

Electronic Supplementary Information

Strongly yellow photo- and electroluminescent palladium(II) complexes via metal-assisted thermally activated delayed fluorescence

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General and Instruments

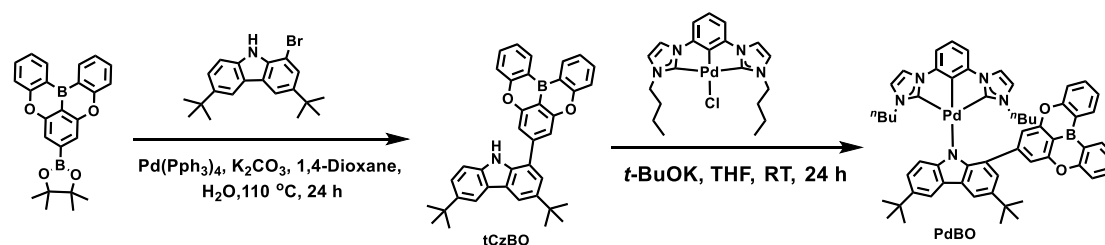
All starting materials were obtained from commercial suppliers and were used without further purification. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in deuterated chloroform (CDCl_3) solution on Bruker Avance 500 MHz FT-NMR spectrometer with tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (CDCl_3 : δ 7.26 ppm for ^1H , DMSO- d_6 : δ 3.33 ppm for ^1H and THF- d_8 : δ 67.21, 25.31 ppm for ^{13}C at room temperature). Elemental analyses were measured on a Vario Micro cube with CHN mode. High resolution mass spectra (HRMS) were measured on a Bruker maxis MALDI-FTMS mass spectrometer. Thermal gravity analysis (TGA) was performed on a TGA-Q50 instrument with a heating rate of 10 $^\circ\text{C}/\text{min}$ from 50 to 800 $^\circ\text{C}$ under a nitrogen atmosphere. The temperature at 5% weight loss was used as the decomposition temperature (T_d). Ultraviolet-Visible (UV-vis) absorption spectra were recorded on a Shimadzu UV-2600 recording spectrophotometer (Shimadzu, Japan). Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer (Hitachi, Japan). The transient photoluminescence spectra were measured using a single photon counting spectrometer (Picoquant, FluoTime 300, Germany). Variable temperature transient photoluminescence decay measurements were performed with the aid of an Oxford 2 Instruments continuous flow cryostat. Absolute PLQYs were obtained using a Quantaaurus-QY measurement system (C9920-02, Hamamatsu Photonics) equipped with a calibrated integrating sphere under argon atmosphere. Cyclic voltammetry (CV) measurements were carried out on a CHI600 electrochemical analyzer (Chenhua, China) at room temperature, with a conventional three-electrode system consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl standard electrode used as the reference electrode. Dichloromethane and tetrabutylammonium hexafluorophosphate (0.1 M) was used as the solvent and supporting electrolyte.

Single Crystal Analysis

Single crystals suitable for X-ray diffraction analysis were obtained by evaporation of a mixture of dichloromethane and n-hexane solution (CH_2Cl_2 : $n\text{-C}_6\text{H}_{14}$ = 1:5) over a period of several days. X-ray single-crystal diffraction data of all compounds were recorded on a Bruker D8 Venture diffractometer using $\text{GaK}\alpha$ radiation ($\lambda = 1.34139 \text{ \AA}$) for **PdBO** and $\text{GaK}\alpha$ radiation ($\lambda = 1.34138 \text{ \AA}$) for **DPdBO**. The crystals were kept at 170 and 200 K during data collection. Full crystallographic information in CIF format has been deposited at the Cambridge Crystallographic Data Center (CCDC) under deposition numbers 2225411 and 2393758 for **PdBO** and **DPdBO**, respectively. The data files can be obtained free of charge from CCDC.

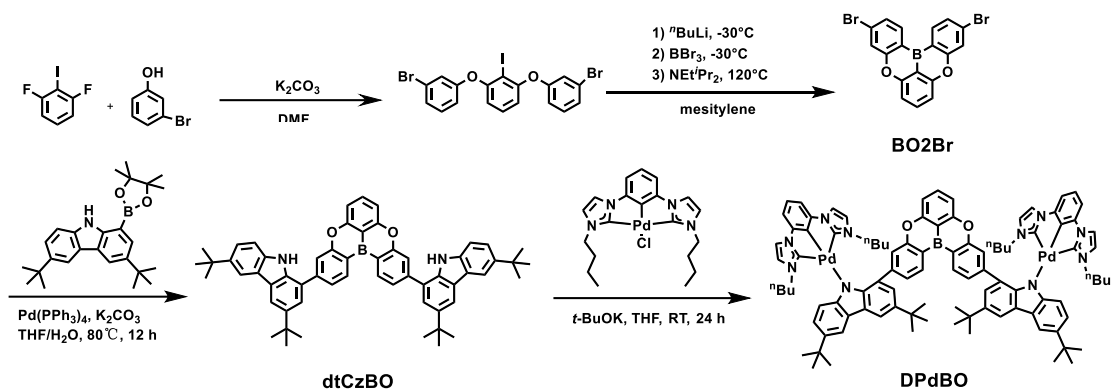
Synthesis

(C[∧]C[∧]C)PdCl: To a round-bottom flask, C[∧]C[∧]C ligand (1 g, 2.06 mmol), PdCl₂ (438 mg, 2.47 mmol), and NaOAc (676 mg, 8.24 mmol) were added. After the flask was evacuated and back-filled with argon (this process was repeated three times), DMF (20 mL) was added to the flask. The mixture was stirred at 140 °C in an oil bath for 3 days. After completion of the reaction, the reaction mixture was extracted with dichloromethane (15 mL × 3). The organic layer was washed with brine and dried over Na₂SO₄. The filtrate was concentrated in vacuo and purified by silica gel column chromatography with hexane/dichloromethane as an eluent. Yield: 167 mg (18%). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 1.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 1.8 Hz, 2H), 6.88 (s, 1H), 6.87 (s, 1H), 4.75 (t, *J* = 7.4 Hz, 4H), 1.87 (m, *J* = 7.6 Hz, 4H), 1.47 (m, *J* = 7.4 Hz, 4H), 0.96 (t, *J* = 7.4 Hz, 6H).



Scheme S1. The synthetic procedure of PdBO.

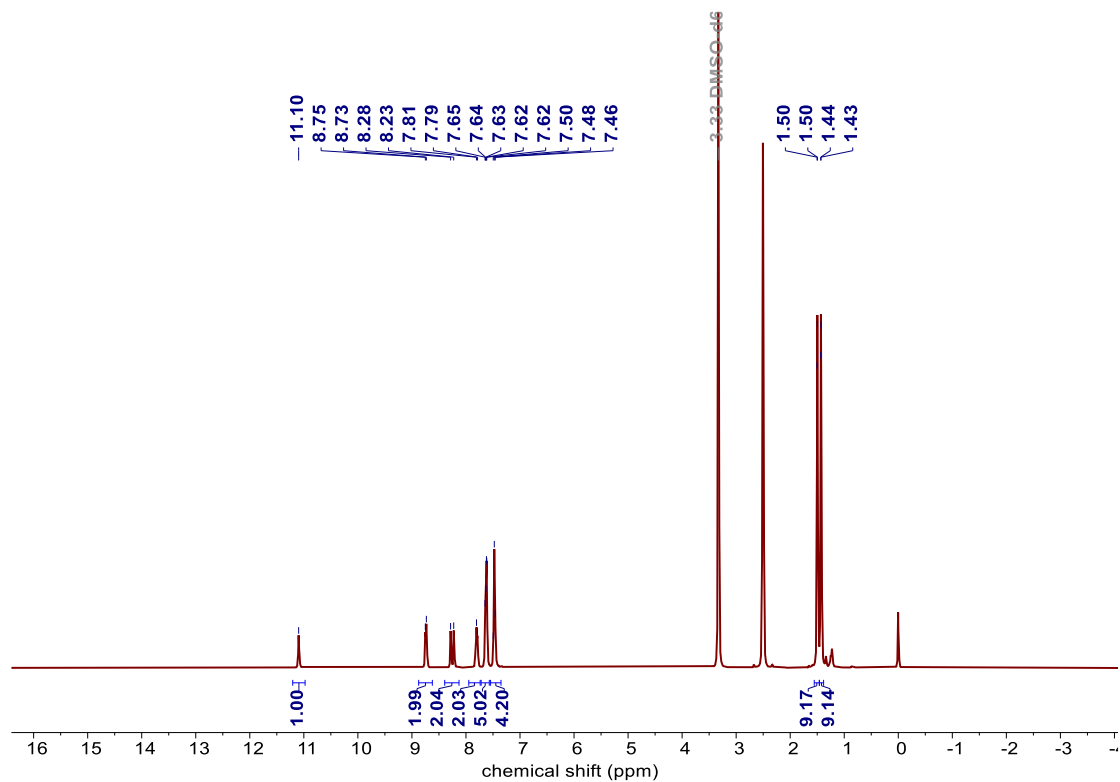
PdBO: tCzBO (200 mg, 0.37 mmol) and ^tBuOK (163 mg, 1.46 mmol) were dissolved in dry THF (20 mL) and stirred for 12 h under argon at room temperature, followed by addition of (C[∧]C[∧]C)PdCl (169 mg, 0.37 mmol). The reaction mixture was stirred for another 24 h. Then, the resulting mixture was filtered through Celite, and the solvent was removed under reduced pressure to afford a yellow solid. The solid was redissolved in dichloromethane, and hexane was added to precipitate the desired product as a yellow powder. Yield: 270 mg (76%). ¹H NMR (500 MHz, CDCl₃) δ 8.51 (dd, *J* = 7.7, 1.7 Hz, 2H), 8.20 (d, *J* = 2.0 Hz, 1H), 8.12 (d, *J* = 1.9 Hz, 1H), 7.62 (ddd, *J* = 8.5, 7.0, 1.7 Hz, 2H), 7.32 (td, *J* = 7.3, 1.1 Hz, 3H), 7.26 (s, 2H), 7.19 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.05 (s, 2H), 6.79 (d, *J* = 1.8 Hz, 2H), 6.72 (d, *J* = 1.9 Hz, 2H), 6.29 (t, *J* = 7.8 Hz, 1H), 5.83 (d, *J* = 7.8 Hz, 2H), 3.28 (ddd, *J* = 13.1, 9.9, 6.5 Hz, 2H), 3.16 (ddd, *J* = 13.1, 9.6, 6.3 Hz, 2H), 1.52 (s, 9H), 1.45 (s, 9H), 1.17 (th, *J* = 9.9, 6.6 Hz, 4H), 0.47 (ddq, *J* = 18.4, 9.0, 5.9 Hz, 2H), 0.38 (t, *J* = 7.1 Hz, 6H), 0.21 (dddd, *J* = 12.8, 9.9, 8.2, 6.1 Hz, 2H). ¹³C NMR (126 MHz, THF-*d*₈) δ 179.48, 161.46, 157.10, 151.88, 151.33, 149.36, 147.54, 146.71, 136.96, 136.23, 135.38, 133.57, 128.07, 127.37, 126.02, 124.38, 123.53, 123.00, 121.55, 121.27, 120.05, 119.21, 116.40, 116.12, 115.64, 115.05, 113.42, 111.28, 107.80, 50.07, 35.29, 35.15, 33.11, 20.14, 14.22. Anal. Calcd for C₅₈H₅₈BN₅O₂Pd: C, 71.50; N, 7.19; H, 6.00. Found: C, 71.43; N, 7.71, H, 5.52. HRMS-ESI: *m/z* calculated for C₈₀H₇₀N₉Pd⁺ [M]⁺ 973.3718, found 973.3703.



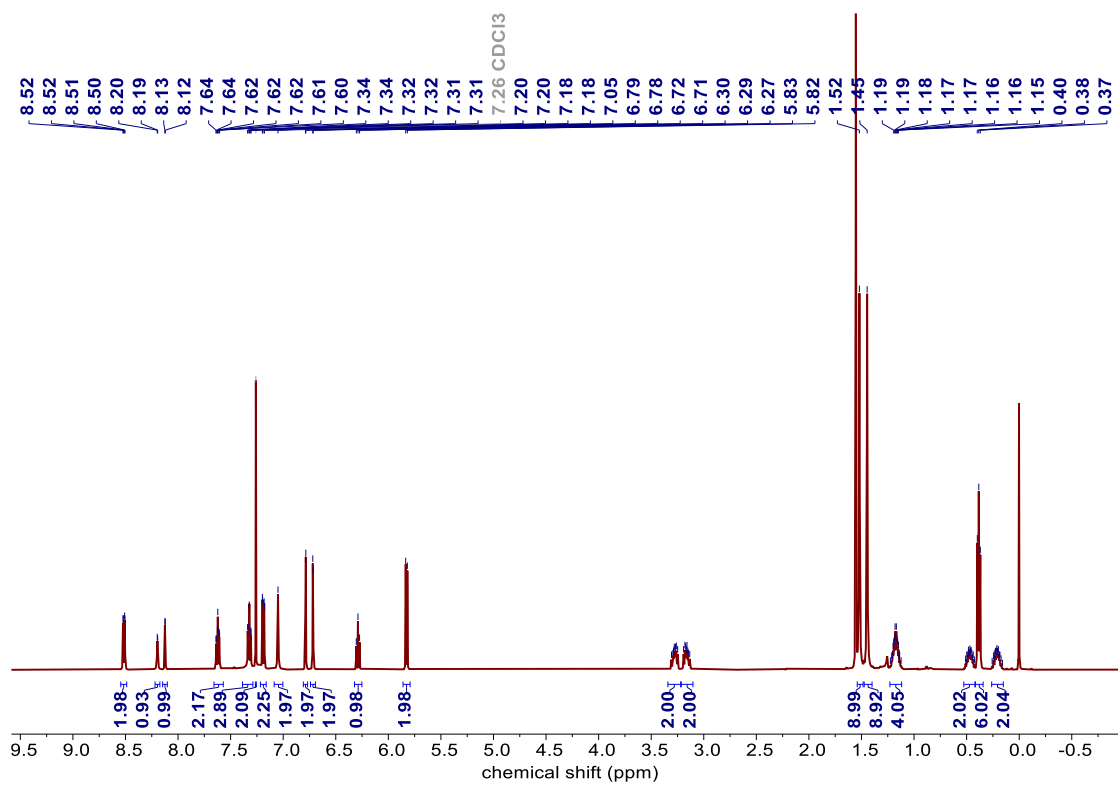
Scheme S2. The synthetic procedure of **DPdBO**.

dtCzBO: A mixture of **BO2Br** (856 mg, 2.00 mmol), **tCz-bpin** (1.783 g, 4.4 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) and K_2CO_3 (1.104 g, 8.00 mmol) was added into a 100 mL round bottle flask. After the flask was evacuated and back-filled with argon by three times, 30 mL THF/H_2O was added into the mixture and then heated at $80^\circ C$ overnight. After reaction and cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified through column chromatography using petroleum ether and dichloromethane as the eluent to give the product as white powder. Yield: 1.402 g, 85%. 1H NMR (500 MHz, $DMSO-d_6$) δ 11.08 (s, 2H), 8.92 (d, $J = 8.1$ Hz, 2H), 8.27 (d, $J = 1.8$ Hz, 2H), 8.21 (d, $J = 1.4$ Hz, 2H), 7.96 – 7.88 (m, 3H), 7.83 (dd, $J = 7.9$, 1.6 Hz, 2H), 7.61 (d, $J = 1.9$ Hz, 2H), 7.46 (d, $J = 1.3$ Hz, 4H), 7.38 (d, $J = 8.1$ Hz, 2H), 1.48 (s, 18H), 1.41 (s, 18H).

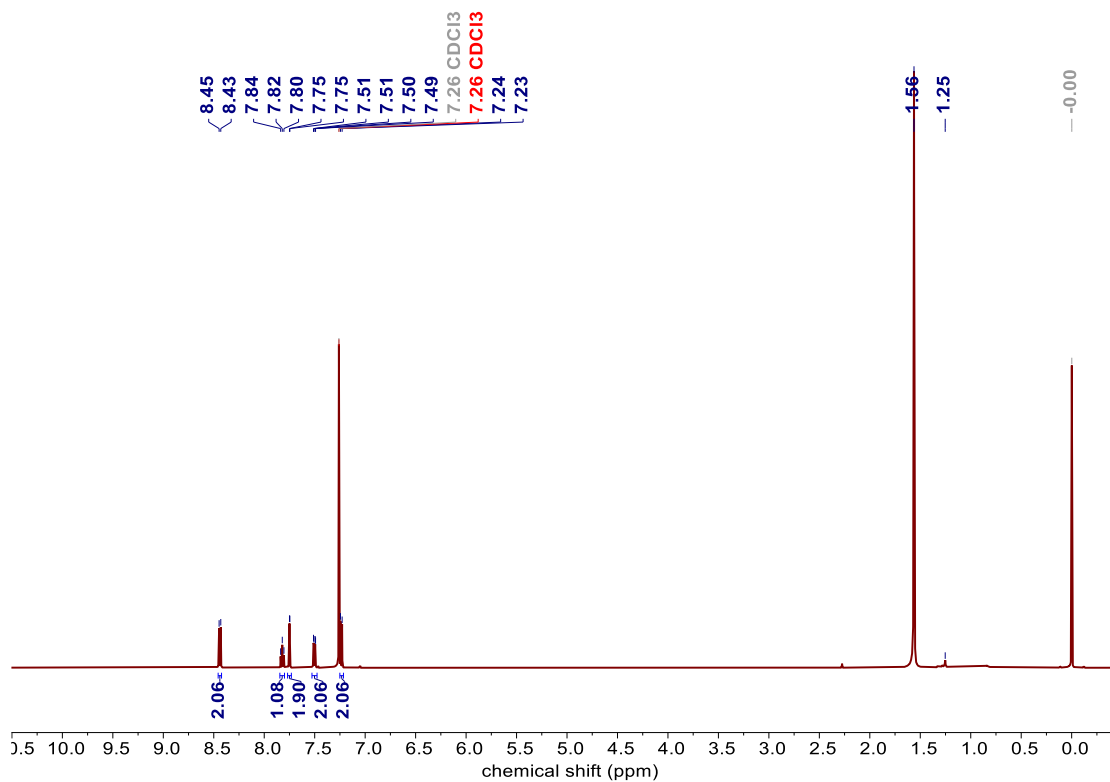
DPdBO: **dtCzBO** (198 mg, 0.24 mmol) and $tBuOK$ (107 mg, 0.96 mmol) were dissolved in dry THF (20 mL) and stirred for 12 h under argon at room temperature, followed by addition of $(C^*C^*C)PdCl$ (109 mg, 0.24 mmol). The reaction mixture was stirred for another 24 h. Then, the resulting mixture was filtered through Celite, and the solvent was removed under reduced pressure to afford a yellow solid. The solid was redissolved in dichloromethane, and hexane was added to precipitate the desired product as a yellow powder. Yield: 331 mg (82%). 1H NMR (500 MHz, $DMSO$) δ 8.15 (d, $J = 2.0$ Hz, 2H), 8.08 (d, $J = 2.0$ Hz, 2H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.70 – 7.62 (m, 3H), 7.58 (d, $J = 1.9$ Hz, 4H), 7.47 (d, $J = 8.5$ Hz, 2H), 7.29 (d, $J = 2.0$ Hz, 2H), 7.25 (d, $J = 1.9$ Hz, 4H), 7.19 (ddd, $J = 9.7$, 8.2, 1.8 Hz, 4H), 6.68 (d, $J = 8.1$ Hz, 2H), 6.20 (d, $J = 7.8$ Hz, 4H), 6.10 (dd, $J = 8.4$, 7.1 Hz, 2H), 3.18 (t, $J = 8.1$ Hz, 8H), 1.51 (s, 18H), 1.42 (s, 18H), 1.22 – 1.00 (m, 8H), 0.40 – 0.25 (m, 16H), 0.05 (dt, $J = 10.6$, 4.6 Hz, 4H). ^{13}C NMR (126 MHz, $THF-d_8$) δ 178.37, 159.06, 157.15, 150.25, 148.25, 148.07, 146.65, 145.63, 143.35, 141.92, 137.42, 135.79, 135.05, 132.34, 131.99, 126.75, 126.36, 124.85, 123.84, 123.11, 120.38, 118.94, 118.86, 115.36, 114.87, 114.42, 114.31, 107.29, 106.87, 48.98, 34.19, 34.07, 31.97, 19.01, 13.11. Anal. Calcd for $C_{98}H_{105}BN_{10}O_2Pd_2$: C, 70.12; N, 8.34; H, 6.31. Found: C, 69.97; N, 8.65; H, 5.81. HRMS-ESI: m/z calculated for $C_{98}H_{105}N_{10}Pd_2^+$ $[M]^+$ 1679.6622, found 1679.6624.



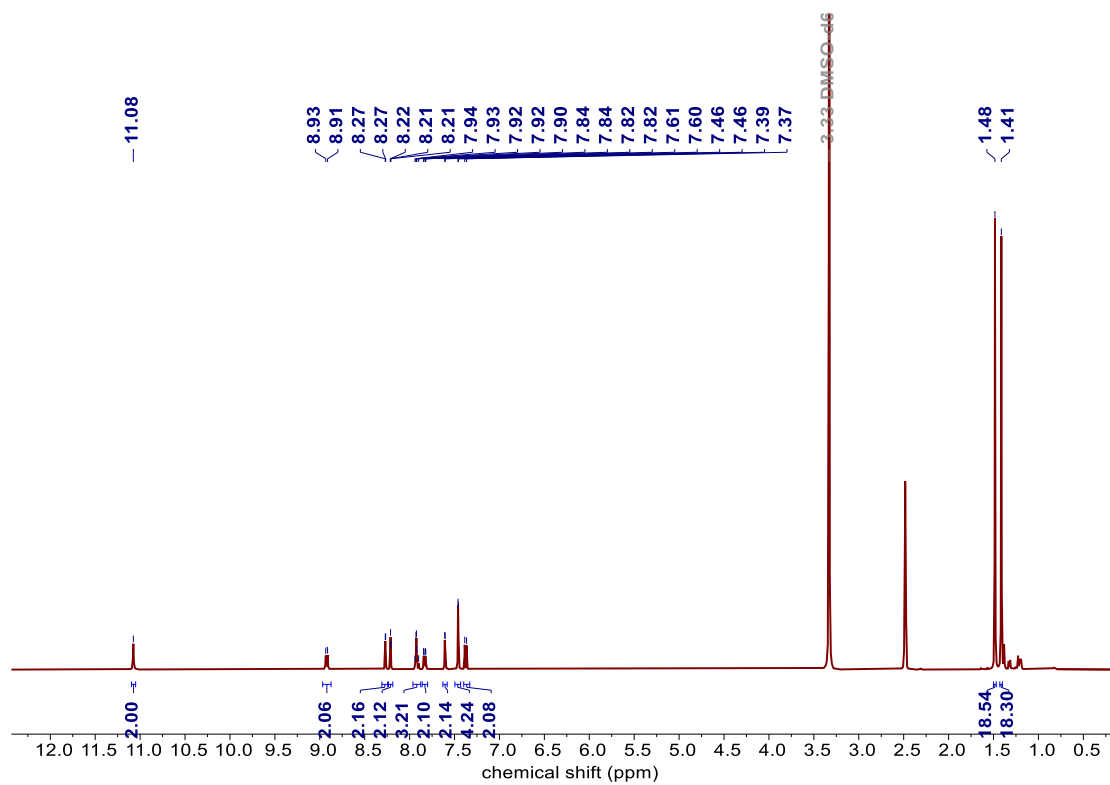
¹H NMR spectrum of tCzBO in DMSO-d₆ (500 MHz)



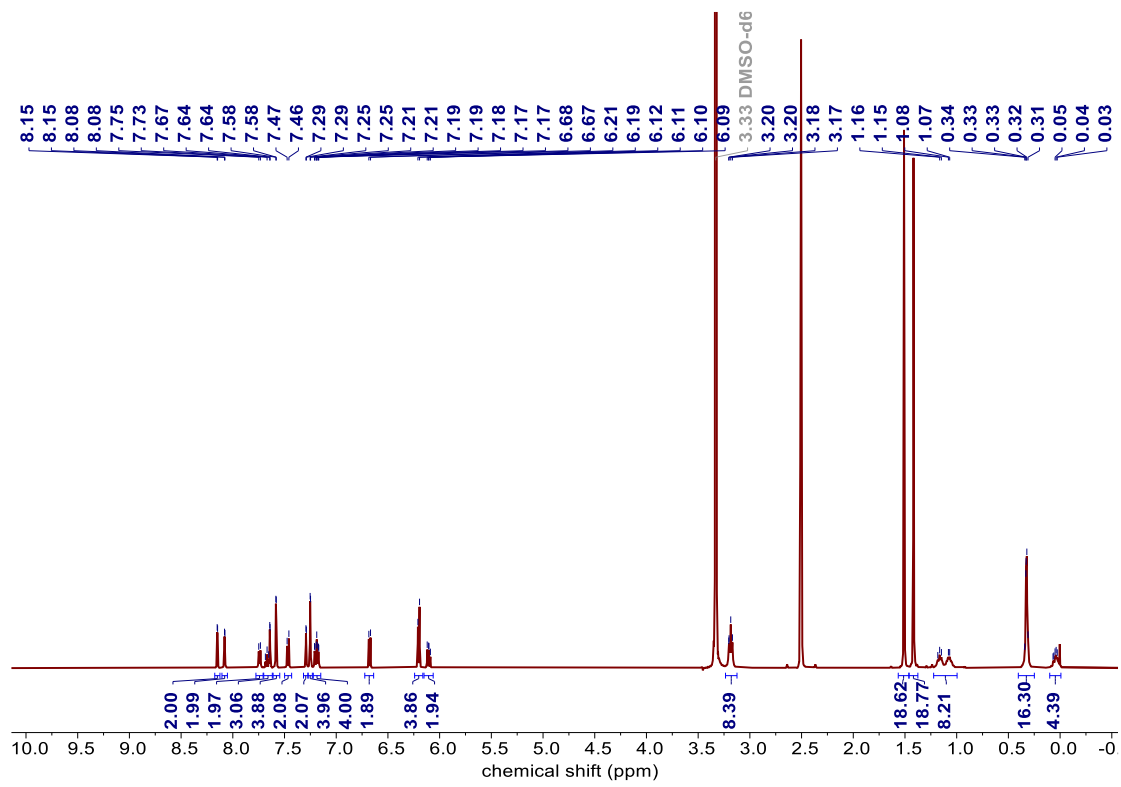
¹H NMR spectrum of PdBO in CDCl₃ (500 MHz).



¹H NMR spectrum of BO₂Br in CDCl₃ (500 MHz).



¹H NMR spectrum of dtCzBO in DMSO-d₆ (500 MHz)



¹H NMR spectrum of **DPdBO** in DMSO-d₆ (500 MHz)

Table S1. Crystal data of **PdBO** and **DPdBO**.

| | PdBO | DPdBO |
|---|---|---|
| CCDC | 2225411 | 2393758 |
| Temperature/K | 170.00 | 200.00 |
| Formula weight | C ₅₈ H ₅₈ BN ₅ O ₂ Pd | C ₁₀₄ H ₁₁₀ BClN ₁₀ O ₂ Pd ₂ |
| Crystal system | monoclinic | monoclinic |
| Space group | P2 ₁ | P2 ₁ /c |
| a (Å) | 13.5254(7) | 14.9978(4) |
| b (Å) | 12.2270(6) | 25.7587(9) |
| c (Å) | 15.1800(7) | 23.6319(8) |
| α (°) | 90 | 90 |
| β (°) | 98.344(2) | 100.619(2) |
| γ (°) | 90 | 90 |
| V (Å ³) | 2483.8(2) | 8973.2(5) |
| Z Value | 2 | 4 |
| ρ _{calc} / g·cm ⁻³ | 1.303 | 1.326 |
| μ/mm ⁻¹ | 2.276 | 2.657 |
| F (000) | 1016.0 | 3736.0 |
| Crystal size | 0.16 × 0.06 × 0.05 | 0.16 × 0.06 × 0.05 |
| 2Theta range (°) | 5.746 to 118.782 | 5.216 to 114.146 |
| GOF on F ² | 1.036 | 1.060 |
| R ₁ /wR ₂ [I>=2σ (I)] | R ₁ = 0.0491, wR ₂ = 0.0860 | R ₁ = 0.0373, wR ₂ = 0.1043 |

Table S2. Selected bond length (Å), and bond angles (degree) for **PdBO** and **DPdBO**.

| | PdBO | DPdBO |
|--|------------------------------------|----------------|
| | Bond length (Å) | |
| Pd-C ₅ /Pd ₁ -C ₉₁ ; Pd ₂ -C ₄₉ | 1.952 | 1.949;1.957 |
| Pd-N ₅ /Pd ₁ -N ₁₅ ; Pd ₂ -N ₁₆ | 2.102 | 2.118;2.121 |
| C ₅ -N ₅ (PdBO)/C ₉ -N ₁₅ ; C ₁₉ -N ₁₆ (DPdBO) | 4.052 | 4.067;4.076 |
| | Bond angles (degree) | |
| C ₅ -Pd-N ₅ /C ₉ -Pd ₁ -N ₁₅ ; C ₄₉ -Pd ₂ -N ₁₆ | 175.96 | 179.28;177.01; |
| | Bond angles around N _{Cz} | |
| C ₂₁ -N ₅ -C ₂₈ (PdBO)/C ₁ -N ₁₅ -C ₇₃ ; C ₃₂ -N ₁₅ -C ₅₀ (DPdBO) | 104.96 | 105.67;105.59 |
| C ₂₁ -N ₅ -Pd/C ₁ -N ₁₅ -Pd ₁ ; C ₃₂ -N ₁₆ -Pd ₂ | 125.95 | 131.31;124.36 |
| C ₂₈ -N ₅ -Pd/C ₇₃ -N ₁₅ -Pd ₁ ; C ₅₀ -N ₁₆ -Pd ₂ | 127.74 | 122.47;129.30 |
| ΣN _{Cz} | 358.65 | 359.45;359.25 |

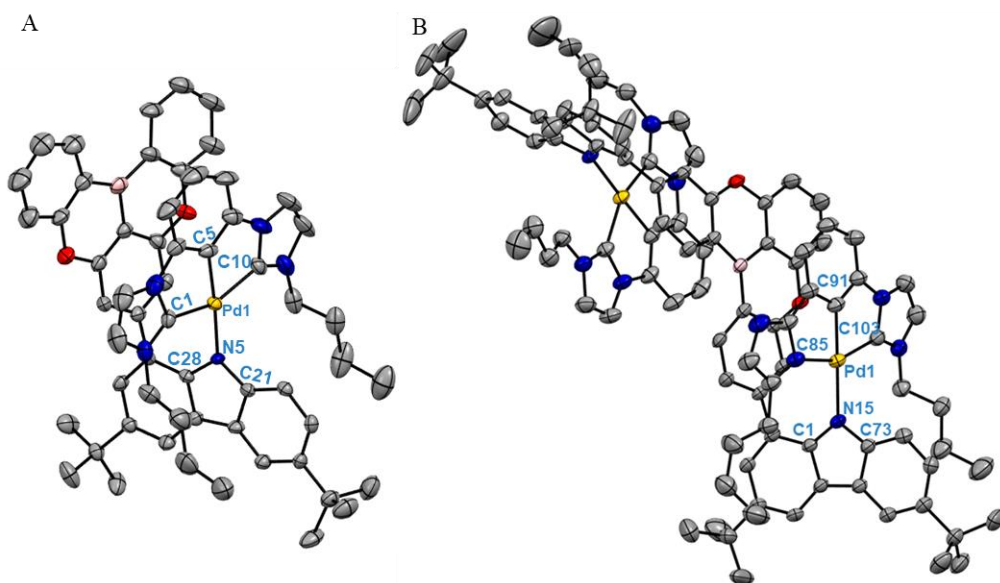


Fig. S1 The perspective views of X-ray crystal structures of **PdBO** and **DPdBO** with labeled atoms.

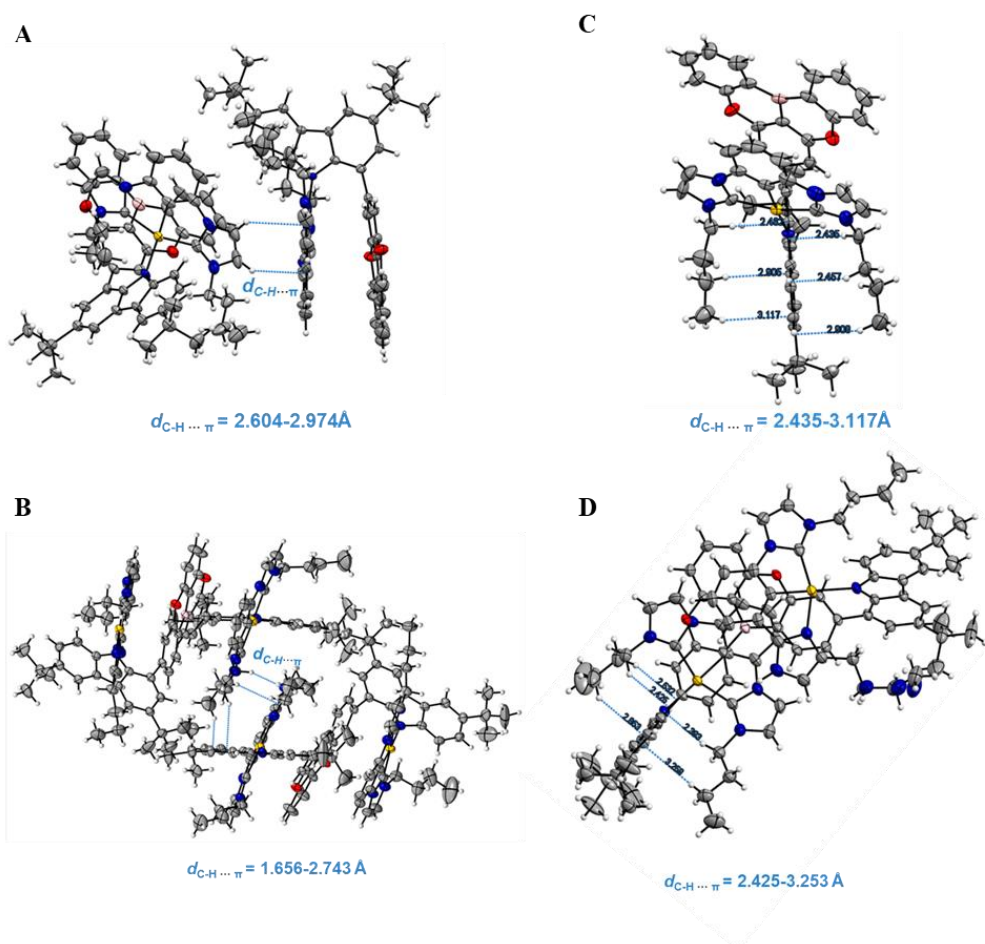


Fig. S2 X-ray crystal structures of **PdBO** and **DPdBO**. Left: the intermolecular short C-H... π contacts in **PdBO** and **DPdBO** with the distances between the C-H Bonds and the (CCC)Pd plane indicated. Right: the intramolecular short C-H... π contacts in **PdBO** and **DPdBO** with the distances between the C-H bonds and the carbazole plane indicated.

Table S3. Electrochemical data and estimated frontier molecular orbital energy levels of **PdBO** and **DPdBO** in CH_2Cl_2 solution.

| | E_{pa}^* [V] | $E_{\text{pc}}^{[a]}$ [V] | $E_{1/2(\text{OX})}^{[a]}$ [V] | $E_{\text{g}}^{[b]}$ [eV] | HOMO ^[c] (eV) | LUMO ^[d] (eV) |
|--------------|--------------------------|------------------------------|-----------------------------------|------------------------------|-----------------------------|-----------------------------|
| PdBO | 0.37 | 0.21 | 0.29 | 2.32 | -4.58 | -2.29 |
| DPdBO | 0.32 | 0.22 | 0.27 | 2.28 | -4.56 | -2.29 |

* Measured in dichloromethane. ^[a] $E_{1/2(\text{OX})} = (E_{\text{pa}} + E_{\text{pc}})/2$. ^[b] Estimated from absorption onset, $E_{\text{g}} = 1240/\lambda$. ^[c] The HOMOs estimated by $E_{\text{HOMO}} = -e[E_{1/2(\text{OX})} - E_{1/2(\text{Fc}^+/\text{Fc})}] - 4.8$ eV. $E_{1/2(\text{Fc}^+/\text{Fc})} = 0.51$ eV. ^[d] $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}$.

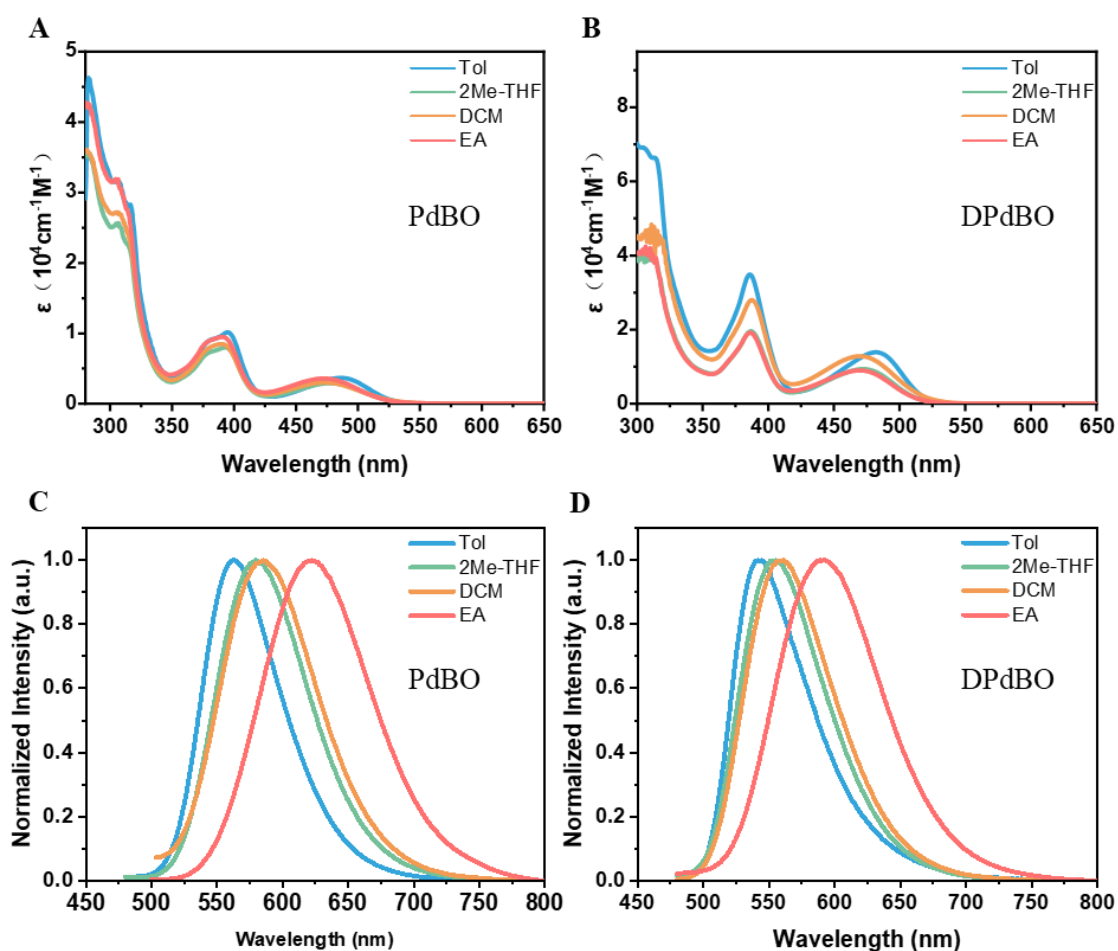


Fig. S3 The normalized absorption spectra (1×10^{-5} M) and emission spectra (1×10^{-4} M) of (A, B) **PdBO** and (C, D) **DPdBO** in different solvents at 298 K.

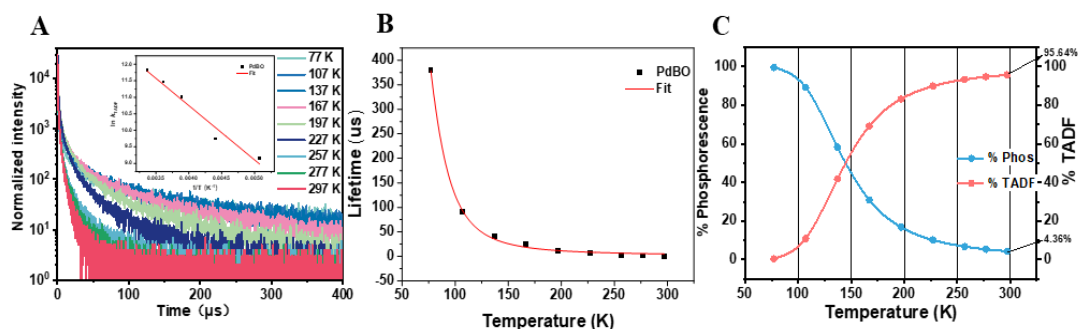


Fig. S4 (A) Variable temperature photoluminescence decay characteristics of **PdBO** in 3 wt% mCP film. Inset: Arrhenius fit of the k_{TADF} value versus temperature for **PdBO** in 3 wt% mCP film (red line). (B) Boltzmann-type fitting of the emission lifetimes of **PdBO** in mCP film at various temperatures. (C) Fractions of TADF and phosphorescence as a function of temperature for **PdBO**.

Table S4. Temperature dependent photophysical properties of **PdBO** in 3 wt% mCP film.

| T (K) | 1/T (K ⁻¹) | τ (μ s) ^[a] | τ_1 (μ s) | τ_2 (μ s) | τ_2 (μ s) | k_{TADF} (10 ⁴ s ⁻¹) ^[b] | ln k_{TADF} |
|-------|------------------------|----------------------------------|---------------------|---------------------|---------------------|---|------------------|
| 197 | 0.00507 | 31.7 | 105.50(24.4%) | 12.40(45.6%) | 1.25(30.0%) | 3.15 | 8.06 |
| 227 | 0.00441 | 15.08 | 55.00 (20.1%) | 7.63(48.9%) | 1.00(31.0%) | 6.63 | 8.80 |
| 257 | 0.00389 | 5.46 | 18.56(21.2%) | 2.85(50.0%) | 0.39 (29.0%) | 6.06 | 9.81 |
| 277 | 0.00361 | 3.73 | 12.63 (19.6%) | 2.26(51.8%) | 0.35 (28.6%) | 18.3 | 10.20 |
| 297 | 0.00336 | 2.68 | 8.87 (18.2%) | 1.82(54.4%) | 0.32 (27.2%) | 37.3 | 10.52 |

[a] Calculated from the weighted average of the three contributions to τ . [b] The k was calculated using the average values of τ . When $T > 200$ K, $k_{TADF} = 1/\tau$.

Table S5. Temperature dependent photophysical properties of **DPdBO** in 3 wt% mCP Film.

| T (K) | 1/T (K ⁻¹) | τ (μ s) ^[a] | τ_1 (μ s) | τ_2 (μ s) | τ_2 (μ s) | k_{TADF} (10 ⁴ s ⁻¹) ^[b] | ln k_{TADF} |
|-------|------------------------|----------------------------------|---------------------|---------------------|---------------------|---|------------------|
| 197 | 0.00507 | 148.30 | 428.00 (26.5%) | 675.00(49.1%) | 8.40(24.4%) | 0.67 | 8.06 |
| 227 | 0.00441 | 49.87 | 410.70 (25.9%) | 24.60(52.0%) | 3.25(22.1%) | 2.00 | 8.80 |
| 257 | 0.00389 | 15.12 | 23.17(59.5%) | 0.00(0.0%) | 3.29 (40.5%) | 6.61 | 9.81 |
| 277 | 0.00361 | 12.54 | 29.30(29.4%) | 1.26(18.0%) | 7.05 (52.6%) | 8.00 | 10.20 |
| 297 | 0.00336 | 7.05 | 2.01(41.5%) | 0.00 (0.0%) | 10.55(58.5%) | 14.1 | 10.52 |

[a] Calculated from the weighted average of the three contributions to τ . [b] The k was calculated using the average values of τ . When $T > 200$ K, $k_{TADF} = 1/\tau$.

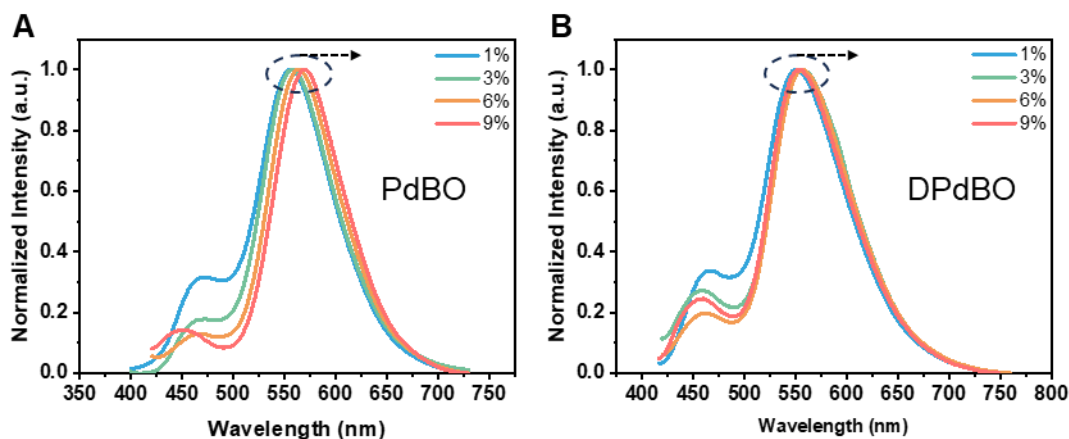


Fig. S5 The PL spectra of PdBO and DPdBO in 1-9 wt% doped S37 films at 298 K.

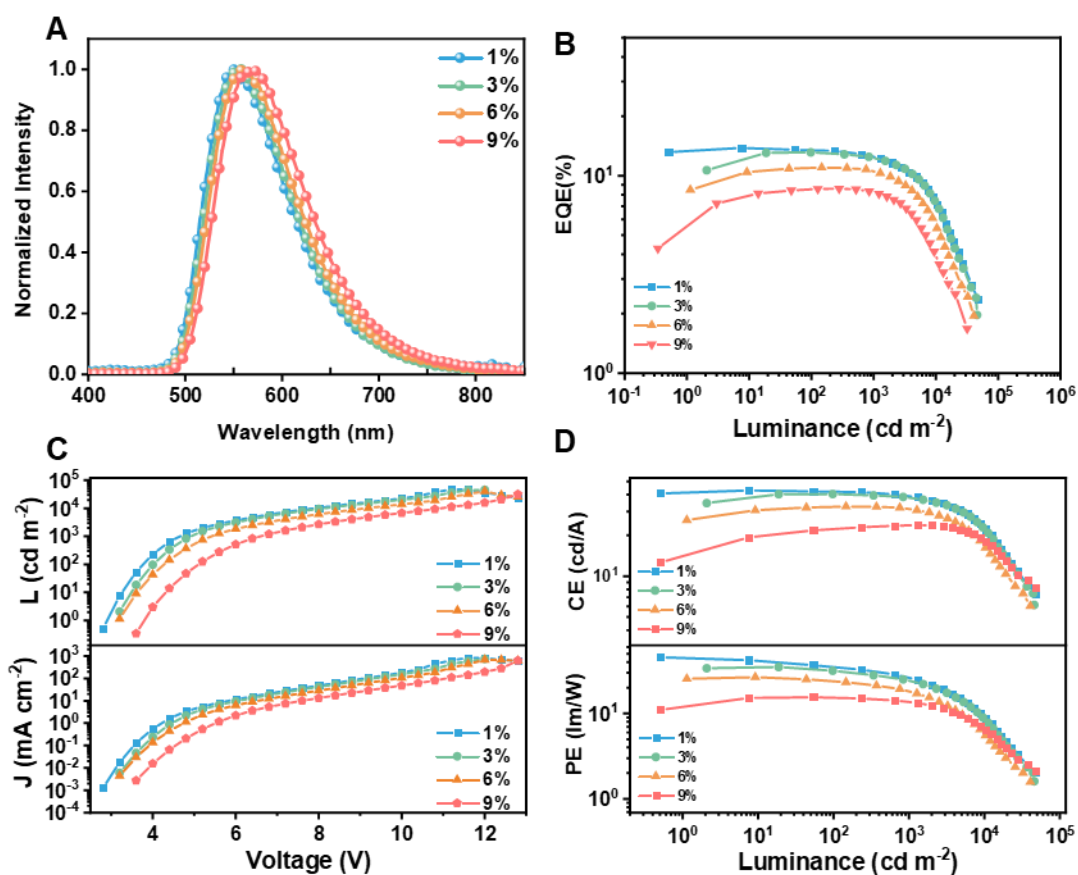


Fig. S6 (A) CE/PE versus luminance curves for PdBO. (B) EQE versus luminance curves. (C) The luminescence and current density versus voltage characteristics. (D) The EL spectra. Device structure: ITO/HAT-CN (5 nm)/TAPC (30 nm)/TCTA (15 nm)/mCBP (10 nm)/S37: PdBO (40 nm)/POT2T (20 nm)/ANT-BIZ (30 nm)/Liq (2 nm)/Al (100 nm).

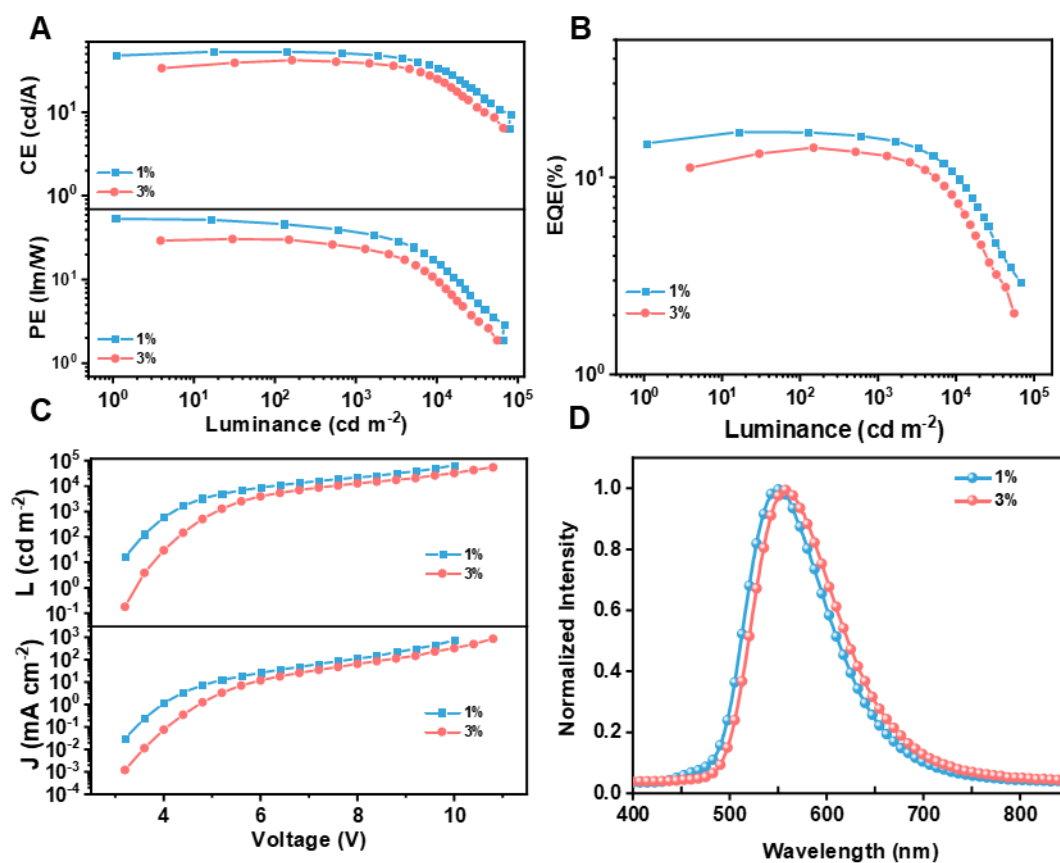


Fig. S7 (A) CE/PE versus luminance curves of **DPdBO**. (B) EQE versus luminance curves. (C) The luminescence and current density versus voltage characteristics. (D) The EL spectra. Device structure: ITO/HAT-CN (5 nm)/TAPC (30 nm)/TCTA (15 nm)/mCBP (10 nm)/S37: **DPdBO** (45 nm)/POT2T (20 nm)/ANT-BIZ (30 nm)/Liq (2 nm)/Al (100 nm).