# Electronic Supplementary Information

## Achieving a Balance between Small Singlet-Triplet Energy Splitting and High Fluorescence Radiative Rate in Quinoxaline-based Orange-red Thermally Activated Delayed Fluorescence Emitter

Ling Yu,<sup>a</sup> Zhongbin Wu,<sup>b</sup> Guohua Xie,<sup>a</sup> Cheng Zhong,<sup>a</sup> Zece Zhu,<sup>a</sup> Hengjiang Cong,<sup>a</sup> Dongge Ma\*<sup>bc</sup> and Chuluo Yang\*<sup>a</sup>

<sup>*a*</sup> Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Department of Chemistry, Wuhan University, Wuhan, 430072, People's Republic of China.

<sup>*b*</sup> State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, University of Chinese Academy of Sciences, Changchun 130022, People's Republic of China.

<sup>c</sup> Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, People's Republic of China

Corresponding Author

\*E-mail: clyang@whu.edu.cn (Chuluo Yang)

\*E-mail: mdg1014@ciac.ac.cn (Dongge Ma)

### **General Information**

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a MERCURY-VX300 spectrometer. HSQC NMR (400 MHz) and <sup>19</sup>F NMR (377 MHz) were measured on a Bruker Advance III spectrometer. Mass spectra were measured on a ZAB 3F-HF mass spectrophotometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. Thermogravimetric analysis (TGA) was recorded on a Netzsch STA 449C instrument. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 20 K min<sup>-1</sup> from 20 to 500 °C under argon. The glass transition temperature (Tg) was determined from the second heating scan at a heating rate of 10 °C min<sup>-1</sup>. UV-vis absorption spectra recorded on а Shimadzu UV-2700 recording were spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. The PL lifetimes were measured from Edinburgh Instruments (FLS920) with a Picosecond Pulsed UV-LASTER (LASTER377) as the excitation yields (PLQYs) were measured on Edinburgh source. Absolute PL quantum FLS920 in films. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (oxidation scan) at room temperature with a CHI voltammetric analyzer. N-Bu<sub>4</sub>PF<sub>6</sub> (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudoreference electrode with ferroceniumferrocene (Fc<sup>+</sup>/Fc) as the internal standard. Cyclic voltammograms were obtained at a scan rate of 100 mV s<sup>-1</sup>. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclicvoltammogram. Single-crystal X-ray diffraction data were obtained from a Bruker APEX II Smart CCD diffractometer.

### **Synthesis**

*6,7-difluoro-2,3-diphenylquinoxaline (FDQ)*: FDQ was prepared by using similar procedure reported in the literature.<sup>16</sup> Shortly, Benzil (1.46 g, 6.94 mmol) was completely dissolved in acetic acid (34 ml), then 4,5-difluoro-1,2-phenylenediamine (1.00 g, 6.94 mmol) was added. The reaction mixture was refluxed for 12 h. After cooled down to room temperature, the mixture was extracted with brine and CH<sub>2</sub>Cl<sub>2</sub>, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the residue was purified by column chromatography on silica gel using dichloromethane/petroleum ether (2:3 by vol.) as the eluent to give white powder (2.16 g, yield: 98%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 7.91 (t, *J* = 9.6 Hz, 2H), 7.49 (t, *J* = 6.0 Hz, 4H), 7.39-7.32 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 153.58, 138.41, 138.34, 129.72, 129.04, 128.27, 114.79, 114.73, 114.67, 114.60. MS (EI): *m/z* 318 [M<sup>+</sup>]. Elemental analysis (%) for C<sub>20</sub>H<sub>12</sub>F<sub>2</sub>N<sub>2</sub>: C 75.46, H 3.80, N 8.80; found: C 75.62, H 4.05, N 8.61.

*10-(7-fluoro-2,3-diphenylquinoxalin-6-yl)-10H-phenoxazine* (*FDQPXZ*): A mixture of phenoxazine (0.63g, 3.45 mmol), sodium hydride (0.11g, 4.58 mmol) and dry tetrahydrofuran solution (60 ml) was stirred under room temperature for 2 h. FDQ (1.00g, 3.14 mmol) solution in dry tetrahydrofuran (30 mL) was added to the mixture

solution. After refluxed for 24 h, the cooling mixture was extracted with brine and CH<sub>2</sub>Cl<sub>2</sub>, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the residue was purified by column chromatography on silica gel using dichloromethane/petroleum ether (2:3 by vol.) as the eluent to give orange powder (0.75g, yield: 37%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 8.31 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 10.5 Hz, 1H), 7.54 (t, J = 6.3 Hz, 4H), 7.42-7.35 (m, 6H), 6.79-6.71 (m, 4H), 6.64 (t, J = 7.8 Hz, 2H), 6.07 (d, J = 7.5 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ [ppm]: 161.80, 159.22, 154.87, 153.45, 143.85, 132.82, 129.77, 129.73, 129.30, 129.15, 128.35, 128.31, 123.34, 122.26, 115.87, 115.63, 115.44, 112.94. MS (EI): m/z 481.2 [M<sup>+</sup>]. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ [ppm]: -114.22. Elemental analysis (%) for C<sub>44</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub>: C 79.82, H 4.19, N 8.73; found: C 79.97, H 4.31, N 8.74.

#### Devices fabrication and characterization

#### Vacuum-deposited device

The fabricated device was grown on clean glass substrates pre-coated with a 180 nm thick layer of ITO with a sheet resistance of 10  $\Omega$  per square. The ITO glass substrates were pre-cleaned carefully and treated by oxygen plasma for 2 min. Then the sample was transferred to the deposition system. MoO<sub>3</sub> (8 nm) was firstly deposited onto the ITO substrate, consecutively followed by TAPC (50 nm), mCP (10 nm), emissive layer (20 nm), and TmPyPB (40 nm). Finally, a cathode composed of lithium fluoride and aluminum was sequentially deposited onto the substrate in the vacuum of 10<sup>-6</sup> Torr. The current–voltage–brightness characteristic was measured by using a Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. The EL spectra were measured by a Spectrascan PR650 spectrophotometer. EQE was calculated from the luminance and current density.

#### **Solution-processed device**

The ITO substrates were degreased in acetone and ethanol consecutively in an ultrasonic bath before UV-ozone treatment for 10 minutes. A layer of 40 nm thick PEDOT:PSS was spin-coated onto the ITO substrate and then baked at 120 °C for 10 minutes. FDQPXZ was spin-coated onto the PEDOT:PSS layer from a chlorobenzene solution. Another baking at 100 °C for 10 minutes was conducted after spin-coating of the emitting layer. A layer of TmPyPB, served as the electron transporting layer, was thermally deposited onto the emitting layer. After the evaporation of the composite Liq/Al cathode, the devices were encapsulated with UV-curable resin. The

current-voltage-luminance characteristic and the EL spectra were measured simultaneously by a customized software controlling a PR735 spectrometer and a Keithley 2400 source measurement unit. The power efficiency and the external quantum efficiency were calculated by assuming a Lambertion emission profile.



**Figure S1.** Thermal gravity analysis (TGA) curves of **FDQPXZ**. Inset: differential scanning calorimetry (DSC) curve.



**Figure S2.** Normalized UV/vis absorption spectrum of FDQPXZ in toluene solution and fluorescence and phosphorescence spectra of FDQPXZ in film.

**Table S1.** Triplet and singlet excitation energies (vertical transition), oscillator strength (f) and transition configurations of FDQPXZ calculated by TDDFT at the b3lyp/6-31g(d).

Compound	state	E (eV)	f	main configuration <sup>[a]</sup>	
FDQPXZ	$\mathbf{S}_1$	2.7297	0.0004	$H \rightarrow L$	0.66562
	S <sub>2</sub>	3.3403	0.0023 -	$H-4 \rightarrow L$	0.28049
				$H-3 \rightarrow L$	0.63372
	<b>S</b> <sub>3</sub>	3.7293	0.1927	$H-2 \rightarrow L$	0.48454
	T <sub>1</sub>	2.6759	0 -	$H-3 \rightarrow L$	0.27583
				$H \rightarrow L$	0.57176
	T <sub>2</sub>		0	$H-3 \rightarrow L$	0.53338
		2.6998		$H-2 \rightarrow L$	0.16227
				$H \rightarrow L+2$	0.11486
	T <sub>3</sub>	2 0024	0 -	$H-3 \rightarrow L$	0.28019
		2.9024		$H-2 \rightarrow L+1$	0.17343

 ${}^{[a]}H \rightarrow L$  represents the HOMO to LUMO transition. Excitation configurations with the highest contributions are presented, together with the corresponding transition symmetry and nature of the involved orbitals.



**Figure S3.** Cyclic voltammogram of FDQPXZ (a) in CH<sub>2</sub>Cl<sub>2</sub> for oxidation scan and (b) in THF for reduction scan.

**Table S2**. Thermal, photophysical, and electrochemical data of FDQPXZ.

Compound	$\begin{array}{c} T_{d}{}^{[a]}\!/T_{g}{}^{[b]}\\ [^{o}C] \end{array}$	$\lambda_{abs}^{[c]}$ [nm]	$\begin{array}{c} \lambda_{PL,max}{}^{[d]} \\ [nm] \end{array}$	HOMO <sup>[e]</sup> /LUMO <sup>[e]</sup> [eV]	Eg <sup>[f]</sup> [eV]	Es [eV]	$E_{T}^{[g]}$ [eV]
FDQPXZ	348/92	336/450	606	-5.06/-2.91	2.37	2.05	2.01

<sup>[a]</sup>Obtained by TGA. <sup>[b]</sup>Obtained by DSC. <sup>[c]</sup>Measured in toluene solution. <sup>[d]</sup>Measured in solid thin film. <sup>[e]</sup>Determined from the onset of the oxidation potential and the reduction potential, respectively. <sup>[f]</sup>Calculated from the absorption edge of the UV/Vis absorption spectrum. <sup>[g]</sup>Measured in film at 77 K.



**Figure S4.** (a) Transient PL decay profile of FDQPXZ in 10<sup>-5</sup> M toluene solution. Blue and pink lines show the profiles before and after the deoxygenation, respectively. The inset shows the transient PL decay of DBQPXZ in film after the deoxygenation.(b) Temperature-dependent transient PL decays of FDQPXZ from 100 to 300 K in film after degassing.

**Table S3.** Summary of the temperature-dependent transient PL decays of FDQPXZfrom 100 to 300 K in film after degassing.

Compound	T (K)	$ au_{\mathrm{F}^{[a]}}\left(\mathrm{ns} ight)$	$ au_{d}^{[b]}(\mu s)$	Ratio of $\tau_{d}^{[c]}$ (%)
	100	29	0.91	5.10
EDODV7	150	28	1.34	7.44
FDQFAL	200	26	2.17	10.82
-	250	24	2.44	15.73
-	300	22	2.34	17.63

<sup>[a]</sup>The lifetime of the prompt component. <sup>[b]</sup>The lifetime of the delayed component. <sup>[c]</sup>Calculated from the integrated intensity of the delayed component divided by the totally integrated intensity of the decay curve.



**Figure S5.** (a) Transient PL decay of Bepp<sub>2</sub>:5% FDQPXZ in film after the deoxygenation; (b) The briefly schematic energy diagram based on the kinetics of the delayed components.



**Figure S6.** (a) The structure of device A and the chemical structures of the employed materials; (b) Current density–voltage–brightness characteristics of device A; (c) EL spectra of device A measured at different voltages.



Figure S7. Normalized PL spectrum of BePP<sub>2</sub>: 5% FDQPXZ in film.

TADF	Von	EQE <sub>Max</sub>	CE <sub>Max</sub>	PE <sub>Max</sub>	LE <sub>Max</sub>	CIE	Reference
emitter	[V]	[%]	[cd A <sup>-1</sup> ]	[lm W <sup>-1</sup> ]	[cd m <sup>-2</sup> ]	(x, y)	
DMAC-PN	3.8	7.2	N.A.	10.7	~10000	(0.55,0.45)	Nanotechnology <sup>21</sup>
Ac-CNP	4.7	13.3	38.1	26.1	70630	(0.47,0.51)	Adv.Funct.Mater. <sup>22</sup>
Px-CNP	5.5	3.0	5.8	3.1	101860	(0.53,0.44)	-
m-Px-2BBP	2.8	4.2	11.1	~15	50820	(0.58,0.36)	Angew.Chem. <sup>20</sup>
b1	3.0	12.5	N.A.	N.A.	10000	(0.61,0.39)	
b2	3.0	9.0	N.A.	N.A.	~	(0.63,0.37)	J.Am.Chem.Soc. <sup>15</sup>
b3	3.0	9.0	N.A	N.A.	30000	N.A	-
b4	3.0	6.9	N.A	N.A		N.A	-
НАР-ЗТРА	4.4	17.5	25.9	22.1	17000	(0.58,0.36)	Adv. Mater <sup>23</sup>
4CzTPN-Ph	N.A.	11.2	N.A.	N.A.	N.A.	N.A.	Nature <sup>14</sup>
FDQPXZ	2.8	13.9	35.3	36.5	43887	(0.50,0.49)	This work

Table S4. Comparison of the device data for the representative orange/red OLEDs.

N.A.: not available.



Figure S8. 2D and 3D AFM images of solution-coated CBP: PBD: FDQPXZ (70:20:10) film.



Figure S9. Current density-voltage-brightness curves of device B.

# **Equations:**

$$EQE = \gamma \eta_{out} [0.25\Phi_{PL} + 0.75 \frac{\Phi_{TADF}}{1 - (\Phi_{PL} - \Phi_{TADF})}]$$
(1)

$$\eta_p = \gamma \eta_{out} 0.25 \Phi_F \tag{2}$$

$$\eta_{d} = \gamma \eta_{out} [0.75 + 0.25(1 - \Phi_{F})] \frac{\Phi_{TADF}}{1 - \Phi_{F}}$$
(3)





