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Dimesitylborane Substituent and Their Green PHOLED  
Performances**

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## COMMUNICATION

## Synthesis of Dibenzothiophene-based Host Materials with Dimesitylborane Substituent and Their Green PHOLED Performances

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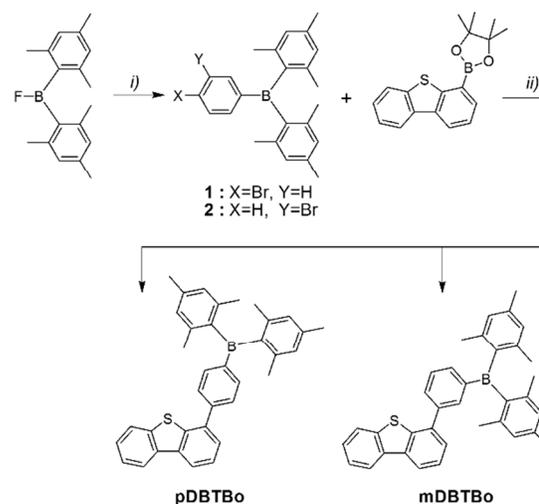
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**In the two isomeric dibenzothiophene-based host materials, the different linkages between dibenzothiophene and dimesitylborane on phenyl spacer dictated their photophysical properties. Whereas, the performances of Ir(ppy)<sub>2</sub>(acac)-based green phosphorescent devices with two isomeric host materials were similar regardless of different linkage position.**

The development of organic light-emitting diodes (OLEDs) based on phosphorescent heavy-metal complexes has drawn tremendous attention because they can harvest both singlet and triplet excitons for light emission, providing the opportunity to accomplish internal electroluminescence (EL) quantum efficiency of close to 100%.<sup>1</sup> However, phosphorescent OLEDs (PHOLEDs) still suffer from severe efficiency roll-off at high current densities caused by triplet-triplet or triplet-polaron exciton annihilation.<sup>2</sup> To compensate suppressed efficiency of PHOLEDs, suitable host materials have been generally employed in the emission layer. Consequently, in PHOLEDs, the device performances (external quantum efficiency, current efficiency, and lifetime *etc.*) should depend on characteristics of the host materials. This is because the triplet energy of the host materials should be higher than those of the phosphorescent dopant, in order to avoid reverse triplet energy transfer from the dopant to the host and to confine triplet excitons to the emission zone. Hence, the designing host materials with these features remains a challenge for material researchers. The main text of the article should go here with headings as appropriate.

Numerous host materials consisting of both electron-rich and electron-deficient functional groups have been reported to remarkably improve the device efficiency due to the hole- and electron-transporting ability. Up to now, carbazole moiety is always an important building unit in design of the most effective host materials for PHOLEDs due to its electron-donating nature. Also, carbazole has a high triplet energy of 3.0 eV, leaving abundant structural modification possibilities. Unfortunately, the lack of electron transporting property in carbazole usually requires the attachment of electron withdrawing group to balance the carrier transport.<sup>3</sup> Recently, new heterocyclic unit similar to carbazole moiety, dibenzothiophene (DBT), was introduced in constructing

new host materials<sup>4</sup> for PHOLEDs because it has also high triplet energy of 3.04 eV and good hole-transporting ability.<sup>5</sup> Here we designed and synthesized two DBT-based structural isomers by finely tuning the linking topology between the two substituents (DBT and dimesityl borane units) and the phenyl group from para-position to meta-positions. We anticipate that the simple modification of linking topology would endow the material with relative high triplet energies. We will present a comprehensive investigation that encompasses the thermal, photophysical, and electrochemical properties of the compounds, and demonstrate the applicability of these materials as host for green PHOLEDs.



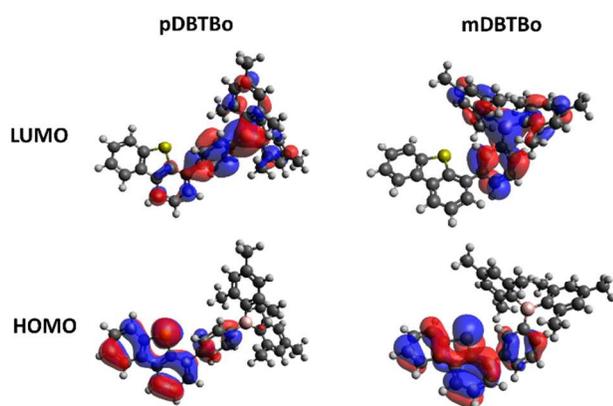
**Scheme 1.** Reagents and conditions: (i) dihalobenzene, *n*-BuLi, THF, -78 °C; (ii) K<sub>2</sub>CO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, reflux.

Two structural isomers, (4-(dibenzo[*b,d*]thiophene-4-yl)phenyl)dimesitylborane (pDBTBo) and (3-(dibenzo[*b,d*]thiophene-4-yl)phenyl)dimesitylborane (mDBTBo), were synthesized by boronation and Suzuki-Miyaura coupling reaction. The intermediates, 1 (73 %) and 2 (66 %), were synthesized by the reaction of 1,4-dibromobenzene or 3-bromoiodobenzene first with *n*-butyllithium to give the lithiated intermediates which were

subsequently treated with fluorodimesityl borane. The intermediates were coupled with 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) dibenzothiophene by Suzuki-Miyaura coupling reaction under basic condition to form the desired pDBTBo (61 %) and mDBTBo (65 %). The desired host materials were fully characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and mass spectrometry. The detailed synthetic procedures and structural characterizations were presented in the experimental section. (Scheme 1)

The thermal behavior under heating of the host materials was studied by DSC and TGA under a nitrogen atmosphere. The glass transition temperatures of pDBTBo and mDBTBo were clearly detected at 90.4 °C and 82.2 °C, respectively. These glass transition temperatures were higher than that of the mCP (55 °C)<sup>6</sup> because of their rigid chemical structure. In addition, the decomposition temperatures at which initial 5 wt.-% loss of mass were 241.4 °C (pDBTBo) and 251.8 °C (mDBTBo). From thermal characterization results, they should be suitable to use as PHOLED component for long life time. (See Figure S3 and S4 in ESI<sup>†</sup>)

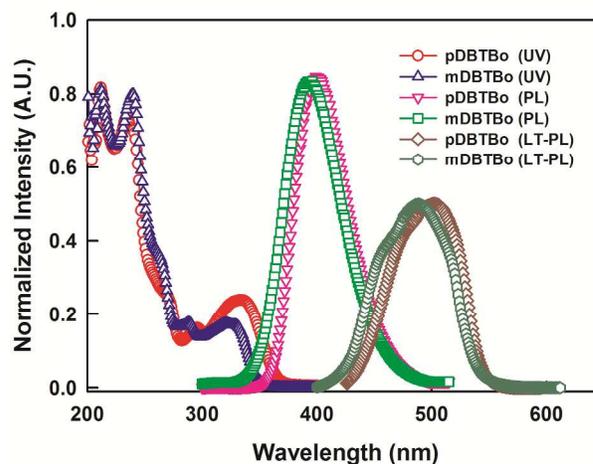
Theoretical molecular orbital distribution of pDBTBo and mDBTBo was calculated with the Gaussian program at the B3LYP/6-31G(d) level, using the density function theory (DFT) for the geometry optimizations. As shown in the Figure 1, the highest occupied molecular orbital (HOMO) of pDBTBo and mDBTBo was mainly dispersed on the DBT and central phenyl group because of stronger electron withdrawing nature of the dimesitylborane moiety. In contrast, their lowest unoccupied molecular orbitals (LUMOs) were localized to the dimesitylborane unit; however, in the case of pDBTBo, a trivial extension of the LUMO to the DBT unit was observed. From these simulation results, the DBT moiety should act as a hole transport unit and the dimesitylborane moiety should play a role as an electron transport unit in the designed host materials.



**Fig. 1** DFT calculations of HOMO and LUMO distribution for pDBTBo and mDBTBo.

Absorption, photoluminescence (PL), and low-temperature PL emission spectra of the synthesized host materials were shown in Figure 2. The relatively weak peaks at around 330 nm which appeared in absorption spectra of all these materials can be attributed to the  $n\text{-}\pi^*$  transitions of DBT group.<sup>7</sup> The absorption peaks below 290 nm could be assigned to  $\pi\text{-}\pi^*$  transitions.<sup>7b</sup> The absorption edges of the UV/vis spectra for pDBTBo and mDBTBo were 366, and 355 nm, which corresponded to the optical bandgap of 3.39 and 3.49 eV, respectively. This discrepancy should be induced by more extended conjugation length of para-substituted pDBTBo compared to meta-substituted mDBTBo. The solution PL emissions of pDBTBo and mDBTBo were observed at 400 and 392 nm, respectively. The narrow bandgap of pDBTBo contributed to the small red-shift (6

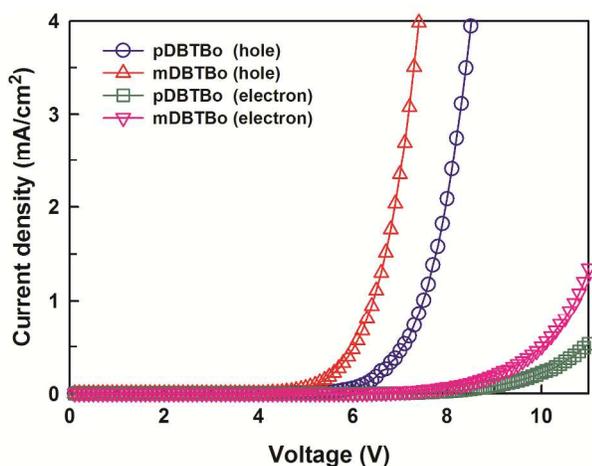
nm) of the PL emission peak compared to that of mDBTBo. The triplet energies of pDBTBo and mDBTBo were 2.673 and 2.71 eV, which could be calculated from the first shoulder PL emission peak of the low temperature (77 K) PL spectra at 4471 and 451 nm, respectively. The obtained low temperature PL emission behaviour showed similar spectrum regardless their different chemical structure (structural isomer). The triplet energy of mDBTBo was higher than that of pDBTBo due to effective breaking of conjugation length through meta-substitution of the mDBTBo. Because the triplet energies of the host materials were higher than the estimated value for Ir(ppy)<sub>2</sub>(acac) ( $E_T = 2.54$  eV),<sup>8</sup> they were sufficient to be used as host materials in Ir(ppy)<sub>2</sub>(acac)-based green PHOLEDs. As reported previously, the higher triplet energy of the host material would facilitate energy transfer from the host to the dopant in host-guest system.<sup>9</sup>



**Fig. 2** UV/vis absorption and PL spectra of pDBTBo and mDBTBo.

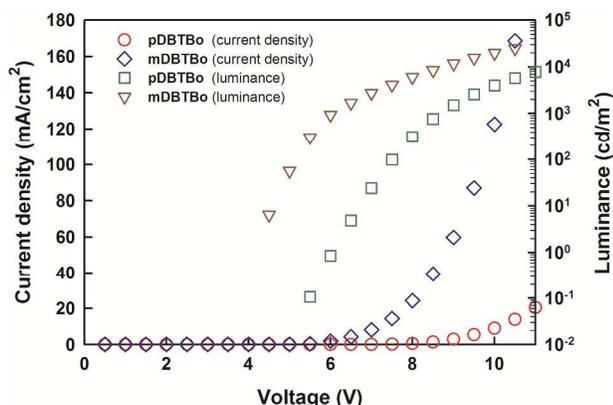
The HOMO levels of pDBTBo and mDBTBo were calculated from the electrochemical oxidation onset potential peak in cyclic voltammogram. All the materials showed distinct oxidation processes corresponding to the oxidation of the sulfur atom and exhibited an irreversible oxidation peaks. (See Figure S5 in ESI<sup>†</sup>) Their HOMO levels were calculated as -5.92 and -6.07 eV, respectively. The LUMO levels of them were -2.53 and -2.58 eV, calculated from the HOMO level and energy bandgap determined from the UV/vis absorption threshold.

Hole- and electron-only devices composed of pDBTBo and mDBTBo were fabricated to compare the hole and electron density of host materials. The structure of these devices based on pDBTBo and mDBTBo were fabricated using following structures: ITO/PEDOT:PSS (60nm)/TAPC (20nm)/mCP (10nm)/ Host (25nm)/TAPC (5nm)/Al (hole); ITO/PEDOT:PSS (60nm)/TSPO1 (10nm)/Host (25nm)/TSPO1 (5nm)/TPBi (30nm)/LiF (0.15nm)/Al (electron). Figure 3 showed the current density-voltage curves of hole- and electron-only devices bearing pDBTBo and mDBTBo. Hole and electron current densities of mDBTBo were higher than those of pDBTBo, which indicates that mDBTBo shows better performance than pDBTBo, in terms of charge transportation. Generally, the hole and electron current densities reflect charge injection and charge transport properties. However, in the case of pDBTBo and mDBTBo, the hole and electron densities are related with only charge transport properties as there was no barrier for charge injection in both materials. Therefore, it can be estimated that mDBTBo is better than pDBTBo in terms of charge transport.



**Fig. 3** Current density-voltage curves of hole- and electron-only devices for pDBTBo and mDBTBo.

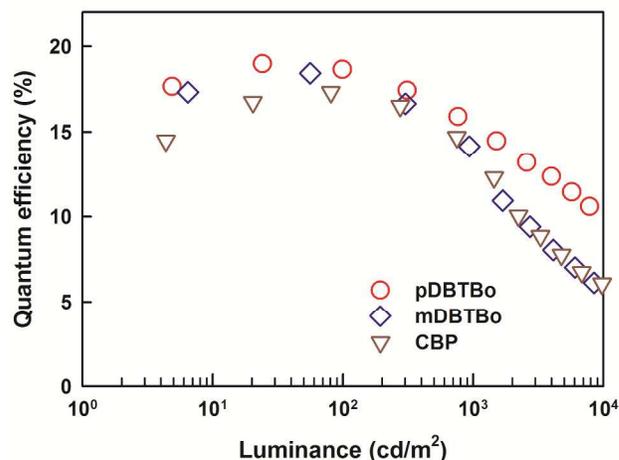
As synthesized host materials showed the HOMO/LUMO levels for good hole and electron injection, and high triplet energy for energy transfer to green emitting Ir(ppy)<sub>2</sub>(acac), they were investigated as the host materials for Ir(ppy)<sub>2</sub>(acac)-based green PHOLEDs. Figure 4 showed the current density-voltage-luminance curves of the green PHOLEDs with two different structural isomer derived host materials. The green-emitting Ir(ppy)<sub>2</sub>(acac) dopant was optimized at a doping concentration of 5 wt.-% and the device performances were compared. The current density in the mDBTBo device was higher than that in the pDBTBo device because of high hole and electron current densities of mDBTBo.<sup>10</sup> The luminance showed the same tendency as the current density.



**Fig. 4** Current density-voltage-luminance curves of pDBTBo and mDBTBo green PHOLEDs.

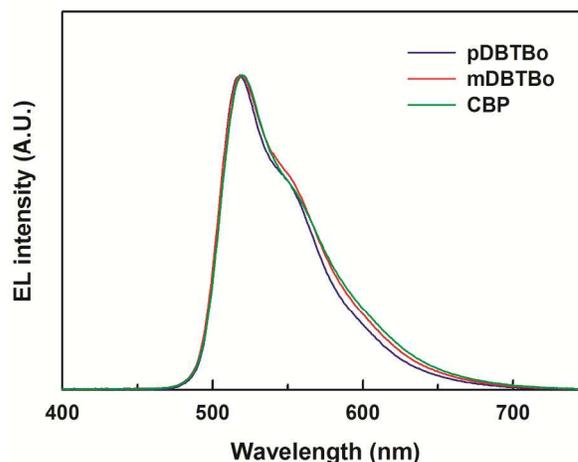
We investigated the device performances based on two structural isomeric hosts and also compared them with commercial available host, 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP), based green PHOLED. Quantum efficiency-luminance curves of the green PHOLED based on pDBTBo, mDBTBo and CBP were presented in Figure 5. The maximum quantum efficiency of the mDBTBo device was similar to that of pDBTBo device but CBP device showed slightly low efficiency compared to DBTBo devices. While the maximum quantum efficiency and quantum efficiency at 1000 cd/m<sup>2</sup> of the mDBTBo device were 17.3 and 13.9 %, the mDBTBo device were 19.0 and 15.4 %, respectively, compared with the 18.4 and 14.1 % values obtained with the pDBTBo device. These results imply that the design concept for constructing new bipolar hosts is adequate to improve the efficiency of PHOLEDs. Both devices showed similar

external quantum efficiencies at low and high luminance. Although the hole and electron current densities of mDBTBo were higher than those of pDBTBo, the relative ratio of the hole current density to the electron current density was similar in the employed PHOLEDs with two isomeric host materials. Therefore, a similar high quantum efficiency was obtained in the two isomeric host materials. The high quantum efficiency of the two host materials was due to the balanced charge density in the emitting layer. The power efficiency was high in the mDBTBo device due to low driving voltage of the mDBTBo device. (See Figure S6 in ESI<sup>†</sup>)



**Fig. 5** Quantum efficiency-luminance curves of pDBTBo, mDBTBo and CBP green PHOLEDs.

The electroluminescence (EL) spectra of the green PHOLEDs were shown in Figure 6. The green emission spectra of typical Ir(ppy)<sub>2</sub>(acac) device with a maximum emission peak at 520 nm and vibrational shoulder peak at 552 nm were exhibited in Figure 6. Furthermore, no other emission peak was observed, suggesting complete energy transfer from the pDBTBo and mDBTBo host to the Ir(ppy)<sub>2</sub>(acac), and charge confinement inside the emitting layer. Thus, high quantum efficiencies were achieved in the green PHOLED with pDBTBo and mDBTBo host materials. The color coordinate of the green PHOLEDs were (CIE<sub>x,y</sub> = 0.31, 0.63) for pDBTBo device, (CIE<sub>x,y</sub> = 0.33, 0.62) for mDBTBo device and (CIE<sub>x,y</sub> = 0.31, 0.63) for CBP device.



**Fig. 6** EL spectra of pDBTBo, mDBTBo and CBP green PHOLEDs.

## Conclusions

In summary, two structural isomers, (4-(dibenzo[b,d]thiophen-4-yl)phenyl)dimesitylborane (pDBTBo) and (3-(dibenzo[b,d]thiophen-4-yl)phenyl)dimesitylborane (mDBTBo), were synthesized as green host materials, successfully. Although the substitution position of strong electron withdrawing group, dimesitylborane moiety, on the host material affected their photophysical properties depending on the conjugation length between DBT and dimesitylborane moieties, they were not much affecting the performances for employed Ir(ppy)<sub>2</sub>(acac)-based green devices. Using the employed Ir(ppy)<sub>2</sub>(acac)-based green device structures, the maximum quantum efficiencies of the pDBTBo and mDBTBo devices were as high as 19.0 and 18.4 %, respectively. This newly designed host materials should be useful for the future development of high triplet energy host materials for green PHOLEDs.

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### Notes and references

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## &lt;Graphical Abstract&gt;

Two structural isomers composed by linking between dibenzothiophene and dimesitylborane moieties on the phenyl group were synthesized and showed similar green device performance regardless of their different linkage positions.

