

Supporting Information for

**Highly efficient organic light emitting diodes based on a D-A-D type
dibenzothiophene derivative exhibiting thermally activated delayed
fluorescence with small ΔE_{ST}**

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S-1 General Methods

General information

All the reagents and solvents used for the syntheses were purchased from Aldrich and Acros and used as received. The ^1H NMR spectra were recorded on Bruker AVANCE 500 spectrometer at 500 MHz at 298 K, using DMSO- D_6 as solvent and tetramethylsilane (TMS) as internal standard. The elemental analysis were performed by a Flash EA 1112, CHNS-O elemental analysis instrument. The MALDI-TOF-MS mass spectra were measured using an AXIMA-CFRTM plus instrument. Thermal gravimetric analysis (TGA) was measured on a Perkin-Elmer thermal analysis system from 30 °C to 900 °C at a heating rate of 10 K/min under nitrogen flow rate of 80 mL/min. Differential scanning calorimetry (DSC) was performed on a NETZSCH (DSC-204) unit from 30 °C to 400 °C at a heating rate of 10K/min under nitrogen atmosphere. The electrochemical properties (oxidation and reduction potentials) were carried out via cyclic voltammetry (CV) measurements by using a standard one-compartment, three-electrode electrochemical cell given by a BAS 100B/W electrochemical analyzer. Tetrabutylammoniumhexafluorophosphate (TBAPF6) in anhydrous dimethyl formamide (DMF) or anhydrous dichloromethane (0.1 M) were used as the electrolyte for negative or positive scan. UV-vis and fluorescence spectra were recorded on a Shimadzu UV-3100 spectrophotometer using 1 cm path length quartz cells. The fluorescence lifetime and PLQY (Φ_F) of the prepared films were measured by FLS920 spectrometer. The Φ_F of different solutions were determined by using 0.1 M quinine sulfate as a reference ($\Phi_F = 0.546$) and were calculated by using the following formula:

$$Q_x = Q_r \left(\frac{A_r(\lambda_r)}{A_x(\lambda_x)} \right) \left(\frac{I(\lambda_r)}{I(\lambda_x)} \right) \left(\frac{n_x^2}{n_r^2} \right) \left(\frac{D_x}{D_r} \right)$$

Where Q is the PLQY, A is the value of absorbance, I is the intensity of excitation source, n is the refractive index of solvent, D is the area of emission spectra, λ is the corresponding wavelength. The subscript r stands for the reference while x stands for test subject. The excitation wavelength was 340 nm.

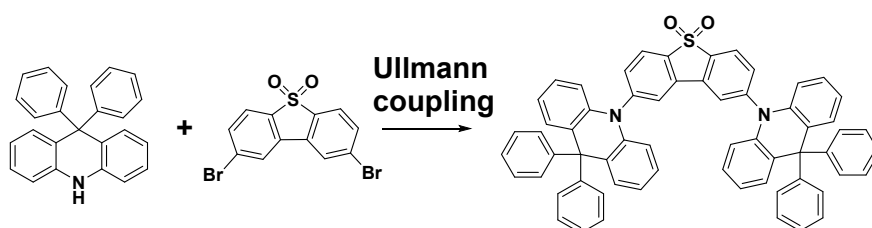
Device fabrication

ITO glass was used as the substrate and the sheet resistance was 20 Ω square $^{-1}$. The ITO glass substrates were cleaned with isopropyl alcohol, acetone, toluene and deionized water, dried in an oven at 120 °C, treated with UV-zone for 20 min, and finally transferred to a vacuum deposition system with a base pressure lower than 5×10^{-6} mbar for organic and metal deposition. The deposition rate of all organic layers was 1.0 \AA s $^{-1}$. The cathode LiF (1 nm) was deposited at a rate of 0.1 \AA s $^{-1}$ and then the capping Al metal layer (100 nm) was deposited at a rate of 4.0 \AA s $^{-1}$. The electroluminescent (EL) characteristics were measured using a Keithley 2400 programmable electrometer and a PR-650 Spectroscan spectrometer under ambient condition at room temperature.

Computational Details

The ground-state (S_0) geometries were optimized at the B3LYP/6-31G(d, p) level. The HOMO/LUMO distributions are calculated on the basis of optimized S_0 state. The higher absorption energy levels of both singlet and triplet states were calculated using TD-M062X/6-31G(d, p) method on the basis of the optimized configuration of S_0 . For the purpose of investigating the properties of excited-states, natural transition orbitals (NTOs) of absorption were evaluated for the five lowest excited-states, involving both singlet and triplet states under TD-M062X/6-31G(d, p) level. This approach provides the most compact representation of the electronic transitions in terms of an expansion into single particle orbitals by diagonalizing the transition density matrix associated with each excitation.

S-2 Synthesis of DPAC-DBTDO



Scheme S1. Synthesis route of DPAC-DBTDO.

Synthesis of DPAC-DBTDO: A solution of 9,9-diphenyl-9,10-dihydroacridine (DPAC) (3.50 g, 10.5 mmol), 2,8-dibromodibenzo[b,d]thiophene 5,5-dioxide (1.87 g, 5 mmol), $\text{Pd}_2(\text{dba})_3$ (115.5 mg, 0.3 mmol), tri-tert-butylphosphine tetrafluoroborate (232 mg, 0.5 mmol) and sodium tert-butoxide (2.54 g, 15 mmol) were dissolved in toluene (30 mL). After degassed, the mixture was refluxed at 110 °C for 24 h under nitrogen. After cooling to room temperature, 50 mL water was added and the mixture was extracted with CH_2Cl_2 . The combined organic layer was dried over anhydrous magnesium sulphate. Then the mixture was concentrated. After recrystallization in ethanol, the light yellow powder was gained (3.69 g). Yield: 84%. ^1H NMR (500 MHz, DMSO, ppm, δ) 8.26 (d, $J = 8.1$ Hz, 2H), 8.03 (s, 2H), 7.36 – 7.18 (m, 14H), 7.13 (dd, $J = 11.3, 4.3$ Hz, 4H), 7.02 – 6.89 (m, 12H), 6.81 (dd, $J = 7.80, 1.4$ Hz, 4H), 6.49 (d, $J = 8.3$ Hz, 4H). MS (MALDI-TOF) m/z : $[\text{M}^+]$ calcd for $\text{C}_{62}\text{H}_{42}\text{N}_2\text{O}_2\text{S}$, 878.30; found, 879.30. Elem. Anal. Calcd for $\text{C}_{62}\text{H}_{42}\text{N}_2\text{O}_2\text{S}$: C, 84.71; H, 4.82; N, 3.19. Found: C, 84.38; H, 4.98; N, 3.22.

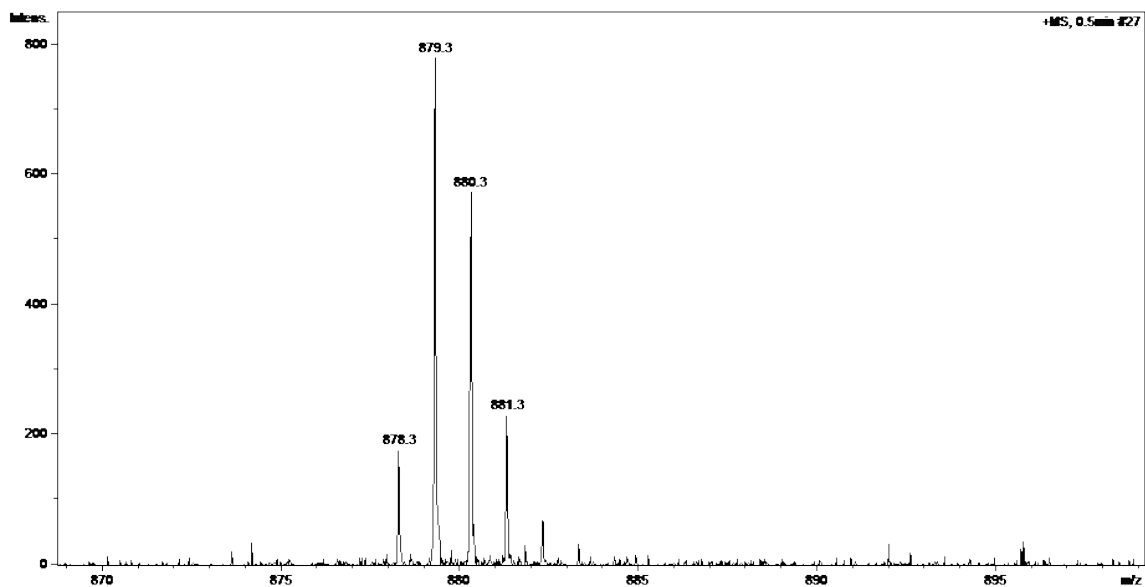


Figure S1. MALDI-TOF spectrum of DPAC-DBTDO.

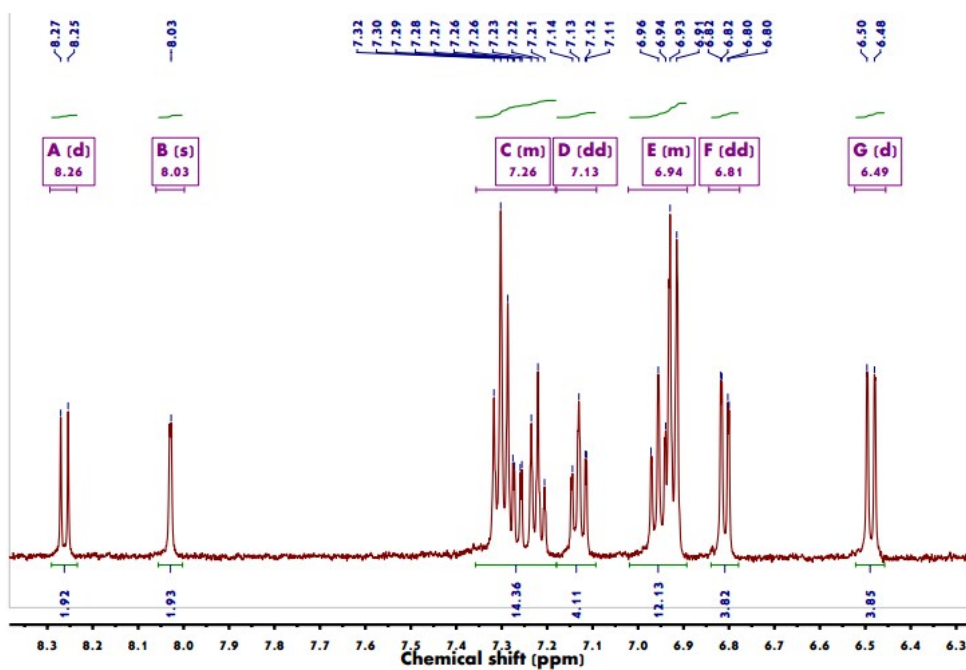


Figure S2. ¹H NMR spectrum of DPAC-DBTDO in DMSO.

S-3 Thermal and Electrochemical Property

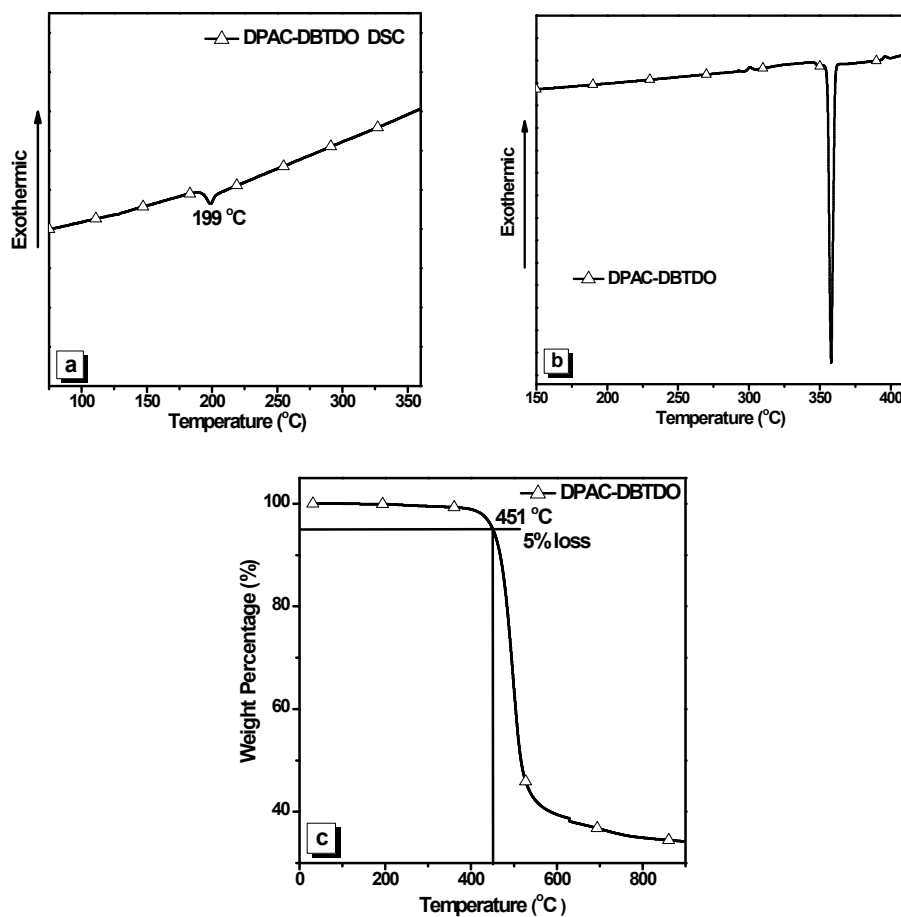


Figure S3. (a) DSC test: glass-transition temperature (T_g) of 199 °C; (b) melt point of 358 °C of DPAC-DBTDO; (c) TGA test: decomposition temperature (T_d) of 451 °C of DPAC-DBTDO.

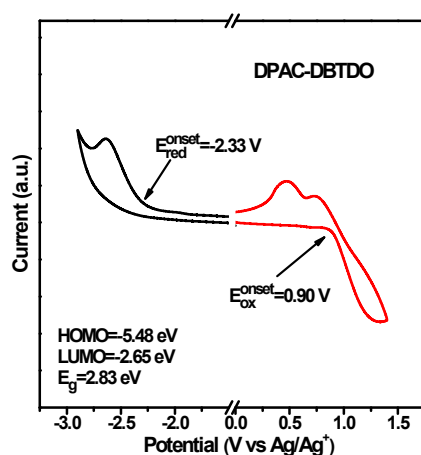


Figure S4. Cyclic voltammetry grams of DPAC-DBTDO. The potentials are calibrated against Fc^+/Fc internal standard.

S-4 Single Crystal Data

The single crystal of DPAC-DBTDO was prepared by vapor deposition method. The diffraction experiments were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a MO-Koandcontrol Software using the RAPID AUTO at 293 (± 2) °C. The crystal structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS programs. All angles and distances in crystals were measured using Mecury 1.4.1 Software.

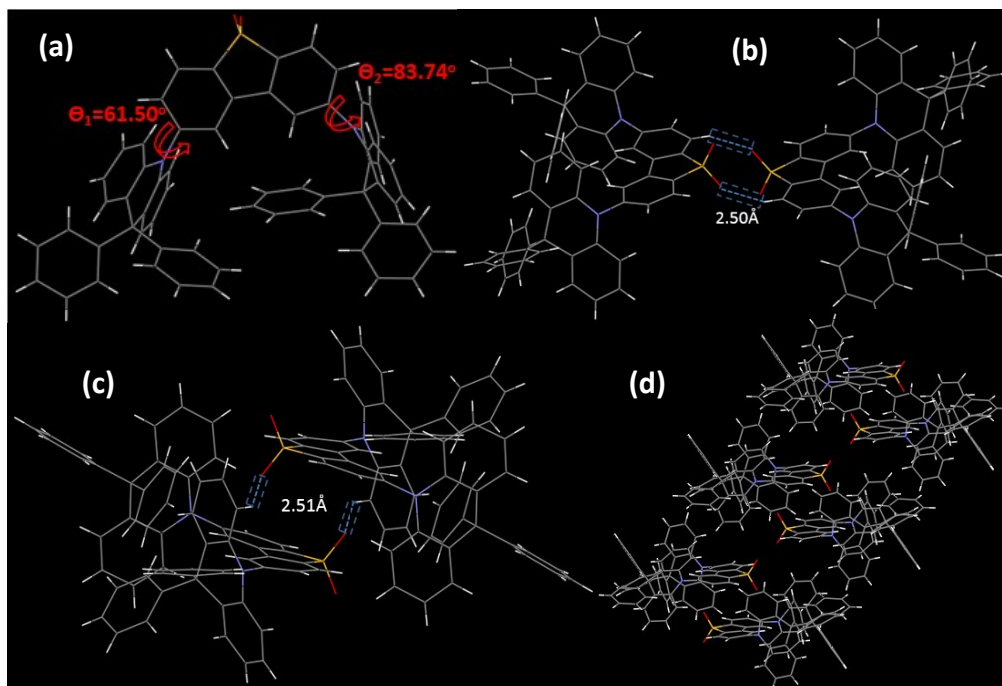


Figure S5. Single crystal structure of DPAC-DBTDO: (a) molecular structure; (b) & (c) Two existent hydrogen bonds; (d) packing structure.

Table S1. Crystallographic Data.

Empirical formula	C ₆₂ H ₄₂ N ₂ O ₂ S
Formula weight	879.04
Crystal size	0.13*0.12*0.10 mm
Temperature	293(2) K
Crystal system	Triclinic
Space group	P -1
a, Å	9.907(2)
b, Å	14.375(3)
c, Å	16.621(3)
α , deg	97.46(3)
β , deg	91.84(3)
γ , deg	105.68(3)
Z	2
Calculated density, g cm ⁻³	1.295

S-5 Theoretical Calculation

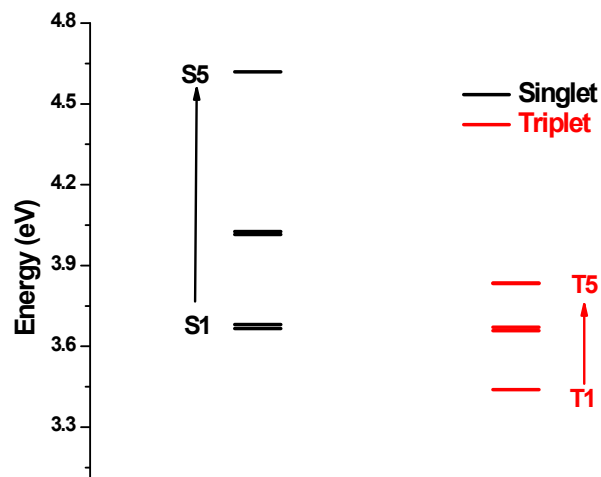
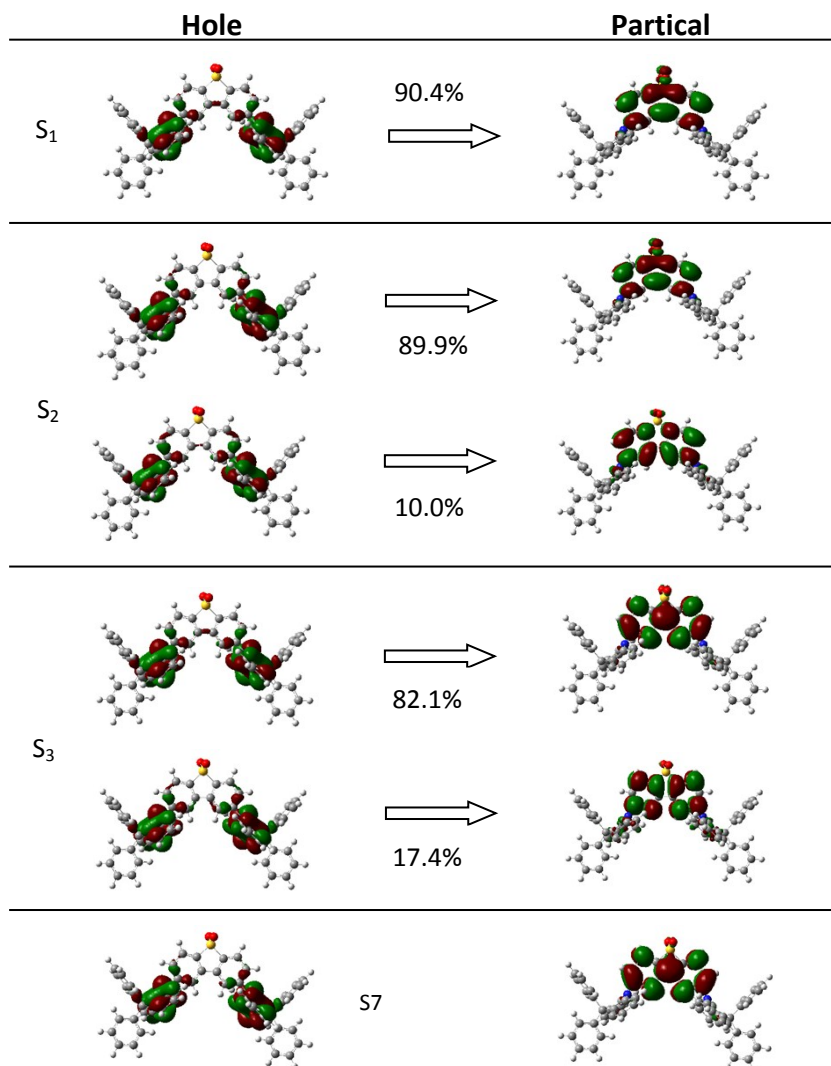


Figure S6. TD-DFT calculation of energy levels of DPAC-DBTDO.

Table S2. Calculated energy of singlet and triplet of DPAC-DBTDO.

	1	2	3	4	5
Singlet (eV)	3.6665	3.6810	4.0156	4.0261	4.6190
Triplet (eV)	3.4394	3.6580	3.6708	3.8334	3.8351



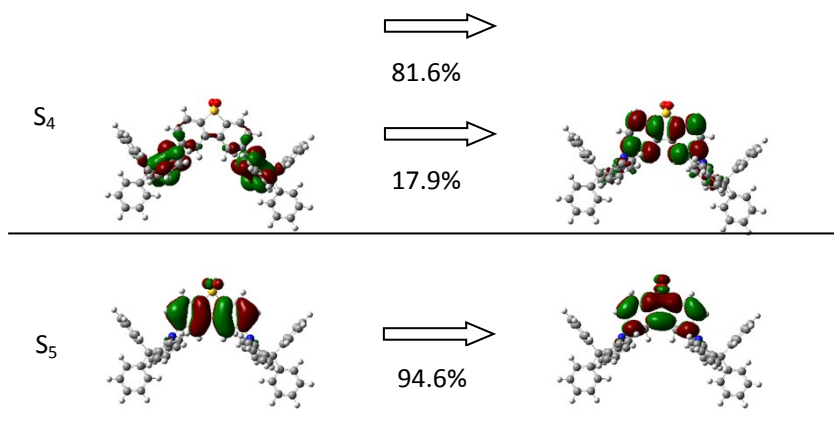
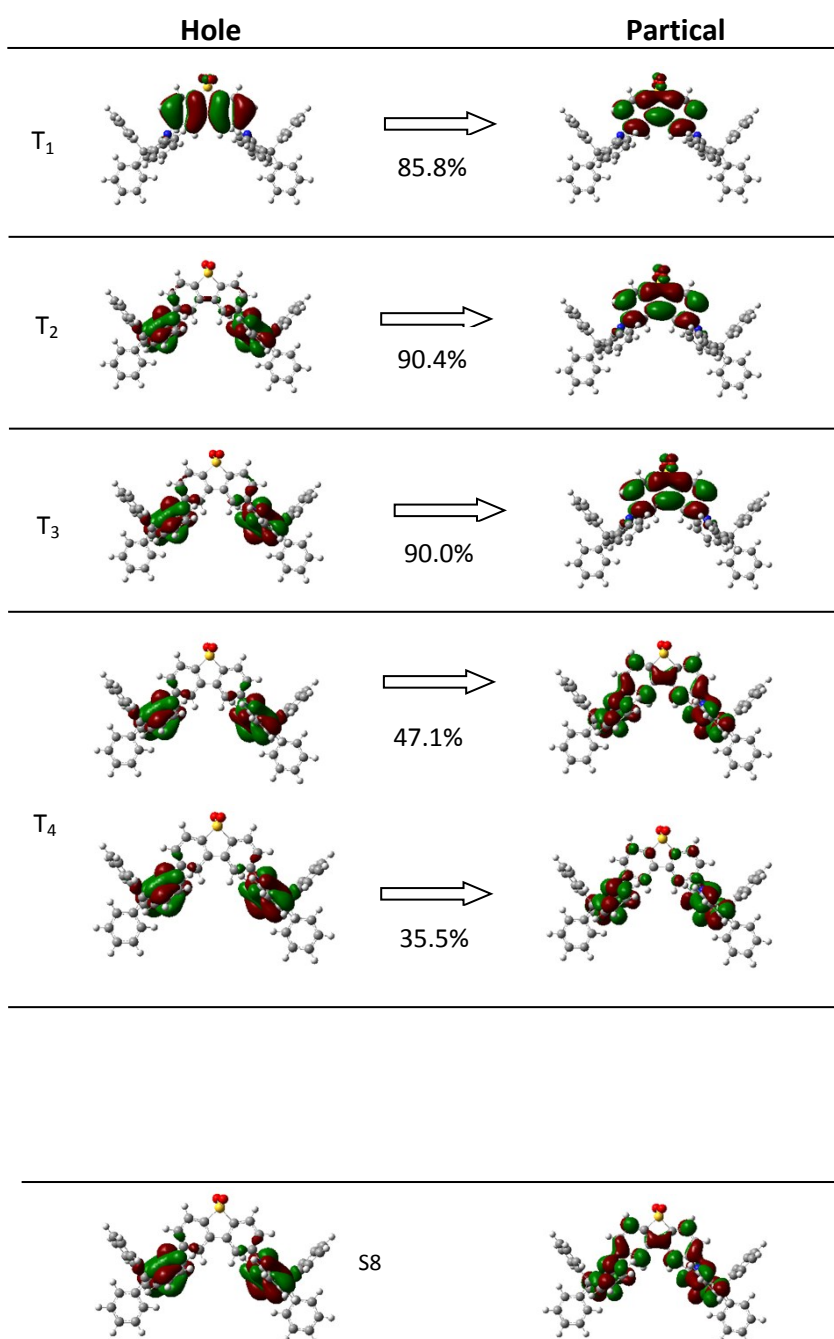


Figure S7. The S_1 to S_5 natural transition orbitals (NTO) of DPAC-DBTDO.



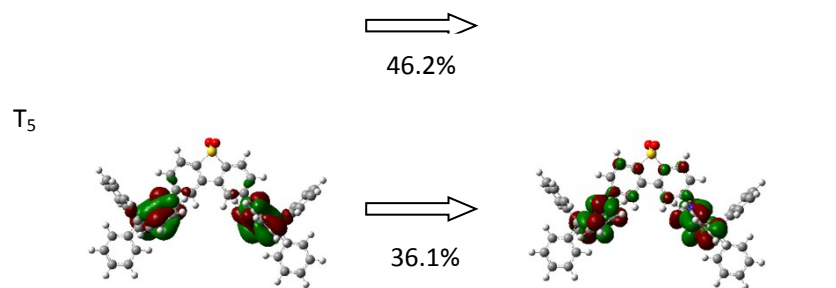


Figure S8. The T_1 to T_5 natural transition orbitals (NTO) of DPAC-DBTDO.

Calculated Geometry Data for DPAC-DBTDO (S_0 optimization: unit Å)

C	-1.68400200	2.46656700	1.53951000
C	-1.97475400	2.90250500	2.83798900
C	-1.49279000	2.19874000	3.94505300
C	-0.72467100	1.06876300	3.71342400
C	-0.41599600	0.61139100	2.42455500
C	-0.90470600	1.32095000	1.32676300
H	-2.58024800	3.79333900	2.96500900
H	-1.71389200	2.52784800	4.95496500
H	-0.69576600	1.00361700	0.31033300
C	0.72467100	-1.06876300	3.71342400
C	1.49279000	-2.19874000	3.94505300
C	1.97475400	-2.90250500	2.83798900
C	1.68400200	-2.46656700	1.53951000
C	0.90470600	-1.32095000	1.32676300
C	0.41599600	-0.61139100	2.42455500
H	1.71389200	-2.52784800	4.95496500
H	2.58024800	-3.79333900	2.96500900
H	0.69576600	-1.00361700	0.31033300
O	1.05063800	0.71102700	5.71111000
O	-1.05063800	-0.71102700	5.71111000
N	-2.20490400	3.21218900	0.43324200
C	-3.41817300	2.80997000	-0.16819400
C	-1.38543000	4.15332000	-0.22842100
C	-3.99049200	1.55850700	0.11293900
C	-4.05181000	3.68349900	-1.07655400
C	-1.97934400	5.05171400	-1.13974300
C	0.00000000	4.20164500	-0.00265600
C	-5.16395100	1.16117400	-0.52141100
H	-3.51492400	0.89256400	0.82224800
C	-5.21595900	3.24707600	-1.71733200
C	-3.51486100	5.11862200	-1.21522000

C	-1.15073100	5.93292500	-1.84202100
H	0.45676200	3.52797100	0.71164500
C	0.79637800	5.10765900	-0.69727000
C	-5.77605200	1.99765700	-1.45259900
H	-5.58926600	0.18889400	-0.29072800
H	-5.70415300	3.91194300	-2.42072400
C	-3.96114900	5.73668700	-2.56094600
C	-4.03710600	5.96281500	-0.00747800
C	0.22773800	5.96839000	-1.63380200
H	-1.60124800	6.62069400	-2.54850100
H	1.86576100	5.12753100	-0.50883100
H	-6.68685700	1.69213500	-1.95762300
C	-3.59124500	5.09877400	-3.75852800
C	-4.71425400	6.91173500	-2.64802800
C	-3.28313100	7.02415500	0.51466600
C	-5.29665100	5.71433300	0.55800800
H	0.84325800	6.67149500	-2.18581200
C	-3.96244800	5.61698400	-4.99579700
H	-3.00518300	4.18598500	-3.71416700
C	-5.08850600	7.43476100	-3.89075900
H	-5.01443500	7.42899900	-1.74464200
C	-3.76881100	7.80747400	1.56303800
H	-2.30386600	7.24233700	0.10452400
C	-5.78410600	6.49639200	1.60624900
H	-5.90448800	4.89953500	0.18183900
C	-4.71589200	6.79219300	-5.06803400
H	-3.66325600	5.10344600	-5.90513000
H	-5.67385500	8.34904700	-3.92954000
C	-5.02204400	7.54709800	2.11655900
H	-3.16021700	8.62095300	1.94803100
H	-6.76232400	6.27770000	2.02533300
H	-5.00675300	7.19862000	-6.03230300
H	-5.39885700	8.15311900	2.93535700
N	2.20490400	-3.21218900	0.43324200
C	3.41817300	-2.80997000	-0.16819400
C	1.38543000	-4.15332000	-0.22842100
C	3.99049200	-1.55850700	0.11293900
C	4.05181000	-3.68349900	-1.07655400
C	1.97934400	-5.05171400	-1.13974300
C	0.00000000	-4.20164500	-0.00265600
C	5.16395100	-1.16117400	-0.52141100
H	3.51492400	-0.89256400	0.82224800
C	5.21595900	-3.24707600	-1.71733200
C	3.51486100	-5.11862200	-1.21522000

C	1.15073100	-5.93292500	-1.84202100
H	-0.45676200	-3.52797100	0.71164500
C	-0.79637800	-5.10765900	-0.69727000
C	5.77605200	-1.99765700	-1.45259900
H	5.58926600	-0.18889400	-0.29072800
H	5.70415300	-3.91194300	-2.42072400
C	3.96114900	-5.73668700	-2.56094600
C	4.03710600	-5.96281500	-0.00747800
C	-0.22773800	-5.96839000	-1.63380200
H	1.60124800	-6.62069400	-2.54850100
H	-1.86576100	-5.12753100	-0.50883100
H	6.68685700	-1.69213500	-1.95762300
C	3.59124500	-5.09877400	-3.75852800
C	4.71425400	-6.91173500	-2.64802800
C	3.28313100	-7.02415500	0.51466600
C	5.29665100	-5.71433300	0.55800800
H	-0.84325800	-6.67149500	-2.18581200
C	3.96244800	-5.61698400	-4.99579700
H	3.00518300	-4.18598500	-3.71416700
C	5.08850600	-7.43476100	-3.89075900
H	5.01443500	-7.42899900	-1.74464200
C	3.76881100	-7.80747400	1.56303800
H	2.30386600	-7.24233700	0.10452400
C	5.78410600	-6.49639200	1.60624900
H	5.90448800	-4.89953500	0.18183900
C	4.71589200	-6.79219300	-5.06803400
H	3.66325600	-5.10344600	-5.90513000
H	5.67385500	-8.34904700	-3.92954000
C	5.02204400	-7.54709800	2.11655900
H	3.16021700	-8.62095300	1.94803100
H	6.76232400	-6.27770000	2.02533300
H	5.00675300	-7.19862000	-6.03230300
H	5.39885700	-8.15311900	2.93535700
S	0.00000000	0.00000000	4.96917300

S-6 Supplementary Photophysical Property

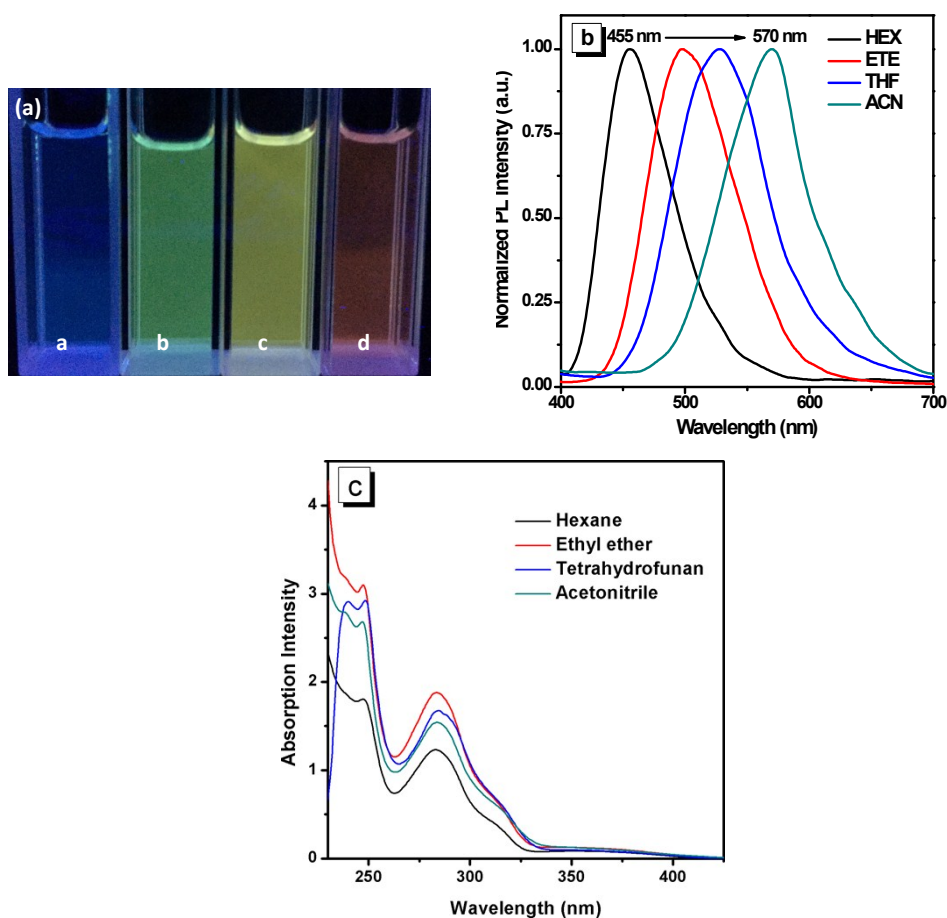


Figure S9. (a) Fluorescent images of DPAC-DBDTO in different solvents upon excitation with a 365 nm light source (from a to d are hexane (HEX), ethyl ether (ETE), tetrahydrofuran (THF) and acetonitrile (ACN), respectively); (b) Fluorescence spectra of DPAC-DBDTO in different solvents with the concentration of 0.01 mM; (c) Absorption spectra of DPAC-DBDTO in different solvents with the concentration of 0.01 mM.

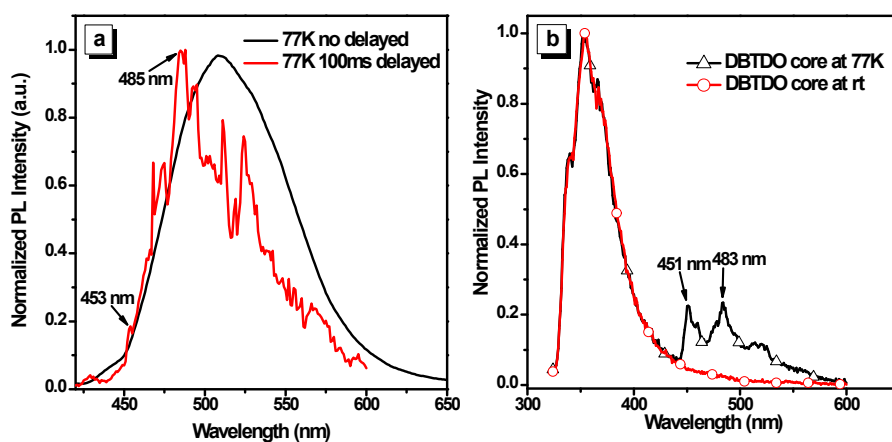


Figure S10. (a) Transient PL spectrum of DPAC-DBDTO in toluene at 77 K (b) Steady state spectrum of DBDTO core in toluene at room temperature and 77 K.

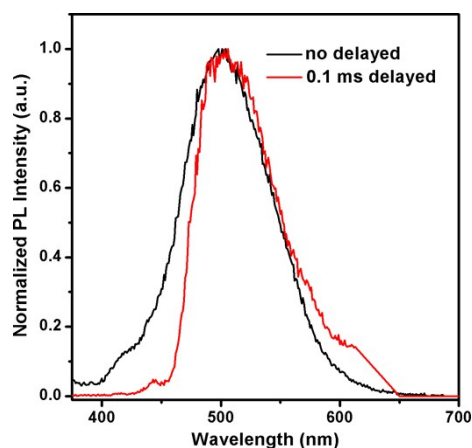


Figure S11. Transient PL spectrum of 15 wt% DPAC-DBTDO:DPEPO doped film at 300 K.

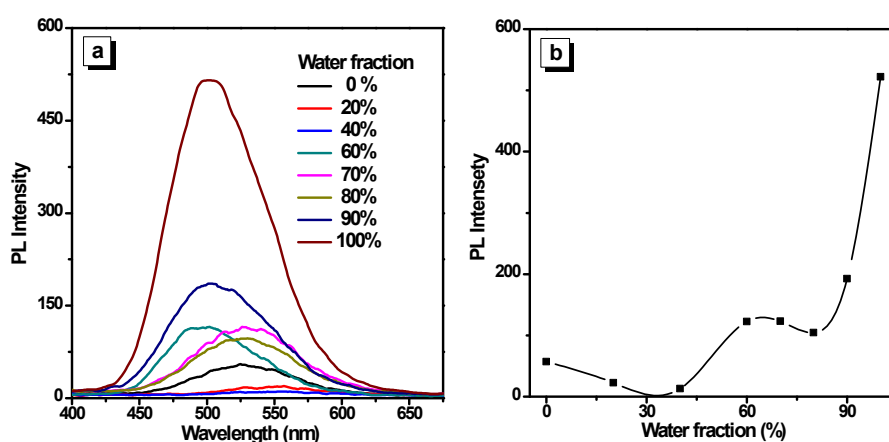


Figure S12. (a) Fluorescence spectra of DPAC-DBTDO in tetrahydrofuran and water mixtures; (b) Changes in the maximum emission intensity of DPAC-DBTDO versus the volume fraction of water in the mixtures of tetrahydrofuran and water.

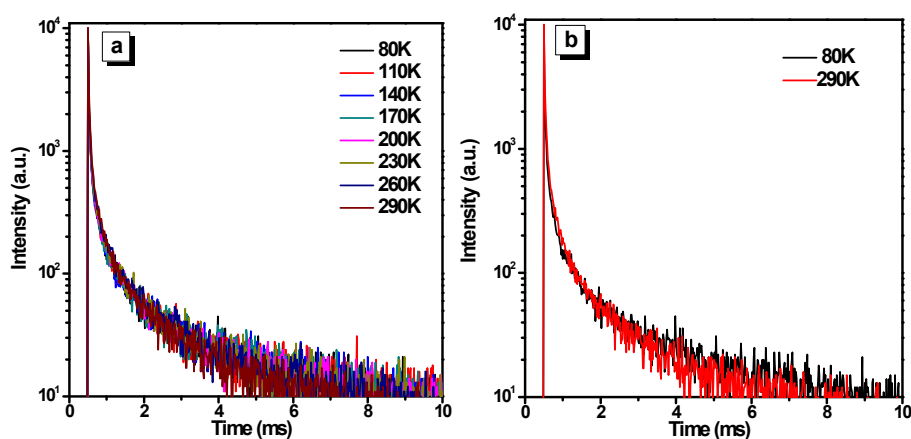


Figure S13. (a) Temperature dependence of transient PL decay of 15 wt% DPAC-DBTDO:DPEPO doped film in the time range of 10 ms; (b) Extracted transient PL decay of 15 wt% DPAC-DBTDO:DPEPO doped film at 80 K and 290 K.

Table S3. Fitting results of the transient PL decay of 15 wt% DPAC-DBTDO:DPEPO doped film in the time range of 10 ms (80 K to 290 K).

	τ_1 (ns)	τ_2 (μ s)	τ_3 (μ s)	χ^2
80 K	26.32	237.6	1957	1.569
110 K	28.37	242.7	1775	1.331
140 K	26.14	231.7	1885	1.454
170 K	24.27	212.3	1959	1.330
200 K	27.15	207.1	1587	1.208
230 K	27.38	202.4	1675	1.501
260 K	26.06	219.6	1632	1.311
290 K	30.41	246.6	1717	1.394

Table S4. Photophysics properties of DPAC-DBTDO.

λ_{Abs} ^a (nm)	λ_{PL} (nm)		Φ_f ^c (%)	Φ_f ^d (%)				E_g ^f (eV)	HOMO/LUMO ^g (eV)
	doped film ^b	neat film		HEX	ETE	THF	ACN		
291, 320	486	498	100	2.4	4.2	2.7	n.o.^e	2.68	-5.43 /-2.44

^a Absorption: measured in neat film. ^b 5 wt% PMMA doped film. ^c Photoluminescent quantum yield by integrating sphere of a 15 wt% DPEPO doped film. ^d Relative fluorescence quantum yield [estimated by using quinine sulfate as standard ($\Phi_f = 54.6\%$ in 0.1 M sulfuric acid solution)]. ^e n.o. = not observed. ^f Optical gap calculated from the absorption onset of neat film. ^g Measured by cyclic voltammetry.

S-7 Electroluminescence Property

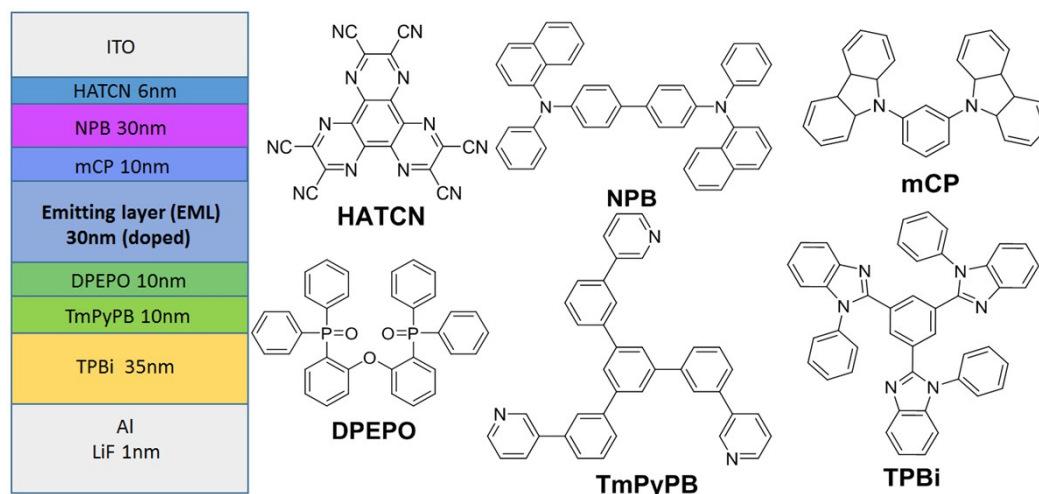


Figure S14. OLED structure and the molecular structures of compounds used in device.

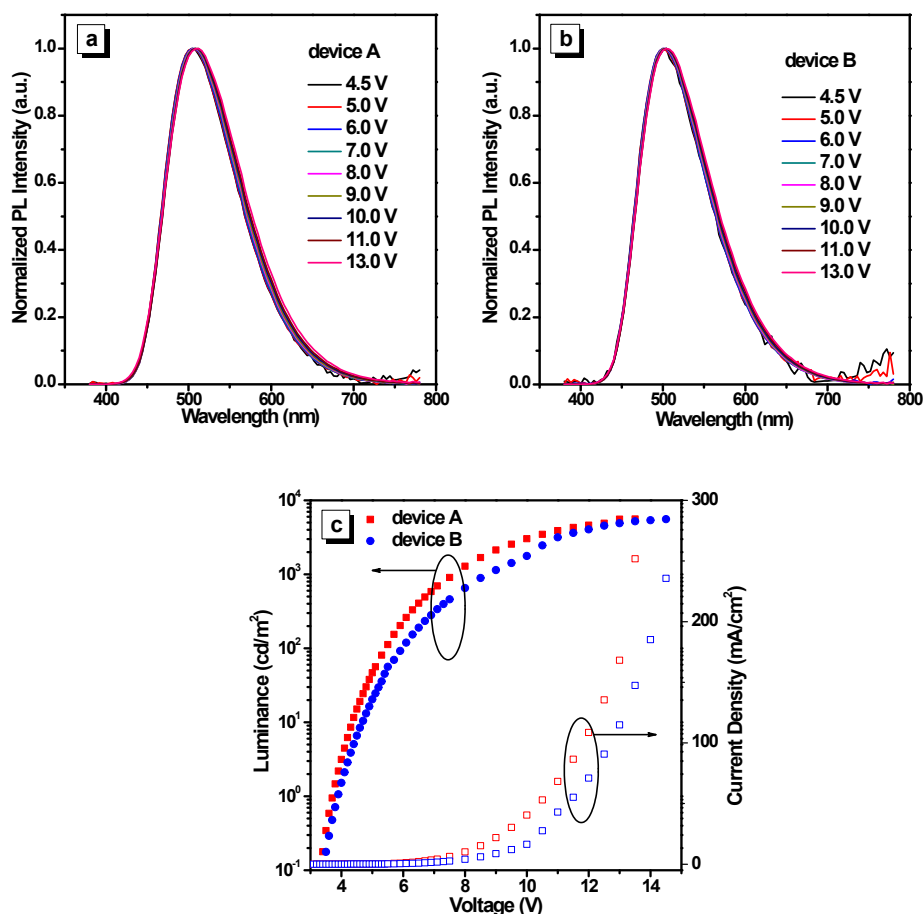


Figure S15. (a) and (b) EL spectra of device A and device B under different voltage, respectively; (c) luminance-voltage-current characteristics of device A and device B. Device A: ITO/HATCN (6 nm)/NPB (30 nm)/mCP (10 nm) /DPAC-DBTBO : DPEPO (15 : 85) (30 nm)/DPEPO (10 nm)/TmPyPB (10 nm)/TPBi (35 nm)/LiF (1 nm)/Al (120 nm); Device B: ITO/HATCN (6 nm)/NPB (30 nm)/mCP (10 nm) /mCP : DPAC-DBTDO 15 wt% (5 nm); DPEPO : DPAC-DBTDO 15 wt% (25 nm)/DPEPO (10 nm)/TmPyPB (10 nm)/TPBi (35 nm)/LiF (1 nm)/Al (120 nm).

Table S5. EL performance of the devices

device	V_{on}^a (V)	L_{max}^b (cd m ⁻²)	PE_{max}^c (lm W ⁻¹)	CE_{max}^d (cd A ⁻¹)	EQE (%) ^e			λ_{EL}^f (nm)	CIE (x, y)
					maximum	at 100 cd m ⁻²	at 1000 cd m ⁻²		
A	3.7	5580	26.1	33.6	12.3	9.5	5.3	504	(0.262,0.469)
B	3.9	5560	26.3	34.2	13.1	9.4	5.7	500	(0.252,0.455)

^a Turn on voltage at a brightness of 1 cd m⁻². ^b Maximum luminance. ^c Maximum power efficiency.

^d Maximum current efficiency. ^e External quantum efficiency. ^f EL peak.