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## Introduction

Deep blue emitters play an irreplaceable role in full-color displays and solid-state lighting.<sup>1–3</sup> Therefore, the realization of efficient and stable deep-blue fluorophores with Commission International de I'Eclairage (CIE) coordinates close to the National Television System Committee (NTSC) standard deep blue CIE (x, y) coordinates of (0.14, 0.08) is essential to the development of organic light-emitting diodes (OLEDs).<sup>4,5</sup> During the past decades, considerable efforts have been made to develop deep blue emitters; however, efficient non-doped deep

<sup>b</sup> State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

## Rational molecular design of phenanthroimidazole-based fluorescent materials towards high-efficiency non-doped deep blue OLEDs<sup>+</sup>

Chunya Du,<sup>a</sup> Tong Lu,<sup>a</sup> Zhuang Cheng,<sup>a</sup> Yulei Chang,<sup>b</sup> Hui Liu,<sup>c</sup> Jun Wang,<sup>d</sup> Liang Wan,<sup>a</sup> Ying Lv<sup>b</sup> and Ping Lu<sup>b</sup>\*<sup>a</sup>

Achieving high external quantum efficiency (EQE) for non-doped deep blue fluorescent organic lightemitting diodes (OLEDs) with the Commission International de l'Eclairage (CIE) coordinate of  $CIE_y < 0.08$  remains a big challenge. Herein, three high-efficiency molecules **PPI-2-DMF**, **PPI-2-DPF** and **PPI-3-SBF** with weak intramolecular charge transfer properties are successfully prepared by connecting phenanthroimidazole (PI) and various fluorene derivatives *via* benzene bridges. The crystallographic study confirms that only  $C-H\cdots\pi$  weak intermolecular interactions exist in these crystals, which is conducive to obtaining high solid-state fluorescence efficiency, and eventually, the photoluminescence quantum yields (PLQYs) of **PPI-2-DMF**, **PPI-2-DPF** and **PPI-3-SBF** reach 57.56, 67.22 and 66.05%, respectively. **PPI-3-SBF** exhibits the shortest conjugation length among the three molecules, leading to the bluest emission. As a result, the non-doped device with **PPI-3-SBF** as an emitting layer realizes a high maximum EQE of 8.41% with CIE coordinates of (0.16, 0.07), accompanied by a relatively low efficiency roll-off. These findings would provide a new strategy of molecular structure design for highly efficient deep blue non-doped OLEDs.

> blue OLEDs are still scarce due to their inherent wide band gaps.<sup>6,7</sup> To achieve 100% internal quantum efficiency, phosphorescence and thermally activated delayed fluorescence (TADF) luminophores have been developed successively.8-11 However, there exist intrinsic difficulties in the molecular structure design of deep blue phosphorescence or TADF emitters. That is, when the emission peaks of phosphorescent materials shift to the deep blue region, the nonradiative transition rate of metal d-orbitals would inevitably increase,<sup>12</sup> which makes it difficult to achieve high efficiency for deep blue phosphorescent OLEDs. Furthermore, classical TADF molecules generally adopt a donoracceptor (D-A) molecular structure with strong charge transfer (CT) characteristics in the excited state, which aims to realize the full utilization of triplet excitons through the reverse intersystem crossing (RISC) process. However, the indispensable strong CT characteristics of TADF materials in the excited state are not conducive to deep blue emission.<sup>13–15</sup> Besides, most phosphorescence and TADF emitters should be fabricated as doped devices for reducing the efficiency roll-offs, which increases the complexity of the device manufacturing process.<sup>16–19</sup> In contrast, using non-doped OLEDs avoids the selection of an appropriate host material and unnecessary precise doping concentration control, which significantly simplifies the fabrication of devices and improves the reproducibility of device performance.<sup>20-22</sup>

<sup>&</sup>lt;sup>a</sup> State Key Laboratory of Supramolecular Structure and Materials, Department of Chemistry, Jilin University, Changchun 130012, China. E-mail: lup@jlu.edu.cn

<sup>&</sup>lt;sup>c</sup> College of Optoelectronic Engineering, Chengdu University of Information Technology, Chengdu 610225, China

<sup>&</sup>lt;sup>d</sup> National & Local Joint Engineering Laboratory for Synthesis Technology of High Performance Polymer, Key Laboratory of High Performance Plastics, Ministry of Education, College of Chemistry, Jilin University, Changchun, 130012, China

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In order to obtain deep blue luminescence, the length of molecular conjugation and the intensity of intramolecular charge transfer (ICT) should be strictly controlled.<sup>23-25</sup> In OLEDs, bipolar D-A structure  $\pi$ -conjugated molecules are usually adopted to achieve balanced carrier transportation.<sup>26,27</sup> However, the combination of donors and acceptors in blue molecules may lead to a relatively wide full width at half maximum (FWHM), which is not beneficial to the improvement of color purity.<sup>28</sup> Phenanthroimidazole (PI) contains two distinct nitrogen atoms with pyrrole-like electron-rich and pyridine-like electron-deficient properties, respectively, endowing PI with a bipolar characteristic.<sup>29,30</sup> With the introduction of the PI unit, the carrier transport balance of the resulting molecules could be significantly promoted, which reduces the necessity of D-A molecular structure construction. Meanwhile, PI possesses a rigid structure and near-ultraviolet emission,<sup>29,31,32</sup> all of which favour the construction of deep blue molecules.

On the other hand, fluorene is an excellent candidate for deep blue emitters with a wide optical gap of 3.9 eV. The rigid planar biphenyl unit not only provides high thermal and chemical stability, but also weakens the excited-state structural relaxations and vibrations, improving the color purities and luminescence efficiencies.33,34 One shortcoming of fluorene is that it often suffers from obvious aggregation-induced quenching due to the  $\pi$ - $\pi$  stacking of its planar skeleton. However, fluorene possesses abundant modification sites; thus, large steric hindrance groups could be introduced to reduce fluorescence quenching. Notably, the sp<sup>3</sup> hybridization carbon atom at the 9-position gives rise to the special spatial configuration of fluorene, which could efficaciously break the conjugation of resulting molecules. Therefore, modification of sterically bulky substituents at the 9-position of fluorene shows little effect on the energy gap between the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) but reduces the overlap of the frontier molecular orbitals (FMOs) and electron exchange with neighbouring molecules,<sup>35–37</sup> which is beneficial to preserve the short  $\pi$ -conjugation length as well as high photoluminescence quantum yield (PLQY) in the solid state.

Based on the above considerations, two fluorene derivatives 9,9-dimethylfluorene (DMF) and 9,9-diphenylfluorene (DPF) with large steric hindrance are selected to connect with PI at the 2-position of fluorene through a benzene bridge to obtain PPI-2-DMF and PPI-2-DPF. In order to further increase the rigidity of the substituent, a 9,9'-spiro-bi(9H-fluorene) (SBF) group with larger rigidity is also adopted to connect with PI at the 3-position to construct PPI-3-SBF. Both photophysical measurements and theoretical calculations demonstrate that their excited states exhibit weak ICT characteristics. PPI-2-DMF, PPI-2-DPF and PPI-3-SBF all realize deep blue emission, of which PPI-3-SBF displays the bluest light color owing to the shortest conjugation length. Moreover, the various molecular structures result in different packing modes in their crystals. PPI-3-SBF exhibits the strongest molecular rigidity and the most abundant C-H $\cdots$  $\pi$  intermolecular interactions among these compounds, which gives a high PLQY of 66.05%. However, PPI-2-DMF has the least weak interactions in the crystal cell, leading to insufficient inhibition of molecular vibration and rotation, resulting in a lower PLQY of 57.56%. Non-doped devices employing these new materials all exhibited deep blue electroluminescence (EL) with emission peaks of 428-436 nm. The device based on PPI-3-SBF displays the best comprehensive EL performance with a maximum external quantum efficiency (EQE) of 8.41% and a deep blue CIE index of (0.16, 0.07), which matches well with the NTSC standard blue CIE coordinates of (0.14, 0.08).

### Results and discussion

#### Synthesis and characterization

The molecular structure and synthetic routes for **PPI-2-DMF**, **PPI-2-DPF** and **PPI-3-SBF** are shown in Scheme 1. PPIB was



Scheme 1 Chemical structures and synthetic procedures of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF.

obtained *via* a two-step synthetic procedure including the dehydration cyclization reaction and the Miyaura borylation reaction according to our previous report.<sup>38</sup> Then, the target compounds **PPI-2-DMF**, **PPI-2-DPF** and **PPI-3-SBF** were prepared through the Suzuki cross-coupling reaction in good yields. After recrystallization and temperature-gradient sublimating purification, all three compounds were fully characterized and verified by <sup>1</sup>H NMR spectroscopy, mass spectroscopy and elemental analysis. The synthetic details and characterization data are described in the ESI.<sup>†</sup>

#### Crystal structures

Single crystals of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF were grown during the temperature-gradient sublimation process. X-ray crystallography data of these crystals were analyzed to reveal the possible effect of molecular packing on solid PLQYs. As shown in Fig. 1, there only existed C-H··· $\pi$  interactions between adjacent molecules, and no  $\pi \cdots \pi$  interactions were observed in all these single crystals. These weak intermolecular interactions could effectively reduce the nonradiative decay by molecular vibration as well as improve the PLQY in the solid state.<sup>39</sup> For **PPI-2-DMF** crystals (Fig. 1a), two types of C–H··· $\pi$ interactions were observed; one was observed between the hydrogen of the benzene ring at the N1 position of PI and the adjacent phenanthrene with a distance of 2.727 Å, and the other C-H··· $\pi$  interaction was between the neighbouring fluorene groups with a distance of 2.896 Å. There were altogether 4 C-H··· $\pi$  interactions in the DMF crystal cell, which was the least among the three fluorophores. Meanwhile, there were no interactions between the methyl groups at the end of the **PPI-2-DMF** and its neighbouring, which might lead to the energy loss of the excited state to a certain extent. In contrast, in **PPI-2-DPF** crystals (Fig. 1b), the relatively flexible benzene bridge, phenyl substituent at the N1 position of PI and two phenyl units on the DPF unit all established intermolecular interactions with surrounding molecules, and the energy loss caused by nonradiative decay would be better inhibited. As for the **PPI-3-SBF** crystal (Fig. 1c), the SBF moieties further enhanced the molecular rigidity, and the most abundant C-H··· $\pi$  intermolecular interactions were observed among these three molecules (10), which guaranteed the high solid-state luminescence efficiency.

#### Theoretical calculations

Density functional theory (DFT) calculations were performed to further investigate the structure-property relationships. As shown in Fig. 2, PPI-2-DMF, PPI-2-DPF and PPI-3-SBF possessed approximately the same torsional angles along the long axis, among which the torsion angles between PI and benzene bridges were 28.6, 25.3 and 25.3°, respectively, as well as the torsion angles between the benzene bridge and fluorene were all about 36°. Such moderate torsion angles facilitated the enhancement of overlap between HOMOs and LUMOs, thus realizing weak ICT and is beneficial for improving the PLQY. It was found that the FMO distributions of PPI-2-DMF and PPI-2-DPF were very similar, and both HOMOs and LUMOs of them were delocalized along the whole long axis of PI, phenyl, and fluorene. However, the FMO distribution of PPI-3-SBF was not extended to the terminal benzene ring of fluorene, demonstrating that the  $\pi$ -conjugation in **PPI-3-SBF** was effectively restricted by



Fig. 1 The single crystal structures and packing modes of (a) PPI-2-DMF (CCDC 2167068), (b) PPI-3-SBF (CCDC 2167072) and (c) PPI-2-DPF (CCDC 2167071) in crystals.

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Fig. 2 So geometries and HOMO/LUMO distributions of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF.

the connection at the 3-position of SBF. Natural transition orbitals (NTOs) were calculated to further explore their excited-state characteristics using the TD-B3LYP/6-31G(d,p) method (Fig. S4, ESI†). The S<sub>1</sub> states of these molecules exhibited weak CT components with a high oscillator strength (1.27–1.64), which was beneficial to obtain high fluorescence efficiency.<sup>40</sup> In addition, there were small energy level splits between S<sub>1</sub> and T<sub>2</sub>/T<sub>3</sub> with hybridized local and charge-transfer (HLCT) characteristics, (Fig. S5, ESI†) which might pave channels for the high-lying RISC

process to utilize triplet excitons efficiently.<sup>41,42</sup> Although the  $T_4$  state of **PPI-3-SBF** showed pure LE dominance, considering the small energy level difference (0.08 eV) between  $T_4$  and  $S_1$ , it was also possible to provide a RISC channel.<sup>43-45</sup>

#### **Photophysical properties**

UV-visible absorption spectra and photoluminescence (PL) spectra of all target molecules in dilution solvents with different polarities were determined. These fluorophores exhibited identical



Fig. 3 (a) Solvation effects on PL spectra of PPI-3-SBF. (b) Absorption and PL spectra of the PPI-2-DMF, PPI-2-DPF and PPI-3-SBF in vacuumevaporated films. (c) Solvatochromic Lippert-Mataga models of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF with the Stokes shift. (d) Radiative transition rates  $(k_r)$  and non-radiative transition rates  $(k_{rr})$  of neat films. (e) Transient PL decay spectra of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF in vacuum-evaporated films. (f) Low-temperature fluorescence and phosphorescence spectra at 77 K of PPI-3-SBF were recorded in a frozen toluene matrix.

absorption spectra in all these solvents (Fig. S6, ESI<sup>†</sup>). All of them displayed an absorption peak around 360 nm, which could be attributed to the  $\pi$ - $\pi$ \* transition of the PI backbone,<sup>46,47</sup> and the short-wavelength absorption peak around 330 nm corresponds to the  $S_0 \rightarrow S_1$  transition of molecules. The PL spectra of **PPI-2-DMF**, PPI-2-DPF and PPI-3-SBF in low polar solvents displayed a locally excited (LE) state characterized by a fine vibration structure. With the increase of the polarity of the solvent, the fine structure became blurred and the spectrum was gradually expanded, and then completely disappeared in the high polarity acetonitrile solvent with one single peak emission (Fig. 3a and Fig. S7, ESI<sup>+</sup>). The emission peak positions in acetonitrile of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF were 435, 433 and 416 nm, respectively, indicating their weak CT properties in the excited state. In addition, due to the enhanced intermolecular interactions between molecules in the solid state, the emission peaks of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF in the non-doped neat films were redshifted to 448, 448 and 434 nm (Fig. 3b), respectively, which were still retained in the deep blue emission range, demonstrating the effectiveness of our molecular design strategy. In order to further investigate the properties of the  $S_1$  state for these three molecules, the linear relationship of Stokes shift  $(v_a - v_f)$  versus the orientation polarization of the solvents  $f(\varepsilon, n)$  was constructed based on the Lippert-Mataga equation. As shown in Fig. 3c, PPI-2-DMF, PPI-2-DPF and PPI-3-SBF exhibited moderate µes of 14.2, 14.3 and 16.6 D, respectively, indicating a quasi-equivalent hybridization character originating from mixed LE and CT states. The key photophysical properties of these compounds are listed in Table 1. The PLOYs of non-doped films of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF were 57.26, 67.22 and 66.05%, respectively. Combined with the decay lifetimes of these films, their radiative transition rates  $(k_r s)$  and non-radiative transition rates  $(k_{nr}s)$  were further calculated. As shown in Fig. 3d, the k<sub>r</sub>s values of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF were 2.63, 3.34 and 2.64  $\times$  10<sup>8</sup> s<sup>-1</sup>, respectively, and the  $k_{\rm nr}$ s values were 1.97, 1.63 and  $1.36 \times 10^8 \text{ s}^{-1}$ . Among them, PPI-2-DMF exhibited the lowest  $k_r$  and the largest  $k_{nr}$ , which resulted in a relatively low PLQY, indicating that the energy loss caused by the molecular vibration rotation was not well suppressed as discussed above. PPI-3-SBF still maintained a high PLQY owing to its stronger molecular rigidity and more abundant intermolecular interactions. It is noteworthy that all three molecules exhibited nanosecond level short lifetimes in both solution and solid states (Fig. 3e and Fig. S9, ESI<sup>†</sup>). Besides, the energy differences between  $S_1$  and  $T_1$  of all three fluorophores were about 0.8 eV (Fig. 3f and



Fig. 4 (a) TGA and (b) DSC profiles of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF.

Fig. S10, ESI $\dagger$ ); such a large energy splitting made it difficult for RISC from T<sub>1</sub> to S<sub>1</sub> to occur, thus ruling out the TADF process.

#### Thermal and electrochemical properties

The thermal properties of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. As displayed in Fig. 4a, the decomposition temperature  $(T_d, 5\%)$ weight loss) was measured to be 464, 514 and 509 °C for PPI-2-DMF, PPI-2-DPF and PPI-3-SBF, respectively, indicating that these materials were resistant to high temperature and would not decompose during equipment manufacture and operation. In addition, the glass transition temperatures  $(T_g)$  of these three compounds were 138, 176 and 190 °C, respectively (Fig. 4b). The crystallization temperature  $(T_c)$  and melting point  $(T_m)$  of **PPI-2**-DMF were as high as 198 and 295 °C, respectively. The excellent thermal stability of all three compounds meets the basic requirements of thermal evaporation for device preparation. Besides, the electrochemical properties of these new materials were investigated by cyclic voltammetry (CV) in solution (Fig. S11, ESI<sup>†</sup>). The HOMOs of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF were at a similar level of -5.48 eV, which were estimated based on the onsets of the initial oxidation potentials. And the LUMOs of three compounds were -2.61, -2.60 and -2.56 eV, respectively. The bandgap between the HOMO and LUMO of PPI-3-SBF (2.92 eV) was lightly wider than those of PPI-2-DMF (2.87 eV) and PPI-2-DPF (2.88 eV) on account of the shorter conjugation length of PPI-3-SBF.

#### **Electroluminescence properties**

To evaluate the EL performance of **PPI-2-DMF**, **PPI-2-DPF** and **PPI-3-SBF** as emitting layers in non-doped OLEDs, devices with

Table 1       Key photophysical properties of PPI-2-DMF, PPI-2-DPF, and PPI-3-SBF												
Compound	$\lambda_{\rm abs}{}^a$ [nm]		$\lambda_{\mathrm{PL}}{}^{b} [\mathrm{nm}]$									
	Sol	Film	Sol	Film	$PLQY^{c}[\%]$	$\tau^{d}$ [ns]	$S_1/T_1^e [eV]$	$\Delta \mathbf{E}_{\mathrm{ST}}^{f}[\mathrm{eV}]$				
PPI-2-DMF PPI-2-DPF PPI-3-SBF	333, 364 332, 361 327, 360	343, 368 347, 368 339, 368	435 433 416	448 448 434	57.26 67.22 66.05	2.17 2.01 2.50	3.09/2.29 3.10/2.27 3.16/2.34	0.80 0.83 0.82				

<sup>*a*</sup> UV-vis absorption peaks in acetonitrile solution ( $10^{-5}$  M) and vacuum-deposited neat films at room temperature. <sup>*b*</sup> Emission peaks in acetonitrile solution ( $10^{-5}$  M) and vacuum-deposited neat films at room temperature. <sup>*c*</sup> Absolute photoluminescence quantum efficiency of vacuum-deposited neat films evaluated using an integrating sphere. <sup>*d*</sup> Fluorescence lifetimes measured in a neat thin film. <sup>*e*</sup> Energies of S<sub>1</sub> and T<sub>1</sub> measured in  $1 \times 10^{-5}$  M toluene solution at 77 K. <sup>*f*</sup> S<sub>1</sub>-T<sub>1</sub> energy gap ( $\Delta E_{ST}$ ) measured in  $1 \times 10^{-5}$  M toluene solution at 77 K.

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the optimized structure of ITO/HATCN (6 nm)/TAPC (25 nm)/ TCTA (15 nm)/EML (20 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (120 nm) were prepared. The corresponding energy levels and molecular structures of the functional materials used in these devices are shown in Fig. 5a and b, (ESI<sup>†</sup>) in which, HATCN (1,4,5,8,9,11-hexaazatriphenylenehexacabonitrile) and TAPC (di-(4-(*N*,*N*-ditolyl-amino)-phenyl) cyclohexane) were used as the hole injecting and transporting layer, respectively. TCTA (tris(4-carbazoyl-9-ylphenyl)amine) was employed as an exciton blocking layer, and LiF and TmPyPB (1,3,5-tri(*m*-pyrid-3-ylphenyl)benzene) served as the electron injecting and transporting layer, respectively, while ITO and Al represented the anode and the cathode. The EL performance of these non-doped devices is listed in Table 2.

These OLEDs showed extremely low turn-on voltages below 3 V, revealing the small carrier injection barrier in these devices. No new peaks were observed at different driving voltages (Fig. S12, ESI†), which indicated that the carrier recombination was well confined to the EML layer and the EL spectra were stable. **PPI-2-DMF** and **PPI-2-DPF** based OLEDs all exhibited deep blue emission with EL emission peaks at 434 nm (Fig. 5c) and the same CIE coordinates of (0.16, 0.09), respectively, approaching the NTSC standard blue index (0.14, 0.08). In addition, the EQEs of **PPI-2-DMF** and **PPI-2-DPF** multilayer devices were 7.57 and 8.48%, respectively. The EQE of the **PPI-2-DMF** based device was relatively low due to the lower PLQY caused by the motion of methyl groups. Furthermore, compared with **PPI-2-DMF** and **PPI-2-DPF**, the EL peak of **PPI-3**-

SBF blue shifted to 428 nm because of its shorter conjugation length. Moreover, profiting from stronger molecular rigidity, the non-doped device of PPI-3-SBF presented a more favourable color purity compared with those of PPI-2-DMF and PPI-2-DPF, with a reduced  $\text{CIE}_{\nu}$  value of 0.07 and a narrower FWHM of 60 nm. More importantly, the PPI-3-SBF based non-doped device simultaneously preserved a high EQE of 8.41% benefiting from its abundant intermolecular interactions. The high exciton utilization efficiencies (EUEs) of 44-66%, 42-63% and 43-62% were realized in the optimized devices based on PPI-2-DMF, PPI-2-DPF and PPI-3-SBF, respectively, assuming an optical outcoupling efficiency of 20-30%<sup>48</sup> according to eqn (S9) (in the ESI<sup>†</sup>). Such high EUEs indicated that in addition to 25% singlet excitons, quite a few triplet excitons also participated in the radiative transition process. As displayed in Fig. S14 (ESI<sup>+</sup>), the horizontal dipole ratios of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF were estimated to be 90.0, 91.0, and 90.5%, respectively, which can improve the optical outcoupling efficiency of the devices and further enhance the device performance. As shown in Fig. S13 (ESI<sup>†</sup>), the device brightness and current density presented a linearity relationship, as a result, the contribution of the triplettriplet annihilation (TTA) mechanism was not dominant.<sup>49</sup> More importantly, we measured the transient EL decay of PPI-2-DMF, PPI-2-DPF and PPI-3-SBF based non-doped devices at different voltages. As shown in Fig. S15 (ESI<sup>+</sup>), the EL intensity of nondoped devices decreased rapidly due to the short fluorescence lifetime, and a delayed EL component was observed with a clear voltage dependence. The delay component is derived from TTA



**Fig. 5** (a) Device structures and energy level diagram of **PPI-2-DMF**, **PPI-2-DPF** and **PPI-3-SBF** based non-doped devices. (b) Molecular structures of HATCN, TAPC, TCTA, and TmPyPB. (c) Normalized EL spectra at 100 cd  $m^{-2}$ . (d) External quantum efficiency *versus* luminance curves. (e) Current efficiency–luminance–power efficiency curves. (f) The curves of luminance–voltage–current density.

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Table 2 Summary of the EL performances of non-doped devices based on PPI-2-DMF, PPI-2-DPF and PPI-3-SBF

Emitting layers	$V_{\mathrm{on}}{}^{a}\left(\mathrm{V}\right)$	$L_{\max}^{b} (\mathrm{cd} \ \mathrm{m}^{-2})$	$\operatorname{CE}_{\max}^{c} (\operatorname{cd} \operatorname{A}^{-1})$	$\operatorname{PE}_{\max}^{d}(\operatorname{Im} \operatorname{W}^{-1})$	$\mathrm{EQE}^{e}$ (%)	$\lambda_{\mathrm{EL}}^{f}(\mathrm{nm})$	$\operatorname{CIE}^{g}(x, y)$	Roll-off <sup><math>h</math></sup> (%)	FWHM <sup>i</sup> (nm)
PPI-2-DMF	2.9	30 145	5.94	5.78	7.57, 6.37	434	(0.16, 0.09)	15	70
PPI-2-DPF	2.9	23 170	6.77	6.24	8.48, 7.02	434	(0.16, 0.09)	17	68
PPI-3-SBF	3.0	16365	4.72	3.69	8.41, 6.77	428	(0.16, 0.07)	19	60

<sup>*a*</sup>  $V_{on}$ : turn-on voltage at a luminescence of 1 cd m<sup>-2</sup>. <sup>*b*</sup>  $L_{max}$ : maximum luminance. <sup>*c*</sup> CE<sub>max</sub>: maximum current efficiency. <sup>*d*</sup> PE<sub>max</sub>: maximum power efficiency. <sup>*e*</sup> EQE: maximum EQE and the EQE value at 1000 cd m<sup>-2</sup>. <sup>*f*</sup>  $\lambda_{EL}$ : emission peak of the EL spectrum. <sup>*g*</sup> CIE: Commission International de l'Éclairage (CIE) coordinates. <sup>*h*</sup> Efficiency roll-off at 1000 cd m<sup>-2</sup>. <sup>*i*</sup> FWHM: full widths at half maximum of the EL spectrum.

instead of recombining the trapped charges.<sup>50,51</sup> As shown in Fig. S16, (ESI<sup>+</sup>) the EL decay curves at 4 V were fitted. According to previous reports,<sup>52,53</sup> taking **PPI-3-SBF** as an example, the intercept value of the linear function (t = 0) was deduced to be 6.86. Therefore, the TTA ratio in the non-doped device of PPI-3-SBF was estimated to be 2.1%. Similarly, in the non-doped devices of PPI-2-DMF and PPI-2-DPF, the ratios of TTA were calculated to be 0.1 and 1.6%, respectively. Thus, TTA is not the dominant triplet exciton utilization mechanism in these nondoped devices. Furthermore, as mentioned above, the large energy difference between the  $S_1$  and  $T_1$  states and the absence of a long lifetime in the transient PL spectra of these molecules were sufficient to exclude the TADF process. Considering the small energy level splits between the  $S_1$  and  $T_2/T_3$  states, the way to mainly utilize triplet excitons was to follow the "hot exciton" channel between the T2/T3 and S1 state to improve EUEs. Moreover, benefiting from the short lifetime of "hot exciton" materials, all these non-doped devices exhibited small efficiency roll-offs of less than 20% at 1000 cd  $m^{-2}$ . These results were comparable to those of highly efficient non-doped deep blue OLEDs with  $\text{CIE}_{\nu} \approx 0.08$  as reported in the literature.54,55

## Conclusion

Three novel deep-blue emission materials PPI-2-DMF, PPI-2-DPF and PPI-3-SBF with weak ICT characteristics have been developed by the rational connection of PI moiety and fluorene derivatives. Different from PPI-2-DMF and PPI-2-DPF, PPI-3-SBF possesses a shorter conjugation length and bluer emission. The crystallographic study indicates that their different stacking patterns significantly affect the intermolecular interactions. Among the crystal cells of these three molecules, the incompletely unrestricted motion of PPI-2-DMF results in relatively lower fluorescence efficiency, while PPI-3-SBF with the most intermolecular interactions exhibits the highest fluorescence efficiency. PPI-2-DMF, PPI-2-DPF and PPI-3-SBF realize different PLQYs of 57.26, 67.22 and 66.05% in neat films, respectively. Non-doped devices of PPI-2-DMF and PPI-2-DPF exhibit the maximum EQEs of 7.57 and 8.48%, respectively, with the same deep-blue CIE indexes of (0.16, 0.09). Benefiting from the shorter conjugation length, stronger molecular rigidity, and richer intermolecular interactions, the non-doped device of PPI-3-SBF achieves a high EQE of 8.41% with better color purity of CIE (0.16, 0.07). Theoretical and experimental investigations also reveal that these materials achieve high EUE mainly through the "hot exciton" mechanism. These results indicate

that it is feasible to construct molecules with weak ICT properties to achieve efficient deep blue emitters through precise molecular structure design, which paves a new way for the preparation of efficient non-doped deep blue OLEDs.

## Conflicts of interest

The authors declare no competing financial interest.

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