Supplementary Material

New Aggregation-Induced Delayed Fluorescence Luminogens with Through-Space Charge Transfer for Efficient Nondoped OLEDs

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All the chemicals and reagents were purchased from commercial sources and used as received without further purification. The final products were subjected to vacuum sublimation to further improve purity before photoluminescence (PL) and electroluminescence (EL) properties investigations. $^1$H and $^{13}$C NMR spectra were measured on a Bruker AV 500 spectrometer in CDCl$_3$ at room temperature. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. Single crystals of TRZ-HPB-DMAC were grown in tetrahydrofuran-hexane mixtures and single crystal X-ray diffraction intensity data were collected at 173 K on a Bruker-Nonices Smart Apex CCD diffractometer with graphite monochromated MoKα radiation. Processing of the intensity data was carried out using the SAINIT and SADABS routines, and the structure and refinement were conducted using the SHELTL suite of X-ray programs (version 6.10). UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. PL spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. PLQY data were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. Cyclic voltammetry was measured in a solution of tetra-$n$-butylammonium hexafluorophosphate (Bu$_4$NPF$_6$, 0.1 M) in acetonitrile containing at a scan rate of 100 mV s$^{-1}$. Three-electrode system (Ag/Ag$^+$, platinum wire and glassy carbon electrode were used as reference, counter and work electrode, respectively) was used in the CV method. HOMO = −$[E_{\text{ox}} + 4.8]$ eV, and LUMO = −$[E_{\text{re}} + 4.8]$ eV. $E_{\text{ox}}$ and $E_{\text{re}}$ represent the onset oxidation and reduction potentials relative to Fc/Fc$^+$, respectively. The ground-state geometries were optimized using the density function theory (DFT) method with BMK functional at the basis set level of 6-31G*, and the $\Delta E_{\text{ST}}$ values were calculated by time-dependent DFT (TDDFT) method at the BMK/6-31G* level (Fan et al., 2017). All the calculations were performed using Gaussian09 package. Differential scanning calorimetry (DSC) analysis was carried out on a DSC Q1000 under dry nitrogen at a heating rate of 10 °C min$^{-1}$, and thermogravimetric analysis was performed on a Netzsch TG 209 F3 under nitrogen with a heating rate of 20 °C min$^{-1}$. 
Figure S1. Molecular packing of TRZ-HPB-DMAC in crystals.

Figure S2. Natural transition orbitals (NTOs) and calculated absorption spectra of (A) TRZ-HPB-PXZ and (B) TRZ-HPB-DMAC corresponding to the $S_0 \rightarrow S_n$ (ground-state geometry) transitions. The contributions of the electron and hole excitations to the transitions are indicated. $f$ is oscillator strength.

There are distinct broad absorption shoulders in the range of 300–350 nm, in order to illuminate the origins of the absorption peaks, natural transition orbitals (NTOs) were calculated and the absorption spectra were analyzed (Lu et al., 2012). As illustrated in Figure S2A, the high-energy band (288 nm) in TRZ-HPB-PXZ is attributed to the $S_0 \rightarrow S_6$ transition, which is associated with the locally excited (LE) state, whereas the lower energy transitions including $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions are obviously assigned to the intramolecular charge transfer (ICT) transition. In other words, the low-
energy band absorption is attributed to ICT transition, corresponding to the broad absorption shoulder in the range of 300–350 nm measured in experiment. Similarly, TRZ-HPB-DMAC shows a high-energy band (291 nm) associated with the $S_0 \rightarrow S_5$ transition related to the LE state, the low-energy band absorption exhibit ICT and agree well with the experimental data (Figure S2B). Notably, the oscillator strength of the lower energy transition of TRZ-HPB-PXZ is distinctly stronger than that of TRZ-HPB-DMAC, which is consistent with stronger charge transfer character of TRZ-HPB-PXZ. In addition, we have also found that many other groups attribute the low-energy band absorption to the ICT transition (Chen et al., 2017; Park et al., 2017).

Figure S3. PL spectra of (A) TRZ-HPB-PXZ and (B) TRZ-HPB-DMAC in various solutions at room temperature.

Figure S4. Fluorescence and phosphorescence spectra of neat films of (A) TRZ-HPB-PXZ and (B) TRZ-HPB-DMAC, measured at 77 K under nitrogen.
Table S1. Transient PL decay data of TRZ-HPB-PXZ and TRZ-HPB-DMAC in THF/water mixtures with different water fractions ($f_w$).

| compound            | $f_w$ | $<\tau>$ [ns] | $<\tau_1>$ [ns] | $<\tau_2>$ [ns] | A<sub>1</sub> | A<sub>2</sub> | R<sub>prompt</sub> [%] | R<sub>delayed</sub> [%] |
|---------------------|-------|---------------|-----------------|-----------------|-------------|-------------|----------------------|------------------------|
| TRZ-HPB-PXZ         | 0     | 15.2          | 14.0            | 102.6           | 158956.0    | 318.9       | 99                   | 1                      |
|                     | 70    | 382.5         | 48.1            | 664.5           | 9562.1      | 821.1       | 46                   | 54                     |
|                     | 80    | 1033.1        | 56.0            | 1366.3          | 18145.9     | 2180.2      | 25                   | 75                     |
|                     | 90    | 1009.0        | 55.3            | 1368.3          | 17945.9     | 1925.3      | 27                   | 73                     |
|                     | 99    | 1212.3        | 59.7            | 1623.3          | 17756.8     | 1831.0      | 26                   | 74                     |
| TRZ-HPB-DMAC        | 0     | 357.5         | 53.0            | 1102.4          | 20732.6     | 407.7       | 71                   | 29                     |
|                     | 70    | 2115.0        | 66.5            | 2573.8          | 16474.5     | 1899.6      | 18                   | 82                     |
|                     | 80    | 3094.2        | 64.3            | 3715.3          | 17652.0     | 1490.9      | 17                   | 83                     |
|                     | 90    | 2874.8        | 61.5            | 3599.6          | 18740.7     | 1242.5      | 20                   | 80                     |
|                     | 99    | 3000.8        | 59.9            | 3863.2          | 19609.3     | 1037.7      | 23                   | 77                     |

Table S2. Transient PL decay data of TRZ-HPB-PXZ and TRZ-HPB-DMAC in THF solutions and neat films, measured at 300 K under nitrogen.<sup>a)</sup>

| compound            | state   | $<\tau>$ [ns] | $<\tau_1>$ [ns] | $<\tau_2>$ [ns] | A<sub>1</sub> | A<sub>2</sub> | R<sub>prompt</sub> [%] | R<sub>delayed</sub> [%] |
|---------------------|---------|---------------|-----------------|-----------------|-------------|-------------|----------------------|------------------------|
| TRZ-HPB-PXZ         | THF solution | 15.2          | 14.0            | 102.6           | 158956.0    | 318.9       | 99                   | 1                      |
|                     | neat film      | 1798.4        | 41.6            | 2114.3          | 2236.2      | 244.5       | 15                   | 85                     |
| TRZ-HPB-DMAC        | THF solution | 357.5         | 53.0            | 1102.4          | 20732.6     | 407.7       | 71                   | 29                     |
|                     | neat film      | 3354.8        | 48.4            | 4733.5          | 7304.2      | 178.9       | 29                   | 71                     |

<sup>a</sup>Transient PL decay data are fitted by multiple-exponential function and the mean fluorescence lifetimes ($<\tau>$) were calculated by $<\tau> = \Sigma A_i \tau_i^2 / \Sigma A_i \tau_i$, where $A_i$ is the pre-exponential for lifetime $\tau_i$. R<sub>prompt</sub> and R<sub>delayed</sub> are individual component ratio for prompt and delayed fluorescence. R<sub>prompt</sub> = $\tau_1 A_1 / (\tau_1 A_1 + \tau_2 A_2 + \tau_3 A_3)$ (Nakagawa et al., 2012), R<sub>delayed</sub> = 1 – R<sub>prompt</sub>. 


Table S3. Transient PL decay data of TRZ-HPB-PXZ and TRZ-HPB-DMAC in neat film at different temperatures.

| compound       | $T$ [K] | $\langle \tau \rangle$ [ns] | $\langle \tau_1 \rangle$ [ns] | $\langle \tau_2 \rangle$ [ns] | $A_1$ | $A_2$ | $R_{\text{prompt}}$ [%] | $R_{\text{delayed}}$ [%] |
|----------------|--------|-----------------|-----------------|-----------------|-----|-----|----------------|----------------|
| TRZ-HPB-PXZ    | 100    | 159.5           | 26.9            | 231.7           | 1157.0 | 247.1 | 35             | 65             |
|                | 150    | 1209.9          | 106.3           | 6019.4          | 11634.4 | 47.1  | 81             | 19             |
|                | 200    | 2663.7          | 100.6           | 3612.1          | 1267.2  | 95.4  | 27             | 73             |
|                | 250    | 2476.5          | 59.2            | 2962.3          | 1727.8  | 171.9 | 17             | 83             |
|                | 300    | 1798.4          | 41.6            | 2114.3          | 2236.2  | 244.5 | 15             | 85             |
| TRZ-HPB-DMAC   | 100    | 113.2           | 21.3            | 159.0           | 1254.6  | 337.5 | 33             | 67             |
|                | 150    | 784.0           | 81.9            | 2133.9          | 1530.8  | 30.6  | 66             | 34             |
|                | 200    | 2284.1          | 79.7            | 4552.2          | 1627.4  | 27.7  | 51             | 49             |
|                | 250    | 4387.2          | 60.9            | 6480.6          | 5931.4  | 115.1 | 33             | 67             |
|                | 300    | 3354.8          | 48.4            | 4733.5          | 7304.2  | 178.9 | 29             | 71             |

Table S4. Photophysical data of TRZ-HPB-PXZ and TRZ-HPB-DMAC in neat films. a)

|                      | TRZ-HPB-PXZ | TRZ-HPB-DMAC |
|----------------------|-------------|-------------|
| $\Phi_{\text{PL}}$ [%] | 61.5        | 51.8        |
| $\tau_{\text{prompt}}$ [ns] | 41.6        | 48.4        |
| $\tau_{\text{delayed}}$ [μs] | 2.1         | 4.7         |
| $R_{\text{delayed}}$ [%] | 84.8        | 70.6        |
| $\Phi_{\text{prompt}}$ [%] | 9.4         | 15.2        |
| $\Phi_{\text{delayed}}$ [%] | 52.1        | 36.6        |
| $\Phi_{\text{ISC}}$ [%] | 84.8        | 70.6        |
| $\Phi_{\text{RISC}}$ [%] | 61.5        | 51.8        |
| $K_F$ [$\times 10^6$ s$^{-1}$] | 2.3         | 3.2         |
| $K_{IC}$ [$\times 10^6$ s$^{-1}$] | 1.4         | 2.9         |
| $K_{ISC}$ [$\times 10^6$ s$^{-1}$] | 20.4        | 14.6        |
| $K_{RISC}$ [$\times 10^5$ s$^{-1}$] | 31.0        | 7.2         |
a) Abbreviations: $\Phi_{PL}$ = absolute photoluminescence quantum yield; $\tau_{\text{prompt}}$ and $\tau_{\text{delayed}}$ = lifetimes calculated from the prompt and delayed fluorescence decay, respectively; $R_{\text{delayed}}$ = the ratio of delayed components; $\Phi_{\text{prompt}}$ and $\Phi_{\text{delayed}}$ = prompt and delayed components, respectively, determined from the total $\Phi_{\text{PL}}$ and the proportion of the integrated area of each component in the transient spectra to the total integrated area; $\Phi_{\text{ISC}}$ = the intersystem crossing quantum yield; $k_F$ = fluorescence decay rate; $k_{\text{IC}}$ = internal conversion decay rate from S$_1$ to S$_0$; $k_{\text{ISC}}$ = intersystem crossing decay rate from S$_1$ to T$_1$; $k_{\text{RISC}}$ = the rate constant of reverse intersystem crossing process.

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\Phi_{\text{prompt}} = \Phi_{\text{PL}} R_{\text{prompt}} \\
\Phi_{\text{delayed}} = \Phi_{\text{PL}} R_{\text{delayed}} \\
k_F = \Phi_{\text{prompt}}/\tau_{\text{prompt}} \\
\Phi_{\text{PL}} = k_F/(k_F + k_{\text{IC}}) \\
\Phi_{\text{prompt}} = k_F(k_F + k_{\text{IC}} + k_{\text{ISC}}) \\
\Phi_{\text{IC}} = k_{\text{IC}}/(k_F + k_{\text{IC}} + k_{\text{ISC}}) \\
\Phi_{\text{ISC}} = k_{\text{ISC}}/(k_F + k_{\text{IC}} + k_{\text{ISC}}) = 1 - \Phi_{\text{prompt}} - \Phi_{\text{IC}} \\
\Phi_{\text{RISC}} = \Phi_{\text{delayed}}/\Phi_{\text{ISC}} \\
k_{\text{RISC}} = (k_p k_d \Phi_{\text{delayed}})/(k_{\text{ISC}} \Phi_{\text{prompt}}) \\
k_p = 1/\tau_{\text{prompt}}; k_d = 1/\tau_{\text{delayed}}
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