1. Experimental

1.1 Materials and instruments

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use.

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 400 or 600 M 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). All the calculations were performed using Gaussian 09 package. 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 °C min⁻¹. Cyclic voltamogramms were measured on a CHI 610E A14297.

1.2 Synthesis

1,2-Bis[4-(dimesitylboranyl)phenyl]-1,2-diphenylethene (TPE-DB): Into a 250 mL two-necked round bottom flask was placed 1.47 g (3.0 mmol) of compound 2. The flask was evacuated under vacuum and flushed with dry nitrogen by three times. Then 80 mL THF was added. The mixture was cooled to −78 °C, and 2.5 mL (2.4 M in hexane, 6.0 mmol) of n-BuLi was added dropwise by a syringe. The mixture was stirred for 2 h at −78 °C and then 1.61 g (6.0 mmol) of dimesitylboron fluoride in 10 mL of THF was slowly injected to the reaction solution. 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. Yellow solid of TPE-DB was obtained in 83% yield. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.21–6.98 (m, 18H), 6.79 (s, 8H), 2.28 (d, 12H), 1.95 (d, 24H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 147.46, 147.35, 143.02, 143.00, 141.87, 141.77, 140.76, 140.71, 138.46, 135.72, 135.49, 131.31, 131.28, 130.96, 130.88, 128.07, 127.69, 127.56, 126.70, 126.65, 23.39, 23.37, 21.22, 21.19. HRMS (C₆₂H₆₂B₂): m/z 828.5047 [M⁺, calcd 828.5038].
1,2-Bis[4’-(dimesitylboranyl)-(1,1’-biphenyl)-4-yl]-1,2-diphenylethene (TPE-BPDB): The procedure was analogous to that described for TPE-DB. Yellow solid, yield 81%. $^1$H NMR (600 MHz, CDCl$_3$, $\delta$ (ppm): 7.59–7.56 (m, 8H), 7.48–7.45 (m, 4H), 7.18–7.08 (m, 14H), 6.85 (s, 8H), 2.34 (d, 12H), 2.05 (d, 24H). $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$ (ppm): 144.52, 143.68, 143.64, 143.63, 143.45, 143.41, 141.76, 140.81, 140.76, 138.58, 138.56, 138.39, 138.30, 137.03, 131.89, 131.42, 128.16, 127.85, 127.70, 126.65, 126.57, 126.46, 126.32, 126.20, 23.45, 21.22. HRMS (C$_{74}$H$_{70}$B$_2$): m/z 980.5659 [M$,^+$, calcd 980.5664].

1,2-Bis[4’’-(dimesitylboranyl)-(1,1’:4’,1’’-terphenyl)-4-yl]-1,2-diphenylethene (TPE-TPDB): Into a 250 mL two-necked round bottom flask was placed compound 5 (1.93 g, 3.0 mmol), 7 (3.33 g, 9.0 mmol), Pd(PPh$_3$)$_4$ (104 mg, 0.09 mmol) and Na$_2$CO$_3$ (1.27 mg, 12.0 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen by 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$_3$), $\delta$ (ppm): 7.73–7.64 (m, 16H), 7.48–7.44 (m, 4H), 7.21–7.14 (m, 14H), 6.88 (s, 8H), 2.36 (s, 12H), 2.08 (s, 24H). $^{13}$C NMR (150 MHz, CDCl$_3$), $\delta$ (ppm): 144.54, 143.76, 143.73, 143.02, 142.98, 141.76, 140.82, 140.75, 139.96, 139.39, 138.59, 138.32, 138.21, 137.12, 131.89, 131.45, 128.18, 127.86, 127.71, 127.49, 127.20, 126.62, 126.54, 126.33, 126.20, 126.07, 23.49, 21.22. HRMS (C$_{86}$H$_{78}$B$_2$): m/z 1132.6315 [M$,^+$, calcd 1132.6290].

1.3 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), TPE-DB, TPE-BPDB and TPE-TPDB were used as the emitting layers, 1,3,5-tri(1-phenyl)-1H-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 electroluminescent 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.

### 1.4 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.

### 2. Additional spectra
Fig. S1 PL spectra of TPE-DB, TPE-BPDB and TPE-TPDB in cyclohexane (10 µM). Excitation wavelength: 360 nm.

Fig. S2 (A) Current density-voltage-luminance characteristics, and (B) external quantum efficiencies vs. the luminance in EL devices of TPE-DB, TPE-BPDB and TPE-TPDB. Device configuration: ITO/HATCN (20 nm)/NPB (40 nm)/emitters (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm).
Fig. S3 (A) Current density-voltage-luminance characteristics, and (B) external quantum efficiencies vs. the luminance in EL devices of TPE-DB, TPE-BPDB and TPE-TPDB. Device configuration: ITO/HATCN (20 nm)/NPB (40 nm)/emitters (60 nm)/ LiF (1 nm)/Al (100 nm).