

Supporting information

Leveraging Quinoxaline Functionalization for the Design of Efficient Orange/Red Thermally Activated Delayed Fluorescence Emitters

Shantaram Kothavale,^a Rajendra Kumar Konidena,^b Hyunjung Lee,^a and Jun Yeob Lee^{a,c}*

^a School of Chemical Engineering, Sungkyunkwan University 2066, Seobu-ro, Jangan-gu, Suwon, Gyeonggi, 16419, Kore. Email: leej17@skku.edu.

^b Department of Chemistry, Indian Institute of Technology-Patna, Bihta Kanpa Rd, Patna, Dayalpur Daulatpur, Bihar 801106, India.

^c SKKU Institute of Energy Science and Technology, Sungkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon, Gyeonggi, 16419, Republic of Korea.

E-mail: leej17@skku.edu

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Experimental section (General Information)

4,5-difluorobenzene-1,2-diamine, sodium hydride (NaH), tetrakis(triphenylphosphine)palladium, tri-tert-butylphosphine were purchased from P&H tech. 4,4'-dibromobenzil, was acquired from Sigma Aldrich. Copper cyanide (CuCN), 18-crown-6, Cu, was purchased from Alfa Aesar. Sodium borohydride (NaBH₄), 1,2-bis(4-bromophenyl)ethane-1,2-dione, and 3,6-Di-tert-butyl-9H-carbazole, were purchased from Tokyo Chemical Industry (TCI) Ltd. *N,N* dimethyl formamide (DMF), *o*-dichlorobenzene (O-DCB), anhydrous THF, and acetic acid were obtained from Duksan Sci. Co. All these chemicals were used without further purification. Column chromatography (Silica Gel 60, 230–400 mesh, Merck) and sublimation (10⁻³ Torr at 300 °C) purification processes were used to obtain pure products before applying for OLED devices.

The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded in deuterated chloroform (CDCl₃) solution on an Avans 500 MHz spectrometer. Chemical shifts of the ¹H and ¹³C NMR signals were quoted relative to tetramethylsilane ($\delta = 0.00$). All coupling constants are reported in Hertz. The ultraviolet–visible (UV–vis) spectra were obtained using a UV–vis spectrophotometer (JASCO, Easton, MD; V-730), and the photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (PerkinElmer, Waltham, MA; LS55). CV measurement was carried out in dichloromethane solution with scan rate at 100 mV/s. The glassy carbon, platinum wire and Ag/AgCl were used as working, counter and reference electrodes respectively. Internal standard was ferrocenium/ferrocene couple and supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAClO₄). The mass spectra were recorded using Advion, Expression LCMS spectrometer in APCI mode. Absolute photoluminescence quantum yields (PLQYs) of 1 wt % doped polystyrene film solid film were measured with a Hamamatsu Quantaurus-QY C11347-11 spectrometer under a nitrogen atmosphere condition. The transient photoluminescence decay characteristics of solid film

samples were recorded using a Quantaurs-Tau fluorescence lifetime measurement system (C11367-31, Hamamatsu Photonics).

Device Fabrication and Measurements

The device structure was indium-tin oxide (ITO, 50 nm)/poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT, 60 nm)/1,1-bis(4-di-p-tolayl-aminophenyl)cyclohexane (TAPC, 20 nm)/1,3-bis(carbazol-9-yl)benzene (mCP, 10 nm)/PBICT:DBTTPI: TADF emitter (25:30 nm: 1wt.)/4-(triphenylsilyl)-phenyldiphenylphosphine oxide (TSPO1, 5 nm)/1,3,5-Tris(N-phenylbenzimidazol-2-yl)benzene (TPBi, 40 nm)/LiF (1.5 nm)/Al (200 nm). All layers of the device structure were deposited by vacuum thermal evaporation under a high pressure of 3.0×10^{-7} Torr. The material was thermally evaporated and then encapsulated with a glass lid in a nitrogen-filled glove box to protect the device from moisture and oxygen. Electrical characterization of the devices was performed using a Keithley 2400 source meter and optical characterization was carried out using a CS 2000 spectroradiometer.

Synthesis

4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole and 1,2-bis(4-(tert-butyl)phenyl)ethane-1,2-dione was synthesized following the reported procedures.^{1,2}

Synthesis of (5s,6s)-4,7-dibromo-5,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)benzo[c][1,2,5]thiadiazole (2)

3,6-Di-tert-butyl-9H-carbazole (10.58 g, 37.88 mmol) was dissolved in N,N-dimethylformamide (DMF) (120 mL) and cooled to 0 °C. NaH (2.18 g, 45.46 mmol, 50wt %) was added slowly to the reaction mixture and stirred for 1 hr at room temperature. The reaction mixture was again cooled to 0 °C. 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (Intermediate 1) (5 g, 15.15 mmol) was added slowly to the reaction mixture and was stirred at 10-15 °C for 3h. After completion, water was added to the reaction mixture. The orange-red solid precipitated out was filtered and dried well. The crude product was further purified by

column chromatography (30% DCM in hexane) to afford the desired product as orange solid (9.8 g, 76.20 %). MS (FAB) m/z 847 [(M + H)⁺]. ¹H NMR (500 MHz, CDCl₃): δ 7.52 (s, 4H), 6.88-6.86 (m, 4H), 6.59 (d, J = 10.0 Hz, 4H). 1.32 (s, 36H).

Synthesis of (5s,6s)-7-bromo-5,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)benzo[c][1,2,5]thiadiazole-4-carbonitrile (3)

Intermediate **2** (5 g, 5.89 mmol) was dissolved in DMF (100 mL). Copper cyanide (0.63 g, 7.06 mmol) was added and the reaction mixture was refluxed for 12 h. After complete conversion of starting material to the product, the reaction mixture was cooled to room temperature, and water was added to it. The solid precipitated out was filtered and dried well. The crude product was further purified with column chromatography (50% DCM in hexane) to obtain the pure product (2.9 g, 62%). MS (FAB) m/z 795 [(M + H)⁺].

Synthesis of (5s,6s,7s)-5,6,7-tris(3,6-di-tert-butyl-9H-carbazol-9-yl)benzo[c][1,2,5]thiadiazole-4-carbonitrile (4)

Intermediate **3** (1 g, 1.25 mmol) was dissolved in *ortho*-dichlorobenzene (30 mL). 3,6-Di-tert-butyl-9H-carbazole (0.45 g, 1.63 mmol), potassium carbonate (0.35 g, 2.51 mmol), copper (0.16 g, 2.51 mmol), 18-crown-6 (0.07 g, 0.25 mmol) were added and the reaction mixture was refluxed for 12 h. After complete conversion of starting material to the product, the reaction mixture was cooled to room temperature, and water was added into it. The solid precipitated out was filtered and dried well. The crude product was further purified with column chromatography (30 % DCM in hexane) to obtain the pure product (0.85 g, 68%). MS (FAB) m/z 994 [(M + H)⁺]. ¹H NMR (500 MHz, CDCl₃): δ 7.69-7.70 (d, J = 2.0 Hz, 2H), 7.56-7.57 (d, J = 2.0 Hz, 2H), 7.17-7.18 (t, J = 1.5 Hz, 2H), 6.83-6.96 (m, 8H), 6.47-6.48 (d, J = 1.5 Hz, 4H), 1.30 (s, 18H), 1.28 (s, 18H), 1.19 (s, 18H).

Synthesis of (4s,5s,6s)-2,3-diamino-4,5,6-tris(3,6-di-tert-butyl-9H-carbazol-9-yl)benzotrile

(5)

Intermediate 4 (0.8 g, 0.80 mmol) was dissolved in anhydrous THF (40 mL) and cooled to 0 °C. lithium aluminum hydride, NaBH₄ (0.15 g, 4.02 mmol) was added slowly to the reaction mixture and it was stirred at room temperature 2-3 hrs. After complete consumption of starting material, the reaction mixture was quenched in ice water and extracted with ethyl acetate. The organic layer was dried over magnesium sulfate and concentrated on a rotary evaporator to obtain a pure product. (0.18 g, 24 %). MS (FAB) m/z 966 [(M + H)⁺].

Synthesis of (6s,7s,8s)-2,3-bis(4-bromophenyl)-6,7,8-tris(3,6-di-tert-butyl-9H-carbazol-9-yl)quinoxaline-5-carbonitrile (6)

Intermediate 5 (1.1 g, 1.14 mmol) and 1,2-bis(4-(*tert*-butyl)phenyl)ethane-1,2-dione (0.42 g, 1.14 mmol) were dissolved in acetic acid (40 mL) and the mixture was heated to reflux for 12 hrs. The reaction mixture was cooled to room temperature and water was added. The solid precipitated out was filtered and dried well as pure product. (0.95 g, 65 %). MS (FAB) m/z 1298 [(M + H)⁺].

Synthesis of (6s,7s,8s)-2,3-bis(4-(tert-butyl)phenyl)-6,7,8-tris(3,6-di-tert-butyl-9H-carbazol-9-yl)quinoxaline-5-carbonitrile (CzQxCN)

Intermediate 5 (0.16 g, 0.16 mmol) and 1,2-bis(4-(*tert*-butyl)phenyl)ethane-1,2-dione (0.05 g, 0.16 mmol) were dissolved in acetic acid (15 mL) and the mixture was heated to reflux for 12 hrs. The reaction mixture was cooled to room temperature and water was added. The orange-colored solid precipitated out was filtered and dried well. The crude product was further purified with column chromatography (30 % DCM in hexane) to obtain the pure product (0.11 g, 55 %). ¹H NMR (500 MHz, CDCl₃): δ 7.81-7.82 (d, *J* = 2.5 Hz, 2H), 7.73-7.75 (d, *J* = 8.5

Hz, 2H), 7.57-7.58 (d, $J = 2.0$ Hz, 2H), 7.38-7.40 (d, $J = 9.0$ Hz, 2H), 7.23-7.24 (d, $J = 2.5$ Hz, 2H), 7.00-7.07 (m, 6H), 6.94-6.96 (d, $J = 8.5$ Hz, 2H), 6.89-6.91 (dd, $J = 8.5$ and 2 Hz, 2H), 6.81-6.83 (d, $J = 9.0$ Hz, 2H), 6.66-6.68 (d, $J = 9.0$ Hz, 2H), 6.56-6.58 (dd, $J = 8.5$ and 2.0 Hz, 2H), 1.34 (s, 27H), 1.33 (s, 18H), 1.22 (s, 18H), 1.21 (s, 9H). ^{13}C NMR (126 MHz,) δ 155.2, 153.6, 153.1, 143.7, 143.3, 142.9, 142.1, 140.4, 139.8, 139.4, 137.6, 136.8, 136.7, 134.9, 134.8, 134.2, 130.1, 130.0, 125.5, 124.9, 124.6, 124.4, 124.3, 123.0, 122.9, 122.3, 115.9, 115.7, 115.1, 113.9, 113.1, 110.9, 109.7, 109.5, 34.9, 34.7, 34.7, 34.6, 34.4, 31.9, 31.9, 31.9, 31.3, 31.2. MS (FAB) m/z 1252 $[(M + H)^+]$.

Synthesis of 4,4'-((6s,7s,8s)-5-cyano-6,7,8-tris(3,6-di-tert-butyl-9H-carbazol-9-yl)quinoxaline-2,3-diyl)dibenzonitrile (CzQx3CN)

Intermediate **6** (0.8 g, 0.61 mmol) was dissolved in DMF (40 mL). Copper cyanide (0.27 g, 3.1 mmol) was added and the reaction mixture was refluxed for 12 h. After complete conversion of starting material to the product, the reaction mixture was cooled to room temperature, and water was added to it. The solid precipitated out was filtered and dried well. The crude product was further purified with column chromatography (60 % DCM in hexane) to obtain the pure product (0.34g, 47 %). ^1H NMR (500 MHz, CDCl_3): δ 7.87-7.88 (d, $J = 8.5$ Hz, 2H), 7.84-7.85 (d, $J = 1.5$ Hz, 2H), 7.72-7.73 (d, $J = 8.5$ Hz, 2H), 7.59-7.60 (d, $J = 2.0$ Hz, 2H), 7.35-7.37 (d, $J = 8.5$ Hz, 2H), 7.27-7.28 (d, $J = 1.5$ Hz, 2H), 7.05-7.09 (m, 4H), 6.89-6.94 (m, 4H), 6.80-6.82 (d, $J = 8.5$ Hz, 2H), 6.66-6.68 (d, $J = 8.5$ Hz, 2H), 6.58-6.60 (dd, $J = 8.5$ Hz and 2.0 Hz, 2H), 1.34 (s, 18H), 1.33 (s, 18H), 1.23 (s, 18H). ^{13}C NMR (126 MHz,) δ 152.5, 151.1, 144.3, 143.9, 143.6, 141.2, 141.1, 140.5, 139.8, 139.6, 137.3, 137.1, 136.5, 135.9, 132.6, 132.1, 130.9, 130.7, 124.8, 124.7, 124.5, 123.2, 123.1, 122.5, 118.0, 116.2, 115.9, 115.3, 114.3, 113.8, 113.5, 113.1, 110.6, 109.6, 109.3, 34.7, 34.6, 34.4, 31.9, 31.9, 31.8. MS (FAB) m/z 1190 $[(M + H)^+]$.

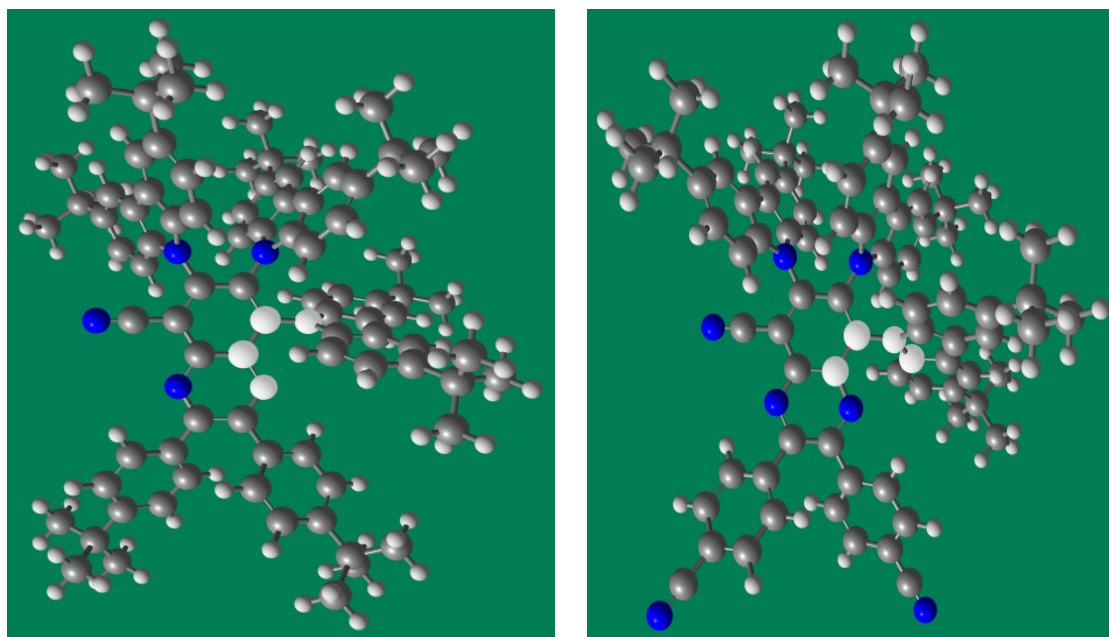


Figure S1. DFT optimized structures of CzQx3CN and CzQx3CN.

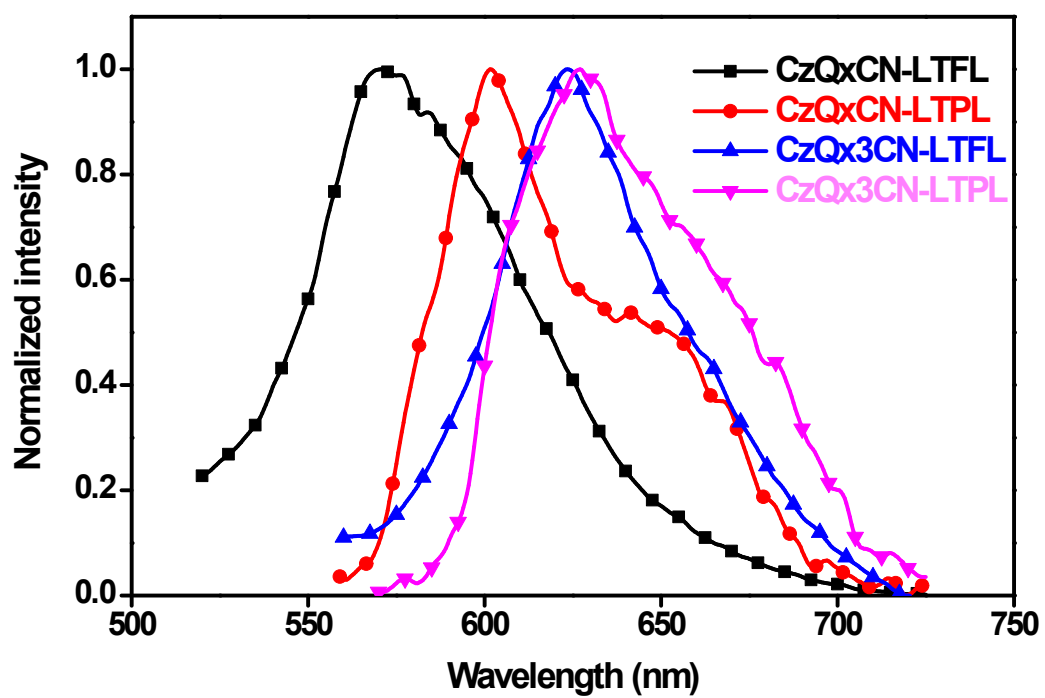


Figure S2. Low temperature fluorescence and phosphorescence spectra of CzQx3CN and CzQx3CN TADF emitters.

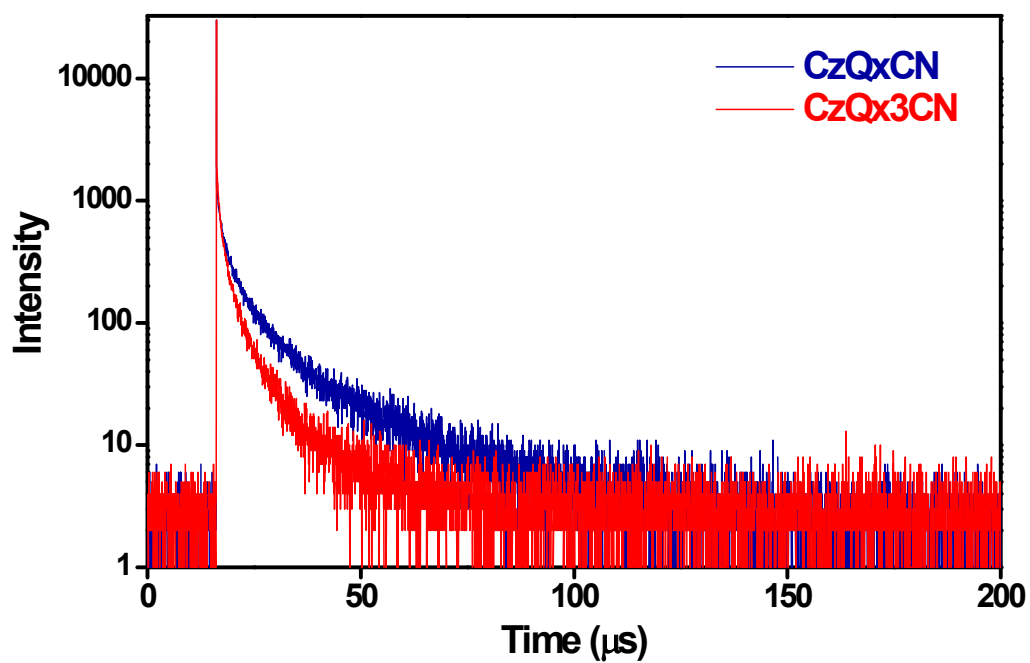


Figure S3. Transient PL of CzQxCN and CzQx3CN.

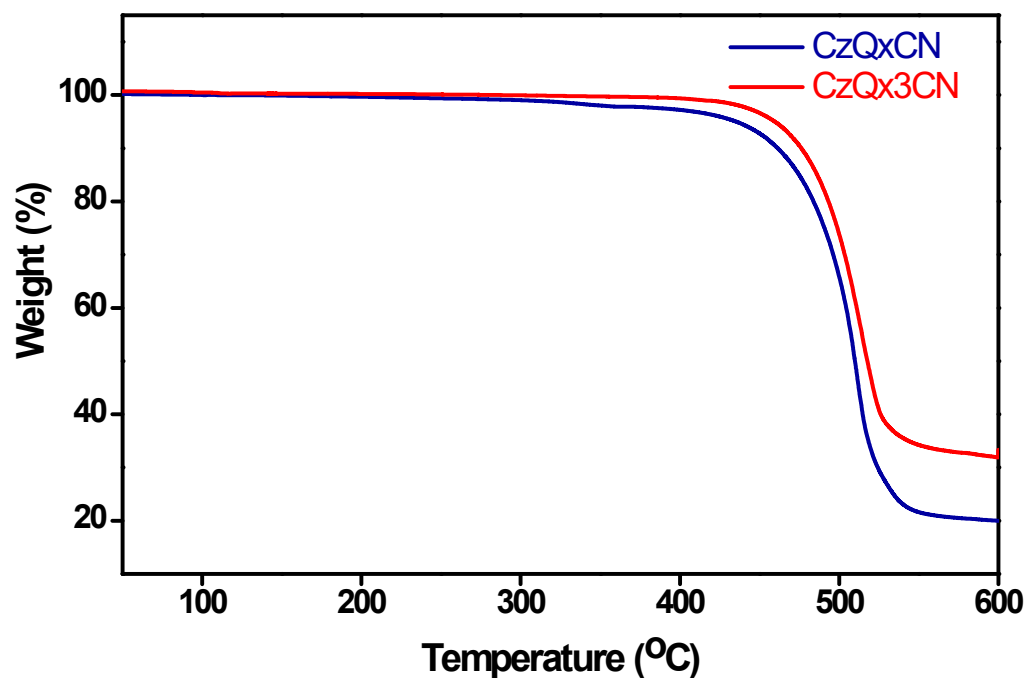


Figure S4. Thermogravimetric analysis (TGA) plot of CzQxCN and CzQx3CN.

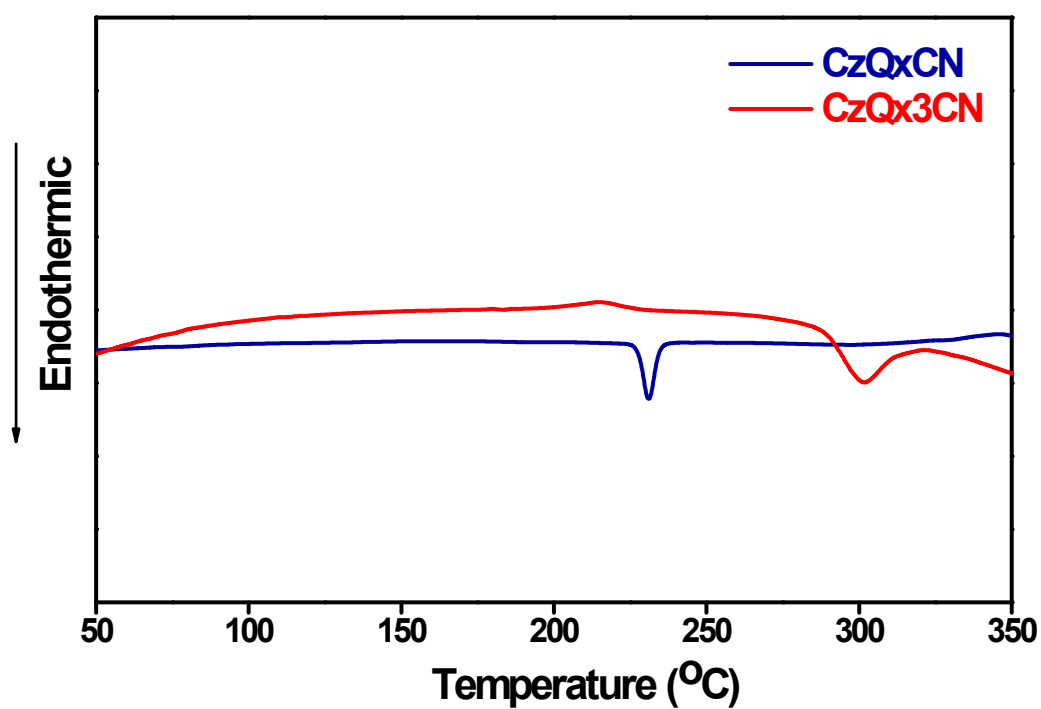


Figure S5. DSC thermograms of CzQxCN and CzQx3CN TADF emitters.

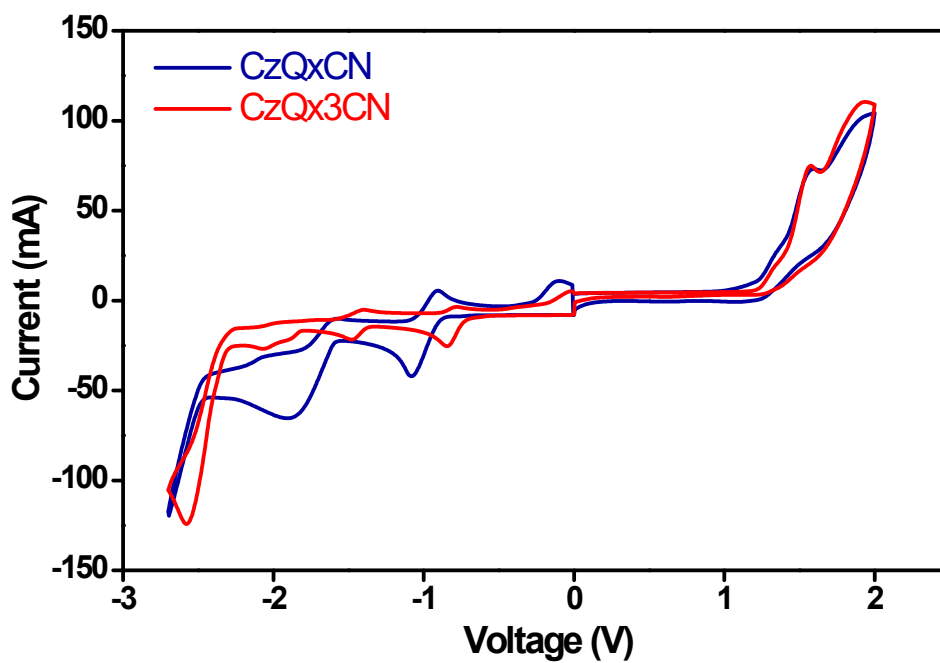


Figure S6. Cyclic voltammogram of CzQxCN and CzQx3CN TADF emitters.

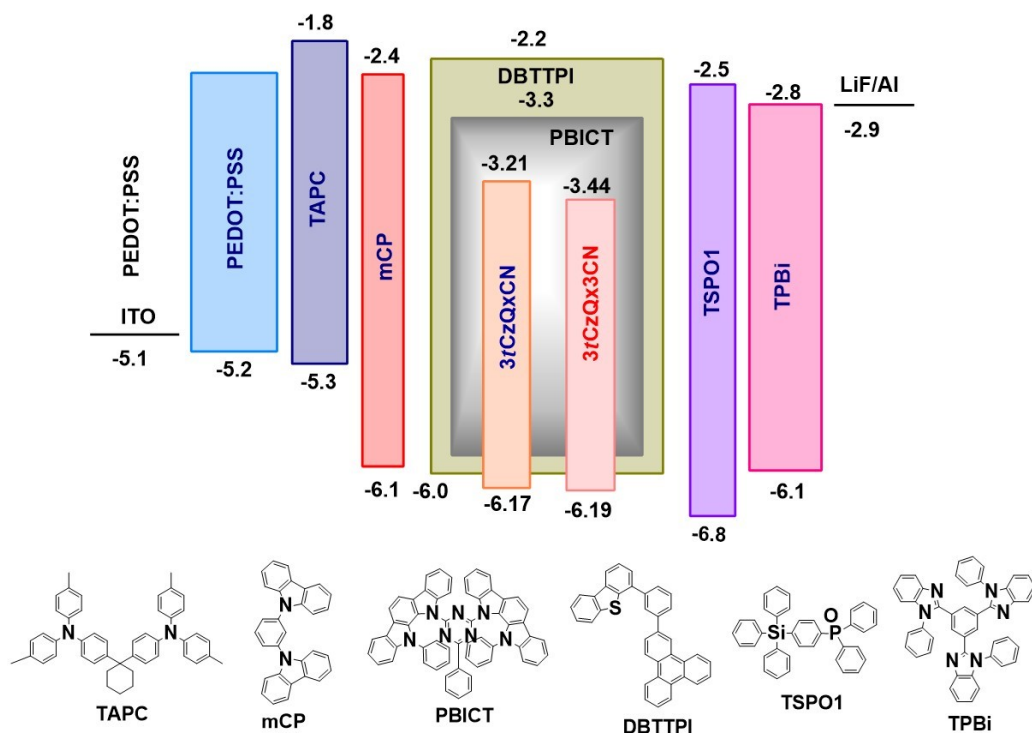


Figure S7. Energy level diagram with chemical structures of layers used in the doped OLEDs of CzQx3CN and CzQx3CN.

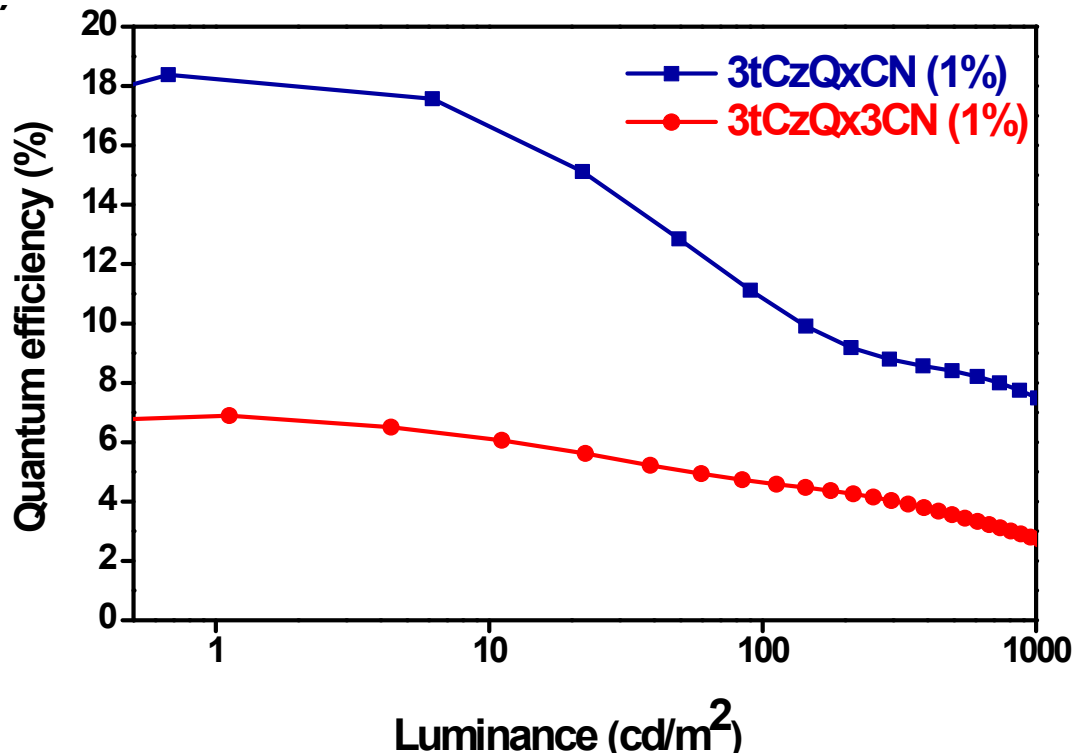


Figure S8. EQE vs Luminance of the CzQx3CN and CzQx3CN.

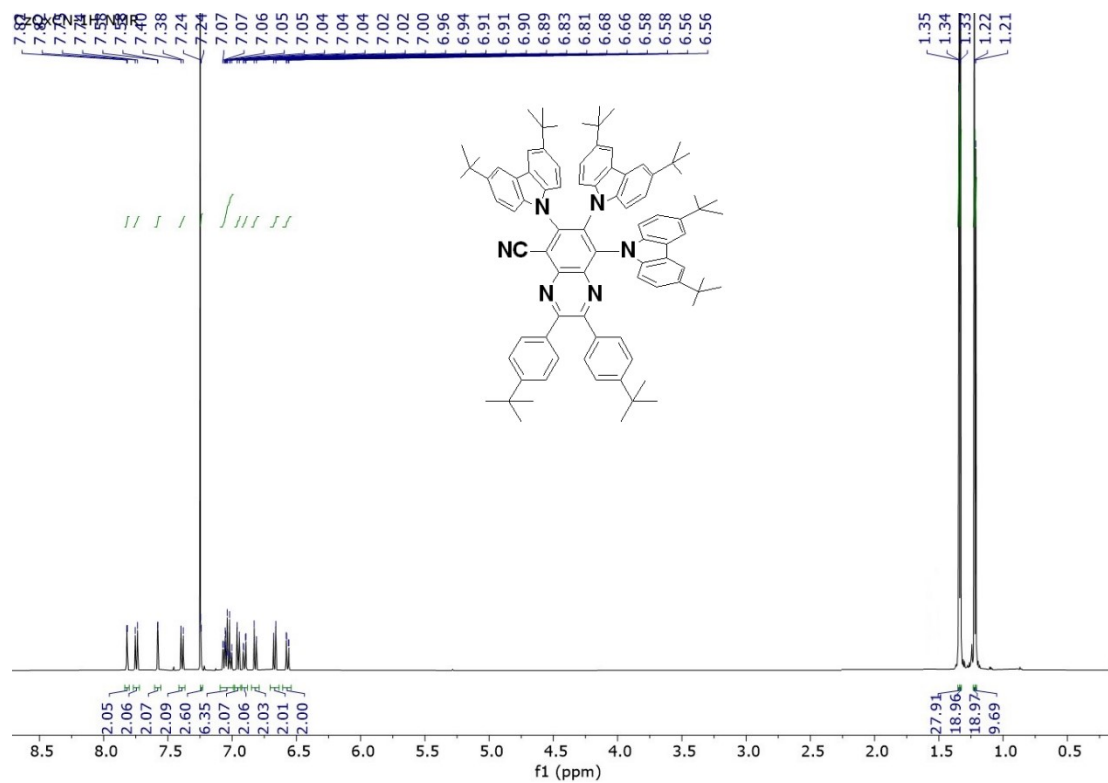


Figure S9. ^1H NMR spectrum of CzQxCN.

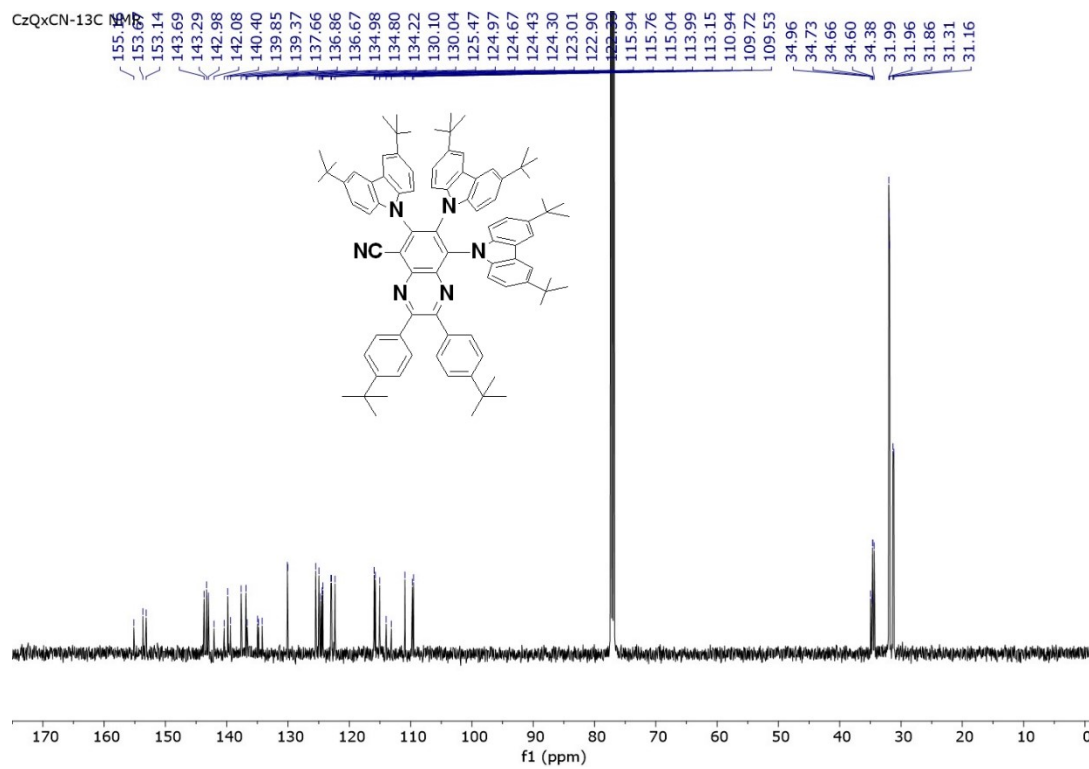


Figure S10. ^{13}C NMR spectrum of CzQxCN.

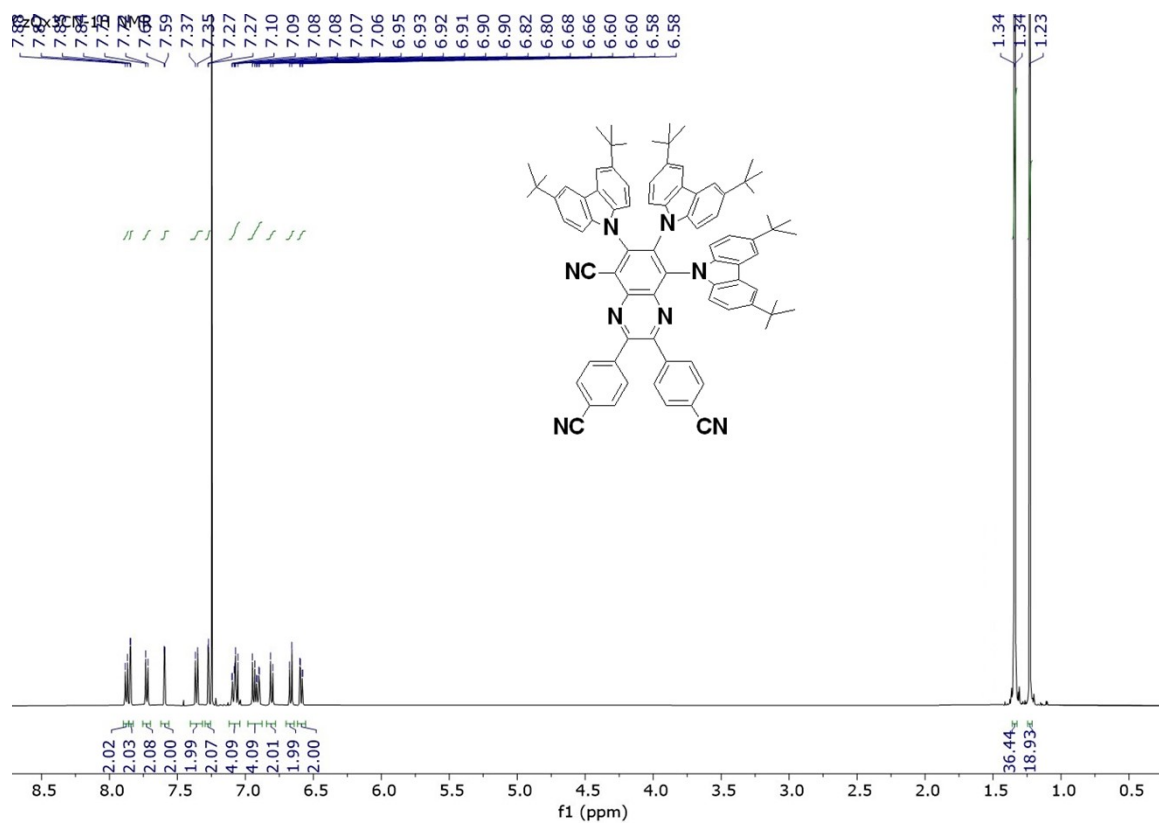


Figure S11. ^1H NMR spectrum of CzQx3CN.

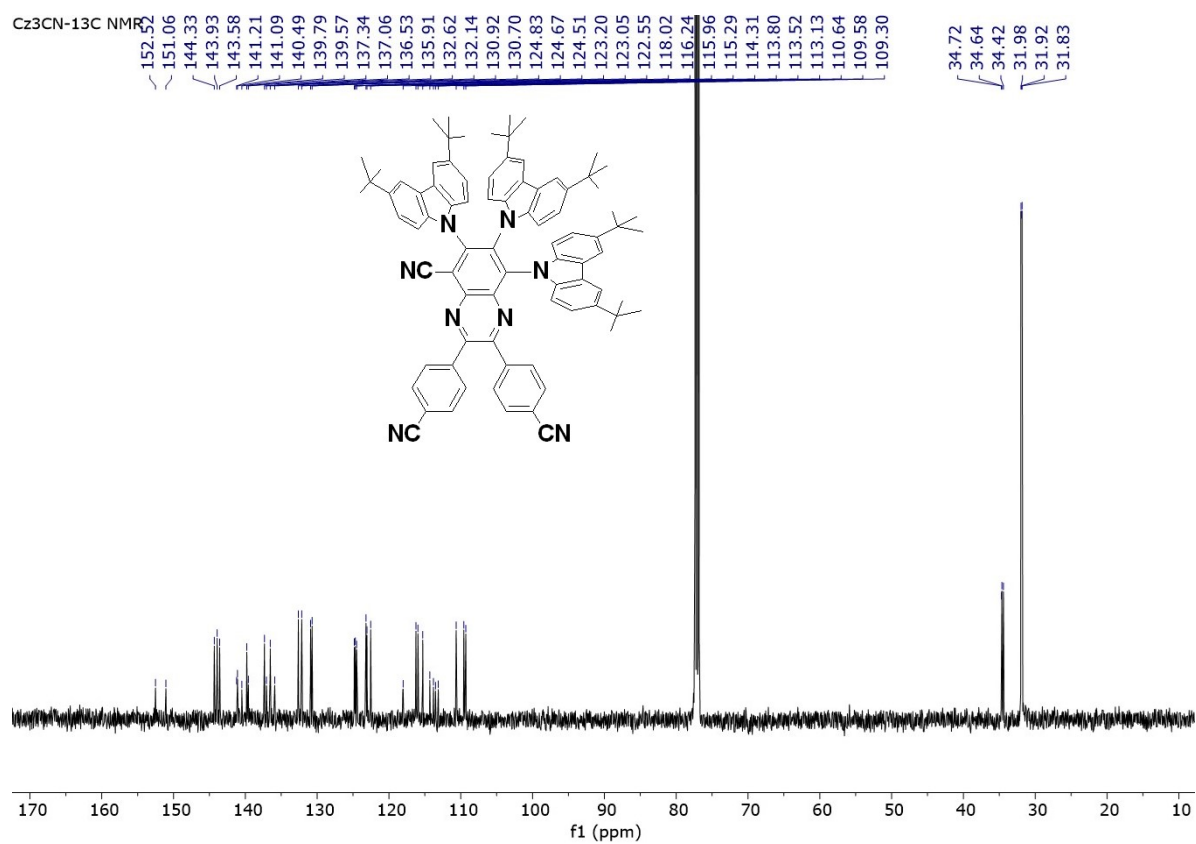


Figure S12. ^{13}C NMR spectrum of CzQx3CN.

Table S1. Summary of the photophysical parameters of the **CzQxCN** and **CzQx3CN** emitters.

Emitter	$\lambda_{\text{abs}}^{\text{a)}$ [nm]	$\lambda_{\text{PL}}^{\text{a)}$ [nm]	$\Phi_{\text{PL}}^{\text{b)}$ [%]	$\tau_{\text{p}}^{\text{c)}$ [ns]	$\tau_{\text{d}}^{\text{c)}$ [μs]	HOMO ^{d)} [eV]	LUMO ^{d)} [eV]	$E_{\text{S}}/E_{\text{T}}^{\text{e)}$ [eV]	$\Delta E_{\text{ST}}^{\text{f)}$ [eV]
CzQxCN	342, 480	597	77	22.6	152.7	-6.17	-3.21	2.34/2.19	0.16
CzQx3CN	353, 511	647	38	24.1	64.5	-6.19	-3.44	2.14/2.10	0.04

a) UV-Vis absorption and photoluminescence λ_{max} measured in a toluene solution. b) Estimated from integrating sphere measurements (1 wt% TADF-emitter-doped PBICT/DBTTPI host film. c) PL lifetimes of the prompt (τ_{p}) and delayed (τ_{d}) decay components measured in a 1 wt% TADF-emitter doped PBICT/DBTTPI host film under nitrogen at 300 K. d) Estimated from the onset of the oxidation and reduction potentials of cyclic voltammetry. e) Singlet (E_{S}) and triplet (E_{T}) energies obtained from the onset of fluorescence and phosphorescence emission spectra. f) $\Delta E_{\text{ST}} = E_{\text{S}} - E_{\text{T}}$.

Table S2. Transient PL related photophysical parameters (Φ_{F} , Φ_{TADF} , k_{p} , k_{d} , k_{ISC} , k_{RISC} , k_{r} , and k_{nr}) of **CzQxCN** and **CzQx3CN**.

Emitter	Φ_{F} [%]	Φ_{TADF} [%]	k_{p} [$\times 10^7 \text{ s}^{-1}$]	k_{d} [$\times 10^4 \text{ s}^{-1}$]	k_{ISC} [$\times 10^7 \text{ s}^{-1}$]	k_{RISC} [$\times 10^6 \text{ s}^{-1}$]	k_{r} [$\times 10^6 \text{ s}^{-1}$]	k_{nr} [$\times 10^3 \text{ s}^{-1}$]
CzQxCN	11	66	4.42	0.65	3.94	4.89	4.39	1.69
CzQx3CN	7	31	4.15	1.55	3.85	7.14	2.99	10.36

Table S3. EL data of **CzQxCN** and **CzQx3CN**.

Emitter	Dopant Conc. [%]	CE_{max} [cd A ⁻¹]	PE_{max} [lm W ⁻¹]	EQE_{max}	EL [nm]	CIE (x, y)
CzQxCN	1	45.2	47.4	18.4	588	(0.53, 0.46)
	3	32.6	33.8	15.4	595	(0.55, 0.44)
	5	24.0	24.6	12.5	598	(0.57, 0.42)
CzQx3CN	1	7.7	7.6	6.9	629	(0.58, 0.39)
	3	3.7	3.7	4.6	640	(0.61, 0.36)
	5	2.6	2.5	3.8	645	(0.62, 0.35)

Table S4. Comparison of the quinoxaline based red emitters.

Emitter	λ_{em} , nm	CIE(x,y)	EQE (%)	Ref.
CzQxCN	588	0.53, 0.46	18.4	This work
FDQPXZ	606	0.53, 0.46	13.9	3
QCN-TPA	594	0.58, 0.42	16.4	4
QCN-2TPA	596	0.58, 0.42	21.4	4
QCN-o-TPA	594	0.58, 0.42	14.6	4
QxPz	598	0.48, 0.50	13.4	5
DPQxPz	612	0.56, 0.43	15.4	5
PXZ-QCN	604	0.56, 0.43	15.3	6
Ac-CNP	580	0.47, 0.51	13.3	7
Px-CNP	606	0.53, 0.44	3.0	7
5,8-DCNQx-DICz	603	0.55, 0.44	12.5	8
tBuTPA-Qx4CN	674	0.58, 0.36	16.3	9
TPA-2DCNQ	596	-	13.6	10
5,8-DCQx-Ac	602	0.55, 0.44	16.4	11
SBDBQ-PXZ	608	0.56, 0.43	5.6	12
DBQ-3PXZ	616	0.60, 0.48	5.3	12

Equations for the calculation of rate constants

$$\tau_p = 1/k_p$$

$$\tau_d = 1/k_d$$

$$k_{ISC} = (1 - \Phi_F) \times k_p$$

$$k_{RISC} = (k_p k_d / k_{ISC}) \times (\Phi_{TADF} / \Phi_F)$$

$$k_r^S = k_p \Phi_F$$

$$k_{nr}^T = k_d - k_{RISC} \Phi_F$$

$$\Phi_F = \Phi_{O_2}$$

$$\Phi_{TADF} = \Phi_{N_2-O_2}$$

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