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Tetrahydrodibenzophenanthridine-Based Boron-Bridged Polycyclic Aromatic Hydrocarbons: Synthesis, Structural Diversity, and Optical Properties

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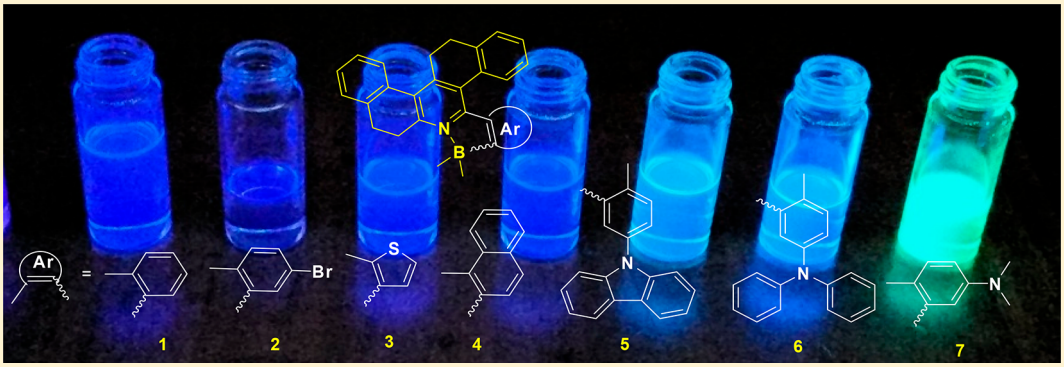
Supporting Information



ABSTRACT: A series of B←N coordinated tetrahydrodibenzo[*a*,*i*]phenanthridine-based polycyclic aromatic hydrocarbons (PAHs) have been designed and synthesized. All of these compounds have been characterized by multinuclear NMR spectroscopy and high-resolution mass spectrometry. Compounds **1**, **2**, **4**, and **7** have also been characterized by single-crystal X-ray diffraction analysis. Our newly synthesized compounds exhibit good luminescence quantum yields in solution and moderate quantum yields in the solid state. Furthermore, the compounds show a large Stokes shift in comparison to the well-known boron−dipyrromethene dyes.

INTRODUCTION

Organic fluorophores, especially polycyclic aromatic hydrocarbons (PAHs), have attracted great attention due to their widespread applications ranging from photodynamic therapy (PDT) and bioimaging to optoelectronics.[1] Despite their wide range of applications, often they have disadvantages such as long-term stability and performance. Different approaches have been used to overcome these shortcomings and to tune the electronic properties of PAHs. Among them, incorporation of main-group elements has become a powerful strategy to produce exciting electronic properties.[2] Tricoordinate boron incorporated PAH compounds have emerged as efficient materials due to strong luminescence and high electron affinities.[3−5] Intramolecular B←N coordination (B−N is isoelectronic with C═C) has become yet another powerful approach to modify PAHs.[6] B←N coordination reinforces the coplanarity and rigidity of the basic structure and also enhances the electron-accepting capability of the resulting materials. The synthesis of B←N coordinated thienylthiazole ligand based ladder-type structures has been explored by Yamaguchi and co-workers.[7] Kawashima and co-workers[8] reported highly luminescent azobenzene- or imine-based B←N coordinated boron compounds. Later, Wang and co-workers[9] developed photochromic B←N coordinated boron compounds based on the 2-phenylpyridine moiety. In 2010 Murakami and co-workers[10] reported the aromatic electrophilic borylation strategy to synthesize phenylpyridine boron complexes. Ingleson and co-workers[6b] applied an electrophilic borylation method to incorporate boron into a π-conjugated acceptor donor system. Recently, Jäkle and co-workers[11] explored a similar strategy to synthesize a B←N coordinated anthracene derivative which has been used for oxygen sensitization. Here, we disclose the synthesis and photophysical properties of tetrahydrodibenzo[*a*,*i*]phenanthridine boron compounds.

RESULTS AND DISCUSSION

Phenanthridine and its derivatives are well-known polycyclic aromatic entities found in natural products and exhibit interesting pharmacological properties such as antitumor and antibacterial.[12] In addition, phenanthridine and its derivatives

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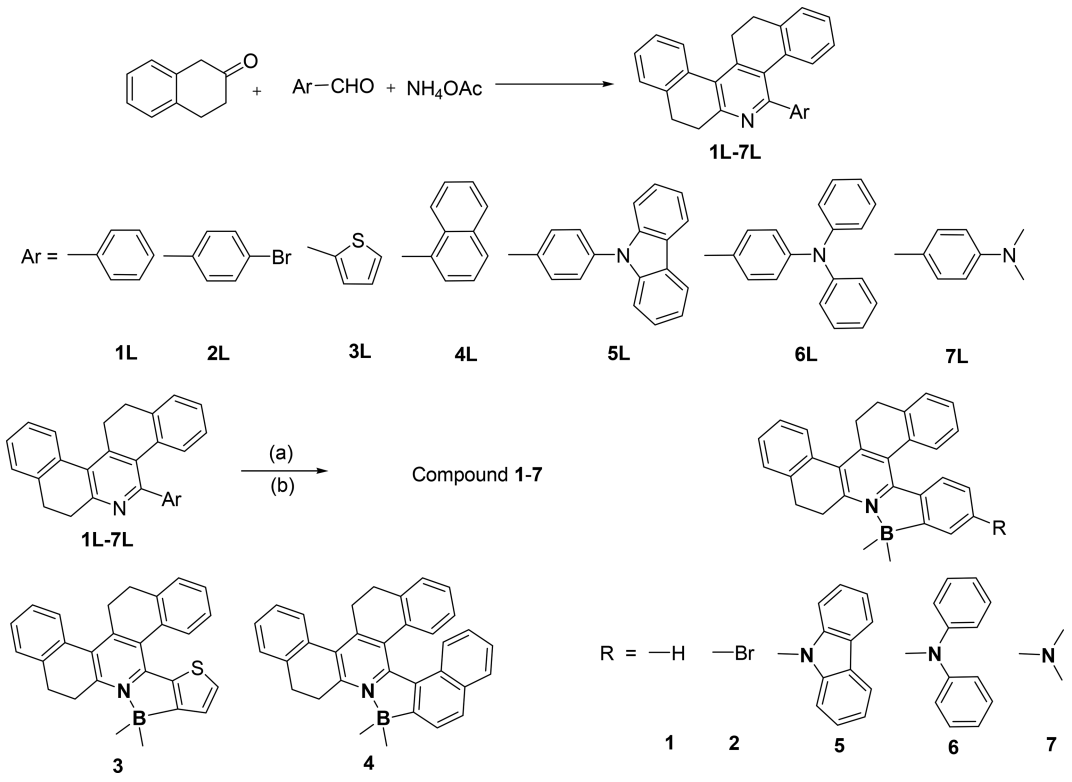
Scheme 1. Synthesis of Compounds 1−7[a]



[a]Legend: (a) BBr_3, $N(i\text{-}Pr)_2Et$, CH_2Cl_2, 0 °C; (b) $AlMe_3$, toluene.

have also found application in photoconduction, optoelectrical switches, and so on.[12g,h] Among the phenanthridine derivatives the tetrahydrodibenzo(*a,i*)phenanthridine core attracted us due to (a) its synthetic methodology which involves one-pot synthesis and (b) tunable functionality. 5-Substituted tetrahydrophenanthridines **1L−7L** were prepared by one-pot reactions using 2-tetralone, arylaldehyde, and ammonium acetate in an ethanol/acetic acid solvent mixture, following the procedure reported in the literature (Scheme 1).[13] All of these compounds were characterized by ^1H and ^{13}C NMR and also HRMS analysis. All of the heteroarenes were subjected to aromatic electrophilic borylation[10,14] using BBr_3 in the presence of *N,N*-diisopropylethylamine to yield the B←N coordinated dibromoboron compounds. Further treatment of B←N coordinated dibromoboron compounds with trimethylaluminum gave the targeted B←N coordinated organoboron compounds **1−7** (Scheme 1). All of the boron compounds are stable toward air and moisture and could be purified by column chromatography. The appearance of new signals around 0.2 ppm in ^1H NMR and 4 ppm (broad) in ^{13}C NMR corresponds to the methyl attached to the boron atom. Furthermore, ^{11}B NMR spectra of compounds **1−7** shows a signal at δ ∼1−3 ppm, which indicates the formation of tetracoordinate boron. The ^1H NMR of compound **4** displays two equally intense signals for the methyl attached to the boron atom, thus indicating the presence of two conformers. However, ^1H NMR spectra of compounds **1−3** and **5−7** show only one signal at ca. 0.2 ppm. To understand this, variable-temperature (VT) ^1H NMR experiments on compound **1**, **4**, and **7** were performed. VT ^1H NMR studies reveal two signals for the methyl attached to the boron in a 1:1 ratio at low temperature, which can be ascribed to the restriction of conformations with decreasing temperature (Figures S1−S3).[15] Moreover, the proposed structures of B←N coordinated boron compounds were confirmed by LC-MS and elemental analysis. Single crystals of compounds **1**, **2**, **4**, and **7** were grown by slow evaporation of a mixture of CH_2Cl_2 and ethanol solvent and studied using single-crystal X-ray diffraction analysis. All of the boron compounds crystallized in the triclinic space group $P\bar{1}$, except compound **1**, which crystallized in the orthorhombic *Pbca* space group. In each of these compounds, the tetracoordinated boron center adopts a typical distorted-tetrahedral geometry. The B−N and B−C bond distances fall in the range 1.646(3)−1.669(2) and 1.583(3)−1.626(3) Å, respectively (Table 1), which are consistent with the values reported in the literature for B←N coordinated boron complexes.[9,11,16] The molecular structures of all the compounds showed that the boron atom coordinates to the pyridyl nitrogen atom to form a five-membered ring (Figure 1). The Ar group attached to pyridyl becomes coplanar due to B←N coordination. The interplanar angles between plane A and plane F vary from 4.3 to 8.1°, those between plane A and Ar vary from 10.4 to 18.9°, and those between plane F and Ar vary from 6.0 to 11.6° (Table 1). Owing to the half-chair formation observed for alicyclic rings B and D, planes C and E showed pronounced deviation up to 41° with respect to plane A. It should be noted that the puckerings of rings B and D are similar in compounds **1**, **2**, and **4** whereas in compound **7** the puckering is in the opposite direction (Figure 2, side view).

All of the tetrahydrodibenzo(*a,i*)phenanthridine ligands (**1L−7L**) displayed absorption maxima at ca. 316−350 nm, which can be attributed to $\pi-\pi^*$ electronic transitions (Table 2 and Figure S6). When they were irradiated at their longer wavelength absorption maxima, compounds **1L−7L** exhibited

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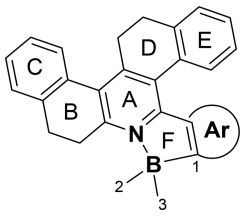
Table 1. Comparison of Bond Length and Angle Data for Compounds 1, 2, 4, and 7



	1	2	4	7
B–C1 (Å)	1.583(3)	1.599(3)	1.599(2)	1.598(2)
B–C2 (Å)	1.625(3)	1.625(3)	1.622(2)	1.621(2)
B–C3 (Å)	1.626(3)	1.616(3)	1.617(2)	1.623(2)
B–N (Å)	1.646(3)	1.669(2)	1.656(2)	1.660(2)
C1–B–N (deg)	96.5(2)	95.6(1)	95.5(1)	95.80(8)
C1–B–C2 (deg)	108.7(2)	111.1 (2)	107.3(1)	113.6(1)
C1–B–C3 (deg)	114.5(2)	113.3(2)	116.0(1)	111.2(1)
C2–B–N (deg)	108.9 (2)	111.2(2)	111.9(1)	110.5(1)
C3–B–N (deg)	111.6(2)	110.6(2)	109.0(1)	111.5(1)
C3–B–C2 (deg)	115.0 (2)	113.7(2)	115.3(1)	113.0(1)
plane A‖C (deg)	25.26	29.37	24.765	29.83
plane A‖E (deg)	40.03	41.53	37.998	40.42
plane A‖F (deg)	4.31	8.10	7.41	7.81
plane F‖Ar (deg)	7.68	7.49	11.63	6.01
plane A‖Ar (deg)	10.45	15.16	18.95	13.33

weak to moderate fluorescence (Table 2 and Figure S7). As expected, the B←N coordinated boron compounds **1**–**7** exhibited red-shifted absorptions and emissions. All of the boron compounds showed limited solubility in protic solvents; hence, the photophysical studies were performed in toluene, CH_2Cl_2, THF, and CH_3CN (Table 2 and Table S1). The absorption spectra of the boron compounds **1**–**7** in CH_2Cl_2 solution (Figure 2) showed absorption maxima at ca. 368–420 nm with moderate molar extinction coefficients at ca. 15800–38700 M^{-1} cm^{-1}. On excitation at their longer wavelength absorption, the emission maxima of these compounds were tuned from 403 nm (compound **1**) to 494 nm (compound **6**) in CH_2Cl_2. Naphthalene (**4**) and thiophene (**3**) substituted B←N coordinated boron chromophores showed red-shifted emissions in comparison to compound **1**. Compounds **1**–**4** did not show any emission changes with solvent polarity, indicating that the stabilization of the excited state by interaction with solvent molecules is modest (Figure S4). However, in the case of compounds **5**–**7**, the emission maxima red-shifted due to intramolecular charge transfer from carbazole, $-NPh_2$, and $-NMe_2$ groups, respectively. The charge transfer emission of these compounds was further supported by the positive solvatochromism with increased solvent polarity from toluene to acetonitrile (Figure S5 and Table S1). The intramolecular charge transfer process present in compounds **5**–**7** is likely responsible for the relatively high Stokes shifts and high fluorescence quantum yields. The highest quantum yield (95% in toluene; Table S1) with large Stokes shift was observed for compound **5** in the solution state. Compound **2** showed a lower fluorescence quantum yield (0.13 in THF; Table S1) in solution; this may be due to the presence of the heavy bromine atom, which induces non-radiative pathways. All of the boron compounds showed single-exponential decay with lifetimes in nanoseconds in THF solution (Table S1 and Figure S8). Moreover, the absolute solid-state fluorescence quantum yields of compounds **1**–**7** (Figure 3 and Table 2) suggest that they are highly emissive in the solid state as well. The solid-state emission of compounds **1**–**7** ranges from 463 nm (deep blue **2**) to 550 nm (yellow **7**), and all are red-shifted in comparison to their solution state (CH_2Cl_2) emission by ∼40 nm. The highest solid-state quantum yield (0.64) was observed for compound **7** with red-shifted emission at 550 nm (Table 2). The emission red shift observed in the solid state (over sthe solution state) for compound **7** (485 nm in CH_2Cl_2, 550 nm in the solid state) is more pronounced in comparison to compound **5** (450 nm in CH_2Cl_2, 470 nm in the solid state). This is probably due to the "carbazole" twist expected in compound **5**, which restricts the planarization of the structure in the excited state. Density functional theory (DFT) calculations were performed to understand the photophysical properties of the B←N coordinated boron compounds. The HOMOs and LUMOs of compounds **1**–**7** are provided in Figure 4. As shown in Figure 4, the HOMOs and LUMOs of compounds **1**–**4** were delocalized over the aromatic rings; in particular the HOMO levels have orbital contributions from Ar, A, and C for compounds **1**–**3** and Ar and A for compound **4**, whereas the LUMO levels have orbital contributions from Ar, A, and C for compounds **1**–**4**. Compound **4**, which contains a naphthyl group, has a slightly higher HOMO energy, consistent with the greater red shift observed for compound **4** in comparison to

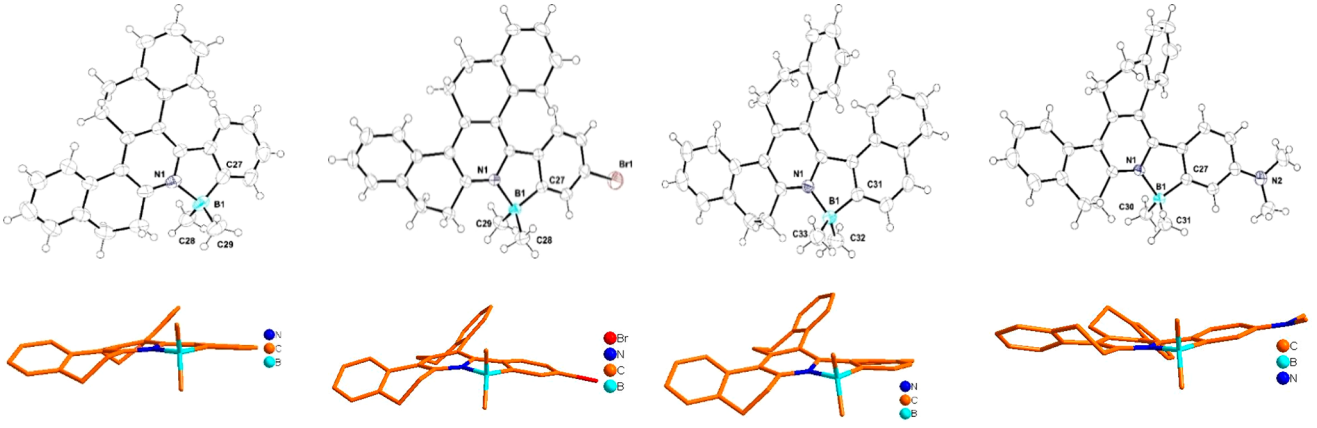


Figure 1. Molecular structures of **1**, **2**, **4**, and **7** (from left to right) with thermal ellipsoids at the 50% probability level (top). Side views of **1**, **2**, **4**, and **7** (from left to right; capped stick model; bottom).

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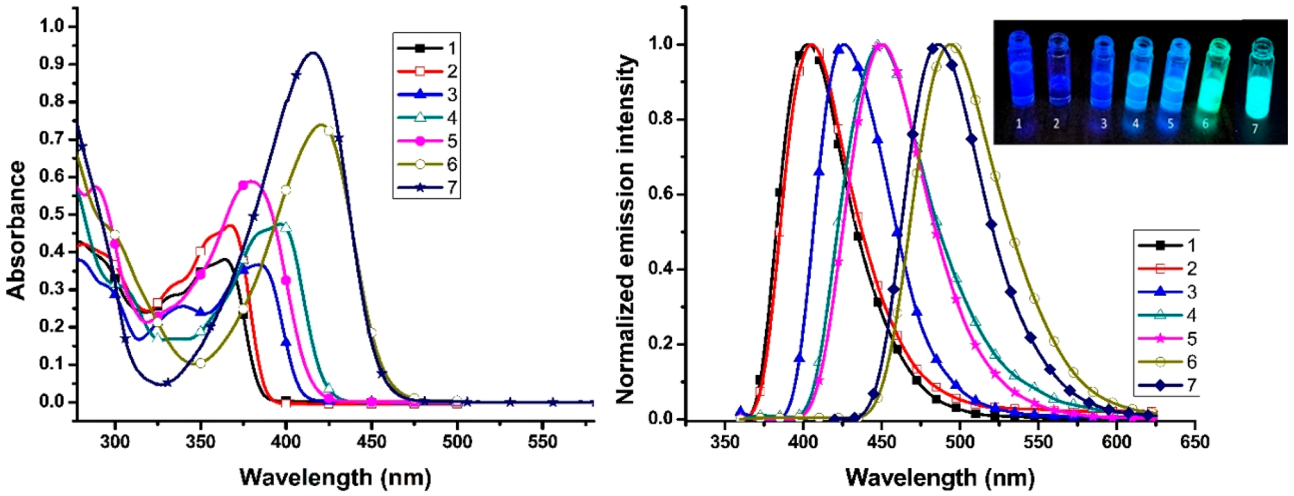

Figure 2. Absorption (left) and normalized emission (right) spectra of boron compounds **1**−**7** (24 μM) in CH_2Cl_2, excited at longer wavelength absorption maxima. Insets (right): fluorescence photograph of compounds **1**−**7** in THF under a hand-held UV lamp at 365 nm.

Table 2. Photophysical Data of Compounds 1L−7L and 1−7

compound	solvent	λ_{max} [a] (nm)	ε_{max} (10^4 M^{-1} cm^{-1})	λ_{em} (nm)[a,b]	Δ (cm^{-1})	Φ_F [c]
1L	CH_2Cl_2	318	1.38	395	6130	0.01
2L	CH_2Cl_2	319	2.00	399	6285	0.03
3L	CH_2Cl_2	342	1.13	421	5486	0.02
4L	CH_2Cl_2	316	1.56	408	7135	0.02
5L	CH_2Cl_2	330	1.92	419	6436	0.18
6L	CH_2Cl_2	350	1.80	459	6784	0.45
7L	CH_2Cl_2	345	2.21	449	6713	0.30
1	CH_2Cl_2	364	1.58	403	2650	0.58
	solid			466		0.21[d]
2	CH_2Cl_2	368	1.96	406	2540	0.15
	solid			463		0.05[d]
3	CH_2Cl_2	384	1.52	426	2560	0.38
	solid			471		0.16[d]
4	CH_2Cl_2	397	1.97	448	2860	0.53
	solid			492		0.06[d]
5	CH_2Cl_2	379	2.45	450	4160	0.90
	solid			470		0.38[d]
6	CH_2Cl_2	420	3.07	494	3560	0.87
	solid			531		0.46[d]
7	CH_2Cl_2	415	3.87	485	3470	0.67
	solid			550		0.64[d]

[a]Absorption maximum (24 μM). [b]Excited at the absorption maximum. [c]Quinine sulfate standard in 0.1 N H_2SO_4. [d]Absolute quantum yields measured using an integrating sphere.

1−**3**. The DFT calculations further indicate that compounds **5**−**7** shows a red-shifted λ_{max} due to an intramolecular charge transfer (ICT) transition from amino-substituted aryl group to phenyl rings A, C, and E. The presence of an electron-donating substituent on phenyl at the 5-position significantly raises the HOMO level, thereby lowering the energy gap in these compounds.

The electrochemical properties of compounds **1**−**7** were investigated by cyclic voltammetry (CV) in deoxygenated dimethoxyethane (DME) at room temperature (Figure S9 and Table S2). All of the compounds (except **3**)[17] exhibit one electron reduction event within the electrochemical window of DME. The reduction potentials range from −2.30 to −2.67 V, which are comparable with those of our recently reported imidazole-based boron complexes.[18] Compound **5** was easily reduced over other compounds due to a more stabilized LUMO level. The cathodic peak potential of compound **7** is highly negative, demonstrating the electron-donating nature of $-NMe_2$. We also investigated the oxidation properties of compounds **5**−**7**. All three compounds exhibit one quasi-reversible oxidation (Figure S10 and Table S3). The oxidation potential of compound **7** is lower than those of **5** and **6** because of the presence of a better electron-donating group. The frontier orbital energies (HOMO and LUMO) were also derived from the onset absorption and E_{pc}.[19] The HOMO−LUMO gaps obtained from these calculations (Table 3) mirror the trend of those obtained from the TD-DFT computations.

CONCLUSIONS

A series of tetrahydrodibenzo[*a*,*i*]phenanthridine compounds (**1L**−**7L**) were synthesized in one pot. By simple electrophilic borylation of these compounds, B←N coordinated boron

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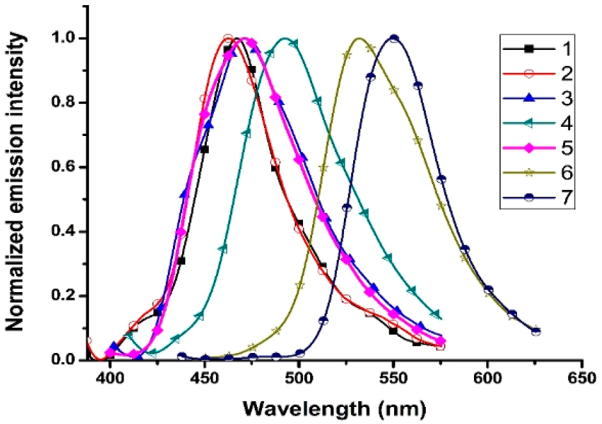

Figure 3. Normalized emission spectra of boron compounds **1**–**7** in the solid state.

compounds **1**–**7** were obtained with good yields. All of these compounds were successfully characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction analyses in the case of compounds **1**, **2**, **4**, and **7**. Large Stokes shifts as well as better quantum yields in both solution and the solid state suggest that this class of compounds could have potential applications in sensing and optoelectronic devices.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of Compounds 1L–7L. To a warm solution of aldehyde (1 equiv) and ammonium acetate (4 equiv) in ethanol and acetic acid (4/1; 40 mL/10 mL) was added 2-tetralone (2 equiv). The reaction mixture was heated for 5 min at 75 °C and then left aside for 24 h at room temperature in open air. The progress of the reaction was monitored by TLC. The reaction mixture was poured into water and extracted with dichloromethane. The combined organic layers were washed with brine solution, dried over Na_2SO_4, and concentrated using a rotary evaporator. The crude reaction mixture was purified by 100–200 silica gel chromatography using an *n*-hexane/dichloromethane mixture as the mobile phase.

Synthesis of Compound ***1L.*** The quantities involved are as follows: benzaldehyde (0.57 mL, 5.67 mmol), 2-tetralone (1.5 mL, 11.34 mmol), and ammonium acetate (1.75 g, 22.68 mmol). Yield: 1.66 g, (82%). Mp: 215 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.51 (m, 1H), 7.46 (dd, J = 6.5, 3.0 Hz, 2H), 7.39–7.29 (m, 6H), 7.27–7.24 (m, 1H), 7.16–7.10 (m, 1H), 6.89 (d, J = 3.9 Hz, 2H), 3.17–3.14 (m, 2H), 3.12–3.09 (m, 2H), 2.98–2.95 (m, 2H), 2.79 (t, J = 8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.11, 153.97, 145.71, 142.08, 139.68, 138.71, 133.07, 133.05, 129.87, 129.68, 128.87, 128.74, 128.40, 127.91, 127.83, 127.69, 127.51, 127.00, 126.91, 126.08, 125.67, 33.20, 29.59, 29.51, 29.25 ppm. HRMS (ESI): calcd for $C_{27}H_{22}N$ ($[M + H]^+$) 360.1747, found 360.1748. Anal. Calcd for $C_{27}H_{21}N$: C, 90.21; H, 5.89; N, 3.90. Found: C, 89.98; H, 6.04; N, 3.87.

Table 3. HOMO and LUMO Levels Derived from UV/Vis Onset Absorption and Electrochemical Data

compound	HOMO–LUMO gap[a]	LUMO[b]	HOMO[c]
1	3.22	−2.26	−5.48
2	3.18	−2.53	−5.71
3	3.04	−2.27	−5.31
4	2.93	−2.41	−5.34
5	3.00	−2.50	−5.50
6	2.72	−2.28	−5.00
7	2.73	−2.13	−4.86

[a]Absorption onset of the longest-wavelength UV band. [b]Calculated from E_{pc} of the first reduction wave with reference to Fc/Fc^+. [c]Calculated from absorption energy and LUMO.

Synthesis of Compound ***2L.*** The quantities involved are as follows: 4-bromobenzaldehyde (1.04 g, 5.67 mmol), 2-tetralone (1.50 mL, 11.34 mmol), and ammonium acetate (1.75 g, 22.68 mmol). Yield: 1.96 g, (79%). Mp: 219 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.48 (m, 3H), 7.38–7.27 (m, 6H), 7.17 (td, J = 7.3, 1.4 Hz, 1H), 6.98–6.91 (m, 2H), 3.18–3.11 (m, 4H), 2.99–2.96 (m, 2H), 2.79 (t, J = 8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.24, 152.35, 146.27, 140.66, 139.72, 138.82, 132.85, 132.63, 131.73, 131.63, 129.65, 129.10, 128.80, 128.04, 127.98, 127.39, 127.16, 126.22, 125.97, 122.35, 33.01, 29.57, 29.46, 29.32 ppm. HR-MS (ESI): calcd for $C_{27}H_{21}BrN$ ($[M + H]^+$) 438.0852, found 438.0841. Anal. Calcd for $C_{27}H_{20}BrN$: C, 73.98; H, 4.60; N, 3.20. Found: C, 73.77; H, 4.75; N, 3.16.

Synthesis of Compound ***3L.*** The quantities involved are as follows: thiophene-2-carbaldehyde (0.53 mL, 5.67 mmol), 2-tetralone (1.5 mL, 11.34 mmol), and ammonium acetate (1.75 g, 22.68 mmol). Yield: 1.38 g, (67%). Mp: 220 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.50 (m, 1H), 7.36–7.26 (m, 6H), 7.19 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 4 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.94 (dd, J = 5.0, 3.7 Hz, 1H), 3.13–3.06 (m, 4H), 2.98–2.94 (m, 2H), 2.76 (t, J = 7.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.35, 147.07, 146.07, 144.65, 139.77, 138.99, 133.06, 132.95, 129.35, 129.09, 128.74, 128.10, 128.01, 127.85, 127.72, 127.51, 127.26, 127.09, 126.82,

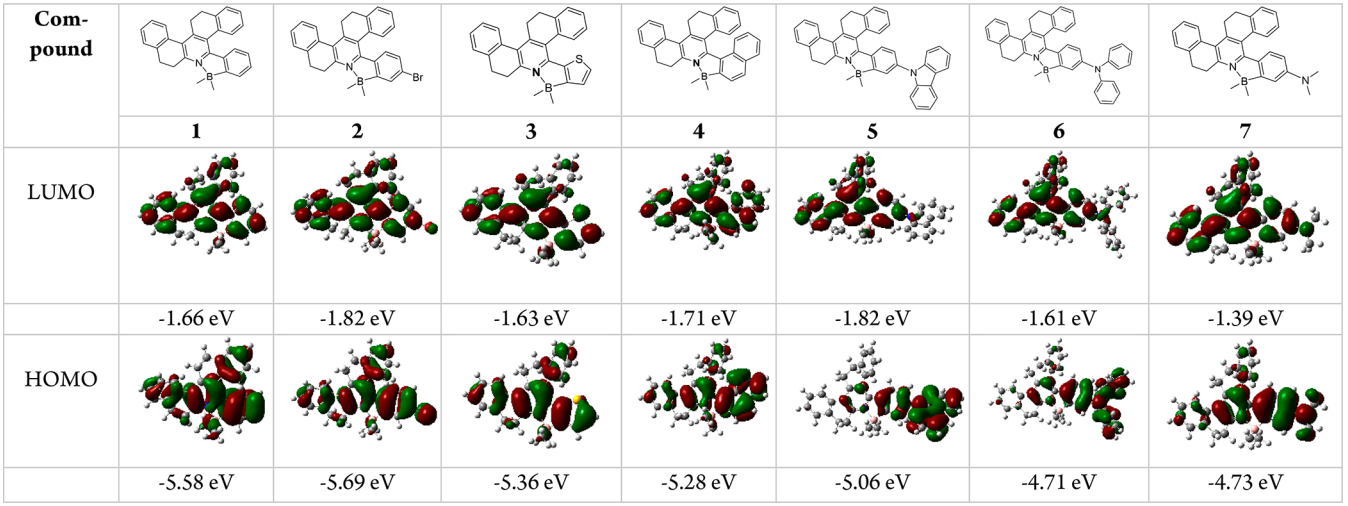

Figure 4. Computed orbitals for compounds **1**–**7**.

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126.18, 125.83, 33.23, 29.62, 29.60, 29.49 ppm. HR-MS (ESI): calcd for $C_{25}H_{20}NS$ ([M + H]$^+$) 366.1311, found 366.1308. Anal. Calcd for $C_{25}H_{19}NS$: C, 82.15; H, 5.24; N, 3.83. Found: C, 82.00; H, 5.38; N, 3.86.

Synthesis of Compound ***4L***. The quantities involved are as follows: 1-naphthaldehyde (0.77 mL, 5.67 mmol), 2-tetralone (1.5 mL, 11.34 mmol), and ammonium acetate (1.75 g, 22.68 mmol). Yield: 1.44 g, (62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, J = 8.0, 4.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 1H), 7.58−7.56 (m, 1H), 7.47−7.42 (m, 2H), 7.40−7.31 (m, 5H), 7.19 (d, J = 7.4 Hz, 1H), 6.99 (td, J = 7.2, 1.8 Hz, 1H), 6.63−6.57 (m, 2H), 3.34−3.27 (m, 1H), 3.20−3.11 (m, 3H), 3.02−2.96 (m, 2H), 2.83−2.74 (m, 2H) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 158.00, 153.25, 145.49, 139.92, 139.84, 138.58, 134.20, 133.16, 132.91, 132.01, 130.49, 129.00, 128.40, 128.36, 128.06, 127.98, 127.92, 127.05, 126.90, 126.31, 126.23, 126.10, 125.88, 125.72, 33.22, 29.78, 29.55, 29.38 ppm. HR-MS (ESI): Calcd for $C_{31}H_{24}N$ ([M + H]$^+$) 410.1903, found 410.1904. Anal. Calcd for $C_{31}H_{23}N$: C, 90.92; H, 5.66; N, 3.42. Found: C, 90.85; H, 5.82; N, 3.43.

Synthesis of Compound ***5L***. The quantities involved are as follows: 4-(9*H*-carbazol-9-yl)benzaldehyde (1.53 g, 5.67 mmol), 2-tetralone (1.5 mL, 11.34 mmol), and ammonium acetate (1.75 g, 22.68 mmol). Yield: 1.54 g, (52%). Mp: 267 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 7.7 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.60−7.55 (m, 3H), 7.50−7.29 (m, 10H), 7.25−7.22 (m, 1H), 7.05 (d, J = 4.0 Hz, 2H), 3.31−3.22 (m, 4H), 3.04−3.01 (m, 2H), 2.83−2.76 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.45, 153.02, 146.07, 141.23, 140.91, 139.81, 139.01, 137.34, 133.05, 132.98, 131.58, 129.80, 129.26, 128.87, 128.06, 127.99, 127.95, 127.44, 127.24, 127.01, 126.24, 126.09, 125.82, 123.56, 120.43, 120.08, 109.97, 33.36, 29.68, 29.59, 29.35 ppm. HR-MS (ESI): calcd for $C_{39}H_{29}N_2$ ([M + H]$^+$) 525.2325, found 525.2320. Anal. Calcd for $C_{39}H_{28}N_2$: C, 89.28; H, 5.38; N, 5.34. Found: C, 89.12; H, 5.23; N, 5.34.

Synthesis of Compound ***6L***. The quantities involved are as follows: 4-(diphenylamino)benzaldehyde (1.55 g, 5.67 mmol), 2-tetralone (1.5 mL, 11.34 mmol), and ammonium acetate (1.75 g, 22.68 mmol). Yield: 1.49 g, (50%). Mp: 238 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53−7.51 (m, 1H), 7.37−7.24 (m, 10H), 7.17−7.12 (m, 5H), 7.07−6.97 (m, 6H), 3.16−3.09 (m, 4H), 2.98−2.95 (m, 2H), 2.77 (t, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.20, 153.71, 147.73, 147.55, 145.78, 139.72, 138.80, 136.15, 133.36, 133.21, 130.93, 129.68, 129.29, 128.85, 128.75, 127.95, 127.68, 127.33, 127.07, 126.97, 126.12, 125.56, 124.48, 123.67, 122.93, 33.36, 29.64, 29.60, 29.32 ppm. HR-MS (ESI): calcd for $C_{39}H_{31}N_2$ ([M + H]$^+$) 527.2482, found 527.2463. Anal. Calcd for $C_{39}H_{30}N_2$: C, 88.94; H, 5.74; N, 5.32. Found: C, 88.81; H, 5.65; N, 5.26.

Synthesis of Compound ***7L***. The quantities involved are as follows: 4-(dimethylamino)benzaldehyde (0.85 g, 5.67 mmol), 2-tetralone (1.5 mL, 11.34 mmol), and ammonium acetate (1.75 g, 22.68 mmol). Yield: 1.27 g, (56%). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.51 (d, J = 8 Hz, 1H), 7.36 (t, J = 8 Hz, 3H), 7.31 (t, J = 8 Hz, 1H), 7.27 (dd, J = 12, 8 Hz, 2H), 7.17−7.07 (m, 2H), 6.96 (t, J = 8 Hz, 1H), 6.69 (d, J = 8.0 Hz, 2H), 3.14−3.09 (m, 4H), 2.98 (s, 6H), 2.97−2.93 (m, 2H), 2.79−2.72 (m, 2H) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 158.13, 154.29, 150.41, 145.73, 139.71, 138.66, 133.86, 133.46, 130.86, 130.13, 129.59, 128.71, 128.37, 127.89, 127.45, 126.85, 126.73, 126.66, 126.06, 125.77, 112.37, 40.67, 33.35, 29.74, 29.69, 29.47 ppm. ESI-MS: calcd for $C_{29}H_{27}N_2$ ([M + H]$^+$) 403.2169, found 403.2160. Anal. Calcd for $C_{29}H_{26}N_2$: C, 86.53; H, 6.51; N, 6.96. Found: C, 86.44; H, 6.45; N, 6.93.

General Procedure for the Synthesis of Compounds 1−7. An oven-dried three-neck round-bottom flask with an addition funnel was degassed and purged using vacuum−nitrogen cycles and charged with a dichloromethane solution of compound **1L**−**7L**. To this solution was added diisopropylethylamine (*i*-Pr_2NEt) at 0 °C, and the mixture was stirred. After 10 min BBr_3 (1.0 M in dichloromethane) was added slowly at the same temperature and the mixture was warmed to room temperature. After the reaction mixture was stirred at room temperature for 24 h, a saturated K_2CO_3 aqueous solution was added and this mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$ and concentrated using a rotary evaporator to afford the crude dibromoboron compound. Without further purification the crude product was placed in a round-bottom flask that was dried using high vacuum and then filled with argon and toluene was added. To this stirred solution was added $AlMe_3$ (2.0 M in toluene) at room temperature. After the mixture was stirred for 1/2 h, the reaction was quenched by adding water and extracted with CH_2Cl_2. The combined organic layers were washed with water and brine. The organic layer was dried over Na_2SO_4 and concentrated using a rotary evaporator. The crude product was purified by silica gel column chromatography using an *n*-hexane/dichloromethane mixture as the mobile phase.

Synthesis of Compound ***1***. The quantities involved are as follows: compound **1L** (0.60 g, 1.67 mmol), *N*,*N*-diisopropylethylamine (0.29 mL, 1.67 mmol), BBr_3 (1.0 M in CH_2Cl_2, 5.01 mL, 5.01 mmol), and $AlMe_3$ (2.0 M in toluene, 1.67 mL, 3.34 mmol). Yield: 0.43 g, (65%). Mp: 251 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.7 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.58−7.54 (m, 2H), 7.41−7.24 (m, 7H), 6.95 (t, J = 8 Hz, 1H), 2.81−4.04 (m, 8H), 0.25 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.22, 155.71, 151.05, 149.83, 139.46, 139.03, 135.70, 131.67, 131.61, 129.70, 129.61, 129.27, 128.94, 128.63, 128.57, 128.40, 127.89, 127.84, 127.26, 126.37, 126.03, 124.82, 123.98, 30.29, 29.35, 28.78, 28.32, 9.16 ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ 2.12 ppm. ESI-MS: calcd for $C_{29}H_{27}BN$ ([M + H]$^+$) 400.2236, found m/z 400.2263. Anal. Calcd for $C_{29}H_{26}BN$: C, 87.22; H, 6.56; N, 3.51. Found: C, 87.02; H, 6.67; N, 3.71.

Synthesis of Compound ***2***. The quantities involved are as follows: compound **2L** (0.73 g, 1.67 mmol), *N*,*N*-diisopropylethylamine (0.29 mL, 1.67 mmol), BBr_3 (1.0 M in CH_2Cl_2, 5.01 mL, 5.01 mmol), and $AlMe_3$ (2.0 M in toluene, 1.67 mL, 3.34 mmol). Yield: 0.49 g, (62%). Mp: 291 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 7.7 Hz, 1H), 7.65 (d, J = 8.3 Hz, 2H), 7.56−7.53 (m, 1H), 7.41−7.30 (m, 5H), 7.28−7.24 (m, 1H), 7.06 (dd, J = 8.5, 2.0 Hz, 1H), 4.04−2.81 (m, 8H), 0.22 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.87, 155.84, 150.11, 150.08, 139.47, 139.17, 134.42, 131.50, 131.40, 129.76, 129.19, 129.08, 128.67, 128.61, 128.31, 127.97, 127.45, 127.13, 126.47, 126.32, 126.19, 125.42, 30.30, 29.34, 28.75, 28.33, 8.79 pppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ 2.66 ppm. ESI-MS: calcd for $C_{29}H_{26}BBrN$ ([M + H]$^+$) 478.1341, found m/z 478.1361. Anal. Calcd for $C_{29}H_{25}BNBr$: C, 72.83; H, 5.27; N, 2.93. Found: C, 72.67; H, 5.21; N, 2.75.

Synthesis of Compound ***3***. The quantities involved are as follows: compound **3L** (0.61 g, 1.67 mmol), *N*,*N*-diisopropylethylamine (0.29 mL, 1.67 mmol), BBr_3 (1.0 M in CH_2Cl_2, 5.01 mL, 5.01 mmol), and $AlMe_3$ (2.0 M in toluene, 1.67 mL, 3.34 mmol). Yield: 0.20 g, (30%). Mp: 239 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28−8.24 (m, 1H), 7.48−7.45 (m, 1H), 7.42−7.37 (m, 4H), 7.32−7.29 (m, 3H), 7.12 (d, J = 4.7 Hz, 1H), 3.44 (br s, 2H), 3.12 (t, J = 8 Hz, 2H), 2.94 (t, J = 6.7 Hz, 2H), 2.73 (t, J = 8 Hz, 2H), 0.23 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.09, 149.48, 148.49, 139.02, 138.82, 133.66, 131.78, 131.24, 130.25, 129.00, 128.68, 128.16, 127.86, 127.71, 127.24, 127.07, 126.60, 126.49, 126.42, 126.14, 30.31, 29.31, 28.68, 28.17, 7.92 ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ 1.67. ESI-MS: Calcd for $C_{27}H_{25}BNS$ ([M + H]$^+$) 406.1800, found m/z 406.1820. Anal. Calcd for $C_{27}H_{24}BNS$: C, 80.00; H, 5.97; N, 3.46. Found: C, 79.85; H, 5.72; N, 3.67.

Synthesis of Compound ***4***. The quantities involved are as follows: compound **4L** (0.68 g, 1.67 mmol), *N*,*N*-diisopropylethylamine (0.29 mL, 1.67 mmol), BBr_3 (1.0 M in CH_2Cl_2, 5.01 mL, 5.01 mmol), and $AlMe_3$ (2.0 M in toluene, 1.67 mL, 3.34 mmol). Yield: 0.32 g, (42%). Mp: 269 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 7.9 Hz, 1H), 7.76 (t, J = 8.1 Hz, 2H), 7.68 (d, J = 7.2 Hz, 1H), 7.40−7.31 (m, 4H), 7.19−7.11 (m, 2H), 7.06 (d, J = 8.5 Hz, 1H), 6.93 (d, J = 7.7 Hz, 1H), 6.83 (t, J = 7.6 Hz, 1H), 6.69 (t, J = 7.4 Hz, 1H), 3.76−3.69 (m, 2H), 3.30−3.22 (m, 1H), 3.08−3.05 (m, 2H), 2.95 (t, J = 8 Hz, 2H), 2.86−2.77 (m, 1H), 0.32 (s, 3H), 0.21 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.20, 155.68, 152.10, 148.91, 139.46, 137.22, 133.78, 133.13, 131.95, 131.27, 130.69, 128.65, 128.56, 128.52,

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128.16, 128.08, 128.01, 127.94, 127.77, 127.07, 126.85, 126.74, 126.51, 125.75, 124.38, 123.55, 29.17, 29.09, 28.83, 28.38, 8.46 ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ 2.63 ppm. ESI-MS: Calcd for $C_{33}H_{29}BN$ ($[M + H]^+$) 450.2393, found m/z 450.2394. Anal. Calcd for $C_{33}H_{28}BN$: C, 88.20; H, 6.28; N, 3.12. Found: C, 87.97; H, 6.15; N, 2.97.

Synthesis of Compound **5**. The quantities involved are as follows: compound **5L** (0.88 g, 1.67 mmol), *N*,*N*-diisopropylethylamine (0.29 mL, 1.67 mmol), BBr_3 (1.0 M in CH_2Cl_2, 5.01 mL, 5.01 mmol), and $AlMe_3$ (2.0 M in toluene, 1.67 mL, 3.34 mmol). Yield: 0.44 g, (47%). Mp: 267 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 7.7 Hz, 2H), 8.09 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 1.8 Hz, 1H), 7.59 (t, J = 7.2 Hz, 3H), 7.44−7.40 (m, 5H), 7.36−7.33 (m, 3H), 7.30−7.27 (m, 2H), 7.17 (dd, J = 8.4, 2.0 Hz, 1H), 4.10−2.85 (m, 8H), 0.31 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.54, 155.96, 150.26, 150.10, 140.82, 139.49, 139.19, 138.70, 134.47, 131.57, 131.56, 129.82, 129.24, 129.17, 128.70, 128.56, 128.06, 127.96, 127.45, 126.47, 126.24, 126.21, 126.00, 125.95, 123.62, 122.18, 120.31, 119.92, 110.50, 30.38, 29.41, 28.81, 28.41, 9.02 ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ 2.28 ppm. ESI-MS: calcd for $C_{41}H_{34}BN_2$ ($[M + H]^+$) 565.2816, found m/z 565.2811. Anal. Calcd for $C_{41}H_{33}BN_2$: C, 87.23; H, 5.89; N, 4.96. Found: C, 87.12; H, 6.13; N, 5.07.

Synthesis of Compound **6**. The quantities involved are as follows: compound **6L** (0.88 g, 1.67 mmol), *N*,*N*-diisopropylethylamine (0.29 mL, 1.67 mmol), BBr_3 (1.0 M in CH_2Cl_2, 5.01 mL, 5.01 mmol), and $AlMe_3$ (2.0 M in toluene, 1.67 mL, 3.34 mmol). Yield: 0.42 g, (45%). Mp: 295 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.5 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.57−7.55 (m, 1H), 7.40−7.24 (m, 15H), 7.09 (t, J = 7.1 Hz, 2H), 6.66 (dd, J = 8.6, 1.8 Hz, 1H), 4.01−2.80 (m, 8H), 0.27 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.95, 155.51, 150.84, 149.61, 149.11, 147.73, 139.27, 138.95, 131.80, 131.77, 129.65, 129.26, 129.00, 128.66, 128.59, 128.50, 128.13, 127.81, 127.18, 126.72, 126.32, 125.94, 125.61, 125.27, 123.19, 121.34, 118.80, 30.27, 29.35, 28.79, 28.29, 9.16 ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ 2.09 ppm. ESI-MS: calcd for $C_{41}H_{36}BN_2$ ($[M + H]^+$) 567.2973, found m/z 567.2969. Anal. Calcd for $C_{41}H_{35}BN_2$: C, 86.92; H, 6.23; N, 4.94. Found: C, 86.73; H, 6.16; N, 5.11.

Synthesis of Compound **7**. The quantities involved are as follows: compound **7L** (0.67 g, 1.67 mmol), *N*,*N*-diisopropylethylamine (0.29 mL, 1.67 mmol), BBr_3 (1.0 M in CH_2Cl_2, 5.01 mL, 5.01 mmol), and $AlMe_3$ (2.0 M in toluene, 1.67 mL, 3.34 mmol). Yield: 0.43 g, (58%). Mp: 260 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.03 (d, J = 7 Hz, 1H), 7.71 (d, J = 7 Hz, 1H), 7.50 (d, J = 7 Hz, 1H), 7.36−7.24 (m, 6H), 6.83 (s, 1H), 6.36 (d, J = 7 Hz, 1H), 3.4−4.4 (m, 2H), 3.06 (s, 6H), 2.78−2.92 (m, 6H), 0.24 (s, 6H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 172.59, 155.35, 151.84, 151.39, 149.31, 139.27, 138.96, 132.35, 132.13, 128.81, 128.45, 128.36, 127.80, 127.76, 127.56, 127.12, 126.27, 125.88, 125.69, 124.51, 110.12, 108.99, 40.46, 30.25, 29.43, 28.90, 28.33, 9.57. ESI-MS: calcd for $C_{31}H_{32}BN_2$ ($[M + H]^+$) 443.2658, found m/z 443.2652. Anal. Calcd for $C_{31}H_{31}BN_2$: C, 84.16; H, 7.06; N, 6.33. Found: C, 84.09; H, 7. 11; N, 6.46.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00853.

General experimental section, emission spectra of compounds **1** and **6** in different solvents, photophysical data of compounds **1**−**7** in different solvents, cyclic voltammograms of compounds **1**−**7** and data table, ^{1}H and ^{13}C NMR spectra for **1L**−**7L**, ^{1}H and ^{13}C NMR and HR-MS spectra for compounds **1**−**7**, and X-ray crystallographic data of compounds **1**, **2**, **4**, and **7** (PDF)

Optimized XYZ coordinates for compounds **1**−**7** and their electronic transitions (XYZ)

Accession Codes

CCDC 1880832−1880835 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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■ REFERENCES

(1) (a) Bendikov, M.; Wudl, F.; Perepichka, D. F. Tetrathiafulvalenes, Oligoacenenes, and Their Buckminsterfullerene Derivatives: The Brick and Mortar of Organic Electronics. *Chem. Rev.* **2004**, *104*, 4891−4946. (b) Anthony, J. E. Functionalized Acenes and Heteroacenes for Organic Electronics. *Chem. Rev.* **2006**, *106*, 5028−5048. (c) Wu, J.; Pisula, W.; Müllen, K. Graphenes as Potential Material for Electronics. *Chem. Rev.* **2007**, *107*, 718−747. (d) Aubry, J. M.; Pierlot, C.; Rigaudy, J.; Schmidt, R. Reversible Binding of Oxygen to Aromatic Compounds. *Acc. Chem. Res.* **2003**, *36*, 668−675. (e) Klaper, M.; Linker, T. Intramolecular Transfer of Singlet Oxygen. *J. Am. Chem. Soc.* **2015**, *137*, 13744−13747. (f) Altinok, E.; Smith, Z. C.; Thomas, S. W. Two-Dimensional, Acene-Containing Conjugated Polymers That Show Ratiometric Fluorescent Response to Singlet Oxygen. *Macromolecules* **2015**, *48*, 6825−6831. (g) Filatov, M. A.; Karuthedath, S.; Polestshuk, P. M.; Savoie, H.; Flanagan, K. J.; Sy, C.; Sitte, E.; Telitchko, M.; Laquai, F.; Boyle, R. W.; Senge, M. O. Generation of Triplet Excited States via Photoinduced Electron Transfer in *meso*-anthra-BODIPY: Fluorogenic Response toward Singlet Oxygen in Solution and in Vitro. *J. Am. Chem. Soc.* **2017**, *139*, 6282−6831.

(2) (a) Narita, A.; Wang, X. Y.; Feng, X. L.; Müllen, K. New advances in nanographene chemistry. *Chem. Soc. Rev.* **2015**, *44*, 6616−6643. (b) Stępień, M.; Gońka, E.; Żyła, M.; Sprutta, N. Heterocyclic Nanographenes and Other Polycyclic Heteroaromatic Compounds:Synthetic Routes,Properties,and Applications. *Chem. Rev.* **2017**, *117*, 3479−3716.

(3) (a) Hashimoto, S.; Ikuta, T.; Shiren, K.; Nakatsuka, S.; Ni, J. P.; Nakamura, M.; Hatakeyama, T. Triplet-Energy Control of Polycyclic Aromatic Hydrocarbons by BN Replacement: Development of Ambipolar Host Materials for Phosphorescent Organic Light-Emitting Diodes. *Chem. Mater.* **2014**, *26*, 6265−6271. (b) Numata, M.; Yasuda, T.; Adachi, C. High efficiency pure blue thermally activated delayed fluorescence molecules having 10*H*-phenoxaborin and acridan units. *Chem. Commun.* **2015**, *51*, 9443−9446. (c) Kushida, T.; Shuto, A.; Yoshio, M.; Kato, T.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2015**, *54*, 6922−6925. (d) Escande, A.; Ingleson, M. J. Fused polycyclic aromatics incorporating boron in the core: fundamentals and applications. *Chem. Commun.* **2015**, *51*, 6257−6274. (e) John, A.; Bolte, M.; Lerner, H. W.; Wagner, M. A. Vicinal Electrophilic Diborylation Reaction Furnishes Doubly Boron-Doped Polycyclic

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Aromatic Hydrocarbons. *Angew. Chem., Int. Ed.* **2017**, *56*, 5588−5592. (f) von Grotthuss, E.; John, A.; Kaese, T.; Wagner, M. Doping Polycyclic Aromatics with Boron for Superior Performance in Materials Science and Catalysis. *Asian J. Org. Chem.* **2018**, *7*, 37−53. (g) Farrell, J. M.; Schmidt, D.; Grande, V.; Würthner, F. Synthesis of a Doubly Boron-Doped Perylene through NHC-Borenium Hydroboration/C-H Borylation/Dehydrogenation. *Angew. Chem., Int. Ed.* **2017**, *56*, 11846−11850. (h) Ji, L.; Griesbeck, S.; Marder, T. B. Recent developments in and perspectives on three-coordinate boron materials: a bright future. *Chem. Sci.* **2017**, *8*, 846−863. (i) Shiotari, A.; Nakae, T.; Iwata, K.; Mori, S.; Okujima, T.; Uno, H.; Sakaguchi, H.; Sugimoto, Y. Strain-induced skeletal rearrangement of a polycyclic aromatic hydrocarbon on a copper surface. *Nat. Commun.* **2017**, *8*, 16089. (j) Neena, K. K.; Thilagar, P. Replacing the non-polarised C = C bond with an isoelectronic polarized B-N unit for the design and development of smart materials. *J. Mater. Chem. C* **2016**, *4*, 11465−11473. (k) Neena, K. K.; Sudhakar, P.; Deepak, K.; Thilagar, P. Diarylboryl-phenothiazene based multifunctional molecular siblings. *Chem. Commun.* **2017**, *53*, 3641−3644.

(4) (a) Hubner, A.; Diefenbach, M.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. Confirmation of an Early Postulate: B-C-B Two-Electron−Three-Center Bonding in Organo(hydro)-boranes. *Angew. Chem., Int. Ed.* **2012**, *51*, 12514−12518. (b) Mercier, L. G.; Piers, W. E.; Parvez, M. Benzo- and Naphthoborepins: Blue-Emitting Boron Analogues of Higher Acenes. *Angew. Chem., Int. Ed.* **2009**, *48*, 6108−6111. (c) Kirschner, S.; Mewes, J.-M.; Bolte, M.; Lerner, H.-W.; Dreuw, A.; Wagner, M. How Boron Doping Shapes the Optoelectronic Properties of Canonical and Phenylene-Containing Oligoacenes:A Combined Experimental and Theoretical Investigation. *Chem. - Eur. J.* **2017**, *23*, 5104−5116. (d) Lulinski, S.; Smetek, J.; Durka, K.; Serwatowski, J. Tandem Synthesis of 9,10-Dihydro-9,10-diboraanthracenes via Elusive ortho-Lithiated Phenylboronates. *Eur. J. Org. Chem.* **2013**, *2013*, 8315−8322. (e) Miyamoto, F.; Nakatsuka, S.; Yamada, K.; Nakayama, K.; Hatakeyama, T. Synthesis of Boron-Doped Polycyclic Aromatic Hydrocarbons by Tandem Intramolecular Electrophilic Arene Borylation. *Org. Lett.* **2015**, *17*, 6158−6161. (f) Osumi, S.; Saito, S.; Dou, C.; Matsuo, K.; Kume, K.; Yoshikawa, H.; Awaga, K.; Yamaguchi, S. Boron-doped nanographene: Lewis acidity, redox properties, and battery electrode performance. *Chem. Sci.* **2016**, *7*, 219−227. (g) Kushida, T.; Shirai, S.; Ando, N.; Okamoto, T.; Ishii, H.; Matsui, H.; Yamagishi, M.; Uemura, T.; Tsurumi, J.; Watanabe, S.; Takeya, J.; Yamaguchi, S. Boron-Stabilized Planar Neutral π-Radicals with Well-Balanced Ambipolar Charge-Transport Properties. *J. Am. Chem. Soc.* **2017**, *139*, 14336−14339. (h) Araneda, J. F.; Piers, W. E.; Sgro, M. J.; Parvez, M. Bronsted acid-catalyzed skeletal rearrangements in polycyclic conjugated boracycles: a thermal route to a ladder diborole. *Chem. Sci.* **2014**, *5*, 3189−3196. (i) Jr Caruso, A.; Tovar, J. D. Conjugated "*B*-Entacenes": Polycyclic Aromatics Containing Two Borepin Rings. *Org. Lett.* **2011**, *13*, 3106−3109. (j) Farrell, J. M.; Schmidt, D.; Grande, V.; Werthner, F. Synthesis of a Doubly Boron-Doped Perylene through NHC-Borenium Hydroboration/C-H Borylation/Dehydrogenation. *Angew. Chem., Int. Ed.* **2017**, *56*, 11846−11850. (k) Warner, A. J.; Lawson, J. R.; Fasano, V.; Ingleson, M. J. Formation of C(sp2)-Boronate Esters by Borylative Cyclization of Alkynes Using BCl_3. *Angew. Chem., Int. Ed.* **2015**, *54*, 11245−11249.

(5) (a) Smith, M. F.; Cassidy, S. J.; Adams, I. A.; Vasiliu, M.; Gerlach, D. L.; Dixon, D. A.; Rupar, P. A. Substituent Effects on the Properties of Borafluorenes. *Organometallics* **2016**, *35*, 3182−3191. (b) Hoefelmeyer, J. D.; Gabbaï, F. P. An Intramolecular Boron−Boron One-Electron σ-Bond. *J. Am. Chem. Soc.* **2000**, *122*, 9054−9055. (c) Kawai, S.; Saito, S.; Osumi, S.; Yamaguchi, S.; Foster, A. S.; Spijker, P.; Meyer, E. Atomically controlled substitutional boron-doping of graphene nanoribbons. *Nat. Commun.* **2015**, *6*, 8098. (d) Cloke, R. R.; Marangoni, T.; Nguyen, G. D.; Joshi, T.; Rizzo, D. J.; Bronner, C.; Cao, T.; Louie, S. G.; Crommie, M. F.; Fischer, F. R. Site-Specific Substitutional Boron Doping of Semiconducting Armchair Graphene Nanoribbons. *J. Am. Chem. Soc.* **2015**, *137*, 8872−8875. (e) Yruegas, S.; Martinez, J. J.; Martin, C. D. Intermolecular insertion reactions of azides into 9-borafluorenes to generate 9,10-B,N-phenanthrenes. *Chem. Commun.* **2018**, *54*, 6808−6811.

(6) (a) Shaikh, A. C.; Ranade, D. S.; Thorat, S.; Maity, A.; Kulkarni, P. P.; Gonnade, R. G.; Munshi, P.; Patil, N. T. Highly emissive organic solids with remarkably broad color tunability based on N,C-chelate, four-coordinate organoborons. *Chem. Commun.* **2015**, *51*, 16115−16118. (b) Crossley, D. L.; Cade, I. A.; Clark, E. R.; Escande, A.; Humphries, M. J.; King, S. M.; Vitorica-Yrezabal, I.; Ingleson, M. J.; Turner, M. L. Enhancing electron affinity and tuning band gap in donor−acceptor organic semiconductors by benzothiadiazole directed C−H borylation. *Chem. Sci.* **2015**, *6*, 5144−5151. (c) Zhao, R. Y.; Dou, C. D.; Xie, Z. Y.; Liu, J.; Wang, L. X. Polymer Acceptor Based on B-N Units with Enhanced Electron Mobility for Efficient All-Polymer Solar Cells. *Angew. Chem., Int. Ed.* **2016**, *55*, 5313−5317. (d) Yusuf, M.; Liu, K. L.; Guo, F.; Lalancette, R. A.; Jäkle, F. Luminescent organoboron ladder compounds via directed electrophilic aromatic C−H borylation. *Dalton Trans.* **2016**, *45*, 4580−4587. (e) Yang, D. T.; Mellerup, S. K.; Peng, J.; Wang, X.; Li, Q.; Wang, S. Substituent Directed Phototransformations of BN-Heterocycles: Elimination vs Isomerization via Selective B−C Bond Cleavage. *J. Am. Chem. Soc.* **2016**, *138*, 11513−11516. (f) Wong, B. Y. W.; Wong, H. L.; Wong, Y. C.; Chan, M. Y.; Yam, V. W. W. Air-Stable Spirofluorene-Containing Ladder-Type Bis(alkynyl)borane Compounds with Readily Tunable Full Color Emission Properties. *Chem. - Eur. J.* **2016**, *22*, 15095. (g) Shen, C.; Srebro-Hooper, M.; Jean, M.; Vanthuyne, N.; Toupet, N.; Williams, J. A. G.; Torres, A. R.; Riives, A. J.; Muller, G.; Autschbach, J.; Crassous, J. Synthesis and Chiroptical Properties of Hexa-, Octa-, and Deca-azaborahelicenes: Influence of Helicene Size and of the Number of Boron Atoms. *Chem. - Eur. J.* **2017**, *23*, 407−418. (h) Grandl, M.; Rudolf, B.; Sun, Y.; Bechtel, D. F.; Pierik, F. J.; Pammer, F. Intramolecular N-B Coordination as a stabilizing scaffold for π-conjugated radical anions with tunable redox potentials. *Organometallics* **2017**, *36* (14), 2527−2535. (i) Grandl, M.; Kaese, T.; Krautsieder, A.; Sun, Y.; Pammer, F. Hydroboration as an Efficient Tool for the Preparation of Electronically and Structurally Diverse N-B-Heterocycles. *Chem. - Eur. J.* **2016**, *22*, 14373−14383. (j) Pais, V. F.; Alcaide, M. M.; Rodriguez, R. L.; Collado, D.; Najera, F.; Inestrosa, E. P.; Alvarez, E.; Lassaletta, J. M.; Fernandez, R.; Ros, A.; Pischel, U. Stongly emissive and Photostable four-coordinate organoboron N,C chelates and their use in fluorescence microscopy. *Chem. - Eur. J.* **2015**, *21*, 15369−15376. (k) Matsuo, K.; Yasuda, T. Enhancing thermally activated delayed fluorescence characteristics by intramolecular B-N coordination in a phenylpyridine-containing donor-acceptor π-system. *Chem. Commun.* **2017**, *53*, 8723−8726. (l) Zhu, C.; Ji, X.; You, D.; Chen, T. L.; Mu, A. U.; Barker, K. P.; Klivansky, L. M.; Liu, Y.; Fang, L. Extraordinary Redox Activities in Ladder-Type Conjugated Molecules Enabled by B←N Coordination-Promoted Delocalization and Hyperconjugation. *J. Am. Chem. Soc.* **2018**, *140*, 18173−18182.

(7) Wakamiya, A.; Taniguchi, T.; Yamaguchi, S. Intramolecular B−N Coordination as a Scaffold for Electron-Transporting Materials: Synthesis and Properties of Boryl-Substituted Thienylthiazoles. *Angew. Chem., Int. Ed.* **2006**, *45*, 3170−3173.

(8) Yoshino, J.; Kano, N.; Kawashima, T. Synthesis of the most intensely fluorescent azobenzene by utilizing the B−N interaction. *Chem. Commun.* **2007**, 559−561.

(9) Rao, Y.-L.; Amarne, H.; Zhao, S.-B.; McCormick, T. M.; Martić, S.; Sun, Y.; Wang, R.-Y.; Wang, S. Reversible Intramolecular C-C Bond Formation/Breaking and Color Switching Mediated by a N,C-Chelate in (2-ph-py)$BMes_2$ and (5-BMes2−2-ph-py)$BMes_2$. *J. Am. Chem. Soc.* **2008**, *130*, 12898−12900.

(10) Ishida, N.; Moriya, T.; Goya, T.; Murakami, M. Synthesis of Pyridine-Borane Complexes via Electrophilic Aromatic Borylation. *J. Org. Chem.* **2010**, *75*, 8709−8712.

(11) Liu, K.; Lalancette, R. A.; Jäkle, F. B-N Lewis Pair Functionalization of Anthracene: Structural Dynamics, Optoelectronic Properties, and O2 Sensitization. *J. Am. Chem. Soc.* **2017**, *139*, 18170−18173.

DOI: 10.1021/acs.organomet.8b00853
Organometallics XXXX, XXX, XXX−XXX

(12) (a) Rouden, J.; Lasne, M.-C.; Blanchet, J.; Baudoux. (−)-Cytisine and Derivatives: Synthesis, Reactivity, and Applications. *Chem. Rev.* **2014**, *114*, 712−778. (b) Donaldson, L. R.; Wallace, S.; Haigh, D.; Patton, E. E.; Hulme, A. N. Rapid synthesis and zebrafish evaluation of a phenanthridine-based small molecule library. *Org. Biomol. Chem.* **2011**, *9*, 2233−2239. (c) Hatae, N.; Fujita, E.; Shigenobu, S.; Shimoyama, S.; Ishihara, Y.; Kurata, Y.; Choshi, T.; Nishiyama, T.; Okada, C.; Hibino, S. Antiproliferative activity of O_4-benzo[c]phenanthridine alkaloids against HCT-116 and HL-60 tumor cells. *Bioorg. Med. Chem. Lett.* **2015**, *25*, 2749−2864. (d) Bakić, M. T.; Jadreško, D.; Hrenar, T.; Horvat, G.; Požar, J.; Galić, N.; Sokol, V.; Tomaš, R.; Alihodžić, S.; Žinić, M.; Frkanec, L.; Tomišić, V. Fluorescent phenanthridine-based calix[4]arene derivatives: synthesis and thermodynamic and computational studies of their complexation with alkali-metal cations. *RSC Adv.* **2015**, *5*, 23900−23914. (e) Chen, J.; Li, K.-T.; Yang, D.-Y. Synthesis of Coumarin/Phenanthridine-Fused Heterocycles and Their Photochemical and Thermochromic Properties. *Org. Lett.* **2011**, *13*, 1658−1661. (f) O'Connor, N. A.; Stevens, N.; Samaroo, D.; Solomon, M. R.; Martí, A. A.; Dyer, J.; Vishwasrao, H.; Akins, D. L.; Kandel, E. R.; Turro, N. J. A covalently linked phenanthridine−ruthenium(II) complex as a RNA probe. *Chem. Commun.* **2009**, 2640−2642. (g) Bakić, M. T.; Jadreško, D.; Hrenar, T.; Horvat, G.; Požar, J.; Galić, N.; Sokol, V.; Tomaš, R.; Al-hodžić, S.; Žinić, M.; Frkanec, L.; Tomišić, V. Fluorescent phenanthridine-based calix[4]-arene derivatives: synthesis and thermodynamic and computational studies of their complexation with alkali-metal cations. *RSC Adv.* **2015**, *5*, 23900−23914. (h) Bo, R.; Li, H.; Liu, H.; Zhuang, H.; Li, N.; Xu, Q.; Lu, J.; Wang, L. Improving of molecular planarity via tailoring alkyl chain within the molecules to enhance memory device performance. *Dyes Pigm.* **2014**, *109*, 155−162.

(13) (a) Sathiyanarayanan, K. I.; Karthikeyan, N. S.; Aravindan, P. G.; Shanthi, S.; Rathore, R. S.; Lee, C. W. Dual behavior of 2-tetralone: A new approach for the synthesis of 5-aryl-7,8,13,14-tetrahydrodibenzo[*a,i*]phenanthridine. *J. Heterocycl. Chem.* **2009**, *46*, 1142−1144. (b) Balijapalli, U.; Udayadasan, S.; Shanmugam, E.; Iyer, S. K. Synthesis, photophysical and acidochromic properties of a series of tetrahydrodibenzo[*a,i*]phenanthridine chromophores. *Dyes Pigm.* **2016**, *130*, 233−244.

(14) Dhanunjayarao, K.; Sa, S.; Aradhyula, B. P. R.; Venkatasubbaiah, K. Synthesis of phenanthroimidazole-based four coordinate organoboron compounds. *Tetrahedron* **2018**, *74*, 5819−5825.

(15) It should be noted that due to the restricted rotation of "naphthyl", compound **4** has two conformers at room temperature.

(16) Wang, S.; Yuan, K.; Hu, M. F.; Wang, X.; Peng, T.; Wang, N.; Li, Q. S. Cleavage of Unstrained C−C Bonds in Acenes by Boron and Light: Transformation of Naphthalene into Benzoborepin. *Angew. Chem., Int. Ed.* **2018**, *57*, 1073−1077.

(17) The origin of the first irreversible reduction is not known; it may be related to bromo reduction.

(18) (a) Mukundam, V.; Dhanunjayarao, K.; Chuang, C.-N.; Kang, D.-Y.; Leung, M.-k.; Hsieh, K.-H.; Venkatasubbaiah, K. Design, synthesis, photophysical and electrochemical properties of 2-(4,5-diphenyl-1-p-aryl-1H-imidazol-2-yl)phenol-based boron complexes. *Dalton Trans.* **2015**, *44*, 10228−10236. (b) Mukundam, V.; Dhanunjayarao, K.; Samal, S.; Venkatasubbaiah, K. Variation of para Substituent on 2-Phenol of Tetraaryl-Substituted Imidazole-Boron Difluoride Complexes: Synthesis, Characterization, and Photophysical Properties. *Asian J. Org. Chem.* **2017**, *6*, 1054−1062. (c) Dhanunjayarao, K.; Mukundam, V.; Chinta, R.V.R.N; Venkatasubbaiah, K. Synthesis of highly fluorescent imidazole based diboron complex. *J. Organomet. Chem.* **2018**, *865*, 234−238.

(19) Mercier, L. G.; Furukawa, S.; Piers, W. E.; Wakamiya, A.; Yamaguchi, S.; Parvez, M.; Harrington, R. W.; Clegg, W. Design, Synthesis and Characterisation of Functionalized Silepins: High Quantum yield Blue Emitters. *Organometallics* **2011**, *30*, 1719−1729.

DOI: 10.1021/acs.organomet.8b00853
Organometallics XXXX, XXX, XXX−XXX