Facile synthesis of multi-resonance ultra-pure-green TADF emitters based on bridged diarylamine derivatives for efficient OLEDs with narrow emission

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Facile synthesis of multi-resonance ultra-pure-green TADF emitters based on bridged diarylamine derivatives for efficient OLEDs with narrow emission

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Abstract

High color-purity emission with a minimum full width at half maximum (FWHM) is critical for high-resolution displays. Despite the increasing demand for narrow-band emission materials with multi-resonance-induced thermally activated delayed fluorescence (MR-TADF), their development remains challenging from the viewpoint of synthetic chemistry. In this study, we developed a novel one-pot borylation method that does not require the use of hazardous tert-BuLi, and for which the starting materials are not limited to aromatic fluorides and carbazole-based materials. We achieved this by making simple modifications to a boron-nitrogen skeleton. By inserting carbon and oxygen into the skeleton, we created two types of highly efficient green-emitting MR-TADF emitters, namely DMAc-BN and PXZ-BN. This design enabled the suppression of aggregation-induced quenching, which was one of the major challenges faced by MR-TADF emitters developed in the past. OLEDs using our DMAc-BN and PXZ-BN emitters
exhibited external quantum efficiencies of 20.3% and 23.3%, respectively, with FWHM values of 49 and 47 nm, respectively. **PXZ-BN** exhibited pure green emission with CIE coordinates of (0.22, 0.67).

**Keywords:** Thermally activated delayed fluorescence • Organoboron compound • Borylation • Organic light-emitting device

**Introduction:**

Highly efficient thermally activated delayed fluorescence (TADF) was first reported by Adachi et al.\cite{1}, and was a major breakthrough for OLEDs, because it paved the way for achieving 100% internal quantum efficiency without the need for precious metal component \cite{2-8}. The small singlet-triplet (S\(_1\)-T\(_1\)) energy gaps (\(\Delta E_{ST}\)) of TADF materials enable efficient reverse intersystem crossing (RISC) from T\(_1\) to S\(_1\) and the use of all generated excitons. To minimize \(\Delta E_{ST}\), conventional TADF materials require electron-rich donors (D) and electron-deficient acceptor (A) fragments that reduce the overlap between the lowest unoccupied molecular orbitals (LUMOs) and the highest occupied molecular orbitals (HOMOs). This strategy has been validated numerous times and can be used to achieve efficient TADF characteristics. A variety of high-performance OLEDs designed using this concept have been manufactured, with external quantum efficiencies (EQEs) of over 30%\cite{9-14}. However, when this strategy is used, structural relaxation occurs in the excited state, and OLEDs exhibit large Stokes shifts and broad emission spectra, which directly impact color purity and device performance.

Instead of conventional D-A conjugated emitters, Hatakeyama et al. reported TADF emitters (**DABNA-1 Scheme 1**) that used a new type of multi-resonance thermally activated delayed fluorescence (MR-TADF) \cite{15-17}. In the compound, due to the complementary resonance effect of
the para-position boron and nitrogen atoms, the electron density between HOMO and LUMO is significantly separated. Because of the rigid molecular framework, a small stroke shift and narrow emission peak were observed, with an FWHM of only 28 nm. However, despite the high EQE ($\text{EQE}_{\text{max}} = 20.2\%$) and high color purity of MR-TADF emitters, their synthesis requires lithiation by $\text{tert}$-BuLi to introduce a boron atom in the first step, making this synthesis extremely hazardous.

In this paper, we report a relatively secure synthesis of the MR effects induced by B-N-containing core-structure molecules ($\text{DMAc-BN}$ and $\text{PXZ-BN}$). We used a one-pot borylation method to simplify the synthesis of $\text{DMAc-BN}$ and $\text{PXZ-BN}$. Initial lithiation is still required for borylation, but $\text{tert}$-BuLi is not used. Additionally, the starting materials are not limited to aromatic fluorides (Ar-F) and carbazole-based materials [18-20], which is a critical advantage that would expand the material science and industrial applications of MR-TADF (Scheme 1). $\text{DMAc-BN}$ and $\text{PXZ-BN}$ show pure green emission, with small FWHMs (33 nm and 38 nm, respectively) and high photoluminescence quantum yields (PLQYs) (88% and 90%, respectively). In addition, the OLED devices that used the emitters had high EQEs: 20.3% for $\text{DMAc-BN}$ and 23.3% for $\text{PXZ-BN}$.

**Results and Discussion:**

The molecular design is illustrated in Scheme 1. Unlike previously reported $\text{DABNA-1}$, $\text{DMAc-BN}$ and $\text{PXZ-BN}$[21-23] are inserted either an $\text{sp}^3$ hybridized carbon or oxygen atom; this inserted atom bridges the molecular skeleton. In contrast, the extension of the frontier molecular orbital to the added phenyl units significantly affects the corresponding photophysical properties. In addition, the presence of non-conjugated $\text{sp}^3$ bonds induces helical molecular structure, and expects to reduce the aggregation-induced quenching, which can ultimately lead to higher EQEs.
The compounds **DMAc-BN** and **PXZ-BN** were synthesized in two steps. Under the conditions of Pd(0) as the catalyst and sodium *tert*-butoxide as the base, 9,9-dimethyl-9,10-dihydroacridine and phenoxazine reacted with the commercially available starting material 1,2,3-tribromobenzene through a Buchwald-Hartwig coupling reaction at 110ºC to produce an intermediate **S1** yield of 30% and **S2** yield of 40% (**Scheme S1**). Through a lithium-bromide exchange reaction with *n*-BuLi to promote the electrophilic capture of boron tribromide, boron atom was introduced into the reactor. In addition, intramolecular borylation occurred in the presence of diisopropylethylamine to produce a 38% yield of **DMAc-BN** and 41% yield of **PXZ-BN**. **DMAc-BN** and **PXZ-BN** were characterized by ¹H NMR, ¹³C NMR, and ¹¹B NMR spectroscopy; mass spectrometry; and elemental analysis, and purified by temperature-gradient vacuum sublimation.

The helical structures of **DMAc-BN** and **PXZ-BN** were determined by X-ray crystallography (**Figure 1**). The single bonds of C–B and C–N can be confirmed from the bond length, such as C–B bonds were 1.508-1.538 Å in length and C–N bonds were 1.400-1.432 Å in length. The C–O bonds were 1.378-1.386 Å in length for **PXZ-BN**, and the C–C bonds were 1.515-1.540 Å in length for **DMAc-BN**. Because of the longer C–B bonds than C–N bonds, the dihedral angles of the nitrogen-connected phenyl rings (A–B: 54.72°, A–B’: 56.44°) are larger than the dihedral angles of the boron-connected phenyl rings (C–C’: 32.57°) for **DMAc-BN**. Similar phenomenon was found for **PXZ-BN**; The dihedral angles of the nitrogen-connected phenyl rings (A–B: 39.75°, A–B’: 46.83°) are larger than the dihedral angles of the boron-connected phenyl rings (C–C’: 35.83°).

MR-dominated frontier orbital distributions were clearly confirmed for **DMAc-BN** and **PXZ-BN** (**Figure 2**), as computed by density functional theory (DFT) calculations. The HOMOs and LUMOs of **DMAc-BN** and **PXZ-BN** spread over the entire skeleton, thereby extending the π-
skeleton, despite their distorted structures. Because of the MR effects, the HOMOs and LUMOs were localized on different atoms, except for the phenyl ring connected to oxygen on the opposition of boron (for **PXZ-BN**) and the phenyl ring connected to carbon on the opposition of boron (for **DMAc-BN**). This can be attributed to the non-conjugated structure caused by the sp³-hybridized carbons of the acridan subunits and lone pairs of oxygen. The stronger electron-donating capacity of the oxygen atom lowers the HOMO and LUMO energy levels and simultaneously narrows the HOMO–LUMO energy gap. The computed HOMO and LUMO energy levels for **DMAc-BN** and **PXZ-BN** support this assumption (**Figure 2**).

The photophysical properties of the thin-film forms of **DMAc-BN** and **PXZ-BN** (3 wt% doping in 3,3-di(9H-carbazol-9-yl)-1,1-biphenyl (**mCBP**)) are summarized in **Table 1**. A strong absorption band can be observed at 460 nm for **DMAc-BN** and 475 nm for **PXZ-BN** from corresponding ultraviolet (UV)-visible absorption spectrum (**Figure 3**). Narrow green emission peak at 484 nm for **DMAc-BN** and 502 nm for **PXZ-BN** can be observed from fluorescence spectrum at 300 K (**Figure 3**). The Stokes shift/FWHM values were significantly small: 24/33 nm for **DMAc-BN** and 27/38 nm for **PXZ-BN**, suggesting that vibrionic coupling during the transition from S₁ to S₀ was minimized by the non-bonding HOMO and LUMO. Their TADF properties can be proofed from the transient photoluminescence, which showed distinct short-lived prompt fluorescence and long-lived delayed fluorescent properties. Short prompt fluorescence lifetimes (τₚפג) of 6.2 and 8.2 ns were observed for **DMAc-BN** and **PXZ-BN**, respectively. Long delayed fluorescence lifetimes (τₜדוג) of 32.9 and 90.7 μs were observed for **DMAc-BN** and **PXZ-BN**, respectively (**Table 1**). Also, we measured PLQYs of **DMAc-BN**, **PXZ-BN** and **DABNA-1** doped **mCBP** films in different doping concentration. The suppression of aggregation-induced quenching
can be confirmed by the doping concentration dependent PLQYs (Figure S6). The PLQYs of DABNA-1-doped films were sharply decreased with increasing of doping concentration, but the PLQYs of DMAc-BN and PXZ-BN-doped films were gradually decreased compared with that of DABNA-1. Note that the PLQYs of DMAc-BN and PXZ-BN-doped films were observed to be apparently higher than that of DABNA-1 at the higher concentration of 10% and 20% most likely due to the helical molecular structure induced by the bridged arylamine units.

To evaluate the device performance of DMAc-BN and PXZ-BN as emitters, we measured the films of emitters doped in mCBP. With respect to solution states, DMAc-BN and PXZ-BN showed similar but broadened emission peaks when doped with mCBP at 3 wt%. DMAc-BN:mCBP- and PXZ-BN:mCBP-doped films produced high PLQY values of 88% for DMAc-BN and 90% for PXZ-BN. These high PLQY values are beneficial to OLED devices. Thus, we fabricated and estimated OLED devices involving DMAc-BN and PXZ-BN as MR-TADF emitters, with the following device organization: [ITO/triphenylamine-containing polymer: 4-isopropyl-4’-methyldiphenyl-iodonium tetrakis(pentafluorophenyl)borate (PPBI) (20 nm) / di-[4-(N,N-ditolyl-amino)-phenyl] cyclohexane (TAPC) (15 nm) / mCBP (5 nm) / 3 wt% guest-doped mCBP (20 nm) / (9-phenyl-9H- carbazole-3,6-diyl)bis(diphenylphosphine oxide) (PO9) [25] (10 nm) / 3,3’’,5,5’-tetra(3-pyridyl)-1,1’;3’,1’’’- terphenyl (B3PyPB) [26] (40 nm) / LiF (0.5 nm) /Al (100 nm)]. mCBP was inserted between TAPC and emission layer to avoid the formation of the electromer of TAPC [27] at high current density. Energy diagrams for OLEDs constructed with either DMAc-BN or PXZ-BN emitters are illustrated in Figure S1. The devices using DMAc-BN and PXZ-BN emitters exhibited green emission at 503 and 516 nm, with FWHMs of 49 and 47 nm and CIE coordinates of (0.18, 0.60) and (0.22, 0.67), respectively (Figure 4). Notably, the two devices had high maximum EQEs of 20.3% and 23.3%, respectively; the PXZ-BN device had a
slightly higher EQE because its PLQY (90%) was higher than that of the DMAc-BN device (88%). Although both DMAc-BN and PXZ-BN have long $\tau_{DF}$s of 30–90 $\mu$s, however, these emitters showed much smaller efficiency roll-off than that of DABNA-1 ($\tau_{DF} = 93.7$ $\mu$s)\cite{15}. It is well-known that the final EQE is determined by the four factors: (i) PLQY, (ii) exciton formation ratio, (iii) outcoupling factor, and (iv) carrier balance. Here, the former three factors, (i)–(iii) are almost similar among DMAc-BN, PXZ-BN, and DABNA-1. Therefore, it can be considered that the suppressed efficiency roll-off was caused by improved carrier balance in different devices. In order to validate this hypothesis, we fabricated three types of devices, Device A–C with DMAc-BN emitter, where we tried to investigate the effects of mCBP and PO9 layers toward the carrier balance factor (Figure S7-S9). Introduction of mCBP in Device B and PO9 in Device C apparently reduced the current density compared with that in Device A without using these two layers (Figure S9). In addition, the much reduced current density was observed when PO9 was used compared with that of mCBP. While, the introduction of PO9 significantly contributed to increase the maximum EQE up to 5% (Device A vs C in Figure S8). Therefore, it can be concluded that PO9 reduced the electron carriers to improve the carrier balance factor contributing to the higher EQEs. Among newly developed two emitters, DMAc-BN exhibited smaller efficiency roll-off compared with the device using PXZ-BN because DMAc-BN has a shorter $\tau_{DF}$ (32.9 $\mu$s) compared to that of PXZ-BN ($\tau_{DF} = 90.7$ $\mu$s).

Conclusion:

In summary, we developed a simplified process for synthesizing novel carbon- and oxygen-bridged MR-TADF emitters (DMAc-BN, PXZ-BN) using non-hazardous $n$-BuLi. Our newly developed MR-TADF emitters exhibit narrow emission peaks at 50 nm and high quantum yields.
Also, aggregation-induced quenching can be suppressed by a helical molecular structure. In particular, the oxygen-bridged MR-TADF emitter **PXZ-BN** exhibits ultra-pure green emission with CIE coordinates of (0.22, 0.67) and an EQE of 23.3%. The emission colors of MR-TADF emitters can be simply tuned using carbon- or oxygen-bridged structures. Our method can aid the development of OLED displays having superior performance and an expanded color range.

Supporting Information

Supporting information is available.

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References:


23 During the preparation of this manuscript, the properties of DMAc-BN and PXZ-BN were independently reported by Jiang, Tao and co-workers (ref 24,25).


Scheme 1. (a) Molecular design strategy and chemical structures of DMAc-BN and PXZ-BN; (b) Synthesis of DMAc-BN and PXZ-BN.
Figure 1. ORTEP drawing of (a) DMAc-BN and (b) PXZ-BN obtained by X-ray crystallography.
Figure 2. Kohn-Sham molecular orbitals (HOMO and LUMO) and oscillator strength (f) of the $S_0$-$S_1$ transition for (a) DMAc-BN and (b) PXZ-BN calculated at the (TD)B3LYP/6-31G(d).
Figure 3. Photophysical properties of DMAc-BN and PXZ-BN. Absorption and fluorescence spectra (at 300 K) in 2-MeTHF (0.02 mM).
Figure 4. Characteristics of OLEDs fabricated with DMAc-BN (black), PXZ-BN (red) as emitters. (a) Normalized EL spectra. (b) EQE versus luminance. (c) PE versus luminance. (d) Current density and luminance versus driving voltage.
Table 1. Summary of photophysical properties.

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<th>Emitter</th>
<th>$\lambda_{\text{abs}}$</th>
<th>$\lambda_{\text{em}}$</th>
<th>$\lambda_{\text{ph}}$</th>
<th>FWHM</th>
<th>$\Delta E_{ST}$</th>
<th>$\Phi_{\text{PL}}$</th>
<th>$\tau_{\text{PF}}$</th>
<th>$\tau_{\text{DF}}$</th>
<th>$k_{\text{F}}$</th>
<th>$k_{\text{IC}}$</th>
<th>$k_{\text{ISC}}$</th>
<th>$k_{\text{RISC}}$</th>
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<tr>
<td>DMAc-BN</td>
<td>460</td>
<td>484</td>
<td>517</td>
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<td>88</td>
<td>6.2</td>
<td>32.9</td>
<td>13.1</td>
<td>17.8</td>
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<tr>
<td>PXZ-BN</td>
<td>475</td>
<td>502</td>
<td>540</td>
<td>38</td>
<td>0.17</td>
<td>90</td>
<td>8.2</td>
<td>90.7</td>
<td>8.2</td>
<td>9.1</td>
<td>3.1</td>
<td>0.9</td>
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*a* Maximum wavelength of UV absorption ($\lambda_{\text{abs}}$, 300 K), fluorescence ($\lambda_{\text{em}}$, 300 K), phosphorescence ($\lambda_{\text{ph}}$, 77 K), FWHM, and $S_1$-$T_1$ energy gap ($\Delta E_{ST}$) measured in 0.02 mM 2-MeTHF; *b* absolute PLQY ($\Phi_{\text{PL}}$), lifetimes calculated from the fluorescence decay, as well as rate constants for singlet radiative decay ($k_{\text{F}}$), non-radiative decay ($k_{\text{IC}}$), intersystem crossing ($k_{\text{ISC}}$), and reverse intersystem crossing ($k_{\text{RISC}}$) measured in 3 wt% doped films of emitters in mCBP.