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# The Strategy to Construct Multifunctional TADF Material for Deep Blue and High Efficiency Yellow Fluorescent Devices

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#### Abstract

Three deep blue thermally activated delayed fluorescence (TADF) molecules are designed by connecting three different sterically hindered electron-donating groups with 2,6-diphenylpyrimidine acceptor. The rigid structures based on carbazole derivatives endow them excellent thermal stability and high photoluminescence quantum yield (PLQY) about 0.72-0.74. A deep blue doped device based on SFI34pPM with a CIE<sub>v</sub> of 0.09 and a high external quantum efficiency (EQE) of 8.2% is achieved. Also, **3CzPhpPM** realizes a maximum EQE of 4.9% with a  $CIE_{xy}$  (0.15, (0.06). The high PLQY and triplet energy ( $\sim 2.84 \text{ eV}$ ) allow three deep blue compounds to be used as hosts for yellow TADF emitter, which realized high-performance yellow devices (EQE<sub>max</sub> = 18.6%) with alleviated efficiency roll-off. What's more, **3CzPhpPM** combining with TADF sensitizer and fluorescence material TBRb achieves a high EQE of 19.1%, which is among the best yellow fluorescent devices. The bipolar transporting ability and harvest of triplet excitions together ensure highly efficient yellow devices. Accordingly, these results shed light on the development of designing multifunctional deep blue TADF materials, particularly offer a smart way to construct high efficiency yellow fluorescence devices.

**Keywords**: thermally activated delayed fluorescence, deep-blue emitters, host, high efficiency, yellow fluorescence devices

#### Introduction

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Organic light-emitting diode (OLED) is known as dreamlike display device. In recent years, a variety of OLED products have entered our lives, such as smart phone, TV, notebook, wearable device and so on. Until now, the cost of OLED applications is still one of the bottlenecks restricting the rapid development of OLED industry. Organic luminescent materials are the core of OLED devices. Emitter molecules, which are able to harvest both singlet excitons and triplet excitons into emitted photons to achieve high device efficiency, become the focus of researchers. Except for expensive phosphorescence materials, the most efficient, inexpensive and easily available emitters are TADF materials.<sup>1,2</sup> The device performance of TADF devices gradually catches up with that of phosphorescent devices.<sup>3</sup> OLED display consists of red, green, and blue pixels. Since the eyes of human are relatively insensitive to blue light, more blue pixels are required in all kinds of display devices.<sup>4</sup> If the power consumption of the blue pixel is reduced, the power consumption of the entire display will be reduced largely. According to statistics, up to 30% of the electric energy is used for direct lighting, such as large-area TV or portable device display lighting. Thus, stable and efficient deep blue OLED is a major economic issue.5-7

In recent years, deep blue TADF materials have aroused extensive attention given the scarcity in OLED industry.<sup>8-11</sup> Several great-performance deep-blue emitters has been reported in recent years.<sup>12</sup> Blue TADF materials based on boron-containing molecules have been extensively investigated due to their narrow full-width at halfmaximum (FWHM) and high efficiency.<sup>13-17</sup> However, the synthetic yields of these compounds are relatively low. Triazine-based deep-blue emitters have also been reported, which need introduce methyl groups in the proper position to moderate electronic interaction.<sup>18, 19</sup> The synthesis process is relatively complicate adding methyl groups to the target compounds. The device stability is also important for blue devices, however the PO-containing and SO-containing materials may not satisfy the industrial demand.<sup>20, 21</sup> Briefly, our goal is to design chemically stable and easily available highefficiency deep blue TADF materials. In view of this, this paper designed three deep blue materials basing on chemical-stable carbazole derivatives, employing readily

available 2.6-diphenylpyrimidine as the acceptor. Apart of this, rigid donorspsuch as /DOTCO0039F carbazole derivatives could not only largely increase the radiative rate constant but also endow the molecules with rigid skeleton, suitable to be host materials.<sup>22</sup> Rare deep blue TADF has been reported with Commission International de L'Eclairage (CIE) coordinates of about (0.14, 0.08), which is the primary blue according to the National Television System Committee (NTSC) standard.<sup>23, 24</sup> In this work, SFI34pPM-based device realizes a high external quantum efficiency (EQE) of 8.2% with a  $CIE_{\nu}$  of 0.09. And the doped device based on **3CzPhpPM** shows a maximum EQE of 4.9% with a  $CIE_{x,v}$  of (0.15, 0.06).

The reported deep blue TADF materials mainly falls into two categories, one is emitter with low PLQY and a relatively small  $\Delta E_{\rm ST}$  (singlet-triplet energy splitting),<sup>25,</sup> <sup>26</sup> the other is molecule with high PLQY and larger  $\Delta E_{\rm ST}$ .<sup>27-30</sup> The latter ones are easy to obtain, but usually suffer from seriously device efficiency roll-off due to the long delayed lifetime of triplet excitons.<sup>31</sup> However, they can be ideal host materials for traditional fluorescence, phosphorescence and TADF materials because of the bipolar charge transport ability of D-A structure of TADF materials, small optical energy gap for carrier injection and relatively higher triplet energy compared with the common bipolar hosts and harvest of triplet excitons.<sup>32-34</sup> The efficient fluorescence OLEDs composed of a wide-energy-gap host, a TADF-assistant dopant and a fluorescent emitter dopant have been studied widely before. Adachi and his coworkers reported three fluorescence-based organic light-emitting diodes with TADF-assisted hosts and conventional hosts realizing EQE as high as 13.4-18.0% for blue, green, yellow and red emission.<sup>35</sup> Recently, Duan et al found, if the wide-gap host had TADF properties, the potential exciton loss pathways, involving Dexter energy transfer from the T<sub>1</sub> of both the host and the TADF sensitizer to that of the fluorescence dopant, could be reduced greatly.<sup>36</sup> However, the wide-energy-gap TADF host materials are hard to find for (2,8-di[t-butyl]-5,11-di[4-(t-butyl)phenyl]-6,12-**TBRb** fluorescence dopant diphenylnaphthacene), which is a normal yellow emitter in white devices.<sup>35, 37-39</sup> In the present work, we allow three deep blue TADF materials to be used as hosts for an yellow TADF emitter 34AcCz-Trz (5-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-

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13,13-dimethyl-8-phenyl-8,13-dihydro-5*H*-indolo[3, 2-*a*]acridine) to realize: high/DOTCO0039F efficiency yellow TADF devices with greatly relieved efficiency roll-off compared to traditional host CBP. Additionally, when using **3CzPhpPM** as the wide-gap host and combing with 34AcCz-Trz sensitizer and TBRb, the yellow device reached a high EQE of 19.1%. All of these demonstrates that **3CzPhpPM** is not only a good deep-blue emitter but also an excellent host material.

#### **Results and Discussion**

#### Synthesis and Characterization

**Scheme 1** depicts the synthetic routes for **SFI34pPM** as well as **SFI23pPM** and **3CzPhpPM**, which named as **PM** derivatives in following description. Firstly, the important intermediate 4-(4-bromophenyl)-2,6-diphenylpyrimidine was prepared according to the reported method previously.<sup>40, 41</sup> Then, the synthesis steps of SFI34 and SFI23 were already reported in our previous work.<sup>42</sup> And 3CzPh was facilely synthesized by Suzuki cross coupling reaction (**Scheme S1**, ESI<sup>†</sup>). Finally, the desired products were obtained from Buchwald-Hartwig coupling reaction with good yields. They were subjected to recrystallization, followed by temperature-gradient vacuum sublimation before the thermodynamics tests, photophysical measurements and device fabrication. The detailed synthesis steps and the confirmation of the chemical structures of the intermediate compounds and final products were described in experimental part.



Scheme 1. The synthesis process of three target compounds.

#### **Theoretical calculations**

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**Fig 1.** Molecular structures, HOMO/LUMO distributions and their energy level diagram for low-lying singlet and triplet excited states of three compounds.

To investigate the highest occupied molecular orbitals (HOMOs)/the lowest unoccupied molecular orbitals (LUMOs) distributions and excited energy states of these carbazole derivatives, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations using the B3LYP/6-31G(d) method were carried out, as illustrated in **Fig 1**. All the compounds show well-separated HOMO and LUMO orbitals, and the HOMO distributions are mainly located on carbazole and the connected five-membered ring and benzene, whereas the LUMO orbital distributions are similarly dispersed on 2,4,6-triphenylpyrimidine except for the 2substituted benzene. Before that, the calculations of three donor groups were conducted (as seen in **Fig S1**). It's obvious that the HOMO energy levels of the donors are gradually become deeper from SFI34 to SFI23 to 3CzPh, suggesting the electrondonating ability decreased gradually. The HOMO energy levels of **SFI34pPM**, **SFI23pPM** and **3CzPhpPM** follow the same trends, whereas the LUMO energy levels do not change apparently. In addition, a small change of the dihedral angles between/DOTCO0039F donors and acceptor of these compounds is seen, about  $52.6^{\circ}-54.5^{\circ}$ , which render them a larger conjugation degree and a higher oscillator strength (f = 0.2390-0.3009) compared to that with more twisted-structure materials. As calculated, the theoretical energy gap between the lowest singlet and triplet states are 0.22-0.32 eV for these **PM** derivatives, which demonstrates these emitters are potential TADF materials.

#### Thermal and electrochemical properties

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Fig 2. The electrochemical properties of the four compounds.

Thermal stability of the compounds was examined by thermogravimetric analysis (TGA) and differential Scanning Calorimeter (DSC) under N<sub>2</sub> atmosphere at a heating rate of 10 °C/min, as shown in Fig S2. The decomposition temperature ( $T_d$ ) is corresponding to the 5% weight loss, and all dyes show  $T_d$  in the range of 405 °C-449 °C. The glass transition temperature ( $T_g$ ) of **3CzPhpPM** is 110 °C. However, no obvious  $T_g$  is seen for **SFI34pPM** and **SFI23pPM** from 30 °C-300 °C. Above all, these compounds have excellent thermal stability. Cyclic voltammetry (CV) measurements on molecules in **Fig 2** were performed in dichloromethane (DCM) and *N*,*N*-dimethylformamide (DMF) via a traditional three-electrode system. The reversible redox peaks indicate their good electrochemical stabilities. Besides, the oxidation peaks are deriving from the electron-donating ability of the donors, which show more variety

than reduction peaks. The HOMO energy levels of **SFI34pPM**, **SFI23pPM**<sup>10</sup>and/DOTCO0039F **3CzPhpPM** are calculated to be -5.48 eV, -5.51 eV and -5.57 eV respectively, by calibrating the onset potential with ferrocene, which are well in good agreement with calculation data. The LUMO energy levels are also estimated from the reduction peaks (as seen in **Table 1**).

#### **Photophysical and TADF properties**



Fig 3. The UV-vis absorption and PL spectra of the compounds in toluene solution.

The photophysical properties of these compounds were investigated by UV-vis absorption and fluorescence spectroscopy in toluene. The absorption band before 314 nm could be ascribed to the  $\pi$ - $\pi$ \* and n- $\pi$ \* transition of the donor groups, and the absorption appearing in the wavelength range 352-367 nm is assigned to the intramolecular charge transfer (ICT) transition. Also, the extinction coefficient ( $\epsilon$ ) of three compounds in toluene was measured as seen in **Fig S3**, and it can be concluded that **3CzPhpPM** possesses the highest ICT transition probabilities among them. From the PL spectra, the emission peaks of **3CzPhpPM**, **SFI23pPM** and **SFI34pPM** are 412 nm, 414 nm and 424 nm, respectively. Compared with **3CzPhpPM**, the observed bathochromic shifts of **SFI23pPM** and **SFI34pPM** can be attributed to the enhanced ICT state, which was resulted from the increased electron-donating capacity of the donors. As shown in **Fig S4**, the emissions of **3CzPhpPM**, **SFI23pPM** and **SFI34pPM** are specified with the increase of solvent polarity from *n*-hexane to dichloromethane, which further manifests their ICT characteristic. Furthermore, the fluorescence and

phosphorescence spectra of three compounds at 77 K in dimethyl tetrahydroftfram are/DOTCO0039F obtained in **Fig S5**. The first singlet/triplet energies can be calculated from the onset of the emission, and the S<sub>1</sub>/T<sub>1</sub> are 3.08/2.84 eV, 3.20/2.84 eV and 3.22/2.83 eV for **SFI34pPM**, **SFI23pPM** and **3CzPhpPM**, respectively. And the energy gaps between singlet and triplet ( $\Delta E_{ST}$ s) are 0.24 eV, 0.36 eV and 0.39 eV, respectively, which are common values for deep blue materials. Further, NTO calculations were carried to demonstrate the property of the excited states as shown in **Fig S6**. Three compounds revealed the typical CT first singlet states, and CT T<sub>1</sub> exited states accompanied by



small contributions from locally excited (LE) states, which were consistent with the

measured phosphorescence spectra.

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**Fig 4.** The transient PL decay curve (air and vacuum) at 300 K for 10 *wt*% of three PM derivatives dopant in zeonex films (a), (b), (c); and in DPEPO films (d), (e) and (f).

To study the influence of host materials on photophysical properties of these compounds, we measured transient PL delay characteristics in zeonex<sup>43</sup> and DPEPO host films as seen in **Fig 4**. Zeonex was used because it has a similar polarity to nonpolar solvents such as methyl cyclohexane, whereas DPEPO has a high polarity. DPEPO host possesses high S<sub>1</sub> and T<sub>1</sub> energies ( $E_S/E_T = 3.5/3.1$  eV), which are large enough to suppress a back energy transfer from the guest emitter to the host and to confine the T<sub>1</sub> excitons within the guest molecules. It is obvious that the decay curves show difference

host, which indicates three compounds are typical TADF materials. Besides, the difference between air and vacuum becomes more apparent for three compounds in zeonex than that of in DPEPO, which could be ascribed to the smaller singlet-triplet energy splitting of the charge-transfer singlet state (<sup>1</sup>CT) and the lowest locally excited triplet state (<sup>3</sup>LE) of materials in higher polarity matrix. The lifetimes of the prompt components of doped films in DPEPO were 5.2-6.6 ns, which demonstrates a fast radiative decay rate. And the lifetimes of the delay parts are in the range of 118-189  $\mu$ s. Moreover, the absolute PL quantum yield (PLQY) of **SFI34pPM**, **SFI23pPM** and **3CzPhpPM** are 0.74, 0.72, and 0.73, respectively. The delayed component included the effect of nonradiative decay, internal conversion decay, intersystem crossing decay and reverse intersystem crossing decay rate, thus the shorter the delayed lifetime the better the TADF emitter.

Table 1. Basic Photophysical and Electrochemical Parameters of PM Derivatives.

Compounds	$\lambda_{abs}^{a}(nm)$	$\lambda_{PL}^{a}(nm)$	Eg <sup>b</sup> (eV)	HOMO/ LUMO <sup>c</sup> (eV)	$\frac{S_1/T_1^{d}}{(eV)}$	$\frac{S_1/T_1^e}{(eV)}$	$T_{\rm g}/T_{\rm d}^{\rm f}$ (°C)
SFI34pPM	314,367	424	3.09	-5.48/-2.64	2.90/2.68	3.08/2.84	-/440
SFI23pPM	308,363	414	3.17	-5.51/-2.63	3.01/2.73	3.20/2.84	-/449
3CzPhpPM	293,352	412	3.18	-5.57/-2.61	3.09/2.77	3.22/2.83	110/405

<sup>a</sup> Measured in toluene solution at 300 K; <sup>b</sup>Estimated from the absorption edges in toluene; <sup>c</sup> Determined by the cyclic voltammetry (CV) measurement.; <sup>d</sup> Calculated by TDDFT; <sup>e</sup> Calculated from the onset of the fluorescence spectra and phosphorescence in 2Me-THF at 77 k; <sup>f</sup> Measured by

#### **Electroluminescent properties**

In order to assess the electroluminescent (EL) properties of these compounds, firstly, we constructed the doped devices  $A_1$ - $A_3$  using DPEPO as host. The configuration of the device  $A_1$ - $A_3$  was indium-tin oxide (ITO)/MoO<sub>3</sub> (10 nm)/TAPC (50 nm)/mCP (10-15 nm)/DPEPO: Emitters (20 nm)/DPEPO (5 nm)/TmPyPB (40 nm)/LiF (1 nm)/A1 (Emitters: 10 *wt*% **SFI34pPM** for device  $A_1$ ; 20 *wt*% **SFI23pPM** for device  $A_2$ ; 20 *wt*% **SC2PhpPM** for device  $A_3$ ), where 1,1-bis[4-[*N*,*N*-di(ptoly1)-amino]phenyl] cyclohexane (TAPC) and 1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB) were used as hole- and electron-transport materials, respectively. Then, the nondoped devices  $B_1$ -

B<sub>3</sub> were also fabricated since they all bear steric structures (the detailed devices/DOTCO0039F structures and EL performance are displayed in **Fig S7**). Inspired by the high PLQY and the matched HOMO/LUMO energy levels with yellow materials, we adopted a yellow TADF material synthesized by our group 34AcCz-Trz (5-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-13,13-dimethyl-8-phenyl-8,13-dihydro-5H-indolo [3,2-a]acridine) using as the dopant and these PM derivatives as hosts.<sup>44</sup>



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**Fig 5.** The detailed device configuration of A<sub>1</sub>-A<sub>3</sub>, B<sub>1</sub>-B<sub>3</sub>, C<sub>1</sub>-C<sub>3</sub>, and D<sub>1</sub>-D<sub>3</sub> and the structure of 34AcCz-Trz and TBRb.



**Fig 6.** (a) Current density–voltage–luminance (C–V–L) curves; (b) CE-Luminance-PE; (0) EQE9/DOTCO0039F Luminance; (d) Normalized EL spectra for doped blue device A<sub>1</sub>-A<sub>3</sub> of three PM derivatives.

Regarding OLED based on the DPEPO: PM derivatives emitting layer (EML), a maximum external quantum effciency (EQE<sub>max</sub>) of 8.2% was achieved by **SFI34pPM**, accompanied with a turn-on voltage of 3.7 V and CIE<sub>x,y</sub> (0.15, 0.09) as shown in **Fig 6**. Although the doped concentrations are different in emitting layers of device A<sub>1</sub>-A<sub>3</sub>, the turn-on voltages of device A<sub>1</sub>-A<sub>3</sub> are the same, because the emitters have a similar LUMO energy levels with TmPyPB (the electron transporting layer) and the electron could directly move on the emitter molecules. Additionally, the other two materials based deep blue devices reach EQE<sub>max</sub> of 5.1% and 4.9% with CIE<sub>x,y</sub> (0.15, 0.10) and (0.15, 0.06) for **SFI23pPM** and **3CzPhpPM** respectively, because of the relatively larger  $\Delta E_{ST}$ s about 0.33 eV for **SFI23pPM** and 0.37 eV for **3CzPhpPM** as seen in **Fig S8**. The exact device data of device A<sub>1</sub>-A<sub>3</sub> are summarized in **Table 2**.

The performances of the nondoped device  $B_1$ - $B_3$  based on three compounds are shown in **Fig S7** and data are listed in **Table 2**. Interestingly, the EL spectra of device  $B_1$  and  $B_2$  exhibit almost no redshift compared to that of the doped device  $A_1$  and  $A_2$ , which may stem from the steric resistance effect and rigid structure of their donors. However, the donor group of **3CzPhpPM** has more planar configuration, which leads to stronger intermolecular interactions and larger bathochromic-shift, and device  $B_3$ shows a CIE<sub>*x,y*</sub> of (0.16, 0.12) compared to (0.15, 0.06) of device  $A_3$ . On the whole, the maximum EQE of device  $B_1$ - $B_3$  are 4.6%, 4.1% and 4.5%, respectively. The good nondoped device performances inspired us to utilize these deep blue emitters as host materials since their bipolar transporting ability and less concentration annihilation effect.

Herein, a yellow TADF material 34AcCz-Trz reported by our group <sup>36</sup> is chosen as the emitter using three PM compounds as hosts (**Fig S9**), and making three yellow devices of  $C_1$ - $C_3$ . The detailed structures of  $C_1$ - $C_3$  are displayed in **Fig 5**, as ITO/MoO<sub>3</sub> (10 nm)/TAPC (80 nm)/TCTA (5 nm)/**SFI34pPM**/ **SFI23pPM**/ **3CzPhpPM**: 3 *wt*% 34AcCz-Trz (25 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al. Besides, a contrast device  $\mathcal{Q}_{4}^{\text{WewArtice Orders}}$ hosted by CBP (4,4'-Bis(9*H*-carbazol-9-yl)biphenyl) with the same structure was made. Finally, the reference device C<sub>4</sub> realized a maximum EQE of 14.5%, 13.2% at 1000 cd/m<sup>2</sup> luminance, and 10.7% at 10000 cd/m<sup>2</sup> luminance. Besides, device C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> showed higher EQE<sub>max</sub> of 17.8%, 17.9% and 18.6%, respectively. More importantly, the efficiency roll-off of device C<sub>1</sub>-C<sub>3</sub> is relieved greatly, as the EQEs are 17.5%, 17.3% and 17.7% at 1000 cd/m<sup>2</sup> luminance, and 14.3%, 14.1% and 14.9% at 10000 cd/m<sup>2</sup> brightness, respectively. This result indicates that PM derivatives can not only achieve highly efficient deep blue TADF OLED, but also efficiently improve the electroluminescence performances of the hosted yellow TADF devices. Moreover, the bipolar transporting property is confirmed by hole-only and electron-only devices as seen in **Fig S10**. The results proved that **3CzPhpPM** represent a more balanced carrier transportation ability, which explained the highest EQE of device C<sub>3</sub>. Nevertheless, the efficiency roll-off depends on both TADF strength and the bipolar transportation property, since **SFI34pPM** shows the smallest efficiency roll-off.



**Fig 7.** (a) The energy transfer process for device  $D_4$ ; (b) the PL decay curves of yellow and yellow doped films; (c) Current density–voltage–luminance (C–V–L) curves; (d) EQE-Luminance and inset: Normalized EL spectra for device  $D_4$ .

As we all know, fluorescence OLED is the most stable devices compared to phosphorescence and TADF OLEDs. Finally, the yellow fluorescence device  $D_4$  was designed using **3CzPhpPM** as the host, 34AcCz-Trz as sensitizer and TBRb as the dopant. From the doping concentration dependent device performances of the TADF sensitized fluorescent devices in **Fig S12**, the device structure of  $D_4$  was more reasonable. The yellow fluorescence device  $D_4$  based on TBRb was constructed with the detailed structure of ITO/MoO<sub>3</sub> (10 nm)/TAPC (60 nm)/TCTA (5 nm)/**3CzPhpPM**: 4*wt*% 34AcCz-Trz: 1*wt*% TBRb (30 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al. Before this, reference device  $D_1$ - $D_3$  were made and hosted by CBP and 34AcCz-Trz respectively, and CBP (host)+34AcCzTrz (sensitizer) in **Fig S11**. Apparently, TADF host +TADF sensitizer improved the device performance greatly, which can be ascribed to the reduced triplet exciton loss compared to that of conventional host (as shown in Fig 7(a)). In order to probe the energy transfer in the yellow device  $C_1$ - $C_3$  and  $D_4$ , the decay curves of doped films were investigated. Since

the delayed lifetime of PM derivatives functioning as the host of 34AcCz-Trz<sup>b</sup>becam<sup>e/DOTCO0039F</sup> much shorter than that of doped in DPEPO host, the three PM-compounds are talented host materials (as seen in Fig 7(b)). Apart from this, the delayed lifetime of the film of **3CzPhpPM**+4*wt*% 34AcCzTrz+1*wt*% TBRb is the shortest one among the yellow and yellow films, which indicated that utilization of triplet excitons with TADF host and TADF sensitizer are the most effective among them. Thus, device D<sub>4</sub> realized a high efficiency of 19.1%, with negotiable efficiency roll-off at 1000 cd/m<sup>2</sup> luminance, as shown in Fig 7(c) and (d). From **Fig S13**, it can be confirmed that the complete energy transfer happened in the TADF sensitized fluorescence devices. This excellent yellow device performance based on TBRb enlightens more usage of the blue TADF materials with long delayed lifetime.

Table 2.	The EL	performance	of three	compounds.
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Device	Emitter	$V_{on}{}^{a}$	CE <sup>b</sup>	PE <sup>b</sup>	EQE <sup>b</sup>	Roll-off <sup>c</sup> (%)	CIEd
		(V)	(cd/A)	(lm/W)	(%)		
$A_1$	SFI34pPM	3.7	8.04	7.89	8.2	-	(0.15, 0.09)
$A_2$	SFI23pPM	3.7	5.81	5.36	5.1	-	(0.15, 0.10)
A <sub>3</sub>	3CzPhpPM	3.7	3.08	2.65	4.9	-	(0.15, 0.06)
$B_1$	SFI34pPM	3.9	4.48	3.57	4.6	-	(0.15, 0.10)
$B_2$	SFI23pPM	4.1	3.41	2.80	4.1	-	(0.16, 0.09)
$B_3$	3CzPhpPM	3.7	4.90	4.09	4.5	-	(0.16, 0.12)
$C_1$	34AcCzTrz	3.1	55.41	44.31	17.8	1.7/19.8	(0.39, 0.55)
$C_2$	34AcCzTrz	3.4	56.44	41.39	17.9	3.5/21.4	(0.38, 0.56)
C <sub>3</sub>	34AcCzTrz	3.5	57.72	43.07	18.6	5.0/20.0	(0.38, 0.56)
$C_4$	34AcCzTrz	3.3	45.10	38.51	14.5	9.1/26.3	(0.40, 0.56)
$D_4$	TBRb	<3.3	56.79	47.39	19.1	0/23.5	(0.49, 0.50)
Ref35	TBRb	3.2	60	58	18.0	39.4/-	(0.45, 0.53)
Ref37	TBRb	4.0	62	-	19.1	12.6/-	(0.43,0.54)

<sup>a.</sup> turn-on voltage (at a brightness of 1 cd m<sup>-2</sup>); <sup>b.</sup> the maximum CE (current efficiency), PE (power efficiency) and EQE (external quantum efficiency); <sup>c.</sup> the EQE roll-off at 1000 cd m<sup>-2</sup> and 10000 cd m<sup>-2</sup>; <sup>d.</sup> CIE: Commission Internationale de l'Eclairage chromaticity coordinates at 100 cd m<sup>-2</sup>.

#### Conclusions

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Finally, we have designed and synthesized a series of bipolar deep blue TADF materials based on 2,6-diphenylpyrimidine (PM) and carbazole derivative donors for use as blue emitters and host materials for yellow TADF emitter. Among them, the doped device

based on SFI34pPM shows a relatively high EQE of 8.2% with  $CIE_{x,y}$  of (0.15;)0:09)?/OTCO0039F 3CzPhpPM also realized a good deep-blue device with a EQE<sub>max</sub> of 4.9% and  $CIE_{x,y}$ of (0.15, 0.06). Besides, these compounds using as host materials not only improve the device efficiency, but also relieve the efficiency roll-off apparently in yellow TADF devices. Especially, the more balanced carrier transporting ability endows the yellow device hosted by 3CzPhpPM a high EQE of 18.6%, which is much higher than that of the reference device hosted by CBP (14.5%). On the other hand, SFI34pPM using as the host exhibits the smallest efficiency roll-off because of the stronger TADF strength. In the end, 3CzPhpPM is also an excellent host in TADF-sensitizing-fluorescence system, which realizes a high efficiency of 19.1% based on TBRb. Accordingly, deep blue materials with rigid structures are ideal candidate for high TADF hosts, and we also present a new approach for design simple and promising TADF molecules as versatile materials in fluorescence devices.

#### **Experimental Section**

The details of experiment conditions and equipments are cited the earlier reports<sup>36</sup> unless otherwise illustrated.

## Synthesis of 5'-(4-(2,6-diphenylpyrimidin-4-yl)phenyl)-5'H-spiro[fluorene-9,12'-indeno[1,2-c]carbazole] (SFI34pPM):

**SFI34pPM** was synthesized according to the similar procedure as described in reported paper<sup>43</sup>, using 5'*H*-spiro[fluorene-9,12'-indeno[1,2-*c*]carbazole] and intermediate **1** as the reactants (yield 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ [ppm]: 8.79-8.77(d, *J* = 8.0 Hz, 2H), 8.55-8.53 (d, *J* = 8.4 Hz, 2H), 8.6-8.33 (d, *J* = 7.6 Hz, 2H), 8.11 (s, 1H), 8.05-8.03 (d, *J* = 7.6 Hz, 2H), 7.99-7.97 (d, *J* = 8.4 Hz, 1H), 7.84-7.82 (d, *J* = 7.2 Hz, 1H), 7.76-7.74 (d, *J* = 8.8 Hz, 2H), 7.61-7.56 (m, 7H), 7.44-7.40 (t, *J* = 7.6 Hz, 2H), 7.32-7.27 (m, 2H), 7.18-7.14 (t, *J* = 8.0 Hz, 1H), 7.09-7.05 (t, *J* = 7.6 Hz, 2H), 7.03-6.99 (t, *J* = 7.6 Hz, 1H), 6.84-6.82 (d, *J* = 7.6 Hz, 2H), 6.74-6.71 (m, 2H), 6.64-6.62 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ [ppm]:165.08, 164.73, 163.85, 149.41, 147.38, 142.23, 141.57, 141.47, 141.44, 140.98, 139.98, 138.01, 137.43, 136.73, 136.14, 130.97, 130.83, 129.00, 128.93, 128.54, 128.11, 128.00, 127.84, 127.36, 126.56,

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## Synthesis of 5'-(4-(2,6-diphenylpyrimidin-4-yl)phenyl)-5'*H*-spiro[fluorene-9,7'indeno[2,1-b]carbazole] (SFI23pPM)

The synthesis process is referred to **SFI34pPM**, employing 5'*H*-spiro[fluorene-9,7'indeno[2,1-*b*]carbazole] and intermediate **1** as the reactants (yield 73%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 8.77-8.75 (d, *J* = 7.6 Hz, 2H), 8.65 (s, 1H), 8.41-8.39 (d, *J* = 7.6 Hz, 2H), 8.35-8.30 (m, 3H), 8.13-8.02 (m, 2H), 7.86-7.86 (d, *J* = 7.6 Hz, 2H), 7.61-7.58 (m, 8H), 7.49-7.37 (m, 6H), 7.16-7.09 (m, 3H), 6.70 (s, 1H), 6.85-6.83 (d, *J* = 7.6 Hz, 2H), 6.72-6.70 (d, *J* = 7.2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 164.91, 164.60, 163.80, 149.67, 148.94, 147.82, 141.91, 141.68, 141.12, 141.01, 139.77, 137.91, 137.34, 136.17, 135.34, 130.94, 130.79, 128.96, 128.90, 128.50, 127.86, 127.74, 127.63, 127.32, 127.10, 126.96, 126.10, 124.20, 123.95, 123.85, 123.68, 120.47, 120.30, 120.06, 119.39, 111.37, 110.26, 109.95, 105.53, 66.03. MS(APCI): cal for C<sub>53</sub>H<sub>33</sub>N<sub>3</sub>: 711.2674, found 712.2679 [M+H]<sup>+</sup>.

# Synthesis of 9-(4-(2,6-diphenylpyrimidin-4-yl)phenyl)-3-phenyl-9*H*-carbazole (3CzPhpPM)

The synthesis of **3CzPhpPM** is similar to that of **SFI34pPM**, using intermediate **1** and intermediate **2** as the reactants (yield 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 8.80-8.78 (d, *J* = 7.2 Hz, 2H), 8.55-8.53 (d, *J* = 8.0 Hz, 2H), 8.38 (s, 1H), 8.36-8.34 (d, *J* = 7.6 Hz, 2H), 8.23-8.21 (d, *J* = 7.6 Hz, 1H), 8.10 (s, 1H), 7.82-7.80 (d, *J* = 8.0 Hz, 2H), 7.76-7.74 (d, *J* = 7.6 Hz, 2H), 7.72-7.70 (d, *J* = 8.4 Hz, 1H), 7.61-7.46 (m, 11H), 7.39-7.34 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 165.03, 164.67, 163.82, 141.87, 141.00, 140.02, 137.99, 137.40, 136.36, 133.93, 130.99, 130.86, 129.01, 128.97, 128.84, 128.56, 127.37, 127.09, 126.70, 126.37, 125.69, 124.24, 123.84, 120.52, 118.94, 110.28, 110.11, 110.02. MS (APCI): cal for C<sub>40</sub>H<sub>27</sub>N<sub>3</sub>: 549.2205, found 550.2211[M+H]<sup>+</sup>.

**Conflicts of interest** 

There are no conflicts to declare.

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#### References

- Y. Tao, K. Yuan, T. Chen, P. Xu, H. Li, R. Chen, C. Zheng, L. Zhang and W. Huang, *Adv. Mater.*, 2014, 26, 7931-7958.
- 2 M. Y. Wong and E. Zysman-Colman, Adv. Mater., 2017, 29, 1605444.
- 3 M. Cazzaniga, F. Cargnoni, M. Penconi, A. Bossi and D. Ceresoli, *Chem. Mater.*, 2019, **31**, 2269-2276.
- R. K. Konidena, K. R. Justin Thomas, S. Sahoo, D. K. Dubey and J.-H. Jou, J.
   *Mater. Chem. C*, 2017, 5, 709-726.
- 5 W.-C. Chen, C.-S. Lee and Q.-X. Tong, *J. Mater. Chem. C*, 2015, **3**, 10957-10963.
- 6 X. Yang, X. Xu and G. Zhou, J. Mater. Chem. C, 2015, 3, 913-944.
- 7 Y. Im, S. Y. Byun, J. H. Kim, D. R. Lee, C. S. Oh, K. S. Yook and J. Y. Lee, *Adv. Funct. Mater.*, 2017, 27, 1603007.
- 8 X. Cai and S.-J. Su, Adv. Funct. Mater., 2018, 28, 1802558.
- 9 K. Matsuo and T. Yasuda, *Chem. Sci.*, 2019, **10**, 10687-10697.

- 10 X. Wang, S. Wang, J. Lv, S. Shao, L. Wang, X. Jing and F. Wang, *Chem*. 1507, 2019, **10**, 2915-2923.
- X. Ban, F. Chen, Y. Liu, J. Pan, A. Zhu, W. Jiang and Y. Sun, *Chem. Sci.*, 2019, 10, 3054-3064.
- J.-H. Lee, C.-H. Chen, P.-H. Lee, H.-Y. Lin, M.-k. Leung, T.-L. Chiu and C.-F. Lin, J. Mater. Chem. C, 2019, 7, 5874-5888.
- 13 D. H. Ahn, S. W. Kim, H. Lee, I. J. Ko, D. Karthik, J. Y. Lee and J. H. Kwon, *Nat. Photonics*, 2019, **13**, 540-546.
- T. Hatakeyama, K. Shiren, K. Nakajima, S. Nomura, S. Nakatsuka, K. Kinoshita,
  J. Ni, Y. Ono and T. Ikuta, *Adv. Mater.*, 2016, 28, 2777-2781.
- S. H. Han, J. H. Jeong, J. W. Yoo and J. Y. Lee, *J. Mater. Chem. C*, 2019, 7, 3082-3089.
- X. Liang, Z. P. Yan, H. B. Han, Z. G. Wu, Y. X. Zheng, H. Meng, J. L. Zuo and
   W. Huang, *Angew. Chem. Int. Ed.*, 2018, 57, 11316-11320.

- Y. Yuan, X. Tang, X.-Y. Du, Y. Hu, Y.-J. Yu, Z.-Q. Jiang, L.-S. Liao and S.-T.
   Lee, *Adv. Optical Mater.*, 2019, 7, 1801536.
- 18 L. S. Cui, H. Nomura, Y. Geng, J. U. Kim, H. Nakanotani and C. Adachi, Angew. Chem. Int. Ed., 2016, 55, 1-6.
- H. L. Lee, K. H. Lee, J. Y. Lee and W. P. Hong, J. Mater. Chem. C, 2019, 7, 6465-6474.
- 20 N. Lin, J. Qiao, L. Duan, L. Wang and Y. Qiu, J. Phys. Chem. C, 2014, 118, 7569-7578.
- 21 S. K. Jeon, H. L. Lee, K. S. Yook and J. Y. Lee, *Adv. Mater.*, 2019, **31**, 1803524.
- T. Serevicius, R. Skaisgiris, J. Dodonova, K. Kazlauskas, S. Jursenas and S. Tumkevicius, *Phys. Chem. Chem. Phys.*, 2019, 22, 265-272.
- 23 S. J. Woo, Y. Kim, S. K. Kwon, Y. H. Kim and J. J. Kim, ACS Appl. Mater. Interfaces., 2019, 11, 7199-7207.
- D. H. Ahn, H. Lee, S.W. Kim, D. Karthik, J. Lee, H. Jeong, J. Y. Lee, and J. H.
   Kwon, ACS Appl. Mater. Interfaces., 2019, 11, 14909-14916.
- 25 S. Y. Lee, C. Adachi, and T. Yasuda, *Adv. Mater.*, 2016, **28**, 4626-4631.

- 26 Y. J. Cho, S. K. Jeon and J. Y. Lee, *Adv. Optical Mater.*, 2016, 4, 688-693.0.1039/D0TC00039F
- Q. Zhang, S. Xiang, Z. Huang, S. Sun, S. Ye, X. Lv, W. Liu, R. Guo and L.
   Wang, *Dyes Pigments.*, 2018, 155, 51-58.
- 28 Q. Zhang, J. Li, K. Shizu, S. Huang, S. Hirata, H. Miyazaki and C. Adachi, J. Am. Chem. Soc., 2012, 134, 14706-14709.
- L. Gan, K. Gao, X. Cai, D. Chen and S. J. Su, *J Phys Chem Lett.*, 2018, 9, 4725-4731.
- 30 X. Cai, B. Gao, X.-L. Li, Y. Cao and S.-J. Su, Adv. Funct. Mater., 2016, 26, 8042-8052.
- 31 X. K. Chen, D. Kim and J. L. Bredas, Acc. Chem. Res., 2018, 51, 2215-2224.
- S. Y. Byeon, D. R. Lee, K. S. Yook and J. Y. Lee, *Adv. Mater.*, 2019, 31, 1803714.
- 33 X.-D. Zhu, Y.-L. Zhang, Y. Yuan, Q. Zheng, Y.-J. Yu, Y. Li, Z.-Q. Jiang and L.-S. Liao, *J. Mater. Chem. C*, 2019, 7, 6714-6720.
- K. P. Guo, H. D. Wang, Z. X. Wang, C. F. Si, C. Y. Peng, G. Chen, J. H. Zhang,
  G. F. Wang and B. Wei, *Chem. Sci.*, 2017, 8, 1259-1268.
- H. Nakanotani, T. Higuchi, T. Furukawa, K. Masui, K. Morimoto, M. Numata,
  H. Tanaka, Y. Sagara, T. Yasuda and C. Adachi, *Nat. Commun.*, 2014, 5, 4016.
- 36 X. Song, D. Zhang, Y. Lu, C. Yin and L. Duan, *Adv. Mater.*, 2019, **31**, 1901923.
- T. Furukawa, H. Nakanotani, M. Inoue and C. Adachi, Sci. Rep., 2015, 5, 8429.
- 38 W. Song, I. Lee and J. Y. Lee, *Adv. Mater.*, 2015, **27**, 4358-4363.
- W. Song, I. H. Lee, S.-H. Hwang and J. Y. Lee, *Org. Electron.*, 2015, 23, 138-143.
- 40 Q. Zhang, S. Sun, X. Lv, W. Liu, H. Zeng, R. Guo, S. Ye, P. Leng, S. Xiang and L. Wang, *Mater. Chem. Front*, 2018, 2, 2054-2062.
- P. Ganesan, R. Ranganathan, Y. Chi, X.-K. Liu, C.-S. Lee, S.-H. Liu, G.-H. Lee,
   T.-C. Lin, Y.-T. Chen and P.-T. Chou, *Chem. Eur. J.*, 2017, 23, 2858-2866.
- X. Lv, W. Zhang, D Ding, C Han, Z. Huang, S. Xiang, Q. Zhang, H. Xu and L. Wang, *Adv. Optical Mater.*, 2018, 6, 1800165.
- 43 X. Lv, R. Huang, S. Sun, Q. Zhang, S. Xiang, S. Ye, P. Leng, F. B. Dias and L.

Journal of Materials Chemistry C Accepted Manuscript

View Article Online DOI: 10.1039/D0TC00039F

Wang, ACS Appl. Mater. Interfaces, 2019, 11, 10758-10767.

44 Q. Zhang, S. Sun, w. liu, P. Leng, X. Lv, Y. Wang, H. Chen, S. Ye, S. Zhuang and L. Wang, *J. Mater. Chem. C*, 2019, **7**, 9487-9495.

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A series of multifunctional deep blue TADF materials is designed and synthesized, when utilizing as the wide-energy-gap host in TADF sensitization system, a high EQE of 19.12% orange fluorescent device is obtained.