Supporting Information

Triplet decay-induced Inverse temperature dependence of the transient PL decay of thermally activated delayed fluorescence emitter

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1. Materials and methods.

1.1 General methods. All solvents and materials were used as received from commercial suppliers without further purification. All reactions were monitored by thin layer chromatographic analysis on a pre-coated silica gel plate, which was visualized by a UV lamp at 254 or 365 nm. Flash column chromatography was performed on glass column of silica gel (100–200 mesh) and solvent ratios were expressed in volume to volume. 1H and 13C NMR spectra for structural characterization were recorded on a NMR spectrometer (400 MHz for ¹H; 100 MHz for ¹³C). All NMR measurements were conducted in CDCl₃ at room temperature. The NMR spectra were recorded on VaRIAN-GEMINI-300 and Bruker Avance II-400 spectrometer at room temperature and tetramethylsilane (TMS) as an internal reference. Mass spectra were recorded using a BIFLEXIII MALDI-TOF mass spectrometer in EI mode. Chemical shifts were reported as parts per million in scale using the solvent residual peak as internal standard

for ¹H and ¹³C NMR. Coupling constants (J) were reported in Hertz (Hz). UV-vis spectra and fluorescence spectra were obtained with Hitachi U-3900 and F- 4600 spectrophotometers, respectively. The phosphorescence spectra were measured in 2-MeTHF glass matrix at 77 K using a Hitachi F-4600 fluorescence spectrometer. Fluorescence quantum yields (Φ_{PL}) of TXO-PhCz1,TXO-PhCz3 and TXO-PhCz4 in solutions were estimated by using quinine sulphate as the reference (Φ_{PL} 54.9% in 1 N H₂SO₄). The absolute fluorescence quantum yields of the solid films are measured with an integrating sphere. Cyclic voltammetry was performed using a CHI600A analyzer with a scan rate of 100mVs⁻¹ at room temperature. The electrolytic cell was a conventional three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a SCE (saturated calomel electrode) reference electrode. The measurement of oxidation potentials was performed in CH2Cl2 with 0.1 M of tetran-butylammonium hexafluorophosphate (n-Bu₄NPF₆) as a supporting electrolyte, and the reduction part was performed in THF with 0.1 M of n-Bu₄NPF₆ as a supporting electrolyte. The DSC measurements were carried out using a TA Instruments DSC 2910 thermal analyzer at a heating rate of 10 °C min⁻¹. The TGA measurements were performed on a TA Instruments TGA 2050 thermal analyzer. The diffraction experiments were carried out on a Rigaku Saturn 724 diffractometer equipped with a Mo-Ka source at about 170 K. Crystal structures were solved with direct methods and refined with a full-matrix least-squares technique, using the SHELXS software package. Mercury (CSD software) was used for crystal structure visualization.



Scheme S1. Synthetic Routes of TXO-PhCz1.

1.2 Synthesis. All solvents and materials were used as received from commercial suppliers without further purification. Synthetic routes of these compounds are shown in scheme S1, S2 and S3.

Synthesis of 2-[(3-Chlorophenyl)thio]benzoic Acid (1) : A suspension of 3.08 g (20 mmol) of α -mercaptobenzoic acid, 2.29 g of 3-chloro-1-bromobenzene,186 mg of Cubronze, and 2.72 g of K₂CO₃ in 40 mL of DMF was stirred under reflux for 4 h. The cooled mixture was poured onto ice-water and then filtered through a bed of Celite. The filtrate was extracted with ether, and after the layers were separated, the aqueous portion was acidified carefully with 3 N HCl. The crystalline solid that separated was collected and dried yield 4.3 g (77%). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J*=7.8 Hz, 1H), 7.57 (s, 1H), 7.46 (d, *J*=7.4 Hz, 1H), 7.44–7.31 (m, 3H), 7.21 (t, *J*=7.5 Hz, 1H), 6.87 (d, *J*=8.2 Hz, 1H). EIMS m/z (%): calcd for C₁₃H₉³⁵ClO₂S, 264.00; found: 264.00.

Synthesis of 1-chloro-9-H-Thioxanthen-9-one(2): 2-[(3-Chlorophenyl)thio]benzoic Acid 2.64g (20 mmol) was added into the concentrated sulfuric acid (20 ml, 98%) .The reaction was stirred for 4h at room temperature, then it was poured into the water. A white precipitate formed. It was filtered off and dried under vacuum. The product was purified by column chromatography (SiO₂) using DCM:PE=1:4 as the eluent .1.5 g of a light yellow solid was obtained (40% yield).¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, *J*=8.1 Hz, 1H), 7.60 (t, *J*=7.5 Hz, 1H), 7.54–7.41 (m, 5H). EIMS m/z (%): calcd for C₁₃H₇³⁵ClOS, 245.99; found: 245.99, 247.99.

Synthesis of 1-chloro-9-H-Thioxanthen-9-one-10,10-dioxide (2): A mixture of 2bromo-9- H-Thioxanthen-9-one (1) (1.22 g,5mmol), glacial acetic acid (40ml) and 34% hydrogen peroxide (10 ml) was boiled for 2 hours at 120 °C, and then was cooled and poured into cold water. The precipitate was collected by filtration under a vacuum, washed with water, and dried in a vacuum oven. The product was recrystallized from ethanol as a white solid (1.26 g, yield: 91%). ¹H NMR (400 MHz, CDCl₃, δ): 8.47 (d, *J*=1.7, 1H), 8.35 (t, *J*=6.1, 1H), 8.18 (d, *J*=8.4, 1H), 8.08–7.98 (m, 2H), 7.90 (dd, *J*=11.0, 4.3, 1H), 7.81 (dd, *J*=9.1, 5.2, 1H); EIMS m/z (%): calcd for C1₃H7³⁵ClO₃S, 277.98; found: 277.98, 279.98.

Synthesis of TXO-PhCz1: 2-bromo-9-H-Thioxanthen-9-one-10, 10-dioxide (2) (4.7 g, 0.0145 mol), tetrakis(triphenylphosphine)palladium(0) (0.08 g, 0.072 mol), 2 M K₂CO₃ (48 ml) and toluene (100ml) were added to a 250 ml three-necked flask under nitrogen. The corresponding (9-phenyl-9H-carbazol-3-yl) boronic acid (3.4g, 0.012 mol) was added to the solution and heated to 110 °C for 5 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane and organic phase was washed with brine. After drying over MgSO₄, the solvent was removed. The resulting crude product was passed through a flash column chromatograph (using ethyl acetate: petroleum ether, 1:10) to remove impurities and recrystallized from toluene to obtain a yellow product. The yield of product was 75%. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, J=7.6 Hz, 1H), 8.18 (d, J=7.7 Hz, 1H), 8.10 (d, J=7.8 Hz, 1H), 8.05 (s, 1H), 7.98 (d, J=7.7 Hz, 1H), 7.82 (q, J=7.4 Hz, 2H), 7.73 (dd, J=12.8, J=7.1 Hz, 2H), 7.63 (m, 4H), 7.54–7.40 (m, 4H), 7.29 (dd, J=10.0, 6.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 181.14, 145.91, 141.97, 141.41, 140.42, 139.64, 137.57, 137.43, 134.58, 133.45, 133.41, 132.62, 131.82, 130.83, 129.95, 128.66, 127.65, 127.18, 126.74, 126.28, 123.44, 123.32, 123.10, 122.67, 120.36, 120.19, 120.16, 110.02, 109.58. EIMS m/z (%): calcd for C₃₁H₁₉NO₃S, 485.11; found: 485.11. Anal. calcd for C₃₁H₂₁NO₃S: C, 76.68; H, 3.94; N, 2.88; found: C, 76.62; H, 3.89; N, 2.90.



Scheme S2. Synthetic Routes of TXO-PhCz3.

4-bromo-2-(phenylsulfanyl)benzonitrile (1): sodium hydride (0.73 g, 30 mmol, 95% dry) was slowly added to a solution of thiophenol (2.56 mL, 25 mmol) in 10 mL dry DMF. To this solution was added at room temperature a solution of 4-bromo-2-fluorobenzonitrile (5 g, 25 mmol) in 10 mL dry DMF. The reaction was then refluxed for 8 hours. After cooling to room temperature, the solution was poured into a cold aqueous solution of NaOH 1M. A white precipitate formed. It was filtered off and dried under vacuum. The solid was purified by column chromatography (SiO₂) using ethyl acetate: petroleum ether, 1:10. The title compound was isolated as a white solid in 72% yield (5.22 g). ¹H NMR (400 MHz, CDCl₃, ppm): 7.14 (d, 1H, *J*=1.5 Hz), 7.36 (dd, 1H, *J*=8.3 Hz, *J*=1.5 Hz), 7.42-7.54 (m, 6H).

4-bromo-2-(phenylsulfanyl)benzoic acid (2): 4-bromo-2-(phenylsulfanyl)benzonitrile (8.4 g, 28.9 mmol)was suspended in 80 mL ethanol and 80 mL of aq. KOH (15 g in 80 mL water) was added. The reaction mixture was refluxed 2 hours. After cooling, the solution was poured into an aq. HCl 6M. The precipitate was filtered off. It was washed with pentane and air-dried (4.96 g, 95% yield). 1H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J*=6.8 Hz, 1H), 7.40 (d, *J*=7.7 Hz, 2H), 7.37–7.29 (m, 3H), 7.16–7.08 (m, 2H). EIMS m/z (%): calcd for C₁₃H₉⁸¹BrO₂S, 289.96; found: 289.96, 291.94.

3-bromo-9H-thioxanthen-9-one (3): 4-bromo-2-(phenylsulfanyl)benzoic acid(2) (2g, 6.87 mmol) was added into the concentrated sulfuric acid (20 ml, 98%) .The reaction was stirred for 2 h at room temperature. The residue was poured into the water. A white precipitate formed. It was filtered off and dried under vacuum. The product was purified

by column chromatography (SiO₂) using DCM:PE=1:4 as the eluent 0.80 g of a yellow solid was obtained (40% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.60 (d, *J*=8.1 Hz, 1H), 8.46 (d, *J*=8.6 Hz, 1H), 7.75 (s, 1H), 7.58 (tt, *J*=29.0, 7.6 Hz, 4H). EIMS m/z (%): calcd for C₁₃H₇⁸¹BrOS, 291.94; found: 289.94, 291.94.

Synthesis of 3-bromo-9-H-Thioxanthen-9-one-10,10-dioxide (4):A mixture of 3bromo-9H-Thioxanthen-9-one (3) (2.92 g,10mmol), glacial acetic acid (80ml) and 34% hydrogen peroxide (20 ml) was boiled for 2 hours at 120 °C, and then was cooled and poured into cold water. The precipitate was collected by filtration under a vacuum, washed with water, and dried in a vacuum oven. The product was recrystallized from ethanol as a white solid (2.95 g,yield: 91%). ¹H NMR (400 MHz, CDCl₃) δ 8.35 (d, *J*=7.8 Hz, 1H), 8.31 (s, 1H), 8.23–8.15 (m, 2H), 7.91 (t, *J*=8.5 Hz, 2H), 7.82 (t, *J*=7.6 Hz, 1H). EIMS m/z (%): calcd for C₁₃H₇⁸¹BrO₃S, 323.93; found: 321.93, 323.93

Synthesis of TXO-PhCz3: 3-bromo-9-H-Thioxanthen-9-one-10, 10-dioxide (4) (4.7 g, 0.0145 mol), tetrakis(triphenylphosphine)palladium(0) (0.08 g, 0.072 mol), 2 M K2CO3 (48 ml) and toluene (100ml) were added to a 250 ml three-necked flask under nitrogen. The corresponding 9-phenyl-9H-carbazol-3-yl) boronic acid (3.4g, 0.012 mol) was added to the solution and heated to 110 °C for 5 h. After cooling to room temperature, the reaction mixture was diluted with diethyl ether and organic phase was washed with brine. After drying over MgSO₄, the solvent was removed. The resulting crude product was passed through a flash column chromatograph (using ethyl acetate: petroleum ether, 1:10) to remove impurities and recrystallized from dichloromethane/ethanol to obtain a yellow product. The yield of product was 70%. ¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, J=4.3 Hz, 2H), 8.41 (dd, J=15.6, 8.0 Hz, 2H), 8.27-8.21 (t, 2H), 8.12 (d, J=8.3 Hz, 1H), 7.89 (t, J=7.6 Hz, 1H), 7.85–7.74 (m, 2H), 7.65 (t, J=7.6 Hz, 2H), 7.59 (d, J=7.7 Hz, 2H), 7.52 (t, J=8.7 Hz, 2H), 7.45 (dd, J=12.3, 7.5 Hz, 2H), 7.37 (t, J=7.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 178.03, 148.64, 141.65, 141.61, 141.56, 141.13, 137.22, 134.46, 133.20, 131.19, 130.91, 130.08, 130.02, 129.63, 129.14, 128.20, 127.95, 127.13, 126.75, 125.30, 124.32, 123.58, 123.18, 121.41, 120.69, 120.61, 119.51, 110.65, 110.21. EIMS m/z (%): calcd for C₃₁H₁₉NO₃S, 485.11; found: 485.11. Anal. calcd for C₃₁H₂₁NO₃S: C, 76.68; H, 3.94; N, 2.88; found: C, 76.60; H, 3.93; N,



Scheme S3. Synthetic Routes of TXO-PhCz4.

Synthesis of 4-bromo-9-H-Thioxanthen-9-one (1): α -mercaptobenzoic acid (10.0 g, 0.065 mol) was added portion-wise to concentrated sulfuric acid (100 ml, 98%) and excess bromobenzene (14 ml, 0.134 mol). The resulting suspension was stirred at room temperature for 24 hours, and then permitted to stand for an additional 1 hour on a steam bath. The color change rapidly from yellow to deep-red and the odor of sulfur dioxide was evident during the reaction. The mixture was cooled and poured slowly over ice, filtered, and washed acid-free. Then extracted with chloroform, and the combined organic extracts were dried over anhydrous MgSO4. After solvent removal, the crude product was further purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:20) as the eluent. The product was isolated as a white solid (1.89 g, yield: 10%). ¹H NMR (400 MHz, CDCl₃) δ 8.61 (dd, *J*=21.6, *J*=8.1 Hz, 2H), 7.90 (d, *J*=7.7 Hz, 1H), 7.70–7.64 (m, 2H), 7.55–7.49 (m, 1H), 7.40 (t, *J*=7.9 Hz, 1H). EIMS m/z (%): calcd for C₁₃H₇⁸¹BrOS, 291.94; found: 289.94, 291.94.

Synthesis of 4-bromo-9-H-Thioxanthen-9-one-10,10 (2): A mixture of 4-bromo-9-H-Thioxanthen-9-one (1) (2.92 g,10mmol), glacial acetic acid (80ml) and 34% hydrogen peroxide (20 ml) was boiled for 2 hours at 120 °C, and then was cooled and poured into cold water. The precipitate was collected by filtration under a vacuum, washed with water, and dried in a vacuum oven. The product was recrystallized from ethanol as a white solid (2.95 g, 4yield: 91%). ¹H NMR (400 MHz, CDCl₃) δ 8.37 (dd, *J*=22.9, 7.9 Hz, 1H), 8.19 (d, *J*=7.9 Hz, 1H), 8.05 (d, *J*=7.9 Hz, 1H), 7.93 (t, *J*=7.7 Hz, 1H), 7.80 (t, *J*=7.7 Hz, 1H), 7.60 (t, *J*=7.9 Hz, 1H). EIMS m/z (%): calcd for C1₃H7⁸¹BrO₃S,

323.93; found: 321.93, 323.93.

Synthesis of TXO-PhCz4: 4-bromo-9-H-Thioxanthen-9-one-10, 10-dioxide (2) (4.7 g, 0.0145mol), tetrakis(triphenylphosphine)palladium(0) (0.08 g, 0.072 mol), 2 M K2CO3 (48 ml) and toluene (100ml) were added to a 250 ml three-necked flask under nitrogen. The corresponding 9-phenyl-9H-carbazol-3-yl) boronic acid (3.4g, 0.012 mol) was added to the solution and heated to 110 °C for 5 h. After cooling to room temperature, the reaction mixture was diluted with diethyl ether and organic phase was washed with brine. After drying over MgSO₄, the solvent was removed. The resulting crude product was passed through a flash column chromatograph (using ethyl acetate: petroleum ether, 1:10) to remove impurities and recrystallized from dichloromethane/ethanol to obtain a yellow product. The yield of product was 75%. ¹H NMR (400 MHz, CDCl₃) δ 8.40 (dd, J=6.2, 2.7 Hz, 1H), 8.32 (d, J=5.8 Hz, 2H), 8.16 (d, J=7.8 Hz, 1H), 8.00 (d, J=7.6 Hz, 1H), 7.77 (dt, J=15.2, J=6.5 Hz, 4H), 7.62 (t, J=6.6 Hz, 5H), 7.54–7.45 (m, 2H), 7.42 (t, J=6.8 Hz, 2H), 7.29 (dd, J=7.8, 3.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 178.03, 148.64, 141.65, 141.61, 141.56, 141.13, 137.22, 134.46, 133.20, 131.19, 130.91, 130.08, 130.02, 129.63, 129.14, 128.20, 127.95, 127.13, 126.75, 125.30, 124.32, 123.58, 123.18, 121.41, 120.69, 120.61, 119.51, 110.65, 110.21. EIMS m/z (%): calcd for C₃₁H₁₉NO₃S, 485.11; found: 485.11. Anal. calcd for C₃₁H₂₁NO₃S: C, 76.68; H, 3.94; N, 2.88; found: C, 76.53; H, 3.90; N, 2.92.

1.3 Theoretical calculations. The molecular geometries of the isomers were optimized by density functional theory (DFT). Based on the optimized geometries, time-dependent DFT (TDDFT) was then used to calculate the lowest singlet (S_1) and triplet (T_1) states. All these calculations were carried out at the B3LYP/6-31G** level with the Gaussian 09 package.

1.4 Transient photophysical measurement. The transient photoluminance decay characteristics were measured using an Edinburgh Instruments FLS920 spectrometer. The temperature dependence experiment is conducted under low temperature refrigeration system from Advanced Research Systems Company. The transient decay curves were fitted with the multi-exponential equation:

$$I(t) = \sum_{i} A_{i} \exp\left(-t / \tau_{i}\right)$$

where A_i is the pre-exponential factor, τ_i is the decay time, and I(t) is the emission intensity. The Φ_{Prompt} and Φ_{TADF} were determined by using total PL quantum efficiency and the ratio between prompt and delayed components. The intensity ratio between prompt (r_1) and delayed (r_2) components were determined using emission life time (τ_1 , τ_2) and fitting parameter (A_1 , A_2). Then, Φ_{Prompt} and Φ_{TADF} were determined using intensity ratio (r_1 , r_2) and total emission quantum yield. To get the solid evidence for the efficient ISC and RISC process and evaluate ΔE_{ST} quantitatively, the triplet formation efficiency (Φ_T) and ΔE_{ST} can be derived from the temperature dependence results according to the Berberan-Santos plot:

$$\ln\left[\frac{I_{\Pr ompt}}{I_{TADF}} - \left(\frac{1}{\Phi_{T}} - 1\right)\right] = \ln\left(\frac{k_{p} + k_{nT}^{T}}{k_{RISC}}\right) + \frac{\Delta E_{ST}}{RT}$$

where $I_{Prompt}/I_{TADF} = \Phi_{Prompt}/\Phi_{TADF}$, k_p is the phosphorescence rate constant, k_{nr}^{T} is the non-radiative rate constant from T₁, k_{RISC} is the RISC rate constant and R is the gas constant. The intersystem crossing constant (k_{ISC}), the radiative rate constants (k_r^s) and the non-radiative rate constant (k_{nr}^s) were also calculated assuming that k_{ISC} was independent of temperature. The energy difference (ΔEsT) and the triplet formation efficiency (Φ_T) were evaluated using a Berberan-Santos plot [s2] from the temperature dependence results according to the above equation. The Berberan-Santos plot gives a maximum linearity when continuous variation of triplet formation efficiency (Φ_T) value. And from the slope we obtained ΔEsT .

$$\Phi_T = \frac{k_{ISC}}{k_r^s + k_{nr}^s + k_{ISC}} = \frac{k_{ISC}}{k_s}$$
$$k_{ISC} = k_s \times \Phi_T = \frac{\Phi_T}{\tau_s}$$
$$\frac{k_r^s}{k_r^s + k_{nr}^s} = \Phi_{Total}$$

Here, k_r^s and k_{nr}^s are the radiative and non-radiative rate constants from S₁ state,

respectively. k_{ISC} is the intersystem crossing rate and $k_{S} = k_{r}^{s} + k_{nr}^{s} + k_{ISC} = \tau_{s}^{-1}$. Where Φ_{T} is the intersystem crossing efficiency estimated from equation (1), τ_{s} is the emission lifetime of the singlet excited state. τ_{s} is taken from the short range lifetime measurements. The values extracted from the transient characterization of emitters are listed in **Table S4**.

1.5 Device fabrication. OLEDs were fabricated on patterned ITO-coated glass substrates with a sheet resistance of 15 Ω/\Box . Before device fabrication, the ITO glass substrates were sequentially cleaned with Decon 90, rinsed in de-ionized water, dried in an oven at 120°C, and treated with oxygen plasma. After that, the clean substrates were transferred into a vacuum deposition system with a base pressure better than 1×10^{-6} mbar for organic and metal deposition. The devices were fabricated by evaporating organic semiconductors onto the substrate sequentially with an evaporation rate of 1-2 Å s⁻¹. The cathode was completed through thermal deposition of LiF at a deposition rate of 0.1 Å s⁻¹, and then capped with Al metal through thermal evaporation at a rate of 10 Å s⁻¹. EL luminescence spectra and CIE color coordinates were measured with a Spectrascan PR650 photometer and the current-voltage characteristics were measured with a computer-controlled Keithley 2400 Source Meter and CS-200 under ambient atmosphere.





Figure S1. ¹H NMR spectrum of TX-2, TX-3, and TX-4.





Figure S2. ¹H NMR spectrum of TXO-PhCz1、TXO-PhCz3 and TXO-PhCz4.





Figure S3. ¹³C NMR spectrum of TXO-PhCz1, TXO-PhCz3, and TXO-PhCz4.





Figure S4. HRMS EI+ spectrum of TXO-PhCz1.

Figure S5. HRMS EI+ spectrum of TXO-PhCz3.



Figure S6. HRMS EI+ spectrum of TXO-PhCz4.



Figure S7. TGA (a) and DSC (b) curves of TXO-PhCz1, TXO-PhCz3 and TXO-PhCz4.



Figure S8. Cyclic voltammogram of TXO-PhCz1, TXO-PhCz3, and TXO-PhCz4. The measurement of oxidation potentials were performed in with 0.1 M of nBu_4NPF_6 as a supporting electrolyte, and the reduction CV were performed in tetrahaydrofuran/DMF with 0.1 M of nBu_4NCIO_4 as a supporting electrolyte.



Figure S9. (a) Absorption spectra of TXO-PhCz1 in different solvent; (b) Fluorescence spectra of TXO-PhCz1 in different solvent. Concentration of TXO-PhCz1 in all cases is $50 \ \mu$ M.



Figure S10. (a) Absorption spectra of TXO-PhCz3 in different solvent; (b) Fluorescence spectra of TXO-PhCz3 in different solvent. Concentration of TXO-PhCz3 in all cases is $50 \ \mu$ M.





Figure S11. (a) Absorption spectra of TXO-PhCz4 in different solvent; (b) Fluorescence spectra of TXO-PhCz4 in different solvent; (c) Normalized fluorescence spectra of TXO-PhCz4 in different solvent. Concentration of TXO-PhCz4 in all cases is $50 \ \mu\text{M}$.



Figure S12. Fluorescence spectra in oxygen-free 2-MeTHF solution at room temperature and fluorescence and phosphorescence spectra in oxygen-free 2-MeTHF solution 77 K of TXO-PhCz1 (a), TXO-PhCz3 (b), and TXO-PhCz4 (c).



Figure S13. Molecular structures in the single crystals of TXO-PhCz1 (a) and TXO-PhCz4 (b); (c) Molecular packing in the single crystal of TXO-PhCz4 along the *a*-axis direction.



Figure S14. (a) PL spectra of 10 wt% TXO-PhCz3:mCP film at 300 K without delay and with a delay of 0.3 μ s; (b) PL spectra of 10 wt% TXO-PhCz4:mCP film at 300 K without delay and with a delay of 3.69 μ s.



Figure S15. Transient PL decay of the doped isomer: mCP film based on (a) TXO-PhCz3 and (b) TXO-PhCz4 in the time range of 200 ns. The doping concentration is 10 ± 1 wt%.



Figure S16. Log plot of the intensity ratio of prompt fluorescence to delayed fluorescence vs 1/T of TXO-PhCz3 (a) and TXO-PhCz4 (b). The error bars represent one standard deviation, calculated from multi-measurement average.



Figure S17. External quantum efficiency versus current density characteristics of the devices based on TXO-PhCz3 and TXO-PhCz4. The solid lines represent the simulated EQE by employing the TTA model.





Figure S18. (a) Device structure of OLEDs based on PPO21 host and TXO-PhCz4 emitter; and (c) Energy levels of the molecules for OLEDs based on PPO21 host and TXO-PhCz4 emitter.



Figure S19. Device characteristic of OLEDs based on PPO21 host and TXO-PhCz4 emitter: (a) Current density-Voltage-Luminance characteristics; (b) Current efficiency-Luminance-Power efficiency characteristics; (c) EQE-Luminance characteristics; and (d) EL spectra at different voltage.



Figure S20. External quantum efficiency versus current density characteristics of OLEDs based on PPO21 host and TXO-PhCz4 emitter. The solid lines represent the simulated EQE by employing the TTA model.

Table S1. Absorption and emission characteristics of TXO-PhCz1 in different solvents.

Solvent	$\lambda_{ab}\left(nm ight)$	$\lambda_{em} \left(nm \right)$	$\Phi_{\rm f}(10^{-3})$
toluene	395	526	12.9
1,4-dioxane	394	537	7.94
choloform	397	583	4.71
ethylacetate	391	579	3.92
THF	393	579	2.56
ethanol	395	n.d.	/
acetonitrile	390	n.d.	/
methanol	390	n.d.	/

Table S2. Absorption and emission characteristics of TXO-PhCz3 in different solvents.

Solvent	$\lambda_{ab}^{}\left(nm ight)$	λ_{em} (nm)	$\Phi_{\rm f}(10^{-3})$
toluene	417	493	26.8
1,4-dioxane	399	513	25.4
choloform	412	564	22.6
ethylacetate	398	550	18
THF	401	563	14.9
ethanol	403	n.d.	5.1
acetonitrile	396	n.d.	/
methanol	401	n.d.	/

Table S3. Absorption and emission characteristics of TXO-PhCz4 in different solvents.

Solvent	λ_{ab} (nm)	λ_{em} (nm)	$\Phi_{\rm F} (10^{-3})$
toluene	400	494	10.9
1,4-dioxane	394	523	9.9
choloform	397	572	2.8
ethylacetate	390	554	0.9
THF	390	n.d	0.37
ethanol	387	n.d.	/
acetonitrile	383	n.d.	/
methanol	386	n.d.	/

Table S4. Lifetime data extracted from the transient characterization of 10 ± 1 wt% TXO-PhCz4: mCP film in the time range of 200 µs at different temperatures.

Temperature	T1 (μs)	Ā1	T2 (μs)	Ā2	T3 (μs)	Ā3
(K)						
300	3.815	42.824	14.800	57.176		
250	1.581	11.756	8.136	53.360	28.293	34.884
200	1.240	9.632	8.579	50.144	37.859	40.222
150	1.143	13.512	10.292	52.844	57.552	33.654
130	1.157	14.33	10.579	51.058	62.852	34.612
100	1.220	22.09	12.707	48.372	92.188	29.538

Table S5. Data extracted from the transient characterization of 10±1 wt% emitter:mCP film at room temperature.

Compounds	Φ _{Total} (%)	Φ _{prompt} (%)	Ф _{ТАD} F (%)	Φ _T (%)	$k_{\mathrm{s}}\left(\mathrm{s}^{\mathrm{-1}} ight)$	$k_{\rm ISC}({ m s}^{-1})$	$k_{\mathrm{TADF}}(\mathrm{s}^{-1})$	K	$k_{\rm r}({\rm s}^{-1})$
TXO-PhCz3	54.66	1.14	53.52	98	4.72×10 ⁷	4.67×10 ⁷	1.72×10 ⁴	0.032	5.38×10 ⁵
TXO-PhCz4	68.98	10.97	58.01	84	2.85×10 ⁷	2.39×10 ⁷	4.07×10 ⁵	0.13	3.13×10 ⁶

In Table S5, K and k_{TADF} were calculated according to the literature.^{1,2} Φ_T was calculated according to the equation: $\frac{\Phi_{prompt}}{\Phi_{TADF}} = \frac{1}{\frac{1}{\Phi_T} - 1};^3 \Phi_T$ of TXO-PhCz3 at room

temperature here is comparable with that obtained from the Berberan-Santos plot. Φ_T of TXO-PhCz4 at room temperature here is lower than that obtained from the Berberan-Santos plot at low temperature. We ascribed to the temperature dependence of the k_{ISC} due to the strong phosphorescent emission at low temperature.

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