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# Highly Efficient Blue Organic Light-Emitting Diodes from COS746F Pyrimidine-Based Thermally Activated Delayed Fluorescence Emitters

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#### Abstract

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Three highly efficient blue thermally activated delayed fluorescence (TADF) emitters, 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM, have been synthesised based on pyrimidine (PM), 2-methylpyrimidine (MPM) and 2-phenylpyrimidine (PPM) as the acceptor and 10H-spiro[acridan-9,9'-fluorene] (2SPAc) as the donor moiety, respectively. With the appropriate molecular design, these emitters successfully achieve small singlet-triplet splitting energies for efficient reverse intersystem crossing, and exhibit high photoluminescence quantum yields. As a result, the TADF OLEDs based on 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM emit blue light peaking at 479-489 nm and generate the very high the external quantum efficiency of 25.56%, 24.34% and 31.45%, respectively. The 2SPAc-PPM based TADF OLEDs also is one of the very few blue TADF emitters with the external quantum efficiency of more than 30% and is the best OLED performance among the pyrimidine-based TADF emitters.

Organic lighting-emitting diodes (OLEDs) with the advantages of such as lightweight, ultra-thin, large-area and flexibility, etc have been considered as one of the most promising applications in the new generation of full-color flat panel displays and solid-state lightings since the first report by Tang in 1987.<sup>1</sup> In order to achieve the near-unity internal quantum efficiency, the utilizations of both singlet (25%) and triplet excitons (75%) should be maximized. In the past decades, noble metals contained phosphorescent OLEDs (ph-OLEDs) has become a representative technology to realize 100% conversion of electrons to photons. The green and red ph-OLEDs containing the phosphorescent iridium-based emitters have been easily achieved with high efficiencies,<sup>2, 3</sup> however the blue ph-OLEDs currently are still suffering the inferior device performances for the practical applications compared to its green and red counterparts, regardless of the critical high cost and stability issues.

Recently, the metal-free pure-organic thermally activated delay fluorescent (TADF) OLEDs have received considerable attentions as the new generation and alternative technology to reach the high efficiency, especially for the blue OLEDs.<sup>4-6</sup> In TADF emitters, the up-conversion of triplet states (T<sub>1</sub>) to emissive singlet states (S<sub>1</sub>) *via* a reverse intersystem crossing (RISC) realizes the harvests of both singlet and triplet excitons, in which a small splitting energy ( $\Delta E_{ST}$ ) between singlet and triplet excited energies is critically important in the thermodynamical RISC process. Regarding the molecular design, TADF emitter normally possesses a twisted intramolecular charge transfer (TICT) framework with a very small spatial overlap between the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO). Employing this strategy, the research efforts have focused on the design of donor-acceptor (D-A) typed TADF emitters for realizing highly efficient TADF OLEDs.<sup>6-9</sup> Various donors and acceptors have been applied by considering their electron-donating or electron-withdrawing capabilities.<sup>9-23</sup> Among theses acceptors, however,

pyrimidine (PM), which is the two nitrogen-contained six-memberedheterocycle Vandete Online possesses an asymmetric molecular structure with the rather strong electron-withdrawing characteristic and the intrinsic high triplet (T<sub>1</sub>) energy level, has received less attentions in constructing the TADF emitters. The current PM-based TADF emitters only possess the external luminescence quantum efficiency ( $\eta_{ext}$ ) of less than 25% in TADF OLEDs mainly due to the relatively low photoluminescence quantum yield induced by the inappropriated molecular orientations and packing behaviors.<sup>4, 8, 24-26</sup> Therefore, the rational molecular design is highly necessary and also challenged with the aim of improving the device performances of PM-based TADF emitters.

In this work, we designed and synthesized three highly efficient blue TADF materials 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM (Scheme 1), which are based on a highly twisted donor-acceptor-donor (D-A-D) structures with pyrimidine (PM), 2-methylpyrimidine (MPM) and 2-phenylpyrimidine (PPM) as the acceptor unit and 10H-spiro[acridan-9,9'fluorene] (SPAc) as the donor moieties, respectively. The bulky, rigid and steric SPAc structure was selected because it could provide the improved photoluminescence quantum yields (PLQYs), strongly horizontally oriented emitting dipoles and even a blue-shifted emission compared to the 9,10-dihydroacridine.<sup>6</sup> 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM exhibit the obvious TADF phenomena with  $\Delta E_{\rm ST}$  of 0.15 eV, 0.19 eV, and 0.16 eV, respectively. The electroluminescence (EL) of three molecules from their TADF OLEDs showed the emission peak ( $\lambda_{em}$ ) of 479-489 nm. The device performances varied with the substitutes of pyrimidine under same device conditions. The highest  $\eta_{ext}$  of these blue TADF OLEDs based on 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM are as high as 25.56%, 24.34% and 31.45%, respectively. To our best knowledge, the device performance of 2SPAc-PPM is the best among the pyrimidine TADF emitters, and is also comparable with those of the state-of-the-art triazine-based TADF and phosphorescent OLEDs.<sup>27, 28</sup>



Scheme 1. The synthetic routes toward 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM.



Fig. 1. The HOMO and LUMO distributions for 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM.

**Results and Discussions** 

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The synthetic rotues for 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM are showing the conversion of the spinol of the spino

Compounds	$T_{\rm m}/T_{\rm d}^{\rm a)}$	HOMO <sup>b)</sup>	LUMO <sup>c)</sup>	$E_{g}^{\text{opt d})}$	$E_{s}^{e)}$	$\boldsymbol{E}_{\mathbf{T}}^{\mathrm{f}}$	$\Delta E_{\rm ST}^{\rm g)}/\Delta E_{\rm ST}^{\rm h)}$
	(°C)	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)
2SPAc-HPM	432/518	-5.46	-2.60	2.86	2.94	2.79	0.15/0.030
2SPAc-MPM	426/487	-5.45	-2.54	2.91	2.98	2.79	0.19/0.018
2SPAc-PPM	461/535	-5.45	-2.57	2.88	2.95	2.79	0.16/0.015

**Table 1.** HOMO, LUMO,  $E_g^{opt}$ ,  $E_S$ ,  $E_T$  and  $\Delta E_{ST}$  values of three TADF molecules.

<sup>a)</sup> $T_{\rm m}$  was measured by DSC;  $T_{\rm d}$  was measure by TGA. <sup>b)</sup>HOMO was calculated from the oxidation potential. <sup>c)</sup>LUMO were calculated from  $E_{LUMO} = E_{HOMO} - E_g^{opt}$ . <sup>d)</sup>  $E_g^{opt}$  was obtained from the absorption edge of normalized absorption spectrum. <sup>e)</sup>Estimated from the onset of fluorescence spectrum in toluene (5 × 10<sup>-5</sup> M) at 300 K. <sup>f)</sup>Estimated from the onset of phosphorescence spectrum in toluene (5 × 10<sup>-5</sup> M) at 77 K. <sup>g)</sup>Singlet-triplet energies splitting determined experimentally using  $\Delta E_{\rm ST} = E_{\rm S} - E_{\rm T}$ . <sup>h)</sup>Singlet-triplet energies splitting calculated using Berberan-Santos plot.

To better understand the molecular orbital distribution of these TADF molecules, we utilized the density function theory (DFT) calculation at the B3LYP/6-31G(d) level to

investigate the geometric and electronic structures of 2SPAc-HPM, 2SPAc-MPM and 2SPActicle Online PPM. As shown in Fig. 1, it can find that the optimized molecular geometrics for the TADF molecules are apparently twisted and show the large dihedral angle of near 90° between the SPAc moiety and the phenyl spacer. The HOMO and LUMO delocalizations of the three TADF molecules are very similar since they have almost identical chemical structures. The HOMO are mainly located on the SPAc moiety with a small portion spreading on the phenyl spacer, while the LUMO are mainly delocalized on the pyrimidine unit with partial extending to the phenyl spacer. It therefore leads to a small frontier molecular orbitals (FMOs) overlap between the HOMO and LUMO delocalizations on the phenyl spacer for each TADF molecule, which can facilitate the radiative decay of 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM.<sup>29</sup> The experimental HOMO and LUMO energy levels of the three TADF molecules are measured by cyclic voltammetry (CV). It can find that each TADF molecule exhibited a reversible oxidation wave (Fig. S2). The HOMO energy levels were calculated from the onset of oxidation potential and were found to be -5.46 eV, -5.45 eV and -5.45 eV, respectively, for 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM. The almost identical HOMO energy levels are the result of the same SPAc moiety in the three TADF molecules, which is also consistent with the theoretical DFT calculations. The LUMO energy levels of 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM were at -2.60 eV, -2.54 eV and -2.57 eV, respectively, which were calculated from the equation of  $E_{LUMO} = E_{HOMO} - E_g^{opt}$ , where  $E_g^{opt}$  is the optical band-gap (Table 1). The slight varies on the LUMO energy levels of these TADF molecules are believed to be from the different substitute on the 2-poistion of pyrimidine unit. The slight higher LUMO energy levels of 2SPAc-MPM and 2SPAc-PPM compared to that of 2SPAc-HPM are mainly induced by the electron-donating properties of the methyl and phenyl groups. These results indicated that the substitutes on the donor and acceptor moieties play an important role on tuning the HOMO and LUMO energy levels of such TADF molecules,

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which are crucial for facilitating the hole and electron injections in the organice online bol: 10:10:99/C/YC05746F electroluminescent device.



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

The UV-Vis absorption and emission spectra of 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM in dilute toluene ( $10^{-5}$  M) are shown in **Fig. 2**. It can be found that these TADF molecules exhibit similar absorption properties and has a higher energy absorption band below 350 nm, which is attributed to the  $\pi$ - $\pi$ \* absorption of the conjugated aromatic moieties, where the much weaker absorption band at 350-425 nm with various peak is assigned to the intramolecular charge transfer (ICT) peak between the pyrimidine unit and the SPAc moiety, which also can be affirmed by **Fig. S3**. Upon the photoexcition of the ICT absorption, the photoluminescence (PL) spectra of 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM showed the intense blue emission with peaks at 469 nm, 460 nm and 464 nm, respectively. The blue-shifted emission peaks of 2SPAc-MPM and 2SPAc-PPM compared with that of 2SPAc-HPM and the slight changes on the ICT absorption are due to the different electron-donating properties of the hydrogen, methyl and phenyl substitutes on the pyrimidine units.<sup>4, 26</sup> For 2SPAc-PPM, the conjugation between pyrimidine and the slowen the an effect on the optical property. It is known that the solvent polarity has an effect

on the optical properties of the TADF materials. As shown in Fig. S4, the UV-Vis absorptionicle Online and PL spectra of the three TADF molecules in various polar solvents were investigated. The absorption spectra of 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM have no obvious solvent effect in various polar solvents as a result of the nonpolar ground states.<sup>30</sup> In contrast, the PL spectra of the three TADF molecules exhibited strong dependence on the solvent polarity (Fig. S4, Table S1). The PL spectra become broad with the full width at half maximum (FWHM) changing from ~55 nm (*n*-hexane,  $\varepsilon$ =1.90) to ~130 nm (DMF,  $\varepsilon$ =37.00) and bathochromically shifted ~100 nm with increasing polarity of solvents from n-hexane to DMF. These results clearly indicate that the emissions of the three TADF molecules are from the ICT states and show the larger transition of the dipole moment from the ground state to the excited state. To further make a quantitative analysis of the fluorescence solvachromism for the three TADF molecules, we plotted the curve of the stokes shift ( $\Delta v_{\text{Fl-Abs}}$ ) versus the orientation polarizability (f) and then calculated the change value of dipole moment ( $\Delta \mu_{e-g}$ ) according to the equations S1-S3.<sup>31</sup> As shown in Fig. S5, a well-fitted linear correlation between the stoke shifts and the orientation polarizability for all three TADF molecules. It demonstrates that the dependence of PL spectra on solvent polarity mainly ascribed to the dipole-dipole interactions between the molecule and solvent. Furthermore, the  $\Delta \mu_{e-g}$  values were calculated to be 4.29 D, 4.22 D and 4.34 D for 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM, respectively (Table S2). 2SPAc-PPM possess larger  $\Delta \mu_{e-g}$  than that of two other compounds, indicated that 2SPAc-PPM possess a more stable polarized excited state in the high polar solvents.

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To further investigate the photophysical and TADF properties of 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM. Fluorescence and phosphorescence spectra of the three TADF molecules are measured in toluene at 300 K and 77 K, respectively, as shown in **Fig. S6**. The  $S_1$  ( $E_S$ ) and  $T_1$  ( $E_T$ ) energies are determined from the onsets of fluorescence and phosphorescence spectra, respectively, and are summarized in **Table 1**. The  $\Delta E_{ST}$  values are obtained to be 0.15 eV, 0.19 eV and 0.16 eV for 2SPAc-HPM, 2SPAc-MPM and 2SPAc-

PPM, respectively. The small  $\Delta E_{ST}$  values support that the three TADF molecules/recaricle Online effectively harvest triplet excitons by the RISC process. It is known that oxygen can effectively quench the triplet state emission, and has no effect on the singlet state emission.<sup>32</sup> To study the delayed fluorescence (DF), the PL spectra in degassed and aerated toluene solution are investigated. As shown in **Fig. S7**, fluorescence intensity become much stronger in the absence of oxygen for 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM than that in the aerated solution, indicating a strong fluorescence quenching by oxygen as a result of suppressing the RISC process. These results exhibited that 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM could possess TADF property..

In order to further confirm the delayed fluorescence behavior of 2SPAc-HPM, 2SPAc-MPM, and 2SPAc-PPM in solid film, the transient PL delay curves of these three compounds in DPEPO host were measured at 300 K. As shown in Fig. 3a, all curves can be divided into the prompt and delayed decay components. The prompt decay component (Fig. 3b) with a transient decay time of 16.67, 13.56 and 16.80 ns were observed for 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM, respectively, corresponding to the relaxation of excitons from  $S_1$  to ground state (S<sub>0</sub>).<sup>33</sup> While the delayed decay component with the lifetimes ( $\tau_d$ ) of 52.23, 53.29, and 56.94 µs for 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM, respectively were estimated and may be rationalized as the thermal up-conversion of excitons from  $T_1$  to  $S_1$ .<sup>33, 34</sup> Moreover, the transient PL decay curves were also investigated under vacuum (Fig. S8) and exhibited that the delayed decay component is extremely sensitive to oxygen, which is different with prompt decay component and shows strong TADF characteristics. In addition, the temperature dependent transient PL decays of 2SPAc-HPM, 2SPAc-MPM, and 2SPAc-PPM were also investigated from 100 to 300 K (Fig. S9). It is found that the prompt decay curves showed no temperature dependence, and the delayed decay components exhibit pronounced temperature dependence. The ratio of delayed component were also gradually increased with increasing

temperature, which further demonstrates the presence of TADF features in the three VPM ticle Online Doi: 10.1039/C/TC05746F based TADF emitters.



**Fig. 3.** a, b)Transient PL characteristics of 10 wt% 2SPAc-HPM, 2SPAc-MPM, and 2SPAc-PPM doped in DPEPO film at 300 K. c) Temperature dependence of the  $\Phi_{PL}(squares)$ ,  $\Phi_{PF}$  (circle), and  $\Phi_{DF}$  (triangles) for 2SPAc-HPM (black), 2SPAc-MPM (red), and 2SPAc-PPM (blue). d) Energy diagram and photoluminescence process of 2SPAc-PPM.

**Table 2.** Physical properties of TADF molecules-doped DPEPO films.

Compounds	$\varPhi_{PL}{}^{ m a)}$	$\Phi_{\it PF}/\Phi_{\it DF}{}^{ m b)}$	$ au_{PF}^{ m c)}$	$\Phi_T$	$ au_{DF}^{d)}$	$k_{PF}$	<i>k</i> <sub>ISC</sub>	<i>k</i> <sub>nr</sub>	<i>k</i> <sub>r</sub>
	(%)	(%)	(ns)	(%)	(µs)	$(10^7 \text{ s}^{-1})$	(10 <sup>7</sup> s <sup>-1</sup> )	(10 <sup>5</sup> s <sup>-1</sup> )	(10 <sup>5</sup> s <sup>-1</sup> )
2SPAc-HPM	96.60	1.54/47.26	16.67	99.4	52.23	6.00	5.96	2.05	1.95
2SPAc-MPM	82.20	0.53/43.25	13.56	99.4	53.29	7.37	7.33	2.25	1.75
2SPAc-PPM	97.00	1.06/61.40	16.80	99.9	56.94	5.95	5.94	0.38	0.63

<sup>a)</sup>Absolute PLQYs measured using an integration sphere in nitrogen atmosphere. <sup>b)</sup>Estimated according to the prompt and delayed components in transient delay curve. <sup>c)</sup>PL lifetimes of prompt decay component. <sup>d)</sup>PL lifetimes of delayed decay component.

The PLQYs of the doped films in DPEPO host were measured at 300 K and listed in Table

2. The PLQYs ( $\Phi_{PL}$ ) of 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM at 20wt% doping ratioscie online are found to be 96.60%, 82.20% and 97.00%, respectively (Table S3), measured at nitrogen atmosphere under 320 nm excitation. It can find that 2SPAc-PPM with the phenyl substitute on PM unit possesses the highest PLQY, where 2SPAc-MPM with the methyl substitute on PM unit exhibits the lowest PLOY compared to that of 2SPAc-HPM. The highest PLOY of 2SPAc-PPM is believed to associate with the restricted torsion of phenyl ring induced by the hydrogen bonding of N-H between PM and phenyl spacer, and also the increased intermolecular distances, which will reduce the self-quenching of 2SPAc-PPM. It is known that the PLQYs are related to the oscillator strength (F) and the transition dipole moment (Q) for fluorescence, and the large F and Q values are necessary for achieving high quantum efficiency. Recent study has shown that the Strickler-Berg equations can also applied in the TADF molecules (equation. S5-S10, Fig. S10).<sup>35</sup> In our cases, the F values for 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM were calculated to be 0.029, 0.027 and 0.033, respectively, where the Q values are 1.62 D, 1.56 D and 1.72 D (**Table S4**), respectively, for 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM. In addition, the temperature dependence of PLQYs for the prompt ( $\Phi_{PF}$ ) and delayed ( $\Phi_{DF}$ ) TADF components are also calculated from  $\Phi_{PL}$  and the PL transient curves (Fig. 3c and Table 2). For all three TADF emitters, the  $\Phi_{PF}$ s are kept almost same at various temperatures and the slight increase with the decreased temperature indicates the suppression of the non-radiative decay from the S<sub>1</sub> to S<sub>0</sub>. However, the  $\Phi_{DF}$ s of all three TADF emitters are significant higher than  $\Phi_{PFS}$  and also show obviously dependence on temperature. The  $\Phi_{DF}$ s increased as the temperature increases, which is the typical phenomenon for TADF emitter and indicates the faster thermodynamically RISC process at higher temperature. Furthermore, the large  $\Phi_{DF}/\Phi_{PL}$  ratio of ~97-99% were also observed for the three TADF emitters from 77K to 300K (Table S5), indicating that a large portion of excited singlets and triplets underwent the efficient ISC and RISC processes between T<sub>1</sub> and  $S_1$  states.<sup>36</sup> The triplet formation efficiencies ( $\Phi_T$ ) were estimated to be 99.4%, 99.4% and

99.9% for 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM, respectively, according to Berberance control Santos equation (equation S4, Fig. S11). The almost 100%  $\Phi_T$  indicates that most of S<sub>1</sub> excitons are converted to T<sub>1</sub> excitons *via* ISC process. It is known that the up-conversion from T<sub>1</sub> to S<sub>1</sub> was dominated by the Arrhenius process.<sup>36, 37</sup> Therefore,  $\Delta E_{STS}$  can also be estimated to be 0.030, 0.018 and 0.015 eV for 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM, respectively (Table 1) based on Berberan-Santos equation. These small  $\Delta E_{ST}$  will ensure the high efficient up-conversion from T<sub>1</sub> excitons to S<sub>1</sub> excitons in these doped films, especially for 2SPAc-PPM. The experimental rate constants of higher  $k_{PF}$  and  $k_{ISC}$  and smaller  $k_{nr}$  and  $k_r$ also further proved the efficient ISC and RISC processes (Table 2). An energy diagram and photoluminescence process of three TADF emitters are shown in Fig. 3d. The high  $\Phi_{PL}$  and small  $\Delta E_{ST}$  in these TADF emitters, especially for 2SPAc-PPM, will make them to be the promising candidates for achieving high efficient blue TADF OLEDs.



Fig. 4. a) The energy level diagrams, b) OLED device structure, and c) the chemical structure of the materials used in the TADF devices.

In order to evaluate the device performances of 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM, multilayer OLEDs were fabricated by doping the three TADF emitters into the high triplet energy DPEPO host as the emissive layer (EML). The doping concentration Viewascle Online optimized for each TADF emitters (see the supporting information, Fig. S12-14, Table S6). The optimized device has the architecture of ITO/HATCN (5 nm)/TAPC (30 nm)/mCP (10 nm)/TADF emitter:DPEPO (x) wt% (20 nm)/DPEPO (5 nm)/TPBi (40 nm)/LiF (0.9 nm)/Al (100 nm). Among them, 2,3,6,7,10,11-hexacyano-1,4,5,8,9,12-hexazatriphenylene (HATCN) and di-[4-(N,N-ditoly-amino)-phenyl]cyclohexane (TAPC) were used as a hole injectionlaver (HTL) and a hole transporting layer (HTL), respectively. 1,3,5-tris(Nphenylbenzimidazol-2-yl)benzene (TPBi) and LiF were the electron transporting layer (ETL) and an electron injection layer (EIL), respectively. N,N-Dicarbazolyl-3,5-benzene (mCP) and (oxybis(2,1-phenylene))bis(diphenylphosphine oxide) (DPEPO) were inserted as excitons blocking layers (EBLs). The  $E_T$  levels of neighboring mCP and DPEPO were 3.00, and 3.30 eV, respectively, which are higher than the  $E_T$  of the three TADF emitters ( $E_T$ =2.79 eV) and can efficiently suppress the triplet excitons quenching and confine the triplet excitons within the EML. The energy level diagrams, OLED device structure, and the chemical structures of the materials used in the TADF devices are illustrated in Fig. 4.



Fig. 5. a) 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.

The EL spectra of the multi-layer OLEDs are exclusively from the three TADF emitters without the emission from the neighboring layers (**Fig. 5a** and **Fig. S12-14**). The devices of 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM exhibited bright blue EL emission with the peaks at 487 nm, 479 nm and 484 nm, respectively, which are consistent with their PL spectra and suggested that all devices possessed the efficient charge carrier injection, transport and recombination in the EML. Futhermore, the EL spectra at different voltages are also provided evaluate the device stability as shown in Fig. S15. The device performances of all TADF OLEDs are summarized in **Table 3**. **Fig. 5b** shows the *J-V-L* characteristics of all TADF OLEDs. The turn-on voltages were found at 3.5-3.6 V for the devices, indicating the similar carrier injection barrier as a result of the similar energy levels. Among the three TADF devices, 2SPAc-PPM device at 30% doping concentration achieved the highest EL

efficiencies with the best  $\eta_{ext}$  of 31.45%, the current efficiency ( $\eta_c$ ) of 68.77 cd  $A_{Det-1}^{-1}$  and there come power efficiency of 56.85 lm W<sup>-1</sup> at the low current densities in the absence of light outcoupling enhancement. The maximum luminance of 2SPAc-PPM device was 5600 cd m<sup>-2</sup>. For 2SPAc-HMP device, the best  $\eta_{ext}$  of 25.56%, the current efficiency ( $\eta_c$ ) of 57.50 cd A<sup>-1</sup> and the power efficiency of 51.60 lm W<sup>-1</sup> were obtained under same device conditions at 20% doping concentration. It is noted that the maximum luminance of 2SPAc-HMP device at 40% doping concentration could reach to 11900 cd m<sup>-2</sup> (**Table S6**). The device performances of 2SPAc-MPM, however, exhibited a lower  $\eta_{ext}$  of 24.34%, the current efficiency ( $\eta_c$ ) of 50.00 cd A<sup>-1</sup> and the power efficiency of 42.45 lm W<sup>-1</sup> compared to that of 2SPAc-PPM and 2SPAc-HPM devices. The 2SPAc-PPM-based TADF OLEDs in this report is one of the very few blue TADF emitters with  $\eta_{ext}$  of more than 30%. This excellent performance further affirmed the efficient up-conversion of triplet excitons from T<sub>1</sub> to S<sub>1</sub> through RISC process, which is also consistent with the above transient PL measurements.

Table 3. Summarized device performance of the 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM devices.

Emitter	<b>V</b> <sup>a)</sup> (V)	ηext <sup>b</sup> max/100/1000 (%)	$\eta_{p}^{b)}_{max/100/1000}$ (lm W <sup>-1</sup> )	$\eta_c  {}^{\rm b)}_{ m max/100/1000}$ (cd A <sup>-1</sup> )	Luminance (cd m <sup>-2</sup> )	CIE <sup>c)</sup>
2SPAc-HPM	3.5	25.56(24.58)/18.86/11.94	51.60(49.62)/26.65/12.98	57.50(55.28)/42.42/26.85	7200	(0.18,0.34)
2SPAc-MPM	3.6	24.34(22.54)/16.14/9.16	42.45(37.00)/20.03/7.68	50.00(46.30)/33.15/18.82	4100	(0.17,0.29)
2SPAc-PPM	3.6	31.45(28.50)/18.34/10.84	56.85(51.54)/23.78/9.55	68.77(62.34)/40.11/23.71	5600	(0.18,0.32)

<sup>a)</sup>Turn-on voltage at the luminance of 1 cd m<sup>-2</sup>; <sup>b)</sup>  $\eta_{ext}$ ,  $\eta_p$ , and  $\eta_c$  is external quantum efficiency, power efficiency, and current efficiency, respectively, averaged efficiency embedded in brackets; <sup>c)</sup>Commission Internationale deL'Eclairage (CIE) coordinates at 1000 cd m<sup>-2</sup>.

#### Conclusion

In summary, we synthesized three pyrimidine based TADF materials 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM with 10H-spiro[acridan-9,9'-fluorene] as the donor moieties and pyrimidine, 2-methylpyrimidine and 2-phenylpyrimidine as the acceptor unit, respectively. These three molecules with highly twisted D-A-D structure endow small  $\Delta E_{ST}$  of 0.15, 0.19,

and 0.16 eV, respectively, supporting the efficient TADF emission with higher PLOY increduce online doped films. As a result, the maximum  $\eta_{ext}$  of these blue TADF OLEDs based on 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM are as high as 25.56%, 24.34%, and 31.45%, respectively. Especially, the 2SPAc-PPM based TADF OLEDs also is one of the very few blue TADF emitters with the external quantum efficiency of more than 30%. To our best knowledge, the device performance is comparable with those of the state-of-the-art triazinebased TADF OLEDs and phosphorescent OLEDs. These confirm that 2SPAc-HPM, 2SPAc-MPM and 2SPAc-PPM are promising for candidates in the organic flat panel displays and solid-state lightings.

#### Electronic supplementary information (ESI) available: The Full experimental

details, additional equations and Figures for the characterizations of the optical properties, and the detailed devices performances.

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## TOC

# Highly Efficient Blue Organic Light-Emitting Diodes fromPyrimidine-BasedThermallyActivatedDelayed

## **Fluorescence Emitters**

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