## 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, ${ }^{\text {a }}$ Zhongbin Wu, ${ }^{\text {b }}$ Guohua Xie, ${ }^{a}$ Cheng Zhong, ${ }^{a}$ Zece Zhu, ${ }^{a}$ Hengjiang Cong, ${ }^{a}$ Dongge $\mathrm{Ma}^{* \mathrm{bc}}$ and Chuluo Yang*a<br>${ }^{a}$ 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.<br>${ }^{b}$ 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.<br>c 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

${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR spectra were measured on a MERCURY-VX300 spectrometer. HSQC NMR ( 400 MHz ) and ${ }^{19} \mathrm{~F}$ 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 $20 \mathrm{~K} \mathrm{~min}^{-1}$ from 20 to $500^{\circ} \mathrm{C}$ under argon. The glass transition temperature ( Tg ) was determined from the second heating scan at a heating rate of $10{ }^{\circ} \mathrm{C} \mathrm{min}^{-1}$. UV-vis absorption spectra were recorded on a Shimadzu UV-2700 recording 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 source. Absolute PL quantum yields (PLQYs) were measured on Edinburgh FLS920 in films. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (oxidation scan) at room temperature with a CHI voltammetric analyzer. $\mathrm{N}^{2} \mathrm{Bu}_{4} \mathrm{PF}_{6}(0.1 \mathrm{M})$ 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 $\left(\mathrm{Fc}^{+} / \mathrm{Fc}\right)$ as the internal standard. Cyclic voltammograms were obtained at a scan rate of $100 \mathrm{mV} \mathrm{s}^{-1}$. 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. ${ }^{16}$ Shortly, Benzil ( $1.46 \mathrm{~g}, 6.94 \mathrm{mmol}$ ) was completely dissolved in acetic acid ( 34 ml ), then 4,5-difluoro-1,2-phenylenediamine $(1.00 \mathrm{~g}, 6.94 \mathrm{mmol})$ was added. The reaction mixture was refluxed for 12 h . After cooled down to room temperature, the mixture was extracted with brine and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, and dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$. After removal of the solvent, the residue was purified by column chromatography on silica gel using dichloromethane/petroleum ether ( $2: 3 \mathrm{by}$ vol.) as the eluent to give white powder ( 2.16 g , yield: $98 \%$ ). ${ }^{1} \mathrm{H}$ NMR (300 MHz, $\mathrm{CDCl}_{3}$ ) $\delta[\mathrm{ppm}]: 7.91(\mathrm{t}, J=9.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.49(\mathrm{t}, J=6.0 \mathrm{~Hz}, 4 \mathrm{H}), 7.39-$ $7.32(\mathrm{~m}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ [ppm]: 153.58, 138.41, 138.34, 129.72, 129.04, 128.27, 114.79, 114.73, 114.67, 114.60. MS (EI): $m / z 318\left[\mathrm{M}^{+}\right]$. Elemental analysis (\%) for $\mathrm{C}_{20} \mathrm{H}_{12} \mathrm{~F}_{2} \mathrm{~N}_{2}$ : 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 $(0.63 \mathrm{~g}, 3.45 \mathrm{mmol})$, sodium hydride $(0.11 \mathrm{~g}, 4.58 \mathrm{mmol})$ and dry tetrahydrofuran solution $(60 \mathrm{ml})$ was stirred under room temperature for 2 h . FDQ $(1.00 \mathrm{~g}, 3.14 \mathrm{mmol})$ solution in dry tetrahydrofuran $(30 \mathrm{~mL})$ was added to the mixturesolution. After refluxed for 24 h , the cooling mixture was extracted with brine and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, and dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$. 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 ( 0.75 g , yield: $37 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta[\mathrm{ppm}]: 8.31(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}$ ), $8.07(\mathrm{~d}, J=10.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.54(\mathrm{t}, J=6.3 \mathrm{~Hz}, 4 \mathrm{H}), 7.42-7.35(\mathrm{~m}, 6 \mathrm{H}), 6.79-6.71(\mathrm{~m}$, $4 \mathrm{H}), 6.64(\mathrm{t}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.07(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ [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): $m / z$ $481.2\left[\mathrm{M}^{+}\right] .{ }^{19} \mathrm{~F}$ NMR ( $377 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta[\mathrm{ppm}]:$-114.22. Elemental analysis (\%) for $\mathrm{C}_{44} \mathrm{H}_{28} \mathrm{~N}_{4} \mathrm{O}_{2}$ : C 79.82, H 4.19, N 8.73 ; found: C 79.97, $\mathrm{H} 4.31, \mathrm{~N} 8.74$.

## 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. $\mathrm{MoO}_{3}(8 \mathrm{~nm})$ 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 $10^{-6}$ 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 $120^{\circ} \mathrm{C}$ for 10 minutes. FDQPXZ was spin-coated onto the PEDOT:PSS layer from a chlorobenzene solution. Another baking at $100^{\circ} \mathrm{C}$ 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 co | ion ${ }^{[a]}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| FDQPXZ | $\mathrm{S}_{1}$ | 2.7297 | 0.0004 | $\mathrm{H} \rightarrow \mathrm{L}$ | 0.66562 |
|  | $\mathrm{S}_{2}$ | 3.3403 | 0.0023 | $\mathrm{H}-4 \rightarrow \mathrm{~L}$ | 0.28049 |
|  |  |  |  | $\mathrm{H}-3 \rightarrow \mathrm{~L}$ | 0.63372 |
|  | $\mathrm{S}_{3}$ | 3.7293 | 0.1927 | $\mathrm{H}-2 \rightarrow \mathrm{~L}$ | 0.48454 |
|  | $\mathrm{T}_{1}$ | 2.6759 | 0 | $\mathrm{H}-3 \rightarrow \mathrm{~L}$ | 0.27583 |
|  |  |  |  | $\mathrm{H} \rightarrow \mathrm{L}$ | 0.57176 |
|  | $\mathrm{T}_{2}$ | 2.6998 | 0 | $\mathrm{H}-3 \rightarrow \mathrm{~L}$ | 0.53338 |
|  |  |  |  | $\mathrm{H}-2 \rightarrow \mathrm{~L}$ | 0.16227 |
|  |  |  |  | $\mathrm{H} \rightarrow \mathrm{L}+2$ | 0.11486 |
|  | $\mathrm{T}_{3}$ | 2.9024 | 0 | $\mathrm{H}-3 \rightarrow \mathrm{~L}$ | 0.28019 |
|  |  |  |  | $\mathrm{H}-2 \rightarrow \mathrm{~L}+1$ | 0.17343 |

${ }^{[a]} \mathrm{H} \rightarrow \mathrm{L}$ 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 $\operatorname{FDQPXZ}$ (a) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ for oxidation scan and (b) in THF for reduction scan.

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

| Compound |  | $\begin{aligned} & \lambda_{\text {abs }}^{[\mathrm{cl]}} \\ & {[\mathrm{nm}]} \end{aligned}$ | $\underset{[\mathrm{nm}]}{\lambda_{\mathrm{PL}, \text { max }}{ }^{[\mathrm{d}]}}$ | $\mathrm{HOMO}^{[\mathrm{c} / \mathrm{LUMO}}{ }^{[\mathrm{e}]}$ [eV] | $\begin{gathered} \mathrm{E}_{\mathrm{E}}^{[f]} \\ {[\mathrm{eV}]} \end{gathered}$ | $\begin{gathered} \mathrm{E}_{\mathrm{S}} \\ {[\mathrm{eV}]} \end{gathered}$ | $\begin{gathered} \mathrm{E}_{\mathrm{E}_{[\mathrm{g}]}} \\ {[\mathrm{eV}]} \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| FDQPXZ | 348/92 | 336/450 | 606 | -5.06/-2.91 | 2.37 | 2.05 | 2.01 |

${ }^{[a]}$ Obtained by TGA. ${ }^{[b]}$ Obtained by DSC. ${ }^{[c]}$ Measured in toluene solution. ${ }^{[d]}$ Measured in solid thin film. ${ }^{[\mathrm{e}]}$ Determined from the onset of the oxidation potential and the reduction potential, respectively. ${ }^{[f]}$ Calculated from the absorption edge of the UV/Vis absorption spectrum. ${ }^{[9]}$ Measured in film at 77 K .


Figure S4. (a) Transient PL decay profile of FDQPXZ in $10^{-5} \mathrm{M}$ 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 FDQPXZ from 100 to 300 K in film after degassing.

| Compound | $\mathrm{T}(\mathrm{K})$ | $\boldsymbol{\tau}_{\mathrm{F}}{ }^{[\text {[] }]}(\mathrm{ns})$ | $\boldsymbol{\tau}_{\mathrm{d}}{ }^{[b]}(\mu \mathrm{s})$ | Ratio of $\boldsymbol{\tau}_{\mathrm{d}}{ }^{[\mathrm{cc}]}(\%)$ |
| :---: | :---: | :---: | :---: | :---: |
| FDQPXZ | 100 | 29 | 0.91 | 5.10 |
|  | 150 | 28 | 1.34 | 7.44 |
|  | 200 | 26 | 2.17 | 10.82 |
|  | 250 | 24 | 2.44 | 15.73 |
|  | 300 | 22 | 2.34 | 17.63 |

${ }^{[a]}$ The lifetime of the prompt component. ${ }^{[b]}$ The lifetime of the delayed component. ${ }^{[c]}$ 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 $\mathrm{Bepp}_{2}: 5 \%$ 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 $\mathrm{BePP}_{2}: 5 \% \mathrm{FDQPXZ}$ in film.

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

| TADF <br> emitter | $\begin{aligned} & \mathbf{V}_{\text {on }} \\ & {[\mathrm{V}]} \end{aligned}$ | $\begin{gathered} \text { EQE }_{\text {Max }} \\ {[\%]} \end{gathered}$ | $\begin{gathered} \mathbf{C E}_{\text {Max }} \\ {\left[\mathbf{c d} \mathbf{A}^{-1}\right]} \end{gathered}$ | $\begin{gathered} \mathbf{P E}_{\text {Max }} \\ {\left[\operatorname{lm} \mathbf{W}^{-1}\right]} \end{gathered}$ | $\begin{gathered} \mathbf{L E}_{\text {Max }} \\ {\left[\mathbf{c d ~ m}^{-2}\right]} \end{gathered}$ | $\begin{gathered} \text { CIE } \\ (\mathbf{x}, \mathrm{y}) \end{gathered}$ | Reference |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| DMAC-PN | 3.8 | 7.2 | N.A. | 10.7 | $\sim 10000$ | $(0.55,0.45)$ | Nanotechnology ${ }^{21}$ |
| Ac-CNP | 4.7 | 13.3 | 38.1 | 26.1 | 70630 | $(0.47,0.51)$ | Adv.Funct.Mater. ${ }^{22}$ |
| Px-CNP | 5.5 | 3.0 | 5.8 | 3.1 | 101860 | $(0.53,0.44)$ |  |
| m-Px-2BBP | 2.8 | 4.2 | 11.1 | $\sim 15$ | 50820 | $(0.58,0.36)$ | Angew.Chem. ${ }^{20}$ |
| 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. ${ }^{15}$ |
| b3 | 3.0 | 9.0 | N.A | N.A. | 30000 | N.A |  |
| b4 | 3.0 | 6.9 | N.A | N.A |  | N.A |  |
| HAP-3TPA | 4.4 | 17.5 | 25.9 | 22.1 | 17000 | $(0.58,0.36)$ | Adv. Mater ${ }^{23}$ |
| 4CzTPN-Ph | N.A. | 11.2 | N.A. | N.A. | N.A. | N.A. | Nature ${ }^{14}$ |
| FDQPXZ | 2.8 | 13.9 | 35.3 | 36.5 | 43887 | (0.50,0.49) | This work |

N.A.: not available.


Figure 58. 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:

$$
\begin{align*}
& E Q E=\gamma \eta_{\text {out }}\left[0.25 \Phi_{P L}+0.75 \frac{\Phi_{\text {TADF }}}{1-\left(\Phi_{P L}-\Phi_{T A D F}\right)}\right]  \tag{1}\\
& \eta_{p}=\gamma \eta_{\text {out }} 0.25 \Phi_{F}  \tag{2}\\
& \eta_{d}=\gamma \eta_{\text {out }}\left[0.75+0.25\left(1-\Phi_{F}\right)\right] \frac{\Phi_{\text {TADF }}}{1-\Phi_{F}} \tag{3}
\end{align*}
$$





