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# Electronic Supplementary Information

## A novel spiro-annulated benzimidazole host for highly efficient blue phosphorescent organic light-emitting devices

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## General information

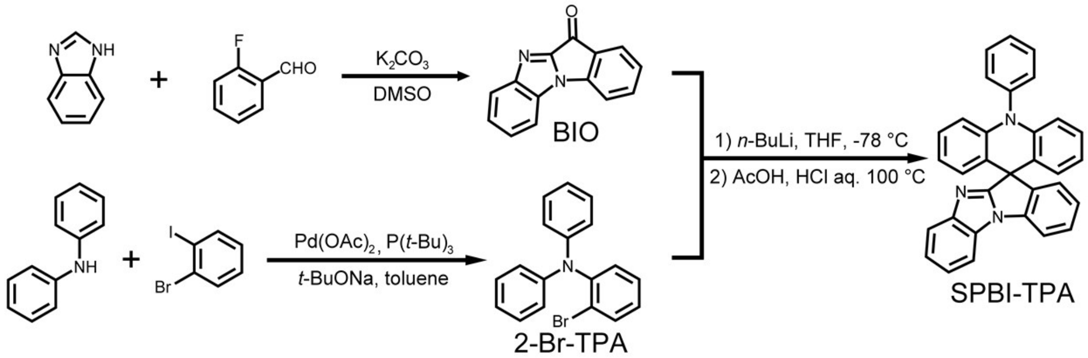
$^1H$ and $^{13}C$ NMR spectra were obtained on a Varian Unity Inova 400 spectrometer. Mass analyses were performed on an Applied Biosystems API-2000 liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS) Triple-Q mass spectrometer with electrospray ionization source. Decomposition and glass transition temperatures were measured respectively on a TA Instrument TGAQ50 and a Perkin-Elmer DSC 7 differential scanning calorimetric at a heating rate of 10 °C minute$^{-1}$ under nitrogen atmosphere. The DCS scanning range is from 50 to 250 °C. UV-vis absorption and photoluminescence spectra were measured on a Perkin-Elmer Lambda 950 UV/vis spectrometer and a Perkin-Elmer LS50B spectrophotometer, respectively. Cyclic voltammetry was scanned on a CHI600 voltammetric analyzer equipped with a three-electrode system (platinum disk: working electrode, platinum wire: auxiliary electrode, Ag/AgCl: reference electrode). $Fc/Fc^+$ with an absolute highest occupied molecular orbital level of -4.80 eV was used as the internal standard. Nitrogen-saturated 0.1 mol L$^{-1}$ tetrabutylammonium hexafluorophosphate dichloromethane solution was used as the supporting electrolyte. All the theoretical calculations were performed using the Gaussian 09 program package. The molecular geometries in the ground state were optimized based on density functional theory (DFT) on the B3LYP/6-31G* level. Mulliken population analysis was carried out to characterize the spin density distributions of unpaired electrons in the triplet states. According to the geometry optimization in the $S_0$ states, the properties of the $S_1$ states are analyzed by natural transition orbitals (NTOs) using time-dependent DFT calculations on the B3LYP/6-31G* level.

## Device fabrication and measurement

Devices were fabricated on indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω/□. Before use, the ITO substrates were swabbed with Decon-90 solution, and treated by 10-min ultrasonic baths in deionized water, and then rinsed with isopropanol. The solvent on the surface was removed with dry $N_2$ flow, and then the substrates were further dried in an oven at 120 °C for at least 2 h. After 15 min UV-ozone treatment, the substrates were loaded into a deposition chamber with vacuum better than $10^{-6}$ Torr. Current density-voltage characteristics and electroluminescence spectrum were recorded with a Keithley 237 power source and a Spectrascan PR650 photometer, respectively. Device measurement was performed under ambient conditions without encapsulation.

## Synthesis detail

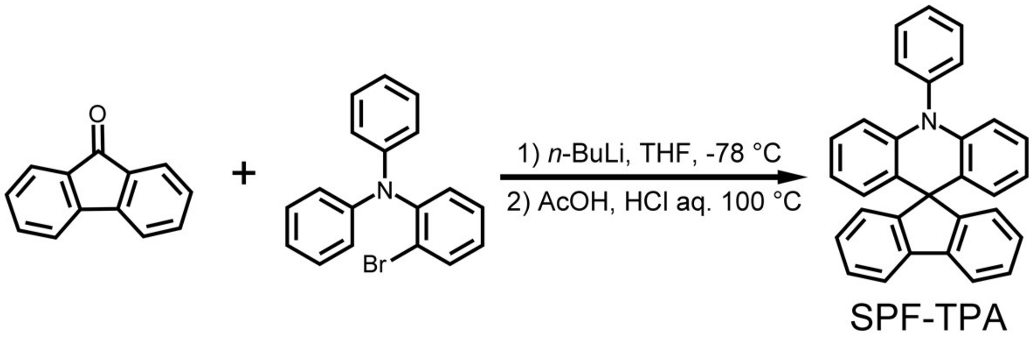
2-bromo-*N*,*N*-diphenylaniline (2-Br-TPA),[1] 2-(4-bromophenyl)-1- phenyl-1*H*-benzo[*d*]imidazole[2] and BI-TPI[3] were prepared according to the references.



**Scheme S1** Synthesis of SPBI-TPA.

11*H*-benzo[4,5]imidazo[1,2-*a*]indol-11-one (BIO): The synthesis of BIO was referred from literature.[4] 1*H*-benzo[*d*]imidazole (3.54 g, 30 mmol), 2-fluorobenzaldehyde (1.86 g, 15 mmol) and $K_2CO_3$ (2.28 g, 16.5 mmol) were added in a three-necked flask with 35 mL anhydrous DMSO. The mixture was stirred under air atmosphere at 120 °C. After 8 h reaction, 1.86 g (15 mmol) 2-fluorobenzaldehyde, 2.28 g (16.5 mmol) $K_2CO_3$ and 35 mL DMSO were added in sequence to the flask, and the mixture was continued to react for further 8 h. After cooling down to room temperature, the raw product was poured to 400 mL ice water, and the pH of the mixture was tuned to ~7 using 1 M HCl aq. Ethyl acetate (3 × 100 mL) was used to extract the product. The organic phase was separated and the solvent was removed by vacuum. Finally, the product was purified with column chromatography (ethyl acetate: $CH_2Cl_2$ = 1:10 as eluent) to give a 2.1 g organic solid (yield: 31.8%). $^1$H NMR (400 MHz, DMSO-d6) $\delta$ [ppm]: 8.11 (d, *J* = 8.2 Hz, 1H), 7.90 (dd, *J* = 4.8, 4.2 Hz, 2H), 7.78 (td, *J* = 7.7, 1.2 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.62 – 7.55 (m, 1H), 7.44 – 7.37 (m, 1H), 7.34 (td, *J* = 7.6, 0.7 Hz, 1H). MS (ESI): *m/z* = 221.1 $[M + H]^+$.

10-phenyl-10*H*-spiro[acridine-9,11'-benzo[4,5]imidazo[1,2-*a*]indole] (SPBI-TPA): 4.21 g 2-Br-TPA (13 mmol) was dissolved in 80 mL dry THF in a 500 mL three-necked flask under $N_2$, and then the mixture was cooled to -78 °C under stirring. 5.42 mL *n*-butyl lithium (13 mmol) was added dropwise using a syringe. The mixture was allowed to stir for 1 h at the same temperature, followed by adding 200 mL BIO THF solution over 30 min via dropping funnel. The reaction was gradually warmed up to room temperature for further 8 h. 10 mL water was added to quench the reaction and the solvent was removed under reduced pressure. The resulting raw product was dissolved in AcOH (100 mL) and hydrochloric acid (10 mL), and the mixture was stirred at 100 °C overnight. After cooling down, the solvent was evaporated via a rotary evaporator. The product was further purified by column chromatography using petroleum ether/$CH_2Cl_2$ (1/1, v/v) as eluent to give a white powder (2.90 g, 62.1%). $^1$H NMR (400 MHz, DMSO-d6) $\delta$ [ppm]: 8.27 (d, $J$ = 8.0 Hz, 1H), 8.10 (d, $J$ = 7.8 Hz, 1H), 7.81 (dd, $J$ = 10.6, 4.8 Hz, 2H), 7.69 (dt, $J$ = 13.8, 7.7 Hz, 2H), 7.64 – 7.59 (m, 2H), 7.54 (td, $J$ = 7.7, 1.1 Hz, 1H), 7.46 (dd, $J$ = 12.4, 4.3 Hz, 2H), 7.41 – 7.33 (m, 1H), 7.26 (td, $J$ = 7.6, 0.8 Hz, 1H), 7.05 (ddd, $J$ = 8.6, 7.3, 1.5 Hz, 2H), 6.71 – 6.63 (m, 2H), 6.40 (dd, $J$ = 7.8, 1.4 Hz, 2H), 6.33 (dd, $J$ = 8.4, 0.8 Hz, 2H). $^{13}$C NMR (151 MHz, DMSO-d6) $\delta$ [ppm]: 166.04, 147.64, 145.94, 140.42, 139.97, 135.33, 131.42, 130.97, 129.17, 128.99, 128.94, 128.30, 127.41, 126.01, 125.63, 122.86, 121.27, 120.86, 120.25, 114.72, 111.84, 111.64, 49.96. MS (ESI): $m/z$ = 448.3 $[M + H]^+$.



**Scheme S2** Synthesis of SPF-TPA.

10-phenyl-10*H*-spiro[acridine-9,9'-fluorene] (SPF-TPA): 2-Br-TPA (1.62 g, 5 mmol) was dissolved in 80 mL dry THF in a 250 mL three-necked flask under $N_2$ and cooled to -78 °C under stirring and then 2.3 mL *n*-butyl lithium (2.4 M) was added dropwise via a syringe. After 1 h stirring, fluorenone (1.08 g, 6 mmol) dissolved in 80 mL dry THF was added dropwise over 30 min. The mixture was stirred for 1 h at -78 °C, and then was gradually warmed up to room temperature overnight. 10 mL water was added to quench the reaction and the solvent was removed under reduced pressure. The organic solid was separated, dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure. The resulting raw product was dissolved in AcOH (50 mL) and hydrochloric acid (5 mL), and the mixture was stirred at 100 °C overnight. After cooling down, 100 mL water was added to the mixture and the product was extracted using $CH_2Cl_2$ (3 × 50 mL). The raw product was obtained under vacuum and was further purified by column chromatography using petroleum ether/$CH_2Cl_2$ (10/1, v/v) as eluent to give a white powder (1.84 g, 90.4%). $^1H$ NMR (400 MHz, DMSO-d6) $\delta$ [ppm]: 7.94 (d, $J$ = 7.6 Hz, 2H), 7.76 (t, $J$ = 7.8 Hz, 2H), 7.63 (t, $J$ = 7.5 Hz, 1H), 7.56 (d, $J$ = 7.1 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.35 (d, $J$ = 7.5 Hz, 2H), 7.27 (td, $J$ = 7.5, 0.9 Hz, 2H), 6.92 (ddd, $J$ = 9.9, 5.9, 2.3 Hz, 2H), 6.57 – 6.52 (m, 2H), 6.25 – 6.22 (m, 2H), 6.20 (dd, $J$ = 7.8, 1.4 Hz, 2H). $^{13}C$ NMR (151 MHz, DMSO-d6) $\delta$ [ppm]: 156.41, 141.27, 140.73, 139.09, 131.83, 131.27, 129.22, 128.99, 128.26, 127.84, 127.47, 125.85, 124.75, 120.84, 120.78, 114.83, 56.67. MS (ESI): $m/z$ = 408.3 $[M + H]^+$.

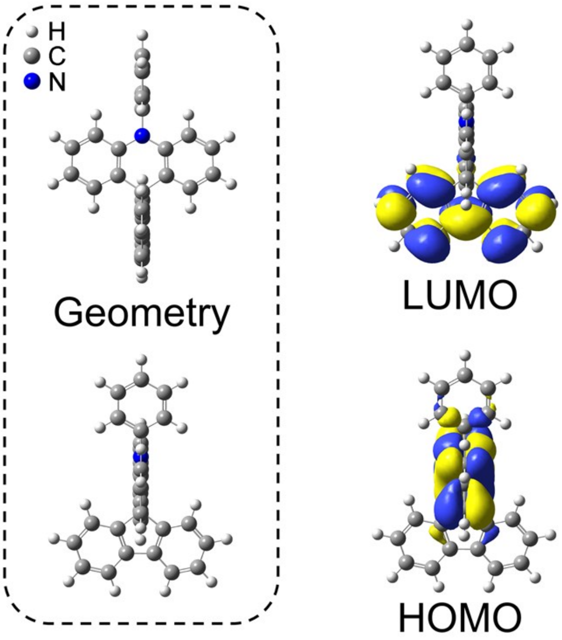


**Fig. S1** Calculated molecular geometry and frontier molecular orbital distribution of SPF-TPA.

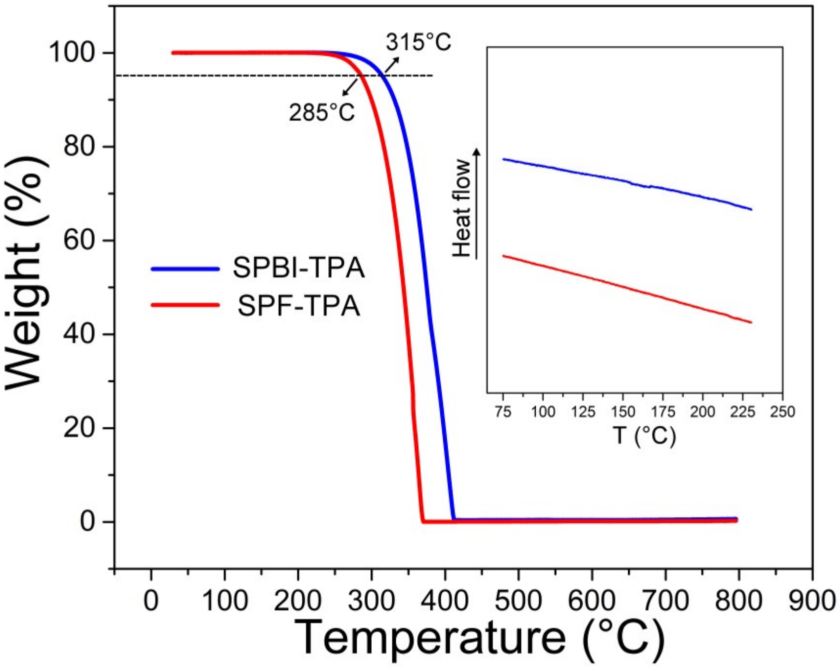


**Fig. S2** TGA and DSC (inset) analyses of SPBI-TPA and SPF-TPA.

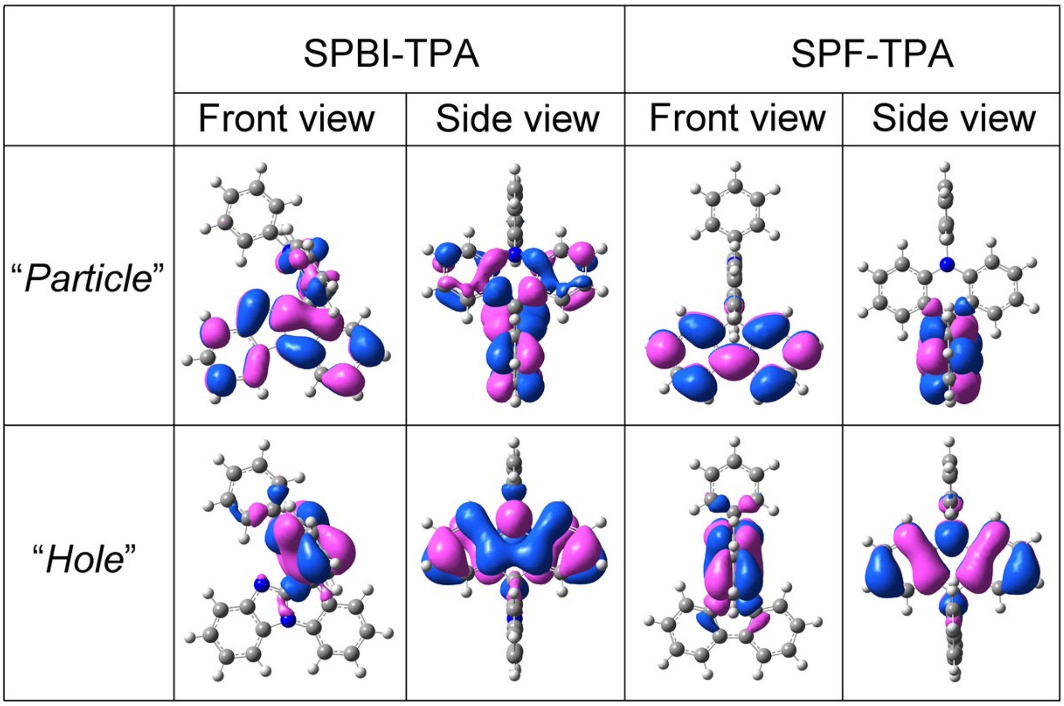


**Fig. S3** $S_0 \rightarrow S_1$ natural transition orbital (NTO) analyses of SPBI-TPA and SPF-TPA.

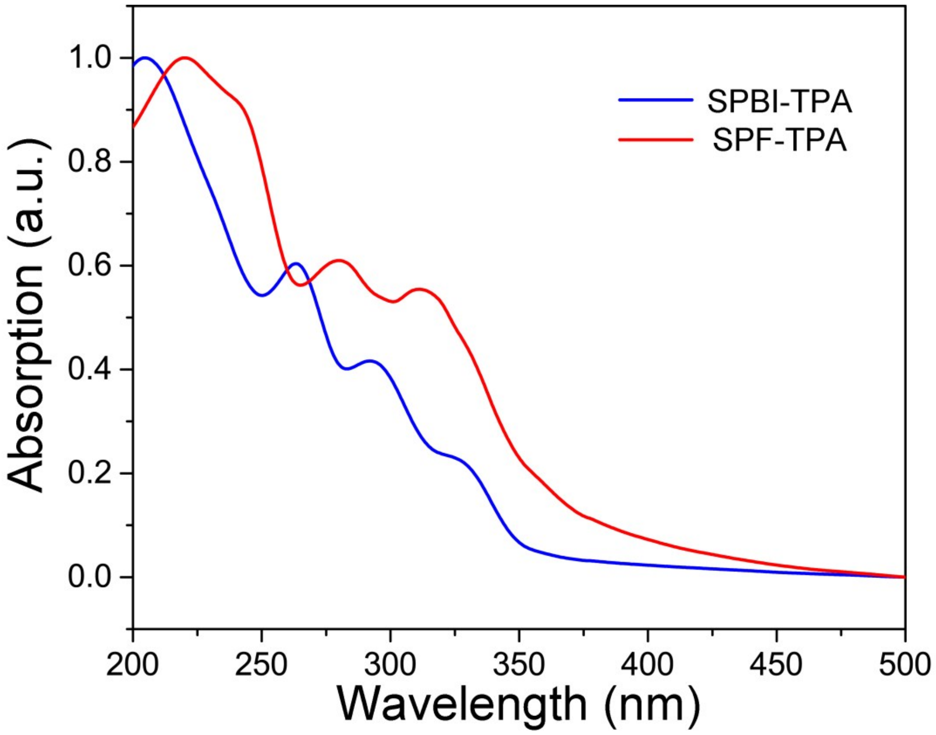


**Fig. S4** Absorption spectra of the thin films prepared on quartz by thermal evaporation.

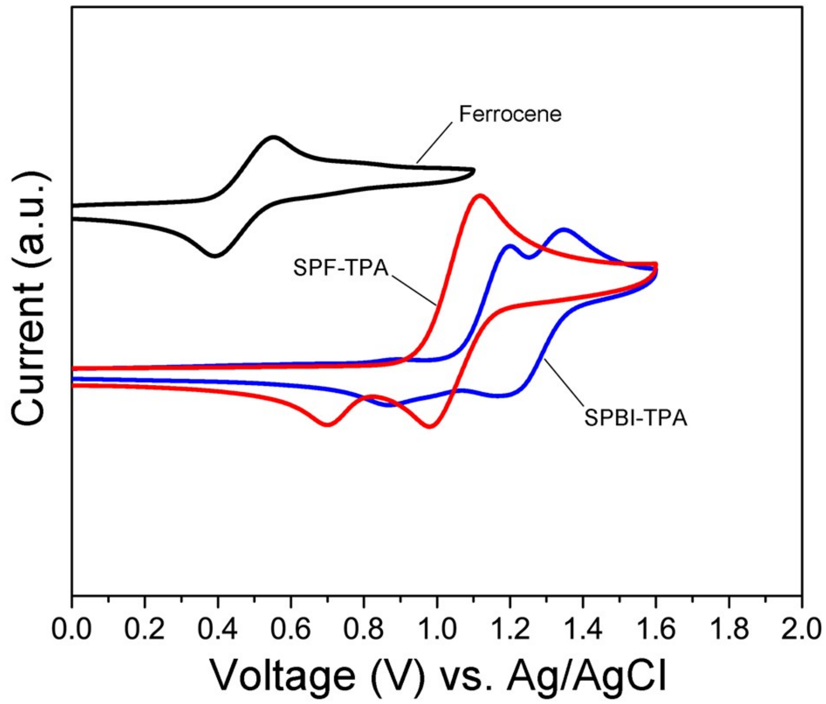


**Fig. S5** Cyclic voltammograms for oxidation of ferrocene (reference), SPBI-TPA and SPF-TPA.

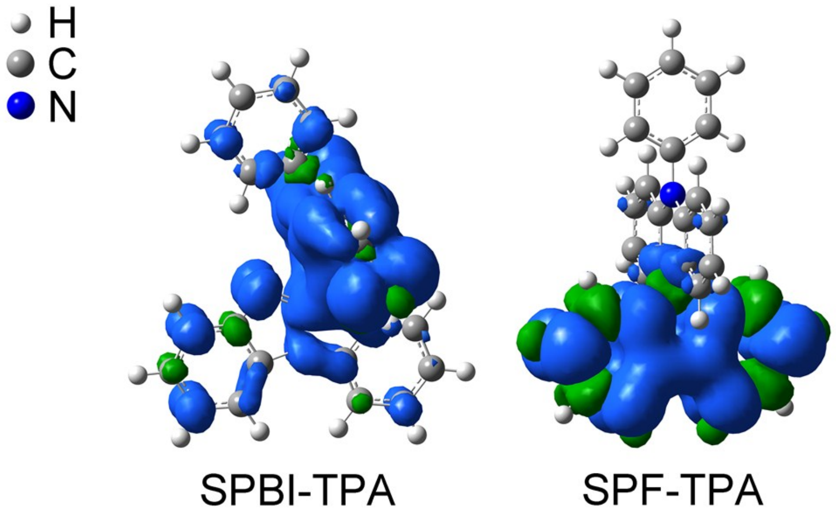


**Fig. S6** Spin density distribution (SDD) in $T_1$ states of SPBI-TPA and SPF-TPA.

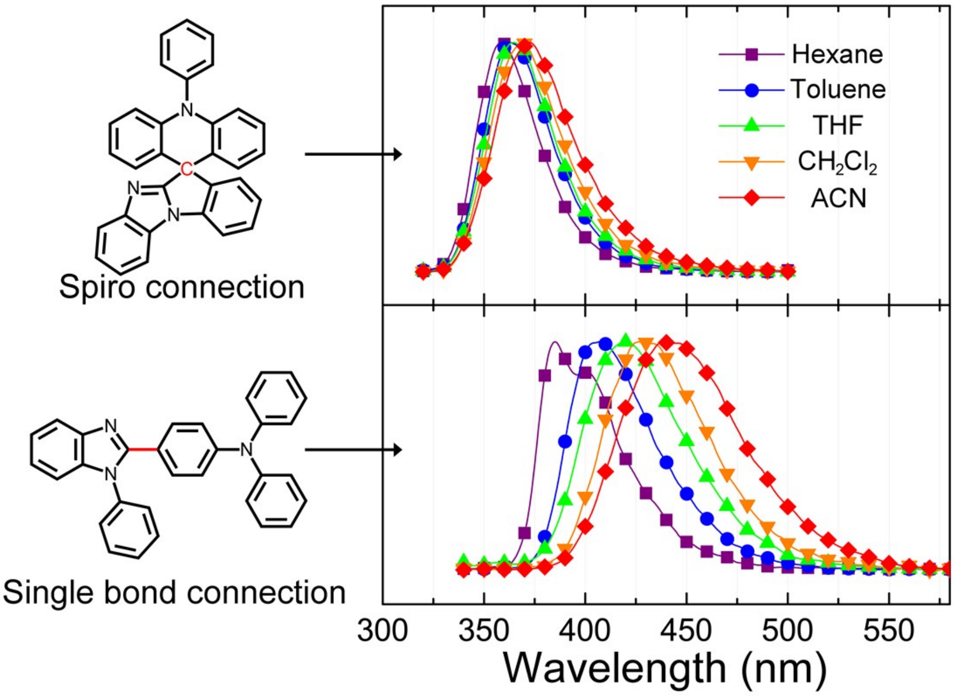


**Fig. S7** Solvent-dependent PL spectra of SPBI-TPA (spiro connection) and BI-TPA (single bond connection).

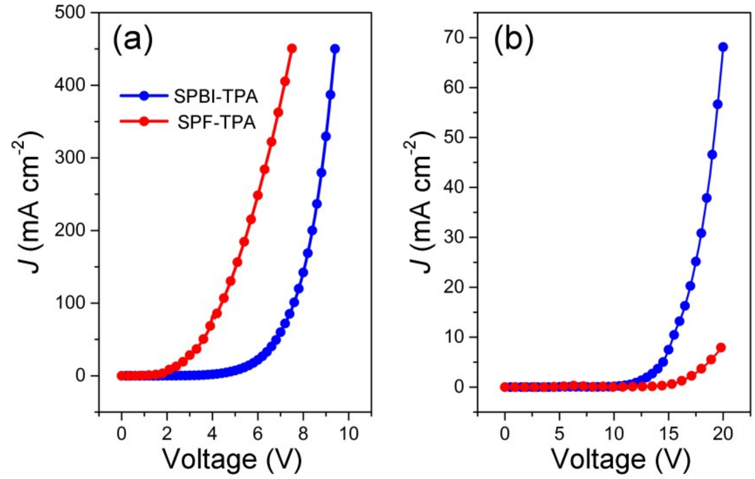


**Fig. S8** Current density-voltage characteristics of (a) hole-only devices (HODs) and (b) electron-only devices (EODs). The HODs and EODs have configurations of respectively ITO /NPB (10 nm)/one of the compounds (70 nm)/NPB (10 nm)/Al (100 nm) and ITO/TmPyPB (10 nm)/one of the compounds (70 nm)/TmPyPB (10 nm)/LiF (1 nm)/Al (100 nm).

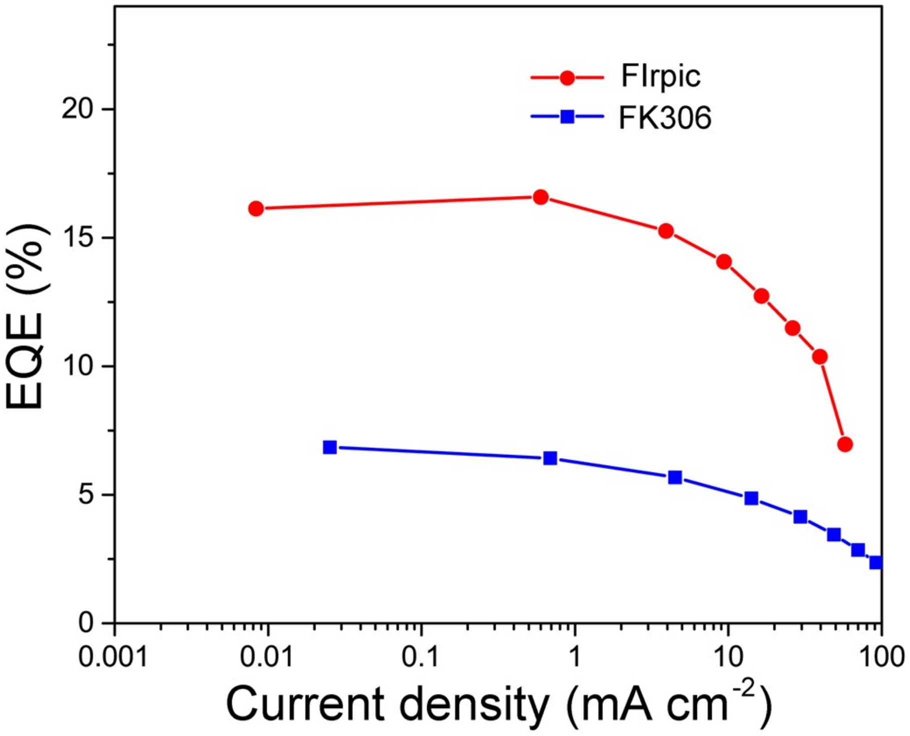


**Fig. S9** EQE-current density curves for the FIrpic-based and the FK306-based PhOLEDs using SPF-TPA as host.

## References

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