Novel carbazole derivative as a host material for blue phosphorescent organic light-emitting diodes

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ABSTRACT

A novel bipolar compound with a thiophene modified 9-phenylcarbazole and phosphine oxide moieties, (5-(4-(9H-carbazol-9-yl)phenyl)thiophen-2-yl)diphenylphosphine oxide (CPTPO), was synthesized and characterized as a high triplet energy host material. Bipolar charge transport character and a high triplet energy of 2.72 eV of CPTPO allowed the development of blue phosphorescent organic light-emitting diodes with an external quantum efficiency of 18.4%.

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1. Introduction

Bipolar host materials have recently been widely employed for phosphorescent organic light-emitting diodes (PHOLEDs) due to efficient exciton formation and high quantum efficiency [1–5]. The operation of PHOLEDs is based on intersystem crossing of triplet exciton from triplet excited state to singlet ground state. Hence, host materials with high triplet energy are prerequisites for proper control of the quantum efficiency of PHOLEDs. To this end, bipolar host materials with efficient electron-donating and electron-withdrawing moieties as well as high triplet energy are necessary.

The carbazole moiety is the most common electron-donating group for host materials due to good hole transport property and high triplet energy [6–12]. For the functionalization of the carbazole moiety, 9H-position has been mostly modified. Various functional groups including triazine, oxadiazole, benzimidazole, and phosphine oxide have been employed for electron-withdrawing

group [13–17]. Among them, phosphine oxide moiety has been widely used for host materials since its tetrahedral geometry affords strong electron withdrawing property without degrading triplet energies of the core structure. Therefore, bipolar host materials containing carbazole and phosphine oxide groups have widely been studied for PHOLEDs [18–21]. For example, Sapochak et al. reported sky-blue PHOLEDs based on N-(4-diphenylphosphoryl phenyl) carbazole(MPO12) as a host material [19]. They showed moderate device performance with external quantum efficiencies of 8–9% at operating voltage of <7 V due to a wide bandgap over 4.00 eV and poor electron injection properties resulted from the shallow LUMO level originated by the wide bandgap. Therefore, the bandgap of the MPO12 host material should be reduced in order to balance holes and electrons in the emitting layer.

In this work, we synthesized (5-(4-(9H-carbazol-9-yl)phenyl) thiophen-2-yl)diphenylphosphine oxide (CPTPO) which is totally new compound as the high triplet energy host material by incorporating a thiophene moiety between phosphine oxide and 9-phenylcarbazole groups. Material characterization, photophysical analysis and device characterization of CPTPO were performed. It

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was revealed that the CPTPO host material could work as the host for blue PHOLEDs and reach a high quantum efficiency of 18.4% in blue PHOLEDs.

2. Experimental

2.1. General methods

Air and/or moisture sensitive reactions were carried out under an argon atmosphere in oven-dried glassware and with anhydrous solvents. All compounds were purchased from commercial sources unless otherwise noted and used without further purification. Solvents were freshly distilled (1,4-dioxane and toluene over sodium) or dried by passing through an alumina column. Thin layer chromatography was carried out on glass plates coated with silica gel SiO_2 60 F_{254} from Merck; visualization with a UV lamp (254 nm) or by staining with a *p*-anisaldehyde or potassium permanganate solution. Flash chromatography was performed with silica gel SiO_2 60 (0.040–0.063 μm, 230–400 mesh), technical solvents, and a head pressure of 0.2–0.4 bar. Proton (^{1}H), carbon (^{13}C), and phosphorous (^{31}P) nuclear magnetic resonance (NMR) spectroscopy was performed on a JEOL ECP-400 spectrometer at 400 MHz (^{1}H), 100 MHz (^{13}C), or 162 MHz(^{31}P) at 294 K. Chemical shifts are reported in ppm relative to the residual protiated solvent (CDCl$_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). The ^{31}P NMR chemical shifts were externally referenced to 85% H_3PO_4. All ^{13}C NMR spectra are proton decoupled. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), m (multiplet), and br (broad). High-resolution mass spectrometry (HRMS) was measured on a JEOL JMS-700 spectrometer. Mass peaks are reported in *m/z* units.

2.2. Synthesis

2.2.1. Synthesis of 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane [22]

n-BuLi (41.18 mL, 65.9 mmol, 1.6 M in hexane) was added dropwise to the stirred solution of thiophene (5.04 g, 59.9 mmol) in THF (50 mL) at −78 °C and the solution was stirred for 30 min at room temperature. After cooling to −78 °C, 2-isopropoxy-4,4,5,5 tetramethyldioxoborolane (11.14 g, 59.9 mmol) in THF (80 mL) was added and the reaction mixture was allowed to stir for 30 min at room temperature. After completion of the reaction (indicated by TLC), solvent was removed under vacuum and the residue was taken up in CHCl$_3$. An aqueous 5 N HCl (50 mL) was added under vigorous stirring. The organic layer was collected and dried over MgSO$_4$. After evaporation of the solvent the product was recrystallized from pentane (10.78 g, 86%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65(d, 3.6 Hz, 1H), 7.63 (d, 4.6 Hz, 1H), 7.20 (dd, 4.7, 3.6 Hz, 1H), 1.34 (s, 12H).

2.2.2. Synthesis of 9-(4-bromophenyl)-9H-carbazole (1) [23]

1,4-Dibromobenzene (14.15 g, 60 mmol), 9H-carbazole (5.02 g, 30 mmol), K$_2$CO$_3$ (16.56 g, 120 mmol), CuI (5.71 g, 30 mmol) and 18-crown-6 ether (3.96 g, 15 mmol) were dissolved in DMAc (120 mL) and the reaction mixture was allowed to reflux under nitrogen atmosphere for 16 h. The crude mixture was filtered, and the residue was washed with CH$_2$Cl$_2$. The combined filtrates were evaporated to dryness under reduced pressure. Then the crude product was purified by flash column chromatography on silica gel to give compound 1 (7.0 g, 73%) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.17 (d, 7.7 Hz, 2H), 7.72 (d, 8.8 Hz, 2H), 7.38–7.48 (m, 6H), 7.30–7.34 (m, 2H).

2.2.3. Synthesis of 9-(4-(thiophen-2-yl)phenyl)-9H-carbazole (2) [23]

A mixture of 9-(4-bromophenyl)-9H-carbazole, 1 (800 mg, 2.48 mmol), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (1.04 g, 4.96 mmol), Pd(PPh$_3$)$_4$ (140 mg, 5 mol%), and Na$_2$CO$_3$ (530 mg, 4.96 mmol) were dissolved in toluene (20 mL), EtOH (10 mL), and H$_2$O (10 mL) and the reaction mixture was refluxed for 6 h. After completion of the reaction (indicated by TLC), the solvent was removed under vacuum, H$_2$O (30 mL) and CH$_2$Cl$_2$ (30 mL) were added. The organic layer was separated and dried over MgSO$_4$. The solvent was removed under reduced pressure and then the crude product was purified by flash column chromatography on silica gel to give compound 2 (710 mg, 87.98%) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.16 (d, 7.7 Hz, 2H), 7.84 (d, 8.4 Hz, 2H), 7.59 (d, 8.4 Hz, 2H), 7.39–7.49 (m, 5H), 7.29–7.37 (m, 3H), 7.15 (dd, 3.6, 4.7 Hz, 1H).

2.2.4. Synthesis of (5-(4-(9H-carbazol-9-yl)phenyl)thiophen-2-yl) diphenylphosphine oxide (CPTPO; 3)

n-BuLi (1.8 mL, 2.86 mmol, 1.6 M in hexane) was added dropwise to the stirred solution of 9-(4-(thiophen-2-yl)phenyl)-9H-carbazole, 2 (846 mg, 2.60 mmol) in dry THF (20 mL) at −78 °C. Then the mixture was allowed to stir for 1 h at 0 °C, cooled the reaction mixture to −78 °C, and chlorodiphenylphosphine (734 mg, 3.12 mmol) was added slowly. The reaction mixture was next allowed to stir for 15 h at room temperature. The reaction mixture was then quenched with aq. NH$_4$Cl, and extracted with CH$_2$Cl$_2$. The combined organic layer was washed with water, once with brine, and dried over MgSO$_4$. After filtration, the solvent was removed in vacuo. The crude residue was dissolved in CH$_2$Cl$_2$ (30 mL) and 5 mL of H$_2$O$_2$ (35% in water) was added. The mixture was next stirred for 20 h after which 50 mL CH$_2$Cl$_2$ was added. The organic phase was washed five times with 20 mL of H$_2$O and then dried over MgSO$_4$. After evaporation of solvent, the crude product was purified by flash column chromatography on silica gel to afford compound 3 (735 mg, 54.04%, brsm yield 80.4%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.14 (d, 7.7 Hz, 2H), 7.78–7.85 (m, 6H), 7.58–7. 62 (m, 4H), 7.39–7.54 (m, 10H), 7.28–7.32 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 152.0, 151.9, 140.4, 137.9, 137.8, 133.7, 133.1, 132.6, 132.26, 132.23, 132.0, 131.8, 131.7, 128.5, 128.4, 127.5, 127.3, 125.9, 124.5, 124.4, 120.3, 120.1, 109.6. ^{31}P NMR (162 MHz, CDCl$_3$): δ 22.8. HRMS-EI(*m/z*): [M$^+$] calcd for C$_{34}$H$_{24}$NOPS, 525.1316; found, 525.1318.

2.3. Device fabrication and characterization

Hole only device with a device structure of indium tin oxide (ITO, 50 nm)/poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) (60 nm)/4,4-(cyclohexane-1,1-diyl)bis(N-phenyl-N-p-tolylaniline) (TAPC, 30 nm)/CPTPO (30 nm)/Al (200 nm) and electron only device with a device structure of ITO (50 nm)/Ca (5 nm)/CPTPO (30 nm)/TSPO1 (25 nm)/LiF(1 nm)/Al (200 nm) were fabricated as single carrier devices. Device stack structure of the blue PHOLEDs with the CPTPO was indium tin oxide (ITO, 50 nm)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 60 nm)/4,4′-cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (TAPC, 20 nm)/1,3-bis(N-carbazolyl)benzene (mCP, 10 nm)/CPTPO:iridium(III) bis[(4,6-difluorophenyl)-pyridinato-N,C^2]picolinate (FIrpic, 25 nm)/diphenylphosphine oxide-4-(triphenylsilyl) phenyl (TSPO1, 35 nm)/LiF (1 nm)/Al (200 nm) as shown in Fig. 1. Doping concentrations of FCNIrpic, as controlled by managing the evaporation rate of 3DCPO and FCNIrpic, were 3, 5, and 10%. All layers (organics, LiF, and Al) except PEDOT:PSS hole injection layer (spin-coating) were deposited by vacuum thermal evaporation. Devices