

Supporting Information

Highly Efficient Deep Blue Fluorescent Organic Light-emitting Diodes Boosted by Thermally Activated Delayed Fluorescence Sensitization

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Materials and synthesis

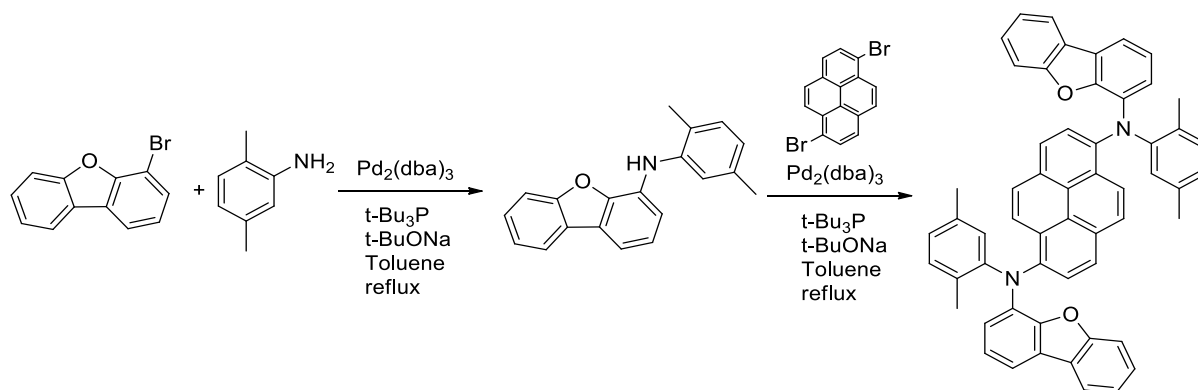
General

All reagents for synthesizing the blue fluorescence dopant materials were purchased from Sigma–Aldrich, TCI (SEJINCI) and used without additional purification. 1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile (HATCN), was purchased from EM Index. 1,1-bis[(di-4-tolylamino) phenyl] cyclo-hexane (TAPC), and 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) were purchased from Jilin OLED Material Tech Co., Ltd. The other materials, 3,5-di(9H-carbazol-9-yl)-N,N-diphenylaniline (DCDPA), bis[2-(diphenylphosphino) phenyl] ether oxide (DPEPO), 2,8-bis(diphenylphosphine oxide) dibenzofuran (DBFPO), diphenyl-4-triphenylsilylphenyl-phosphine oxide (TSPO1), 10,10'-(sulfonylbis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine) (DMAC-DPS), and 2,7-bis(9,9-dimethylacridin-10(9H)-yl)-9,9-dimethyl-9H-thioxanthene 10,10-dioxide (DMAC-DMT) were synthesized by using the previously reported methods.¹⁻⁶ Fabricated OLED device structure was HATCN / TAPC / DCDPA / EML / TSPO1 / TPBi / LiF / Al. HATCN and TAPC was used for hole transport layer (HTL). DCDPA and TSPO1 were used for exciton blocking layer (EBL). DPEPO and DBFPO were used for wide bandgap host of EML. DMAC-DPS and DMAC-DMT were used for TADF dopant and TSH. TPBi was used for electron transport layer (ETL).

Synthesis of N,N'-Bis-dibenzofuran-4-yl-N,N'-bis-(2,5-dimethyl-phenyl)-pyrene-1,6-diamine (BPPyA)

To a mixture of 4-bromodibenzofuran (12.00 g, 48.57 mmol), 2,5-dimethylaniline (5.89 g, 48.57 mmol), tri-tert-butylphosphine (50% solution in toluene, 1.18 g, 2.91 mmol), sodium tert-

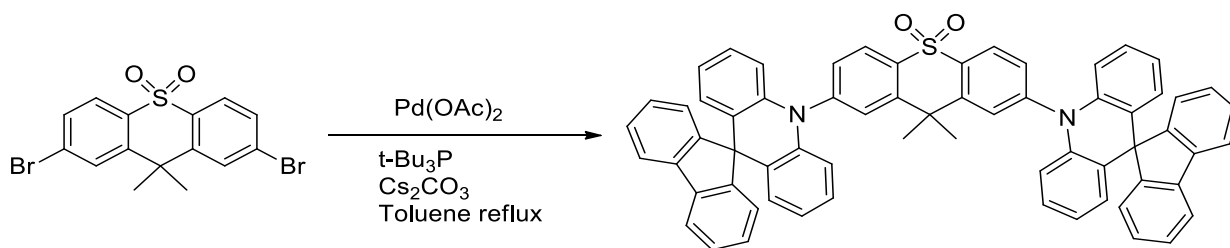
butoxide (14.00 g, 145.70 mmol) in toluene (400 mL) was added tris(dibenzylideneacetone)dipalladium(0) (1.33 g, 1.46 mmol). The mixture was stirred at 110 °C for 12 h under nitrogen. The reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography to afford N-(2,5-dimethylphenyl)dibenzo[b,d]furan-4-amine (10.47 g, 75%). To a mixture of N-(2,5-dimethylphenyl)dibenzofuran-4-amine (10.40 g, 36.18 mmol), 1,6-dibromopyrene (5.21 g, 14.47 mmol), tri-tert-butylphosphine (50% solution in toluene, 0.88 g, 2.17 mmol), and sodium tert-butoxide (10.43 g, 108.54 mmol) in toluene (300 mL) was added tris(dibenzylideneacetone)dipalladium(0) (0.99 g, 1.09 mmol). The mixture was stirred at 110 °C for 12 h under nitrogen. The reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography to yield the desired product as a greenish yellow solid (5.03 g, 45%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.02 (m, 2H), 7.93 (m, 4H), 7.77 (m, 2H), 7.62 (m, 4H), 7.05-7.40 (m, 10H), 6.92 (d, J=5.6 Hz, 2H), 6.65-6.96 (m, 4H), 2.15 (s, 6H), 2.06 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 156.0, 149.0, 131.4, 128.5, 127.1, 126.8, 126.1, 125.8, 125.6, 125.2, 124.5, 123.4, 122.5, 121.4, 120.5, 114.6, 112.1, 21.1, 18.6; HRMS (FAB) m/z: [M+H]⁺ calcd for C₅₆H₄₁N₂O₂, 773.3123, found: 773.3161.



Scheme 1. Synthesis of N,N'-Bis-dibenzofuran-4-yl-N,N'-bis-(2,5-dimethyl-phenyl)-pyrene-1,6-diamine (BPPyA)

Synthesis of 9,9-dimethyl-2,7-di(10H-spiro[acridine-9,9'-fluorene]-10-yl)-9H-thioxanthene 10,10-dioxide (SPAC-DMT)

To a mixture of 2,7-dibromo-9,9-dimethyl-9H-thioxanthene 10,10-dioxide (0.86 g, 2.0 mmol), 10H-spiro[acridine-9,9'-fluorene] (1.50 g, 4.53 mmol), tri-*t*-butyl phosphine (50% solution in toluene, 82 mg, 0.21 mmol), and Cs₂CO₃ (2.00 g, 6.18 mmol) in toluene (20 mL) was added palladium diacetate (23 mg, 0.10 mmol). The reaction mixture was refluxed for 5h under nitrogen. The resulting mixture was cooled to room temperature, diluted with CH₂Cl₂ and then filtered through celite/SiO₂. The crude product was recrystallized from toluene to afford the title compound (1.8 g, 95%) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ [ppm] 8.68 (d, *J*=8.4 Hz, 2H), 7.98 (d, *J*=1.2 Hz, 2H), 7.79-7.86 (m, 6H), 7.41-7.45 (m, 8H), 7.31 (d, *J*=7.2 Hz, 4H), 6.99 (td, *J*=8.4, 1.2 Hz, 4H), 6.65 (t, *J*=7.2 Hz, 4H), 6.47 (d, *J*=8.0, 1.2 Hz, 4H), 6.34 (d, *J*=8.4 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 156.5, 149.2, 146.0, 140.6, 139.3, 136.6, 131.1, 129.4, 128.5, 128.3, 127.8, 127.7, 127.5, 125.7, 125.0, 121.3, 120.0, 114.3, 56.7, 40.1, 31.1; HRMS (FAB) *m/z*: [M+H]⁺ calcd for C₆₅H₄₅N₂O₂S 917.3157, found: 917.3202.



Scheme 2. Synthesis of 9,9-dimethyl-2,7-di(10H-spiro[acridine-9,9'-fluoren]-10-yl)-9H-thioxanthene 10,10-dioxide (SPAC-DMT)

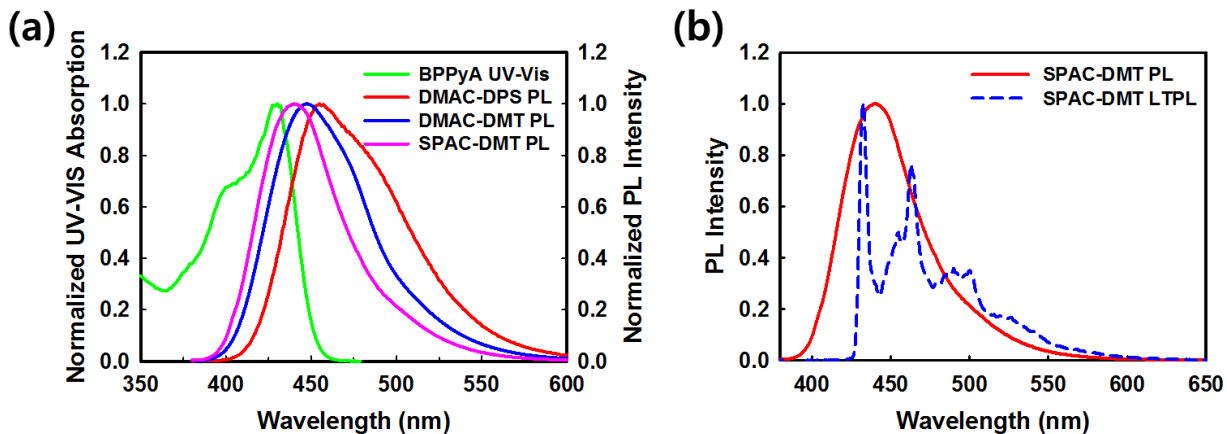


Figure S1. (a) Absorption spectrum of BPPyA and PL spectrum of TADF materials in toluene. (b) Low temperature (77 K) PL spectrum of SPAC-DMT.

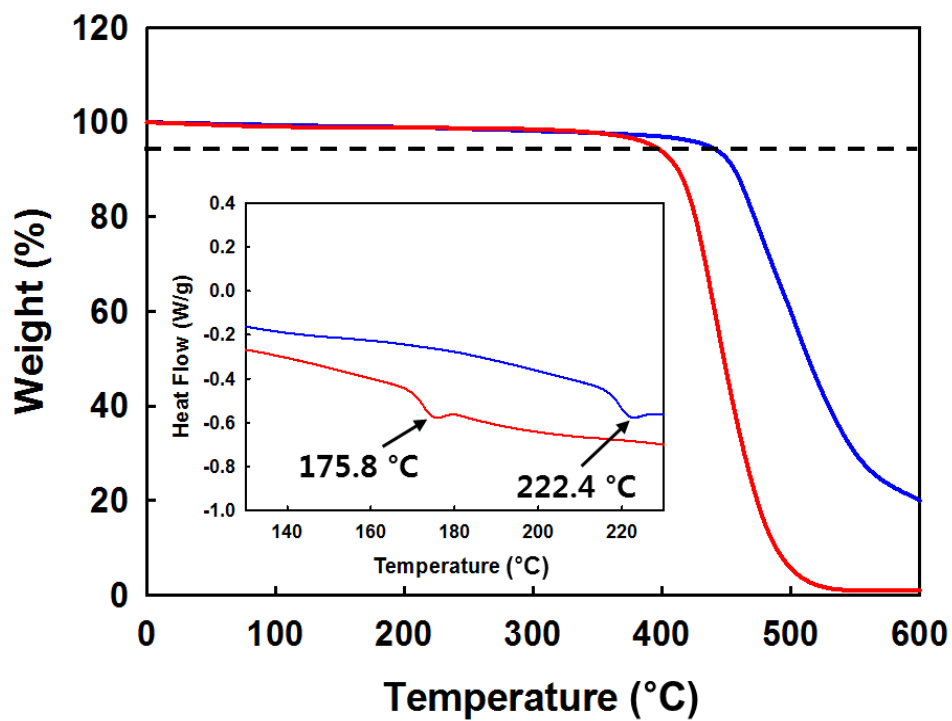


Figure S2. TGA and DSC data of SPAC-DMT (blue line) and BPPyA (red line).

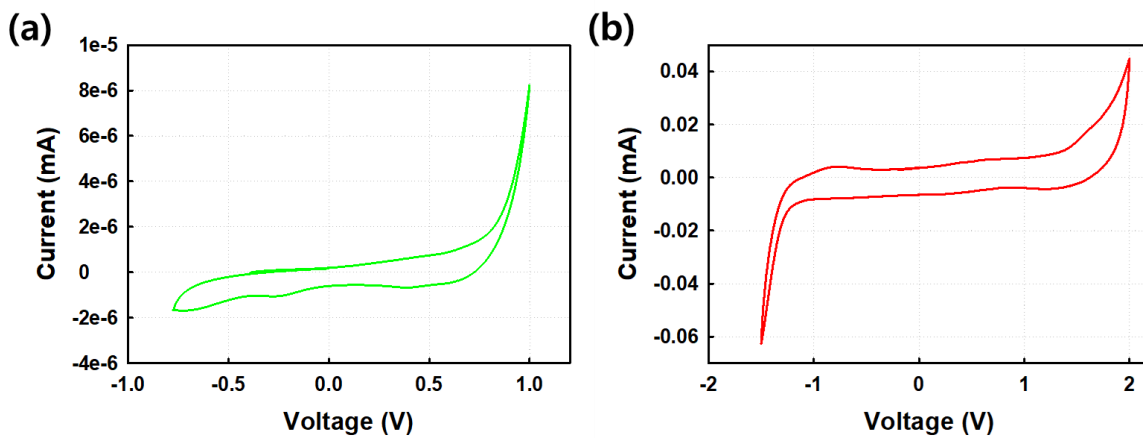


Figure S3. Cyclicvoltammogram of (a) BPPyA and (b) SPAC-DMT

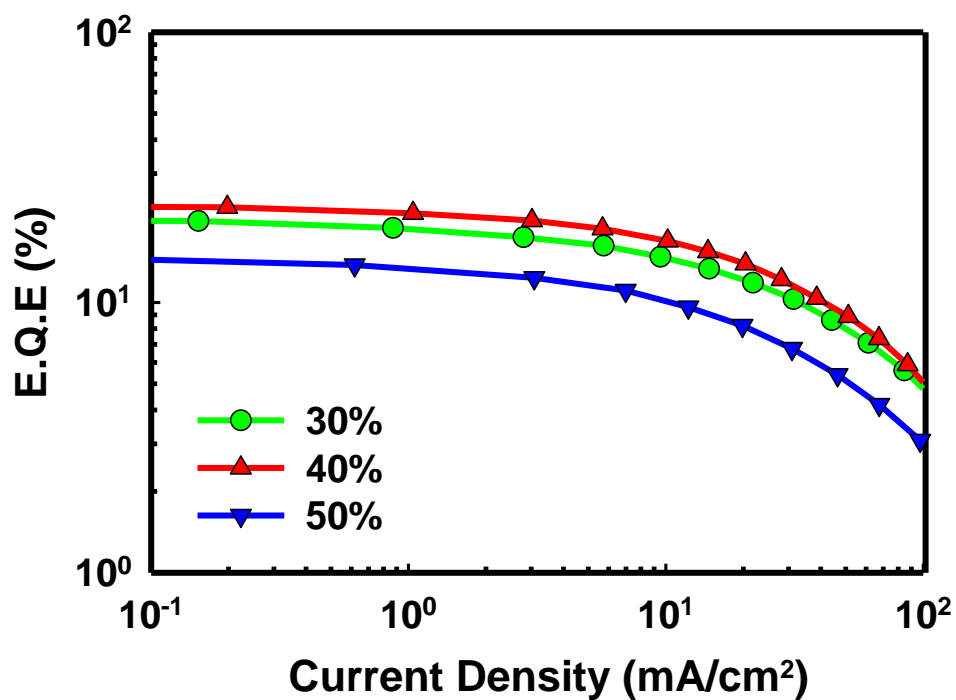


Figure S4. EQE verses current density graph of DMAC-DMT devices with various doping concentration.

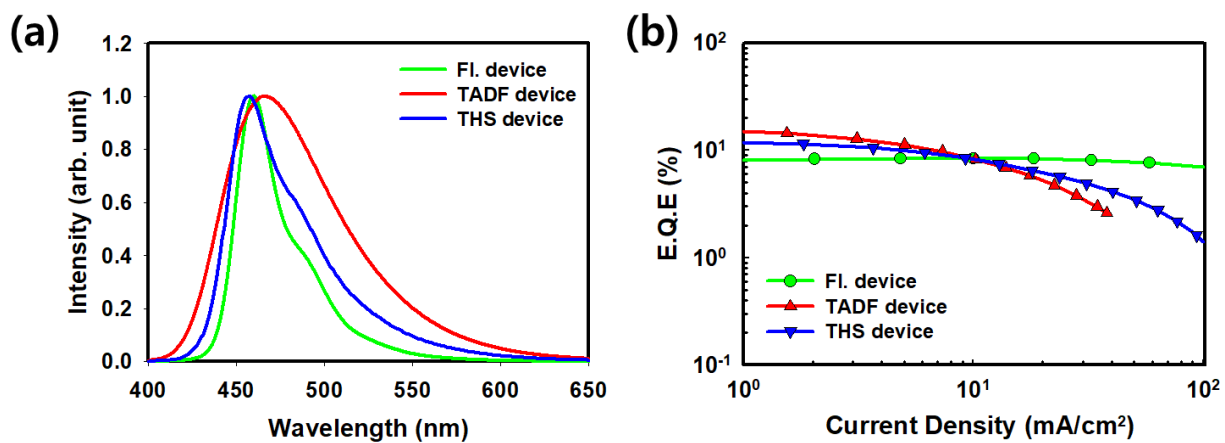


Figure S5. Device performance of fluorescence device (Fl. device) and TADF and THS device of DMAC-DPS. (a) EL spectra (b) EQE verses current density graph.

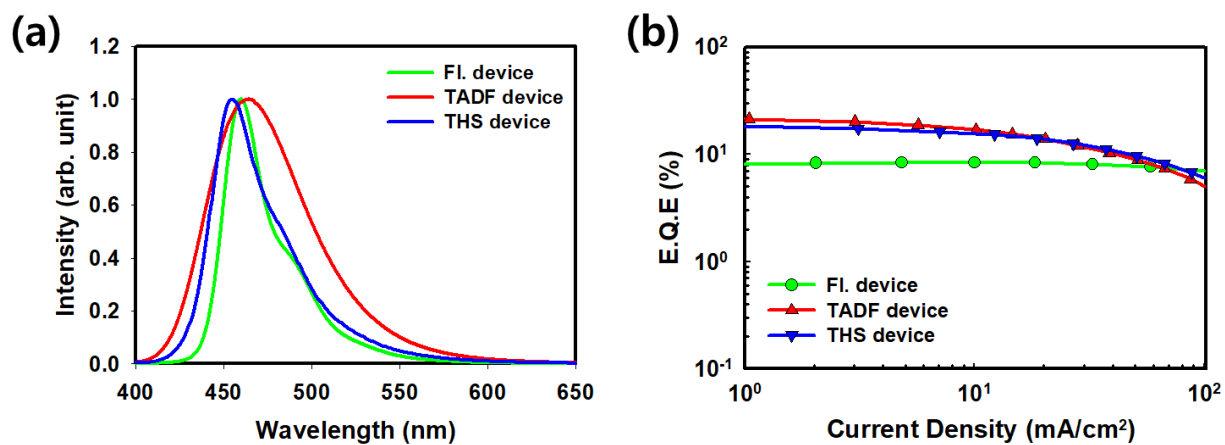


Figure S6. Device performance of fluorescence device (Fl. device) and TADF and THS device of DMAC-DMT. (a) EL spectra (b) EQE verses current density graph.

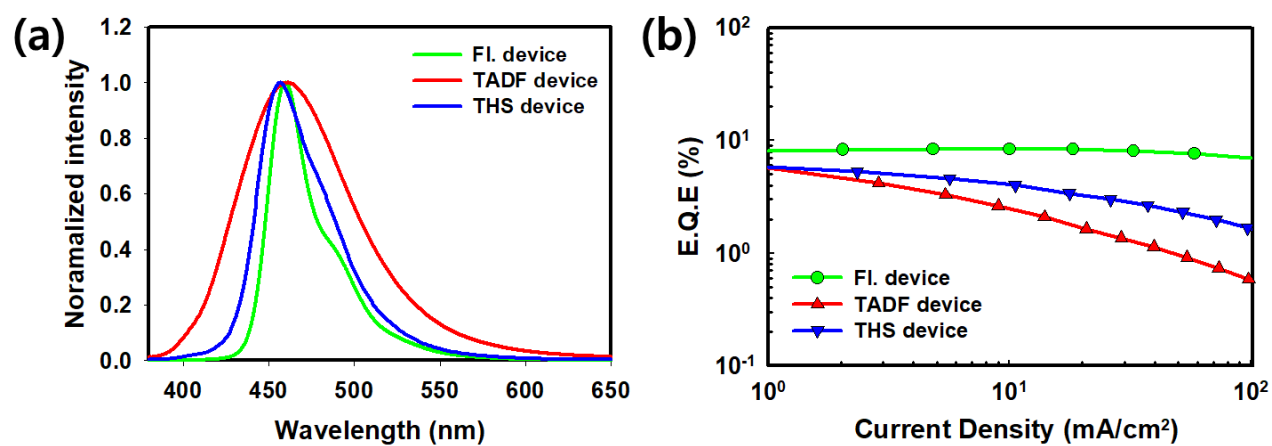


Figure S7. Device performance of fluorescence device (Fl. device) and TADF and THS device of SPAC-DMT. (a) EL spectra (b) EQE verses current density graph.

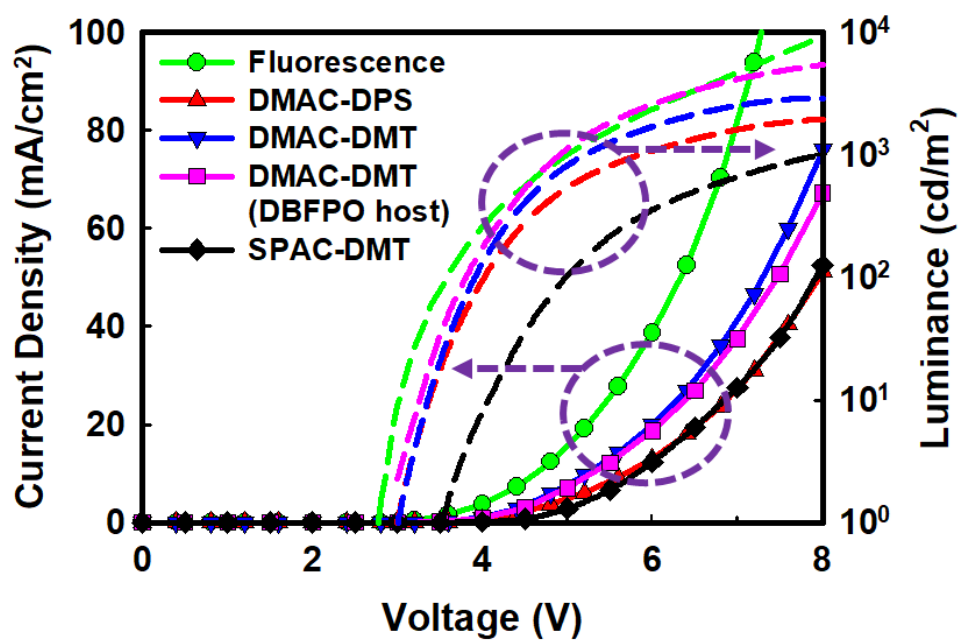


Figure S8. Current density-voltage-luminance characteristic for the device ITO / HATCN / TAPC / DCDPA / DPEPO: 40% TADF: 0.7% BPPyA / TSPO1 / TPBi / LiF/ Al. Only fluorescence device have a different structure of ITO / HATCN / TAPC / MADN : 5% BPPyA / TPBi / LiF / Al.

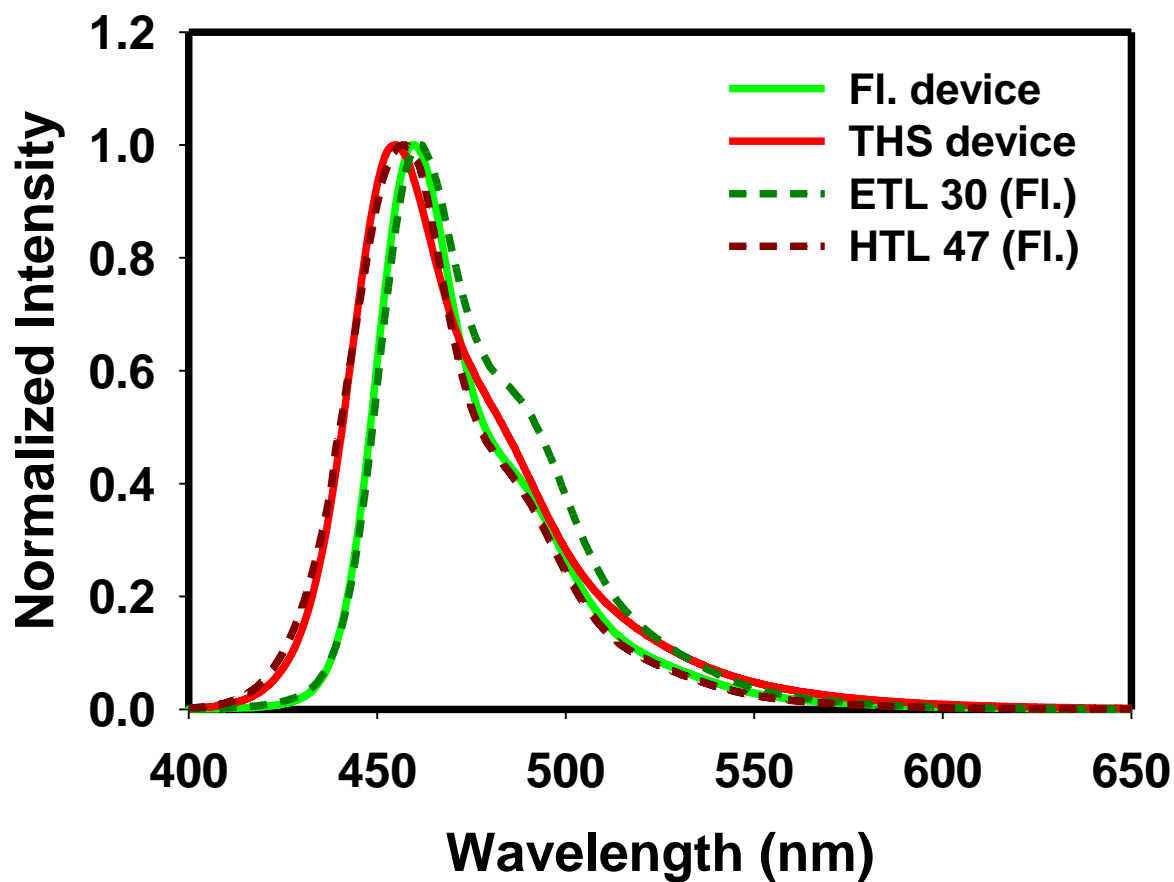


Figure S9. The EL spectrum of Device I (green line) and Device III (red line) of DMAC-DMT, and the EL spectrum of modified Device I (dot lines).

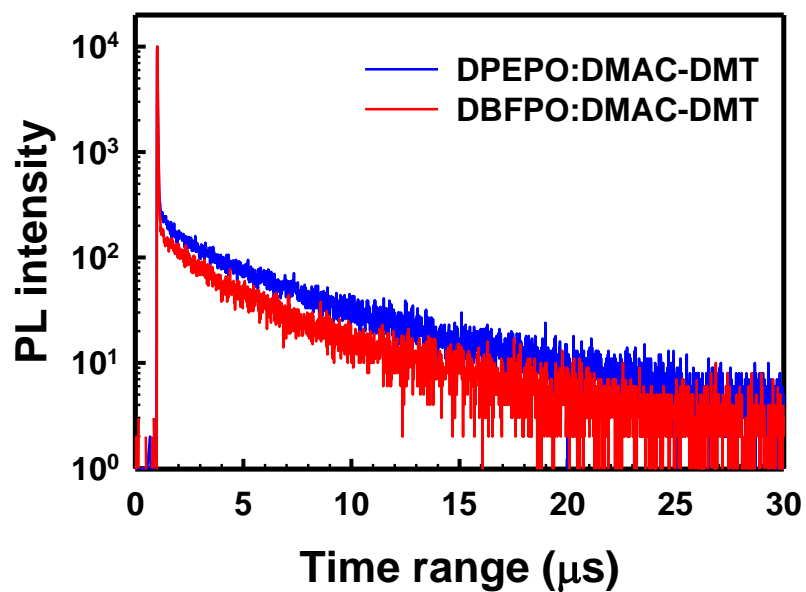


Figure S10. Delayed exciton decay lifetime of DMAC-DMT with different hosts in deposited film. The doping concentration was 40% and the thickness was 50 nm.

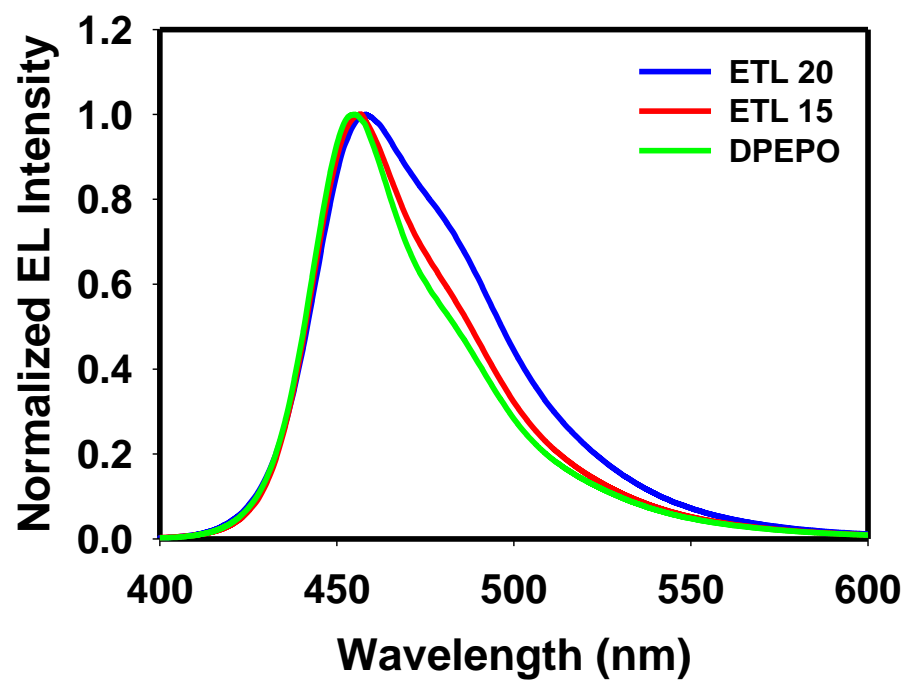


Figure S11. The EL spectrum of DBFPO: DMAC-DMT: BPPyA device (Device III). Almost same spectrum with DPEPO host device can be achieved by reducing ETL thickness.

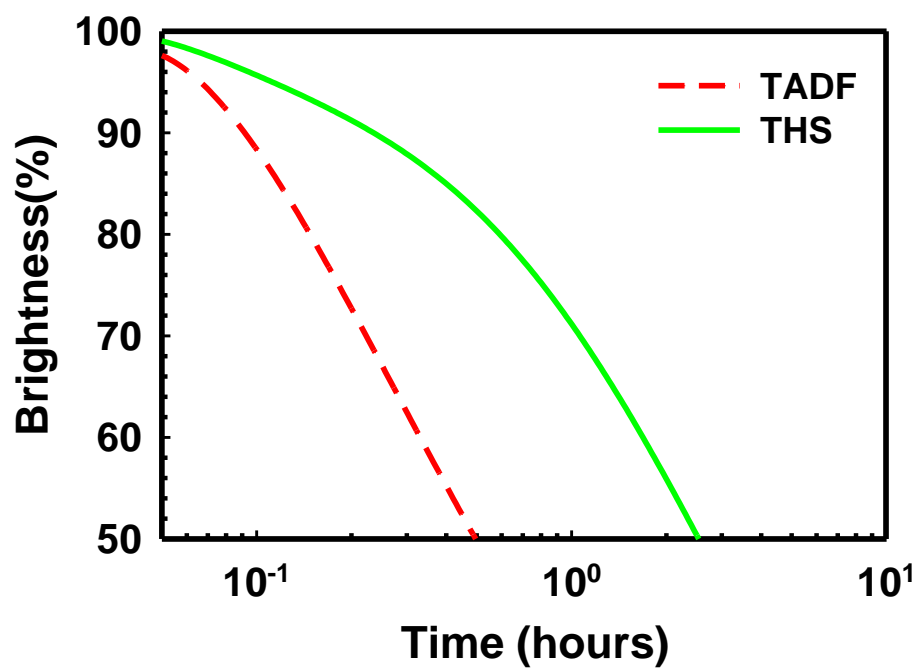


Figure S12. The device operating lifetime of TADF and THS devices. Phosphine oxide series materials have low stability, which results in short device lifetime. In spite of these condition, THS device shows long operating lifetime than TADF device.

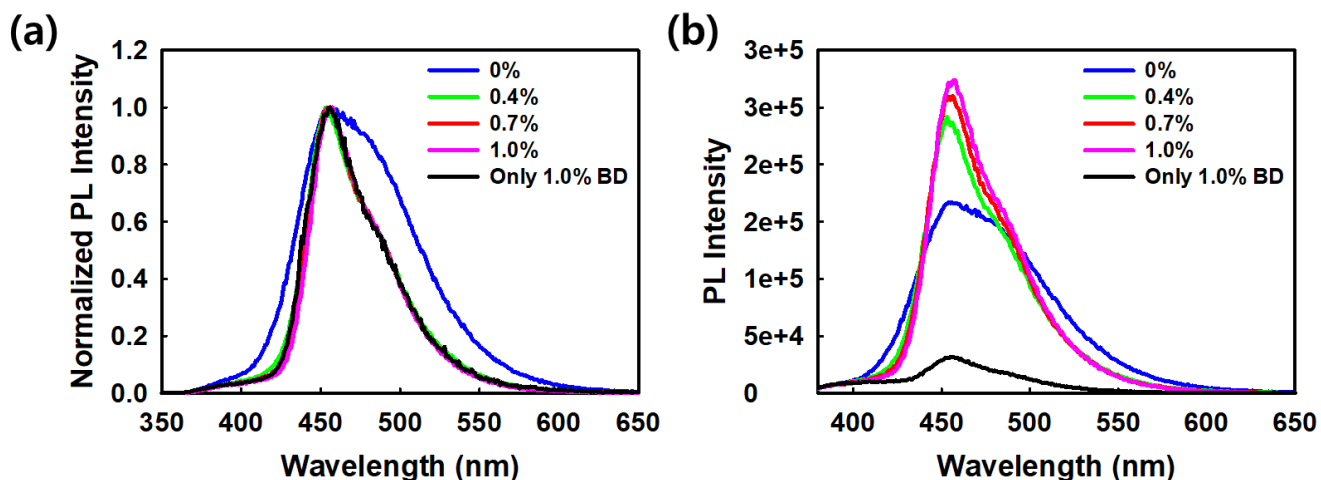


Figure S13. (a) The normalized spectra of DMAC-DMT film and only 1.0% BD means that there is no TADF material in the film. The spectra are all the same under fluorescence doped conditions. (b) Non-normalized spectra of DMAC-DMT film. Even at small doping of 0.4%, the spectral change is large and it shows a much larger intensity in the thin film doped with TADF material at the same 1.0% condition.

Table S1. Calculated PLQY and RISC rate from time resolved spectrum

Materials	Prompt (ns)	Delayed (μ s)	Φ_{PF}	Φ_{DF}	k_{PF} ($\times 10^7 \text{ s}^{-1}$)	k_{DF} ($\times 10^5 \text{ s}^{-1}$)	k_{ISC} ($\times 10^7 \text{ s}^{-1}$)	k_{RISC} ($\times 10^6 \text{ s}^{-1}$)
DMAC-DMT	24.5	2.49	0.22	0.68	4.1	4.0	3.3	1.8

Reference

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