



Orange phosphorescent organic light-emitting diodes based on spirobenzofluorene type carbazole derivatives as a host material

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ABSTRACT

Spiro-type orange phosphorescent host materials, 9-carbazole-spiro[benzo[c]fluorene-7,9'-fluorene] (**OPH-1C**) and 5-carbazole-spiro[benzo[c]fluorene-7,9'-fluorene] (**OPH-2C**) were designed and successfully prepared by the amination reaction. The EL characteristics of **OPH-1C** and **OPH-2C** as orange host materials doped with iridium(III) bis(2-phenylquinoline)acetylacetonate (Ir(pq)₂acac) were evaluated. The electroluminescence spectra of the indium tin oxide (ITO, 150 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, 30 nm)/9-carbazole-spiro[benzo[c]fluorene-7,9'-fluorene] (**OPH-1C**): Ir(pq)₂acac (30 nm, 3%)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline(BCP, 5 nm)/tris(8-hydroxyquinoline)aluminum (Alq₃, 20 nm)/LiF (1 nm)/Al (200 nm) devices show a narrow emission band with a full width at half maximum of 73 nm and a $\lambda_{\text{max}} = 596$ nm. The device obtained from **OPH-1C** doped with 3% Ir(pq)₂acac showed an orange color purity of (0.595, 0.387) and efficiency of 17.6 cd/A at 6.0 V.

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1. Introduction

Organic light-emitting diodes (OLEDs) have been the focus of both academic research and industrial interest in the past two decades, because of their potential application in flat-panel displays and solid lighting resources [1–5]. In particular, intensive studies have been conducted on the development of transitional metal complex based phosphorescent OLEDs (PHOLEDs), owing to their potential ability to achieve an internal quantum efficiency of 100% by harvesting both singlet and triplet excitons [6]. However, orange PHOLEDs are challenging, because of the difficulty of finding a suitable host material with an E_T (triple energy) exceeding that of the commonly used orange phosphorescent dyes. Orange phosphorescent dyes can be used for white organic light-emitting diodes (WOLEDs). White OLED (WOLED) technology can replace the back lights used in LCDs owing to their potential as low-cost and large-area full color displays and solid-state lightings. From the standpoint of their environment friendliness and low electric consumption, WOLEDs constitute a good candidate for high efficiency light units [7–9]. However, it was not until the discovery of

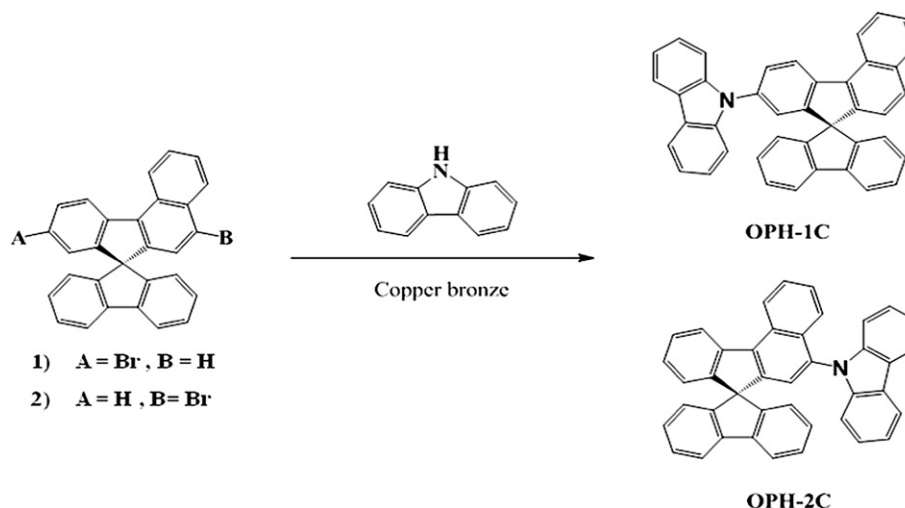
organic phosphorescent materials that researchers began seriously looking into the possibility of using WOLEDs for thin-film solid state lighting. Recent results have shown continually improved WOLEDs, which are now surpassing incandescent lamps in terms of their efficiency and lifetime [10]. Carbazole derivatives are photoconductors with good hole-transport properties [11–14]. Recently, carbazole based host materials have been effective as host materials for deep blue PHOLEDs due to the high triplet energy of the carbazole unit [15,16]. However, more studies are required to develop high efficiency deep blue PHOLEDs.

The spirobifluorene and spirobilabifluorene derivatives were widely used for new amorphous host and dopant materials possessing high morphological stability [17–23]. Spirobifluorene with a high glass transition temperature also showed an excellent nondispersive hole transporting and ambipolar carrier transporting properties [24,25]. Recently spirofluorenebenzofluorene would be a useful strategy to expand the application of spiro compounds [26–32].

In this study, new spirobenzofluorene based carbazole compounds were developed and evaluated as red phosphorescent host materials. The devices based on these spiro complexes emit orange light at 593 nm with exceedingly high brightness and external quantum, current and power efficiencies. The device performances of the orange PHOLEDs with the **OPH-1C** and **OPH-2C** hosts were investigated according to the doping concentration of red dopant.

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Scheme 1. Chemical structures of Orange phosphorescent host materials.

2. Experimental

2.1. Materials and measurements

Carbazole (95%), potassium carbonate (99%), copper powder (99%), dichloromethane (95%) and nitrobenzene (Aldrich Chem. Co.) were used without further purification. Ammonia water (Duksan Chem. Co.) was used as received. Tetrahydrofuran was distilled over sodium and calcium hydride. 9-bromospiro[benzo[*c*]fluorene-7,9'-fluorene] and 5-bromospiro[fluorene-7,9'-benzofluorene] were prepared as previously reported [28–30].

The photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (Jasco FP-6500) and the UV–vis spectra were obtained by means of a UV–vis spectrophotometer (Shimadzu, UV-1601PC). The energy levels were measured with a low-energy photo-electron spectrometer (Riken-Keiki AC-2). The FT-IR spectra were obtained with a Thermo Fisher Nicolet 850 spectrophotometer and the elemental analyses were performed using a CE Instrument EA1110. The DSC measurements were performed on a Shimadzu DSC-60 differential scanning calorimeter under nitrogen at a heating rate of 10 °C/min. The TGA measurements were performed on a Shimadzu TGA-50 thermo gravimetric analyzer at a heating rate of 5 °C/min. The low and high resolution mass spectra were recorded using a JEOL JMS-AX505WA spectrometer in FAB mode.

2.2. Synthesis of 9-carbazole-spiro[benzo[*c*]fluorene-7,9'-fluorene] (**OPH-1C**)

A mixture of 9-bromospiro[benzo[*c*]fluorene-7,9'-fluorene] (5.00 g, 11.23 mmol), carbazole (2.06 g, 12.35 mmol), potassium carbonate (3.1 g, 22.45 mmol) and copper bronze (0.71 g, 11.23 mmol) in nitrobenzene (80 ml) was refluxed with vigorous stirring under a nitrogen atmosphere for 18 h. After the removal of the solvent in vacuo, ammonia solution (80 ml) was added and the mixture was left to stand for 2 h. Dichloromethane (150 ml) and distilled water (100 ml) were then added and the organic layer was separated. After the organic layer was evaporated with a rotary evaporator, the resulting powdery product was purified by column chromatography using a mixture of dichloromethane/hexane (v/v, 1/1) as eluent to give a white crystalline **OPH-1C**.

Yield 64%. Mp 261 °C. ¹H-NMR (500 MHz, CDCl₃) δ 8.88–8.87 (d, 1H, Ar-CH- benzene), 8.62–8.61 (d, 1H, Ar-CH-carbazole), 8.05–8.04 (d, 2H, Ar-CH-naphthalene), 7.94–7.92 (d, 1H, Ar-CH-carbazole),

7.82–7.81 (d, 2H, Ar-CH-carbazole), 7.75–7.74 (t, 1H, Ar-CH-carbazole), 7.67–7.66 (d, 2H, Ar-CH-benzene), 7.60–7.58 (t, 1H, Ar-CH-fluorene), 7.37–7.34 (t, 2H, Ar-CH-fluorene), 7.34–7.33 (t, 1H, Ar-CH-fluorene), 7.33–7.32 (d, 1H, Ar-CH-carbazole), 7.28–7.22 (m, 1H, Ar-CH-c), 7.20–7.18 (m, 3H, Ar-CH-benzene), 7.18–7.14 (t, 2H, Ar-CH-benzene), 7.11–6.99 (s, 1H, Ar-CH-benzene), 6.87–6.84 (d, 2H, Ar-CH-benzene), 6.84–6.82 (d, 1H, Ar-CH-carbazole), ¹³C NMR (CDCl₃) δ 152.0, 148.2, 147.5, 142.3, 142.1, 140.8, 136.4, 135.9, 134.3, 129.6, 129.4, 128.2, 128.1, 127.3, 126.4, 126.0, 125.9, 124.1, 124.0, 123.8, 123.5, 122.7, 122.2, 120.4, 120.4, 120.0, 109.9, 77.4, 77.2, 76.9, 66.4. FT-IR (KBr, cm⁻¹) 3052, 3037 (aromatic C–H), 1268 (aromatic C–N). Anal. Calcd for C₄H₂₅N (Mw, 531.64): C, 92.63; H, 4.74; N, 2.63. Found: C, 92.59; H, 4.68; N, 2.71. MS (FAB) *m/z* 531.6 [(M + 1)⁺]. UV–vis (THF): λ_{max} (Absorption) = 345 nm, λ_{max} (Emission) = 395 nm.

2.3. Synthesis of 5-carbazole-spiro[benzo[*c*]fluorene-7,9'-fluorene] (**OPH-2C**)

A mixture of 5-bromospiro[benzo[*c*]fluorene-7,9'-fluorene] (4.00 g, 8.98 mmol), carbazole (1.65 g, 9.88 mmol), potassium carbonate (2.5 g, 17.96 mmol) and copper bronze (0.57 g, 8.98 mmol) in nitrobenzene (70 ml) was stirred and refluxed under a nitrogen atmosphere for 18 h. After the removal of the solvent in vacuo, ammonia solution (70 ml) was added and the mixture was left to stand for 2 h. Dichloromethane (150 ml) and water (100 ml) were added and the organic phase was separated. The organic solution was washed with water (100 ml × 2) twice. After the resulting solution was evaporated with rotary evaporator, the resulting powdery product was purified by column chromatography using a mixture of dichloromethane/hexane (v/v, 1/1) as eluent to give **OPH-2C** as a white solid.

Yield 68%. Mp 371 °C ¹H-NMR (500 MHz, CDCl₃) δ 9.02–9.00 (d, 1H, Ar-CH- benzene), 8.54–8.52 (d, 1H, Ar-CH-carbazole), 8.11–8.10 (d, 1H, Ar-CH-naphthalene), 8.10–8.09 (d, 1H, Ar-CH-carbazole), 7.78–7.77 (d, 1H, Ar-CH-benzene), 7.76–7.75 (d, 2H, Ar-CH-carbazole), 7.52–7.51 (t, 1H, Ar-CH-benzene), 7.37–7.36 (t, 1H, Ar-CH-carbazole), 7.35–7.34 (d, 3H, Ar-CH-benzene), 7.24–7.23 (t, 1H, Ar-CH-carbazole), 7.23–7.22 (t, 1H, Ar-CH-carbazole), 7.20–7.19 (m, 3H, Ar-CH-fluorene), 7.13–7.12 (d, 2H, Ar-CH-benzene), 7.12–7.11 (s, 1H, Ar-CH-fluorene), 6.96–6.87 (d, 1H, Ar-CH- benzene), 6.83–6.81 (m, 3H, Ar-CH-benzene), 6.84–6.82 (d, 1H, Ar-CH-carbazole), ¹³C NMR (CDCl₃) δ 150.2, 148.1, 147.5, 142.4, 142.3, 142.1, 137.4, 134.2, 131.3, 130.8, 128.2, 128.1, 127.7, 126.6, 126.0, 125.1, 124.6, 124.4, 124.0,

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