## Electronic Supplementary Information

# Axially chiral thermally activated delayed fluorescent emitters with dual emitting core for efficient organic light-emitting diode

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#### 1. General information

All the reagents were purchased from commercial sources and used without further purification. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on AVIII 500 MHz NMR spectrometers in CDCl<sub>3</sub> solutions. High resolution mass spectra were measured on a Thermo Fisher<sup>®</sup> Exactive high resolution LC-MS spectrometer. The calculation was carried out with the Gaussian 09 software package. Geometry optimizations were conducted under the M06-2X/6-31g(d) level of theory. TGA was performed on a TA Instruments TGA 2050 thermal analyzer at a heating rate of 10 °C min<sup>-1</sup> in nitrogen. Cyclic voltammetry was performed using a CHI600A analyzer with a scan rate of 100 mV/s at room temperature to investigate the oxidation potentials. A conventional three electrode cell was used as electrolytic cell with a glassy carbon working electrode, an Ag/Ag+ (0.01 M AgNO<sub>3</sub>) as the reference electrode, and Pt wire as the counter electrode. The oxidation potential was measured in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M of tetra-nbutylammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) as a supporting electrolyte. Ferrocene used as internal standard for calibrating the reference electrode.

UV-Vis spectra were recorded on PerkinElmer<sup>®</sup> UV/Vis/NIR spectrometer (Lambda 950), and the fluorescence spectra were recorded on HITACHI<sup>®</sup> F-7000 Fluorescence Spectrometer at room temperature. The transient PL decay characteristics, delayed PL emission spectra and absolute PLQY were measured on an Edinburgh Instruments FLS 980 spectrometer. HPLC analysis were performed on Agilent 1260 Infinity. Analytical injections were performed on chiral stationary phase using the column (Chiralpak<sup>®</sup> ID, 5  $\mu$ m, 4.6 mm × 250 mm) and the mobile phase of hexane and dichloromethane. CD spectra were recorded on a JASCO J810 spectropolarimeter, CPL spectra were performed with a JASCO CPL-300 spectrometer at room temperature.

The OLED devices were fabricated by vacuum deposition onto pre-coated ITO glass substrates at a low pressure  $(1 \times 10^{-5} \text{ mbar})$  for organic and metal deposition successively, with deposition rate of 0.5~3 Å s<sup>-1</sup>. Before the fabrication of devices, the ITO glass substrates were cleaned with Decon 90, rinsed in ultrapure water and ethanol,

dried in an oven at 120 °C, then by plasma cleaning process. The electroluminescence and current-voltage-luminance characteristics of the devices were measured with a computer-controlled Spectrascan PR 670 spectrophotometer and Keithley 2400 SourceMeter after device packaging.



#### 2. Synthetic procedures and characterized data

Scheme S1 Synthetic routes of (a) 2tBuCzPN and (b) 4tBuCzPN.

Synthesis of 2tBuCzPN: To a dried DMF (20 mL) solution containing KO<sup>t</sup>Bu (1.68g, 15 mmol) under argon atmosphere was added dropwise 3,6-di-*tert*-butylcarbazole (3.35 g, 12 mmol) in dried DMF (20 mL) for 15 min. The mixture was stirred for 3 h and then added dropwise 3,5-difluorobenzonitrile (0.7 g, 5 mmol) in dried DMF (10 mL) for 15 min. After the reaction mixture was stirred at 80 °C for 10 h, water (200 mL) was then added into the mixture and the white precipitate was filtered and dried in vacuum. The crude product was purified by column chromatography to give the target material as a white powder (2.76 g, 84 %). M.p.: > 280 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.14 (d,

*J* = 1.9 Hz, 4H), 8.08 (t, *J* = 2.0 Hz, 1H), 7.92 (d, *J* = 2.0 Hz, 2H), 7.53–7.42 (m, 8H), 1.47 (s, 36H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 144.2, 141.1, 138.3, 128.3, 127.3, 124.2, 124.0, 117.5, 116.7, 115.4, 108.8, 34.8, 31.9. HR-MS (APCI): *m/z* calcd for C<sub>47</sub>H<sub>52</sub>N<sub>3</sub> [M + H]<sup>+</sup> 658.4156, found 658.4154.

Synthesis of 3,5-difluoro-4-iodobenzonitrile (2): The solution of 2-amino-3,5difluorobenzonitrile (1) (4.62 g, 30 mmol) and *p*-toluenesulfonic acid monohydrate (17.12 g, 90 mmol) in acetonitrile was cooled to 10-15 °C and then added NaNO<sub>2</sub> (4.14g, 60 mmol) and KI (12.45g, 75 mmol) in water (18 mL). The reaction mixture was stirred for 10 min at 10-15 °C and then warmed to room temperature for 2 h. After that, water (200 mL), NaHCO<sub>3</sub> (1 M, 100 mL) and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (2 M, 100mL) was added into the reaction mixture successively. The reaction suspension was extracted with ether and purified on column chromatography to give the target material as a white powder (2.39g, 30%). M.p.: 80-81 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.29–7.23 (m, 1H), 7.09 (td, *J* = 7.9, 2.7 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  163.9, 163.8, 163.7, 161.9, 161.8, 161.8, 161.7, 122.78, 122.75, 122.70, 122.66, 117.9, 117.8, 117.7, 117.6, 117.40, 117.37, 117.3, 109.1, 108.9, 108.9, 108.7, 81.4, 81.3, 81.1, 81.1. HR-MS (APCI): *m/z* calcd for C<sub>7</sub>H<sub>3</sub>F<sub>2</sub>IN [M + H]<sup>+</sup> 265.9273, found 265.9295.

Synthesis of 4,4',6,6'-difluoro-[1,1'-biphenyl]-2,2'-dicarbonitrile (3): The solution of compound 2 (2.12g, 8 mmol) and copper (I) thiophene-2-carboxylate (CuTC) (3.8 g, 20.0 mmol) in DMF (40 mL) under argon was stirred at 110 °C for 24 h. After that, the reaction mixture was diluted with ethyl acetate (60 mL), and the resulting slurry was passed through a plug of SiO<sub>2</sub> by using ethyl acetate as eluent. The combined organic layer was washed with saturated brine, dried over anhydrous MgSO<sub>4</sub>, and then concentrated under reduced pressure. The residue was purified on column chromatography to give the target material as a white powder (0.48 g, 43%). M.p.: 107-108 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.46–7.39 (m, 2H), 7.29 (td, *J* = 8.4, 2.5 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  164.4, 164.3, 162.4, 162.3, 161.5, 161.4, 159.5, 159.4, 119.0, 118.9, 118.79, 118.76, 117.10, 117.07, 116.90, 116.87, 116.5, 116.42,

116.37, 116.3, 114.83, 114.79, 114.76, 110.20, 110.17, 110.0, 109.8. HR-MS (APCI): *m*/*z* calcd for C<sub>14</sub>H<sub>5</sub>F<sub>4</sub>N<sub>2</sub> [M + H]<sup>+</sup> 277.0383, found 277.0396.

Synthesis of 4tBuCzPN: Similar to the synthetic procedure for 2tBuCzPN, compound 4tBuCzPN was obtained in 81% yield by the reaction of 3,6-di-*tert*-butylcarbazole (2.23 g, 8 mmol) and compound 3 (0.44g, 1.6 mmol) in the presence of KO<sup>t</sup>Bu (1.12g, 10 mmol). M.p.: 166-167 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.27–8.26 (m, 2H), 8.08–8.07 (m, 4H), 7.87–7.86 (m, 2H), 7.63–7.62 (m, 2H), 7.55–7.54 (m, 2H), 7.49–7.46 (m, 2H), 7.44–7.41 (m, 4H), 7.25–7.18 (m, 6H), 6.69–6.66 (m, 2H), 5.64–5.63 (m, 2H), 1.49 (d, *J* = 3.1 Hz, 18H), 1.44 (d, *J* = 2.9 Hz, 36H), 1.30 (d, *J* = 3.1 Hz, 18H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  144.3, 143.9, 143.2, 141.3, 140.8, 139.2, 138.13, 138.06, 133.4, 131.1, 130.1, 124.6, 124.3, 124.1, 124.0, 123.3, 123.1, 119.1, 117.8, 116.6, 116.5, 115.1, 109.5, 109.1, 108.8, 34.8, 34.7, 34.5, 32.0, 31.9, 31.8. HR-MS (APCI): *m/z* calcd for C<sub>94</sub>H<sub>101</sub>N<sub>6</sub> [M + H]<sup>+</sup> 1313.8082, found 1313.8100.

#### 3. Thermal properties



Fig. S1 TGA curves of 2tBuCzPN and 4tBuCzPN.

## 4. Theoretical calculations



**Fig. S2** HOMO/LUMO distributions of **2tBuCzPN** and **4tBuCzPN** calculated at the B3LYP/6-31G (d,p) level..

#### 6. Photophysical properties



**Fig. S3** UV-Vis absorption of **2tBuCzPN** in different solutions ( $c = 1.0 \times 10^{-5}$  M).



**Fig. S4** PL spectra of **2tBuCzPN** in different solutions ( $c = 1.0 \times 10^{-5}$  M).



**Fig. S5** UV-Vis absorption of **4tBuCzPN** in different solutions ( $c = 1.0 \times 10^{-5}$  M).



**Fig. S6** PL spectra of **4tBuCzPN** in different solutions ( $c = 1.0 \times 10^{-5}$  M).

solvent	$\lambda_{abs}$ (nm)	$\lambda_{\rm em}  ({\rm nm})$
hexane	325, 339	399
toluene	328, 341	418
THF	326, 340	440
ethyl acetate	326, 340	439
dichloromethane	326, 341	455
acetonitrile	326, 340	471

**Table S1** Absorption and emission characteristics of **2tBuCzPN** in different solvents at room temperature ( $c = 1.0 \times 10^{-5}$  M)

**Table S2** Absorption and emission characteristics of **4tBuCzPN** in different solvents at room temperature ( $c = 1.0 \times 10^{-5}$  M)

solvent	$\lambda_{abs}$ (nm)	$\lambda_{ m em}$ (nm)
hexane	341	484
toluene	343	497
THF	342	517
ethyl acetate	342	514
dichloromethane	342	530
acetonitrile	342	540



**Fig. S7** UV-Vis absorption in neat film, fluorescence and phosphorescence spectra at 77K in 25 wt% doped DPEPO films of **2tBuCzPN**.



**Fig. S8** UV-Vis absorption in neat film, fluorescence and phosphorescence spectra at 77K in 25 wt% doped DPEPO films of **4tBuCzPN**.

Table S3 The physical properties of 2tBuCzPN and 4tBuCzPN.

Compound	HOMO <sup>a</sup> /LUMO <sup>b</sup> (eV)	$\lambda_{abs}/\lambda_{em}^{c}$ (nm)	$\lambda_{ m FL}/\lambda_{ m PL}{}^{ m d}$ (nm)	S <sub>1</sub> /T <sub>1</sub> (eV)	$\Delta E_{\rm ST}$ (eV)	$\eta_{\mathrm{PL}}^{\mathrm{e}}$ (%)	$ au^{e}$ (µs)
2tBuCzPN	-5.70/-2.54	341/418	420,445/450,474	3.23/2.90	0.33	29	14.1
4tBuCzPN	-5.60/-2.63	343/497	476/477	2.87/2.82	0.05	74	4.0

#### 6. HPLC analysis

HPLC analysis conditions:

Column: Chiralpak<sup>®</sup> ID 5  $\mu$ m, 4.6 mm × 250 mm

Mobile phase: hexane: dichloromethane = 75:25

Flow rate: 1.0 mL/min

Abs. detector: 340 nm



Fig. S9 HPLC profile of *rac*-4tBuCzPN.

**Table S4** The column performance report of *rac*-4tBuCzPN.

Compound	Ret Time (min)	Height (mAU)	Area (mAU s)	Area (%)
(+)-4tBuCzPN	5.042	86.63538	1025.09558	50.5312
(-)-4tBuCzPN	6.404	50.15479	1003.54443	49.4688





Fig. S11 HPLC profile of (-)-4tBuCzPN.

## 7. OLEDs performances



**Fig. S12** Current efficiency–luminance–power efficiency characteristics of the OLEDs based on **4tBuCzPN**.



**Fig. S13** Current efficiency–luminance–power efficiency characteristics of the OLEDs based on **2tBuCzPN** as emitters.



Fig. S14 Luminance-voltage-current density curves for devices 4tBuCzPN.



Figure S15.  $\ln(A/A_0) = k$  (time, min) plot for (+)-4tBuCzPN at 473 K.

As shown in Figure S14, we achieved a first order kinetic equation *via* the representation of  $\ln(A/A_0)$  against time, in which A is the concentration of the enantiomer and  $A_0$  is the respective initial concentration. The reaction rate constant k and  $t_{1/2}$  were estimated to be  $1.86797 \times 10^{-3}$  min<sup>-1</sup> and 3711 min from the linear fitting, respectively. according to the Eyring equation (Equation 1).

$$\Delta G^{\ddagger} = -RTln(\frac{k_T \cdot h}{\kappa \cdot k_B \cdot T}) \qquad (\text{Equation 1})$$

Where *R* is gas constant ( $R = 8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$ ), *T* is absolute temperature (K),  $\kappa$  is transition factor ( $\kappa = 0.5$ ), *h* is Planck's constant ( $h = 6.62606896 \times 10^{-34} \text{ J s}$ ),  $k_{\text{T}}$  is reaction rate constant, and  $k_{\text{B}}$  is Boltzamann's constant ( $k_{\text{B}} = 1.380662 \times 10^{-23} \text{ J K}^{-1}$ ).



Fig. S16 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2tBuCzPN.

-144.23 -141.09 -138.28	128.26 127.29 124.15 1124.03 117.52 115.35	-100.01 77.26 77.00	-34,81 -34,81 -34,93
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8. Copies of <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of new compounds



-1.56

-0.00



Fig. S19<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 2.



-0.00

-1.54



Fig. S21  $^{13}\mathrm{C}$  NMR (101 MHz, CDCl<sub>3</sub>) of 3.





Fig. S22 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 4tBuCzPN.





Fig. S23 <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 4tBuCzPN.