

Electronic Supplementary Information

Acceptor modification of diindolocarbazole embedded multiple-resonance emitters for efficient narrowband deep-blue OLEDs with CIE_y ≤ 0.08 and alleviated efficiency roll-off

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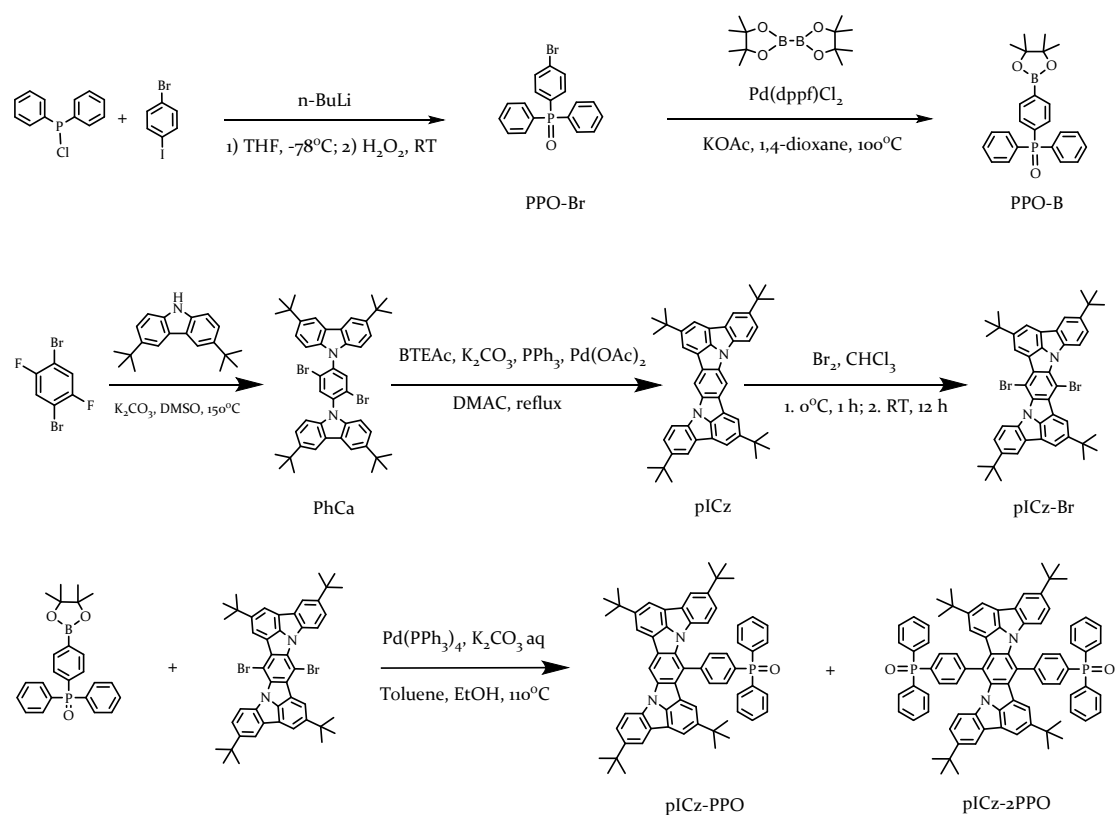
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ESI-1. Synthesis and Characterization

All the reagents and solvents used for the synthesis were purchased from commercial suppliers and used without further purification.



Scheme S1. The synthetic routes for pICz-PPO and pICz-2PPO.

Synthesis of PPO-Br

Under the N₂ atmosphere, 1-bromo-4-iodo-benzene (0.22g, 1.0 mmol) was dissolved in anhydrous tetrahydrofuran (10 mL). The solution was cooled to -78 °C and then n-BuLi (0.48 mL, 1.2 mmol, 2.5 M in hexane) was added dropwise. After stirring for 45 min, chlorodiphenylphosphine (0.18 mL, 1.0 mmol) was added to the mixture and reacted at room temperature overnight. Dilute hydrochloric acid was added to the mixture to adjust the pH value to ca. 7.0. The mixture was washed with deionized water and extracted with dichloromethane, and the organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was dissolved in tetrahydrofuran (10 mL), and H₂O₂ (2 mL, 30%) was added to the solution dropwise. After reacting at room temperature for 2 h, the mixture was extracted with dichloromethane, the organic layer was washed with water and dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by silica gel chromatography (hexane: ethyl acetate = 1: 1) to give the yellow solid. (0.25 g, 69.4%). ¹H NMR (400 MHz, Chloroform-d) δ (ppm): 7.87 (s, 2H), 7.63 (s, 6H), 7.51 (s, 2H), 7.42 (s, 4H), 1.36 – 1.28 (m, 12H).

Synthesis of PPO-B

PPO-Br (0.36 g, 1.0 mmol), bis(pinacolato)diboron (0.31 g, 1.2 mmol), and potassium acetate (0.49 g, 5.0 mmol) were added to dioxane (15 mL) in a N₂ atmosphere and the mixture was stirred at 100 °C for 12 h. After cooling to room temperature, deionized water was added. The mixture was extracted with dichloromethane. The collected organic phase was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography (hexane: ethyl acetate = 1: 1) to afford the product as a white solid (0.28 g, 79%). ¹H NMR (400 MHz, Chloroform-*d*) δ (ppm): 7.87 (s, 2H), 7.64 (s, 6H), 7.52 (s, 2H), 7.43 (s, 4H), 1.32 (s, 12H).

Synthesis of PhCa

In a N₂ atmosphere, 3,6-di-*tert*-butyl-carbazole (0.61 g, 2.2 mmol), dibromo-difluorobenzene (0.27 g, 1 mmol), and K₂CO₃ (0.37 g, 2.7 mmol) were mixed in dimethyl sulfoxide (DMSO, 5 mL). The system was heated to 150 °C and then stirred for 12 h. After cooling to room temperature, the mixture was poured into deionized water. The precipitate was filtered and washed with water. The crude product was purified by silica gel chromatography (hexane: dichloromethane = 3: 1) to afford the product as a white solid (0.59 g, 76%). ¹H NMR (400 MHz, Chloroform-*d*) δ (ppm): 8.18 (d, *J* = 2.0 Hz, 4H), 7.94 (s, 2H), 7.54 (dd, *J* = 8.6, 1.9 Hz, 4H), 7.18 (d, *J* = 8.6 Hz, 4H), 1.50 (s, 36H).

Synthesis of pICz

A mixture of 9,9'-(2,5-dibromo-1,4-phenylene)bis(3,6-di-*tert*-butyl-9*H*-carbazole) (0.79 g, 1 mmol), benzyl triethylammonium chloride (0.46 g, 2 mmol), K₂CO₃ (1.34 g, 10 mmol), triphenylphosphine (0.26 g, 2.8 mmol) and palladium(II) acetate (0.67 g, 3 mmol) in 15 mL *N,N*-dimethylacetamide (DMAC) was stirred and heated to reflux for 10 h under the N₂ atmosphere. Then it was cooled to room temperature and poured into ice-water. The resulting precipitate was filtered to give the crude product as a dark green solid and then washed with deionized water and EtOH. The residue was purified by silica gel chromatography (hexane: dichloromethane=1:1) to afford the product as a yellow solid (0.46 g, 73%). ¹H NMR (400 MHz, Chloroform-*d*) δ (ppm): 8.54 (s, 2H), 8.28 (s, 2H), 8.20 (s, 4H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.64 (dd, *J* = 8.4, 1.9 Hz, 2H), 1.64 (s, 18H), 1.52 (s, 18H).

Synthesis of pICz-Br

A solution of Br₂ (0.27 mL, 5 mmol) in 10 mL CHCl₃ was added dropwise to a suspension of pICz (1.26 g, 2 mmol) in 100 mL CHCl₃ at 0 °C. The resulting mixture was stirred for 1 h at 0 °C and stirred at room temperature for another 12 h. After the reaction was complete, the reaction mixture was treated with saturated sodium sulfite solution.

The organic layer was collected and washed with excess deionized water. The organic solvent was evaporated and recrystallized using CHCl₃/EtOH to give the crude product as a yellow solid. The residue was purified by silica gel chromatography (hexane: dichloromethane=1:1) to afford the product as a yellow solid (1.29 g, 82.2%). ¹H NMR (400 MHz, Chloroform-*d*) δ (ppm): 8.94 (d, *J* = 8.9 Hz, 2H), 8.72 (s, 2H), 8.17 (s, 2H), 8.11 (d, *J* = 2.1 Hz, 2H), 7.56 (dd, *J* = 9.0, 2.1 Hz, 2H), 1.63 (s, 19H), 1.52 (s, 18H).

Synthesis of pICz-PPO and pICz-2PPO

PPO-B (4.0 g, 10 mmol), pICz-Br (1.6 g, 2 mmol), Pd(PPh₃)₄ (0.23 g, 0.2 mmol), K₂CO₃ (2 M, 10 mL), ethanol (10 mL) and toluene (150 mL) were mixed in a 500 mL round-bottom flask. The reaction mixture was heated at reflux for 12 h under the N₂ atmosphere. The solvents were evaporated under vacuum and the resulting residue was extracted with DCM and washed with deionized water. The organic phase was collected, dried with Na₂SO₄, and then evaporated to dryness. The residue was purified by silica gel chromatography (hexane: dichloromethane =5:1) to give yellow solids of pICz-PPO (0.91g, 51%) and pICz-2PPO (0.47 g, 20%). ¹H NMR for pICz-PPO (400 MHz, Chloroform-*d*) δ (ppm): 8.61 (s, 1H), 8.32 (s, 1H), 8.20 (dd, *J* = 11.5, 7.7 Hz, 4H), 8.12 (s, 1H), 8.07 (s, 1H), 8.05 – 8.00 (m, 3H), 7.95 (dd, *J* = 12.2, 7.6 Hz, 4H), 7.64 (dd, *J* = 18.4, 6.3 Hz, 7H), 7.02 (s, 1H), 6.85 (d, *J* = 8.8 Hz, 1H), 5.41 (d, *J* = 8.8 Hz, 1H), 1.64 (s, 9H), 1.52 (s, 9H), 1.40 (s, 9H), 1.35 (s, 9H). ¹³C NMR for pICz-PPO (151 MHz, Chloroform-*d*) δ 146.61, 146.13, 144.65, 144.45, 144.23, 143.96, 137.77, 137.15, 134.57, 134.48, 133.53, 133.16, 132.85, 132.79, 132.72, 132.47, 132.29, 132.27, 132.17, 132.10, 131.57, 131.49, 129.95, 129.91, 129.85, 128.86, 128.78, 128.26, 124.08, 123.51, 122.05, 119.73, 118.99, 118.33, 118.18, 117.79, 117.32, 116.82, 116.50, 115.90, 112.94, 111.51, 105.24, 35.98, 35.66, 34.93, 34.64, 32.84, 32.61, 31.94, 31.81. HRMS (ESI): *m/z* calcd for C₆₄H₆₁N₂OPNa⁺ [*M*+Na]⁺: 927.4419, found: 927.4438. ¹H NMR for pICz-2PPO (400 MHz, Chloroform-*d*) δ (ppm): ¹H NMR for pICz-2PPO (400 MHz, Chloroform-*d*) δ 8.24 (dd, *J* = 11.5, 7.7 Hz, 4H), 8.07 – 8.03 (m, 7H), 7.96 (dd, *J* = 12.1, 6.9 Hz, 8H), 7.71 – 7.57 (m, 12H), 6.95 (d, *J* = 1.2 Hz, 2H), 6.85 (dd, *J* = 8.8, 2.1 Hz, 2H), 5.40 (d, *J* = 8.8 Hz, 2H), 1.39 (s, 18H), 1.32 (s, 18H). ¹³C NMR for pICz-2PPO (101 MHz, Chloroform-*d*) δ 146.16, 144.43, 142.46, 142.43, 137.62, 134.10, 133.97, 133.33, 132.94, 132.84, 132.35, 132.33, 132.33, 132.22, 132.12, 131.75, 131.63, 129.92, 128.93, 128.81, 128.59, 123.60, 121.30, 118.99, 118.24, 117.50, 117.23, 116.44, 112.96, 35.61, 34.67, 32.56, 31.81. HRMS (ESI): *m/z* calcd for C₈₂H₇₅N₂O₂P₂⁺ [*M*+H]⁺: 1181.5304, found: 1181.5321.

ESI-2. Measurements

Instrumentation for structure characterization: ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Ultra Shield Plus 400 MHz instrument (400 MHz for ¹H and 101 MHz for ¹³C, respectively) with chloroform-*d* (CDCl₃) as the solvent and tetramethylsilane (TMS, δ = 0.00 ppm) as the internal standard. High-resolution mass spectra (HRMS) were performed by the Agilent 6540 QTOP-MS operating in positive ionization mode.

Thermal stability measurements: Thermal properties of the deep-blue emitters were investigated by thermogravimetric analysis (TGA). TGA measurements were performed using a Perkin Elmer Pyris 6 under a nitrogen atmosphere with a heating rate of $10^{\circ}\text{C min}^{-1}$ from $30\text{-}800^{\circ}\text{C}$.

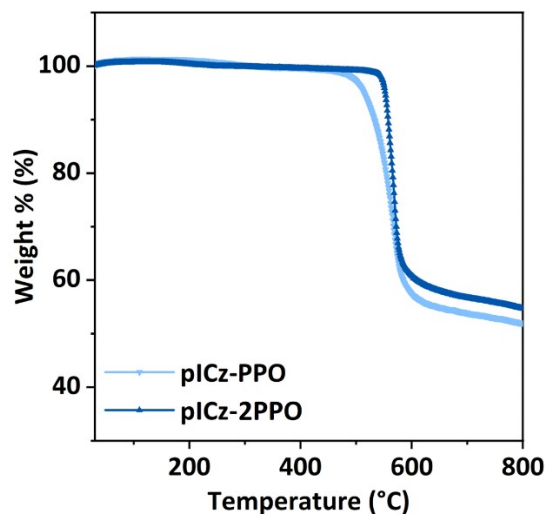


Figure S1. TGA curves of pICz-PPO and pICz-2PPO.

Electrochemical property measurements: Cyclic voltammetry (CV) measurements were performed at room temperature on a CHI660E system in a typical three-electrode cell with a working electrode (glass carbon), a reference electrode (Ag/Ag^+ , referenced against ferrocene/ferrocenium (FOC)), and a counter electrode (Pt wire) in acetonitrile solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) at a sweeping rate of 100 mV s^{-1} . The highest occupied molecular orbital (HOMO) energy levels (E_{HOMO}) of the materials were estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum) according to Equation S1:

$$E_{\text{HOMO}} = - \left(E_{\text{onset}}^{\text{Ox}} - E_{(\text{Fc}/\text{Fc}^+)} + 4.8 \right) \text{ eV} \quad (\text{S1})$$

where $E_{(\text{Fc}/\text{Fc}^+)}$ is the onset potential of oxidation wave of ferrocene (Fc) vs Ag/Ag^+ and $E_{\text{onset}}^{\text{Ox}}$ is the onset potential of the oxidation wave of the materials deposited as thin films on the surface of the working electrode. The lowest unoccupied molecular orbital (LUMO) energy level (E_{LUMO}) was estimated by adding the optical bandgap (E_g) to the corresponding HOMO energy level.

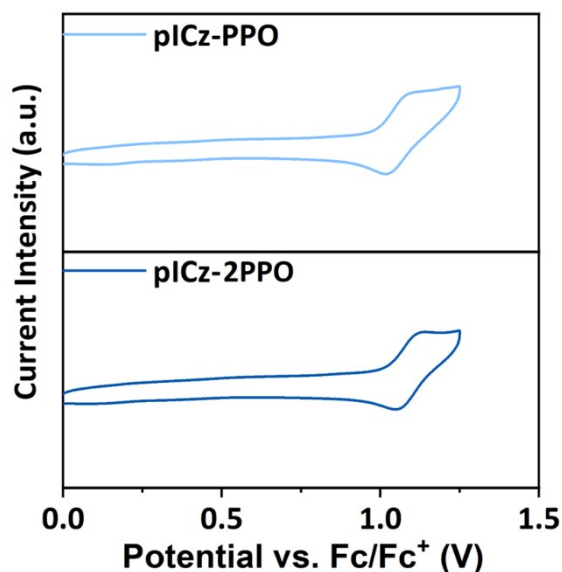


Figure S2. Cyclic voltammograms of pICz-PPO and pICz-2PPO.

Photophysical property measurements: Ultraviolet-visible (UV-Vis) spectra were recorded on a Varian Cary 4000 UV-Visible spectrophotometer. The photoluminescent (PL) spectra were obtained on an Fluoromax-4 spectrophotometer. Transient PL decay curves were collected using an Edinburgh FLS 1000 fluorescence spectrophotometer at room temperature. The absolute photoluminescence quantum yield (PLQY) was obtained on an Edinburgh FLS1000 fluorescence spectrophotometer with an integrating sphere. The single and triplet energy values were obtained from the prompt fluorescent spectra and phosphorescent spectra with a 5 ms delay, respectively, measured at 77 K using liquid nitrogen.

ESI-3. Theoretical Calculations

The density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were conducted using Gaussian program with b3lyp/6-31g(d) basis set.

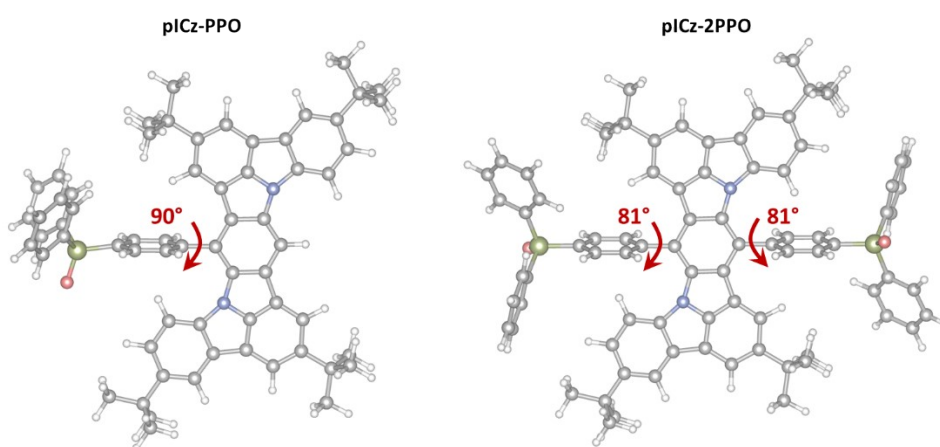


Figure S3. Optimized ground state geometries of pICz-PPO and pICz-2PPO.

ESI-4. Photophysical Properties

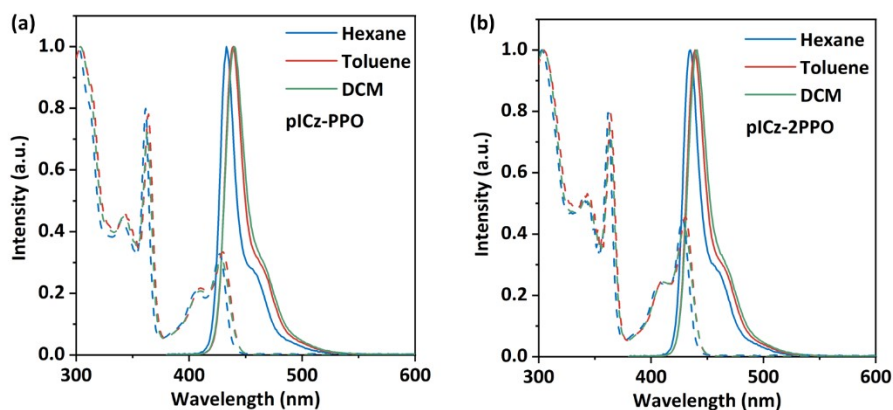


Figure S4. The normalized UV-Vis and fluorescence spectra of pICz-PPO (a) and pICz-2PPO (b) in hexane, toluene, and dichloromethane (DCM) solution (10^{-5} mol L $^{-1}$). The dash and solid lines denote the UV-Vis and fluorescence spectra, respectively.

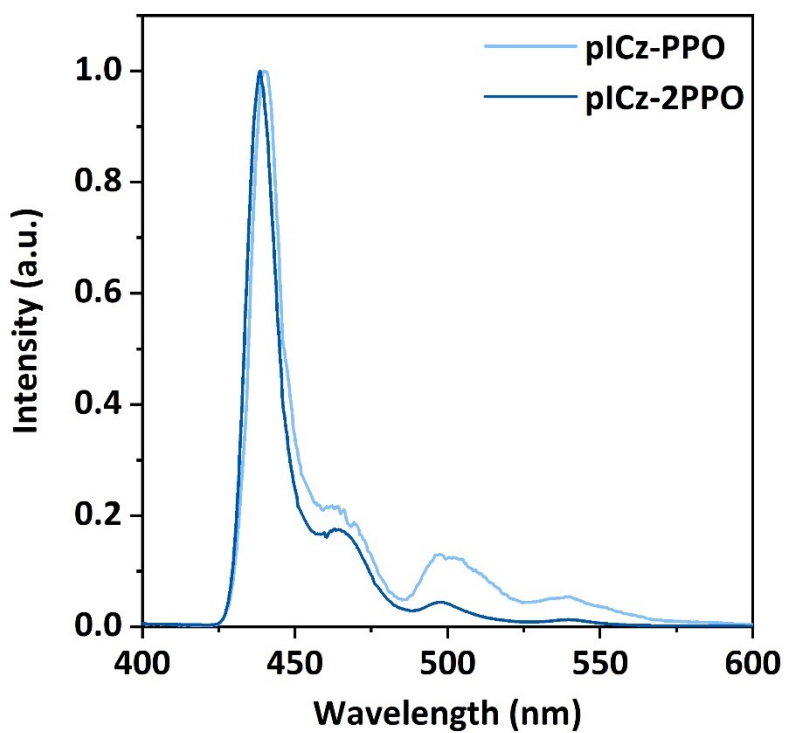


Figure S5. The normalized fluorescence spectra of pICz-PPO and pICz-2PPO in toluene solution (10^{-5} mol L $^{-1}$) measured at 77 K.

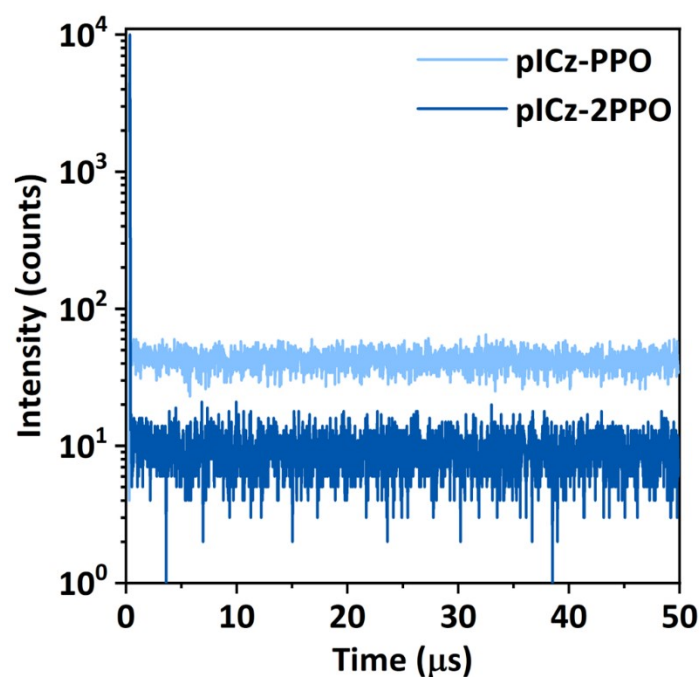


Figure S6. The photoluminescence decay curves of pICz-PPO and pICz-2PPO in doped thin films with PPF as the host.

ESI-5. Device Fabrication

Before device fabrication, the ITO glass substrates were pre-cleaned carefully. Then the sample was transferred to the deposition system. The devices were prepared in vacuum at a pressure of 5×10^{-6} Torr. The organic layers were thermally evaporated at a rate of 1.0 \AA s^{-1} . After the organic film deposition, 0.5 nm of LiF and 150 nm of aluminum were thermally evaporated onto the organic surface. All of the organic materials used were purified by a vacuum sublimation approach. The electrical characteristics of the devices were measured with a Keithley 2400 source meter. The electroluminescence spectra and luminance of the devices were obtained on a PR650 spectrometer. All the device fabrication and characterization steps were carried out at room temperature under ambient laboratory conditions.

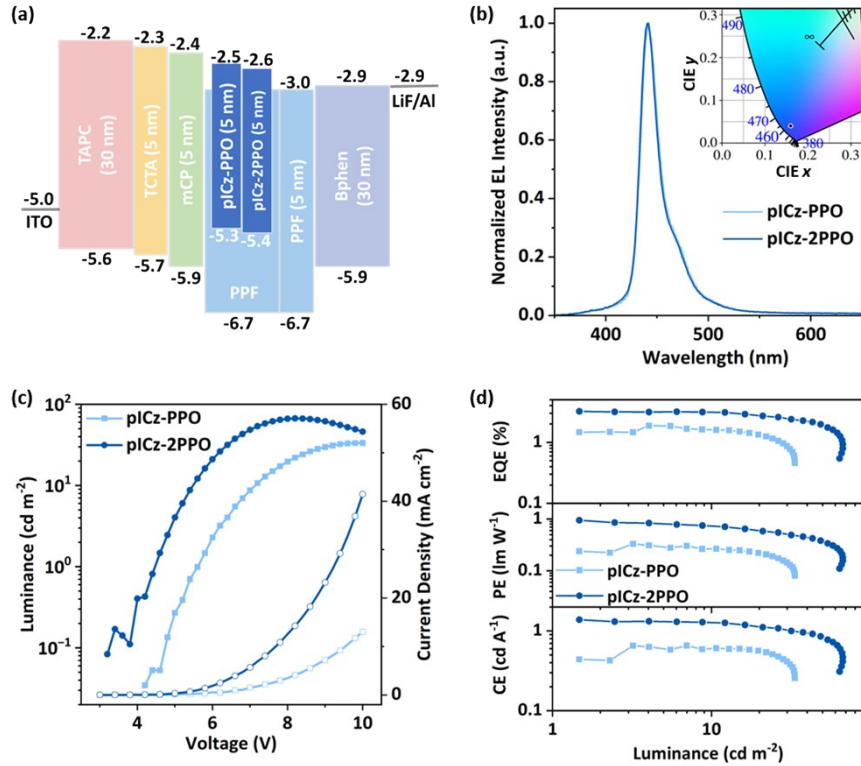


Figure S7. (a) Energy level diagram; (b) electroluminescence spectra (inset shows the corresponding CIE coordinates); (c) luminance-voltage-current density plots and (d) efficiency-luminance characteristics of the OLEDs with PPF: 1 wt% pICz-PPO / pICz-2PPO as emitting layer.

Table S1. Critical parameters for the EL performance of OLEDs with PPF: 1 wt% pICz-PPO / pICz-2PPO as emitting layer.

Device	λ_{EL} (nm)	FWHM (nm)	CIE (x,y)	EQE _{Max} (%)	V _{on} (V)	PE _{max} (lm·W ⁻¹)	CE _{max} (cd·A ⁻¹)
pICz-PPO	441	20	(0.16,0.04)	1.9	5.6	0.4	0.8
pICz-2PPO	441	20	(0.16,0.04)	3.2	4.6	1.0	1.4

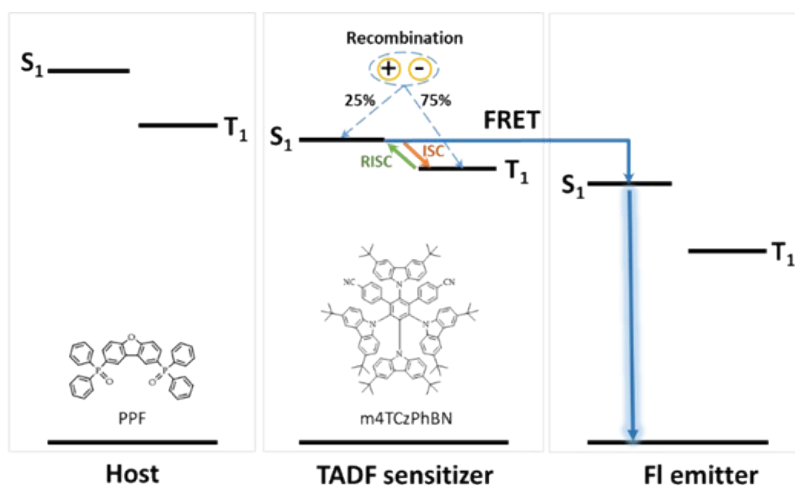


Figure S8. The scheme of energy transfer process of device with the TADF sensitized fluorescence mechanism.

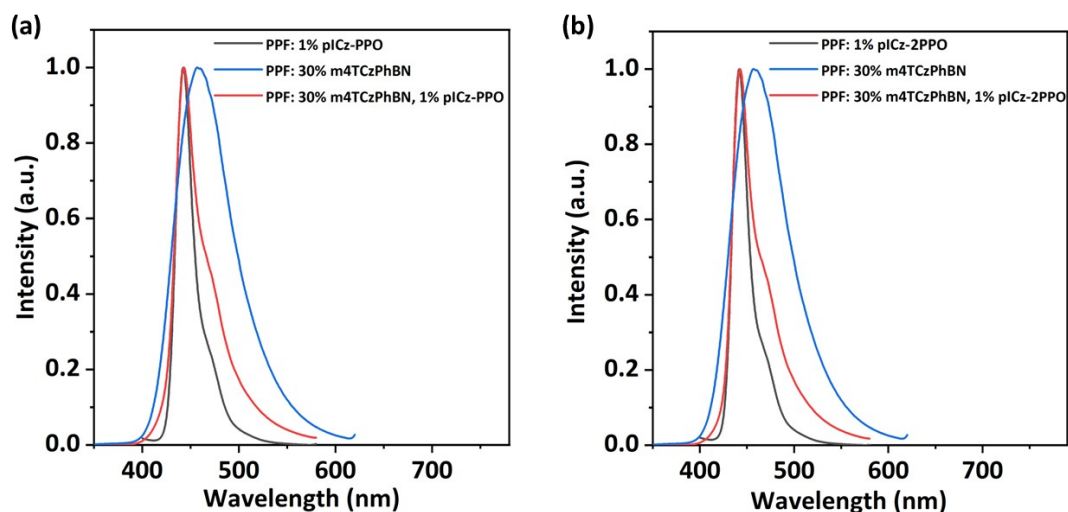


Figure S9. The photoluminescence spectra of the mixed film of (a) PPF: 30% m4TCzPhBN, PPF: 1% pICz-PPO, PPF: 30% m4TCzPhBN: 1% pICz-PPO, and (b) PPF: 30% m4TCzPhBN, PPF: 1% pICz-2PPO, PPF: 30% m4TCzPhBN: 1% pICz-2PPO.

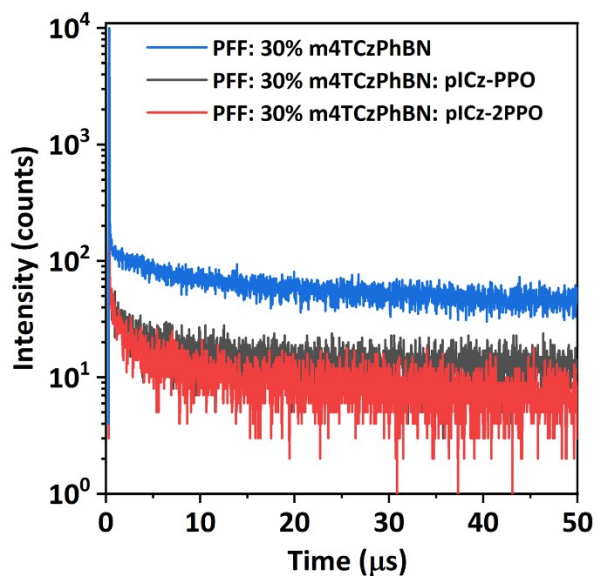


Figure S10. The photoluminescence decay curves of PFF: 30% m4TCzPhBN, PFF: 30% m4TCzPhBN: 1% pICz-PPO, PFF: 30% m4TCzPhBN: 1%pICz-2PPO.

ESI-6. Nuclear Magnetic Resonance Spectra and High-Resolution Mass Spectra

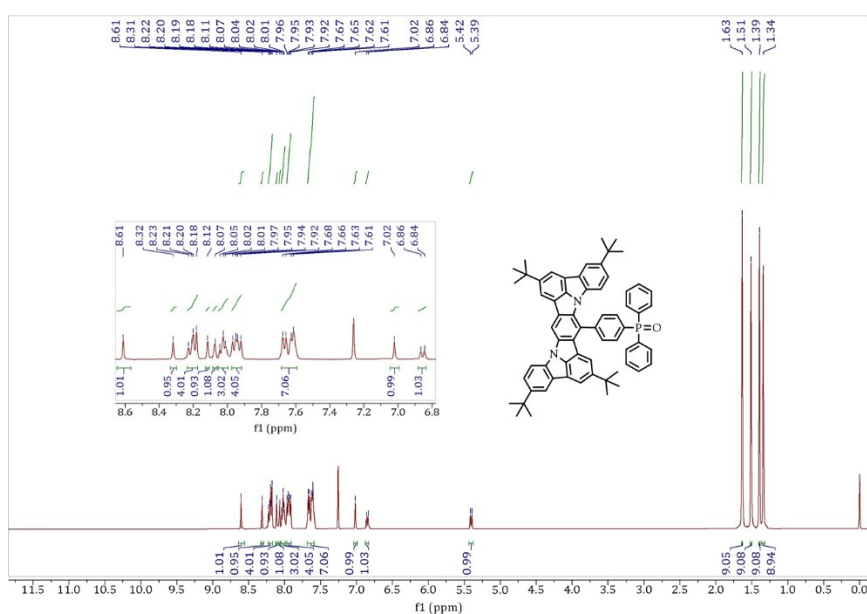


Figure S11. ^1H NMR spectrum of pICz-PPO in CDCl_3 .

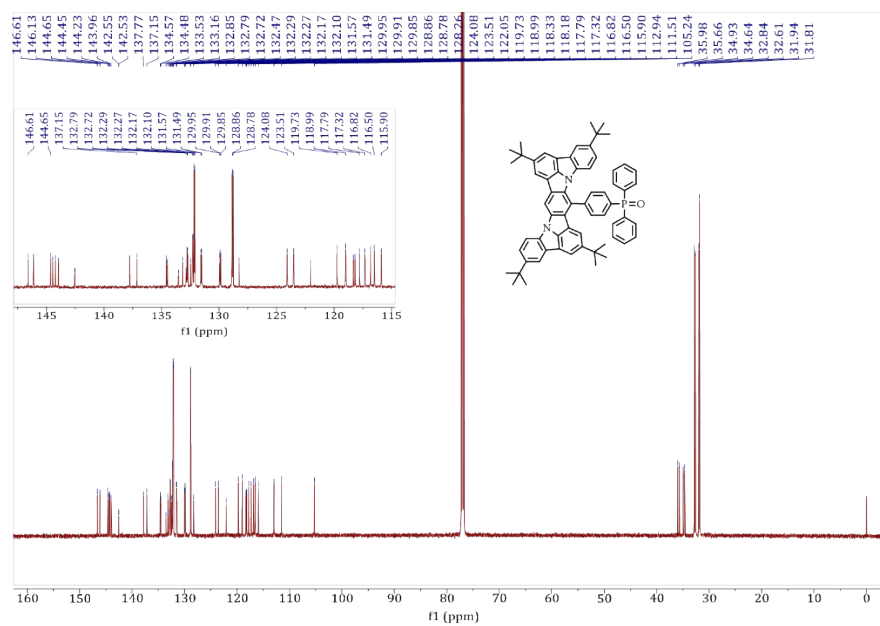


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of pCz-PPO in CDCl_3 .

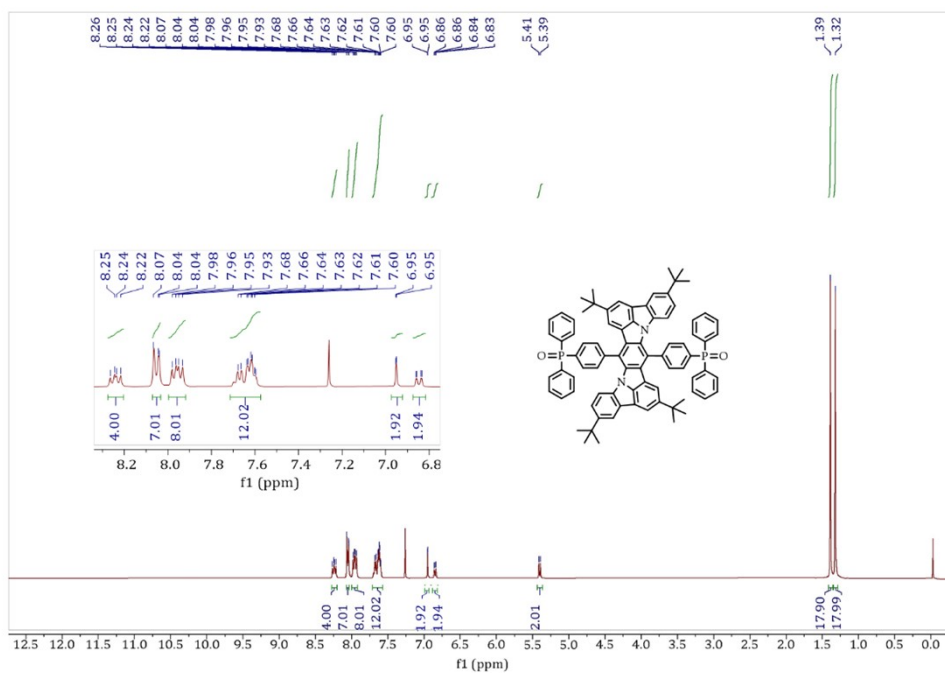


Figure S13. ^1H NMR spectrum of pCz-2PPO in CDCl_3 .

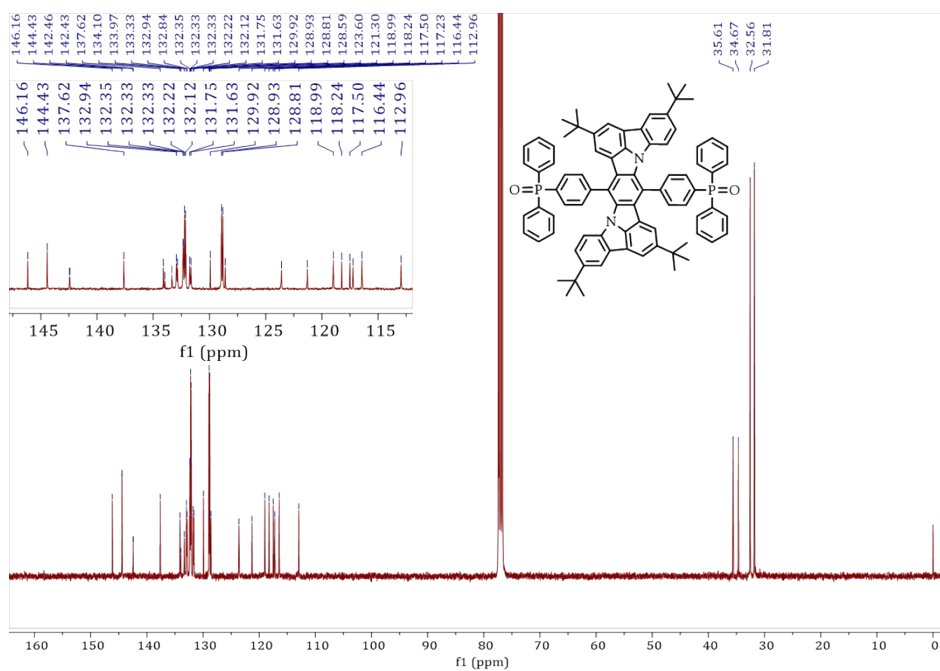


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of pCz-2PPO in CDCl_3 .

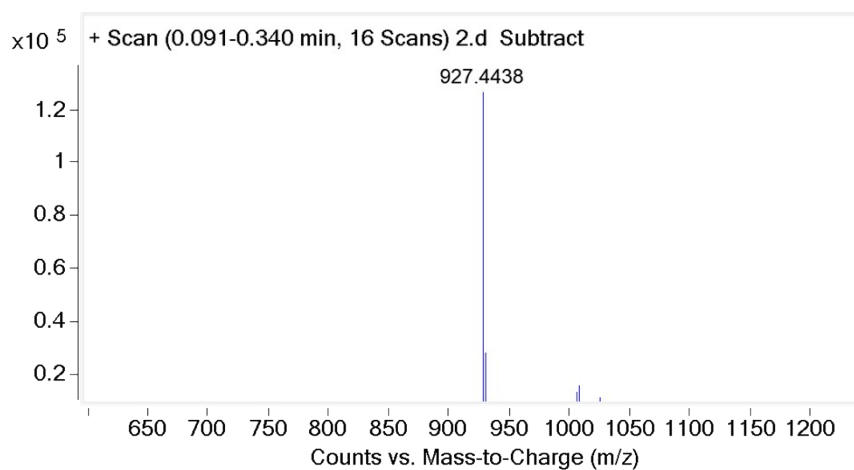


Figure S15. High-resolution mass spectrum of pCz-PPO.

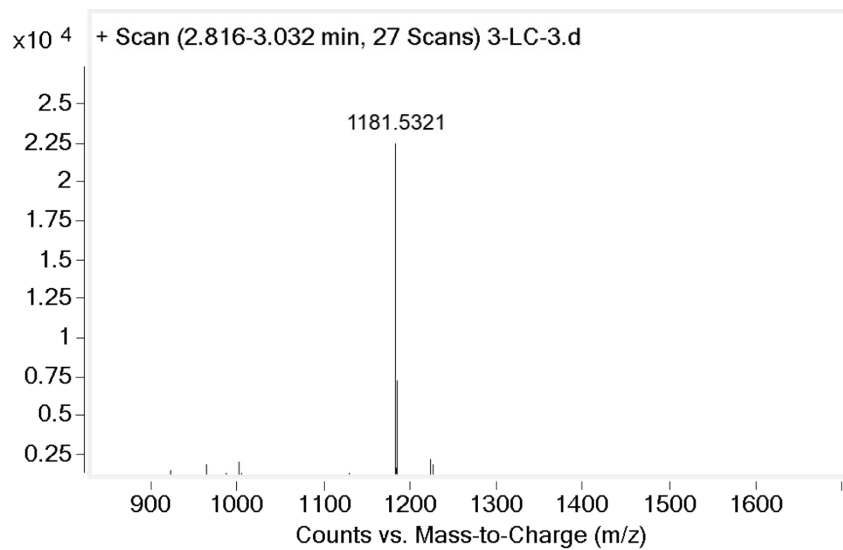


Figure S16. High resolution mass spectrum of pICz-2PPO.