Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information For

Molecular Engineering of Thermally Activated Delayed Fluorescence Emitters to Concurrently Achieve High Performance and Reduced Efficiency Roll-off in Organic Light-Emitting Diodes

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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 Electrochemical Characterization

The oxidation potential was determined by cyclic voltammetry using 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in CH_2Cl_2 (CV) as a supporting electrolyte and a scan rate of 100 mV s^{-1}. 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^+) redox couple in $CH_2Cl_2/TBAPF_6$ occurs at E'_o = + 0.48 V. HOMO levels were conducted from the oxidation half-wave 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.

1.4 Photophysical Characterization

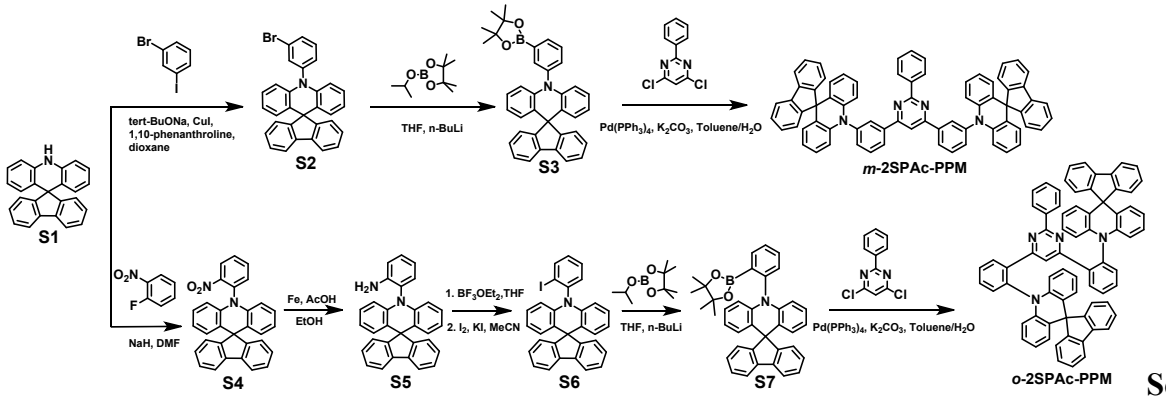
Absorption spectra were studied using a UV-vis-NIR spectrophotometer (UV-1650 PC, Shimadzu). Photoluminescence (PL) spectra and phosphorescence spectra were performed at

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.

1.5 OLED Fabrication and Characterization

OLEDs were fabricated on patterned ITO-coated glass substrates with a sheet resistance of 15 Ω/□. 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^{-6} mbar for organic and metal deposition. The devices were fabricated by evaporating organic onto the ITO glass sequentially with an evaporation rate of 1–2 Å s^{-1}. The cathode was completed through thermal deposition of LiF at a deposition rate of 0.04-0.05 Å s^{-1}, and then capped with Al metal through thermal evaporation at a rate of 10 Å s^{-1}. 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.

1.6 Synthetic procedure



Scheme S1. Synthetic routes of *o*-2SPAc-PPM and *m*-2SPAc-PPM.

Compounds S1, S2, S3, S6, and S7 are synthesized according to our previous work.[S1]

Synthesis of *o*-2SPAc-PPM: A mixture of **S7** (1.20 g, 2.55 mmol), 4,6-dichloro-2-phenylpyrimidine (0.211 g, 0.9 mmol) in toluene (55 mL), an aqueous solution (10 mL) of potassium carbonate (0.933 g, 6.75 mmol) and 10 mL anhydrous alcohol was added to the mixture, which was stirred, bubbled using N_2 for 40 min, and $Pd(PPh_3)_4$ (0.078 g, 0.0675 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_2Cl_2 and recrystallized using THF to give *o*-2SPAc-PPM as a light-yellow solid (yield = 0.72 g, 81%). This compound was further purified by temperature-gradient sublimation under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.71 (t, *J* = 7.4 Hz, 2H), 7.64 (t, *J* = 8.4 Hz, 4H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.55 (s, 1H), 7.51 (d, *J* = 6.4 Hz, 4H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.29 – 7.22 (m, 4H), 7.16 – 7.04 (m, 5H), 6.88 (t, *J* = 7.4 Hz, 2H), 6.78 (t, *J* = 7.6 Hz, 4H), 6.63 (t, *J* = 7.4 Hz, 2H), 6.45 (t, *J* = 7.4 Hz, 4H), 6.32 (d, *J* = 7.7 Hz, 2H), 6.28 (d, *J* = 8.2 Hz, 4H), 6.20 (d, *J* = 7.7 Hz, 4H). MALDI-TOF: *m/z* calcd for $C_{66}H_{42}N_4$ $[M]^+$ 967.1, found 966.4

Synthesis of *m*-2SPAc-PPM: This compound was synthesized according to the same procedure as described above for the synthesis of *m*-2SPAc-PPM, except that **S3** (1.20 g, 2.25 mmol) was used as the reactant instead of **S7**. 2DPAc-PPM was obtained as a light-yellow solid (yield = 0.86 g, 89%), and was further purified by temperature-gradient sublimation under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 8.77 (d, *J* = 7.0 Hz, 2H), 8.61 (d, *J* = 7.8 Hz, 2H), 8.45 (s, 2H), 8.18 (s, 1H), 7.94 (t, *J* = 7.5 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 4H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 5.6 Hz, 3H), 7.48 (d, *J* = 7.5 Hz, 4H), 7.37 (t, *J* = 7.3 Hz, 4H), 7.18 (dd, *J* = 21.2, 13.5 Hz, 4H), 6.95 (t, *J* = 7.8 Hz, 4H), 6.60 (t, *J* = 7.4 Hz, 4H), 6.46 (t, *J* = 6.7 Hz, 8H). MALDI-TOF: *m/z* calcd for $C_{72}H_{46}N_4$ $[M]^+$ 967.1, found 966.4.

2. Supplementary Equations, Figures, and Tables

2.1 Equations

The intensity ratio between prompt (A_1), delayed (A_2), or/and phosphorescent (A_3) component were determined using emission life time (t_1, t_2, or/and t_3) and fitting parameter (B_1, B_2, or/and B_3). As following:

$$I(t) = B_1 e^{-\frac{1}{t_1}} + B_2 e^{-\frac{1}{t_2}} + B_3 e^{-\frac{1}{t_3}} \tag{S1}$$

$$A_1 = \frac{B_1 t_1}{B_1 t_1 + B_2 t_2 + B_3 t_3} \tag{S2}$$

$$A_2 = \frac{B_2 t_2}{B_1 t_1 + B_2 t_2 + B_3 t_3} \tag{S3}$$

$$A_3 = \frac{B_3 t_3}{B_1 t_1 + B_2 t_2 + B_3 t_3} \tag{S4}$$

2.2 Figures

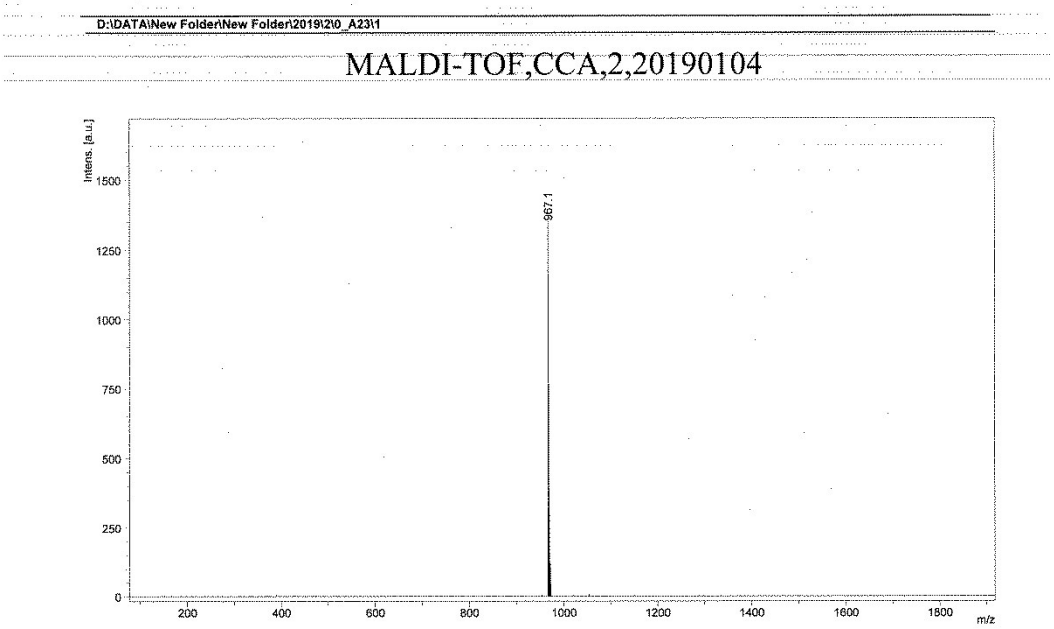


Fig.S1 Mass spectra of *m*-2SPAc-PPM

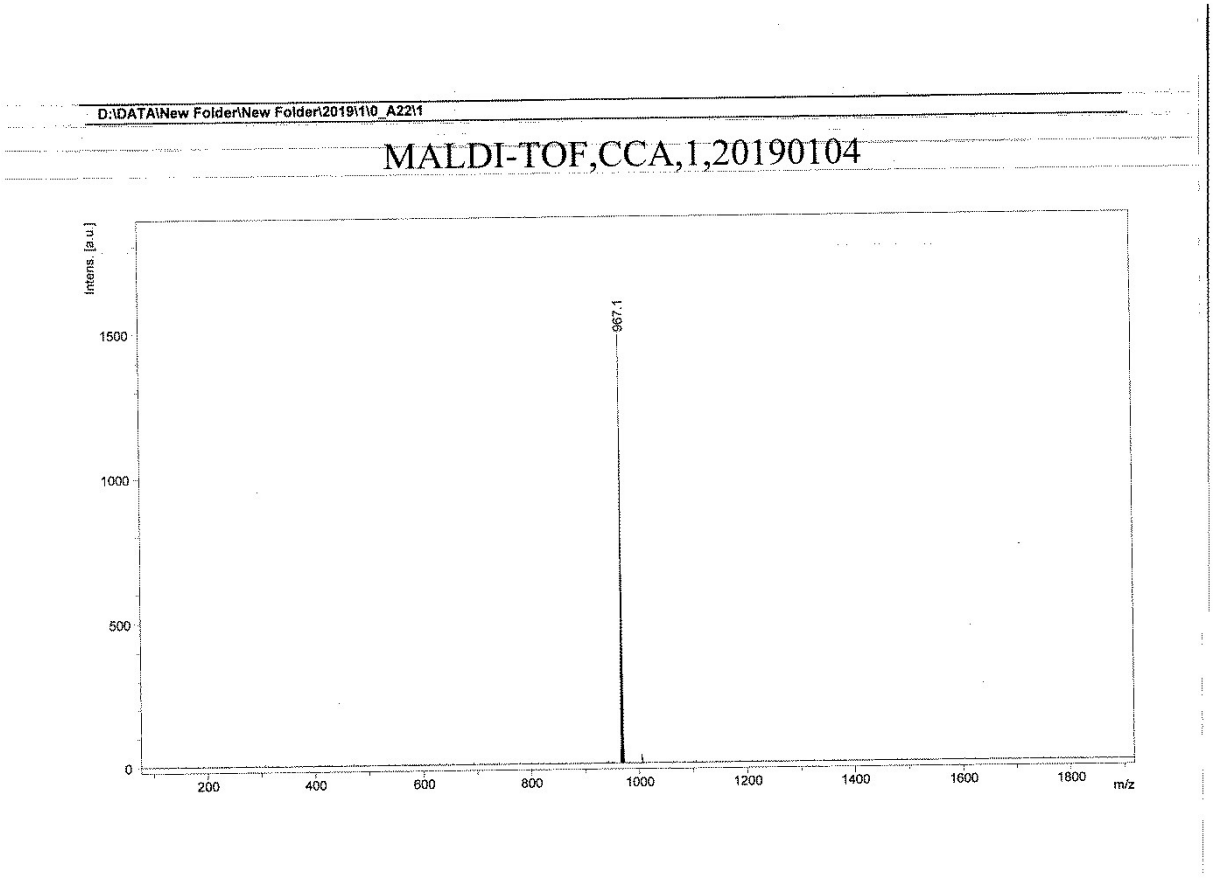


Fig.S2 Mass spectra of *o*-2SPAc-PPM

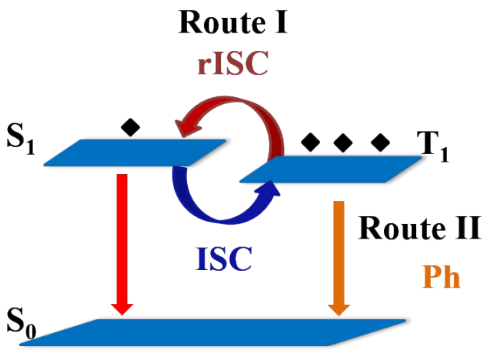


Fig. S3. The triplet exciton dynamic processes for routes I and II.

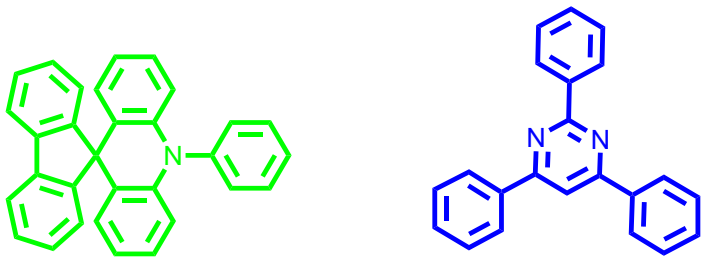


Fig. S4. The chemical strucutres of model donor 2SPAc-Ph and acceptor PPM-Ph.

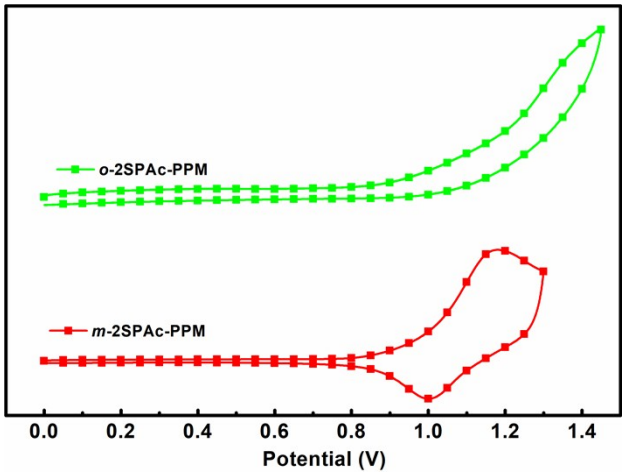


Fig. S5. Cyclic voltammogram of *o*-2SPAc-PPM and *m*-2SPAc-PPM.

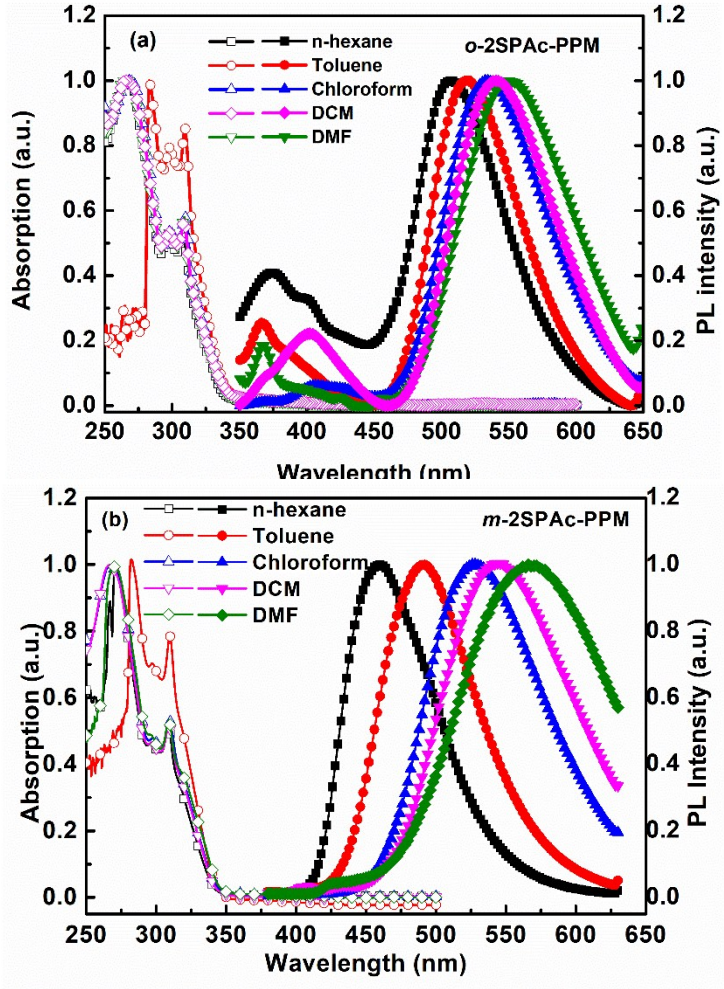


Fig. S6. UV-Vis absorption and emission spectra of *o*-2SPAc-PPM (a) and *m*-2SPAc-PPM (b) in various solvent (10^{-5} M) at room temperature.

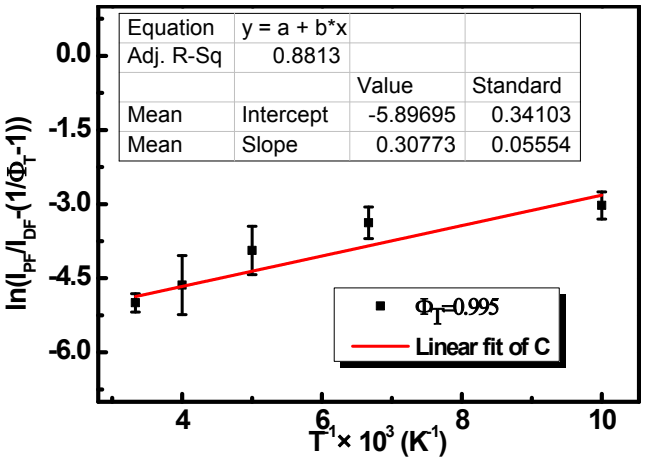


Fig. S7. The Berberan-Sanotos plot of *o*-2SPAc-PPM.

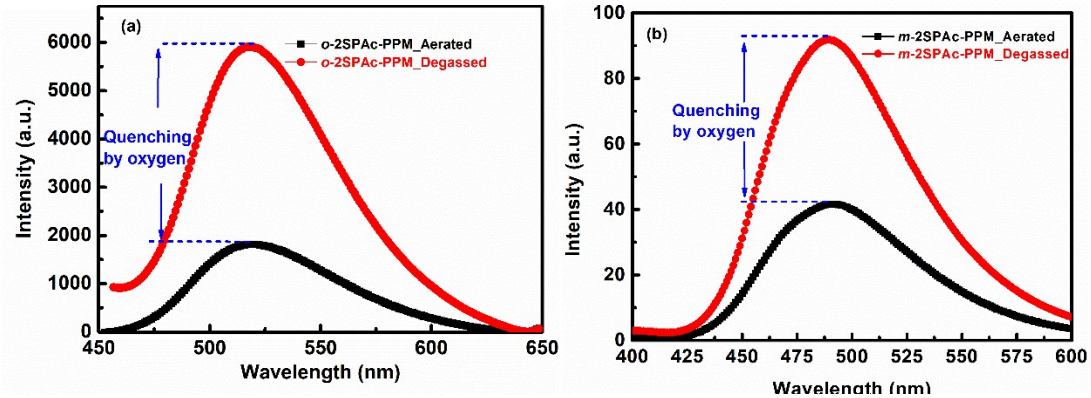


Fig. S8. PL spectra of *o*-2SPAc-PPM (a) and *m*-2SPAc-PPM (b) in degassed (N_2 treatment) and aerated toluene solution.

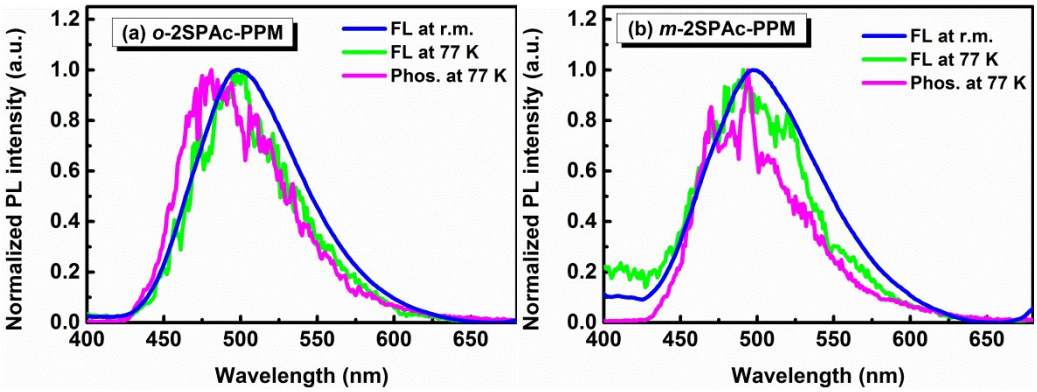


Fig. S9. Fluorescence and phosphorescence spectra of *o*-2SPAc-PPM (a) and *m*-2SPAc-PPM (b) in doped films.

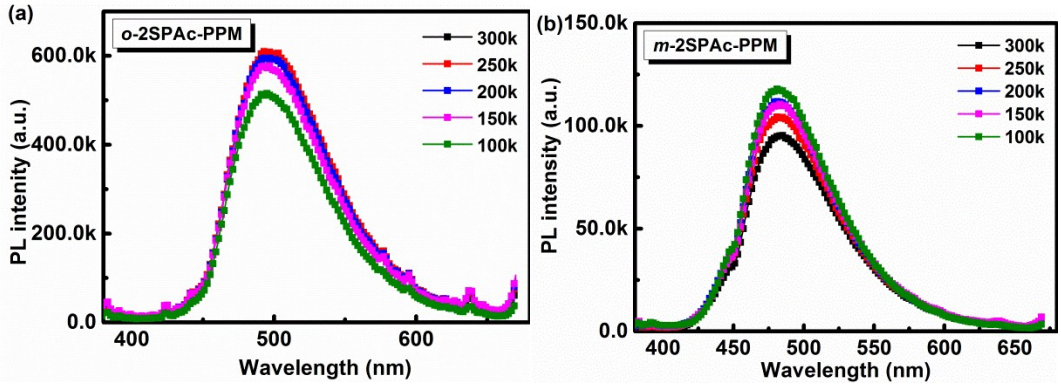


Fig. S10. PL spectra of *o*-2SPAc-PPM (a) and *m*-2SPAc-PPM (b) doped films at different temperature (100, 150, 200, 250, and 300 K).

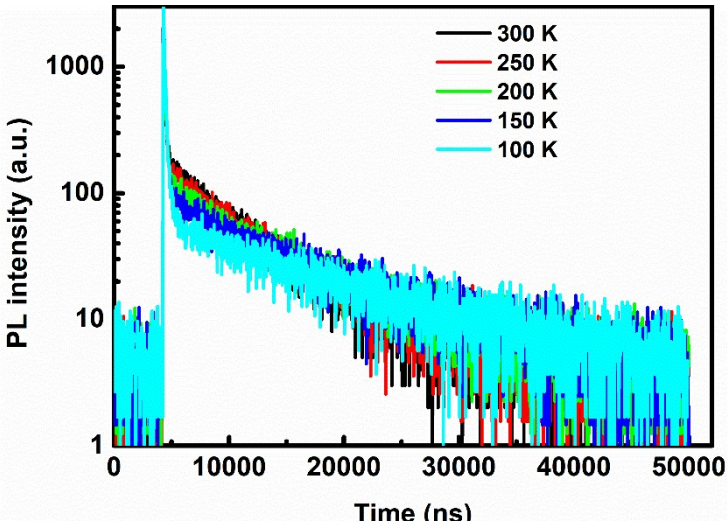


Fig. S11. Temperature dependence of PL decay *o*-2SPAc-PPM in 10 wt % doped DPEPO film.

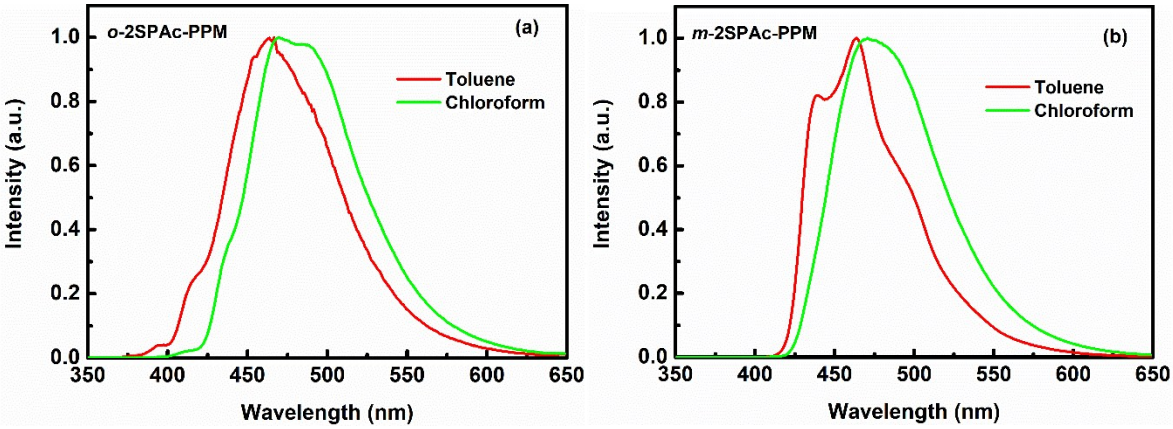


Fig. S12. Phosphorescence spectra of *o*-2SPAc-PPM and *m*-2SPAc-PPM in toluene and chloroform solution. The phosphorescence with vibronic structure in toluene solution indicates that the T_1 state has LE character. However, the phosphorescence spectra have the solvatochromism. Thus, the T_1 state originates from CT charcter.

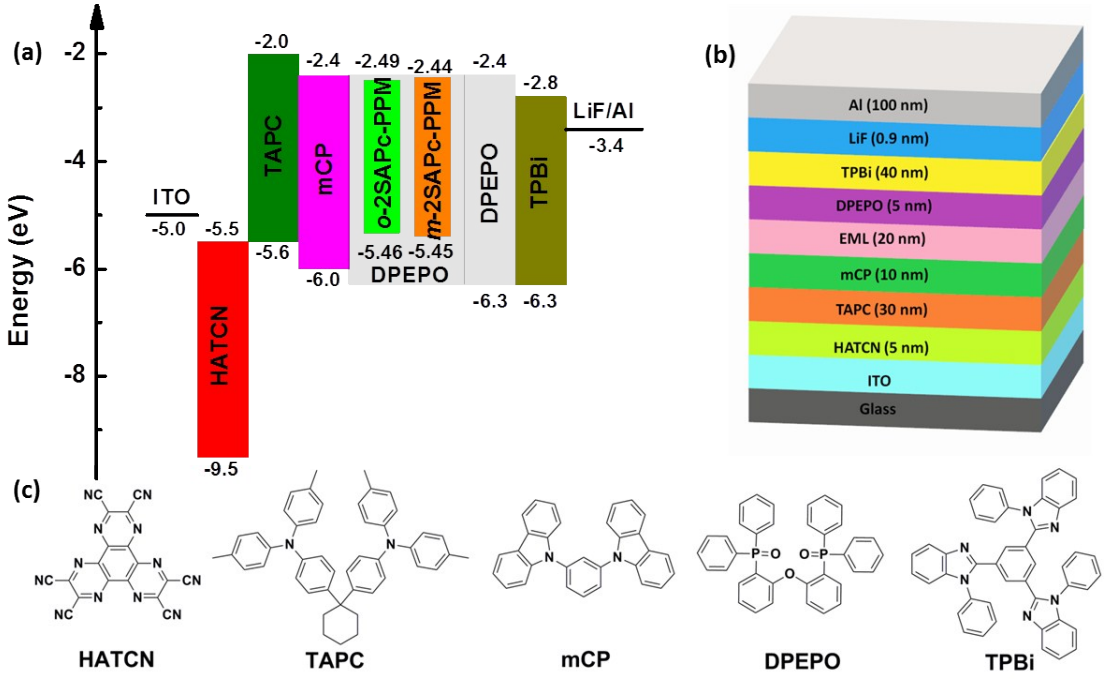


Fig. S13. (a) The energy level diagrams, (b) OLED device structure, and (c) the chemical structure of the materials used in the TADF devices.

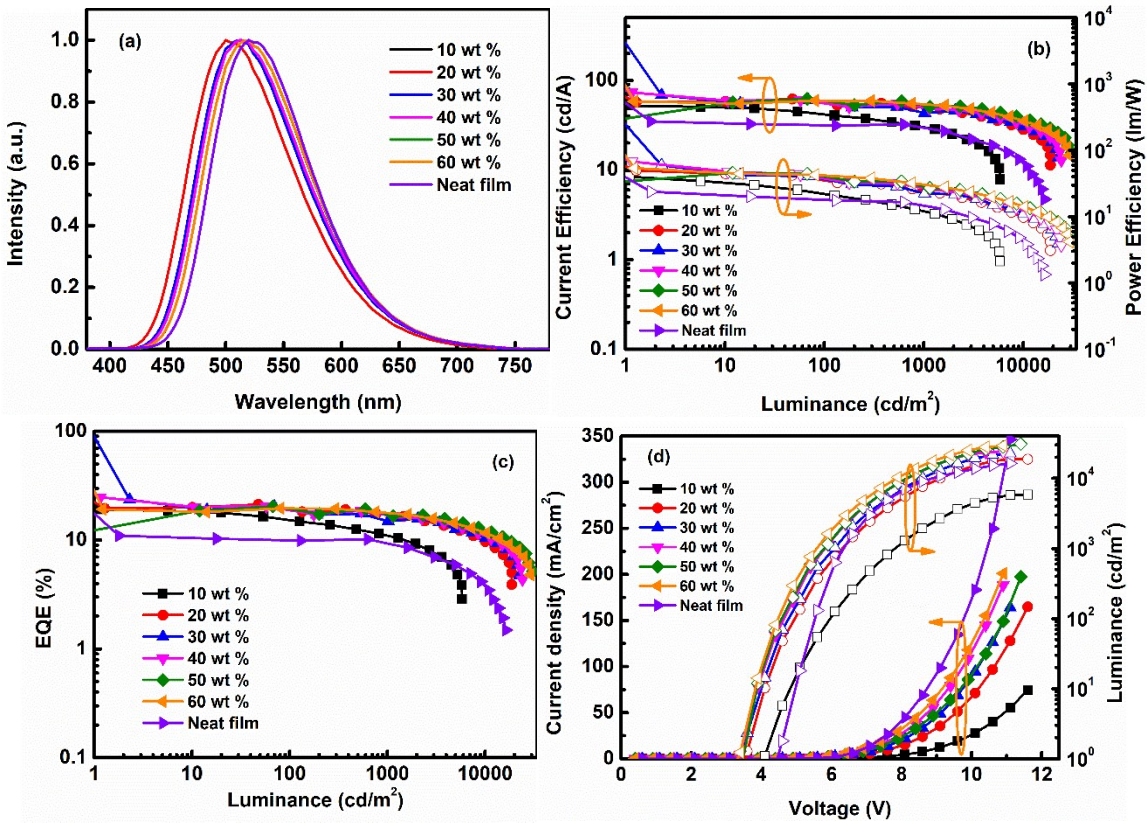


Fig. S14. The performance of OLED device with *x* wt. % *o*-2SPAc-PPM doped in DPEPO as emitting layer (*x* = 10, 20, 30, 40, 50, 60, and neat film): (a) EL spectra of the TADF OLEDs at 8 V. (b) Current efficiency-luminance-power efficiency. (c) External quantum efficiency (EQE) versus current density plots, (d) Current density and luminance versus voltage (*J*-*V*-*L*) characteristics.

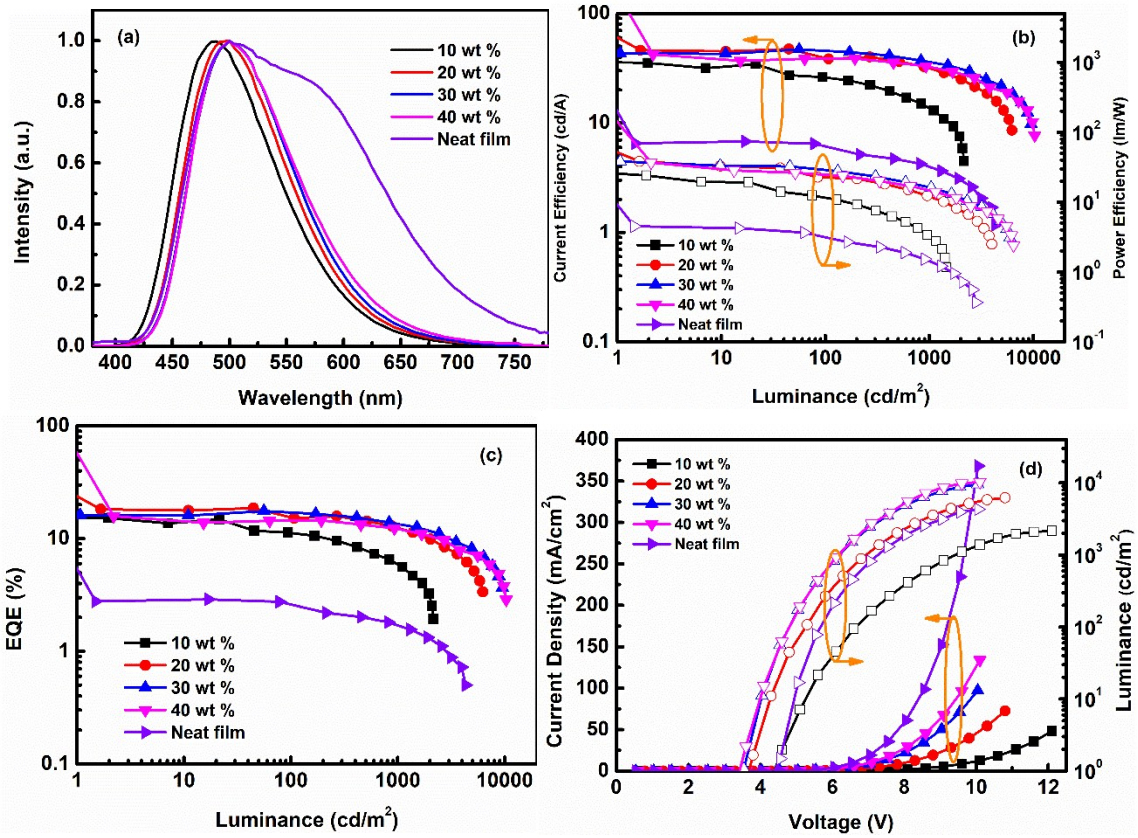


Fig. S15. The performance of OLED device with *x* wt% *m*-2SPAc-PPM doped in DPEPO as emitting layer (*x* = 10, 20, 30, 40, and neat film): (a) EL spectra of the TADF OLEDs at 8 V. (b) Current efficiency-luminance-power efficiency. (c) External quantum efficiency (EQE) versus current density plots, (d) Current density and luminance versus voltage (*J*-*V*-*L*) characteristics.

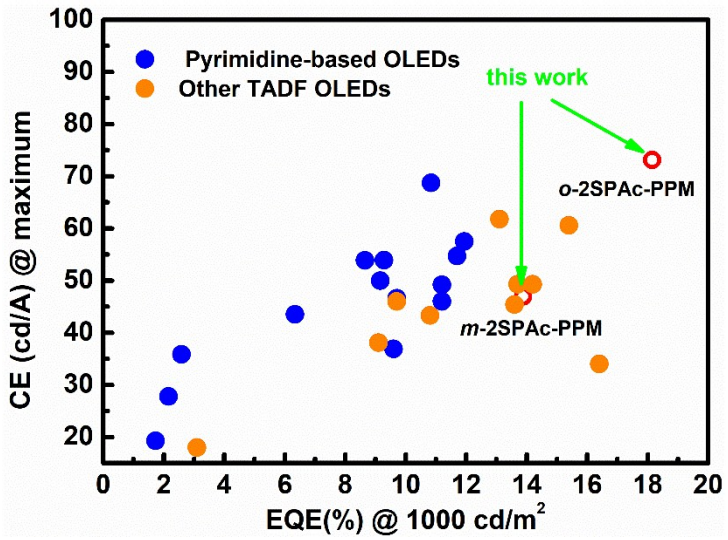
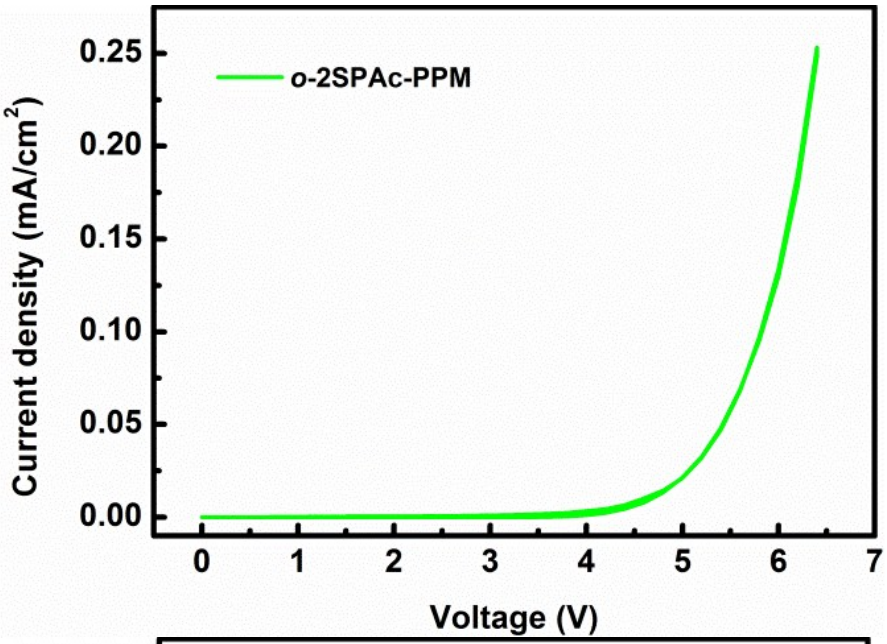
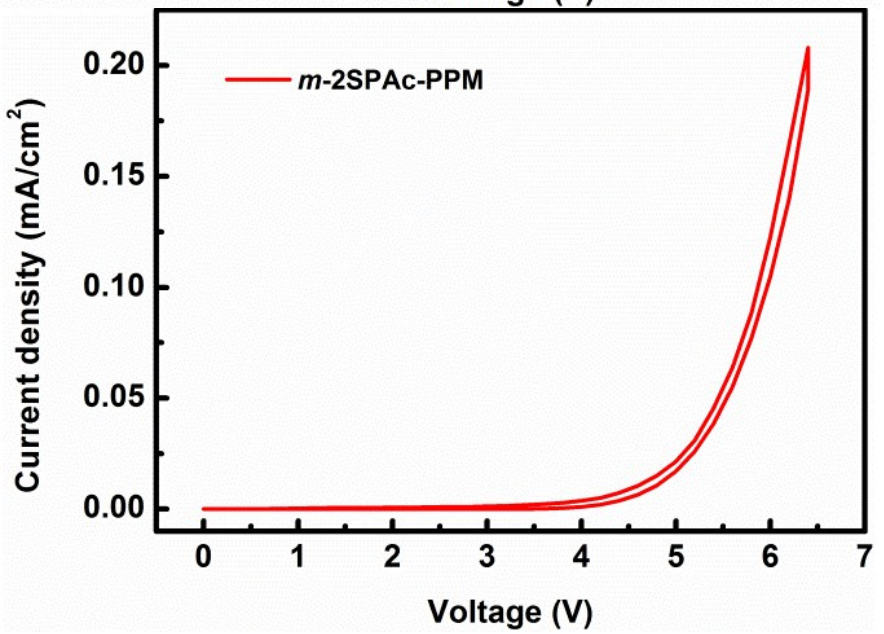


Fig. S16. The EQE at 1000 cd m^{-2} and the maximum of CE of OLEDs in this work compared with reported pyrimidine-based OLEDs and other efficient TADF OLEDs.


o-2SPAc-PPM
Current density (mA/cm2)
Voltage (V)
0.25
0.20
0.15
0.10
0.05
0.00
0
1
2
3
4
5
6
7


m-2SPAc-PPM
Current density (mA/cm2)
Voltage (V)
0.20
0.15
0.10
0.05
0.00
0
1
2
3
4
5
6
7

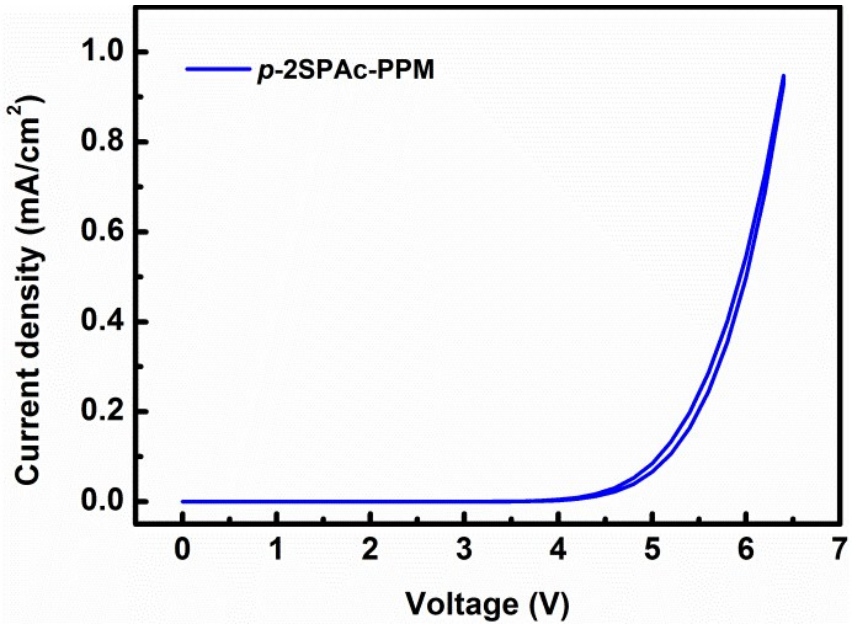


Fig. S17. Double sweep of the I-V curve for *p*-2SPAc-PPM, *m*-2SPAc-PPM and *o*-2SPAc-PPM-based OLEDs, respectively.

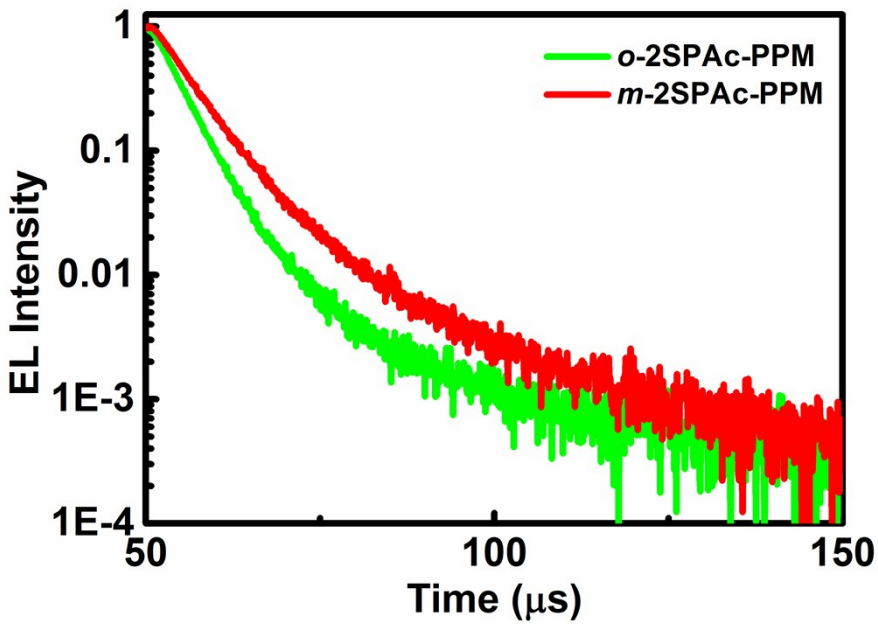


Fig. S18. Transient EL delayed curve of *o*-2SPAc-PPM- and *m*-2SPAc-PPM-based TADF OLEDs.

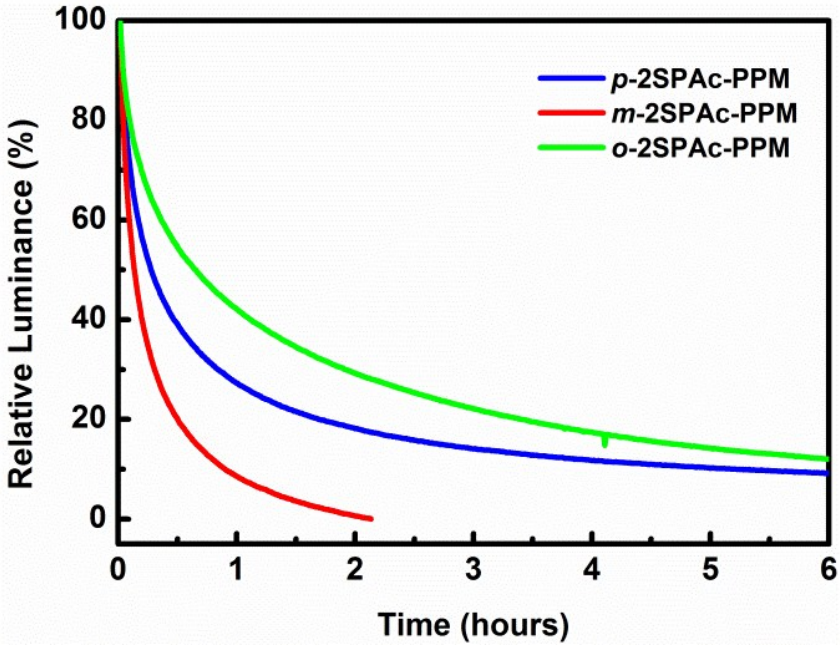


Fig. S19. Relative luminance of the OLEDs as a function of operating time at a constant voltage. The initial luminance was 500 cd m^{-2} for each OLED for *p*-2SPAc-PPM, *m*-2SPAc-PPM and *o*-2SPAc-PPM-based OLEDs, respectively.

2.3 Tables

Table S1. Lifetime data extracted from the transient characterization of 10 wt% *o*- or *m*-2SPAc-PPM: DPEPO film in the time range of 200 μs at different temperatures.

Compounds	Parameters	100 K	150 K	200 K	250 K	300 K
***m*-2SPAc-PPM**	Φ_{PL}[a] (%)	-	-	-	-	92.30
	Φ_{PL}[b] (%)	66.85	64.43	64.26	61.12	56.15
	Φ_{F}[b] (%)	0.17	0.18	0.16	0.19	0.20
	Φ_{DF}[b] (%)	14.21	14.14	15.51	16.61	17.09
	Φ_{Ph}[b] (%)	52.49	50.11	48.59	44.32	38.85
	τ_1[c] *(ns)*	307.10	347.20	313.00	384.30	348.80
	A_1[c] (%)	0.22	0.25	0.24	0.34	0.41
	τ_2 *(us)*	17.72	13.98	12.00	10.77	9.36
	A_2 (%)	20.95	21.68	23.57	27.04	30.21
	τ_3 *(us)*	79.11	70.60	61.97	56.94	50.33
	A_3 (%)	78.83	78.06	76.19	72.63	69.38
***o*-2SPAc-PPM**	Φ_{PL}[a] (%)	-	-	-	-	95.50
	Φ_{PL}[b] (%)	63.09	74.26	77.00	78.65	76.41
	Φ_{F}[b] (%)	2.80	1.72	2.48	0.46	0.40
	Φ_{DF}[b] (%)	60.29	72.53	74.52	78.20	76.01
	τ_1 *(ns)*	93.48	93.43	93.24	97.00	92.87
	A_1(%)	4.45	2.33	3.22	0.58	0.53
	τ_2 *(us)*	11.44	9.63	8.19	6.65	5.61
	A_2(%)	95.55	97.67	96.78	99.42	99.47

[a)]Absolute PLQYs for the 10% wt%-doped DPEPO films measured using an integration sphere under N_2 atomosphere. [b)]Absolute PLQYs for the 10% wt%-doped DPEPO films measured using an integration sphere under

air. [b)]Estimated according to the prompt and delayed components in transient delay curve. [c)]measured in the time range of 200 μs.

Table S2. Physical properties of 10 wt% *o*-2SPAc-PPM and *m*-2SPAc-PPM doped DPEPO films at 300 K.

Compounds	τ_p[a)] (ns)	τ_d[b)] (μs)	τ_{Ph}[b)] (us)	k_P (10^7 s^{-1})	k_r^s (10^5 s^{-1})	k_{ISC} (10^7 s^{-1})	k_{rISC} (10^7 s^{-1})	k_{nr}^T (10^4 s^{-1})	k_{Ph}* (10^3 s^{-1})
m-2SPAc-PPM	50.12	9.35	56.97	2.00	0.40	2.00	0.91	8.90	7.72
o-2SPAc-PPM	92.45	5.36	-	1.08	0.43	1.08	3.55	0.80	-
p-2SPAc-PPM	16.80	56.94	-	5.90	0.22	5.88	0.29	0.68	-

[a)]Measured in the time range of ~200 ns. [b)] Measured in the time range of 200 μs. * $k_{Ph} = \Phi_{Ph}/(\tau_{Ph}\Phi_{ISC})$ according to the reference[1], where $\Phi_{ISC} = k_{ISC}/k_F$

Table S3. Summarized device performances of compounds *o*-2SPAc-PPM and *m*-2SPAc-PPM.

Compounds	wt%	$EQE_{max/100/1000/10000}$ [%]	$PE_{max/100/1000/10000}$ [lm/W]	$CE_{max/100/1000/10000}$ [cd/A]
***o*-2SPAc-PPM**	10	19.15/14.82/11.48/N.A.	40.01/20.82/12.94/N.A.	52.22/40.42/31.30/N.A.
	20	21.23/18.19/17.43/9.71	42.21/32.62/26.14/9.76	61.81/52.96/50.75/28.27
	30	23.52/20.60/14.91/10.53	59.61/40.86/22.30/11.17	68.31/59.82/43.30/30.58
	40	24.80/20.50/16.62/11.69	67.58/43.17/26.10/13.71	73.14/60.46/49.01/34.47
	50	20.43/20.43/16.66/11.83	44.39/44.39/27.00/13.47	62.18/62.18/50.70/36.01
	60	19.58/19.58/18.15/11.61	42.52/42.52/32.11/14.04	59.55/59.55/55.20/35.31
	Neat	10.09/9.56/9.91/N.A.	21.83/16.99/16.16/-	31.96/30.28/31.38/N.A.
***m*-2SPAc-PPM**	10	15.28/11.32/6.49/N.A.	24.18/12.49/5.19/N.A.	35.41/26.24/15.03/N.A.
	20	18.22/15.16/12.9/N.A.	38.25/22.82/15.15/N.A.	46.27/38.49/32.78/N.A.
	30	17.58/16.61/13.88/N.A.	32.48/27.65/19.28/N.A.	46.94/44.36/37.07/N.A.
	40	15.84/14.51/12.34/N.A.	36.94/23.89/16.99/N.A.	42.33/38.79/32.99/N.A.
	Neat	2.78/2.78/1.81/N.A.	4.50/3.66/1.89/N.A.	6.51/6.46/4.24/N.A.

Table S4. Recently reported pyrimidine based TADF OLEDs.

Compounds	V (V)	$EQE_{max/100/1000/10000}$ [%]	$PE_{max/100/1000/10000}$ [lm/W]	$CE_{max/100/1000/10000}$ [cd/A]	Ref.
o-2SPAc-PPM[a]	3.40	24.80/20.50/16.62/11.69	67.58/43.17/26.10/13.71	73.14/60.46/49.01/34.47	**This work**
o-2SPAc-PPM[b]	3.40	19.58/19.58/18.15/11.61	42.52/42.52/32.11/14.04	59.55/59.55/55.20/35.31	**This work**
m-2SPAc-PPM	3.50	17.58/16.61/13.88/N.A.	32.48/27.65/19.28/N.A.	46.94/44.36/37.07/N.A.	**This work**
2DPAc-PPM	3.60	20.80/12.40/N.A./N.A.	31.50/14.60/N.A./N.A.	38.10/23.50/N.A./N.A.	[S2]
2DPAc-MPM	3.60	19.00/9.40/N.A./N.A.	27.90/11.10/ N.A./N.A.	32.00/16.50/N.A./N.A.	[S2]
Ac-HPM	2.85	20.90/17.60/11.70/N.A.	60.30/38.20/20.00/N.A.	54.70/46.00/30.60/N.A.	[S3]
Ac-PPM	2.93	19.00/16.60/11.20/N.A.	52.80/33.80/17.40/N.A.	49.20/43.20/29.00/N.A.	[S3]
Ac-MPM	2.93	20.40/16.10/9.70/N.A.	49.90/29.20/13.20/N.A.	46.60/36.80/22.10/N.A.	[S3]
Ac-NPM	2.88	14.4/5.61/2.16/N.A.	30.50/8.19/1.86/N.A.	27.80/10.80/3.97/N.A.	[S4]
Ac-1MHPM	3.16	24.00/19.00/11.20/N.A.	45.10/26.20/11.60/N.A.	46.00/26.20/11.60/N.A.	[S5]
Ac-2MHPM	3.24	19.80/15.90/9.60/N.A.	35.80/20.90/9.50/N.A.	36.90/29.70/18.00/N.A.	[S5]
Ac-3MHPM	3.25	17.80/10.40/ N.A./N.A.	19.60/7.90/ N.A./N.A.	19.90/11.70/N.A./N.A.	[S5]
Ac-46MHPM	2.95	11.80/4.48/1.73/N.A.	19.70/5.45/1.29/N.A.	19.30/6.96/2.46/N.A.	[S6]
Ac-26MHPM	2.87	18.60/11.90/6.34/N.A.	43.50/21.20/8.61/N.A.	43.50/21.20/8.61/N.A.	[S6]
CzAc-26MHPM	2.87	22.80/14.90/9.28/N.A.	59.20/29.30/14.10/N.A.	53.90/35.30/21.90/N.A.	[S6]
T1	3.20	7.20/5.60/N.A./N.A.	12.00/8.20/N.A./N.A.	13.40/10.40/N.A./N.A.	[S7]
T2	3.00	12.60/12.60/N.A./N.A.	29.80/21.00/N.A./N.A.	34.20/28.10/N.A./N.A.	[S7]
T3	3.00	11.80/4.20/N.A./N.A.	19.60/4.70/N.A./N.A.	18.80/6.50/N.A./N.A.	[S7]
T4	3.00	11.80/10.3/N.A./N.A.	21.50/15.50/N.A./N.A.	24.00/21.00/N.A./N.A.	[S7]
2SPAc-PPM	3.60	31.45/18.34/10.84/N.A.	56.85/23.78/9.55/N.A.	68.77/40.11/23.71/N.A.	[S8]
2SPAc-HPM	3.60	25.56/18.86/11.94/N.A.	51.60/26.65/12.98/N.A.	57.50/42.42/26.85/N.A.	[S8]
2SPAc-MPM	3.60	24.34/16.14/9.16/N.A.	42.45/20.03/7.68/N.A.	50.00/33.15/18.82/N.A.	[S8]
DPAc-4PyPM	4.60	24.34/17.53/8.65/N.A.	36.79/17.74/5.89/N.A.	53.89/39.54/19.51/N.A.	[S9]

DPAc-3PyPM	4.80	22.42/11.27/2.59/N.A.	23.45/7.20/1.04/N.A.	35.85/18.80/4.45/N.A.	[S9]
DPAc-TPPM	4.2	16.80/6.86/N.A./N.A.	19.49/4.90/N.A./N.A.	26.07/10.93/N.A./N.A.	[S9]

N.A: not available. [a]40 wt% *o*-2SPAc-PPM doped DPEPO. [b]60 wt% *o*-2SPAc-PPM doped DPEPO.

Table S5. Recently reported efficient TADF OLEDs.

Compounds	V (V)	$EQE_{max/100/1000/10000}$ [%]	$PE_{max/100/1000/10000}$ [lm/W]	$CE_{max/100/1000/10000}$ [cd/A]	Ref.
DBT-BZ-PXZ	3.2	19.2/N.A./15.4/N.A.	59.2/N.A./21.8/N.A	60.6/N.A./48.6/N.A	[S10]
DBT-BZ-PTZ	3.2	15.1/N.A./9.7/N.A.	43.3/N.A./13.6/N.A	46.0/N.A./29.5/N.A	[S10]
5PXZ-PIDO	N.A.	14.40/N.A./10.80/4.60	33.10/N.A./19.90/5.60	43.30/N.A./32.30/13.50	[S11]
5,6PXZ-PIDO	N.A.	16.90/N.A./14.20/8.10	38.70/N.A./26.20/10.80	49.30/N.A./26.20/23.60	[S11]
DCzIPN	4.0	16.40/N.A./7.60/N.A.	15.90/N.A./4.80/N.A.	N.A./N.A./N.A./N.A.	[S12]
DDCzIPN	3.5	18.90/N.A./15.80/N.A.	38.30/N.A./21.50/N.A.	N.A./N.A./N.A./N.A.	[S12]
Cz-VPN	4.4	8.70/4.80/3.10/ N.A.	12.30/3.80/1.7/ N.A.	18.00/10.00/6.40/N.A.	[S13]
Ac-VPN	4.5	18.90/18.00/16.40/N.A.	51.70/45.50/41.50/N.A.	34.10/27.10/22.30/N.A.	[S13]
Px-VPN	4.7	14.90/14.90/13.60/N.A.	26.70/19.90/11.80/N.A.	45.40/43.00/33.20/N.A.	[S13]
Ac-CNP	4.7	13.00/12.00/9.10/N.A.	26.10/15.30/9.10/N.A.	38.10/34.10/26.00/N.A.	[S13]
Px-CNP	5.5	3.00/3.00/2.80/N.A.	3.10/2.90/1.70/N.A.	5.80/5.80/5.10/N.A.	[S13]
ACRDSO2	3.5	19.20/17.60/13.10/N.A.	N.A./N.A./N.A./N.A.	61.80/N.A./N.A./N.A.	[S14]
PXZDSO2	3.7	16.70/16.30/13.70/N.A.	N.A./N.A./N.A./N.A.	49.30/N.A./N.A./N.A.	[S14]

N.A: not available.

Cartesian coordinates of the optimized structures for *o*-2SPAc-PPM

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.094729	2.292336	-0.203945
2	6	0	-0.530232	1.212558	0.289505
3	6	0	-0.178991	-0.067892	-0.144483
4	6	0	0.854014	-0.179418	-1.085379
5	7	0	1.458885	0.905232	-1.586765
6	6	0	1.047901	2.099488	-1.131329
7	6	0	1.686214	3.314417	-1.703303
8	6	0	2.630520	3.204494	-2.735197
9	6	0	3.224155	4.345259	-3.272599
10	6	0	2.883927	5.610115	-2.787692
11	6	0	1.942717	5.727417	-1.761513
12	6	0	1.346240	4.589594	-1.223101
13	6	0	-1.492104	1.464691	1.419669
14	6	0	1.234718	-1.520838	-1.629721
15	6	0	-0.840915	2.105235	2.491854
16	6	0	-1.423771	2.292326	3.734161
17	6	0	-2.706692	1.798570	3.928948
18	6	0	-3.399359	1.208796	2.879759
19	6	0	-2.864200	1.064491	1.578862
20	6	0	2.543013	-2.078837	-1.708742
21	6	0	2.692565	-3.241569	-2.494245
22	6	0	1.613012	-3.904155	-3.068120
23	6	0	0.318765	-3.423819	-2.889242
24	6	0	0.158255	-2.234281	-2.187579
25	6	0	-4.761798	3.331832	-1.743302
26	6	0	-6.103637	3.013307	-1.945125
27	6	0	-6.629688	1.853604	-1.378899
28	6	0	-5.849804	1.016977	-0.573311
29	6	0	-4.506700	1.385909	-0.313147
30	6	0	-3.965642	2.514923	-0.944265
31	6	0	-6.377243	-0.316957	-0.014737
32	6	0	-5.184925	-1.307075	-0.088068
33	6	0	-3.867879	-0.844086	0.172905
34	7	0	-3.685063	0.539851	0.514035

35	6	0	-5.356632	-2.649713	-0.447255
36	6	0	-4.271556	-3.513781	-0.577041
37	6	0	-2.981218	-3.034198	-0.376491
38	6	0	-2.784126	-1.703309	-0.016631
39	6	0	-7.593625	-0.850253	-0.785035
40	6	0	-8.709146	-1.010519	0.049093
41	6	0	-8.343886	-0.589609	1.400525
42	6	0	-6.995373	-0.169515	1.404961
43	6	0	-7.680721	-1.165170	-2.138760
44	6	0	-8.889991	-1.646433	-2.651429
45	6	0	-9.999629	-1.812238	-1.815494
46	6	0	-9.917145	-1.495531	-0.459261
47	6	0	-9.119559	-0.546945	2.560362
48	6	0	-8.546555	-0.075548	3.739930
49	6	0	-7.218085	0.349830	3.746996
50	6	0	-6.444040	0.302448	2.580916
51	6	0	2.224766	-2.456673	2.294556
52	6	0	3.191387	-1.935721	3.145135
53	6	0	4.336289	-1.361303	2.606094
54	6	0	4.520017	-1.256951	1.223359
55	6	0	3.487966	-1.683166	0.356684
56	6	0	2.373463	-2.342279	0.913582
57	6	0	5.851932	-0.767819	0.630531
58	6	0	6.125118	-1.612859	-0.626565
59	6	0	5.012389	-1.962603	-1.462093
60	7	0	3.703749	-1.517532	-1.085069
61	6	0	7.403054	-2.094095	-0.929570
62	6	0	7.601776	-2.882692	-2.060042
63	6	0	6.529681	-3.188486	-2.900944
64	6	0	5.608608	-1.494265	-2.640776
65	6	0	6.998213	-0.879689	1.642805
66	6	0	7.596586	0.371599	1.869270
67	6	0	6.915863	1.374717	1.043079
68	6	0	5.888044	0.745701	0.313600
69	6	0	7.466308	-2.013974	2.299316
70	6	0	8.536994	-1.890181	3.190692
71	6	0	9.130791	-0.643343	3.419364
72	6	0	8.665426	0.495773	2.760693
73	6	0	7.157602	2.742205	0.902925
74	6	0	6.364086	3.481458	0.022862
75	6	0	5.345062	2.856956	-0.702770
76	6	0	5.100833	1.485192	-0.562654
77	1	0	-0.660577	-0.949880	0.247584
78	1	0	2.889495	2.220741	-3.107779
79	1	0	3.954513	4.241669	-4.070650
80	1	0	3.347789	6.499417	-3.207062
81	1	0	1.672642	6.708717	-1.379727
82	1	0	0.614546	4.669845	-0.427111
83	1	0	0.177120	2.440268	2.318333
84	1	0	-0.880484	2.788770	4.532389
85	1	0	-3.189999	1.873969	4.899731
86	1	0	-4.390194	0.852905	3.076671
87	1	0	3.683676	-3.642199	-2.658022
88	1	0	1.798626	-4.800386	-3.654596
89	1	0	-0.541098	-3.936456	-3.309067
90	1	0	-0.832930	-1.801777	-2.095981
91	1	0	-4.325360	4.206336	-2.218066
92	1	0	-6.734582	3.649361	-2.559531
93	1	0	-7.662783	1.585152	-1.572099
94	1	0	-2.914023	2.745391	-0.810240
95	1	0	-6.356445	-3.025144	-0.634249

96	1	0	-4.438127	-4.552730	-0.847070
97	1	0	-2.122769	-3.688070	-0.503022
98	1	0	-1.787901	-1.330509	0.137007
99	1	0	-6.821343	-1.037484	-2.791309
100	1	0	-8.967502	-1.891676	-3.707154
101	1	0	-10.932888	-2.188650	-2.225895
102	1	0	-10.780957	-1.623595	0.187930
103	1	0	-10.156331	-0.873488	2.545512
104	1	0	-9.134693	-0.038416	4.652870
105	1	0	-6.775999	0.726181	4.665899
106	1	0	-5.428828	0.644511	2.610703
107	1	0	1.351548	-2.961755	2.698042
108	1	0	3.073833	-2.000225	4.223182
109	1	0	5.112529	-1.001113	3.271789
110	1	0	1.620786	-2.760255	0.266090
111	1	0	8.234989	-1.854789	-0.277440
112	1	0	8.593504	-3.281005	-2.266105
113	1	0	6.667995	-3.818177	-3.775844
114	1	0	5.066373	-0.790189	-3.272600
115	1	0	7.007245	-2.982850	2.123540
116	1	0	8.910255	-2.769290	3.708936
117	1	0	9.961673	-0.561706	4.115174
118	1	0	9.129523	1.462045	2.940559
119	1	0	7.953170	3.225054	1.464940
120	1	0	6.540675	4.546818	-0.099355
121	1	0	4.729917	3.439577	-1.383086
122	1	0	4.296897	1.023321	-1.124115

Cartesian coordinates of the optimized structures for *m*-2SPAc-PPM .

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.139483	-4.156052	-0.401910
2	6	0	-1.141919	-2.763186	-0.400996
3	6	0	-0.000044	-2.051697	0.000140
4	6	0	1.141811	-2.763210	0.401286
5	6	0	1.139340	-4.156076	0.402219
6	6	0	-0.000080	-4.857162	0.000160
7	6	0	-0.000025	-0.566250	0.000126
8	7	0	1.161526	0.053012	0.265010
9	6	0	1.164024	1.394554	0.282223
10	6	0	0.000006	2.118798	0.000130
11	6	0	-1.164021	1.394585	-0.281990
12	7	0	-1.161552	0.053038	-0.264776
13	6	0	2.455720	2.059730	0.598727
14	6	0	-2.455696	2.059778	-0.598532
15	6	0	3.657985	1.367375	0.387259
16	6	0	4.884178	1.968400	0.669451
17	6	0	4.925082	3.270796	1.179544
18	6	0	3.734771	3.963083	1.401901
19	6	0	2.509282	3.364693	1.112606
20	6	0	-2.509217	3.364749	-1.112413
21	6	0	-3.734679	3.963147	-1.401782
22	6	0	-4.925013	3.270868	-1.179491
23	6	0	-4.884150	1.968477	-0.669401
24	6	0	-3.657977	1.367438	-0.387132
25	7	0	6.104689	1.248945	0.437674
26	7	0	-6.104707	1.249069	-0.437706
27	6	0	6.761130	1.389141	-0.799537
28	6	0	7.960634	0.699899	-1.063893

29	6	0	8.609123	-0.244093	-0.045500
30	6	0	7.817623	-0.293766	1.266094
31	6	0	6.624880	0.429944	1.458069
32	6	0	-6.760609	1.388399	0.799885
33	6	0	-7.959822	0.698717	1.064406
34	6	0	-8.608866	-0.244420	0.045587
35	6	0	-7.817159	-0.294308	-1.265879
36	6	0	-6.624637	0.429737	-1.457966
37	6	0	6.219010	2.227851	-1.796180
38	6	0	6.852442	2.382877	-3.022209
39	6	0	8.043744	1.706317	-3.289518
40	6	0	8.576609	0.877159	-2.309521
41	6	0	8.293821	-1.093678	2.313024
42	6	0	7.630044	-1.195034	3.529892
43	6	0	6.448778	-0.474194	3.713223
44	6	0	5.952250	0.327737	2.693999
45	6	0	-6.218259	2.226714	1.796739
46	6	0	-6.851123	2.380830	3.023174
47	6	0	-8.042072	1.703730	3.290698
48	6	0	-8.575204	0.875028	2.310463
49	6	0	-8.293149	-1.094485	-2.312696
50	6	0	-7.629375	-1.195794	-3.529570
51	6	0	-6.448323	-0.474632	-3.713015
52	6	0	-5.952000	0.327562	-2.693897
53	6	0	10.078076	0.140422	0.209266
54	6	0	10.947348	-0.896412	-0.178354
55	6	0	10.144645	-2.010394	-0.704144
56	6	0	8.784478	-1.655252	-0.637049
57	6	0	-10.077433	0.141503	-0.209409
58	6	0	-10.947719	-0.894692	0.177647
59	6	0	-10.146129	-2.009561	0.703260
60	6	0	-8.785631	-1.655605	0.636602
61	6	0	10.579066	1.320950	0.743834
62	6	0	11.962770	1.464439	0.891741
63	6	0	12.829587	0.434947	0.507625
64	6	0	12.328992	-0.752704	-0.029992
65	6	0	10.526262	-3.254277	-1.212533
66	6	0	9.536019	-4.135804	-1.651163
67	6	0	8.184181	-3.779904	-1.583012
68	6	0	7.801281	-2.534358	-1.074101
69	6	0	-10.577238	1.322657	-0.743697
70	6	0	-11.960778	1.467420	-0.891901
71	6	0	-12.828602	0.438564	-0.508360
72	6	0	-12.329196	-0.749714	0.028979
73	6	0	-10.528973	-3.253268	1.211164
74	6	0	-9.539618	-4.135817	1.649740
75	6	0	-8.187447	-3.781099	1.582016
76	6	0	-7.803321	-2.535729	1.073601
77	1	0	-2.028191	-4.695659	-0.718193
78	1	0	-2.020921	-2.211164	-0.713912
79	1	0	2.020828	-2.211206	0.714193
80	1	0	2.028035	-4.695700	0.718508
81	1	0	-0.000095	-5.944075	0.000166
82	1	0	0.000016	3.201189	0.000154
83	1	0	3.627491	0.355779	-0.001061
84	1	0	5.885923	3.726241	1.399362
85	1	0	3.761596	4.969727	1.809255
86	1	0	1.592082	3.908704	1.316866
87	1	0	-1.591998	3.908749	-1.316619
88	1	0	-3.761473	4.969792	-1.809135
89	1	0	-5.885840	3.726314	-1.399365

90	1	0	-3.627506	0.355837	0.001179
91	1	0	5.294434	2.758298	-1.605115
92	1	0	6.409128	3.035871	-3.769403
93	1	0	8.547691	1.820273	-4.244658
94	1	0	9.501461	0.342494	-2.506436
95	1	0	9.213757	-1.650089	2.157742
96	1	0	8.027013	-1.825378	4.320046
97	1	0	5.906673	-0.533023	4.653328
98	1	0	5.034370	0.880154	2.852009
99	1	0	-5.293944	2.757560	1.605514
100	1	0	-6.407641	3.033535	3.770522
101	1	0	-8.545554	1.816948	4.246171
102	1	0	-9.499818	0.339994	2.507506
103	1	0	-9.212925	-1.651139	-2.157324
104	1	0	-8.026197	-1.826327	-4.319647
105	1	0	-5.906212	-0.533432	-4.653118
106	1	0	-5.034266	0.880197	-2.851987
107	1	0	9.906848	2.120879	1.043275
108	1	0	12.367900	2.382685	1.308569
109	1	0	13.902298	0.560810	0.628759
110	1	0	13.006769	-1.549307	-0.326593
111	1	0	11.575053	-3.535241	-1.267775
112	1	0	9.817800	-5.107044	-2.049270
113	1	0	7.425375	-4.476792	-1.928816
114	1	0	6.750825	-2.259900	-1.022674
115	1	0	-9.904235	2.122090	-1.042699
116	1	0	-12.364994	2.386169	-1.308511
117	1	0	-13.901170	0.565418	-0.629727
118	1	0	-13.007755	-1.545820	0.325130
119	1	0	-11.578028	-3.533308	1.266071
120	1	0	-9.822356	-5.106933	2.047470
121	1	0	-7.429344	-4.478776	1.927768
122	1	0	-6.752611	-2.262183	1.022516

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3. References

[S1] W. J. Zhao, Z. K. He, J. W. Y. Lam, Q. Peng, H. L. Ma, Z. G. Shuai, G. X. Bai, J. H. Hao, B. Z. Tang, *Chem*, *1*, 592.

[S2] B. W. Li, Z. Y. Li, T. P. Hu, Y. Zhang, Y. Wang, Y. P. Yi, F. Y. Guo, L. C. Zhao, *J. Mater. Chem. C* **2018**, *6*, 2351.

[S3] I. S. Park, J. Lee, T. Yasud, *J. Mater. Chem. C* **2016**, *4*, 7911.

[S4] R. Komatsu, H. Sasabe, Y.Seino, K. Nakao, J. Kido, *J. Mater. Chem. C* 2016, *4*, 2274.

[S5] R. Komatsu, H. Sasabe, K. Nakao, Y. Hayasaka, T. Ohsawa, J. Kido, *Adv. Opt. Mater.* **2017**, *5*, 1600675.

[S6] R. Komatsu, T. Ohsawa, H. Sasabe, K. Nakao, Y. Hayasaka, J. Kido, *ACS Appl. Mater. Interfaces*, **2017**, *9*, 4742.

[S7] P. Ganesan, R. Ranganathan, Y. Chi, X. K. Liu, C.-S. Lee, S.-H. Liu, G.-H. Lee, T.-C. Lin, Y.-T. Chen, P.-T. Chou, *Chem. Eur. J.* **2017**, *23*, 2858.

[S8] K. Nakao, H. Sasabe, R. Komatsu, Y. Hayasaka, T. Ohsawa, J. Kido, *Adv. Opt. Mater.* **2017**, *5*, 1600843.

[S9] Q. Zhang, S. Q. Sun, X. L. Lv, W. Liu, H. X. Zeng, R. D. Guo, S. F. Ye, P. P. Leng, S. P. Xiang, L. Wang, *Mater. Chem. Front.* **2018**, *2*, 2054.

[S10] J. J. Guo, X. L. Li, H. Nie, W. W. Luo, R. R. Hu, A. J. Qin, Z. J. Zhao, S. J. Su, B. Z. Tang, *Chem. Mater.* **2017**, *29*, 3623.

[S11] Y. P. Xiang, Z. L. Zhu, D. J. Xie, S. L. Gong, K. L. Wu, G. H. Xie, C.-S. Lee, C. L. Yang, *J. Mater. Chem. C*, **2018**, *6*, 7111.
[S12] Y. J. Cho, S. K. Jeon, B. D. Chin, E. Yu, J. Y. Lee, *Angew. Chem., Intl. Ed.* **2015**, *54*, 5201.
[S13] I. S. Park, S. Y. Lee, C. Adachi, T. Yasuda, *Adv. Funct. Mater.* **2016**, *26*, 1813.
[S14] G. Z. Xie, X. L. Li, D. J. Chen, Z. H. Wang, X. Y. Cai, D. C. Chen, Y. C. Li, K. K. Liu, Y. Cao, S. J. Su, *Adv. Mater.* **2016**, *28*, 181.