

Sequential Multiple Borylation Toward an Ultrapure Green Thermally Activated Delayed Fluorescence Material

Shigetada Uemura^{†,‡}, Susumu Oda[‡], Masahiro Hayakawa[†], Ryosuke Kawasumi[§], Naoya Ikeda[‡], Yi-Ting Lee[#], Chin-Yiu Chan[#], Youichi Tsuchiya[#], Chihaya Adachi[#], and Takuji Hatakeyama^{†,*}

[†]Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan.

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

[§]SK JNC Japan Co., Ltd. 5-1 Goikaigan, Ichihara, Chiba 290-8551, Japan.

[#]Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, Fukuoka 819-0395, Japan

Supporting Information Placeholder

ABSTRACT: Multiple-resonance thermally activated delayed fluorescence (MR-TADF) emitters have emerged as an important component of organic light-emitting diodes (OLEDs) owing to their narrowband emission and high exciton utilization efficiency. However, the chemical space of MR-TADF emitters remains mostly unexplored owing to the lack of suitable synthetic protocols. Herein, we demonstrate a sequential multiple borylation reaction that provides new synthetically accessible chemical space. **ω-DABNA**, the proof-of-concept material, exhibited narrowband green TADF with a full width at half maximum of 22 nm and a small singlet–triplet energy gap of 13 meV. The OLED employing it as an emitter exhibited electroluminescence at 512 nm, with Commission International de l’Éclairage coordinates of (0.13, 0.73) and a high external quantum efficiency (EQE) of 31.1%. Moreover, the device showed minimum efficiency roll-off, with an EQE of 29.4% at 1000 cd m⁻².

Organic light-emitting diodes (OLEDs) have emerged as an important component of commercial displays owing to their excellent color reproducibility, high contrast ratio, fast response time, and good panel flexibility.¹ However, the power consumption and luminance of commercial OLED displays are not satisfactory because the electroluminescence (EL) spectra of conventional blue emitters are broader than those required for broadcasting standards. A color filter and/or an optical microcavity is usually required to improve the color purity of the original EL spectra, leading to efficiency loss. To address this, herein we proposed the utilization of the multiple-resonance (MR) effect of boron and nitrogen/oxygen atoms.² The resulting non-bonding frontier orbitals minimized the vibronic coupling between electronic excitation and stretching vibrations to realize extraordinary narrowband emission

with a full width at half maximum (FWHM) of <30 nm, as well as a high photoluminescence quantum yield (PLQY) of >90%. Because of these ideal features, a variety of boron-based MR emitters, such as DABNA derivatives,^{2a} have been developed and are now widely implemented as blue emitters for triplet–triplet annihilation (TTA)-driven fluorescent devices combined with anthracene-based host materials in commercial OLED displays. Because of their alternating HOMO-LUMO pattern, most MR emitters have small singlet–triplet energy gaps (ΔE_{ST}) and exhibit thermally activated delayed fluorescence (TADF),³ affording OLEDs with 100% internal quantum efficiency via efficient reverse intersystem crossing (RISC). This phenomenon, which is known as “MR-TADF,” has been extensively harnessed in the last few years.⁴ The most effective protocol to construct boron-based MR structures is the “one-pot borylation”⁵ method involving lithiation, transmetalation, and tandem bora-Friedel-Crafts reaction (electrophilic arene borylation),⁶ which was first reported in 2011⁷ and subsequently established for the synthesis of **DOBNA**^{2a} and **DABNA**^{2b} (Figure 1a). Although this protocol provides synthetically accessible chemical space for MR-TADF emitters,⁸ it requires directing groups or halogen atoms for borylation, thus limiting the number of boron atoms introduced. Therefore, in 2018, we developed “one-shot borylation,”⁹ which involved inter- and intramolecular tandem bora-Friedel-Crafts reaction (Figure 1b). This protocol provided facile access to π -extended MR-TADF emitters containing multiple boron atoms.¹⁰ Such emitters, which also include **v-DABNA**,^{10a} have excellent photophysical properties because of the delocalization of short-range charge-transfer character.^{11d} However, borylation preferably proceeds at the most sterically accessible carbon atom with a certain HOMO distribution,¹² and most of the chemical space remains unexplored. To address this issue, herein we report a new protocol—sequential multiple

borylation—consisting of one-pot borylation, amination, and one-shot borylation (Figure 1c). As a proof-of-concept, an ultrapure green MR-emitter, viz. **ω-DABNA**, was synthesized. The omega-shaped MR skeleton contains three boron atoms and four nitrogen atoms, which conventional borylation protocols could never construct.

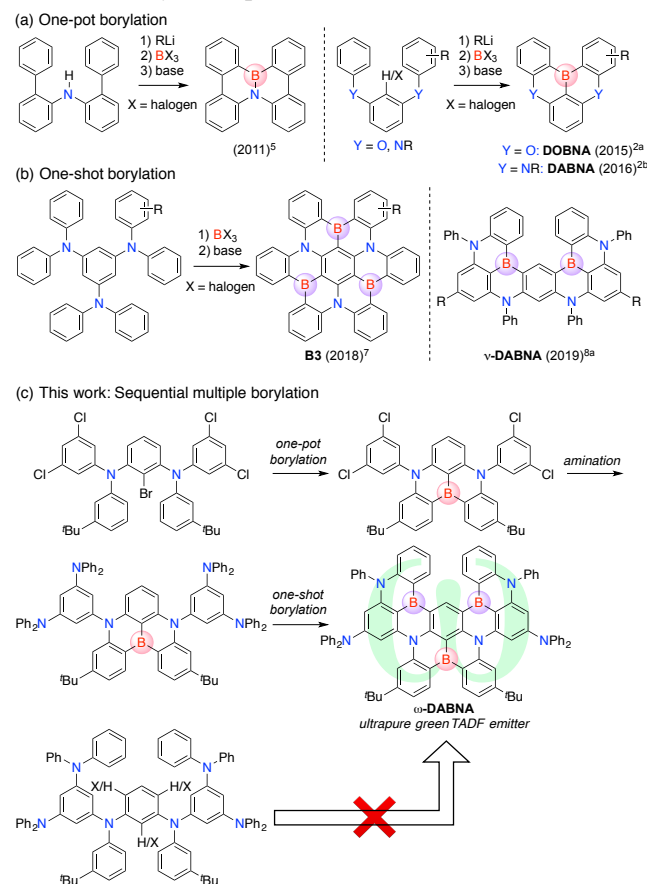


Figure 1. Previously reported and currently developed synthetic protocols for MR-TADF emitters.

To evaluate the MR-TADF properties of **ω-DABNA**, SCS-CC2 calculations were performed on model compounds **v-DABNA-core** and **ω-DABNA-core** (Figure 2a and b). The energy for the transition from the ground state to the first excited singlet state (S_0 – S_1) in **ω-DABNA-core** (2.847 eV) was lower than that in **v-DABNA-core** (3.213 eV), suggesting a bathochromic shift in the emission spectrum of the former with respect to that of the latter. Furthermore, the ΔE_{ST} of **ω-DABNA-core** (39 meV) was larger than that of **v-DABNA-core** (20 meV). Notably, the spin-orbit coupling (SOC) matrix elements ($SOC = \langle S_n | \hat{H}_{SOC} | T_n \rangle$) of **ω-DABNA-core** (S_1 – T_1 : 0.090 cm^{-1} , S_1 – T_2 : 1.414 cm^{-1}) were much larger than those of **v-DABNA-core** (S_1 – T_1 : 0.018 cm^{-1} , S_1 – T_2 : 0.157 cm^{-1}) because of the unique twisted structure of the former, which consists of five [4]helicene units. Despite larger $\Delta E_{S_1-T_1}$ and $\Delta E_{S_1-T_2}$, **ω-DABNA** is expected to exhibit an RISC rate constant (k_{RISC}) comparable to that of **v-DABNA** (2.0

$\times 10^5 \text{ s}^{-1}$) owing to large SOC, based on the following relationship: $k_{RISC} \propto \langle S_n | \hat{H}_{SOC} | T_n \rangle^2 / \Delta E_{ST}$.¹¹

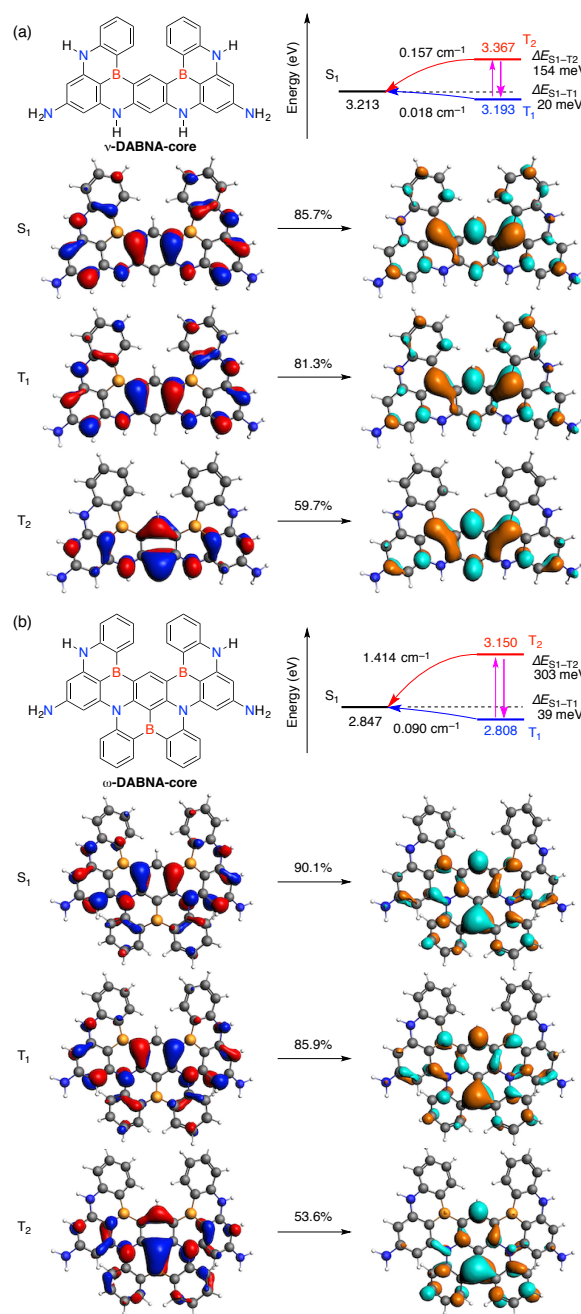


Figure 2. Molecular structure, energy level diagram, and associated natural transition orbitals (NTOs) for the singlet and triplet excited states of (a) **ω-DABNA-core** and (b) **v-DABNA-core** at the S_1 geometry. Transition energies for S_1 , T_1 , and T_2 were calculated at the SCS-CC2/def2TZVP//M062X/6-31G(d) level of theory. NTOs and SOC matrix elements between the T_n and S_n states were calculated at the M062X/TZP//M062X/6-31G(d) level of theory.

Scheme 1. Synthesis of **ω -DABNA**.

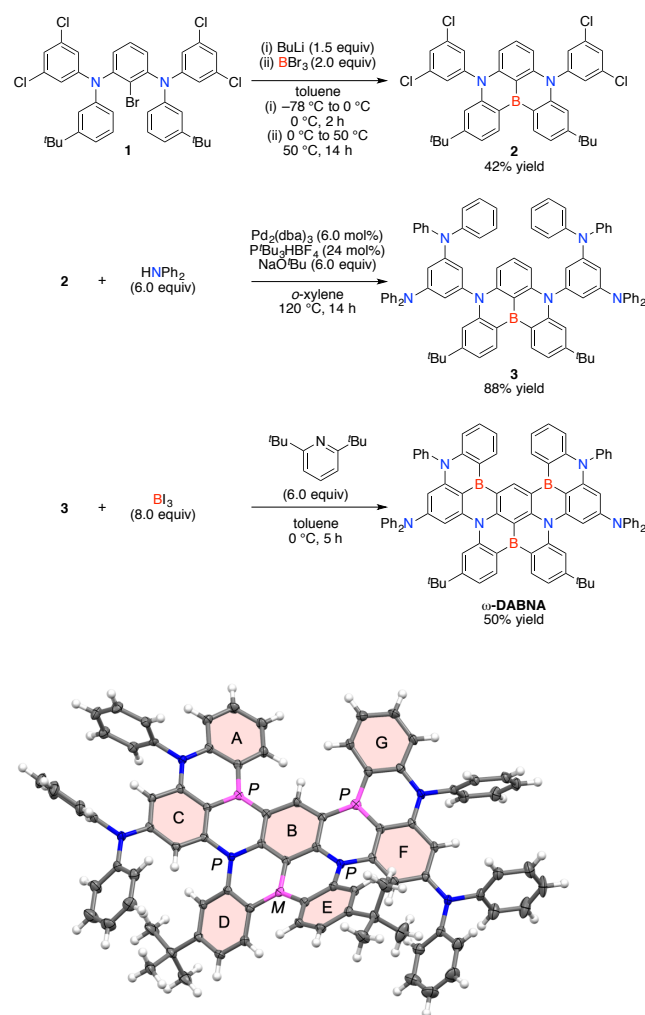


Figure 3. Molecular structure of **ω -DABNA** determined by single-crystal X-ray diffraction analysis (thermal ellipsoids are plotted for 50% probability). Chlorobenzenes incorporated as crystallization solvents have been omitted for clarity.

The synthesis of **ω -DABNA** by sequential multiple borylation is schematically shown in Scheme 1. Precursor **1**, bearing four chlorine atoms and one bromine atom, was prepared in two steps from a commercially available source by iterative Buchwald–Hartwig aminations (details in Supporting Information). The first key step, i.e., the one-pot borylation of **1**, was the construction of a DABNA skeleton bearing four chlorine atoms. The subsequent bora-Friedel-Crafts reaction using 2 equiv. of BBr_3 , i.e., the bromine-lithium exchange reaction of **1**, afforded DABNA derivative **2** bearing four chlorine atoms in 42% yield. The second key step, i.e., the introduction of four diphenylamino groups into **2**, was achieved by Buchwald–Hartwig amination with diphenylamine, affording **3** in 88% yield. The third key step is the one-shot borylation of **3**. Importantly, the HOMO of **3** was localized on the DABNA skeleton, and regioselective

borylation reactions were expected. Indeed, in the presence of 2,6-di-*tert*-butylpyridine, the double bora-Friedel-Crafts reaction of **3** using 8 equiv. of BI_3 afforded **ω -DABNA**, a novel MR-TADF material, in 50% yield. Notably, a significantly reduced yield (4%) was observed and a considerable amount of **3** (80%) was recovered without using 2,6-di-*tert*-butylpyridine (Eq. S1). This indicated that sterically hindered 2,6-di-*tert*-butylpyridine selectively captured *in situ* generated hydrogen iodide to promote borylation and suppress deborylation. The one-shot borylation of **3** using boron tribromide (BBr_3) was carried out at 180 °C to afford **ω -DABNA** in 23% yield (Eq. S2), which is lower than that under standard conditions (50%) due to the lower reactivity of BBr_3 .

The single-crystal X-ray diffraction analysis of **ω -DABNA** unequivocally revealed a highly twisted structure owing to the incorporation of the five [4]helicene moieties in the molecule (Figure 3). The A–B, C–D, D–E, E–F, and B–G angles between the least-squares planes of the rings at both termini of the [4]helicene moieties were 27.6°, 51.2°, 41.3°, 50.6°, and 26.3°, respectively. The helicities of these [4]helicene moieties were *P-P-M-P-P* and the other enantiomer with completely inverted helicities (*M-M-P-M-M*) was located adjacent to this enantiomer (Figure S3). Notably, the dihedral angle of the [4]helicene moieties between the planes of the terminal rings, especially the two nitrogen-center [4]helicene moieties (C–D and E–F) and the molecular center of the [4]helicene moiety (D–E), was much larger than that of pristine [4]helicene (26.7°).¹³ As a result, the entire molecule adopted a highly twisted structure, which is advantageous in preventing aggregation-induced quenching and increasing the efficiency of OLEDs.

The photophysical properties of **ω -DABNA** in a poly(methyl methacrylate) (PMMA) dispersion film (1 wt%) are shown in Figure 4. **ω -DABNA** exhibited an extremely sharp green emission at 509 nm with an FWHM of 22 nm (0.11 eV) and a high PLQY of 87%. In addition, the Stokes shift is extremely small (14 nm), which is in good agreement with the low reorganization energy (108 meV) calculated at the B3LYP/TZP level of theory. These desirable properties are attributed to the non-bonding character of the HOMO and LUMO, which completely suppresses the vibronic coupling between the S_1 – S_0 transition and the stretching/scissoring vibration. Based on the fluorescence and phosphorescence emission maxima (Figure 4b), ΔE_{ST} was determined to be 13 meV from the peak tops, which is significantly smaller than that of previously reported pure green MR-TADF emitters.¹⁴ This ΔE_{ST} value is smaller than the predicted value (39 meV), which is attributed to the negligence of the solvent effects and the simplified molecular structure according to the calculations. Transient spectra were recorded to investigate the TADF properties (Figure 4c). The transient decay curves showed two components, corresponding to prompt decay and delayed decay, with lifetimes of 5.92 ns and 8.95 μs ,

respectively. The rate constants of fluorescence (k_F), internal conversion (k_{IC}), intersystem crossing (k_{ISC}), and k_{RISC} were calculated based on the above-mentioned quantum yields and lifetimes.¹⁵ Notably, the k_{RISC} value of **ω -DABNA** was $1.2 \times 10^5 \text{ s}^{-1}$, which is consistent with the results of the TD-DFT calculations. Similar photophysical properties were observed for the 1 wt%

DOBNA-Ph doped film (Figure S5). Furthermore, the transient spectra at different temperatures showed that the TADF component decreased at lower temperatures (Figure S6). From the Arrhenius plots of $k_{RISC}T^{0.5}$ and $k_{ISC}T^{0.5}$ versus $1/T$, the activation energies for the RISC (ΔE_a^{RISC}) and ISC (ΔE_a^{ISC}) processes were estimated to be 14 and 15 meV, respectively.

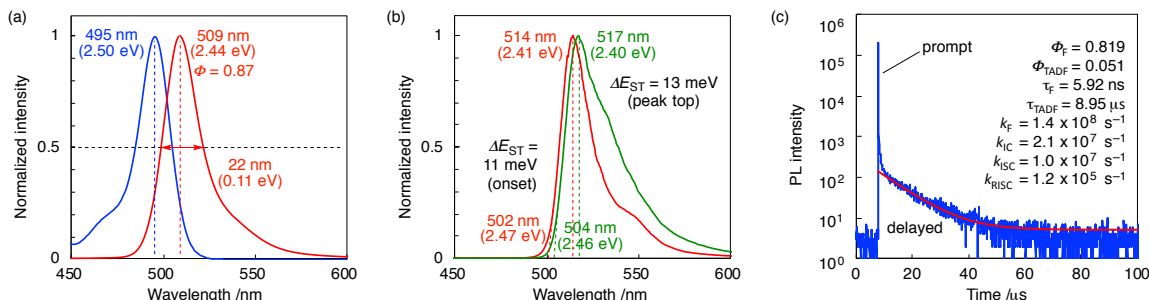


Figure 4. Photophysical properties of **ω -DABNA** in PMMA (1 wt% doped film). (a) Normalized absorption (blue, 300 K) and fluorescence (red, 300 K) spectra. (b) Fluorescence (red, 77 K) and phosphorescence (green, 77 K, 25-ms delay) spectra. (c) Transient decay spectrum at 300 K and its relevant parameters. The red curve shows the single exponential fitting (background = 5). Φ_F and Φ_{TADF} : quantum yields of the fluorescent and TADF components, respectively; τ_F and τ_{TADF} : lifetimes of the fluorescent and TADF components, respectively.

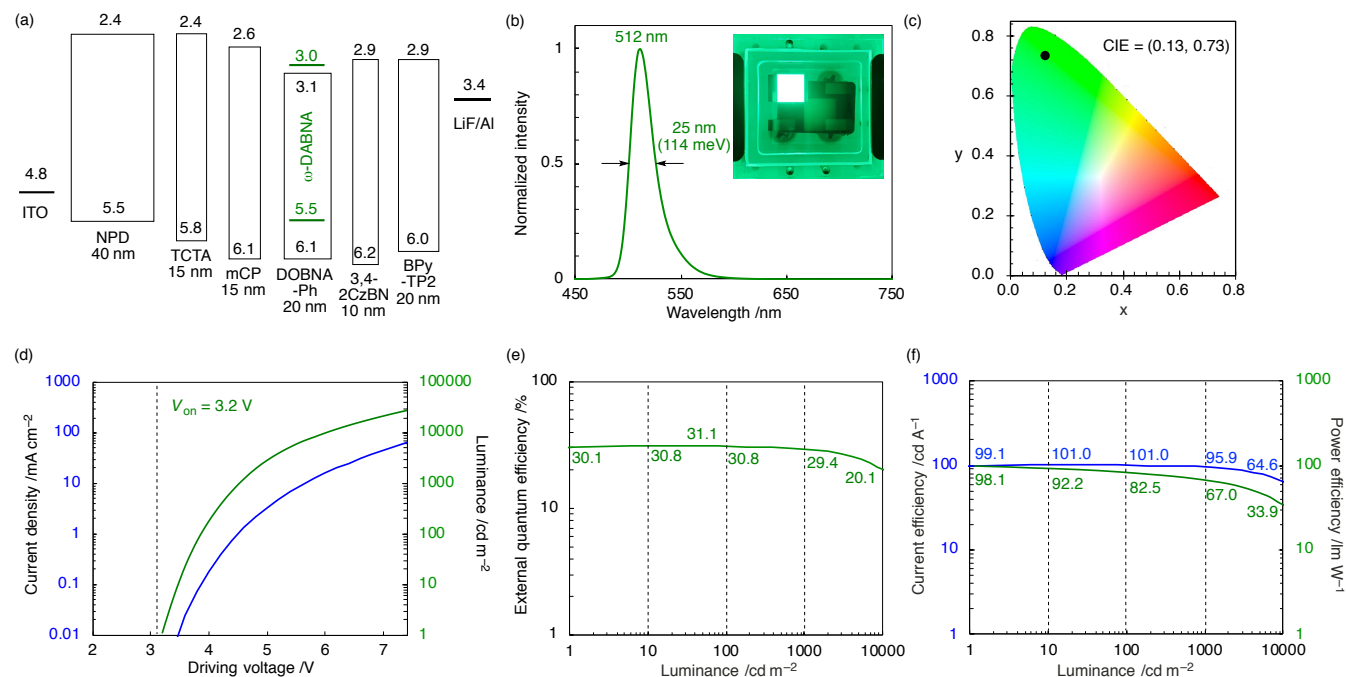


Figure 5. EL characteristics of OLED device fabricated with **ω -DABNA**. (a) Device structure with energy level diagram (in eV). (b) Normalized EL spectrum with a photograph of EL emission. (c) CIE(x,y) coordinates. (d) Current density (blue) and luminance (green) versus driving voltage. (e) EQE versus luminance. (f) CE (blue) and PE (green) versus luminance.

To demonstrate the potential utility of **ω -DABNA**, an OLED device employing **ω -DABNA** as an emitter was fabricated according to the following device structure: indium tin oxide (ITO, 50 nm), *N,N'*-di(1-naphthyl)-*N,N'*-

diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPD, 40 nm), tris(4-carbazolyl-9-ylphenyl)amine (TCTA, 15 nm), 1,3-bis(N-carbazolyl)benzene (mCP, 15 nm), 0.5 wt% **ω -DABNA-CN-Me** emitter, 99.5 wt% **DOBNA-Ph**^{2a} (20

nm), 3,4-di(9H-carbazol-9-yl)benzotrile (3,4-2CzBN,¹⁶ 10 nm), 2,7-bis(2,2'-bipyridine-5-yl)triphenylene (BPy-TP2,¹⁷ 20 nm), LiF (1 nm), and Al (100 nm). The EL characteristics are shown in Figure 5. The device exhibited pure green emission at 512 nm, with an FWHM of 25 nm and CIE coordinates of (0.13, 0.73), which are very close to the color space parameter (0.17, 0.80) of the primary green color in the BT.2020 standard, which is required for ultra-high-definition displays with a wide color gamut (Figure 5b and c). The device can be driven using voltages as low as 3.2 V (Figure 5d) and showed an excellent maximum external quantum efficiency (EQE) of 31.1% (Figure 5e). In addition, this device achieved satisfactory values for both current efficiency (CE) and power efficiency (PE) of 101.0 cd A⁻¹ and 98.1 lm W⁻¹, respectively (Figure 5f). Moreover, remarkably high EQE values of 29.4%, and 20.1% were achieved even at 1000 and 10000 cd m⁻², respectively. The small efficiency roll-off was especially noteworthy (1.4% and 10.7% at 1000 and 10000 cd m⁻², respectively). This is attributed to the use of **DOBNA-Ph** as a host material, which improved the carrier balance and enabled efficient charge recombination even at high luminance. The operational lifetime (LT₈₀) was 292 h at an initial luminance of 1000 cd m⁻² (Figure S10), which is relatively long among green MR-TADF OLED devices and could be further improved by using an assist dopant.¹⁸

In conclusion, herein we proposed sequential multiple borylation as a novel synthetic protocol for B,N-embedded MR-TADF materials. We synthesized **ω-DABNA** with five [4]helicene substructures using this protocol, and the obtained **ω-DABNA** exhibited narrowband green TADF with an FWHM of 22 nm and a small singlet–triplet energy gap of 13 meV. The OLED employing **ω-DABNA** as an emitter exhibited emission at 512 nm with an FWHM of 25 nm and CIE coordinates of (0.13, 0.73). Because of its high PLQY and high *k*_{RISC} value, a high maximum EQE of 31.1% and an extremely small efficiency roll-off (1.4% at 1000 cd m⁻²) were achieved. To the best of our knowledge, this is the best performance reported to date for any green MR-TADF emitter (Table S5). Thus, sequential multiple borylations can be useful for the further development of MR-TADF materials in unexplored chemical spaces.

ASSOCIATED CONTENT

Supporting Information

Synthesis, analytical data, NMR spectra, DFT studies, fabrication of OLED devices (PDF), and X-ray crystallography data (CIF). Supporting information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

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

Notes

The authors declare no competing financial interest.

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