

Supporting Information for;

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

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General procedure:

Chemicals were commercially purchased and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets precoated SiO₂ (Baker-flex; IB2-F) and visualized by UV light. Column chromatography was conducted by using silica gel (60-200 mesh; Fisher Scientific Co.). Melting point was determined on melting point apparatus (MEL-TEMP; model 1102D). ¹H and ¹³C NMR spectra were recorded on JEOL JNM-LA400 FT NMR spectrometer using CDCl₃, as the solvent, except where noted. Mass spectra were obtained on LC/mass spectrometer (Agilent Technology 6120). Photophysical properties were analyzed by using UV/vis spectrometer (Scinco Co.; S-3100) and photoluminescence (PL) spectrometer (Hitachi High Technologies; F-7000). The host material was dissolved in THF and 2-methoxyethanol at a concentration of ca. 1.0 × 10⁻⁴ M for UV/vis and PL measurements, respectively. Triplet energy of the host material was calculated from low temperature PL spectrum measured in the liquid nitrogen (77 K) condition. Cyclic voltammetry (CV) measurement was conducted by using potentiostat (SP-50; Bio-Logic Science Instruments) in electrolyte solution, which is CH₃CN with tetrabutylammonium perchlorate at 0.1 M concentration. Ag was used as the reference electrode and Pt was the counter electrode. The host material was coated on indium-tin-oxide substrate and immersed in the electrolyte solution for measurement. Ferrocene was used as a standard material of the CV measurement. Glass transition temperature and thermal decomposition temperature were measured by using a differential scanning calorimeter (TA, DSC Q2000) and thermogravimetric analyzer (TA, TGA Q50) at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere, respectively.

Synthesis:

(4-bromophenyl)dimesitylborane (1). A solution of 1,4-dibromobenzene (3.5 g, 14.9 mmol) in THF (80 mL) was stirred under argon atmosphere. After cooling to -78°C, n-BuLi (2.5M in hexanes, 5.96 mL, 14.9 mmol) was added to the solution dropwise over 20 min and the mixture was maintained at -78°C for further 1 hr under inert atmosphere. Then dry dimesitylboron fluoride (2 g, 7.45 mmol) in THF (30 mL) was added to the reaction mixture dropwise. After 1 hr, temperature was raised slowly to ambient temperature and kept stirring overnight. The distilled water was added to the reaction mixture to quench the procedure and the solvent was removed by rotary evaporation. The mixture was extracted with dichloromethane and washed with distilled water three times. The organic layer was separated and dried over anhydrous MgSO₄. The crude product was collected by filtration and was purified by column chromatography (SiO₂) eluting with a n-hexane to give a white solid powder (2.2 g, 73 %): m.p. 189-190 °C; ¹H NMR (400 MHz, δ) 7.48 (d, 2H), 7.36 (d, 2H), 6.83 (s, 4H), 2.31 (s, 6H), 2.00 (s, 12H); ¹³C NMR (100 MHz, δ) 140.92, 139.08, 137.94, 131.45, 128.41, 127.51, 23.57, 21.36.

(3-bromophenyl)dimesitylborane (2). This compound was synthesized according to the same procedure employed for (4-bromophenyl)dimesitylborane (1), except that 3-bromiodobenzene was used instead of 1,4-dibromobenzene. Final product was obtained as a white solid powder (2.0 g, 66 %): m.p. 153-155 °C; ¹H NMR (400 MHz, δ) 7.70 (s, 1H), 7.63 (d, 1H), 7.47 (d, 1H), 7.25 (t, 1H), 6.89 (s, 4H), 2.32 (s, 6H), 2.06 (s, 12H); ¹³C NMR (100

MHz, δ) 148.72, 141.31, 140.93, 139.22, 138.40, 134.71, 134.58, 129.95, 128.74, 128.66, 128.48, 128.18, 123.07, 23.58, 21.37.

General procedure of Suzuki-Miyaura coupling reaction. Aryl bromide compound (1 equivalent) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzothiophene (1.15 equivalent) were dissolved in toluene and 2M K_2CO_3 aqueous solution (2.3 equivalent) was added. The mixture were stirred and bubbled with N_2 gas for 30min. *tetrakis*(triphenylphosphine)palladium(0) (2 mol.-%) was quickly added to the mixture and refluxed with vigorous stirring for 24 hrs. After cooling to room temperature, the mixture was extracted with ethyl acetate and washed with distilled water three times. The organic layer was separated and dried over anhydrous $MgSO_4$. The crude product was collected by filtration and was purified by column chromatography (SiO_2) eluting with a mixture of CH_2Cl_2 : n-hexane (1:20; v/v).

(4-(dibenzo[b,d]thiophen-4-yl)phenyl)dimesitylborane (pDBTBo). White solid powder (1.0 g, 61 %): m.p. 219-220 °C; 1H NMR (400 MHz, δ) 8.17-8.22 (m, 2H), 7.83 (m, 1H), 7.74 (d, 2H), 7.66 (d, 2H), 7.56 (m, 2H), 7.47 (m, 2H), 6.87 (s, 4H), 2.34 (s, 6H), 2.09 (s, 12H); ^{13}C NMR (100 MHz, δ) 144.036, 141.02, 139.70, 138.86, 138.67, 137.02, 136.90, 136.47, 135.86, 128.37, 127.92, 127.13, 126.98, 125.24, 124.54, 122.73, 121.86, 120.90, 23.67, 21.39; ESI-MS: $m/z = 507.5$ $[M-H]^+$ (calcd. $m/z = 507.2$)

(3-(dibenzo[b,d]thiophen-4-yl)phenyl)dimesitylborane (mDBTBo). White solid powder (0.9 g, 65 %): m.p. 221-222 °C; 1H NMR (400 MHz, δ) 8.16 (m, 1H), 8.12 (d, 1H), 7.81 (m, 3H), 7.41-7.60 (m, 6H), 6.83 (s, 4H), 2.30 (s, 6H), 2.08 (s, 12H); ^{13}C NMR (100 MHz, δ) 140.984, 140.39, 139.85, 138.89, 137.24, 136.24, 135.91, 135.78, 135.71, 131.73, 128.56, 128.38, 127.03, 126.86, 125.11, 124.45, 122.72, 121.85, 120.50, 23.64, 21.38; ESI-MS: $m/z = 507.5$ $[M-H]^+$ (calcd. $m/z = 507.2$)

Fabrication of PHOLED device and measurements

The device structure of green PHOLEDs was indium tin oxide (ITO, 150 nm)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 60 nm)/4,4'-cyclohexylidenebis[*N,N*-bis(4-methylphenyl)benzenamine] (TAPC, 20 nm)/*N,N'*-dicarbazolyl-3,5-benzene (mCP, 10 nm)/host material: Ir(ppy) $_2$ (acac) (25 nm, x wt.-%)/4-(triphenylsilyl) phenyldiphenylphosphine oxide (TSPO1, 5 nm)/ 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBi, 30 nm)/LiF (1.5 nm)/Al (200 nm). The doping concentrations of Ir(ppy) $_2$ (acac) in the devices was 5%. The device performances of the green PHOLEDs was measured with Keithley 2400 source measurement unit and Minolta CS-1000 spectroradiometer.

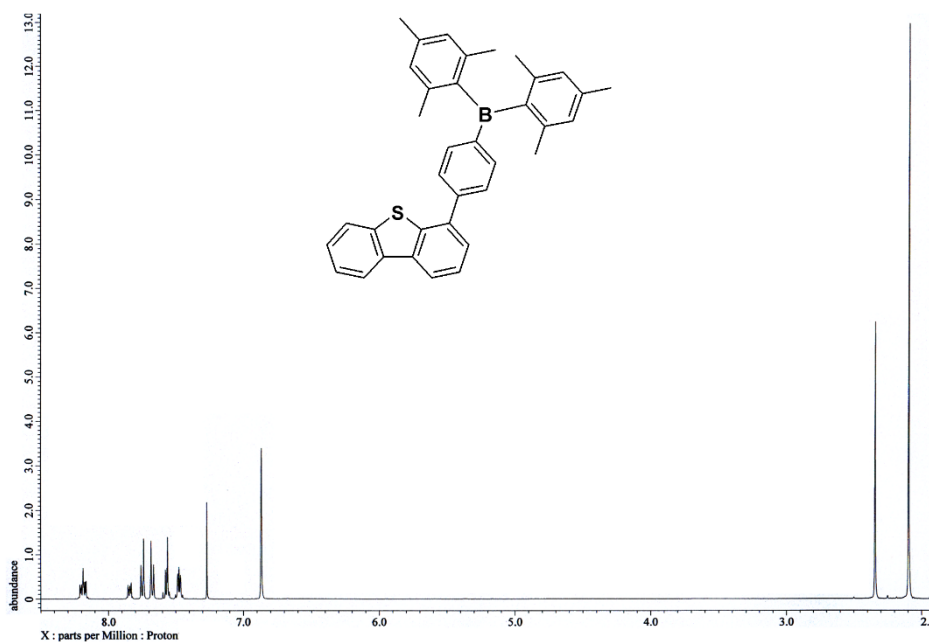


Figure S1. ^1H NMR spectrum of pDBTBo host material.

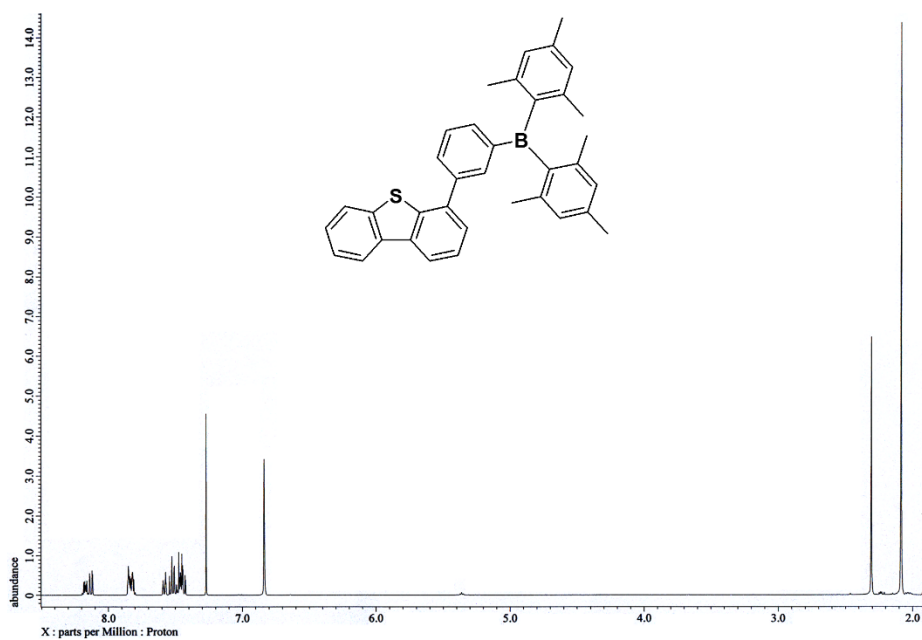


Figure S2. ^1H NMR spectrum of mDBTBo host material.

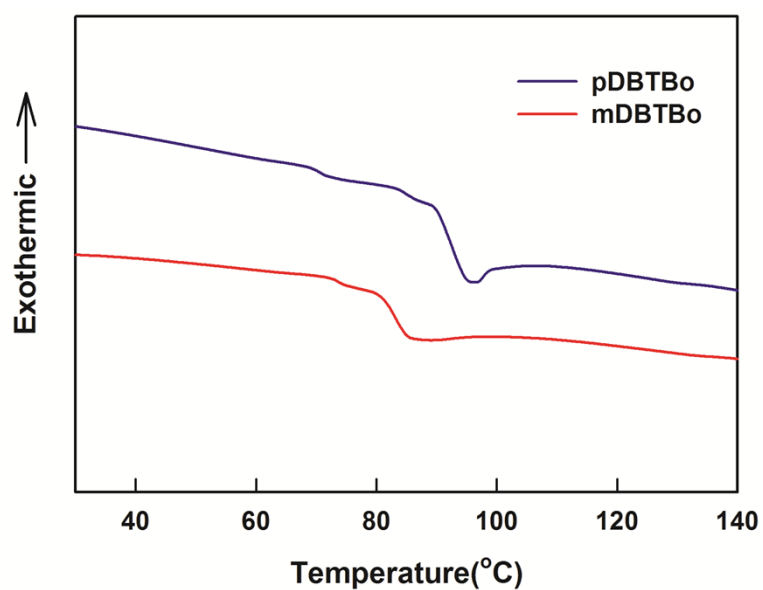


Figure S3. DSC thermograms for pDBTBo and mDBTBo host materials.

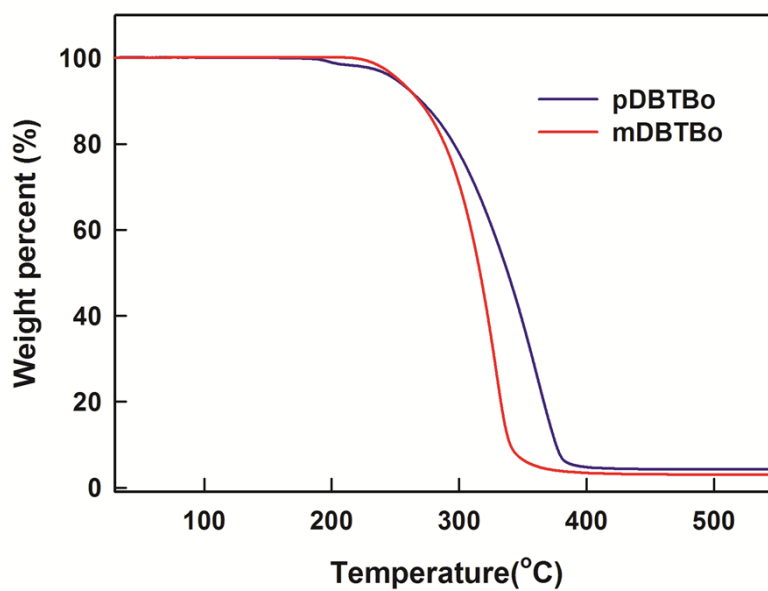


Figure S4. TG thermograms for pDBTBo and mDBTBo host materials.

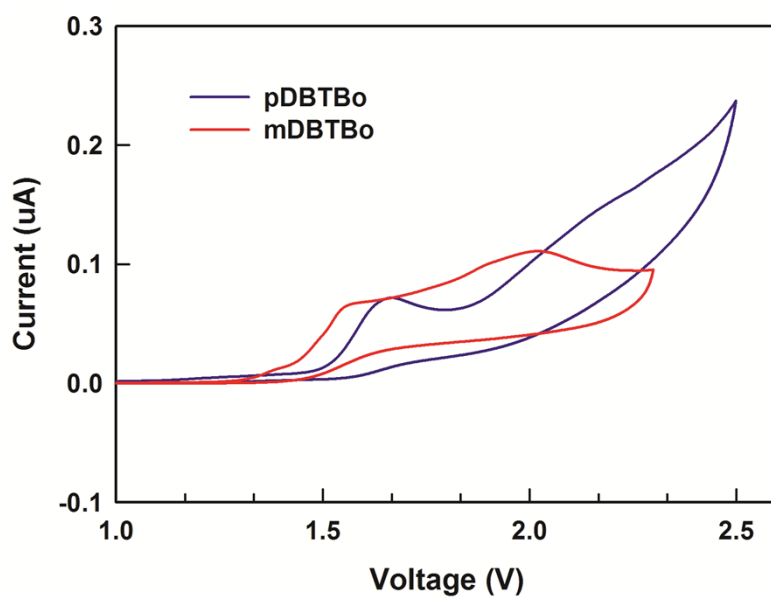


Figure S5. Cyclic voltammogram for pDBTBo and mDBTBo host materials.

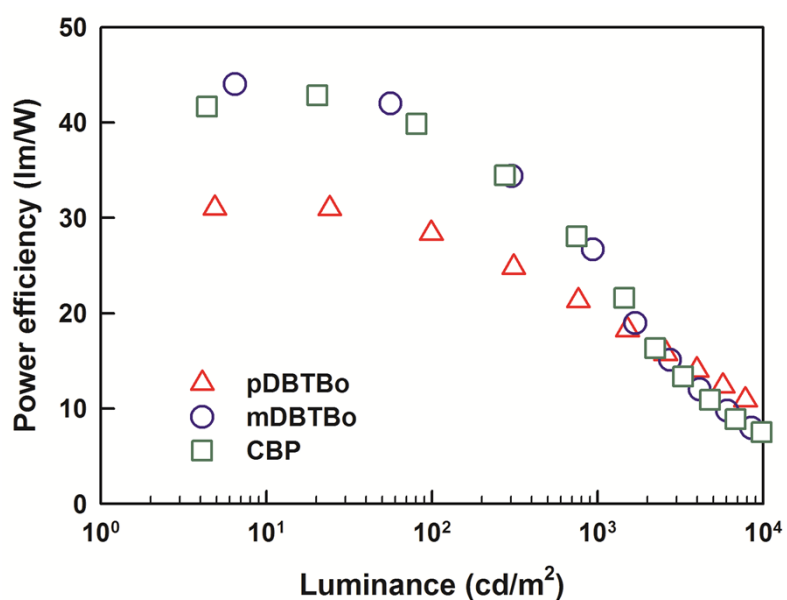


Figure S6. Power efficiency-luminance curves of pDBTBo, mDBTBo and CBP green PHOLEDs.

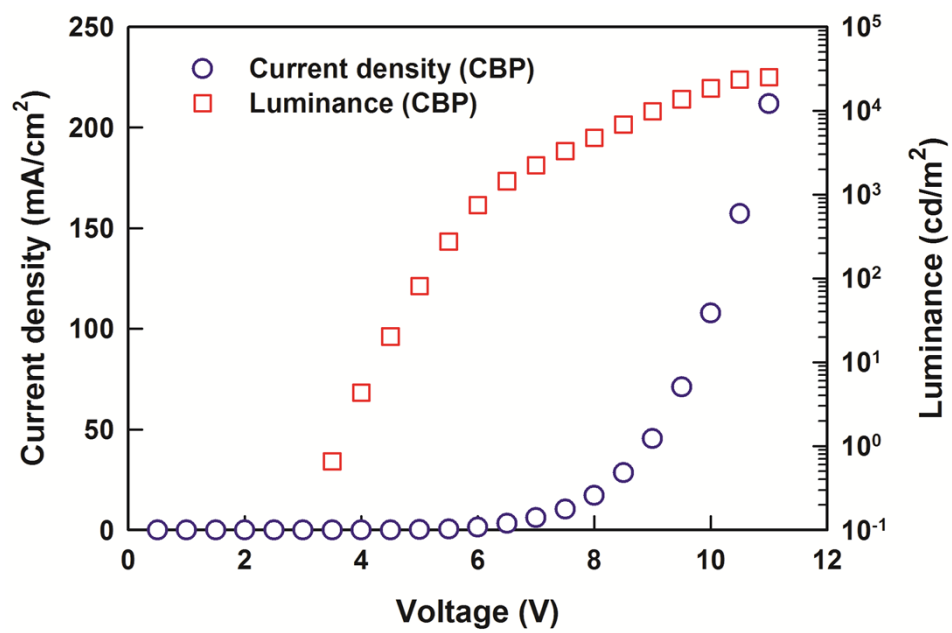


Figure S7. Current density-voltage-luminance curves of CBP green PHOLEDs.