Organic light-emitting diodes (OLEDs) play an important role in new-generation flat-panel displays and solid-state lighting. The internal quantum efficiency (IQE) of OLEDs employing a conventional fluorophore is up to 25% because triplet excitons, constituting 75% of the electrically generated excitons, do not contribute to the emission. The IQE can be increased to ≈100% using phosphorescent materials such as Ir and Pt complexes owing to the heavy-atom effect that accelerates the intersystem crossing (ISC). However, phosphorescent OLEDs present potential drawbacks such as the high cost of the heavy metals and the limited availability of pure blue phosphorescent materials. Therefore, even the newest OLED displays employ blue fluorophores together with triplet–triplet annihilation, for which the theoretical maximum IQE is only 62.5%. Recently, another promising pathway—thermally activated delayed fluorescence (TADF)—achieved an IQE of ≈100% without employing any precious heavy metals. In order to achieve the optimal performance in TADF-based OLEDs through efficient upconversion from the T1 state to the S1 state, a fluorophore with a small energy gap (ΔE ST ) between S1 and T1 is required. A common strategy for minimizing ΔE ST involves introducing donor and acceptor groups, which can separate the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) and reduce the exchange interaction between singly occupied molecular orbitals (SOMOs) in the excited states. However, such a strategy enhances the structural relaxation in the excited states and increases the Stokes shift, resulting in a broadening of the electroluminescence (EL) peaks, whose typical full-width at half-maximum (FWHM) is 70–100 nm. Since commercial OLED displays employ a color filter and/or an optical microcavity in order to satisfy the Commission Internationale de l’Eclairage (CIE) coordinate requirements defined by broadcasting standards, the broadening of the original EL peaks significantly reduces the external quantum efficiency (EQE) of the OLED displays. An improved approach to overcome these issues might involve the establishment of a new strategy to minimize ΔE ST of the fluorophores without broadening of the fluorescence peaks.

Here, we report a novel design of organic molecules that exhibit ultrapure blue fluorescence based on TADF (Figure 1b). The molecule shown in the figure is triphenylboron, possessing two nitrogen atoms, which combine neighboring phenyl groups to construct a rigid polycyclic aromatic framework. Since the nitrogen atom exhibits the opposite resonance effect of the boron atoms, para-substitution relative to it can enhance the resonance effect and can significantly separate the HOMO and LUMO without the need to introduce donor or acceptor groups. The calculated molecular orbitals of the parent molecule DABNA-1 are shown in Figure 2: the LUMOs are localized on the boron atom and at the ortho and para positions relative to it, whereas the HOMOs are localized on the nitrogen atoms and at the meta position relative to the boron atom.

Because of the rigid π-conjugated framework and the large oscillator strength of the S0–S1 transition (f = 0.205), OLEDs employing DABNA-1 exhibited an emission at 459 nm with an FWHM of 28 nm, CIE coordinates of (0.13, 0.09), and a high EQE of 13.5%. The introduction of substituents improved the oscillator strength (f = 0.415) without affecting the localization of MOs, as demonstrated by derivative DABNA-2 in Figure 2, which enabled us to fabricate a blue OLED exhibiting an emission at 467 nm with an FWHM of 28 nm, CIE coordinates of (0.12, 0.13), and an EQE of 20.2%.

Compound DABNA-1 was synthesized in two steps from a commercially available starting material, 1-bromo-2,3-dichlorobenzene, as shown in Scheme 1, left. In the presence of a catalytic amount of dichlorobis(di-tert-butylyphosphino)palladium(II) and a stoichiometric amount of sodium tert-butoxide, a cross-coupling reaction with diphenylamine smoothly took place at 80–120 °C to give intermediate 1 in 66% yield. A boron atom was introduced in one pot via a lithium–chloride exchange reaction with tert-butyllithium, electrophilic trapping with boron tribromide, and tandem electrophilic arené borylation in the presence of a stoichiometric amount of diisopropylethylamine to give DABNA-1 in 32% yield. According to the same strategy,
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DABNA-2 was synthesized in three steps from 1-bromo-2,3-dichlorobenzene (Scheme 1, right). A sequential cross-coupling with $N_1, N_1, N_3$-triphenylbenzene-1,3-diamine ($90^\circ$C) and $N_1$-(2,3-dichlorophenyl)-$N_1, N_3, N_3$-triphenylbenzene-1,3-diamine ($120^\circ$C) gave intermediate 2 in 71% yield, which was readily converted to DABNA-2 in 31% yield via the one-pot borylation reaction. Notably, the tandem electrophilic arene borylation took place at the para position relative to the diphenylamino group probably because of its electron-donating property and bulkiness. These processes were robust and scalable and thus enabled us to prepare 6.0 g of the target compounds.

The photophysical properties of the two compounds are listed in Table 1. The UV–visible absorption spectra measured in CH$_2$Cl$_2$ exhibit a strong absorption band corresponding to the HOMO–LUMO transition with maxima at 437 and 444 nm for DABNA-1 and DABNA-2, respectively. The 298 K fluorescence spectra of DABNA-1 and DABNA-2 exhibit strong and sharp emission bands at 462 and 470 nm. Notably, the Stokes shifts and FWHMs are very small, 25 and 33 nm for DABNA-1 and 26 and 34 nm for DABNA-2, respectively, because of their rigid π-conjugated framework. Similar emission spectra were observed in EtOH, suggesting negligible interaction between the boron atoms of these compounds and the oxygen atom of EtOH. Similar photophysical properties were observed for 1 wt%-doped films of DABNA-1 and DABNA-2 in 3,3′-bis(N-carbazolyl)-1,1′-biphenyl (mCBP), one of the more common host materials for blue emitters. Notably, high absolute PL quantum efficiencies ($\Phi = 0.84–0.90$) were observed for both compounds, not only in solution but also in the solid state. To estimate $\Delta E_{ST}$ value, we obtained the emission spectra of the solutions and films with various delay times at 77 K (see the Supporting Information for details); two independent emissions with different lifetimes were observed and assigned to fluorescence and phosphorescence, respectively. $\Delta E_{ST}$ values in the range of 0.14–0.18 eV were estimated from the emission maxima of each spectra. As shown in Table 2, the quantum yields ($\Phi_F$, $\Phi_{TADF}$) and lifetimes ($\tau_F$, $\tau_{TADF}$) of the fluorescence and TADF components were determined from the total $\Phi$ and
Photophysical data of DABNA-1 and DABNA-2.

Table 1. Photophysical data of DABNA-1 and DABNA-2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conditions</th>
<th>T [K]</th>
<th>λ_{abs}</th>
<th>log ε</th>
<th>λ_{em}</th>
<th>E_{FL}</th>
<th>FWHM</th>
<th>Φ</th>
<th>τ_F</th>
<th>τ_S</th>
<th>ΔE_{ST}</th>
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<tbody>
<tr>
<td>DABNA-1</td>
<td>2.0 × 10^{-3} wt in CH_{2}Cl_{2}</td>
<td>298</td>
<td>437</td>
<td>4.39</td>
<td>462</td>
<td>2.68</td>
<td>33</td>
<td>0.89</td>
<td>9.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Saturated in EtOH</td>
<td>298</td>
<td>–</td>
<td>–</td>
<td>458</td>
<td>2.71</td>
<td>36</td>
<td>0.84</td>
<td>11.1</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Saturated in EtOH</td>
<td>77</td>
<td>–</td>
<td>–</td>
<td>453</td>
<td>2.74</td>
<td>48</td>
<td>–</td>
<td>–</td>
<td>478</td>
<td>2.59</td>
</tr>
<tr>
<td></td>
<td>1 wt% in mCBP</td>
<td>298</td>
<td>–</td>
<td>–</td>
<td>460</td>
<td>2.70</td>
<td>30</td>
<td>0.88</td>
<td>8.3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>DABNA-2</td>
<td>2.0 × 10^{-3} wt in CH_{2}Cl_{2}</td>
<td>298</td>
<td>444</td>
<td>4.63</td>
<td>470</td>
<td>2.64</td>
<td>34</td>
<td>0.85</td>
<td>7.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Saturated in EtOH</td>
<td>298</td>
<td>–</td>
<td>–</td>
<td>463</td>
<td>2.68</td>
<td>34</td>
<td>0.90</td>
<td>7.3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Saturated in EtOH</td>
<td>77</td>
<td>–</td>
<td>–</td>
<td>458</td>
<td>2.71</td>
<td>24</td>
<td>–</td>
<td>–</td>
<td>485</td>
<td>2.56</td>
</tr>
<tr>
<td></td>
<td>1 wt% in mCBP</td>
<td>298</td>
<td>–</td>
<td>–</td>
<td>469</td>
<td>2.64</td>
<td>28</td>
<td>0.90</td>
<td>6.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1 wt% in mCBP</td>
<td>77</td>
<td>–</td>
<td>–</td>
<td>475</td>
<td>2.61</td>
<td>40</td>
<td>–</td>
<td>–</td>
<td>503</td>
<td>2.47</td>
</tr>
</tbody>
</table>

*Maximum wavelength of ultraviolet–visible absorption and emission; singlet and triplet energies estimated from the emission maxima. ΔE_{ST} = E_S − E_T; full-width at half-maximum; absolute photoluminescence quantum yield; lifetime calculated from the fluorescence decay; deposited thin films of 3,3′-bis(N-carbazolyl)-1,1′-biphenyl (mCBP) doped with DABNA-1 or DABNA-2; measured at 300 K.
Table 2. Photophysical data of DABNA-1 and DABNA-2 in mCBP films (1 wt%) at 300 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Phi^{a}$</th>
<th>$\Phi^{b}$</th>
<th>$\Phi^{\text{TADF}}^{b}$</th>
<th>$\tau^{f}$ [ns]</th>
<th>$\tau^{\text{TADF}}$ [ps]</th>
<th>$k^{f} \times 10^{7}$ [s$^{-1}$]</th>
<th>$k^{TADF} \times 10^{7}$ [s$^{-1}$]</th>
<th>$k^{\text{ISC}} \times 10^{7}$ [s$^{-1}$]</th>
<th>$k^{\text{RISC}} \times 10^{6}$ [s$^{-1}$]</th>
<th>$\Delta E_{ST}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DABNA-1</td>
<td>0.880</td>
<td>0.845</td>
<td>0.035</td>
<td>8.8</td>
<td>93.7</td>
<td>9.6</td>
<td>1.3</td>
<td>4.5</td>
<td>9.9</td>
<td>0.20</td>
</tr>
<tr>
<td>DABNA-2</td>
<td>0.897</td>
<td>0.843</td>
<td>0.054</td>
<td>6.0</td>
<td>65.3</td>
<td>14.1</td>
<td>1.6</td>
<td>10.1</td>
<td>14.8</td>
<td>0.20</td>
</tr>
</tbody>
</table>

$^{a}$Absolute photoluminescence quantum yield; $^{b}$the fluorescent and TADF components are determined from the total $\Phi$ and the proportion of the integrated area of each of the components in the transient spectra to the total integrated area; $^{f}$lifetimes calculated from the fluorescence decay; $^{TADF}$fluorescence decay rate ($k^{f}$), internal conversion decay rate from $S_1$ to $S_0$ ($k^{IC}$), intersystem crossing decay rate from $S_1$ to $T_1$ ($k^{ISC}$), reverse intersystem crossing decay rate from $T_1$ to $S_1$ ($k^{RISC}$), and $\Delta E_{ST}$ are calculated from $\Phi$, $\Phi^{f}$, $\Phi^{\text{TADF}}$, $\tau^{f}$, and $\tau^{\text{TADF}}$ according to Adachi’s method reported in refs. [11] and [16].

7.9 lm W$^{-1}$, respectively, at 100 cd m$^{-2}$). The maximum IQE was estimated to be $\approx 100\%$ by assuming that the light out-coupling efficiency was 20%. Since derivative DABNA-2 exhibited comparable values of $\Phi$ and $\Delta E_{ST}$ to those of DABNA-1, its higher $k^{f}$ (DABNA-1: 9.6 $\times$ 10$^{7}$ s$^{-1}$, DABNA-2: 14.1 $\times$ 10$^{7}$ s$^{-1}$) and $k^{RISC}$ (DABNA-1: 9.9 $\times$ 10$^{3}$ s$^{-1}$, DABNA-2: 14.8 $\times$ 10$^{3}$ s$^{-1}$) may account for the significant improvement.\[^{[9,11,12]}\] Unfortunately, the maximum luminance cannot reach 1000 cd m$^{-2}$ owing to the serious efficiency roll-off. Since the roll-off was slightly improved by using 5 wt% of DABNA,

\[^{[27]}\] we currently assume that the relatively small $k^{RISC}$ and charge carrier imbalance in the devices cause bimolecular quenching process such as triplet–triplet and exciton–polaron annihilation at high current densities.\[^{[28]}\] Notably, the EL spectrum of DABNA-2 was slightly redshifted ($\lambda_{\text{em}} = 467$ nm, CIE = (0.12, 0.13)) but not broadened at all (FWHM = 28 nm) compared to that of DABNA-1, probably because of the localization of the HOMO and LUMO at the rigid-core structure rather than at the substituents (Figure 2). These results suggest that the device performance can be further improved by an appropriate choice of substituents without a significant loss in the color purity.

In conclusion, we have designed and synthesized organoboron-based ultrapure blue emitters having small $\Delta E_{ST}$, high $\Phi$, and excellent color purity. The device employing emitter DABNA-2 exhibited pure blue emission at 467 nm with a narrow FWHM of 28 nm, CIE coordinates of (0.12, 0.13), and an IQE of $\approx 100\%$, which represent record-setting performance for blue OLEDs. We believe that the novel molecular design for

Figure 3. Characteristics of OLED devices using DABNA-1 (blue line) and DABNA-2 (red line) as the emitter. a) Electroluminescence spectra, b) current-density–driving-voltage characteristics, c) luminance–driving-voltage characteristics, d) external-quantum-efficiency–luminance characteristics, e) current-efficiency–luminance characteristics, and f) power-efficiency–luminance characteristics.

Figure 4. Energy diagram of OLED materials fabricated in this study. The ionization potential and electron affinity (in eV) for each material are displayed.
separating the HOMO and LUMO and minimizing $\Delta E_{ST}$ can be used to prepare not only excellent TADF emitters but also assistant dopants for fluorescent emitters and host materials for phosphorescent emitters.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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[19] The FWHMs of the RGB emission spectra of the Galaxy S5 (Samsung) were 23, 33, and 43 nm (see the Supporting Information for details).
[27] The use of 5 wt% content of DABNA-2 improved the device performance (EQE, current efficiency, and power efficiency of 20.0%, 23.8 cd A$^{-1}$, and 17.0 lm W$^{-1}$ at 4.1 cd m$^{-2}$ and of 14.8%, 18.0 cd A$^{-1}$, and 10.1 lm W$^{-1}$ at 100 cd m$^{-2}$, respectively), but the EL spectrum was redshifted ($\lambda_{em} = 471$ nm, CIE = (0.12, 0.17)) because of concentration quenching (see the Supporting Information for details).