



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} cm²/Vs) based on holes and electrons were observed. Hole or electron-only devices containing these compounds with *p*-type doping with MoO₃ 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:MoO₃ (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%.

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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. ^1H 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 KEI-KI 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. ^1H 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), $\text{PdCl}_2(\text{dppf})$ (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), $\text{PdCl}_2(\text{dppf})$ (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%. ^1H 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 $\text{C}_{58}\text{H}_{48}\text{N}_2$: 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), $\text{Pd}(\text{OAc})_2$ (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. ^1H 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), $\text{PdCl}_2(\text{dppf})$ (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), $\text{PdCl}_2(\text{dppf})$ (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%. ^1H 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 $\text{C}_{58}\text{H}_{52}\text{N}_2$: 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. ^1H 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. ^1H 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).

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