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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 guenching 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

Corresponding author. E-mail address: leej17@skku.edu (J.Y. Lee). 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 PHO-LEDs. 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.





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) *miz* 436.2 [(M)⁺].

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).

¹H NMR (400 MH_Z, CDCl₃): 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) *miz* 646.7 [(M)⁺]. Elemental Analysis (calculated for $C_{42}H_{26}N_6S$): 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

2,7-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) *miz* 420.2 [(M)⁺].

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%).

 ^{1}H NMR (400 MHz, CDCl₃): 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) miz 630.7 [(M)⁺].

2.3. Device fabrication and measurements

The device structure of the blue PHOLEDs, indium tin oxide/ DNTPD (60 nm)/BPBPA (30 nm)/mCBP: $Ir(dbi)_3$ (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(9*H*-carbazol-9-yl)biphenyl (mCBP): tris[1-(2,4-diisopropyldibenzo[*b*,*d*]furan-3-yl)-2phenylimidazole] iridium(III) (Ir(dbi)_3) emitting layer and 9,10di(naphthalene-2-yl)anthracen-2-yl-(4,1-phenylene)(1-phenyl-1Hbenzo[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.

DBFTrz







Fig. 2. UV-vis, Solution PL and low temperature PL spectra of DBTTrz and DBFTrz.



Fig. 3. Reduction curves of DBTTrz and DBFTrz during cyclic voltammetry scan.

were collected at 1000 cd/m^2 at a fixed current. Luminance change and voltage rise were traced according to driving time of the devices.



Fig. 4. Current density-voltage-luminance curves of DBTTrz and DBFTrz devices.



Fig. 5. Current density-voltage plots of single charge devices of DBTTrz and DBFTrz.

3. Results and discussion

Two important parameters to be considered in the design of the stable exciton blocking materials for high EQE and stable lifetime are triplet energy and bond dissociation energy of chemical moieties included in the molecular structure. From the chemical



Fig. 6. Quantum efficiency-luminance curves of the blue PHOLED devices.



Fig. 7. Energy level diagram of the blue PHOLED devices.



Fig. 8. Lifetime curves of the blue PHOLED devices. Lifetime was measured at an initial luminance of 1000 cd m^{-2} .

stability point of view, pure aromatic moieties are favourable due to high dissociation energy of the chemical bond in the aromatic moieties. Small dihedral angle between aromatic moieties is also favoured because extended conjugation structure stabilizes the chemical bond between aromatics and can extend the lifetime of the devices. From the EQE point of view, only high triplet energy moieties need to be used to construct the exciton blocking materials and conjugation between aromatic moieties should be minimized. Therefore, the two main requirements of high triplet energy and long lifetime can be satisfied by proper management of chemical structure of the exciton blocking materials.

Main backbone structures of two exciton blocking materials designed in this work were dibenzothiophene and dibenzofuran for high triplet energy and chemical stability. Those moieties were already proven as chemical units for long lifetime in the design of host materials due to rigidity and planar molecular structure. It was reported that the dibenzothiophene and dibenzofuran moieties are superior to biphenyl for long lifetime in the blue PHOLEDs, which encouraged us to use those moieties in the design of exciton blocking materials. Moreover, those moieties may increase thermal stability of the exciton blocking materials due to rigidity. However, the two core moieties have weak electron carrying ability as electron transport type exciton blocking materials, which was compensated by modification of the core structures with a diphenyltriazine moiety which has good electron transporting character, chemical stability and high triplet energy. Therefore, the DBTTrz and DBFTrz exciton blocking materials which have high triplet energy and stable chemical building blocks may fulfil the requirement of the electron transport type exciton blocking materials.

The preparation of DBTTrz and DBFTrz was made by simple Suzuki coupling reaction of boronic ester modified dibenzofuran and dibenzothiophene with chlorinated diphenyltriazine. Pd catalyst assisted the coupling reaction and production yields of DBTTrz and DBFTrz were 90% and 73%, respectively. The DBTTrz and DBFTrz compounds were ascertained by nuclear magnetic resonance, mass and elemental analysis. Scheme 1 shows synthetic route of DBTTrz and DBFTrz.

The appropriateness of the two compounds as exciton blocking materials was investigated by calculating the molecular orbital with Gaussian 09 Software. A B3LYP 6-31G* basis set based calculation result in Fig. 1 represents the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of DBTTrz and DBFTrz. The HOMO and LUMO of DBTTrz and DBFTrz were similarly distributed with the HOMO localization on the dibenzothiophene and dibenzofuran core, and the LUMO extension from the core to the triazine moiety. The strong electron deficiency of the triazine moiety determined the HOMO and LUMO distribution. As the LUMO electronic orbital was uniformly spread over the core and two triazine moieties, the DBTTrz and DBFTrz compounds are expected to transport electrons effectively through large overlap integral for electron hopping.

Two important photophysical parameters, HOMO-LUMO gap and triplet energy, were extracted from ultraviolet-visible (UV-vis) absorption and low temperature photoluminescence (PL) spectra in Fig. 2. Tetrahydrofuran solution of the two materials was used for the photophysical analysis. Main UV-vis absorption peaks of DBTTrz and DBFTrz corresponding to $\pi - \pi^*$ transition were of little difference, but the UV–vis absorption edge reflecting n- π^* transition was different. The UV-vis absorption edge was extended to long wavelength in the DBTTrz by the loosely bound non-bonding electron of dibenzothiophene. HOMO-LUMO gaps of DBTTrz and DBFTrz from the UV-vis absorption edge were 3.41 eV and 3.57 eV, respectively. Phosphorescent emission peak from low temperature PL measurement provided a high triplet energy of 2.80 eV and 2.94 eV in DBTTrz and DBFTrz, respectively. The assembly of the high triplet energy core and diphenyltriazine gave high triplet energy in the DBTTrz and DBFTrz.

Estimation of the HOMO and LUMO levels is essential to study the applicability of DBTTrz and DBFTrz as exciton blocking layers. Therefore, cyclic voltammetry (CV) analysis of DBTTrz and DBFTrz was carried out to estimate ionization potential (IP) and electron affinity (EA). However, IP could not be calculated because oxidation behaviour was not stable possibly due to poor electron donating character of DBTTrz and DBFTrz. Only the reduction behaviour was



Fig. 9. Dihedral angle between diphenyltriazine and core moieties.



Fig. 10. DSC thermograms of DBTTrz and DBFTrz.

clear from reverse bias scan of CV. Reduction curves of DBTTrz and DBFTrz in Fig. 3 suggested reduction onsets of -1.61 V and -1.73 V, which were changed into -3.19 eV and -3.07 eV as EA values of DBTTrz and DBFTrz using ferrocene as a standard material. Therefore, the HOMO/LUMOs of DBTTrz and DBFTrz were proposed as -6.60/-3.19 eV and -6.64/-3.07 eV, respectively, using the measured LUMO values and HOMO-LUMO gap from absorption edge of the UV–vis measurement. The HOMO and LUMO of DBTTrz and DBFTrz were deep enough for hole blocking and electron injection as exciton blocking materials.

As DBTTrz and DBFTrz were confirmed to have triplet energy for triplet exciton blocking, HOMO level for hole blocking and LUMO level for electron injection, they were inserted as an exciton blocking layer of blue PHOLEDs. Voltage scan of the blue PHOLEDs produced the current density-voltage and luminance-voltage curves in Fig. 4. A reference device without the DBTTrz or DBFTrz exciton blocking layer was also evaluated to judge the effectiveness of the exciton blocking materials. The current density and luminance of the DBFTrz device were higher than those of the DBTTrz device, indicating that electron carrying ability of DBFTrz is better than that of DBTTrz, which was verified by electron current density of electron only devices in Fig. 5. The high electron current density of the DBFTrz electron only device supports the good electron transport character of DBFTrz, which is due to high electronegativity of oxygen of DBFTrz. The relatively electron withdrawing character of oxygen to sulfur enhances electron accepting character of the DBFTrz, improving electron transport performance. However, the current density of the DBFTrz device was not increased compared to that of the reference device without the exciton blocking layer.

EQE plot obtained from the current density and luminance data of the blue PHOLEDs is shown in Fig. 6. Dramatic increase of

maximum EQE from 8.3% to 13.0% was demonstrated by inserting the DBTTrz and DBFTrz exciton blocking layers. As can be easily projected from the energy level diagram in Fig. 7, triplet exciton blocking and hole blocking effect of DBTTrz and DBFTrz were dominant factors for the enhanced EQE.

The stable molecular structure of DBTTrz and DBFTrz may be helpful to stabilize the blue PHOLEDs for long term driving. Therefore, the effect of the exciton blocking materials on the lifetime of the blue PHOLEDs was examined by collecting luminance data according to driving time at a constant current driving mode. Luminance decay curves in Fig. 8 suggests that the DBTTrz and DBFTrz exciton blocking materials had little negative effect on the lifetime of the blue PHOLEDs. Although initial drop of luminance was slightly significant in the DBTTrz and DBFTrz devices, the luminance decay after initial decrease was similar. Typically, it is difficult to introduce the high triplet energy exciton blocking layer because they quickly degrade the blue PHOLEDs due to intrinsic chemical instability of the high triplet energy compound. However, the DBTTrz and DBFTrz are composed of stable chemical moieties and are widely conjugated by small dihedral angle (0°) between the dibenzothiophene or dibenzofuran core and diphenyltriazine moiety (Fig. 9), which allowed them to maintain the lifetime of the reference device without the exciton blocking layer. Additionally, high glass transition temperature of DBTTrz (195 °C) and DBFTrz (140 °C) as shown in differential scanning calorimeter (DSC) thermograms in Fig. 10 thermally stabilized the DBTTrz and DBFTrz exciton blocking materials and made a contribution to the stable operation of the DBTTrz and DBFTrz devices. Therefore, the DBTTrz and DBFTrz enhanced the EQE of blue PHOLEDs without any degradation of long-term stability.

4. Conclusions

Design, synthesis, and device evaluation of DBTTrz and DBFTrz exciton blocking materials were investigated and the two compounds were effective to improve the EQE of blue PHOLEDs without any degradation of device lifetime. Small dihedral angle between aromatic moieties of DBTTrz and DBFTrz was proposed as the key factor for the stable operation of the blue PHOLEDs in the presence of the high triplet energy exciton blocking materials. Therefore, the dibenzothiophene or dibenzofuran derived triazine type compounds can be suitable for developing stable blue PHOLEDs and various modifications of the DBTTrz and DBFTrz may produce better exciton blocking materials than DBTTrz and DBFTrz in terms of EQE and efficiency.

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