An Alternative Host Material for Long-Lifespan Blue Organic Light-Emitting Diodes Using Thermally Activated Delayed Fluorescence

Soo-Ghang Ihn, Namheon Lee, Soon Ok Jeon, Myungsun Sim, Hosuk Kang, Yongsik Jung, Dal Ho Huh, Young Mok Son, Sae Youn Lee, Masaki Numata, Hiroshi Miyazaki, Rafael Gómez-Bombarelli, Jorge Aguilera-Iparraguirre, Timothy Hirzel, Álán Aspuru-Guzik, Sunghan Kim,* and Sangyoon Lee*

It has been challenging to find stable blue organic light emitting diodes (OLEDs) that rely on thermally activated delayed fluorescence (TADF). Lack of stable host materials well-fitted to the TADF emitters is one of the critical reasons. The most popular host for blue TADF, bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO), leads to unrealistically high maximum external quantum efficiency, DPEPO is however an unstable material and has a poor charge transporting ability, which in turn induces an intrinsic short OLED operating lifespan. Here, an alternative host material is introduced which educates the potential efficiency and device lifespan of given TADF emitters with the appropriateness of replacing the most popular host material, DPEPO, in developing blue TADF emitters. It simultaneously provides much longer device lifespan and higher external quantum efficiency at a practical brightness due to its high material stability and electron-transport-type character well-fitted for hole-transport-type TADF emitters.
DPEPO has been employed mostly because it can boost EQEmax OLEDs were achieved only with the DPEPO providing no efficiency data. Although no device lifespan data while the long-lifespan OLEDs were at least in part. It makes us lose one of the advantages of the host-dopant system letting dopant molecules reduce electrical stress. In this paper, we present a long lifespan of a blue TADF OLED introducing an alternative host material. Simultaneously it exhibits practically high EQE which is much higher than those of fluorescent OLEDs. Its LT80 of 21 h was achieved with 8.7% EQE at the initial luminance (500 cd m⁻²) using 5,8-bis(4-(2,6-di(9H-carbazol-9-yl)phenyl)-5,8-dihydroindolo[2,3-c]carbazole (BDpyInCz) and 3’,5-di(9H-carbazol-9-yl)-1,1’-biphenyl]-3-carbonitrile (mCBP-CN) as an emitter and a host, respectively.

mCBP-CN is well-fitted for BDpyInCz having shallow LUMO and the highest occupied molecular orbital (HOMO) because mCBP-CN has an ET-type character with deep LUMO, and so the emitting layer composed of mCBP-CN and the highly doped BDpyInCz works like a mixed host system. The electrons are mainly injected into and transported through the ET-type host material while a considerable number of holes are probably injected into TADF emitters and transported through the percolation pathway composed of the emitters having a hole transporting (HT)-type character in our device (Figure 1b). To achieve ET-type host having deep LUMO, which is fitted for the HT-type TADF emitters, we have tried to synthesize and attach cyano-groups to various positions of mCBP. It is expected to have efficient electron-injection and electron-transport due to the strong electron-withdrawing character of the cyano-group and resultingly to improve OLED performances. They are also known to have good electrochemical and thermal stability.

The mCBP-CN-based OLED exhibits a slight blue shift comparing to DPEPO-based one while increasing the content of BDpyInCz induces a slight red-shift in EL (Figure 2a). The diode turn-on voltages and OLED operating voltages of the mCBP-CN-based OLEDs at 500 cd m⁻² are quite lower than those of the DPEPO-based ones (Figure 2b). The smaller $E_g$ and deeper LUMO of mCBP-CN and the contribution of BDpyInCz to hole-transport lead to the lower operating voltage of the mCBP-CN-based OLEDs. The DPEPO-based OLEDs show severe 10–500 cd m⁻² efficiency roll-off of 75.6%, 52.5%, and 44.7% for 10%, 15%, and 20% doping ratio, respectively. Although $E_{QEMax}$ of the mCBP-CN-based device is lower than that of the DPEPO-based one, its EQE at 500 cd m⁻² is
higher due to the better charge balance. Still severe efficiency roll-off (40.8%, 38.5%, and 36.0% for 10%, 15%, and 20% doping ratio) of the mCBP-CN-based TADF OLEDs despite their improved charge balance is induced by severe triplet–triplet annihilation and singlet–triplet annihilation caused by the long excited-state lifetime of BDpyInCz ($\tau_{\text{TADF}} = 32$ µs).[17] The efficiency roll-off decreases according to the increased doping ratio without increment of driving voltage ($V_d$) indicating charge trapping.[18] This is additional evidence that BDpyInCz works like an HT-type host forming a mixed host-like system with both hosts. Detailed device characteristics are summarized in Table 1. The role of BDpyInCz as a hole transporting pathway is verified again by significantly decreased $V_d$ of the hole-only devices (HODs) of mCBP-CN:BDpyInCz and DPEPO:BDpyInCz compared to those of mCBP-CN and DPEPO (Figure 2c).

In contrast with the HOD cases, $V_d$ of the electron-only devices (EODs) of mCBP-CN:BDpyInCz and DPEPO:BDpyInCz are slightly higher than those of mCBP-CN and DPEPO, respectively (Figure 2d). In the case of DPEPO, BDpyInCz works as a deep trap according to the significant increment of $V_d$ (Figure 2d). However, in the case of mCBP-CN, because LUMO of mCBP-CN is deeper than that of BDpyInCz, we believe that the resistivity of the layer was possibly increased by the highly doped BDpyInCz (15%), decreasing the volume of mCBP-CN and the main electron transporting pathway. The increased resistivity induced the slight increment of $V_d$ (Figure 2d). The fact that the same phenomenon was observed in the EODs of mCBP-2CN and mCBP-3CN having deeper LUMO than that of mCBP-CN supports our inference (Figure S20, Supporting Information). It is worthwhile to note that mCBP-CN shows better transporting ability requiring lower $V_d$ for the same

### Table 1. Device performances of BDpyInCz-based OLEDs.

<table>
<thead>
<tr>
<th></th>
<th>$V_d$</th>
<th>CIEx</th>
<th>CIEy</th>
<th>$\lambda_{\text{EL}}$</th>
<th>Quantum efficiency</th>
<th>LT80</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[nm]</td>
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<td>[h]</td>
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<tr>
<td>DPEPO:BDpyInCz (10%)</td>
<td>7.34</td>
<td>0.178</td>
<td>0.255</td>
<td>467</td>
<td>13.1</td>
<td>3.2</td>
</tr>
<tr>
<td>DPEPO:BDpyInCz (15%)</td>
<td>5.37</td>
<td>0.196</td>
<td>0.340</td>
<td>485</td>
<td>17.7</td>
<td>8.2</td>
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<tr>
<td>DPEPO:BDpyInCz (20%)</td>
<td>5.01</td>
<td>0.211</td>
<td>0.359</td>
<td>486</td>
<td>15.0</td>
<td>8.3</td>
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<tr>
<td>mCBP-CN:BDpyInCz (10%)</td>
<td>4.95</td>
<td>0.162</td>
<td>0.204</td>
<td>464</td>
<td>12.0</td>
<td>7.1</td>
</tr>
<tr>
<td>mCBP-CN:BDpyInCz (15%)</td>
<td>4.78</td>
<td>0.167</td>
<td>0.240</td>
<td>470</td>
<td>13.0</td>
<td>10.6</td>
</tr>
<tr>
<td>mCBP-CN:BDpyInCz (20%)</td>
<td>4.74</td>
<td>0.173</td>
<td>0.266</td>
<td>472</td>
<td>13.6</td>
<td>11.2</td>
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$^a$Driving voltage at 500 cd m$^{-2}$; $^b$EL wavelength.
current density for both hole and electron according to lower $V_d$ of its HOD and EOD than those of DPEPO under the same current density (Figure 2c,d).

In addition to higher EQE at practical brightness, the mCBP-CN:BDpyInCz device shows about 43 times longer lifespan than that of the DPEPO:BDpyInCz device (Figure 3a). The longer lifespan was achieved due to its lower operating current at the same luminance and higher stability of mCBP-CN than that of DPEPO. Figure 3b shows $V_d$ of EODs under the same current density as a function of time for comparison of the solid state electrochemical stability while Figure 3c shows $V_d$ of HODs. Increment of $V_d$, which is equivalent to increment of resistivity induced by material degradation,[19] of the DPEPO-based devices is larger than those of the mCBP-CN-based ones within the same operating time. The voltage change of EOD of DPEPO is much dramatic than HOD. It indicates that electron transport through DPEPO is a harsher stress to DPEPO than hole transport even though DPEPO has been known as an ET-type host, whereas the voltage changes of both EOD and HOD of mCBP-CN are negligible. It reveals that the mCBP-CN layer degrades much slower than the DPEPO layer under the same electrical stress as we expected. We believe that the improved lifespan is attributed to the high electrochemical stability and ET-type character of mCBP-CN, which is well-fitted for HT-type BDpyInCz forming a mixed host system-like emitting layer. It can be also inferred from the improvement in current density–voltage and luminance–voltage characteristics as the content of BDpyInCz increases (Figure 2b).

Because excited-state unstability can be another source of OLED degradation,[20] we performed photoluminescence (PL) stability study. Figure 3d shows normalized PL spectra of a 50 nm mCBP-CN film on a quartz substrate measured after deposition and after 3 h UV-laser-exposure. The film was glass-encapsulated in a nitrogen-filled glove box right after the vacuum deposition. Normalization was performed by dividing them by the PL peak intensity of the as-deposited film. The
PL spectrum of the mCBP-CN film after 3 h exposure to UV-laser keeps its shape but loses peak intensity down to 0.93. On the other hand, we have unfortunately no result of the same experiment on DPEPO because we could not achieve PL from the DPEPO film because our highest-energy UV-laser (325 nm) cannot put the wide-E_{\chi} DPEPO to excited state. Instead, we can presume that DPEPO is photochemically unstable by extrapolating from a report of low photochemical stability of phosphine oxide (PO) materials.[21] In addition, we have a couple of phosphine oxide materials showing low PL stability such as [9-(3-(9H-carbazol-9-yl)phenyl)-9H-carbazol-3-yl]diphenylphosphine oxide (mCPP01)[22] (Figure 3e) and [9-(6-(9H-carbazol-9-yl)pyrindin-2-yl)-9H-carbazol-3-yl]diphenylphosphine oxide (mCPyPO) (Figure 3f). They lose peak intensity down to 0.31 and 0.14, respectively. It indicates the PO materials are photochemically more unstable than mCBP-CN in solid state. We expect that if we were able to introduce a certain TADF emitter exhibiting photochemically higher stability and shorter device lifespan could be accomplished with higher EQE at a relevant practical brightness, nor even noticeable device lifespan.

We thus believe that the shoulder PL comes out of a twisted intramolecular charge transfer (TICT) molecule having different dihedral angles between electron donating and accepting moieties leading to spatial separation of HOMO and LUMO phases.[6,25] The difference of dihedral angles can be changed by electrostatic interactions with host molecules. It is possible to produce various forms of chemical structures called rotamers, a class of conformers, in TICT molecules.[26] Changing host may form various rotamers and exhibit dual fluorescence (Figure 4c). Lippert et al. discovered the dual fluorescence strongly depending on the solvent polarity[27] and so we presume that the host matrix can also affect the phenomenon in the same way. We can find another evidence of the TICT transition in Figure 4d, noticeable change of the PL peak wavelength of the TADF emitters according to the employed hosts. The TADF emitters are working in the various hosts in the same way as in various solvents having different polarities. Even though we do not have any helpful information of the polarity of DPEPO, it seems safe to think DPEPO has an appropriate polarity to suppress dual fluorescence with LE transition and to manifest ICT transition of DpylnCz. In addition, according to more significant PL shift for DPEPO than other hosts (Figure 4d), we can presume that the polarity of DPEPO is quite different from those of other hosts. We will not discuss the polarity of DPEPO which may suppress dual fluorescence further because it is not our primary interest in this work. The important message is that certain emitters work only with DPEPO which is hardly employed for practical or commercial applications and it means DPEPO does not have an ability to screen out practically useless candidates for TADF emitters. We thus believe DPEPO must be replaced in the study of blue TADF OLEDs from now except for estimation of the maximum ability of TADF emitters in terms of EQE.

TICT molecules, the most popular TADF emitters, have a potential risk that some of them possibly work only with DPEPO or DPEPO-like host materials suppressing dual fluorescence.
This bias in selecting a host material leaves no room for utilizing device engineering to educate the potential ability of a given TADF emitter. Because of the limitation, we cannot say the newly reported DpyInCz in this work is practically useful though DpyInCz works anyhow in the DPEPO matrix as a blue TADF emitter. We would thus like to suggest that it is better to replace DPEPO with a stable host well-fitted for a given blue TADF emitter to accelerate the advance of TADF technology. The introduced mCBP-CN successfully replaces DPEPO and helps accomplish a remarkably long lifespan in a blue TADF OLED with high efficiency at a practical brightness as educating the potential ability of a given blue TADF emitter despite its relatively long $\tau_{\text{TADF}}$.

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