# ORGANOMETALLICS

# BN-Heterocycles Bearing Two BN Units: Influence of the Linker and the Location of BN Units on Electronic Properties and Photoreactivity

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S Supporting Information

ABSTRACT: Four diboron BN-heterocycles bearing two BN units have been synthesized via double lithiation/borylation with the aim to examine their thermal and photoelimination properties. In two of the BN-heterocycles, (BN)<sub>2</sub>-1 and (BN)<sub>2</sub>-4, the BN units share the central linker unit, while the other two BN-heterocycles (BN)<sub>2</sub>-2 and (BN)<sub>2</sub>-3 are isomers with a benzene ring in the middle of the backbone separating the two chelate units. Only compound (BN)<sub>2</sub>-3 can thermally and photochemically undergo complete double elimination producing green fluorescent  $(BN)_2$ -3a due to the highly crowded boron centers.  $(BN)_2$ -2 can partially convert (~56%)



to  $(BN)_2$ -2a under 350 nm UV irradiation.  $(BN)_2$ -1 and  $(BN)_2$ -4 are either inactive or unstable toward photolysis. The molecular structures and electronic properties of these (BN)2-heterocycles have been investigated experimentally as well as computationally using TD-DFT to further elucidate the origin of differences in optical and electronic properties.

# INTRODUCTION

The incorporation of BN units into arenes has attracted growing attention<sup>1</sup> due to the unique optical and electronic properties of the resulting BN-arenes which have a number of potential applications such as optoelectronic materials<sup>2</sup> and sensors.<sup>3</sup> Particularly, replacing a C-C unit by a BN unit in conjugated systems can lead to a lower LUMO energy and improved electron affinity, which enhances election transport.4,5 Our group recently found that nonconjugated BNheterocycles could undergo thermal and photoeliminations to generate highly fluorescent azaborines/BN-arenes.<sup>6</sup> We also reported double elimination of (BN)2-pyrene driven by excitons (EDE) generated electrically within electroluminescent (EL) devices, forming rare yellow fluorescent (BN)2-pyrenes that contain two BN units7 (Scheme 1). In addition, the BNheterocyclic precursor compounds are important and interesting in their own right because a number of closely related compounds have been demonstrated to be good electron acceptors in devices such as organic photovoltaics (OPV).<sup>5</sup> Therefore, we have been very interested in further exploring the chemistry and applications of this class of compounds. To further our investigation on photoresponsive boron-containing compounds, we extended the study to new BN-heterocycles (BN)<sub>2</sub>-1, (BN)<sub>2</sub>-2, (BN)<sub>2</sub>-3, and (BN)<sub>2</sub>-4 (Scheme 1) that contain two BN units and investigated their thermal and phototransformations. The aim of this work is to determine the influence of the location and the number of BN units within the heterocyclic skeleton on the electronic structure and the

Scheme 1. Examples of BN-Heterocycles Investigated for Elimination Reactions Stimulated by Heat and Light/ Excitons



photophysical/photochemical properties of this class of compounds.

Aside from different locations of the BN units, the other key difference of these four compounds is the linking unit: In  $(BN)_2$ -1 and  $(BN)_2$ -4, the boron units are fused with the linker,

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while in  $(BN)_2$ -2 and  $(BN)_2$ -3 they are separated by a phenyl ring. In addition, TD-DFT calculation data predicts that the optical energy gap of the double elimination products follows the order of  $(BN)_2$ -1a  $(1.74 \text{ eV}) < (BN)_2$ -4a  $(2.69 \text{ eV}) < (BN)_2$ -3a (2.78 eV) and  $(BN)_2$ -2a (2.82 eV)  $((BN)_2$ -1a represents the expected double elimination product of  $(BN)_2$ -1, and so forth), making it interesting to examine and compare this group of compounds if it were possible to produce them via double elimination. However, unlike the previously reported monoboron and diboron compounds shown in Scheme 1 that all undergo photoelimination, only  $(BN)_2$ -2 and  $(BN)_2$ -3 among the new diboron compounds were found to undergo photoelimination. The details are presented herein.

# RESULTS AND DISCUSSION

**Syntheses and Structures.** The ligands N2-1, N2-2, and N2-3 were synthesized by double Suzuki coupling of diboronic acid or boronic pinacol ester and corresponding bromoprecursors, while ligand N2-4 was prepared by the condensation reaction of ethanebis(thioamide) with 2-methylbenzaldehyde (see the Experimental Section and Supporting Information). Compounds (BN)<sub>2</sub>-1, (BN)<sub>2</sub>-2, and (BN)<sub>2</sub>-3 were synthesized in good yields using the procedure shown in Scheme 2 which involves double lithiation using <sup>t</sup>BuLi, followed

#### Scheme 2. Synthetic Procedures



by the addition of 3 equiv of Mes<sub>2</sub>BF reagent.<sup>5</sup> The double lithiation/borylation only succeeds when <sup>t</sup>BuLi was used as lithiation reagent in diethyl ether solution rather than <sup>n</sup>BuLi/ TEMDA in THF solution. The *n*-heptyl group was introduced to improve the solubility of the ligands as well as the final (BN)<sub>2</sub>-heterocyles. (BN)<sub>2</sub>-4 can only be obtained in low yield from the reaction of N2-4 with 2.5 equiv of LDA at -78 °C, followed by the addition of 2.5 equiv of Mes<sub>2</sub>BF. All (BN)<sub>2</sub>heterocyles were fully identified and characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B NMR, and HRMS. Furthermore, single crystals suitable for X-ray diffraction analysis were obtained for (BN)<sub>2</sub>-2, (BN)<sub>2</sub>-3, and (BN)<sub>2</sub>-4.

The crystal structures of  $(BN)_2$ -2,  $(BN)_2$ -3, and  $(BN)_2$ -4 are shown in Figures 1–3, respectively. All three compounds possess a crytallographically imposed inversion center. Compounds  $(BN)_2$ -2 and  $(BN)_2$ -3 are isomers. For  $(BN)_2$ -2, the pyridyl rings are the outermost ring, while for  $(BN)_2$ -3 the benzyl rings are the outermost. As a result of the location difference of the pyridyl, benzyl ring, and the heptyl substituents,  $(BN)_2$ -3 is sterically much more congested than



**Figure 1.** Crystal structure of  $(BN)_2$ -2: top view and side view (the 5 linked aryl rings are shown in red) with 35% ellipsoid. Important bond lengths (Å): B(1)-N(1) 1.646(6), B(1)-C(1) 1.657(6), B(1)-C<sub>Mes</sub> 1.655(6)/1.666(7).



**Figure 2.** Crystal structure of  $(BN)_2$ -3: top view and side view (the 5 linked aryl rings are shown in red) with 35% ellipsoid. Important bond lengths (Å): B(1)-N(1) 1.683(3), B(1)-C(1) 1.641(3), B(1)-C<sub>Mes</sub> 1.654(3)/1.655(3).



Figure 3. Crystal structure of  $(BN)_2$ -4: top view and side view (the 5 linked aryl rings are shown in red) with 35% ellipsoid. Important bond lengths (Å): B(1)-N(1) 1.653(2), B(1)-C(1) 1.645(2), B(1)-C<sub>Mes</sub> 1.651(2)/1.656(2).

 $(BN)_2$ -2. As shown by the side view in Figures 1 and 2, the five aryl rings in the backbone of  $(BN)_2$ -2 are essentially coplanar with the largest torsion angle between these rings being 20°. In contrast, the five aryl rings in  $(BN)_2$ -3 are significantly out of coplanarity with the torsion angle between the central benzene ring and the pyridyl ring being 44°. In addition, the B–N bond in  $(BN)_2$ -3 (1.683(3) Å) is much longer than that in  $(BN)_2$ -2 (1.646(6) Å), again a consequence of the greater steric congestion in  $(BN)_2$ -3. This structural difference has a significant impact on the electronic properties of these two

isomeric molecules, which will be discussed in next section. The aryl rings of the backbone in  $(BN)_2$ -4 have a good coplanarity with the torsion angle between the benzene ring and the fused bis-thiazole ring being 18°.

**Electronic Properties.** All four  $(BN)_2$ -heterocycles possess strong absorption bands between 300 and 480 nm as shown in Figure 4 and Table 1. Compound  $(BN)_2$ -1 has a low energy



Figure 4. UV/vis spectra of  $(BN)_2$ -1,  $(BN)_2$ -2,  $(BN)_2$ -3, and  $(BN)_2$ -4 in THF (1.0 × 10<sup>-5</sup> M).

absorption band at ~394 nm. As structural isomers, the absorption bands of (BN)2-3 are hypsochromically shifted by ~20 nm compared to  $(BN)_2$ -2, which agrees with the greater coplanarity, hence better extended  $\pi$ -conjugation of the backbone in  $(BN)_2$ -2, as revealed by the crystal structures. Furthermore,  $(BN)_2$ -2 has a much bigger extinction coefficient at the low energy absorption band ( $\varepsilon = 3.98 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\lambda$ = 359 nm) than that of  $(BN)_2$ -3 ( $\varepsilon$  = 2.21 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> at 340 nm). These all support that the steric congestion has a great impact on the electronic properties of isomeric structures. Among the four BN-heterocycles,  $(BN)_2$ -4 has the most bathochromically shifted absorption band with the absorption edge at ~475 nm, followed by  $(BN)_2$ -1 which has the absorption edge at ~450 nm. The sharing of the same central chelate unit by the two BMes<sub>2</sub> units in  $(BN)_2$ -1 and  $(BN)_2$ -4 clearly is more effective in lowering the energy of the absorption edge than the insertion of the benzene linker to extend the  $\pi$ -conjugation in  $(BN)_2$ -1 and  $(BN)_2$ -4, which can be attributed to the effective conjugation and better coplanarity of the backbone in the former. Compounds  $(BN)_2-1-(BN)_2-4$ are not fluorescent.

The electrochemical data revealed that the four BNheterocycles  $(BN)_2$ -1- $(BN)_2$ -4 display the characteristic oneelectron reduction peak at  $E_{\rm red} = -2.11$ , -2.18, -2.33, and

-1.68 V, respectively (relative to FcH/FcH<sup>+</sup>, Table 1 and Supporting Information). The electrochemical data indicate that compound  $(BN)_2$ -4 is likely a good electron acceptor for organic devices such as photovoltaics due to its deep LUMO (-3.12 eV), which will be examined in a future study. To understand UV/vis spectral difference and electrochemical data, TD-DFT calculations were performed at the B3LYP/6-31g(d) level of theory on the optimized geometries of all four BNheterocycles.<sup>8</sup> In addition, we also performed DFT calculations for N2-1-N2-3 in order to compare the change of HOMO/ LUMO energy levels between ligands N2-1-N2-3 and corresponding  $(BN)_2$ -1- $(BN)_2$ -3. After boron chelation, the HOMO levels of these three BN-heterocycles are raised by about 0.57 eV, while their LUMO levels are stabilized by up to 1.09 eV, supporting the idea that embedding the boron chelate units into heterocycles can enhance the electron affinity of the molecule and reduce the HOMO-LUMO gap, in agreement with the general trend observed for previously reported boronchelate compounds.<sup>4,5</sup> On the basis of the DFT data, the low energy absorption band of  $(BN)_2$ -1– $(BN)_2$ -4 can be assigned to a mesityl  $\rightarrow$  backbone charge transfer (CT) transition. The calculated absorption spectral patterns and the trend of the first symmetry allowed vertical excitation energy for (BN)2-1- $(BN)_2$ -4 match approximately with the experimental data as shown in Table 1 (and the Supporting Information). The main deviation is the HOMO and LUMO energies of (BN)<sub>2</sub>-4 that are much higher than the experimental values. Since the reduction potential of  $(BN)_2$ -4 was determined in DMF due to its low solubility, the inconsistency between the experimentally observed redox trend and the calculated one may be due to solvent effects which were not accounted for in TD-DFT calculations. For (BN)<sub>2</sub>-2 and (BN)<sub>2</sub>-3, the TD-DFT calculated values change significantly with the dihedral angles between the central benzene ring and its neighboring rings in the backbone. The data shown in Table 1 for these two molecules are based on crystal structural parameters which were further optimized by DFT. In the optimized structure of  $(BN)_2$ -2, the central benzene ring has a much larger dihedral angle with its neighboring rings than that observed in the crystal structure, leading to its calculated optical energy gap being similar to that of  $(BN)_{2}-2$ .

**Thermal and Photoreactivity.** To establish if  $(BN)_2$ heterocycles  $(BN)_2$ -1,  $(BN)_2$ -2,  $(BN)_2$ -3, and  $(BN)_2$ -4 can act as precursors for the generation of double BN-doped fully  $\pi$ conjugated systems, their thermal and photoreactivity were examined and summarized in Scheme 3. Upon irradiation with 350 nm UV light, the  $C_6D_6$  solution of all four compounds gradually become fluorescent and displayed distinct fluorescent colors (Scheme 3). However, when these photoreactions were monitored by <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy, only  $(BN)_2$ -3 eliminates two mesitylene molecules cleanly and produces a

Table 1. Electrochemical and Photophysical Properties of (BN)<sub>2</sub>-Heterocycles

compd	$E_{\rm red}$ (V) <sup><i>a</i></sup>	$\lambda_{\rm abs} \ (\varepsilon, \ 10^4 \ { m M}^{-1} \ { m cm}^{-1}) \ { m (nm)}^b$	optical gap Exp/DFT (nm) <sup>c</sup>	HOMO $Exp/DFT (eV)^d$	LUMO Exp/DFT (eV) <sup>e</sup>
$(BN)_{2}-1$	-2.11	394 (0.70)	450/454	-5.48/-5.19	-2.69/-2.15
$(BN)_{2}-2$	-2.18	359 (3.98)	420/445	-5.64/-5.26	-2.62/-1.94
$(BN)_{2}-3$	-2.33	340 (2.21)	400/445	-5.69/-5.33	-2.47/-1.99
$(BN)_{2}-4$	-1.68	402 (2.03)	475/470	-5.73/-5.18	-3.12/-2.59

"Relative to FcH/FcH<sup>+</sup> recorded in THF for  $(BN)_2$ -1– $(BN)_2$ -3 and in DMF for  $(BN)_2$ -4 with  $[Bu_4N][PF_6]$  as the electrolyte. <sup>b</sup>10<sup>-5</sup> M in THF at 298 K. <sup>c</sup>The experimental value is from the absorption edge, and the DFT value is from the first symmetry allowed vertical excitation. <sup>d</sup>Calculated using to absorption edge and reduction potential. <sup>e</sup>Estimated from the reduction potential.

Scheme 3. Thermal and Photoreactivity of  $(BN)_2$ -1,  $(BN)_2$ -2,  $(BN)_2$ -3, and  $(BN)_2$ -4



new diazaborine,  $(BN)_2$ -3a in ~90% yield.  $(BN)_2$ -2 only undergoes partial conversion ( $\sim$ 56%) to (BN)<sub>2</sub>-2a along with the formation of an unidentified product under 350 nm. Irradiation of (BN)2-1 generated unidentifiable species with orange color and bright yellow emission. (BN)2-4's behavior appears to be similar to that of  $(BN)_2$ -1. Although <sup>11</sup>B NMR data indicated that (BN)2-4 may partially form the doubleeliminated product  $(BN)_2$ -4a, upon irradiation at either 300 or 365 nm, the chemical shifts of the aromatic protons are mostly absent or very broad in the <sup>1</sup>H NMR spectrum with unidentifiable peaks in the aliphatic region (see Supporting Information). Furthermore, both (BN)<sub>2</sub>-1 and (BN)<sub>2</sub>-4 only display detectable changes by NMR after a long exposure to UV light. Perhaps the rigid structures imposed by the two boron units sharing the central linker unit in (BN)2-1 and  $(BN)_{2}$ -4 makes the elimination reaction difficult, although the details are not understood yet. The different photoreactivities of  $(BN)_2$ -2 and  $(BN)_2$ -3 are probably caused by the different locations of the two BN units and heptyl groups, which led to a highly congested structure for (BN)2-3, compared to that of  $(BN)_2$ -2. The steric congestion likely makes the photoelimination of  $(BN)_2$ -3 more efficient and is responsible for its relatively clean double elimination.

Besides phototransformation, previously we have also shown that related BN-chelate compounds can display either retro-1,1-hydroboration (deborylation) or mesitylene elimination upon heating.<sup>6b</sup> To determine if the new BN-heterocycles display similar reactivities, their thermal reaction was examined.  $(BN)_2$ -1,  $(BN)_2$ -2, and  $(BN)_2$ -4 produce unidentifiable products in mineral oil at 230 °C. In contrast, compound  $(BN)_2$ -3 undergoes a clean thermal elimination upon heating at 230 °C, producing  $(BN)_2$ -3a nearly quantitatively (see the Supporting Information).

(BN)<sub>2</sub>-3a was fully characterized by NMR and HRMS. The <sup>11</sup>B chemical shift of (BN)<sub>2</sub>-3a (36 ppm) is consistent with that of azaborines.<sup>6</sup> (BN)<sub>2</sub>-3a has a low-energy absorption band at ~476 nm with well-resolved vibrational features and bright green-yellow fluorescent emission ( $\lambda_{em} = 510$  nm,  $\Phi_{FL} = 0.14$ ; Figure 5), which is similar to that of the corresponding mono-BN-phenanthrene reported previously.<sup>6</sup> This suggests that increasing  $\pi$  conjugation via a phenyl linker does not significantly change the absorption and fluorescent properties of BN-phenanthrene. The most stable form of (BN)<sub>2</sub>-3a has an approximate *syn*-conformation with the two BMes units on the



1.2

1.0

0.8

0.6

0.4

0.2

A/I



Figure 5. Absorption (red) and fluorescence (black) spectra of  $(BN)_2$ -3a in THF. Inset: photograph showing the emission color of  $(BN)_2$ -3a in THF.

same side as shown in Figure 6, based on DFT structural optimization. The central benzene ring has a torsion angle of



Figure 6. Left: DFT-optimized structure of  $(BN)_2$ -3a. Right: HOMO and LUMO diagrams of  $(BN)_2$ -3a.

 $\sim$ 58° with the two neighboring BN-phenanthrene rings. This confirms the poor conjugation between these three units in (BN)<sub>2</sub>-3a and explains the lack of the influence of the central benzene linker on the electronic properties of the bis-BN-phenanthrene molecule (BN)<sub>2</sub>-3a.

TD-DFT computation studies (Supporting Information) confirmed that the  $S_0 \rightarrow S_1$  transition of (**BN**)<sub>2</sub>-**3a** involves primarily the HOMO and LUMO orbitals (83%), localized predominantly on the BN-phenanthrene units with a very high oscillator strength (0.168, Figure 6). This transition is believed to be responsible for the green fluorescence of (**BN**)<sub>2</sub>-**3a**. Compound (**BN**)<sub>2</sub>-**3a** displays two pseudoreversible reduction waves in the CV diagram (in THF) at -2.22 and -2.47 V, respectively, and an irreversible oxidation at 0.64 V (vs FcH/FcH<sup>+</sup>, Supporting Information), which correspond to approximately LUMO, LUMO+1, and HOMO levels of -2.58, -2.33, and -5.44 eV, respectively.

# CONCLUSIONS

Four new diboron BN-heterocycles with extended conjugated backbones have been synthesized. The impact of the linker unit and the location of the boron chelate unit on the electronic properties and photoreactivity of this class of compounds have been examined. The experimental and computational data suggest that the location of BN units, the steric congestion, and the linker unit within the  $\pi$ -conjugated backbone can greatly affect the electronic structure of these molecules as well as their photophysical/photochemical properties. Diboron BN-heterocycles that share the central linker unit appear to be either unstable or have a poor reactivity toward light while those that do not share the central linker can undergo double photoelimination with the sterically congested one being more effective.

# EXPERIMENTAL SECTION

General Information. 2-Bromo-4-heptylpyridine and 2,5-dibromo-4-heptylpyridine were prepared according to a modified reported procedure.9 Compounds N2-2 pre and N2-3 pre were prepared using  $Pd(PPh_3)_4$  (5 mol %) and  $Na_2CO_3$  (3 equiv) at reflux conditions for Suzuki-coupling reactions (See Supporting Information). All other chemicals were obtained from commercial sources and were used without further purification. THF and diethyl ether were distilled over Na under a nitrogen atmosphere. All the synthetic procedures were performed under N<sub>2</sub> using the standard Schlenk techniques. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 400 or 500 MHz Bruker spectrometer. High-resolution mass spectra (HRMS) were obtained from an Applied Biosystems Qstar XL spectrometer. UV-visible spectra were recorded using a Varian Cary 50 UV/vis spectrophotometer. Cyclic voltammetry experiments were conducted on a BAS CV-50W analyzer with a scan rate of 100 mVs<sup>-1</sup>. The electrochemical cell was a standard three-compartment cell composed of a glassy carbon working electrode, a Pt auxiliary electrode, and a Pt wire reference electrode. All measurements were performed using 0.1 M  $[Bu_4N][PF_6]$  in THF as the supporting electrolyte, except for those of compound  $(BN)_2$ -4, which were recorded using DMF as the solvent. The potentials are reported relative to the ferrocene/ferrocenium couple. <sup>1</sup>H NMR scale photoelimination reactions were carried out under  $N_2$  using  $C_6D_6$  as the solvent, quartz J. Young NMR tubes as the reaction vessels, and a Rayonet Photochemical Reactor as the light source. The mineral oil used in the thermal reaction was purchased from Sigma-Aldrich Corp. (76235, 500 mL), heated over sodium metal, and stored under nitrogen prior to use. The purity of the new compounds has been established by NMR after column chromatography on silica gel or recrystallization.

**DFT Calculation Details.** All calculations were performed using the Gaussian 09 suite of programs on the High-Performance Computing Virtual Laboratory (HPCVL) at Queen's University. Initial input coordinates were taken from the corresponding crystal structure data where applicable, while all others were generated in Gaussian 09.<sup>10</sup> DFT and TD-DFT calculations were performed using the B3LYP/6-31G(d) level of theory.<sup>8</sup>

Synthesis of Compound N2-1. This compound was synthesized using a modified Suzuki coupling procedure. A mixture of THF (60 mL) and water (20 mL) was stirred and purged by nitrogen for 1 h. Diboron esters (2.1 g, 5.9 mmol), 2-bromo-4-heptylpyridine (3 g, 11.8 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (410 mg, 0.354 mmol), and Na<sub>2</sub>CO<sub>3</sub> (3.7 g, 35.4 mmol) were added to the mixed solvents. The mixture was stirred and refluxed for 24 h. The organic solvents were removed under vacuum. The water layer was separated and extracted with  $CH_2Cl_2$  (3 × 50 mL). The combined organic layers were washed by brine and dried over magnesium sulfate, and the solvents were evaporated under reduced pressure. Purification of the crude product by column chromatography afforded the product N2-1 as a white solid in 45% yield (1.2 g).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.60 (d, J = 5.0 Hz, 2H), 7.36 (s, 2H), 7.26 (d, J = 1.6 Hz, 2H), 7.09 (dd, J = 5.1, 1.7 Hz, 2H), 2.68 (t, J = 7.7 Hz, 4H), 2.39 (s, 6H), 1.76–1.62 (m, 4H), 1.42–1.27 (m, 16H), 0.95–0.85 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 159.57, 151.74, 149.10, 140.35, 132.99, 131.98, 124.35, 121.89, 35.38, 31.75, 30.40, 29.19, 29.08, 22.63, 19.78, 14.08. HR-ESIMS (m/z): M + 1]<sup>+</sup> calcd for C<sub>32</sub>H<sub>45</sub>N<sub>2</sub>: 457.35773; found: 457.35591.

Synthesis of Compound N2-2. A mixture of THF (30 mL) and water (10 mL) was stirred and purged by nitrogen for 1 h. Boronic acid (204 mg, 1.23 mmol), compound N2-2 pre (870 mg, 2.5 mmol), Pd(dppf)Cl<sub>2</sub> (18 mg, 0.024 mmol), and Na<sub>2</sub>CO<sub>3</sub> (782 mg, 7.37 mmol) were added to the mixed solvents. The mixture was stirred and reflux for 24 h. The organic solvents were removed under vacuum. The water layer was separated and extracted with  $CH_2Cl_2$  (3 × 40 mL). The combined organic layers were washed by brine and dried over magnesium sulfate, and the solvents were evaporated under reduced pressure. Purification of the crude product by column chromatography afforded the product N2-2 as a colorless oil in 78% yield (590 mg, 0.97 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>2</sub>)  $\delta$  8.65 (d, *J* = 5.1 Hz, 2H), 7.79 (d, J = 3.8 Hz, 4H), 7.68–7.57 (m, 6H), 7.29 (s, 2H), 7.09 (dd, J = 5.1, 1.5 Hz, 2H), 2.52 (s, 6H), 1.79–1.57 (m, 8H), 1.30 (d, J = 15.2 Hz, 16H), 0.91 (t, J = 6.7 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 159.40, 155.57, 149.24, 140.48, 139.91, 136.21, 130.29, 129.42, 127.53, 127.40, 124.57, 13.77, 121.38, 45.79, 36.34, 31.77, 29.37, 27.51, 22.66, 20.63, 14.12. HR-ESIMS (m/z):  $[M + 1]^+$  calcd for  $C_{44}H_{53}N_2$ : 609.42033; found: 609.41839.

**Synthesis of Compound N2-3.** Compound N2-3 was synthesized using the same procedure of synthesis as that for compound N2-2 as a colorless oil in 60% yield (600 mg, 0.99 mmol). <sup>1</sup>H NMR (499 MHz, CDCl<sub>3</sub>)  $\delta$  8.61 (s, 2H), 7.52 (m, 6H), 7.40 (s, 2H), 7.34 (p, *J* = 3.7 Hz, 6H), 2.79–2.70 (m, 4H), 2.48 (s, 6H), 1.61 (td, *J* = 7.9, 3.9 Hz, 4H), 1.32–1.23 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  158.88, 149.67, 149.24, 140.43, 137.33, 135.84, 135.08, 130.78, 129.69, 129.53, 128.23, 125.90, 124.34, 32.58, 31.68, 30.36, 29.34, 28.96, 22.61, 20.45, 14.09. HR-ESIMS (*m*/*z*): [M + 1]<sup>+</sup> calcd for C<sub>44</sub>H<sub>53</sub>N<sub>2</sub>: 609.42033; found: 609.41840.

**Synthesis of Compound N2-4.** A solution of ethanebis-(thioamide) (0.454 g, 3.7 mmol) and 2-methylbenzaldehyde (1.0 g, 8.3 mmol) in DMF (10 mL) was refluxed for 4 h. After being cooled to room temperature, the solvents were then removed under reduced pressure. The crude product was purified by silica gel chromatography (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1). Compound N2-4 was obtained as a pale yellow solid in 64% yield (0.768 g, 2.38 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.76 (d, *J* = 7.5 Hz, 2H), 7.43–7.28 (m, 6H), 2.69 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.98, 151.03, 137.09, 133.37, 131.87, 130.16, 126.41, 21.70. HR-ESIMS (*m*/*z*): [M + 1]<sup>+</sup> calcd for C<sub>18</sub>H<sub>15</sub>N<sub>2</sub>S<sub>2</sub>, 323.06766; found 323.06415.

Synthesis of Compound  $(BN)_2$ -1. <sup>t</sup>BuLi (4.0 mL, 1.7 M in hexane, 6.78 mmol) was added to a solution of compound N2-1 (700 mg, 1.54 mmol) in Et<sub>2</sub>O (25 mL) at -78 °C. After stirring at this temperature for 1 h, the precooled boron reagent Mes<sub>2</sub>BF (1.23g, 4.62 mmol) in THF was added via cannula transfer with vigorous stirring at -78 °C. The mixture was stirred for another hour at -78 °C, then allowed to warm slowly to room temperature and stirred overnight. The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> and water. The organic phase was dried over magnesium sulfate and filtered. The filtrate was purified by column chromatography on silica gel to afford product (BN)2-1 (514 mg, 0.54 mmol, 35% yield) as a yellow solid. <sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ )  $\delta$  8.38 (d, J = 6.2 Hz, 2H, py), 7.59 (s, 2H, py), 7.16– 7.07 (m, 2H, py), 7.03 (s, 2H, benzene ring), 6.59 (s, 8H, Mes), 2.79 (t, J = 7.8 Hz, 4H, CH<sub>2</sub>), 2.69 (s, 4H, B-CH<sub>2</sub>), 2.16 (s, 12H, Me), 1.84 (m, 24H, Mes), 1.74 (br, 4H, CH<sub>2</sub>), 1.42–1.31 (m, 16H, CH<sub>2</sub>), 0.93 (t, J = 6.6 Hz, 6H, Me in heptyl). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ 157.98, 154.95, 147.28, 142.89, 141.59, 133.18, 132.37, 129.55, 126.00, 123.45, 123.20, 35.32, 31.64, 29.77, 29.66, 29.05, 28.95, 24.56, 22.58, 20.28, 13.81. <sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 2.6. HR-ESIMS (*m*/*z*):  $[M + 1]^+$  calcd for  $C_{68}H_{87}B_2N_2$ : 953.70499; found: 953.70893.

Synthesis of Compound (BN)<sub>2</sub>-2. Compound (BN)<sub>2</sub>-2 was synthesized using the same procedure of synthesis as that for compound (BN)<sub>2</sub>-1. The mixture was recrystallized by ethyl acetate and hexanes to afford product (BN)<sub>2</sub>-2 (632 mg, 0.57 mmol, 60% yield) as a yellow solid, which was confirmed by X-ray diffraction analysis. <sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ )  $\delta$  8.44 (d, J = 6.2 Hz, 2H, py), 7.83 (d, J = 2.0 Hz, 2H, py), 7.69 (d, J = 8.1 Hz, 2H, ph), 7.56 (s, 4H, benzene linker), 7.36 (dd, J = 8.0, 1.9 Hz, 2H, ph), 7.17 (dd, J = 6.2, 1.9 Hz, 2H, py), 7.09 (d, J = 1.9 Hz, 2H, ph), 6.60 (s, 8H, Mes), 2.83 (br, 8H, CH<sub>2</sub> and B-CH<sub>2</sub>), 2.15 (s, 12H, Mes), 1.90 (s, 24H, Mes),

1.78 (br, 4H, CH<sub>2</sub>), 1.44–1.32 (m, 16H, CH<sub>2</sub>), 0.94 (t, *J* = 6.7 Hz, 6H, Me in heptyl). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  158.19, 155.25, 148.36, 147.23, 142.27, 141.63, 139.66, 133.38, 129.78, 129.57, 127.18, 126.72, 126.48, 123.27, 123.18, 122.74, 35.42, 31.68, 30.41, 29.88, 29.04, 28.98, 24.62, 22.59, 20.27, 13.84. <sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.6. HR-ESIMS (*m*/*z*): [M + 1]<sup>+</sup> calcd for C<sub>80</sub>H<sub>95</sub>B<sub>2</sub>N<sub>2</sub>: 1105.76759; found: 1105.77307.

**Synthesis of Compound (BN)**<sub>2</sub>-3. Compound (BN)<sub>2</sub>-3 was synthesized using the same procedure of synthesis of compound (BN)<sub>2</sub>-1 to provide product (BN)<sub>2</sub>-3 (497 mg, 0.45 mmol, 50% yield) as a yellow solid, which was confirmed by X-ray diffraction analysis. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.43 (s, 2H, py), 7.91 (s, 2H, py), 7.67 (br, 2H, ph), 7.26 (br, 4H, ph), 7.13 (br, 4H, ph), 6.91 (br, 2H, ph), 6.57 (s, 8H, Mes), 2.83 (br, 8H, CH<sub>2</sub> and B-CH<sub>2</sub>), 2.15 (s, 12H, Mes), 1.90 (s, 24H, Mes), 1.71–1.59 (m, 4H, CH<sub>2</sub>), 1.29 (br, 16H, CH<sub>2</sub>), 0.90 (t, *J* = 6.5 Hz, 6H, Me in heptyl). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 155.59, 154.46, 147.82, 147.64, 146.81, 141.66, 136.17, 135.95, 133.37, 130.62, 130.32, 129.63, 129.54, 128.51, 125.99, 124.24, 123.77, 32.74, 31.59, 29.91, 29.12, 28.85, 24.68, 22.53, 20.26, 13.82. <sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 1.8. HR-ESIMS (*m*/*z*): [M + 1]<sup>+</sup> calcd for C<sub>80</sub>H<sub>95</sub>B<sub>2</sub>N<sub>2</sub>: 1105.76759; found: 1105.76845.

Synthesis of Compound (BN)<sub>2</sub>-4. To a solution of N2-4 (0.1 g, 0.31 mmol) in anhydrous THF (10 mL) a solution of lithium diisopropylamide in THF (1 mL, 0.78 mmol) was added dropwise in a  $N_2$  atmosphere at -78 °C. The mixture was stirred at -78 °C for 2 h and Mes<sub>2</sub>BF (0.195 g, 0.78 mmol) in anhydrous THF (10 mL) was added. The mixture solution was warmed up to room temperature and stirred for 12 h. After removal of the solvent under the reduced pressure, the resulting crude product was purified by silica gel chromatography (petroleum ether/ $CH_2Cl_2 = 3.1$ ) as a yellow solid in 4% yield (0.011 g, 0.013 mmol). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  6.91 (d, J = 7.6 Hz, 2H, ph), 6.82 (s, 8H, Mes), 6.74 (d, J = 7.6 Hz, 2H, ph), 6.62 (t, J = 7.5 Hz, 2H, ph), 6.33 (t, J = 7.5 Hz, 2H, ph), 2.96 (s, 4H, B-CH<sub>2</sub>), 2.17 (br, 36H, Me). <sup>13</sup>C NMR (176 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$ 172.71, 147.94, 143.62, 133.74, 130.88, 126.40, 126.06, 125.13, 20.94. <sup>11</sup>B NMR (128 MHz,  $C_6D_6$ ):  $\delta$  2.3. HR-ESIMS (m/z):  $[M + 1]^+$  calcd for C<sub>54</sub>H<sub>57</sub>B<sub>2</sub>N<sub>2</sub>S<sub>2</sub>, 819.41438; found 819.41334.

Formation of (BN)<sub>2</sub>-3a via Photoelimination. <sup>1</sup>H NMR scale photoelimination reactions were carried out under  $N_2$  using  $C_6 D_6$  as the solvent, quartz J. Young NMR tubes as the reaction vessels, and a Rayonet Photochemical Reactor as the light source. Compound  $(BN)_2$ -3 (~5 mg) was dissolved in C<sub>6</sub>D<sub>6</sub> (0.5 mL) in a quartz J. Young NMR tube and sealed under nitrogen. The NMR tube was then irradiated with 350 nm UV light and the reaction progress was monitored by <sup>1</sup>H and <sup>11</sup>B NMR spectra until it reached completion (~90% yield by NMR). <sup>1</sup>H NMR (499 MHz,  $C_6D_6$ )  $\delta$  8.57 (s, 2H, py), 8.42 (d, J = 11.3 Hz, 2H, ph), 8.39 (s, 2H, py), 7.78 (d, J = 8.4 Hz, 2H, ph), 7.37 (dd, J = 8.2, 6.7 Hz, 2H, ph), 7.30 (s, 2H, CH bound to B), 7.10 (dd, J = 8.2, 6.7 Hz, 2H, ph), 7.03 (s, 4H, Mes), 6.92 (s, 4H, benzene linker), 2.49–2.45 (m, 4H, CH<sub>2</sub>), 2.30 (s, 12H, Me in Mes), 2.26 (s, 6H, Me in Mes), 1.36-1.07 (m, 20H, CH<sub>2</sub>), 0.90 (t, J = 7.2Hz, 6H, Me in heptyl). <sup>13</sup>C NMR (126 MHz,  $C_6D_6$ )  $\delta$  145.61, 143.01, 142.05, 140.34, 137.35, 136.79, 136.48, 135.90, 131.39, 128.96, 128.83, 128.27, 124.80, 121.10, 119.91, 118.55, 33.17, 31.73, 29.86, 29.34, 29.05, 22.80, 22.72, 21.16, 14.06. <sup>11</sup>B NMR (160 MHz, C<sub>6</sub>D<sub>6</sub>) δ 36.4. HR-ESIMS (m/z):  $[M + 1]^+$  calcd for C<sub>62</sub>H<sub>71</sub>B<sub>2</sub>N<sub>2</sub>: 865.57979; found: 865.57965.

**Formation of (BN)**<sub>2</sub>**-3a via Thermal Elimination.** In a glovebox, compound (BN)<sub>2</sub>**-3** (10 mg) was placed in a J. Young NMR tube containing a few drops of mineral oil. The J. Young NMR tube was heated for 2 h at 230 °C using a sand bath. The reaction mixture was then transferred into a glovebox again and dissolved in  $C_6D_6$ . <sup>1</sup>H NMR shows that (BN)<sub>2</sub>-3a was produced nearly quantitatively.

**X-ray Diffraction Analysis.** The crystal data of  $(BN)_2$ -2 and  $(BN)_2$ -3 were collected on a Bruker Apex II X-ray diffractometer with Mo-target ( $\lambda = 0.71073$  Å) at 180 K while the crystal structure of  $(BN)_2$ -4 was determined on a Bruker D8-Venture diffractometer with Mo target at 180 K. Data were processed on a PC with the aid of the Bruker SHELXTL software package and corrected for absorption effects.<sup>11</sup> Complete crystal structural data have been deposited at the

Cambridge Crystallographic Data Centre [CCDC No. 1542183  $(BN)_2$ -2, 1542182  $(BN)_2$ -3, and 1542181  $(BN)_2$ -4]. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif].

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00261.

Experimental data for the synthesis of organic substrates, NMR spectral data, electrochemical analysis data, and data showing the change of compounds  $(BN)_2$ -2,  $(BN)_2$ -3, and  $(BN)_2$ -4 upon irradiation by UV light, and computational details (PDF)

Crystal structural data for BN-heterocycles (XYZ)

# Accession Codes

CCDC 1542181–1542183 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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