

Electronic Supplementary Information (ESI)

A π -extended tercarbazole-core multi-resonance delayed fluorescence emitter exhibiting efficient narrowband yellow electroluminescence

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1. Materials and general methods

All reagents and anhydrous solvents were purchased from Tokyo Chemical Industry (TCI), Fujifilm Wako Pure Chemical Corp., or Sigma-Aldrich, and were used without further purification unless otherwise noted. 2,3,6,7,10,11-Hexacyano-1,4,5,8,9,12-hexaazatriphenylene (HAT-CN), 1,1-bis[4-[*N,N*-di(*p*-tolyl)amino]phenyl]cyclohexane (TAPC), 3,3'-di(carbazole-9-yl)-1,1'-biphenyl (mCBP), and 8-quinolinolato lithium (Liq) were procured from LG Chem Ltd., Luminescence Technology Corp., TCI, and e-Ray Optoelectronics Technology Co., Ltd., respectively, and used as received. Compound **1**^[S1] and 1,3-bis[3,5-di(pyridin-3-yl)phenyl]benzene (B3PyPB)^[S2] was prepared according to the literature procedure and purified by vacuum sublimation prior to use.

NMR spectra were recorded on an Avance III 400 spectrometer (Bruker). ¹H and ¹³C NMR chemical shifts were determined relative to the signals of tetramethylsilane ($\delta = 0.00$) and CDCl₃ ($\delta = 77.0$), respectively. Elemental analysis was carried out using an MT-5 CHN corder (Yanaco). Vacuum sublimation was performed using a P-100 system (ALS Technology). Thermogravimetric analysis (TGA) was performed on a TG/DTA7300 analyzer (Hitachi High-Tech Science) under a N₂ atmosphere.

2. Computational methods

The density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed using the ADF2021 program package.^[S3] The ground-state (*S*₀) geometry was initially optimized employing the B3LYP functional with the DZP basis set in the gas phase. The vertical excitation calculations were carried out using the optimized *S*₀ geometry, and the geometry optimizations in the excited *S*₁ and *T*_{*n*} (*n* = 1–2) states were performed using TD-DFT at the same level of theory. For the *S*₀ → *S*₁ and *S*₀ → *T*_{*n*} transitions, the natural transition orbitals (NTOs) with their adiabatic excitation energies were simulated using the optimized *S*₁ and *T*_{*n*} geometries, respectively. Using the respective *T*_{*n*} geometries, spin-orbit coupling (SOC) matrix elements, $\langle S_1 | \hat{H}_{\text{SOC}} | T_n \rangle$, were calculated using a scalar relativistic TD-DFT with the two-component zeroth-order relativistic approximation (ZORA)^[S4] at the same level of theory. The contributions of the three degenerate triplet states (*T*_{*n,x*}, *T*_{*n,y*}, and *T*_{*n,z*}) were taken into account by calculating the root sum square of the real and imaginary parts (Re and Im, respectively) of the matrix elements, as expressed by the following equation:^[S5]

$$\langle S_1 | \hat{H}_{\text{SOC}} | T_n \rangle = \left\{ \sum_{a=x,y,z} \left(\text{Re}^2 \langle S_1 | \hat{H}_{\text{SOC}} | T_{n,a} \rangle + \text{Im}^2 \langle S_1 | \hat{H}_{\text{SOC}} | T_{n,a} \rangle \right) \right\}^{1/2} \quad (\text{Eq. S1})$$

3. Photophysical measurements

The emitter doped films for photophysical analysis were deposited onto quartz substrates via vacuum deposition ($< 7 \times 10^{-5}$ Pa) using an E-200 vacuum evaporation system (ALS Technology). UV-vis absorption and PL data were collected using a V-670Y spectrometer (Jasco) and an FP-8600Y spectrophotometer (Jasco), respectively. The absolute PL quantum yields (Φ_{PL}) were determined using an ILF-835 integrating sphere system (Jasco) under a N_2 atmosphere. Transient PL decay measurements were carried out using a C11367 Quantaaurus-tau fluorescence lifetime spectrometer (Hamamatsu Photonics) with an LED excitation source ($\lambda_{\text{ex}} = 340$ nm, pulse width = 100 ps, repetition rate = 20 Hz) under a N_2 atmosphere. The emission lifetimes were extracted from the resulting decay curves by performing exponential fitting and deconvolution with the instrument response function. The rate constants for radiative decay (k_r), non-radiative decay (k_{nr}), intersystem crossing (k_{ISC}), and reverse intersystem crossing (k_{RISC}) were calculated according to the literature method.^[S6]

4. Synthesis

Compound 2: A mixture of **1** (3.8 g, 5.0 mmol), 1-bromo-2-nitrobenzene (1.0 g, 5.0 mmol), potassium carbonate (2.1 g, 15 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (5 mol%) in THF and water (3:1, v/v) was purged N_2 for 10 min. The mixture was refluxed for 12 h under N_2 . After cooling to room temperature, the reaction mixture was added into water and then extracted with chloroform. The combined organic layer was washed with water and dried over anhydrous Na_2SO_4 . After filtration and evaporation, the crude product was purified by silica gel column chromatography (eluent: hexane/chloroform = 3:2, v/v) to afford **2** (3.1 g, 80%) as a yellow solid. ^1H NMR (400 MHz, CDCl_3): δ 9.16 (s, 2H), 8.50 (s, 2H), 8.32-8.38 (m, 6H), 8.06 (d, $J = 8.8$ Hz, 1H), 7.80-7.65 (m, 5H), 1.7 (s, 18H), 1.5 (s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 149.94, 145.59, 144.91, 144.45, 141.95, 141.85, 141.71, 138.23, 136.67, 132.42, 132.14, 129.86, 128.81, 127.16, 124.56, 124.13, 123.80, 121.68, 120.80, 117.27, 114.04, 107.72, 35.20, 34.80, 32.19, 31.80.

Compound 3: A solution of **2** (3.0 g, 3.9 mmol) and PPh_3 (3.0 g, 12 mmol) in *o*-dichlorobenzene (*o*-DCB) was stirred at 180 °C for 24 h. After cooling to room temperature, the reaction mixture was added into water and then extracted with chloroform. The combined organic layer was washed with water and dried over anhydrous Na_2SO_4 . After filtration and evaporation, the crude product was purified by silica gel column chromatography (eluent: hexane/chloroform = 3:2, v/v) to afford **3** (1.4 g, 50%) as a red solid. ^1H NMR (400 MHz, CDCl_3): δ 9.19 (d, $J = 8.5$ Hz, 2H), 9.09 (s, 1H), 8.67 (d, $J = 8.6$ Hz, 1H), 8.5 (d, $J = 8.0$ Hz,

2H), 8.4 (d, $J = 7.2$ Hz, 1H), 8.3 (s, 1H), 8.26 (s, 1H), 7.98 (d, $J = 6.0$ Hz, 1H), 7.7 (d, $J = 7.5$ Hz, 1H) 7.69-7.64 (m, 1H), 7.60-7.53 (m, 2H), 7.46-7.42 (m, 1H), 1.73-1.70 (m, 18 H), 1.59-1.54 (m, 18H). ^{13}C NMR (CDCl_3 , 100.00 MHz): δ 144.34, 143.98, 143.58, 143.53, 142.80, 141.36, 140.81, 139.42, 137.32, 136.72, 136.51, 128.83, 128.25, 127.67, 127.49, 127.42, 126.83, 126.43, 126.20, 125.63, 123.19, 122.98, 122.55, 122.47, 122.07, 119.93, 119.67, 119.56, 118.76, 116.72, 116.20, 112.32, 110.18, 99.89, 76.86, 76.30, 75.97, 75.66, 34.26, 34.15, 33.91, 33.80, 31.34, 31.26, 30.94, 30.92.

CzCzB: A solution of **3** (1.2 g, 4.9 mmol) in dry DMF was slowly added to NaH (0.12 g, 4.9 mmol) at room temperature. After stirring for 10 min, iodomethane (1.3 mL, 10 mmol) was added to the mixture, which was allowed to stir at room temperature for 30 min. After completion of the reaction, NaH was quenched with water. The reaction mixture was extracted with chloroform, washed with water, and dried over anhydrous Na_2SO_4 . After filtration and evaporation, the crude product was purified by silica gel column chromatography (eluent: hexane/chloroform = 3:1, v/v) to afford **CzCzB** (0.6 g, 60%) as a red solid. ^1H NMR (400 MHz, CDCl_3): δ 9.18 (s, 1H), 9.14 (d, $J = 8.0$, 2H), 8.68 (d, $J = 7.5$ Hz, 1H), 8.53 (s, 2H), 8.41-8.34 (m, 4H), 8.01 (d, $J = 7.5$ Hz, 1H), 7.78 (d, $J = 8.5$ Hz, 1H), 7.7-7.5 (m, 3H), 7.39-7.35 (m, 1H), 1.71 (s, 18H), 1.59-1.56 (m, 18H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.08, 145.24, 145.07, 144.77, 144.08, 142.46, 141.76, 139.44, 138.48, 138.23, 132.31, 130.01, 129.47, 129.00, 128.19, 127.76, 126.82, 125.80, 124.94, 124.58, 124.32, 123.81, 123.23, 121.12, 120.77, 120.50, 120.41, 117.27, 116.90, 114.24, 113.65, 111.39, 100.45, 35.88, 35.31, 35.18, 34.83, 32.31, 32.28, 31.95, 31.92. Anal. calcd (%) for $\text{C}_{53}\text{H}_{54}\text{BN}_3$: C 85.58, H 7.32, N 5.65; found: C 85.52, H 7.35, N 5.66.

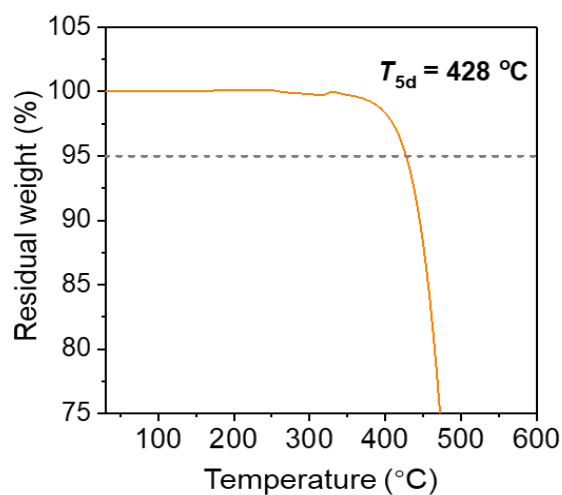


Fig. S1 TGA thermogram of **CzCzB** recorded at a heating rate of 10 °C min^{-1} under N_2 .

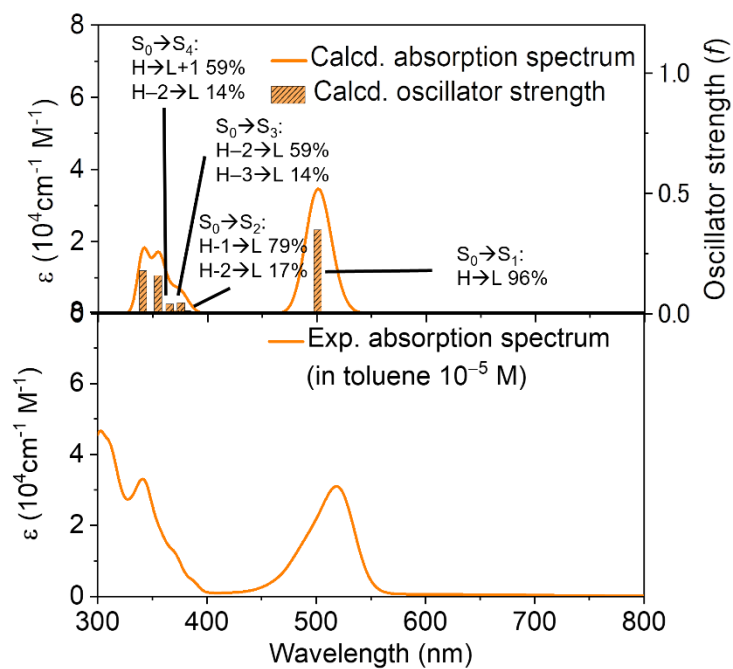


Fig. S2. Comparison between the theoretical and experimental absorption spectra of **CzCzB**.

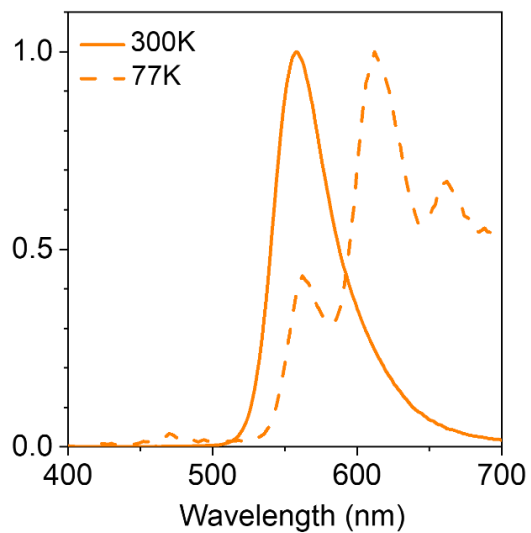


Fig. S3 Fluorescence (300 K) and phosphorescence (77 K) spectra of **CzCzB** in toluene.

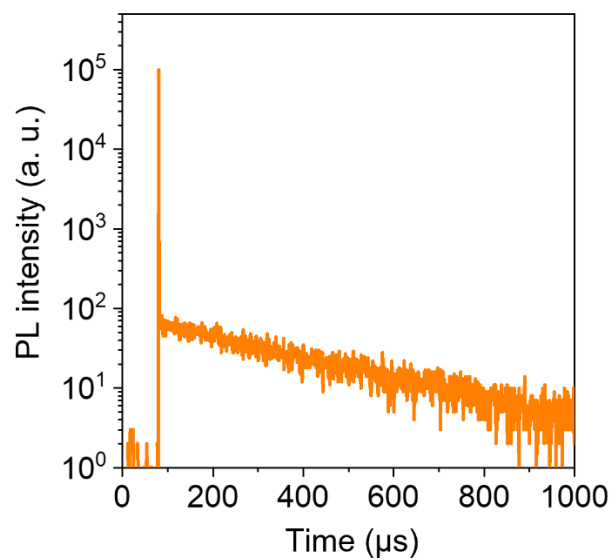


Fig. S4 Transient PL decay profile of **CzCzB** in deoxygenated toluene (10^{-5} M^{-1}).

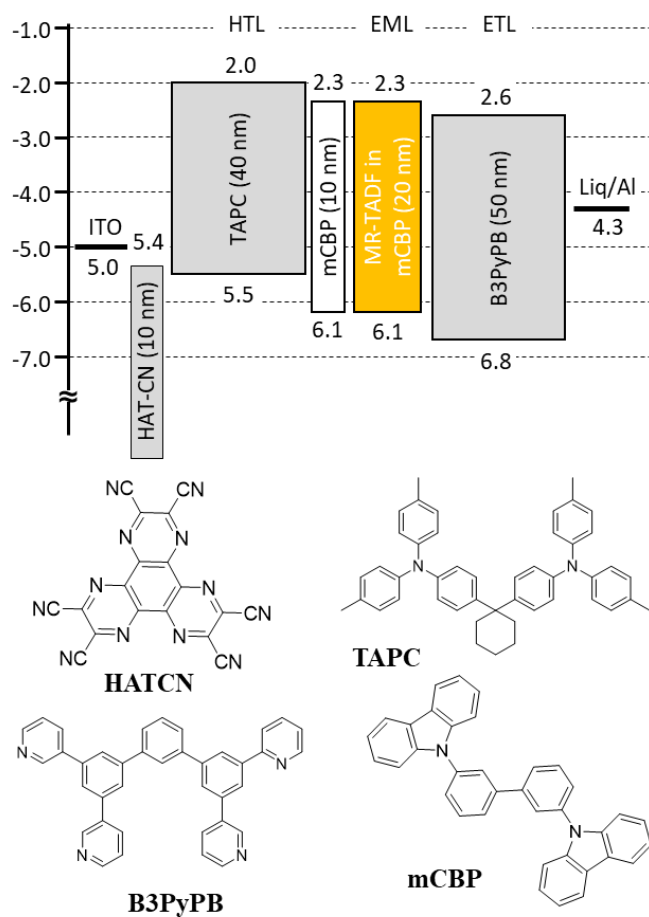


Fig. S5 Energy-level diagram and chemical structures of the materials used for TADF-OLEDs based on **CzCzB**.

Table S1 EL data for **CzCzB**

λ_{EL} (nm)	FWHM (nm)	V_{on} (V)	EQE_{max} (%)	$\text{EQE}_{100/1000}$ (%)	CE_{max} (cd A^{-1})	PE_{max} (lm W^{-1})	CIE (x, y)
559	48	6.4	19.0	9.7/6.7	74.8	36.3	(0.43, 0.56)

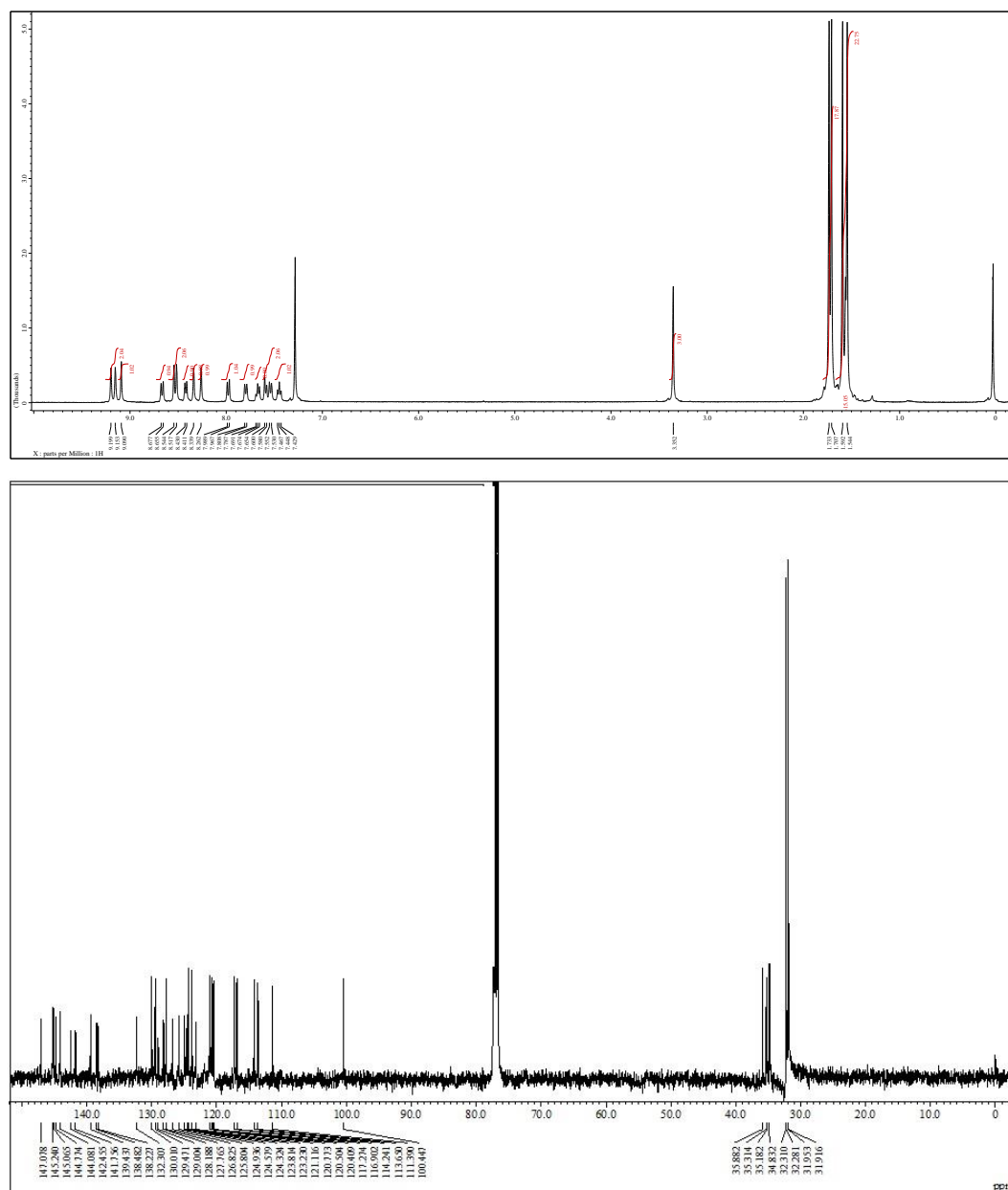


Fig. S6 ¹³C NMR spectra of CzCzB in CDCl₃.

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