

**Efficient deep-blue multiple-resonance emitters based on azepine-decorated  $\nu$ -DABNA for CIE<sub>y</sub> below 0.06**

*Masashi Mamada,<sup>1</sup> Akio Aoyama,<sup>2</sup> Ryota Uchida,<sup>1</sup> Junki Ochi,<sup>1</sup> Susumu Oda,<sup>3</sup> Yasuhiro Kondo,<sup>4</sup> Masakazu Kondo,<sup>5</sup> Takuji Hatakeyama<sup>1\*</sup>*

Dr. M. Mamada, R. Uchida, Dr. J. Ochi, Prof. T. Hatakeyama

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

E-mail: hatake@kuchem.kyoto-u.ac.jp

A. Aoyama

Department of Chemistry, Graduate School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan

Prof. S. Oda

Department of Applied Chemistry, Graduate School of Science and Engineering, Toyo University, 2100 Kujirai, Kawagoe, Saitama 350-8585, Japan

Y. Kondo

SK JNC Japan Co., Ltd., 5-1 Goi Kaigan, Ichihara, Chiba 290-8551, Japan

Dr. M. Kondo

JNC Co., Ltd. 5-1 Goi Kaigan, Ichihara, Chiba 290-8551, Japan

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Ultrapure deep-blue emitters are in high demand for organic light-emitting diodes (OLEDs). Although color coordinates serve as straightforward parameters for assessing color purity, precise control over the maximum wavelength and full-width at half-maximum is necessary to optimize OLED performance, including luminance efficiency and luminous efficacy. Multiple-resonance (MR) emitters are promising candidates for achieving ideal luminescence properties; consequently, a wide variety of MR frameworks have been developed. However, most of these emitters experience a wavelength displacement from the ideal color, which limits their practical applicability. Therefore, a molecular design that is compatible with MR emitters for modulating their energy levels and color output is particularly valuable. Here, we demonstrate that the azepine donor unit induces an appropriate blue-shift in the emission maximum while maintaining efficient MR characteristics, including high photoluminescence quantum yield, narrow emission, and a fast reverse intersystem crossing rate. OLEDs using newly developed MR emitters based on the  $\nu$ -DABNA framework simultaneously exhibit a high quantum efficiency of  $\sim 30\%$ , luminous efficacy of  $\sim 20 \text{ lm W}^{-1}$ , exceptional color purity with Commission Internationale de l'Éclairage coordinates as low as (0.14, 0.06), and notably high operational stability. These results demonstrate unprecedentedly high levels compared with those observed in previously reported deep-blue emitters.

## 1. Introduction

Organic light-emitting diodes (OLEDs) have been successfully commercialized for full-color displays in mobile phones and televisions owing to their advantages in terms of contrast ratio and viewing angle.<sup>1</sup> Consequently, the performance requirements of OLEDs, which are intrinsically related to the properties of their materials, present significant and unique challenges. The key criteria for assessing OLEDs include color purity, efficiency, durability, and cost. Although blue OLEDs have yet to meet these criteria, they are essential for reducing power consumption. Therefore, highly efficient blue organic emitters have been in high demand over recent decades.<sup>2</sup> Color purity can be defined by the color gamut range specified by the Commission Internationale de l'Éclairage (CIE) coordinates.<sup>3</sup> Pure blue is specified as CIE (x, y) coordinates of (0.14, 0.08) by the National Television System Committee (NTSC) and (0.15, 0.06) by the European Broadcast Union (EBU). Moreover, in the recent BT.2020 standard for ultrahigh-definition television, the CIE values are (0.131, 0.046), which are equivalent to a monochromatic light source of 467 nm.<sup>4</sup> Although high efficiencies have been achieved for blue OLEDs using phosphorescent or thermally activated delayed fluorescence (TADF) emitters,<sup>5,6</sup> the discrepancy in CIE coordinates necessitates the use of a color filter, resulting in

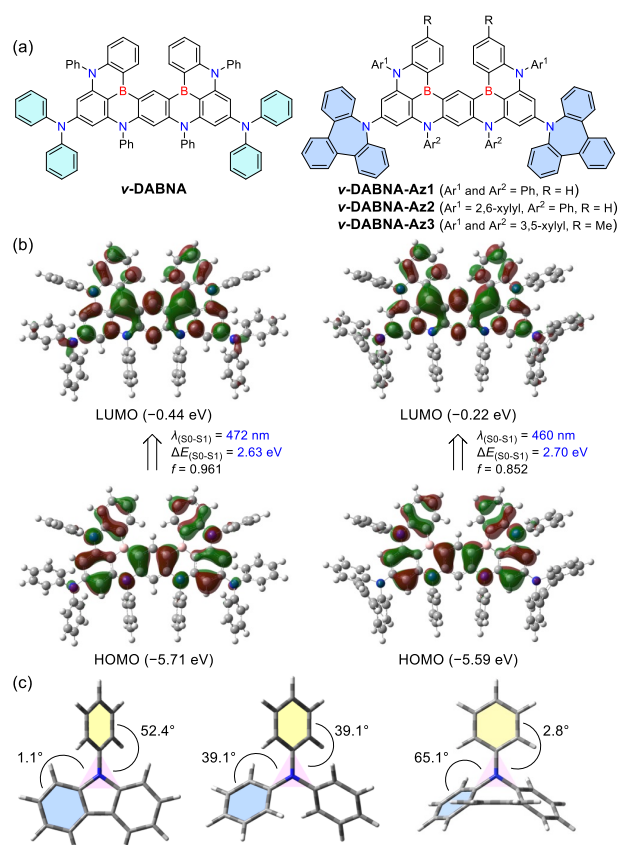
significant emission loss. Therefore, the development of blue emitters must target deep-blue and narrowband emission with a peak maximum at ~460 nm and a full-width at half-maximum (FWHM) of <20 nm, while maintaining high efficiencies.

A promising molecular design for emitters that enables favorable control of the excited-state dynamics is a multiple-resonance (MR) system.<sup>7–11</sup> The electron-donating nitrogen and electron-withdrawing boron atoms in the ortho position provide complementary resonance effects on the same benzene rings, allowing for alternative localization of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). This feature facilitates the reduction of the energy gap ( $\Delta E$ ) between the first singlet and triplet excited states ( $S_1$  and  $T_1$ ) to achieve TADF. In addition, the relatively small structural relaxation in the excited states and the suppression of stretching vibrations during the transition through non-bonding HOMO–LUMO separation yield a small FWHM without pronounced vibronic peaks. The initial MR material, **DABNA-1**, exhibited a high photoluminescence quantum yield (PLQY) of 88%, TADF property with a reverse intersystem crossing (RISC) rate constant ( $k_{\text{RISC}}$ ) of  $9.9 \times 10^3 \text{ s}^{-1}$ , external quantum efficiency (EQE) of 13.5%, and deep-blue emission at 459 nm with a small FWHM of 28 nm, resulting in a CIE of (0.13, 0.09).<sup>7</sup> Subsequent development of a  $\pi$ -extended  $\nu$ -**DABNA** consisting of two fused **DABNA-1** units improved PLQY (90%),  $k_{\text{RISC}}$  ( $2.0 \times 10^5 \text{ s}^{-1}$ ), EQE (34.4%), and FWHM (18 nm) and contributed to prolonging device durability; however, a slight red-shift of the emission maximum (469 nm) resulted in CIE values of (0.12, 0.11).<sup>8</sup> Therefore, achieving simultaneous optimization of both emission efficiency and color purity is an exceedingly difficult task. Moreover, almost no material exhibits a high EQE with adequately small CIE values based on a narrow FWHM (<20 nm), especially for  $\text{CIE}_y < 0.06$ .<sup>12–14</sup> Notably, the visual sensitivity of the human eye, which is related to the current efficiency (CE, luminance efficiency) and power efficiency (PE, luminous efficacy), significantly diminishes for ultra-deep-blue emission. Hence, although small CIE values can be obtained for emissions <450 nm despite a relatively large FWHM, the peak emission maximum should ideally exceed 455 nm.<sup>15</sup>

In this study, we showcase highly efficient ultrapure deep-blue emission, achieving a  $\text{CIE}_y$  as low as  $\leq 0.06$  by incorporating tribenzo[*b,d,f*]azepine (Az) moieties into the  $\nu$ -**DABNA** framework (**Figure 1**). Although some efforts have been made to blue-shift the emission of  $\nu$ -**DABNA**, such as replacing nitrogen atoms with oxygen or sulfur atoms and substituting fluorine atoms, these strategies are expected to compromise device durability,<sup>12,13</sup> highlighting the need for alternative chemical modification strategies. The emission wavelength can be controlled by introducing electron-donating or electron-withdrawing substituents at positions

with HOMO–LUMO distributions. For example, electron-withdrawing cyano groups substituted at carbons with large LUMO coefficients decrease the LUMO level and promote a bathochromic shift.<sup>16</sup> Conversely, electron-donating groups have the opposite effect on the energy levels. Since ***ν*-DABNA** already has a large molecular weight and additional substituents make vacuum evaporation challenging, we propose using a stronger donor unit instead of diphenyl amine connected to the carbons exhibiting LUMO distributions (Figure 1b).

The electronic properties of Az derivatives compared with those of carbazole (Cz) and diarylamine (DPA) derivatives are related to their geometries (Figure 1c). The dihedral angles between the yellow phenyl rings and the red center planes consisting of three C–N bonds are 52.4°, 39.1°, and 2.8° for *N*-phenyl-Cz (Ph-Cz), triphenylamine (Ph-DPA), and *N*-phenyl-substituted Az (Ph-Az), respectively. In contrast, the angles between the blue phenyl rings and the red center planes are 1.1°, 39.1°, and 65.1°, respectively. Thus, the lone-pair electrons on the Az nitrogen atom are more strongly delocalized to the yellow phenyl ring than those on the other nitrogen atoms. This is further evidenced by the larger HOMO distribution and the higher energy of the LUMO+n with coefficients on the yellow phenyl ring for Ph-Az (Figure S1). Thus, the emission wavelengths of *ν*-DABNA-Az derivatives are expected to be blue-shifted by 10 nm compared with that of ***ν*-DABNA**. Although some reports of MR compounds using the Az moiety were published while preparing this manuscript based on the patents we filed,<sup>17,18</sup> they do not clearly feature the effects of Az substitutions. First, these studies focused on the role of the perpendicular geometry of the Az moiety in preventing aggregation-caused quenching (ACQ) without explaining the donor strength of the Az moiety. Second, the overall OLED performance was unsatisfactory in terms of color purity and efficiency roll-off. Finally, and most importantly, device durability was not appropriately investigated; therefore, concerns remain about the stability of the Az moiety in OLEDs. In contrast, our results confirm the validity of Az substitution for the development of stable and ultrapure deep-blue MR emitters.



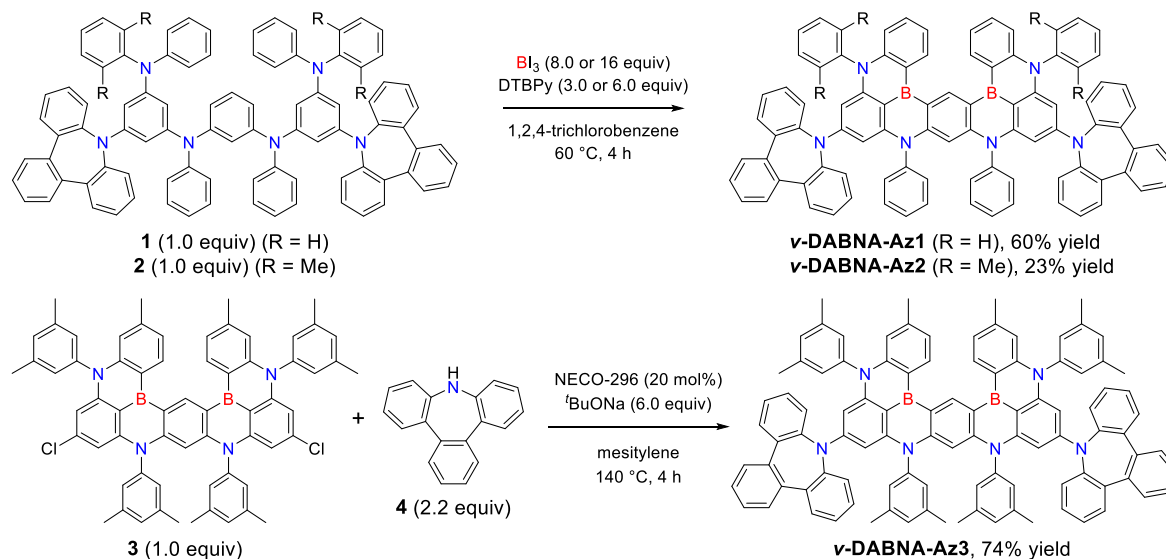
**Figure 1.** a) Design of MR-TADF materials by the substitution of tribenzo[ $b,d,f$ ]azepine. b) Kohn–Sham frontier orbitals of  $\nu$ -DABNA and  $\nu$ -DABNA-Az1 calculated at the M06-2X/6–31G(d) level of theory and their oscillator strength ( $f$ ) and  $S_0$ – $S_1$  transition energy ( $\Delta E$ ,  $\lambda$ ) at the TDA-B2PLYP( $c_x = 0.40$ ,  $c_c = 0.23$ )/6-31G//M062X/6-31G(d) level of theory. c) Dihedral angles of  $N$ -phenylcarbazole ( $C_2$  symmetry), triphenylamine ( $C_3$  symmetry), and  $N$ -phenyltribenzo[ $b,d,f$ ]azepine ( $C_s$  symmetry) at the M06-2X/6-31G(d) level of theory.

## 2. Results and Discussion

To gain insight into the emission properties, including the TADF behavior of  $\nu$ -DABNA-Az derivatives, detailed results of time-dependent double-hybrid density functional theory (TD-DHDF) and spin-orbit coupling (SOC) calculations (Methods S1) for  $\nu$ -DABNA and its parent Az derivative ( $\nu$ -DABNA-Az1) are summarized in Figure S2.<sup>19</sup> The calculations accurately reproduced the  $S_0$ – $S_1$  transition energy (emission wavelength) of  $\nu$ -DABNA, indicating a reasonable prediction for these processes. The emission wavelength of  $\nu$ -DABNA-Az1 is expected to be 460 nm, which is ideal for balancing between small CIE and high luminance. The SOC matrix elements ( $\langle S_n | \hat{H}_{\text{SOC}} | T_n \rangle$ ) calculated at the M062X/TZP level of theory for  $\nu$ -DABNA-Az1 ( $S_1$ – $T_1$ :  $0.056$   $\text{cm}^{-1}$ ,  $S_1$ – $T_2$ :  $0.316$   $\text{cm}^{-1}$ ) were larger than those for  $\nu$ -DABNA

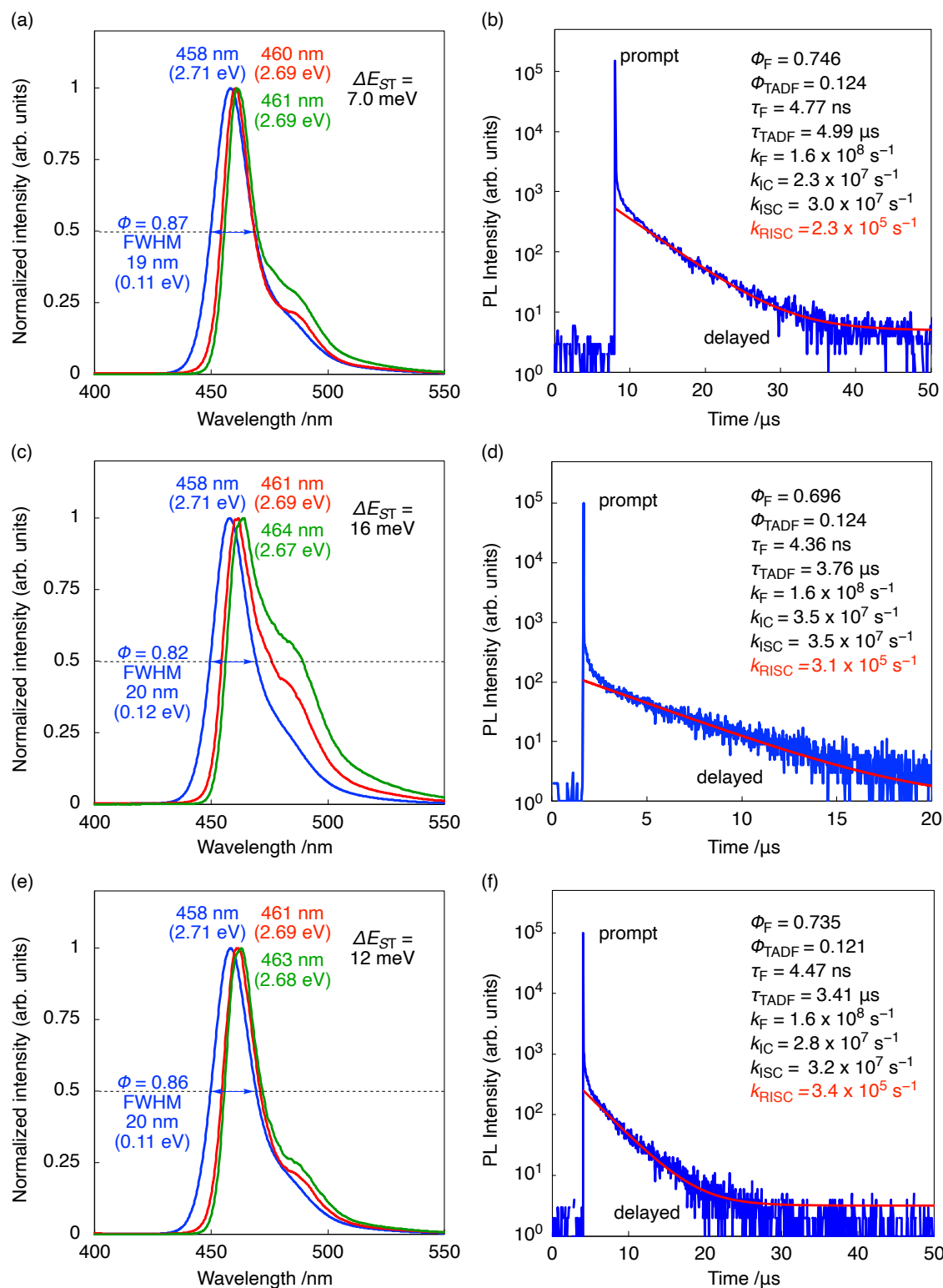
( $S_1-T_1$ : 0.013 cm<sup>-1</sup>,  $S_1-T_2$ : 0.234 cm<sup>-1</sup>). Considering the slightly increased activation energy for the RISC through the  $T_2$  level ( $\Delta E_{S_1-T_1}$  = 111 meV and  $\Delta E_{S_1-T_2}$  = 157 meV for ***v*-DABNA-Az1** versus  $\Delta E_{S_1-T_1}$  = 125 meV and  $\Delta E_{S_1-T_2}$  = 91 meV for ***v*-DABNA**), ***v*-DABNA-Az** derivatives are expected to exhibit a high  $k_{RISC}$  ( $>10^5$  s<sup>-1</sup>) relative to ***v*-DABNA**.<sup>20</sup>

Although *N*-aryl groups have less impact on the electronic structure, the introduction of bulky groups can alter intermolecular interactions in the solid state, including the aggregation of emitters and  $\pi$ - $\pi$  interaction between the emitter and host material.<sup>21</sup> Consequently, ***v*-DABNA-Az2** and ***v*-DABNA-Az3** with steric protection were also prepared. The synthesis of ***v*-DABNA-Az1** and ***v*-DABNA-Az2** follows the same procedure, involving stepwise Buchwald–Hartwig amination reactions to introduce the Az moiety, resulting in precursor compounds **1** and **2** (Methods S2 and Schemes S1–S3). This is subsequently followed by one-shot double borylation (**Scheme 1**).<sup>8</sup> The synthesis of ***v*-DABNA-Az3** follows that of the compound with the same aryl groups.<sup>12</sup> Therefore, the core skeleton was constructed via one-shot double borylation to yield precursor compound **3** (Scheme S4), with the Az moiety introduced by substituting chlorine atoms (Scheme 1). These two procedures were classified as early- and late-stage functionalizations relative to borylation cyclization, and both schemes successfully provided Az derivatives in high yields.



**Scheme 1.** Synthesis of ***v*-DABNA-Az** derivatives.

The photophysical properties of 1-wt%- $\nu$ -DABNA-Az-derivative-doped films of poly(methyl methacrylate) (PMMA) are summarized in **Figure 2** and **Table 1**. The excited state characters of the  $\nu$ -DABNA-Az derivatives are similar to those of  $\nu$ -DABNA, resulting in narrow emission spectra, a relatively small Stokes shift (Figures S3 and S4), small  $\Delta E_{ST}$ , and large  $k_{RISC}$  owing to excellent MR effects. However, the spectra of the  $\nu$ -DABNA-Az derivatives appeared in the deeper blue region, which is consistent with the theoretical investigations. All  $\nu$ -DABNA-Az derivatives exhibited emission maxima at 458 nm, representing a 7 nm blue-shift from that observed for  $\nu$ -DABNA under identical experimental conditions (Figures S5 and S6). An important feature is the retention of a narrow FWHM of < 20 nm, in contrast to the broadening of the FWHM observed in the strategy using chalcogen atoms instead of nitrogen to blue-shift the emission wavelength.<sup>12,13</sup> The PLQY values of the  $\nu$ -DABNA-Az derivatives were sufficiently high (>80%), although they were slightly lower than that of  $\nu$ -DABNA, probably because of intermolecular interactions between azepine units with a fused structure. In addition, the  $\Delta E_{ST}$  values based on the emission maxima of the fluorescence and phosphorescence spectra at 77 K were small (<20 meV). Consequently, their rate constants, including  $k_{RISC}$  calculated from emission lifetimes (Methods S3 and Figures S7–S11),<sup>22</sup> were comparable to those of  $\nu$ -DABNA, which aligns with the SOC calculations. Since the  $k_{RISC}$  of DABNA-1-based derivatives is generally low ( $\sim 10^4$  s<sup>-1</sup>),<sup>10</sup> the  $\nu$ -DABNA core inherently offers significant advantages. The Az decoration strategy was found to enhance color purity without compromising photophysical properties.



**Figure 2.** Photophysical properties of 1-wt%-doped PMMA films of a,b) ***v*-DABNA-Az1**, c,d) ***v*-DABNA-Az2**, and e,f) ***v*-DABNA-Az3**. a,c,e) Steady-state PL (fluorescence) spectra at 300 K (blue) and 77 K (red) without delay time and phosphorescence spectra at 77 K (green) with a delay time of 25 ms. b,d,f) Transient photoluminescence decay curves at 300 K and their relevant parameters. The red curves represent the single exponential fitting data based on background values of b) 5, d) 1, and f) 3.

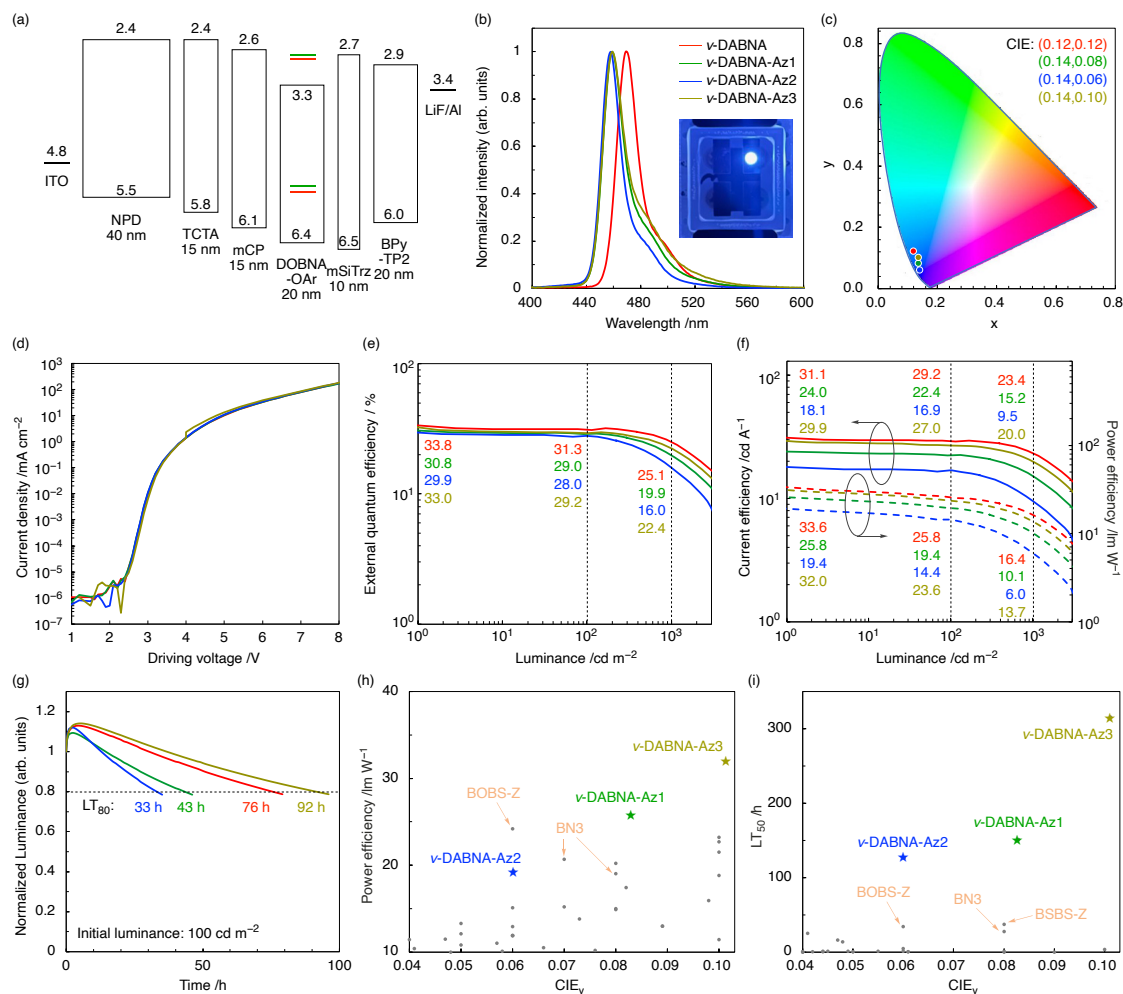
**Table 1.** Photophysical properties of ***v*-DABNA**, ***v*-DABNA-Az1**, ***v*-DABNA-Az2**, and ***v*-DABNA-Az3** in PMMA.

| Compound                  | $\lambda_{\text{PL,max}}$<br>[nm] | FWHM<br>[nm] | $\Delta E_{\text{ST}}$<br>[meV] <sup>a)</sup> | $\Phi$<br>[-] <sup>b)</sup> | $\Phi_{\text{F}}$<br>[-] <sup>c)</sup> | $\Phi_{\text{TADF}}$<br>[-] <sup>c)</sup> | $\tau_{\text{F}}$<br>[ns] <sup>d)</sup> | $\tau_{\text{TADF}}$<br>[ $\mu\text{s}$ ] <sup>d)</sup> | $k_{\text{F}}$<br>[ $10^7 \text{ s}^{-1}$ ] <sup>e)</sup> | $k_{\text{IC}}$<br>[ $10^7 \text{ s}^{-1}$ ] <sup>e)</sup> | $k_{\text{ISC}}$<br>[ $10^7 \text{ s}^{-1}$ ] <sup>e)</sup> | $k_{\text{RISC}}$<br>[ $10^5 \text{ s}^{-1}$ ] <sup>e)</sup> |
|---------------------------|-----------------------------------|--------------|-----------------------------------------------|-----------------------------|----------------------------------------|-------------------------------------------|-----------------------------------------|---------------------------------------------------------|-----------------------------------------------------------|------------------------------------------------------------|-------------------------------------------------------------|--------------------------------------------------------------|
| <b><i>v</i>-DABNA</b>     | 465                               | 18           | 12                                            | 0.91                        | 0.79                                   | 0.12                                      | 4.0                                     | 3.9                                                     | 20                                                        | 2.0                                                        | 3.4                                                         | 3.0                                                          |
| <b><i>v</i>-DABNA-Az1</b> | 458                               | 19           | 7                                             | 0.87                        | 0.76                                   | 0.12                                      | 4.8                                     | 5.0                                                     | 16                                                        | 2.3                                                        | 3.0                                                         | 2.3                                                          |
| <b><i>v</i>-DABNA-Az2</b> | 458                               | 19           | 16                                            | 0.82                        | 0.70                                   | 0.12                                      | 4.4                                     | 3.8                                                     | 16                                                        | 3.5                                                        | 3.5                                                         | 3.1                                                          |
| <b><i>v</i>-DABNA-Az3</b> | 458                               | 19           | 12                                            | 0.86                        | 0.74                                   | 0.12                                      | 4.5                                     | 3.4                                                     | 16                                                        | 2.8                                                        | 3.2                                                         | 3.4                                                          |

<sup>a)</sup>Singlet–triplet energy gap estimated from the emission maxima of fluorescence and phosphorescence at 77 K; <sup>b)</sup>Absolute photoluminescence quantum yield under N<sub>2</sub>; <sup>c)</sup>Fluorescence and TADF components determined from the total  $\Phi$  and contribution of the integrated area of each component in the transient spectra to the total integrated area; <sup>d)</sup>Lifetimes calculated from fluorescence decay; <sup>e)</sup>Rate constants of fluorescence ( $k_{\text{F}}$ ), internal conversion from S<sub>1</sub> to S<sub>0</sub> ( $k_{\text{IC}}$ ), intersystem crossing from S<sub>1</sub> to T<sub>1</sub> ( $k_{\text{ISC}}$ ), and reverse intersystem crossing from T<sub>1</sub> to S<sub>1</sub> ( $k_{\text{RISC}}$ ) calculated from  $\Phi$ ,  $\Phi_{\text{F}}$ ,  $\Phi_{\text{TADF}}$ ,  $\tau_{\text{F}}$ , and  $\tau_{\text{TADF}}$  according to the reported methods.<sup>22</sup>

To harness the potential of Az derivatives as emitters for deep-blue OLEDs, we investigated the electroluminescence (EL) properties of devices with the structure shown in **Figure 3**. Details of the device fabrication and chemical structures of the materials are provided in the Supporting Information (Methods S4 and Figure S12). The host material, DOBNA-OAr, is compatible with *v*-DABNA derivatives because of its relatively high T<sub>1</sub> level and HOMO–LUMO energy level alignment, thereby facilitating efficient charge recombination (**Figures 3a** and **S13**).<sup>8</sup> Similar to the PL spectra in PMMA, the EL spectra of *v*-DABNA-Az derivatives with emission maxima of 458–459 nm were visibly blue-shifted compared with that of ***v*-DABNA** (Figure 3b). Notably, the PL spectra of *v*-DABNA-Az derivatives in DOBNA-OAr showed a relatively large emission from DOBNA-OAr (Figure S14). This result indicates that the strong carrier trap capability of the MR compounds causes direct charge recombination in OLEDs.<sup>23</sup> On the other hand, the incomplete energy transfer from the host, as observed in the PL measurements, suggests weaker interactions between the *v*-DABNA-Az derivatives and DOBNA-OAr due to the steric hindrance of the Az moiety, which contributes to preventing the

red-shift of the emission maxima and keeping the FWHM narrower than 20 nm. In particular, ***v*-DABNA-Az2** had steric protection, which implies fewer interactions, and exhibited a better EL spectrum. Thus, the minor variations in FWHM among the three *v*-DABNA-Az derivatives depending on the *N*-aryl groups were likely due to interactions with the host molecules. Consequently, these emitters achieved significantly enhanced color purity, with CIE coordinates of (0.136, 0.083) for ***v*-DABNA-Az1** and (0.140, 0.060) for ***v*-DABNA-Az2**, meeting the pure blue definition outlined by the NTSC and EBU standards (Figure 3c). The devices exhibited excellent semiconducting properties with a low turn-on voltage of 3.0 V (Figure 3d) and adequately high EQE values exceeding 30% (Figure 3e). Note that the device based on ***v*-DABNA** reproduced the reported OLED characteristics despite minor changes in ETL materials aimed at improving stability.<sup>8</sup> The roll-off characteristics seem to be related to charge transport properties due to host–guest interactions, as evidenced by the nearly identical  $k_{\text{RISC}}$  of these emitters and the corresponding changes in the FWHM. Higher doping concentrations improved the roll-off characteristics of these emitters (Figure S15), whereas color purity was enhanced at lower doping concentrations. These emitters demonstrated notably high CE and PE (Figure 3f), which are essential features expected for high-performance deep-blue emitters. Another crucial performance factor for blue emitters is device durability. The operational lifetime of ***v*-DABNA-Az3** was similar to that of ***v*-DABNA** despite the blue-shifted emission maximum (Figure 3g), indicating that the Az moiety is robust and useful as a building block for OLED materials. Consequently, these emitters exhibited remarkably long LT<sub>50</sub> values up to 300 h at 100 cd m<sup>-2</sup>, estimated using the equation  $\text{LT}_{50}@100 \text{ cd m}^{-2} = \text{LT}_{50}@500 \text{ cd m}^{-2} \times (500 \text{ cd m}^{-2}/100 \text{ cd m}^{-2})^n$ , where the *n* values were estimated from the acceleration aging tests of the OLEDs (Figures S16 and S17). This result offers great promise for hyperfluorescence devices to exhibit lifetimes comparable to those of commercial blue OLEDs.<sup>24</sup> Overall, the Az-incorporated ***v*-DABNA** exhibited exceptional performance as a deep-blue emitter compared with previously reported materials, as demonstrated in the plots of PE and operational lifetime as a function of CIE<sub>y</sub> (Figures 3h and 3i, and Table S1).<sup>10,13–15,25</sup>



**Figure 3.** OLED characteristics of devices using  $\nu$ -DABNA-Az1 (green lines and symbols),  $\nu$ -DABNA-Az2 (blue lines and symbols),  $\nu$ -DABNA-Az3 (yellow lines and symbols), and  $\nu$ -DABNA (red lines and symbols). a) Device structure with the estimated energy levels of each component in eV. b) Normalized EL spectra at 1000  $\text{cd m}^{-2}$  (inset: electroluminescence of the  $\nu$ -DABNA-Az1 device). c) Commission Internationale de l'Éclairage (CIE) (x,y) coordinates. d) Current density–voltage ( $J$ – $V$ ) characteristics. e) EQE–luminance (EQE– $L$ ) characteristics. f) Current efficiency (CE)– $L$  (solid lines) and power efficiency (PE)– $L$  (dashed lines) characteristics. g) Change in luminance versus operational time at an initial luminance of 100  $\text{cd m}^{-2}$ . h) Comparison of maximum PE values of reported blue OLEDs with  $\text{CIE}_y \leq 0.1$ . g) Comparison of  $\text{LT}_{50}$  values of reported deep-blue OLEDs with  $\text{CIE}_y \leq 0.1$  at 100  $\text{cd m}^{-2}$ .

### 3. Conclusion

We successfully developed advanced deep-blue MR-TADF emitters based on the  $\nu$ -DABNA framework by incorporating Az units. This molecular design preserves the high PLQY and efficient TADF properties of  $\nu$ -DABNA while shifting the emission spectra to the ultrapure blue region, with an emission maximum lower than 460 nm and an FWHM of less than 20 nm. Thus, color purity was significantly enhanced compared with that of  $\nu$ -DABNA. Consequently, OLEDs using these emitters demonstrated not only high EQE exceeding 30% but also high CE and PE values, with excellent CIE coordinates of (0.136, 0.083) for  $\nu$ -DABNA-Az1 and (0.140, 0.060) for  $\nu$ -DABNA-Az2. In addition, these devices exhibited outstanding durability compared with previously reported deep-blue emitters. Currently, the operational lifetime is the key parameter that must be significantly enhanced for practical use, although highly luminescent deep-blue emitters have been developed using different strategies.<sup>26</sup> We emphasize again that the Az moiety does not cause low stability while it efficiently blue-shifts the emission wavelength. We conclude that the Az decoration strategy is versatile and applicable to various MR compounds, despite its simplicity.

### Supporting Information

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

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