Electronic supplementary information (ESI) for

Solution-Processible Phosphonate Functionalized Deep-Blue Fluorescent Emitter for Efficient Single-Layer Small Molecule Organic Light-Emitting Diodes

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Experimental

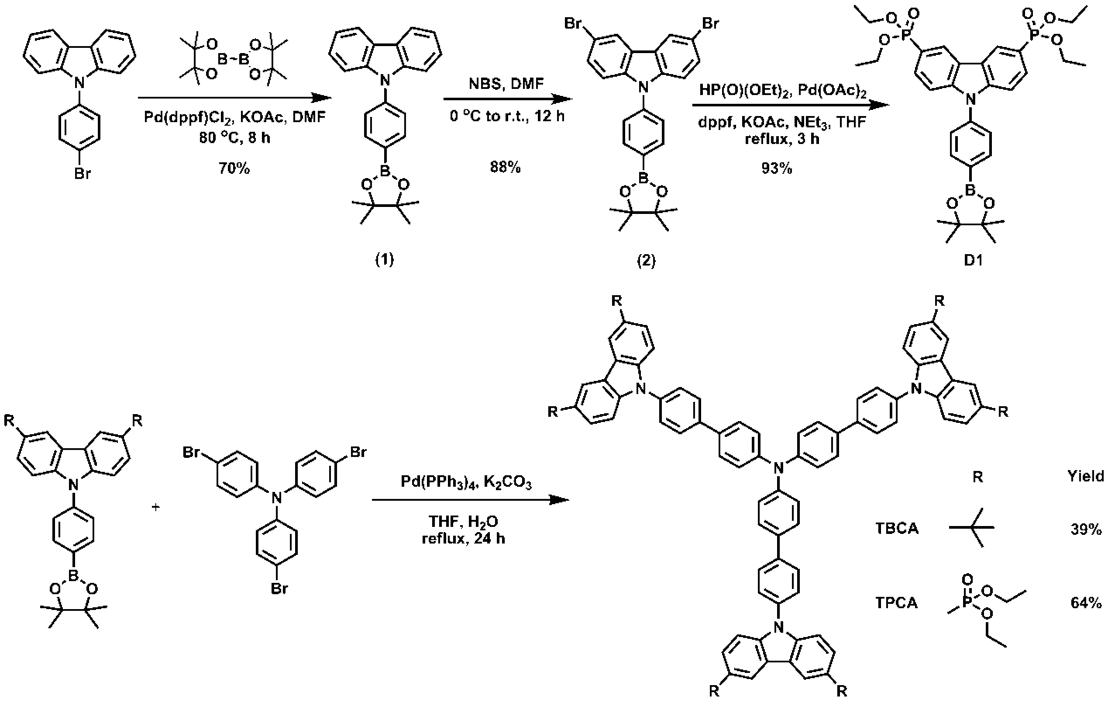
General Information: ^{1}H NMR spectra and ^{31}P NMR spectrum were recorded at room temperature on a Bruker Avance 300 NMR spectrometer. ^{31}P NMR spectrum was referenced to external 85 % H_3PO_4 (0 ppm). Elementary analysis was carried out on a Bio-Rad elemental analysis system. MALDI-TOF mass spectrum was performed on an AXIMA CFR MS apparatus (COMPACT). UV-visible absorption and photoluminescence spectra were recorded on Perkin-Elmer Lambda 35 UV–vis spectrometer and Perkin-Elmer LS 50B spectrofluorometer, respectively. Cyclic voltammetry was performed on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system. The sample was tested in 1 mM solution, at a scanning rate of 100 mV/s. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (n-Bu_4NClO_4), with ferrocene as reference.

Device fabrication and characterization condition:

The substrates were the commercially available indium tin oxide (ITO) coated glass with a sheet resistance of 20 Ω/square. The substrates were pre-cleaned carefully, and then treated by oxygen plasma for 25 min. The PEDOT:PSS solution was spin-coated onto the substrates with 40 nm and then baked at 120 °C for 40 min in the air. The sample solutions were spin-coated at the 1.5 krpm for 1 min, at the concentration of 35 mg/mL under nitrogen atmosphere. In succession, a 1-nm-thick film of LiF and a 100-nm-thick film of aluminium were vacuum deposited onto the active layer under the pressure of 10^{-4} Pa. The typical active area of the devices was 0.14 cm^2. By using a PR650 spectra colorimeter, the EL spectra were measured. By using a Keithley 2400/2000 source meter and a calibrated silicon photodiode, the current-voltage and brightness-voltage curves of devices were measured. The device performance was tested at room temperature under ambient conditions.

Synthesis:

All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures. The intermediates 9-(4-bromophenyl)-9*H*-carbazole[1], 9-(4-bromophenyl)-3,6-di-tert-butyl-9*H* -carbazole[2], and 3,6-di-tert-butyl-9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole,[3] were prepared according to the literature procedures.



Scheme S1. Synthetic Route of TBCA and TPCA.

9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole (1):

DMSO (18 mL) was added to the mixture of 9-(4-bromophenyl)-9*H*-carbazole (0.99 g, 3.07 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (0.87 g, 3.43 mmol), PdCl$_2$(dppf) • CH$_2$Cl$_2$ (71 mg, 87.1 μmol), KOAc (0.90 g, 9.18 mmol) under inert atmosphere. The solution was stirred at 80 ^{o}C for 8 h and turned out to be black suspension. Then the mixture was poured into 200 mL water. The gray precipitate was filtered, washed with plenty of water and dried under vacuum. The raw product was purified by column chromatography on silica gel. The eluent was composed of the mixed petroleum and dichloromethane with decrease proportion from $V_{petroleum}$ ： $V_{dichloromethane}$ = 5 ： 1 to 3 : 1. The final product was obtained as white solid (3.21 g, 69.8 %). ^{1}H NMR(CDCl$_3$, 300 MHz): δ 8.14 (d, *J* = 7.7 Hz, 2H), 8.05 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.42 (m, 4H), 7.30 (d, *J* = 6.7 Hz, 2H), 1.40 (s, 12H).

3,6-dibromo-9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole (2):

Compoud **1** (3.21, 8.69 mmol) was dissolved in 90 mL DMF, and stirred with ice/water bath for 30min. 20 mL DMF solution of NBS (3.12 g, 17.5 mmol) was added dropwise to this solution. The solution was stirred for 12 h, and then poured into 500 mL water. The precipitate was filtered and dry under vacuum. Final product was obtained from crystalization from the mixture solvent of dichloromethane and ethanol, as light yellow crystals of 4.02 g (87.7%). M. p. 233-234 °C. ^{1}H NMR($CDCl_3$, 300 MHz): δ 8.19 (d, *J* = 1.8 Hz, 2H), 8.05 (d, *J* = 8.3 Hz, 2H), 7.56-7.48 (m, 4H), 7.29 (s, 2H), 1.40 (s, 12H).

Tetraethyl 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole-3,6-diyldiphosphonate (D1):

A mixture of $Pd(OAc)_2$ (85.3 g, 0.38 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf, 0.42 g, 0.77 mmol), anhydrous KOAc (0.15 g, 1.52 mmol) and THF (70 mL) were stirred at reflux temperature under inert atmosphere for 15min. After the solution turned into dark red, a solution of compound **2** (4.02 g, 7.62 mmol) and diethyl phosphite (2.86 mL, 16.8 mmol) in 20 mL THF was added to the catalytic solution. The solution became orange, and was stirred under reflux for 8 hours. After THF was removed by distillation, dichloromethane was added to dissolve the residue, and then the dichloromethane solution was washed by saturated aqueous sodium chloride. After being dried by anhydrous Na_2SO_4, the solution was filtered and the solvent was completely removed by rotary evaporator. The raw product was purified by column chromatography on silica gel, using mixed solvent of $V_{dichloromethane}$: $V_{methanol}$ = 20 : 1 as eluent. The final product was obtained as light yellow solid (4.20 g, 93.3 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.70 (d, *J* = 13.8 Hz, 2H), 8.10 (t, *J* = 8.1 Hz, 2H), 7.89 (dd, J_1 = 12.3 Hz, J_2 = 8.5 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.48 (dd, J_1 = 8.5 Hz, J_2 = 3.0 Hz, 2H), 4.27 – 4.06 (m, 8H), 1.41 (s, 12H), 1.36 (t, *J* = 7.1 Hz, 12H).

Dodecaethyl (9,9',9''-(nitrilotris([1,1'-biphenyl]-4',4-diyl))tris(9*H*-carbazole-9,6,3-triyl))hexakis(phosphonate) (TPCA):

Under inert atmosphere, 6 mL K_2CO_3 water solution (2 M) and 18 mL dry THF were added to the mixture of tris(4-bromophenyl)amine (0.88 g, 1.84 mmol), **D1** (3.61 g, 6.07 mmol) and $Pd(PPh_3)_4$ (0.19 g, 0.17 mmol). The mixture was stirred under reflux for 24 h. Then the solvent was removed by vacuum distilling. Dichloromethane was added to solve the residue, and the solution was washed with saturated NaCl aqueous solution and water sequentially. After being dried by anhydrous Na_2SO_4, the organic solution was filtered and the solvent was completely removed by rotary evaporator. The raw product was purified by column chromatography on silica gel using mixed solvent of $V_{\text{ethyl acetate}} : V_{\text{methanol}} = 5 : 1$ as eluent. Final product was obtained as white solid (2.10 g, 64.0%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 8.88 (d, J = 13.7 Hz, 6H), 8.04 (d, J = 8.5 Hz, 6H), 7.89 – 7.82 (m, 12H), 7.79 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.5 Hz, 6H), 7.59 (dd, J_1 = 8.5 Hz, J_1 = 3.0 Hz, 6H), 4.07 (m, 24H), 1.27 (t, J = 7.0 Hz, 36H). ^{13}C NMR (DMSO, 151 MHz): δ 147.04, 143.33, 140.15, 134.96, 134.25, 130.33 (d, $J_{\text{C-P}}$ = 17.6 Hz), 128.53, 127.97, 125.93 (d, $J_{\text{C-P}}$ =11.5 Hz), 124.83, 122.73 (d, $J_{\text{C-P}}$ = 17.4 Hz), 121.02, 119.76, 110.91 (d, $J_{\text{C-P}}$ = 15.8 Hz), 16.70 (d, $J_{\text{C-P}}$ = 5.8 Hz). ^{31}P NMR (DMSO, 121 MHz): δ 20.56. Anal. Calcd. For $C_{96}H_{102}N_4O_{18}P_6$: C, 64.57; H, 5.76; N, 3.14; Found: C, 64.11; H, 5.86; N, 2.84. Calcd. Mass: 1784.7; MALDI-TOF Found (m/z): 1784.6 [M$^+$], 1807.6 [M + Na$^+$].

Tris(4'-(3,6-di-tert-butyl-9*H*-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)amine (TBCA):

Under inert atmosphere, 3.5 mL K_2CO_3 water solution (2 M) and 10.5 mL dry THF were added to the mixture of tris(4-bromophenyl)amine (0.28 g, 0.57 mmol), 3,6-di-tert-butyl-9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole (1.00 g, 2.06 mmol) and $Pd(PPh_3)_4$ (99.0 mg, 85.7 mmol). The mixture was stirred under reflux for 24 h. Then the solvent was removed by vacuum distilling. Dichloromethane was added to solve the residue, and the solution was washed with saturated NaCl aqueous solution and water sequentially. After being dried by anhydrous Na_2SO_4, the solution was filtered and the solvent was completely removed by rotary evaporator. The raw product was purified by column chromatography on silica gel using mixed solvent of $V_{petraleum}$: $V_{dichloromethane}$ = 4 : 1 as eluent. Final product was obtained as white solid (0.29 g, 38.7%). ^{1}H NMR (CD_3Cl, 300 MHz): δ 8.19 (d, *J* = 1.4Hz, 6H), 7.85 (d, *J* = 8.2Hz, 6H)，7.68 (t, 12H), 7.53-7.39 (m, 12H),7.38 (d, *J* = 7.2Hz, 6H), 1.50 (s, 54H). ^{13}C NMR (1,2-dichlorobenzene-d_4,, 75 MHz): δ 147.49, 143,36, 139.53, 139.25, 137.62, 135.20, 128.38, 128.25, 127.05, 125.18, 124.29, 116.83, 109.95, 35.01, 32.39. Anal. Calcd. For $C_{96}H_{96}N_4$: C, 88.30; H, 7.41; N, 4.29; Found: C, 87.81; H, 7.42; N, 4.10. Calcd. Mass: 1304.8; MALDI-TOF (m/z): 1304.8 [M^+].

(1) Zhang, Q.; Chen, J.; Cheng, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. *J. Mater. Chem.* 2004, ***14***, 895.
(2) Liu, Y.; Nishiura, M.; Wang, Y.; Hou, Z. *J. Am. Chem. Soc.* 2006, ***128***, 5592.
(3) Lai, W.-Y.; He, Q.-Y.; Chen, D.-Y.; Huang, W. *Chem. Lett.* 2008, ***37***, 986.

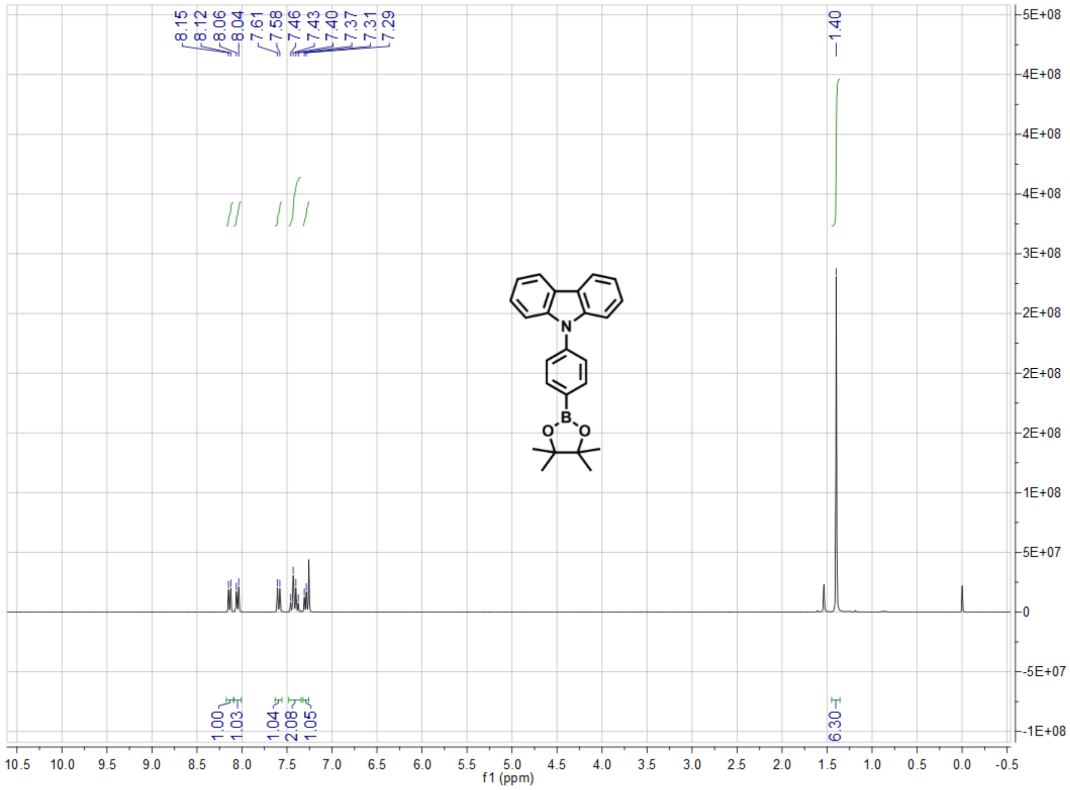


Fig. S1 ^{1}H NMR spectrum of compound **1**.

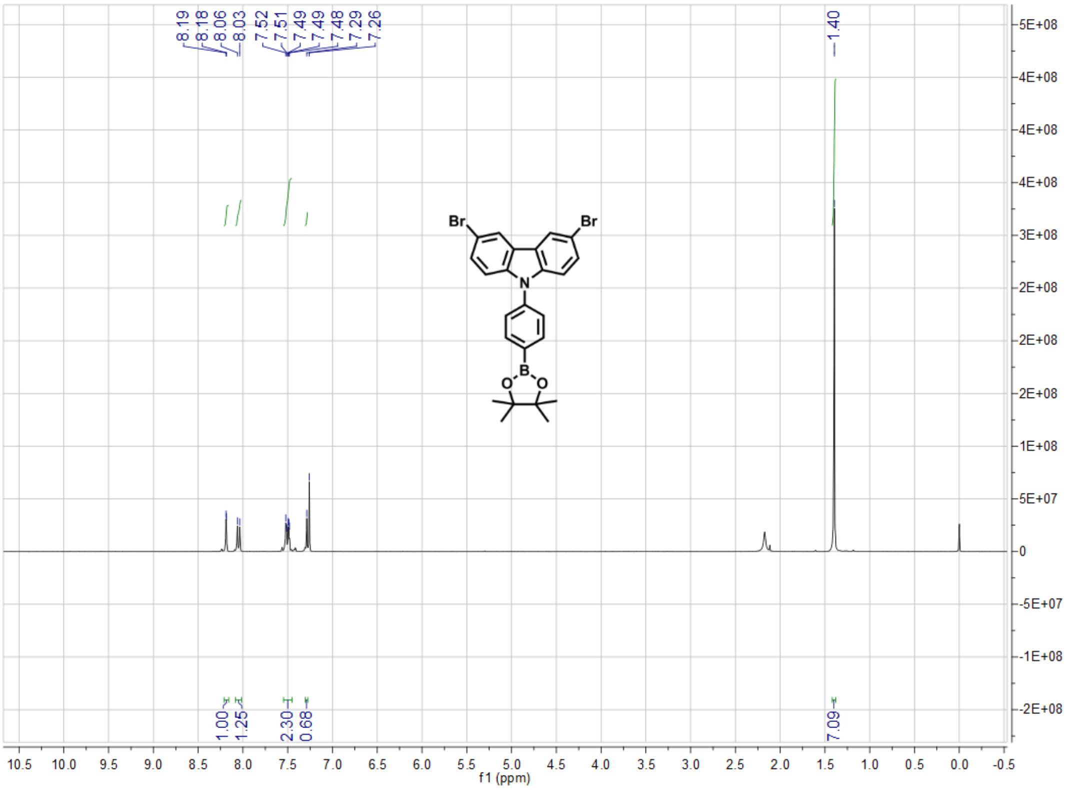


Fig. S2 ^{1}H NMR spectrum of compound **2**.

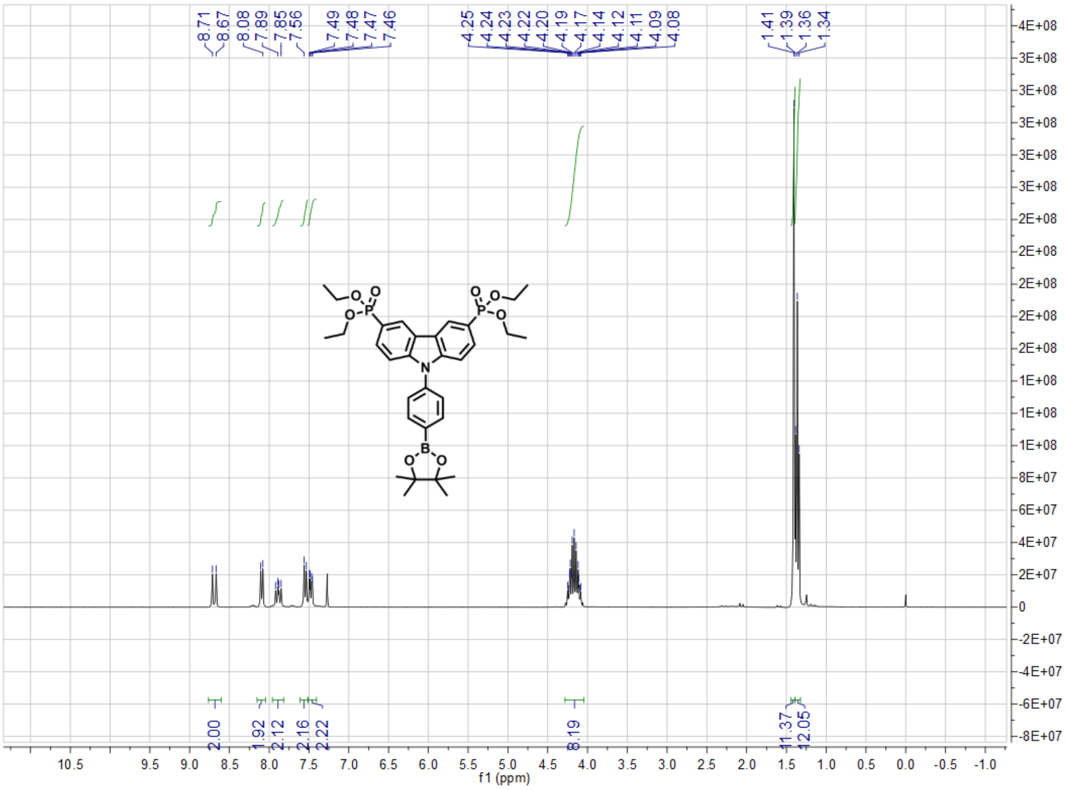


Fig. S3 ^{1}H NMR spectrum of compound **D1**.

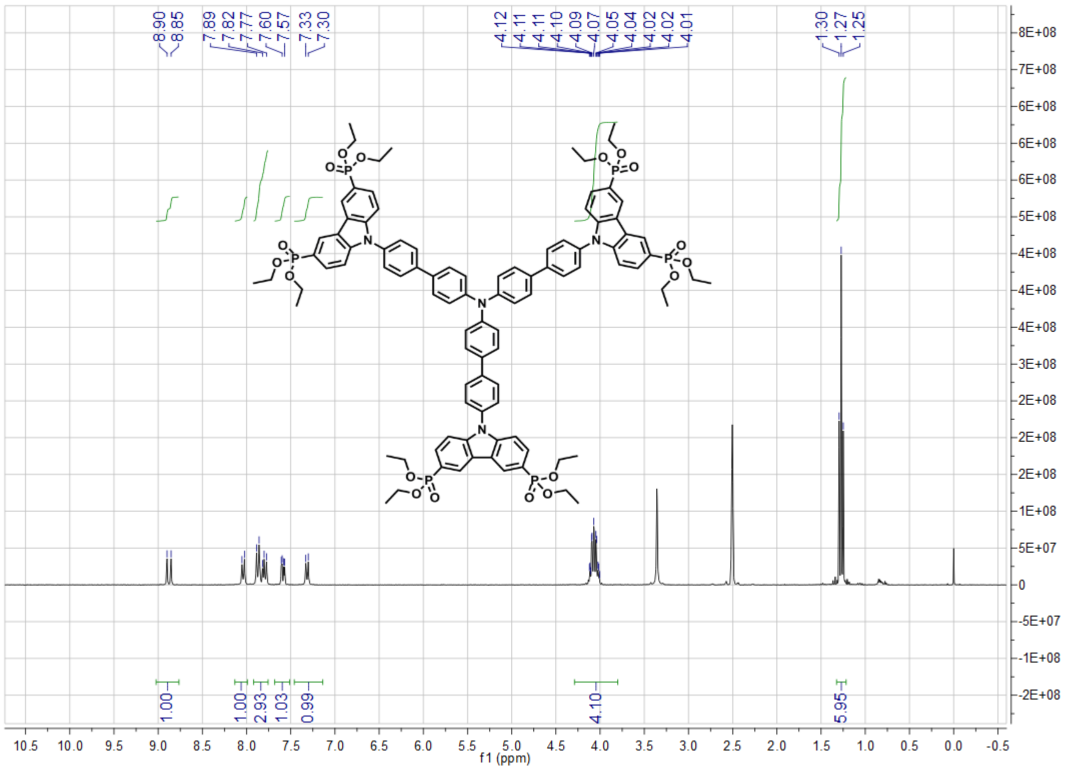


Fig. S4 ^{1}H NMR spectrum of **TPCA**.

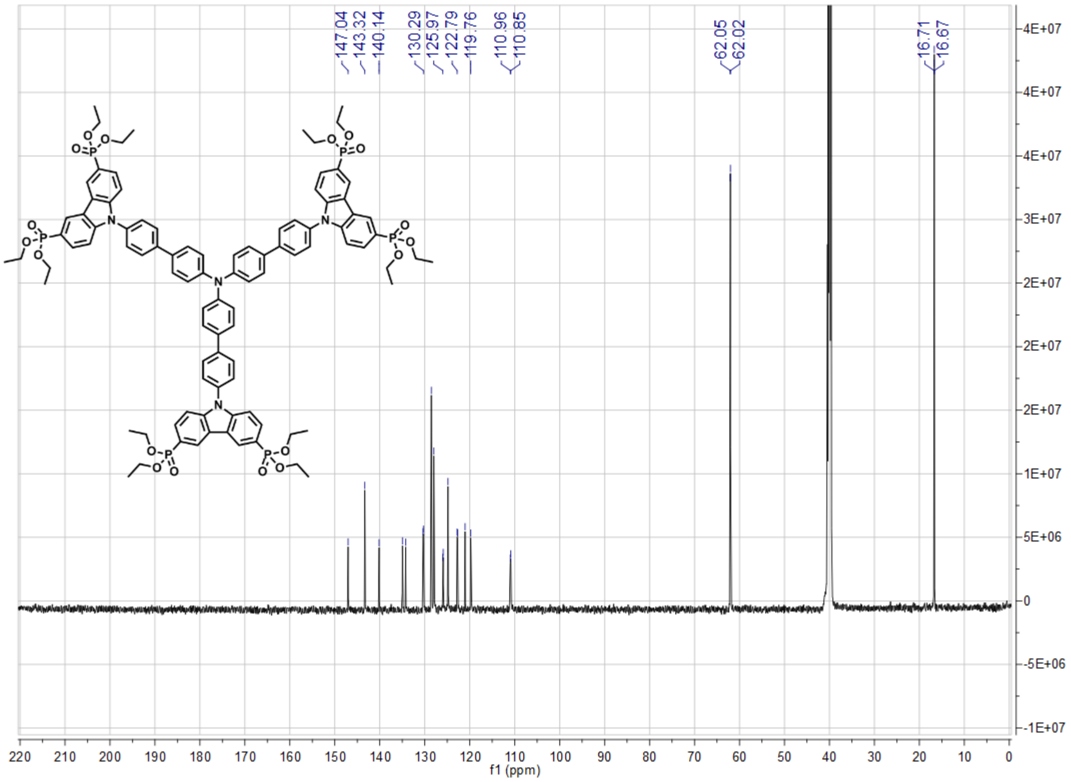


Fig. S5 ^{13}C NMR spectrum of **TPCA**.

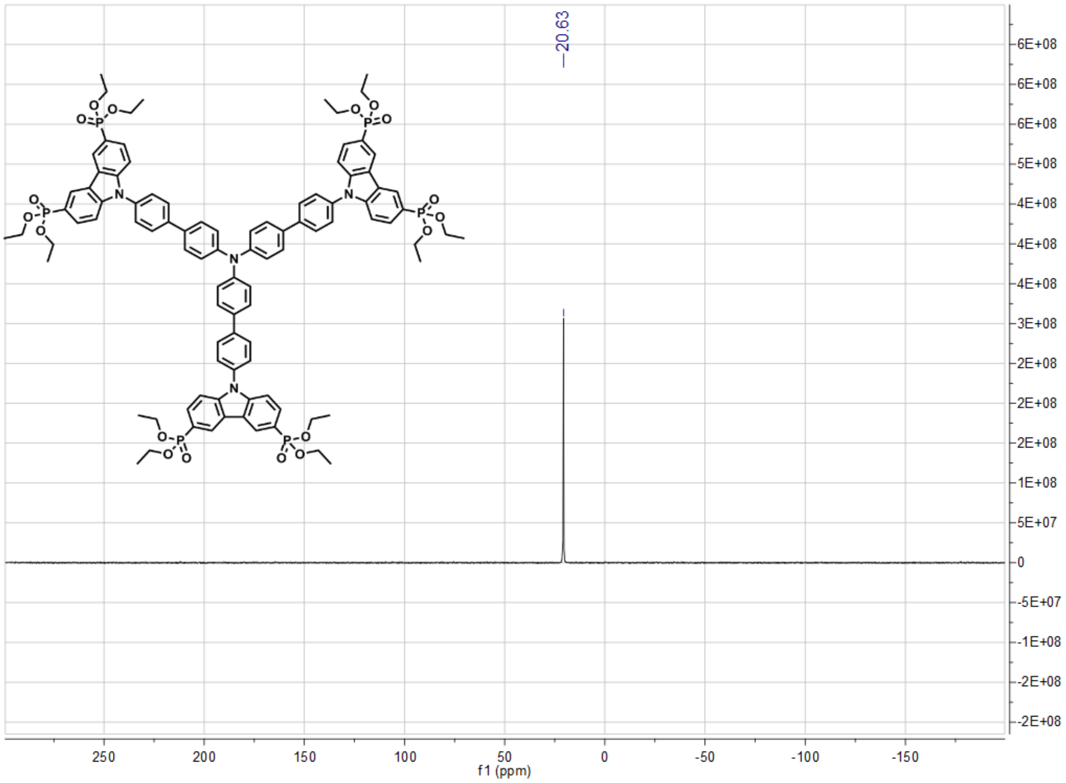


Fig. S6 ^{31}P NMR spectrum of **TPCA**.

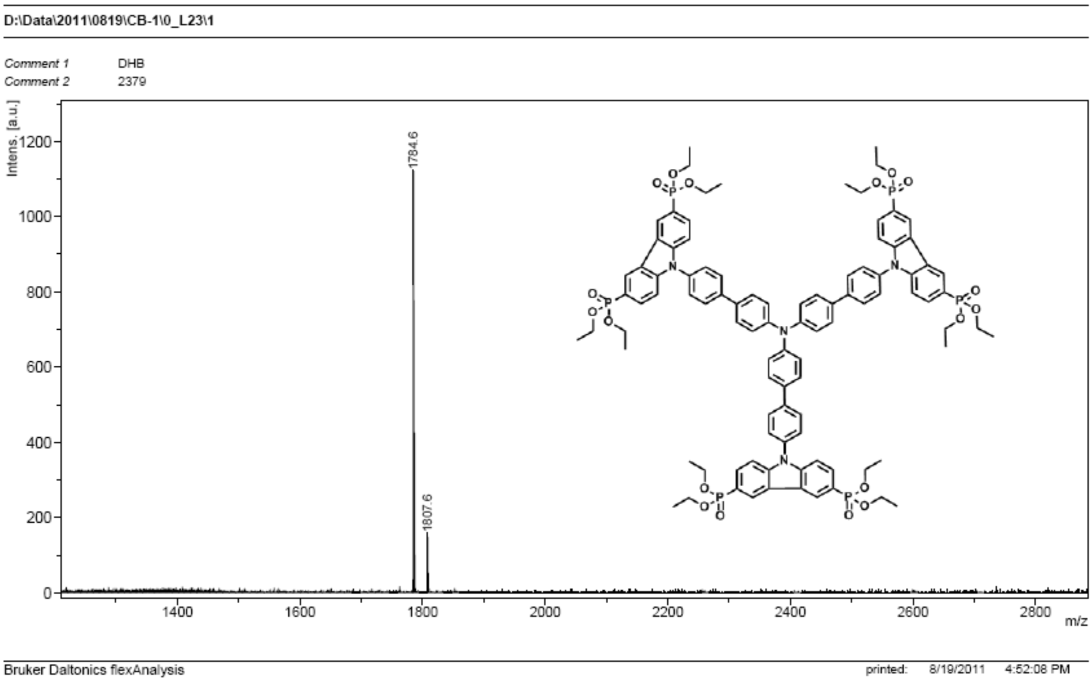


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Fig. S7 MALDI-TOF spectrum of **TPCA**.

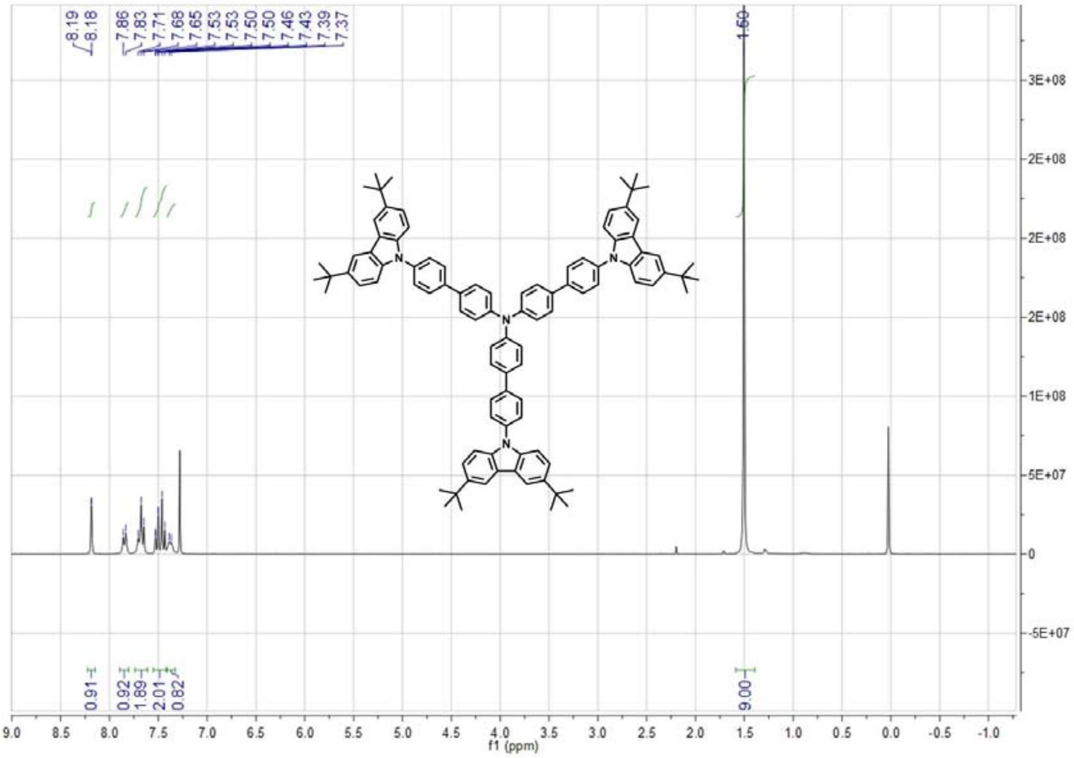


Fig. S8 ^{1}H NMR spectrum of **TBCA**.

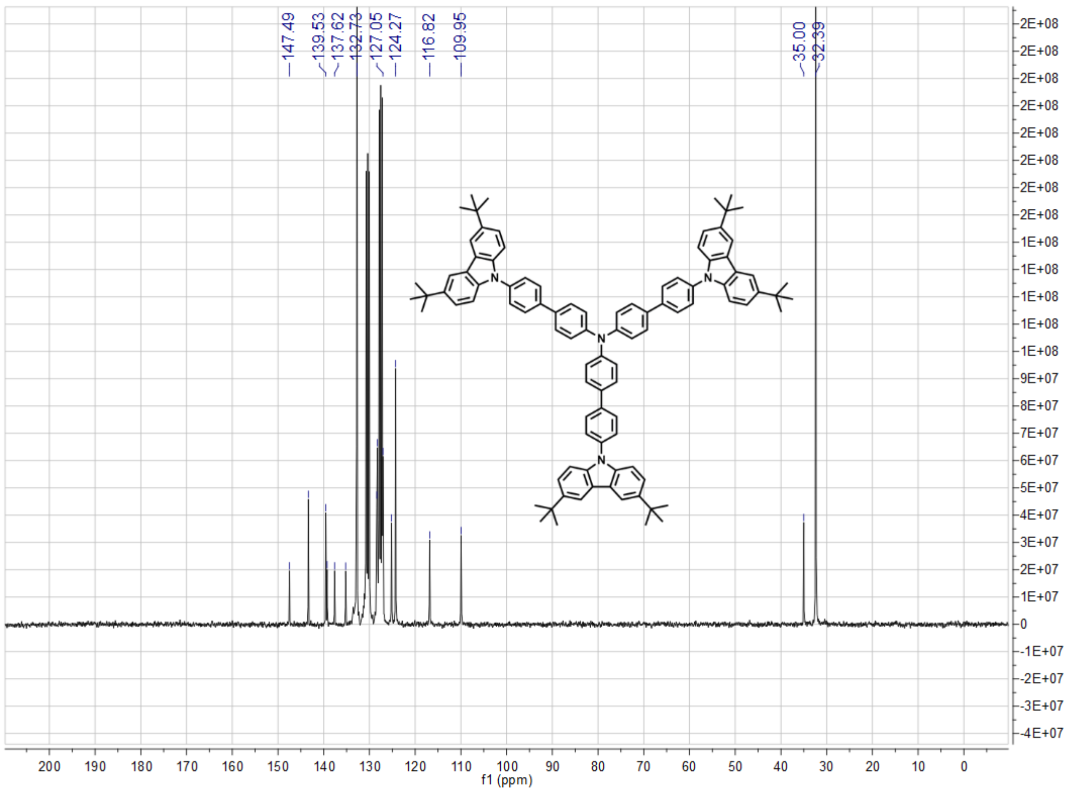


Fig. S9 ^{13}C NMR spectrum of **TBCA**.

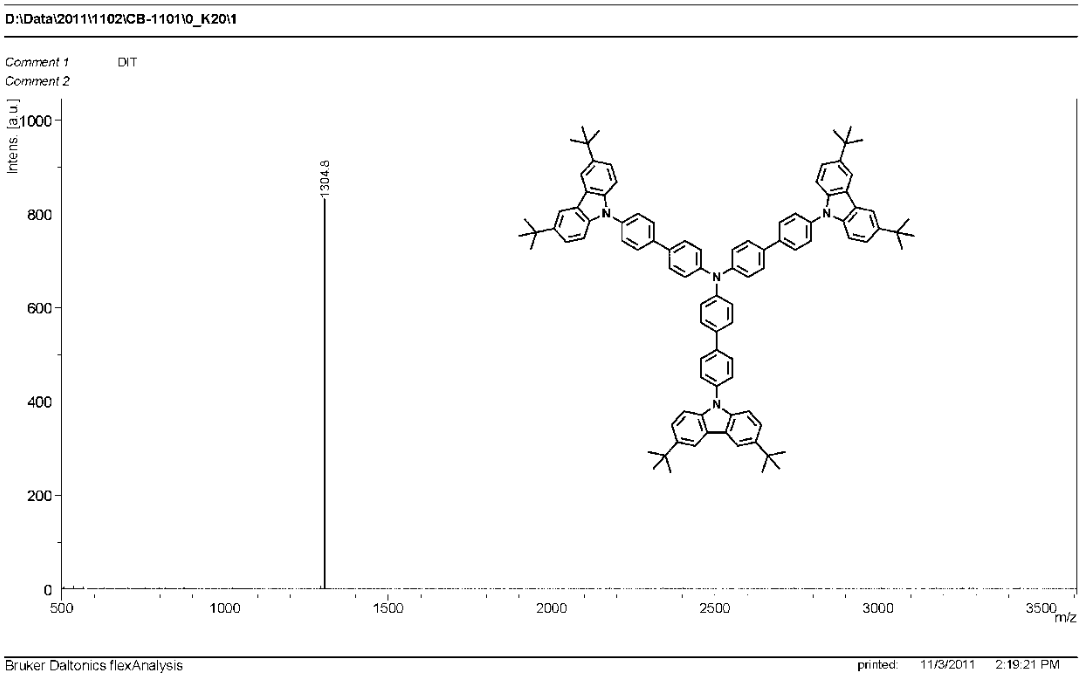


Fig. S10 MALDI-TOF spectrum of **TBCA**.

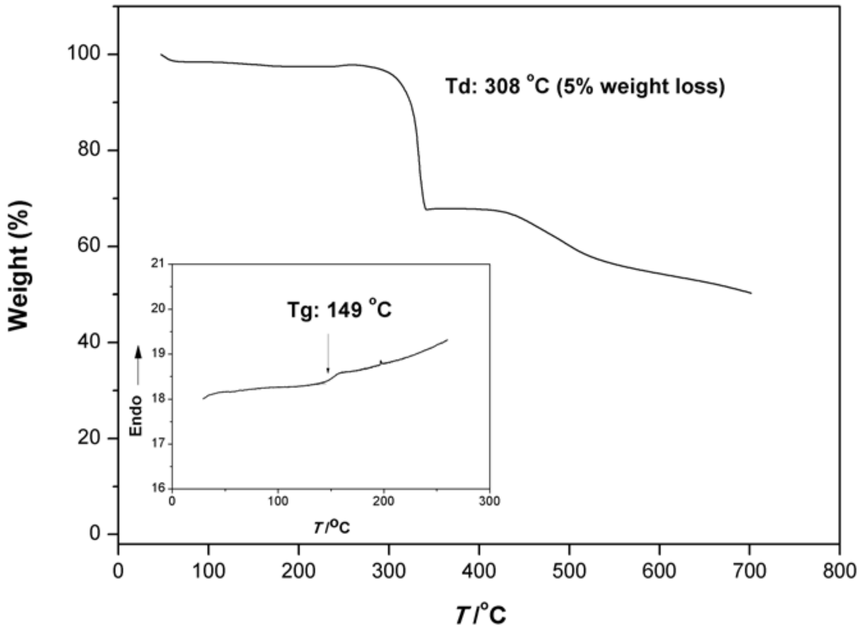
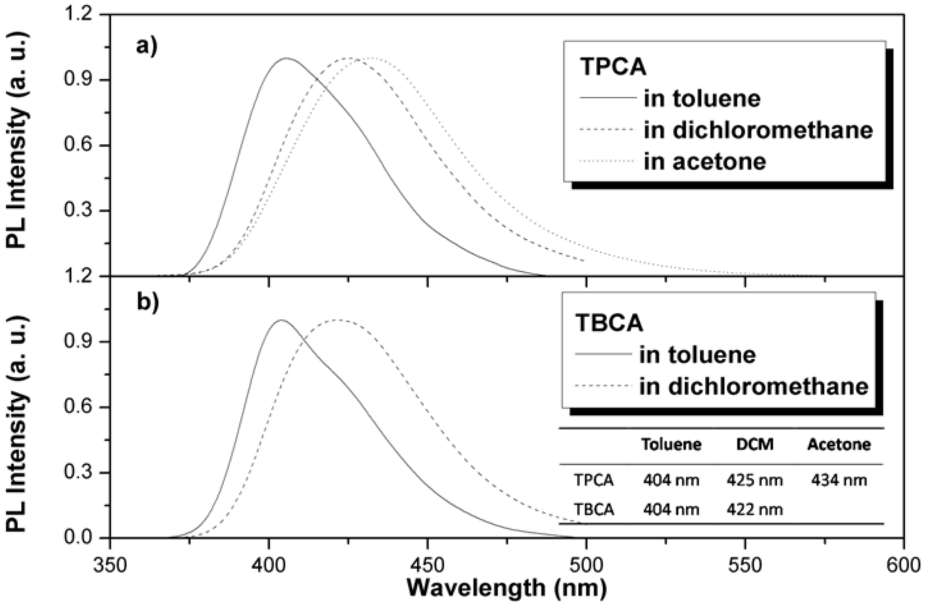


Fig. S11 The TGA curve of **TPCA** measured at a heating rate of 10 °C/min under N_2 atmosphere. Inset: the DSC curve of the second heating cycle for **TPCA**.



	Toluene	DCM	Acetone
TPCA	404 nm	425 nm	434 nm
TBCA	404 nm	422 nm	

Fig. S12 The PL spectra of **TPCA** (a) and **TBCA** (b) in various solvents (10^{-6} M). For clearness, the emission maxima are also listed in the inset table.

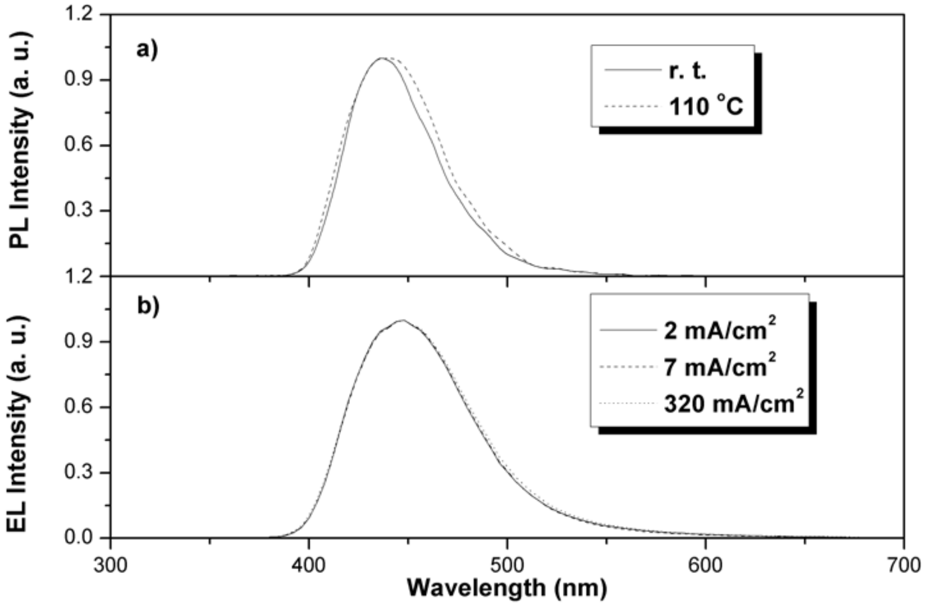


Fig. S13 a) The PL spectra of **TPCA** films before and after thermal annealing for 0.5 h, and b) the EL spectra of **TPCA** under different current densities.