Electronic Supplementary Information

Exciton energy transfer and bi-exciton annihilation in the emitting layers of thermally activated delayed fluorescence-based OLEDs

Hyunchul Kang,[1] Han Jin Ahn,[2] Gyeong Woo Kim,[2] Ji-Eun Jeong,[1] Han Young Woo,[1] Jun-Yun Kim,[2,] and Sungnam Park[1,]**

[1]Department of Chemistry and Research Institute for Natural Science, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul, 02841, Republic of Korea

[2]LG Display Co. Ltd., LG Science Park, 30, Magokjungang 10-ro, Gangseo-gu, Seoul, 07796, Republic of Korea

Corresponding Authors:

*E-mail: windwart@lgdisplay.com (J. Y. Kim) and spark8@korea.ac.kr (S. Park)

1. TADF kinetic model with the concentration quenching of triplet excitons

Time-resolved PL (TRPL) spectra of DPEPO:TDBA-DI films were analyzed by a conventional TADF kinetic model with a concentration quenching of triplet excitons. The coupled differential equations for the concentrations of singlet and triplet excitons ($[S_1]$ and $[T_1]$) can be written by,

$$\frac{d[S_1](t)}{dt} = -(k_r^S + k_{nr}^S + k_{ISC})[S_1](t) + k_{RISC}[T_1](t) \quad \text{(s1)}$$

$$\frac{d[T_1](t)}{dt} = k_{ISC}[S_1](t) - (k_{nr}^T + k_{RISC})[T_1](t) - k_{TTA}[T_1]^2(t) \quad \text{(s2)}$$

where k_r^S is the radiative rate constant of the excited singlet state, k_{nr}^S is the non-radiative rate constant of the excited singlet state, k_{ISC} is the intersystem crossing rate constant from the excited singlet state to the excited triplet state, k_{RISC} is the reverse intersystem crossing rate constant from the excited triplet state to the excited singlet state, k_{nr}^T is the non-radiative rate constant of the excited triplet state, and k_{TTA} is the rate constant of the concentration quenching of triplet excitons. The solution of Eqs. (s1) and (s2) is obtained by

$$[S_1](t) = A_{PF}\exp(-t/\tau_{PF}) + A_{DF}\exp(-t/\tau_{DF}) \quad \text{(s3)}$$

where $\tau_{PF} = 1/k_{PF}$ and $\tau_{DF} = 1/k_{DF}$ were obtained by fitting a multi-exponential function $I(t) = \sum_{i=1}^{n} A_i \exp(-t/\tau_i)$ to TRPL signals. The prompt and delayed fluorescence rate constants, k_{PF} and k_{DF}, are given by

$$k_{PF} + k_{DF} = k_r^S + k_{nr}^S + k_{ISC} + k_r^T + k_{nr}^T + k_{RISC} + k_{TTA}^{'} \quad \text{(s4)}$$

$$k_{PF}k_{DF} = (k_r^S + k_{nr}^S + k_{ISC})(k_r^T + k_{nr}^T + k_{RISC} + k_{TTA}^{'}) - k_{ISC}k_{RISC} \quad \text{(s5)}$$

where $k_{TTA}^{'} = k_{TTA}[T_1]$. By assuming that $k_{PF} >> k_{DF}$, $k_r^S >> k_{nr}^S, k_{RISC}$, $k_{RISC} >> k_r^T$, k_{nr}^T, $k_{TTA}^{'}$, and $k_{nr}^S \approx 0$, $k_{nr}^T \approx 0$ because of high PLQY, the rate constants can be simply obtained as,

$$k_{PF} = 1/\tau_{PF} \approx k_r^S + k_{ISC} \quad \text{(s6)}$$

$$k_{DF} = 1/\tau_{DF} \quad \text{(s7)}$$

$$k_r^S = k_{PF} \cdot \Phi_{PF} \quad \text{(s8)}$$

$$k_{ISC} \simeq k_{PF} \cdot (1 - \Phi_{PF}) \quad \text{(s9)}$$

$$k_{RISC} = (k_{DF} - k_{nr}^T)/\Phi_{PF} \simeq k_{DF}/\Phi_{PF} \quad \text{(s10)}$$

On the other hand, when the concentration quenching of triplet excitons occurs and $k_{TTA}^{'}$ is comparable to k_{RISC}, Eqs. (s4) and (s5) are reduced to

$$k_{PF} + k_{DF} \approx k_r^S + k_{ISC} + k_{RISC} + k_{TTA}^{'} \quad \text{(s11)}$$

$$k_{PF}k_{DF} \approx k_r^S k_{RISC} + k_r^S k_{TTA}^{'} + k_{ISC}k_{TTA}^{'} \quad \text{(s12)}$$

Solving Eqs. (s11) and (s12) for $k_{TTA}^{'}$,

$$k_{TTA}^{'} = \frac{1}{2}\left(k_{PF} + k_{DF} - 2k_{RISC} - \sqrt{\left(k_{PF} - k_{DF}\right)^2 - 4k_{ISC}k_{RISC}}\right) \quad \text{(s13)}$$

The rate constant for the concentration quenching of triplet states $k_{TTA}^{'} = k_{TTA}[T_1]$ can be determined once k_{PF}, k_{DF}, k_{ISC}, and k_{RISC} are experimentally measured.

In our experiments, k_{ISC} and k_{RISC} were assumed to be concentration-independent for DPEPO:TDBA-DI films. The k_{ISC} and k_{RISC} values obtained from DPEPO:TDBA-DI film (90:10 wt%) were used to determine $k_{TTA}^{'}$ for DPEPO:TDBA-DI films (70:30 and 50:50 wt%).

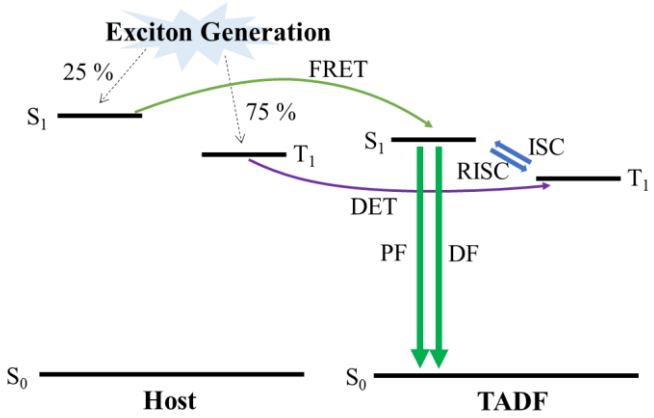

Figure S1. Electroluminescence (EL) mechanism of TADF-based OLEDs.

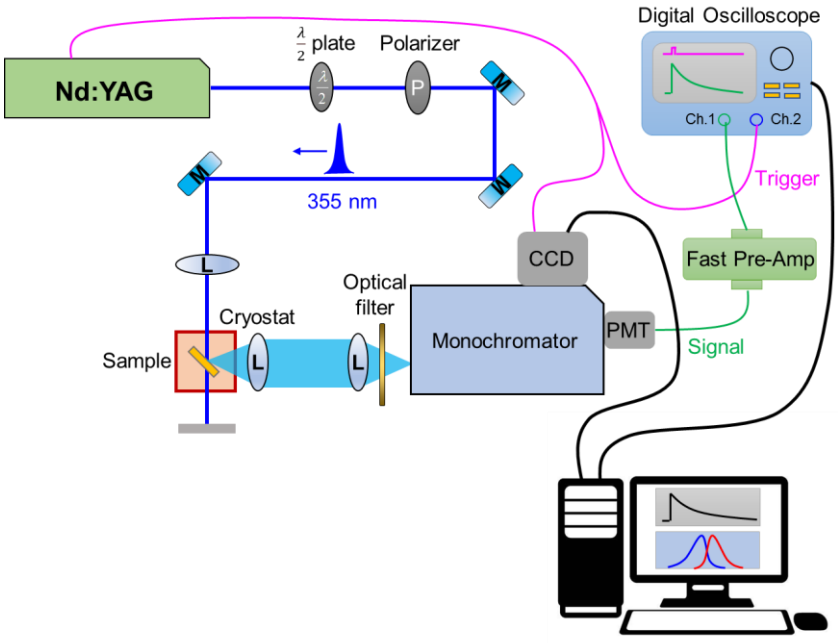

Figure S2. Schematic illustration of our TRPL experimental setup.

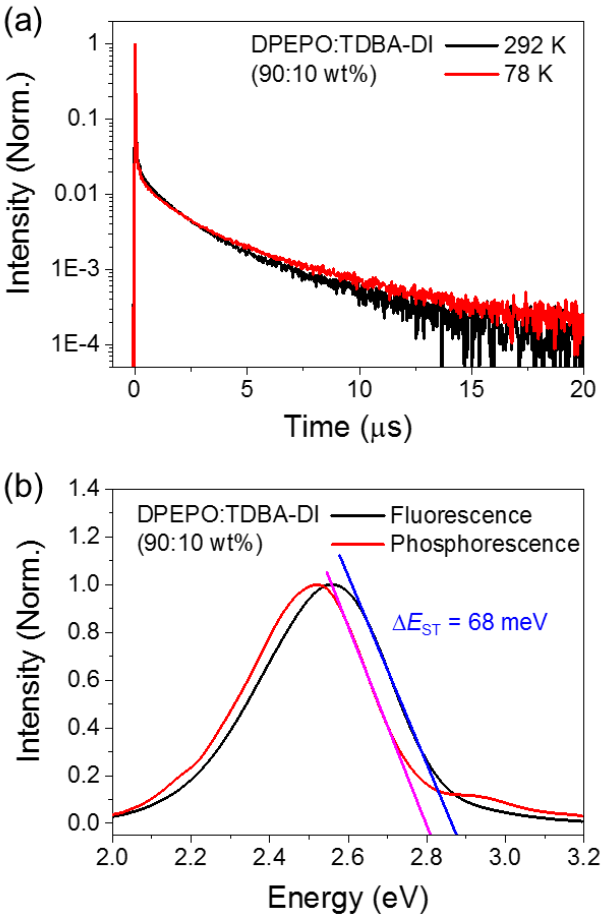

Figure S3. (a) TRPL signals of DPEPO:TDBA-DI film (90:10 wt%) measured at 292 K and 78 K. (b) Fluorescence and phosphorescence spectra of DPEPO:TDBA-DI film (90:10 wt%) measured at 78 K (ΔE_{ST} = 68 meV).

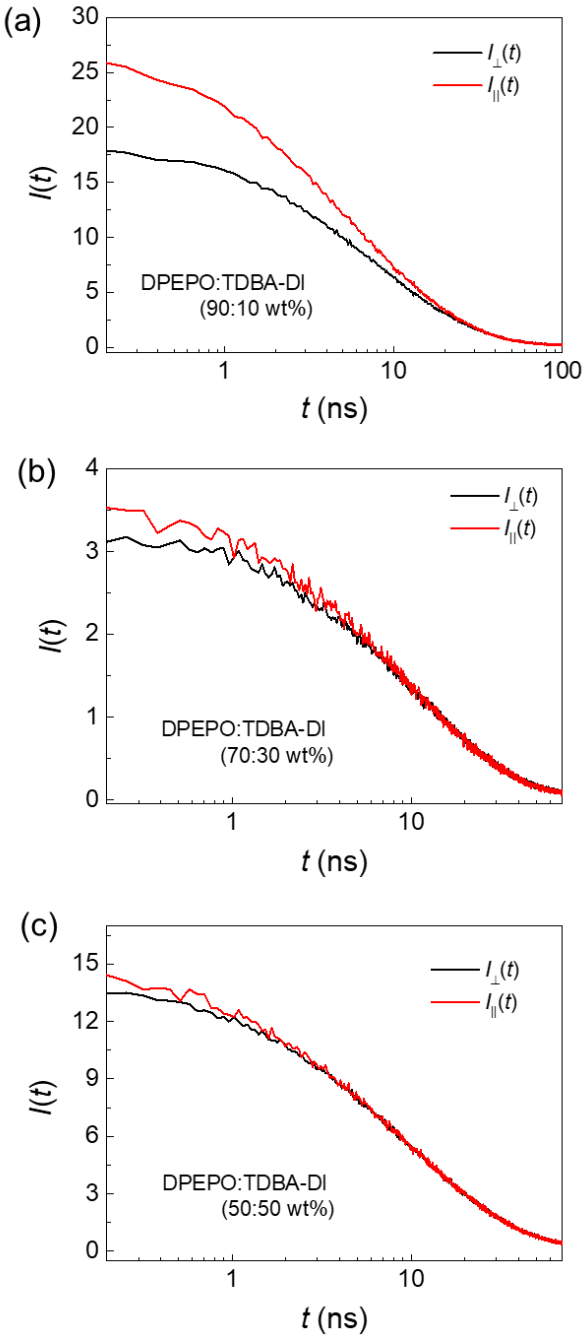

Figure S4. Intensity-calibrated $I_{\parallel}(t)$ and $I_{\perp}(t)$ measured with DPEPO:TDBA-DI films. (a) 90:10, (b) 70:30, and (c) 50:50 wt%.

Table S1. The number of host and dopant molecules (n_{host} and n_{dopant}) used for the MD simulations. The volume, V_{box}, of the simulation box for DPEPO:TDBA-DI films.

DPEPO:TDBA-DI (wt%)	n_{host}	n_{dopant}	V_{box} (nm^3)
90 : 10	560	39	497.8
70 : 30	467	133	565.6
50 : 50	359	240	628.5

Table S2. Parameters for the fit of a Gaussian function to the distribution of the minimum distances of all pairs of TDBA-DI molecules in films: mean, $d_{min,center}$, standard deviation, w, and R^2 values.

DPEPO:TDBA-DI (wt%)	$d_{min,center}$ (nm)	w (nm)	R^2
90 : 10	1.30	0.87	0.51
70 : 30	0.85	0.58	0.87
50 : 50	0.72	0.48	0.95

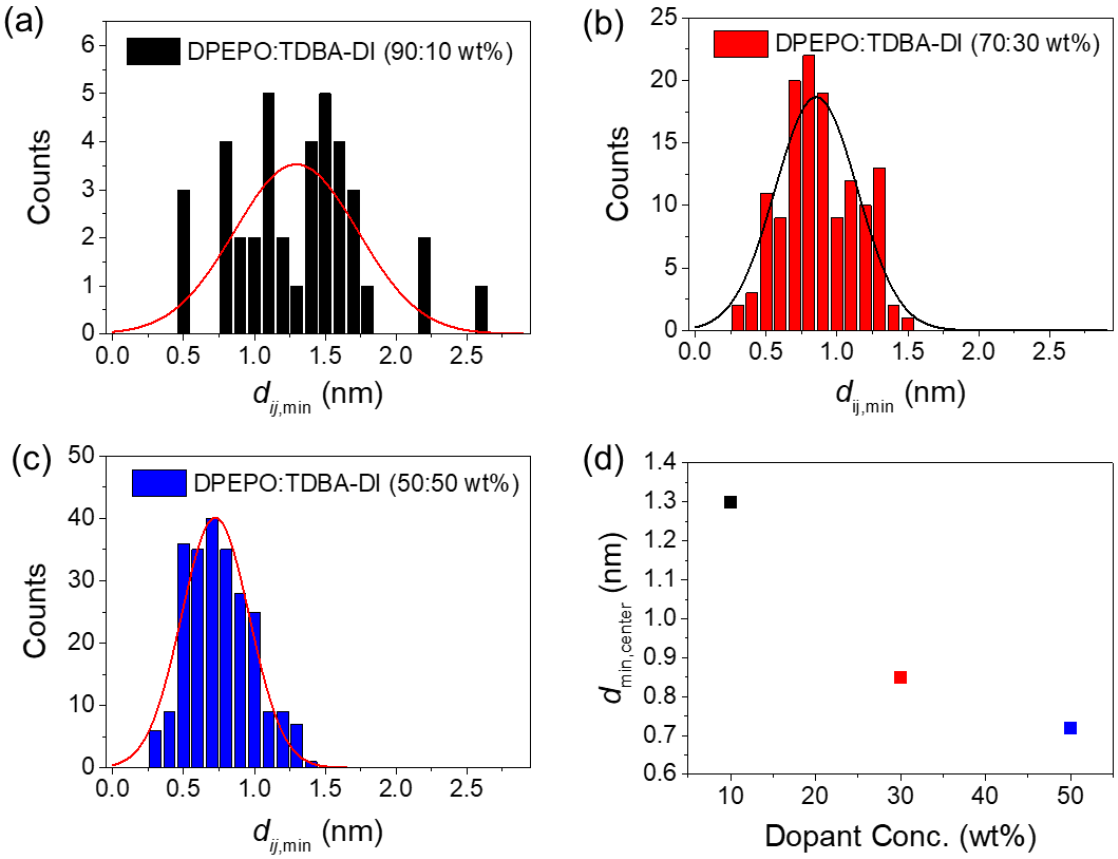

Figure S5. Distribution of the minimum distances, $d_{ij,min}$, of all pairs of neighboring TDBA-DI molecules in films: (a) 90:10, (b) 70:30, and (c) 50:50 wt%. The distribution is fitted by a Gaussian function. (d) Comparison of the average minimum distances of neighboring TDBA-DI molecules in films.

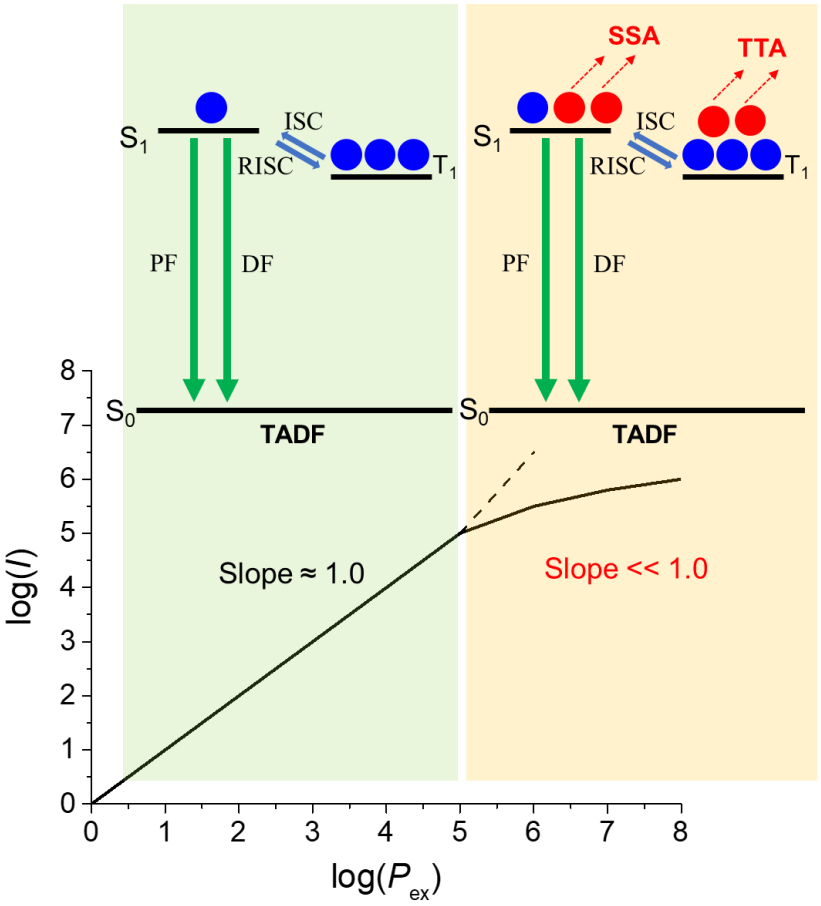

Figure S6. Exciton-exciton annihilation mechanism (bi-exciton recombination) in TADF-based OLEDs when the excitation laser power is increased.

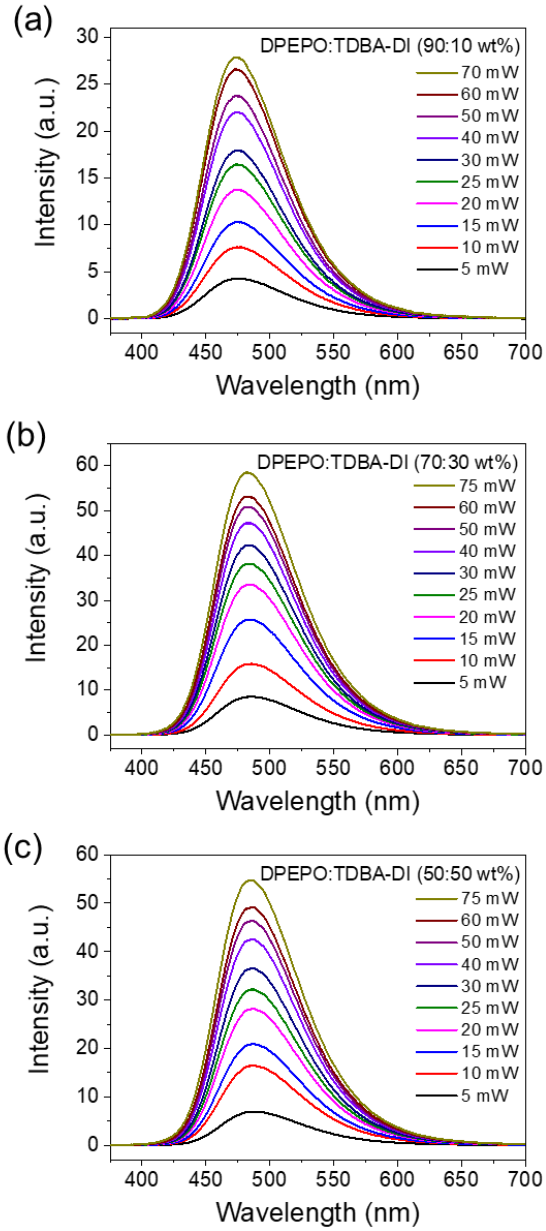

Figure S7. Excitation power-dependent PL spectra of DPEPO:TDBA-DI films. (a) 90:10, (b) 70:30, and (c) 50:50 wt%.

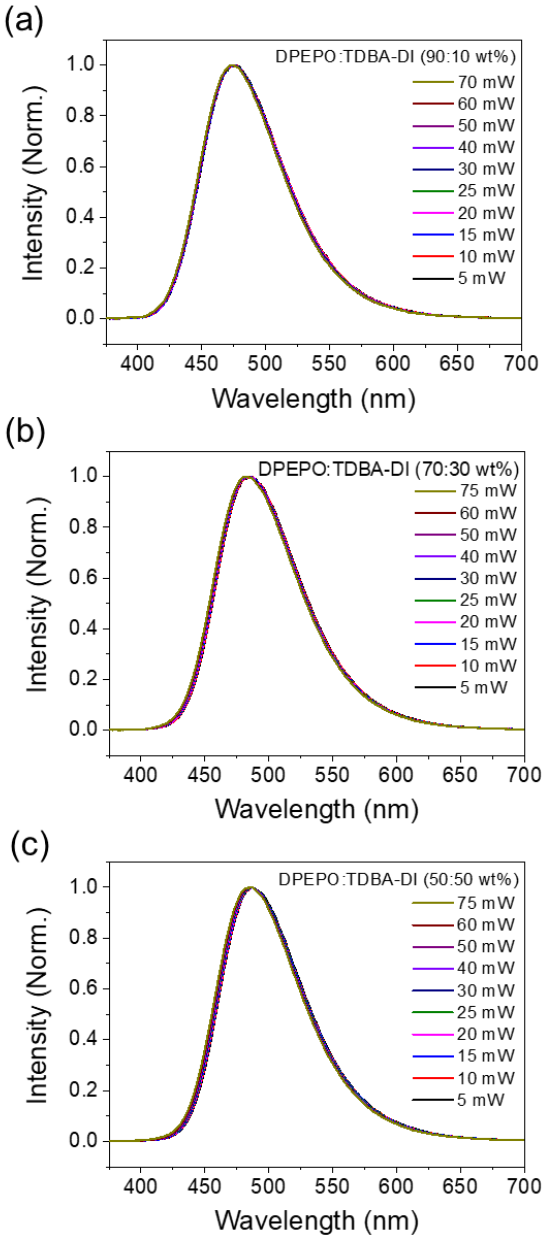

Figure S8. Normalized excitation power-dependent PL spectra of DPEPO:TDBA-DI films. (a) 90:10, (b) 70:30, and (c) 50:50 wt%.