

One-Shot Construction of BN-Embedded Heptadecacene Framework Exhibiting Ultra-Narrowband Green Thermally Activated Delayed Fluorescence

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Supporting Information Placeholder

ABSTRACT: BN-embedded nonacene, tridecacene, and heptadecacene frameworks were constructed using one-shot quadruple, sextuple, and octuple borylation reactions, respectively. The key to success is the judicious choice of borylating reagents and long-chain alkyl-substituted carbazolyl groups as boron-trapping groups, which suppressed the decrease in HOMO energy and insolubilization associated with borylation. Judging from the product yields, each electrophilic C–H borylation occurred in >99% yield, which is the best efficiency reported so far for C–H borylation reactions. Owing to the multiple resonance effects of boron and nitrogen, the prepared acenes exhibited ultra-narrowband green thermally activated delayed fluorescence with full-width at half-maximum of 12–16 nm; moreover, their k_{RISC} values were in the order of 10^5 s^{-1} . We fabricated an organic light-emitting diode by employing the nonacene as an emitter, which exhibited high external quantum efficiency (EQE) of 28.7%. The device also showed a minimum efficiency roll-off with an EQE of 25.8% at 1000 cd m^{-2} .

Organic light-emitting diodes (OLEDs) were first developed by Tang and VanSlyke;^[1] currently, they are essential components of commercial displays owing to their outstanding features, such as high contrast, design flexibility, lightweight, fast response times, and wide viewing angles. However, the power consumption and brightness of OLEDs have been far from the theoretical limit because fluorescent emitters only utilize singlet excitons. Therefore, in order for the utilization of triplet excitons to be efficient, intensive efforts have been devoted to develop phosphorescent and thermally activated delayed fluorescence (TADF) materials after the pioneering works by Forrest^[2] and Adachi^[3], respectively. However, because of the significant charge transfer (CT) character of their electronic excitations, such materials exhibit broader emission bands than those required for broadcasting standards, with a full width at half maximum (FWHM) of 50–100 nm. Therefore, a color filter and/or an optical microcavity is usually required to improve the color purity of the original electroluminescence (EL) spectra, which

subsequently leads to efficiency loss. To overcome this problem, we used the multiple-resonance (MR) effect of boron and nitrogen/oxygen atoms.^[4] Because of the resulting alternating HOMO-LUMO pattern, boron-based emitters have small singlet–triplet energy gaps (ΔE_{ST}) and exhibit TADF,^[5] enabling OLEDs to have an internal quantum efficiency of 100% via efficient reverse intersystem crossing (RISC). Furthermore, the resulting non-bonding frontier orbitals minimize the vibronic coupling between the electronic excitation and stretching vibrations^[6] to realize narrowband emission with an FWHM of <30 nm, as well as a high photoluminescence quantum yield (PLQY) of >90%. This phenomenon, which is known as “MR-TADF,” has been extensively used in the past few years.^[7] The most promising way to utilize the MR effect is to extend it to a fully resonating π -skeleton with multiple boron and nitrogen atoms.^[8] Therefore, we have developed the one-shot borylation reaction in our previous study,^[9] which involved inter- and intramolecular tandem bora-Friedel-Crafts reactions (electrophilic C–H borylation).^[10] However, the borylation reaction is accompanied by a decrease in HOMO energy and insolubilization of the resulting intermediate, and therefore only proceeds up to three times with one exception.^[9a]

Herein, we report quadruple, sextuple, and octuple borylation reactions, which were used to construct the largest MR-core structures comprising BN-embedded nonacene^[9], tridecacene, and heptadecacene frameworks, respectively (Figure 1, **CzB4**, **CzB6**, **CzB8**). This was achieved by carefully choosing the borylating reagents, boron triiodide combined with 2,6-di(*tert*-butyl)pyridine, and by using long-chain alkyl-substituted carbazolyl groups, which effectively capture boron atoms to counteract the decrease in HOMO energy associated with sequential borylation and solubilize the intermediates by interfering with π -stacking. Notably, the molecules exhibited extremely narrowband green TADF with an FWHM of 12–16 nm. The HOMO/LUMO spread over the large acene frameworks to reduce the exchange interaction and ΔE_{ST} . The k_{RISC} value increased with the framework expansion and reached $6.5 \times 10^5 \text{ s}^{-1}$. To demonstrate the usefulness of this protocol, we synthesized sterically protected nonacene (**CzB4-oPh**) and used it as

an emitter to fabricate an organic light-emitting diode (OLED); consequently, **CzB4-oPh** exhibited high color purity and external quantum efficiency.

Figure 2 summarizes the theoretical simulations of the sequential borylation of triarylamine-based precursors (model **A** and **B**). In the case of model **A**, the HOMO energy gradually decreases from -4.80 to -5.47 eV after the introduction of bromoboryl groups because of the resonance effect of the vacant 2p orbitals of boron atoms and the inductive effect of bromine atoms. In contrast, model **B** contains carbazolyl groups; therefore, the HOMO energy gradually increases from -5.02 to -4.77 eV after the introduction of boron atoms. This is because carbazolyl groups effectively expand π -conjugation by capturing boron atoms upon replacement of bromine atoms. These simulations clearly suggest that carbazolyl groups may enable the construction of larger acene frameworks by multiple borylation.

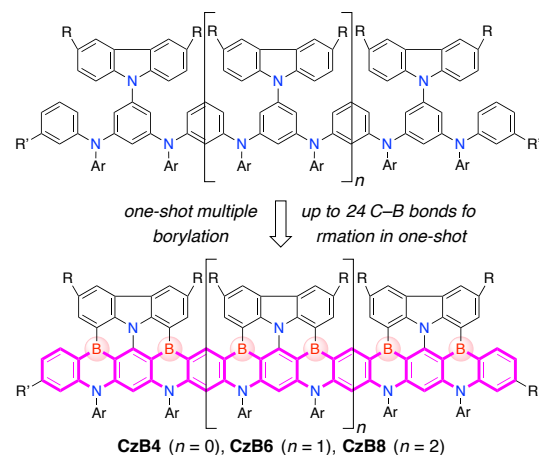


Figure 1. One-shot construction of BN-embedded large acene frameworks.

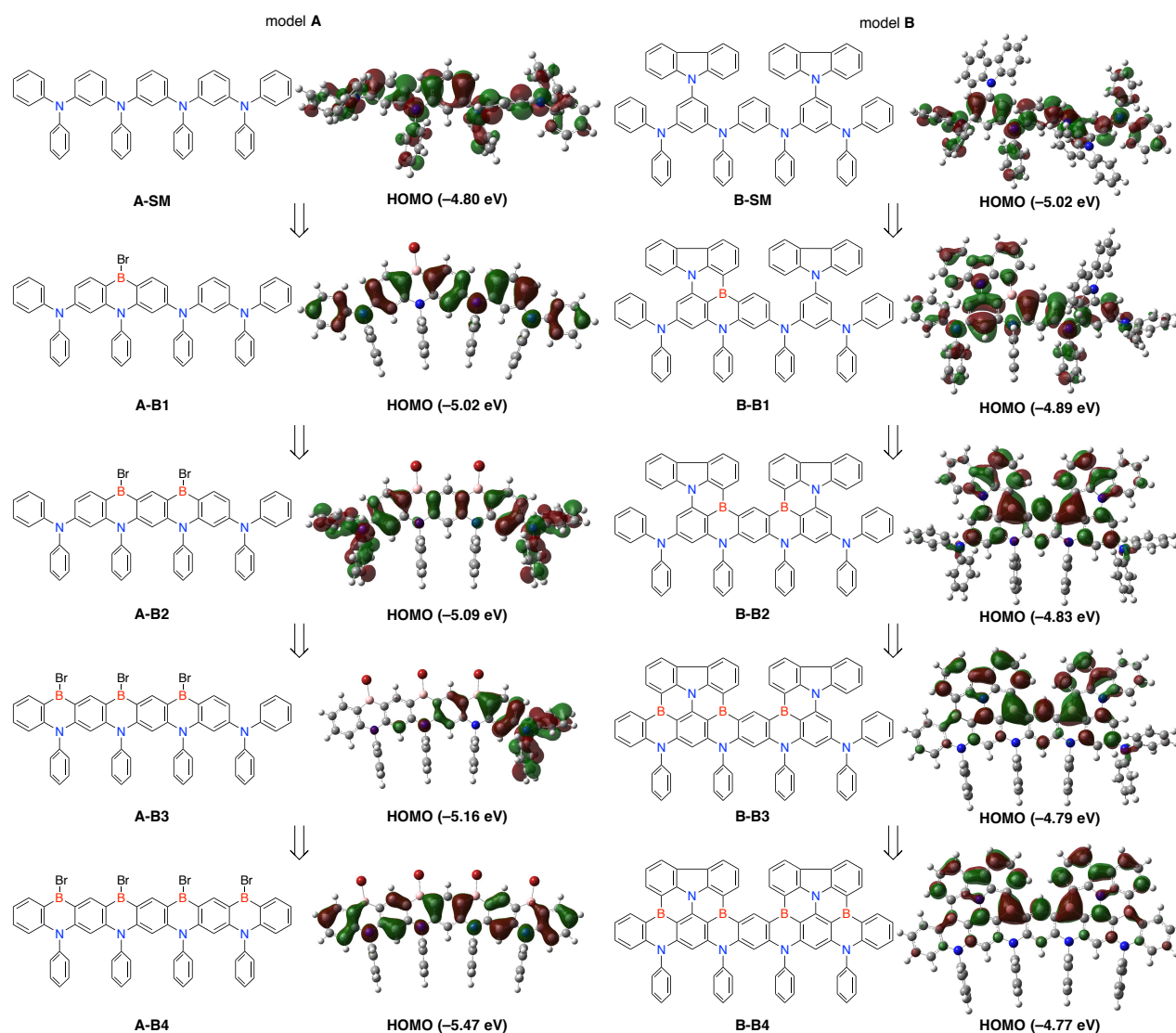


Figure 2. HOMO energies of model **A** and **B**, and borylated intermediates at the B3LYP/6-31G(d) level of theory.

To elucidate the effect of the expansion of acene framework on the TADF properties, double hybrid time-dependent density

functional theory (DH-TD-DFT)^[11] calculations were performed on model compounds with C_2 symmetry, namely **CzB4-**

core, **CzB6-core**, and **CzB8-core** (Figure 3). The S_0 – S_1 transition energies were 2.785, 2.732, and 2.699 eV with the oscillator strength (f) of 0.769, 2.233, 3.565, respectively, indicating red-shift emission. Based on the energy gap between S_1 and T_1 , the ΔE_{ST} of **CzB4-core**, **CzB6-core**, and **CzB8-core** were estimated to be 96, 66, and 8.1 meV, respectively. Moreover, the spin–orbit coupling (SOC) matrix elements of **CzB4-core**,

CzB6-core, and **CzB8-core** between the S_1 and T_1 states were 0.250, 0.339, and 0.344 cm^{-1} , respectively. Thus, an increase in the number of boron atoms resulted in larger f , smaller ΔE_{ST} , and larger SOC matrix elements, leading to the enhancement of a rate constant for reverse intersystem crossing (k_{RISC}) based on the following relationship: $k_{\text{RISC}} \propto \langle S_n | \hat{H}_{\text{SOC}} | T_n \rangle^2 / \Delta E_{ST}$.^[12]

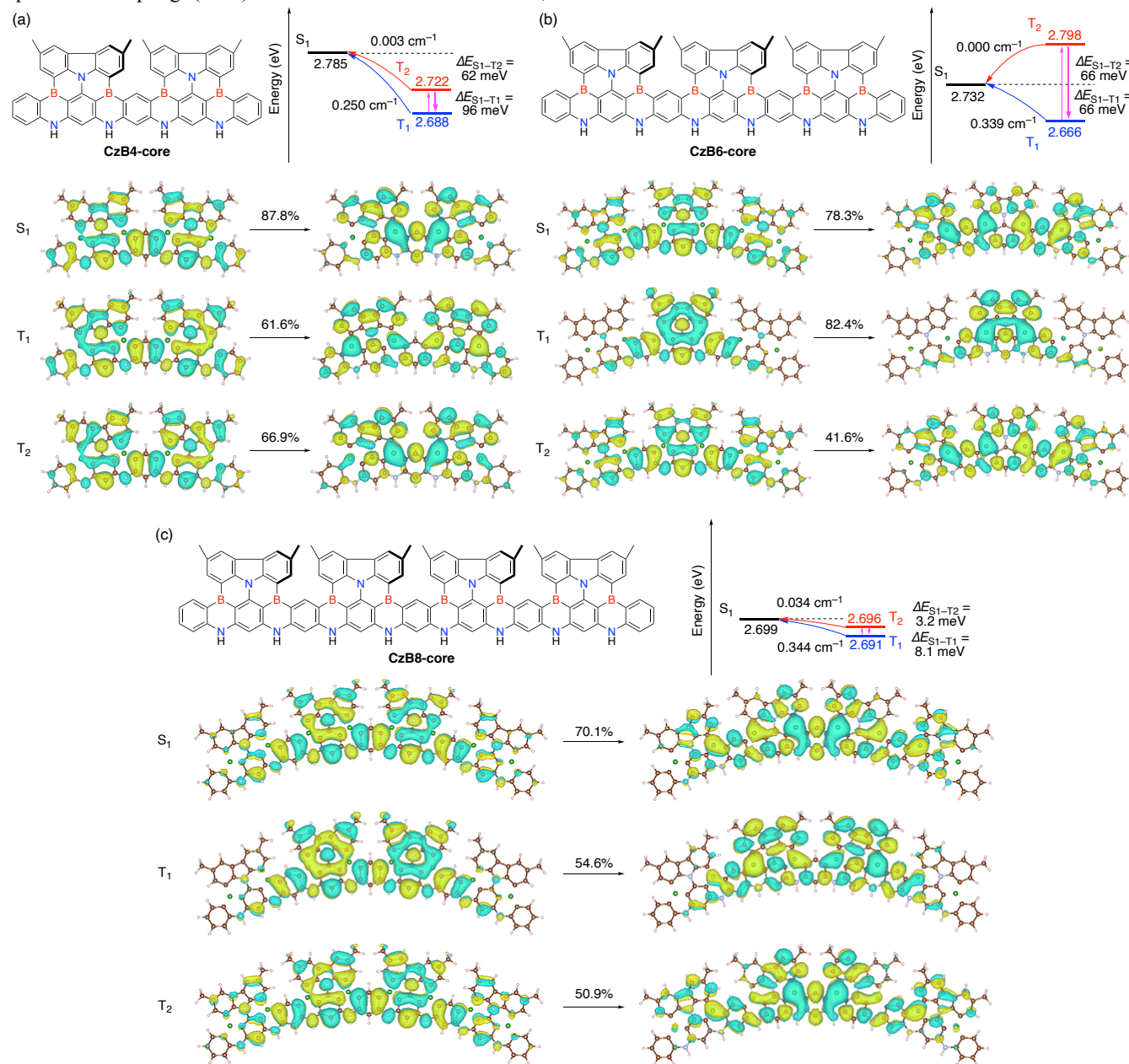


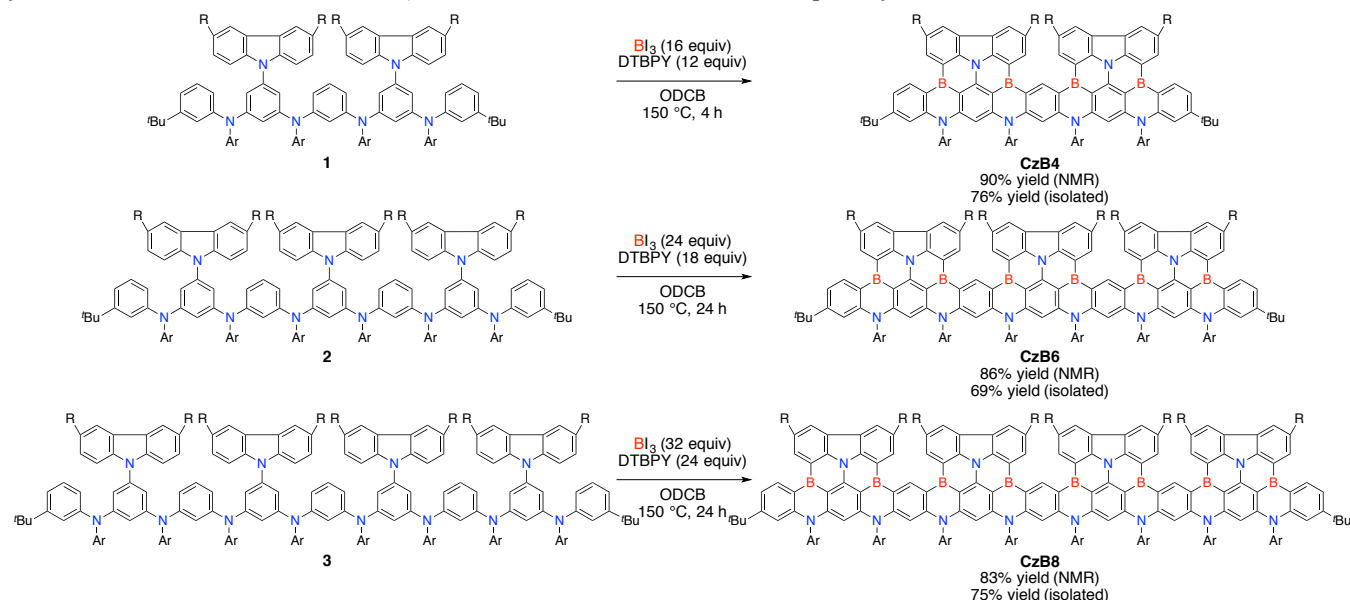
Figure 3. Molecular structure, energy level diagram, and associated natural transition orbitals (NTOs) for singlet and triplet excited states. (a) **CzB4-core**, (b) **CzB6-core**, and (c) **CzB8-core** at the T_1 geometry. Transition energies for S_1 , T_1 , and T_2 , NTOs, and SOC matrix elements between the T_n and S_n states were calculated at the TDA-B2PLYP($c_s=0.40$, $c_c=0.21$)/6-31G//B3LYP/DZP level of theory. The isomers with the largest SOC matrix elements between the S_1 and T_1 states are shown among the conformational isomers for **CzB6-core** and **CzB8-core** (Figures S1 and S2).

The synthesis of **CzBn** is shown in Scheme 1. To suppress the insolubilization associated with borylation, we designed precursors **1** and **2** possessing 2-ethylhexyl-substituted carbazolyl groups, which facilitated borylation and suppressed the insolubilization of the resulting intermediates. In addition, *tert*-butyl and 3,5-dimethylphenyl groups were introduced to prevent

undesired peripheral borylations. Precursors **1–3** were synthesized in 52–66% yield in five to seven steps from commercially available sources (Schemes S1–S3). In the presence of 16–32 equiv. of boron triiodide (BI_3) and 12–24 equiv of a bulky Brønsted base, 2,6-di(*tert*-butyl)pyridine (DTBPY), the one-shot multiple borylation of **1**, **2**, and **3** proceeded at 150 °C to

obtain **CzB4**, **CzB6**, and **CzB8** in 90%, 86%, and 83% yield, respectively. Notably, the efficiency for each C–H borylation was calculated to be >99%, which is among the highest efficiencies reported for borylation reactions.^[10,13] The isolated yields of **CzB4**, **CzB6**, and **CzB8** (76%, 69%, and 75%,

respectively) are not as high as the NMR yields because of the difficulty in removing the side products with similar molecular weights or polarities. However, the current protocol can significantly expand the chemical space of organoboron-based materials^[14], especially MR-TADF materials^[5].



Scheme 1. Synthesis of **CzB4**, **CzB6**, and **CzB8** (R = 2-ethylhexyl, Ar = 3,5-dimethylphenyl).

The photophysical properties of **CzB4**, **CzB6**, and **CzB8** in a polystyrene (PS) dispersion film (0.1 wt%) are shown in Figures 4a, c, e, and Table S1. The fluorescence maximum wavelengths of **CzB4**, **CzB6**, and **CzB8** were 483 nm, 488 nm, and 491 nm, respectively, which slightly red-shifted after the π -extension. These fluorescence emissions have extremely narrow FWHMs of 14 nm, 12 nm, and 12 nm, with high PLQYs (Φ) of 0.916, 0.940, and 0.922, respectively. Based on the low-temperature photoluminescence spectra of **CzB4**, **CzB6**, and **CzB8**, their ΔE_{ST} were determined to be 12 meV, 21 meV, and 3.9 meV from the onset (4.2 meV, 3.1 meV, and 3.0 meV from the peak tops) shown in Figures 4a, 4c, and 4e, respectively. These significant small ΔE_{ST} values can be attributed to the effectively spread HOMO/LUMO orbitals over the large acene skeletons (Figures S3–S5). To evaluate the TADF properties, the transient spectra were measured (Figures 4b, 4d, 4f, and S8–S10). The transient decay curves of **CzB4**, **CzB6**, and **CzB8** showed two components corresponding to prompt lifetimes of 5.3 ns, 3.3 ns, and 3.1 ns, respectively, and delayed lifetimes of 5.0 μ s, 2.9 μ s, and 1.4 μ s, respectively. Based on the above quantum yields and lifetimes, the radiative decay rate constants of fluorescence (k_F), intersystem crossing (k_{ISC}), and reverse intersystem crossing (k_{RISC}) were determined as per Adachi's method (Tables 1 and S3).^[15,16] Notably, the larger the acene skeleton resulted in the higher the k_{RISC} values, which reached up to $6.5 \times 10^5 \text{ s}^{-1}$ for **CzB8**. As per our theoretical calculations and spectroscopic results, this relatively high k_{RISC} value should be attributed to the extremely small ΔE_{ST} value (3.9–21 meV). The spectroscopic measurements of these compounds in organic solution showed results similar to those of the PS dispersion films (Figure S7).

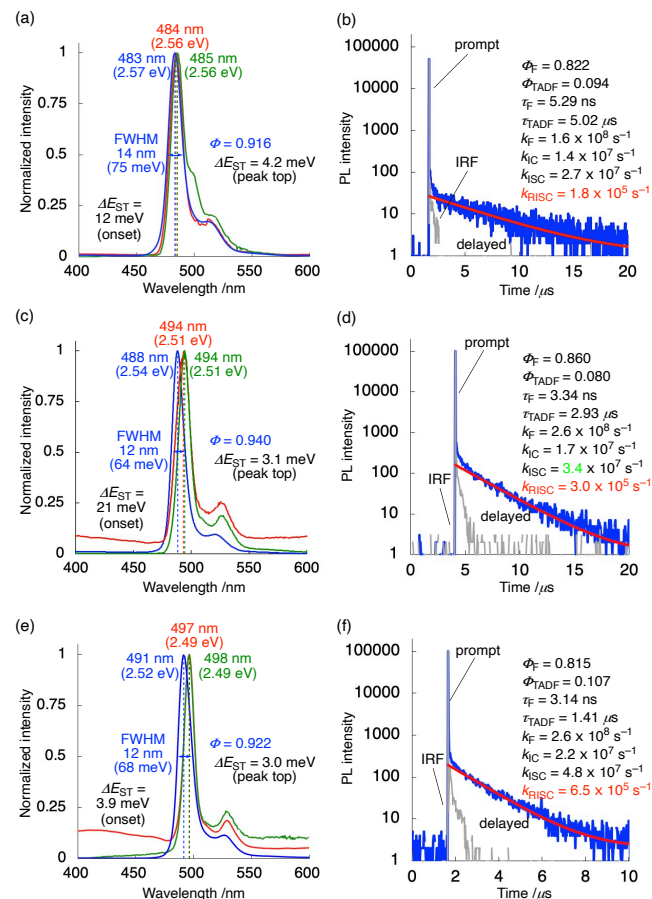


Figure 4. Photophysical properties of **CzB4** (a,b), **CzB6** (c,d), and **CzB8** (e,f). (a, c, e) Normalized fluorescence (blue, 300 K; red, 77 K) and phosphorescence (green, 77 K, 25 μ sec delay) spectra of the 0.1 wt%-doped PS films of the three compounds with

absorption/emission maxima (nm, eV), absolute fluorescence quantum yield (Φ), full width at half maximum (nm, eV), and energy gap between the S_1 and T_1 states (ΔE_{ST} , meV). (b, d, f) Transient decay spectrum at 300 K and its relevant parameters. The red curve shows the single exponential fitting (background = 5). The gray line shows the instrument response function (IRF). Φ_F and Φ_{TADF} indicate quantum yields of the fluorescent and TADF components, respectively; τ_F and τ_{TADF} indicate the lifetimes of the fluorescent and TADF components, respectively.

Table 1. Summary of Photophysical Data of 0.1 wt%-doped PS Films of CzBn Derivatives.

compound	Φ^a [%]	Φ_F^b [%]	Φ_{TADF}^c [%]	τ_F^d [ns]	τ_{TADF}^e [μ s]	k_F^f [10^7 s $^{-1}$]	k_{IC}^f [10^7 s $^{-1}$]	k_{ISC}^f [10^7 s $^{-1}$]	k_{RISC}^f [10^5 s $^{-1}$]
CzB4	91.6	82.2	9.40	5.29	5.02	16	1.4	2.7	1.8
CzB6	94.0	86.0	8.00	3.34	2.93	26	1.7	3.4	3.0
CzB8	92.2	81.5	10.7	3.14	1.41	26	2.2	4.8	6.5
CzB4-oPh	92.5	77.7	14.8	5.24	16.0	15	1.2	3.7	0.64

^aAbsolute photoluminescence quantum yield. ^bQuantum yield of fluorescent (prompt) component. ^cQuantum yield of TADF (delay) component. ^dLifetime of fluorescent (prompt) component. ^eLifetime of TADF (delay) component. ^f k_F , k_{IC} , k_{ISC} , k_{RISC} are rate constants for fluorescence, internal conversion, intersystem crossing and reverse intersystem crossing, respectively. These values were calculated by the method in ref [15] and corrected by the method in ref [16].

Although **CzB4**, **CzB6**, and **CzB8** exhibited enhanced photophysical characteristics as emitters, we were unable to fabricate OLED devices using these compounds by vapor deposition due to their large molecular weight. Therefore, we synthesized a new nonacene derivative, **CzB4-oPh**, to demonstrate the usefulness of this synthetic protocol and used it to develop an OLED emitter (Figure 5a). The structure design of **CzB4-oPh** consists of the following steps: (1) 2-ethylhexyl groups were replaced with methyl groups to reduce the molecular weight and sublimation temperature, and (2) 3,5-dimethylphenyl groups on the nitrogen atoms were replaced with large steric *o*-biphenyl groups to disrupt the intermolecular π - π interaction for maintaining superior photophysical properties and ensuring solubility. Similar to the case of **CzBn**, **CzB4-oPh** was synthesized by the one-shot quadruple borylation of the corresponding precursor (Scheme S4) in 54% isolated yield as a mixture of *syn*- and *anti*- isomers with different configurations of two *o*-diphenyl groups. The photophysical properties of **CzB4-oPh** in the PS dispersion film (0.1 wt%) were evaluated (Figure 5b). The fluorescence maximum wavelength of **CzB4-oPh** is 478 nm, which is slightly blue-shifted than that of **CzB4**. The FWHM and Φ of **CzB4-oPh** are 16 nm and 0.925 respectively, which are comparable to those of **CzB4**. Based on the fluorescence and phosphorescence emission maxima of **CzB4-oPh** (Figure 5b), its ΔE_{ST} was determined to be 19 meV from the onset (87 meV from peak tops), which is slightly higher than that of **CzB4** (12 meV from onset). The transient decay curves of **CzB4-oPh** also showed two components, which corresponded to prompt decay with a lifetime of 5.2 ns and delayed decay with a lifetime of 16.0 μ s (Figure 5c). Based on the above quantum yields and lifetimes, k_F , k_{ISC} , and k_{RISC} were determined. The k_{RISC} value of **CzB4-oPh** (6.4×10^4) is smaller than that of **CzB4** (1.8×10^5), which is attributed to the larger ΔE_{ST} of **CzB4-oPh**.

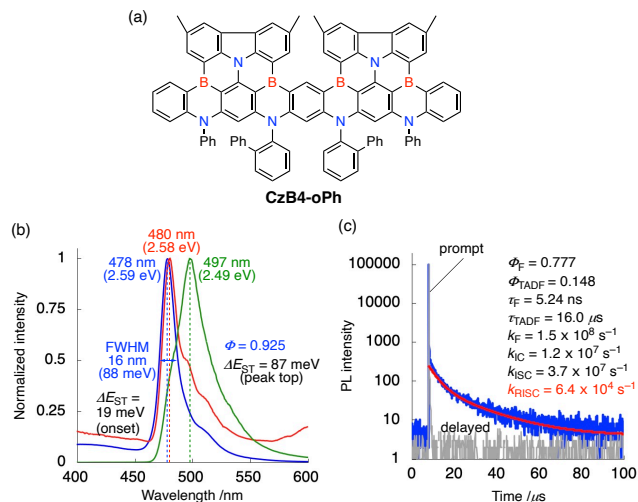


Figure 5. (a) Molecular structure of **CzB4-oPh**. (b) Normalized fluorescence (blue, 300 K; red, 77 K) and phosphorescence (green, 77 K, 25 μ s delay) spectra of 0.1 wt%-doped PS films of **CzB4-oPh** with absorption/emission maxima (nm, eV), absolute fluorescence quantum yield (Φ), full width at half maximum (nm, eV), and energy gap between the S_1 and T_1 states (ΔE_{ST} , meV). (c) Transient decay spectrum of 0.1 wt%-doped PS films of **CzB4-oPh** at 300 K and its relevant parameters. The red curve shows the single exponential fitting (background = 5). The gray line shows the instrument response function (IRF). Φ_F and Φ_{TADF} indicate quantum yields of the fluorescent and TADF components, respectively; τ_F and τ_{TADF} indicate lifetimes of the fluorescent and TADF components, respectively.

To demonstrate the potential utility of the **CzBn** series as emitters for OLED, we fabricated an OLED device employing **CzB4-oPh** as an emitter according to the following device structure (Figure 6): 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), 1.0 wt% **CzB4-oPh** emitter, 99.0 wt% DOBNA-Ph^[4a] (20 nm), 3,4-di(9*H*-carbazol-9-yl)benzotrile (3,4-2CzBN,^[17] 10 nm), 2,7-bis(2,2'-bipyridine-5-yl)triphenylene (BPy-TP2,^[18] 20 nm), LiF (1 nm), and Al (100 nm). The EL characteristics of the device exhibited ultra-narrowband green emission at 490 nm with an FWHM of 21 nm (Figure 6b) and corresponding Commission International de l'Éclairage (CIE) coordinates of (0.09, 0.45) (Figure 6c). In addition, the device could be operated at 3.2 V (Figure 6d) and showed a high maximum external quantum efficiency (EQE) of 28.7% (Figure 6e). Furthermore, the device showed a current efficiency of 55.0 cd A $^{-1}$ and 50.8 cd A $^{-1}$, and a power efficiency of 44.0 lm W $^{-1}$ and 33.8 lm W $^{-1}$ at 100 cd m $^{-2}$ and 1000 cd m $^{-2}$, respectively (Figure 6f). The operational lifetime (LT80) was 43 h at an initial luminance of 1000 cd m $^{-2}$ (Figure S14). Notably, the high EQE is maintained even with increasing luminance, and the EQE values of 27.8% and 25.8% were achieved at 100 cd m $^{-2}$ and 1000 cd m $^{-2}$, respectively (Figure 6e). Furthermore, the orientational order parameter (*S*) was determined to be -0.226 (Figure S13), which is not comparable to those of the latest MR-TADF emitters due to its moderate planarity.^[7b,7h] Therefore, further improvement of EQE is expected by optimizing substituents. These results demonstrate the usefulness of BN-embedded higher-order acenes as TADF materials.

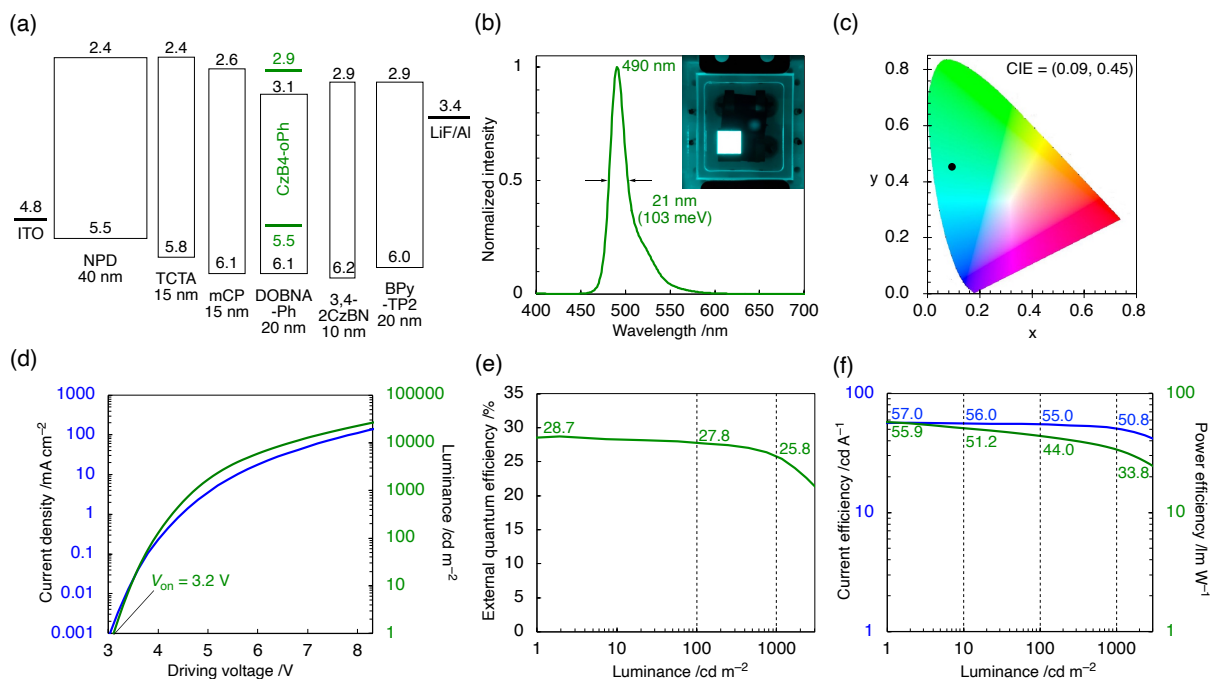


Figure 6. EL characteristics of OLED device fabricated with **CzB4-oPh**. (a) Device structure with energy level diagram (in eV). (b) Normalized EL spectrum with a photograph of EL emission. Inset: electroluminescence of the device. (c) CIE(x,y) coordinates. (d) Current density (blue) and luminance (green) versus driving voltage. (e) EQE versus luminance. (f) CE (blue) and PE (green) versus luminance.

In conclusion, we successfully synthesized **CzB4**, **CzB6**, **CzB8**, and **CzB4-oPh**, consisting of BN-embedded higher-order acene frameworks. Unprecedented multiple borylations were carried out up to eight times by using boron triiodide as the borylating reagents and appropriate precursors. Judging from the product yields, each electrophilic C–H borylation occurred in >99% yield, which is the best efficiency reported so far for C–H borylation reactions. The obtained **CzBn** series exhibited ultra-narrowband TADF (FWHM of 12–16 nm) with high PLQY (0.916–0.940). In addition, the framework expansion of the acene leads to improvements in ΔE_{ST} and k_{RISC} , reaching 3.9 meV and $6.5 \times 10^5 \text{ s}^{-1}$, respectively, for **CzB8**. The OLED employing **CzB4-oPh** as an emitter exhibited emission at 490 nm with an FWHM of 21 nm and CIE coordinates of (0.09, 0.45). The fabricated OLED device showed a high maximum EQE of 28.7% and a small efficiency roll-off (2.9% at 1000 cd m⁻²), which were attributed to its high PLQY and high k_{RISC} value. The **CzBn** compounds are the largest MR-TADF core structures reported so far, and the present protocol will significantly expand the chemical space of MR-TADF materials and pave the way for the controlled synthesis of BN-embedded nanocarbons.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details include synthesis, DFT studies, and fabrication of OLED devices and NMR spectra for newly synthesized compounds (PDF).

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