Supporting Information for

# Highly Efficient Blue Organic Light-Emitting Diodes from Pyrimidine-Based Thermally

# **Activated Delayed Fluorescence Emitters**

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### **1. Experimental Procedures**

#### 1.1 General information

All regents and solvents used for the synthesis of the compound were purchased from commercial source and used without further purification.

#### **1.2 Quantum Chemical Calculations**

All of the theoretical simulations for the investigated molecules were performed using the Gaussian 09 program package. The electron density distribution of frontier molecular orbital (FOM) were visualized with Gaussview 3.0. Structure optimizations were carried out using density functional theory (DFT) calculations. The ground state structures were optimized with B3LYP/6-31G (d) level set in the gas phase.

#### **1.3 Thermal Properties**

Thermogravimetric analysis (TGA) was undertaken with a Q600 Simultaneous TG-DSC instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their 5% weight loss while heating at a rate of 10 °C min<sup>-1</sup>.

#### **1.4 Electrochemical Characterization**

The oxidation potential was determined by cyclic voltammetry using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in CH<sub>2</sub>Cl<sub>2</sub> (CV)

as a supporting electrolyte and a scan rate of 100 mV s<sup>-1</sup>. ITO, Ag/AgCl and Pt mesh were used as working electrode, reference electrode and counter electrode, respectively. A 3-electrode cell comprising silver/silver chloride (Ag/AgCl), a platinum mesh and ITO as the reference, counter, and working electrodes, respectively, were used. All potentials were recorded versus Ag/AgCl (saturated) as a reference electrode. Oxidation of the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple in CH<sub>2</sub>Cl<sub>2</sub>/TBAPF<sub>6</sub> occurs at  $E'_{o} = + 0.48$  V. HOMO levels were conducted from the oxidation halfwave potential with the formula:  $E_{HOMO} = - (E_{oxi. v.s. Fc^+/Fc} + 4.8)$  (eV),  $E_{LUMO} = E_{HOMO} + E_g^{opt}$ , thereinto,  $E_g^{opt}$  was obtained from the absorption edges of normalized absorption spectra.

#### **1.5 Photophysical Characterization**

Absorption spectra were studied using a UV-vis-NIR spectrophotometer (UV-1650 PC, Shimadzu). Photoluminescence (PL) spectra and phosphorescence spectra were performed at 77 K using a HITACHI F-4600 spectrophotometer. The transient photoluminance decay characteristics were measured using an Edinburgh Instruments FLS920 spectrometer. The temperature dependence experiment is conducted under low temperature refrigeration system from Advanced Research Systems Company. The absolute fluorescence quantum yields of the solid films are measured with an integrating sphere.

#### **1.6 OLED Fabrication and Characterization**

OLEDs were fabricated on patterned ITO-coated glass substrates with a sheet resistance of 15  $\Omega/\Box$ . Before device fabrication, the ITO glass substrates were cleaned with Decon 90, rinsed in de-ionized water, dried in an oven at 120°C, treated with UV-ozone, and transferred to a vacuum deposition system with a base pressure better than 1×10<sup>-6</sup> mbar for organic and metal deposition. The devices were fabricated with an evaporation rate

of 1–2 Å s<sup>-1</sup>. The cathode was completed through thermal deposition of LiF at a deposition rate of 0.1 Å s<sup>-1</sup>, and then capped with Al metal through thermal evaporation at a rate of 10 Å s<sup>-1</sup>. EL luminescence spectra and CIE color coordinates were measured with a Spectrascan PR650 photometer and the current-voltage characteristics were measured with a computer-controlled Keithley 2400 SourceMeter under ambient atmosphere.

#### 1.7 Synthetic procedure



Scheme S1. Synthetic routes of 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM.

Synthesis of 2-Bromo-N-phenylbenzenamine (S1)<sup>[S1]</sup>: A mixture of aniline (6.89 g, 74.00 mmol), 2-bromoiodobenzene (20.93 g, 74.00 mmol),

and NaOtBu (14.22 g, 148.0 mmol) were stirred 10 min in dry toluene (200 mL) at room temperature under N<sub>2</sub> and were added DPPF (1.03 g, 1.85 mmol) and Pd<sub>2</sub>(dba)<sub>3</sub> (0.85 g, 0.93 mmol). After heating at 80°C for 12 h the reaction mixture was filtered through a celite pad with chloroform, and the filtrate was dried. The crude product was purified by column chromatography on silica gel (eluent: hexane/ dichloromethane = 9:1, v/v), and then concentrated under reduced pressure to afford **S1** as a white solid. (yield = 16.63 g, 91%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 7.52 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 6.7 Hz, 1H), 7.16 (t, *J* = 6.1 Hz, 3H), 7.04 (t, *J* = 7.4, 1H), 6.73 (t, *J* = 7.4Hz, 1H), 6.03 (s, 1H). HR-MS (ESI): *m/z* calcd for C<sub>12</sub>H<sub>10</sub>BrN [M]<sup>+</sup> 248.2, found 247.8.

Synthesis of 10H-spiro[acridan-9,9'-fluorene] (1)<sup>[S2]</sup>: To a solution of S1 (7.20 g, 29.1 mmol) in dry THF (150 mL), n-BuLi (2.5 M in hexane, 25.6 mL, 64.0 mmol) was added dropwise at -78°C. After stirring for 2 h, fluorenone (5.76 g, 110.00 mmol) was added as a solution while stirring the solution at -78°C for 30 min. The reaction mixture was allowed to warm to room temperature and stirred for overnight. After quenching by a large amount of water, the resulting mixture was extracted three with CHCl<sub>2</sub>. A combined CHCl<sub>2</sub> solution was dried over anhydrous MgSO<sub>4</sub> and concentrated to afford a hydroxy intermediate, after filtration and evaporation. The crude hydroxyl intermediate was dissolved in CHCl<sub>3</sub> (150 mL), and methane sulfonic acid (6.15 g, 64.02 mmol) was added and then refluxed for 10 h. After cooling to room temperature, the resulting solution was carefully poured into an excess amount of NaHCO<sub>3</sub> aqueous solution and stirred for 20 min. The product was extracted by CHCl<sub>2</sub>, dried over anhydrous MgSO<sub>4</sub>. After filtration and evaporation, the crude product was purified by column chromatography on silica gel (hexane/CH<sub>2</sub>Cl<sub>2</sub> = 4:1, v/v) filtered off, and then dried under reduced pressure to afford S2 as a white solid (yield = 4.88 g, 51%). <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$ (ppm) 9.25 (s, 1H), 7.92

(d, J = 7.5 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.28 - 7.14 (m, 4H), 7.05 (t, J = 7.5 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.49 (t, J = 7.4 Hz, 2H), 6.12 (d, J = 7.7 Hz, 2H). HR-MS (ESI): *m/z* calcd for C<sub>25</sub>H<sub>17</sub>N [M]<sup>+</sup> 331.4, found 332.0.

Synthesis of 10-(4-bromophenyl)-spiro[acridan-9,9'-fluorene] (2): A mixture of S2 (1.66 g, 5.00 mmol), sodium *tert* butoxide (0.96 g, 10.00 mmol) in 1,4-dioxane (80 mL) were stirred for 30 min at room temperature under N<sub>2</sub>. After, copper (1) iodide (0.10 g, 0.50 mmol), 1,10-phenanthroline (0.10 g, 0.50 mmol), and 4-bromoiodobenzene (1.69 g, 6.00 mmol) were added to the reaction mixture. The mixture was refluxed for 24 h. After cooling to room temperature, the mixture were filtered through a Celite pad and dried. Then the crude product was purified by column chromatography on silica gel (hexane/chloroform = 5:1, v/v) and concentrated under reduced pressure to give S3 as a white solid (yield = 1.83 g, 75%). <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$ (ppm) 7.98 (dd, *J* = 8.1, 3.2 Hz, 4H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 6.97 (dd, *J* = 11.3, 4.3 Hz, 2H), 6.59 (t, *J* = 7.0 Hz, 2H), 6.28 (d, *J* = 7.6 Hz, 2H), 6.23 (dd, *J* = 7.8, 1.5 Hz, 2H). HR-MS (ESI): *m/z* calcd for C<sub>31</sub>H<sub>20</sub>BrN [M]<sup>+</sup>486.4, found 485.8.

Synthesis of 10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)-spiro[acridan-9,9'-fluorene] (3): To a solution of 3 (5.0 g, 10.2 mmol) in dry THF(400 mL) was added dropwise *n*-butyllithium (2.5 M, 4.7 mL, 12.30 mmol) at -78°C under N<sub>2</sub>. The mixture was stirred for 30 min and further reacted for 1.5 h at that temperature. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.30 g, 12.3 mmol) was quickly added to the mixture at -78 °C. The reaction mixture was further stirred for overnight at room temperature. The resulting mixture was added into water, and then extracted with chloroform. The combined organic layers were washed with water, and dried over anhydrous MgSO<sub>4</sub>. After filtration and evaporation, the crude product was purified by column chromatography on silica gel (hexane/ chloroform = 2:1, v/v) to afford S4 as a white solid

(yield = 4.0 g, 73%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 8.22 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.30 (dd, *J* = 12.7, 5.3 Hz, 2H), 6.95 (t, *J* = 7.7 Hz, 2H), 6.61 (t, *J* = 7.4 Hz, 2H), 6.46 (d, *J* = 7.7 Hz, 2H), 6.41 (d, *J* = 8.3 Hz, 2H), 1.48 (s, 12H). HR-MS (ESI): *m/z* calcd for C<sub>37</sub>H<sub>32</sub>BNO<sub>2</sub> [M]<sup>+</sup> 533.4, found 534.0.

Synthesis of 2SPAc-HPM: A mixture of 3 (1.33 g, 2.50 mmol), 4,6-dichloropyrimidine (4, 0.148 g, 1.00 mmol) in toluene (55 mL), an aqueous solution (10 mL) of potassium carbonate (1.06 g, 7.50 mmol) and 10 mL anhydrous alcohol was added to the mixture, which was stirred, bubbled using N<sub>2</sub> for 40 min, and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.09 g, 0.08 mmol) was added quickly, then refluxed under nitrogen atmosphere for 6 h. After cooling to room temperature, the reaction mixture was extracted with chloroform and the solvent was removed under reduced pressure. The crude product was washed twice with CH<sub>2</sub>Cl<sub>2</sub> and recrystallized using THF to give 2SPAc-HPM as a light-yellow solid (yield = 0.72 g, 81%). This compound was further purified by temperature-gradient sublimation under vacuum. <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$ (ppm) 9.52 (s, 1H), 9.03 (s, 1H), 8.87 (d, *J* = 8.4 Hz, 4H), 8.00 (d, *J* = 7.5 Hz, 4H), 7.87 (d, *J* = 8.5 Hz, 4H), 7.44 (dd, *J* = 12.2, 7.1 Hz, 8H), 7.34 (t, *J* = 7.4 Hz, 4H), 7.04 – 6.99 (m, 4H), 6.63 (t, *J* = 7.7 Hz, 4H), 6.40 (d, *J* = 8.2 Hz, 4H), 6.28 (d, *J* = 7.6 Hz, 4H). HR-MS (ESI): *m/z* calcd for C<sub>66</sub>H<sub>42</sub>N<sub>4</sub> [M]<sup>+</sup> 891.1, found 890.9.

Synthesis of 2SPAc-MPM: This compound was synthesized according to the same procedure as described above for the synthesis of 2SPAc-MPM, except that 4,6-dichloro-2-methylpyrimidine (5, 0.16 g, 1.00 mmol) was used as the reactant instead of 4,6-dichloropyrimidine. 2DPAc-MPM was obtained as a light-yellow solid (yield = 0.78 g, 87%), and was further purified by temperature-gradient sublimation under vacuum. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 8.54 (d, *J* = 8.1 Hz, 4H), 8.17 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 4H), 7.72 (d, *J* = 8.1 Hz, 4H), 7.46 (d, *J* = 7.5 Hz, 4H), 7.40 (t, *J* = 7.4 Hz), 7.40 (t, J = 7.4 Hz), 7.4

4H), 7.29 (d, *J* = 7.4 Hz, 4H), 6.95 (t, *J* = 7.8 Hz, 4H), 6.60 (t, *J* = 7.4 Hz, 4H), 6.48 – 6.40 (m, 8H), 3.01 (s, 3H). HR-MS (ESI): *m/z* calcd for C<sub>67</sub>H<sub>44</sub>N<sub>4</sub> [M]<sup>+</sup> 905.1, found 904.9.

Synthesis of 2SPAc-PPM: This compound was synthesized according to the same procedure as described above for the synthesis of 2SPAc-PPM, except that 4,6-dichloro-2-phenylpyrimidine (**6**, 0.23 g, 1.00 mmol) was used as the reactant instead of 4,6-dichloro-2-methylpyrimidine. 2DPAc-PPM was obtained as a light-yellow solid (yield = 0.86 g, 89%), and was further purified by temperature-gradient sublimation under vacuum. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 8.85 (d, *J* = 7.8 Hz, 2H), 8.71 (d, *J* = 8.3 Hz, 4H), 8.29 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 4H), 7.76 (d, *J* = 8.2 Hz, 4H), 7.66 – 7.58 (m, 3H), 7.48 (d, *J* = 7.5 Hz, 4H), 7.40 (t, *J* = 7.4 Hz, 4H), 7.29 (t, *J* = 7.4 Hz, 4H), 6.97 (t, *J* = 7.7 Hz, 4H), 6.61 (t, *J* = 7.4 Hz, 4H), 6.47 (dd, *J* = 13.7, 8.1 Hz, 8H). HR-MS (ESI): *m/z* calcd for C<sub>72</sub>H<sub>46</sub>N<sub>4</sub> [M]<sup>+</sup>967.2, found 966.9.

#### 2. Supplementary Equations, Fig.s, and Tables

#### 2.1 Equations

$$\Delta v_{Fl-Abs} = k\Delta f + C \tag{S1}$$

 $\Delta v_{\text{Fl-Abs}}$  represents the solvent dependent stokes shifts,  $\Delta f$  is the orientation polarizability, *k* represents the slope of Lippert-Mataga plot for 2SPAc-HPM, 2SPAc-PPM, and 2SPAc-MPM.

$$\Delta \mu_{e-g} = \left(2\pi\varepsilon_0 hca^3 k\right)^1 \tag{S2}$$

$$a = 3(M/4N\pi\rho)^{1/3}$$
(S3)

 $\varepsilon_0$  is the permittivity of free space (its value is approximately equal to  $8.854 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$ ), *h* is the Planck's constant, *c* is the speed of light in classical vacuum, *a* the Onsager radius of the solute, *N* is  $6.02 \times 10^{23}$ , M,  $\rho$  is molecular weight of the solute and density (*d* = 1.0 g·cm<sup>-1</sup> in this calculation), respectively. Therefore, a high *k* value can obtain a high  $\Delta \mu_{e-g}$ .

$$\ln\left[\frac{I_{prompt}}{I_{delayed}} - \left(\frac{1}{\Phi_T} - 1\right)\right] = \ln\left(\frac{k_p + k_{nr}}{k_{RISC}}\right) + \frac{\Delta E_{ST}}{RT}$$
(S4)

where  $\Phi_T$  is the formation efficiency,  $k_p$  is the phosphorescence rate constant,  $k_{nr}$  is the non-radiative rate constant from T<sub>1</sub>,  $k_{RISC}$  is the reverse intersystem crossing rate constant from T<sub>1</sub> to S<sub>1</sub>. *R* is the gas constant.

A large photoluminescence quantum yield of the prompt component of fluorescence ( $\Phi_{PF}$ ) is important for achieving excellent internal quantum efficiency ( $\eta_{int}$ ). According to the **equation S5**, can be calculated from the experimental radiative decay rate of fluorescence ( $k_f$ ) using **equation S6** and **S7**.

$$\eta_{int} = n_{r,S} \Phi_{PF} + n_{r,T} \Phi_{TADF} + n_{r,T} \frac{\Phi_{TADF}}{\phi_T}$$
(S5)

$$\Phi_{PF} = k_f \tau_{PF} \tag{S6}$$

$$\tau_{PF} = 1/\left(k_f + k_{ic} + k_{isc}\right) \tag{S7}$$

where  $n_{r,S}$  is the singlet exciton production efficiency,  $n_{r,T}$  is the triplet exciton production efficiency,  $\Phi_{TADF}$  is the photoluminescence quantum yield of TADF,  $\Phi_T$  is the quantum yield of intersystem crossing from S<sub>1</sub> to T<sub>1</sub>,  $t_{PF}$  is the lifetime of the prompt component of fluorescence. It is known that in a molecule with the larger overlap of HOMO and LUMO, the relationship between  $k_f$  and the absorption coefficient can be expressed with Strickler-Berg equation (equation S8). Recent studies however have showed that the Strickler-Berg equation can also be applied in the TADF molecule that has the small FOMs overlap of HOMO and LUMO. In such case, the main contribution of fluorescence emissions originate from CT state. Therefore, the absorption coefficient ( $\varepsilon$ ) could be attributed to CT absorption. The absorption spectra in toluene solution are fitted based on the Gaussian model (see the Supporting information, Fig. S12) to obtain  $\int \varepsilon (v_a) d \ln v_a$  and  $k_f$  (Table S6).

$$k_f = 2.88 \times 10^{-9} n \left\langle \overline{v}_f^{-3} \right\rangle^{-1} \int \varepsilon(v_a) d \ln v_a$$
(S8)

$$\left\langle \overline{\nu}_{f}^{-3} \right\rangle^{-1} = \frac{\int f\left(\nu_{f}\right) l \nu_{f}}{\int f\left(\nu_{f}\right) \gamma_{f}^{-3} d \nu_{f}}$$
(S9)

$$F = 4.32 \times 10^{-9} n^{-1} \int \varepsilon(v_a) dv_a = \left(\frac{8\pi^2 m_e c \langle v_f \rangle}{3he^2}\right) |Q|^2$$
(S10)

In addition, based on interim parameter  $\int \varepsilon(v_a) d \ln v_a$ , the oscillator strength for fluorescence (F) and the transition dipole moment for fluorescence (Q) can be calculated using **equation S10**. From this equation, in turn, we can observe that large F and Q are critical parameters for achieving large  $\Phi_{PF}$  in designing the TADF molecules.

#### 2.2 Fig.s



Fig. S1. TGA and DSC curves of 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM



Fig. S2. Cyclic voltammogram of 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM





Fig. S3. UV-Vis absorption spectra of 2SPAc-HPM, 2SPAc, and PPM-Br in toluene solution (10<sup>-5</sup> M) at room temperature.





**Fig. S4.** UV-Vis absorption and emission spectra of 2SPAc-HPM, 2SPAc-HPM and 2SPAc-PPM in various solvent (10<sup>-5</sup> M) (n-hexane, toluene, chloroform, DCM, and DMF) at room temperature.



**Fig. S5.** The plot of stokes shift ( $\Delta v_{\text{Fl-Abs}}$ ) as a function of orientation poparizability (*f*).



Fig. S6 Fluorescence spectra (300 K) and phosphorescence spectra (77 K) of 2SPAc-HPM, 2SPAc-MPM, and 2SPAc-PPM in toluene (10-3).



Wavelength (nm)



Fig. S7. PL spectra of (a) 2SPAc-HPM, (b)2SPAc-MPM, (c) 2SPAc-PPM in degassed (N<sub>2</sub> treatment) and aerated toluene solution



Fig. S8. Emission decay of 10 wt% emitters: (a), (b) 2SPAc-HPM, (c), (d) 2SPAc-MPM, (e), (f) 2SPAc-PPM doped in DPEPO after Nitrogen flow

for 30 mins.



Fig. S9. Temperature-dependence of the transient PL spectra for 10 wt% emitters: (a), (b) 2SPAc-HPM; (c), (d) 2SPAc-MPM; (e), (f) 2SPAc-PPM

### doped in DPEPO.





Fig. S10. Absorption characteristics of emitters: (a) 2SPAc-HPM, (b) 2SPAc-MPM, (c) 2SPAc-PPM in toluene solution.





Fig. S11. Log plot of the intensity ratio of prompt fluorescence to delayed fluorescence vs. 1/T, (a) 2SPAc-HPM, (b) 2SPAc-MPM, (c) 2SPAc-PPM.



Fig. S12. Device performance of the 2SPAc-HPM device under different doping concentration, (a) is EL spectra of the TADF OLEDs at 8 V, (b) Current density and luminance versus voltage (*J-V-L*) characteristics, (c) External quantum efficiency ( $\eta_{ext}$ ) versus current density plots, (d) Current efficiency-luminance-power efficiency.



Fig. S13. Device performance of the 2SPAc-MPM device under different doping concentration, (a) is EL spectra of the TADF OLEDs at 8 V, (b)Current density and luminance versus voltage (*J-V-L*) characteristics, (c) External quantum efficiency ( $\eta_{ext}$ ) versus current density plots, (d) Current efficiency-luminance-power efficiency.



Fig. S14. Device performance of the 2SPAc-PPM device under different doping concentration. (a) is EL spectra of the TADF OLEDs at 8 V, (b) Current density and luminance versus voltage (*J-V-L*) characteristics, (c) External quantum efficiency ( $\eta_{ext}$ ) versus current density plots, (d) Current efficiency-luminance-power efficiency.



Fig. S15 EL spectra of HPM-2SPAc, HPM-2SPAc, and HPM-2SPAc at different voltages

## 2.3 Tables

				2SPAc-HPM		2SPAc-MPM			2SPAc-PPM			
Solvents	Е	п	f(ε,n)	$\lambda_{Abs}$	$\lambda_{\mathrm{Pl}}$	V <sub>Abs-Pl</sub>	$\lambda_{Abs}$	$\lambda_{Pl}$	V <sub>Abs-Pl</sub>	$\lambda_{Abs}$	$\lambda_{Pl}$	$v_{Abs-Pl}$
				(nm)	(nm)	(cm <sup>-1</sup> )	(nm)	(nm)	(cm <sup>-1</sup> )	(nm)	(nm)	(cm <sup>-1</sup> )
n-hexane	1.90	1.375	0.001	-	460	-	-	450	-	-	449	-
Toluene	2.38	1.494	0.014	383	469	4788	379	461	4793	384	464	4490
Chloroform	4.80	1.447	0.147	382	529	7275	377	515	7108	384	513	6649
DCM	8.93	1.427	0.217	375	542	8217	370	529	8123	376	534	7879
DMF	37.00	1.427	0.276	371	568	9348	368	554	9123	374	554	8687

# **Table S1.** Detailed parameters of photophysicals data of 2SPAc-HPM, 2SPAc-MPM, and 2SPAc-PPM

Compound	M	а	k	$\Delta \mu_{e-g}$
Compound	(g/mol)	(Å)		(D)
2SPAc-HPM	890.34	6.82	17184	4.29
2SPAc-MPM	904.36	6.86	16441	4.22
2SPAc-PPM	966.37	7.01	16199	4.34

**Table S2.** Detailed parameters of photophysicals data of 2SPAc-HPM, 2SPAc-MPM, and 2SPAc 

 PPM

**Table S3.** The PLQYs of 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM at different doping ratio

in DPEPO films excited at 320 nm in nitrogen atmosphere.

Compound	10wt%	20wt%	30wt%	40wt%
2SPAc-HPM	58.50%	96.60%	85.60%	96.00%
2SPAc-MPM	80.20%	82.20%	84.30%	85.40%
2SPAc-PPM	91.10%	97.00%	92.00%	95.10%

**Table S4.** Photophysicals date of 2SPAc-HPM, 2SPAc-PPM, and 2SPAc-SPAc in toluene (10<sup>-5</sup> M)

Compound	$\int \varepsilon(v_a) d \ln v_a$	$k_{ m f}$	F	Q	<b>PL</b> <sub>max</sub>	va
Compound	$(10^3 \text{ cm}^3)$	$(10^7 \text{ s}^{-1})$	Г	(D)	(nm)	(nm)
2SPAc-HPM	0.40	2.31	0.029	1.62	468	383
2SPAc-MPM	0.36	2.16	0.027	1.56	460	380
2SPAc-PPM	0.44	2.60	0.033	1.72	465	384

Temper2SPAc-HPM			2SPAc-MPM				2SPAc-PPM					
ature	$arPhi_{ ext{PL}}$	$arPhi_{ m PF}$	$arPsi_{ m DF}$	$arPsi_{ m DF}/arPsi_{ m PL}$	$arPhi_{ ext{PL}}$	$arPhi_{ m PF}$	$arPsi_{ m DF}$	$arPsi_{ m DF} / arPsi_{ m PL}$	$arPhi_{ ext{PL}}$	$arPhi_{ m PF}$	$arPsi_{ m DF}$	$arPsi_{ m DF} / arPsi_{ m PL}$
(K)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
77	31.90	0.64	31.26	98.0	21.36	0.68	20.68	96.8	40.91	1.08	39.83	97.4
100	31.50	0.46	31.10	98.7	23.33	0.40	22.93	98.3	43.82	0.80	43.03	98.2
150	40.40	0.41	39.99	99.0	29.65	0.41	29.24	98.6	53.92	0.39	53.53	99.3
200	44.30	0.43	43.87	99.0	31.81	0.38	31.43	98.8	58.38	0.46	57.92	99.2
250	45.80	0.30	45.49	99.3	35.59	0.31	35.29	99.2	59.83	0.64	59.19	98.9
300	48.80	0.33	48.47	99.3	43.78	0.57	43.21	98.7	62.46	0.37	62.09	99.4

**Table S5.** PL quantum yield ( $\Phi_{PL}$ ) and PL quantum yield for prompt ( $\Phi_{PF}$ ) and delayed ( $\Phi_{DF}$ ) fluorescence at temperature between 77 to 300 K.

TADE omittous	<b>Doping Concentration (x wt%) in DPEPO host</b>									
TADT emitters		10 (device 1)	20 (device 2)	30 (device 3)	40 (device 4)					
	$V_{\rm oc}$ (V)	4.2	3.5	3.4	3.4					
	EQE (%)	$18.33(\pm 0.40)$	24.58(±0.99)	22.74(±3.32)	$19.42(\pm 1.00)$					
2SPAc-HPM	PE (lm/W)	26.01(±2.73)	49.62(±1.99)	49.02(±10.47)	44.43(±2.29)					
	CE (cd/A)	37.58(±0.84)	55.28(±2.22)	56.17(±8.21)	48.08(±2.48)					
	Luminance (cd/m <sup>2</sup> )	2000	7200	11600	11900					
	$V_{\rm oc}$ (V)	4.0	3.6	3.6	3.4					
	EQE (%)	20.84(±2.39)	22.54(±2.27)	21.87(±1.59)	20.17(±1.87)					
2SPAc-MPM	PE (lm/W)	29.09(±5.38)	37.00(±5.45)	40.47(±2.95)	35.83(±4.69)					
	CE (cd/A)	39.37(±4.52)	46.30(±3.70)	46.38(±3.38)	43.69(±4.10)					
	Luminance (cd/m <sup>2</sup> )	1900	4100	5200	5700					
	$V_{\rm oc}({ m V})$	4.2	3.7	3.6	3.5					
2SPAc-PPM	EQE (%)	21.16(±2.96)	$25.65(\pm 1.49)$	28.50(±2.94)	$25.61(\pm 0.41)$					
	PE (lm/W)	30.68(±4.30)	46.34(±2.71)	51.54(±5.31)	50.21(±0.79)					

**Table S6.** Key EL date for TADF OLEDs based on 2SPAc-HPM, 2SPAc-MPM, and 2SPAc-PPM

CE (cd/A)	42.97(±6.02)	56.04(±3.29)	62.34(±6.43)	57.54(±0.90)
Luminance (cd/m <sup>2</sup> )	1900	5300	5600	7500

#### 3. Reference

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