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Supporting Information

High-Efficiency Near-Infrared Fluorescent Organic Light-Emitting Diodes with Small Efficiency Roll-Off Based on AIE-active Phenanthro[9,10-d]imidazole Derivatives

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1. Experimental section

General information

All the reagents and solvents were used as received without further purification. ^{1}H NMR and ^{13}C NMR were recorded by Bruker AVANCE 500 spectrometer at 500 MHz or 125 MHz with tetramethylsilane (TMS) as the internal standard, DMSO-d_6, CD_2Cl_2 and $CDCl_3$, as solvent. Elemental analysis was carried out on a Flash EA 1112, CHNSO elemental analysis instrument. MALDI-TOF-MS mass spectra were obtained from an AXIMA-CFRTM plus instrument. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer thermal analysis system from 30 °C to 900 °C. Differential scanning calorimetry (DSC) was measured by NETZSCH (DSC-204) unit from 30 °C to 400 °C. The electrochemical properties (oxidation and reduction potentials) were carried out via cyclic voltammetry (CV) measurements by using a standard one compartment, three-electrode electrochemical cell given by a BAS 100B/W electrochemical analyzer. Tetrabutylammoniumhexafluorophosphate (TBAPF6) in anhydrous dimethyl formamide (DMF) or anhydrous dichloromethane (0.1 M) were used as the electrolyte for negative or positive scan. A glass-carbon disk electrode was used as the working electrode, a Pt wire was used as the counter electrode, and Ag/Ag^+ was used as the reference electrode together with ferrocene as the internal standard at a scan rate of 100 mV s^{-1}. Ag/Ag^+ reference electrode was commercially available and was constituted of (1) one silver wire; (2) $AgNO_3$ solution (0.01 M) in which the $AgNO_3$ was solute and acetonitrile was solvent and (3) tetrabutylammoniumhexafluorophosphate (TBAPF6) (0.1 M) which was used as supporting electrolyte. The concentration of Ag^+ was not constant since the Ag^+ may react with other trace impurities. Hence the authentic potential of the Ag/Ag^+ electrode was unknown. What's more, there may be different liquid junction potentials for Ag/Ag^+ electrode when used in different solvents such as DMF and dichloromethane. Hence, the experimental potential of our sample which was directly related to the Ag/Ag^+ electrode was not valid and we need internal standard to eliminate the uncertainty of Ag/Ag$^+$ electrode. Following the IUPAC recommendation,[1] we used ferrocenium/ferrocene (Fc$^+$/Fc) redox couple as the internal standard because the formal potential of Fc$^+$/Fc varies little in different solvents and such variations can be neglect in our measurement.[2] According to some early literatures, the formal potential of Fc$^+$/Fc was 4.8 eV below vacuum.[3] All potentials relative to Ag/Ag$^+$ electrode obtained from CV measurement were eventually referenced against Fc$^+$/Fc to calculate HOMO/LUMO energy levels. As a result, the Ag/Ag$^+$ electrode was just a pseudo reference and the uncertainty of Ag/Ag$^+$ electrode was eliminated. The HOMO/LUMO levels were calculated according to the following formalism:

$$\mathrm{HOMO} = -\,(E_{\mathrm{ox}}\ \mathrm{vs.\ Fc^+/Fc} + 4.8)\ \mathrm{eV} \qquad \text{Equation S1}$$

$$\mathrm{LUMO} = -\,(E_{\mathrm{red}}\ \mathrm{vs.\ Fc^+/Fc} + 4.8)\ \mathrm{eV} \qquad \text{Equation S2}$$

where the E_{ox} vs. Fc$^+$/Fc and E_{red} vs. Fc$^+$/Fc are oxidation and reduction onset potentials relative to Fc$^+$/Fc reference, respectively. UV-vis and fluorescence spectra were recorded on a Shimadzu UV-3100 spectrophotometer using 1 cm path length quartz cells. The fluorescence lifetime and photoluminescence quantum efficiency (PLQY) of solid film were measured by FLS920 Spectrometer. The PLQY values of different solutions were measured by using Rhodamine B as a reference (PLQY = 0.7 in ethanol) and were calculated by using the following formula:

$$Q_X = Q_r\left(\frac{A_r(\lambda)}{A_x(\lambda)}\right)\left(\frac{I(\lambda_r)}{I(\lambda_x)}\right)\left(\frac{n_x^2}{n_r^2}\right)\left(\frac{D_x}{D_r}\right) \qquad \text{Equation S3}$$

Where Q is the PLQY, A is the value of absorbance, I is the intensity of excitation source, n is the refractive index of solvent, D is the area of emission spectra, λ is the corresponding wavelength. The subscript r stands for the reference while x stands for test subject. The excitation wavelengths were their absorption maxima.

Device fabrications and measurements

ITO coated glasses with a sheet resistance of 20 Ω square^{-1} were used as the substrate and cleaned by deionized water, isopropyl alcohol, acetone and toluene. Then the ITO glasses were irradiated in UV-zone for 30 min. The deposition system for organic and metal deposition has a base pressure lower than 5×10^{-6} mbar. The hole injecting layer HATCN was deposited at 0.1 Å s^{-1}. The deposition rate of all other organic layers was 1.0 Å s^{-1}. The electron injecting layer LiF was deposited at a rate of 0.1 Å s^{-1} and then the capping Al metal layer was deposited at a rate of 4.0 Å s^{-1}. The EL characteristics were measured using a Keithley 2400 programmable electrometer and a PR-650 Spectroscan spectrometer under ambient condition.

Computational Details

The ground-state (S_0) and the lowest singlet excited state (S_1) geometries were optimized at the B3LYP/6-31G(d, p) level, which is a common method to provide molecular geometries and the optimized outcome is in good agreement with the experiment result. The HOMO/LUMO distributions are calculated on the basis of optimized S_0 state. The high excitation energy levels of both singlet and triplet states were calculated using TD-M062X/6-31G(d, p) method on the basis of the optimized configuration of S_1. For the purpose of investigating the properties of excited-states, natural transition orbitals (NTOs) of emission were evaluated for the ten lowest excited-states, involving both singlet and triplet states under TD-M062X/6-31G(d, p) level. This approach provides the most compact representation of the electronic transitions in terms of an expansion into single particle orbitals by diagonalizing the transition density matrix associated with each excitation.

Lippert-Mataga calculation

The properties of ground state (S_0) and the lowest singlet excited state (S_1) can be better understood through solvatochromic experiment. One reliable way to explore the influence of solvent environment on the optical property of our sample is by using the Lippert-Mataga equation, a model that describes the interactions between the solvent and the dipole moment of solute:

$$hc(v_a - v_f) = hc(v_a^0 - v_f^0) - \frac{2(u_e - u_f)^2}{a^3} f(\varepsilon, n) \qquad \text{Equation S4}$$

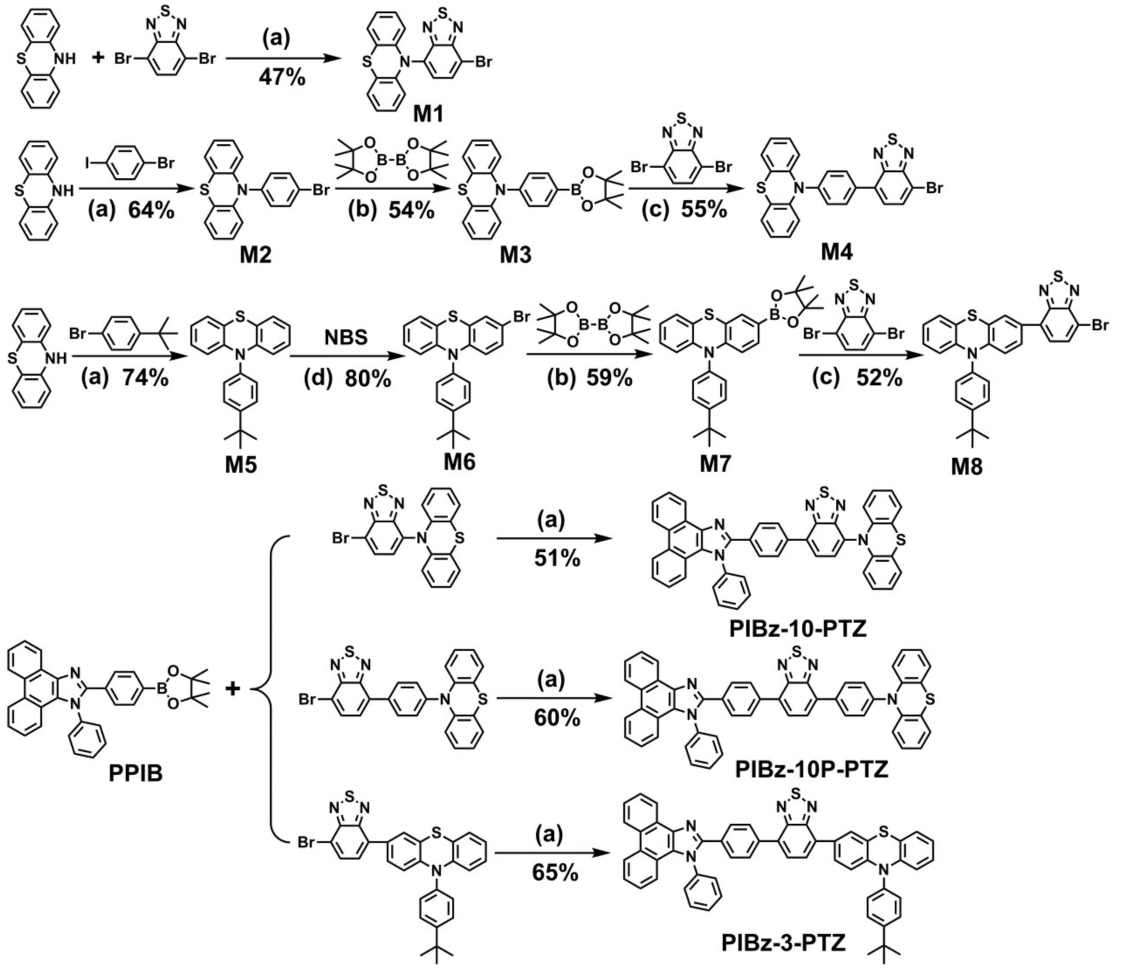
where f is the orientational polarizability of solvents, μ_e is the dipole moment of excited state, μ_g is the dipole moment of ground state; a is the solvent cavity

(Onsager) radius, derived from the Avogadro number (N), molecular weight (M), and density (d = 1.0 g cm^{-3}); ε and n are the solvent dielectric and the solvent refractive index, respectively. f(ε,n) and a can be calculated respectively as follows

$$f(\varepsilon,n)=\frac{\varepsilon-1}{2\varepsilon+1}-\frac{n^2-1}{2n^2+1} \qquad \text{Equation S5}$$

$$a=(3M/4N\pi d)^{1/3} \qquad \text{Equation S6}$$

2. Synthesis and Characterization



Scheme S1. Synthetic procedures. (a) Ullmann coupling: Na^{t}OBu, PH^{t}Bu$_3$BF$_4$, Pd$_2$(dba)$_3$, toluene, 110 ℃, 12 h, under N$_2$ atmosphere; (b) n-BuLi, -78 °C, stirring for 3 hours under N$_2$ atmosphere, then adding isopropoxyboronic acid pinacol ester and stirring overnight under N$_2$ atmosphere; (c) Suzuki coupling: Pd(PPh$_3$)$_4$, K$_2$CO$_3$ (2 M aq), toluene, 90 °C, 24 hours under N$_2$ atmosphere; (d) NBS, THF, room temperature and stirring 4 h.

The synthesis of PPIB were according to previous reports.

10-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)-10H-phenothiazine (M1)

In a 100 mL round flask, a mixture of phenothiazine (0.60 g, 3 mmol), 4,7-dibromobenzo[c][1,2,5]thiadiazole (1.45 g, 5 mmol), $Pd_2(dba)_3$ (82 mg, 0.09 mmol), $PH^tBu_3BF_4$ (44 mg, 0.15 mmol), Na^tOBu (0.48 g, 5 mmol) and 40 mL toluene was stirred and refluxed at 110 °C under N_2 atmosphere for 12 hours. The reaction was then quenched by water and extracted with dichloromethane. The organic phase was collected and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified via column chromatography by using petroleum ether/dichloromethane (5:1, v/v) as eluent to afford black solid. (580 mg, yield: 47%). 1H NMR (500 MHz, DMSO-D_6, 25 °C, TMS) δ (ppm): 8.25 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.10 (dd, J = 7.5, 1.6 Hz, 2H), 6.85 (m, J = 7.5, 3.7 Hz, 2H), 6.83 - 6.76 (m, 2H), 6.05 (dd, J = 8.2, 1.1 Hz, 2H). MALDI-TOF MS (mass m/z): Calcd for $C_{18}H_{10}BrN_3S_2$, 410.95; Found, 411.21 [M^+].

10-(4-bromophenyl)-10H-phenothiazine (M2)

In a 100 mL round flask, a mixture of phenothiazine (1.80 g, 9 mmol), 1-bromo-4-iodobenzene (4.23 g, 15 mmol), $Pd_2(dba)_3$ (264 mg, 0.27 mmol), $PH^tBu_3BF_4$ (132 mg, 0.45 mmol), Na^tOBu (1.44 g, 15 mmol) and 60 mL toluene was stirred and refluxed at 110 °C under N_2 atmosphere for 12 hours. The reaction was then quenched by water and extracted with dichloromethane. The organic phase was collected and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified via column chromatography by using petroleum ether/dichloromethane (8:1, v/v) as eluent to afford the pure white solid. (2.03 g, yield: 64%). ^1H NMR (500 MHz, DMSO-D_6, 25 °C, TMS) δ (ppm): 7.83 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 7.3 Hz, 2H), 7.00 (t, J = 7.4 Hz, 2H), 6.92 (t, J = 7.2 Hz, 2H), 6.29 (d, J = 8.0 Hz, 2H). MALDI-TOF MS (mass m/z): Calcd for $C_{18}H_{12}BrNS$, 352.99; Found, 352.76 [M^+].

10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-10H-phenothiazine (M3)

In a 100 mL round flask, A mixture of 10-(4-bromophenyl)-10H-phenothiazine (1.77

g, 5 mmol), bis(pinacolato)diboron (2.54 g, 10 mmol), Pd(dppf)Cl_2 (117 mg, 0.15 mmol), KOAc (1.48 g, 15 mmol), and 1,4-dioxane (40 mL) was stirred and refluxed at 90 °C under N_2 protection for 72 hours. The mixture was washed three times with 40 mL water and extracted with dichloromethane. The organic phase was collected and dried by anhydrous Na_2SO_4, and then the solvent was evaporated. The residue was purified via column chromatography eluting with petroleum ether-dichloromethane (2:1, v/v) mixtures to afford white solid. (1.08 g, yield: 54%).^{1}H NMR (500 MHz, DMSO-D_6, 25 °C, TMS) δ (ppm): 7.98 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 6.98 (m, 6H), 6.26 (d, J = 7.9 Hz, 2H), 1.32 (d, J = 7.9 Hz, 12H). MALDI-TOF MS (mass m/z): Calcd for $C_{24}H_{24}BNO_2S$, 410.16; Found, 410.58 [M^+].

10-(4-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)phenyl)-10H-phenothiazine (M4)

In a 100 mL round flask, a mixture of 10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-10H-phenothiazine (1.00 g, 2.5 mmol), 4,7-dibromobenzo[c][1,2,5] thiadiazole (0.73 g, 2.5 mmol), K_2CO_3 (5.52 g, 40 mmol), 20 mL distilled water, 40 mL toluene and $Pd(PPh_3)_4$ (115 mg, 0.10 mmol) was added and refluxed at 90 °C under N_2 atmosphere for 24 hours. The mixture was poured into water to quench the reaction and then extracted with dichloromethane, the organic phase was collected and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified via column chromatography by using petroleum ether/dichloromethane (2:1, v/v) as eluent to afford red solid. (670 mg, yield: 55%). ^{1}H NMR (500 MHz, DMSO-D_6, 25 °C, TMS) δ (ppm): 8.24 (d, J = 7.4 Hz, 2H), 8.19 (d, J = 7.1 Hz, 1H), 7.91 (d, J = 6.7 Hz, 1H), 7.58 (d, J = 7.2 Hz, 2H), 7.17 (d, J = 7.4 Hz, 2H), 7.04 (t, J = 7.5 Hz, 2H), 6.94 (t, J = 7.3 Hz, 2H), 6.43 (d, J = 8.1 Hz, 2H). MALDI-TOF MS (mass m/z): Calcd for $C_{24}H_{14}BrN_3S_2$, 486.98; Found, 487.35 [M^+].

10-(4-(tert-butyl)phenyl)-10H-phenothiazine (M5)

In a 250 mL round flask, a mixture of phenothiazine (4.00 g, 20 mmol), 1-bromo-4-(tert-butyl)benzene (4.24 g, 20 mmol), $Pd_2(dba)_3$ (550 mg, 0.60 mmol), $PH^tBu_3BF_4$ (300 mg, 1.00 mmol), Na^tOBu (2.88 g, 30 mmol) and 100 mL toluene was stirred and refluxed at 110 °C under N_2 atmosphere for 12 hours. The reaction was then quenched by water and extracted with dichloromethane. The organic phase was collected and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified via column chromatography by using petroleum ether as eluent to afford the blue solid. (4.90 g, yield: 74%). ^1H NMR (500 MHz, DMSO-D_6, 25 °C, TMS) δ (ppm): 7.68 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 7.5 Hz, 2H), 6.95 (t, J = 7.5 Hz, 2H), 6.85 (t, J = 7.5 Hz, 2H), 6.15 (d, J = 8.2 Hz, 2H), 1.38 (s, 9H). MALDI-TOF MS (mass m/z): Calcd for $C_{22}H_{21}NS$, 331.14; Found, 331.45 [M^+].

3-bromo-10-(4-(tert-butyl)phenyl)-10H-phenothiazine (M6)

10-phenyl-10H-phenoxazine (3.31 g, 10 mmol) was added into 100 mL THF. The mixture was stirring under lucifugal environment. And then NBS (1.96 g, 11 mmol) was added into the mixture every 20 minutes for 4 times. The mixture was reacted at room temperature and refluxed under a N_2 atmosphere for 4 h. The mixture was washed by NaCl aqueous solution and extracted with dichloromethane consecutively. The organic phase was collected and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified via column chromatography by using petroleum ether as eluent to afford the blue solid. (3.25 g, yield: 80%). ^1H NMR (500 MHz, DMSO-D_6, 25 °C, TMS) δ (ppm): 7.70 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.24 (s, 1H), 7.20 (d, J = 8.3 Hz, 1H), 7.05 (d, J = 7.7 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.85 (t, J = 7.5 Hz, 1H), 6.13 (d, J = 8.3 Hz, 1H), 6.05 (d, J = 8.2 Hz, 1H), 1.38 (s, 9H). MALDI-TOF MS (mass m/z): Calcd for $C_{22}H_{20}BrNS$, 409.05; Found, 409.61 [M^+].

10-(4-(tert-butyl)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (M7)

In a 100 mL round flask, A mixture of 3-bromo-10-(4-(tert-butyl)phenyl)-10H-phenothiazine (2.05 g, 5 mmol), bis(pinacolato)diboron (2.54 g, 10 mmol), Pd(dppf)Cl_2 (117 mg, 0.15 mmol), KOAc (1.48 g, 15 mmol), and 1,4-dioxane (40 mL) was stirred and refluxed at 90 ℃ under N_2 protection for 72 hours. The mixture was washed three times with 40 mL water and extracted with dichloromethane. The organic phase was collected and dried by anhydrous Na_2SO_4, and then the solvent was evaporated. The residue was purified via column chromatography eluting with petroleum ether-dichloromethane (5:1, v/v) mixtures to afford blue solid. (1.35 g, yield: 59%).^{1}H NMR (500 MHz, DMSO-D$_6$, 25 °C, TMS) δ (ppm): 7.70 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.24 (s, 1H), 7.20 (d, J = 7.8 Hz, 1H), 7.05 (d, J = 7.0 Hz, 1H), 6.91 (d, J = 7.4 Hz, 1H), 6.86 (d, J = 7.2 Hz, 1H), 6.13 (d, J = 8.4 Hz, 1H), 6.05 (d, J = 7.5 Hz, 1H), 1.38 (s, 9H), 1.26 (s, 12H). MALDI-TOF MS (mass m/z): Calcd for $C_{28}H_{32}BNO_2S$, 457.22; Found, 457.93 [M^+].

3-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)-10-(4-(tert-butyl)phenyl)-10H-phenothiazine (M8)

In a 100 mL round flask, a mixture of 10-(4-(tert-butyl)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (1.15 g, 2.5 mmol), 4,7-dibromobenzo[c][1,2,5] thiadiazole (0.73 g, 2.5 mmol), K_2CO_3 (5.52 g, 40 mmol), 20 mL distilled water, 40 mL toluene and $Pd(PPh_3)_4$ (115 mg, 0.10 mmol) was added and refluxed at 90 °C under N_2 atmosphere for 24 hours. The mixture was poured into water to quench the reaction and then extracted with dichloromethane, the organic phase was collected and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified via column chromatography by using petroleum ether/dichloromethane (1:1, v/v) as eluent to afford red solid. (700 mg, yield: 52%). ^{1}H NMR (500 MHz, DMSO-D$_6$, 25 °C, TMS) δ (ppm): 8.08 (d, J = 7.5 Hz, 1H), 7.73 (m, J = 17.4, 9.5 Hz, 4H), 7.55 (d, J = 8.6 Hz, 1H), 7.42 (d, J = 7.5 Hz, 2H), 7.11 (d, J = 6.8 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H), 6.23 (d, J = 8.1 Hz, 1H), 6.16 (d, J = 7.8 Hz, 1H), 1.40 (s, 9H). MALDI-TOF MS (mass m/z): Calcd for $C_{18}H_{22}BrN_3S_2$, 543.04; Found, 543.69 [M^+].

10-(4-(tert-butyl)phenyl)-3-(7-(4-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)phenyl)benzo[c][1,2,5]thiadiazol-4-yl)-10H-phenothiazine (PIBz-3-PTZ)

In a 100 mL round flask, A mixture of M8 (543 mg, 1 mmol), PPIB (496 mg, 1 mmol), K_2CO_3 (2.76 g, 20 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), 10 mL distilled water and 20 mL toluene was stirred and refluxed at 90 °C under N_2 protection for 24 hours. The mixture was washed three times with 30 mL water and extracted with dichloromethane. The organic phase was collected and dried by anhydrous Na_2SO_4, and then the solvent was evaporated. The residue was purified via column chromatography eluting with petroleum ether-dichloromethane (1:2, v/v) mixtures to afford red solid. (424 mg, yield: 51%). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, TMS) δ (ppm): 8.88 (d, J = 6.0 Hz, 1H), 8.84 (d, J = 6.6 Hz, 1H), 8.79 (d, J = 6.8 Hz, 1H), 8.00 (d, J = 6.7 Hz, 2H), 7.82 (m, 4H), 7.72 (m, 10H), 7.57 (t, J = 7.3 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.33 (t, J = 5.9 Hz, 1H), 7.25 (d, J = 6.6 Hz, 1H), 7.07 (d, J = 5.5 Hz, 1H), 6.95 – 6.82 (m, 2H), 6.37 (d, J = 6.9 Hz, 1H), 6.27 (d, J = 6.7 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm): 157.04, 156.31, 154.97, 149.37, 147.23, 142.62, 141.48, 130.41, 129.69, 129.25, 127.77, 125.99, 125.65, 122.12, 112.26. MALDI-TOF MS (mass m/z): Calcd for $C_{55}H_{39}N_5S_2$, 833.26; Found, 883.78 [M^+]. Anal. Calcd (%) for $C_{55}H_{39}N_5S_2$: C, 79.20; H, 4.71; N, 8.40; S, 7.69. Found: C, 79.29; H, 4.63; N, 8.33; S, 7.71.

10-(4-(7-(4-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)phenyl)benzo[c][1,2,5]thiadiazol-4-yl)phenyl)-10H-phenothiazine (PIBz-10P-PTZ)

In a 100 mL round flask, A mixture of M4 (487 mg, 1 mmol), PPIB (496 mg, 1 mmol), K_2CO_3 (2.76 g, 20 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), 10 mL distilled water and 20 mL toluene was stirred and refluxed at 90 °C under N_2 protection for 24 hours. The mixture was washed three times with 30 mL water and extracted with dichloromethane. The organic phase was collected and dried by anhydrous Na_2SO_4, and then the solvent was evaporated. The residue was purified via column chromatography eluting with petroleum ether-dichloromethane (1:2, v/v) mixtures to afford red solid. (470 mg, yield: 60%). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, TMS) δ (ppm): 8.85 (d, J = 8.2 Hz, 1H), 8.79 (d, J = 8.1 Hz, 1H), 8.27 (d, J = 7.4 Hz, 2H), 8.06 (d, J = 7.7 Hz, 2H), 7.94 (d, J = 7.5 Hz, 2H), 7.78 (m, J = 38.3, 26.9, 7.2 Hz, 10H), 7.58 (t, J = 10.5 Hz, 3H), 7.34 (t, J = 7.7 Hz, 1H), 7.25 (d, J = 7.9 Hz, 1H), 7.13 (d, J = 7.3 Hz, 2H), 7.00 (t, J = 7.5 Hz, 2H), 6.93 (t, J = 7.2 Hz, 2H), 6.54 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm): 153.97, 150.24, 143.95, 141.66, 138.85, 137.47, 135.43, 132.73, 132.45, 131.35, 130.35, 129.99, 129.55, 129.45, 129.22, 129.07, 128.29, 128.19, 127.35, 127.00, 126.95, 126.33, 125.72, 125.00, 124.16, 123.15, 122.95, 121.75, 120.91, 117.37 MALDI-TOF MS (mass m/z): Calcd for $C_{51}H_{31}N_5S_2$, 777.20; Found, 776.82 [M^+]. Anal. Calcd (%) for $C_{51}H_{31}N_5S_2$:

C, 78.74; H, 4.02; N, 9.00; S, 8.24. Found: C, 78.65; H, 4.03; N, 8.93; S, 8.39.

10-(7-(4-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)phenyl)benzo[c][1,2,5]thiadiazol-4-yl)-10H-phenothiazine (PIBz-10-PTZ)

In a 100 mL round flask, A mixture of M1 (411 mg, 1 mmol), PPIB (496 mg, 1 mmol), K_2CO_3 (2.76 g, 20 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), 10 mL distilled water and 20 mL toluene was stirred and refluxed at 90 °C under N_2 protection for 24 hours. The mixture was washed three times with 30 mL water and extracted with dichloromethane. The organic phase was collected and dried by anhydrous Na_2SO_4, and then the solvent was evaporated. The residue was purified via column chromatography eluting with petroleum ether-dichloromethane (1:2, v/v) mixtures to afford red solid. (455 mg, yield: 65%). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, TMS) δ (ppm): 8.85 (d, J = 6.7 Hz, 1H), 8.80 (d, J = 6.5 Hz, 1H), 8.07 (d, J = 6.2 Hz, 2H), 7.99 (d, J = 5.9 Hz, 1H), 7.90 (m, J = 10.3, 6.2 Hz, 3H), 7.86 – 7.65 (m, 3H), 7.60 (t, J = 6.0 Hz, 1H), 7.35 (t, J = 5.9 Hz, 1H), 7.26 (d, J = 6.5 Hz, 1H), 7.11 (d, J = 5.9 Hz, 2H), 6.88 (t, J = 5.7 Hz, 2H), 6.82 (t, J = 6.0 Hz, 2H), 6.12 (d, J = 6.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm): 174.15, 164.28, 154.77, 153.69, 150.14, 147.07, 145.05, 143.55, 138.81, 137.60, 135.88, 134.48, 132.69, 130.35, 130.01, 139.60, 129.42, 129.21, 128.47, 127.29, 126.96, 126.92, 126.35, 125.77, 125.05, 124.18, 123.18, 122.97, 122.83, 121.16, 120.93, 120.69, 119.45, 115.80. MALDI-TOF MS (mass m/z): Calcd for $C_{45}H_{27}N_5S_2$, 701.17; Found, 701.85 [M^+]. Anal. Calcd (%) for $C_{45}H_{27}N_5S_2$: C, 77.01; H, 3.88; N, 9.98; S, 9.14. Found: C, 77.09; H, 3.94; N, 10.00; S, 9.13.

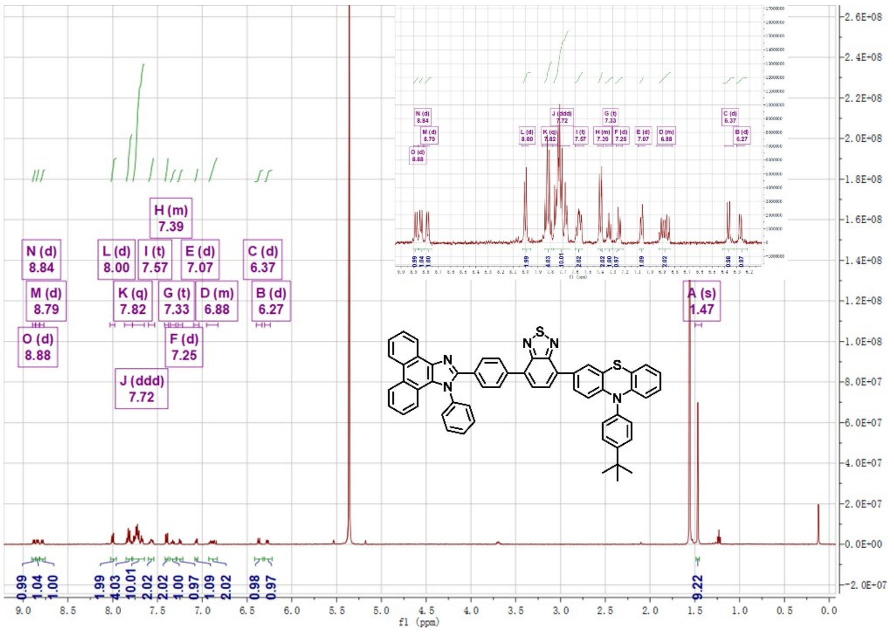


Fig. S1 ^{1}H NMR spectra of **PIBz-3-PTZ** in deuterated CD_2Cl_2.

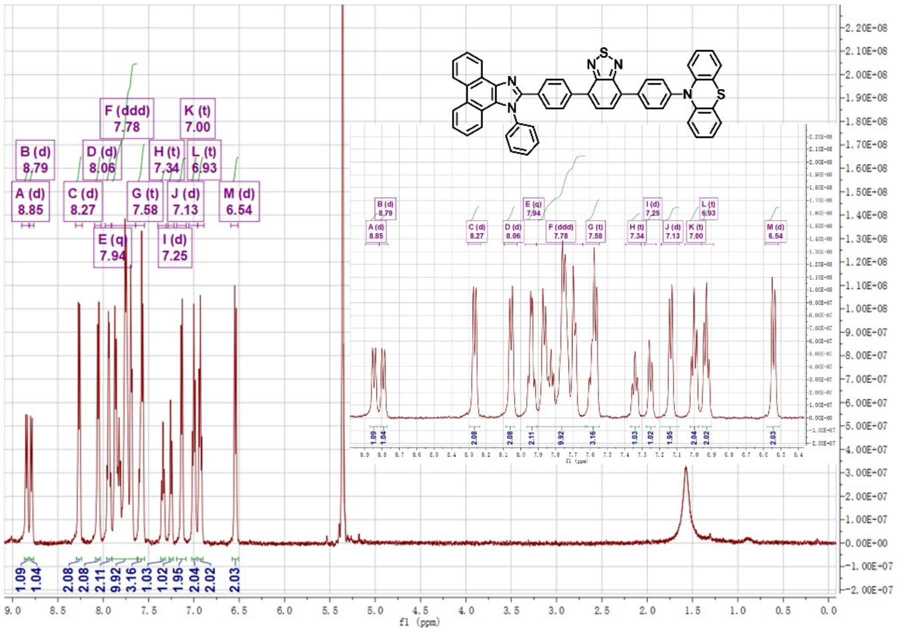


Fig. S2 ^{1}H NMR spectra of **PIBz-10P-PTZ** in deuterated CD_2Cl_2.

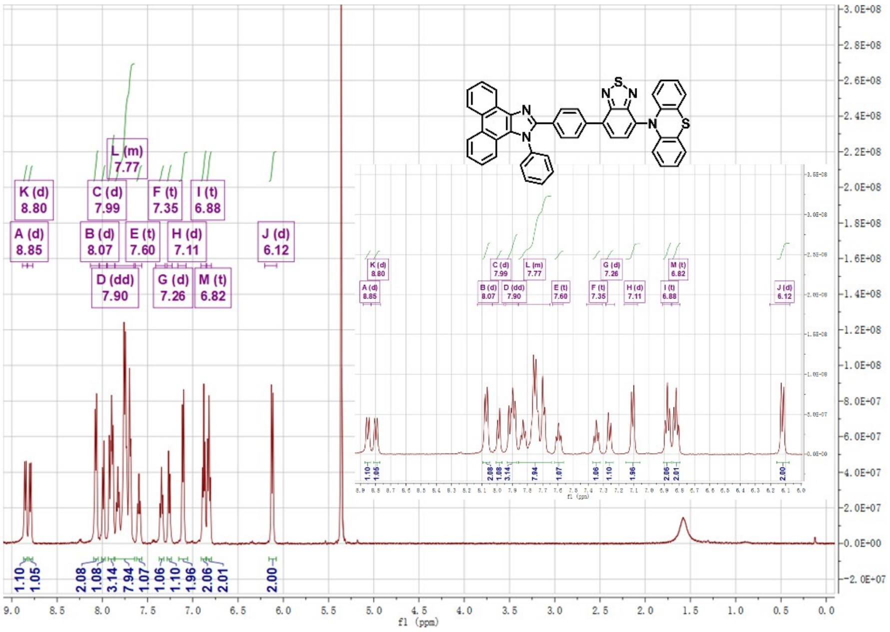


Fig. S3 ^{1}H NMR spectra of **PIBz-10-PTZ** in deuterated CD_2Cl_2.

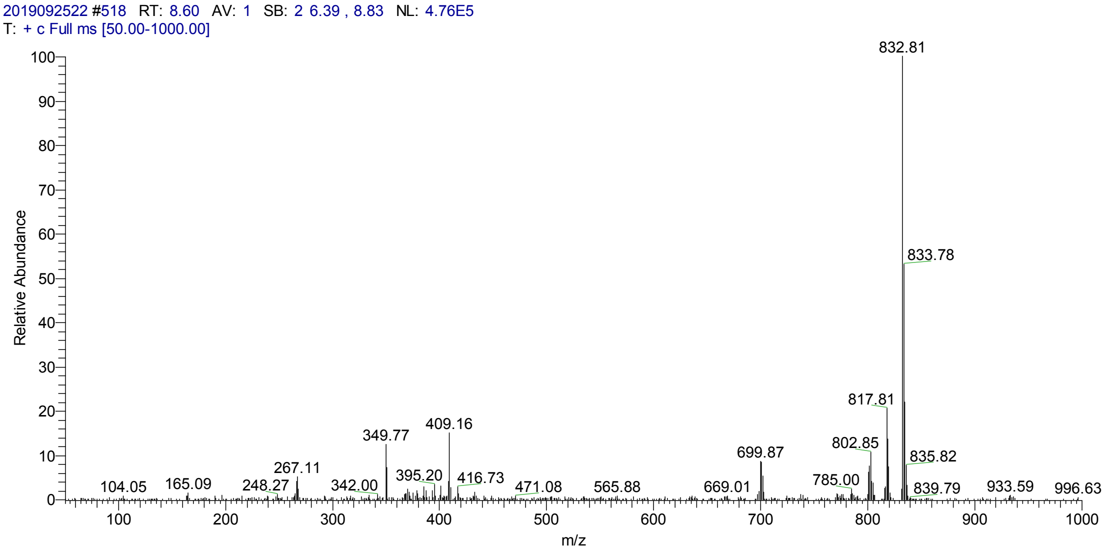


Fig. S4 MALDI-TOF spectrum of **PIBz-3-PTZ**.

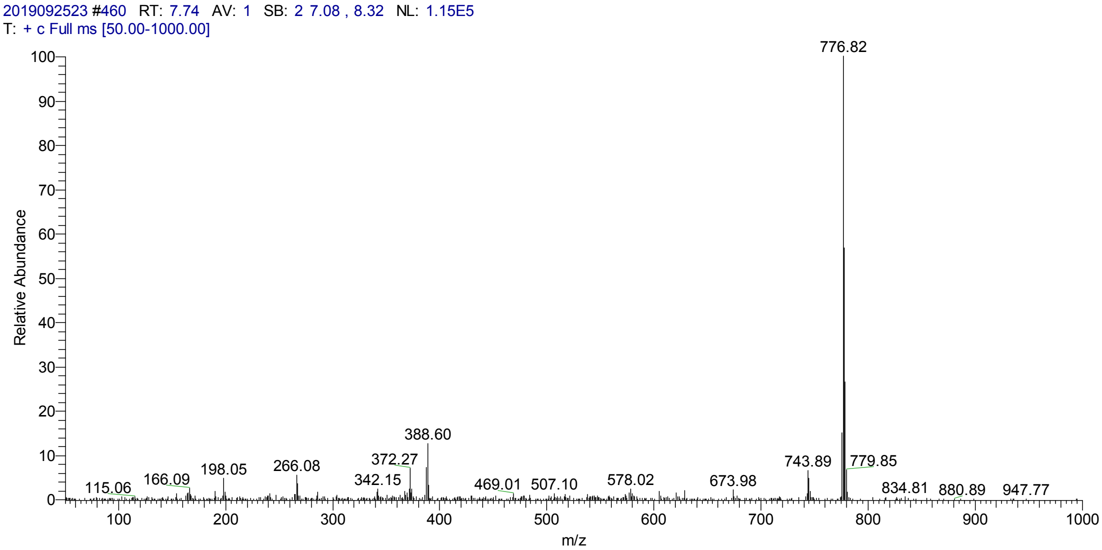


Fig. S5 MALDI-TOF spectrum of **PIBz-10P-PTZ**.

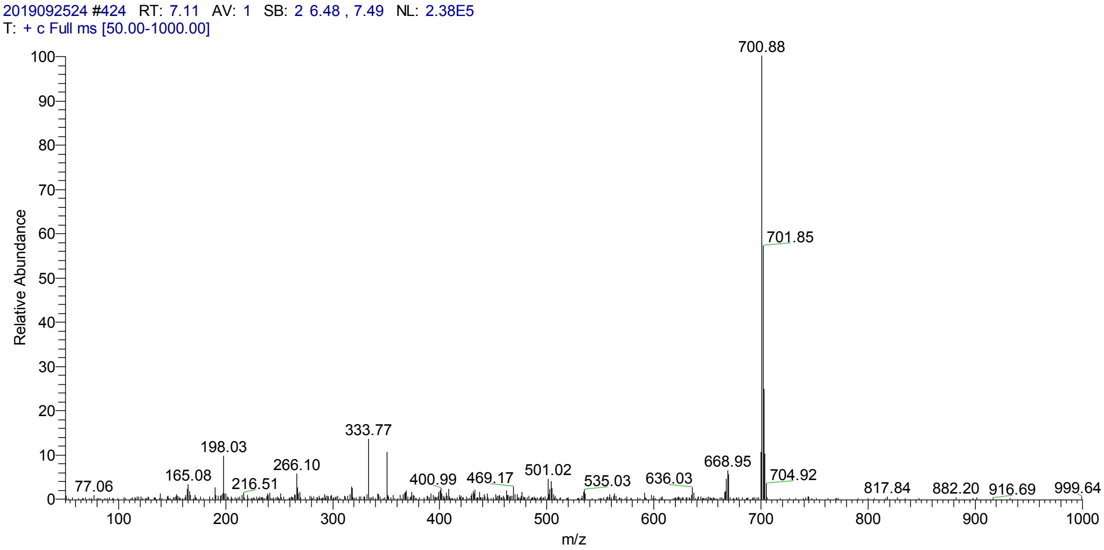


Fig. S6 MALDI-TOF spectrum of **PIBz-10-PTZ**.

3 Theoretical Calculations

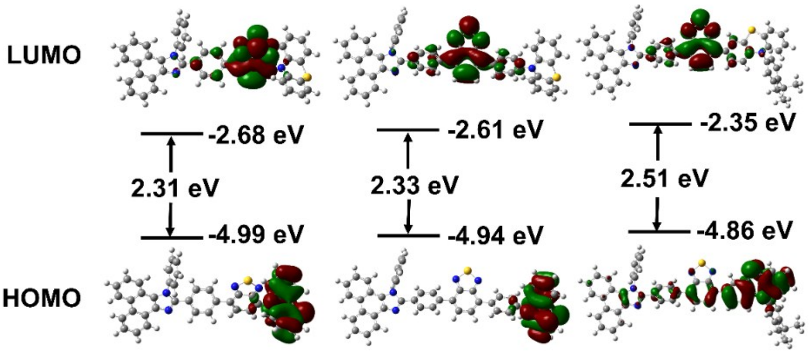


Fig. S7 The spatial distributions and energy levels of frontier molecular orbitals of **PIBz-10-PTZ**, **PIBz-10P-PTZ** and **PIBz-3-PTZ**.

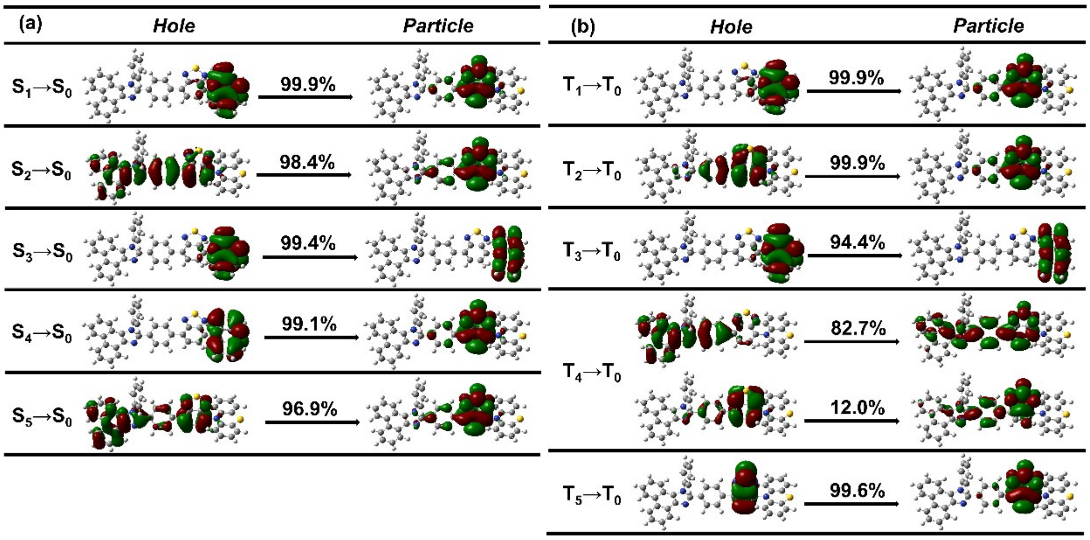


Fig. S8 Natural transition orbital (NTO) analysis for **PIBz-10-PTZ**.

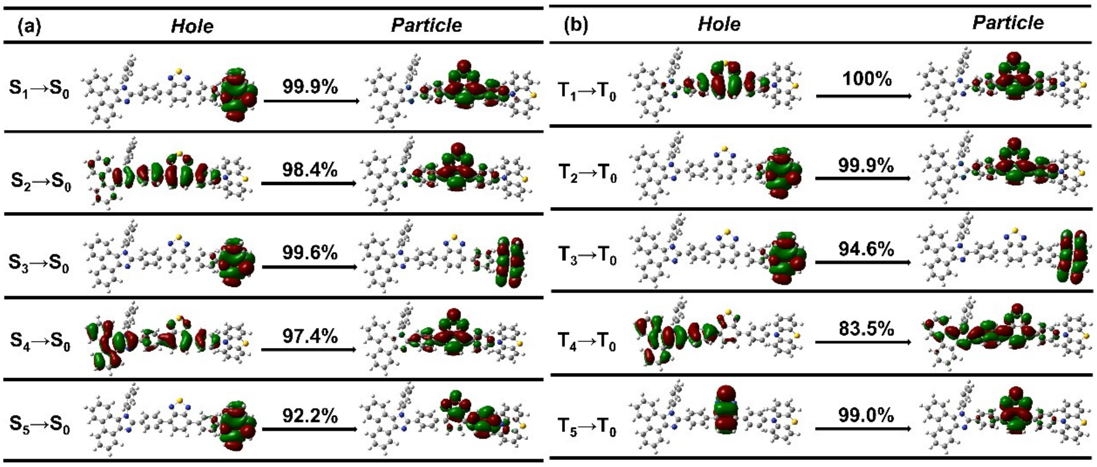


Fig. S9 Natural transition orbital (NTO) analysis for **PIBz-10P-PTZ**.

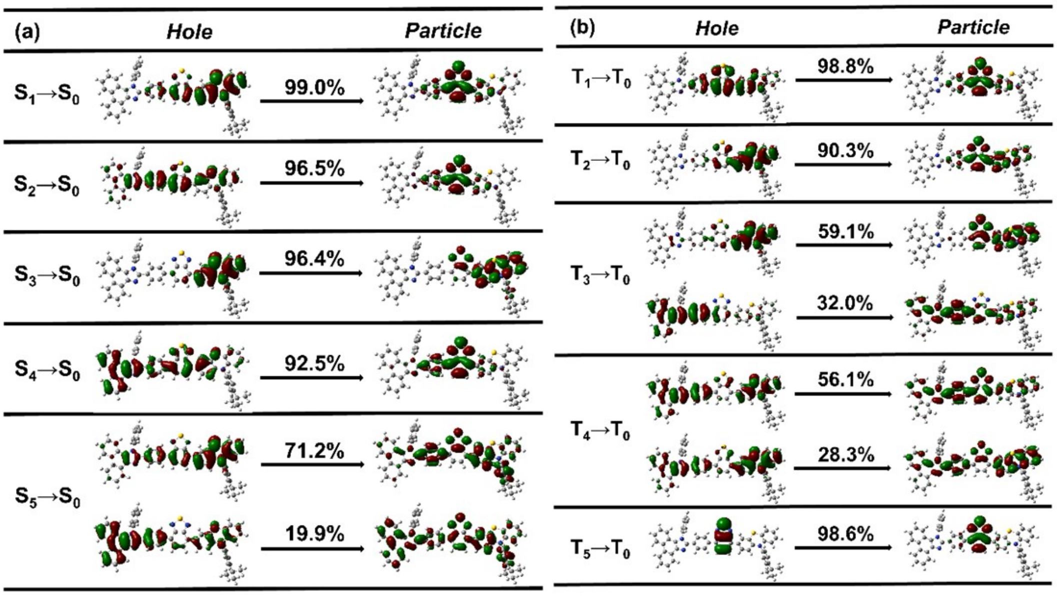


Fig. S10 Natural transition orbital (NTO) analysis for **PIBz-3-PTZ**.

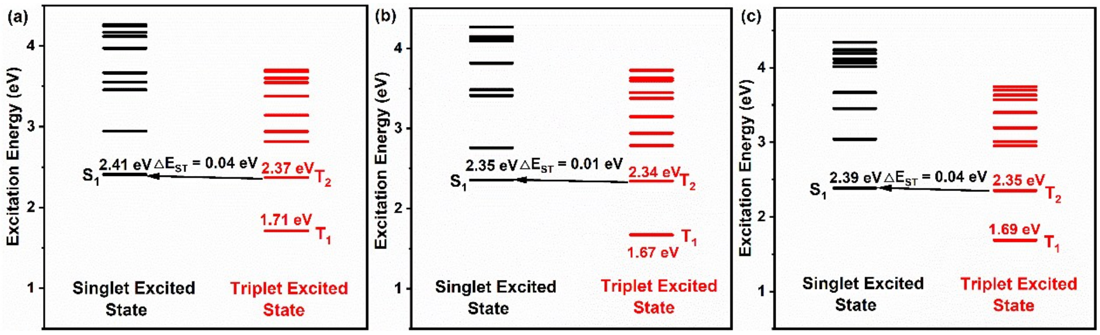


Fig. S11 Energy diagram of calculated singlet and triplet excited states of **PIBz-10-PTZ** (a), **PIBz-10P-PTZ** (b) and **PIBz-3-PTZ** (c).

4 Photophysical Properties

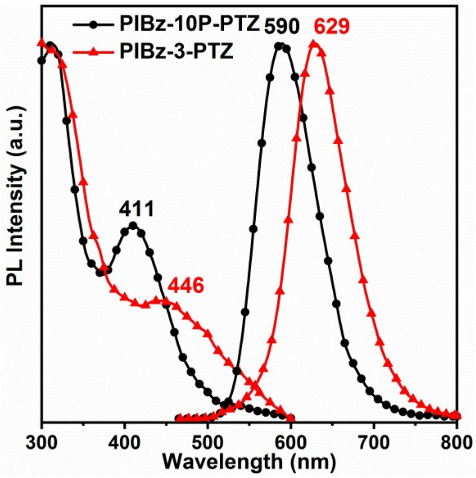


Fig. S12 Absorption and PL spectra of 5% doped polymethyl methacrylate (PMMA) films.

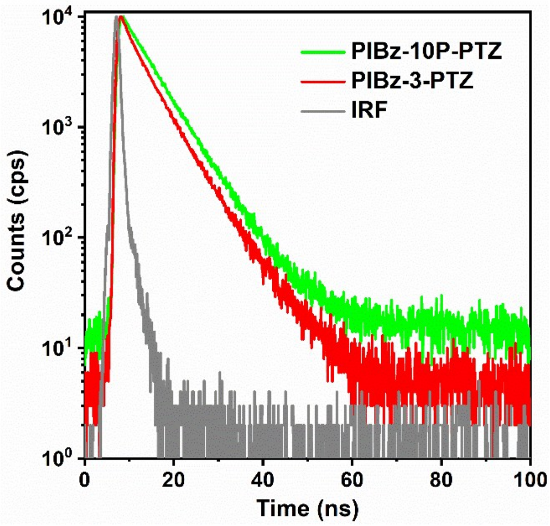


Fig. S13 Lifetime measurement of **PIBz-10P-PTZ** and **PIBz-3-PTZ** in thin films.

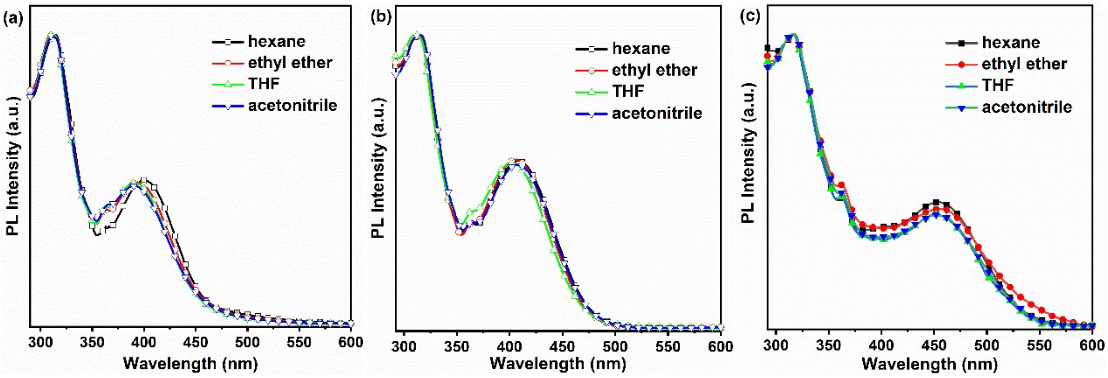


Fig. S14 Solvation effects on UV-vis absorption of **PIBz-10-PTZ** (a), **PIBz-10P-PTZ** (b) and **PIBz-3-PTZ** (c).

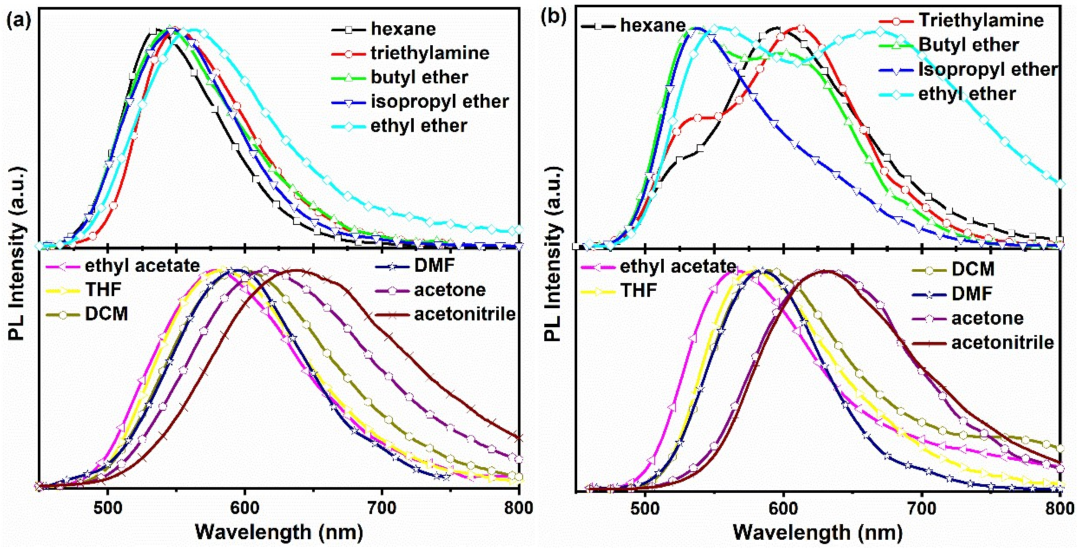


Fig. S15 Solvatochromic PL spectra of **PIBz-10P-PTZ** (a) and **PIBz-3-PTZ** (b) in different solvents.

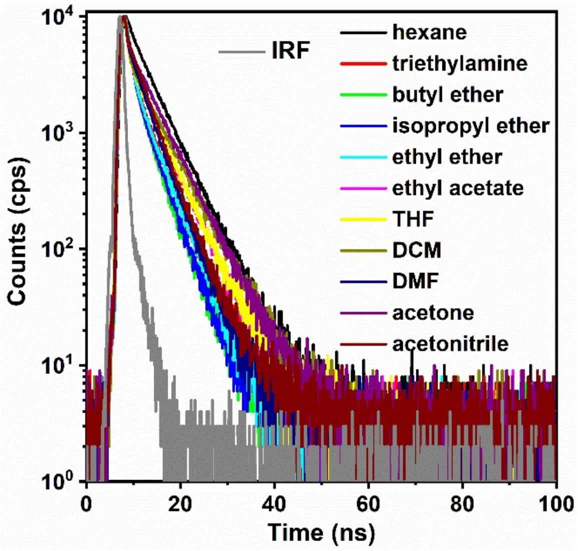


Fig. S16 Lifetime measurement of the **PIBz-10P-PTZ** in different solvents.

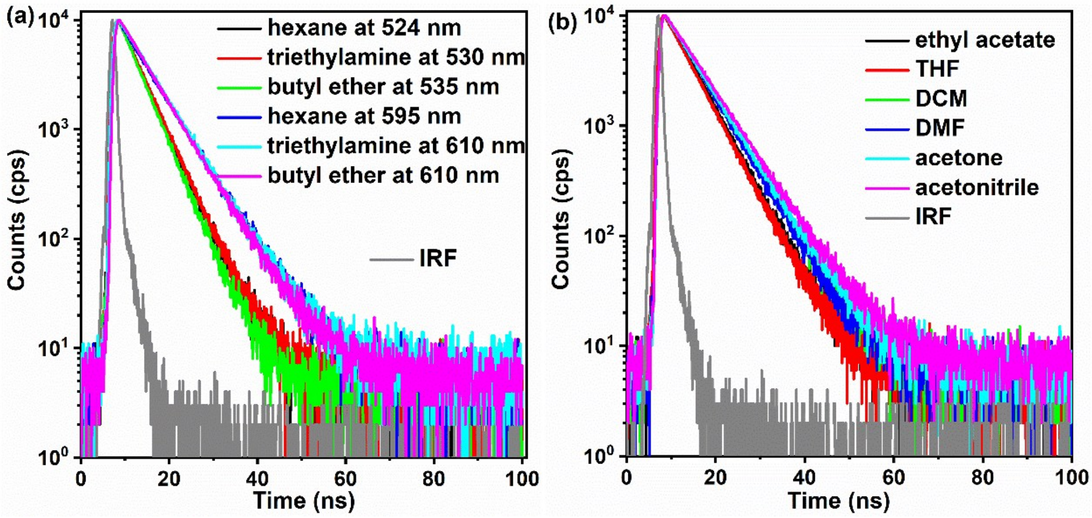


Fig. S17 (a) Lifetime measurement of the **PIBz-3-PTZ** in hexane, trimethylamine and butyl ether at different wavelength. (b) Lifetime measurement of the **PIBz-3-PTZ** in other solvents.

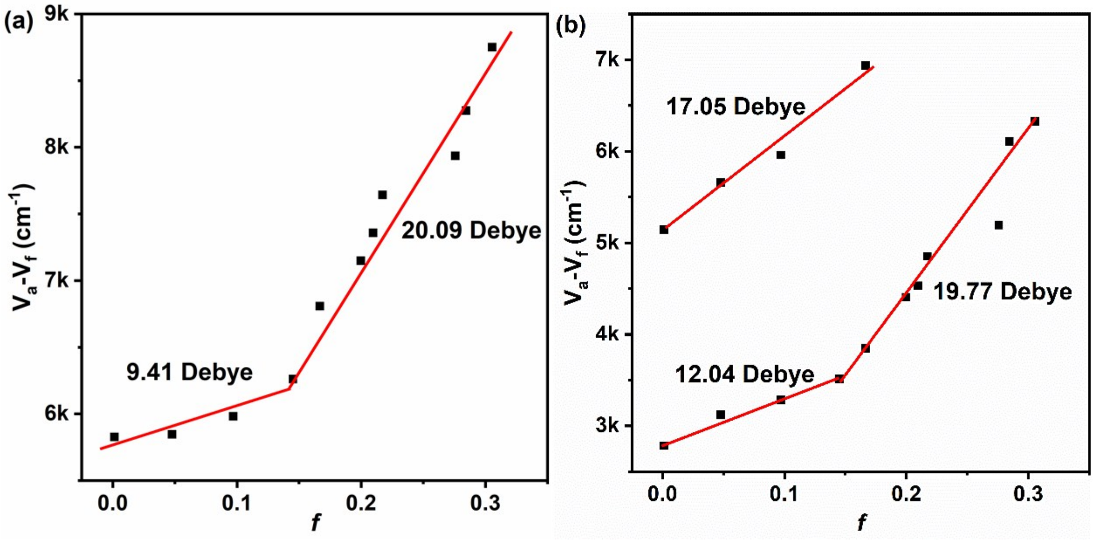


Fig. S18 Linear correlation of orientation polarization (*f*) of solvent media with the Stokes shift ($\upsilon_a - \upsilon_f$; a: absorbed light; f: fluorescence) for **PIBz-10P-PTZ** (a) and **PIBz-3-PTZ** (b).

Table S1. Detailed photophysical data of **PIBz-10P-PTZ** in different solvents

solvents	f (ε,n)	**PIBz-10P-PTZ**			PLQY
		λ_a (nm)	λ_f (nm)	υ_a-υ_f (cm^{-1})	(%)
n-hexane	0.0012	409	537	5827.90382	40.2
Triethylamine	0.048	411	541	5846.61189	38.6
Butyl ether	0.096	411	545	5982.27639	34.1
Isopropyl ether	0.145	408	548	6261.62874	30.2
ethyl ether	0.167	407	563	6808.03523	25.6
ethyl acetate	0.200	409	578	7148.83969	6.0
THF	0.210	407	584	7358.32061	2.5
DCM	0.217	408	595	7643.15506	1.1
DMF	0.276	409	599	7936.05105	0.6
acetone	0.284	408	616	8276.03769	-
acetonitrile	0.305	409	637	8751.29062	-

f: the orientational polarizability of the solvent; λ_a: absorption maximum; λ_f: emission maximum; υ_a-υ_f : the Stokes shifts.

Table S2. Detailed photophysical data of **PIBz-3-PTZ** in different solvents

solvents	f (ε,n)	**PIBz-3-PTZ**					PLQY
		λ_a (nm)	λ_f (nm)		υ_a-υ_f (cm^{-1})		(%)
n-hexane	0.0012	453	523	596	2884.16401	5143.00514	78.8
Triethylamine	0.048	453	533	610	3172.84004	5659.81961	68.2
Butyl ether	0.096	451	537	598	3286.43319	5959.81961	67.6
Isopropyl ether	0.145	449	538	-	3516.23258	-	56.9
ethyl ether	0.167	452	554	669	3846.64192	6937.32081	51.3
ethyl acetate	0.200	449	566	-	4407.21066	-	49.5
THF	0.210	451	580	-	4531.19554	-	45.0
DCM	0.217	455	588	-	4854.73431	-	23.2
DMF	0.276	451	585	-	5195.02031	-	5.1
acetone	0.284	456	632	-	6107.03975	-	1.6
acetonitrile	0.305	455	634	-	6326.1055	-	-

f: the orientational polarizability of the solvent; λ_a: absorption maximum; λ_f: emission maximum; υ_a-υ_f : the Stokes shifts.

5 Electroluminescence properties

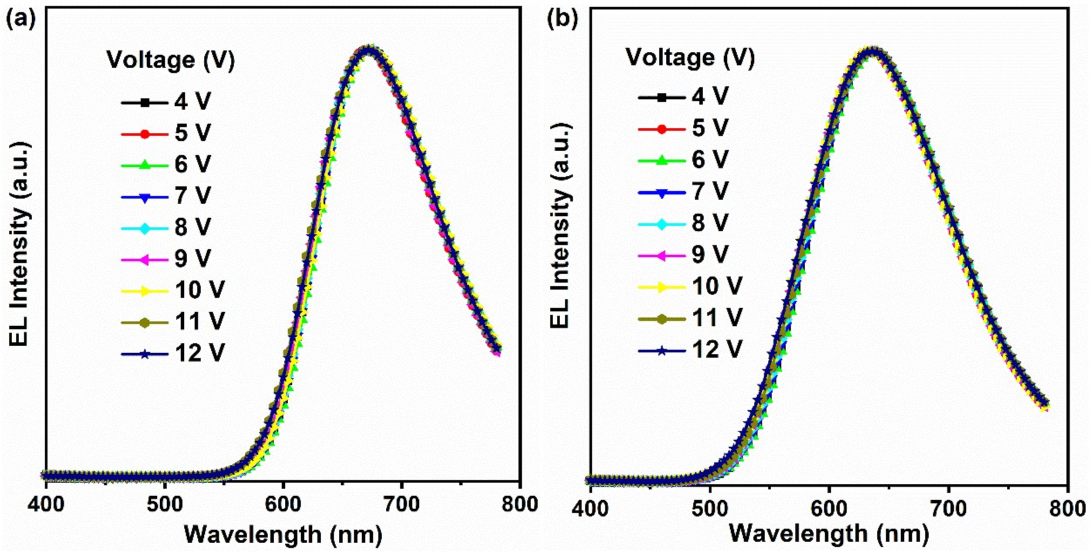


Fig. S19 The EL spectra of the nondoped device **PIBz-10P-PTZ** (a) and **PIBz-3-PTZ** (b) under the different voltages.

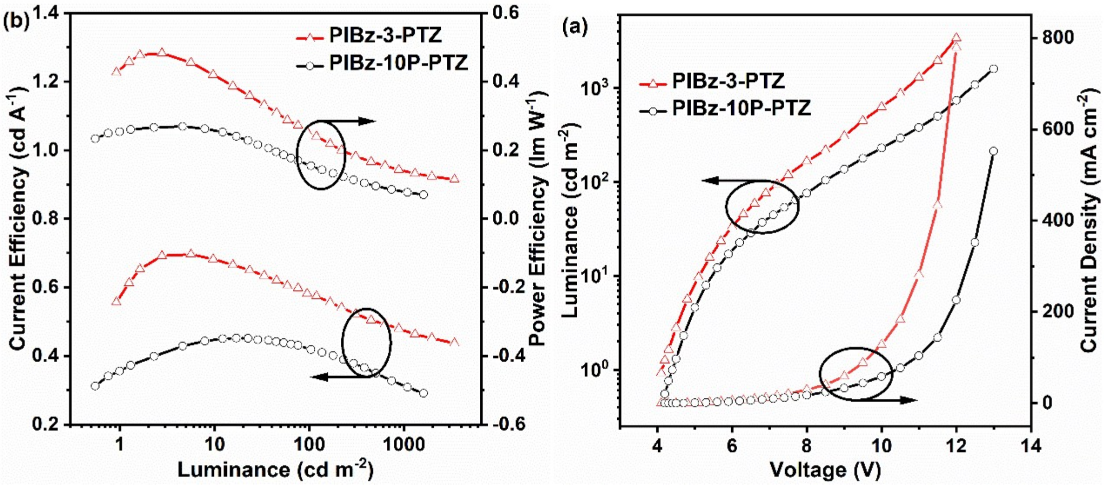


Fig. S20 (a) Luminance-voltage-current density characteristics. (b) Current efficiency-luminance-power efficiency curves of the nondoped device **PIBz-10P-PTZ** and **PIBz-3-PTZ**.

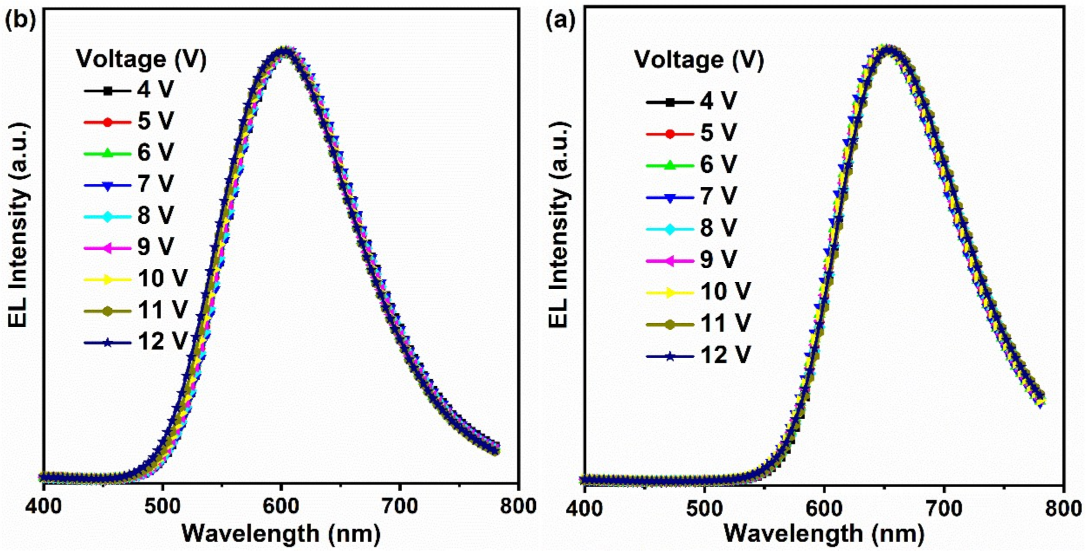


Fig. S21 The EL spectra of the doped device **PIBz-10P-PTZ** (a) and **PIBz-3-PTZ** (b) under the different voltages.

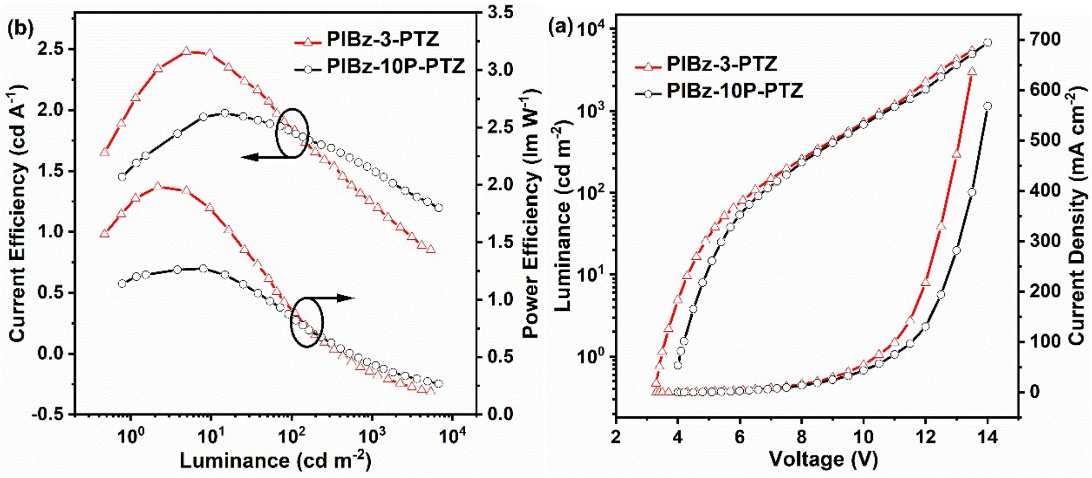
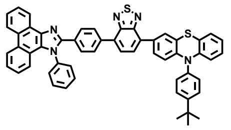
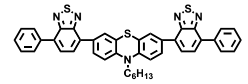
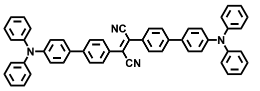
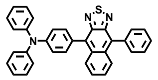
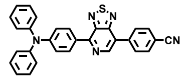
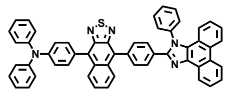
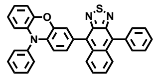
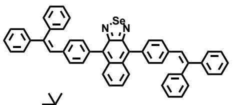
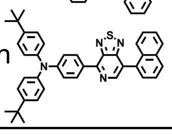


Fig. S22 (a) Luminance-voltage-current density characteristics. (b) Current efficiency-luminance-power efficiency curves of the doped device **PIBz-10P-PTZ** and **PIBz-3-PTZ**.

Table S3. Relevant devices performance data of other reported high-efficiency DR/NIR nondoped fluorescent OLEDs

Compound	Structure	*L*maxa [cd m-2]	EQEb [%] max/100/1000 cd	EL λmaxc	CIEd (x, y)
PIBz-3-PTZ This work		3403	2.02/1.69/1.37	672	(0.67,0.32)
PTZ-BZP Ref 4		780	1.54/-/-	700	(0.70,0.30)
TPATCN Ref 5		7025	2.58/-/-	675	(0.67,0.32)
TPA-NZP Ref 6		4574	2.8/1.7/1.6	~670	(0.67,0.32)
p-TPA-PT-CN Ref 7		640	1.47/1.35/-	700	(0.70,0.30)
TNZPPI Ref 8		1938	2.48/-/-	686	(0.69,0.30)
PXZ-3-NZP Ref 9		780	0.82/-/-	738	(0.70,0.29)
NSeD Ref 10		-	1.1/1.1/1.1	688	(0.69,0.30)
TPA-N-pyT-naph Ref 11		~2000	0.96/-/-	630	(0.62,0.38)

[a] L_{max}: maximum luminance; [b] EQE: external quantum efficiency of maximum/at 100 cd m^{-2}/1000 cd m^{-2}; [c] EL λ_{max}: EL emission peak of EL spectrum at 100 cd m^{-2}; [d] CIE: Commission International de l'Éclairage (CIE) coordinates at 100 cd m^{-2}.

6 Notes and references

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