Supporting Information

Molecular Design of Thermally Activated Delayed Fluorescent Emitters for Narrowband Orange–Red OLEDs: Boosted by a Cyano-Functionalization Strategy

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I. General Remarks

All commercially available reagents and chemicals were used as received without further purification. Unless otherwise noted, all reactions were carried out using Schlenk techniques under a nitrogen atmosphere. The solvents were dried and purified using an Innovative Technology PS-MD-5 Solvent Purification System. NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The $^1$H NMR (400 MHz) chemical shifts were measured relative to CDCl$_3$ as the internal reference (CDCl$_3$: $\delta = 7.26$ ppm). The $^{13}$C NMR (100 MHz) chemical shifts were given using CDCl$_3$ as the internal standard (CDCl$_3$: $\delta = 77.16$ ppm). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). X-Ray single-crystal diffraction data were collected on an Oxford Xcalibur E single crystal diffraction. UV-Vis spectra were measured on a HITACHI U-2910. Fluorescence spectra and photoluminescence quantum yield were collected on a Horiba Jobin Yvon-Edison Fluoromax-3 fluorescence spectrometer with a calibrated integrating sphere system. Phosphorescence spectra were collected on a HITACHI F-7100 fluorescence spectrophotometer. Transient photoluminescence decay spectra were obtained with Horiba Single Photon Counting Controller: FluoroHub and Horiba TBX Picosecond Photon Detection. Thermogravimetric analysis (TGA) was carried out using DTG-60(H) at a rate of 10 °C/min under nitrogen atmosphere. Cyclic voltammogram were performed on LK2005A with a solution of tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$, 0.1 M) in DCM as electrolyte and ferrocene/ferrocenium (Fc/Fc$^+$) as standard. Three-electrode system (Ag/Ag$^+$, platinum wire and glassy carbon electrode as reference, counter and work electrode respectively) was used in the CV measurement.

II. OLED Fabrication and Characterization

Indium-tin-oxide (ITO) coated glass with a sheet resistance of 15 $\Omega$ sq$^{-1}$ was used as the anode substrate. Prior to film deposition, patterned ITO substrates were cleaned with alkaline detergent, boiled deionized water, and deionized water thoroughly in ultrasonic bath, dried in an oven, and finally treated with oxygen plasma for 10 min to
enhance the surface work function of ITO anode. All of the organic layers were deposited with the rate of 0.1 nm·s⁻¹ under high vacuum. The doped and co-doped layers were prepared by co-evaporating dopant and host material from two or three individual sources, and the doping concentrations were modulated by controlling the evaporation rates of dopant.

**Measurements:** Current density-voltage-Luminance (J-V-L) characteristics were measured by using KEYSIGHT B1500A. The luminance and EL spectra were collected with model DLM-100Z photometer and OPT2000 spectrophotometer, respectively.

### III. Synthesis and Characterization

**Scheme S1.** Synthetic route to CNCz-BNCz. DMF: N,N-dimethylformamide; THF: tetrahydrofuran; EtN(i-Pr₂): N,N-diisopropylethylamine.

**Synthesis of 9,9',9''(3,6-Dibromobenzene-1,2,4,5-tetrayl)tetrakis(3,6-di-tert-butyl-9H-carbazole) (compound 2).** A dried round bottom flask with a magnetic stir bar was charged with 3,6-di-tert-butyl-9H-carbazole (6.29 g, 22.5 mmol), NaH (1.08 g, 60%, 27.0 mmol), and 50 mL of DMF under an air atmosphere. After stirring for 0.5 h under room temperature, 1,4-dibromotetrafluorobenzene (1.54 g, 5 mmol) was added to the reaction mixture and stirred for 12 h at 140 °C. After cooling to room temperature, the mixture was filtered and the solid was washed with DMF. The residue was dissolved in THF and the insoluble matter was filtered off. The product was evaporated under reduced pressure to provide compound 2 as a white solid in 95% yield (6.39 g, 4.75 mmol). ¹H NMR (CDCl₃, 400 MHz): δ = 1.38 (s, 72H), 6.97 (d, J = 8.4 Hz, 8H), 7.09
(dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 8H), 7.61 (d, $J = 2.0$ Hz, 8H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 32.1$, 34.7, 110.2, 115.6, 122.7, 123.9, 129.6, 137.2, 138.5, 143.1 ppm. HRMS (ESI$^+$): calcd for C$_{86}$H$_{96}$Br$_2$N$_4$Na $[M+Na]^+$, 1367.5879 (100%), 1368.5913 (79.0%), 1365.5899 (51.4%), 1369.5859 (48.6%); found 1367.5875, 1368.5910, 1365.5874, 1369.5885.

Synthesis of BrCz-BNCz (compound 3). In a dried round bottom flask with a magnetic stir bar, a solution of n-BuLi in hexane (1.05 mL, 2.5 M, 2.625 mmol) was added slowly to a solution of compound 2 (3.36 g, 2.5 mmol) in toluene (100 mL) at -60 °C under a nitrogen atmosphere. After stirring for 1.0 h the reaction mixture was allowed to warm to -40 °C. After addition of boron tribromide (0.355 mL, 3.75 mmol), the reaction mixture was stirred at room temperature for 1.0 h. N,N-Diisopropylethylamine (1.75 mL, 10.0 mmol) was added at 0 °C and then the reaction mixture was allowed to warm to 120 °C. After stirring for 8 h, the reaction mixture was cooled to room temperature. The solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 20:1, v/v) and recrystallized from dichloromethane and methanol as orange powder in 45% yield (1.43 g, 1.125 mmol).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.21$ (s, 18H), 1.42 (s, 36H), 1.70 (s, 18H), 6.14 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 2H), 6.63 (d, $J = 8.8$ Hz, 2H), 7.17 (br, 8H), 7.55 (d, $J = 2.0$ Hz, 2H), 7.85 (s, 4H), 8.26 (d, $J = 1.6$ Hz, 2H), 9.17 (d, $J = 2.0$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 31.6$, 32.1, 32.3, 34.4, 34.8, 35.4, 113.4, 114.8, 116.0, 120.4, 121.6, 121.7, 122.2, 123.5, 125.1, 125.2, 129.0, 129.5, 136.8, 137.5, 137.6, 141.7, 142.9, 143.3, 145.0, 145.4 ppm. HRMS (ESI$^+$): calcd for C$_{86}$H$_{95}$BrN$_4$ $[M+H]^+$, 1273.6833 (100.0%), 1275.6813 (97.3%); found 1273.6844, 1275.6814.

Synthesis of CNCz-BNCz (compound 4).[11] In a dried round bottom flask with a magnetic stir bar, a solution of n-BuLi in hexane (0.44 mL, 2.5 M, 1.1 mmol) was added slowly to a solution of compound 3 (1.274 g, 1.0 mmol) in THF (30 mL) at -78 °C under a nitrogen atmosphere. After stirring for 1.0 h, dimethylmalononitrile
(141.2 mg, 1.5 mmol) was added and then the reaction mixture was allowed to slowly warm to room temperature. After stirring for 8 h at room temperature, the solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 5:1, v/v) and recrystallized from dichloromethane and methanol as red powder in 26% yield (317.4 mg, 0.26 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.20\) (s, 18H), 1.41 (s, 36H), 1.71 (s, 18H), 6.19 (dd, J\(_1\) = 8.8 Hz, J\(_2\) = 2.0 Hz, 2H), 6.56 (d, J = 8.8 Hz, 2H), 7.00 (br, 4H), 7.32 (br, 4H), 7.59 (d, J = 1.6 Hz, 2H), 7.87 (s, 4H), 8.31 (d, J = 1.6Hz, 2H), 9.19 (d, J = 1.6Hz, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 31.6, 32.1, 32.3, 34.4, 34.8, 35.5, 108.7, 113.0, 114.7, 115.1, 116.4, 120.5, 122.1, 122.2, 122.7, 123.7, 123.9, 124.6, 125.2, 125.3, 129.3, 136.8, 137.8, 139.9, 143.1, 143.5, 145.5, 146.0 ppm. HRMS (ESI\(^+\)): calcd for C\(_{87}\)H\(_{94}\)BN\(_5\)[M+H]\(^+\) 1220.7681, found 1220.7678. Anal. Calcd (%) C\(_{87}\)H\(_{94}\)BN\(_5\): C, 85.61; H, 7.76; N, 5.74; Found: C, 85.59; H, 7.73; N, 5.83. (B is not analyzed by elemental analysis)

Scheme S2. Synthetic route to CN-BCz-BN. DMF: N,N-dimethylformamide; THF: tetrahydrofuran.

**Synthesis of 9,9’-(5-Bromo-2-iodo-1,3-phenylene)bis(3,6-di-tert-butyl-9H-carbazole) (compound 5).** A dried round bottom flask with a magnetic stir bar was charged with 3,6-di-tert-butyl-9H-carbazole (3.35 g, 12 mmol), NaH (576 mg, 60%, 14.4 mmol), and DMF 50 mL under an air atmosphere. After stirring for 0.5 h under room temperature, 4-bromo-2,6-difluoriodobenzene (1.56 g, 5 mmol) was added to
the reaction mixture and stirred for 12 h at 140 °C. After cooling to room temperature, 
the solution was filtered through a celite pad and washed with dichloromethane. The 
filtrate was evaporated under reduced pressure and the residue was purified by column 
chromatography on silica gel (petroleum ether/dichloromethane = 10:1, v/v) to provide 
compound 5 as a white solid in 78% yield (3.27 g, 3.9 mmol). 1H NMR (CDCl₃, 400 MHz): δ = 1.49 (s, 36H), 7.12 (d, J = 8.8 Hz, 4H), 7.53 (dd, J₁ = 8.4 Hz, J₂ = 2.0 Hz, 4H), 7.69 (s, 2H), 8.17 (d, J = 2.0 Hz, 4H) ppm. 13C NMR (100 MHz, CDCl₃): δ = 32.2, 35.0, 104.3, 109.6, 116.7, 123.4, 123.6, 124.1, 133.5, 139.0, 143.5, 144.7 ppm. HRMS (ESI⁺): calcd for C₄₆H₅₀BrI₂N₂Na [M+Na]⁺, 859.2100 (100.0%), 861.2079 (97.3%); found 859.2085, 861.2080.

Synthesis of Br-BCz-BN (compound 6). In a dried round bottom flask with a magnetic 
stir bar, a solution of n-BuLi in hexane (1.05 mL, 2.5 M, 2.625 mmol) was added 
slowly to a solution of 9,9’-(5-bromo-2-iodo-1,3-phenylene)bis(3,6-di-tert-butyl-9H-
carbazole) (compound 5) (2.1 g, 2.5 mmol) in toluene (50 mL) at -60 °C under a 
nitrogen atmosphere. After stirring for 1.0 h the reaction mixture was allowed to 
warm to 40 °C. After addition of boron tribromide (0.355 mL, 3.75 mmol), the 
reaction mixture was stirred at room temperature for 1.0 h. N, N-
Diisopropylethylamine (1.75 mL, 10.0 mmol) was added at 0 °C and then the 
reaction mixture was allowed to warm to 120 °C. After stirring for 8 h, the 
reaction mixture was cooled to room temperature. The solution was filtered through 
a celite pad and washed with dichloromethane. The filtrate was evaporated under 
reduced pressure and the residue was purified by column chromatography on silica gel 
(petroleum ether/dichloromethane = 5:1, v/v) to provide compound 6 as yellow 
powder in 42% yield (755 mg, 1.05 mmol). 1H NMR (400 MHz, CDCl₃): δ = 1.53 (s, 
18H), 1.67 (s, 18H), 7.60 (dd, J₁ = 8.8 Hz, J₂ = 2.0 Hz, 2H), 8.13 (dd, J₁ = 8.8 Hz, J₂ = 
1.6 Hz, 2H), 8.16 (d, J = 2.0 Hz, 2H), 8.20 (d, J = 1.6 Hz, 2H), 8.38 (d, J = 1.6 Hz, 2H), 
9.00 (d, J = 2.0 Hz, 2H) ppm. 13C NMR (100 MHz, CDCl₃): δ = 32.0, 32.3, 34.9, 35.3, 
110.8, 114.1, 117.3, 120.9, 121.5, 123.7, 124.6, 127.2, 127.7, 129.8, 138.0, 141.4, 144.6, 
144.9, 145.6 ppm. HRMS (ESI⁺): calcd for C₄₆H₄₉BBrN₂ [M+H]⁺, 719.3172 (100.0%),
721.3152 (97.3%); found 719.3169, 721.3153.

**Synthesis of CN-BCz-BN (compound 7).** A dried round bottle flask with a magnetic stir bar was charged with compound 6 (144 mg, 0.2 mmol), and CuCN (26.9 mg, 0.3 mmol) in DMF (5 mL) at 150 °C under nitrogen atmosphere for 12 h. After cooling to room temperature, the solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 2:1, v/v) to provide compound 7 as a yellow solid in 58% yield (77.2 mg, 0.116 mmol). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.54 (s, 18H), 1.67 (s, 18H), 7.65 (dd, $J_1$ = 8.8 Hz, $J_2$ = 2.0 Hz, 2H), 8.20-8.22 (m, 4H), 8.34 (s, 2H), 8.44 (d, $J$ = 2.0 Hz, 2H), 9.03 (d, $J$ = 2.0 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CS$_2$/CDCl$_3$ = 1:1, v/v): $\delta$ = 31.8, 32.1, 34.6, 35.0, 110.2, 114.0, 115.9, 117.6, 119.1, 121.5, 124.0, 124.9, 127.2, 129.9, 137.8, 141.2, 144.0, 145.2, 146.0 ppm. HRMS (ESI$^+$): calcd for C$_{47}$H$_{48}$BN$_3$ [M+H]$^+$ 666.4020, found 666.4018. Anal. Calcd (%): C$_{47}$H$_{48}$BN$_3$: C, 84.80; H, 7.27; N, 6.31; Found: C, 84.57; H, 7.17; N, 6.29. (B is not analyzed by elemental analysis)

**IV. Method of Theoretical Calculations**

All theoretical calculations were performed using Gaussian 09$^{[2]}$ serials software. The ground-state structures and FMOs were obtained by B3LYP$^{[3]}$ density functional method with basis set 6-31G*. The S$_1$ and T$_1$ energies were calculated by time-dependent DFT (TD-DFT) method with the same parameters for ground-state calculations. The HOMO and LUMO distributions were visualized using Gaussview 5.0 software.
# V. Crystal Data

**Table S1. Crystal Data for CNCz-BNCz**

| Property                      | Value                                      |
|-------------------------------|--------------------------------------------|
| **Identification code**       | CNCz-BNCz                                  |
| **Empirical formula**         | C₈₇H₉₄BN₅                                  |
| **Formula weight**            | 1220.48                                    |
| **Temperature/K**             | 150.0                                      |
| **Crystal system**            | monoclinic                                 |
| **Space group**               | P₂₁/c                                      |
| **a/Å**                       | 18.299(3)                                  |
| **b/Å**                       | 29.627(5)                                  |
| **c/Å**                       | 14.364(3)                                  |
| **α/°**                       | 90                                          |
| **β/°**                       | 104.263(10)                                |
| **γ/°**                       | 90                                          |
| **Volume/Å³**                 | 7547(2)                                    |
| **Z**                         | 4                                           |
| **ρ calc/g/cm³**              | 1.074                                       |
| **μ/mm⁻¹**                    | 0.466                                       |
| **F(000)**                    | 2624.0                                      |
| **Crystal size/mm³**          | 0.3 × 0.2 × 0.2                             |
| **Radiation**                 | CuKα (λ = 1.54178)                         |
| **2Θ range for data collection/°** | 4.982 to 138.382                          |
| **Index ranges**              | -21 ≤ h ≤ 22, -35 ≤ k ≤ 33, -17 ≤ l ≤ 17 |
| **Reflections collected**     | 75860                                       |
| **Independent reflections**   | 13757 [R_{int} = 0.0992, R_{sigma} = 0.0888] |
| **Data/restraints/parameters**| 13757/0/929                                |
| **Goodness-of-fit on F²**     | 1.068                                       |
| **Final R indexes [I>2σ(I)]** | R₁ = 0.0923, wR₂ = 0.2561                    |
| **Final R indexes [all data]**| R₁ = 0.1416, wR₂ = 0.3044                    |
| **Largest diff. peak/hole / e Å⁻³** | 0.50/-0.33                                 |
VI. Additional Spectra and Data

| Molecule          | HOMO | LUMO | Energy Level |
|-------------------|------|------|--------------|
| BCz-BN            |      |      |              |
| CN-BCz-BN         |      |      |              |
| m-Cz-BBCz         |      |      |              |
| BBCz-Y            |      |      |              |
| CNCz-BNCz         |      |      |              |

**Fig. S1.** Theoretical calculation results of the FMOs distributions and energy levels of BCz-BN, CN-BCz-BN, m-Cz-BBCz, BBCz-Y and CNCz-BNCz.

**Fig. S2.** Emissions of BCz-BN, CN-BCz-BN, BBCz-Y and CNCz-BNCz in toluene solution at $1 \times 10^{-3}$ mol L$^{-1}$. 
**Fig. S3.** (a) TGA thermogram of CNCz-BNCz recorded at a heating rate of 10 °C/min. (b) Cyclic voltammograms of CNCz-BNCz, measured in dry dichloromethane containing 0.1 M of tetrabutylammonium hexafluorophosphate.

**Fig. S4.** (a) Normalized UV-vis absorption spectrum of CNCz-BNCz and (b) normalized photoluminescence spectrum of CNCz-BNCz in solvents with different polarity at $2 \times 10^{-5}$ mol L$^{-1}$.

**Fig. S5.** (a) Normalized UV-vis absorption spectrum of CNCz-BNCz and (b) normalized photoluminescence spectrum of CNCz-BNCz in toluene solution at different concentrations.
Fig. S6. Normalized photoluminescence spectrum of CNCz-BNCz in PS at different concentrations.

Fig. S7. (a) Fluorescence spectrum and (b) phosphorescence spectrum of CNCz-BNCz in PS (3 wt% doped film) at different temperature.

Fig. S8. Fluorescence spectrum of CNCz-BNCz in polystyrene film (3 wt%) at room temperature (298 K) and 77 K.
\textbf{Fig. S9.} (a) Fluorescence spectrum and (b) transient photoluminescence spectrum of CNCz-BNCz in CBP film (3 wt\%) at 298 K.

\textbf{Fig. S10.} Current density and luminance versus voltage curves of Device A, B and C.
Fig. S11. (a) EL spectra at the luminance of 1000 cd m$^{-2}$. (b) EQE and power efficiency versus luminance curves of doped OLEDs and (c) Current density and luminance versus voltage curves. Devices configuration: ITO/TAPC (30 nm)/TCTA (10 nm)/32alCTRZ: 20 wt% DACT-II: x wt% CNCz-BNCz (20 nm)/TmPyPb (50 nm)/LiF (0.8 nm)/Al, where $x$ is 1, 2, 3 and 5 for device D, E, C and F, respectively.

Fig. S12. Histogram of EQEs$_{\text{max}}$. An average EQE$_{\text{max}}$ of 29.2% and a highest EQE$_{\text{max}}$ of 33.7%.
Table S2: Summary of physical properties for CNCz-BNCz.

| Compound    | $T_d$ [°C] | HOMO[a] [eV] | LUMO[b] [eV] | $\lambda_{abs}$[c] [nm] | $\lambda_{em}$[c] [nm] |
|-------------|------------|--------------|--------------|------------------------|------------------------|
| CNCz-BNCz   | 409        | -5.33        | -3.19        | 345/547                | 581                    |

| Compound    | $E_g$[d] [eV] | $E_S$[e] [eV] | $E_{T1}$[f] [eV] | $\Delta E_{ST}$[g] [eV] | $\Phi_{PL}$[h] [%] |
|-------------|---------------|---------------|------------------|--------------------------|---------------------|
| CNCz-BNCz   | 2.14          | 2.28          | 2.10             | 0.18                     | 90                  |

[a] Measured in dry dichloromethane solution (1 × 10⁻³ M) where $E_{HOMO} = -4.8 - (E_{ox} - E_{Fc})$. [b] Estimated according to the absorption spectrum and the HOMO energy level. [c] Measured in toluene solution (1 × 10⁻⁵ M) at room temperature. [d] Calculated from the absorption spectrum. [e] Estimated from the onset wavelength of room-temperature photoluminescence measured in toluene solution (1 × 10⁻⁵ M). [f] Estimated from the onset wavelength of low-temperature photoluminescence measured in toluene solution (1 × 10⁻⁵ M) at 77 K. [g] Calculated from $E_{S1}$ and $E_{T1}$. [h] Measured in oxygen-free toluene solution (1 × 10⁻⁵ M).

Table S3: Transient PL decay data of CNCz-BNCz in toluene solution (1 × 10⁻⁵ M) measured at room temperature under nitrogen atmosphere.

| Compound    | $\tau_p$[a] [ns] | $\tau_d$[b] [μs] | C₁[c] [%] | C₂[d] [%] | $k_{RISC}$[e] $\times 10^5$ s⁻¹ | $k_r$[f] $\times 10^7$ s⁻¹ | $k_{ISC}$[g] $\times 10^7$ s⁻¹ |
|-------------|------------------|------------------|--------|--------|-------------------------------|--------------------------|-------------------------------|
| CNCz-BNCz   | 28.4             | 3.4              | 70.2   | 29.8   | 4.2                           | 2.2                      | 1.1                           |

[a] Prompt lifetime. [b] Delayed lifetime. The proportion of [c] prompt and [d] delayed components which are calculated from transient spectra. [e] Calculated from $k_{RISC} = 1/(C_1\tau_d)$. [f] Calculated from $k_r = C_1\Phi_{PL,N2}/\tau_p$. [g] Calculated from $k_{ISC} = (1-C_1)/\tau_p$.

Table S4: Summary of photophysical properties for CNCz-BNCz in CBP film (3 wt%).

| Compound    | $\lambda_{em}$ [nm] | $\Phi_{PL}$ [%] | $\tau_p$ [ns] | $\tau_d$ [μs] |
|-------------|----------------------|-----------------|----------------|---------------|
| CNCz-BNCz   | 582                  | 96              | 17.7           | 60.4          |

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Table S5: Summary of EL characteristics for OLED devices.

| Device | $\text{EL}_{\text{peak}}$ [nm] | $V_{\text{on}}$ [V] | FWHM [nm] | EQE$_{\text{max}}$ [%] | PE$_{\text{max}}$ [lm W$^{-1}$] | CIE$^{[d]}$ [x, y] | at 100 cd m$^{-2}$ | at 1000 cd m$^{-2}$ |
|--------|-------------------------------|------------------|----------|-----------------|------------------|-----------------|----------------|----------------|
| C      | 583                           | 2.7              | 49       | 33.7            | 117.8            | [0.54, 0.46]    | 27.7           | 69.1           |
| D      | 577                           | 2.6              | 49       | 27.9            | 107.5            | [0.50, 0.49]    | 21.3           | 61.8           |
| E      | 581                           | 2.7              | 50       | 27.7            | 94.8             | [0.53, 0.47]    | 22.6           | 57.8           |
| F      | 584                           | 2.7              | 51       | 27.8            | 83.0             | [0.55, 0.45]    | 21.2           | 51.8           |

[a] Turn-on voltage. [b] External quantum efficiency. [c] Power efficiency. [d] Commission Internationale de l’Eclairage (CIE) coordinates. Current density and luminance versus voltage curves. Devices configuration: ITO/TAPC (30 nm)/TCTA (10 nm)/32alCTRZ: 20 wt% DACT-II: $x$ wt% CNCz-BNCz (20 nm)/TmPyPb (50 nm)/LiF (0.8 nm)/Al., where $x$ is 1, 2, 3 and 5 for device D, E, C and F, respectively.
Table S6: Performance summary of TADF-OLEDs with emission peaks from 550 nm to 650 nm.

| Emitter          | EL-peak[a] [nm] | FWHM [nm] | $V_{on}$ [V] | $C_{F}^{max}$ [cd A$^{-1}$] | $P_{F}^{max}$ [lm W$^{-1}$] | $EQE_{max}$ [%] | $EQE_{col}$ [%] | Reference |
|------------------|-----------------|-----------|--------------|-----------------------------|-----------------------------|----------------|----------------|-----------|
| CzBNCz           | 583             | 49        | 2.7          | 101.3                      | 117.8                       | 33.7           | 27.7           | This work |
| QBP-PXZ          | 550             | --        | 3.4          | 53.6                       | 52.6                        | 16.6           | 15.2           | 4         |
| FDQCNAc          | 554             | --        | --           | 90.8                       | 91.6                        | 27.6           | --             | 5         |
| SBPQ-DPAC        | 556             | --        | 3.2          | 65.7                       | 59.0                        | 20.0           | 19.0           | 6         |
| 2SDAcBPy         | 558             | --        | 3.5          | 71.6                       | 59.7                        | 19.6           | --             | 7         |
| Me-PXZ           | 562             | --        | 3.0          | 54.4                       | 48.2                        | 21.1           | --             | 8         |
| SpAcDBA          | 567             | 96        | 3.0          | 84.7                       | 76.6                        | 29.5           | 28.9           | 9         |
| 6,7-DNQx-DICz    | 578             | --        | --           | 63.1                       | 62.3                        | 23.9           | --             | 10        |
| 6,7-DQx-Ac       | 578             | --        | --           | 56.8                       | 50.9                        | 21.1           | --             | 11        |
| Ac-CNP           | 580             | --        | 4.7          | 38.1                       | 26.1                        | 13.3           | 12.0           | 12        |
| 3,6,11-TriAC-BPQ | 581             | --        | 2.9          | 44.2                       | 46.3                        | 22.0           | --             | 13        |
| dmAcDBA          | 583             | 98        | 3.2          | 58.3                       | 48.6                        | 24.9           | 23.1           | 9         |
| NAI-DPAC         | 584             | --        | 3.0          | 76.2                       | 79.7                        | 29.2           | 13.0           | 14        |
| Ac-CNBQx         | 585             | --        | 2.8          | 34.0                       | 33.3                        | 14.0           | 13.9           | 15        |
| DMAC-11-DPPZ     | 588             | 95        | 3.6          | 50.8                       | 41.0                        | 23.8           | --             | 16        |
| DPXZ-PQM         | 590             | 114       | 3.6          | 28.6                       | 23.2                        | 17.1           | --             | 17        |
| T-DA-1           | 590             | --        | 3.0          | 49.2                       | 51.4                        | 20.3           | 10.6           | 18        |
| DMAC-Ph-DCPP     | 596             | --        | 3.3          | 34.5                       | 32.8                        | 16.9           | --             | 22        |
| NAI-DMAC         | 597             | --        | 3.0          | 50.7                       | 53.1                        | 23.4           | 13.6           | 14        |
| FBPCNAc          | 597             | --        | --           | 55.7                       | 57.8                        | 23.8           | --             | 5         |
| $\sigma$TPA-DPPZ | 600             | --        | 3.1          | 41.8                       | 42.3                        | 18.5           | 17.0           | 23        |
| BPPZ-PXZ         | 604             | --        | --           | 37.0                       | 41.0                        | 25.2           | 21.0           | 24        |
| oDTBPZ-DPZZ      | 604             | --        | 3.5          | 38.1                       | 29.2                        | 20.1           | 14.1           | 25        |
| 3DMAC-BP         | 606             | 90        | 3.1          | 38.2                       | 36.4                        | 22.0           | 17.5           | 26        |
| W1               | 608             | --        | 4.1          | 40.0                       | 38.3                        | 25.0           | 8.7            | 27        |
| HAP-3TPA         | 609             | --        | --           | 25.9                       | 22.1                        | 17.5           | 12.8           | 28        |
| POZ-DPHZH        | 610             | --        | --           | --                         | --                          | 16.0           | --             | 29        |
| DPXZ-BPPZ        | 612             | --        | 3.1          | 30.2                       | 30.9                        | 20.1           | 19.6           | 30        |
| ANQDC-DMAC       | 615             | --        | 2.7          | 47.6                       | 53.1                        | 27.5           | 19.3           | 31        |
| NAI_R3           | 622             | --        | 7.0          | 28.3                       | 9.4                         | 22.5           | --             | 32        |
| mDPPBZ-PXZ       | 624             | --        | --           | 25.0                       | 21.0                        | 21.7           | 19.0           | 24        |
| B1               | 624             | --        | --           | --                         | --                          | 12.5           | 8.1            | 33        |
| TPAAQ            | 630             | --        | --           | --                         | --                          | 15.8           | 2.8            | 34        |
| B2               | 637             | --        | --           | --                         | --                          | 9.0            | 5.7            | 33        |

S17
|       |       | 640  | 644  | 648  | 3.0  | 14.3 | 20.0 | 14.9 | 28.1 | 6.4  | 22.5 | 26.3 | 22.5 | 26.3 | 24.0 | 35  |
|-------|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|-----|-----|
| T-DA-2|       |      |      |      |      |      |      |      |      |      |      |      |      |      |     |     |
| TPA-QCN|      | 644  |      |      |      |      |      |      |      |      |      |      |      |      |     |     |
| TPA-PZCN|    | 648  |      |      |      |      |      |      |      |      |      |      |      |      |     |     |

[a] Emission peak. [b] Turn-on voltage. [c] Maximum current efficiency. [d] Maximum Power efficiency. [e] Maximum External quantum efficiency. [f] External quantum efficiency at 100 cd m$^{-2}$.

VII. References

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VIII. Copies of NMR spectra

$^1$H NMR spectra of 2 (CDCl$_3$)

$^{13}$C NMR spectra of 2 (CDCl$_3$)
$^1$H NMR spectra of 3 (CDCl$_3$)

$^{13}$C NMR spectra of 3 (CDCl$_3$)
$^1$H NMR spectra of 4 (CDCl$_3$)

$^{13}$C NMR spectra of 4 (CDCl$_3$)
$^1$H NMR spectra of 5 (CDCl$_3$)

$^{13}$C NMR spectra of 5 (CDCl$_3$)
$^1$H NMR spectra of 6 (CDCl$_3$)

$^{13}$C NMR spectra of 6 (CDCl$_3$)
$^1$H NMR spectra of 7 (CDCl$_3$)

$^{13}$C NMR spectra of 7 (CDCl$_3$)