Supplementary information for:

Thioxanthone-containing blue thermally activated delayed fluorescent emitter

Natsuko Kanno, Yongxia Ren, Yu Kusakabe, Katsuaki Suzuki, Katsuyuki Shizu, Hiroyuki Tanaka, Yoshimasa Wada, Hiromichi Nakagawa, Jan Geldsetzer, and Hironori Kaji*

Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611-0011, Japan
E-mail: kaji@scl.kyoto-u.ac.jp

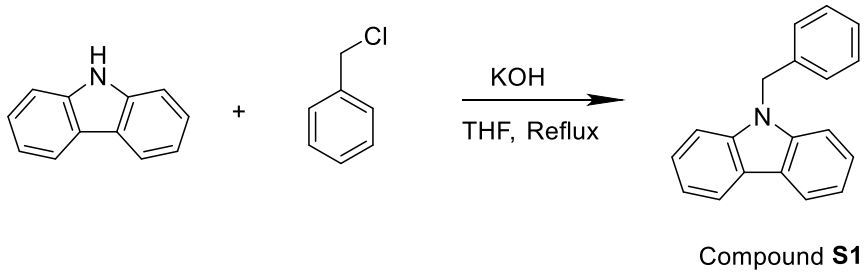
1. Synthesis and characterization

1.1. Procedure for material characterization

^{1}H and ^{13}C NMR spectra were obtained with JEOL ECA (600 MHz for ^{1}H and 151 MHz for ^{13}C) with a 5-mm CPTCI triple resonance inverse detection cryoprobe. $CDCl_3$ was used as a deuterated solvent and all measurements were performed at 300 K. Chemical shifts are reported in δ ppm, using tetramethylsilane for ^{1}H NMR and solvent peaks for ^{13}C NMR spectra as internal standards. Atmospheric pressure chemical ionization (APCI) mass spectra were measured with a Bruker micrOTOF-Q II (Bruker, Germany).

1.2. Synthesis procedure

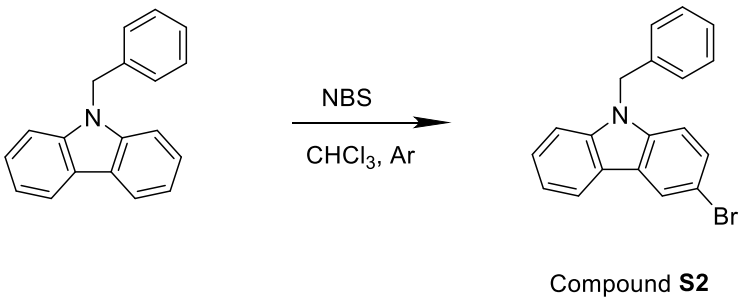
1.2.1. Synthesis of compound **S1**



Supplementary Scheme 1. Synthesis of compound **S1**.

Carbazole (25.1 g, 150 mmol, 1 eq) and potassium hydroxide (41.0 g, 730 mmol, 4.2 eq) were placed in a two-necked flask equipped with a magnetic stirrer and a reflux condenser. The flask was evacuated and backfilled with argon. Then, 250 mL of THF was added to the mixture followed by the addition of benzyl chloride (57.0 g, 450 mmol, 3 eq). The reaction mixture was heated to reflux for 66 h. After cooling to room temperature, the suspension was poured into water, extracted three times with dichloromethane. The combined organic phase washed sequentially with a saturated ammonium chloride solution, water and brine. After drying over Na_2SO_4, the solvent was removed under reduced pressure and the crude product was recrystallized from ethanol to give white needles (compound **S1**, 35.3 g, 137 mmol, 92%). The crystals were thoroughly washed with hexane to remove excess benzyl chloride which would interfere with the subsequent bromination reactions. The analytical data matched Ref. S1.

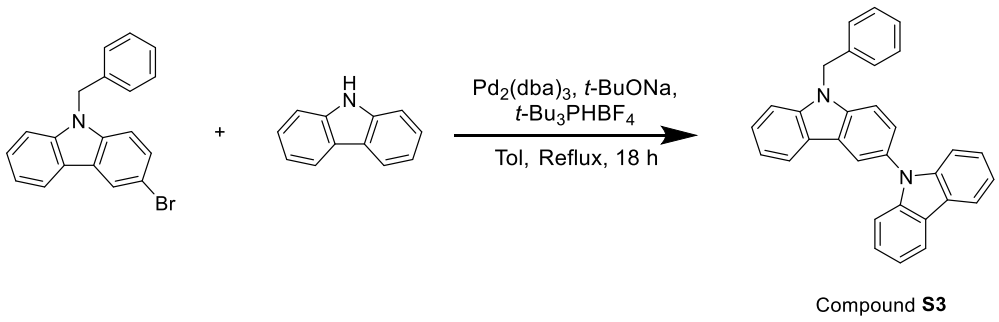
1.2.2. Synthesis of compound **S2**



Supplementary Scheme 2. Synthesis of compound **S2**.

N-benzylcarbazole (Compound **S1**, 10.3 g, 40 mmol, 1 eq) and *N*-bromosuccinimide (NBS) (4.84 g, 41 mmol, 1.025 eq) were dissolved in 200 mL of chloroform. The flask was flushed with argon and stirred in the dark at 30 °C for 3 h. The crude reaction mixture was washed sequentially with a sodium thiosulfate solution, water and brine. The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was recrystallized from ethanol yielding 10.8 g of white needles which were found to be 70% of desired product and 30% of recovered starting material by NMR analysis (27.9 mmol isolated product, 70% yield, compound **S2**). As unbrominated, protected carbazole was deemed inconsequential to the following cross-coupling reactions, the reaction product was not purified further. The analytical data matched Ref S2.

1.2.3. Synthesis of compound **S3**

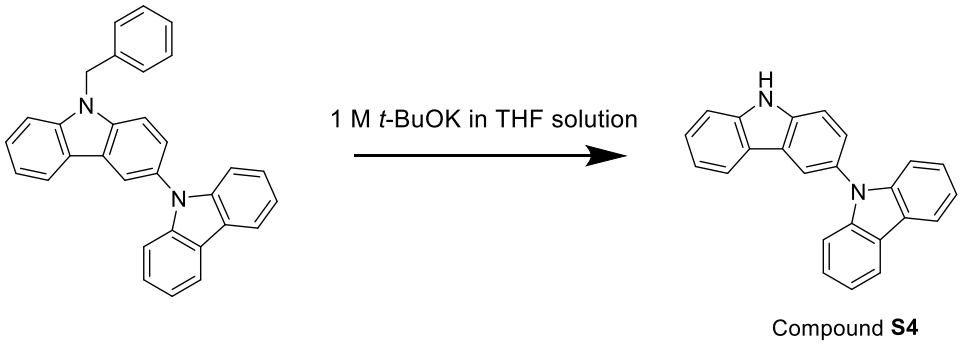


Supplementary Scheme 3. Synthesis of compound **S3**.

N-benzyl-3-bromocarbazole (Compound **S2**, 1.68 g, 5 mmol, 1 eq), carbazole (836 mg, 5

mmol, 1 eq), sodium *tert*-butoxide (*t*-BuONa, 961 mg, 10 mmol, 2 eq), tris(dibenzylideneacetone) dipalladium ($Pd_2(dba)_3$, 137 mg, 150 µmol, 3 mol-%) and tri-*tert*-butylphosphonium tetrafluoroborate (*t*-Bu_3PHBF_4, 87 mg, 300 µmol, 6 mol-%) were added to a Schlenk flask equipped with a magnetic stirrer. The flask was evacuated and backfilled with argon. After adding 50 mL of dry toluene, the flask was sealed and heated to 125 °C for 18 h. The reaction mixture was allowed to cool to room temperature before being filtrated through celite and washed down with ethyl acetate. The crude product was purified by column chromatography (hexane:ethyl acetate =15:1) and the coupling product (Compound **S3**, 1.75g, 4.13 mmol, 83%) was isolated as a white powder. The analytical data matched Ref S3.

1.2.4. Synthesis of compound **S4**

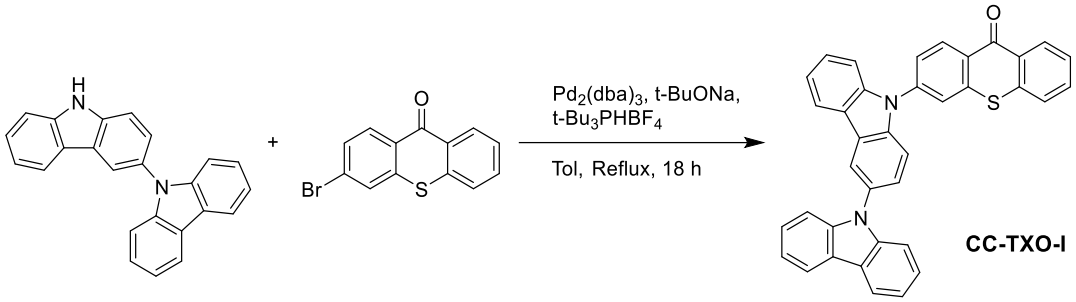


Supplementary Scheme 4. Synthesis of compound **S4**.

Benzyl-protected carbazolylcarbazole (Compound **S3**, 1.94 g, 4.58 mmol, 1 eq) were dissolved in 143 mL of DMSO in a two-necked flask equipped with a magnetic stirrer. 45.8 mL freshly prepared 1 M of potassium *tert*-Butoxide solution (5.61 g in 50 mL dry THF) was added rapidly under stirring. After 10 min, air was bubbled through the solution, which was closely monitored to prevent spillage as stable bubbles tended to develop at various times. After 3 h, bubbling was terminated and the solution poured into 200 mL of water to which about 1 g of NaCl had been added; this suspension was stirred for approximately 1 h. Thereafter, the top of the beaker was covered with aluminium foil and the suspension allowed to rest in the fridge over 3 nights. The precipitate was collected by filtration and dried in vacuum. The desired product (Compound **S4**, 1.51 g, 4.54 mmol) were isolated as a

white powder and shown to require no further purification. The analytical data matched Ref S3.

1.2.5. Synthesis of compound **CC-TXO-I**

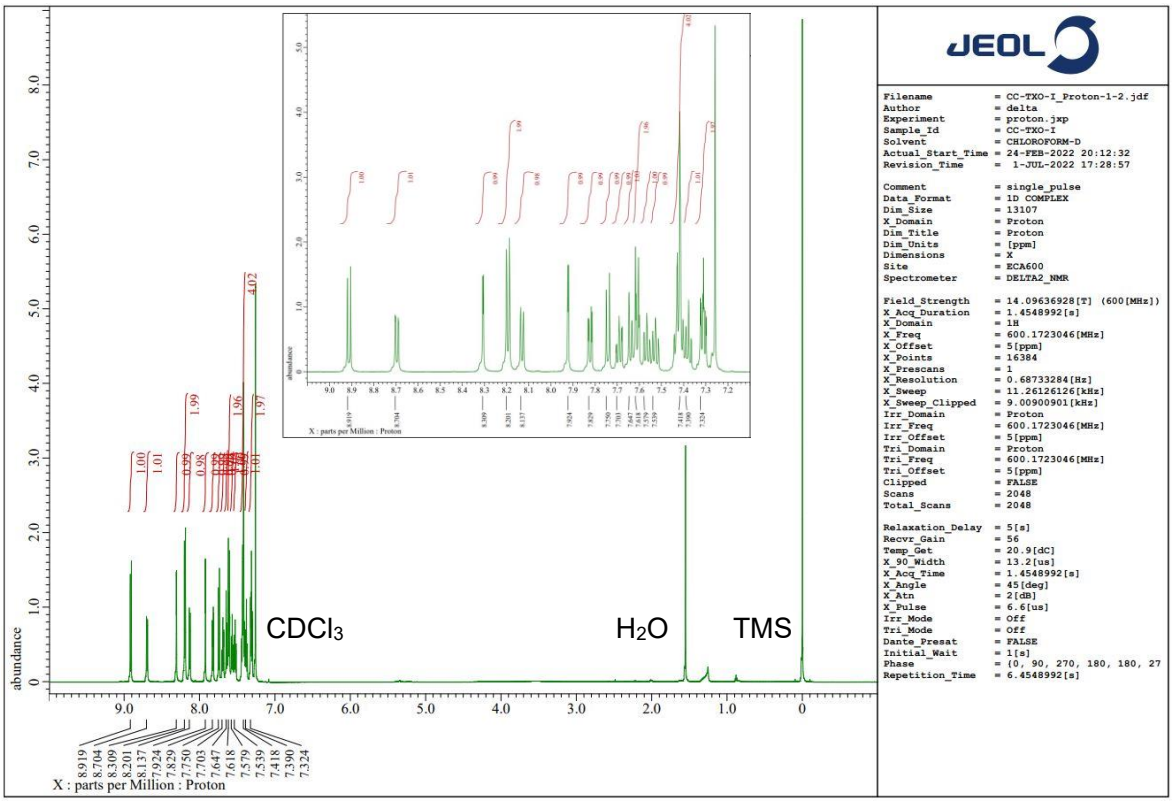


Supplementary Scheme 5. Synthesis of **CC-TXO-I**.

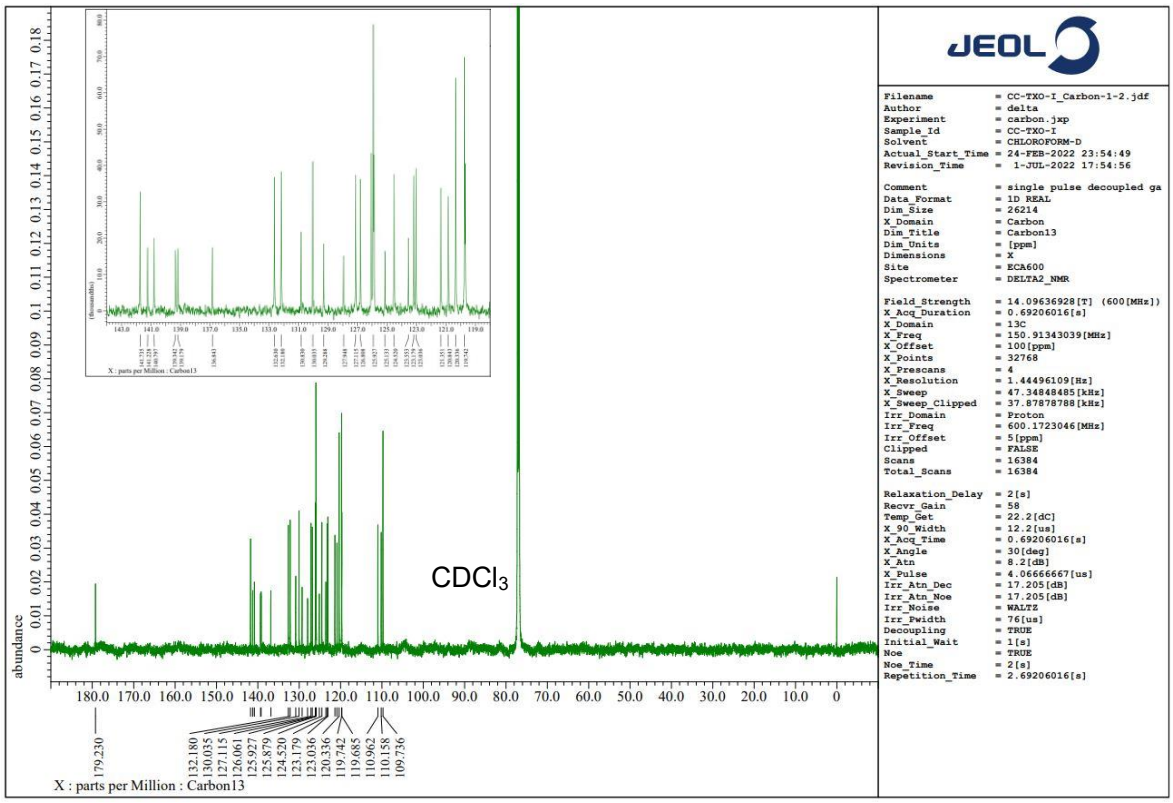
3-carbazolyl-carbazole (Compound **S4**, 665 mg, 2 mmol, 1 eq), 3-bromothioxanthone (582 mg, 2 mmol, 1 eq), sodium *tert*-butoxide (*t*-BuONa, 384 mg, 4 mmol, 2 eq), tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$, 91.6 mg, 100 µmol, 5 mol-%) and tri-*tert*-butylphosphonium tetrafluoroborate (*t*-Bu_3PHBF_4, 58.0 mg, 200 µmol, 10 mol-%) were added to a Schlenk flask equipped with a magnetic stirrer. The flask was evacuated and backfilled with argon three times and 20 mL of dry toluene were added. The flask was sealed and heated to reflux for 18 h. During this time, a yellow precipitate began gathering on the walls of the flask. After cooling to room temperature, the crude reaction mixture was filtrated through celite, washed with excess dichloromethane until the filtrate no longer fluoresced under 360 nm UV light. The product was purified by column chromatography (hexane:DCM =1:1) and subsequent recrystallization from chloroform/hexane. Bright yellow crystals (861 mg, 1.59 mmol, 79%) were isolated.

^{1}H-NMR (600 MHz, CDCl3): δ (ppm) = 8.92 (d, J = 8.2 Hz, 1 H), 8.70 (dd, J = 8.2, 1.4 Hz, 1 H), 8.31 (d, J = 1.4 Hz, 1 H), 8.20 (d, J = 7.6 Hz, 2 H), 8.14 (d, J = 7.6 Hz, 1 H), 7.93 (d, J = 2.0 Hz, 1 H), 7.83 (dd, J = 8.9, 2.0 Hz, 1 H), 7.75 (d, J = 8.3 Hz, 1 H), 7.70 (td, J = 7.6, 1.3 Hz, 1 H), 7.65 (d, J = 7.6 Hz, 1 H), 7.62 (dd, J = 8.2, 1.4 Hz, 2 H), 7.58 (t, J = 7.6 Hz, 1 H), 7.53 (t, J = 8.3 Hz, 1 H), 7.40-7.46 (m, 4 H), 7.39 (t, J = 7.6 Hz, 1 H), 7.32 (td, J = 8.3, 1.4 Hz, 2 H); ^{13}C-NMR (150 MHz, CDCl3): δ (ppm) = 179.2, 141.8, 141.3, 140.8, 139.4, 139.2, 136.9, 132.6, 132.2, 130.9, 130.0, 129.3, 128.0, 127.1, 126.8, 126.1, 126.0, 125.9, 125.1, 124.5, 123.6, 123.2, 123.1, 121.4, 120.8, 120.3, 119.8, 119.7, 111.0, 110.2,

109.7; APCI-MS (*m/z*): $[M+H]^+$ calcd. for $C_{37}H_{22}N_2OS$, 543.1526; found. 543.1525.



^{1}H NMR spectrum of CC-TXO-I after train sublimation.



^{13}C NMR spectrum of CC-TXO-I after train sublimation.

1.3. Photophysical characterizations

The oxygen-free toluene solution of CC-TXO-I at a concentration of 1×10^{-4} M was prepared in a glove box (UniLab, MBraun, Germany). The concentrations of oxygen and water in the glove box were less than 0.1 ppm. To prepare solution-processed films, spin coating was conducted with solutions in 2.5 mg mL^{-1} with 1000 rpm for 30 seconds on fused quartz substrates, and the fabricated films were dried at 30 ℃ for 30 minutes under N_2 atmosphere. Also, vacuum-processed films were deposited on fused quartz substrates with vacuum-deposition equipment (SE-4260, ALS Technology, Japan). The pressure in the chamber was $\sim10^{-5}$ Pa and the thickness of films were 50 nm.

For photophysical characterizations, a UV-vis spectrophotometer (UV-2600, SHIMADZU, Japan), a spectrofluorometer (FluoroMax Plus, HORIBA, Japan), and an absolute photoluminescence (PL) quantum yield (Φ_{PL}) spectrometer (C9920-02, Hamamatsu Photonics, Japan) were used. In addition, the transient PL decay curves were obtained by a fluorescence lifetime measurement system (Quantaurus-Tau C11367-01, Hamamatsu Photonics, Japan), and it was used in combination with a cryostat (Optistat DN2, Oxford Instruments, UK) for a temperature-dependent transient PL decay. Fig. S1 shows an example of a transient PL measurement for 6 vol% CC-TXO-I:PPF doped film.

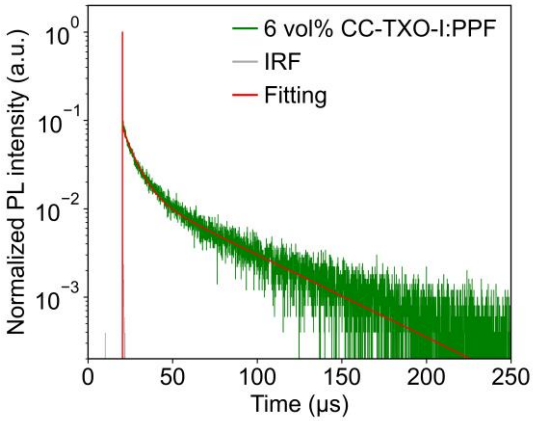


Fig. S1. Transient PL decay curve of 6 vol% CC-TXO-I:PPF doped film; experimental data (green line), fitting curve (red line), and instrument response function (gray line).

1.4. Fabrication of OLEDs

First, a patterned indium tin oxide (ITO) glass substrate was cleaned by UV-ozone treatment for 15 minutes. Then, each layer was deposited at the pressure of ~10^{-4} Pa with vacuum-deposition equipment (SE-4260, ALS Technology, Japan). After deposition of organic layers and an electrode, the device was sealed by a UV-curable resin in the glove box.

An OLED performance was characterized with a source meter (2400, Keithley, USA) and an EQE measurement system (C9920-12, Hamamatsu Photonics, Japan).

2. Supplementary figures and tables

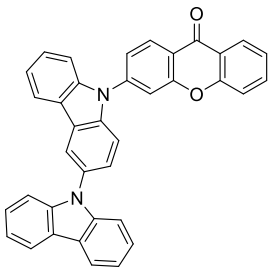


Fig. S2. Chemical structure of CCX-I.[4)]

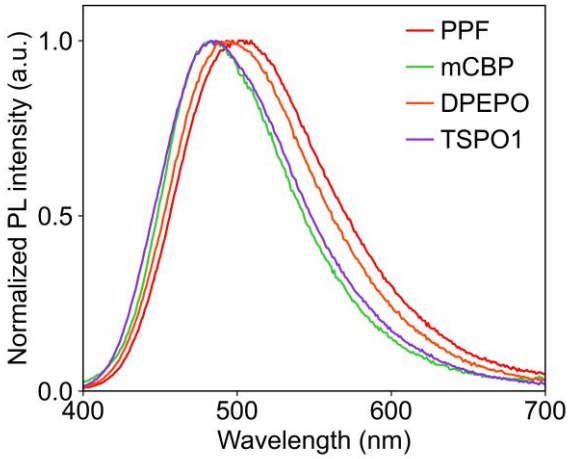


Fig. S3. PL spectra of solution-processed doped films of 6 wt% CC-TXO-I.

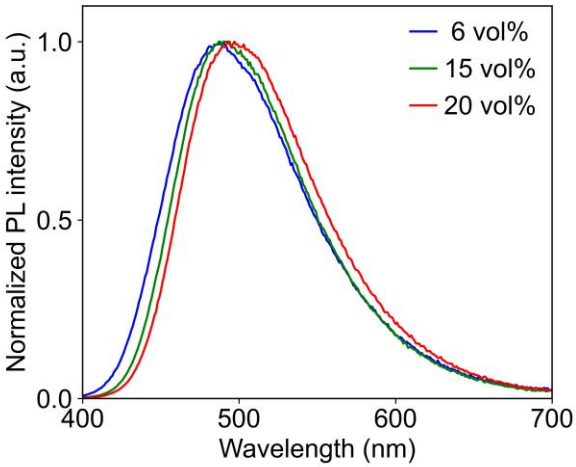


Fig. S4. PL spectra of vacuum-processed doped films of *X* vol% CC-TXO-I:PPF (*X* = 6, 15, 20).

Table SI. Photophysical properties of solution-processed doped films of 6 wt% CC-TXO-I.

Host	λ_{MAX}[a)] (nm)	Φ_{PL}[b)] (%)
PPF	506	68
mCBP	483	15
DPEPO	493	67
TSPO1	486	57

a) Emission peak maximum wavelength excited at 365 nm. b) Φ_{PL} excited at 365 nm.

Table SII. Photophysical properties of vacuum-processed doped films of *X* vol% CC-TXO-I:PPF.

X (vol%)	λ_{MAX}[a)] (nm)	Φ_{PL}[b)] (%)
6	486	84
15	488	83
20	493	84

a) Emission peak maximum wavelength excited at 365 nm. b) Φ_{PL} excited at 365 nm.

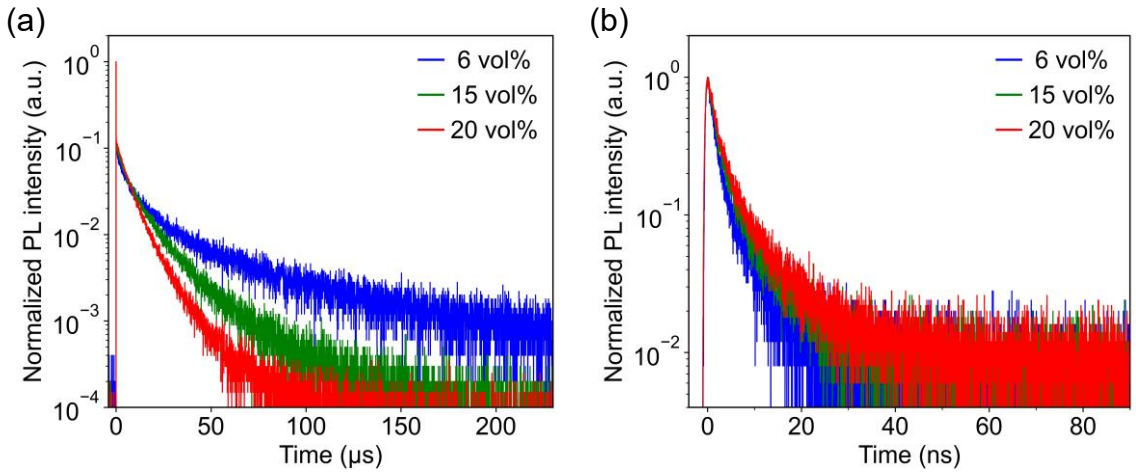


Fig. S5. Transient PL decay curves of vacuum-processed films of *X* vol% CC-TXO-I:PPF excited at 280 nm. (a) All region. (b) Prompt region.

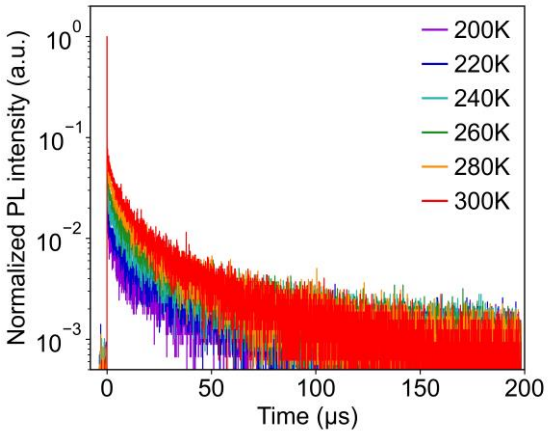


Fig. S6. Transient PL decay curves of 6 vol% CC-TXO-I:PPF vacuum-processed film measured at 200, 220, 240, 260, 280, and 300 K.

Table SIII. Photophysical properties of doped films of the reported TXO-based TADF emitters and performance of OLEDs using those doped films as EMLs.

Emitter	λ_{MAX}[a] (nm)	Φ_{PL} (%)	EQE_{max}[b] (%)	Reference
6 vol% CC-TXO-I:PPF	486	84	19.0	This work
10 wt% CzTXO:DPEPO	N.A.[c]	29.6	11.2	[5]
10 wt% DCz-TXO:DPEPO	N.A.[c]	34.8	11.5	[5]
3 wt% 3,6-2TPA-TX:CBP	N.A.[c]	35.0	23.7[d]	[6]
10 wt% 1,6-2TPA-TX:CBP	N.A.[c]	2.5	2.23	[6]
10 wt% MCz-TXT:mCBP	490	92	25.8	[7]
5 vol% MCz-TXO:CzSi	475	64.7	17.4	[8]
50 wt% Dye1:TFB	472	33	2.23	[9]
50 wt% Dye2:TFB	464	51	3.16	[9]

a) Emission peak maximum wavelength of a doped film. b) Maximum EQE of OLEDs based on the doped film. c) No data was provided. d) Judging from the Φ_{PL} value of 35.0%, the EQE_{max} is considered to be too high.

References

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