

## Supporting Information

### **Singlet-Triplet Splitting Energy Management for Thermally Activated Delayed Fluorescence Emitters: Up-Conversion of Acceptor Triplet into Charge Transfer Singlet State**

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### 1. Experimental Procedures

#### 1.1 General information

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

#### 1.2 Quantum Chemical Calculations

All of the theoretical simulations for the investigated molecules were performed using the Gaussian 09 program package. The electron density distribution of frontier molecular orbital (FOM) were visualized with Gaussview 3.0. Structure optimizations were carried out using density functional theory (DFT) calculations. The ground state structures were optimized with B3LYP/6-31G (d) level set in the gas phase.

#### 1.3 Electrochemical Characterization

The oxidation potential was determined by cyclic voltammetry using 0.1 M

tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in CH<sub>2</sub>Cl<sub>2</sub> (CV) as a supporting electrolyte and a scan rate of 100 mV s<sup>-1</sup>. ITO, Ag/AgCl and Pt mesh were used as working electrode, reference electrode and counter electrode, respectively. A 3-electrode cell comprising silver/silver chloride (Ag/AgCl), a platinum mesh and ITO as the reference, counter, and working electrodes, respectively, were used. All potentials were recorded versus Ag/AgCl (saturated) as a reference electrode. Oxidation of the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple in CH<sub>2</sub>Cl<sub>2</sub>/TBAPF<sub>6</sub> occurs at  $E_o = + 0.48$  V. HOMO levels were conducted from the oxidation half-wave potential with the formula:  $E_{\text{HOMO}} = - (E_{\text{oxi. v.s. Fc}^+/\text{Fc}} + 4.8)$  (eV),  $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{\text{opt}}$ , thereinto,  $E_g^{\text{opt}}$  was obtained from the absorption edges of normalized absorption spectra.

#### 1.4 Photophysical Characterization

Absorption spectra were studied using a UV-vis spectrophotometer (TU-1901, PERSEE). Photoluminescence (PL) spectra and phosphorescence spectra were performed using a HITACHI F-4600 spectrophotometer. The transient fluorescence decay characteristics were measured using an Edinburgh Instruments FLS920 spectrometer. The absolute fluorescence quantum yields of the solid films are measured with an integrating sphere.

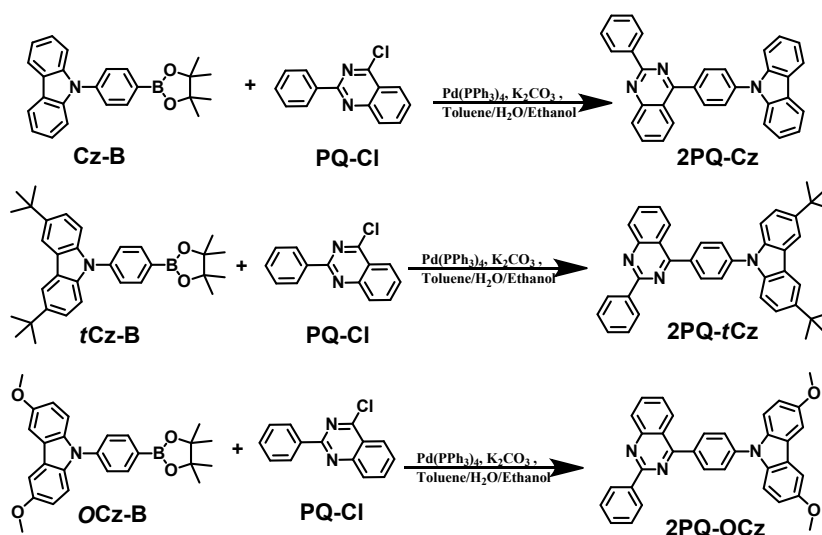
#### 1.5 OLED Fabrication and Characterization

Organic light-emitting devices were fabricated on glass substrates precoated with 150 nm ITO. The substrates should be cleaned with detergent, ultrasonicated in water, acetone and ethyl alcohol firstly, and subsequently dried at 75 °C (15 min) in an oven. Afterwards the substrates were exposed to oxygen plasma (10 min) in order to remove organic residues and improve the work function of ITO. Then the substrates were

transferred to a thermal evaporation chamber with a pressure lower than  $4 \times 10^{-4}$  Pa for organic semiconductor layers and metal cathode deposition. The devices were fabricated by evaporating organic layer sequentially with an evaporation rate of 1-2 Å s<sup>-1</sup>. The cathode was completed through thermal deposition of LiF at a deposition rate of 0.1 Å s<sup>-1</sup>, and then capped with Al metal through thermal evaporation at a rate of 2 Å s<sup>-1</sup>. The transient PL decay characteristics were measured using an Edinburgh Instruments FLS920 spectrometer. The electroluminescence (EL) spectra were measured by a Spectra scan PR655 photometer. The current-voltage-brightness characteristics were measured by using a computer-controlled Keithley source measurement unit (Keithley 2400) with a Konica Minolta CS-200 luminance-meter under dark and ambient atmosphere. External quantum efficiencies (EQE, %), current efficiencies (cd/A) and power efficiencies (lm/W) were calculated from the electrical and optical properties. For this calculation we assumed Lambertian light distribution.

### 1.6 Synthesis procedure

The synthesis of Cz-B, tCz-B, and OCz-B are following the previous report.[1]



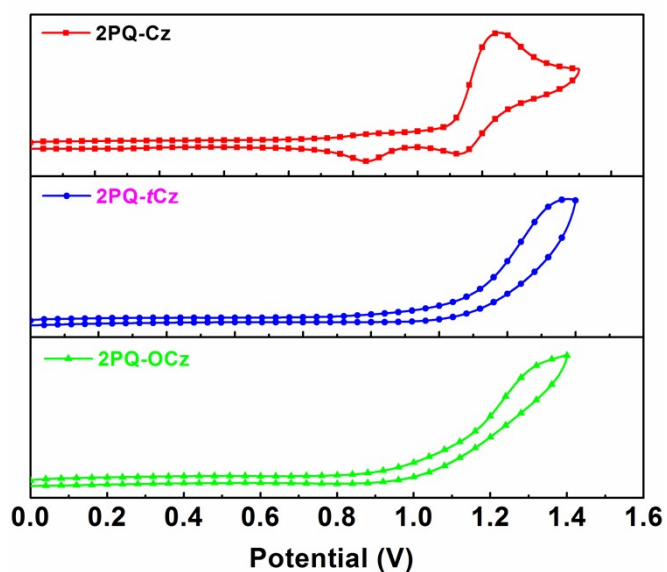
**Scheme S1** Synthetic procedure of 2PQ-Cz, 2PQ-tCz, and 2PQ-OCz.

Synthesis of 2PQ-Cz. The synthesis of 2PQ-Cz is following the previous report.[1] A mixture of **Cz-B** (0.58 g, 1.6 mmol), PQ-Cl (0.36 g, 1.5 mmol) in toluene (55 mL), an aqueous solution (10 mL) of potassium carbonate (0.67 g, 4.8 mmol) and 10 mL anhydrous alcohol was added to the mixture, which was stirred, bubbled using N<sub>2</sub> for 40 min, and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.06 g, 0.05 mmol) was added quickly, then refluxed under nitrogen atmosphere for 6 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/dichloromethane = 3:2, v/v) to give 2PQ-Cz as a light yellow solid (yield = 0.62 g, 85%). This compound was further purified by temperature-gradient sublimation under vacuum. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) 8.74 (d, 2H), 8.29 (d, 1H), 8.19 (dd, 5H), 7.95 (t, 1H), 7.84 (d, 2H), 7.60 (ddt, 6H), 7.48 (t, 2H), 7.34 (t, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ(ppm) 167.30, 160.34, 152.18, 140.58, 139.49, 138.11, 136.49, 133.81, 131.89, 130.67, 129.39, 128.70, 128.64, 127.31, 126.91, 126.80, 126.16, 123.68, 121.62, 120.46, 120.36, 109.88.

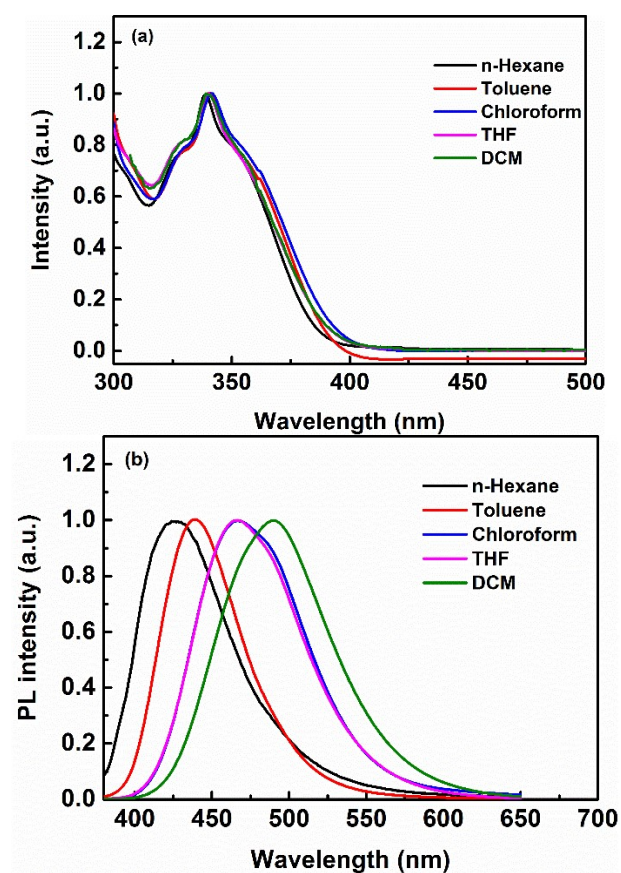
Synthesis of 2PQ-*t*Cz. The synthesis of 2PQ-*t*Cz was applied similar procedure by using *t*Cz-B and PQ-Cl. A mixture of ***t*Cz-B** (0.61 g, 1.26 mmol), PQ-Cl (0.29 g, 1.2 mmol) in toluene (55 mL), an aqueous solution (10 mL) of potassium carbonate (0.52 g, 3.7 mmol) and 10 mL anhydrous alcohol was added to the mixture, which was stirred, bubbled using N<sub>2</sub> for 40 min, and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 g) was added quickly, then refluxed under nitrogen atmosphere for 6 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane and the solvent was removed under

reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/dichloromethane = 3:2, v/v) to give 2PQ-*t*Cz as a light yellow solid (yield = 0.59 g, 88%). This compound was further purified by temperature-gradient sublimation under vacuum. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) 8.74 (d, J = 7.6 Hz, 2H), 8.28 (d, J = 8.4 Hz, 1H), 8.23 – 8.12 (m, 5H), 7.94 (t, J = 7.6 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.61 – 7.47 (m, 7H), 1.49 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ(ppm) 167.41, 160.34, 152.18, 143.34, 140.05, 138.95, 138.15, 135.95, 133.72, 131.78, 130.61, 129.37, 128.70, 128.61, 127.24, 126.85, 126.43, 123.79, 123.73, 121.64, 116.37, 109.33, 34.79, 32.02.

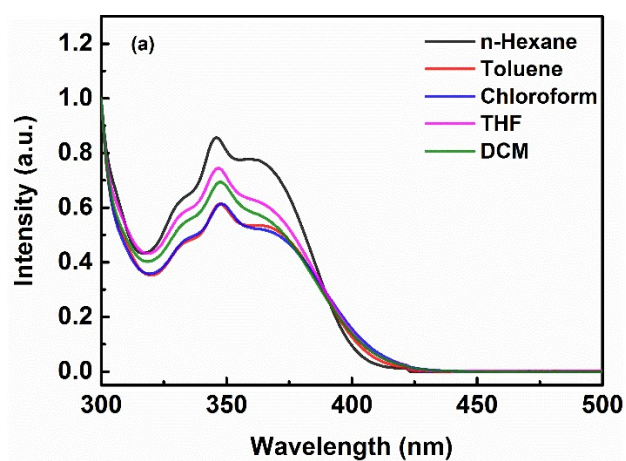
Synthesis of 2PQ-OCz. The synthesis of 2PQ-OCz was applied similar procedure by using OCz-B and PQ-Cl. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) 8.78 (d, 2H), 8.32 (d, 1H), 8.26 (d, 1H), 8.19 (d, 2H), 7.99 (t, 1H), 7.85 (d, 2H), 7.68-7.54 (m, 8H), 7.14 (dd, 2H), 4.01 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ(ppm) 167.38, 160.30, 154.32, 140.01, 138.08, 135.89, 133.80, 131.85, 130.67, 129.31, 128.70, 128.63, 127.29, 126.83, 126.33, 124.03, 121.61, 115.34, 110.86, 102.97, 56.13.

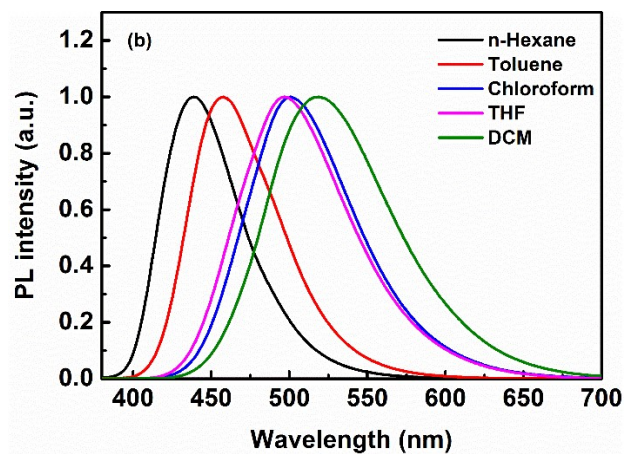


**Fig. S1.** Cyclic voltammogram of 2PQ-Cz, 2PQ-*t*Cz, and 2PQ-OCz.

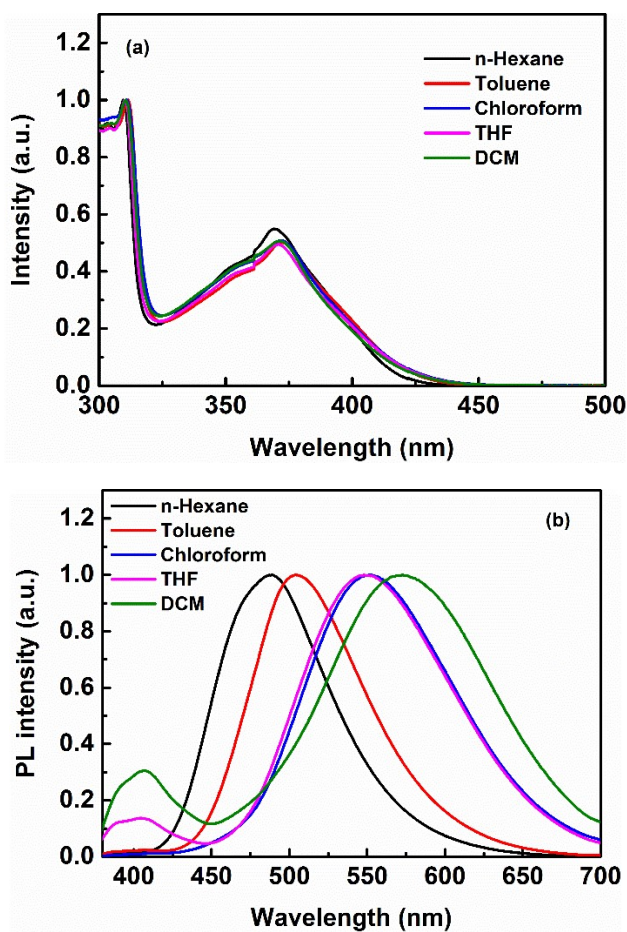


**Fig. S2.** UV-Vis absorption of 2PQ-Cz in different solutions: n-hexane, toluene, chloroform, THF, and DCM.





**Fig. S3.** UV-Vis absorption of 2PQ-*t*Cz in different solutions: n-hexane, toluene, chloroform, THF, and DCM.



**Fig. S4.** UV-Vis absorption of 2PQ-OCz in different solutions: n-hexane, toluene, chloroform, THF, and DCM.



[1] Li B, Song X, Jiang X, et al. Stable deep blue organic light emitting diodes with CIE of  $y < 0.10$  based on quinazoline and carbazole units[J]. Chinese Chemical Letters, 2020, 31, 1188.