Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting information

Positive Impact of Chromophore Flexibility on the Efficiency of Red Thermally Activated Delayed Fluorescence Materials

Yuan-Yuan Wang,†[a] Kai-Ning Tong,†[a] Kai Zhang,†[b] Chen-Han Lu,[c] Xing Chen,[a] Jing-Xing Liang,[a] Chuan-Kui Wang,*[b] Chung-Chih Wu,[c] Man-Keung Fung*[a] and Jian Fan*[a]

[a] *Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu 215123, China*

[b] *Shandong Province Key Laboratory of Medical Physics and Image Processing Technology, School of Physics and Electronics, Shandong Normal University, 250014 Jinan, China.*

[c] *Department of Electrical Engineering, Graduate Institute of Electronics Engineering and Graduate Institute of Photonics and Optoelectronics, National Taiwan University Taipei 10617, Taiwan*

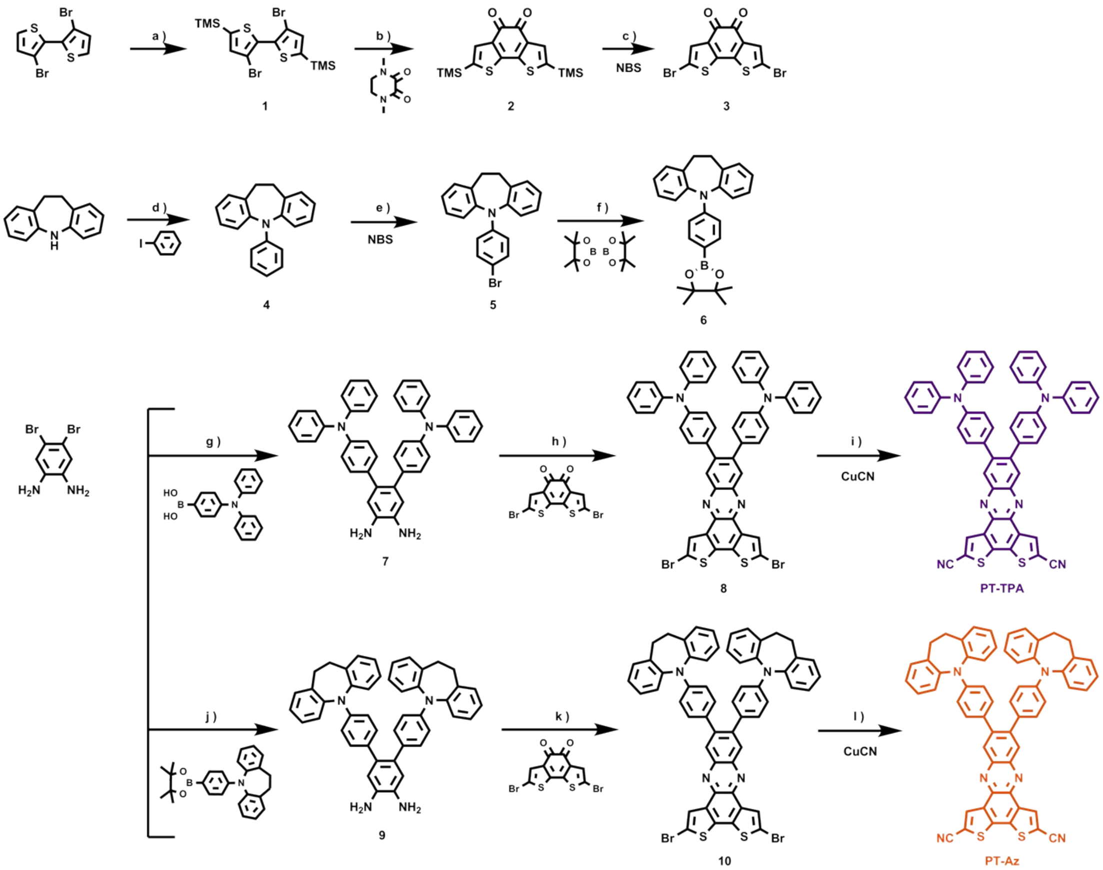
E-mail: ckwang@sdnu.edu.cn, mkfung@suda.edu.cn, jianfan@suda.edu.cn

†These authors contribute equally to this work.

General information

All chemicals and reagents were used as received without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) was performed on a BRUKER ultrafleXtreme MALDI-TOF spectrometer. UV-vis absorption spectra were recorded on a PerkinElmer Lambda 750 spectrophotometer. PL spectra and phosphorescence spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a TA DSC 2010 unit and a TA SDT 2960 instrument, respectively under nitrogen. The glass transition temperatures (Tg) were determined from the second heating scan. Cyclic voltammetry (CV) was performed on a CHI600 voltammetric analyzer at room temperature with ferrocenium–ferrocene (Fc/Fc$^+$) as the internal standard at a scan rate of 100 mV s^{-1}. The geometric and electronic data for ground state and excited states were calculated by Gaussian 16 package.[1] The rate parameters of k_r, and k_nr were calculated by Molecular Materials Property Prediction Package program (MOMAP).[2]

Determination of the emitting dipole orientation in an emitting layer: To determine the emitting dipole orientation in a molecular emitting film, angle-resolved and polarization-resolved PL measurements were performed.[3] The sample consisted of a glass substrate with the 20-nm-thick CBP film doped with emitters. The sample was attached to a fused silica half cylinder prism by index matching liquid. The excitation of the samples was performed with the 325-nm line of the continuous-wave He:Cd laser with a fixed excitation angle of 45°. The emission angle was changed by use of a rotation stage. The spectra were measured using a fiber optical spectrometer and a polarizing filter to distinguish p- and s-polarized light. The angle-dependent p-polarized emission intensity at the peak wavelength of the PL spectrum of the emitting layer was detected. The emitting dipole orientation (the horizontal dipole ratio $\theta_{//}$) was then determined by comparing the measured angle-dependent p-polarized emission intensity with those calculated assuming different horizontal dipole ratios ($\theta_{//}$). The simulation was conducted using the dipole-based electromagnetic model for layered organic emitting structures as described below.



Scheme S1. Synthetic procedure of **PT-TPA**, **PT-Az:** a) TMSCl, LDA, THF, -78 ^{o}C~0 ^{o}C, overnight; b) *n*-BuLi, THF, -78 ^{o}C~R.T., 1h; c) NBS, THF, R.T., 24h; d) S-Phos, NaOt-Bu, Pd(dba)$_2$, toluene, 120 ^{o}C, overnight; e) NBS, DMF, 0 ^{o}C~R.T., 12h; f) KOAc, Pd(dppf)Cl$_2$, 1,4-dioxane, 115 ^{o}C, 12h; g)/j) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, 1,4-dioxane/H$_2$O, 85 ^{o}C, 24h; h)/k) AcOH, 125 ^{o}C, overnight; i)/l) CuCN, NMP, 180 ^{o}C, MW, 2h.

(3,3'-dibromo-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylsilane) (1)

A mixture of 3,3'-dibromo-2,2'-bithiophene (8 mmol, 2.6 g) and 80 mL dry THF was cooled to -78 ^{o}C under nitrogen atmosphere, and added lithium diisopropylamide (2.0 M, 24 mmol, 12 mL) dropwise and stirred for 30 minutes. The mixture was warmed to -10 ^{o}C for 3 hours and cooled to -78 ^{o}C again, then added trimethylchlorosilane (24 mmol, 2.61 g) subsequently. The resulting solution was allowed to warm to room temperature slowly and stirred overnight. Water was used to quench the reaction, and the solution was concentrated under reduced pressure. Applying DCM to extract the residue, and the row material was purified by column chromatography with PE to afford the compound **1** (3.58 g, 95.6%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 (s, 2H), 0.34 (s, 18H).

2,7-bis(trimethylsilyl)benzo[2,1-b:3,4-b']dithiophene-4,5-dione (2)

Compound **1** (4.27 mmol, 2 g) was blended with 80 mL dry THF and cooled to -78 ^{o}C under nitrogen atmosphere. *n*-BuLi (6.67 mL, 10.68 mmol, 1.6 M in hexane) was added slowly. 1,4-dimethylpiperazine-2,3-dione (5.56 mmol, 790 mg) was added after the solution was stirred at -78 ^{o}C for 1.5 hours. The resulting mixture was reacted at room temperature for 1 hour. 1.5M HCl solution was added after the reaction finished, and the row mixture was extracted with DCM. After removing the solvent, PE/DCM (2/3, v/v) was used to purified the residue by silica gel. 480 mg dark red solid was obtained. Yield: 30.8%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.59 (s, 2H), 0.36 (s, 18H).

2,7-dibromobenzo[2,1-b:3,4-b']dithiophene-4,5-dione (3)

To a solution of compound **2** (1.31 mmol, 477 mg) in 30 mL dry THF, NBS (2.75 mmol, 490 mg) was added and the mixture was protected from light. After 24 hours reaction at room temperature, the solvent was removed under reduced pressure, then DCM was used for extracting. The crude product was purified by column chromatography with PE/EA (10/1, v/v) to get 453 mg dark solid. Yield: 92.0%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.46 (s, 2H).

5-phenyl-10,11-dihydro-5H-dibenzo[b,f]azepine (4)

10,11-dihydro-5H-dibenzo[b,f]azepine (5 mmol, 975 mg) and iodobenzene (6 mmol, 1.224 g) were dissolved in 30 mL toluene. S-Phos (0.5 mmol, 205 mg), NaOt-Bu (10 mmol, 960 mg) and $Pd_2(dba)_3$ (0.25 mmol, 229 mg) were added. After overnight reaction at 120 ^{o}C, the mixture was cooled to room temperature and the toluene was removed. Purification of the residue on silica gel with PE gave 1.02 g product. Yield: 75.24%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.28 – 7.14

(m, 6H), 7.08 (t, *J* = 7.9 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 8.1 Hz, 2H), 2.97 (s, 4H).

5-(4-bromophenyl)-10,11-dihydro-5H-dibenzo[b,f]azepine (5)

Compound **4** (11.5 mmol, 3.12 g) was blended with 50 mL DMF and stirred at 0 °C, with addition of NBS (17.25 mmol, 3.07 g) dissolved in 30 mL DMF. The solution was slowly warmed to room temperature. After 12 hours reaction the resulting mixture was poured into water and extracted with diethyl ether. The solvent was removed by rotary evaporation. The product (3.175 g) was obtained by column chromatography with PE. Yield: 78.9%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 7.41 – 7.32 (m, 4H), 7.29 (t, J = 5.8 Hz, 4H), 7.24 (d, J = 9.0 Hz, 2H), 6.36 (d, J = 8.9 Hz, 2H), 2.91 (s, 4H).

5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-10,11-dihydro-5H-dibenzo[b,f]azepine (6)

A mixture of compound **5** (3.5 g, 10 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (3.81 g, 15 mmol), Pd(dppf)Cl$_2$ (366 mg, 0.5 mmol), KOAc (1.96 g, 20 mmol), 1,4-dioxane (100 mL) was heated at 115 °C for 12 hours under nitrogen atmosphere. After removing the solvent, the remaining material was extracted with DCM and water. PE/DCM (2/1, v/v) was used as eluent on silica gel to acquire 1.28 g white solid. Yield: 32.24%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 6.0 Hz, 6H), 6.57 (d, *J* = 8.5 Hz, 2H), 2.97 (s, 4H), 1.29 (s, 12H).

N4,N4,N4'',N4''-tetraphenyl-[1,1':2',1''-terphenyl]-4,4',4'',5'-tetraamine (7)

4-(diphenylamino)phenylboronic acid (7.5 mmol, 2.17 g), 4,5-dibromobenzene-1,2-diamine (3 mmol, 798 mg), K$_2$CO$_3$ (12 mmol, 1.66g), Pd(PPh$_3$)$_4$ (0.15 mmol, 174 mg), 1,4-dioxane (100 mL) and H$_2$O (10 mL) was mixed and deaerated at 85 °C for 24 hours. Then the solution was poured into water and extracted with DCM. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Purification by column chromatography with PE/EA (2/1, v/v) to afford the compound **7** (1.29 g, 72%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 7.23 (m, *J* = 7.7 Hz, 8H), 6.98 (d, *J* = 13.6, 5.2 Hz, 8H), 6.93 (t, *J* = 9.6 Hz, 8H), 6.83 (d, *J* = 8.2 Hz, 4H), 6.59 (s, 2H).

4,4'-(2,5-dibromodithieno[3,2-a:2',3'-c]phenazine-9,10-diyl)bis(N,N-diphenylaniline) (8)

Compound **7** (1.1 mmol, 650 mg) and compound **3** (1 mmol, 378 mg) was suspended in AcOH (30 mL) and heated at 60 °C overnight under nitrogen. The mixture was cooled down to room temperature. Filtering the product with suction and washing with water.

The crude product was re-crystallized in DCM to afford compound **8** (740 mg, 71.2%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.42 (s, 2H), 8.31 (s, 2H), 7.28 (d, *J* = 13.2 Hz, 8H), 7.20 (d, *J* = 7.9 Hz, 4H), 7.14 (d, *J* = 7.5 Hz, 8H), 7.05 (m, *J* = 7.6 Hz, 8H).

4,4''-bis(10,11-dihydro-5H-dibenzo[b,f]azepin-5-yl)-[1,1':2',1''-terphenyl]-4',5'-diamine (9)

The synthesized procedure of compound **9** was similar to the compound **7**. Yield: 70.36%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 6.4 Hz, 4H), 7.22 (m, 12H), 6.79 (d, *J* = 8.2 Hz, 4H), 6.70 (s, 2H), 6.36 (d, *J* = 8.7 Hz, 4H), 2.94 (s, 8H).

2,5-dibromo-9,10-bis(4-(10,11-dihydro-5H-dibenzo[b,f]azepin-5-yl)phenyl)dithieno[3,2-a:2',3'-c]phenazine (10)

The synthetic method of compound **10** was in common with compound **8**. Yield: 85.18%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (s, 2H), 8.19 (s, 2H), 7.45 (d, *J* = 6.5 Hz, 4H), 7.27-7.33 (m, 12H), 7.02 (d, *J* = 8.8 Hz, 4H), 6.48 (d, *J* = 8.5 Hz, 4H), 2.99 (s, 8H). MALDI-TOF-MS: m/z calcd for $C_{56}H_{36}Br_2N_4S_2$: 988.037, found: 989.244.

9,10-bis(4-(diphenylamino)phenyl)dithieno[3,2-a:2',3'-c]phenazine-2,5-dicarbonitrile (PT-TPA)

Compound **8** (0.79 mmol, 740 mg) and CuCN (1.98 mmol, 176 mg) was dissolved in 1-methyl-2-pyrrolidinone (20 mL). This reaction was carried out at 180 ^{o}C by microwave irradiation for 2 hours. Removing the solvent by decompress distillation. The crude product was washed with aqueous solution of ferric chloride hexahydrate and then purified by column chromatography with PE/DCM (4/5,v/v) as eluent to afford the compound **PT-TPA** (438 mg, 42.12%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.99 (s, 2H), 8.36 (s, 2H), 7.30 (d, *J* = 7.7 Hz, 8H), 7.21 (d, *J* = 8.2 Hz, 4H), 7.15 (d, *J* = 7.9 Hz, 8H), 7.06 (m, *J* = 12.0, 7.8 Hz, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.58,147.43, 145.28, 141.80, 138.82, 136.35, 135.32, 133.40, 130.78, 129.42, 124.82, 123.37, 122.39, 113.44, 110.12. MALDI-TOF-MS: m/z calcd for $C_{54}H_{32}N_6S_2$: 828.213, found: 828.195.

9,10-bis(4-(10,11-dihydro-5H-dibenzo[b,f]azepin-5-yl)phenyl)dithieno[3,2-a:2',3'-c]phenazine-2,5-dicarbonitrile (PT-Az)

Compound **PT-Az** was synthesized as the same procedure for **PT-TPA**. Yield: 37.38%. ^{1}H NMR (400 MHz, 1,2-Dichlorobenzene-*d*) δ 8.68 (s, 2H), 8.28 (s, 2H), 7.31 - 7.20(m, 20H), 6.53 (d, *J* = 5.9 Hz, 4H), 2.71 (s, 8H). ^{13}C NMR measurement was not available because of low solubility. MALDI-TOF-MS: m/z calcd for $C_{58}H_{36}N_6S_2$: 880.244, found: 880.228.

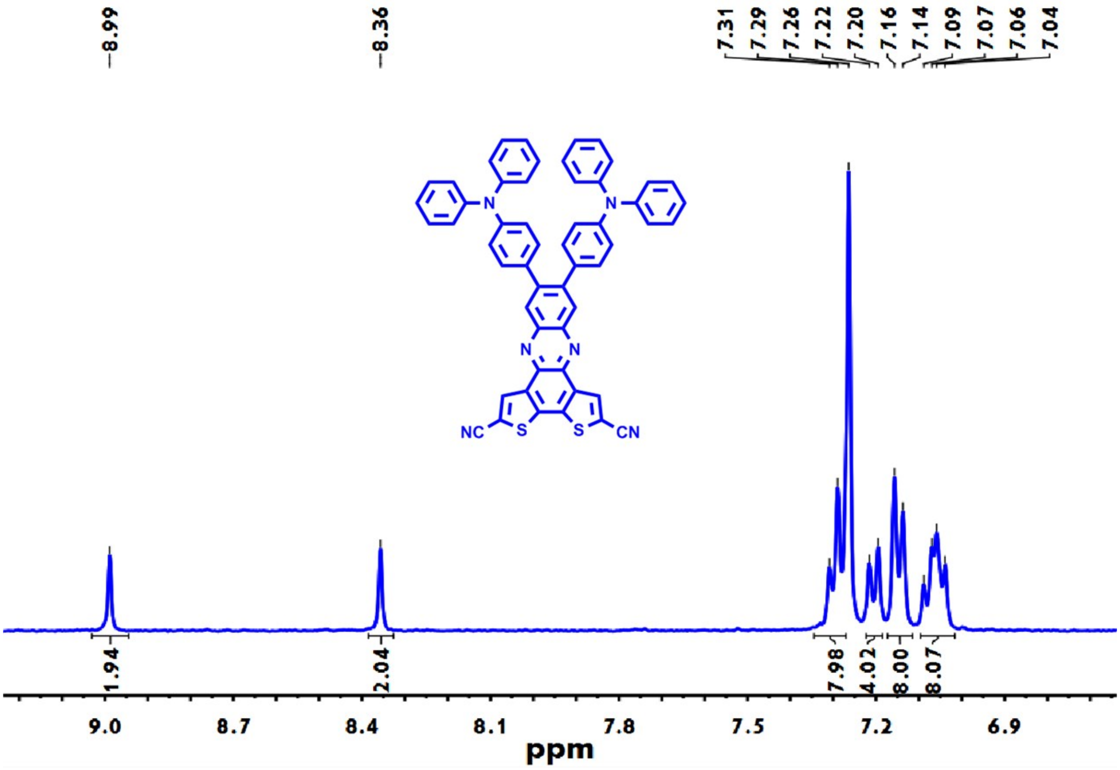


Figure S1 ^{1}H NMR spectrum of PT-TPA in chloroform-*d*.

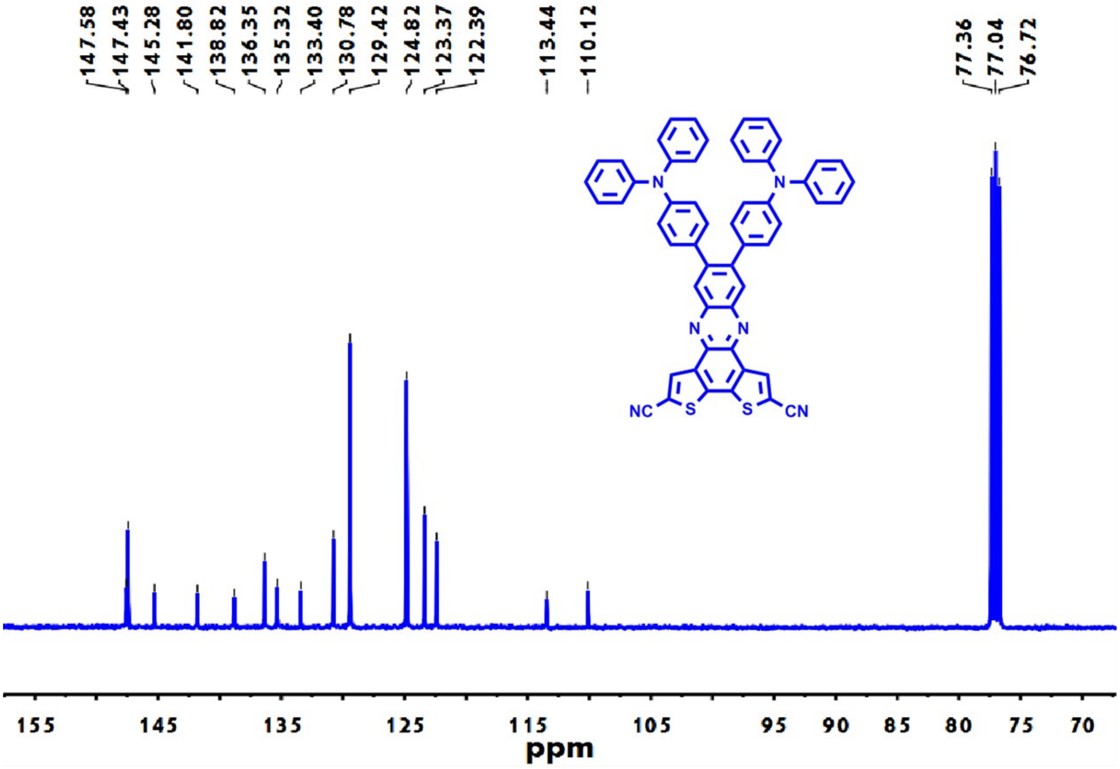


Figure S2 ^{13}C NMR spectrum of PT-TPA in chloroform-*d*.

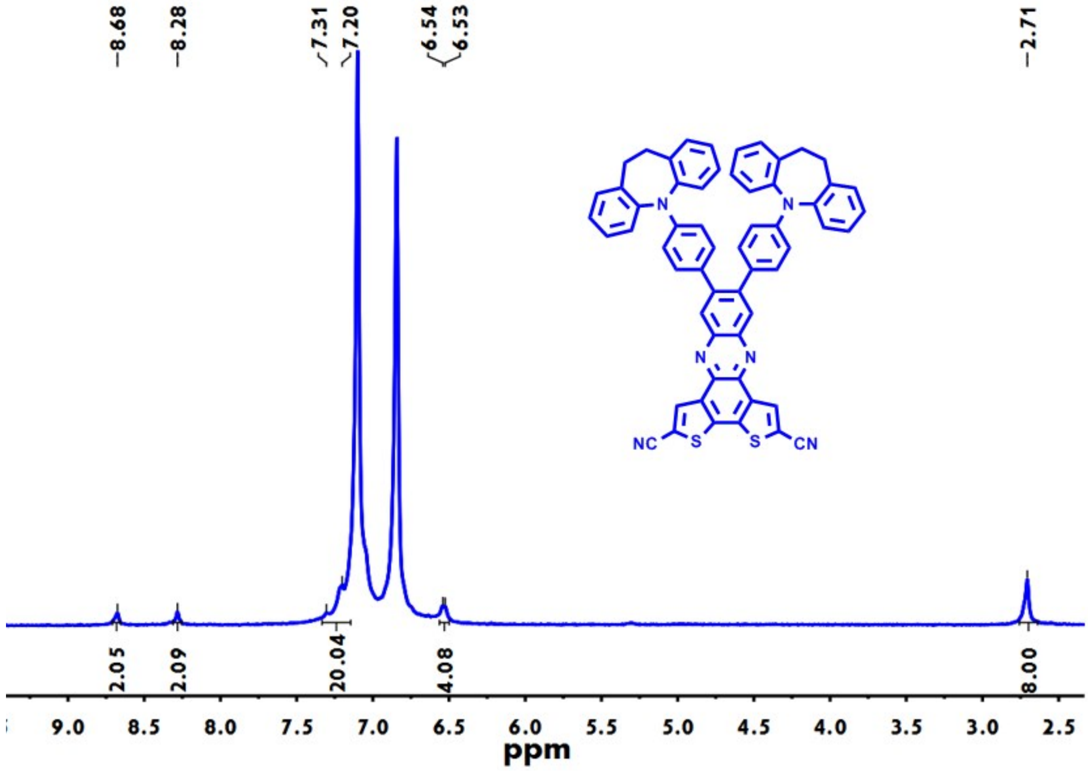


Figure S3 ^{1}H NMR spectrum of PT-Az in 1,2-dichlorobenzene-D4.

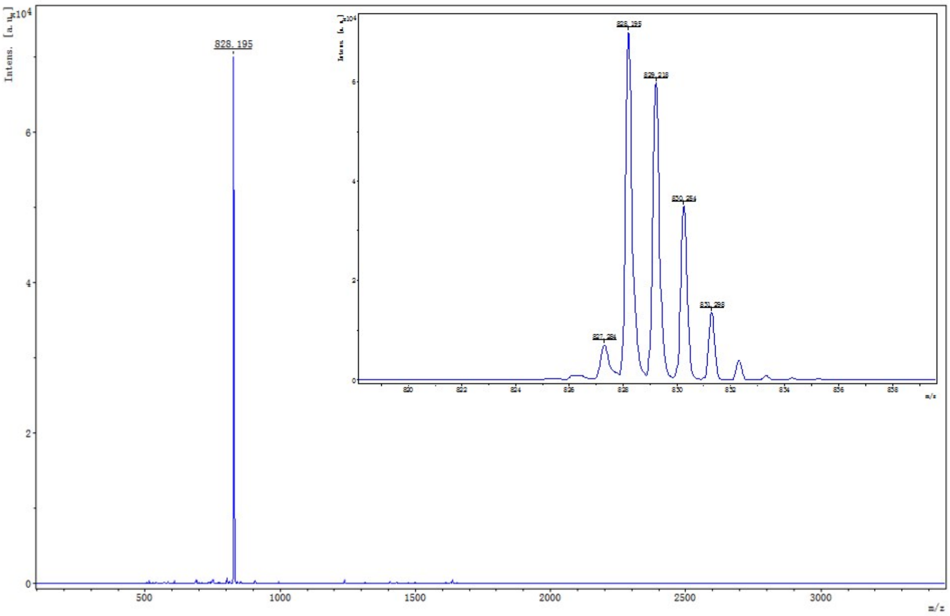


Figure S4 MALDI-TOF mass spectrum of PT-TPA.

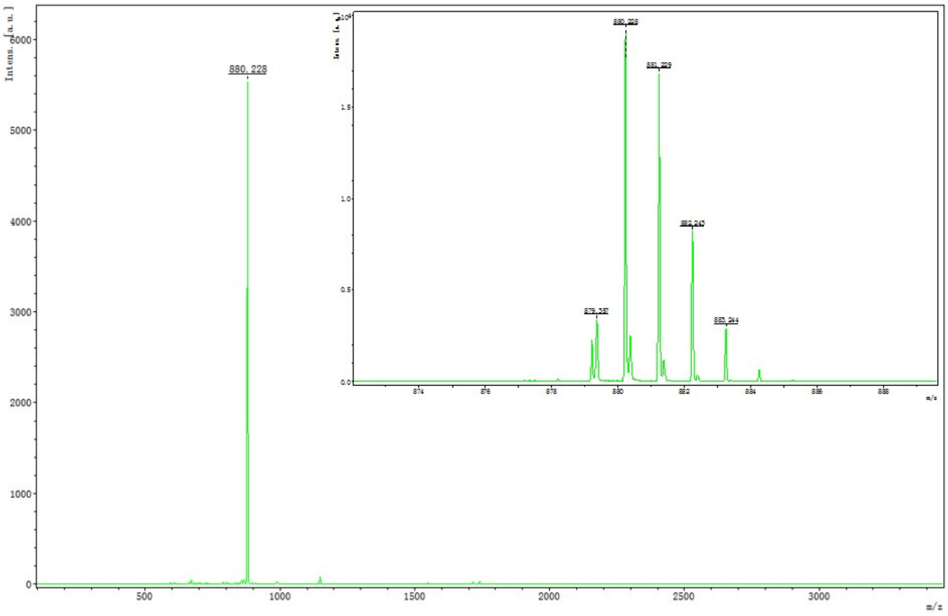


Figure S5 MALDI-TOF mass spectrum of PT-Az.

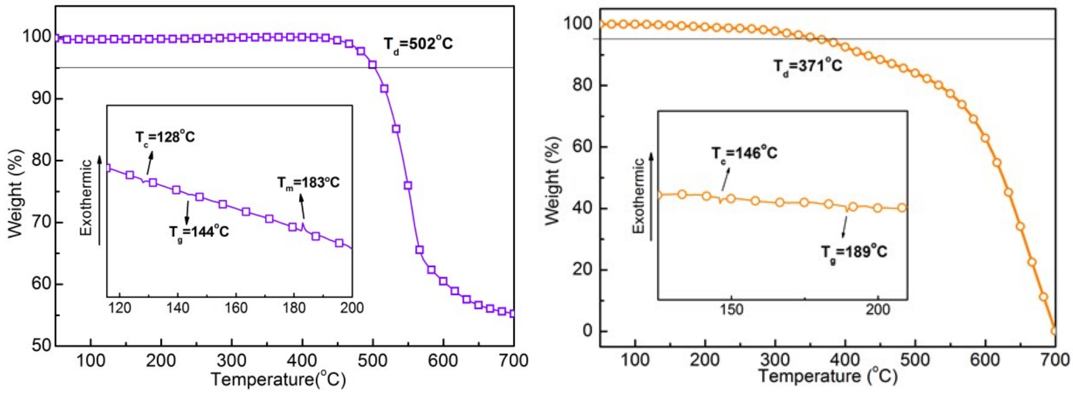


Figure S6 TGA and DSC (inset) curves of PT-TPA and PT-Az at a heating rate of 10 ^{o}C/min under nitrogen atmosphere.

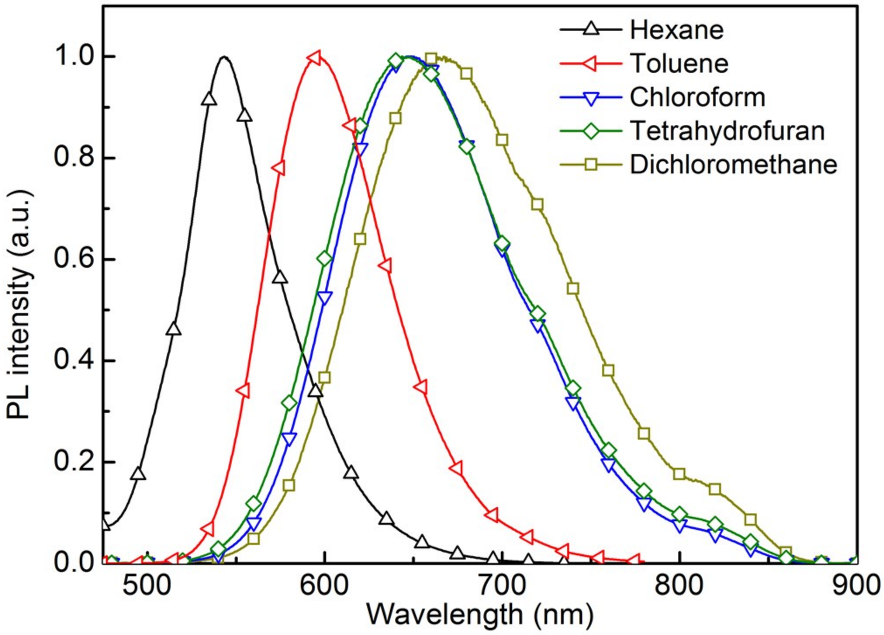


Figure S7 Normalized PL spectra of PT-TPA in various solutions (1.0×10^{-5} M) with different polarities.

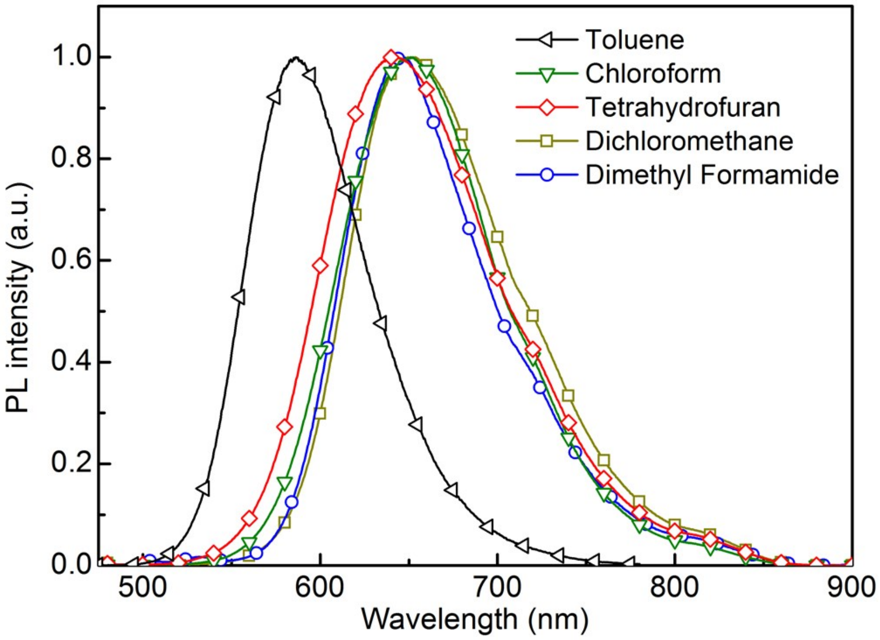


Figure S8 Normalized PL spectra of PT-Az in various solutions (1.0×10^{-5} M) with different polarities.

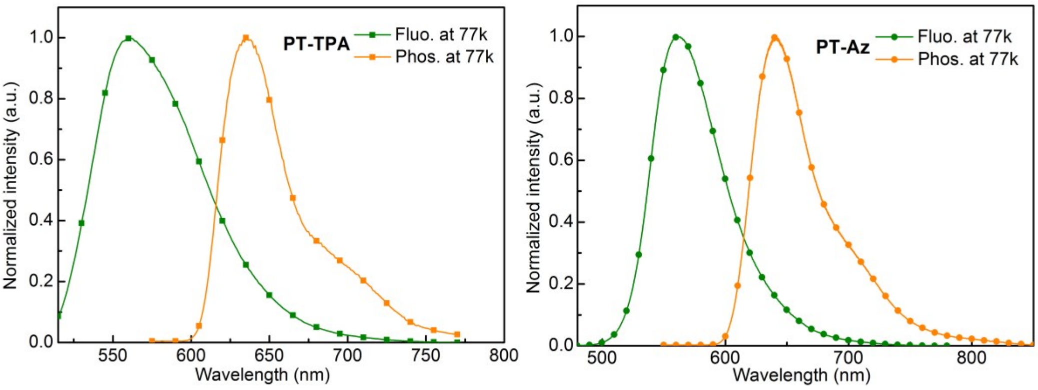


Figure S9 Normalized fluorescence and phosphorescence spectra of PT-TPA and PT-Az in toluene at 77 K.

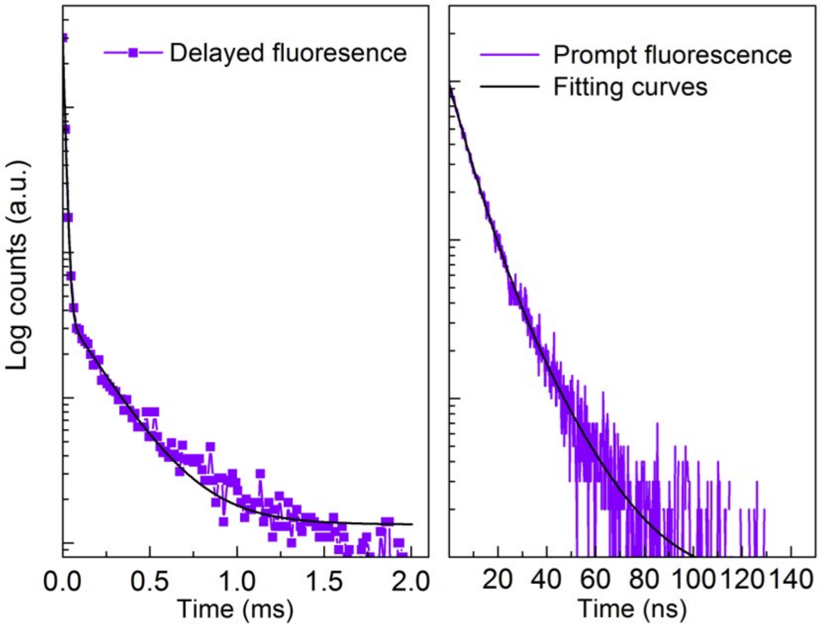


Figure S10 Time decay curves and fitting results of PT-TPA in 15 wt% doped CBP film.

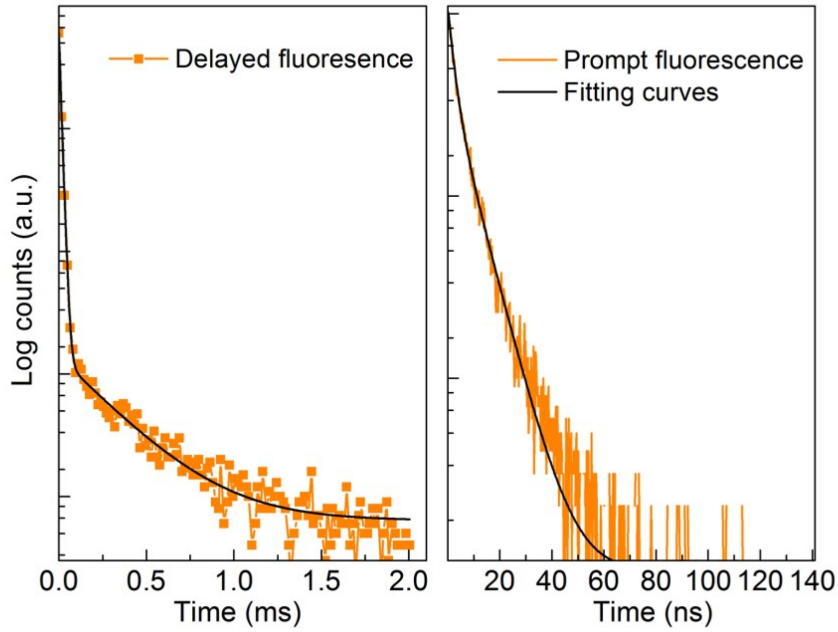


Figure S11 Time decay curves and fitting results of PT-Az in 10 wt% doped CBP film.

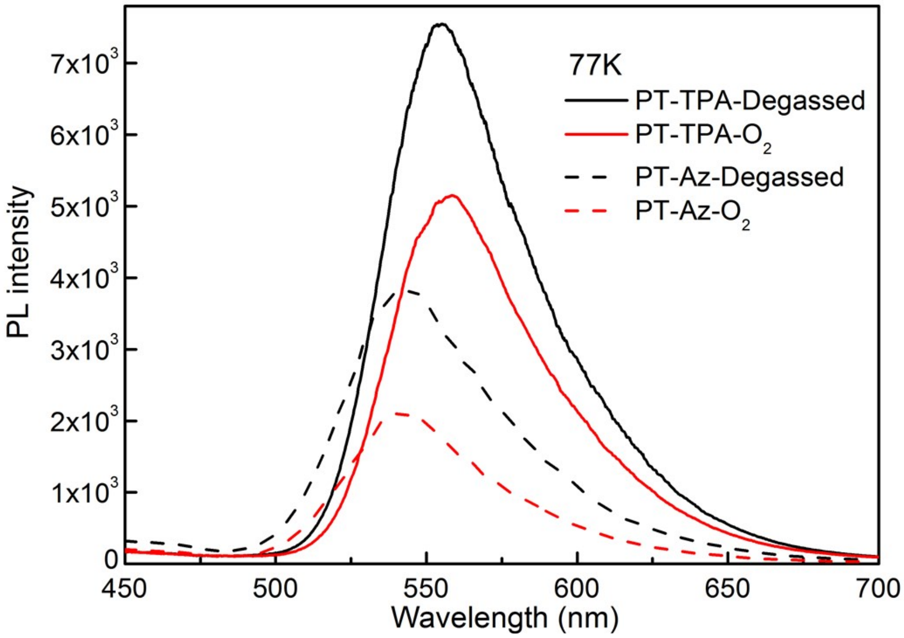


Figure S12 PL spectra of the toluene solutions (1.0 ×10^{-5} M) of PT-TPA and PT-Az at 77K.

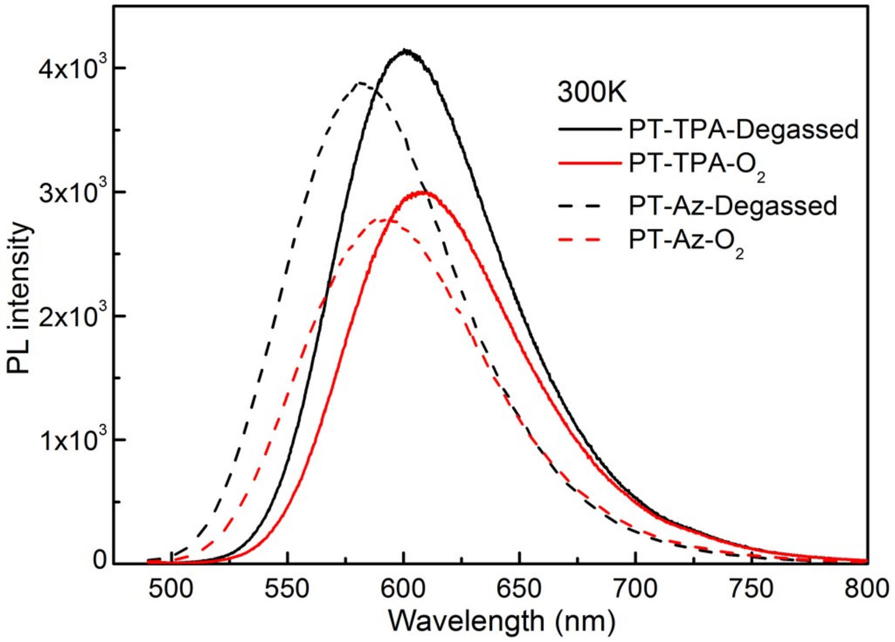


Figure S13 PL spectra of the toluene solutions (1.0 ×10^{-5} M) of PT-TPA and PT-Az at 300K.

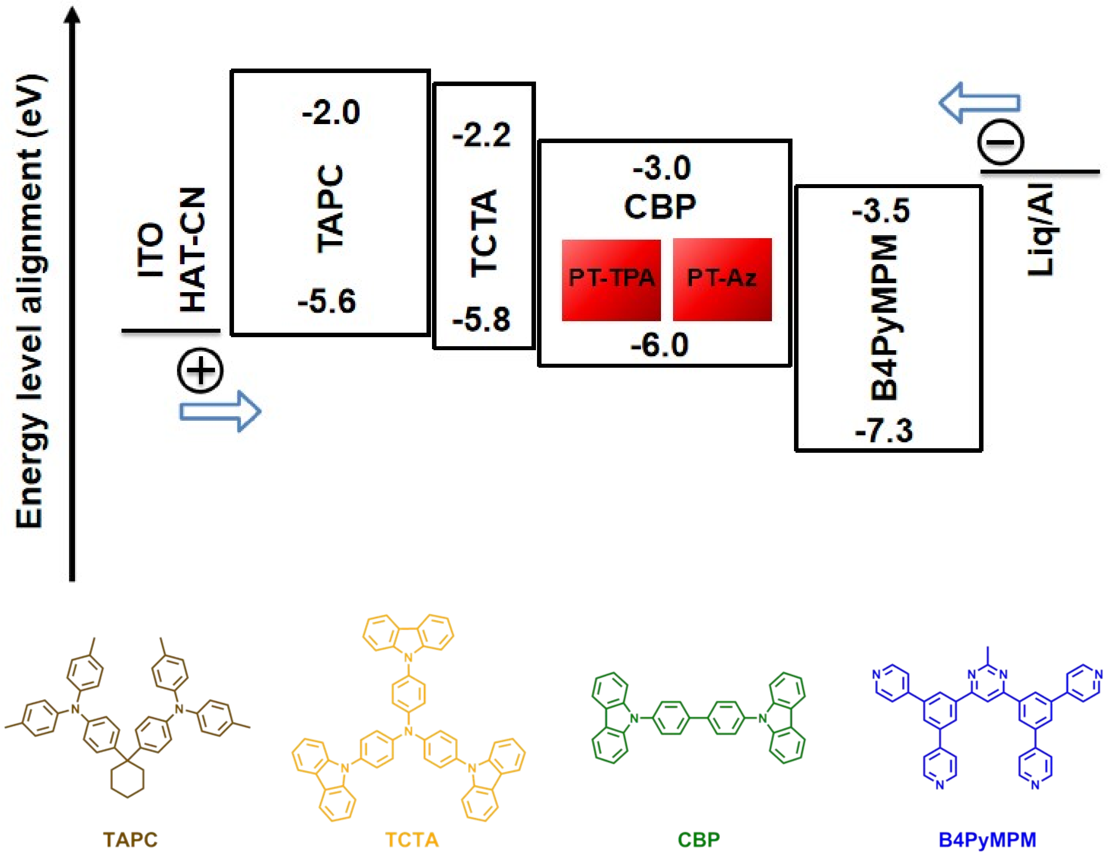


Figure S14 Energy level diagram and molecular structures of materials used in PT-TPA/PT-Az based device.

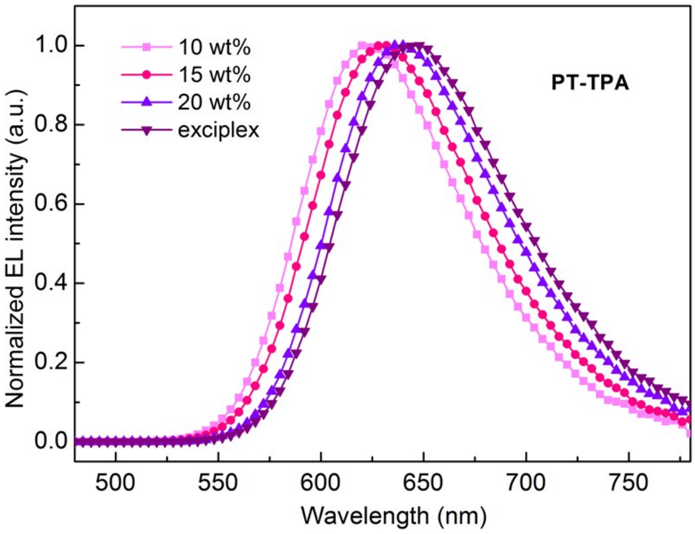


Figure S15 Electroluminescence (EL) spectra curve of PT-TPA at 0.1 mA cm^{-2}.

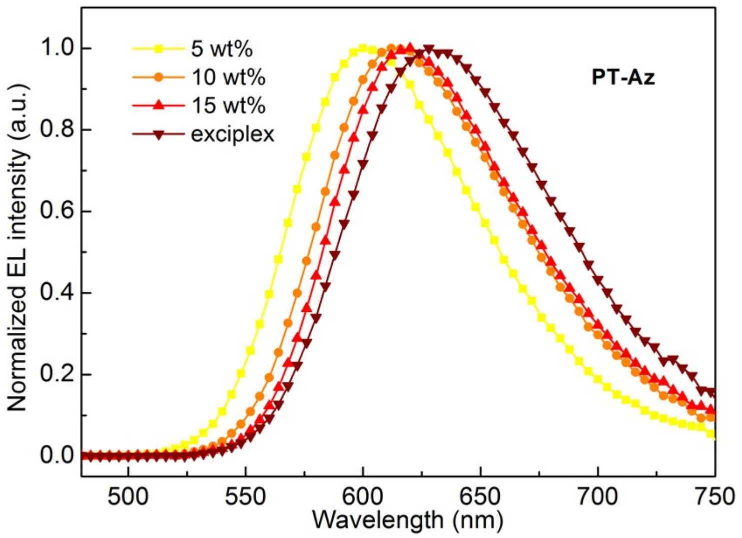


Figure S16 Electroluminescence (EL) spectra curve of PT-Az at 0.1 mA cm^{-2}.

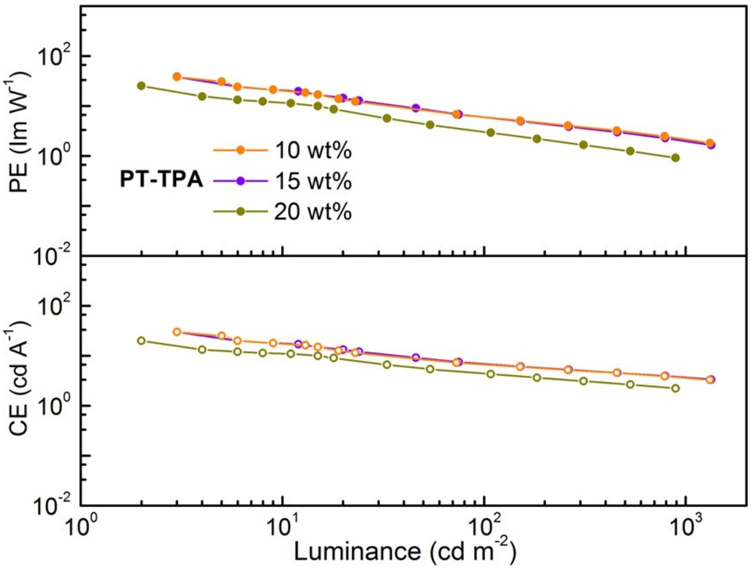


Figure S17 Power/Current Efficiency *vs.* Luminance relationships of PT-TPA-based device.

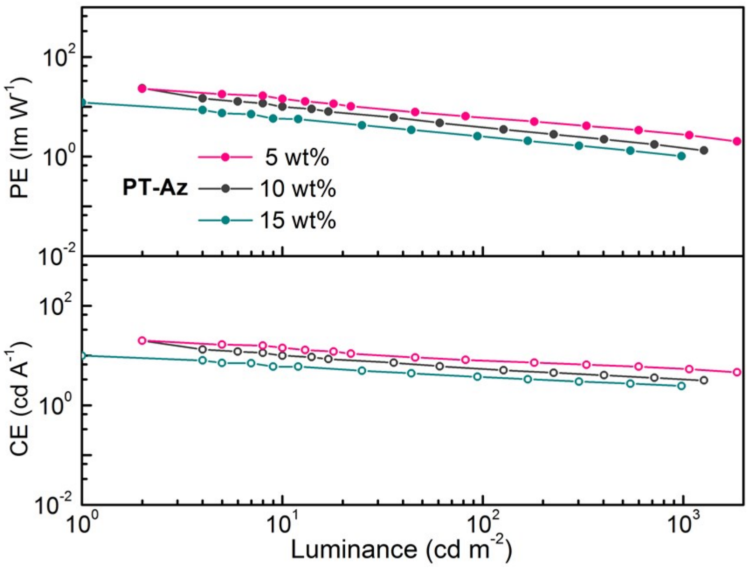


Figure S18 Power/Current Efficiency *vs.* Luminance relationships of PT-Az-based device.

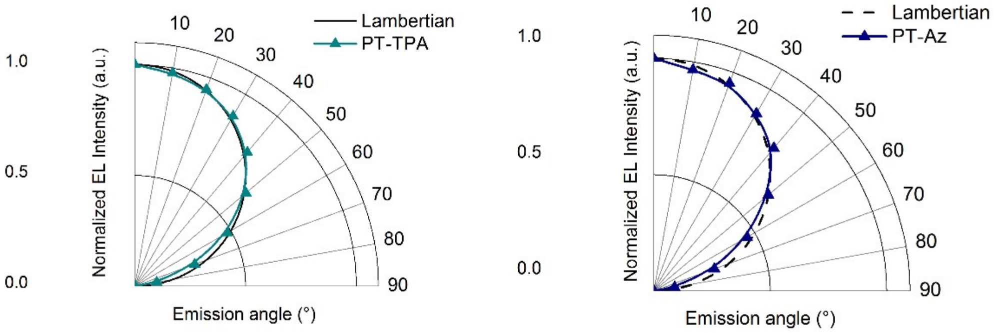


Figure S19 Angle-dependent EL emission pattern of the devices based on PT-TPA (left) and PT-Az (right). The black line is the Lambertian distribution.

Table S1 Properties of devices based on PT-TPA with different doping concentration.

	V^{b} [V]	CE ^{c} [cd/A]	PE ^{c} [lm/W]	EQE ^{c} [%]	CIE ^{d} (x,y)	λ_{EL} ^{e} [nm]	Φ_{PL} ^{f} (%)
10 wt%	2.55	30	38.1	24.3	0.633,0.364	620	86.7
15 wt%	2.55	30	38.5	29.7	0.645,0.352	632	99.7
20 wt%	2.77	20	25.4	25.2	0.659,0.337	640	93.8
15 wt% - exciplex	2.71	20	24.9	28.8	0.664,0.332	648	-
100 wt%	3.22	1	1.18	5.3	0.695, 0.301	692	50.0

Table S2 Properties of devices based on PT-Az with different doping concentration.

	V^{b} [V]	CE ^{c} [cd/A]	PE ^{c} [lm/W]	EQE ^{c} [%]	CIE ^{d} (x,y)	λ_{EL} ^{e} [nm]	Φ_{PL} ^{f} (%)
5 wt%	2.90	20	23.0	10.6	0.585,0.409	600	54.7
10 wt%	2.90	20	23.7	14.1	0.613,0.382	612	68.9
15 wt%	3.00	10	12.2	8.0	0.625,0.369	620	52.7
10 wt% - exciplex	3.41	10	11.3	9.7	0.634,0.358	628	-
100 wt%	6.71	0.0125	0.006	0.04	0.687,0.313	672	2.1

[a] Measured at room temperature in doped film.

[b] Voltage at 5 cd m^{-2}.

[c] Maximum efficiencies.

[d] Commission Internationale de L'Eclairage coordinates.

[e] All the λ_{EL} were measured at 0.1 mA cm^{-2}, except for PT-Az in non-doped film, which was measured at 10 mA cm^{-2} because the luminance at low current density is essentially zero.

[f] Measured at room temperature under nitrogen condition in doped film.

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