# ORGANOMETALLICS

## Influence of Extended Conjugation on Photophysical/Electronic **Properties and Photoelimination of BN-Heterocycles**

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S Supporting Information

ABSTRACT: A 1,1-hydroboration reaction was used successfully to create brominated BN-heterocyclic compounds, which are amenable to Stille coupling reactions for the construction of new BN-heterocyclic compounds, including a new polymeric BN-heterocycle that has an extended  $\pi$ conjugated backbone. The conjugated backbone of the new BN-heterocycles was found to have a great influence on the photophysical and electronic properties of this class of compounds. In addition, the photoelimination reactivity of the new BN-heterocycles was also found to be greatly



dependent on the extent of the conjugated backbone. Several new 1,2,4-triazole-fused boranaphthalenes have been obtained successfully via photoelimination.

#### ■ INTRODUCTION

BN-embedded aromatic compounds (BN-arenes) are an attractive class of materials that have attracted much recent research attention,<sup>1,2</sup> mainly because of their unique electronic/ photophysical properties and versatile applications in organic optoelectronic materials/devices.<sup>3,4</sup> Various synthetic methods have been developed for achieving a variety of B,N-arenes.<sup>3-6</sup> In particular, B,N-heterocycles such as A in Scheme 1 have been found to be convenient precursors for the generation of B,N-arenes B via photoelimination (PE) reactions.<sup>7</sup> One advantage of the PE reaction is that the precursor B,Nheterocycle may be readily prepared either by lithiation of the appropriate substrate, followed by the addition of BR<sub>2</sub>X, or by the catalyst-free 1,1-hydroboration of pyrido[1,2-a]isoindole and derivatives.<sup>7b</sup> 1,1-Hydroboration has also been realized for analogues of pyrido [1,2-a] isoindole, leading to new B,Nheterocycles such as 1a, which also undergoes a PE reaction, forming B,N-arenes such as 1c.<sup>7d</sup> Pammer and co-workers have shown that 1,2-hydroboration of 2-(2-vinylphneyl)pyridine and derivatives is also an effective strategy for the synthesis of B,Nheterocycles such as D, which contains an asymmetric carbon atom, although the photochemistry of D has not been established.<sup>8</sup> These new synthetic methods make it possible to access a large variety of B,N-heterocyclic compounds and carry out a comprehensive study of the PE phenomenon. Our recent successful demonstration of exciton-driven elimination (EDE) of B,N-heterocycles for in situ generation of B,N-arenes in OLEDs<sup>9</sup> opens up the possibility of using B,N-heterocyclic precursor compounds for the in situ generation of functional B,N-arenes in optoelectronic devices such as organic field effect transistors (OFETs) and organic solar cells. For these applications, extended  $\pi$ -conjugated molecules or polymers for easy processing and achieving the desired energy levels/

optical energy gap are necessary. However, the effect of extended  $\pi$ -conjugation on the photophysical/electronic properties and the PE reactivity of B,N-heterocycles with a core structure such as 1a has not been established. Therefore, we set out to develop synthetic methods for extended  $\pi$ conjugated molecules containing a PE active B,N-heterocyclic unit

We have found that postmodification of molecules that have a benzyl-pyridyl backbone such as A and its halogen-substituted derivatives for C-C coupling to extend the backbone conjugation is difficult. On the other hand, we have discovered that bromo-substituted B,N-heterocycle 1a is amenable for post C-C cross-coupling reactions. Therefore, in this study, we selected 1a as the core structure and progressively increased extended conjugation of the backbone via compounds 2b-5b shown in Scheme 1. Investigation of these new molecules revealed the distinct effect of extended conjugation on the electronic properties and PE reactivity of the B,N-heterocycles and luminescence of the corresponding B,N-arenes. The details are presented herein.

#### **RESULTS AND DISCUSSION**

Syntheses and Structures of BN-Heterocycles 2b-5b. 1-Methyl-2-phenyl-1*H*-[1,2,4]triazolo[5,1-a]isoindole (the heterocycle L in Scheme 1) can be obtained readily and undergoes facile 1,1-hydroboration as pyrido[2,1-a]isoindole does, providing easy access to B,N-heterocycles.<sup>7d</sup> The precursor B,N-

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Scheme 1. Examples of Hydroboration for B,N-Heterocycle Synthesis and B,N-Arene Formation via Photoelimination



heterocycles **2a** and **3a** for the target compounds examined in this work were prepared using this approach. The key starting materials are the monobrominated and dibrominated 1-methyl-2-phenyl-1*H*-[1,2,4]triazolo[5,1-*a*]isoindole (**L**-**b**), which can be prepared by the procedure shown in Scheme 2 via **L**-**I**. The





corresponding precursors (L-a) were prepared in high yields via the condensation reaction shown in Scheme 2. Methylation of L-a by dimethyl sulfate, followed by anion exchange with iodide, produced the iodide salts L-I in good yields. Treatment of the iodide salts by 3 equiv of KO<sup>t</sup>Bu generated L-b in situ, which could not be isolated due to their high sensitivity to air. The addition of 2 equiv of HBMes<sub>2</sub> to the solution of L-b led to the formation of the corresponding B,N-heterocycles. For comparison, the yields of 1a and its precursor compounds are also shown in Scheme 2. The one-pot 1,1-hydroboration of L-I with KO<sup>t</sup>Bu and HBMes<sub>2</sub> produced compounds 2a and 3a in 45% and 31% yields, respectively, which are lower than that of **1a** (72%). Nonetheless, this is the first successful demonstration of 1,1-hydroboration involving brominated substrates. The low hydroboration yield can be attributed to the inductive electron-withdrawing nature of bromine atom that destabilizes the key intermediate—the adduct of borane with L-b.<sup>7b</sup>

To extend the  $\pi$ -conjugation of the backbone, we introduced thienyl units to the central core. First, we attempted to connect the thienyl units to 2a and 3a via Suzuki coupling methods. However, this approach failed to produce the desired product because it led to deborylation of the BMes<sub>2</sub> group, attributable to the basic conditions (Na<sub>2</sub>CO<sub>3</sub> was used as the base) of the Suzuki coupling method (see the Supporting Information). To avoid the use of basic conditions, Stille coupling was investigated as a general method to attach thienyl rings to compounds 2a and 3a, which turned out to be effective. Using tris(dibenzylideneacetone)dipalladium  $(Pd_2(dba)_3)$  as the catalyst and trimethyltin-functionalized thienyl/bis-thienyl units as the coupling partners, in the presence of  $P(o-tolyl)_{3}$ , thienyl/bis-thienyl units can be attached to 2a and 3a successfully, producing compounds 2b-4b, respectively, as shown in Scheme 3. The hexyl group at the ortho position of

#### Scheme 3. Synthesis of Compounds 2b-5b



SnMe<sub>3</sub>-functionalized thiophene employed in the synthesis of **2b** and **3b** may be responsible for the relatively low yields of the products due to steric hindrance in Stille coupling. To reduce steric hindrance and improve the yield of bis-thienyl-linked B,N-heterocycle polymers, we prepared (3,3'-dihexyl[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane), according to a literature procedure,<sup>10</sup> and used this tin reagent for the synthesis of the polymeric compound **5b**. Using the same reaction conditions as employed for **2b**-**4b** synthesis, the reaction of **3a** with the tin reagent in a 1:1 ratio and the end-capping reagent bromobenzene produced successfully polymer **5b** in 42% yield. All four compounds are stable in solution and in the solid state under ambient conditions.

Compounds 2b-5b were fully characterized by NMR, HRMS, or GPC analyses. All four compounds display a <sup>11</sup>B chemical shift at -1.4, -1.9, 1.1, and 3.1 ppm, respectively, which is characteristic of four-coordinate boron.<sup>7</sup> The polymer **5b** has a mean  $M_n$  value of 6888, corresponding to about 8

repeating units. The mean PDI value of 5b was determined to be 1.5 (see the Supporting Information for details). The crystal structure of 4b was determined by single-crystal X-ray diffraction analysis and is shown in Figure 1. The B–C bond



Figure 1. (top) Crystal structure of 4b with labeling schemes and 35% thermal ellipsoids. H atoms are omitted for clarity. Important bond lengths (Å) and angles (deg): B(1)-N(1) 1.621(4), B(1)-C(1) 1.665(5), B(1)-C(11) 1.652(4), B(1)-C(20) 1.648(5); C(1)-B(1)-N(1) 99.1(2), C(1)-B(1)-C(11) 118.6(3), C(1)-B(1)-C(20) 103.0(2), C(11)-B(1)-N(1) 104.9(2), C(20)-B(1)-N(1) 113.1(3). (bottom) DFT optimized structure of the hexyl-substituted analogue 4b', showing the twist of the thienyl rings.

lengths in 4b are similar and comparable to those of 2-(otolyl)pyridine-BMes<sub>2</sub> and precursor compound 1a. However, the B–N bond in 4b (1.628(2) Å) is shorter than that in 1a (1.636(2) Å). The bis-thienyl units in **4b** are essentially coplanar, as indicated by the dihedral angles between the S1 and S2 rings  $(2.4^{\circ})$  and between the S3 and S4 rings  $(11.6^{\circ})$ . The dihedral angles between the S3 ring and the C40 benzene ring and between the S1 ring and the C5 benzene ring are 17.5 and 42.0°, respectively, while that between the C40 benzene ring and the triazole ring is 49.3°, indicating good conjugation between these units. The hexyl-substituted analogue of 4b (4b'), which could serve as a model compound for the repeating unit in polymer 5b, was not prepared. Nonetheless, as shown by the DFT optimized structure of 4b' in Figure 1, the thienyl rings in 4b' are nearly perpendicular to each other due to the interactions between the hexyl substituents, which supports the notion that the repeating unit in the polymer 5b is less conjugated than the backbone of 4b.

Photophysical and Electronic Properties of 2b-5b. The UV/vis spectra recorded in THF for compounds 2b-5b along with that of 1a are shown in Figure 2. The impact of



Figure 2. Absorption spectra of 1a and 2b-4b in THF ( $\sim 1 \times 10^{-5}$  M).

extended  $\pi$ -conjugation on the electronic properties of B,Nheterocycles is evident. From 1a to 5b, the absorption edge is red-shifted. The absorption bands of 4b and polymer 5b are bathochromically shifted by 30–50 nm, relative to other molecules. Although 5b contains about eight repeating units, the energy of its absorption band/edge is only slightly smaller than that of 4b, which is clearly caused by the poor conjugation between the two neighboring thienyl units in 5b.

Compound **4b** displays two well-resolved reversible reduction peaks in its CV diagram, while others show either irreversible or pseudoreversible peaks in the CV diagrams that are at potentials much more negative than that of **4b** (see the Supporting Information). To better define the reduction potential of this group of compounds, differential pulse voltammetry was performed for all compounds, and the data are shown in Figure 3 and Table 1. In general, with an increase



**Figure 3.** Differential pulse voltammetry diagrams of 1a and 2b-5b recorded in DMF with [NBu<sub>4</sub>]PF<sub>6</sub> as the electrolyte, relative to FC/FC<sup>+</sup>.

in the backbone conjugation, the first reduction potential becomes less negative, consistent with a decrease in the LUMO energy level. The exception is between **4b** and **5b**, because **4b** has a more positive reduction potential and a lower LUMO level in comparison to those of **5b**. Again, this can be attributed to the disruption of conjugation between the two hexyl-substituted thienyl rings in **5b**. The DFT calculated trend of the LUMO energy level for **1a** and **2b–4b** agree with the electrochemical data, as shown in Figure 4.

Table 1. Photophysical and Electrochemical Data

absorption		nuorescence				
$\lambda_{\max} (nm)^a$	$E_{g}^{opt} (eV)^{b}$	$\lambda_{\rm em}~({\rm nm})$	$\Phi_{ m FL}$	$E_{\rm red} \; ({\rm eV})^d$	HOMO (eV) exptl <sup>e</sup> /DFT <sup>f</sup>	LUMO (eV) exptl <sup>e</sup> /DFT <sup>f</sup>
310	3.35			$-2.80^{c}$	-5.35/-5.10	-2.00/-1.64
310	3.35			$-2.67^{\circ}$	-5.48/-5.10	-2.13/-1.66
330	3.18			$-2.53^{\circ}$	-5.45/-5.16	-2.27/-1.79
365	2.82	425	0.050	$-2.58, -2.30^{c}$	-5.30/-5.12	-2.50/-2.04
352	2.75	475	0.020	$-2.40^{\circ}$	-5.15/-	-2.40/-
404	2.70	478	0.13		-/-4.70	-/-1.33
405	2.70	478	0.14		-/-4.71	-/-1.42
410	2.53	488	0.25		-/-4.76	-/-1.47
340	2.53	505	0.17		-/4.78	-/-1.90
	$\begin{array}{c} & absolution \\ \hline \lambda_{max} \ (nm)^{a} \\ 310 \\ 310 \\ 330 \\ 365 \\ 352 \\ 404 \\ 405 \\ 410 \\ 340 \\ \end{array}$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Horisectic $\overline{\lambda_{max} (nm)^a}$ $E_g^{opt} (eV)^b$ $\overline{\lambda_{em} (nm)}$ $\Phi_{FL}$ $E_{red} (eV)^d$ 3103.35-2.80°3103.35-2.67°3303.18-2.53°3652.824250.0503522.754750.0204042.704780.134052.704780.144102.534880.253402.535050.17	IndetSetter $\overline{\lambda_{max} (nm)^a}$ $\overline{E_g^{opt} (eV)^b}$ $\overline{\lambda_{em} (nm)}$ $\Phi_{FL}$ $E_{red} (eV)^d$ HOMO (eV) exptl <sup>e</sup> /DFT <sup>f</sup> 3103.35 $-2.80^c$ $-5.35/-5.10$ 3103.35 $-2.67^c$ $-5.48/-5.10$ 3303.18 $-2.53^c$ $-5.45/-5.16$ 3652.824250.050 $-2.58, -2.30^c$ $-5.30/-5.12$ 3522.754750.020 $-2.40^c$ $-5.15/-$ 4042.704780.13 $-/-4.70$ 4052.704780.14 $-/-4.71$ 4102.534880.25 $-/-4.76$ 3402.535050.17 $-/4.78$

<sup>*a*</sup>The first low-energy, resolved absorption band in THF. <sup>*b*</sup> $E_g^{opt}$  = absorption edge. <sup>*c*</sup>In DMF with [NBu<sub>4</sub>]PF<sub>6</sub> as the electrolyte. Potentials vs Fc/Fc<sup>+</sup>. <sup>*d*</sup>Determined from the first reduction peak positions in DPV diagrams which agree well with  $E^{1/2}$  from the CV diagrams (see the Supporting Information). <sup>*e*</sup> $E_{LUMO} = -(4.8 + E_{red})$ ;  $E_{HOMO} = E_{LUMO} - E_g^{opt}$ . <sup>*f*</sup>DFT calculations were performed using the B3LYP/6-31G(d) level of theory.



**Figure 4.** HOMO and LUMO energy levels of compounds **1a** and **2b–5b**: (blue bars) experimentally estimated values; (black bars) DFT calculated values (not calculated for **5b** due to its large size).

BN-heterocycles such as **A** and **1a** are in general not fluorescent.<sup>7</sup> It is therefore not surprising that compounds **2b** and **3b** are also not fluorescent. Interestingly, however, **4b** and **5b** are fluorescent with  $\lambda_{em}$  at 425 and 475 nm, respectively, albeit with a low quantum efficiency in THF (Figure 5). The polymer **5b** is also fluorescent in the solid state with  $\lambda_{em} \approx 500$  nm and a low quantum efficiency (~1%). The red shift of the emission band of **5b** in the solid state can be attributed to intermolecular interactions. TD-DFT data indicate that the vertical transitions to the first three singlet excited states (S<sub>1</sub>, S<sub>2</sub>,



Figure 5. Fluorescence spectra of 1c-4c and 4b-5b in THF (~1 ×  $10^{-5}$  M).

and  $S_3$ ) are predominantly charge-transfer transitions from the Mes groups to the chelate backbone with relatively low oscillator strengths (~0.001 to 0.007) for compounds 1a, 2b, and 3b. For 4b and 4b', the transitions to  $S_1$  and  $S_2$  are CT transitions similar to those of 1a, 2b, and 3b. However, the transition to the  $S_3$  state by 4b and 4b', which is close in energy to the  $S_2$  state, involves a large contribution from the  $\pi$ -orbital of the backbone (36% and 46%, respectively) in addition to the Mes group. Thus, as the backbone conjugation increases, the  $\pi$  to  $\pi^*$  transition localized on the backbone has increased contributions to the low-lying excited states of the BN-heterocycles, which may be responsible for the fluorescence of 4b and 5b. The calculated  $S_0 \rightarrow S_1$  transition energy for 4b' is 0.11 eV greater than that of 4b, in agreement with the twisted structure of 4b' shown in Figure 1.

Photoreactivity of 2b-5b and Photophysical Properties of 2c-5c. When they are subjected to UV irradiation at either 300 or 350 nm in a THF, benzene, or toluene solution, the monoboron compounds 2b-4b undergo photoelimination, producing the corresponding triazole-fused boranaphthalenes 2c-4c, respectively, in a manner similar to that for the parent molecule 1a (Scheme 4). In contrast, compound 5b does not show any photoreactivity on irradiation under the same conditions for 22 h. The lack of photoreactivity of 5b may be

Scheme 4. Photoreactivity of 2b-5b



DOI: 10.1021/acs.organomet.7b00290 Organometallics XXXX, XXX, XXX–XXX attributed to the extended  $\pi$ -conjugated backbone, which leads to the backbone-dominated excited states and the lack of significant contributions from the  $-CH_2-BMes_2$  portion to the low-lying excited states accessible at 300 or 350 nm excitation.

<sup>1</sup>H and <sup>11</sup>B NMR spectral tracking at ~0.01 M concentration showed that the transformation of 2b-4b to 2c-4c is quantitative (see the Supporting Information). Compounds 2c-4c display a characteristic <sup>11</sup>B chemical shift at 32.8, 33.6, and 34.3 ppm, respectively, similar to that<sup>9</sup> of 1c. Under the same irradiation conditions, the time needed to achieve full conversion in the NMR experiments is  $\sim$ 22 h for 2b to 2c,  $\sim$ 24 h for 3b to 3c, and  $\sim$ 72 h for 4b to 4c, respectively. The less efficient photoelimination of 4b is consistent with its greater extended  $\pi$ -conjugation of the backbone, relative to those of **2b** and 3b, where electronic transitions localized on the backbone that do not contribute to the photoreaction pathway can compete effectively for the excitation energy, hence resulting in a less efficient photoreaction. The photoelimination process of 2b-4b was also tracked by UV/vis and fluorescence spectroscopy at  $\sim 1 \times 10^{-5}$  M concentration. The photophysical data for 2c-4c are summarized in Table 1. For 2b and 3b, a new low-energy absorption band at 405 and 410 nm, respectively, appears as the photoreaction proceeds, which is similar to that of 1c and is assigned to the BN-arenes 2c and 3c, respectively. In contrast, on irradiation, the absorption band of 4b at 352 nm is gradually replaced by an intense high-energy band with wellresolved vibrational features at 340 nm and a very weak shoulder peak in the 390-460 nm region (see the Supporting Information).

To understand the different electronic properties of 2c-4c, TD-DFT computational studies for these three compounds were performed and the results are summarized in Table 1, Figure 6, and the Supporting Information. As shown in Figure 6, the  $S_0 \rightarrow S_1$  transition for all three compounds involves HOMO–LUMO orbitals (98%). The HOMO compositions for all three compounds are similar—located exclusively on the central triazole-boranaphthalene unit. However, the LUMO composition varies considerably. For 2c, the LUMO is dominated by the phenyl ring and the triazole unit. For 3c,



**Figure 6.** Diagrams for orbitals involved in  $S_0 \rightarrow S_1$  ( $S_0 \rightarrow S_2$ ) vertical excitation of **2c-4c** obtained by TD-DFT calculations (B3LYP/6-31G(d)).

there is a much greater contribution from the fused benzene ring to LUMO in comparison to that in 2c. For 4c, the LUMO has essentially no contribution from the central core; instead, it is localized on the phenyl-bis-thienyl unit and the HOMO to LUMO transition has a low oscillator strength and may be described as a charge-transfer transition. On the other hand, the  $S_0 \rightarrow S_2$  transition in 4c involves mainly the LUMO+1 orbital (93%) that has significant central core contributions and the bis-thienyl units as well with a much higher oscillator strength. Therefore, the typical  $\pi \rightarrow \pi^*$  transition of the central azaborine core is no longer the lowest in energy for 4c, which is clearly caused by the presence of the conjugated bis-thienyl units. As a result, the main absorption band of 4c appears at a higher energy in comparison to those of 2c and 3c.

The new triazole-boranaphthalene compounds are all brightly fluorescent, as shown in Scheme 4. In the fluorescence spectra, with irradiation of 2b and 3b, a peak at 478 and 488 nm (Figure 5), respectively, appears, which is responsible for the characteristic blue-green fluorescent colors of 2c and 3c. The fluorescent quantum efficiency of 2c (0.14) is similar to that of 1c (0.13), while that of 3c is much higher (0.25). The extra thienyl ring in 3c that is bound to the boranaphthalene ring seems effective in red-shifting the emission energy and enhancing  $\Phi_{\rm FI}$ , relative to that of 1c. For 4b, under irradiation, its fluorescent color changes from blue to green, and a new fluorescent band at 505 nm, which is red-shifted by more than 80 nm in comparison to that of 4b, appears, which is assigned to the photoelimination product 4c and likely originates from the HOMO to LUMO+1 transition shown in Figure 6. The fluorescence quantum yield of 4c is 0.17, comparable to those of 1c and 2c.

#### CONCLUSIONS

In summary, we have demonstrated that brominated Nheterocyclic compounds L-I can be successfully converted to BN-heterocycles via one-pot 1,1-hydroboration reactions. Furthermore, we have shown that brominated BN-heterocycles based on a triazolyl-benzyl chelate core can be further functionalized on the backbone via Stille coupling to produce extended  $\pi$ -conjugated BN-heterocycles. All monoboron species produced in this manner have been found to undergo quantitative photoelimination, producing the corresponding triazole-fused boranaphthalenes, which are brightly fluorescent. The photoelimination reaction efficiency decreases with an increase in the extended conjugation of the backbone. A polyboron compound with a conjugated backbone was obtained successfully, which does not show any photoreactivity due to the effective competition of electronic transitions localized on the  $\pi$ -conjugated backbone with the photoelimination pathway in the excited state. These findings provide valuable guides for the future design of photoresponsive boronbased materials.

#### EXPERIMENTAL SECTION

**General Procedure.** All solvents were freshly distilled over sodium metal and stored under nitrogen prior to use. All starting materials were purchased from Energy Chemical. HBMes<sub>2</sub>,<sup>11</sup> 3-hexyl-2-(trimethyltin)thiophene,<sup>12</sup> 5-trimethylstannyl-2,2'-bithiophene,<sup>13</sup> and (3,3'-dihexyl[2,2'-bithiophene]-5,5'-diyl)bis[trimethylstannane]<sup>10</sup> were synthesized according to procedures reported in the literature. All reactions were performed under nitrogen and in dry solvents. <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectra were recorded on a 400 or 700 MHz spectrometer. <sup>1</sup>H and <sup>13</sup>C chemical shifts are in ppm, relative to the

signals corresponding to the residual nondeuterated solvents (CDCl<sub>3</sub>, <sup>1</sup>H 7.26 ppm, <sup>13</sup>C 77.23 ppm; *d*<sub>6</sub>-DMSO, <sup>1</sup>H 2.50 ppm, <sup>13</sup>C 39.52 ppm; C<sub>6</sub>D<sub>6</sub>, <sup>1</sup>H 7.16 ppm, <sup>13</sup>C 128.06 ppm). <sup>11</sup>B chemical shifts are in ppm, relative to BF<sub>3</sub>·OEt<sub>2</sub> (0.00 ppm). High-resolution electrospray ionization mass spectra data were obtained via an ESI (Agilent (Q-TOF 6520)) analyzer. UV/vis spectra were obtained on an Agilent Cary 300 UV/vis spectrophotometer. Fluorescence spectra were recorded on a Photon Technologies International Quanta Master Model C-60 spectrometer. Fluorescent quantum efficiencies were determined using a Hamamatsu Quantaurus-QY spectrometer (C11347). Cyclic voltammetry experiments were conducted on an AUTOLAB-CV-75W analyzer with a scan rate of 100 mV s<sup>-1</sup>. The electrochemical cell was a standard three-compartment cell composed of a Pt working electrode, a Pt auxiliary electrode, and a Pt-wire reference electrode. All measurements were performed using 0.10 M of NBu<sub>4</sub>PF<sub>6</sub> in DMF as the supporting electrolyte. The potentials are reported relative to the ferrocene/ferrocenium couple. The purity of all compounds reported here was established by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra.

**DFT Calculation Details.** Geometry optimization and TD-DFT calculations were carried out using the Gaussian 09 software<sup>15</sup> at the High Performance Computing Virtual Laboratory (HPCVL) at Queen's University. All computations were performed at the B3LYP level of theory using the 6-31G(d) basis set<sup>14</sup> for all atoms.

Synthesis of Compounds L-I1-L-I3. The precursor compounds L-1a-L-3a were prepared using a modified procedure reported previously for L-1a.9 See the Supporting Information for details. The reaction was performed in air. A mixture of compound L-a (0.2 mmol) and dimethyl sulfate (0.5 mL) was stirred for 5 min at 155 °C and then another 30 min at 100 °C. The mixture was poured slowly into ethyl ether (4 mL). Filtration gave a light gray solid intermediate. The solid was dissolved in 1.5 mL of water and reprecipitated by adding 0.5 mL of 30% aqueous potassium iodide and filtered; the residue was then treated with water  $(1 \text{ mL} \times 3)$  and dried to give L-I. Data for L-I1: light yellow solid (yield: 66%); <sup>1</sup>H NMR (300 MHz,  $d_6$ -DMSO)  $\delta$ 8.43 (d, J = 7.7 Hz, 1H), 7.97-7.71 (m, 8H), 5.78 (s, 2H), 4.21 (s, 3H). Data for L-I2: light yellow solid (yield: 90%); <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  8.44 (d, J = 7.7 Hz, 1H), 8.06 (s, 1H), 8.01–7.94 (m, 2H), 7.90 (dd, J = 13.0, 4.9 Hz, 2H), 7.81 (t, J = 7.6 Hz, 1H), 7.69 (t, J = 7.9 Hz, 1H), 5.79 (s, 2H), 4.21 (s, 3H). Data for L-I3: gray solid (yield: 83%); <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  8.39 (d, J = 8.4 Hz, 1H), 8.24 (s, 1H), 8.07–8.02 (m, 2H), 7.99 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.68 (t, J = 7.9 Hz, 1H), 5.78 (s, 2H), 4.20 (s, 3.10 Hz)3H).

1,1-Hydroboration of L-I1-L-I3 and Syntheses of Compounds 1a-3a. KO'Bu (0.84 mmol) and the correponding salt L-I (0.27 mmol) were reacted in toluene (10 mL) at room temperature for 10 h. The insoluble solid and excess base KO<sup>t</sup>Bu were removed by filtration. The filtrate was concentrated by vacuum until half of the solvent was left. HBMes<sub>2</sub> (0.54 mmol) was added to the filtrate at room temperature and the mixture was stirred overnight, at which point the volatiles were removed in vacuo and the product was isolated by column chromatography on silica gel using a solvent mixture of hexanes and ethyl acetate (10/1) as the eluent. Data for 1a: white solid (yield: 72%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.66 (dd, J = 7.7, 1.5 Hz, 2H), 7.62–7.49 (m, 4H), 7.29 (dt, J = 12.9, 7.3 Hz, 2H), 7.20 (t, J = 7.5 Hz, 1H), 6.62 (s, 4H), 4.02 (s, 3H), 2.96 (s, 2H), 2.18 (s, 6H), 2.04 (s, 12H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.58, 150.43, 149.59, 147.67, 140.35, 132.05, 131.08, 130.59, 130.26, 128.56, 128.47, 128.28, 124.27, 123.29, 123.23, 119.53, 34.66, 31.88, 23.92, 19.85; <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  –1.80; HR-ESIMS (m/z) [M + 1]<sup>+</sup> calcd for C<sub>34</sub>H<sub>37</sub>BN<sub>3</sub> 498.3081, found 498.3054. Data for 2a: white solid (yield: 45%); <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  7.91–7.83 (m, 2H), 7.78 (d, J = 7.0 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.58 (t, J = 7.9 Hz, 1H), 7.28–7.19 (m, 2H), 7.04 (d, J = 7.3 Hz, 1H), 6.42 (s, 4H), 4.03 (s, 3H), 2.79 (s, 2H), 2.05 (s, 6H), 1.89 (s, 12H); <sup>13</sup>C NMR (176 MHz, d<sub>6</sub>-DMSO) δ 152.28, 151.51, 148.95, 140.76, 134.01, 131.60, 129.94, 129.28, 128.47, 127.83, 127.29, 125.15, 124.45, 122.19, 120.48, 35.39, 24.48, 22.08, 20.36; <sup>11</sup>B NMR (225 MHz,  $d_6$ -DMSO)  $\delta$  -3.72; HR-ESIMS (m/z) [M + 1]<sup>+</sup> calcd for C<sub>34</sub>H<sub>36</sub>BBrN<sub>3</sub> 576.2186, found

576.2245. Data for 3a: white solid (yield: 31%); <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  7.35 (s, 1H), 7.15–7.14 (m, 1H), 7.10 (dd, *J* = 7.9, 3.7 Hz, 2H), 7.04 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.88 (s, 4H), 6.58 (d, *J* = 8.3 Hz, 1H), 6.48 (t, *J* = 7.9 Hz, 1H), 3.17 (s, 2H), 2.39 (s, 12H), 2.29 (s, 3H), 2.22 (s, 6H); <sup>13</sup>C NMR (176 MHz,  $C_6D_6$ )  $\delta$  153.37, 152.18, 151.46, 141.32, 134.38, 133.98, 133.56, 131.06, 130.92, 130.64, 128.63, 127.37, 126.92, 125.31, 122.73, 119.38, 33.85, 25.37, 20.97; <sup>11</sup>B NMR (225 MHz,  $C_6D_6$ )  $\delta$  –1.84; HR-ESIMS (*m*/*z*) [M + 1]<sup>+</sup> calcd for  $C_{34}H_{35}BBr_2N_3$  654.1291, found 654.1341.

Synthesis of Compound 2b. In an oven-dried Schlenk flask were placed 2a (50 mg, 0.087 mmol), 3-hexyl-2-(trimethyltin)thiophene (32 mg, 0.095 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (4 mg, 0.0044 mmol), and P(o-(5 mg, 0.017 mmol). The flask was evacuated and filled with N<sub>2</sub> three times, and then dried toluene (4 mL) was injected into the mixture. The resulting solution was stirred at 100 °C for 12 h under N2. 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/CH2Cl2, 2/1). 2b was obtained as a white solid in 40% yield (23 mg): <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  7.44 (s, 1H), 7.35 (d, J = 7.7 Hz, 1H), 7.22 (d, J = 7.8 Hz, 1H), 7.11 (d, J = 7.4 Hz, 1H), 6.93 (dd, J = 6.7, 4.9 Hz, 4H), 6.90 (s, 4H), 6.82 (dd, J = 12.8, 6.6 Hz, 2H), 3.34 (s, 2H), 2.66 (s, 3H), 2.59-2.51 (m, 2H), 2.48 (s, 12H), 2.24 (s, 6H), 1.50 (dt, J = 15.3, 7.6 Hz, 2H), 1.24–1.13 (m, 6H), 0.84 (t, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (176 MHz, C<sub>ε</sub>D<sub>ε</sub>) δ 153.13, 152.09, 150.98, 141.51, 139.83, 136.44, 135.99, 133.20, 132.16, 131.85, 131.63, 130.52, 129.95, 129.68, 129.54, 128.80, 128.52, 128.33, 125.78, 124.83, 124.21, 124.03, 120.74, 34.23, 31.98, 31.24, 29.46, 28.94, 25.45, 22.97, 21.04, 14.30; <sup>11</sup>B NMR (225 MHz,  $C_6D_6$ )  $\delta$  -1.37; HR-ESIMS (m/z) [M + 1]<sup>+</sup> calcd for  $C_{44}H_{51}BN_3S$ 664.3897, found 664.3929.

Synthesis of Compound 3b. In an oven-dried Schlenk flask were placed 3a (50 mg, 0.076 mmol), 3-hexyl-2-(trimethyltin)thiophene (71 mg, 0.21 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (7 mg, 0.0076 mmol), and P(o-tolyl)<sub>3</sub> (9.3 mg, 0.03 mmol). The flask was evacuated and filled with  $N_2$  three times, and then dried toluene (9 mL) was injected into the mixture. The resulting solution was stirred at 100 °C for 12 h under an N2 atmosphere. 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). 3b was obtained as a light yellow oil in 25% yield (14 mg): <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  7.45 (s, 2H), 7.36 (d, J = 7.7 Hz, 1H), 7.23 (d, J = 7.9 Hz, 2H), 7.01–6.92 (m, 4H), 6.90 (d, J = 7.8 Hz, 4H), 6.81 (dd, J = 5.2, 2.4 Hz, 2H), 3.34 (s, 2H), 2.68 (s, 3H), 2.62-2.52 (m, 4H), 2.53-2.42 (m, 12H), 2.26 (s, 6H), 1.53 (ddd, J = 26.3, 14.7, 7.2 Hz, 4H), 1.35–1.16 (m, 12H), 0.87 (dt, J = 13.8, 4.9 Hz, 6H); <sup>13</sup>C NMR (176 MHz,  $C_6D_6$ )  $\delta$  153.09, 151.80, 151.38, 141.42, 140.28, 139.85, 137.24, 136.45, 136.00, 133.18, 131.94, 130.48, 130.20, 129.95, 129.69, 129.54, 128.58, 128.33, 125.79, 125.26, 124.78, 124.50, 119.48, 34.20, 32.17, 31.46, 31.24, 29.47, 28.95, 25.44, 22.97, 21.05, 14.30; <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -1.91; HR-ESIMS (m/z) [M + 1]<sup>+</sup> calcd for C54H65BN3S2 830.4713, found 830.4726.

Synthesis of Compound 4b. In an oven-dried Schlenk flask were placed 3a (40 mg, 0.06 mmol), 5-trimethylstannyl-2,2'-bithiophene (50 mg, 0.15 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (6 mg, 0.006 mmol), and P(o-tolyl)<sub>3</sub> (7.3 mg, 0.024 mmol). The flask was evacuated and filled with  $N_2$ three times, and then dried toluene (9 mL) was injected into the mixture. The resulting solution was stirred at 100 °C for 12 h under an N2 atmosphere. 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). 4b was obtained as a yellow solid in 71% yield (35 mg): <sup>1</sup>H NMR (400 MHz,  $C_6 D_6 \delta$  7.58 (d, J = 1.5 Hz, 1H), 7.47 (t, J = 1.6 Hz, 1H), 7.35– 7.31 (m, 1H), 7.25 (dd, J = 8.1, 1.8 Hz, 1H), 7.20-7.17 (m, 1H), 7.08 (dd, J = 3.6, 1.1 Hz, 1H), 7.03 (dd, J = 3.5, 1.1 Hz, 1H), 6.99-6.95 (m, 2H), 6.94 (s, 4H), 6.91–6.80 (m, 4H), 6.74 (td, J = 5.5, 1.1 Hz, 2H), 6.68 (ddd, J = 6.5, 5.1, 3.6 Hz, 2H), 3.42 (s, 2H), 2.67 (s, 3H), 2.55 (s, 12H), 2.24 (s, 6H); <sup>13</sup>C NMR (176 MHz,  $C_6D_6$ )  $\delta$  153.16, 151.74, 141.98, 141.44, 137.54, 137.30, 135.16, 133.41, 130.67, 130.07, 128.62, 128.35, 126.13, 125.80, 125.68, 125.36, 125.14, 124.97, 124.38, 121.42, 119.64, 34.28, 30.23, 25.57, 21.03;  $^{11}\mathrm{B}$  NMR (128 MHz, C\_6D\_6)  $\delta$ 

-1.08; HR-ESIMS  $(m/z)~[{\rm M}+1]^+$  calcd for  ${\rm C}_{50}{\rm H}_{45}{\rm BN}_3{\rm S}_4$  826.2589, found 826.2686.

Synthesis of Compound 5b. In an oven-dried Schlenk flask were placed 3a (110 mg, 0.16 mmol), (3,3'-dihexyl[2,2'-bithiophene]-5,5'diyl)bis[trimethylstannane] (110 mg, 0.16 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (6 mg, 0.0064 mmol), and P(o-tolyl)<sub>3</sub> (10 mg, 0.032 mmol). The flask was evacuated and filled with N2 three times, and then dried toluene (8 mL) was injected into the mixture. The resulting solution was stirred at 120 °C for 48 h under N2. The end-capping reaction was carried out by adding (3,3'-dihexyl[2,2'-bithiophene]-5,5'-diyl)bis-[trimethylstannane] (9 mg, 0.013 mmol), and the solution was stirred at 120 °C for 12 h under N2. Finally, bromobenzene (126 mg, 0.8 mmol) was added and the mixture was stirred at 120 °C for 24 h under N2. After being cooled to room temperature, the resulting organic phase was extracted with  $CH_2Cl_2$  (10 mL  $\times$  3) and washed with water. After the solvents were removed, the residue was dispersed in a small amount of dichloromethane and added dropwise to a stirred acetonitrile solution and the precipitate was collected. The obtained yellow solid was next dispersed in methanol and the precipitate was collected. Then the yellow solid was dispersed in acetonitrile once again and the precipitate was collected. Finally, the obtained yellow solid was dispersed in diethyl ether and the precipitate was collected and dried in vacuo to afford the desired polymer **5b** (55 mg, 42%): <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.27-7.08 (m, 22H), 6.58 (br, 4H), 4.05 (br, 3H), 3.00 (br, 2H), 2.60 (br, 8H), 2.14 (br, 6H), 2.02 (br, 12H), 1.60 (br, 8H), 1.28 (br, 24H), 0.87 (br, 12H); <sup>11</sup>B NMR (225 MHz,  $CD_2Cl_2$ )  $\delta$  3.14; GPC (polystyrene standard, 25 °C)  $M_p$  = 6888, PDI = 1.5.

Formation of 2c-4c via Photoelimination. <sup>1</sup>H NMR scale photoelimination reactions were carried out using  $C_6D_6$  as the solvent and quartz J. Young NMR tubes as the reaction vessels under N2 and a Shanghai Si-Le Photochemical Reactor as the light source. The azaborine products 2c-4c were characterized by NMR and HRMS analysis. For NMR, UV/vis, and fluorescence spectroscopic tracking data, see the Supporting Information. Data for 2c: <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  7.97 (s, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.76 (d, J = 8.8Hz, 1H), 7.41 (t, J = 8.6 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.10 (s, 2H), 7.03-6.98 (m, 2H), 6.93 (d, J = 5.3 Hz, 2H), 6.80 (d, J = 5.1 Hz, 1H), 2.92 (s, 3H), 2.64 (s, 6H), 2.53 (t, J = 7.8 Hz, 2H), 2.36 (s, 3H), 1.52-1.47 (m, 2H), 1.15-1.21 (m, 6H), 0.83 (t, J = 6.8 Hz, 3H);  $^{13}C$ NMR (176 MHz, C<sub>6</sub>D<sub>6</sub>) δ 153.80, 146.92, 144.23, 141.16, 139.73, 138.96, 136.52, 135.98, 131.81, 130.98, 130.70, 129.88, 129.64, 129.41, 129.14, 128.92, 127.66, 126.42, 125.97, 124.83, 123.03, 117.78, 107.71, 34.90, 31.96, 31.22, 29.42, 28.95, 23.76, 22.93, 21.33, 14.28; <sup>11</sup>B NMR (128 MHz,  $C_6D_6$ )  $\delta$  32.8; HR-ESIMS (m/z) [M + 1]<sup>+</sup> calcd for C<sub>35</sub>H<sub>39</sub>BN<sub>3</sub>S 544.2958, found 544.2941. Data for 3c: <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  8.13 (d, J = 1.4 Hz, 1H), 7.78 (d, J = 8.9 Hz, 1H), 7.45–7.39 (m, 2H), 7.31 (dd, J = 8.9, 1.7 Hz, 1H), 7.18 (d, J = 1.4 Hz, 1H), 7.11-7.08 (m, 2H), 7.04-7.00 (m, 2H), 6.93 (dd, J = 5.1, 2.4 Hz, 3H), 6.80 (d, J = 5.2 Hz, 1H), 2.93 (s, 3H), 2.87 (d, J = 8.3 Hz, 2H), 2.63 (s, 6H), 2.53 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H), 1.70-1.64 (m, 2H), 1.52–1.47 (m, 2H), 1.19 (ddd, J = 14.5, 7.3, 2.9 Hz, 12H), 0.82 (d, J = 7.0 Hz, 6H); <sup>13</sup>C NMR (176 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  153.84, 146.75, 144.28, 141.12, 139.74, 139.53, 138.96, 138.82, 136.50, 136.01, 134.61, 132.09, 131.85, 130.69, 130.02, 129.89, 129.46, 129.14, 128.92, 127.67, 127.04, 126.33, 124.85, 124.59, 124.31, 123.47, 119.77, 106.57, 34.85, 32.01, 31.51, 31.22, 29.60, 29.43, 28.96 23.74, 22.98, 22.74, 21.55, 14.28; <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>6</sub>) δ 33.6; HR-ESIMS (m/z)  $[M + 1]^+$  calcd for  $C_{45}H_{53}BN_3S_2$  710.3774, found 710.3790. Data for 4c: <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  8.23 (d, J = 1.7 Hz, 1H), 7.77 (d, J = 9.0 Hz, 1H), 7.56-7.53 (m, 1H), 7.51 (t, J = 1.6 Hz, 1H), 7.11 (s, 2H), 7.08-7.05 (m, 3H), 6.97-6.94 (m, 3H), 6.83 (dd, J = 5.4, 3.8 Hz, 2H), 6.75 (ddd, J = 4.5, 3.3, 1.3 Hz, 3H), 6.69 (dd, J = 5.2, 3.5 Hz, 3H), 2.89 (s, 3H), 2.70 (s, 6H), 2.35 (s, 3H); <sup>13</sup>C NMR (176 MHz,  $C_6D_6$ )  $\delta$  155.10, 154.45, 142.40, 142.26, 141.16, 139.81, 138.96, 137.91, 137.58, 135.86, 135.20, 131.29, 129.65, 129.59, 127.00, 126.81, 126.15, 125.14, 124.89, 124.27, 123.24, 116.17, 106.72, 31.70, 23.80, 21.33, 20.25; <sup>11</sup>B NMR (128 MHz,  $C_6D_6$ )  $\delta$  34.3; HR-ESIMS (m/z)  $[M + 1]^+$  calcd for C<sub>41</sub>H<sub>33</sub>BN<sub>3</sub>S<sub>4</sub> 706.1650, found 706.1658.

**X-ray Diffraction Analysis.** The crystal data of **4b** were collected on a Bruker D8-Venture diffractometer with Mo target ( $\lambda = 0.71073$ Å) at 180 K. Data were processed on a PC with the aid of the Bruker SHELXTL software package<sup>16</sup> and corrected for absorption effects. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. The detail of crystal data, collection parameters, and results of analyses are provided in the Supporting Information. The crystal data of **4b** were deposited with the Cambridge Crystallographic Data Center with the deposition number CCDC 1544199. 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 website at DOI: 10.1021/acs.organo-met.7b00290.

Synthetic details, characterization data, TD-DFT data, photoelimination experiments, UV/vis spectra, and crystal data of **4a** (PDF)

Cartesian coordinates of the calculated structures (XYZ)

#### Accession Codes

CCDC 1544199 contains 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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