



Pyridine and carbazole modified biphenyl as a host for blue phosphorescent organic light-emitting diodes



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ABSTRACT

A new biphenyl substituted with a carbazole unit and a pyridine unit, 9-(2'-(pyridin-3-yl)-[1,1'-biphenyl]-3-yl)-9H-carbazole, was synthesized as the host material for blue phosphorescent organic light-emitting diodes. A high triplet energy of 2.96 eV was obtained by inclusion of pyridine at *ortho*-position of biphenyl moiety. The new biphenyl was applied as the host material for blue phosphorescent organic light-emitting diodes and a high quantum efficiency of 18.4% was achieved.

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1. Introduction

High triplet energy host materials play a key role of improving the device performances of blue phosphorescent organic light-emitting diodes (PHOLEDs) through energy transfer and charge balance because the host materials manage holes and electrons density in the emitting layer and transfer host emission energy to the triplet emitter. Therefore, the host materials are required to have bipolar charge transport properties and high triplet energy.

The high triplet energy host materials should possess hole transport units and electron transport units in the molecular structure for bipolar charge transport properties and short conjugation length for high triplet energy. Various electron donating units such as triphenylamine [1–4] and carbazole [5–11] have been used as the hole transport moieties and electron withdrawing units such as diphenylphosphine oxide [12–18], pyridine [19–21] and imidazole [22–24] have been popular as the electron transport moieties. The hole and electron transport moieties were directly connected or linked through an aromatic linkage to develop high triplet energy host materials for blue PHOLEDs. However, it was rather difficult to obtain high triplet energy above 2.90 eV by combining the hole and electron transport moieties in the

molecular structure because of extended conjugation structure [22,23]. Therefore, a new molecular design is required to develop high triplet energy host materials with bipolar charge transport properties.

In this work, a new high triplet energy host material derived from carbazole and pyridine, 9-(2'-(pyridin-3-yl)-[1,1'-biphenyl]-3-yl)-9H-carbazole (PyBPCz), was synthesized as the bipolar host material with a high triplet energy above 2.90 eV and the device performances of PyBPCz were investigated. It was demonstrated that the PyBPCz host had bipolar charge transport properties and a high triplet energy of 2.96 eV. A high quantum efficiency of 18.4% was achieved using the PyBPCz host material in blue PHOLEDs doped with bis((3,5-difluorophenyl)pyridine) iridium picolinate (Flrpic).

2. Experimental section

2.1. General information

9-(2'-Bromo-[1,1'-biphenyl]-3-yl)-9H-carbazole was prepared using the method previously reported in the literature [25]. 3-Pyridylboronic acid was purchased from TCI Chemicals Ltd. and was used without further purification. ¹H and ¹³C NMR were measured on Bruker Avance 500 spectrometer in CDCl₃. Fourier transform-infrared (FT-IR) spectrum was recorded on in KBr pellet a Nicolet 380 FTIR spectrometer. Mass spectrum (in fast atom bombardment mode) was obtained on a JEOL JMS-600W

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spectrometer. Elemental analysis was determined using Thermo-fisher Flash2000 analyzer. The differential scanning calorimetric (DSC) measurements and thermo gravimetric analysis (TGA) were performed on a Mettler DSC822e and Mettler TGA, respectively. Thermal analyses were carried out under a nitrogen flow at a heating rate of 10 °C/min from room temperature. The ultraviolet–visible (UV–Vis) absorption spectrum was taken using a Shimadzu UV-2501PC spectrometer in tetrahydrofuran. The room temperature photoluminescence (PL) spectrum was obtained using a HITACHI F-7000 spectrophotometer, while low temperature PL spectrum was recorded on a PerkinElmer LS-55 spectrofluorimeter at 77 K. Cyclic voltammetry measurements of PyBPCz were carried out with tetrabutylammonium perchlorate in acetonitrile as the electrolyte solution. Ag/AgCl was utilized as reference electrode, with a Pt wire counter electrode.

2.2. Synthesis

2.2.1. Synthesis of 9-(2'-(pyridin-3-yl)-[1,1'-biphenyl]-3-yl)-9H-carbazole (PyBPCz)

9-(2'-Bromo-[1,1'-biphenyl]-3-yl)-9H-carbazole (2.00 g, 5.02 mmol) and 3-pyridinylboronic acid (0.93 g, 7.53 mmol), potassium carbonate (1.39 g, 10.04 mmol), tetrahydrofuran (100 mL) and distilled water (33 mL) were placed in a two-necked round bottom flask equipped with a reflux condenser and a nitrogen inlet. This mixture was stirred and bubbled with nitrogen gas for 30 min and then tetrakis(triphenylphosphine)palladium(0) (0.29 g, 0.25 mmol) was added to the solution. The solution was refluxed for 24 h under nitrogen and was cooled down to room temperature, extracted with ethyl acetate and distilled water. The ethyl acetate layer was evaporated and the crude product was dried under vacuum. The crude product was purified by column chromatography on silica gel using *n*-hexane/dichloromethane (1/3) as an eluent. Additional purification by sublimation resulted in 1.5 g of PyBPCz as a white powder.

PyBPCz: Yield 75%. Tg 58 °C, Tm N.D. FT-IR 711.3, 748.7, 804.3, 849.4, 926.2, 1001.6, 1024.5, 1117.6, 1166.0, 1229.1, 1313.8, 1336.2, 1407.5, 1451.0, 1592.1, 1928.3, 3053.1 cm⁻¹ ¹H NMR (500 MHz, CDCl₃): δ 6.94 (d, 2H, *J* = 4.3 Hz), 7.20–7.26 (m, 4H), 7.31 (t, 2H, *J* = 5.3 Hz), 7.36 (d, 1H, *J* = 3.8 Hz), 7.40–7.55 (m, 7H), 8.06 (d, 2H, *J* = 3.8 Hz), 8.53 (s, 1H), 8.58 (d, 1H, *J* = 3.2 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 109.5, 119.9, 120.1, 123.2, 123.3, 125.4, 125.9, 128.2, 128.4, 128.6, 128.7, 129.9, 130.7, 130.8, 136.8, 137.0, 137.4, 140.0, 140.6, 142.9, 147.9, 150.6. Mass (FAB) *m/z* 397 [(M+H)⁺]. Element analysis Calcd. for C₂₉H₂₀N₂ C(87.85%) H(5.08%) N(7.07%); found C(87.85%) H(5.08%) N(7.06%).

2.3. Device fabrication and measurement

Device structure of the blue PHOLEDs was comprised of indium tin oxide (ITO, 120 nm)/N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (NPB, 60 nm)/4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (TAPC, 20 nm)/1,3-bis(*N*-carbazolyl)benzene (mCP, 10 nm)/PyBPCz (25 nm)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 35 nm)/LiF (1 nm)/Al (200 nm). Doping concentrations of Flrpic were 5 and 10%. Device structure of hole only device was ITO (120 nm)/NPB (60 nm)/TAPC (20 nm)/mCP (10 nm)/PyBPCz (25 nm)/NPB (5 nm)/Al (200 nm) and the device structure of electron only device was ITO (120 nm)/Ca (10 nm)/PyBPCz (25 nm)/TSPO1 (35 nm)/LiF (1 nm)/Al (200 nm). All organic materials were vacuum deposited on the ITO substrate at a vacuum pressure of 1.0 × 10⁻⁷ torr. LiF and Al electrode were also formed by vacuum thermal evaporation. After Al evaporation, the device was encapsulated in the glove box with a glass lid. A CaO desiccant was inserted inside the device to remove oxygen and moisture permeated from outside. Device performances were

measured using Keithley 2400 source measurement unit and CS 2000 spectroradiometer in ambient condition.

3. Results and discussion

High triplet energy host materials for blue PHOLEDs should be designed to minimize the degree of conjugation of the molecular structure. In order to reduce the degree of conjugation of the backbone structure, a hole transport moiety and an electron transport moiety should be linked with an aromatic moiety which limits the extension of conjugation. Our approach was to link a hole transport type carbazole with an electron transport type pyridine using a biphenyl linkage. However, *para*- or *meta*-linkage could not maintain the high triplet energy of carbazole and pyridine [26]. Therefore, an *ortho*-linkage was introduced in the molecular structure to maintain the high triplet energy of carbazole and pyridine [25,27]. The PyBPCz host was designed to possess high triplet energy by attaching the carbazole moiety at a *meta*-position of phenyl and the pyridine moiety at an *ortho*-position of phenyl.

Synthetic scheme of PyBPCz is shown in Scheme 1. 9-(2'-Bromo-[1,1'-biphenyl]-3-yl)-9H-carbazole was prepared according to the method reported in the literature [25] and was coupled to 3-pyridinylboronic acid by Suzuki coupling reaction. Synthetic yield of PyBPCz was 75% after purification by column chromatography. PyBPCz was further purified by vacuum train sublimation and a high purity over 99% was obtained. The chemical structure of PyBPCz was confirmed by ¹H NMR, ¹³C NMR, elemental analysis and mass analysis.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) distribution of PyBPCz was simulated using Gaussian 09 program with density functional theory of B3LYP with 6-31G* basis sets. The HOMO and LUMO distribution of PyBPCz is shown in Fig. 1. The HOMO of PyBPCz was mostly dispersed over the carbazole unit, whilst the LUMO was distributed over the pyridine modified biphenyl moiety due to electron donating character of carbazole and electron withdrawing character of pyridine. Therefore, hole transport properties and the HOMO level of PyBPCz would be dominated by the carbazole moiety, while electron transport properties and the LUMO level of PyBPCz would be determined by the pyridine modified biphenyl. Donor character of carbazole and acceptor character of pyridine separated the HOMO and LUMO of PyBPCz. In addition, the ground state geometry of PyBPCz was simulated by the same calculation method. The dihedral angles between central phenyl unit and 3-pyridinyl unit or phenyl unit were 131° and -52°, respectively. The distorted structure of PyBPCz due to *ortho*-substitution can cause suppression of the extension of conjugation length, which can limit the decrease of triplet energy.

The HOMO and LUMO levels of PyBPCz were measured by cyclic voltammetry (CV). Oxidation and reduction curves of PyBPCz are shown in Fig. 2. Oxidation potential and reduction potential of PyBPCz were 1.25 V and -2.28 V, respectively, which corresponded to an ionization potential of -6.05 eV and an electron affinity of -2.52 eV. The ionization potential–electron affinity gap of PyBPCz was 3.53 eV. Therefore, the HOMO and LUMO of PyBPCz can be estimated to be -6.05 eV and -2.52 eV, respectively. The HOMO of PyBPCz was similar to that of other carbazole compounds, but the LUMO was not stabilized as much as that of other pyridine compounds because the LUMO is extended over the biphenyl unit.

Photophysical properties of PyBPCz were analyzed using ultraviolet–visible (UV–Vis) and photoluminescence (PL) measurements. Fig. 3 shows UV–Vis, solution PL and low temperature delayed PL spectra of PyBPCz. PyBPCz exhibited typical UV–Vis absorption of carbazole derivatives above 300 nm by *n*-π* transition of carbazole and below 300 nm by π-π* transition of the

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