Electronic Supplementary Material (ESI) for Materials Horizons.

Suppressing Singlet-triplet Annihilation Process to Achieve Highly Efficient Deep-Blue AIE-Based OLEDs

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Section S1. Photophysical Equations

The rate constants were determined using the following basic photophysical functions:

$$\phi_{PF} = \phi_{PL} R_{prompt} \quad \text{(S1)}$$

$$\phi_{DF} = \phi_{PL} R_{delayed} \quad \text{(S2)}$$

$$k_r^S = \phi_{PF}/\tau_{PF} \quad \text{(S3)}$$

$$\phi_{PL} = k_r^S/(k_r^S + k_{nr}^S) \quad \text{(S4)}$$

$$\phi_{PF} = k_r^S/(k_r^S + k_{nr}^S + k_{ISC}) \quad \text{(S5)}$$

$$\phi_{ISC} = k_{ISC}/(k_r^S + k_{nr}^S + k_{ISC}) \quad \text{(S6)}$$

$$k_{hRISC} = \frac{k_{PF} k_{DF} \emptyset_{DF}}{k_{ISC} \emptyset_{PF}} \quad \text{(S7)}$$

$$k_{IC}^{T_n} = k_{DF} - k_{hRISC} \phi_{DF} \quad \text{(S8)}$$

$$\phi_{hRISC} = k_{hRISC}/(k_{hRISC} + k_{IC}^{T_n}) \quad \text{(S9)}$$

$$k_{PF} = 1/\tau_{PF} \quad \text{(S10)}$$

$$k_{DF} = 1/\tau_{DF} \quad \text{(S11)}$$

here ϕ_{PL} is the photoluminescence quantum yield (PLQY). ϕ_{PF} and ϕ_{DF} are the prompt and delayed fluorescence efficiencies, respectively. ϕ_{ISC} and ϕ_{hRISC} are the ISC and hRISC efficiencies, respectively. τ_{PF} and τ_{DF} are the prompt and delayed fluorescent lifetimes, respectively. k_r^S, k_{nr}^S, k_{ISC}, k_{hRISC}, $k_{IC}^{T_n}$, k_{PF} and k_{DF} are the rates of singlet radiation, singlet non-radiation, ISC, hRISC, IC from T_n state to T_1 state, prompt fluorescence and decay fluorescence processes, respectively. R_{prompt} and $R_{delayed}$ are the component ratios of prompt and delayed fluorescence, respectively.

Section S2. Steady-state dynamics

Taking account of all the possible hRISC, TTA and STA processes, the time evolution of singlet and triplet excited state decay of AIE by electrical pulse excitation can be modeled as

$$\frac{dS_1}{dt} = \gamma(J)\frac{J}{4ed} - \left(k_r^S + k_{nr}^S + k_{ISC}\right)S_1 + k_{hRISC} T_n - k_{STA} S_1 T_1 + \frac{\alpha}{2} k_{TTA} T_1^2 \quad \text{(S12)}$$

$$\frac{dT_n}{dt} = \gamma(J)\frac{3J}{4ed} - k_{IC}^{T_n}T_n - k_{hRISC}T_n + k_{ISC}S_1 \quad \text{(S13)}$$

$$\frac{dT_1}{dt} = k_{IC}^{T_n}T_n - k_T T_1 - \frac{1+\alpha}{2}k_{TTA}T_1^2 \quad \text{(S14)}$$

To exclude the influence of singlet–triplet annihilation, we only explore the dynamic process at low current density. Therefore, $k_{STA}S_1T_1 \approx 0$. Because $k_r^S + k_{nr}^S \gg k_{ISC}$, $k_{ISC}S_1$ can be negligible. The evaluation of T_n can be solved using Equation S13 and is expressed as

$$T_n = \frac{3\gamma(J)J}{4ed(k_{IC}^{T_n} + k_{hRISC})} \quad \text{(S15)}$$

under low current density region, where the triplet monomolecular decay dominates and the bimolecular can be negligible ($k_{nr}^T T_1 \gg \frac{1+\alpha}{2}k_{TTA}T_1^2$), the evaluation of T_1 can be solved using Equation S14 and S15 and is expressed as

$$T_1 = \frac{3\gamma(J)k_{IC}^{T_n}J}{4ed(k_{IC}^{T_n} + k_{hRISC})k_T} \quad \text{(S16)}$$

the evaluation can be solved using Equation S12, S15 and S16 and is expressed as

$$S_1 = \frac{1}{(k_r^S + k_{nr}^S)}\left[\frac{3\gamma(J)}{4ed}\left(\frac{k_{hRISC}}{k_{hRISC} + k_{IC}^{T_n}}\right) + \frac{\gamma(J)}{4ed}\right]J + \frac{k_{TTA}\alpha}{2k_T{}^2(k_r^S + k_{nr}^S)}\left[\frac{3\gamma(J)}{4ed}\frac{k_{IC}^{T_n}}{k_{hRISC} + k_{IC}^{T_n}}\right]^2 J^2 \quad \text{(S17)}$$

Because $\frac{k_{hRISC}}{k_{hRISC} + k_{IC}^{T_n}} = \emptyset_{hRISC}$ and $\gamma(J) = 1$, Equation S17 is abbreviated

$$S_1 = \frac{1}{(k_r^S + k_{nr}^S)}\left[\frac{3}{4ed}\emptyset_{hRISC} + \frac{1}{4ed}\right]J + \frac{k_{TTA}\alpha}{2k_T{}^2(k_r^S + k_{nr}^S)}\left[\frac{3}{4ed}(1 - \emptyset_{hRISC})\right]^2 J^2 \quad \text{(S18)}$$

As discussed above, the overall singlets contain two components. The first part is the singlets from the direct charge recombination and hRISC process, which are linearly dependent on current density as expected for the whole investigated current range. The second part is the singlets indirectly produced via TTA, which are proportional to the square of current density. Since the EL intensity is proportional to the singlet density, the ratio of the EL intensity from the two parts, donated as $R = EL_T/EL_S$, can be, respectively, described by

$$R = \frac{9 \cdot k_{TTA} \cdot \gamma(J) \cdot \alpha \cdot (1 - \emptyset_{hRISC})^2}{8{k_T}^2 ed \cdot (3 \cdot \emptyset_{hRISC} + 1)} \cdot J \tag{S19}$$

Because α =0.25. Equation S18 is expressed as

$$R = \frac{9 \cdot k_{TTA} \cdot \gamma(J) \cdot (1 - \emptyset_{hRISC})^2}{32{k_T}^2 ed \cdot (3 \cdot \emptyset_{hRISC} + 1)} \cdot J \tag{S20}$$

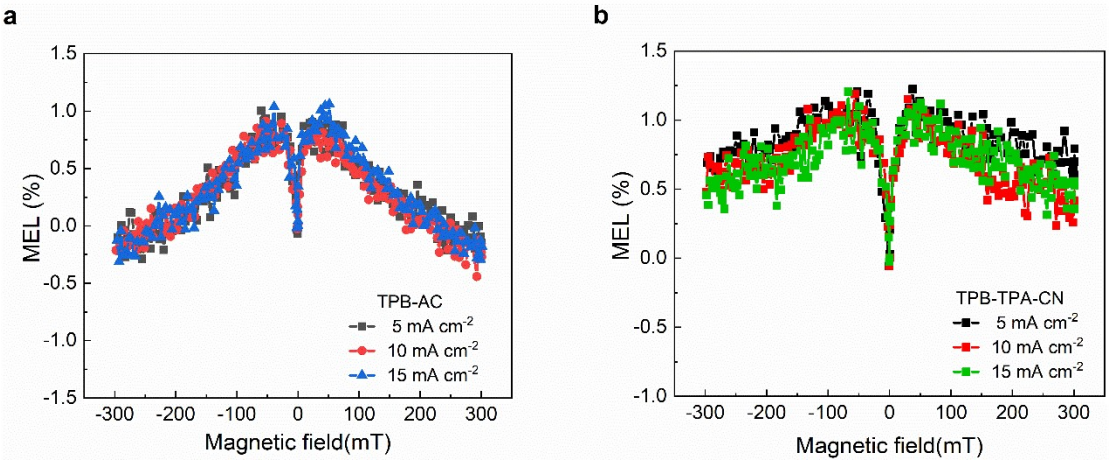

Figure S1. MEL responses of the (a) non-doped TPB-AC, and (b) non-doped TPB-TPA-CN devices at different current densities.

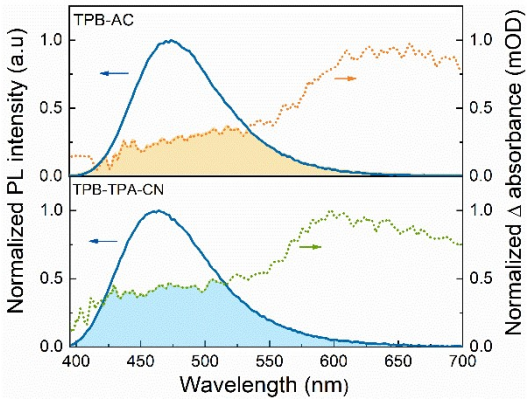

Figure S2. PL spectra of TPB-AC and TPB-TPA-CN in chlorobenzene solution, and triplet absorption spectra of TPB-AC and TPB-TPA-CN in chlorobenzene solution.

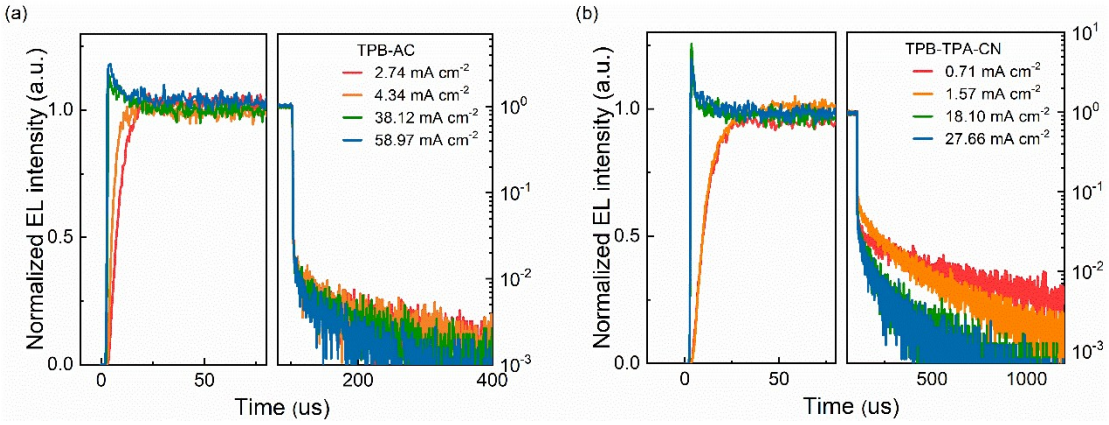

Figure S3. (a) Transient-EL decay curves of the non-doped TPB-AC OLEDs at different current densities. (c) Transient-EL decay curves of the non-doped TPB-TPA-CN OLEDs at different current densities.

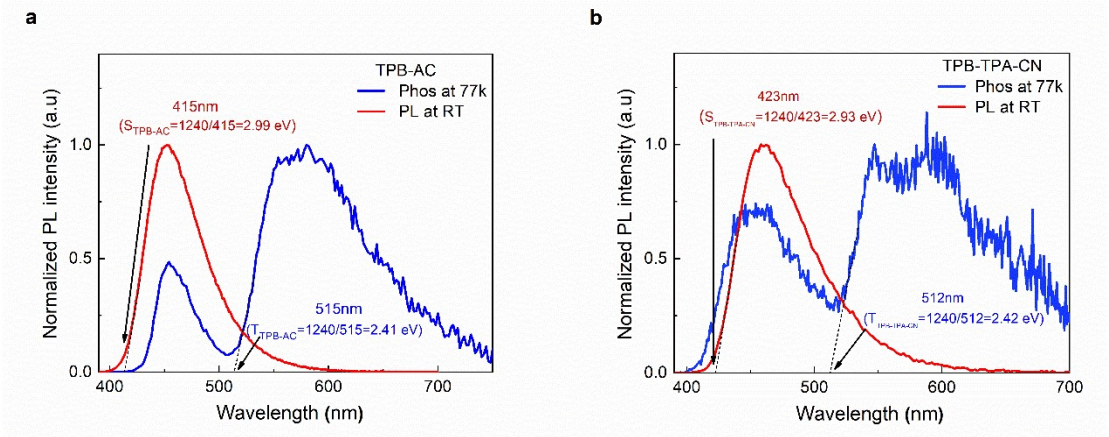

Figure S4. Normalized PL spectra of (a) TPB-AC and (b) TPB-TPA-CN films at room temperature (RT) and 77 K.

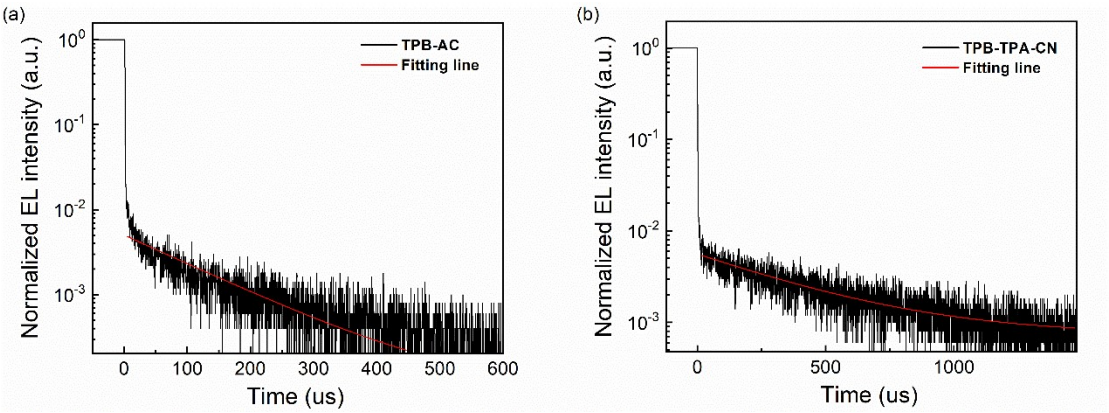

Figure S5. TREL charateristics of AIE-OLEDs with emitter of a) TPB-AC, b) TPB-TPA-CN. The red lines are fitting line for obtaining the lifetime values of up-conversion fluorescence.

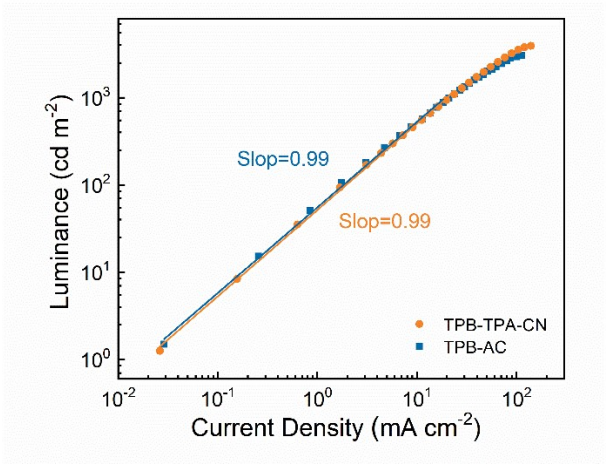

Figure S6. Current-density–luminance curves of the non-doped TPB-AC and TPB-TPA-CN OLEDs.

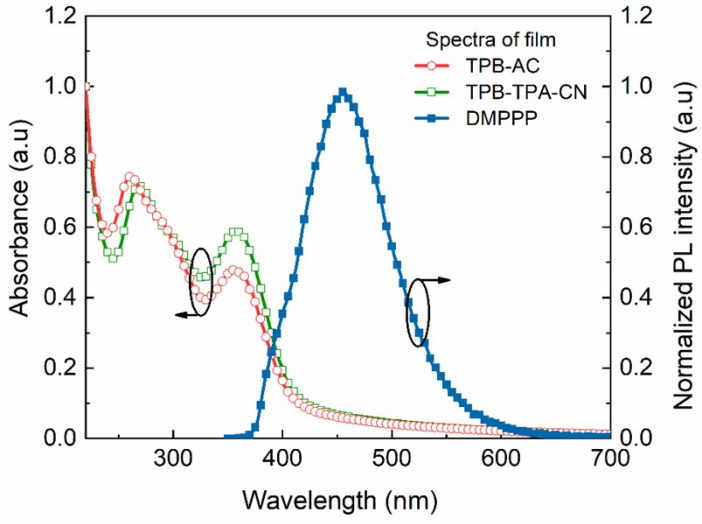

Figure S7. UV spectra of TPB-AC and TPB-TPA-CN neat films, and PL spectra of DMPPP neat film.

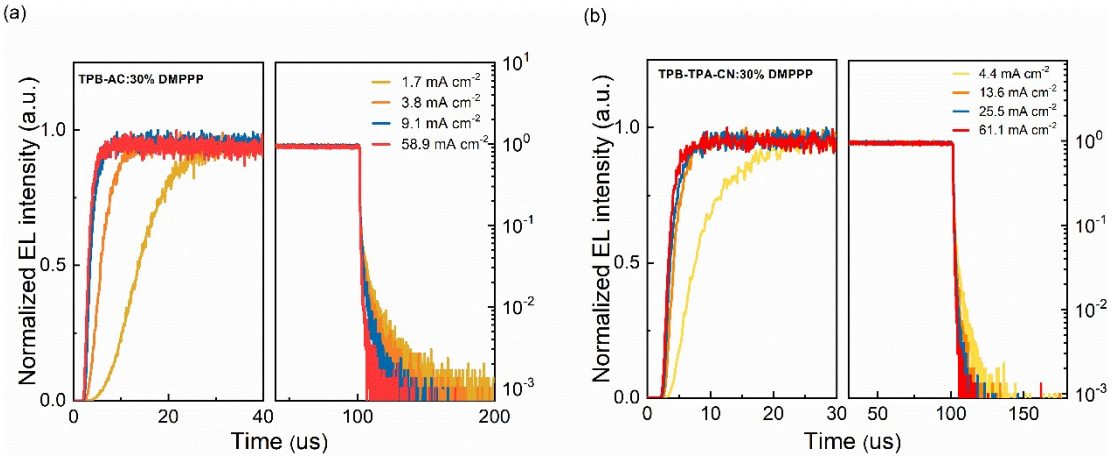

Figure S8. (a) Transient-EL decay curves of the TPB-AC:30% DMPPP OLEDs at different current densities. (b) Transient-EL decay curves of the TPB-TPA-CN:30%

DMPPP OLEDs at different current densities.

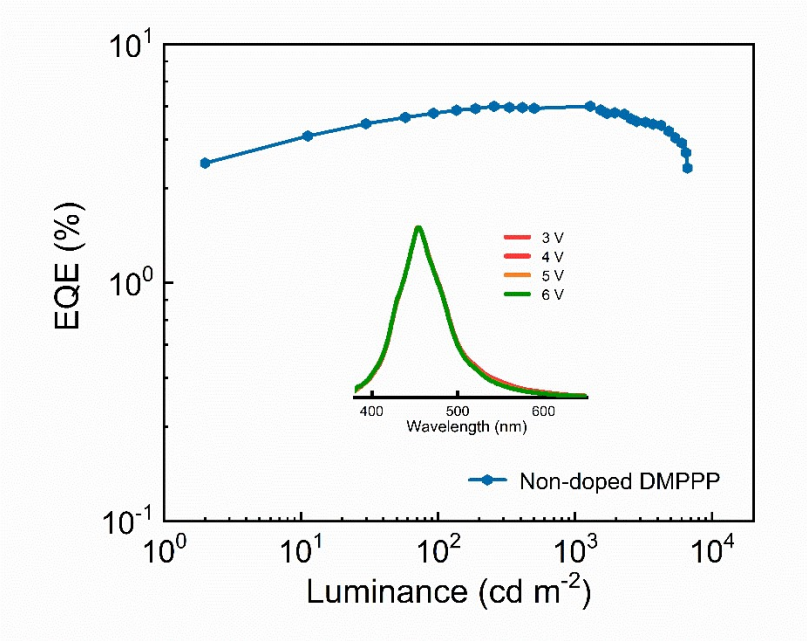

Figure S9. EQE versus luminance characteristic of the resulting non-doped DMPPP OLEDs. The inset shows the electroluminescent (EL) spectra at different voltages.

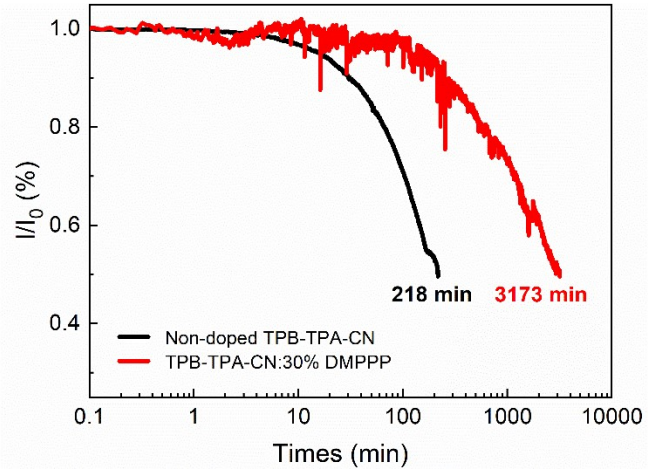

Figure S10. Lifetimes of the non-doped TPB-TPA-CN and TPB-TPA-CN: 30% DMPPP OLEDs at 500 cd m^{-2}. The device structures are as follows: ITO/HAT-CN (10 nm)/NPB (60 nm)/TCTA (5 nm)/ emitting layer (11 nm)/TPBi (30nm)/LiF (1nm)/Al (100nm). NPB is *N*,*N*′-diphenyl-*N*,*N*′-bis(1-napthyl)-1,1′-biphenyl-4,4′-diamine. TPBi is 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene.

Table S1. Electroluminescent data of the optimized devices based on the two AIE materials

EML	L_{max} [cd m^{-2}]	CE_{max} [cd A^{-1}]	EQE_{max} [%]	PE_{max} [lm W^{-1}]	Roll-off at 1000 cd m^{-2} [%]	EL peak [nm]	CIE (x,y)
Non-doped TPB-AC	3911	5.9	8.7	5.5	16.1	453	(0.14,0.07)
Non-doped TPB-TPA-CN	3043	6.3	7.7	6.5	18.2	453	(0.15,0.07)
TPB-AC: 30% DMPPP	12340	7.4	11.1	6.3	0.0	453	(0.15,0.07)
TPB-TPA-CN: 30% DMPPP	7579	8.6	11.8	8.2	0.0	452	(0.15,0.07)

L_{max}: the maximum luminance; CE_{max}: the maximum current efficiency; EQE_{max}: the maximum external quantum efficiency; PE_{max}: the maximum power efficiency; EL peak: the peak of the EL spectrum; CIE(x,y): the CIE coordinates at 5 V.

Table S2. Photophysical properties of the BD-doped TPB-PAPC films.

Compound	ϕ_{PL}[a] [%]	τ_{PF}[b] [ns]	τ_{DF}[c] [ns]	k_{PF}[d] [$10^8 s^{-1}$]	k_{DF}[e] [$10^8 s^{-1}$]	k_{ISC}[f] [$10^8 s^{-1}$]	k_{hRISC}[g] [$10^8 s^{-1}$]	k_r^S[h] [$10^8 s^{-1}$]	k_{nr}^S[i] [$10^7 s^{-1}$]	k_{IC}^{Tn}[j] [$10^8 s^{-1}$]	ϕ_{ISC}[k] [%]	ϕ_{hRISC}[l] [%]	ϕ_{hRISC}/ϕ_{ISC} [%]	k_T[n] [$10^3 s^{-1}$]	k_{TTA}[m] [10^{-16} cm^3 s^{-1}]	k_{STA}[O] [10^{-10} cm^3 s^{-1}]
TPB-AC	98	2.3	5.3	4.4	1.9	0.8	2.3	3.5	0.7	1.5	18	61	3.4	4.0	8.7	3.9
TPB-TPA-CN	93	2.1	8.9	4.8	1.1	0.9	1.4	3.5	2.7	0.9	20	62	3.1	1.4	7.5	7.5

[a] PL quantum yield; [b] the prompt fluorescent lifetime; [c] the delayed fluorescent lifetime; [d] Rate constants of prompt fluorescence, [e] decay fluorescence, [f] ISC, [g] hRISC; [h] singlet radiation; [i] singlet non-radiation, and [j] IC of highly-lying excitation triplet; [k] ISC efficiency; [l] hRISC efficiency; [n] triplet monomolecular recombination; [m] TTA up-conversion; [o] STA process.