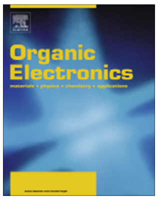
Organic Electronics 13 (2012) 351–355

Contents lists available at SciVerse ScienceDirect

Organic Electronics

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



Synthesis of an aromatic amine derivative with novel double spirobifluorene core and its application as a hole transport material

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ARTICLE INFO

Article history:
Received 18 August 2011
Received in revised form 25 October 2011
Accepted 22 November 2011
Available online 14 December 2011

Keywords:
Double spirobifluorene core
Hole transport material
High efficiency
High glass transition temperature

ABSTRACT

A synthetic method to prepare a novel double spirobifluorene core structure was developed and a hole transport type exciton blocking material with the double spirobifluorene core was synthesized. A two step ring closing method was used to synthesize the double spirobifluorene core. The double spirobifluorene core based hole transport material showed high glass transition temperature due to rigid structure, and high quantum efficiency in green phosphorescent organic light emitting diodes because of efficient hole injection and triplet exciton blocking properties.

1. Introduction

Organic light-emitting diodes (OLEDs) have been developed for more than 20 years and are being used in display and lighting applications. Various organic emitters and charge transport materials were synthesized for OLED applications and one of the well-known core structures is spirobifluorene. The spirobifluorene core has been widely used due to the merits of thermal stability, morphological stability, chemical stability, chemical versatility and high triplet energy [1–10].

As the spirobifluorene moiety was effective as the core structure of hole transport materials and emitters, many derivatives of the spirobifluorene were synthesized [11–17]. Among the various spirobifluorene compounds, dispirobifluorene based compounds were better than spirofluorene in terms of light-emitting efficiency, thermal and morphological stability [18–22]. Dispirofluorene–indenofluorene based compounds were synthesized as the double spiro type compounds [18–22]. Other than these, several dispiro-fused fluorene compounds were reported [23,24]. However, further development of new double spirobifluorene based compounds is required.

In this work, a new core structure with a double spirobifluorene moiety was developed as a thermally stable core and the synthetic procedure to prepare the double spirobifluorene structure was studied. It was demonstrated that two step ring closing procedure can be used to synthesize the double spirobifluorene core. In addition, the application of the new double spirobifluorene core based compound as the hole transport material for phosphorescent organic light emitting diodes (PHOLEDs) was investigated.

2. Experimental

2.1. General information

1,2-Dibromobenzene, *n*-butyllithium (*n*-BuLi), sodium-*t*-butoxide, palladium(II)acetate, diphenylamine and chlorodiphenylphosphine (Aldrich Chem. Co.) were used without further purification. Hydrogen peroxide (Duksan Sci. Co.) and 2,7-dibromofluorenone (P&H Co.) were used as received. Tetrahydrofuran (THF) was distilled over sodium and calcium hydride.

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doi:10.1016/j.orgel.2011.11.028

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian 200 (200 MHz) spectrometer. The photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (HITACHI, F-7000) and the ultraviolet–visible (UV–Vis) spectra were obtained using UV–Vis spectrophotometer (Shimadzu, UV-2501PC). Samples were dissolved in THF at a concentration of 1.0×10^{-4} M. The differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 822 under nitrogen at a heating rate of 10 °C/min. The mass spectrometry (MS) was performed using a JEOL, JMS-AX505WA spectrometer in fast atom bombardment mode. Cyclic voltametry (CV) measurement of organic material was carried out in acetonitrile solution with tetrabutylammonium perchlorate at 0.1 M concentration. Ferrocene was used as the internal standard material. Elemental analysis of the materials was carried out using EA1110 (CE instrument).

2.2. Synthesis

2.2.1. 2′,7′-Dibromo-spiro(cyclopenta[def]fluorene-1,5,9′9″-bifluorene)

4-Bromo-9,9′-spirobi[fluorene] (5.70 g, 14.40 mmol) was dissolved in anhydrous THF (76 mL) under ambient atmosphere. The reaction flask was cooled to −78 °C and *n*-BuLi (2.5 M in hexane, 7.49 mL) was added dropwise slowly. Stirring was continued for 2 h at −78 °C, followed by addition of a solution of 2,7-dibromo-fluorenone (6.33 g, 18.70 mmol) in anhydrous THF (123 mL) under nitrogen atmosphere. The resulting mixture was gradually warmed to ambient temperature and quenched by adding saturated, aqueous sodium bicarbonate (200 mL). The mixture was extracted with dichloromethane. The combined organic layers were dried over magnesium sulfate, filtered, and evaporated under reduced pressure. A yellow powdery product was obtained. The crude residue was placed in another two-neck flask (250 mL) and dissolved in acetic acid (150 mL). A catalytic amount of sulfuric acid (15 mL) was then added and the whole solution was refluxed for 12 h. After cooling to ambient temperature, purification by silica gel chromatography using dichloromethane/*n*-hexane gave a white powder.

^{1}H NMR (200 MHz, $CDCl_3$): 8.26 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 7.2 Hz, 2H), 7.71∼7.54 (m, 4H), 7.39 (t, J = 7.2 Hz, 2H), 7.17 (t, J = 7.1 Hz, 2H), 6.85 (d, J = 7.4 Hz, 2H), 6.62 (d, J = 7.2 Hz, 2H), 6.50 (d, J = 7.6 Hz, 2H), 6.25 (s, 2H).

^{13}C NMR (50 MHz, $CDCl_3$): 150.1, 149.0, 141.9, 140.0, 139.5, 135.0, 131.6, 130.6, 129.4, 128.6, 127.6, 124.7, 123.8, 122.2, 121.7, 121.3, 120.8, 119.8, 65.9, 50.0. MS (FAB) m/z 637 [$(M+H)^+$]. Anal. Calcd for $C_{38}H_{20}Br_2$: C, 71.72; H, 3.17 Found: C, 69.94; H, 3.31.

2.2.2. N,N,N′,N′-Tetraphenyl-spiro(cyclopenta[def]fluorene-1,5,9′,9″-bifluorene)-2′,7′-diamine (DSPN)

2′,7′-Dibromo-spiro(cyclopenta[def]fluorene-1,5,9′,9″-bi fluorene) (1.00 g, 15.71 mmol) diphenylamine (0.66 g, 39.20 mmol) and palladium acetate (0.02 g, 0.94 mmol) were dissolved in anhydrous toluene under a nitrogen atmosphere. To the reaction mixture was added a solution of tri-*t*-butylphosphine (1 M, 0.31 g, 15.71 mmol) and sodium-*t*-butoxide (0.37 g, 39.20 mmol) dropwise slowly. The reaction mixture was stirred for 12 h at 100 °C. The mixture were diluted with dichloromethane and washed with distilled water (50 mL) three times. The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo to give the crude product, which was purified by column chromatography using *n*-hexane. The final yellowish powdery product was obtained in 75% yield.

^{1}H NMR (200 MHz, $CDCl_3$): 8.05 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 7.2 Hz, 4H), 7.61 (d, J = 7.4 Hz, 4H), 7.38–6.67 (m, 20H), 6.50 (d, J = 7.6 Hz, 8H), 6.06 (s, 2H).

^{13}C NMR (50 MHz, $CDCl_3$): 149.6, 149.2, 147.8, 146.7, 142.0, 141.9, 140.1, 136.9, 136.4, 135.8, 129.8, 128.8, 128.5, 127.5, 127.11, 124.9, 123.9, 123.3, 122.3, 121.3, 120.7, 119.5, 65.7, 50.9. MS (FAB) m/z 814 [$(M+H)^+$]. Anal. Calcd for $C_{62}H_{40}N_2$: C, 91.60; H, 4.96; N, 3.45. Found: C, 91.67; H, 4.90; N, 3.37.

2.3. Device fabrication

The basic device structure used to evaluate DSPN was indium tin oxide (ITO, 50 nm)/*N*,*N*′-diphenyl-*N*,*N*′-bis-[4-(phenyl-*m*-tolyl-amino)-phenyl]-biphenyl-4,4′-diamine (DNTPD, 60 nm)/*N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (NPB) or DSPN (30 nm)/bis-9,9′-spirobi[fluoren-2-yl]-methanone (BSFM):tris(2-phenylpyridine) iridium ($Ir(ppy)_3$)(30 nm, 10%)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl(TSPO1, 25 nm)/LiF (1 nm)/Al (100 nm). All organic materials were deposited by vacuum thermal evaporation. Devices were encapsulated with a glass lid and a CaO getter in glove box after device fabrication. Hole only device with a device structure of ITO/DNTPD/NPB or DSPN/Al was also fabricated to compare hole injection and transport properties of DSPN and NPB. Current density–voltage–luminance characteristics of the devices were measured with Keithley 2400 source measurement unit and CS1000 spectroradiometer.

3. Results and discussion

The double spirobifluorene moiety was designed as the core structure to obtain good thermal stability due to the twisted structure and rigidity of the double spirobifluorene core. A two step ring closing method was used to synthesize the double spirobifluorene core structure with two substituents at the spirobifluorene core. One spirobifluorene unit can be formed by lithiating only one bromine unit of 2,2′-dibromobiphenyl followed by reaction with fluorenone and ring closing reaction. The other bromine unit can be lithiated and reacted with 2,7-dibromofluorenone followed by ring closing reaction, yielding the double spirobifluorene structure. The two step synthetic process can be used to functionalize only one spirobifluorene of the double spirobifluorene core. The functionalized double spirobifluorene core can be used to synthesize various materials and a hole transport material, DSPN, was synthesized as the hole transport material for green PHOLEDs in this work. Synthetic scheme of the DSPN is shown in Scheme 1. The DSPN was designed as the high triplet energy hole transport material for green PHOLEDs. The