

Electronic Supplementary Information:

**Efficient Thermally Activated Delayed Fluorescence Carbazole Derivatives with a Cofacial Acceptor/Donor/Acceptor Chromophore: Comparable Luminescent Properties to their Counterparts with an Opposite Configuration of Donor/Acceptor/Donor**

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**General information:**

All chemical reagents were used as received from commercial sources without further purification. 3,6-Di(tert-butyl)-9-(4-iodophenyl)carbazole was prepared according to reference.<sup>1</sup> NMR spectra were recorded with Bruker Avance spectrometers (400 or 500 MHz for <sup>1</sup>H NMR and 126 MHz for <sup>13</sup>C NMR). Elemental analyses were carried out on Bio-Rad elemental analysis system. Thermal gravimetric analysis (TGA) was performed on Perkin-Elmer-TGA 7 at heating rate of 10°C/min with continuous nitrogen flow.

**Optical measurements:**

The solution samples (10<sup>-5</sup> M) were degassed with nitrogen for several minutes prior to using. Thin film samples were deposited on quartz glass substrates by spin-coating and measured under an argon atmosphere. UV-visible (UV-vis) absorption and steady state photoluminescence spectra were measured with a Perkin-Elmer Lambda 35 UV-vis spectrometer and a Perkin-Elmer LS 50B spectrofluorometer, respectively. Fluorescence lifetime and quantum efficiency were carried out with Edinburgh fluorescence spectrometer (FLS980) with an integrating sphere.

**Electrochemical measurements:**

Cyclic voltammetry (CV) was carried out on electrochemical workstation (CHI610E) with a typical three-electrode cell (glassy-carbon work electrode, calomel reference electrode and platinum counter electrode). The samples were tested in degassed dichloromethane using ferrocene as an internal reference and tetra-butyl ammonium hexafluorophosphate as the supporting electrolyte. The highest

occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were calculated according to the equations of  $E_{\text{HOMO}} = - [E (\text{onset, ox vs Fc/Fc}^+) + 4.8] (\text{eV})$  and  $E_{\text{LUMO}} = - [E (\text{onset, re vs Fc/Fc}^+) + 4.8] (\text{eV})$ .

#### **Crystal structure determination:**

The crystal of PTBPAC was obtained by slow evaporation of toluene/ethanol solution at room temperature. The single crystal X-ray diffraction experiment was carried out using a Bruker Smart APEX diffractometer with CCD detector and graphite monochromator, Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The intensity data was recorded with  $\omega$  scan mode [187(2) K]. Lorentz, polarization factors were made for the intensity data and absorption corrections were performed using SADABS program.<sup>2</sup> The crystal structure was determined using the SHELXTL program and refined using full matrix least squares.<sup>3</sup> All non-hydrogen atoms were assigned with anisotropic displacement parameters, whereas hydrogen atoms were placed at calculated positions theoretically and included in the final cycles of refinement in a riding model along with the attached carbons. The detailed data can be obtained free of charge from the Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) with CCDC 2347370 for PTBPAC.

#### **Theoretical calculation:**

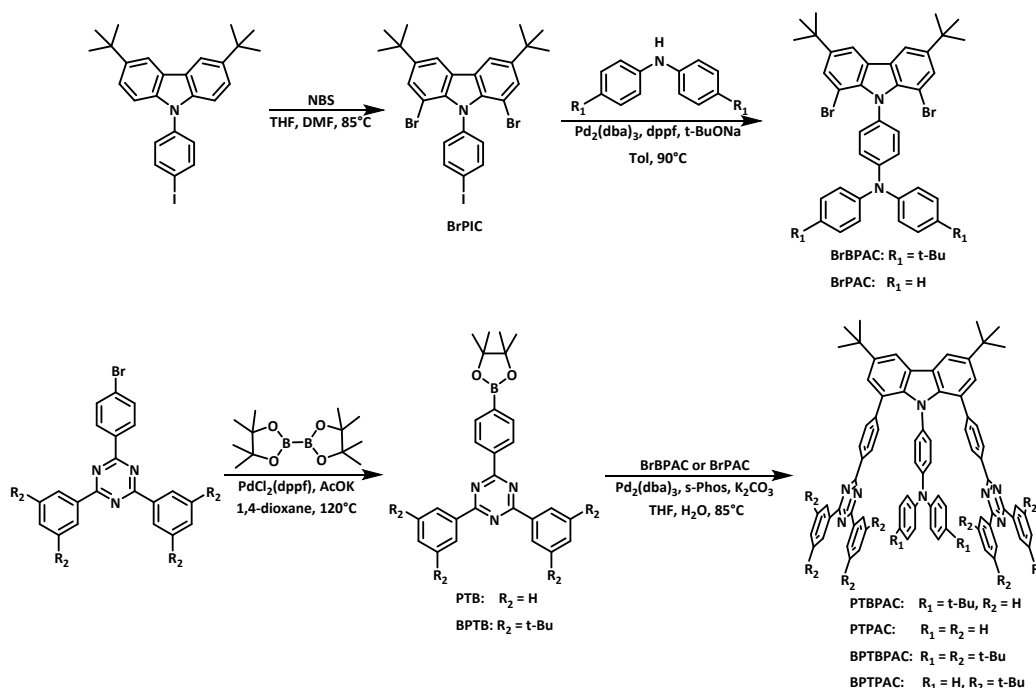
Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were performed using the Gaussian 09 program package. The ground state geometries were optimized using DFT, B3LYP/6-31G(d) method, without imposing any symmetry constraints.

#### **Device fabrication and measurements:**

The prepared OLEDs have a configuration of ITO/PEDOT:PSS (40 nm)/SimCP2:emitter (40 nm)/TmPyPB (60nm)/LiF (1 nm)/Al (120 nm) or ITO/PEDOT:PSS (40 nm)/TCTA:emitter (40 nm)/TmPyPB (60nm)/LiF (1 nm)/Al (120 nm). Here, PEDOT:PSS is poly(ethylenedioxythiophene):poly(styrenesulfonate), TmPyPB is 1,3,5-tri(m-pyrid-3-ylphenyl)benzene, TCTA is 4,4',4''-tris(carbazole-9-yl)triphenylamine and SimCP2 is bis(3,5-di(carbazole-9-yl)phenyl)diphenylsilane. The PEDOT:PSS (AI 4083) was spin-coated onto the pre-cleaned ITO substrate and annealed at 120°C for 30 min in air

condition. Then the device substrates were transferred into a nitrogen-filled glovebox to prepare the corresponding emissive layer. Emitters were dissolved in fresh chlorobenzene solvent and then stirring at 60°C for 1 hour before spin-coating them to form ca. 40nm-thick emissive layer. The devices were then annealed at 100°C for 30 min in the glovebox. The other layers including TmPyPB (60 nm)/LiF (1 nm)/Al (120 nm) were evaporated in a vacuum chamber at a base pressure less than  $2 \times 10^{-7}$  Tor. The J-L-V characteristics were measured by a Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. The EL spectra of the devices were measured by PR-655 spectra radiometer. All measurements were carried out at room temperature under ambient conditions. External quantum efficiencies of the devices were calculated from the luminance, current density and EL spectrum, assuming a Lambertian distribution.

### Synthesis:



**Scheme S1.** Synthesis of PTBPAC, PTPAC, BPTBPAC and BPTPAC.

#### BrPIC: 1,8-dibromo-3,6-di(tert-butyl)-9-(4-iodophenyl)carbazole

3,6-Di(tert-butyl)-9-(4-iodophenyl)carbazole (4.81 g, 10 mmol) was dissolved in a mixed solvent of 10 mL tetrahydrofuran (THF) and 20 mL N,N-dimethylformamide

(DMF) under dark condition. Then, N-bromosuccinimide (NBS) (5.34 g, 30 mmol) was added to the solution. The mixture was heated to 85°C and stirred for 12 h. After cooled to room temperature, the mixture was poured into 100 mL water and extracted with CH<sub>2</sub>Cl<sub>2</sub> (DCM) three times. The organic layer was washed with water and brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solution was filtered and then concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether (PE)) to give white solid. Yield: 5.09 g, 80%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 8.03 (d, J = 1.8 Hz, 2H), 7.78-7.74 (m, 2H), 7.59 (d, J = 1.8 Hz, 2H), 7.21-7.16 (m, 2H), 1.43 (s, 18H).

**BrBPAC: 1,8-dibromo-3,6-di(tert-butyl)-9-(4-(di(4-tert-butylphenyl)amino)phenyl)carbazole**

BrPIC (1.27 g, 2 mmol), bis(4-tert-butylphenyl)amine (0.53 g, 1.9 mmol), tris(dibenzylideneacetone)dipalladium (Pd<sub>2</sub>(dba)<sub>3</sub>) (0.0915 g, 0.1 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf) (0.1108 g, 0.2 mmol) and sodium tert-butoxide (0.38 g, 4 mmol) were dissolved in toluene (5 mL) under an argon atmosphere. The mixture was heated to 90°C and stirred for 12 h. After cooled to room temperature, the mixture was poured into 100 mL water, and extracted with DCM three times. The organic layer was washed with water and brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solution was filtered and then concentrated in vacuo. The crude product was washed by a small amount of DCM and filtered to give white solid. Yield: 0.82 g, 55%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 8.05 (d, J = 1.6 Hz, 2H), 7.63 (d, J = 1.6 Hz, 2H), 7.31 (d, J = 8.6 Hz, 4H), 7.23 (d, J = 8.7 Hz, 2H), 7.11 (dd, J = 12.9, 8.7 Hz, 6H), 1.45 (s, 18H), 1.33 (s, 18H).

**PTB: 2,4-diphenyl-6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine**

2-(4-Bromophenyl)-4,6-diphenyl-1,3,5-triazine (1.16 g, 3 mmol), pinacol diboronate (3.05 g, 12 mmol), (1,1'-bis(diphenylphosphino)ferrocene)dichloropalladium(II) (PdCl<sub>2</sub>(dppf)) (0.0365 g, 0.05 mmol) and potassium acetate (1.24 g, 9 mmol) were dissolved in 1,4-dioxane (10 mL) under an argon atmosphere. The mixture was stirred at 120°C for 12 h. After cooled to room temperature, the mixture was poured into 100 mL water, and extracted with DCM three times. The organic layer was

washed with water and brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solution was filtered and then concentrated in vacuo. The crude product was purified by silica gel column chromatography (PE/DCM = 1/2) to give white solid. Yield: 1.24 g, 95%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 8.81-8.74 (m, 6H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.63-7.56 (m, 6H), 1.41 (s, 12H).

**PTBPAC:** 1,8-bis(4-(4,6-diphenyl-1,3,5-triazine-2-yl)phenyl)-3,6-di(tert-butyl)-9-(4-di(4-tert-butylphenyl)amino)phenyl)carbazole

BrBPAC (0.31 g, 0.4 mmol), PTB (0.43 g, 1 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.0183 g, 0.02 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (S-Phos) (0.0328 g, 0.08 mmol) and potassium carbonate (0.22 g, 1.6 mmol) were dissolved in a mixed solvent of THF (5 mL) and water (2 mL) under an argon atmosphere. The mixture was heated to 85°C and stirred for 24 h. After cooled to room temperature, the mixture was poured into 100 mL water, and extracted with DCM three times. The organic layer was washed with water and brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solution was filtered and then concentrated in vacuo. The crude was purified by silica gel column chromatography (PE/DCM = 15/1) to give yellow green solid. Yield: 0.42 g, 85%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 8.90-8.70 (m, 8H), 8.53 (d, *J* = 8.2 Hz, 4H), 8.33 (d, *J* = 1.8 Hz, 2H), 7.60 (dq, *J* = 9.6, 4.6 Hz, 4H), 7.56 (t, *J* = 7.3 Hz, 8H), 7.42 (d, *J* = 1.7 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 4H), 6.59 (d, *J* = 5.7 Hz, 4H), 6.41 (d, *J* = 7.8 Hz, 6H), 5.97 (s, 2H), 1.58 (s, 18H), 0.88 (s, 18H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, ppm) δ 184.93, 170.02, 144.79, 142.39, 137.81, 134.09, 129.99, 129.89, 128.67, 127.68, 127.34, 125.87, 125.38, 124.41, 123.02, 119.48, 115.49, 39.59, 34.66, 32.00, 28.95. Anal. Calcd for C<sub>88</sub>H<sub>80</sub>N<sub>8</sub>: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.56; H, 6.482; N, 8.93%.

**BrPAC:** 1,8-dibromo-3,6-di(tert-butyl)-9-(4-(diphenylamino)phenyl)carbazole

The compound was prepared from BrPIC (0.25 g, 0.4 mmol) and diphenylamine (0.17 g, 1 mmol) by the same procedure of BrBPAC. White solid. Yield: 0.13 g, 50%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 8.06 (d, *J* = 1.7 Hz, 2H), 7.64 (d, *J* = 1.7 Hz, 2H), 7.33-7.26 (m, 6H), 7.21 (d, *J* = 7.5 Hz, 4H), 7.15-7.11 (m, 2H), 7.06 (dd, *J* = 10.5, 4.2 Hz, 2H), 1.46 (s, 18H).

**BPTB: 2,4-bis(3,5-di(tert-butyl)phenyl)-6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine**

The compound was prepared from 2-(4-bromophenyl)-4,6-di(3,5-di(tert-butyl)phenyl)-1,3,5-triazine (1.50 g, 3 mmol), pinacol diboronate (3.05 g, 12 mmol) by the same procedure of PTB. White solid. Yield: 1.88 g, 95%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 8.76 (d, *J* = 8.2 Hz, 2H), 8.66 (d, *J* = 1.9 Hz, 4H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.71 (t, *J* = 1.9 Hz, 2H), 1.46 (s, 36H), 1.40 (s, 12H).

**PTPAC: 1,8-bis(4-(4,6-diphenyl-1,3,5-triazine-2-yl)phenyl)-3,6-di(tert-butyl)-9-(diphenylamino)phenyl)carbazole**

The compound was prepared from BrPAC (0.27 g, 0.4 mmol) and PTB (0.43 g, 1 mmol) by the same procedure of PTBPAC. Yellow green solid. Yield: 0.29 g, 64%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 8.74 (d, *J* = 7.3 Hz, 8H), 8.52 (d, *J* = 7.8 Hz, 4H), 8.28 (s, 2H), 7.55 (dt, *J* = 14.3 Hz, 7.0 Hz, 12H), 7.36 (s, 2H), 7.22 (d, *J* = 7.7 Hz, 4H), 6.68 (t, *J* = 7.3 Hz, 4H), 6.63-6.45 (m, 8H), 6.13 (d, *J* = 8.0 Hz, 2H), 1.54 (s, 18H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, ppm) δ 171.58, 136.24, 133.60, 132.44, 128.99, 128.60, 127.64, 77.27, 77.02, 76.76, 32.04. Anal. Calcd for C<sub>80</sub>H<sub>64</sub>N<sub>8</sub>: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.20; H, 5.614; N, 9.95%.

**BPTBPAC: 1,8-bis(4-(4,6-di(3,5-di(tert-butyl)phenyl)-1,3,5-triazine-2-yl)phenyl)-3,6-di(tert-butyl)-9-(4-di(4-tert-butyl)phenyl)amino)phenyl)carbazole**

The compound was prepared from BrBPAC (0.31 g, 0.4 mmol) and BPTB (0.66 g, 1 mmol) by the same procedure of PTBPAC. Yellow green solid. Yield: 0.54 g, 80%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 8.69 (s, 8H), 8.58 (d, *J* = 8.0 Hz, 4H), 8.32 (s, 2H), 7.70 (s, 4H), 7.39 (s, 2H), 7.24 (s, 2H), 7.20 (d, *J* = 7.2 Hz, 2H), 6.57 (d, *J* = 7.4 Hz, 4H), 6.53 (d, *J* = 8.1 Hz, 2H), 6.39 (d, *J* = 6.5 Hz, 4H), 6.13 (d, *J* = 6.4 Hz, 2H), 1.56 (s, 18H), 1.45 (s, 72H), 0.79 (s, 18H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, ppm) δ 171.99, 171.32, 151.10, 146.26, 145.04, 143.77, 142.21, 137.70, 135.70, 133.74, 130.28, 127.47, 127.34, 126.81, 125.73, 124.13, 123.13, 116.93, 115.51, 77.30, 77.04, 76.79, 35.04, 34.74, 33.77, 32.09, 31.51, 30.98. Anal. Calcd for C<sub>120</sub>H<sub>144</sub>N<sub>8</sub>: C, 84.86; H, 8.55; N, 6.60. Found: C, 84.75; H, 8.512; N, 6.44%.

**BPTPAC: 1,8-bis(4-(4,6-di(3,5-di(tert-butyl)phenyl)-1,3,5-triazine-2-yl)phenyl)-3,6-di(tert-butyl)-9-(diphenylamino)phenyl)carbazole**

The compound was prepared from BrPAC (0.27 mg, 0.4 mmol) and BPTB (0.66 g, 1 mmol) by the same procedure of PTBPAC. Yellow green solid. Yield: 0.46 g, 73%. <sup>1</sup>H

NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  8.64 (d,  $J = 1.3$  Hz, 8H), 8.56 (d,  $J = 8.1$  Hz, 4H), 8.28 (d,  $J = 1.5$  Hz, 2H), 7.69 (s, 4H), 7.31 (d,  $J = 1.5$  Hz, 2H), 7.28 (s, 2H), 6.73 (t,  $J = 7.7$  Hz, 4H), 6.65 (d,  $J = 8.5$  Hz, 2H), 6.53 (d,  $J = 8.0$  Hz, 4H), 6.49 (t,  $J = 7.4$  Hz, 2H), 6.26 (d,  $J = 8.6$  Hz, 2H), 1.53 (s, 18H), 1.43 (s, 72H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  172.02, 171.26, 151.06, 146.86, 146.52, 145.11, 142.46, 137.98, 135.65, 134.00, 132.62, 130.19, 130.13, 128.97, 127.64, 127.58, 126.69, 125.96, 125.17, 124.45, 123.12, 123.06, 119.99, 115.52, 77.26, 77.00, 76.75, 35.02, 34.70, 32.02, 31.46. Anal. Calcd for  $\text{C}_{112}\text{H}_{128}\text{N}_8$ : C, 84.80; H, 8.13; N, 7.06. Found: C, 84.65; H, 8.098; N, 6.92%.

## Figures and Tables

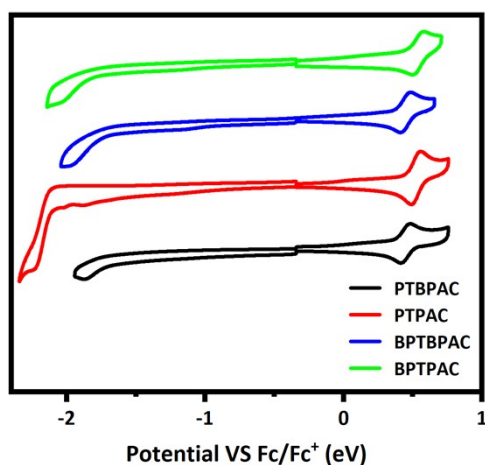


Fig S1. Cyclic voltammogram of four compounds.

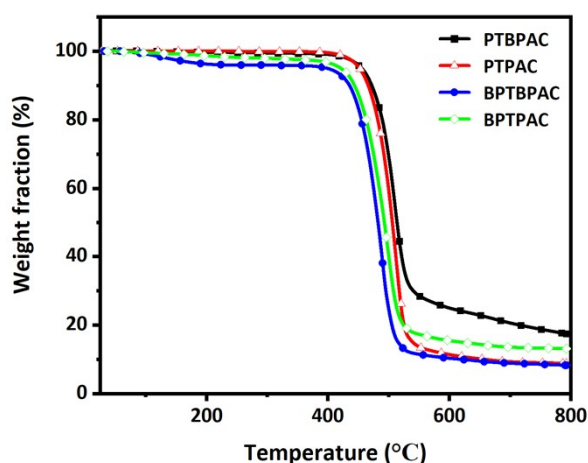
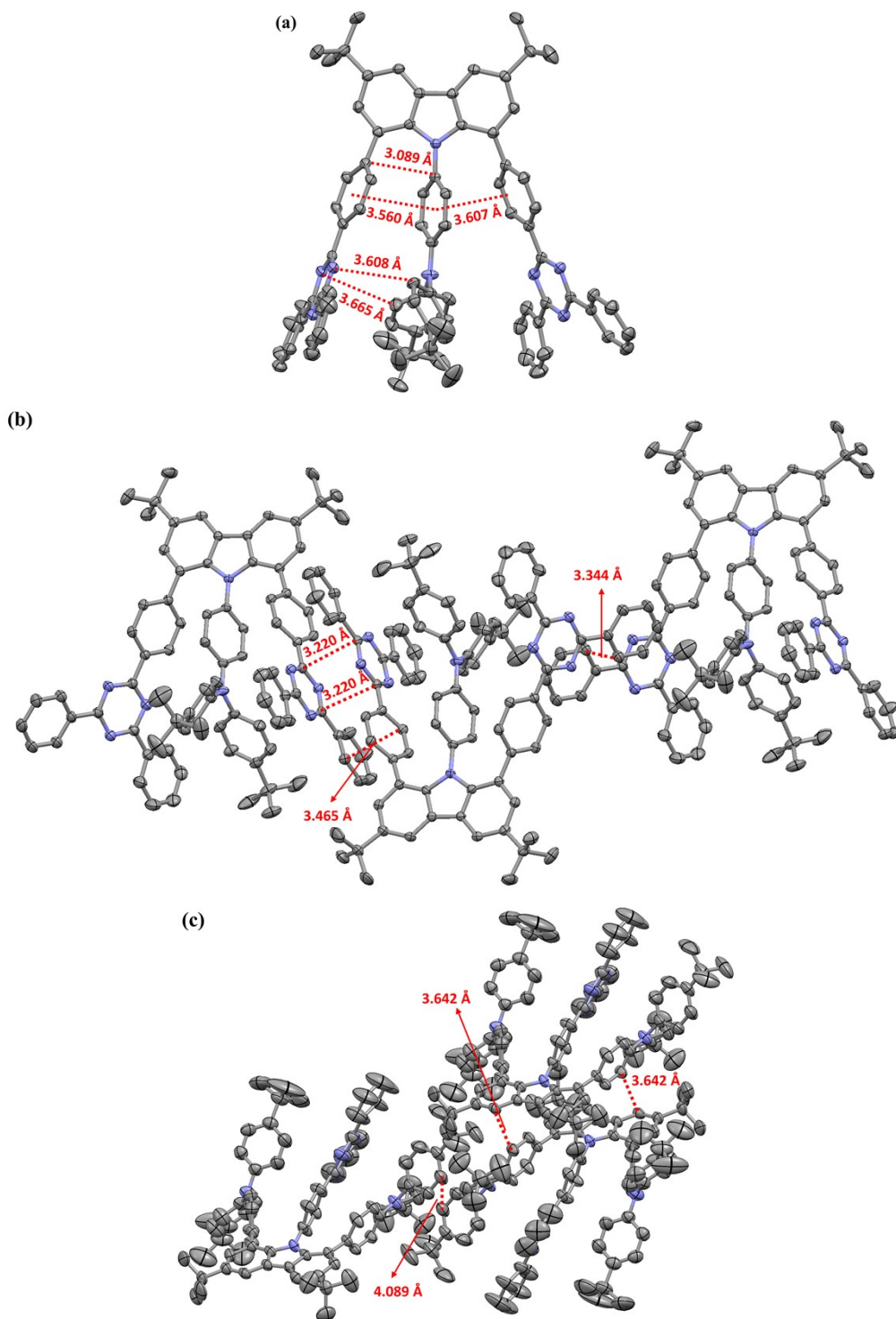
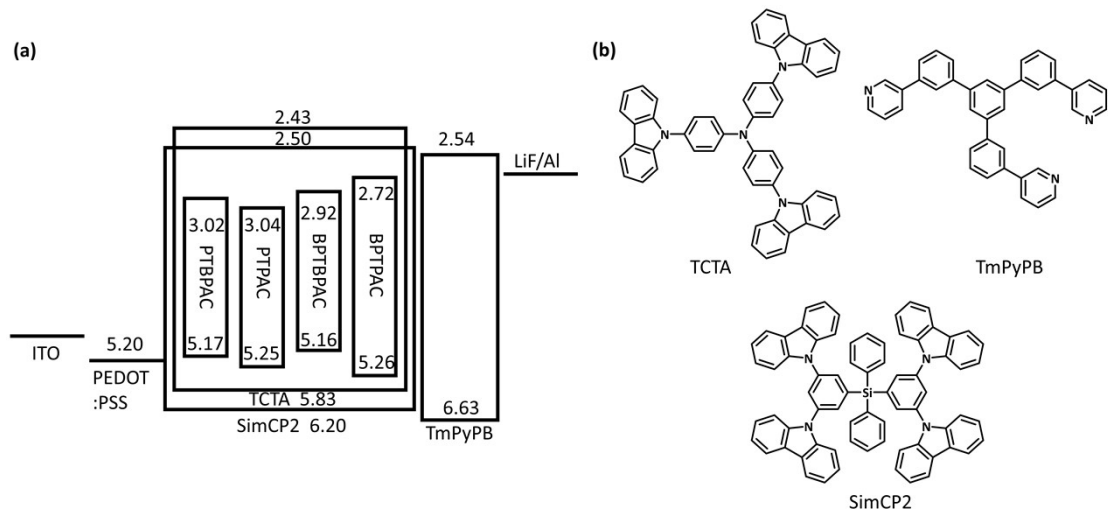


Fig S2. TGA traces recorded at a heating rate of  $10^\circ\text{C min}^{-1}$ .

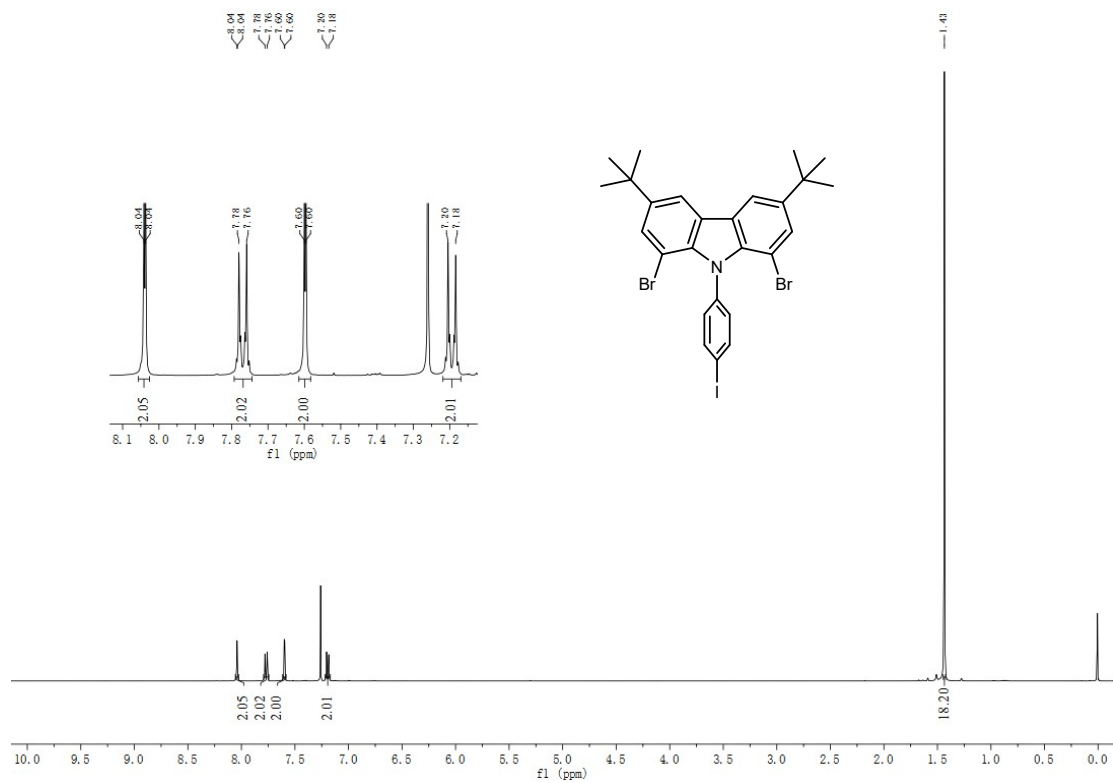


**Fig S3.** (a) Crystal structure and (b) crystal packing of PTBPAC, (c) crystal packing of BPAPTC. Hydrogen atoms have been omitted for clarity. In crystal packing of PTBPAC, the stronger intermolecular  $\pi$ - $\pi$  interactions are observed among adjacent molecules with the shortest distance of 3.220 Å, and the interactions occur between two triazine acceptors with face-to-face contacts. There are also intermolecular  $\pi$ - $\pi$  interactions among adjacent molecules in crystal packing of BPAPTC, however, the interactions merely occur between carbazole and linker phenylene rings with the shortest distance of 3.642 Å and edge-to-face contacts, rather than between chromophores.





**Fig S4.** a) Energy levels of the EL devices; b) Chemical structures of TCTA, SimCP2 and TmPyPB.



**Fig S5.**  $^1\text{H}$  NMR spectrum of compound BrPIC.

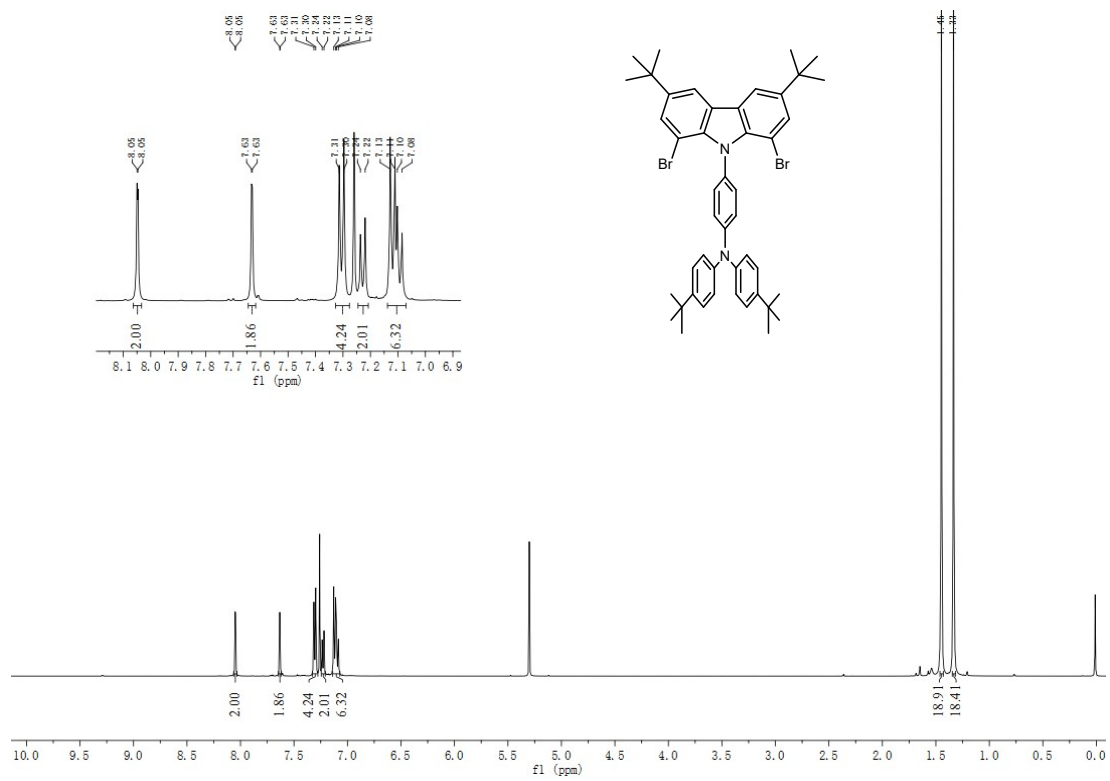


Fig S6. <sup>1</sup>H NMR spectrum of BrBPAC.

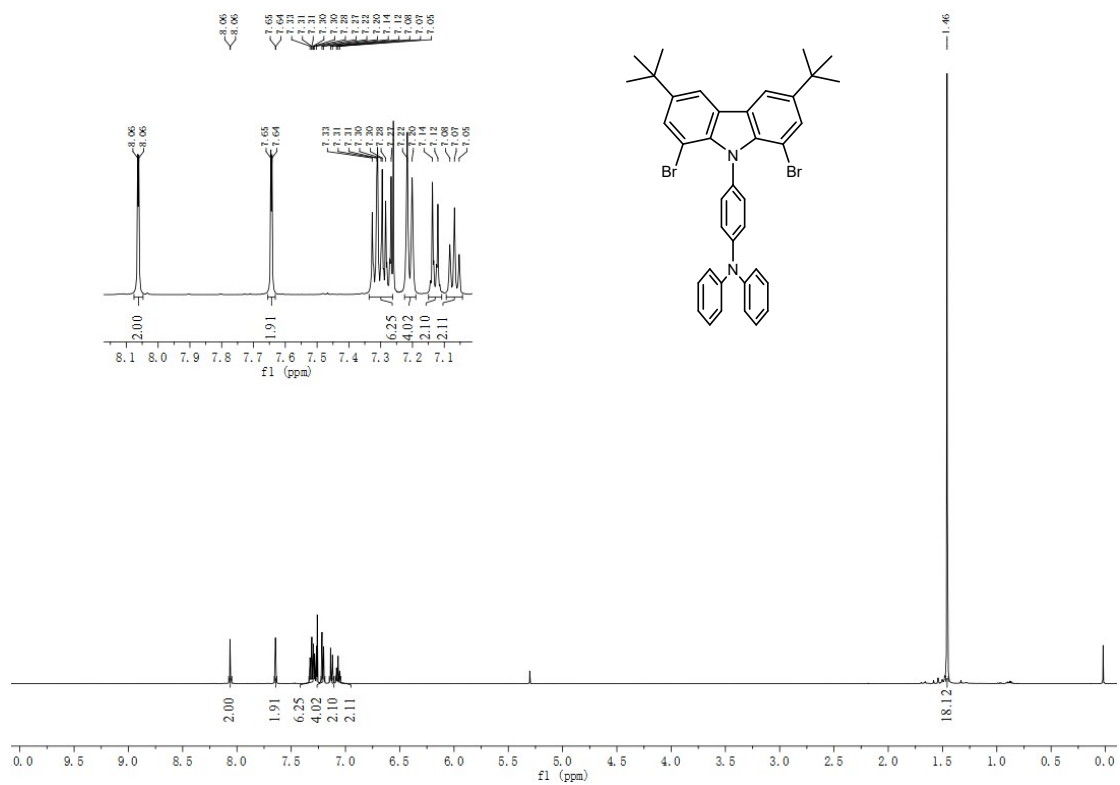


Fig S7. <sup>1</sup>H NMR spectrum of BrPAC.

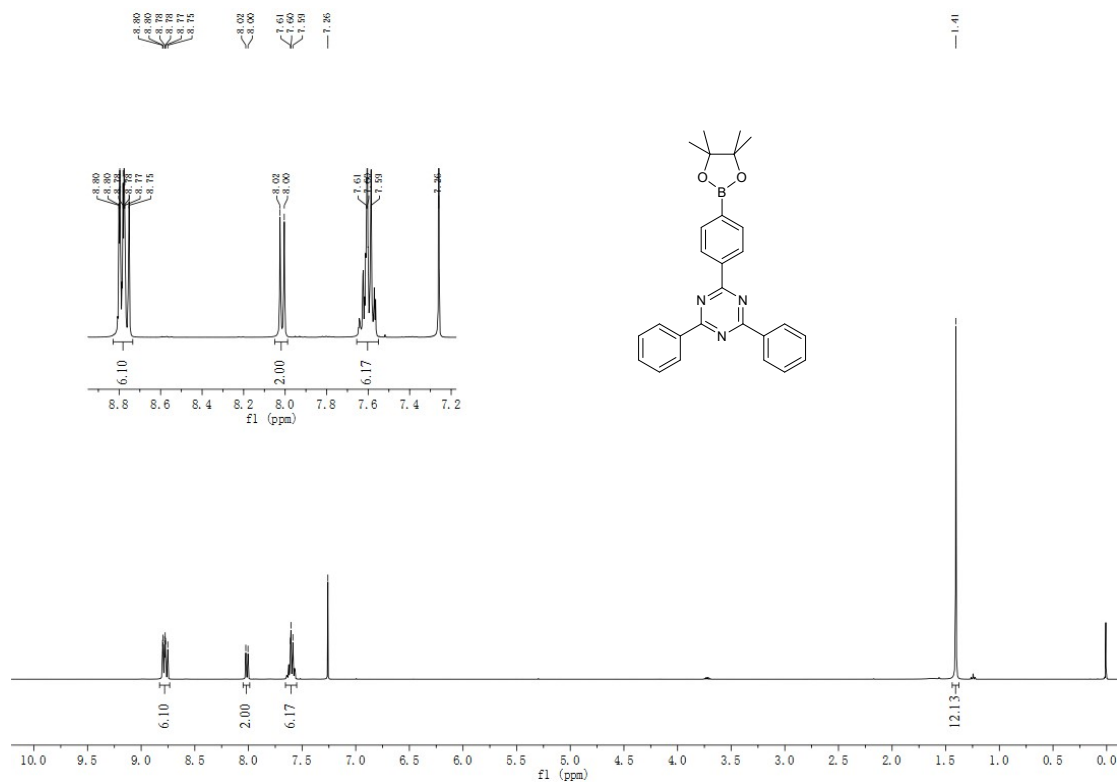


Fig S8. <sup>1</sup>H NMR spectrum of PTB.

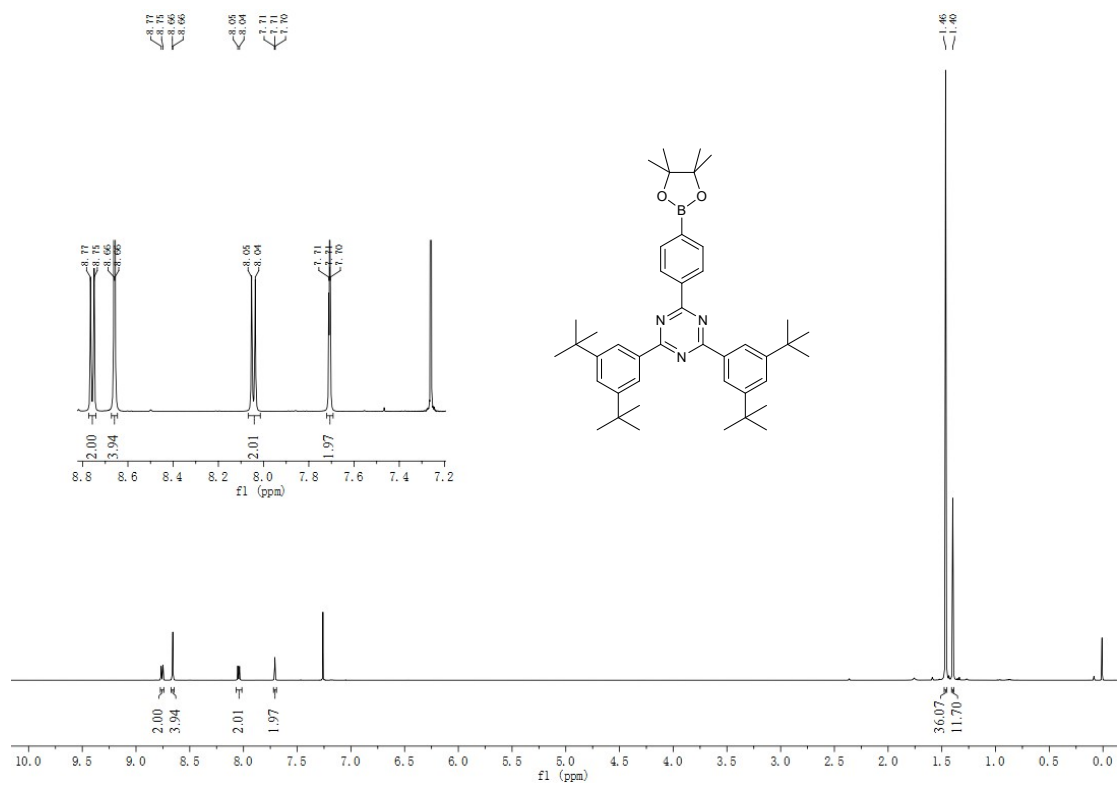


Fig S9. <sup>1</sup>H NMR spectrum of BPTB.

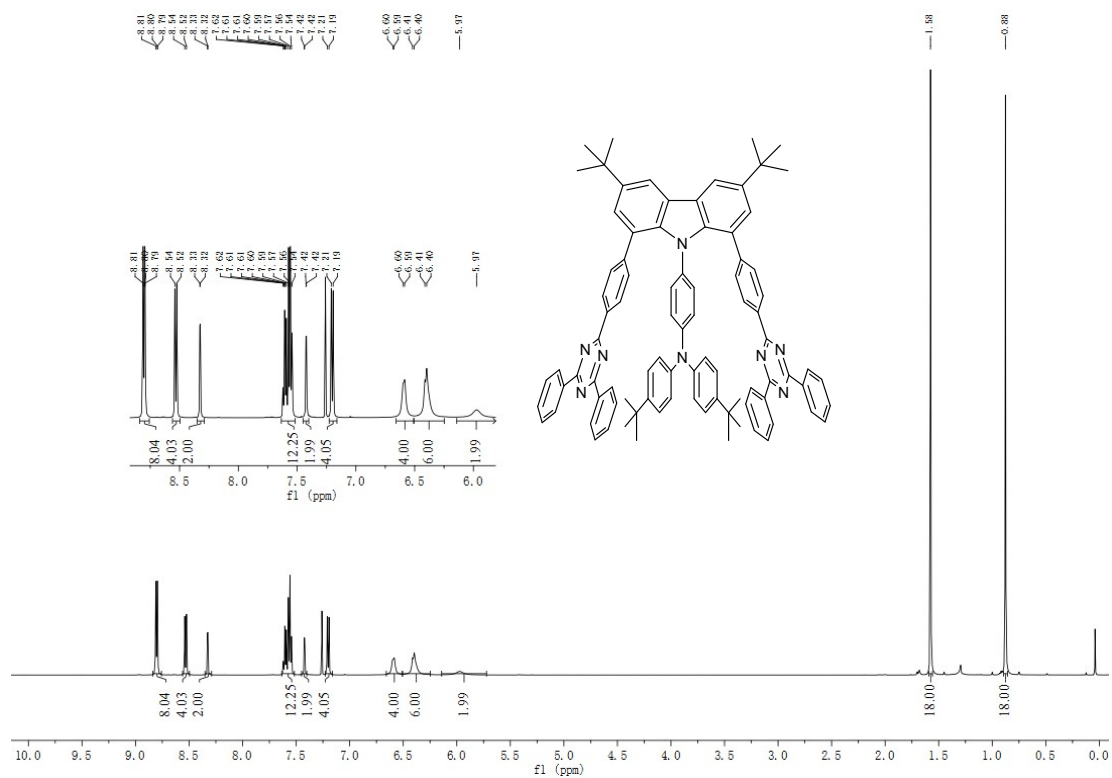


Fig S10. <sup>1</sup>H NMR spectrum of PTBPAC.

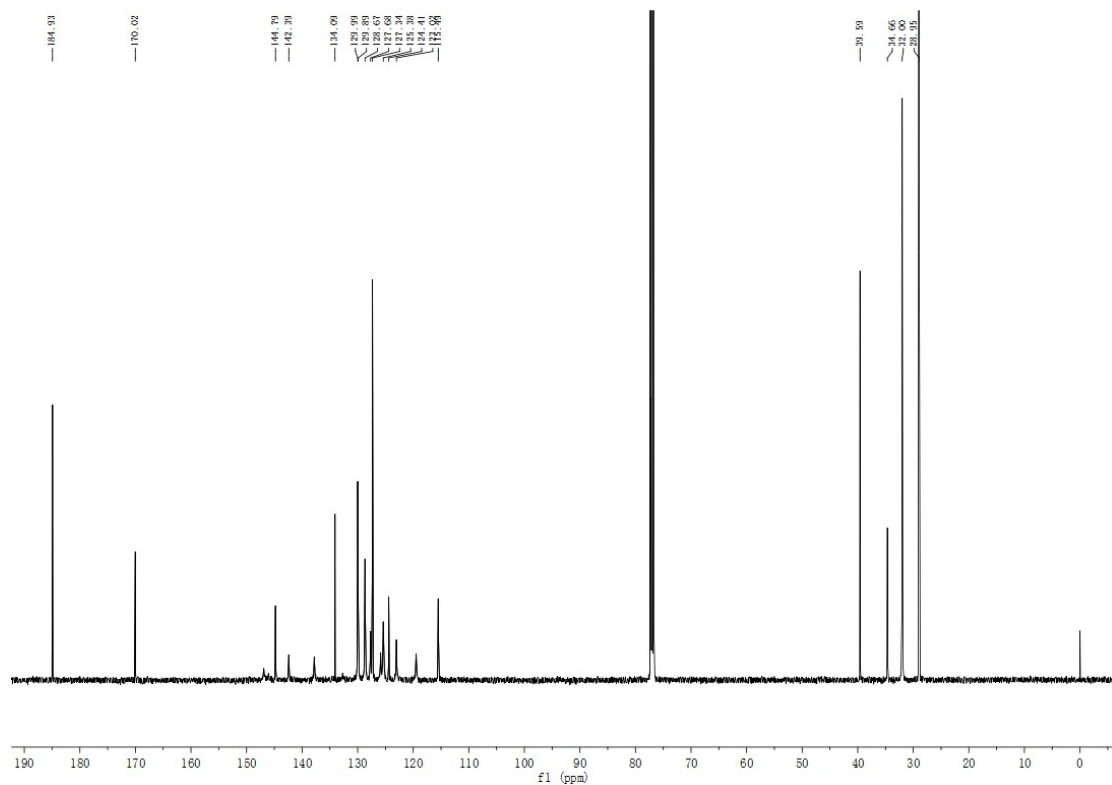


Fig S11. <sup>13</sup>C NMR spectrum of PTBPAC.

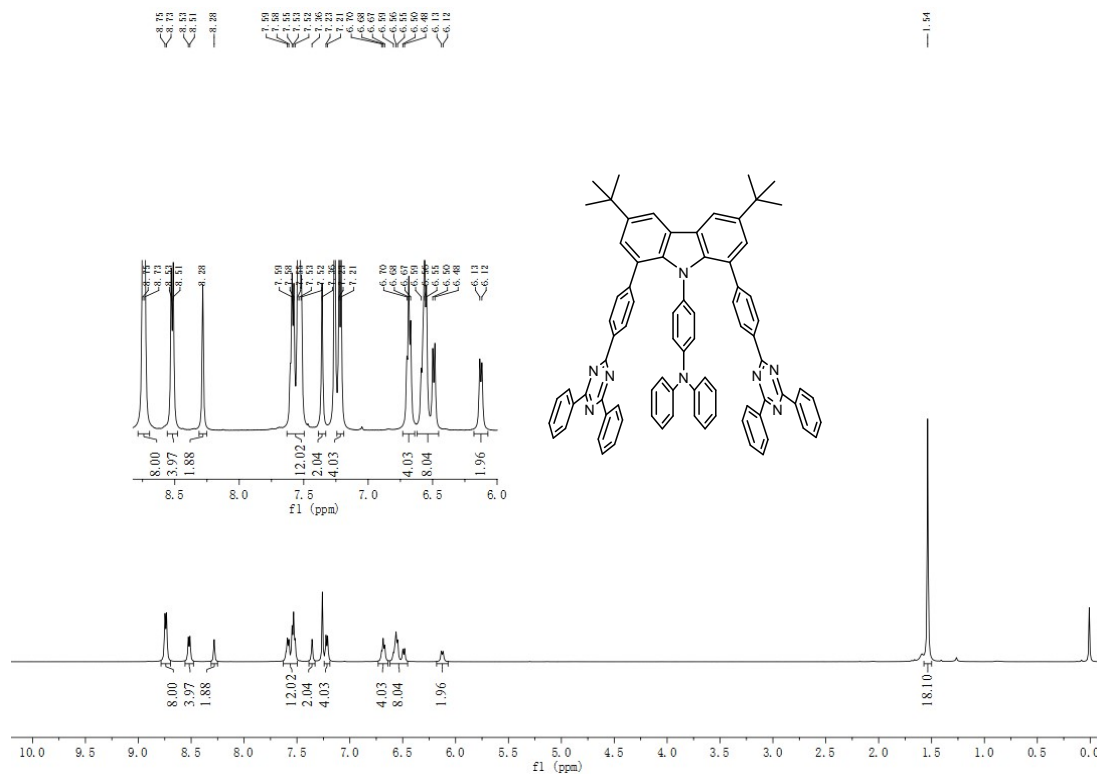


Fig S12. <sup>1</sup>H NMR spectrum of PTPAC.

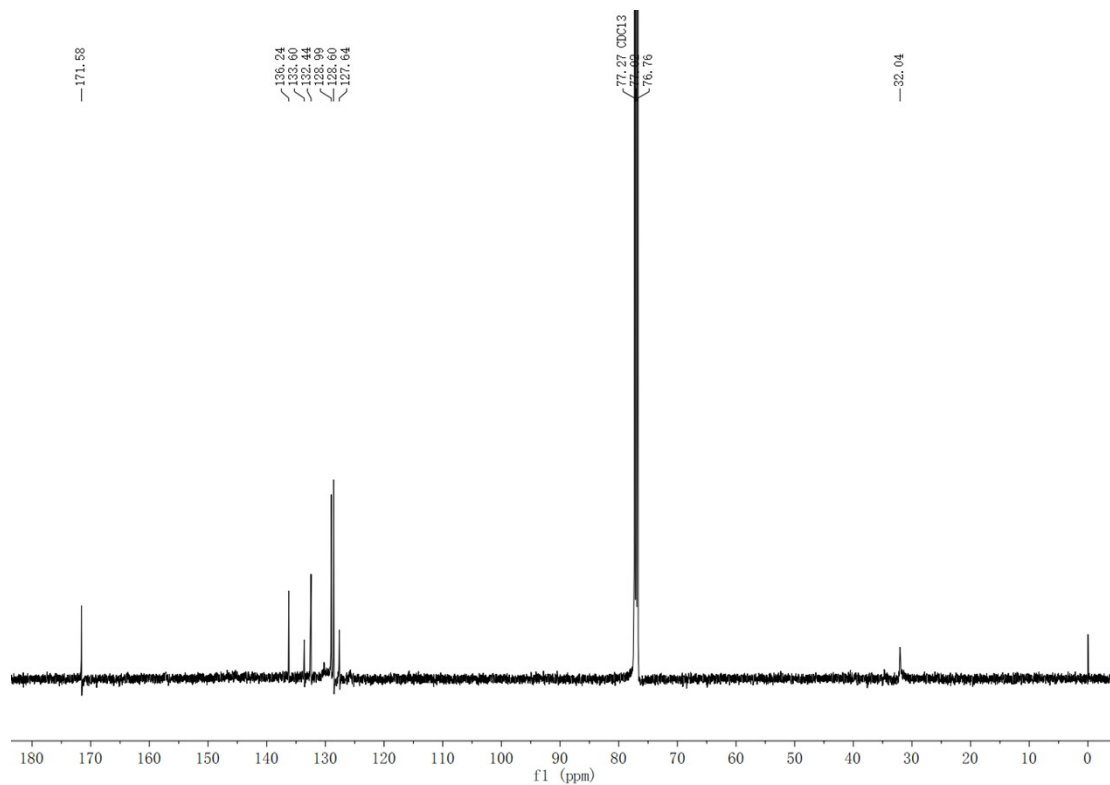


Fig S13. <sup>13</sup>C NMR spectrum of PTPAC.

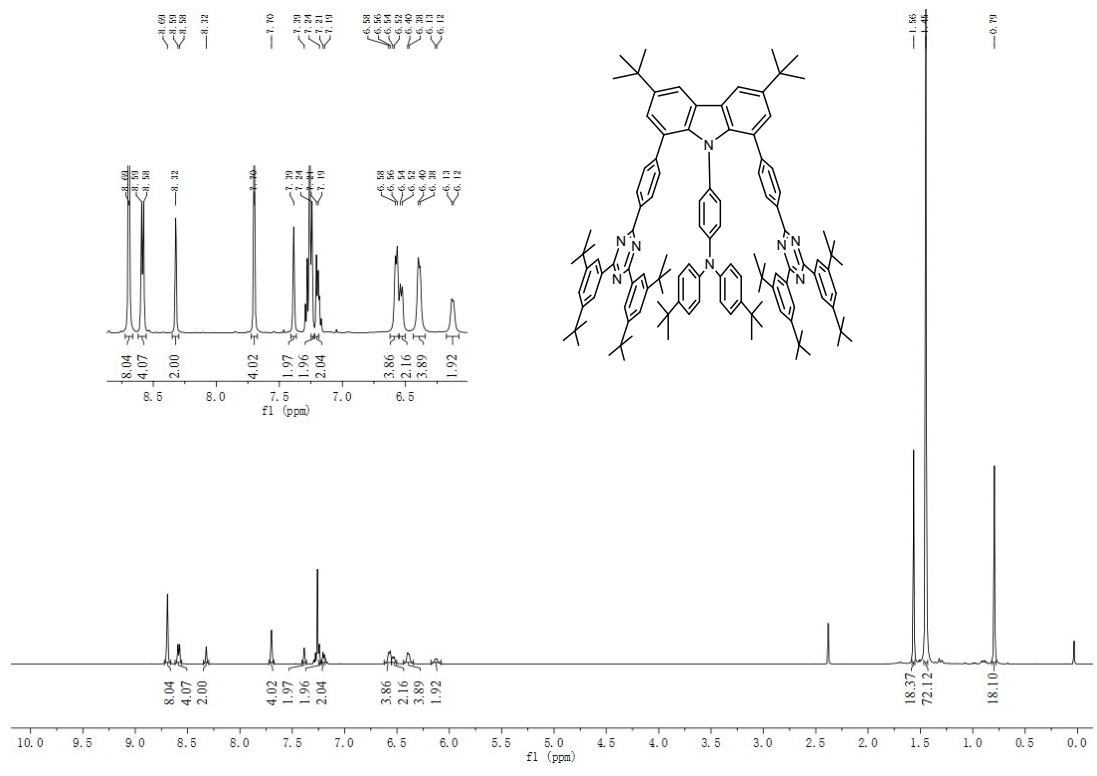


Fig S14.  $^1\text{H}$  NMR spectrum of BPTBPAC.

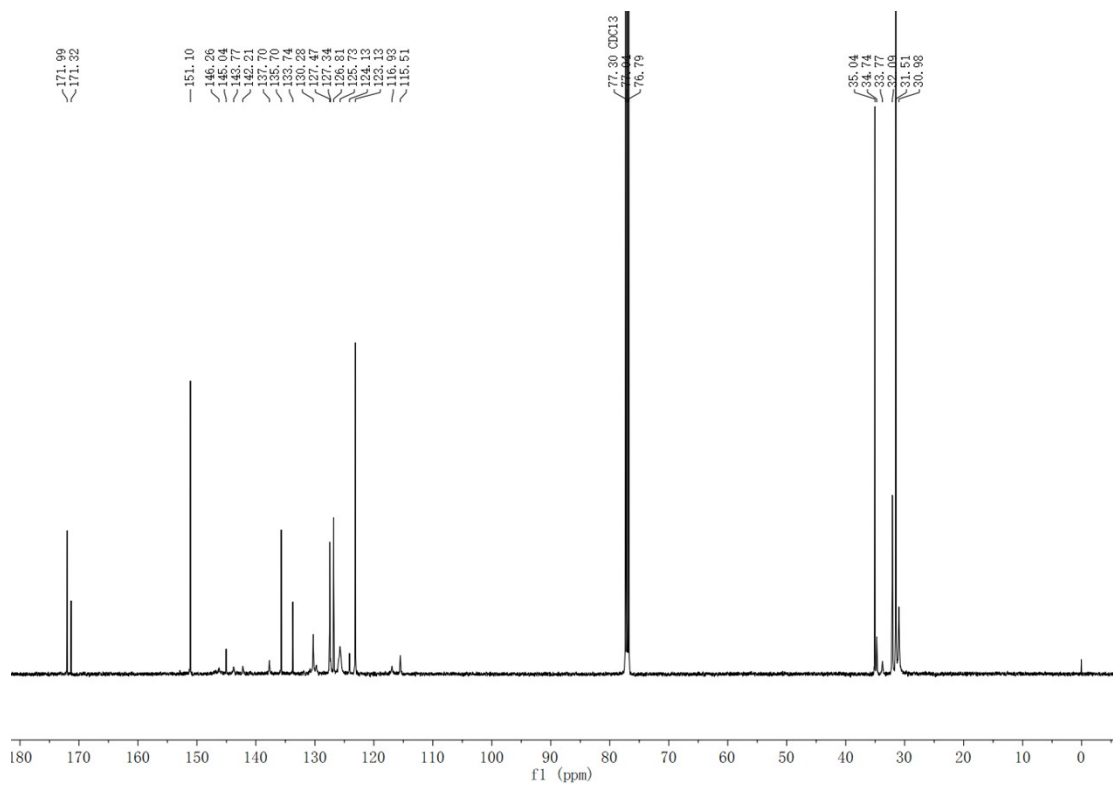


Fig S15.  $^{13}\text{C}$  NMR spectrum of BPTBPAC.

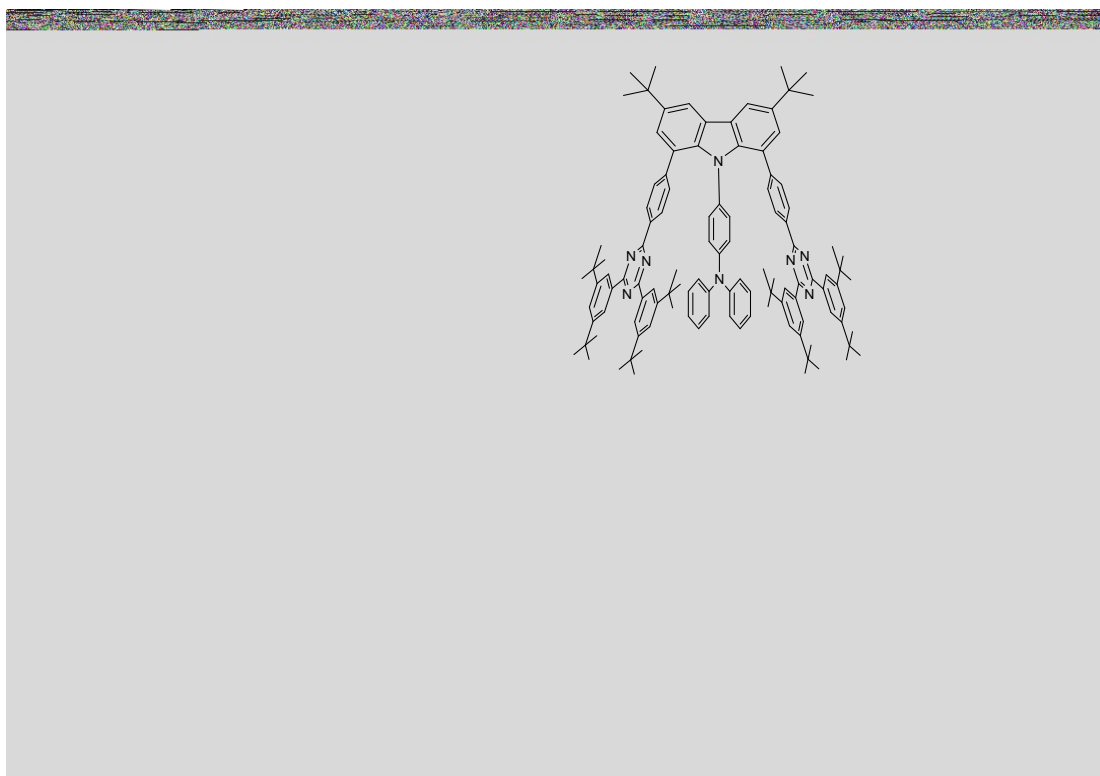


Fig S16.  $^1\text{H}$  NMR spectrum of BPTPAC.

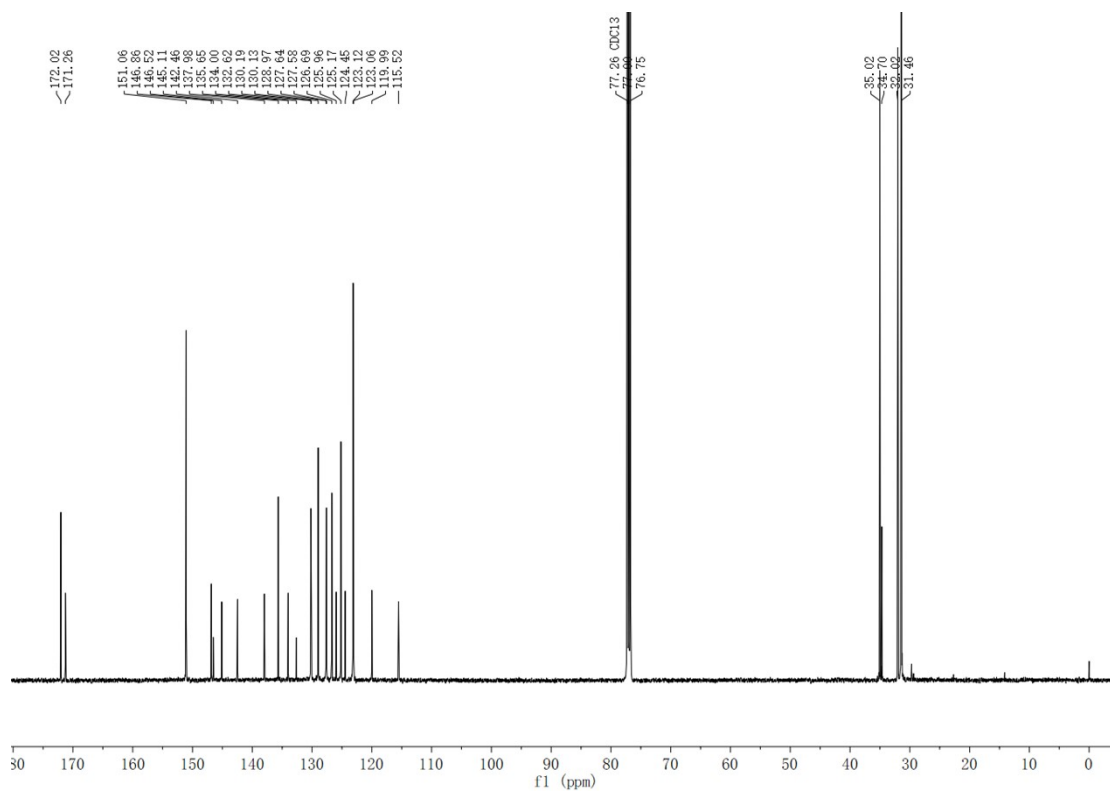
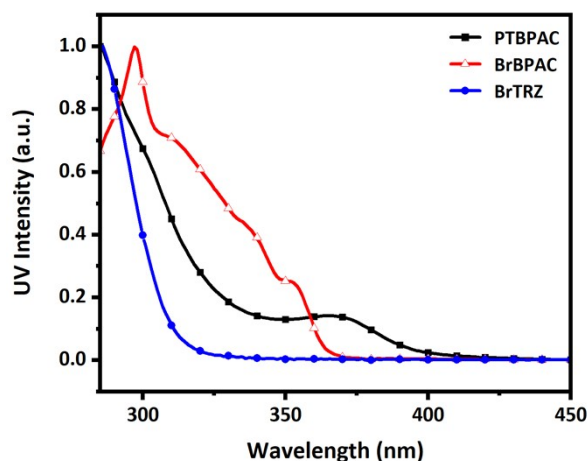
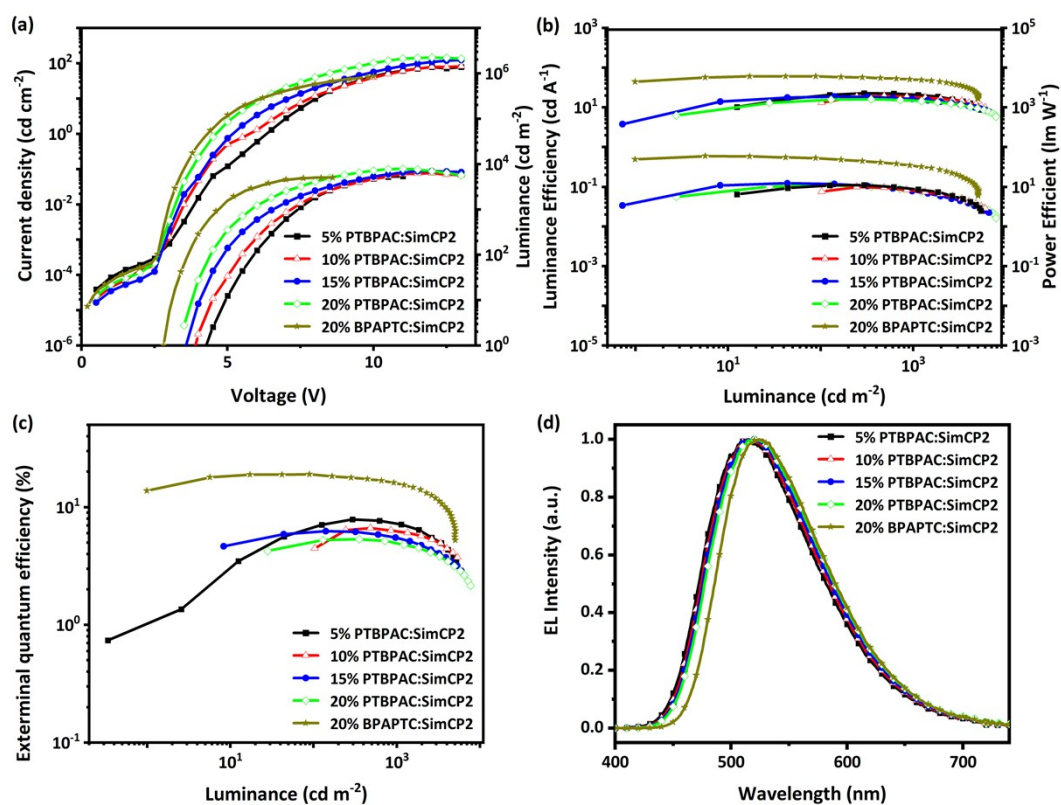


Fig S17.  $^{13}\text{C}$  NMR spectrum of BPTPAC.

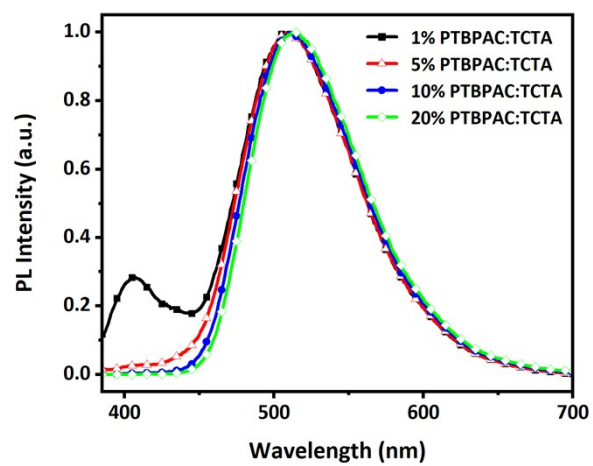


**Fig S18.** UV-vis absorption spectra of PTBPAC, BrBPAC and BrTRZ in toluene with the concentration of  $10^{-5}$  M.



**Fig S19.** EL performance of 5, 10, 15, 20 wt% PTBPAC and 20 wt% BPAPTC doped in SimCP2: (a) current density-voltage-luminance curves; (b) current efficiency-luminance-power efficiency curves; (c) EQE-luminance curves and; (d) EL spectra.





**Fig S20.** PL of PTBPAC doped in TCTA with different ratios.

**Table S1.** EL performance of 5, 10, 15, 20 wt% PTBPAC and 20 wt% BPAPTC doped in SimCP2.

Device	EL [nm]	$V_{on}$ [V]	Max performance				Device performance at 500/1000 cd m <sup>-2</sup>			
			L	LE	PE	EQE	CIE	LE	PE	EQE
			[cd m <sup>-2</sup> ]	[cd A <sup>-1</sup> ]	[lm W <sup>-1</sup> ]	[%]		[cd A <sup>-1</sup> ]	[lm W <sup>-1</sup> ]	[%]
PTBPAC: SimCP2 (0.5:9.5 mg/mL)	514	4.2	5401	22.9	11.0	7.8	(0.30, 0.51)	22.3/20.7	10.0/8.7	7.6/7.1
PTBPAC: SimCP2 (1:9 mg/mL)	515	3.9	6337	19.6	9.4	6.6	(0.30, 0.51)	19.0/18.6	9.0/8.3	6.4/6.3
PTBPAC: SimCP2 (1.5:8.5 mg/mL)	515	3.5	6999	18.6	11.7	6.2	(0.31, 0.52)	17.4/16.4	9.1/7.9	5.8/5.5
PTBPAC: SimCP2 (2:8 mg/mL)	520	3.4	7833	16.1	10.1	5.3	(0.32, 0.52)	15.5/14.4	8.8/7.6	5.1/4.8
BPAPTC: SimCP2 (2:8 mg/mL)	524	3.0	5049	60.5	52.7	19.1	(0.35, 0.56)	54.8/50.9	40.9/34.7	17.3/16.1

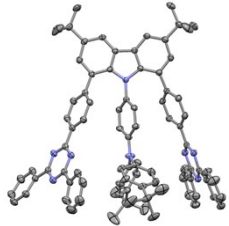
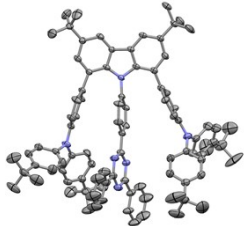
**Table S2.** The PLQYs of PTBPAC doped in TCTA with different ratios.

Emitter: TCTA	PLQY%			
	20 wt%	10 wt%	5 wt%	1 wt%
	52	70	90	57
PTBPAC	PL [nm]			
	513	511	511	511

**Table S3.** The photophysical properties and dynamic parameters of 5 wt% PTBPAC, PTPAC, BPTBPAC and BPAPTC doped in TCTA.

Compound	$\Phi_{PF}$ [%]	$\Phi_{DF}$ [%]	$k_p$ [10 <sup>6</sup> s <sup>-1</sup> ]	$k_d$ [10 <sup>5</sup> s <sup>-1</sup> ]	$k_{ISC}$ [10 <sup>6</sup> s <sup>-1</sup> ]	$k_{RISC}$ [10 <sup>5</sup> s <sup>-1</sup> ]	$k_r$ [10 <sup>6</sup> s <sup>-1</sup> ]	$k_{nr}$ [10 <sup>4</sup> s <sup>-1</sup> ]
PTBPAC	29	61	4.00	1.39	2.72	4.35	1.15	1.39
PTPAC	42	45	8.19	0.85	4.26	1.79	3.42	1.11
BPTBPAC	39	52	5.84	0.94	3.33	2.19	2.29	0.85
BPTPAC	31	26	6.67	0.53	3.00	0.97	2.09	2.30
BPAPTC	17	73	2.05	1.59	1.66	8.43	0.35	1.58

**Table S4.** Structural parameters, Photophysical , electrochemical and EL properties of the isomers PTBPAC and BPAPTC.

Items		PTBPAC	BPAPTC	
Chemical structure	Single crystal structure			
	Structural parameters			
	torsion angles between carbazole ring and linker phenylene group	62.8, 57.4 and 62.0°	67.1, 70.5 and 77.9°	
	the shortest distance between linker phenylene groups	3.089 Å	3.081 Å	
	the shortest distance between donor and acceptor	3.608 Å	3.358 Å	
Photophysical properties	PL wavelength in solution	517 nm	520 nm	
	Phosphorescence peak in solution at 77 K	507 nm	500 nm	
	PL wavelength in doped film	511 nm (1% TCTA)	-	
		511 (5%)	-	
		511 (10%)	-	
		513 (20%)	519 nm (20% SimCP2)	
	UV-vis absorption	365 nm	356 and 389 nm	
	PLQYs in doped film	57% (1% TCTA)	90% (20% SimCP2)	
		90% (5%)	93 (40%)	
		70% (10%)	92 (60%)	
		52% (20%)	90 (80%)	
	Kinetic parameter (5 wt% doped in host)	$k_d$ [ $10^5$ s <sup>-1</sup> ]	1.39	1.59
		$k_p$ [ $10^6$ s <sup>-1</sup> ]	4.00	2.05
		$k_{RISC}$ [ $10^5$ s <sup>-1</sup> ]	4.35	8.43
$k_r$ [ $10^6$ s <sup>-1</sup> ]		1.15	0.35	
$k_{nr}$ [ $10^4$ s <sup>-1</sup> ]		1.39	1.58	
Lifetime and proportion	$\tau_p$ [ns] (%)	72 (32)	83 (19)	
	$\tau_d$ [ $\mu$ s] (%)	4.4 (68)	4.6 (81)	
Electrochemical properties	HOMO/LUMO [eV]	-5.17/-3.02	-5.12/-2.93	
	$E_{S1}/E_{T1}$ ( $\Delta E_{ST}$ ) [eV]	2.74/2.69 (0.05)	2.68/2.62 (0.06)	
Thermal stability	$T_d$ [°C]	456	462	
EL performances (the best values obtained from this work)	EL peak	527	524	
	$V_{on}$ (V)	2.9	3.0	
	L [cd m <sup>-2</sup> ]	3007	5049	
	EQE <sub>max</sub> (%)	18.4	19.1	
	EQE (%) at 1000 cd m <sup>-2</sup>	14.1	16.1	

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