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Aggregation-enhanced emission active tetraphenylbenzene-cored efficient blue light emitter

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Experimental Section

Materials: Phenyl boronic acid, 4-cyanophenyl boronic acid, *n*-butyllithium were purchased from J&K; 4-bromotriphenylamine was purchased from Enengy, 1,4-dibromo-2,5-diiodobenzene was purchased from TCI; 2-iIsopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was purchased from Matrix; $Pd(PPh_3)_4$ was purchased from J&K and used as received without further purification. Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use.

Instrumentation: ^1H and ^{13}C NMR spectra were measured on a Mercury plus 400MHz NMR spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. High-resolution mass spectra (HRMS) were taken on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. Photoluminescence spectra were measured on a Perkin-Elmer LS 55 spectrofluorometer. UV-visible absorption spectra were measured on a Varian CARY 100 Biospectrophotometer. Relative PL quantum yield was measured with standard quinine sulfate in 0.1 N H_2SO_4 ($\Phi_F = 0.54$), and absolute quantum yield was measured with a Hamamatsu Quantaurus-QY C11347 spectrometer. Thermalgravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted on a Perkin-Elmer DSC 7 under nitrogen atmosphere at a heating rate of 10 ^oC/min.

Device fabrication: Electroluminescence device was fabricated on a 170 nm ITO-coated glass possessing a sheet resistance of 10 Ω/sq. Before loaded into the pretreatment chamber, the ITO coated glass was soaked in ultrasonic acetone and semiconductor cleaning solution for one time, followed by two times of ultrasonic de-ionized water and finally one time of ultrasonic isopropanol. 10 min was used for each time. Then, after baking the glass at 80 ℃ for 1 h in oven, treat it with oxygen plasma for 5 min. Subsequently, transfer ITO-coated glass into the chamber with a reduced pressure of 7×10^{-7} Torr for depositing the organic layers, LiF and Al at a rate of 1-2 Å/s, 0.1 Å/s and 0.1 Å/s, respectively. The active area of OLED was 3 mm × 3 mm. The current density-voltage- luminescence characteristics of OLED were measured on Keithley 2420 and Konica Minola chromameter CS-200 analyzers. The EL spectra were measured with a Photo Research PR-750 spectrofluorometer. All measurements here were conducted in air at room temperature without device encapsulation.

Synthesis of *2,5-dibromo-1,4-diphenylbenzene (1)* : 1,4-dibromo-2,5-diiodobenzene (974.5 mg, 2 mmol), phenylboronic acid (609.5 mg, 5 mmol), and $Pd(PPh_3)_4$ (115.6mg, 0.1mmol) were added into a 100 mL two necked round flask under N_2 protection. THF (20 mL) and potassium carbonate solution (2 M, 10 mL) were injected into the flask and the mixture was stirred at 74 ^oC, after refluxed for 8h, the solution was poured into water and extracted with DCM. The organic layer was washed with brine and dried over magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica gel-column chromatography, using petroleum ether (PE) as eluent. White product was obtained with the yield 63.7%. ^1H NMR (400 MHz, $CDCl_3$): δ (TMS, ppm) 7.64(s, 2H), 7.44(m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (TMS, ppm) 143.0, 135.5, 129.3, 128.1, 121.4.

Synthesis of *intermediate 2*: In a two necked round bottle, 4-bromotriphenylamine (3.3 g, 10 mmol) was dissolved in 50 mL distilled THF under N_2 atmosphere, then the flask was cooled to -78 ^{o}C, then *n*-butyllithium of 1.6 M (6.8 mL, 11 mmol) was added into the flask by drop and was kept at -78 ^{o}C for an hour, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.2 mL, 11 mmol) was injected into the reaction system and then the flask was wormed to room temperature and stirred overnight. After the reaction, hydrochloric acid was added into the system to stop the reaction, then th extracted with dichloromethane and the organic layer dried by anhydrous sodium sulfate. The filtrated organic layer was then evaporated and purified by silicon column with PE:DCM = 20:1. The color-less solid was got at the yield of 81.2%. ^{1}H NMR (400 MHz, aceton-*d*$_6$): *δ* (TMS, ppm) 7.51(d, 2H), 7.23(t, 4H), 7.00(t, 6H), 6.86(d, 2H), 1.22(s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (TMS, ppm) 150.6, 147.4, 135.9, 129.4, 125.0, 123.4, 121.8, 24.9.

Synthesis of *intermediate 3*: compound **1** (385.9 mg, 1 mmol), compound **2** (186 mg, 0.05mmol) and $Pd(PPh_3)_4$ (46.2 mg, 0.04 mmol) were added into a 100 two necked round bottom under N_2 protection, then distill THF (20 mL), $K_2CO_{3(aq)}$ (2 M, 10 mL) were injected. Then compound **2** (186 mg, 0.05 mmol) was dissolved in 2 mL distilled THF and injected into the system three times in 5 hours. The reaction continued overnight and was then stopped, exacted with DCM. The organic layer was washed with brine solution and dried by anhydrous sodium sulfate. The product was got by evaporate the organic layer and running the silicon column with yield 65.7%. ^{1}H NMR (400 MHz, aceton-*d*$_6$): *δ* (TMS, ppm) 7.66(m, 4H), 7.50(d, 1H), 7.45(t, 2H), 7.36(t, 1H), 7.20(m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (TMS, ppm) 141.5, 141.7, 141.0, 140.6, 139.6, 131.2, 130.0, 129.9, 129.5, 128.9, 127.5, 127.2, 126.7, 126.6, 126.2.

Synthesis of TPB-AC: The synthesis of TPB-AC was similar to **1**, the only difference lies in that the solvent was changed into distilled toluene (10 mL), dry ethanol (5 mL) and $K_2CO_{3(aq)}$ (2M, 5 mL).The light green product was got with the yield 87.3%. ^{1}H NMR (400 MHz, *d*-DMSO): δ (TMS, ppm) 7.75(d, 2H), 7.47(d, 2H), 7.43(d, 2H), 7.29 (m, 14H), 7.12(d, 2H), 7.05(t, 2H), 7.00(t, 4H), 6.86(d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (TMS, ppm) 147.6, 146.7, 146.0, 140.5, 140.2, 140.0, 139.8, 137.4, 134.4, 132.9, 132.6, 131.8, 130.7, 130.6, 129.8, 129.3, 128.3, 128.1, 127.1, 127.0, 124.4, 123.1, 123.0, 119.09, 110.4. HRMS (MALDI-TOF): m/z 574.2393 ($[M]^+$, calcd for $C_{43}H_{30}N_2$ 574.2409).

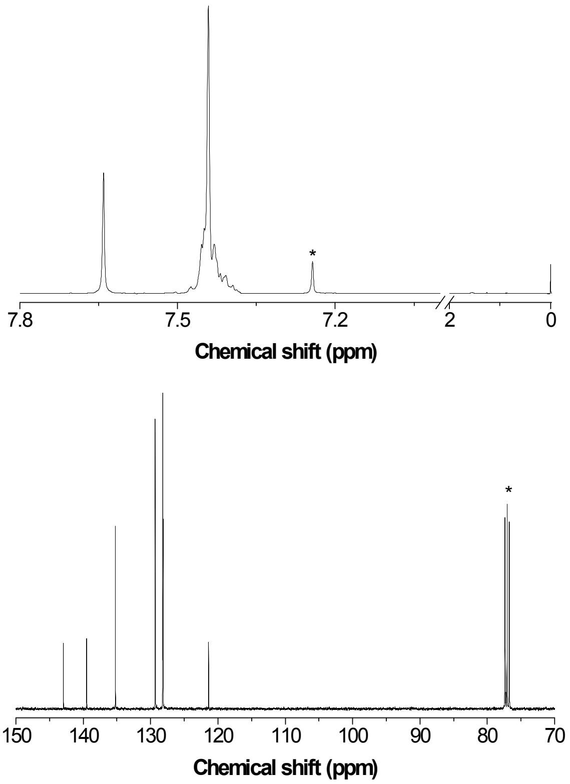

Figure S1. ^{1}H NMR spectra and ^{13}C NMR spectra of compound **1** in $CDCl_3$. The solvent peaks are marked with asterisks.

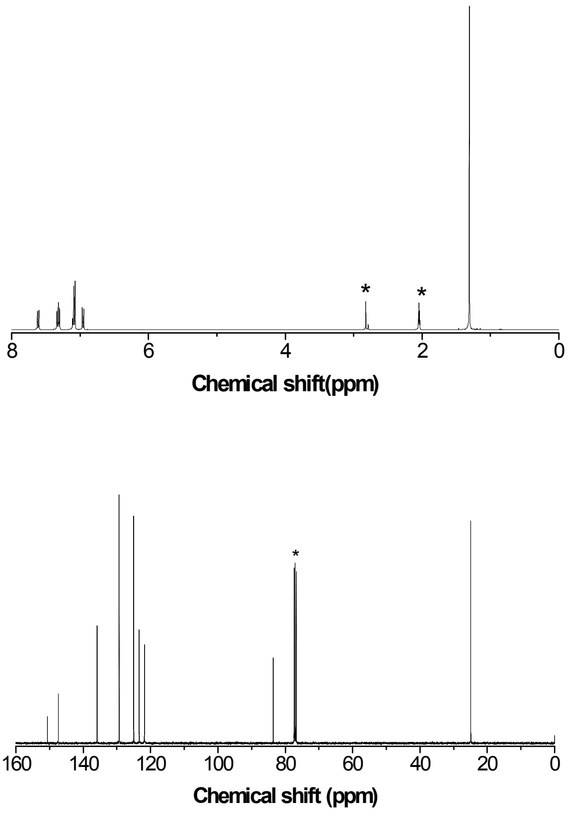

Figure S2. ^{1}H NMR spectra in aceton-d_6 and ^{13}C NMR spectra in $CDCl_3$ of compound **2**. The solvent peaks are marked with asterisks.

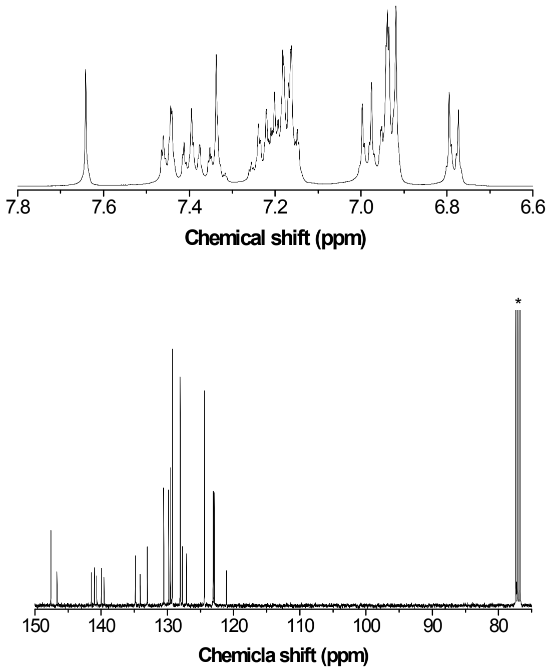

Figure S3. ^{1}H NMR spectra in aceton-d_6 and ^{13}C NMR spectra in $CDCl_3$ of compound **3**. The solvent peaks are marked with asterisks.

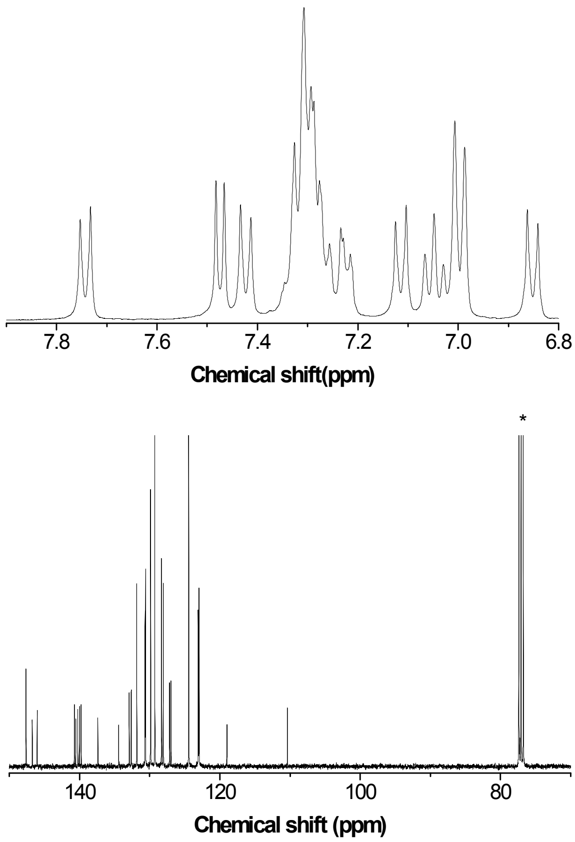

Figure S4. ^{1}H NMR spectra of TPB-AC in DMSO-d_6 and ^{13}C NMR speatra in CDCl$_3$. The solvent peaks are marked with asterisks.

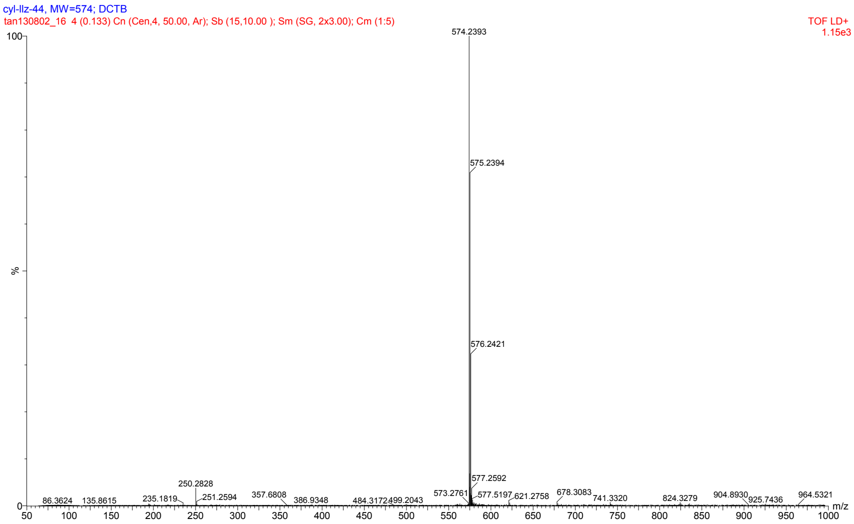

Figure S5. Mass spectra of TPB-AC.

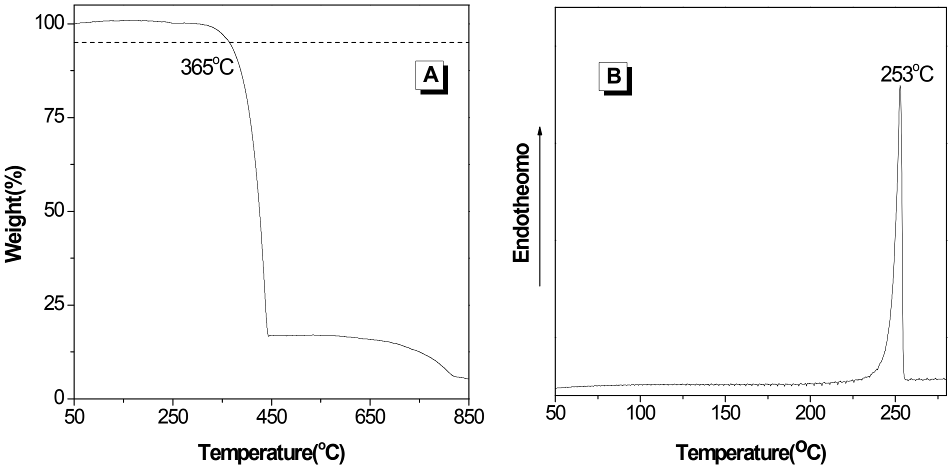

Figure S6. TGA thermograms (A) and DSC curve (B) of TPB-AC, recorded under nitrogen at a heating rate of 10 °C/min.

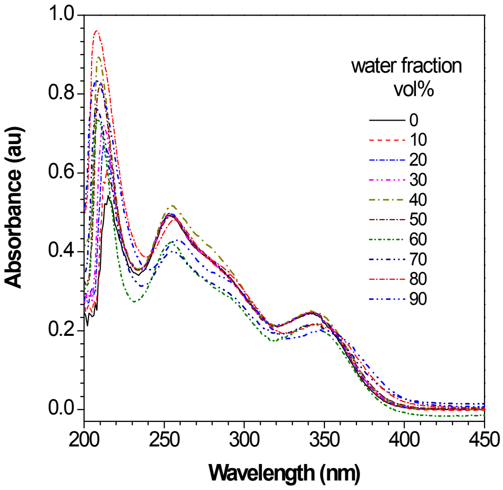

Figure S7. Absorption spectra of TPB-AC in THF/water mixtures with different water fraction (concentration : 10^{-5} M).

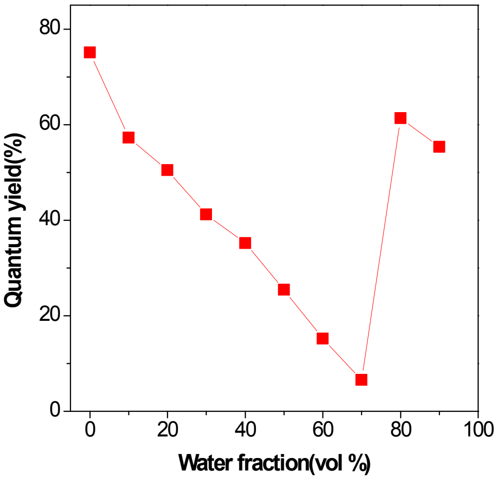

Figure S8. Quantum yields of TPB-AC in THF/water mixtures tested using quinine sulfate in 0.1 N sulfuric acid as standard.

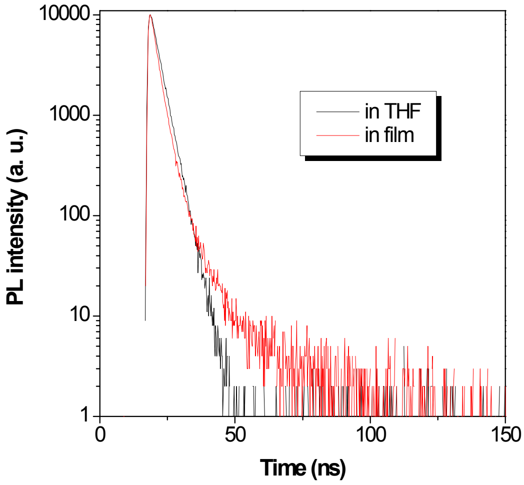

Figure S9. PL decay curves of TPB-AC in THF and thin-solid film.

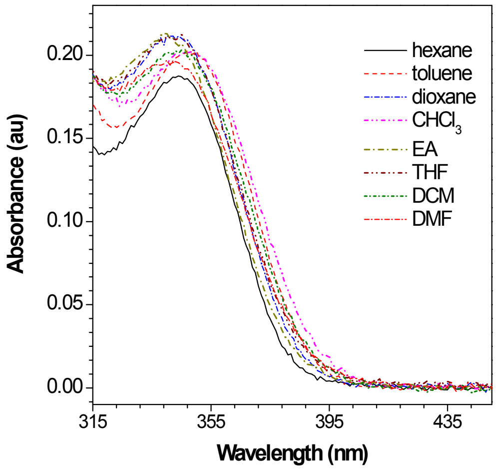

Figure S10. UV spectra of TPB-AC in solvents with different polarity parameters (Δf). (concentration : 10^{-5} M).

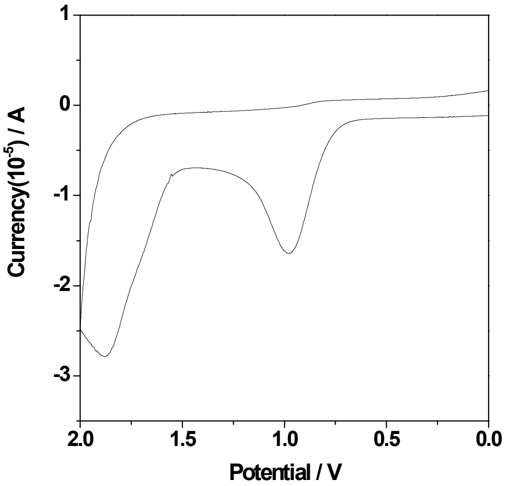

Figure S11. The cyclic voltammograms in DCM/ 0.1 M $[nBu4N]^{+}[PF6]^{-}$ at a rate of 50 mV s^{-1} (left) of TPB-AC**.**