Judicious Heteroatom Doping Produces High Performance Deep Blue Multiresonant Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes

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Abstract

We show how borylation of an acceptor-donor-acceptor (A-D-A) thermally activated delayed fluorescence (TADF) emitter, DIDOBNA-N, transforms the compound into a multi-resonant TADF (MR-TADF) emitter, MesB-DIDOBNA-N. DIDOBNA-N emits bright blue light ($\lambda_{PL} = 444$ nm, FWHM = 64 nm, $\Phi_{PL} = 81\%$, $\tau_d = 23$ $\mu$s, 1.5 wt% in TSPO1). The deep blue organic light-emitting diode (OLED) based on this compound shows a very high maximum external quantum efficiency ($\text{EQE}_{\text{max}}$) of 15.3% for a device with CIE$_y$ of 0.073. The MR-TADF emitter, MesB-DIDOBNA-N shows efficient and narrowband violet emission ($\lambda_{PL} = 402$ nm, FWHM = 19 nm, $\Phi_{PL} = 74.7\%$, $\tau_d = 133$ $\mu$s, 1.5 wt% in TSPO1). The OLED with MesB-DIDOBNA-N shows outstanding efficiency for a violet OLED at 9.3% and CIE$_y = 0.044$, which is the bluest EL reported for a MR-TADF OLED to date. Noteworthy are the CIE coordinates of (0.166, 0.045), which are very close to the Rec.2020 standard for blue (0.131,
0.046). The EQE\textsubscript{max} values were improved from 9.3% to 13.6% by increasing the concentration of the emitter in the host from 1.5 wt% to 5 wt%.

**Introduction**

Organic light-emitting diodes (OLEDs) are rapidly becoming the preferred display technology for a range of consumer electronics, from smartwatches, mobile phones and laptops to large screen televisions and displays used in the automotive industry.\textsuperscript{1} Ultra-high-definition displays must meet ever more stringent industry color standards, the most recent of which being Rec 2020., which are defined according to the Commission International de l’Éclairage (CIE) 1931 as (0.131, 0.046), (0.17, 0.797) and (0.708, 0.292) for blue, green, and red, respectively.\textsuperscript{2} Presently commercial vacuum-deposited OLEDs rely on phosphorescent complexes as emitter materials for the red and green sub-pixels and organic fluorescent materials for the blue sub-pixel. Significant research has been devoted to developing sustainable organic emitters that operate at comparable efficiencies to phosphorescent complexes and so can replace noble metal-based emitters for red and green OLEDs, and for blue OLEDs can lead to much higher efficient devices.\textsuperscript{3, 4} Organic compounds that exhibit thermally activated delayed fluorescence (TADF) have the most potential to act as replacement emitters in OLEDs as this class of material can harvest 100% of the electrically generated excitons and convert these to light emission.\textsuperscript{5, 6} Though TADF OLEDs now show comparable efficiencies to phosphorescent OLEDs for each of the red, green and blue devices, the typically employed donor-acceptor design results in emission from a charge-transfer (CT) state that is broad and unstructured, leading to poor chromaticity in the device. A subclass of TADF emitters, multi-resonant TADF (MR-TADF), however, shows great promise to address the issue of colour purity. MR-TADF emitters show very narrowband emission (full width half maximum, FWHM <40 nm),\textsuperscript{7} which is due to their very rigid polycyclic aromatic structure and their short range charge transfer (SRCT) excited state.\textsuperscript{8, 9} Their use in OLEDs would obviate the need for the use of color filters, leading to more energy efficient devices.

Since the first report of an MR-TADF compound from the group of Hatakeyama, over two hundred separate MR-TADF materials have been identified as hosts or emitters for OLEDs\textsuperscript{8, 10} with examples
of their use in high-efficiency blue, green and red OLEDs. Near UV and violet emitters for OLEDs are one class where there is a dearth of reports. Potential uses of short wavelength OLEDs are for sensing, photocopying, high density information storage and sterilization. Most of the reported efficient near UV OLEDs (<400 nm) using purely organic emitters to date contain materials that emit from a hybridized local and charge transfer excited state (HLCT) where triplets are harvested through a hot exciton channel mechanism involving reverse intersystem crossing (RISC) from higher lying triplet (Tn) states to S1. A recent report from Tang et al. demonstrated record setting performance values for an HLCT emitter-based near UV-OLED [λel = 396 nm, EQEmax = 10.79%, CIE (0.161, 0.031)]. There are also a small number of reports of near UV TADF and MR-TADF emitters and their use in OLEDs (Figure 1). The first report of a near UV-emitting MR-TADF compound is based on a boron, oxygen doped triangulene type structure reported by Hatakeyama, (λPL = 398 nm, FWHM = 33 nm, ΔESt = 0.18 eV, τD = 66 μs in 1wt% PMMA). This compound, also known as DOBNA, was initially identified as a potential host material due to its large band gap and high triplet energy. In the same report, phenyl derivatives of 2a were employed as host materials in phosphorescent OLEDs. Other reports have mostly documented the use of the DOBNA fragment as a weak acceptor in D-A type violet (λPL < 450 nm) TADF emitters. In 2015, Kwon et al. reported two deep blue emitters containing the DOBNA fragment as the acceptor. The OLED with the acridine donor-based emitter, TDBA-Ac presented an EQEmax of 21.5% and an excellent CIEy of 0.06. Choi et al. reported devices using related tercarbazole donor-based TB-3Cz and TB-P3Cz emitters that showed EQEmax of 9.9% and 6.1%, respectively, with corresponding CIEy values were 0.07 and 0.08, respectively for TB-3Cz and TB-P3Cz. A structurally related deep blue emitter containing a spiroacridan donor was reported by Kim et al., TDBA-SAF-based device achieved an EQEmax of 28.2% and a CIEy of 0.09. Recently, Choi et al. reported two deep blue solution-processible emitters containing extended carbazole donor units connected to DOBNA acceptor, BO-tCzPhICz and BO-tCzDICz. The solution-processed OLEDs showed EQEmax of 17.8% and 14.8%, respectively, and with CIEy of 0.07 and 0.062, respectively. Hong et al. reported two tri-spiral acridine donor based blue emitters, OBOtSAc and tBuOBOtSAc and their use in OLEDs. Both emitters showed efficient (ΦPL above 90%) deep blue
emission at 452 nm (FWHM = 50 nm) and 446 nm (FWHM = 48 nm), respectively for OBOtSAc and tBuOBOtSAc. Both devices achieved very high EQE\textsubscript{max} of 31.2% and 28.2% with CIE\textsubscript{y} of 0.092 and 0.061, respectively. Tong \textit{et al.} reported OLEDs using two deep blue emitters TDBA-PAS and TDBA-DPAC that can achieve EQE\textsubscript{max} of 22.4% and 24.6% at CIE\textsubscript{y} of 0.042 and 0.085, respectively.\textsuperscript{27} These two emitters each show two different conformers in the solid state and the authors contend that one conformer acts as a host for the other, evidenced by the improved performance in the device at high doping concentrations (≤ 50 wt%). Su \textit{et al.} reported a disk-like emitter based on a DOBNA acceptor decorated with three diphenylamine units, BO3N, which showed narrowband blue emission (λ\textsubscript{PL} = 424 nm, FWHM = 34 nm) with high Φ\textsubscript{PL} of 80% in toluene solution. The OLED with the emitter BO3N showed an EQE\textsubscript{max} of 10.4% and CIE\textsubscript{y} value of 0.08.\textsuperscript{28}

The DOBNA fragment has thus been shown to be a promising motif used in the construction of D-A type efficient deep blue TADF emitters. An alternative design for UV emitters was highlighted by Lee \textit{et al.} where they reported a fused indolocarbazole (tDIDCz) derivative that presented incredibly narrowband EL (FWHM = 14 nm, λ\textsubscript{EL} = 401 nm) with CIE coordinates of (0.164, 0.018) in the device.\textsuperscript{29} Though this compound shows the characteristic pattern of alternating increasing and decreasing electron density on adjacent atoms in the excited state, the ∆E\textsubscript{ST} of 0.44 eV is too large due to the very different natures of the S\textsubscript{1} and T\textsubscript{1} excited states resulting in the absence of delayed fluorescence.\textsuperscript{30} The absence of triplet harvesting in the OLED limited the EQE\textsubscript{max} to only 2.75% (Table S7).
Figure 1. (a) Chemical structures of previously reported violet MR-TADF emitters (b) α-3BNMes, (c) D-A TADF emitters with CIE$_y \leq$0.1 with DOBNA acceptor fragment, and (d) chemical structures of our molecules.

In 2020, we reported a near UV emitting linear ladder type B,N-doped heptacene (Figure 1), α-3BNOH ($\lambda_{PL} = 390$ nm, FWHM = 31 nm, $\Delta E_{ST} = 0.31$ eV in THF) that showed an emission resulting from TADF and TTA and narrow deep blue emission in solution.$^{31}$ By replacing the OH group attached to boron with mesityl units in α-3BNOH, a red shift of the emission was observed for α-3BNMes ($\lambda_{PL} = 443$ nm, FWHM = 30 nm, THF, $\Delta E_{ST} = 0.28$ eV, 1 wt% in PMMA).$^{32}$ Here, we report two emitters, one based on an A-D-A design containing two DOBNA acceptor groups that emits in the deep blue (DIDOBNA-N), and a second B,N,O doped heptacene MR-TADF compound that emits in the near UV (MesB-DIDOBNA-N). Both compounds exhibit weak TADF due to their moderately large $\Delta E_{ST}$ of 0.23 and 0.24 eV yet demonstrate high $\Phi_{PL}$ of 81 and 75% for DIDOBNA-N and MesB-DIDOBNA-N, respectively. The OLED with DIDOBNA-N showed deep blue emission at 444 nm (FWHM = 64 nm) corresponding to CIE coordinates of (0.152, 0.073) with an EQE$_{max}$ of 15.2%. The OLED with
**MesB-DIDOBNA-N** showed near UV emission with $\lambda_{EL}$ of 401 nm, FWHM = 22 nm, corresponding to CIE coordinates of (0.165, 0.044). By increasing the doping concentration of **MesB-DIDOBNA-N** in the emitting layer of the device, from 1.5 wt% to 3 wt% and 5 wt%, the EQE$_{max}$ increased from 9.3%, 11.3% and 13.6% respectively. Only minor variances were observed in the emission maxima and CIE$_y$ value with increasing doping concentration. The EQE$_{max}$ value of the 5 wt% doped device represents the most efficient device among those employing purely organic violet emitters.\textsuperscript{10,11}

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**Results and Discussion**

**MesB-DIDOBNA-N** was obtained in three steps from compound 1 (Figure 2). DOBNA-Br, a key intermediate, was obtained through a sequence of S$_N$Ar and electrophilic borylation in good yield; the borylation reaction proceeded in 73% yield. DIDOBNA-N was obtained in 57% yield following a Buchwald-Hartwig cross-coupling reaction of two equivalents of DOBNA-Br with 2,4-dimethylaniline. DIDOBNA-N was then subjected to electrophilic borylation with BBr$_3$ and quenching with Mes-MgBr to afford **MesB-DIDOBNA-N** in 74% yield. The identity and purity of the synthesized molecules were established from a combination of $^1$H and $^{13}$C NMR spectroscopy, high-resolution mass spectrometry (HRMS), elemental analysis (EA), and gel permeation chromatography (GPC) (Figures S1-S15).
Single crystals of **DOBNA-Br** were obtained directly from the reaction mixture. **DIDOBNA-N** crystals were obtained following temperature-gradient sublimation, and **MesB-DIDOBNA-N** were obtained by slow diffusion of hexane into saturated solution of the emitter in THF. Their structures are shown in Figure 2b-d. No intermolecular hydrogen bonding or π-π stacking interactions were observed for **DIDOBNA-N** and **MesB-DIDOBNA-N**. In **MesB-DIDOBNA-N**, the B-C$_{Mes}$ bond is longer [1.587(3) Å] than the B-C bonds within the DOBNA fragment [1.536(3) and 1.540(3) Å], a structural feature previously observed in other compounds containing a mesitylated borane.\(^{33}\) This emitter has a planar structure and the two aryl moieties attached to the B and N positioned are oriented approximately orthogonal to the acene core.

![Figure 3. a) HOMO and LUMO electron density distribution and orbital energies of DIDOBNA-N and MesB-DIDOBNA-N calculated at PBE0/6-31G(d,p) in the gas phase, isovalue = 0.02; b) Difference density plots and energies for the lowest two lying singlet and triplet excited states for DIDOBNA-N and MesB-DIDOBNA-N calculated at SCS-CC2/cc-pVDZ in the gas phase (isovalue = 0.001). Blue color represents an area of decreased electron density, and yellow represents an increased electron density between the ground and excited states. \(f\) denotes the oscillator strength for the transition to the excited singlet state.](image)
We then undertook a computational study to understand the ground and excited state properties of MesB-DIDOBNA-N as well as the A-D-A system DIDOBNA-N (Figure 3). Ground state calculations were carried out using Density Functional Theory (DFT) at the PBE0/6-31G(d,p) level in the gas phase. The DFT calculations predict a 0.12 eV increase in the band gap from DIDOBNA-N to MesB-DIDOBNA-N, despite the apparent increase in conjugation length. Both DIDOBNA-N and MesB-DIDOBNA-N display similar electron density distribution patterns for their LUMOs, with a pattern that is reminiscent of the DOBNA moiety (Figure S16). However, DIDOBNA-N and MesB-DIDOBNA-N show distinct electron density distribution patterns for their HOMOs. The electron density of the HOMO in DIDOBNA-N is reminiscent of triphenylamine, a good electron donor, while the electron density of the HOMO in MesB-DIDOBNA-N is localized on the DOBNA units, similar to the DOBNA core, and with a nodal plane passing through the central nitrogen and boron atoms of the molecule. Excited state calculations were performed using wavefunction based methods using the spin-component scaling second-order approximate coupled-cluster (SCS-CC2) in tandem with the cc-pVDZ basis set, which we have previously shown to be a sufficient level of theory to accurately predict $\Delta E_{ST}$ in MR-TADF emitters. The $S_1$ energy of DIDOBNA-N of 3.67 eV is slightly higher than that of MesB-DIDOBNA-N at 3.63 eV. Despite their similar $S_1$ energies, the oscillator strengths ($f$) for the $S_0$-$S_1$ transition are starkly different at 0.63 and 0.05 for DIDOBNA-N and MesB-DIDOBNA-N, respectively. The much-attenuated $f$ in MesB-DIDOBNA-N is likely the result of the higher symmetry of this compound (Figure S17). Notably, a similar change in the properties of the singlet excited state was predicted for DABNA-1 compared to its more symmetric fused derivative TABNA. Identical $T_1$ energies of 3.47 eV were predicted for DIDOBNA-N and MesB-DIDOBNA-N, resulting in $\Delta E_{ST}$ of 0.20 eV and 0.16 eV, respectively. An intermediate triplet state was predicted to exist in both compounds, which is acknowledged to facilitate RISC via spin-vibronic coupling in D-A TADF emitters. Difference density plots of the $S_1$, $S_2$, $T_1$ and $T_2$ states are shown in Figure 2b. For MesB-DIDOBNA-N each excited state possesses the typical alternating pattern of increasing and decreasing electron density of MR-TADF compounds that is characteristic of an excited state possessing SRCT character. The magnitude of the CT character of the excited state was quantified using two separate metrics: (1) the distance of charge transfer (D$_{CT}$) and (2) the amount of charge transferred (q$_{CT}$). These two metrics
reveal that there is a greater CT character in the excited states of **DIDOBNA-N** compared to that of **MesB-DIDOBNA-N** (Tables S1-3), pointing towards a more distinct long-range charge transfer (LRCT) character for the former compound; however, the magnitude of the CT character of **DIDOBNA-N** is still modest compared to conventional D-A TADF emitters, with $D_{CT}$ reported to be 1.1 Å here while typical D-A TADF emitters show $D_{CT}$ of $>1.6$ Å.\(^{39}\) Notably, the orbital types for the $T_2$ states of both compounds are different from those of $S_1$ and so spin-orbit coupling is expected to be non-negligible.

The electrochemical properties of both emitters were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in deaerated DCM with 0.1 M [nBu$_4$N]PF$_6$ as the supporting electrolyte and Fc$^+$/Fc as the internal reference ($0.46$ V vs SCE).\(^{40}\) Scan rate = 50 mV s$^{-1}$. (b) Solution-state absorption and steady-state emission spectra at 300 K measured in THF. $\lambda_{exc} = 365$ nm.

Figure 4. (a) Cyclic and differential pulse voltammograms measured in degassed DCM with 0.1 M [nBu$_4$N]PF$_6$ as the supporting electrolyte and Fc$^+$/Fc as the internal reference (0.46 V vs SCE).\(^{40}\) Scan rate = 50 mV s$^{-1}$. (b) Solution-state absorption and steady-state emission spectra at 300 K measured in THF. $\lambda_{exc} = 365$ nm.
MesB-DIDOBNA-N, which correspond to respective LUMO levels of -2.40 eV and -2.24 eV. The DFT calculations corroborate the trend in LUMO levels. The LUMO energy level of DIDOBNA-N is similar to other reported D-A type deep blue emitters having a DOBNA fragment as the acceptor.\textsuperscript{22, 25, 41, 42}
Reductions for both emitters were broad, in the case of DIDOBNA-N a second reduction peak appeared at -2.10 V, which is likely due to the reduction of second DOBNA unit. The electrochemical band gap is calculated to be 3.08 eV and 3.49 eV, respectively for DIDOBNA-N and MesB-DIDOBNA-N. Moving from DIDOBNA-N to MesB-DIDOBNA-N, the addition of the B-Mes unit resulted in a destabilization of the LUMO by 0.16 eV and a stabilization of the HOMO by 0.25 eV. The increasing band gap from DIDOBNA-N to MesB-DIDOBNA-N is consistent with the trend predicted by DFT.

Table 1. Photophysical properties of DIDOBNA-N and MesB-DIDOBNA-N.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>$\lambda_{\text{abs}}$ / nm</th>
<th>$\lambda_{\text{em}}$ / nm</th>
<th>FW HM / nm</th>
<th>$E_{\text{ex}}$ / eV</th>
<th>$E_{\text{em}}$ / eV</th>
<th>$\Delta E_{\text{ex}}$ / eV</th>
<th>$\Phi_{\text{PL}}$ / %</th>
<th>$\tau_{\text{prompt PL}}$ / ns</th>
<th>$\tau_{\text{delayed PL}}$ / µs</th>
<th>$k_{\text{ISC}}$ / s$^{-1}$</th>
<th>$k_{\text{RISC}}$ / s$^{-1}$</th>
<th>$k_{\text{keff}}$ / s$^{-1}$</th>
<th>$k_{\text{kr}}$ / s$^{-1}$</th>
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<td>DIDOBNA-N</td>
<td>Sol. a</td>
<td>384 (66)</td>
<td>43</td>
<td>3.08 g</td>
<td>2.86 g</td>
<td>0.22</td>
<td>75a</td>
<td>3.07</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>film b</td>
<td>-</td>
<td>444</td>
<td>64</td>
<td>3.12</td>
<td>2.89</td>
<td>0.23</td>
<td>80.8</td>
<td>6.83</td>
<td>13.7</td>
<td>1.55 × 10$^7$</td>
<td>1.19 × 10$^8$</td>
<td>2.77 × 10$^7$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MesB-DIDOBNA-N</td>
<td>Sol. c</td>
<td>388 (26)</td>
<td>399</td>
<td>3.17 g</td>
<td>2.93 g</td>
<td>0.24</td>
<td>33a</td>
<td>2.63</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>film b</td>
<td>-</td>
<td>402</td>
<td>19</td>
<td>3.18</td>
<td>2.94</td>
<td>0.24</td>
<td>74.7</td>
<td>5.09</td>
<td>95.9</td>
<td>6.18 × 10$^7$</td>
<td>9.81 × 10$^3$</td>
<td>1.47 × 10$^5$</td>
<td>4.97 × 10$^7$</td>
<td></td>
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</table>

*In THF solutions (10$^{-6}$ M).\textsuperscript{2}Measured in evaporated thin films consisting of 1.5 wt% emitter in TSPO1 host under vacuum. $\lambda_{\text{exc}}$ = 280 nm.\textsuperscript{3}Lowest energy absorbance peak, Absorptivity (ε) in parenthesis (/10$^4$ M$^{-1}$ cm$^{-1}$).\textsuperscript{4}Steady-state emission maximum at 300 K. $\lambda_{\text{exc}}$ = 365 nm.\textsuperscript{5}Full width at half maximum of emission peak. $\lambda_{\text{em}}$ and $\lambda_{\text{ex}}$ energies were obtained from the onsets of the respective prompt fluorescence (delay: 1 ns; gate time: 100 ns) and phosphorescence spectra (delay: 1 ms; gate time: 9 ms) at 77 K. $\lambda_{\text{exc}}$ = 343 nm.\textsuperscript{6}Solution samples for $\Delta E_{\text{ST}}$ measurements were prepared in 2-MeTHF (10$^{-6}$ M).\textsuperscript{7}$\Delta E_{\text{ST}} = E(S_0) - E(T_1)$.\textsuperscript{8}Relative $\Phi_{\text{PL}}$ in solutions were measured by a comparative method using quinine sulfate as a standard ($\Phi_{\text{PL}}$ = 54.6% in 1 N H$_2$SO$_4$).\textsuperscript{9}while absolute $\Phi_{\text{PL}}$ of the thin films were measured using an integrating sphere.\textsuperscript{10}Prompt and delayed lifetimes were obtained by TCSPC and MCS, respectively. $\lambda_{\text{em}}$ = 378 nm.\textsuperscript{11}Inter-system and reverse intersystem crossing rates were calculated using steady-state approximation method as described in literature.\textsuperscript{12}

The photophysical properties were studied by measurements of absorption and photoluminescence (PL), PL quantum yield ($\Phi_{\text{PL}}$) and time-resolved PL in 10$^{-6}$ M THF. Figure 4b shows the absorption and PL properties of DIDOBNA-N and MesB-DIDOBNA-N and these together with other photophysical data are collated in Table 1. There is excellent agreement between the experimental and simulated
absorption spectra (Figure S17). Intense absorption bands were noted for DIDOBNA-N and MesB-DIDOBNA-N around 250 nm, reflected in the molar absorptivity ($\varepsilon$) values of $92 \times 10^4$ M$^{-1}$ cm$^{-1}$ and $50 \times 10^4$ M$^{-1}$ cm$^{-1}$, respectively. An intense band at 340 nm ($\varepsilon = 79 \times 10^4$ M$^{-1}$ cm$^{-1}$) was observed for MesB-DIDOBNA-N, which has a similar alternating increasing/decreasing electron density pattern to S$_1$ that is indicative of a SRCT state (Figure S17). For DIDOBNA-N there is an intense band at 384 nm ($\varepsilon = 66 \times 10^4$ M$^{-1}$ cm$^{-1}$), a feature also observed in the absorption spectra of other D-A systems containing DOBNA acceptor fragment.\textsuperscript{22, 24, 41} The lowest energy absorption band in DIDOBNA-N is blue-shifted compared to that in MesB-DIDOBNA-N, which aligns with the predicted SCS-CC2 calculations (vide supra). The intensity at the lowest energy absorption band is higher for DIDOBNA-N than MesB-DIDOBNA-N. This is qualitatively consistent with the predicted higher oscillator strength of S$_1$ and S$_2$ of DIDOBNA-N compared to those of MesB-DIDOBNA-N, where the oscillator strength is weak ($<0.1$) for S$_1$.

The PL spectra in solution state at RT reveal deep-blue and near UV emission (Figure 4b) for DIDOBNA-N and MesB-DIDOBNA-N, respectively. DIDOBNA-N shows an unstructured emission peaking at $\lambda_{PL} = 426$ nm and a moderate FWHM of 43 nm (0.29 eV). The emission from this compound is among the bluest D-A compounds containing a DOBNA acceptor moiety.\textsuperscript{22, 23, 24, 25, 26, 27, 28, 45} MesB-DIDOBNA-N emits in the violet at $\lambda_{PL} = 399$ nm, with a very small FWHM of 23 nm (0.17 eV); and a low energy shoulder at 417 nm. This emission is narrower than that reported for DOBNA ($\lambda_{PL} = 398$ nm, FWHM = 34 nm in DCM, Figure 1).\textsuperscript{19} The Stokes shifts of DIDOBNA-N and MesB-DIDOBNA-N are 42 nm and 11 nm, respectively, reflecting the small reorganization energies in the excited states of these two compounds, especially for the MR-TADF emitter. The singlet-triplet energy gaps ($\Delta E_{ST}$), determined from the difference in energy of the onsets of the prompt fluorescence and phosphorescence spectra at 77 K in 2Me-THF glass (Figure S18) are 0.22 eV and 0.24 eV, respectively, for DIDOBNA-N and MesB-DIDOBNA-N, values in line with the predicted ones (Figure 3b). DIDOBNA-N and MesB-DIDOBNA-N possess similar triplet energy levels of 2.86 eV and 2.93 eV, respectively. The $\Phi_{PL}$ in degassed dilute THF solutions are 75% and 33% for DIDOBNA-N and MesB-DIDOBNA-N,
respectively. The \( \Phi_{\text{PL}} \) values decrease to 61% and 26%, respectively, upon exposure to air. Both emitters showed a small decrease in \( \Phi_{\text{PL}} \) upon exposure to air that can be attributed to singlet quenching\(^{46}\) as there was no delayed emission detected in the transient PL measurements (Figure S19).

Figure 5. Co-evaporated thin film of 1.5 wt% emitter in TSPO1. a) Steady-state PL spectra at room temperature under vacuum, \( \lambda_{\text{exc}}(\text{DIDOBNA-N}) = 385 \text{ nm}, \lambda_{\text{exc}}(\text{MesB-DIDOBNA-N}) = 344 \text{ nm} \); b) Time-resolved PL decay at RT and 77 K of DIDOBNA-N, \( \lambda_{\text{exc}} = 379 \text{ nm} \); c) Time-resolved PL decay at RT and 77 K of MesB-DIDOBNA-N, \( \lambda_{\text{exc}} = 379 \text{ nm} \); d) Decay of emission signal at RT plotted together with IRF signal.

To avoid possible intermolecular interactions or concentration-induced quenching, both molecules were doped into high triplet energy (\( E_T \)) hosts at a low doping concentration. Three high triplet energy widely used phosphine-oxide-based hosts, TSPO1, DPEPO, and PPT, were compared, among which TSPO1 showed the best performance in terms of \( \Phi_{\text{PL}} \) (Table S6) and device EQE that are due to its high \( E_T \) (3.36 eV) and tendency to better bipolar carrier transport than the other host materials.\(^{47}\) The \( \Phi_{\text{PL}} \) values for 1.5 wt% doped TSPO1 films containing DIDOBNA-N and MesB-DIDOBNA-N are 81% and 75%, respectively (Table S6). Figure 5a shows the steady state photophysical properties of evaporated thin
films with a doping concentration of 1.5 wt% in TSPO1. **DIDOBNA-N** shows a deep blue emission at 444 nm with FWHM of 64 nm (0.38 eV), which is red-shifted and broader than that in dilute THF solution \([\lambda_{pl} = 426 \text{ nm} \text{ and } \text{FWHM} = 43 \text{ nm} (0.29 \text{ eV})]\). The red-shift and spectral broadening of the emission are attributed to the polarization effect of the host matrix on the different excited state properties as CT-type TADF emitters are sensitive to the host polarity.\(^{48,49}\) By contrast, **MesB-DIDOBNA-N** showed negligible changes in its steady-state PL spectrum in the thin film \([\lambda_{pl} = 402 \text{ nm} \text{ and } \text{FWHM} = 19 \text{ nm} (0.15 \text{ eV})]\) compared to that in solution \([\lambda_{pl} = 399 \text{ nm} \text{ and } \text{FWHM} = 23 \text{ nm} (0.17 \text{ eV})]\). The observed narrowband emission spectra of **DIDOBNA-N** and **MesB-DIDOBNA-N** translate to deep blue and violet emission at Commission Internationale de l’Éclairage (CIE) coordinates of (0.150, 0.063), and (0.165, 0.022), respectively, which match well the blue CIE coordinates of BT.709 and BT.2020 standards for HDTV and UHDTV, i.e., (0.150, 0.06), and (0.131, 0.046), respectively.

The \(S_1/T_1\) energies for **DIDOBNA-N** and **MesB-DIDOBNA-N** in 1.5 wt% doped TSPO1 films were determined from the onsets of the respective prompt fluorescence and phosphorescence spectra at 77 K, which are 3.12 eV/2.89 eV and 3.18 eV/2.94 eV, respectively. The corresponding \(\Delta E_{ST}\) values are 0.23 eV and 0.24 eV, respectively, which are consistent with those determined in 2-MeTHF.

We next acquired temperature-dependent time-resolved PL decays of the TSPO1 doped films using multi-channel scaling (MCS). The decays, which are presented in Figures 5b-c, show both prompt (PF) and delayed fluorescence (DF) components for both emitters. Whereas the prompt component exhibited negligible temperature dependence, the intensity of the DF decreased significantly with decreasing temperature, behavior that is characteristic of TADF compounds. The lifetimes of both PF and DF were estimated by fitting the decays with a multi-exponential decay fitting (for details of the fitting of the decays see page S4, ESI). The prompt, \(\tau_p\), and delayed, \(\tau_d\), lifetimes are \(\tau_p/\tau_d = 6.83 \text{ ns}/13.72 \mu\text{s}\) and 5.09 ns/95.91 \(\mu\text{s}\) for **DIDOBNA-N** and **MesB-DIDOBNA-N**, respectively. Both emitters exhibited high radiative rates in the order of \(10^8 \text{ s}^{-1}\) (Table 1); however, RISC rates are slow at \(3.14 \times 10^4 \text{ s}^{-1}\) and \(9.81 \times 10^3 \text{ s}^{-1}\), respectively for **DIDOBNA-N** and **MesB-DIDOBNA-N**; deep blue D-A DOBNA-containing TADF compounds have been reported to show \(k\text{RISC}\) on average on the order of \(10^6 \text{ s}^{-1}\).\(^\text{22,23,24,25}\) More generally, deep blue MR-TADF compounds rarely show \(k\text{RISC}\) above \(10^4 \text{ s}^{-1}\).\(^\text{50,51,52}\) The
$k_{\text{RISC}}$ for DOBNA was reported to be $1.6 \times 10^4$ s$^{-1}$ in 1 wt% PMMA,\textsuperscript{20} which is just slightly faster than that of MesB-DIDOBNA-N ($9.81 \times 10^3$ s$^{-1}$).

Device performance

The potential of the emitters in deep-blue and violet electroluminescent (EL) devices was next assessed. To confine the excitons on the emitter, the high triplet energy material TSPO1 was selected as the host. Since TSPO1 has a dominant electron-transport character, the recombination zone inside the emission layer (EML) is believed to be located near the interface between the emission layer (EML) and the hole transport layer (HTL). To avoid exciton loss into the HTL, an exciton blocking layer of 10 nm thick CzSi [(9-(4-tert-butylphenyl)-3,6-bis(triphenylsilyl)-9H-carbazole, $E_T = 3.0$ eV)]\textsuperscript{53} was inserted between the EML and HTL. Furthermore, the doping concentration ($c_D$: 1.5 wt% - 5.0 wt%) of the emitter was carefully tuned to investigate its effects on device performance and color purity.

Figure 6. OLED device data for MesB-DIDOBNA-N and DIDOBNA-N as emitters. a) EL spectrum of both emitters at 5 V. b) and c) are images of operating devices of DIDOBNA-N and MesB-DIDOBNA-N, respectively under 5 V. d) EQE$_{\text{max}}$ comparison in terms of EL peak wavelength of present emitters to reported fluorescent (Fluo.), and D-A-TADF emitters in OLEDs. Source references for
the plotted data are given in Table S7. e) Dependence of external quantum efficiency (EQE) and power efficiency (PE) on the luminance. f) Current density-voltage-luminance (J–V–L) characteristics of the device.

Using either of the emitters, the optimized device structure was: indium tin oxide (ITO)/hexaazatriphenylenehexacarbonitrile (HAT-CN, 5 nm)/N,N’-di(1-naphthalyl)-N,N’-diphenyl-(1,1’-biphenyl)-4,4’-diamine (NPB, 40 nm)/tris(4-carbazoyl-9-ylphenyl)amine (TCTA, 10 nm)/CzSi (10 nm)/MesB-DIDOBNA-N or DIDOBNA-N or:TSPO1 (cD, 20 nm)/TSPO1 (10 nm)/1,3,5-tris(3-pyridyl-3-phenyl)benzene (TmPyPB, 20 nm)/LiF (0.8 nm)/Al (100 nm), where HAT-CN, NPB, TCTA, CzSi, TSPO1, TmPyPB, LiF are the hole injection (HIL), hole transport (HTL), electron blocking (EBL), exciton blocking, hole blocking (HBL), electron transport (ETL), and electron injection layers (EIL), respectively. The device structure and energy levels of each layer are illustrated in Figure S20.

Focusing first on the OLEDs with MesB-DIDOBNA-N, both device efficiency and color purity depend sensitively on the doping concentration (cD) of the emitter. To identify the optimum emitter doping level, devices were fabricated at different doping concentrations of MesB-DIDOBNA-N from 1.5 to 3.0 to 5.0 wt%. High cD devices presented lower turn-on voltage (Von, voltage at 1 cd m⁻²), higher brightness, higher maximum external quantum efficiency (EQE_max), and higher power efficiency (PE) as shown in Figure 6 and Table 2. At the lowest doping level of 1.5 wt%, the EL peak (λ_EL = 402, FWHM = 22 nm) was nearly identical to the λ_PL in dilute THF solution (λ_PL = 399 nm, FWHM = 23 nm). Figure 6a shows the EL spectrum of MesB-DIDOBNA-N, which is the bluest of all the MR-TADF OLEDs reported to date. In addition, the MesB-DIDOBNA-N devices exhibited the shortest λ_EL and narrowest FWHM among the reported purely organic molecule-based violet OLEDs. With increasing of cD, the λ_EL red-shifted slightly to 404 nm (3wt%) and 405 nm (5wt%) while the FWHM increased to 25 nm and 31 nm, respectively. The spectral broadening resulted mainly from the increase in intensity of the low energy shoulder peak at 430 nm. Despite these undesired spectral changes with increasing cD, devices showed extraordinary color purity, with CIE coordinates of (0.165, 0.044), (0.166, 0.045), and (0.166, 0.055) for the MesB-DIDOBNA-N OLEDs with cD of 1.5, 3, and 5wt%, respectively. Those values, especially that with cD of 3 wt%, are very close to the BT.2020 standard for the primary blue color of UHDTV [i.e., CIE coordinates of (0.131, 0.046)].
Considering the HOMO/LUMO levels of the emitter, **MesB-DIDOBNA-N** (5.73 eV/2.24 eV) and the host, TSPO1 (6.79 eV/2.50 eV), holes and electrons are mainly transported via the emitter and the host molecules, respectively. In other words, the injected holes are mostly trapped on the emitters, which then capture the mobile electrons hopping via the transporting sites of the TSPO1 host, i.e., the trap-assisted recombination mechanism. Therefore, at a low C_D of 1.5 wt%, it has a certain percentage of electrons that can migrate through the EML without being transferred to the emitters, which then leak into the TCTA layer and induce EL there. Indeed, EL at around 380 nm was observed in **MesB-DIDOBNA-N** device, which was attributed to the emission from TCTA. When the C_D is above 3 wt%, sufficient recombination is achieved, and the EL originates only from **MesB-DIDOBNA-N**. The EQE_{max} increased from 9.3 to 11.3 and 13.6% for the devices with emitter C_D of 1.5, 3.0 and 5.0 wt%, respectively (Figure 6e). The **MesB-DIDOBNA-N** OLED has the highest EQE_{max} among all the reported fluorescent and TADF emitters with \( \lambda_{EL} \) around 400 nm (Figure 6d and Table S7). It is noted that the maximum luminance \( (L_{max}) \) of the device is limited by the severe efficiency roll-off, which is attributed to a combination of carrier imbalance commonly observed in devices with low emitter doping in combination with high-energy band gap hosts and long-lived triplets that lead to an enhanced probability for bimolecular annihilation processes such as singlet-triplet annihilation, triplet-triplet annihilation processes, and triplet-polaron quenching.54, 55 Low \( L_{max} \) is endemic in deep blue TADF OLEDs with similar CIE{ subst } values, such as devices with tDIDCz (CIE{ subst } = 0.02) of 200 cd m\(^{-2}\) at 8 V,29 DCzBN1 (CIE{ subst } = 0.05) of 320 cd m\(^{-2}\) at 10 V,56 B-O-dpa (CIE{ subst } = 0.05) of 180 cd m\(^{-2}\) at 8 V,57 and tBuOBOTSAc (CIE{ subst } = 0.06) of 350 cd m\(^{-2}\) at 12 V,58 implying that factors other than the nature of the emitter need to be addressed in order to improve device performance, such as the stability of high triplet-energy host materials and the device structure.

The A-D-A compound **DIDOBNA-N** also presented a highly desirable set of photophysical properties in TSPO1. Using the same device structure as that of **MesDIDOBNA-N**, the OLED with **DIDOBNA-N** showed deep-blue unstructured EL (\( \lambda_{EL} = 429 \) nm, FWHM = 70 nm, CIE = 0.152, 0.073) at C_D of 1.5 wt% (Figure 6a), which corresponds well to the NTSC standard of (0.14, 0.08) for blue emission. Interestingly, The peak of the EL of **DIDOBNA-N** at 429 nm is close to the PL peak in dilute THF.
solutions (426 nm), although the EL spectrum is broader. The $V_{\text{on}}$ was 4.2 V, and the EQE$_{\text{max}}$ was high at 15.2%, which decreased to 3.8% at 100 cd m$^{-2}$. Like the MesB-DIDOBNA-N OLED, the DIDOBNA-N device is among the most efficient devices at this $\lambda_{\text{EL}}$ (Figure 6d and Table S7).\textsuperscript{10,11}

Table 2. Device performance of DIDOBNA-N and MesB-DIDOBNA-N.

<table>
<thead>
<tr>
<th>Emitter</th>
<th>cd / wt%</th>
<th>$V_{\text{on}}$ / V</th>
<th>$\lambda_{\text{EL}}$ / nm</th>
<th>FWHM / nm</th>
<th>CIE (x,y)</th>
<th>EQE$<em>{\text{max}}$ (EQE$\times$1000 cd m$^{-2}$) / PE$</em>{\text{max}}$ / % / lm W$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIDOBNA-N</td>
<td>1.5</td>
<td>4.2</td>
<td>429</td>
<td>70</td>
<td>(0.152, 0.073)</td>
<td>15.2 (3.8) / 6.46</td>
</tr>
<tr>
<td>MesB-DIDOBNA-N</td>
<td>1.5</td>
<td>4.5</td>
<td>402</td>
<td>22</td>
<td>(0.165, 0.044)</td>
<td>9.3 (-) / 1.14</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>4.5</td>
<td>404</td>
<td>25</td>
<td>(0.166, 0.045)</td>
<td>11.3 (-) / 1.78</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>4.2</td>
<td>405</td>
<td>31</td>
<td>(0.165, 0.055)</td>
<td>13.6 (-) / 3.08</td>
</tr>
</tbody>
</table>

Conclusions

Two new easy-to-access TADF emitters have been synthesised in good yields. The A-D-A emitter DIDOBNA-N showed efficient pure blue emission and TADF in 1.5 wt% TSPO1 films ($\lambda_{\text{PL}} = 444$ nm, FWHM = 64 nm, $\Phi_{\text{PL}} = 81\%$, $\tau_{\text{d}} = 23$ $\mu$s). The electroluminescence is blue-shifted ($\lambda_{\text{EL}} = 429$ nm, FWHM = 70 nm, CIE$_y = 0.073$), corresponding well to the NTSC standard of (0.14, 0.08). The OLED shows an excellent EQE$_{\text{max}}$ of 15.3%, which is the highest reported for a deep blue emitter with a $\lambda_{\text{EL}}<430$ nm.\textsuperscript{10,25} The MR-TADF emitter, MesB-DIDOBNA-N was obtained from DIDOBNA-N in one step by installing a bridging mesitylated borane unit. This compound represents a rare example of a non triangulene type $\pi$-extended violet MR-TADF emitter. The molecular design utilized two electronically distinct acceptor boron atoms in combination with mixed donor nitrogen, and oxygen atoms. This emitter shows narrowband pure violet emission in the 1.5 wt% TSPO1 film ($\lambda_{\text{PL}} = 402$ nm, FWHM = 19 nm, $\Phi_{\text{PL}} = 75\%$, $\tau_{\text{d}} = 133$ $\mu$s), which translated into record-setting near UV MR-TADF OLED EQE$_{\text{max}}$ of 9.3% ($\lambda_{\text{EL}} = 402$ nm, FWHM = 22 nm, CIE$_y = 0.044$). The EL from the MesB-DIDOBNA-N device is the bluest of all the MR-TADF OLEDs reported to date.\textsuperscript{10,11} Notably, the CIE$_y$ value of the
**MesB-DIDOBNA-N** device is very close to the Rec.2020 standard for blue of (0.131, 0.046). The EQE\textsubscript{max} value of the **MesB-DIDOBNA-N** device could be enhanced to 13.6% by increasing the doping concentration of the emitter to 5 wt%\textsuperscript{11}.

**Supporting Information**

\textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra, GCMS, HRMS and reverse phase and gel permeation (GPC) HPLC; supplementary computational data and coordinates; Crystallographic data (CIF). **DOBNA-Br** (CCDC 2171188); **DIDOBNA-N** (CCDC 2171190); **MesB-DIDOBNA-N** (CCDC 2171189). Additional photophysical and OLED data.

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**References**


TOC graphic
Transformation of a deep-blue acceptor-donor-acceptor TADF emitter, DIDOBNA-N, to a multiresonant TADF emitter, MesB-DIDOBNA-N is demonstrated. Efficient deep-blue OLEDs with EQE_max and CIE_2 ordinate of 15.3% and 0.073 with DIDOBNA-N and 9.3% and 0.044 with MesB-DIDOBNA-N illustrate the promise of the molecular design of these emitters.