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# Methoxy Substituents Activated Carbazole-Based Boron Dimesityl TADF Emitters

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Keywords: boron, carbazole, charge transfer, TADF, OLEDs

#### ABSTRACT

View Article Online DOI: 10.1039/C9TC07020F

N-borylated emitters bearing both boron dimesityl acceptor (Mes)<sub>2</sub>B and phenoxazine or acridine donors are a class of efficient TADF emitters; however, switching to carbazole donor nullifies the TADF characteristics. This work is targeted at improving the TADF characteristics of the carbazole based (Mes)<sub>2</sub>B emitters by introduction of up to two methoxy substituents at the carbazoles. We hereby report the design and synthesis of three methoxy substituted carbazoles (Cz-1, Cz-2 and Cz-3) and the corresponding directly N-borylated emitters, CzBM-1, CzBM-2 and CzBM-3. Moreover, a p-phenylene spacer was also introduced between the (Mes)<sub>2</sub>B unit and carbazole, giving CzPBM-2 and CzPBM-3. As confirmed by the bi-exponential transient decay analyses, all titled compounds exhibit prominent TADF character, while the parent molecule CzBM-0 and CzPBM-0 without methoxy groups show no TADF characteristics. The results manifest the importance of donor strength of substituents and degrees of spatial orthogonality in harnessing the charge transfer property, minimalizing  $S_1$ - $T_1$  energy gap and facilitating reversed intersystem crossing process. OLED devices with doped CzBM-2 and CzPBM-3 emitters exhibited a maximum external quantum efficiency of 12.5 % and 13.3 %, respectively, confirming the potential of methoxy substituents in improving their TADF characteristics.

# 1. Introduction

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Organic light emitting diodes (OLEDs) has been rapidly developed in the past three decades and found promising applications in flat panel displays and solid state lighting luminaires.<sup>1-5</sup> Two major luminescent materials can achieve unitary internal quantum efficiency (IQE) via converting both singlet and triplet excitons into light, achieving very high external quantum efficiencies (EQE) that are extensively tested for the next generation OLEDs.<sup>6-8</sup> On the one hand, noble-metal-based organometallic phosphores constitute one class of such materials due to the highly efficient phosphorescence.<sup>9</sup> In this scenario, phosphorescent OLEDs exhibited EQE higher than 30% with varied emission colors were documented.<sup>10-14</sup> On the other hand, Adachi and coworkers reported distinctive organic compounds possessing unitary quantum efficiency via thermally activated delayed

fluorescence (TADF).<sup>15</sup> Furthermore, with the assistance of the horizontal aligned transition dipole moment, external quantum efficiency (EQE) of over 37% with simple planar architecture has been successfully obtained for TADF based OLEDs.<sup>16</sup> For both the full-color display and lighting applications, it is essential to achieve emission with all three elementary colors, i.e. blue, green and red.<sup>17</sup> Although the library of green and red emitting materials are widely established, there is a strong demand for stable, high efficient blue emitters.<sup>18</sup> Pure blue emission requires enlarged HOMO/LUMO energy gap and sets a tough challenge in emitters. However, TADF materials showing both true blue and blue emissions are emerging in the past few years,<sup>19</sup> despite that the wide energy gap of blue emitters is expected to lead exciton instability, limited charge injection and poor device lifetime.<sup>20</sup>

In view of molecular design, traditional TADF molecules consist of electron donating and accepting moieties, which are linked in different arrangements such as donor-acceptor (D-A), D-A-D, A-D-A and etc., enabling the triplet excitons to undergo fast reversed intersystem crossing (RISC) that leads to unitary IQE.<sup>21</sup> Typical donors such as phenoxazine and phenothiazine give red emission, while acridine and analogues provided the required blue shifted emission.<sup>22-24</sup> However, in view of long term stability it will be better to switch to alternative donor such as carbazole and functional analogues, which are also widely utilized in blue emitting TADF.<sup>25</sup> Among acceptors, electron deficient triazine, pyrimidine, pyridine, sulfone, phosphine oxide, polycyclic borazine, boron dimesityl, etc. were successfully utilized in achieving the needed TADF characters.<sup>26-31</sup> In recent years, functional boron based acceptors have received much attention in the development of TADF emitters.<sup>32, 33</sup> These boron compounds can be categorized into the boron-fused heteroaromatics,<sup>34</sup> three coordinate<sup>35-37</sup> and four coordinate boron compounds.<sup>38</sup> The electron accepting property of the three coordinate boron compounds is related to its lower lying vacant p-orbital that facilitates the charge transfer upon excitation.<sup>35</sup> Earlier reports on three coordinate boron TADF compounds generally possess a phenylene spacer between the boron dimesityl acceptor and donor segment.<sup>39</sup> The relative position between donor and boron dimesityl fragments was an important factor in realizing TADF. For instance, the utilization of psubstituted linkage affords only fluorescence, while switching the o-appended phenylene

yields the desired TADF.<sup>40</sup> Hence, it is believed that the sterically congested *o*-arrangement<sup>CO7020F</sup> gives the vertical arranged donor and acceptor and, hence, smaller gap between S<sub>1</sub> and T<sub>1</sub> states (i.e.  $\Delta E_{ST}$ ), faster intersystem crossing (ISC) rates and notable delayed fluorescence.<sup>41,</sup>

Recently, Thilagar, his co-workers and our groups have independently reported the directly N-borylated stimuli and shape responsive materials and efficient TADF emitters based on phenothiazine, acridine and phenoxazine donors.<sup>43-45</sup> However, upon switching to carbazole, although charge transfer character was clearly observed for the corresponding N-borylated compound, no TADF properties has been detected.<sup>46</sup> Based on the aforementioned discussion and hence a goal to realize the possible TADF behavior, we then shifted gear to study the carbazole substituted N-borylated compounds. In this study, the methoxy substituent(s) were strategically added to carbazole at various position(s) in an attempt to achieve the desired electronic and steric properties (c.f. **Scheme 1**).<sup>47-49</sup> Furthermore, the tradeoff between steric interaction and donor strength is critical in maintaining the required blue emission and TADF character.<sup>50</sup> Detail of results and discussion is elaborated as follows.



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Scheme 1. Structural drawings of carbazole with varied methoxy substituents.

**Scheme 1** displays our designs of carbazole donor molecules. The methoxy groups are inserted at the selected location in maximizing the resonance effect, while the 1-position will also afford large steric encumbrance to the adjacent fragment, thereby satisfying the condition of higher donor strength and better orthogonality for realizing TADF character. As depicted in **Scheme 1**, Cz-1 possesses 1-methoxy substituent and, to further enhance the donor strength, we also introduced a second 3-methoxy substituent in giving Cz-2, while Cz-3 comprises of the 1,6-dimethoxy substituents. Hence, comparison of Cz-2 and Cz-3 will offer

the distinctive structural effect. Next, we synthesized both the boron dimesity (BM)<sup>3</sup> and <sup>CO7020F</sup> phenylene bridged boron dimesityl (PBM) type of emitters, giving **CzBM-1**, **2** and **3** series and **CzPBM-2** and **3** series, respectively, which are depicted in **Scheme 2**. In sharp contrast to the reference **CzBM-0**<sup>46</sup> and **CzPBM-0**<sup>39</sup> compounds (see **Scheme 2**) that were reported to have no TADF character, remarkable TADF was observed for all titled methoxy-substituted compounds. Among them, some exhibit the highly demanding blue emission, which adds another niche to this investigation. Detail of results and discussion is elaborated as follows.



Scheme 2. Structural drawings of various carbazole based TADF emitters.

#### 2. RESULTS AND DISCUSSION

#### 2.1. Syntheses and Characterization.

All carbazoles are synthesized in accordance to the protocols shown in **Scheme S1** of **Supporting information**. As indicated, Cz-1 and Cz-2 were synthesized using 2-haloanilines and methoxy substituted halobenzenes. Subsequent Buchwald-Hartwig amination yields intermediates which are subjected to C-H activation and ring closure to form the required Cz-1 and Cz-2.<sup>51</sup> For Cz-3, we employed Pd(II)-catalyzed oxidative carbon-carbon bond formation for the needed ring closure reaction.<sup>52</sup> The directly N-borylated **BM** compounds, **CzBM-1** to **3**, were synthesized via in situ deprotonation of respective carbazole with *n*-BuLi in THF at –78°C, followed by treatment with B(Mes)<sub>2</sub>F under reflux. The N-phenyl carbazoles were next synthesized by Ullmann coupling of dimethoxy substituted Cz-2 and Cz-3 and 1-bromo-4-iodobenzene, and the **PBM** compounds (**CzPBM-2** and **-3**) were prepared from

aforementioned N-phenyl carbazole and B(Mes)<sub>2</sub>F at RT. All the **BM** and **PBM** compounds are air-stable and, hence, enable facile purification by sequential column chromatography and vacuum sublimation. Finally, all boron compounds were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies, FAB mass spectrometry and elemental analysis.

Notably, <sup>1</sup>H NMR spectral patterns of both the *o*- and *p*-methyl groups in the mesityl unit are strongly influenced by their individual structures (**Figure S1**). The *o*-methyl signals of **CzBM-3** appeared as four broadened signals, while those of **CzPBM-3** appeared as one sharp signal at RT. This difference is mainly due to a large barrier of the restricted rotation of mesityl groups in solution at RT. Introducing the phenylene spacer to **CzBM-3** in forming **CzPBM-3** reduces the rotational barrier and gives rise to only one sharp signal. This observation was akin to the NMR spectral behaviors observed for other three coordinate N-borylated compounds reported in literature.<sup>53</sup>

CzBM-1, CzBM-3, and CzPBM-3 were characterized by single-crystal X-ray diffraction study, and their molecular structures are displayed in Figures 1 and 2. Generally speaking, both CzBM-1 and CzBM-3 display trigonal planar core arrangement as evidenced from the sum of all angles around B(1) atom being ~360°. The observed B-N distance of 1.458 Å and 1.454 Å for CzBM-1 and CzBM-3, respectively, falls in the range of 1.442–1.472 Å as observed for other N-borylated pyrrole derivatives, which is shorter than the tetravalent borylated compounds.<sup>31</sup> This is mainly due to the larger s-character of the sp<sup>2</sup>-hybridized trivalent boron atom that enhances the B-N bond strength compared to the sp<sup>3</sup>-hybridized tetravalent boron compounds. The torsional angles between the N(1)-C(1)-C(12) and B(1)-C(15)-C(25) planes of CzBM-1 and CzBM-3 are measured to be 38.75° and 40.37°, respectively, confirming the reduced p-orbital overlap between the N-donor and B-acceptor.

Concurrently, introducing phenylene in forming **CzPBM-3** does not alter the trigonal geometry of (Mes)<sub>2</sub>B as displayed in **Figure 2**. The dihedral angle between the carbazole and phenylene is measured to be 58.73° which is akin to the relevant structural parameters reported in literature.<sup>32, 39</sup> Although this dihedral angle is smaller than that of the phenoxazine or acridine donors, our attached methoxy substituents enhance the electron donating ability of carbazole that, in turn, assists the localization of the HOMO on the carbazole moiety,

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reduces the spatial overlap between the HOMO and LUMO as well as favors smaller  $\Delta E_{sT}^{OI: 10.1039/C9TC07020F}$ better TADF character (*vide infra*).<sup>54, 55</sup>

Their thermal and morphological properties were analyzed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. The corresponding TGA and DSC graphs are shown in **Figure S2** and the numeric data are summarized in **Table S1**. The decomposition temperature (T<sub>d</sub>) for **CzBM-2** and **CzBM-3** occurred at 276 and 286 °C respectively, which was slightly higher than that of 1-methoxy substituted **CzBM-1** (264 °C). In addition, T<sub>d</sub> of **CzPBM-3** occurred at ~308 °C, revealing an increase of 22 °C in comparison to that of **CzBM-3**, which is attributed to the addition of a phenylene spacer. The glass transition temperature (T<sub>g</sub>) of **CzBM-1** to **3** was observed between 192 to 196 °C, while the introduction of phenylene spacer decreases T<sub>g</sub> to 136 and 141 °C for **CzPBM-2** and **3**, respectively.

# 2.2. Photophysical properties

The UV-vis absorption and photoluminescence (PL) spectra were measured in solvents with different polarity, as well as in neat film and doped film to validate the influence on their photophysical properties. The corresponding spectra and data are displayed in **Figures 3** and **4** and **Table 1**. It appears that alternation of methoxy substituents and solvent polarity renders no significant influence in their absorption behavior. All the N-borylated compounds possess two absorption bands, among which the higher energy above 300 nm is attributed to  $\pi \rightarrow \pi^*$  transitions, while the lower energy band below 320 nm is assigned to a charge transfer (CT) transition. Red shift of absorption from ~330 to ~370 nm was observed in respective **BM** and **PBM** compounds that correspond to the extended  $\pi$ -conjugation imposed by the inserted *p*-phenylene fragment.

As can be seen, addition of methoxy substituents exerts significant influence on their photoluminescence. For example, the emission maximum of 1-methoxy substituted **CzBM-1** in toluene is observed at 462 nm. Upon introducing 1,3-dimethoxy substituents in affording **CzBM-2**, the emission maximum is shifted to 501 nm, revealing an increased electron donation on Cz-2 compared to Cz-1 as shown in **Figure 3**. Furthermore, the emission of **CzBM-**

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**3** is blue shifted by 9 nm from **CzBM-2** in toluene, indicating a slightly reduction of charge transfer. Moreover, their emissions are highly sensitive to the solvent polarity. For example, **CzBM-1** displays a prominent red shifting of 40 nm by switching from cyclohexane (440 nm) to CH<sub>2</sub>Cl<sub>2</sub> (480 nm), while CzBM-2 and CzBM-3 exhibit a red shifting of 49 nm and 43 nm, respectively. CzPBM-2 and CzPBM-3 with phenylene bridge show an emission max. at 417 nm and 406 nm in cyclohexane and at 519 nm and 499 nm in CH<sub>2</sub>Cl<sub>2</sub>. This change of luminescence confirms the extensive charge transfer character at the excited state, which is one important criterion for the TADF behavior.

Although the decrease in the emission energy gap upon increasing solvent polarity in both **BM** and **PBM** series of compounds can be attributed to the solvent relaxation, i.e. solvatochromism, their emissive hues have greatly different from each other. For instance, both CzPBM-2 and CzPBM-3 exhibit emission max. at 464 nm and 452 nm in toluene, both are blue-shifted by approx. ~40 nm in comparison to their N-borylated counterpart CzBM-2 (501 nm) and CzBM-3 (492 nm). Hence, in addition to the solvatochromism, another relaxation process is considered to take place in BM based compounds to account for the large Stokes-shifted emission in nonpolar solvent (i.e. toluene). Accordingly, from a molecular structure point of view, the lack of phenylene in BM compounds may induce the large steric hindrance between carbazole and (Mes)<sub>2</sub>B unit, resulting in a more rigid molecular structure. Furthermore, upon optical excitation in all solution states, the rigid structures can undergo structural relaxation in its S<sub>1</sub> state potential energy surface to relief the steric constrains, obtaining the large Stokes-shifted emission (see Figure 3). On the contrary, owing to the addition of phenylene bridge in PBM compounds, they can retain their original, more relaxed geometries upon excitation and exhibit less Stokes-shifted emission (see Figure 4).<sup>31</sup> Verifications of the structural relaxations and its corresponding geometries are discussed in the theoretical calculations sections (vide infra).

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TADF characteristics were preliminarily confirmed by measurement of their photoluminescence properties in aerated versus degassed solutions. As displayed in Table 1, the quantum yields were found to increase by two to three folds in degassed solutions, endorsing the suppression of oxygen quenching and efficient reversed intersystem crossing (RISC) from  $T_1 \rightarrow S_1$  excited states. To validate these properties, the time-resolved delayed PL spectra were conducted for all the molecules in CH<sub>2</sub>Cl<sub>2</sub> as shown in Figure S3. The prompt emission components can be acquired at zero delay time and a gate width of 50 ns by an intensified charge-coupled detector, whereas the delayed emission components were acquired at a delayed time of 10  $\mu$ s and a gate width of 10  $\mu$ s. The proximity of the spectral onsets between fluorescence and the delayed components apparently affirm the appearance of delayed fluorescence and the possibility of TADF character. Next, transient PL decay dynamics were then measured in different solvent, and as neat film and doped film. The pertinent lifetime results are tabulated in Table 1, while the spectra taken in degassed solutions are displayed in Figures S4 to S8. All the compounds exhibited bi-exponential decays comprising prompt and delayed components. For example, CzBM-2 exhibited two decay kinetics in degassed  $CH_2Cl_2$ , with a short time constant of 11 ns that corresponds to  $S_1 \rightarrow S_0$ fluorescence and the other long decay of 3.5 µs that arises from RISC, followed by the delayed  $S_1 \rightarrow S_0$  emission. These observations confirm the TADF property in the **BM** compounds and validates the usefulness of methoxy groups. Moreover, the long decay lifetime of CzPBM-2 (1.6 µs) and CzPBM-3 (1.2 µs) in neat film confirm their TADF characters, which is in contrast to the parent CzPBM-0,<sup>55, 56</sup> for which the lack of TADF reveals the positive influence imposed by methoxy substituents.

# 2.4 Theoretical calculation

Computations were performed to gain further insights into the basic photophysical and electronic properties of titled molecules. Their ground-state geometries were optimized using density function theory (DFT) calculation, while the excited-state properties were computed by the time-dependent-DFT method with a m062x hybrid functional. In this section, the  $S_0 \rightarrow S_1$  absorption and the vertical  $S_1 \rightarrow S_0$  transition were calculated from the structurally optimized  $S_0$  and  $S_1$  states to obtain the transitional energy gap as tabulated in **Table S4** to **S14**, respectively. For a fair comparison, the reported **CzBM-0**<sup>46</sup> and **CzPBM-0**<sup>39</sup> were also computed based on the same functional and basis sets. Detailed procedures are provided in the **SI**.

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As shown in Figure 5, for all CzBM and CzPBM series, the results of computational data indicate that the electron distributions in HOMO and LUMO are mainly localized at carbazole (donor) and boron dimesityl (acceptor) moieties, respectively. Therefore, the emission possessing charge transfer (CT) character for all titled boron complexes is unambiguous. However, as for CzBM-0 and CzPBM-0 (see Figure 5), careful analysis of frontier orbital indicates their subtle difference from the rest of BM and PBM compounds anchored with methoxy groups, in which CzBM-0 and CzPBM-0 has non-negligible overlap between HOMO and LUMO at CzBM-O's N(1), C(1) and C(2) as well as CzPBM-O's C(6) and C(8) atoms (see Figure 5). The result indicates an appreciable electronic coupling between locally excited (LE) and CT states, diminishing the TADF character by its enlarged  $\Delta E_{ST}$ . Conversely, the overlap between HOMO and LUMO at C(6) and C(8) atoms is nearly non-observable for CzPBM-2 and CzPBM-3, indicating mainly a CT character in their emissive states. The difference, in a qualitative manner, can be rationalized by the anchoring of methoxy group in CzPBM-2 and CzPBM-3 to raise the carbazole HOMO level. The relatively large CT/LE mixing in CzPBM-0 increases the electron exchange energy and hence leads to a large energy splitting between  $S_1$  and  $T_1$  state, i.e.  $\Delta E_{ST}$ , <sup>53-54</sup> making TADF vanished. To the contrary, **CzPBM-2** and **CzPBM-3** with predominant CT character reveal prominent TADF. Similar dominant CT character was resolved for CzBM-1, 2 and 3, consistent with their observable TADF behavior.

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Despite the sameness of the CT characters of all molecules in this study, the distinct differences lie in the optimized geometries of both **BM** and **PBM** compounds. It is notable that **CzBM-1**, **2** and **3** exhibits smaller torsional angle ( $\theta_t$ ) of 41.13°, 38.36° and 38.27° (cf. 88.46° and 85.63° of **CzPBM-2** and **3**) as shown in **Figure 6**, respectively. These results indicate that the phenylene bridge provides better orthogonality between carbazole donor and (Mes)<sub>2</sub>B acceptor. Furthermore, at the optimized geometries of at the lowest lying excited state, the  $\theta_t$  angle increased in all N-borylated compounds, together with the expansion of the bending angle in (Mes)<sub>2</sub>B fragments ( $\theta_b$ ). The orthogonal orientation may result in a poor donor-acceptor  $\pi$ -orbital overlap, to which the resulting smaller exchange energy is expected to lower  $\Delta E_{ST}$  and facilitate RISC. In order to increase  $\theta_t$  angle for better orthogonality, the B-N distance is elongated in **BM** molecules, combining with the increased  $\theta_b$  angle in the boron

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dimesityl fragments. For example,  $\theta_t$  was changed from 38.36° into 59.90° in ground/excitedstate optimized structure of **CzBM-2** as shown in **Figure 6**. Moreover, the B-N distance and  $\theta_{b}$ angle were varied from 1.452 Å to 1.545 Å and from 121.13° to 128.93° in CzBM-2, respectively. Similar structurally relaxed processes were also observed in CzBM-1 and CzBM-3. The computational results clearly support the occurrence of excited-state structural relaxations in N-borylated molecules (i.e. CzBM-1 to 3), including rotation of the donor and acceptor moieties, elongation of B-N distance and expansion of the boron dimesityl fragments.

On the contrary, owing to the phenylene spacer in PBM molecules, CzPBM-2 and 3 already exhibit nearly orthogonal orientations in their optimized ground-state geometries, in which  $\theta_t$  and  $\theta_b$  are recorded as 88.46° and 121.46° for **CzPBM-2** and 85.63° and 121.65° for CzPBM-3 as shown in Figure 6. Moreover, CzPBM-2 and 3 show very small structural relaxation upon excitation, indicating the less steric restriction in PBM molecules compared to the **BM** series. These observations indicate that they had reached their stable geometries in an absence of steric confinements, which are consistent with the small Stokes-shifted emission and the previously reported **PBM** type of TADF molecules.<sup>31</sup>

#### 2.4. Electrochemical properties

Redox parameters of the title compounds are necessary with an aim to access optimized device architecture for OLEDs. Accordingly, cyclic voltammetry measurements were conducted to analyze their electrochemical behavior, for which the voltammograms and numerical data are displayed in Figure S9 and Table S3. As can be seen, the anodic sweep resulted in two reversible oxidation peaks for CzBM-2 and CzPBM-2, both possess 1,3dimethoxy substituted carbazole, while only one reversible oxidation peak was observed for their isomeric 1,6-derivatives CzBM-3 and CzPBM-3. Specifically, the first oxidation peak of CzBM-2 and CzPBM-2 appeared at 0.37 V and 0.44 V, indicating the shallow HOMO energy level of 1,3-dimethoxy compounds in comparison to that of 1,6-dimethoxy substituted CzBM-3 and CzPBM-3 (i.e. 0.56 V and 0.61 V). Meanwhile, both phenylene bridged CzPBM-2 and CzPBM-3 exhibit more stabilized HOMO than the corresponding N-borylated derivatives

(CzBM-2 and CzBM-3, respectively). In good agreement with these observation, we also measured the oxidation potentials of the parent carbazoles Cz-2 and C-3, which occurred at 0.36 V and 0.57 V, respectively. These results confirmed the higher oxidation potentials of all Cz-3 based N-borylated emitters as well as the blue-shifting of emission in comparison to their Cz-2 analogues.

Moreover, CzBM-1 exhibited the highest oxidation peak potential at 0.66 V, indicating the lowest donor strength for its carbazole among all studied derivatives. As for the reduction process, the peak potentials occurred between -2.57 to -2.65 V and -2.40 to -2.48 V for the **BM** and **PBM** derivatives respectively, affirming the greater stabilization of LUMO by  $\pi$ conjugated phenylene.

#### 2.5 OLED device fabrication

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Electroluminescent (EL) properties of the five TADF blue emitters were then studied with a device structure of indium tin oxide (ITO)/N,N'-bis(naphthalen-1-yl)-N,N'bis(phenyl)benzidine (NPB, 40 nm)/4,4',4"-tris(carbazol-9-yl)triphenylamine (TCTA, 20 nm)/1,3-bis(carbazol-9-yl)benzene (mCP, 10 nm)/bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO) : 6 wt% emitter (20 nm)/DPEPO (10 nm)/1,3,5-tri[(3-pyridyl)-phen-3yl]benzene (TmPyPB, 35 nm)/LiF (1 nm)/Al (100 nm). The device performances are shown in Figure 7 and the key performance parameters are listed in Table 2. Based on the current density-voltage-luminance (J-V-L) curves shown in Figure 7(a), the fabricated devices presented an approximately ten-time difference in current efficiency as recorded in Table 2. Figure 7(b) shows the EL spectra measured at 100 cd m<sup>-2</sup>. As indicated, all the EL characters were akin to their PL measured in thin films that possess an identical composition to the doped emitting layer in OLED. Among them, CzBM-1 emitted a deep-blue electroluminescence with a CIE(y) value as low as 0.11 with emission peak wavelength located at 444 nm. However, owing to low PLQY and wide energy gap of CzBM-1, the associated devices showed the lowest current efficiency (1.4 cd/A), power efficiency (1.1 lm/W) and external quantum efficiency (1.8%) among all fabricated TADF OLED devices. Alternatively, CzBM-2, CzBM-3, CzPBM-2 and CzPBM-3 exhibit much better EL performances with EQEs

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ranging from 9.5 to 13.3% (**Fig. 7c**), owing to better TADF characteristics and higher PLQYs in doped thin films. The highly twisted molecular conformation induced by the phenylene spacer between N-donor and B-acceptor in PBM molecules may influence their electrical properties and carrier balances in the emissive layer, leading to higher turn-on voltages in the devices based on CZBM-2 and CZBM-3. Although their EL peak wavelength spanned the true-blue region from 444 nm to 468 nm, their max. EQE values are higher than those of the EQE expected for conventional fluorescent OLED (i.e. 5%). These results affirm their characteristics in harvesting both the singlet and triplet excitons via RISC and, thus, giving direct evidence for the TADF characters.

#### 3. Conclusion

In summary, we have designed and synthesized three methoxy substituted carbazoles (Cz-1, Cz-2 and Cz-3) in an attempt to enhance the electron donating strength and to create a relatively enlarged steric encumbrance. These donors were then linked to boron dimesityl acceptor, forming the **BM** emitters (**CzBM-1**, **CzBM-2** and **CzBM-3**) and phenylene bridged **PBM** emitters (**CzPBM-2** and **CzPBM-3**). Absorption and photoluminescence measurements in different solvents reveal strong solvatochromism induced by the CT processes. Drastically different from lack of TADF for reference compounds CzBM-0 and CzPBM-0 being reported previously, all synthesized emitters showed notable delayed fluorescence, validating the methoxy substitution as one useful strategy to harness the electron donating strength and special orthogonality in achieving the TADF characteristics. Furthermore, these compounds were then employed as dopant in fabrication of OLEDs, in which their EL peak wavelengths span the region from 444 nm to 468 nm. OLED based on **CzBM-2** and **CzPBM-3** achieved max. EQEs of 12.5% and 13.3% respectively, demonstrating their potentials in the development of highly efficient blue TADF emitters.

#### 4. Supporting Information

Detailed synthetic conditions for both donor and acceptor moieties as well as well as the contract of the studied TADF molecules are recorded.

**Crystallographic data.** The X-ray crystallographic coordinates for the compounds reported in this article has been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC 1900690 (**CzBM-1**), 1900691 (**CzBM-3**) and 1900692 (**CzPBM-3**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac</u>

#### 5. Notes

The authors declare no competing financial interests.

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# 7. Author Contributions

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# 8. Acknowledgment

Prof. Chi and Chou thanks for Ministry of Science Technology (MOST) of Taiwan and the Higher Education Sprout Project administrated by Ministry of Education (MOE) of Taiwan for finical supports. This work was also supported by the funding from City University of Hong Kong, Hong Kong SAR. The authors are grateful to the National Center for the Highperformance Computing (NCHC) of Taiwan for the computer facilities.

	state	$\lambda_{em}$ [nm]	PLQY [%] ª	τ [ns] and pre-exp. factor	ΔE <sub>st</sub> , (eV) <sup>b</sup>	
CzBM-1	cyclohexane	440	11 / 13	4.19 (1.000)		_
	toluene	462	18 / 26	9.8 (0.996), 212(0.004)	0.113	
	$CH_2CI_2$	480	20 / 33	14.57 (0.998), 764 (0.002)	0.131	
	Neat film	442	30	5.97 (0.999), 721.4 (0.001)	0.149	
CzBM-2	cyclohexane	475	24 / 42	10.98 (0.997), 629(0.003)	0.121	_
	toluene	501	21 / 57	15.29 (0.992), 2840 (0.008)	0.096	
	$CH_2CI_2$	524	16 / 26	11.53 (0.998), 3520 (0.002)	0.131	
	Neat film	481	32	1.13 (0.997), 4259 (0.003)	0.121	
	DPEPO doped film	478	55	4.94 (0.999), 26633 (0.001)	0.149	
CzBM-3	cyclohexane	467	20 / 25	9.98 (0.997), 868 (0.003)	0.121	
	toluene	492	20 / 51	15.48 (0.997), 3087 (0.003)	0.121	
	$CH_2CI_2$	510	15 / 42	20.77 (0.997), 6955 (0.003)	0.121	
	Neat film	479	57	3.58 (0.992), 2657 (0.008)	0.096	
	DPEPO doped film	476	70.3	8.47 (0.999) 5578 (0.001)	0.149	
CzPBM-2	cyclohexane	417	53 / 88	6.42 (1.000)		_
	toluene	464	55 / 100	16.40 (0.998), 10000 (0.002)	0.131	
	CH <sub>2</sub> Cl <sub>2</sub>	519	50 / 71	18.42 (0.998), 10008 (0.002)	0.131	
	Neat film	475	68	12.31 (0.999), 1609 (0.001)	0.149	_
	DPEPO doped film	474	94	18.11 (0.999), 2218 (0.001)	0.149	
CzPBM-3	cyclohexane	406	70 / 95	5.65 (0.999), 10000 (0.001)	0.149	_
	toluene	452	75 / 100	12.59 (0.999), 5582 (0.001)	0.149	_
	CH <sub>2</sub> Cl <sub>2</sub>	499	42 / 100	21.81 (0.998), 19277 (0.002)	0.131	
	Neat film	463	72	12.49 (0.997), 1251 (0.003)	0.121	
	DPEPO doped film	458	94	31.00 (0.997), 9880 (0.003)	0.121	

 Table 1. Selected photophysical properties of the studied boron compounds in both solution and thin film states at RT.

<sup>a</sup> The solution quantum yields are recorded in both the aerated and degassed conditions and separated by slash.

<sup>b</sup> The energy differences were analyzed by the equations as descripted in **Table S2.** 

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 Table 2. Key OLED device performance parameters.

Emitter	V <sub>on</sub> a (V)	$\lambda_{\scriptscriptstyle EL}{}^{\scriptscriptstyle b}$ (nm)	CIE <sup>c</sup> (x, y)	CE <sub>max</sub> <sup>d</sup> (cd/A)	PE <sub>max</sub> <sup>d</sup> (Im/W)	EQE <sub>max</sub> <sup>d</sup> (%)
CzBM-1	3.9	444	0.16, 0.11	1.4, 0.1	1.1, 0.2	1.8, 0.4
CzBM-2	3.7	468	0.18, 0.24	19.8, 7.3	17.3, 4.4	12.5, 4.2
CzBM-3	3.5	468	0.17, 0.22	19.3, 9.2	16.8, 5.8	11.7, 5.6
CzPBM-2	4.5	467	0.19, 0.27	13.8, 4.6	9.6, 2.1	9.5, 2.8
CzPBM-3	5.0	467	0.18, 0.19	9.4, 2.2	6.5, 0.8	13.3, 1.8

<sup>a</sup>Voltage measured at 1 cd m<sup>-2</sup>; <sup>b</sup>color index measured at 100 cd m<sup>-2</sup>; <sup>c</sup>electroluminescence peak at 100 cd m<sup>-2</sup>; <sup>c</sup>device performances measured at maximum and 100 cd m<sup>-2</sup>, respectively.

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**Figure 1**. Structural drawing of (a) **CzBM-1**, B(1)-N(1) = 1.458(3) Å; torsional angle ( $\theta_t$ ) between the N(1)-C(1)-C(12) and B(1)-C(13)-C(22) planes: 38.75° and (b) **CzBM-3**, B(1)-N(1) = 1.454(16) Å; torsional angle ( $\theta_t$ ) between the N(1)-C(1)-C(12) and B(1)-C(15)-C(25) planes: 40.37°. The ellipsoids were shown at the 30% probability.

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**Figure 2**. Structural drawing of **CzPBM-3** with ellipsoids shown at the 30% probability level. B(1)-C(4) = 1.570(17) and C(1)-N(1) = 1.427(15) Å; dihedral angle between the C(6)-C(1)-C(2) and C(7)-N(1)-C(18) planes:  $58.73^{\circ}$ .





**Figure 3**. Absorption and emission spectra of (a) **CzBM-1**, (b) **CzBM-2** and (c) **CzBM-3**, in cyclohexane (blue), toluene (red), CH<sub>2</sub>Cl<sub>2</sub> (brown), neat film (black) and doped film (magenta) at 298 K.



**Figure 4**. Absorption and emission spectra of (a) **CzPBM-2**, and (b) **CzPBM-3** in cyclohexane (blue), toluene (red),  $CH_2Cl_2$  (brown), neat film (black) and doped film (magenta) at 298 K.



**Figure 5**. Optimized molecular structures in their ground-states and the associated HOMO and LUMO for **CzBM-0** to **3** and **CzPBM-0**, **2** and **3**.



**Figure 6.** Optimized molecular structures in the ground-states and excited-states for **CzBM-1** to **3** and **CzPBM-2** and **3**.  $\theta_t$  indicates the torsional angle between the mean planes C(1)-N(1)-C(2) and C(3)-B(1)-C(4) of the carbazole donor and the (Mes)<sub>2</sub>B unit, respectively.  $\theta_b$  represents the bending angle between the two mesityl groups in the acceptor, which is recorded by the angle of C(3)-B(1)-C(4).

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**Figure 7.** (a) current density-voltage-luminance characteristics; (b) electroluminescent spectra at 100 cd m<sup>-2</sup>; (c) EQE-current density curves.

# References

View Article Online DOI: 10.1039/C9TC07020F

- 1. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913-915.
- 2. J. Kido, M. Kimura and K. Nagai, *Science*, 1995, **267**, 1332-1334.
- 3. B. W. D'Andrade and S. R. Forrest, *Adv. Mater.*, 2004, **16**, 1585-1595.
- 4. Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson and S. R. Forrest, *Nature*, 2006, **440**, 908-912.
- 5. S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Luessem and K. Leo, *Nature*, 2009, **459**, 234-238.
- 6. C. Adachi, M. A. Baldo, M. E. Thompson and S. R. Forrest, *J. Appl. Phys.*, 2001, **90**, 5048.
- 7. K.-H. Kim, J.-L. Liao, S. W. Lee, B. Sim, C.-K. Moon, G.-H. Lee, H. J. Kim, Y. Chi and J.-J. Kim, *Adv. Mater.*, 2016, **28**, 2526-2532.
- 8. Y. Zhang and S. R. Forrest, *Phys. Rev. Lett.*, 2012, **108**, 267404.
- 9. B. Minaev, G. Baryshnikov and H. Agren, *Phys. Chem. Chem. Phys.*, 2014, **16**, 1719-1758.
- 10. C.-Y. Kuei, W.-L. Tsai, B. Tong, M. Jiao, W.-K. Lee, Y. Chi, C.-C. Wu, S.-H. Liu, G.-H. Lee and P.-T. Chou, *Adv. Mater.*, 2016, **28**, 2795-2800.
- 11. D. Liu, L. Deng, W. Li, R. Yao, D. Li, M. Wang and S. Zhang, *Adv. Opt. Mater.*, 2016, **4**, 864-870.
- 12. Z. Yan, Y. Wang, J. Wang, Y. Wang, J. Ding and L. Wang, *J. Mater. Chem. C*, 2017, **5**, 10122-10125.
- 13. G.-Z. Lu, n. Su, H. Yang, Q. Zhu, W.-W. Zhang, Y. Zheng, L. Zhou, J.-L. Zuo, Z.-X. Chen and H. Zhang, *Chem. Sci.*, 2019, **10**, 3535-3542.
- 14. H. Shin, Y. H. Ha, H.-G. Kim, R. Kim, S.-K. Kwon, Y.-H. Kim and J.-J. Kim, *Adv. Mater.*, 2019, **31**, 1808102.
- 15. H. Uoyama, K. Goushi, K. Shizu, H. Nomura and C. Adachi, *Nature*, 2012, **492**, 234-238.
- 16. T.-A. Lin, T. Chatterjee, W.-L. Tsai, W.-K. Lee, M.-J. Wu, M. Jiao, K.-C. Pan, C.-L. Yi, C.-L. Chung, K.-T. Wong and C.-C. Wu, *Adv. Mater.*, 2016, **28**, 6976-6983.
- 17. Z. He, W. Zhao, J. W. Y. Lam, Q. Peng, H. Ma, G. Liang, Z. Shuai and B. Z. Tang, *Nat. Commun.*, 2017, **8**, 416.
- 18. T. Miwa, S. Kubo, K. Shizu, T. Komino, C. Adachi and H. Kaji, Sci. Rep., 2017, 7, 284.
- 19. X. Cai and S.-J. Su, Adv. Funct. Mater., 2018, 28, 1802558.
- 20. M. Liu, R. Komatsu, X. Cai, K. Hotta, S. Sato, K. Liu, D. Chen, Y. Kato, H. Sasabe, S. Ohisa, Y. Suzuri, D. Yokoyama, S.-J. Su and J. Kido, *Chem. Mater.*, 2017, **29**, 8630-8636.
- 21. Y. Im, M. Kim, Y. J. Cho, J.-A. Seo, K. S. Yook and J. Y. Lee, *Chem. Mater.*, 2017, **29**, 1946-1963.
- 22. J. H. Kim, J. H. Yun and J. Y. Lee, Adv. Opt. Mater., 2018, 6, 1800255.
- 23. P. Ganesan, D.-G. Chen, J.-L. Liao, W.-C. Li, Y.-N. Lai, D. Lo, C.-H. Chang, C.-L. Ko, W.-Y. Hung, S.-W. Liu, G.-H. Lee, P.-T. Chou and Y. Chi, *J. Mater. Chem. C*, 2018, **6**, 10088-10100.
- 24. D.-G. Chen, T.-C. Lin, Y.-A. Chen, Y.-H. Chen, T.-C. Lin, Y.-T. Chen and P.-T. Chou, *J Phys Chem C*, 2018, **122**, 12215-12221.
- 25. B. Wex and B. R. Kaafarani, J. Mater. Chem. C, 2017, 5, 8622-8653
- 26. T. Hatakeyama, K. Shiren, K. Nakajima, S. Nomura, S. Nakatsuka, K. Kinoshita, J. Ni, Y. Ono and T. Ikuta, *Adv. Mater.*, 2016, **28**, 2777-2781.
- 27. C. Duan, J. Li, C. Han, D. Ding, H. Yang, Y. Wei and H. Xu, *Chem. Mater.*, 2016, **28**, 5667-5679.
- 28. X. Cao, D. Zhang, S. Zhang, Y. Tao and W. Huang, J. Mater. Chem. C, 2017, 5, 7699-7714.
- 29. N. Jürgensen, A. Kretzschmar, S. Höfle, J. Freudenberg, U. H. F. Bunz and G. Hernandez-Sosa, *Chem. Mater.*, 2017, **29**, 9154-9161.
- 30. S. Nakatsuka, H. Gotoh, K. Kinoshita, N. Yasuda and T. Hatakeyama, *Angew. Chem. Int. Ed.*, 2017, **56**, 5087-5090.
- D.-G. Chen, T.-C. Lin, C.-L. Chen, Y.-T. Chen, Y.-A. Chen, G.-H. Lee, P.-T. Chou, C.-W. Liao, P.-C. Chiu, C.-H. Chang, Y.-J. Lien and Y. Chi, ACS Appl. Mater. Interfaces, 2018, 10, 12886-12896.

Journal of Materials Chemistry C Accepted Manuscript

- 32. K. Suzuki, S. Kubo, K. Shizu, T. Fukushima, A. Wakamiya, Y. Murata, C. Adachi and Hticle Online Kaji, Angew. Chem. Int. Ed., 2015, **54**, 15231-15235.
- 33. Y.-J. Shiu, Y.-C. Cheng, W.-L. Tsai, C.-C. Wu, C.-T. Chao, C.-W. Lu, Y. Chi, Y.-T. Chen, S.-H. Liu and P.-T. Chou, *Angew. Chem. Int. Ed.*, 2016, **55**, 3017-3021.
- 34. H. Hirai, K. Nakajima, S. Nakatsuka, K. Shiren, J. Ni, S. Nomura, T. Ikuta and T. Hatakeyama, *Angew. Chem. Int. Ed.*, 2015, **54**, 13581-13585.
- 35. L. Ji, S. Griesbeck and T. B. Marder, *Chem. Sci.*, 2017, **8**, 846-863.
- 36. Y. Liu, G. Xie, K. Wu, Z. Luo, T. Zhou, X. Zeng, J. Yu, S. Gong and C. Yang, *J. Mater. Chem. C*, 2016, *4*, 4402-4407.
- 37. Y. Liu, H. Huang, T. Zhou, K. Wu, M. Zhu, J. Yu, G. Xie and C. Yang, *J. Mater. Chem. C*, 2019, **7**, 4778-4783.
- 38. D. Li, H. Zhang and Y. Wang, *Chem. Soc. Rev.*, 2013, **42**, 8416-8433.
- 39. Y. Kitamoto, T. Namikawa, T. Suzuki, Y. Miyata, H. Kita, T. Sato and S. Oi, *Org. Electron.*, 2016, **34**, 208-217.
- 40. Y. H. Lee, S. Park, J. Oh, J. W. Shin, J. Jung, S. Yoo and M. H. Lee, *ACS Appl. Mater. Interfaces*, 2017, **9**, 24035-24042.
- 41. X.-L. Chen, J.-H. Jia, R. Yu, J.-Z. Liao, M.-X. Yang and C.-Z. Lu, *Angew. Chem. Int. Ed.*, 2017, **56**, 15006-15009.
- 42. Y. H. Lee, S. Park, J. Oh, S.-J. Woo, A. Kumar, J.-J. Kim, J. Jung, S. Yoo and M. H. Lee, *Adv. Opt. Mater.*, 2018, **6**, 1800385.
- 43. S. Mukherjee and P. Thilagar, J. Mater. Chem. C, 2016, 4, 2647-2662.
- 44. K. K. Neena, P. Sudhakar, K. Dipak and P. Thilagar, *Chem. Commun.*, 2017, **53**, 3641-3644.
- 45. Y.-J. Lien, T.-C. Lin, C.-C. Yang, Y.-C. Chiang, C.-H. Chang, S.-H. Liu, Y.-T. Chen, G.-H. Lee, P.-T. Chou, C.-W. Lu and Y. Chi, *ACS Appl. Mater. Interfaces*, 2017, **9**, 27090-27101.
- 46. T. Taniguchi, J. Wang, S. Irle and S. Yamaguchi, *Dalton Trans.*, 2013, **42**, 620-624.
- 47. X. Sallenave, A. Bucinskas, S. Salman, D. Volyniuk, O. Bezvikonnyi, V. Mimaite, J. V. Grazulevicius and G. Sini, *J. Phys. Chem. C*, 2018, **122**, 10138-10152.
- 48. Z. Chen, F. Ni, Z. Wu, Y. Hou, C. Zhong, M. Huang, G. Xie, D. Ma and C. Yang, *J. Phys. Chem. Lett.*, 2019, **10**, 2669-2675.
- 49. J. S. Ward, R. S. Nobuyasu, M. A. Fox, J. A. Aguilar, D. Hall, A. S. Batsanov, Z. Ren, F. B. Dias and M. R. Bryce, *J. Org. Chem.*, 2019, **84**, 3801-3816.
- 50. C. Tu and W. Liang, *ACS Omega*, 2017, **2**, 3098-3109.
- 51. M. E. Budén, V. A. Vaillard, S. E. Martin and R. A. Rossi, *J. Org. Chem.*, 2009, **74**, 4490-4498.
- 52. B. Liégault, D. Lee, M. P. Huestis, D. R. Stuart and K. Fagnou, *J. Org. Chem.*, 2008, **73**, 5022-5028.
- 53. Y. Cui, F. Li, Z.-H. Lu and S. Wang, *Dalton Trans.*, 2007, 2634-2643.
- 54. K. Shizu, H. Tanaka, M. Uejima, T. Sato, K. Tanaka, H. Kaji and C. Adachi, *J. Phys. Chem. C*, 2015, **119**, 1291-1297.
- 55. Y. Gao, T. Su, L. Zhao, Y. Geng, Y. Wu, M. Zhang and Z.-M. Su, *Org. Electron.*, 2017, **50**, 70-76.
- 56. Y. Geng, L.-S. Cui, J. U. Kim, H. Nakanotani and C. Adachi, *Chem. Lett.*, 2017, **46**, 1490-1492.

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