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# A New Benzothienoindole-based Bipolar Host Material for Efficient Green

# **Phosphorescent Organic Light-Emitting Diodes with Extremely Small**

# **Efficiency Roll-Off**

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# Abstract

In this contribution, two new hole-transport units, 10*H*-benzo[4,5]thieno[3,2-*b*]indole (BTI) and 10*H*-benzofuro[3,2-*b*]indole (BFI), were developed to design and synthesize bipolar host materials namely 10-(3-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10*H*-benzo[4,5]thieno[3,2-*b*]indole (**mBTITrz**) and 10-(3-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10*H*-benzofuro[3,2-

blindole (**mBFITrz**), for phosphorescent organic light-emitting diodes (PhOLEDs). The effect of heteroatoms in the hole-transport unit on the physicochemical and electroluminescence properties of the hosts were investigated in detail. Interestingly, the phosphorescence of the compounds was highly dependent on the hole-transport unit, because it originated from their local excited state (<sup>3</sup>LE), which was attributed to the interrupted strong electronic communication between donor and acceptor units by meta-mode of conjugation on the phenyl linker. Consequently, the **mBTITrz** showed high triplet energy  $(E_T)$ of ~ 2.88 eV compared to its counterpart **mBFITrz** ( $E_{\rm T}$  ~ 2.65 eV). Both compounds displayed marked thermal stability with high thermal decomposition temperatures of above 410°C and glass-transition temperatures of above 103°C. In addition, the single carrier device studies revealed a bipolar charge transporting character for the compounds. Furthermore, the compounds were evaluated as bipolar hosts for green PhOLEDs by employing Ir(ppy)<sub>3</sub> dopant. The **mBTITrz**-hosted device demonstrated much better performance than did the mBFITrz-hosted device, with a maximum external quantum efficiency of 21.3% and maximum current efficiency of 76.0 cd/A. Notably, the mBTITrz-based device exhibited excellent efficacy stability with uncompromised efficiency roll-off at 1000 cd/m<sup>2</sup> and an extremely low efficiency roll-off of 3.2% at 5000  $cd/m^2$  and 9.0% at 10,000  $cd/m^2$ .

# Introduction

During the past three decades, organic light-emitting diodes (OLEDs) received enormous impetus from both the academic and industrial laboratories due to their versatile applications in next generation energy saving displays and solid state lightings.<sup>1-9</sup> Also, OLEDs possess numerous attractive features such as ultra-thinness, inexpensive, light weight, flexible and low power consumption compared to traditional display technologies.<sup>1-9</sup> In the OLEDs, as per the spin statistics the recombination of charge carriers generates singlet and triplet excitons in

1:3 ratio.<sup>4-6</sup> Conventional fluorescent materials can harvest only singlet excitons for light emission due to the spin forbidden transition rules, which limited their internal quantum efficiency to 25%.<sup>4-6</sup> In order to resolve this, Forrest *et al.* developed heavy metal-based phosphorescent emitters (PhOLEDs) to exploit both singlet and triplet excitons for light emission, which enabled 100% IQE.<sup>4,5</sup> After the pioneering work, tremendous research efforts have been dedicated to improve the device performance of PhOLEDs.<sup>10-23</sup> In general, PhOLEDs constructed by the host-guest device architecture by doping the phosphorescent emitter in a suitable host to alleviate the unwanted concentration quenching and triplet-triplet annihilation.<sup>10-15</sup> As the host materials occupy the major portion of the emitting layer, they plays an important role in controlling the charge injection and transportation, location of charge recombination zone and device stability.<sup>10-15</sup> Nevertheless, engineering of the host materials is as crucial as the dopant emitters for fabricating efficient PhOLEDs. In general, an ideal host should have sufficiently high triplet energy compared to dopant, suitable HOMO and LUMO energy levels with neighboring layers, high thermal stability and a broad recombination zone of the charge carriers in the EML.<sup>10-15</sup>

It has been demonstrated that the bipolar host materials consisting of both the holetransporting (electron donor) and electron-transporting (electron acceptor) units can improve the balanced charge transport in emitting layer and thus are good for promoting the device performance and reducing the efficiency roll-off at high brightness compared to the unipolar hosts.<sup>10-15</sup> Previous reports illustrated that the choice of donor and acceptor units and their structural combination of bipolar host materials should be examine carefully because they dominates the charge-transport ability and overall device performance in many cases.<sup>10-15, 24-<sup>29</sup>. Therefore, the understanding of the structure and property relationships of bipolar host materials is highly desirable for good device performances. Until now, several electrondeficient units, such as triazine, cyano, triazole, pyrazole, pyridine, triazolopyridine,</sup>

phosphine oxide, benzimidazole, and oxadiazole, has been examined as electron transporting units for developing bipolar host materials for green/blue PhOLEDs.<sup>10-15</sup> However, the potential donors are limited to carbazole and its derivatives because of their excellent holetransporting property, thermal stability, and high triplet state.<sup>10-15,24-44</sup> Thus, the development of novel hole-transport units with the aforementioned criteria is highly desirable to execute new designs of high-quality bipolar host materials for PhOLEDs. Besides, the green PhOLEDs have surpassed the maximum theoretical limit of EQE (20%).<sup>33-43</sup> However, typical PhOLEDs encounter significant efficacy roll-off issues at high brightness (> 1000  $cd/m^2$ ) in spite of high maximum EQE ( $\eta_{max}$ ), which is a challenging issue of green PhOLEDs. For example, recently, Su et al. reported a new bipolar host featuring triazolopyridine electron-transport unit and demonstrated  $\eta_{max}$  of 25.0% and reduced efficacy roll-off of 7.6% at 1000 cd/m<sup>2</sup>.<sup>34</sup> Wei *et al.* developed an indenocarbazole-based bipolar host and demonstrated  $\eta_{max}$  of 23.6% and reduced efficacy roll-off of 8.9% at 1000 cd/m<sup>2.35</sup> Similarly, Liu *et al.* reported highly efficient triazole-featured bipolar host and found a  $\eta_{max}$  of 28.0% and suppressed efficiency roll-off of 6.0% at 1000 cd/m<sup>2</sup>.<sup>36</sup> However, the efficiency roll-off of the aforementioned devices is still large at practical luminance range of  $5000 \text{ cd/m}^2$ . Therefore, the development of proficient bipolar hosts with extremely low efficiency roll-off for PhOLEDs remained as challenging work for researchers.

Inspired by the above discussions and with our continuing interest in the development of new bipolar hosts for PhOLEDs,<sup>44-47</sup> herein we report two new hole-transport units, 10*H*-benzo[4,5]thieno[3,2-*b*]indole (BTI) and 10*H*-benzofuro[3,2-*b*]indole (BFI), for designing bipolar host materials, 10-(3-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10*H*-benzo[4,5]thieno[3,2-*b*]indole (**mBTITrz**) and <math>10-(3-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10*H*-benzofuro[3,2-*b*]indole (**mBTITrz**), by integration with a moderate aryltriazine electron-transport unit for efficient green PhOLEDs, respectively. Although some

synthetic attempts have been documented for BTI and BFI in the literature, their potential as hole-transport units in developing functional materials for electroluminescent applications was not explored in the literature.<sup>48</sup> To this end, here we explored their potential applications as hole-transport units in developing bipolar hosts for OLED applications. The donor and acceptor units were connected in a meta-conjugation mode through a phenyl linker to avoid the extension of conjugation and maintain high triplet energy for the host materials. The effect of heteroatoms in the hole-transport unit on photophysical and device performances was evaluated in detail. Interestingly, the compounds showed similar behavior in fluorescence spectra, whereas their phosphorescence spectra were dominated by the holetransport units. The phosphorescence of the compounds predominantly originated from the local excited state (<sup>3</sup>LE) of donor units, and their corresponding triplet energies were 2.88 eV for **mBTITrz** and 2.65 eV for **mBFITrz**. Both compounds exhibited high thermal stability, with a decomposition temperature  $(T_d)$  above 410 °C and a glass-transition temperature  $(T_g)$ above 103°C. In addition, the single carrier device studies revealed a bipolar chargetransporting feature for the compounds. Furthermore, the compounds were evaluated as bipolar host materials for green PhOLEDs by employing Ir(ppy)<sub>3</sub> dopant. The **mBTITrz**hosted device demonstrated much better performance than did the mBFITrz-hosted device, with a maximum EQE of 21.3% and a maximum current efficiency of 76.0 cd/A. Notably, the mBTITrz-hosted device exhibited excellent efficiency stability, with an uncompromised efficiency roll-off at 1000 cd/m<sup>2</sup> and an extremely small efficiency roll-off of 3.2% at 5000 cd/m<sup>2</sup> and 9.0% at 10,000 cd/m<sup>2</sup>.



Scheme 1. Synthetic scheme of the compounds mBTITrz and mBFITrz.

# **Results and Discussion**

#### Synthesis and Characterization

Our molecular design was mainly focused on the study of the effect of heteroatoms (oxygen or sulfur) in the hole-transport unit on physicochemical and electroluminescent properties of the host materials. We envisaged that the integration of electron-donating BTI or BFI units with an aryltriazine acceptor through a phenyl linker *via* a *meta*-conjugation mode would impart a bipolar charge-transport feature for **mBTITrz** and **mBFITrz**, and maintain their triplet energy sufficiently higher than the common green phosphorescent emitter Ir(ppy)<sub>3</sub>. The key precursors, BFI and BTI, were synthesized according to the procedure in the literature.<sup>48</sup> The aforementioned donors was reacted with 2-(3-bromophenyl)-4,6-diphenyl-1,3,5-triazine under a palladium-catalyzed Buchwald-Hartwig reaction<sup>49</sup> to accomplish the desired materials, **mBFITrz** and **mBTITrz**, in reasonable yields. A synthetic scheme for **mBFITrz** and **mBTITrz** is shown in Scheme 1. The chemical structures of the compounds were confirmed by the nuclear magnetic resonance spectroscopy (<sup>1</sup>H and <sup>13</sup>C NMR) and mass spectral analysis. Also, the two host materials were purified by the vacuum train sublimation process before applying in the OLED devices.

# **Thermal properties**

Thermal stability of the host materials is one of the important parameters in fabricating efficient OLED devices with higher operational stability. The thermogravimetric analysis

(TGA) and differential scanning calorimetry (DSC) measurements were employed to investigate the thermal stability of the compounds **mBTITrz** and **mBFITrz**. The corresponding TGA and DSC traces of the compounds are portrayed in Figure 1, and pertinent data were shown in Table 1. Thermal decomposition temperatures corresponding to the 5% weight loss ( $T_d$ ) of the compounds **mBTITrz** and **mBFITrz** are of 414°C and 413°C, respectively indicates their excellent thermal stabilities. Such superior thermal stability of the compounds **mBTITrz** and **mBFITrz** is ascribed to the robust chemical structures of the BTI, BFI, and aryltriazine units, and aromatic unit based backbone structures. Furthermore, the DSC curves showed the definite glass transition temperatures ( $T_g$ ) of 106°C for **mBTITrz and** 103°C for **mBFITrz** during a second heating cycle. Evidently, these materials showed significantly better  $T_g$  than that of the conventional host materials namely 1,3-bis(*N*carbazolyl)-benzene (mCP; 60°C) and 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP; 62°C).<sup>50</sup> The results suggests that the compounds **mBTITrz** and **mBFITrz** possess excellent thermal stabilities and tolerate high temperatures during the vacuum evaporation process of OLED device fabrication and device operation.





Figure 1. a) TGA and b) DSC traces of the hosts mBTITrz and mBFTTrz.

# **Electrochemical properties**

To investigate the electrochemical behavior of the new compounds **mBTITrz** and **mBFTTrz**, the cyclic voltammetry measurements were collected in dilute dichloromethane solution. The oxidation potentials of the compounds was referenced to Fc/Fc+ redox couple, and the relevant data were tabulated in Table 1. In general, the electron-donating strength of the chromophores can be evaluated based on their oxidation propensity.<sup>51</sup> Therefore, to understand the effect of the heteroatoms in the hole-transport units on their electron donating strength, the oxidation potentials of the BTI and BFI were collected. Interestingly, the BTI possessed a smaller oxidation potential (+ 0.90 V) than did the BFI (+ 0.95 V), which indicates its strong electron donor character, which probably results because the BTI unit contains a sulfur atom, which is less electronegative than is the oxygen atom in the BFI unit.<sup>52</sup> Indeed, **mBTITrz** showed more facile oxidation than that of **mBFITrz** because of

having a BTI donor that is stronger than the relatively weak BFI donor in the latter. Upon reduction sweep, the compounds showed irreversible reduction waves with almost similar reduction potentials attributed to the presence of same aryltriazine acceptor in both the compounds. The corresponding HOMO and LUMO energy levels of the compounds was calculated from their onset potentials of oxidation and reduction peaks, respectively. Accordingly, the HOMO/LUMO energy levels of the compounds were -5.78/-3.22 eV for **mBTITrz** and -5.83/-3.19 eV for **mBFITrz**. The HOMO levels of the **mBTITrz** and **mBFITrz** were shallower than those of common hole-transport type hosts such as CBP (-6.0 eV) and mCP (-6.1 eV), suggesting good hole-related properties.<sup>50</sup> Additionally, the deep LUMO levels propose good electron-related properties. Therefore, good bipolar properties are expected from the two hosts. The HOMO level became shallow and resulted in a smaller HOMO-LUMO gap ( $E_g = 2.56 \text{ eV}$ ) in the **mBTITrz** than in the **mBFITrz** ( $E_g = 2.64 \text{ eV}$ ).

#### **Theoretical calculation**

Density functional theoretical (DFT) calculations was performed on the model compounds of the new host materials **mBTITrz and mBFITrz** using the B3LYP/6-31G\* basis set on the Gaussian 09 program package to understand their electronic structure and frontier molecular orbital distributions (HOMO and LUMO). The optimized geometrical structures of the compounds and their HOMO/LUMO orbitals are displayed in Figure 2. In both the compounds **mBTITrz** and **mBFITrz**, the HOMO orbitals are exclusively localized on the BTI and BFI electron donating moieties with little contributions from the phenyl linker, whereas the LUMO orbitals are delocalized on the aryltriazine acceptor unit and extended into phenyl linker. These HOMO and LUMO distribution results suggest that the BTI and BFI would function as the hole-transporting units, whereas the aryltriazine moiety would behave as the electron-transporting unit. As shown in the optimized geometries, both

compounds exhibited non-planar geometries, with a large twisting between the hole-transport unit and phenyl linker with a large dihedral angle of above  $51^{\circ}$ . The calculated HOMO and LUMO energies and band gap ( $E_g$ ) of the host materials are of -5.14 eV, -2.03 eV, and 3.11 eV for **mBTITrz** and -5.17 eV, -2.00 eV and 3.17 eV for **mBFITrz**, respectively. The trends in the computed HOMO, LUMO and band gap ( $E_g$ ) values are in good agreement with the experimentally deduced values.



Figure 2 a) Optimal geometrical configurations and b) orbital distributions of the **mBTITrz** and **mBFITrz** estimated by DFT methods.

# **Photophysical properties**

The photophysical properties of the compounds was analyzed by absorption and emission spectral measurements using  $10^{-5}$  M THF solutions and the corresponding spectral profiles are shown in Figure 3 and the pertinent data were fitted in Table 1. Both compounds showed multiple absorption bands in the range of 260-375 nm. The high energy absorption bands seeming below ~ 335 nm correspond to the localized  $\pi$ - $\pi$ \* electronic transitions of different aromatic conjugative segments in the compounds. The long-wavelength absorption band with

mediocre intensity appearing above ~ 345 nm is assigned to the intramolecular charge transfer (ICT) transitions from the BTI or BFI donor to the aryltriazine acceptor. The observed weak intensity of ICT band is attributed to the interrupted strong electronic communication between the BTI or BFI donor and aryltriazine acceptor by virtue of nonconjugative meta-mode of linkage between them. The dilute solutions of the compounds showed green fluorescence under the visible light. Both compounds showed featureless emission profiles, with an emission maximum of 538 nm for mBTITrz and 534 nm for mBFITrz, showing that the singlet transition originating from the CT states (vide infra). Comparatively, that **mBTITrz** exhibited a slight bathochromic shift with a broader emission profile than that of its counterpart **mBFITrz** is attributed to a relatively stronger CT excited state generated by the charge transfer from the BTI donor to the aryltriazine acceptor. Furthermore, the excited state CT of these compounds is certified by their observed bathochromic shift in emission profiles form non-polar toluene (TOL) to polar THF solution with a large full width at half maximum (FWHM). Such a red-shifted emission with broadened spectral profiles in polar solvents is a feature of CT induced electronic perturbations in the excited state of bipolar compounds.<sup>51</sup> However, the extent of CT is minimal in these compounds according to the small bathochromic shift ( $\Delta \lambda_{em} > 48$  nm) from TOL to THF solvents caused by the meta-conjugation linkage between the donor and acceptor moities.<sup>53</sup> The low-temperature PL spectra (LTPL) of the compounds were recorded in a frozen THF at 77 K. In contrast to the fluorescence spectra, the phosphorescence spectra were largely dominated by the donor units in the compounds. As shown in Figure 3, the phosphorescence spectra of the mBTITrz and mBFITrz were almost indistinguishable in both the profile and the peak wavelength from those of BTI and BFI units, respectively. This clearly indicates that the phosphorescence in these compounds stems from the local triplet excited states (<sup>3</sup>LE) of the hole-transport units, perhaps because of the poor electronic

coupling between the hole-transport and electron-transport units resulting from the nonconjugative *meta*-mode linkage between them.<sup>54,55</sup> The triplet energy ( $E_T$ ) of the **mBTITrz** and **mBFITrz** were calculated from the onset wavelengths of the phosphorescence spectra and are of 2.88 eV and 2.65 eV, respectively. The  $E_T$  of these compounds is sufficiently superior than the common green Ir(ppy)<sub>3</sub> phosphor to ensure efficient forward energy transfer and prevent back energy transfer when employed as hosts for green PhOLEDs.



**Figure 3.** UV-visible Absorption recorded in THF and emission spectra collected in THF and TOL solutions and phosphoresce spectra measured at 77K (LTPL) of the compounds.

Compound	$\lambda_{abs}$ , nm $(\epsilon_{max}, M^{-1} \text{ cm}^{-1} \times 10^3)^a$	$\lambda_{\rm em}$ $(\rm nm)^{a}$	$E_{\rm T}$ (eV) <sup>b</sup>	HOMO/LUM O (eV) <sup>c</sup>	$E_{g}$ (eV)	$T_{5d}$ (°C) <sup>e</sup>	$T_g (^{\mathrm{o}}\mathrm{C})^{\mathrm{f}}$
mBTITrz	350 (7.12), 313 (sh), 261 (74.0)	538	2.88	-5.78/-3.22	2.56	414	106
mBFITrz	349 (sh), 332 (s h), 319 (33.1), 2 68 (66.3)	534	2.65	-5.83/-3.19	2.64	413	103

Table 1. Physicochemical and thermal properties of the compounds

<sup>a</sup>Measured in THF solution. <sup>b</sup>Estimated from onset of phosphorescence spectra. <sup>c</sup>HOMO and LUMO estimated from the cyclic voltagrams. <sup>d</sup>Band gap estimated from the electrochemical measurements. <sup>e</sup>Thermal decomposition temperature ( $T_{5d}$ ). <sup>f</sup>Glass transition temperature ( $T_g$ ).

# **Carrier transport properties**

The bipolar charge-transport character of the host materials is one of the most essential parameters to facilitate the injection and transport of charge carriers, balance the holeelectron distribution, increase the recombination probability, and achieve the superior device performance with low efficiency roll-off in the PhOLEDs. As discussed above, electrochemical and theoretical studies was indirectly demonstrated the bipolar chargetransport feature of **mBTITrz** and **mBFITrz**. Furthermore, single carrier devices were fabricated to certify this. The electric-field-dependent current-density data of the single carrier devices were displayed in Figure 4. The hole-only (HOD) and electron-only (EOD) devices of the hosts **mBTITrz** and **mBFITrz** exhibited significantly superior current densities compared to the conventional host material 3,3-di(9H-carbazol-9-yl)biphenyl (mCBP), suggesting that the new host materials possess appropriate hole and electrontransporting ability and have the bipolar charge-transport feature. It is noted that the two compounds **mBTITrz** and **mBFITrz** exhibited superior hole current density than the mCBP, shows that the new hole-transport units (BTI and BFI) are more efficient for hole-transport than is carbazole. Comparing the two host, the **mBTITrz** displayed a hole current density higher than that of the **mBFITrz** because the BTI has better hole-transport properties than does the BFI hole-transport unit. Besides, the EOD have comparable current-densities, indicating that the two hosts have comparable electron-transport properties, because the same electron-transport units were used in the two hosts. From these results, it is expected that the **mBTITrz** and **mBFITrz** work well as the host balancing carriers because of the bipolar charge-transport property.



Figure 4. I-V characteristics of a) hole-only and b) electron-only devices of mBTITrz,

### mBFITrz and mCBP.



#### **Electroluminescence properties**

Figure 5. Energy level alignment and materials chemical structures used in the devices.

The high triplet energy, bipolar charge-transport character, and excellent thermal stability of these compounds motivated us to explore their potential applicability as bipolar host materials for green PhOLEDs using a well-known green  $Ir(ppy)_3$  dopant. The emitting layer (EML) was composed by doping of 5wt% of  $Ir(ppy)_3$  in either **mBTITrz** (Device G1, G denotes green phosphorescence) or **mBFITrz** (Device G2) hosts. The energy-level alignment

and the chemical structures of each layer used in the device were displayed in Figure 5. The EL spectra, current density (J)-voltage (V)-luminance (L) and EQE vs luminance plots of the green devices are shown in Figure 6, and their detailed EL parameters are tabulated in Table 2. In EL spectra (Figure 6a), both G1 and G2 devices emitted pure green emission corresponds to the Ir(ppy)<sub>3</sub> dopant, with peak wavelengths of 517 nm and 514 nm and CIE coordinates of (0.30, 0.63) and (0.31, 0.63), respectively. The absence of any other emission peaks corresponding to the hosts or other layers from the devices, suggesting efficient energy transfer from the hosts **mBTITrz** or **mBFITrz** to the  $Ir(ppy)_3$  dopant and exciton imprisonment in the EML. Comparatively, the **mBTITrz-**hosted device G1 showed slightly higher current-density and luminance than did the mBFITrz-based G2 device because of its good hole-transport property, as shown in the single carrier device data. The maximum EQE and current efficiency (CE) of the devices are of 21.3% and 76.0 cd/A for device G1, and 15.7% and 56.3 cd/A for device G2. The superior performance of the mBTITrz-hosted device G1 compared to that of the **mBFITrz** hosted device G2 is attributed to its sufficiently higher triplet energy than the dopant for efficient energy transfer and good bipolar chargetransporting property for balanced charge carrier injection and transport. The EQE vs luminance plots of the compounds are portrayed in Figure 6c. Notably, the device G1 exhibited extremely low efficacy roll-off at high brightness. At the luminance of 1000 cd/m<sup>2</sup>, the device G1 exhibited EQE of 21.3%, which is almost unchanged compared to their maximum EQE value. Even at the high brightness level of 5000 cd/m<sup>2</sup>, the device G1 revealed excellent efficiency stability (EQE = 20.6%) with a small efficacy roll-off of 3.2%. Furthermore, even at 10,000 cd/m<sup>2</sup>, the **mBTITrz**-hosted G1 device maintained a high EQE of 19.4%. The efficiency drop at 10,000  $cd/m^2$  was only 9.0%, indicating its excellent efficiency stability at a practical brightness range. Undoubtedly, this is attributed to the balanced charge transport of the **mBTITrz** host. From these results, it is evident that the BTI



unit is a potential hole-transport unit for developing highly efficient bipolar hosts for PhOLEDs.

Figure 6. a) EL plot, b) J-V-L plots, c) EQE brightness and d) CE vs luminance plots of the

green PhOLED devices.

 Table 2. Summarized EL performances of the devices

Host	Voltage $(V_{on})^{a}$	EQE (%)			CE (cd/A)			EL peak (n m)	CIE (x, y)
		Max.	@1000 $cd/m^2$	$@5000  ext{ cd/m}^2$	Max.	@1000 c d/m <sup>2</sup>	@5000 c d/m <sup>2</sup>	,	
mBTITrz	3.9	21.3	21.3	20.6	76.0	75.9	73.3	515	0.30, 0.63
mBFITrz	4.0	15.7	15.6	14.3	56.3	56.3	51.3	517	0.31, 0.63
<sup>a</sup> turn-on volt	age (V) at 1 cd/m <sup>2</sup>			tin Mr					

# Conclusions

In summary, we have designed and synthesized two new bipolar host materials *viz.*, **mBTITrz** and **mBFITrz**, using BTI or BFI as the hole-transport units and aryltriazine as the electron-transport unit for green PhOLEDs. The introduction of the BTI and BFI hole-transport units allowed a high triplet energy over 2.65 eV, a high thermal decomposition temperature over 410 °C and a glass-transition temperature above 103 °C. DFT computations and single carrier device studies revealed bipolar charge transporting feature for the compounds. Further, the green PhOLEDs were fabricated using these new compounds as bipolar host materials by employing Ir(ppy)<sub>3</sub> emitter. The **mBTITrz**-hosted device worked better than the **mBFITrz**-hosted device, with maximum EQE of 21.3% and CE of 76.0 cd/A. Moreover, the **mBTITrz**-hosted device maintained uncompromised EQE of 21.3% at 1000 cd/m<sup>2</sup> and high EQE of 20.6% at 5000 cd/m<sup>2</sup> with an extremely low efficiency roll-off of 3.2%. These results suggest that BTI is a potential hole-transport unit for developing highly proficient bipolar hosts for PhOLEDs and expands the library of donor units.

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**Key words:** organic light-emitting diodes (OLEDs); green PhOLEDs; bipolar host; holetransport unit; efficiency roll-off.

#### References

1. Burroughes, J. H.; Bradly, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend,

R.H.; Holmes, A.B. Light-emitting diodes based on conjugated polymers. Nature, 347 (1990) 539-541.

2. Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly efficient organic light-emitting diodes from delayed fluorescence. Nature, 492 (2012) 234-238.

3. Ren, Z.; Nobuyasu, R. S.; Dias, F. B.; Monkman, A. P.; Yan, S.; Bryce, M. R. Pendant Homopolymer and Copolymers as Solution-Processable Thermally Activated Delayed Fluorescence Materials for Organic Light-Emitting Diodes. Macromolecules, 49 (2016) 5452-5460.

4. Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. Highly efficient phosphorescent emission from organic electroluminescent devices. Nature, 395 (1998) 151-154.

5. Adachi, C.; Baldo, M. A.; S. R. Forrest. High-efficiency organic electrophosphorescent devices with tris(2-phenylpyridine)iridium doped into electron-transporting materials. App. Phys. Lett. 77 (2000) 904.

 Yang, Z.; Mao, Z.; Xie, Z.; Zhang, Y.; Liu, S.; Zhao, J.; Xu, J.; Chi, Z.; Aldred, M. P. Recent advances in organic thermally activated delayed fluorescence materials. Chem. Soc. Rev. 46 (2017) 915-1016.

7. Guo, J.; Zhao, Z.; Tang, B. Z. Purely Organic Materials with Aggregation-Induced Delayed Fluorescence for Efficient Nondoped OLEDs. Adv. Optical Mater. 6 (2018) 1800264.

8. Chen, W. C.; Lee, C. S.; Tong, Q. X. Blue-emitting organic electrofluorescence materials: progress and prospective. J. Mater. Chem. C, 3 (2015), 10957-10963.

9. Sharma, R.; Volyniuk, D.; Popli, C.; Bezvikonnyi, O.; Grazulevicius, J. V.; Misra, R. Strategy Toward Tuning Emission of Star-Shaped Tetraphenylethene-Substituted Truxenes for Sky-Blue and Greenish-White Organic Light-Emitting Diodes. J. Phys. Chem. C, 122 (2018) 15614-15624.

10. Ma, D.; Tsuboi, T.; Qiu, Y.; Duan, L. Recent Progress in Ionic Iridium(III) Complexes for Organic Electronic Devices. Adv. Mater. 29 (2017) 1603253.

11. Tao, Y.; Yang, C.; Qin, J. Organic host materials for phosphorescent organic light-emitting diodes. Chem. Soc. Rev. 40 (2011) 2943-2970.

12. Chaskar, A.; Chen, H. F.; Wong, K. T. Bipolar host materials: a chemical approach for highly efficient electrophosphorescent devices. Adv. Mater. 23 (2011) 3876-3895.

13. Sasabe, H.; Kido, J. Recent Progress in Phosphorescent Organic Light-Emitting Devices.Eur J. Org. Chem. 2013, 7653

14. Yang, X.; Zhou, G.; Wong, W. Y. Functionalization of phosphorescent emitters and their host materials by main-group elements for phosphorescent organic light-emitting devices. Chem. Soc. Rev. 44 (2015) 8484-8575.

15. Yook, K. S.; Lee, J. Y. Organic Materials for Deep Blue Phosphorescent Organic Light-Emitting Diodes. Adv. Mater. 24 (2012) 3169-3190.

16. Chi, Y.; Chou, P. T. Transition-metal phosphors with cyclometalating ligands: fundamentals and applications. Chem. Soc. Rev. 39 (2010) 39, 638-655.

17. Chan, A. K. W.; Ng, M.; Wong, Y. C.; Chan, M. Y.; Wong, W. T.; Yam, V. W. W. Synthesis and Characterization of Luminescent Cyclometalated Platinum(II) Complexes with Tunable Emissive Colors and Studies of Their Application in Organic Memories and Organic Light-Emitting Devices. J. Am. Chem. Soc. 139 (2017) 10750-10761

18. Pal, A. K.; Krotkus, S.; Fontani, M.; Mackenzie, C. F. R.; Cordes, D. B.; Slawin, A. M.;

D. W. F. Samuel, Colman, E. Z. High-Efficiency Deep-Blue-Emitting Organic Light-Emitting Diodes Based on Iridium(III) Carbene Complexes. Adv. Mater. 30 (2018)1804231.

19. Zhu, Z. Q.; Klimes, K.: Holloway, S.; Li, J. Efficient Cyclometalated Platinum(II) Complex with Superior Operational Stability. 29 (2017) 1605002.

20. 18. Hu, Y. X.; Xia, X.; He, W. Z.; Tang, Z. J.; Lv, Y. L.; Li, Xiao, Zhang, D. Y. Recent developments in benzothiazole-based iridium(III) complexes for application in OLEDs as electrophosphorescent emitters. Organic Electronics, 66 (2019) 126-135.

21. Wu, C.; Wang, B.; Wang, Y.; Hu, J.; Jiang, J.; Ma, D.; Wang, Q. A universal host material with a simple structure for monochrome and white phosphorescent/TADF OLEDs. J. Mater. Chem. C, 7 (2019) 558-566.

22. Chen, D.; Su, S. J.; Cao, Y. Nitrogen heterocycle-containing materials for highly efficient phosphorescent OLEDs with low operating voltage. J. Mater. Chem. C, 2 (2014) 9565-9578.

23. Shin, H.; Lee, J. H.; Moon, C. K.; Huh, J. S.; Sim, B.; J. J. Kim Sky-Blue Phosphorescent OLEDs with 34.1% External Quantum Efficiency Using a Low Refractive Index Electron Transporting Layer. Adv. Mater. 28 (2016) 4920-4929.

24. Chen, W. C.; Yuan, Y.; Zhu, Z. L.; Jiang, Z. Q.; Su, S. J.; Liao, L. S.; Lee, C. S. De novo design of D–s–A molecules as universal hosts for monochrome and white phosphorescent organic light-emitting diodes. Chem. Sci. 9 (2018) 4062-4070

25. Chang, S. Y.; Lin, G. T.; Cheng, C. Y.; Huang, J. J.; Chang, C. L.; Lin, C. F.; Lee, J. H.; Chiu, T. L.; Leung, M. K. Construction of Highly Efficient Carbazol-9-yl-Substituted Benzimidazole Bipolar Hosts for Blue Phosphorescent Light Emitting Diodes: Isomer and Device Performance Relationships. ACS Appl. Mater. Interfaces 10 (2018) 42723-42732.

26. Xhao, J.; Xie, G, H.; Yin, C. R.; Xie, L. H.; H. C. M.; Chen. R. F.; Xu, H.; Yi, M. D.;

Deng, Z. P.; Chen, S. F.; Zhao, Y.; Liu, S. Y.; Huang, W. Harmonizing Triplet Level and

Ambipolar Characteristics of Wide-Gap Phosphine Oxide Hosts toward Highly Efficient and Low Driving Voltage Blue and Green PHOLEDs: An Effective Strategy Based on Spiro-Systems. Chem. Mater. 23 (2011) 5331-5339.

27. Wagner, D.; Hoffmann, S. T.; Heinemeyer, U.; Munster, I.; Kohler, A.; Strohriegl, P. Triazine Based Bipolar Host Materials for Blue Phosphorescent OLEDs. Chem. Mater. 25 (2013) 25, 3758-3765.

28. Lin, M. J.; Huang, M. J.; Chiu, M. P.; Huang, C. C.; Chang, C. Y.; Liao, K. M.; Chiang, Y. J.; Shiau, T. Y.; Chou, L. K.; Chu, H.; Lin, W.; Cheng, C. H. Molecular Design of Highly Efficient Thermally Activated Delayed Fluorescence Hosts for Blue Phosphorescent and Fluorescent Organic Light-Emitting Diodes. Chem. Mater. 29 (2017) 1527-1537.

29. Wu, Q.; Wang, M.; Cao, X.; Zhang, D.; Sun, N.; Wan, S.; Tao, Y. Carbazole/α-carboline hybrid bipolar compounds as electron acceptors in exciplex or non-exciplex mixed cohosts and exciplex-TADF emitters for high-efficiency OLEDs. J. Mater. Chem. C, 6 (2018) 8784-8792.

30. Huang, H.; Wang, Y.; Pan, B.; Yang, X.; Wang, L.; Chen, J.; Ma, D.; Yang, C. Simple Bipolar Hosts with High Glass Transition Temperatures Based on 1,8-Disubstituted Carbazole for Efficient Blue and Green Electrophosphorescent Devices with "Ideal" Turn-on Voltage. Chem. Eur. J. 19 (2013) 19, 1828-1834

31. Yao, C.; Yang, Y.; Li, L.; Bo, M.; Peng, C.; Wang, J. Ge-based bipolar small molecular host for highly efficient blue OLEDs: multiscale simulation of charge transport. J. Mater. Chem. C, 6 (2018) 6146-6152.

32. Ban, X.; Jiang, Q.; Sun, K.; Xie, X.; Peng, L.; Dong, H.; Sun, Y.; Huang, B.; Duan, L.; Qiu, Y. Bipolar Host with Multielectron Transport Benzimidazole Units for Low Operating Voltage and High Power Efficiency SolutionProcessed Phosphorescent OLEDs. ACS Appl. Mater. Interfaces, 7 (2015) 7303-7314. 33. Liu, D.; Li, D.; Wang, M.; Li, W. 1,2,4-Triazole-containing bipolar hosts for blue and green phosphorescent organic light-emitting diodes. J. Mater. Chem. C, 4 (2016) 7260-7268.

34. Song, W.; Shi, L.; Gao, L.; Hu, P.; Mu, H.; Xia, Z.; Huang, J.; Su, J. [1,2,4]Triazolo[1,5a]pyridine as Building Blocks for Universal Host Materials for High-Performance Red, Green, Blue and White Phosphorescent Organic Light-Emitting Devices. ACS Appl. Mater. Interfaces, 10 (2018) 5714-5722.

35. Guo, K.; Wang, H.; Wang, Z.; Si, C.; Peng, C.; Chen, G.; Zhang, J.; Wang, G.; Wei, B. Stable green phosphorescence organic light-emitting diodes with low efficiency roll-off using a novel bipolar thermally activated delayed fluorescence material as host. Chem. Sci. 8 (2017) 1259-1268.

36. Liu, D.; Wang, F.; Yao, R. Molecular evolution of host materials by regular tuning of n/p ratio for high-performance phosphorescent organic light-emitting diodes. J. Mater. Chem. C, 6 (2018) 7839-7846.

37. Liu, X. K.; Zheng, C. J.; Xiao, J.; Ye, J.; Liu, C. L.; Wang, S. D.; Zhao, V. M.; Zhang, X.
H. Novel bipolar host materials based on 1,3,5-triazine derivatives for highly efficient phosphorescent OLEDs with extremely low efficiency roll-off. Phys. Chem. Chem. Phys. 14 (2012) 14255-14261.

38. Li, W.; Li, J.; Liu, D.; Li, D.; Wang, F. Cyanopyridine Based Bipolar Host Materials for Green Electrophosphorescence with Extremely Low Turn-On Voltages and High Power Efficiencies. ACS Appl. Mater. Interfaces, 8 (2016) 21497-21504.

39. Chen, M.; Yang, J.; Ye, Z.; Wang, S.; Tang, Z.; Chen, G.; Zheng, Y.; Shi, Y.; Wei, B.; Wong, W. Y. Extremely low-efficiency roll-off of phosphorescent organic light-emitting diodes at high brightness based on acridine heterocyclic derivatives. J. Mater. Chem. C, 6 (2018) 9713-9722.

40. Li, W.; Li, J.; Liu, D.; Jin, Q. Simple Bipolar Host Materials for High-Efficiency Blue, Green, and White Phosphorescence OLEDs. ACS Appl. Mater. Interfaces, 8 (2016) 22382-22391.

41. Song, W.; Chen, Y.; Xu, Q.; Mu, H.; Cao, J.; Huang, J.; Su, J. [1,2,4]Triazolo[1,5-a]pyridine-Based Host Materials for Green Phosphorescent and Delayed-Fluorescence OLEDs with Low Efficiency Roll-Off. ACS Appl. Mater. Interfaces, 10 (2018) 24689-24698.
42. Kim, G. H.; Lampande, R.; Park, M. J.; Bae, H. W.; Kong, J. H.; Kwon, J. H.; Park, J. W.; Park, Y. W.; Song, C. E. Highly Efficient Bipolar Host Materials with Indenocarbazole and Pyrimidine Moieties for Phosphorescent Green Light-Emitting Diodes. J. Phys. Chem. C, 118 (2014) 28757-28763.

43. Wang, S.; Lee, C. W.; Lee, J. Y.; Hwang, S. H. Synthesis and green phosphorescent OLED device performance of cyanofluorene-linked phenylcarbazoles as host material. New J. Chem. 42 (2018) 5059-5065.

44. Byeon, S. Y.; Han, S. Y.; Lee, J. Y. Molecular Design of Blue Phosphorescent Host Materials for Phenylimidazole-Type Blue Triplet Emitters to Extend Operational Lifetime. Adv. Optical Mater. 6 (2018) 1701263.

45. Konidena, R. K.; Lee, K. H.; Lee, J. Y. Decoration of Dibenzofuran Using Cyanocarbazole via 6-Position as a Molecular Design Approach for High-Triplet-Energy Bipolar Host Materials. Chem. Asian. J. 14 (2019) 313-321.

46. Kim, M.; Lee, J. Y. Engineering of Interconnect Position of Bicarbazole for High External Quantum Efficiency in Green and Blue Phosphorescent Organic Light-Emitting Diodes. ACS Appl. Mater. Interfaces. 6 (2014)14874-14880.

47. Shin, S. K.; Han, S. H.; Lee, J. Y. High triplet energy exciplex host derived from a CN modified carbazole based n-type host for improved efficiency and lifetime in blue phosphorescent

organic light-emitting diodes. J. Mater. Chem. C, 6 (2018) 10308-10314.

48. Srour, H.; Doan, T. H.; Silva, E. D.; Whitby, R. J.; Witulski, B. Synthesis and molecular properties of methoxy-substituted diindolo[3,2-b:2',3'-h]carbazoles for organic electronics obtained by a consecutive twofold Suzuki and twofold Cadogan reaction. J. Mater. Chem. C, 4 (2016) 6270.

49. F. Paul, J. Patt, J. F. Hartwig, Palladium-catalyzed formation of carbon-nitrogen bonds. Reaction intermediates and catalyst improvements in the hetero cross-coupling of aryl halides and tin amides. J. Am. Chem. Soc. 116 (1994) 5969-5970.

50. M. H. Tsai, Y. H. Hong, C. H. Chang, H. C. Su, C. C. Wu, A. Matoliukstyte, J. Simokaitiene, S. Grigalevicius, J. V. Grazulevicius, C. P. Hsu. 3-(9-Carbazolyl)carbazoles and 3,6-Di(9-carbazolyl)carbazoles as Effective Host Materials for Efficient Blue Organic Electrophosphorescence. Adv. Mater. 19 (2007) 862-866.

51. Konidena, R. K.; Thomas, K. R. J.; Pathak, A.; Dubey, D. K.; Sahoo, S.; Jou, J. H. Tuning the Photophysical and Electroluminescence Properties in Asymmetrically Tetrasubstituted Bipolar Carbazoles by Functional Group Disposition. ACS Appl. Mater. Interfaces, 10 (2018) 24013-24027.

52. Jia, H.; Ju, X.; Zhang, M.; Ju, Z.; Zheng, H. Effects of heterocycles containing different atoms as  $\pi$ -bridges on the performance of dye-sensitized solar cells. Phys. Chem. Chem. Phys. 17 (2015) 16334-16340.

53. Konidena, R. K.; Thomas, R. K. Star-Shaped Asymmetrically Substituted Blue Emitting Carbazoles: Synthesis, Photophyscial, Electrochemical and Theoretical Investigations. Chemistryselect, 2 (2017) 7514-7524.

54. Ryoo, C. H.; Cho, I.; Han, J.; Yang, J. H.; Kwon, J. E.; Kim, S.; Jeong, H.; Lee, C.; Park, S. Y. Structure–Property Correlation in Luminescent Indolo[3,2-b]indole (IDID) Derivatives: Unraveling the Mechanism of High Efficiency Thermally Activated Delayed Fluorescence

(TADF). ACS Appl. Mater. Interfaces, 9 (2017) 41413-41420.

- Bipolar hosts with new hole transport units for high external quantum efficiency
- Small efficiency roll-off in green phosphorescent organic light-emitting diodes using the bipolar hosts
- Effect of heteroatom in the hole transport unit on the physical and device performances of the hosts

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