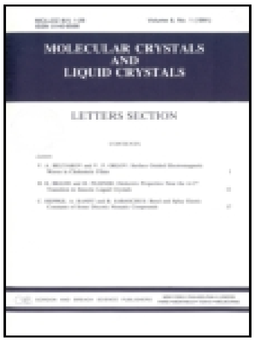

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Hyung Jong Kim, Ik Rang Choe, Tae Ryang Hong, Ju Sik Kang, Hyun Ah Um, Min Ju Cho & Dong Hoon Choi (2015) Synthesis and Characterization of New Dibenzothiophene-based Host Materials for Blue Phosphorescent Organic Light-Emitting Diodes, Molecular Crystals and Liquid Crystals, 621:1, 31-39, DOI: 10.1080/15421406.2015.1095835

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1095835

Mol. Cryst. Liq. Cryst., Vol. 621: pp. 31–39, 2015
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1095835

Synthesis and Characterization of New Dibenzothiophene-based Host Materials for Blue Phosphorescent Organic Light-Emitting Diodes

HYUNG JONG KIM, IK RANG CHOE, TAE RYANG HONG,
JU SIK KANG, HYUN AH UM, MIN JU CHO,
AND DONG HOON CHOI*

Department of Chemistry, Research Institute for Natural Sciences,
Korea University, Seoul, Republic of Korea

*A series of bipolar host materials containing dibenzo[*b,d*]thiophene (DBT) or dibenzo[*b,d*]thiophene 5,5-dioxide core were successfully synthesized, and their physical, photophysical, and electrochemical properties were investigated. The three host materials showed well-localized electron distribution at the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states, as evidenced by theoretical calculations. Triplet energies of the new host materials are higher than 2.6 eV, and the blend film with bis[2-(4,6-difluorophenyl)pyridinato-C^2,N](picolinato)iridium(III) (FIrpic) as a blue phosphorescent dopant showed highly efficient energy transfer between the host material and dopant.*

Keywords bipolar host material; triplet energy; energy transfer; phosphorescence

Introduction

Organic light-emitting diodes (OLEDs) have been recognized as a practical technology for the development of future flat panel and flexible displays. The significant progress in OLED technology for practical applications has been supported by the development of a number of small organic molecules for use in display devices. Most conventional OLED materials that show semiconducting properties are fluorescent and phosphorescent molecules. In particular, phosphorescent dye molecules have attracted much attention, since both singlet and triplet excitons can provide highly efficient OLEDs with a theoretical internal quantum efficiency of 100%. [1–3] In particular, cyclometalated Ir(III) complexes show high phosphorescent efficiency, and in recent times, have been frequently employed for fabricating practical OLED devices. Although various Ir(III) complex dopants exhibit red, green, and blue emission, further study is required to obtain highly efficient and long-lifetime blue phosphorescent OLEDs (PhOLEDs), since blue dopants require a larger energy bandgap and higher triplet energy (E_T). [4–6] In addition to the characteristics

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*Address correspondence to Dong Hoon Choi, Department of Chemistry, Research Institute for Natural Sciences, Korea University, Seoul 136-701, Republic of Korea. E-mail: dhchoi8803@korea.ac.kr

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shown by Ir(III) dopants, host materials also require a large E_T, high charge transport ability, and thermal and morphological stability to produce improved device efficiency. [7–9] So far, various types of high-E_T host materials have been synthesized in attempts to improve the performance of blue PhOLEDs, including structures designed with large-bandgap-inducing moieties such as carbazole, arylsilane, and DBT. [10–12[Among them, carbazole is the most widely used hole-transport moiety because of a high E_T and a rigid molecular framework. In addition, the carbazole moiety is easily substituted with various electron transport units for preparing the bipolar host. To design highly efficient bipolar host materials, carbazole, carboline, diphenylphosphine oxide, oxadiazole, or triazole can be combined through conjugative units such as benzene, pyridine and triazine. [13–16[After selecting the proper moieties, the geometry of the resultant host material should be considered for increasing the triplet and bandgap energies.

In this work, we designed and synthesized a new series of bipolar host materials containing either DBT or dibenzo[*b,d*]thiophene 5,5-dioxide, and characterized their structures. In addition, their physical, photophysical, and electrochemical properties were investigated and theoretical calculations were performed. The three host materials showed moderately high triplet energies, in the range of 2.66–2.76 eV, in the low-temperature photoluminescence spectra (at 77K). Thermal analysis determined that the glass transition temperature is around 113–153°C, which is favorable for promoting morphological stability after blending the blue-emitting dopants. The theoretical calculations also supported the potential of our bipolar host materials for blue PhOLEDs. With an E_T higher than 2.6 eV, a blend film of the new host materials with FIrpic as a blue phosphorescent dopant exhibited highly efficient exothermic energy transfer from host material to dopant.

Experimental Section

Materials

All reagents were purchased from Acros, TCI, and Sigma-Aldrich Co. and used without further purification, unless otherwise stated. The reagent-grade solvents used in this study were freshly dried using standard distillation methods. Intermediate 3,6-diphenyl-9*H*-carbazole (**1**) and 2-(dibenzo[*b,d*]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**) were prepared by following the published procedures. [17, 18[

*9-(3-Bromophenyl)-3,6-diphenyl-9*H*-carbazole (2).* Under an argon atmosphere, **1** (2.91 g, 9.11 mmol), 1-bromo-3-iodobenzene (2.83 g. 10.0 mmol), potassium phosphate tribasic (K_3PO_4, 9.67 g, 45.6 mmol), CuI (0.35 g, 1.82 mmol), and *trans*-1,2-diaminocyclohexane (0.52 g, 4.56 mmol) were added to dry toluene (40 mL), and the mixture was stirred at 100°C for 18 h. After completion of the reaction, the mixture was filtered through celite and washed with methylene chloride (MC). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel column chromatography (eluent: MC : hexane = 1:3) to give 3.37 g (a 78% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.38 (s, 2H), 7.79 – 7.78 (s, 1H), 7.74 - 7.71 (d, J = 7.95 Hz, 3H), 7.69 – 7.66 (d, J = 8.52 Hz, 2H), 7.63 – 7.57 (t, J = 7.68 Hz, 2H), 7.55 – 7.50 (d, J = 11.52 Hz, 2H), 7.49 – 7.45 (d, J = 8.25 Hz, 6H), 7.38 – 7.32 (t, J = 7.68 Hz, 2H); Anal. Calcd. for $C_{30}H_{20}BrN$: C, 75.95; H, 4.25; Br, 16.84; N, 2.95, found : C, 75.89; H, 4.29; Br, 16.79; N, 3.02

*9-(3-(Dibenzo[*b,d*]thiophen-2-yl)phenyl)-3,6-diphenyl-9*H*-carbazole (4, DBT-P-BPC).* **3** (2.42 g, 7.81 mmol) and **2** (3.37 g, 7.11 mmol) were dissolved in dry toluene (35 mL). Pd(PPh_3)$_4$ (0.16 g, 0.14 mmol), K_2CO_3 (10.7 mL, 2 M in H_2O), and a few drops of Aliquat 336 were added to the reaction mixture, which was then stirred at 90°C for 18 h. The reaction mixture was poured into distilled water and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and concentrated. The crude mixture was purified by silica gel column chromatography (eluent: MC: hexane = 1:1) to give 3.20 g (a 78% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.43 (s, 2H), 8.21 (m, 1H), 7.98 – 7.95 (d, J = 8.79 Hz, 1H), 7.87 – 7.84 (d, J = 6.30 Hz, 2H), 7.80 – 7.71 (m, 7H), 7.66 – 7.64 (d, J = 7.71 Hz, 2H), 7.60 – 7.58 (d, J = 8.25 Hz, 3H), 7.52 – 7.47 (m, 6H), 7.39 – 7.34 (t, J = 6.87 Hz, 3H); Anal. Calcd. for $C_{42}H_{27}NS$: C, 87.31; H, 4.71; N, 2.42; S, 5.55, found : C, 87.38; H, 4.68; N, 2.49; S, 5.45.

*9-(6-Bromopyridin-2-yl)-3,6-diphenyl-9*H*-carbazole (5).* Under an argon atmosphere, **1** (1.34 g, 4.21 mmol), 2-bromo-6-iodopyridine (1.31 g. 4.61 mmol), K_3PO_4 (4.45 g, 21.0 mmol), CuI (0.16 g, 0.84 mmol), and *trans*-1,2-diaminocyclohexane (0.24 g, 2.10 mmol) were added to dry toluene (30 mL), and the mixture was stirred at 100°C for 18 h. After completion of the reaction, the reaction mixture was filtered through celite and washed with MC. The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel column chromatography (eluent: MC: hexane = 1:2) to give 1.38 g (69% yield).

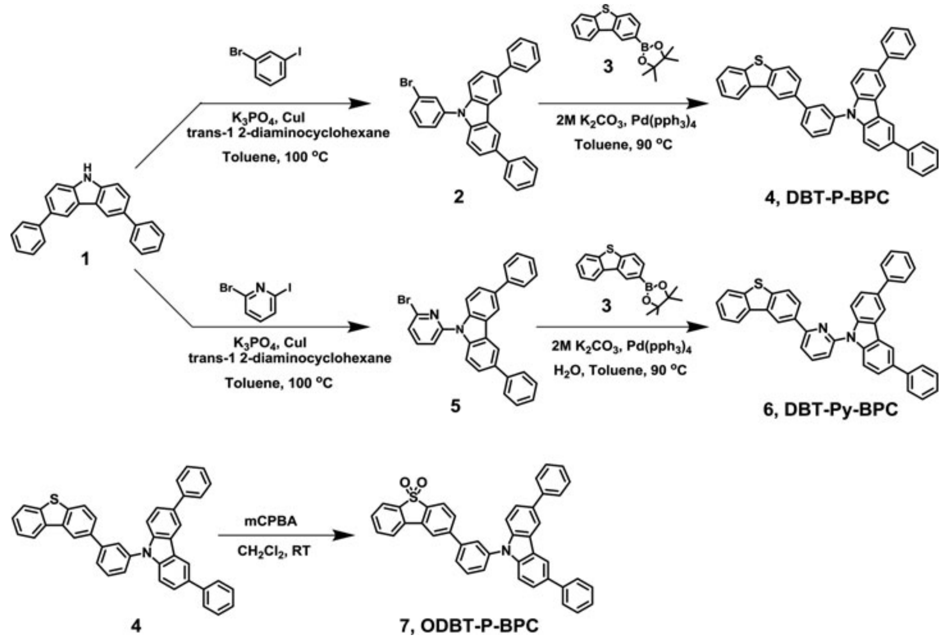
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.35 (s, 1H), 8.00 – 7.97 (d, J = 8.52 Hz, 2H), 7.83 – 7.66 (m, 10H), 7.52 – 7.47 (s, 4H), 7.39 – 7.34 (t, J = 7.41 Hz, 2H); Anal. Calcd. for $C_{29}H_{19}BrN_2$: C, 73.27; H, 4.03; Br, 16.81; N, 5.89, found : C, 73.32; H, 4.01; Br, 16.72; N, 5.95.

*9-(6-(Dibenzo[*b,d*]thiophen-2-yl)pyridin-2-yl)-3,6-diphenyl-9*H*-carbazole (6, DBT-Py-BPC).* **3** (0.99 g, 3.19 mmol), **5** (1.38 g, 2.90 mmol), and dry toluene (30 mL, degassed with nitrogen for 30 min) were added to a 100 mL three-necked round-bottom flask. Pd(PPh_3)$_4$ (0.07 g, 0.06 mol), K_2CO_3 (4.34 mL, 2 M in H_2O), and a few drops of Aliquat 336 were added to the mixture, which was stirred at 90°C for 18 h. The reaction mixture was poured into water and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, and then purified by silica-gel column chromatography (eluent: MC: hexane = 1:1) to give 1.21 g (72% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.01 (s, 1H), 8.44 – 8.42 (s, 2H), 8.31 – 8.25 (d, J = 8.49 Hz, 2H), 8.11 – 8.04 (m, 3H), 8.01 – 7.98 (d, J = 8.79 Hz, 1H), 7.95 – 7.92 (d, J = 7.98 Hz, 1H), 7.90 – 7.87 (m, 1H), 7.79 – 7.74 (m, 6H), 7.67 – 7.65 (d, J = 7.68 Hz, 1H), 7.53 – 7.48 (m, 6H), 7.40 – 7.35 (t, J = 7.41 Hz, 2H); Anal. Calcd. for $C_{41}H_{26}N_2S$: C, 85.09; H, 4.53; N, 4.84; S, 5.54, found : C, 85.12; H, 4.48; N, 4.89; S, 5.51.

*2-(3-(3,6-Diphenyl-9*H*-carbazol-9-yl)phenyl)dibenzo[*b,d*]thiophene 5,5-dioxide (7, ODBT-P-BPC).* An excess of 3-chloroperoxybenzoic acid (mCPBA) was added to a solution of **4** (1.58 g, 2.73 mmol) in CH_2Cl_2 (30 mL) while being stirred at 0°C. After being stirred for 4 h, the reaction mixture was quenched with a 2 M K_2CO_3 solution and extracted with CH_2Cl_2. The combined organic layer was dried with anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel column chromatography (eluent: MC: hexane = 2:1) to give 1.05 g (63% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.45 (s, 1H), 8.05 (s, 1H), 7.97 – 7.93 (m, 2H), 7.89 – 7.85 (d, J = 8.22 Hz, 3H), 7.82 – 7.66 (m, 11H), 7.60 – 7.49 (m, 7H), 7.40 – 7.33



Scheme 1. Synthetic procedure for DBT-based host materials.

(m, 2H); Anal. Calcd. for $C_{42}H_{27}NO_2S$: C, 82.73; H, 4.46; N, 2.30; O, 5.25; S, 5.26, found : C, 82.78; H, 4.41; N, 2.36; O, 5.23; S, 5.22.

Instruments. ^{1}H NMR spectra were recorded with a Varian Mercury 300 MHz spectrometer (Varian, Palo Alto, CA) using deuterated chloroform ($CHCl_3$) purchased from Cambridge Isotope Laboratories (Andover, MA). Elemental analysis was performed using an EA1112 elemental analyzer (Thermo Electron, West Chester, PA). The thermal properties were studied under a nitrogen atmosphere on a Mettler 821e differential scanning calorimeter (DSC) (Mettler, Greifensee, Switzerland). Absorption spectra of the three host materials were obtained using a UV-Vis absorption spectrometer with a photodiode array (HP 8453) in the wavelength range of 190–1100 nm. Photoluminescence (PL) spectra were recorded with a Hitachi F-7000 fluorescence spectrophotometer at room temperature. The E_T of the compound was determined by the highest-energy vibronic subband of the phosphorescence spectrum at 77 K in 2-methyltetrahydrofuran (2-MeTHF). The redox properties were examined through cyclic voltammetry with an eDAQ EA161 potentiostat. Thin films were drop-casted on a Pt plate using $CHCl_3$ as the solvent. The electrolyte solution was 0.10 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in freshly dried acetonitrile. The reference electrode was Ag/AgCl and the counter electrode was a Pt wire (0.5 mm in diameter). The scan rate was 50 mV s^{-1}.

Results and Discussion

Bipolar host materials are avidly studied for use in high performing PhOLEDs, in an effort to achieve well-balanced charge carriers in an emitting layer. By selecting the proper electron-accepting and -donating moieties, three different DBT-based bipolar host molecules were synthesized in this study, the synthetic procedures for which are displayed in **Scheme 1**.

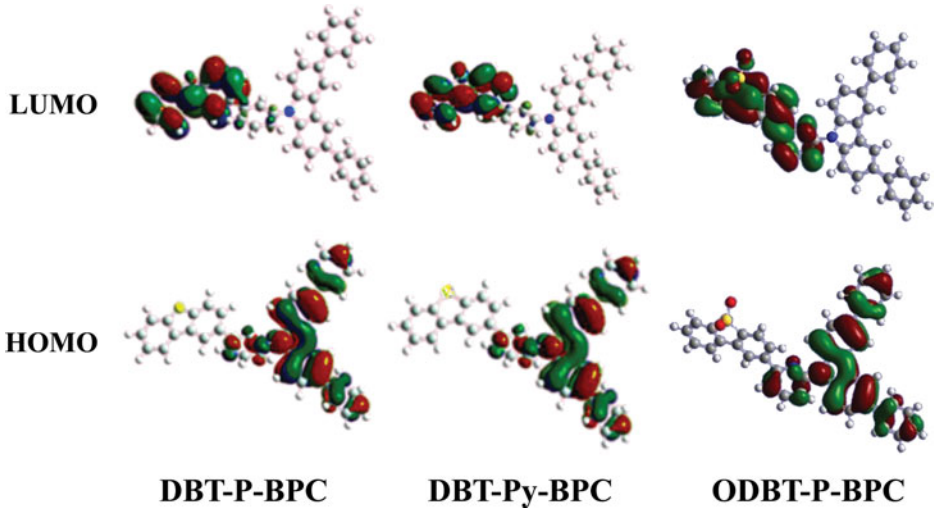


Figure 1. DFT-calculated molecular orbitals of the DBT-based host materials.

In cases of **DBT-P-BPC** and **DBT-Py-BPC**, DBT and carbazole subunits were connected through the 1,3-positions of benzene in a typical conjugated bridge and the 2,6-positions of a pyridine ring, respectively. The Suzuki coupling reaction gave **DBT-P-BPC** (**4**) and **DBT-Py-BPC** (**6**) in a high yield (above 70%) using compounds **2**, **3**, and **5**. To promote the electron-accepting ability, the **ODBT-P-BPC** molecule was then prepared by oxidizing **DBT-P-BPC**.

To investigate the electron distribution of the building blocks used in this study, density functional theory (DFT) calculations were carried out for the three host molecules. As shown in Fig. 1, the HOMOs of the three host materials were locally distributed over the carbazole

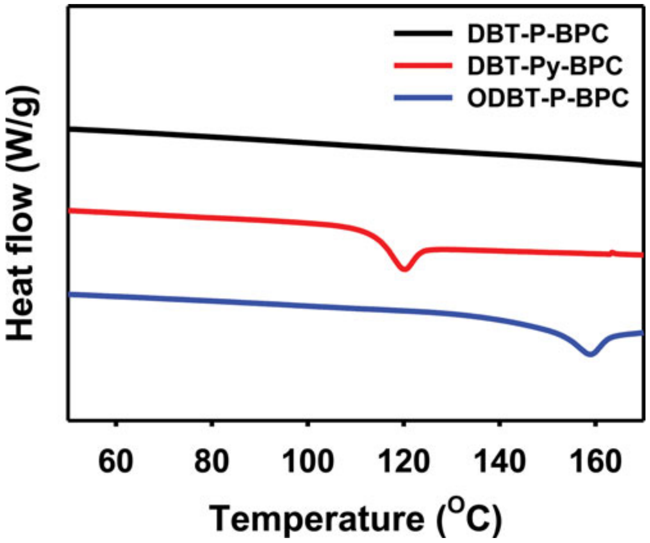


Figure 2. DSC curves for DBT-based host materials.

Table 1. Physical, optical, and electrochemical properties of DBT-based host materials

Host material	T_g (°C)	Absorbance (nm)	PL (nm)	$\lambda_{cut\ off}$ (nm)	E_g^{opt} (eV)	E_T (eV)	E_{ox} (V)	HOMO (eV)	LUMO (eV)
DBT-P-BPC	—	253, 294, 355	387	369	3.36	2.76	1.19	−5.62	−2.26
DBT-Py-BPC	113	254, 296, 351	399	368	3.37	2.70	1.13	−5.66	−2.29
ODBT-P-BPC	149	262, 295, 355	470	371	3.34	2.66	1.17	−5.60	−2.26

moiety and the π-bridge units of the benzene and pyridine rings. On the other hand, the LUMO distributions were localized on the DBT units, which indicate that the three host materials could have strong bipolar character, and therefore highly efficient electron and hole transport pathways.

The thermal properties of the DBT-based host materials were investigated using DSC under nitrogen. As shown in Fig. 2, the glass transition temperatures (T_g) are 113°C and 149°C for **DBT-Py-BPC** and **ODBT-P-BPC**, respectively. Unfortunately, the **DBT-P-BPC** molecule did not show clear transition behavior in the temperature range of 25-180°C.

UV-Vis absorption, PL, and low-temperature PL (LT-PL) spectra of the three host materials were measured in dilute methylene chloride solutions (Fig. 3). The spectroscopic parameters of the three materials are summarized in Table 1.

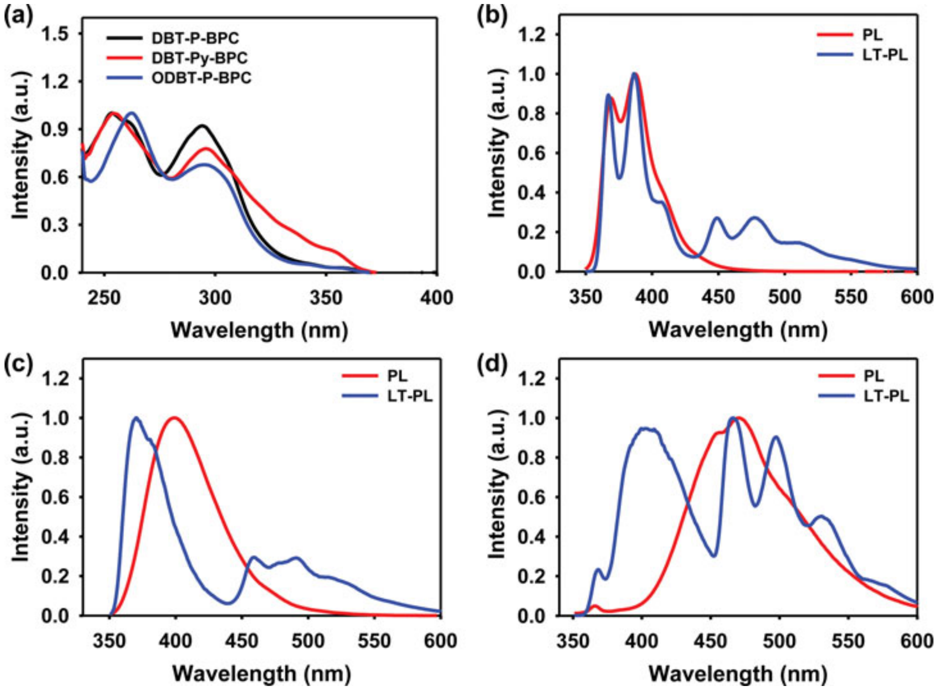


Figure 3. (a) UV-Vis absorption spectra of DBT-based host materials; PL and LT-PL (recorded at 77K) spectra of (b) DBT-P-BPC, (c) DBT-Py-BPC, and (d) ODBT-P-BPC.

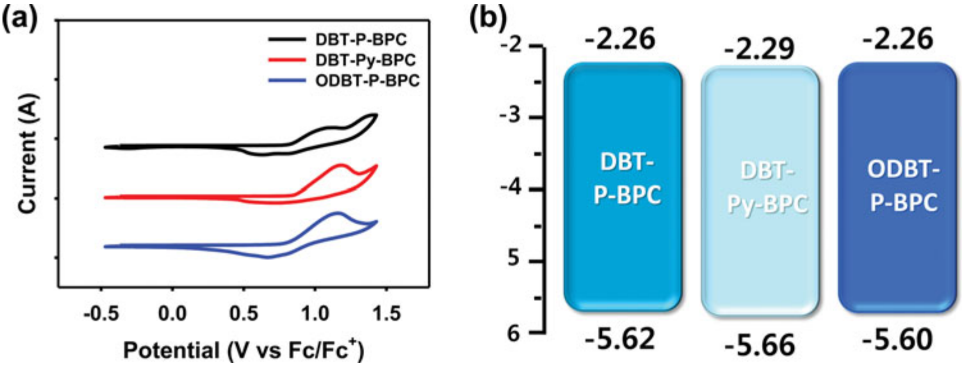


Figure 4. (a) Cyclic voltammogram curves and (b) HOMO-LUMO energy gap diagram for **DBT-P-BPC**, **DBT-Py-BPC**, and **ODBT-P-BPC**.

In the absorption spectra of the solutions, clear $\pi-\pi^*$ transitions of the three DBT-based host materials appeared below 300 nm. The optical band gap energies (E_g^{opt}) were determined from the absorption edges ($\lambda_{cut\text{-}off}$) as 3.36, 3.37, and 3.34 eV for **DBT-P-BPC**, **DBT-Py-BPC**, and **ODBT-P-BPC**, respectively. To investigate the excited E_T levels of the host molecules, LT-PL spectra were obtained at 77 K, which gave the triplet energies to be 2.76 eV for **DBT-P-BPC**, 2.70 eV for **DBT-Py-BPC,** and 2.66 eV for **ODBT-P-BPC**. These moderately high E_T values of over 2.6 eV indicate that all three molecules are suitable for application as host materials for blue PhOLEDs.

The HOMO and LUMO levels of the host materials in PhOLEDs are critical for governing efficient charge transport between the hole transport layer and the emitting layer. The electrochemical properties of the DBT-based host materials were examined by cyclic voltammetry; the results are displayed in Fig. 4 and Table 1. The oxidation potentials (E_{ox}) of **DBT-P-BPC**, **DBT-Py-BPC**, and **ODBT-P-BPC** were found to be 1.19, 1.13, and 1.17 V, respectively. The HOMO levels of the three host molecules were calculated from the oxidation potentials and are in the range of −5.60 to −5.66 eV, again making them suitable for use as emitting layers in blue PhOLEDs. The LUMO levels are −2.26 eV for **DBT-P-BPC**, −2.29 eV for **DBT-Py-BPC**, and −2.26 eV for **ODBT-P-BPC**, as calculated from the energies of the HOMO levels and E_g^{opt}.

Finally, in order to examine the functionality of DBT-based molecules as host materials in blue PhOLEDs, FIrpic as blue dopant was mixed into the synthesized DBT-based molecules at four different concentrations in monochlorobenzene. Thin films were then fabricated on glass substrates by the spin-coating method in order to obtain the PL spectra. Fig. 5 shows the variation in the PL spectra with the FIrpic concentration in the range of 5–20 wt %. As the FIrpic concentration increases, the PL intensity of host materials around 400 nm decreases drastically. The optimal concentration of FIrpic was found to be 20 wt % in the host material, since at that concentration there was a complete disappearance of the original PL peak of the host material, but the intensity of blue emission was maintained. In brief, the PL studies of the doped matrices unambiguously demonstrated that a highly efficient energy transfer from host material to FIrpic could successfully be achieved.

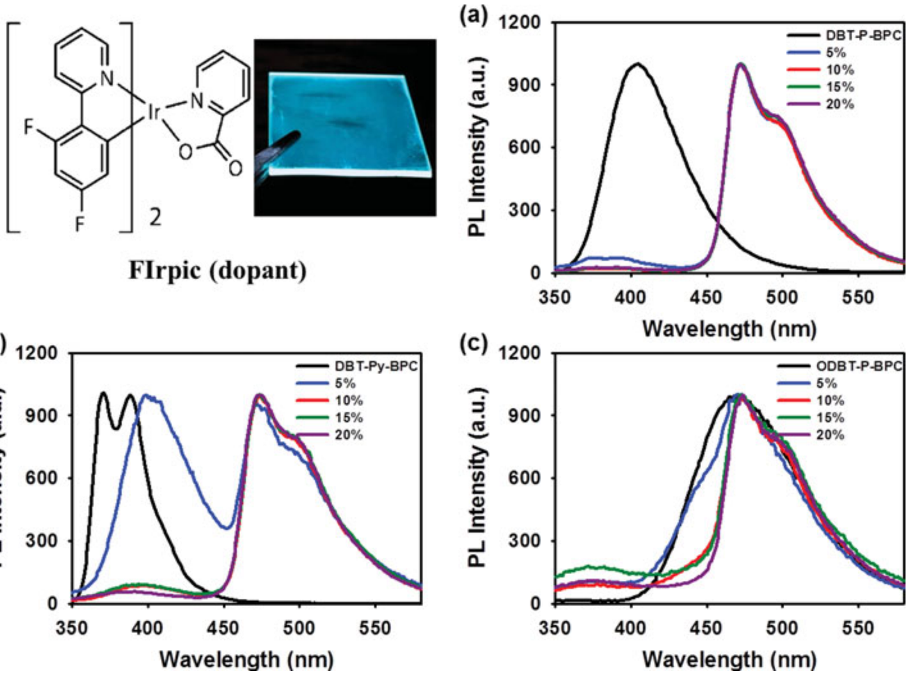


Figure 5. PL spectra of the DBT-based host materials doped with FIrpic in varying concentrations, in thin film states: (a) **DBT-P-BPC**, (b) **DBT-Py-BPC**, and (c) **ODBT-P-BPC**.

Conclusion

We have successfully synthesized and characterized a new series of bipolar host materials containing DBT or dibenzo[*b,d*]thiophene 5,5-dioxide for blue phosphorescent OLEDs. The triplet energies of the three host materials were found to be suitable for sky-blue phosphorescent OLEDs, with moderately high glass transition temperatures and promising potential improvements in morphological and device stability when blended with blue emitting dopants. We confirmed their unique function as bipolar host materials by observing a highly efficient energy transfer from host to FIrpic dopants, though PL spectroscopy. Our study obviously demonstrates that DBT or dibenzo[*b,d*]thiophene 5,5-dioxide-containing host materials can be utilized for fabricating highly efficient blue PhOLED devices.

Acknowledgments

This research was supported by National Research Foundation of Korea (NRF2012R1A2A1A01008797 & 20110026418) and by Key Research Institute Program through the NRF funded by the Ministry of Education, Science and Technology (NRF20100020209).

References

[1] Forrest, S. R. (2004). *Nature*., *428*, 911.
[2] Misra, A. *et al.* (2006). *Semicond. Sci. Technol.*, *21*, R35.
[3] D'Andrade, B. W., & Forrest, S. R. (2004). *Adv. Mater.*, *16*, 1585.

[4] Su, S. J. *et al.* (2008). *Chem. Mater.*, *20*, 1691.
[5] Gong, S. *et al.* (2010). *Adv. Mater.*, *22*, 5370.
[6] Chou, H. H., & Cheng, C. H. (2010). *Adv. Mater.*, *22*, 2468.
[7] Schrogel, P. *et al.* (2011). *J. Mater. Chem.*, *21*, 2266.
[8] He, J. *et al.* (2009). *J. Phys. Chem. C.*, *113*, 6761.
[9] Tao, Y. *et al.* (2010). *Adv. Funct. Mater.*, *20*, 2923.
[10] Tao, Y. *et al.*(2008). *Angew. Chem. Int. Ed.*, *47*, 8104.
[11] Gong, S. *et al.* (2011). *Adv. Funct. Mater.*, *21*, 1168.
[12] Han, C. *et al.* (2012). *J. Am. Chem. Soc.*, *134*, 19179.
[13] Kim, S. J. *et al.* (2013) *Chem. Commun.*, *49*, 6788.
[14] Koech, P. K. *et al.* (2010). *Org. Lett.*, *12*, 5534.
[15] Tao, B. Y. *et al.* (2010). *Adv. Funct. Mater.*, *20*, 304.
[16] Tao, Y. *et al.* (2010). *J. Phys. Chem.*, *114*, 601
[17] Inoue, M. *et al.* (2003). *J. Am. Chem. Soc.*, *125*, 1140
[18] Kim, C. S. *et al.* (2014). *WO Pat. 2014054912 A1*