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## **ARTICLE TYPE**

### Spiro-Annulated Triarylamine Based Hosts Incorporating Dibenzothiophene for Highly-Efficient Single Emitting Layer White Phosphorescent Organic Light-Emitting Diodes

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Four novel host materials were designed and synthesized, incorporating fluorene-spiro-annulated triphenylamine/carbazole (ST/SCz) and dibenzothiophene (DBT) blocks. A *meta*-linking strategy was applied by introducing DBT moieties to ST/SCz skeletons on C3 position of the fluorene backbones. As

- <sup>10</sup> expected, high triplet energies (over 2.80 eV) were achieved in all these four materials despite the different linking positions on DBTs. All four materials show high  $T_g$  from 149 to 163 °C, which is benefitted from their spiro-structure. Their thermal, electrochemical and photo-physical properties were fully characterized. Highly efficient blue and white PHOLEDs were fabricated using these four materials as host. Triphenylamine-containing STDBT4 and STDBT2 demonstrate better device performances due
- <sup>15</sup> to their relatively high-lying HOMO compared to carbazole-containing SCzDBT4 and SCzDBT2. Maximum  $\eta_{ext}$  of 19.6%/18.4% (STDBT4/STDBT2) were achieved for FIrpic based devices, and 23.7%/22.2% (STDBT4/STDBT2) for two color based white PHOLEDs with double emitting layers using PO-01 as yellow dopant. Finally a highly efficient single emitting layer white PHOLED with maximum efficiencies of (24.0%, 77.0 cd A<sup>-1</sup>, 63.2 lm W<sup>-1</sup>) and CIE coordinator of (0.38, 0.48) was <sup>20</sup> realized using the device configuration of ITO/HAT-CN/TAPC/STDBT4: 8 wt% FIrpic: 0.8 wt% PO-

01/TmPyPB/Liq/Al. And the device shows good color stability and low efficiency roll-off. Even at a high luminance of 10000 cd m<sup>-2</sup>, it still maintain very high efficiencies of (17.9%, 56.4 cd A<sup>-1</sup>, 26 lm W<sup>-1</sup>).

#### Introduction

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- After over two decades of research and development, organic <sup>25</sup> light emitting diode (OLED) have proved itself to be a practical technique in display with outstanding performance.<sup>1</sup> OLED display panels have already been commercialized and monetized in portable electronic devices. And large size OLED TVs are on their way to mass production. After the success in flat-panel <sup>30</sup> display, the next big thing for OLED is its application in general lighting.<sup>2</sup> Kido's early research on white OLED revealed its potential and advantages in solid-state lighting.<sup>3</sup> But the efficiency of conventional fluorescent white OLED cannot compete with fluorescent tube or LED lighting device, since it <sup>35</sup> could only utilize singlet excitons. In 1998, Forrest and Thempson reported highly afficient phoephorescent organic light
- Thompson reported highly efficient phosphorescent organic lightemitting diodes (PHOLEDs),<sup>4</sup> which boosted the theoretical internal quantum efficiency (IQE) from 25% to 100% by utilizing both singlet and triplet excitons. The significant progress made it <sup>40</sup> possible to develop white PHOLED with efficiency comparable
- <sup>40</sup> possible to develop while THOLED with efficiency comparable to fluorescent tube. This was realized by K. Leo who developed a highly efficient white PHOLED using elegantly designed triemitting layers.<sup>5</sup> By applying light outcoupling techniques, the power efficiency can outran fluorescent tube. But there is another <sup>45</sup> critical issue baffling the industrialization of white PHOLED for

general lighting, the cost. Constructing the multilayer structure of OLED is the prime part of the total cost. The more the layers, the higher the cost. The short cut to decrease the layers without compromising the efficiency is to simplify the emitting layer.<sup>6</sup> <sup>50</sup> Thus developing highly efficient white PHOLED with single emitting layers is a promising strategy for the commercialization of white PHOLED.

A typical PHOLED adopts a host-guest-strategy by doping 55 emitting layer with heavy metal-containing complexes (Ir, Pt or Os etc.) as emitting dopant, homogeneously dispersed into appropriate host material. In this regard, host materials play a crucial role in PHOLEDs. Developing host materials with supreme performance is as important as the design of efficient 60 phosphorescent emitters for realizing highly efficient PHOLEDs for practical usage.<sup>7</sup> Especially in PHOLED with single emitting layer, the physical properties of host material need to be finely tuned to fit all the dopants involved. Firstly, the triplet energy  $(E_{\rm T})$  level of host material must be higher than that of guest in 65 order to prevent reverse energy transfer from the guest back to the host and to confine the triplet excitons in the emission zone. Since the triplet energy of the commonly used blue dopant FIrpic is 2.65 eV, host materials with triplet energies over 2.7 eV are favorable for blue and white PHOLEDs.<sup>8</sup> Besides adequate triplet

55



level, a good host material still have other criteria to meet, such 5 as good carrier mobility, matched HOMO and LUMO energy levels, good thermal stability etc.<sup>7</sup> mCP, which is a widely used host materials, has very high  $E_{\rm T}$  of 2.9 eV and good holetransporting property. But its low glass transition temperature (60 <sup>o</sup>C) greatly restricts its application.<sup>9</sup> During the past decade, 10 numerous host materials were developed to replace mCP from the perspectives of increasing  $T_{\rm g}$ , adjusting energy levels, balancing carrier transporting, etc.7 Spiro-annulated structures normally have very high  $T_{\rm g}$  due to their bulky and orthogonal configuration.<sup>10</sup> And the central sp<sup>3</sup> hybridized spiro-carbon 15 could disconnect the conjugation of the two units on each side of spiro-carbon, and hence preserve  $E_{\rm T}$ . In addition, the properties of the spiro-annulated materials can be easily tuned by introducing different functional groups or atoms on each side of the spirocarbon, forming symmetric or asymmetric structures.<sup>11</sup> All these 20 features make them good skeletons for developing high performance host materials. Various spiro-structures were explored as host materials for PHOLEDs, incorporating phosphine oxide,<sup>12</sup> triphenylsilane,<sup>13</sup> cyano group,<sup>14</sup> oxadiazole,<sup>15</sup> etc.<sup>16</sup> Dibenzothiophene (DBT) is another building block that 25 receives growing attentions. DBT has high triplet energy of 3.04 eV and good hole-transporting ability, which makes it a good candidate for constructing host materials. Recently a few DBT based host materials were reported with very good device performances.<sup>17</sup> For instance, Han reported a DBT based 30 phosphine oxide DBTSPO with a maximum EQE of 13.9% for white PHOLED,<sup>18</sup> In our previous work, we reported a DBT based host material incorporating spirobifluorene through an ortho-linkage.<sup>19</sup> The maximum EQE for white PHOLED reached 16.9%. And very recently, Wong reported a fluorene based host 35 material CzFCN linking through the C3 position to form a meta-

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- <sup>35</sup> material CZFCN mixing infolgin the CS position to form a metalinkage.<sup>20</sup> The white PHOLED using CZFCN as host showed a maximum EQE of 14.2%. We also developed a spirobifluorene based phosphine oxide SF3PO linked though the C3 position of the fluorene ring.<sup>21</sup> The triplet energy of SF3PO is significantly
- <sup>40</sup> higher than its *para*-linking analog SPPO1, which is a widely used host based on spirobifluorene. To integrate above advantages about spiro-structures and further elevate the device performance, in this paper, we designed and synthesized four novel host materials incorporating spiro-annulated triarylamine
- <sup>45</sup> and DBT units using *meta*-linking strategy (Scheme 1). DBT unit is connected through the C3 position of fluorene. Both C2 and C4 position of DBT unit are explored, forming a total *meta*-linkage with the fluorene ring. As expected, all four materials have very high  $E_{\rm T}$  of over 2.8 eV. For comparison, a *para*-linking analog 50 ST2DBT4 was also synthesized. Its triplet energy plummets to

2.48 eV due to the greatly extended conjugation by *para*-linkage. The high  $E_{\rm T}$ s qualify them as hosts



Scheme 2 Synthetic routes of host materials. i) n-BuLi, THF, -78 °C. ii) HCl (11 M), AcOH, reflux. iii) Pd(PPh<sub>3</sub>)<sub>4</sub>, THF/K<sub>2</sub>CO<sub>3</sub> (2M) (3/1, v/v), 70 °C.

- for blue and white PHOLEDs. Electron-donating triarylamines are introduced to raise the HOMO levels of these materials, aiming to facilitate the hole injection. And the energy levels can also be tuned by different arylamines. By installing triphenylamine or *N*-phenylcarbazole unit on the fluorene ring through a spiro-carbon, the resulting spiro-annulated hosts not only inherit the good hole injection, but also show enhanced thermal stability. All these materials presented high  $T_g$  ranging from 149 to 163 °C. The device performances of these host materials were evaluated using common device structures. Triphenylamine containing materials showed better performances than their *N*-phenylcarbazole containing counterparts. Maximum efficiencies of 19.6%/47.0 cd A<sup>-1</sup>/38.7 lm W<sup>-1</sup> and 18.4%/44.5 cd A<sup>-1</sup>/37.8 lm W<sup>-1</sup> for FIrpic based blue PHOLEDs were achieved
- <sup>70</sup> by STDBT4 and STDBT2. Afterwards, highly efficient white PHOLEDs were fabricated using both double emitting layer and single emitting layer configuration, using FIrpic and PO-01 as dopants. Devices hosted by STDBT4 show the best performances with maximum efficiencies of 23.7%/75.0 cd A<sup>-1</sup>/65.0 lm W<sup>-1</sup> for 75 double and 24.0%/77.0 cd A<sup>-1</sup>/63.2 lm W<sup>-1</sup> for single emitting
- layer white PHOLED. The white PHOLEDs also exhibit low efficiency roll-off and good color stability.

#### **Results and Discussion**

#### Synthesis and Characterization

Scheme 2 illustrates the synthetic routes to target materials. 2-Bromo-triphenylamine or 9-(2-bromophenyl)-9*H*-carbazole was treated with *n*-BuLi at -78 °C, followed by reaction with 3bromofluorenone to afford corresponding alcohol intermediates. Then, the resulting intermediates were used without purification to obtain the bromine substituted spiro-annulated triarylamines (STBr3 and SCzBr3) via a Friedel-Crafts intramolecular ringclosure in the presence of acid. The final products were readily afforded by classic Suzuki-Miyaura reaction between STBr3 or SCzBr3 and corresponding boronic acid of dibenzothiophene in 90 good yields. ST2DBT4 was synthesized following similar procedure. The final products were characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopies, mass spectrometry and elemental analysis. Before device fabrication, all the materials were further

purified by vacuum sublimation. STDBT4 and SCzDBT4, which link through the position 4 of DBT unit, could be readily dissolved in common organic solvent (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, THF etc.)



**Fig. 1** DSC traces recorded at a heating rate of 10 °C min<sup>-1</sup>.

due to their twisted structure. Their good solubility also qualifies them to be potential solution processible host materials in the future study. On the contrary, STDBT2 and SCzDBT2 exhibited very poor solubility and precipitated from solutions during <sup>10</sup> reaction. On the other hand, this greatly simplified their purification process, and pure samples of STDBT2 and SCzDBT2 can be obtained by just filtration followed by vacuum sublimation to remove catalyst residues.

#### **Thermal Analysis**

- <sup>15</sup> The thermal stabilities of the compounds were measured by thermogravimetric analysis (TGA). All four materials exhibited high decomposition temperatures (*T*<sub>d</sub>, corresponding to 5% weight loss, Fig S1) ranging from 363 °C to 464 °C. Their glass transition temperatures (*T*<sub>g</sub>, Fig 1) were observed at 149 °C and 20 151 °C for STDBT4 and STDBT2, 161 °C and 163 °C for SCzDBT4 and SCzDBT2 by differential scanning calorimetry (DSC), indicating that it is the difference of configurations at spiro-moieties not the DBT linking ways which determined the morphological stability. Benefitted from the more rigid *N*-25 phenylcarbazole, SCzDBT4 and SCzDBT2 showed both higher *T*<sub>d</sub> and *T*<sub>g</sub> than their triphenylamine counterparts. The good thermal stabilities of these materials are beneficial to their device
- thermal stabilities of these materials are beneficial to their device applications by improving the film morphology and reducing the possibility of crystallization and phase separation upon heating.

#### **30 Photophysical Properties**

The UV-Vis absorption and photo-luminescence spectra in dilute toluene solutions, phosphorescent spectra in 2-methy THF at 77 K are presented in Fig 2. Detailed photo-physical data are summarized in Table 1. In the absorption spectra of SCzDBT4 <sup>35</sup> and SCzDBT2, the relatively weak shoulder peaks at ca. 360 nm

- are attributed to the  $n-\pi^*$  transitions of carbazole group. As a result, the optical band gaps of SCzDBT4 and SCzDBT2 are smaller than those of STDBT4 and STDBT2 by ca. 0.2 eV. STDBT4 and STDBT2 exhibited broad structureless PL spectra with  $\lambda$  and  $\lambda$  and  $\lambda$  are as a 270 nm. On the other hand, the PL spectra of
- <sup>40</sup> with  $\lambda_{max}$  ca. 370 nm. On the other hand, the PL spectra of SCzDBT4 and SCzDBT2 were almost identical with vibronic

structure consisting of a  $\lambda_{max}$  at 365 nm and a shoulder peak at 382 nm. The PL and absorption spectra results suggest that the different substitution positions on DBT moieties have limited <sup>45</sup> effect on electronic structures of the materials. We also tested



Fig. 2 UV-Vis absorption and PL spectra measured in toluene solution at 10<sup>-5</sup> M; phosphorescence spectra measured in frozen 2-methyltetrahydrofuran (2-MeTHF) matrix at 77 K.

50 their PL and absorption spectra in thin films (Fig S2), which are similar to the solution spectra with only slight red shifts. The triplet energies were estimated from the highest vibronic band of their low temperature phosphorescent spectra. STDBT4 and SCzDBT4, which link through the C4 position on the DBT units, 55 exhibit sharp peaks at ca. 440 nm corresponding to the T<sub>1</sub> band. While in the spectra of their counterparts linking through the C2 position of DBT, the vibronic bands at 440 nm shrink to less obvious shoulder peaks. Nevertheless, all four compounds possessed high  $E_{\rm T}$  over 2.8 eV, which qualify them to be potential 60 hosts for blue and white PHOLEDs. The  $E_{\rm T}$  of ST is about 2.87 eV (Fig S3), which is inherited by these materials with little compromise. For comparison, ST2DBT4, the analogue of STDBT4 which adopts a *para*-linkage, exhibits a dramatically lowered  $E_{\rm T}$  of 2.48 eV (Fig S3). It is obvious that our meta-65 linking strategy on fluorene moiety successfully reduces the effective conjugation length and preserves the high triplet energy of the backbone. Time-dependence DFT was utilized to simulate the natural transition orbitals (NTOs)<sup>22</sup> using the optimized structures of the S<sub>0</sub> state. Fig 3 illustrates the spatial distribution 70 of the lowest and highest NTOs of the host materials. The NTOs mainly locate on the fluorene ring and one adjacent benzene ring of DBT moiety, indicating the triplet energies of these materials are determined by the linking ways of DBT to the spiro-structure. This explains well why the materials with the same linking 75 configuration on DBT exhibited similar phosphorescent spectra. STDBT4 and SCzDBT4 linked through the C4 position on DBT adopt more twisted structures with dihedral angles of ca. 48° (between fluorene and DBT), about 10° larger than that of STDBT2 and SCzDBT4, resulting in sharper T<sub>1</sub> bands.

#### 80 Electrochemical Properties and FMO Energy Levels

The electrochemical behaviors of these materials were probed by cyclic voltammetry (CV) using a typical tri-electrode configuration with ferrocene as internal standard. Both distinct oxidation and reduction processes were observed (Fig 4). On the ss oxidation side, they all exhibited a reversible oxidation peak followed by a quasi-reversible oxidation process, corresponding to the oxidation of the nitrogen center of ST/SCz and the DBT

ring respectively. While their reduction processes are less characteristical compared to oxidation ones. The oxidation onsets of the ST-containing compounds are 0.2 eV lower than their SCz-

containing counterparts. This implies the HOMO levels of  $_{\rm 5}$  STDBT4 and STDBT2 are about 0.2 eV higher than SCzDBT4

Table 1 Physical Properties

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	Abs λ <sub>max</sub> solution <sup>a</sup> /film <sup>b</sup> [nm]	PL λ <sub>max</sub> solution <sup>a)</sup> /film <sup>b)</sup> [nm]	$E_{\rm T}^{\rm c}$ [eV]	<i>T</i> <sup>d</sup> <sub>m</sub> <sup>d</sup> [°C]	<i>T</i> <sup>d</sup> <sub>g</sub> <sup>d</sup> [°C]	<i>T</i> <sub>d</sub> <sup>d</sup> [°C]	HOMO <sup>e</sup> [eV]	LUMO <sup>f</sup> [eV]	Eg <sup>g</sup> solution [eV]	Eg <sup>g</sup> film [eV]
STDBT4	319/322	373/380	2.83	>350	149	383	5.69	2.17	3.57	3.52
STDBT2	317/320	371/378	2.82	297	151	363	5.74	2.17	3.59	3.57
SCzDBT4	355, 336, 319/	365, 382/	2.82	>350	161	464	5.91	2.58	3.39	3.33
	359, 340, 292	3/3, 38/								
SCzDBT2	360, 319, 294/ 360, 320, 295	365, 382/ 372, 389	2.81	>350	163	397	5.94	2.61	3.40	3.33

<sup>*a*</sup> Measured in toluene solution at room temperature; <sup>*b*</sup> vacuum-deposited thin film (50 nm); <sup>*c*</sup> measured in 2-MeTHF glass matrix at 77 K; <sup>*d*</sup>  $T_m$ : melting temperatures,  $T_g$ : glass transition temperatures,  $T_d$ : decomposition temperatures; <sup>*e*</sup> HOMO levels were calculated from UPS data; <sup>*f*</sup>LUMO levels were calculated from HOMO and  $E_g$  in solid films; <sup>*g*</sup> $E_g$ : The band gap energies were calculated from the corresponding absorption onset.



Fig. 3 NTOs of the materials.

and SCzDBT2. The CV results only reflect the electrochemical behavior of materials in solution. Given that the devices are in <sup>15</sup> solid films, it is not appropriate to use the HOMO or LUMO levels calculated directly from the oxidation or reduction process in the device energy diagram.<sup>23</sup> In order to get more accurate and reliable frontier molecular orbital (FMO) energy levels, ultraviolet photoemission spectroscopy (UPS) was employed to

- <sup>20</sup> determine the HOMO levels (Fig S4 to S7). And LUMO levels were calculated from energy band gaps in solid films (Fig S2) and HOMO levels. All the data are summarized in Table 1. The HOMO levels of STDBT4/STDBT2 are 5.69/5.74 eV, about 0.2 eV higher than SCzDBT4/SCzDBT2 (5.91/5.94 eV), matching
- <sup>25</sup> perfectly with the CV results. The relatively high lying HOMO of STDBT4/STDBT2 may facilitate the hole injection to the emitting layer in devices. SCzDBT4 and SCzDBT2 show significantly lowered LUMO levels, which are a result of their lowered HOMO levels compounded with narrowed optical band

<sup>30</sup> gaps compared to STDBT4 and STDBT2. The LUMO levels of these new materials are comparable to many bipolar host

materials reported even not any electron-withdrawing groups are introduced.<sup>7, 20</sup> This may facilitate the electron injection and help balancing the carrier recombination to some degree. To better <sup>35</sup> understand the electronic structures of these materials, DFT calculations were utilized to simulate their FMO spatial distributions. As Fig 5 illustrates, these materials have divided HOMO and LUMO, separated by the central spiro-carbon. The HOMOs of these materials locate at the electron-rich nitrogen <sup>40</sup> centers. The HOMO-1s distribute on the fluorene ring and spread heavily on the sulfur center of DBT unit with similar distribution patterns as the HOMO of DBT (Fig S8). The HOMO and HOMO-1 match with the CV results, corresponding to the first and second oxidation process, respectively. STDBT4 and <sup>45</sup> SCzDBT4 have similar LUMO distributions with LUMO spreading on part of the fluorene ring. On the other hand,



Fig. 4 Cyclic voltammogram of host materials. The measurement of oxidation and reduction potentials were performed in  $CH_2Cl_2$  and DMF respectively with 0.1 M of n-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte.

<sup>5</sup> STDBT2 and SCzDBT4 show much different LUMO distributions. As a result of sulfur induced polarization, the C2 and C8 positions of DBT don't have LUMO distribution, which restrain the LUMO of STDBT2 on the DBT ring. In the case of SCzDBT2, the energy of unoccupied FMO on ST is higher than <sup>10</sup> that on SCz. The LUMO of SCz merged with the LUMO of DBT forming a near-degenerate orbital. Nevertheless, the FMO energy levels are mainly determined by the amine parts of the materials. The different linking ways of DBT show limited affect on the FMO energy levels because the *meta*-linking strategy greatly <sup>15</sup> restricts the conjugation.

#### **EL performance of PHOLEDs**

To evaluate the performance of these four materials as host materials, FIrpic based blue phosphorescent devices were fabricated using the structure of ITO/HAT-CN (10 nm)/TAPC <sup>20</sup> (45 nm)/Host:8 wt% FIrpic (20 nm)/TmPyPB (40 nm)/Liq (2 nm)/Al. STDBT4 (B1), STDBT2 (B2), SCzDBT4 (B3) or SCzDBT2 (B4) were doped with 8 wt% FIrpic to form emitting layer (EML). To confine triplet excitons in the EML, TAPC and TmPyPB which have high  $E_{\rm T}$  and carrier mobility were served as

- <sup>25</sup> hole-transporting/electron-blocking (HTL/EBL) and electrontransporting /hole-blocking layer (ETL/HBL) respectively. And to ensure efficient charge injection, HAT-CN and Liq were utilized as hole injection layer (HIL) and electron injection layers (EIL), respectively.
- <sup>30</sup> Fig 6a illustrates the efficiencies of blue phosphorescent devices. The detail performance data were summarized in Table 2. High efficiencies were achieved by device B1~4. The maximum efficiency of B1 (STDBT4) reached 47.0 cd A<sup>-1</sup> for current efficiency (CE), 38.7 lm W<sup>-1</sup> for power efficiency (PE) and
- <sup>35</sup> 19.6% for external quantum efficiency (EQE). B2 (STDBT2) shows similar performance with slightly lowered maximum efficiencies of 44.5 cd A<sup>-1</sup> for CE, 37.8 lm W<sup>-1</sup> for PE and 18.4% for EQE. Although the performance of B3 (SCzDBT4)/B4 (SCzDBT2) are relatively lower than that of B1/B2, maximum

40 efficiencies of 37.3/29.3 cd A<sup>-1</sup> for CE, 27.0/21.9 lm W<sup>-1</sup> for PE and 15.3%/11.7% for EQE were still realized. All four devices show rather low efficiency roll-off at low current density. At a brightness of 1000 cd m<sup>-2</sup>, the EQE of B1~4 maintains over 90% of their initial values. But with the increase of current density 45 from 5 mA cm<sup>-2</sup> to 40 mA cm<sup>-2</sup>, the efficiencies of B1 and B2 decay more rapidly than that of B3 and B4. At a high brightness of 10000 cd m<sup>-2</sup>, device B1~4 finally reach similar performances with EQE of ca. 12%. Although B4 presented the lowest efficiencies among these devices, it shows very low roll-off with 50 only 13% drop of EQE even at 10000 cd m<sup>-2</sup>. All four devices show relativley greenish blue CIE of ca. (0.16, 0.39) compared to typical FIrpic based devices. These red-shifts of CIE are common in literatures.<sup>20, 24</sup> This phenomenon can be attributed to the micro-cavity effect caused by different distance between emission 55 zone (EMZ) and cathode.<sup>25</sup> The CIE of blue devices can be further altered by manipulating the thickness of charge transporting layers. But in the application of solid-state lighting, the CIE of blue devices is not so critical. The better performance of B1 and B2 may be attributed to the relatively higher HOMO 60 level of STDBT4/STDBT2. The hole/electron injection barriers are about 0.2 eV/0.5 eV for STDBT4/STDBT2 and 0.4 eV/0.1 eV for SCzDBT4/SCzDBT2 (Fig 7). Considering these four materials are hole-transporting type hosts (Fig S9), holes can be efficiently injected into EML. Based on the energy diagram, SCz 65 based materials should reduce hole injection and facilitate electron injection, resulting in more balanced charge injection and an improvement of the quantum efficiency of the device. However, it is also important to consider the energy levels of the dopant when discussing efficiency. FIrpic has low lying LUMO 70 level that is below that of the electron transporting material TmPyPB. The ST based materials have higher LUMOs compared to the SCz based materials. As such, when electrons are injected into the emitting layer, there is a greater likelihood that there will be direct recombination on the dopant when the ST based 75 materials are used compared to the SCz based materials. In essence, the dopant acts as stronger electron traps for the ST based materials and the resulting direct recombination on the dopant produced a high efficiency. In contrast, the SCz based materials have LUMO levels that are close to those of the dopant 80 and the ability of the dopant to trap electrons is reduced. When electrons are injected into the emitting layer containing the SCz based hosts, there is less direct recombination on the dopant and the efficiency is lower due to a charge imbalance. As long as the hole can be efficiently recombined with electrons, then the 85 efficiencies of ST based devices can be higher than the SCz based devices. But as the voltage increases, in the case of B1 and B2, holes can on longer be efficiently recombined with electrons because of limited dopant in EML. The unbalanced charge injection results in excessive holes at the EML/ETL interface, 90 leading to efficiency roll-off at high current density. While in the contrast, as a merit of the relatively low LUMO levels of SCzDBT4/SCzDBT2, B3 and B4 have much smaller electron injection barrier (0.1 eV), which lead to more balanced charge injection and low efficiency roll-off at high current density. These 95 four materials proved themselves to be very good host materials for blue PHOLEDs. STDBT4 and STDBT2 with maximum EQE of 19.6% and 18.4% are among the best-performed blue host

#### materials.

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The excellent performance of blue PHOLEDs qualified them as potential host materials for white PHOLEDs. There are two

<sup>5</sup> possible layouts to generate white light in PHOLEDs, three colorbased (R+G+B) and two color-based (B+Y or B+O) devices. Generally, RGB white PHOLED usually can obtain very high color rendering index (CRI) and its CIE can be tuned in a wide



Fig. 5 Optimized geometry and HOMO-LUMO spatial distributions.

Table 2 Electroluminescence characteristics of the devices

Device <sup>a</sup>	Device <sup>a</sup> Host		$\eta_{ce}^{c} [cd A^{-1}]$	$\eta_{\rm pe}^{\ \rm c}  [ m lm \ W^{-1}]$	$\eta_{\rm ext}^{\ \rm c}$ [%]	$\operatorname{CIE}\left[x,y\right]^{\mathrm{d}}$	CCT [K] <sup>e</sup>	
B1	STDBT4	4.8	47.0, 41.9, 28.4	38.7, 27.6, 12.2	19.6, 17.6, 11.9	0.15, 0.38	-	
B2	STDBT2	4.8	44.5, 42.5, 30.9	37.8, 28.2, 13.6	18.4, 17.5, 12.7	0.16, 0.39	-	
В3	SCzDBT4	5.1	37.3, 37.2, 30.6	27.0, 23.0, 12.8	15.3, 15.2, 12.5	0.16, 0.40	-	
B4	SCzDBT2	5.1	29.3, 29.2, 25.6	21.9, 17.9, 10.5	11.7, 11.7, 10.2	0.17, 0.41	-	
W1	STDBT4	4.2	75.0, 72.7, 55.8	65.0, 54.1, 26.5	23.7, 22.7, 17.5	0.39, 0.49	4337	
W2	STDBT2	4.3	67.7, 67.3, 55.8	57.5, 49.9, 27.6	22.2, 21.9, 17.8	0.36, 0.48	4817	
W3	SCzDBT4	4.8	59.0, 57.1, 47.8	45.8, 37.2, 21.7	20.0, 18.8, 15.6	0.35, 0.47	5109	
W4	SCzDBT2	4.8	44.4, 44.1, 41.2	33.8, 29.1, 18.8	15.1, 15.0, 13.6	0.33, 0.46	5656	
WS1		4.7	56.5, 51.0, 35.2	46.6, 34.0, 15.2	20.7, 18.9, 13.2	0.25, 0.42	8518	
WS2	GTDDT4	4.6	76.5, 71.7, 55.2	61.5, 48.8, 25.1	24.0, 22.6, 17.7	0.37, 0.48	4651	
WS3	S1DB14	4.6	77.0, 72.8, 56.4	63.2, 50.1, 26.0	24.0, 22.8, 17.9	0.38, 0.49	4536	
WS4		4.6	76.2, 75.5, 60.9	62.0, 52.1, 28.4	23.2, 23.0, 18.8	0.41, 0.50	4086	

<sup>a</sup> The notation 1~4 in device B1~B4 and W1~W4 indicate the corresponding device fabricated with STDBT4, STDBT2, SCzDBT4 and SCzDBT2 as host respectively. Device configuration: B1~B4, ITO/HAT-CN (10 nm)/TAPC (45 nm)/Host:8 wt% FIrpic (20 nm)/TmPyPB (40 nm)/Liq (2 nm)/Al;
 <sup>15</sup> W1~W4, ITO/HAT-CN (10 nm)/TAPC (45 nm)/Host:8 wt% FIrpic (19 nm)/Host:6 wt% PO-01 (1 nm)/TmPyPB (40 nm)/Liq (2 nm)/Al; WS1~WS4, ITO/HAT-CN (10 nm)/TAPC (45 nm)/STDBT4: 8 wt% FIrpic: x wt% PO-01 (20 nm)/TmPyPB (40 nm)/Liq (2 nm)/Al; WS1~WS4, ITO/HAT-CN (10 nm)/TAPC (45 nm)/STDBT4: 8 wt% FIrpic: x wt% PO-01 (20 nm)/TmPyPB (40 nm)/Liq (2 nm)/Al; WS1~WS4, ITO/HAT-CN (10 nm)/TAPC (45 nm)/STDBT4: 8 wt% FIrpic: x wt% PO-01 (20 nm)/TmPyPB (40 nm)/Liq (2 nm)/Al; WS1~WS4, ITO/HAT-CN (10 nm)/TAPC (45 nm)/STDBT4: 8 wt% FIrpic: x wt% PO-01 (20 nm)/TmPyPB (40 nm)/Liq (2 nm)/Al, WS1~WS4, x = 0.2, 0.5, 0.8, 1.2.
 <sup>b</sup> Voltages at 1000 cd m<sup>-2</sup>. <sup>c</sup> efficiencies in the order of maximum, at 1000 cd m<sup>-2</sup> and at 10000 cd m<sup>-2</sup>. <sup>d</sup> Commission International de l'Eclairage coordinates measured at 5 mA cm<sup>-2</sup>. <sup>e</sup> Correlated color temperature at 5 mA cm<sup>-2</sup>.

range.<sup>2</sup> But with three dopants involved, the device fabrication <sup>20</sup> process will be complicated and the device efficiency may also be compromised due to the multiple recombination interfaces. Even all the dopants been doped into one layer to simplify the device structure, the control of doping concentration of low  $E_{\rm T}$  dopants can still be tricky. By comparison, two color-based PHOLED has

<sup>25</sup> more simplified device structure with fewer variables. With less interfaces involved, the charge recombination zone can be more easily adjusted. Furthermore, single EML devices can be realized by doping two dopants into one layer. And the CIE can be easily tuned by the doping ratio of yellow or orange dopant. Although <sup>30</sup> the CIE is hard to reach (0.33, 0.33) by manipulating two colors, the spectra can still be tuned from cold white to warm white, which is more desirable in human-friendly lighting.<sup>26</sup> Considering all these features, a two color-based device configuration was adopted in our experiments. White PHOLEDs with double EMLs <sup>35</sup> were fabricated using these four materials as host. The device structure is similar to previous blue PHOLEDs: ITO/HAT-CN (10 nm)/TAPC (45 nm)/Host:8 wt% FIrpic (19 nm)/Host:6 wt% PO-01 (1 nm)/TmPyPB (40 nm)/Liq (2 nm)/Al (W1~4). A thin yellow EML was inserted between blue EML and ETL using PO-40 01 as dopant. As expected, device W1~4 exhibited excellent performances (Fig 6b). Similar to the blue PHOLEDs, W1 (STDBT4) and W2 (STDBT2) showed better performance

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Fig. 6 Current efficiency, power efficiency and external quantum efficiency as a function of luminance for Device B1~4 (a) and Device W1~4 (b)



s Fig. 7 Proposed energy level diagram showing HOMO and LUMO levels and the molecular structures for the materials used in Device W1~4 and WS1~4.

than W3 (SCzDBT4) and W4 (SCzDBT2). The best-performed W1 reached maximum efficiencies as high as 75.0 cd A<sup>-1</sup> for CE, 65 lm W<sup>-1</sup> for PE and 23.7% for EQE with a CIE coordinator of (0.39, 0.49). The maximum EQE of W2 and W3 also exceed 20% <sup>10</sup> with 67.7 and 59.0 cd A<sup>-1</sup> for CE, 57.5 and 45.8 lm W<sup>-1</sup> for PE. Even the least-performed device W4 still has an EQE over 15%. W1 and W2 show much flatter efficiency decay curves as a function of brightness than corresponding blue devices. And W3 and W4 still preserve their low efficiency roll-off as B3 and B4. <sup>15</sup> At a brightness of 1000 cd m<sup>-2</sup>, the efficiencies of W1~4 maintain as high as over 96% for CE, 80% for PE and 95% for EQE

compared to their maximum values. And at high luminance of 10000 cd m<sup>-2</sup>, their EQEs still stay above 73% of the maximum values. It is worth to notice that device W1~4 possess the same <sup>20</sup> device configuration, but exhibit different CIE coordinates, which show a gradually blue shift from (0.39, 0.49) for W1 to (0.33, 0.46) for W4. According to the energy diagram, the main carrier recombination zone of W1 will locate at the interface of PO-01 layer and ETL, since the hole injection barrier (0.2 eV) is much <sup>25</sup> smaller than electron injection barrier (0.5 eV). Triplet excitons can be transfer to PO-01 more easily because the band gap and T<sub>1</sub> of PO-01 are smaller than those of FIrpic. But the PO-01 layer is

very thin, which means part of the triplet excitons can migrate to or formed in the adjacent FIrpic layer, resulting a warm white of (0.39, 0.49) with color temperature of 4337 K. STDBT2, SCzDBT4 and SCzDBT2 have sequentially lowered HOMOs 5 compared to STDBT4, which may cause the recombination zone gradually shift towards the anode. More and more excitons can migrate or be formed in the blue EML, resulting in progressive blue shifts in CIE coordinates of W2, W3 and W4. This also explains the lower efficiency roll-off of W1 and W2 compared to

10 B1 and B2 because that the carrier recombination zone of W1 and W2 mainly locate in the more efficient yellow EML with smaller efficiency roll-off. In the case of W3 and W4, the carrier recombination zones shift towards the less efficient blue EML due to their lower HOMO levels, resulting in the similar 15 efficiency decay trend as B3 and B4.

Apparently, these four materials showed excellent performance in white PHOLEDs. Among them, W1 hosted by STDBT4 exhibited the best performance at 1000 cd m<sup>-2</sup>, with efficiency of  $_{\rm 20}$  72.7 cd  $A^{\rm -1}$  for CE, 54.1 lm  $W^{\rm -1}$  for PE and 22.7% for EQE. And W1 also had the best color stability with CIE nearly unchanged

(Fig S13) when the current density varied from 0.2 mA cm<sup>-2</sup> to 40 mA cm<sup>-2</sup>. To further simplify the device structure, devices with single EML were fabricated by doping FIrpic and PO-01 into 25 STDBT4. The device structure of W1~4 has proved itself applicable and efficient. So we merged the double EMLs together leaving only one variable, the doping concentration of PO-01 in the single EML. When doping two triplet emitters into one layer, the doping concentration of the dopant with lower  $E_{\rm T}$ , in this case 30 PO-01, should be smaller in order to get a white emission since the excitons tend to be transferred to the emitters with lower  $E_{\rm T}$ . Four concentrations of PO-01 were adopted, 0.2%, 0.5%, 0.8% and 1.2% for WS1~4 respectively, resulting emissions from cold white (0.25, 0.42) to warm white (0.41, 0.50). All four devices 35 show excellent performances with EOE exceeding 20%. Fig 8 illustrates their efficiency curves as a function of luminance and emission characteristics. Since the dopants were integrated into one EML, WS1~4 show quite stable CIE coordinates (Fig 8a).

40 CIE of (0.25, 0.42) and CCT of 8518 K. The EL spectrum of WS1 is dominated by blue emission from FIrpic due to the relatively low doping concentration of PO-01. And the

Device WS1 with 0.2% PO-01 exhibit a cold white emission with



efficiencies are also compromised since most of the excitons are captured by less efficient FIrpic. By raising the doping rate of PO-01 to 0.5% and 0.8%, the emissions of WS2 and WS3 were tuned to more desirable warm white light with CIE of (0.37, 0.48)50 and (0.38, 0.49); CCT of 4651 K and 4536 K, respectively. The maximum efficiencies of WS3 reach 77.0 cd A<sup>-1</sup> for CE, 63.2 lm

W<sup>-1</sup> for PE and 24.0% for EQE. WS2 trails closely behind WS3 with similar performances. Both WS2 and WS3 had very low efficiency roll-off. Compared to the maximum values, their 55 efficiencies maintain over 93% for CE, 79% for PE and 94% for EQE at 1000 cd m<sup>-2</sup>. Even at 10000 cd m<sup>-2</sup>, the efficiencies of WS3 still preserve 56.4 cd A<sup>-1</sup> for CE, 26.0 lm W<sup>-1</sup> and 17.9% for



EQE, which makes it very tolerable to voltage variation. Further increase of the PO-01 concentration to 1.2% rendered the CIE coordinate into the yellow region, resulting in a yellowish white light emission of WS4 with CIE of (0.41, 0.50) and CCT of 4086 5 K. WS4 also exhibits very high efficiencies of 76.2 cd A<sup>-1</sup> for CE.

- <sup>5</sup> K. WS4 also exhibits very high efficiencies of 76.2 cd A<sup>-1</sup> for CE, 62.0 lm W<sup>-1</sup> and 23.2% for EQE with even better efficiency rolloff, since the spectrum is dominated by yellow emission from more efficient PO-01. Compared with double emitting layer device W1, WS3 have slightly higher efficiencies and similar CIE
- <sup>10</sup> coordinates. The CIE coordinates of WS3 show a small blue shift with increasing current density. Since that all the dopants are integrated into one layer, electron injection into EML is facilitated by dopants at low current density. As the current density increases, the recombination zone gradually move toward
- <sup>15</sup> cathode due to the hole transporting nature of the host, resulting blue shift in CIE value caused by the micro-cavity effect. Nevertheless, the CIE coordinates of simplified devices are still quite stable. Again, the supreme performances of single EML white PHOLEDs have proved STDBT4 an excellent host material
- <sup>20</sup> for cost-effective white PHOLED. Its efficiencies are among the best performed single EML white PHOLED.<sup>27</sup> In the upcoming research, the efficiencies of our single EML white PHOLEDs could easily outrun fluorescent tube by applying state-of-the art outcoupling techniques.

#### 25 Conclusions

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Four new host molecules based on spiro-annulated triarylamine incorporating dibenzothiophene were synthesized and fully characterized. The DBT moieties were introduced through monosubstituted *meta*-linking strategy on the C3 position of the <sup>30</sup> fluorene ring to preserve  $E_{\rm T}$ . This molecular design is rarely reported before and endowed the materials with high thermal stability and high triplet energy. And the FMO energy levels can be tuned by different arylamines to balance the charge injection. The PHOLED results have proved this series of materials

- <sup>35</sup> competent for both blue and white devices. The best performed STDBT4 exhibits maximum EQE of 19.6% for blue and 23.7% for double EML white PHOLED using common device structures. Highly efficient cost effective single EML white PHOLEDs were also fabricated using STDBT4 as host with very
- <sup>40</sup> low efficiency roll-offs. Maximum efficiencies of (24.0%, 77.0 cd A<sup>-1</sup>, 63.2 lm W<sup>-1</sup>) were reached with CIE coordinator of (0.38, 0.48). At 1000 cd m<sup>-2</sup> and 10000 cd m<sup>-2</sup>, the EQE still preserved 22.8% and 17.9% respectively. These performances are among the highest efficiencies achieved by single EML white
- <sup>45</sup> PHOLEDs. To the best of our knowledge, STDBT4 is so far the best performed host materials based on spiro-structures for white PHOLEDs. Given the high efficiencies achieved, the performance of our single EML white PHOLEDs have the potential to exceed fluorescent tube efficiency by applying <sup>50</sup> outcoupling layers in further research.

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The alignments of spiro-triarylamine and DBT unit are successfully utilized in the host materials of phosphorescent OLEDs. Benefitted from optimized linking way, four new host materials with high triplet energies and matched HOMO/LUMO are obtained. In particular, the host STDBT4 could achieve impressively high efficiencies not only in blue but also in warm white (double-layer or single-layer) with quite low roll-offs.

361x135mm (300 x 300 DPI)