g, 7.16 mmol), $Pd_2(dba)_3$ (34.9 mg, 0.0382 mmol), tri(*tert*-butyl)phosphine (0.0114 ml, 0.0477 mmol) and sodium *tert*-butoxide (0.688 g, 7.16 mmol) in toluene (60 ml) was stirred under reflux for 24 h under nitrogen. After cooling to room temperature the mixture was poured into water and then extracted with toluene. The combined organic phases were washed with brine and dried over $MgSO_4$. The crude mixture was purified by column chromatography on silica gel (chloroform/hexane = 1/2), affording *CzDABF* (2.17 g, 58.7%) as a white solid. The product was further purified by train sublimation. Yield: 0.801 g, 51.7%. ^1H NMR (400 Mz, $CDCl_3$, ppm) δ 0.44 (6H, t, $J = 7.0$ Hz), 0.51 (6H, t, $J = 6.8$ Hz), 1.9–2.2 (8H, m), 7.00–7.07 (3H, m), 7.14 (5H, d, $J = 7.2$ Hz), 7.25–7.30 (6H, m), 7.44 (4H, d, $J = 3.6$ Hz), 7.53–7.72 (8H, m), 7.85 (1H, d, $J = 8.2$ Hz), 7.94 (1H, d, $J = 7.8$ Hz), 8.17 (2H, d, $J = 7.8$ Hz). Elemental Anal. Calcd for $C_{58}H_{50}N_2$: C, 89.88; H, 6.50; N, 3.61. Found C, 89.75; H, 6.51; N, 3.58%.

2.2. Device fabrication and characterization

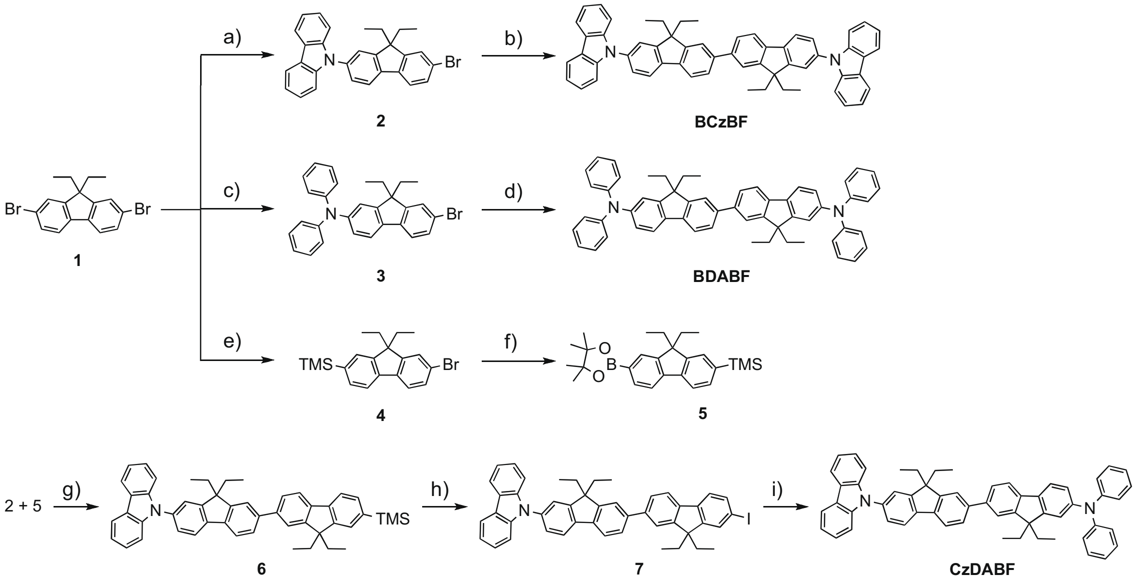
Light emitting devices were fabricated on indium tin oxide (ITO) coated glass substrates, which were prepared by ultrasonication sequentially in detergent, methanol, 2-propanol and acetone, then exposed to UV-ozone under ambient conditions for 15 min. MoO_3, Cs, rubrene and the bipolar materials were deposited by thermal evaporation at less than 1×10^{-4} Pa. Finally, the aluminum cathode was deposited through a shadow mask at less than 1×10^{-4} Pa. The active area of each device is 2 mm × 2 mm. Layer thickness calibration was performed using a Dektak 3 surface profilometer. The EL spectra were measured on a Hamamatsu PMA-11 photonic multichannel analyzer. The current–voltage (I–V) characteristics and luminance of the devices were measured using a Keithley 2400 Source Meter and Konica Minolta CS-200 chromameter, respectively. External quantum efficiencies were calculated assuming a Lambertian emission pattern and considering all spectral features in the visible region.

3. Results and discussion

Scheme 1 shows the synthetic routes to the carbazole and/or diphenylamine substituted-difluorene derivatives. Monocarbazolyl compound **2** was synthesized by an Ullmann coupling reaction between **1** and carbazole. After synthesis of the boronic ester derivative of **2** by the reaction of *bis*-(pinacolato)diboron and **1** with a palladium catalyst, dicarbazolyl compound BCzBF was synthesized successively in the same pot, *via* palladium-catalyzed Suzuki coupling of **2** with the boronic ester derivative of **2**. **3** was synthesized by palladium-catalyzed C–N coupling between **1** and diphenylamine. BDABF was synthesized in the same manner as BCzBF. In the synthesis of CzDABF, the coupling reaction between **2** and the boronic ester of **3** and the coupling reaction between **3** and boronic ester **2** gave a small amount of BCzBF or BDABF, respectively, as byproducts because of a homocoupling side reaction. These byproducts are difficult to remove from CzDABF because of their similar structure and polarity. Therefore, CzDABF was synthesized using a different route. **6** was obtained from a coupling reaction between **2** and **5**, then reacted with ICl to form **7**. Finally, a diphenylamine group was introduced to **7**, giving CzDABF.

TGA showed that the decomposition temperatures (T_d) with loss of 5 wt.% of the compounds were over 400 °C. The glass transition temperatures (T_g) of BDABF and CzDABF determined by DSC were higher than 100 °C. On the other hand, a T_g for BCzBF, which has a symmetrical structure and rigid carbazole substituents, was not observed in our experiment, probably because of its high crystallinity.

The UV absorption and PL spectra of the compounds were measured in the solution state and in the film state on a quartz substrate (Table 1). Absorption and PL maxima exhibited red shifts as the number of diphenylamine groups increased, suggesting that the electron donating diphenylamine group reduced the HOMO (highest occupied molecular orbital)–LUMO (lowest unoccupied molecular orbital) gap of the compounds. The ionization potentials (I_p) of the compounds were measured by ultraviolet photoelectron yield spectroscopy under atmospheric conditions. The I_p increased as the number of diphenylamine groups increased because diphenylamine moieties are better at donating electron density than carbazole moieties, which increases the HOMO energy level. Tentative electron affinity (E_a) values were estimated from the difference between I_p and the optical energy gap obtained from the edge of the UV absorption of the films. As the number of diphenylamine groups increased, the E_a of the compounds decreased and the I_p increased. DFT calculations



Scheme 1. Synthetic route to the bipolar compounds. (a) carbazole, Cu, K_2CO_3, dichlorobenzene, 180 °C, 20 h, (b) (i) $Pd(dppf)Cl_2$, KOAc, bis(pinacolato)diboron, DMF, 80 °C 3 h; (ii) **2**, $Pd(dppf)Cl_2$, K_2CO_3, 80 °C, 20 h, (c) diphenylamine, $Pd(OAc)_2$, 1,1′-bis(diphenylphosphino)ferrocene, NaO-*t*-Bu, toluene, reflux, 20 h, (d) (i) $Pd(dppf)Cl_2$, KOAc, bis(pinacolato)diboron, DMF, 80 °C 3 h; (ii) **3,** $Pd(dppf)Cl_2$, K_2CO_3, 80 °C 20 h, (e) (i) *n*-BuLi, −78 °C 1 h; (ii) $(CH_3)_3SiCl$, −78 °C to r.t., 20 h, (f) (i) *n*-BuLi, −78 °C 1 h; (ii) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, −78 °C to r.t., 9 h, (g) $Pd(PPh_3)_4$, K_2CO_3 *aq*., toluene, ethanol, reflux, 20 h, (h) ICl, dichloromethane, 0 °C, 1 h, (i) $Pd_2(dba)_3$, tri(*t*-butyl)phosphine, NaO-*t*-Bu, toluene, reflux, 24 h.

Table 1
Thermal and optoelectrochemical properties and charge mobilities of the bipolar compounds.

	T_g (°C)	$T_{d5\%}$ (°C)	UV[a] (nm)	PL[a] (nm)	I_p (eV)	E_a[b] (eV)	E_g^{OPT}[a] (eV)	HOMO[c] (eV)	LUMO[c] (eV)	μ_h ($cm^2V^{-1}s^{-1}$)	μ_e ($cm^2\ V^{-1}s^{-1}$)
BCzBF	N.D.	477	350, 297	425	5.98	2.89	3.09	5.51	1.85	2.3×10^{-3}	1.5×10^{-3}
BDABF	106	417	380, 310	452	5.57	2.69	2.88	5.16	1.72	1.0×10^{-3}	N.D.
CzDABF	126	447	377, 299	449	5.76	2.79	2.93	5.02	1.58	1.3×10^{-4}	1.3×10^{-3}

[a] Neat film.
[b] $E_a = I_p - E_g^{OPT}$.
[c] Obtained from DFT calculations using B3LYP 6311+G(d,p)//631G(d).

showed that the HOMO energy levels of BCzBF and BDABF are delocalized over the whole molecule, while the HOMO of CzDABF is localized on the diphenylamine and bifluorene units. On the other hand, the LUMOs of all three compounds are localized on the bifluorene unit (Fig. S1). HOMO and LUMO levels estimated from the calculations were consistent with the values obtained experimentally for I_p and E_a.

The charge transport properties of the compounds were investigated by the TOF transient photocurrent technique at room temperature (Fig. 1). The carrier transit times were determined from the folding point in the double-logarithmic plots of the data (insets in Fig. 1). The hole mobilities of all three compounds were high, comparable to the mobilities of common hole transporting materials [15]. BDABF did not exhibit a photocurrent during measurement of electron mobility. On the other hand, BCzBF and CzDABF showed sufficient electron photocurrent to determine their electron mobilities. The electron mobilities of these two compounds were as high as their hole mobilities, and much higher than the electron mobility of 10^{-6}–$10^{-7}\ cm^2V^{-1}s^{-1}$ of the well-known electron transporting material, *tris*-(8-hydroxyquinoline) aluminum (Alq_3). These results demonstrate that the diphenylamine group increased the hole transport ability of bifluorene, while the carbazole group gave the compound bipolar charge transport abilities. The bipolar charge transport properties of these carbazole compounds are consistent with previously reported bipolar compounds such as CBP [9].

Fig. 2 shows the current density–voltage (*J*–*V*) characteristics of the hole-only devices containing *p*-doped bipolar compounds (ITO/bifluorene:MoO_3 50 mol% (120 nm)/Au) and undoped bifluorene (ITO/bifluorene (120 nm)/Au). While the undoped hole-only devices exhibited low current densities, the current density of the *p*-doped hole-only devices increased considerably in an Ohmic manner. The conductivities of the *p*-doped devices at $4.0 \times 10^5\ Vcm^{-1}$ were $1.5 \times 10^{-6}\ Scm^{-1}$, $1.7 \times 10^{-6}\ Scm^{-1}$ and $1.1 \times 10^{-6}\ Scm^{-1}$ for BCzBF, BDABF and CzDABF, respectively. Similarly, electron-only devices containing

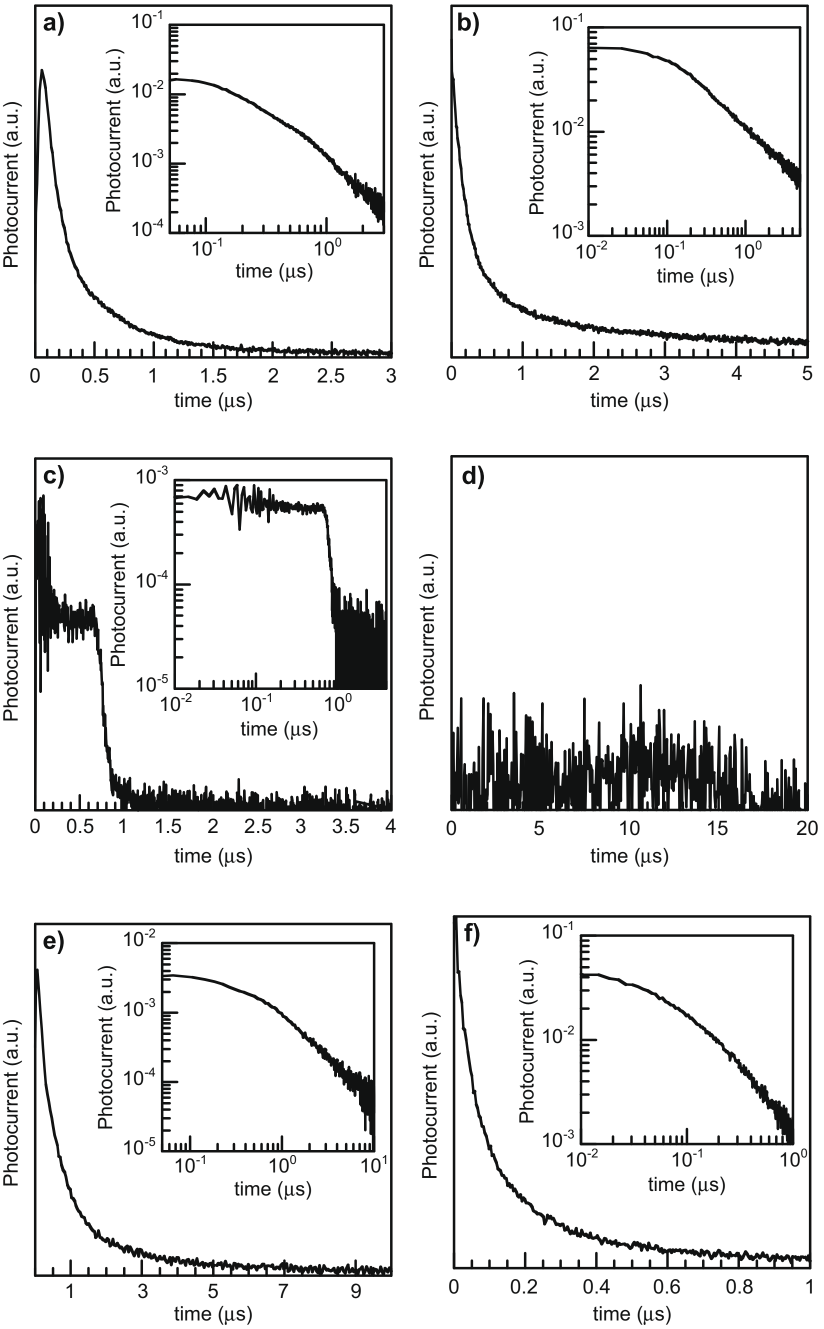


Fig. 1. Time-of-flight (TOF) transients of the bipolar compounds: (a) BCzBF, hole, $E^{1/2} = 700\ (\mathrm{V/cm})^{1/2}$, $d = 3.0\ \mu\mathrm{m}$. (b) BCzBF, electron, $E^{1/2} = 700\ (\mathrm{V/cm})^{1/2}$, $d = 8.0\ \mu\mathrm{m}$. (c) BDABF, hole, $E^{1/2} = 700\ (\mathrm{V/cm})^{1/2}$, $d = 3.0\ \mu\mathrm{m}$. (d) BDABF, electron, $E^{1/2} = 700\ (\mathrm{V/cm})^{1/2}$, $d = 3.0\ \mu\mathrm{m}$. (e) CzDABF, hole, $E^{1/2} = 700\ (\mathrm{V/cm})^{1/2}$, $d = 3.0\ \mu\mathrm{m}$. (f) CzDABF, electron, $E^{1/2} = 700\ (\mathrm{V/cm})^{1/2}$, $d = 3.0\ \mu\mathrm{m}$.

n-doped bipolar compounds (ITO/BCP (10 nm)/bifluorene:Cs 30 wt.% (120 nm)/Au) and undoped bipolar compounds (ITO/BCP (10 nm)/bifluorene (100 nm)/Au) were fabricated. The Cs-doped electron-only devices exhibited conductivities that were seven orders of magnitude higher than the undoped electron-only devices. At $4.0 \times 10^{5}\ \mathrm{Vcm}^{-1}$, the conductivities of the *n*-doped electron-only devices were $4.7 \times 10^{-6}\ \mathrm{Scm}^{-1}$, $1.0 \times 10^{-6}\ \mathrm{Scm}^{-1}$ and $1.2 \times 10^{-6}\ \mathrm{Scm}^{-1}$ for BCzBF, BDABF and CzDABF, respectively. These results demonstrate that the bifluorene compounds have small enough I_p to be *p*-doped and E_a to be *n*-doped effectively, in addition to their bipolar charge transport ability in an undoped state.

OLEDs with a homo-junction structure were fabricated containing BCzBF and CzDABF with the device configurations: device I = ITO/bifluorene:$\mathrm{MoO_3}$ (50 mol%, 20 nm)/

bifluorene (80 nm)/bifluorene:Cs (30 wt.%, 20 nm)/Al (80 nm) and device II = ITO/bifluorene:MoO_3 (50 mol%, 20 nm)/ bifluorene (10 nm)/bifluorene: rubrene (20 wt.%, 60 nm)/ bifluorene (10 nm)/bifluorene: Cs (30 wt.%, 20 nm)/Al (80 nm). Fig. 4a shows the PL spectra of the bipolar compounds and the EL spectra of the OLED. The EL spectra of device I did not correspond to the PL spectra of the bipolar compounds. This might be caused by absorption in the blue region by a radical species in the doped layers or exciplex emission in the interface between the doped and undoped layers. External quantum efficiencies (EQE) of device I were low at around 0.5% at 100 cd m^{-2} (Table 2). The low EQE of these devices were probably caused by the lack of an energy barrier between the layers making charge recombination poor and exciton quenching caused by the close proximity of doped layers to the emission zone. Device II was fabricated with rubrene doped into the emission layer to efficiently trap carriers and undoped bifluorene layers between the emission layer and the doped layers to prevent quenching. For device II, only yellow emission derived from

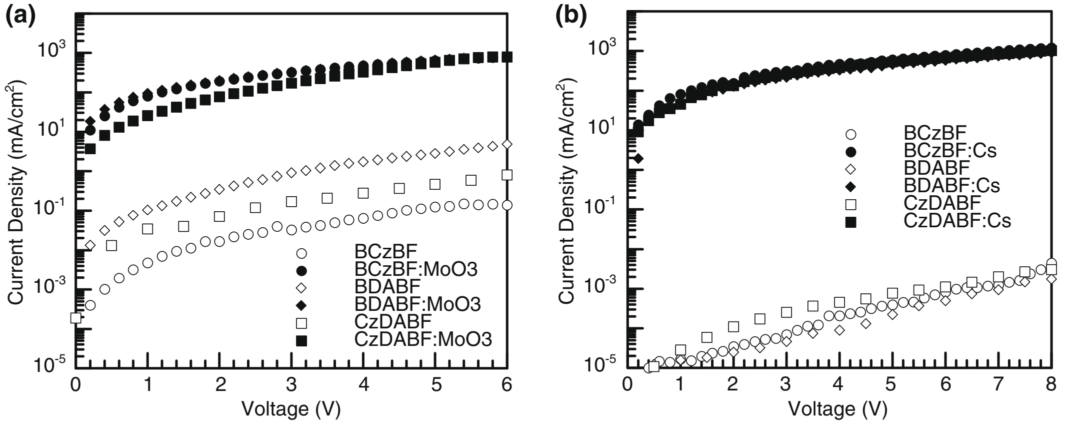


Fig. 2. Current density–voltage characteristics of (a) hole-only devices (ITO/bifluorene or bifluorene:MoO_3 (120 nm)/Au) and (b) electron-only devices (ITO/ BCP (10 nm)/bifluorene or bifluorene:Cs (100 nm)/Al).

Table 2
Turn-on voltage at 1 cd m^{-2} and efficiencies at 100 cd m^{-2} and 1000 cd m^{-2} of OLEDs containing bipolar compounds.

EML	V_{on} (V)	100 cd m^{-2}				1000 cd m^{-2}			
		Voltage (V)	P.E. (lm W^{-1})	C.E. (cd A^{-1})	E.Q.E. (%)	Voltage (V)	P.E. (lm W^{-1})	C.E. (cd A^{-1})	E.Q.E. (%)
BCzBF	3.0	5.5	0.68	1.2	0.56	8.8	0.27	0.75	0.37
BCzBF:rubrene	3.8	7.0	2.9	6.5	2.1	10.4	1.4	4.5	1.5
CzDABF	3.0	5.2	0.76	1.3	0.49	8.2	0.32	0.84	0.35
CzDABF:rubrene	3.1	4.6	3.1	4.6	1.5	6.9	1.5	3.4	1.1

P.E., power efficiency; C.E., current efficiency; E.Q.E., external quantum efficiency.

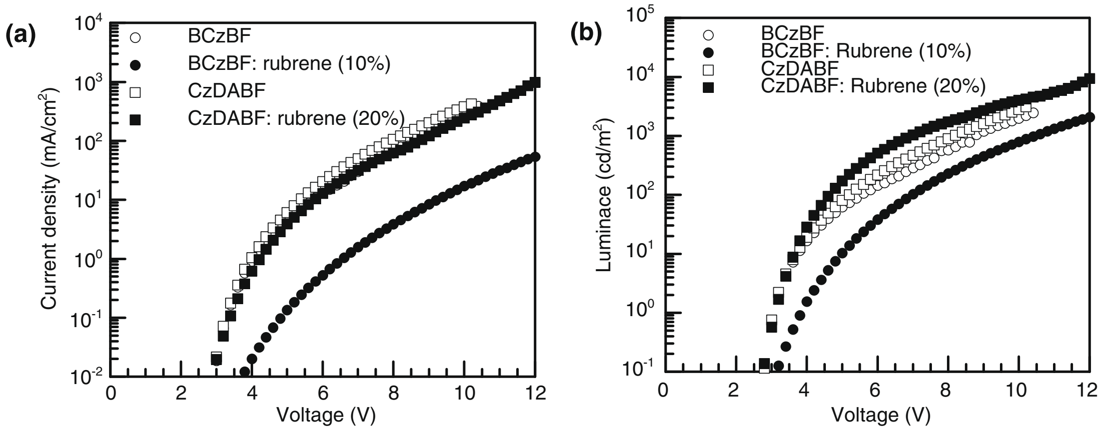


Fig. 3. (a) Current density–voltage and (b) luminance–voltage characteristics of OLEDs.

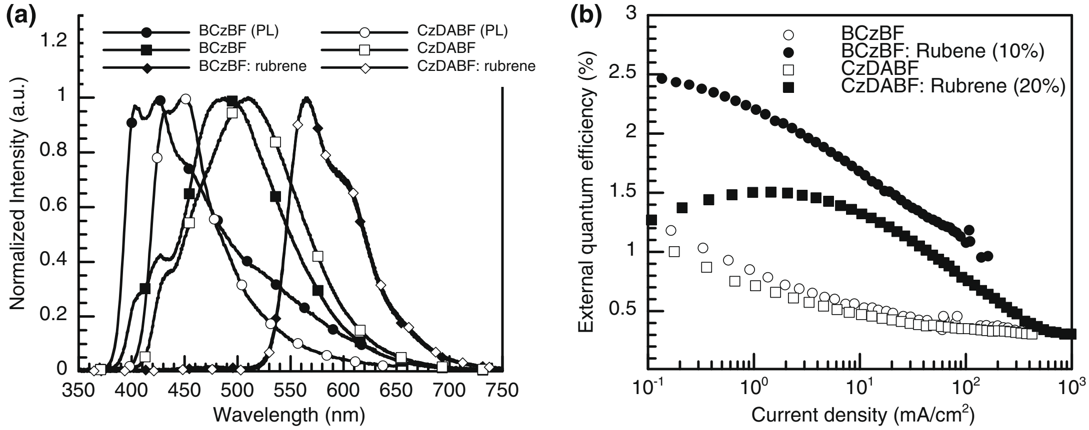


Fig. 4. (a) EL spectra and (b) quantum efficiency–current density characteristics of OLEDs containing the bipolar compounds.

rubrene was observed (Fig. 4a). Although the driving voltages increased compared to those of device I because of carrier trapping by rubrene (Fig. 3a), device II exhibited higher EQEs than that of device I (Fig. 4b). The maximum EQE of 1.5% for device II containing CzDABF is consistent with the theoretical EQE of 1.35% estimated from the PL quantum yield of 27% of 20 wt.% rubrene in CzDABF. Doping concentrations of rubrene of less than 20 wt.% increase the PL quantum yield, but incomplete carrier trapping causes emission from the bifluorene host and results in lower overall EQE. The homo-junction structure of the OLEDs was expected to extend the lifetimes of the devices because of a lack of organic interfaces but the lifetime measurements did not show an improvement over typical device structures. Further detailed investigations are under way and will be presented in the future.

4. Conclusion

Bipolar fluorene compounds were synthesized by palladium-catalyzed C–C and C–N coupling reactions. The energy levels of these compounds were related to the number of carbazole and diphenylamine groups. TOF measurements demonstrated that these compounds have bipolar charge transport abilities. Hole mobilities were as high as that of NPD and electron mobilities were much higher than that of Alq_3. These bifluorene compounds have small enough I_p to be *p*-doped and E_a to be *n*-doped. Hole- and electron-only devices containing these compounds with *p*-type doping with MoO_3 and *n*-type with Cs showed Ohmic current density–voltage characteristics. OLEDs with a homo-junction structure containing these bipolar compounds as the emitting material exhibited poor efficiencies. Addition of rubrene as an emitting material into these devices improved the EQEs to 1.5–2.0%.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.orgel.2010.01.010.

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