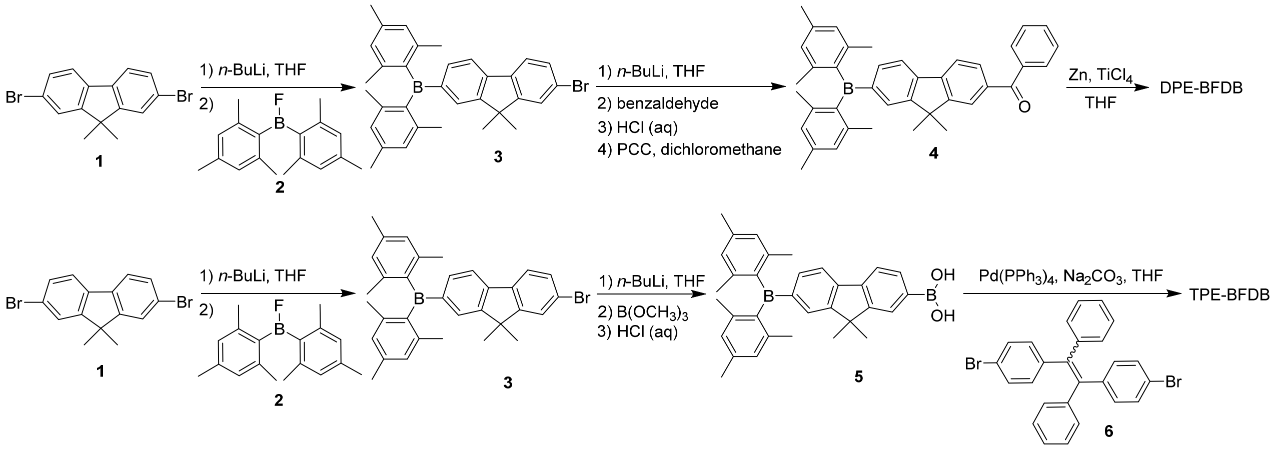
Electronic Supplementary Information (ESI)

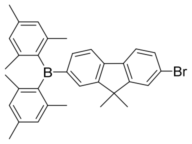
1. General

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Compound **6**[1] and pyridinium chlorchromate[2] (PCC) were prepared according to the known procedures. All other chemicals and reagents were purchased from commercial sources and used as received without further purification. NMR spectra were obtained on a Bruker AV 500 or 600 spectrometer. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. The ground-state geometries were optimized using the density functional with B3LYP hybrid functional at the basis set level of 6-31G(d). UV-vis absorption spectra were measured on a SHIMADZU UV-2600 spectrophotometer. Fluorescence spectra were recorded on a Horiba Fluoromax-4 fluorescence spectrophotometer. Fluorescence quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. TGA analysis was carried on a TA TGA Q5000 and DSC analysis was evaluated on DSC Q1000 under dry nitrogen at a heating rate of 10 ^{o}C min^{-1}. Cyclic voltamogramms were measured on a CHI 610E A14297.

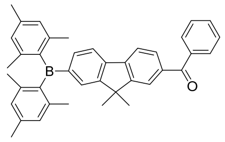
Synthesis and Characterization



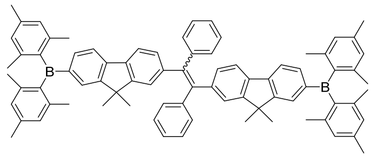
Scheme S1. Synthetic routes to DPE-BFDB and TPE-BFDB.



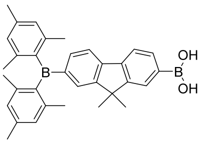
(7-Bromo-9,9-dimethyl-9H-fluoren-2-yl)dimesitylborane **(3)**: Into a 250 mL two-necked round bottom flask was placed 3.52 g (10.0 mmol) of **1**. The flask was evacuated under vacuum and flushed with dry nitrogen for three times. Then 80 mL THF was added. The mixture was cooled to −78 °C, and 4.2 mL (2.4 M in hexane, 10.0 mmol) of *n*-BuLi was added dropwise by a syringe. The mixture was stirred for 2 h at −78 °C and then 2.95 g (11.0 mmol) of dimesitylboron fluoride in 20 mL of THF was slowly injected to the reaction mixture. The mixture was warmed slowly to room temperature and kept stirring for 1 h. The mixture was poured into water and extracted with dichloromethane by three times. The combined organic layers were dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the crude product was purified by silica-gel column chromatography. White solid of **3** was obtained in 85% yield. ^{1}H NMR (600 MHz, CDCl$_3$), δ (ppm): 7.65 (d, 1H, J = 7.8 Hz), 7.61–7.60 (m, 2H), 7.55 (d, 1H, J = 1.8 Hz), 7.52 (d, 1H, J = 7.8 Hz), 7.47 (dd, 1H, J_1 = 1.8 Hz, J_2 = 7.8 Hz), 6.83 (s, 4H), 2.32 (s, 6H), 2.01 (s, 12H), 1.43 (s, 6H). ^{13}C NMR (150 MHz, CDCl$_3$), δ (ppm): 156.80, 152.67, 141.85, 140.88, 138.53, 137.82, 136.32, 130.80, 130.18, 128.19, 126.28, 122.03, 121.97, 119.50, 47.04, 26.73, 23.55, 21.24. HRMS ($C_{33}H_{34}BBr$): *m/z* 520.1960 [M^+, calcd 520.1937].



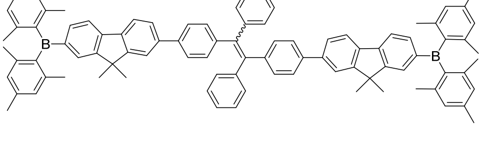
[7-(Dimesitylboranyl)-9,9-dimethyl-9H-fluoren-2-yl](phenyl)methanone **(4)**: Into a 250 mL two-necked round bottom flask was placed 5.20 g (10.0 mmol) of **3**. The flask was evacuated under vacuum and flushed with dry nitrogen for three times. Then 80 mL THF was added. The mixture was cooled to −78 °C, and 4.2 mL (2.4 M in hexane, 10.0 mmol) of *n*-BuLi was added dropwise by a syringe. The mixture was stirred for 2 h at −78 °C and then 1.17 g (11.0 mmol) of benzaldehyde was added to the reaction solution. The mixture was warmed slowly to room temperature and kept stirring for 3 h. The reaction was finally quenched with HCl (2.0 M, 40 mL). Then the mixture was poured into water (100mL) and extracted with dichloromethane by three times. The combined organic layers were dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the crude product was dissolved in anhydrous dichloromethane (50 mL) and then 3.23 g of PCC (15.0 mmol) was added to the solution. The mixture was stirred at room temperature for 5 h. Then the mixture was poured into water and extracted with dichloromethane by three times. The combined organic layers were dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the crude product was purified by silica-gel column chromatography. White solid of compound **4** was obtained in 61% yield. ^1H NMR (600 MHz, $CDCl_3$), δ (ppm): 7.94 (s, 1H), 7.83−7.78 (m, 4H), 7.76 (d, 1H, J = 7.5 Hz), 7.66 (s, 1H), 7.62−7.59 (m, 1H), 7.56 (d, 1H, J = 7.5 Hz), 7.52−7.49 (m, 2H), 6.85 (s, 4H), 2.33 (s, 6H), 2.02 (s, 12H), 1.48 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm): 196.71, 154.83, 154.21, 143.22, 141.53, 140.92, 138.67, 138.16, 136.90, 136.15, 132.24, 130.83, 130.07, 129.99, 128.28, 128.24, 124.46, 120.39, 120.16, 47.02, 26.72, 23.56, 21.26. HRMS ($C_{40}H_{39}BO$): *m/z* 547.3185 [M^+, calcd 546.3094].



1,2-Bis[7-(dimesitylboranyl)-9,9-dimethyl-9H-fluoren-2-yl]-1,2-diphenylethene **(DPE-BFDB)**: Into a 250 mL two-necked round-bottom flask with a reflux condenser was placed **4** (3.28 g, 6.0 mmol), zinc dust (780 mg, 12.0 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen by three times, and then dry THF (100 mL) was added. After the mixture was cooled to −78 °C, $TiCl_4$ (1.14 g, 6.0 mmol) was then added dropwise by a syringe. After stirring for 15 min at −78 °C, the mixture was slowly warmed to room temperature and then was heated to reflux overnight. The mixture was quenched with 10 % aqueous sodium carbonate and extracted with dichloromethane by three times. The combined organic layers were washed with water and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the crude product was purified by silica gel column chromatography. Yellow solids of DPE-BFDB were obtained in 60% yields. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 7.61 (d, 1H, J = 7.5 Hz), 7.54–7.52 (m, 3H), 7.49–7.46 (m, 3H), 7.44 (d, 1H, J = 7.5 Hz), 7.13–7.08 (m, 12H), 7.02–7.00 (m, 2H), 6.83–6.81 (m, 8H), 2.32–2.31 (m, 12H), 2.01–1.98 (m, 24H), 1.16–1.12 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm): 154.32, 154.07, 153.46, 153.34, 144.24, 143.95, 143.77, 143.56, 142.86, 142.79, 141.99, 141.63, 141.56, 140.91, 140.87, 138.38, 138.35, 137.09, 136.98, 136.20, 131.51, 130.76, 130.66, 130.44, 130.33, 128.13, 128.11, 127.75, 127.68, 126.57, 126.53, 126.24, 119.91, 119.36, 119.28, 46.34, 26.62, 26.57, 23.50, 21.23. HRMS ($C_{80}H_{78}B_2$): *m/z* 1060.6288 [M^+, calcd 1060.6290].



[7-(Dimesitylboranyl)-9,9-dimethyl-9H-fluoren-2-yl]boronic acid **(5)**: Into a 250 mL two-necked round bottom flask was placed 5.20 g (10.0 mmol) of **3**. The flask was evacuated under vacuum and flushed with dry nitrogen for three times. Then 80 mL THF was added. The mixture was cooled to −78 °C, and 4.2 mL (2.4 M in hexane, 10.0 mmol) of *n*-BuLi was added dropwise by a syringe. The mixture was stirred for 2 h at −78 °C and then 1.15 g (11.0 mmol) of trimethyl borate was added to the reaction solution in one portion. The mixture was warmed slowly to room temperature and kept stirring for 12 h. The reaction was finally quenched with HCl (2.0 M, 40 mL). Then the mixture was poured into water (100mL) and extracted with dichloromethane three times. The combined organic layers were dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the crude product was purified by silica-gel column chromatography. White solid of compound **4** was obtained in ~70% yield. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 8.33–8.32 (m, 2H), 7.95 (d, 1H, J = 7.5 Hz), 7.81 (d, 1H, J = 7.5 Hz), 7.7 (s, 1H), 7.58 (d, 1H, J = 7.5 Hz), 6.86 (s, 4H), 2.35 (s, 6H), 2.04 (s, 12H), 1.58 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm): 154.18, 153.96, 145.87, 143.28, 142.49, 141.96, 140.96, 138.56, 138.52, 136.15, 134.91, 130.91, 129.60, 128.22, 120.27, 120.18, 46.84, 26.93, 23.59, 21.27. HRMS ($C_{32}H_{36}B_2O_2$): *m/z* 486.2892 [M^+, calcd 486.2901].



1,2-Bis(4-(7-(dimesitylboranyl)-9,9-dimethyl-9H-fluoren-2-yl)phenyl)-1,2-diphenylethene (TPE-BFDB): Into a 250 mL two-necked round bottom flask was placed compound **6** (1.47 g, 3.0 mmol), **5** (4.37 g, 9.0 mmol), $Pd(PPh_3)_4$ (104 mg, 0.09 mmol) and Na_2CO_3 (1.27 g, 12.0 mmol).

The flask was evacuated under vacuum and flushed with dry nitrogen for three times and then 80 mL THF and 20 mL water were added. The reaction mixture was refluxed for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane by three times. The combined organic layers were dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the crude product was purified by silica-gel column chromatography. Yellow solid of TPE-TPDB was isolated in 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$, δ (ppm): 7.77–7.76 (m, 2H), 7.69–7.66 (m, 2H), 7.63–7.61 (m, 4H), 7.57–7.43 (m, 8H), 7.19–7.08 (m, 14H), 6.84–6.83 (m, 8H), 2.33–2.32 (m, 12H), 2.03–2.02 (m, 24H), 1.46–1.45 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm): 155.49, 153.31, 144.80, 143.82, 142.88, 142.70, 141.99, 140.91, 140.70, 140.54, 139.17, 138.41, 138.01, 136.34, 131.90, 131.48, 130.85, 128.16, 127.86, 127.70, 126.52, 126.39, 126.24, 125.98, 121.10, 120.97, 119.47, 46.84, 26.94, 23.56, 21.24. HRMS ($C_{92}H_{86}B_2$): *m/z* 1212.6906.1713 [M^+, calcd 1212.6916].

2. Devices Fabrication

The multilayer OLEDs were fabricated by the vacuum-deposition method. Organic layers were deposited by high-vacuum (5×10^{-4} Pa) thermal evaporation onto a glass (3 cm × 4 cm) substrate pre-coated with an indium tin oxide (ITO) layer. Dipyrazinoquinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN) was used as the hole-injecting layer, *N,N*-bis(naphthalene)-*N,N*-bis(phenyl)benzidine (NPB) was used as the hole-transporting layer (HTL), DPE-BFDB and TPE-BFDB were used as the emitting layers, 1,3,5-tri(1-phenyl-1*H*-benzo[d]imidazol-2-yl)phenyl (TPBi) was used as the electron-transporting layer (ETL) and LiF/Al was used as the cathode. All organic layers were deposited sequentially.

Thermal deposition rates for the organic materials, LiF and Al were 0.5, 0.5 and 1 Å S^{-1}, respectively. The active area of each device was 12 mm^2. The electroluminescence spectra were measured on a Hitachi MPF-4 spectrofluorometer. The current density-voltage (J-V) characteristics of the OLEDs were recorded on a Keithley 2400 Source Meter. The current density-voltage-luminance curves (J-V-L) characterizations were carried out with a 3645 DC power supply combined with a 1980A spot photometer and they were recorded simultaneously. All measurements were done at room temperature under ambient conditions.

3. Preparation of Nanoaggregates

Stock THF solutions of the luminogens with a concentration of 10^{-4} M were prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under vigorous stirring to furnish 10^{-5} M solutions with different water contents (0–90 vol %). The PL measurements of the resultant solutions were then performed immediately.

4. Additional Data

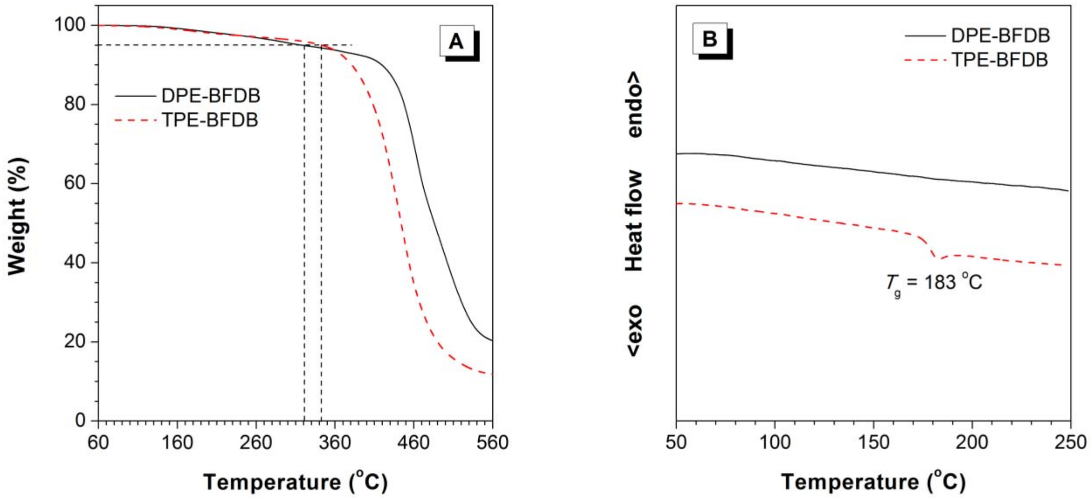


Fig. S1 (A) TGA and (B) DSC of DPE-BFDB and TPE-BFDB, recorded under nitrogen at a heating rate at 10 °C min^{-1}.

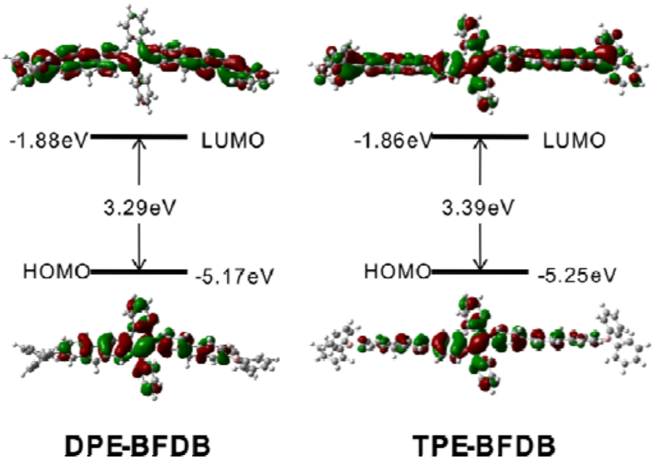


Fig. S2 B3LYP/6-31G(d) calculated molecular orbital amplitude plots and energy levels of HOMOs and LUMOs of DPE-BFDB and TPE-BFDB.

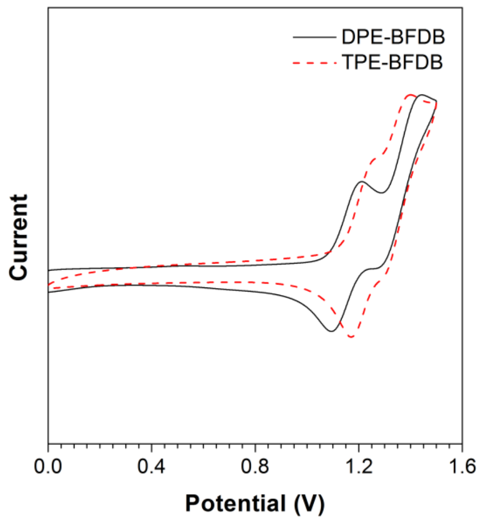


Fig. S3 Cyclic voltammograms of DPE-BFDB and TPE-BFDB, measured in dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate. Scan rate: 100 mV s^{-1}.

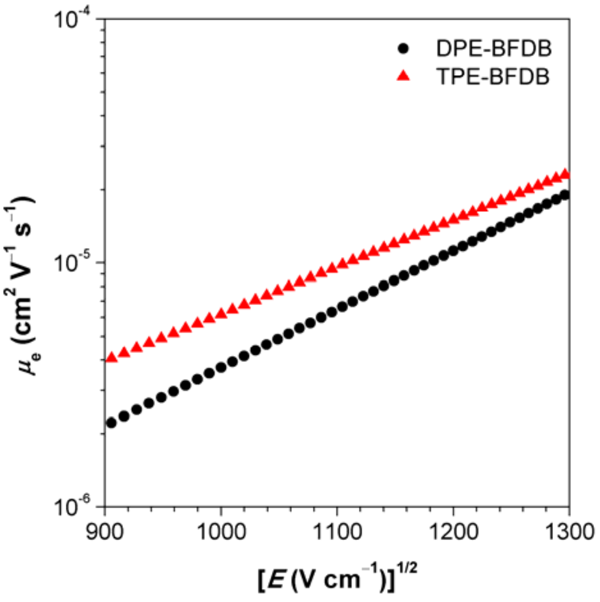


Fig. S4 Electric field-dependent electron mobility (μ_e) for the thin solid films of DPE-BFDB and TPE-BFDB, measured from electron only devices with a configuration of ITO/TmPyPB (10 nm)/ DPE-BFDB or TPE-BFDB (100 nm)/LiF (1 nm)/Al at room temperature. TmPyPB: 1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene.

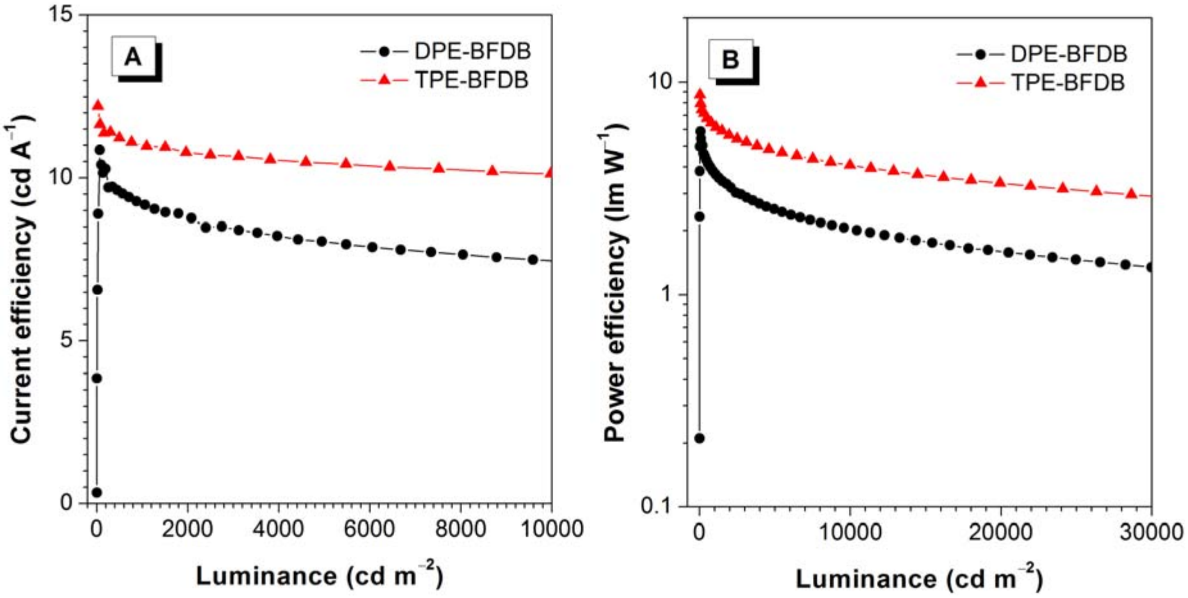


Fig. S5 (A) Current efficiencies and (B) power efficiencies with the luminance in OLED devices based on DPE-BFDB and TPE-BFDB. Device configuration: ITO/HATCN (20 nm)/NPB (40 nm)/emitters (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm).

Reference

1. R. Hu, J. L. Maldonado, M. Rodriguez, C. Deng, C. K. W. Jim, J. W. Y. Lam, M. M. F. Yuen, G. Ramos-Ortiz and B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 232.
2. G. Piancatelli, A. Scettri and M. D'Auria, *Synthesis*, 1982, **4**, 245.