



# High triplet energy electron transport type exciton blocking materials for stable blue phosphorescent organic light-emitting diodes



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## ABSTRACT

High triplet energy electron transport materials with dibenzothiophene and dibenzofuran cores modified with a diphenyltriazine unit were investigated as electron transport type exciton blocking materials for stable blue phosphorescent organic light-emitting diodes. The two exciton blocking materials showed high triplet energy above 2.80 eV and enhanced quantum efficiency of the blue phosphorescent devices by more than 40% while maintaining stability of the pristine blue devices without the high triplet energy exciton blocking layer.

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## 1. Introduction

Blue phosphorescent organic light-emitting diodes (PHOLEDs) require triplet exciton blocking functional layers specially designed to have high triplet energy above 2.70 eV to put down triplet exciton quenching and leakage [1–3]. The triplet exciton blocking functional layers are essential in the blue PHOLEDs and are inserted at the interface between phosphorescent emitting layers and charge transport layers. Both hole transport type and electron transport type exciton blocking layers are inserted because triplet excitons can diffuse into both hole and electron transport layers [4–12]. Therefore, the development of the triplet exciton blocking layers was a challenging issue to promote the light-emitting performances of the blue PHOLEDs.

Intense research and development of the exciton blocking materials upgraded external quantum efficiency (EQE) of the blue PHOLEDs by suppressing leakage and quenching of triplet excitons by charge transport materials. Several groups demonstrated above 20% EQE in the blue PHOLEDs by development of hole and electron transport type exciton blocking functional layers [6–8]. Carbazole or aromatic amine functionalized organic materials worked efficiently as a hole transport type exciton blocking materials by

confining excitons and injecting holes [6,9–12]. However, most high triplet energy hole transport type exciton blocking materials had negative effect on the operational lifetime of the blue PHOLEDs because of instability of the exciton blocking materials. The degradation of the blue PHOLEDs was even more serious when electron transport type exciton blocking materials were adopted [13–16]. Therefore, most stable blue PHOLEDs could not use any electron transport type exciton blocking materials in spite of low EQE by triplet exciton quenching caused by low triplet energy of common electron transport materials [17]. The problem of the low EQE of the stable blue PHOLEDs can be resolved by design and synthesis of stable electron transport type exciton blocking materials.

In this work, two electron transport type exciton blocking materials, 2,8-bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[*b,d*]thiophene (DBTTrz) and 2,8-bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[*b,d*]furan (DBFTrz) were introduced as the stable high triplet energy exciton blocking functional materials of blue PHOLEDs. DBTTrz and DBFTrz had only stable aromatic moieties in the molecular structure and enhanced the EQE of the blue PHOLEDs with the lifetime of the blue PHOLEDs unchanged. Therefore, the DBTTrz and DBFTrz exciton blocking materials can be used to increase the EQE of stable blue PHOLEDs.

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## 2. Experimental

### 2.1. General information

2-Chloro-4,6-diphenyl-1,3,5-triazine (Sun fine global Co.), tetrakis(triphenylphosphine)palladium(0) (P&H Tech), potassium carbonate, n-hexane, magnesium sulfate anhydrous (Duksan Sci. Co.). These chemical were used without further purification. Tetrahydrofuran was distilled over sodium and calcium hydride. Chemical analysis of the synthesized materials referred to the method reported in other literature [8].

### 2.2. Synthesis

#### 2.2.1. 2,8-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene

Under nitrogen, 2,8-dibromodibenzo[b,d]thiophene (1.0 g, 3.0 mmol), Bis(pinacolato)diboron (1.85 g, 8.0 mmol) and potassium acetate (0.9 g, 10.0 mmol) were dissolved in 100 ml of 1,4-dioxane. [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride dichloromethane adduct (7.1 mg, 0.1 mmol) are added in the mixture. It was refluxed for overnight and quenched with distilled water followed by extracting with ethyl acetate. The mixture was purified by column chromatography on silica gel using ethyl acetate and hexane. The yellowish white powder was obtained to 1.2 g. MS (APCI) *m/z* 436.2 [(M)<sup>+</sup>].

#### 2.2.2. 2,8-Bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[b,d]thiophene (DBTTrz)

2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene (0.6 g, 1.3 mmol), and 2-chloro-4,6-diphenyl-1,3,5-triazine (0.8 g, 3.1 mmol) were dissolved in 10 ml of anhydride tetrahydrofuran. After stirring for 30 min at room temperature, tetrakis(triphenylphosphine)palladium(0) (0.01 g, 0.1 mmol) was added and 2 M aqueous potassium carbonate (2.8 g in 10 ml distilled water) was put to the reaction mixture instantly. The reaction mixture was refluxed overnight and a white powder are formed. The crude product was separated by filtration and purified by washing using tetrahydrofuran and hexane. A white product was finally obtained (1.2 g, 90% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 9.83 (s, 1H), 8.98–8.96 (d, 1H, J = 5.0 Hz), 8.91–8.87 (d, 4H, J = 4.8 Hz), 8.10–8.08 (t, 2H, J = 2.93 Hz), 7.71–7.63 (m, 12H), 7.54–7.51 (m, 6H) MS (APCI) *m/z* 646.7 [(M)<sup>+</sup>]. Elemental Analysis (calculated for C<sub>42</sub>H<sub>26</sub>N<sub>6</sub>S): C, 78.00; H, 4.05; N, 12.99. Found: C, 78.46; H, 4.25; N, 12.99.

#### 2.2.3. 2,8-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]furan

2,8-Diiodobenzene (4.0 g, 12.0 mmol), Bis(pinacolato)diboron (6.0 g, 26.0 mmol) and potassium acetate (3.0 g, 36.0 mmol) were dissolved in 250 ml of 1,4-dioxane. [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride dichloromethane adduct (0.3 g, 0.4 mmol) are added in the mixture and it was refluxed for overnight. After cooling the solution to room temperature, it was quenched with distilled water and the solution was extracted using methylene chloride. The crude product was purified by column chromatography on silica gel using n-hexane/MC and the product was obtained as a yellowish white powder after sublimation (2.5 g, yield 65%). MS (APCI) *m/z* 420.2 [(M)<sup>+</sup>].

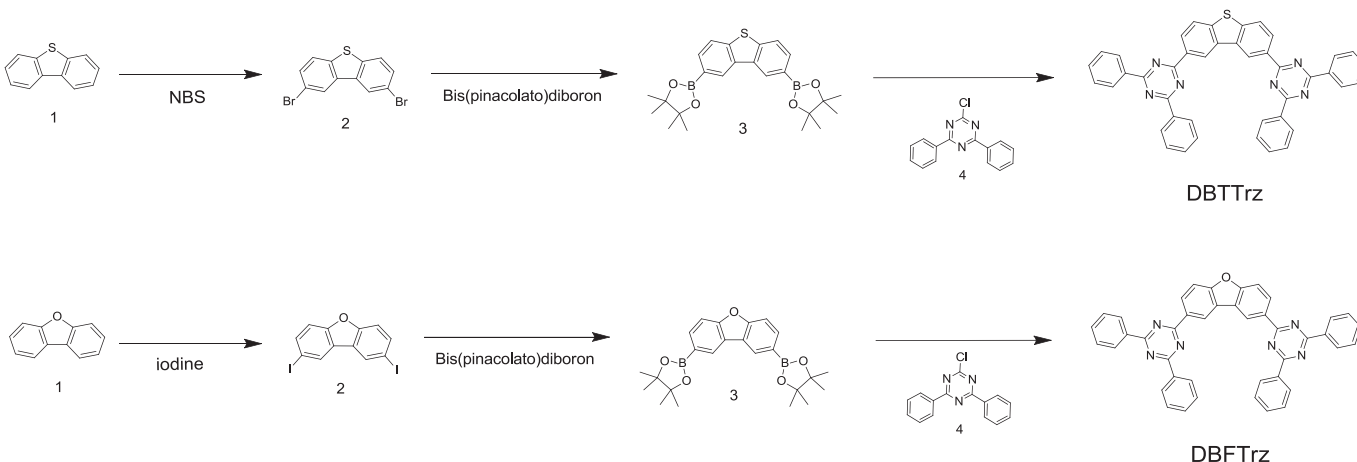
#### 2.2.4. 2,8-Bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[b,d]furan (DBFTrz)

2,8-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]furan (0.7 g, 1.6 mmol) and 2-chloro-4,6-diphenyl-1,3,5-triazine (1.0 g, 3.8 mmol) were dissolved in 10 ml of anhydride tetrahydrofuran. After stirring for 30 min at room temperature, tetrakis(triphenylphosphine)palladium (12.0 mg, 0.1 mmol) was added in mixture and followed by addition of 2 M aqueous potassium carbonate (2.8 g in 10 ml distilled water). Work-up procedure of DBFTrz was the same as that of DBTTrz and the product was obtained as a white powder after sublimation (1.1 g, yield 73%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 9.57–9.56 (d, 1H, J = 0.8 Hz), 9.04–9.01 (d, 1H, J = 5.2 Hz), 8.87–8.85 (d, 4H, J = 5.0 Hz), 7.81 (s, 1H), 7.79 (s, 1H), 7.72–7.63 (m, 12H), 7.54–7.51 (m, 6H) MS (APCI) *m/z* 630.7 [(M)<sup>+</sup>].

### 2.3. Device fabrication and measurements

The device structure of the blue PHOLEDs, indium tin oxide/DNTPD (60 nm)/BPBPA (30 nm)/mCBP: Ir(dbi)<sub>3</sub> (25 nm, 10% doping)/LG201 (35 nm)/LiF (1 nm)/Al (200 nm), was the same as that described in the literature [18]. The only difference was that DBTTrz or DBFTrz was inserted between 3,3-di(9H-carbazol-9-yl)biphenyl (mCBP): tris[1-(2,4-diisopropylidibenzo[b,d]furan-3-yl)-2-phenylimidazole] iridium(III) (Ir(dbi)<sub>3</sub>) emitting layer and 9,10-di(naphthalene-2-yl)anthracen-2-yl-(4,1-phenylene)(1-phenyl-1H-benzo[d]imidazole (NAPIm) electron transport layer. DNTPD and BPBPA were *N,N'*-diphenyl-*N,N'*-bis[4-(phenyl-*m*-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine, *N,N,N',N'*-tetra[(1,1'-biphenyl)-4-yl]-(1,1'-biphenyl)-4,4'-diamine, respectively. The thickness of the exciton blocking layer was 5 nm. Lifetime data of the blue PHOLEDs



**Scheme 1.** Synthetic scheme of DBTTrz and DBFTrz.

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