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Electronic and Optical Properties of Ladder-Type Heteraborins

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Abstract: Ladder-type π-conjugated molecules bearing heteraborin (azaborine or thiaborin) units were synthesized, and X-ray crystallographic analysis of pentacene-type molecules showed that these molecules have rigid and planar structures. UV-visible spectroscopy and theoretical calculations revealed the enhancement of electronic interaction between heteraborin units, the decrease in HOMO–LUMO energy gaps, and the strong effect of the bridging main-group elements (nitrogen or sulfur) on the electronic states. The ladder-type molecules emitted strong fluorescence both in solution and in the solid state, and the emission-band shapes were different from each other, indicating the existence of intermolecular interactions in the solid state. Complex formation of the ladder molecules with fluoride ion was monitored by UV-visible spectroscopy, which revealed that the Lewis acidity of these molecules can be controlled by the elongation of π systems and the change of the bridging main-group elements.

Keywords: conjugation • heterocycles • optical properties • pi interactions • X-ray crystallography

Introduction

π-Conjugated molecules bearing main-group elements (hetero-π-conjugated molecules) have attracted much attention in various research fields such as fundamental chemistry, supramolecular chemistry, material chemistry, and industrial chemistry. This is because atomic orbitals of main-group elements can interact with π orbitals on parent hydrocarbons and differentiate the electronic structures of the molecules substantially, and hence novel properties are expected to appear in such molecules. Hetero-π-conjugated molecules bearing nitrogen, oxygen, or sulfur have been investigated over recent decades; indeed, some of these molecules have been applied to, for example, organic electroluminescence devices. However, the compounds with other main-group elements have not been used so much, in spite of their valuable electronic properties.[1] Among such main-group element compounds, silicon- or phosphorus-containing π-conjugated molecules, especially heteracyclopentadienes (heteroles), have recently been investigated because they exhibit anomalous and fruitful electronic and optical properties due to their weak aromaticity and negative hyperconjugation derived from their low-lying σ* orbitals (σ* orbitals of Si−R or P−R bonds). In fact, these molecules have a decreased HOMO–LUMO energy gap relative to the parent cyclopentadiene, and the weak aromaticity enhances delocalization of π electrons over the butadiene moiety.[2,3]

On the one hand, a boron atom is very attractive when it is introduced to a hetero-π-conjugated system, such as triarylborane-based π-conjugated molecules.[4] A tricoordinated boron atom has a vacant 2p orbital and acts as a strong electron acceptor through its efficient overlap of π orbitals. Another interesting feature of boranes is reversible structural and electronic transformation upon complexation with Lewis bases. When boranes form complexes with Lewis bases, the resulting tetracoordinated boron complexes no longer exhibit the conjugated electronic properties that tricoordinated boron compounds do. Thus, both the electronic and optical properties of borane-based π-conjugated molecules can be controlled by external stimuli, leading to the application to chemical sensors. Such properties allow triarylboranes to be good candidates for many applications, such as luminescence polymers,[5] nonlinear optics,[6] electroluminescence,[7] electron-carrier materials,[8] and chemical sensors for Lewis bases.[9] The structural diversity of hetero-π-conjugated systems, however, is still insufficient to construct the various types of functional materials desired. For example, many boron-containing π-conjugated molecules must have a Mes_2B unit for effective steric protection around boron centers, and the freedom of molecular design is limited.

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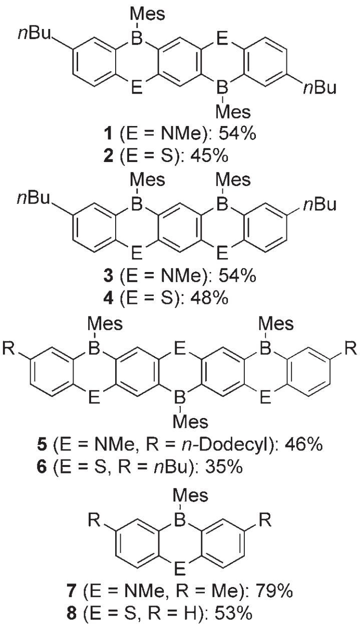
On the other hand, molecular planarity is known to be an important parameter for enhancement of π conjugation because interactions between conjugated π orbitals and atomic orbitals on main-group elements are maximized in planar framework. Fixation of a π-conjugated system into a rigid and planar structure not only enhances the π delocalization but also intensifies luminescence emission because such a structure can prevent thermal degradation from the excited states. A ladder-type molecule is an efficient motif for construction of a planar and rigid π-conjugated system.[10] From such a view point, hybrid systems of ladder-type π-conjugated molecules and hetero-π-conjugated molecules have been recently reported. For example, ladder-type molecules bearing silicon[11] or chalcogen (sulfur, selenium, or tellurium)[12] in the conjugated backbones have exhibited improved optical or electronic properties, such as strong blue luminescence or good organic-field effect transistor property.

Dibenzoheteraborin is one of the hetero-π-conjugated molecules based on a dihydroanthracene framework bearing a boron atom and another main-group element.[13,14] In this rigid and planar molecule, the synergistic electronic interactions were expanded into three factors, that is, a boron 2p orbital, a lone pair of the main-group element, and π orbitals of the conjugation system, and photoluminescence efficiency will be increased. Besides the enhancement of the photoluminescence property, the rigid structure furnishes enough stability to the triarylborane moiety. Thus, dibenzoheteraborin is expected to be a good candidate for organic electronic and optical materials. However, the reported dibenzoheteraborins are limited to only four molecules; diborin, azaborin, oxaborin, and thiaborin, and the electronic and optical properties of these heteraborins have not been investigated precisely.[15]

Recently, we reported the electronic and optical properties of new hetero-π-conjugated molecules based on dibenzoheteraborin units.[16] In the previous communication, we reported the synthesis and preliminary study on optical properties of ladder-type azaborines.[17] UV-visible spectra of these molecules showed red shift of absorption maxima in accordance with extension of the π systems, indicating enhancement of π conjugation through the ladder-type molecular framework. Here we report the synthesis of the ladder-type heteraborins containing nitrogen or sulfur atoms as bridging main-group elements and the systematic study of their optical properties, as well as their complexation abilities against fluoride ion.[18,19]

Results and Discussion

Synthesis of ladder-type heteraborins: The synthesized ladder-type molecules have two or three heteraborin units connected by phenylene linkages (Scheme 1). The syntheses of pentacene-type azaborines **1** and **3** as well as heptacene-type azaborine **5** have been already reported.[17]



1 (E = NMe): 54%
2 (E = S): 45%

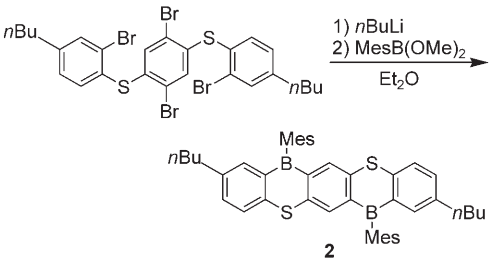
3 (E = NMe): 54%
4 (E = S): 48%

5 (E = NMe, R = *n*-Dodecyl): 46%
6 (E = S, R = *n*Bu): 35%

7 (E = NMe, R = Me): 79%
8 (E = S, R = H): 53%

Scheme 1. Ladder-type heteraborins and parent dibenzoheteraborins.

They were synthesized from the corresponding polybromides, and the synthesis of **2** is shown as a representative procedure (Scheme 2); the tetrabromide was lithiated with *n*BuLi in Et_2O, and the generated tetralithio derivative was treated with $MesB(OMe)_2$ to give pentacene-type thiaborin **2** as yellow solids.



2
45%

Scheme 2. Synthesis of ladder-type thiaborin **2**.

It is important to add $MesB(OMe)_2$ at room temperature (around 300 K) as slowly as possible to obtain reproducible results. Otherwise, many unidentified products were generated, and, especially in the synthesis of **5**, the yield of the ladder-type molecules decreased drastically by rapid addition. The syntheses of ladder-type thiaborins **4** and **6** as well as parent dibenzothiaborin **8** were achieved in the similar manner (see Experimental Section). The ladder-type heteraborins were obtained in good to moderate yields, and all the compounds were stable against air and moisture.

X-ray crystallographic analysis of pentacene-type thiaborin 2: A single crystal of **2** was obtained by recrystallization from $CHCl_3$/EtOH, and the molecular structure of **2** is shown in Figure 1. The crystal of **2** contains two independent molecules in the unit cell, and one of the two molecules is

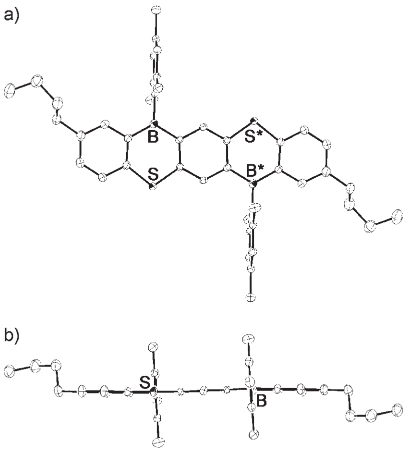


Figure 1. ORTEP drawings of pentacene-type thiaborin **2** (50 % probability). Hydrogen atoms are omitted for clarify. a) Top view. b) Side view.

shown here. The molecular structures of **1** and **2** are nearly the same,[17] and both molecules have a planar and rigid framework as expected, indicating that the ladder framework is effective for extension of π conjugation to improve the photoluminescence properties (see below). Intermolecular interactions, such as π–π stacking of the pentacene moiety or CH–π interaction, are not observed in the packing diagrams of **1** and **2**, probably due to the steric congestion of Mes groups.

UV-visible spectra of ladder-type heteraborins: UV-visible absorption spectra of the ladder-type heteraborins in cyclohexane are shown in Figure 2, and the optical data are summarized in Table 1. The absorption maxima of the ladder-type heteraborins with *para*-type substitution mode were red shifted according to the elongation of π conjugation from the anthracene-type (**7** or **8**) to the heptacene-type molecules (**5** or **6**), whereas *meta*-type substitution molecules **3** and **4** showed almost the same absorption maxima as those of **7** and **8**.

Table 1. Optical data of the ladder-type heteraborins in cyclohexane at 298 K.

	λ_{max} [nm][a] (log ε)	λ_{em} [nm][b]	ΔE[c] [cm^{-1}]	τ [ns]
1	523 (4.23)	534 (0.69)	3.9×10^2	18
2	499 (4.04)	517 (0.72)	7.0×10^2	–
3	415 (3.94)	428 (0.21)	7.3×10^2	–
4	399 (3.81)	420 (0.06)	1.3×10^3	–
5	609 (4.28)	626 (0.55)	4.5×10^2	33
6	558 (3.95)	580 (0.61)	6.8×10^2	–
7	405 (4.02)	421 (0.48)	9.4×10^2	9.3
8	387 (3.94)	403 (0.39)	1.0×10^3	–

[a] Absorption maxima in UV-visible spectra and absorption coefficiency in parenthesis. [b] Emission maxima of fluorescence spectra and quantum yield in parenthesis. [c] $\Delta E = 1/\lambda_{max} - 1/\lambda_{em}$.

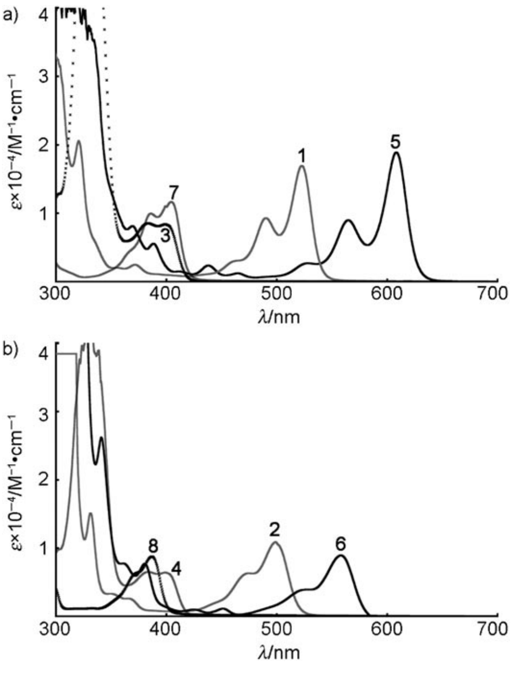


Figure 2. UV-visible spectra of the ladder-type heteraborins in cyclohexane at 298 K. a) Azaborines. b) Thiaborins.

The HOMO–LUMO energy gaps of these *para*-substituted molecules are decreased in accordance with the elongation of π-conjugation systems, indicating that the electronic communication between the heteraborin units and delocalization of π electrons are more effectively operated in the *para*-substitution mode than in the *meta*-substitution mode. Thus, the *para*-type substitution mode provides a better contribution to the extension of π conjugation than the *meta*-type substitution mode.

Comparing the spectra of the azaborines with those of the thiaborins, the former series always showed more red shifted absorption bands and larger absorption coefficients than the latter series. The longest absorption bands of the ladder-type heteraborins arise from intramolecular charge transfer from bridging main-group elements (nitrogen or sulfur) to boron atoms, and the donor–acceptor interaction between nitrogen and boron atoms is stronger than that between sulfur and boron atoms. The stronger donor–acceptor interaction of the azaborines than that of the thiaborins can be interpreted to provide the azaborines with more decreased HOMO–LUMO energy gaps as well as more enhanced oscillator strength of optical absorption.

Evaluation of effective conjugation length of ladder-type heteraborins: It is well known that transition energy (E) of π-conjugated oligomers or polymers can be expressed empirically as a linear function of a reciprocal number of repeating units (n) [Eq. (1)].[20]

$$E = E_\infty + \Delta E \times (1/n) \tag{1}$$

E_∞ is the infinitive value of E when $n \rightarrow \infty$, and thus this value indicates the effective conjugation length of the π-conjugated oligomers or polymers. These parameters can be obtained simply by plotting the observed transition energy against the number of repeating units and by using the least-square fitting method.

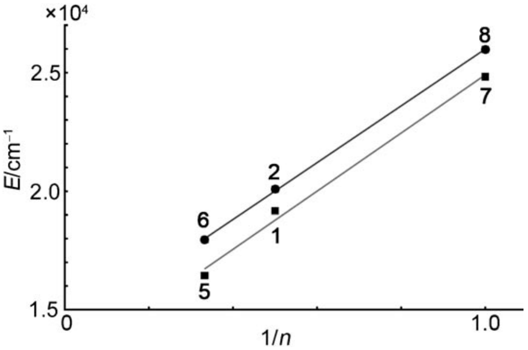


Figure 3. Plot of transition energy (E [cm^{-1}]) obtained from UV-visible spectra versus reciprocal number of heteraborin units (n) of the ladder-type hetetaborins. Least-square fitting lines are also shown. ■: azaborines, ●: thiaborins.

This method was applied to the ladder-type azaborines and thiaborins, and the results are shown in Figure 3. By using the least-square fitting method, we found the following regression Equations (2) and (3) for the azaborines and thiaborins, respectively (n: number of heteraborin units per molecule):

$$E \times 10^{-4}\ \mathrm{cm}^{-1} = 1.22 \times (1/n) + 1.26\ (R^2 = 0.9935) \tag{2}$$

$$E \times 10^{-4}\ \mathrm{cm}^{-1} = 1.20 \times (1/n) + 1.40\ (R^2 = 0.9997) \tag{3}$$

E_∞ values of the ladder-type azaborines and thiaborins were estimated to be 1.26×10^4 cm^{-1} (1.3 eV) and 1.40×10^4 cm^{-1} (1.5 eV), respectively. These values are comparable with the theoretical limits of transition energy of several conjugated molecules based on fully π-conjugated carbon frameworks (Figure 4).[21] The E_∞ values of the ladder-type heteraborins are larger than that of polyacene that has isoelectronic structure with the ladder-type heteraborins, and thus delocalization of π electrons over the ladder-type heteraborins is weaker and π electrons are relatively localized on the benzene rings and the bridging main-group elements (nitrogen or sulfur).

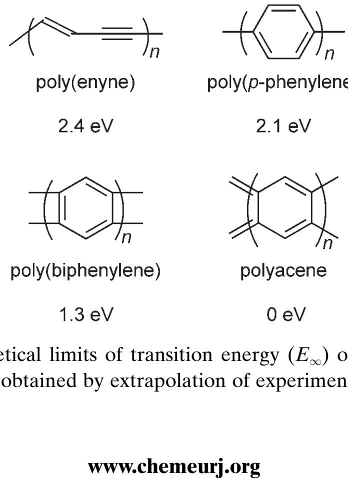


Figure 4. Theoretical limits of transition energy (E_∞) of several π-conjugated polymers obtained by extrapolation of experimental data.

Theoretical calculations on frontier orbitals of the ladder-type heteraborins:[22,23] Electronic structures of the ladder-type heteraborins were investigated by using the DFT method (B3LYP/6–31G(d)), and the energy levels of the frontier orbitals are summarized in Table 2. Theoretical calculations were carried out on model ladder-type heteraborins bearing hydrogen atoms instead of alkyl and mesityl groups in the real systems in order to reduce the computation burden.

Table 2. Calculated frontier orbital energy and energy gaps.[a]

	HOMO [eV]	LUMO [eV]	ΔE [eV]
1	−5.33	−2.34	2.99
2	−5.75	−2.71	3.04
3	−5.71	−2.03	3.68
4	−6.03	−2.31	3.72
5	−5.10	−2.61	2.49
6	−5.61	−2.95	2.66
7	−5.98	−1.71	4.27
8	−6.03	−2.12	3.91

[a] Level of calculations: B3LYP/6–31G(d)//B3LYP/6–31G(d).

As indicated by the UV-visible spectra in the previous section, elongation of the molecular framework showed the decrease in HOMO–LUMO energy gaps due to effective π conjugation in the *para*-type substitution, but *meta*-substituted molecules **3** and **4** did not show the effective extension of π conjugation. The ladder-type azaborines have higher-energy frontier orbitals because the molecular orbitals of the azaborines should move to higher energies due to the strong electron donation from the nitrogen atoms. In contrast, the frontier orbitals of the ladder-type thiaborins lie at lower energy levels, reflecting the weaker electron donation from sulfur compared with that of nitrogen. As a result, the HOMO–LUMO energy gaps did not differ so much between the azaborines and the thiaborins. In addition, a plot of energy gaps (ΔE) against the reciprocal number of repeating units (n) (Figure 5) gave linear regression Equations (4) and (5) for the azaborines and the thiaborins with *para*-substitution mode, respectively.

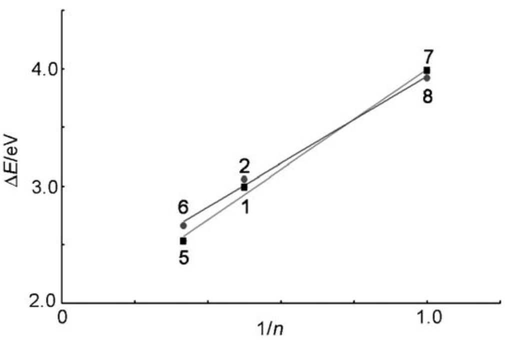


Figure 5. Theoretical energy gap (ΔE [eV]) of the model ladder-type heteraborins against the reciprocal number of heteraborin units per molecule (n). ■: ladder-type azaborines, ●: ladder-type thiaborins.

$$\Delta E\ [\mathrm{eV}] = 2.13 \times (1/n) + 1.87 \tag{4}$$

$$\Delta E\ [\mathrm{eV}] = 1.85 \times (1/n) + 2.08 \tag{5}$$

These equations show that the theoretical limits of the energy gaps of the ladder-type azaborines and thiaborins are 1.9 and 2.1 eV, respectively. The existence of limitation in HOMO–LUMO energy gaps is in marked contrast to the case of polyacenes because infinite polyacene is revealed to have no energy gap and becomes true organic metal or semimetal.[21d,e] Such a difference is considered to arise from the localization of π electrons in the ladder-type heteraborins.

Fluorescence spectra of the ladder-type heteraborins: Steady-state fluorescence spectra of the heteraborins were recorded in cyclohexane at 298 K (Figure 6), and the optical properties of these molecules are summarized in Table 1. Reflecting the red shift of the absorption maxima in the UV-visible spectra, emission maxima of the ladder-type heteraborins also showed red shift, going from **7** and **8** to **5** and **6**, respectively. Stokes shifts of the ladder-type heteraborins are still small (10^2–10^3 cm^{-1}), indicating that the structural relaxation is very small in these ladder-type molecules due to the molecular rigidity. Fluorescence quantum yields of the ladder-type heteraborins increased relative to those of the parent dibenzoheteraborins **7** and **8**, except for the *meta*-type substituted molecules **3** and **4**. These photoluminescence properties imply that the *para*-substituted ladder-type molecules are expected to be used for optical devices. In addition, the fluorescence of the ladder-type molecule **5** contained at least three components, indicating the generation of other photoexcited states than the lowest excited state. For the *para*-substituted ladder-type azaborines, time-resolved fluorescence spectra were also measured in cyclohexane at 298 K, and the fluorescence lifetimes (τ/ns) are shown in Table 1. The fluorescence lifetime increased in accordance with the extension of the π-conjugated framework. Investigations of these two interesting phenomena are now under way.

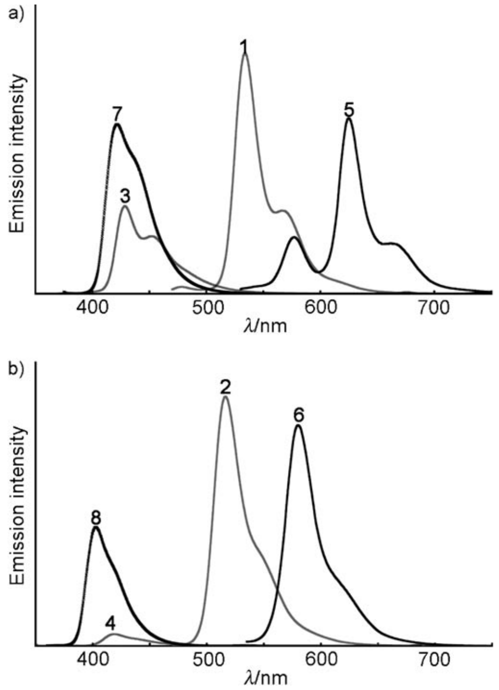


Figure 6. Steady-state fluorescence spectra of the ladder-type heteraborins in cyclohexane at 298 K. a) Azaborines. b) Thiaborins.

Solid-state fluorescence spectra of the ladder-type heteraborins: Solid-state fluorescence spectra of the ladder-type heteraborins are shown in Figure 7, and the spectral data are summarized in Table 3. The photoimages of the powder samples are available in the Supporting Information. These molecules showed intense photoluminescence in the solid state as well as in solution, except for heptacene-type molecules **5** and **6**, probably because the bulky Mes groups prohibit aggregation that results in degradation from the excit-

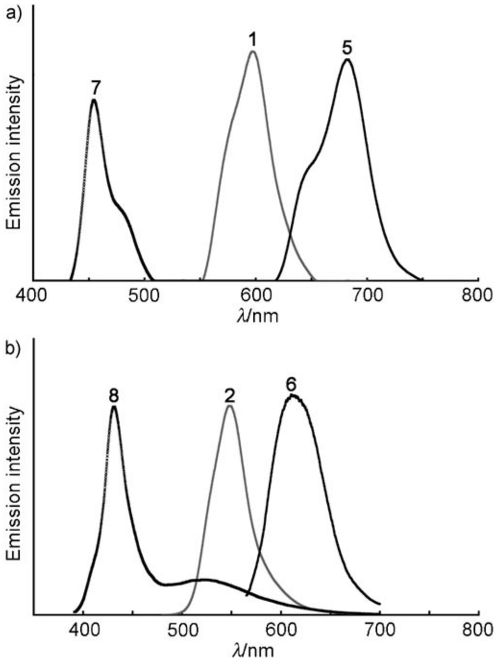


Figure 7. Solid-state fluorescence spectra of the ladder-type heteraborins (powder sample). a) Azaborines. b) Thiaborins.

Table 3. Optical data of the ladder-type heteraborins in the solid state.

	λ_{max}[a] [nm]	λ_{em}[b] [nm]	ΔE[c] [cm^{-1}]
1	556	599	1.3×10^3
2	519	550	1.1×10^3
5	645	683	8.6×10^2
6	590	613	6.4×10^2
7	430	456	1.3×10^3
8	405	432	1.5×10^3

[a] Excitation spectrum maxima in the solid state. [b] Emission maxima of fluorescence spectra in the solid state. [c] $\Delta E = 1/\lambda_{max} - 1/\lambda_{em}$.

ed state through nonradiation processes. The photoluminescence intensities of **5** and **6** in the solid state were moderate because substantial overlap of the absorption and emission bands of these molecules may result in self quenching of the fluorescence emission. The wavelengths of emission maxima, however, are shifted relative to those of the fluorescence in solution, and the shifts of the ladder-type azaborines **1** and **5** increased by almost twice that of parent dibenzoazaborine **7**, indicating the existence of intermolecular dipole–dipole interactions in the excited states. Although direct π–π stacking is ruled out by steric repulsion, it is likely that the long-range interaction between excited dipoles may influence fluorescence emission in the solid state. In addition, the solid-state fluorescence spectrum of parent dibenzothiaborin **8** exhibited two emission maxima at 432 and 540 nm. The latter emission peak may originate from excimer formation in the solid state because the single crystals of this molecule contained π–π dimeric structure, shown by X-ray crystallographic analysis (Figure 8).

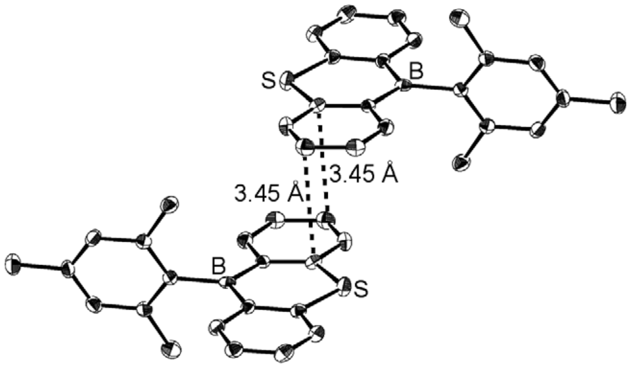


Figure 8. ORTEP drawing of dibenzothiaborin **8** (50% probability). Hydrogen atoms were omitted for clarify. Shortest contacts between two molecules in the dimeric structure are indicated by dashed lines.

Table 4. Complex-formation constants of the ladder-type heteraborins with fluoride ion.

	K_1 [M^{-1}]	K_2 [M^{-1}]	K_3 [M^{-1}]
1	$7(1)\times10^4$	$1.1(1)\times10^2$	–
2	$3.2(7)\times10^5$	$2.0(1)\times10^3$	–
5	$2.8(8)\times10^5$	$5.5(5)\times10^2$	–[a]
6	$8(4)\times10^6$	$4(3)\times10^5$	$2.3(1)\times10^3$

[a] Complex formation was not observed.

Complex formation with fluoride ion: As the ladder-type heteraborins have several boron atoms in one molecule, these molecules are expected to function as a multistep fluoride ion sensor.[9d,24] Upon the complex formation, the electronic state of the ladder-type heteraborins is switched, and it will cause multistep colorimetric change that can be monitored by UV-visible spectroscopy. The complex formation was carried out in THF by using (nBu)$_4$NF (TBAF) as a fluoride ion source. The spectral changes of the heptacene-type heteraborins **5** and **6** are shown in Figure 9, and the complex formation constants are summarized in Table 4. Heptacene-type azaborine **5** formed monofluoroborate upon the addition of three equivalents of TBAF with color change from red to orange (Figure 9a), but further reaction hardly occurred in spite of the addition of a large excess of TBAF (Figure 9b). Heptacene-type thiaborin **6**, however, reacted with up to three equivalents of TBAF quantitatively to form

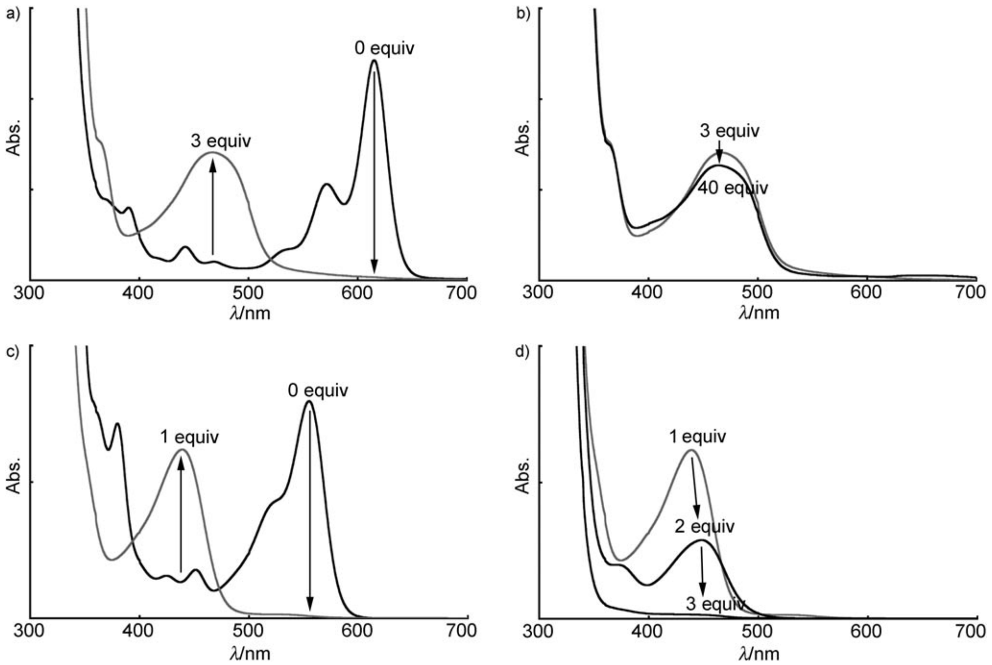


Figure 9. UV-visible spectral change upon addition of TBAF in THF. (a) and (b) **5**. (c) and (d) **6**.

mono-, di-, and trifluoroborates in a stepwise fashion, followed by color change from pink to colorless via yellow, indicating the increased Lewis acidity of boron centers (Figures 9c and d). Comparing the formation constants of the fluoroborates, extension of π systems or change of the bridging main-group elements from nitrogen to sulfur seems to increase the Lewis acidity. The explanations for such phenomena are as follows: 1) extension of π systems decreased the LUMO energy level, 2) the thiaborins have lower LUMO energy levels than those of the azaborines due to a weaker donating ability of a sulfur atom.

Conclusion

We synthesized the ladder-type π-conjugated molecules based on heteraborins (azaborine or thiaborin) units. These molecules were shown to have a rigid and planar framework, judging from X-ray crystallographic analysis and theoretical calculations. UV-visible and fluorescence spectroscopy as well as theoretical calculations proved that the ladder-type structures are effective for the improvement of electronic communication between the heteraborin units and delocalization of π electrons. The ladder-type azaborines emitted intense fluorescence both in solution and in the solid state because of the rigid framework and inhibition of strong intermolecular interactions such as π–π stacking. Lewis acidity of these molecules can be controlled by the extension of the π system or the change of bridging main-group elements, as demonstrated in the complex formation with fluoride ion.

Experimental Section

General procedure: General chemicals were used as received. Cyclohexane and THF for spectrochemical or fluorometric grade (Dojindo) were used for optical measurements. All manipulations were carried out using Schlenk techniques under an argon atmosphere. Solvents were purified by using the MBRAUN MB-SPS system. Wet column chromatography (WCC) was performed by using Kanto Silica Gel 60N. Gel permeation liquid chromatography (GPLC) was performed using LC-918 or LC-908 with JAIGEL 1H+2H columns (Japan Analytical Industry) by using chloroform or toluene as solvents, respectively. NMR spectra were recorded by using a JEOL AL-400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{11}B, 128 MHz), a JEOL ECX-400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz), a Bruker DRX-500 spectrometer (^{1}H, 500 MHz; ^{13}C, 126 MHz), or a Bruker AV-500 spectrometer (^{1}H, 500 MHz; ^{13}C, 126 MHz). Chemical shifts are reported in δ. ^{1}H NMR spectra are referenced to residual protons in deuterated solvent; ^{13}C NMR spectra are referenced to carbon-13 in the deuterated solvent; ^{11}B NMR spectra are referenced to an external standard of $BF_3{\cdot}Et_2O$. Low-resolution mass spectra were obtained with a JEOL JMS-700P by using *m*-nitrobenzyl alcohol (*m*NBA) as a matrix. High-resolution mass spectra were recorded by using a JEOL JMS-700P with PEG400, PEG600, or Ultramark as internal standards. UV/Vis spectra were recorded by using a JASCO V-530 spectrophotometer. Fluorescence spectra were recorded by using a HITACHI F4500 fluorescence spectrophotometer. All melting points were measured by using a Yanaco MP-S3 and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo. 2-Bromo-4-butylaniline,[17] 1,4-dibromo-2,5-diiodobenzene and 1,5-dibromo-2,4-diiodobenzene,[25] and bis(2-bromophenyl) sulfide[26] were synthesized according to literature procedures.

10-Mesityl-10*H*-9-thia-10-boraanthracene (8): To a Et_2O (100 mL) solution of bis(2-bromophenyl)sulfide (0.50 g, 1.5 mmol) was added *t*BuLi (2.2 M in pentane, 3.4 mL, 7.5 mmol) at −75 °C, and the mixture was stirred for 30 min at this temperature and then for 30 min at room temperature. To this mixture was added $MesB(OMe)_2$ (0.34 mL, 1.6 mmol), and the mixture was refluxed for 4 h. The precipitates were filtered off, and the crude products were subjected to GPLC. After the solvents were removed under reduced pressure, vacuum drying gave **8** as pale-yellow solids (0.25 g, 53 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.93 (s, 6H), 2.40 (s, 3H), 6.94 (s, 2H), 7.30 (td, J=7.4, 1.0 Hz, 2H), 7.62 (td, J=7.6, 1.5 Hz, 2H), 7.78 (d, J=8.1 Hz, 2H), 7.87 ppm (dd, J=7.7, 1.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ=21.3, 22.9, 124.6, 125.2, 126.9, 132.2, 136.8, 138.7, 139.6, 144.3 ppm (two signals corresponding to the ipso-carbons of the boron atom could not be observed due to broadening by a quadrupole moment of ^{11}B nuclei); ^{11}B NMR (128 MHz, $CDCl_3$): δ= 58.6 ppm; UV/Vis (cyclohexane): λ_{max} (log ε)=387 nm (3.94); HRMS (FAB$^+$): m/z: calcd for $C_{21}H_{19}{}^{32}S^{10}B$: 313.1337; found: 313.1304; elemental analysis calcd (%) for $C_{21}H_{19}BS$: C 80.26, H 6.09; found: C 80.04, H 6.28.

2-Bromo-4-butylbenzenethiol: To a suspension of 2-bromo-4-butylaniline (50 g, 0.22 mol) in aq. HCl (6 M, 400 mL) at −5 °C was added dropwise a solution of $NaNO_2$ (23 g, 0.33 mol) in H_2O (100 mL), and the mixture was stirred for 1 h. To the mixture was added a solution of $EtOCS_2K$ (60 g, 0.38 mol) in H_2O (100 mL), and the solution was stirred at 80 °C for 4 h. The aqueous layer was extracted with Et_2O, and the organic layer was dried over Na_2SO_4. After the evaporation of the solvents, the crude products were dissolved in anhydrous THF (100 mL), and the mixture was slowly added to the suspension of $LiAlH_4$ (20 g, 0.53 mol) in THF (200 mL) at 0 °C. After stirring at RT for 10 h, the mixture was poured into a mixture of concd HCl (100 mL) and crushed ice (caution: strong stench!). The aqueous layer was extracted with Et_2O, and the organic layer was dried over Na_2SO_4. The solvents were evaporated, and the crude material was purified by distillation (3 mmHg, 130 °C) to give the title compound as colorless oil (38 g, 71 %). B.p. 130 °C (3 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.91 (t, J=7.3 Hz, 3H), 1.32 (sext, J= 7.4 Hz, 2H), 1.55 (q, J=7.6 Hz, 2H), 2.52 (t, J=7.7 Hz, 2H), 3.98 (s, 1H), 6.98 (dd, J=7.5, 1.6 Hz, 1H), 7.24 (d, J=7.5 Hz, 1H), 7.35 ppm (d, J=1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.9, 22.3, 33.4, 34.7, 122.2, 128.1, 129.5, 130.1, 132.8, 142.0 ppm; HRMS (FAB$^+$): m/z: calcd for $C_{10}H_{13}{}^{79}BrS$: 243.9922; found: 243.9938.

1,4-Dibromo-2,5-bis(2-bromo-4-butylphenylsulfanyl)benzene (9):[27] A mixture of 2-bromo-4-butylbenzenethiol (2.9 g, 12 mmol), 1,4-dibromo-2,5-diiodobenzene (2.9 g, 5.9 mmol), $[Pd(dba)_2]$ (69 mg, 0.12 mmol) (dba=(*E*,*E*)-dibenzylideneacetone), DPPF (66 mg, 0.12 mmol) (DPPF= 1,1′-bis(diphenylphosphino)ferrocene), NaO*t*Bu (1.7 g, 18 mmol), and toluene (50 mL) was stirred at 80 °C for 1 d. The reaction was quenched by the addition of aqueous NH_4Cl, and the aqueous layer was extracted with C_6H_6. The organic layer was dried with Na_2SO_4, and the solvents were evaporated. The crude product was separated by column chromatography (SiO_2, eluent: hexane) to give **9** as colorless solid (2.7 g, 64 %). M.p. 126–128 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.91 (t, J=8.6 Hz, 6H), 1.35 (sext, J=7.4 Hz, 4H), 1.60 (q, J=7.6 Hz, 4H), 2.60 (t, J= 7.8 Hz, 4H), 7.04 (s, 2H), 7.12 (dd, J=7.3, 1.8 Hz, 2H), 7.24 (d, J= 7.3 Hz, 2H), 7.52 ppm (d, J=1.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ=13.9, 22.3, 33.1, 34.9, 122.8, 127.5, 128.8, 130.1, 133.4, 133.8, 134.3, 136.9, 145.9 ppm; LRMS (FAB$^+$): m/z: 718 [M^+]; elemental analysis calcd for (%) $C_{26}H_{26}Br_4S_2$: C 43.24, H 3.63; found: C 43.14, H 3.64.

1,5-Dibromo-2,4-bis(2-bromo-4-butylphenylsulfanyl)benzene (10): A mixture of 2-bromo-4-butylbenzenethiol (2.4 g, 9.8 mmol), 1,5-dibromo-2,4-diiodobenzene (2.4 g, 4.9 mmol), $[Pd(dba)_2]$ (0.28 g, 0.48 mmol), DPPF (0.27 g, 0.49 mmol), NaO*t*Bu (1.4 g, 15 mmol), and toluene (50 mL) was stirred at 80 °C for 2 d. The reaction was quenched by the addition of aqueous NH_4Cl, and the aqueous layer was extracted with C_6H_6. The organic layer was dried with Na_2SO_4, and the solvents were evaporated. To the crude mixture was added hexane, and the mixture was triturated to give **10** as colorless solids. Recrystallization from EtOH/CHCl$_3$/hexane gave pure **10** (2.1 g, 60%). M.p. 110–112°C; ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 0.95$ (t, $J = 7.5$ Hz, 6H), 1.36 (sext, $J = 7.4$ Hz, 4H), 1.59 (q, $J = 7.6$ Hz, 4H), 2.58 (t, $J = 7.9$ Hz, 4H), 6.21 (s, 1H), 7.01 (dd, $J = 8.0$, 2.0 Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 2.0$ Hz, 2H), 7.74 ppm (s, 1H); ^{13}C NMR (126 MHz, CDCl$_3$): $\delta = 13.9$, 22.4, 33.1, 35.1, 119.9, 128.5, 129.0, 129.6, 133.6, 135.3, 136.1, 137.8, 145.8, 148.7 ppm; HRMS (FAB$^+$, *m*NBA, PEG600): m/z: calcd for $C_{26}H_{26}{}^{79}Br_4{}^{32}S_2$: 717.8210; found: 717.8212; elemental analysis calcd (%) for $C_{26}H_{26}Br_4S_2$: C 43.24, H 3.63; found: C 43.45, H 3.65.

2,9-Dibutyl-7,14-dimesityl-7,14-dihydro-5,12-dithia-7,14-diborapentacene (2): To a Et$_2$O solution (500 mL) of **9** (0.50 g, 0.69 mmol) at 0°C was added *n*BuLi (1.6 M in hexane, 2.2 mL, 3.5 mmol), and the mixture was stirred for 20 min at 0°C. To this mixture was added MesB(OMe)$_2$ (0.36 mL, 1.7 mmol). The resulting fluorescent green suspension was refluxed for 1 h, and the solvents were removed under reduced pressure. The resulting red solids were extracted with CHCl$_3$, and the solvent was evaporated. The crude product was subjected to GPLC to give **2** as yellow solids (0.21 g, 45%). M.p. 278–280°C (dec.); ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 0.87$ (t, $J = 7.4$ Hz, 6H), 1.29 (sext, $J = 7.4$ Hz, 4H), 1.52 (q, $J = 7.7$ Hz, 4H), 1.95 (s, 12H), 2.45 (s, 6H), 2.59 (t, $J = 7.7$ Hz, 4H), 6.98 (s, 4H), 7.46 (dd, $J = 8.2$, 1.8 Hz, 2H), 7.66 (d, $J = 8.2$ Hz, 2H), 7.68 (d, $J = 1.8$ Hz, 2H), 8.23 ppm (s, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): $\delta = 13.9$, 21.4, 22.2, 23.0, 33.9, 35.2, 125.3, 127.1, 131.5, 133.4, 133.6, 136.1, 136.9, 138.7, 139.2, 139.4, 139.8, 142.2 ppm; ^{11}B NMR (128 MHz, CDCl$_3$): $\delta = 58.6$ ppm ($h_{1/2} = 1900$ Hz); UV/Vis (cyclohexane): λ_{max} (log ε) = 499 (4.04), 475 (3.80), 331 nm (4.18); HRMS (FAB$^+$): m/z: calcd for $C_{44}H_{48}S_2{}^{10}B^{11}B$: 661.3420; found: 661.3377; elemental analysis calcd (%) for $C_{44}H_{48}B_2S_2 \cdot H_2O$: C 77.65, H 7.40; found: C 77.81, H 7.37.

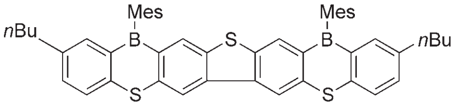
2,10-Dibutyl-12,14-dimesityl-12,14-dihydro-5,7-dithia-12,14-diborapentacene (4): To a Et$_2$O solution (300 mL) of **10** (0.20 g, 0.28 mmol) at −75°C was added *t*BuLi (2.2 M in pentane, 1.1 mL, 2.4 mmol), and the mixture was stirred for 20 min at −75°C. To this mixture was added MesB(OMe)$_2$ (0.14 mL, 0.68 mmol). This mixture was refluxed for 10 h, and the solvents were removed under reduced pressure. The resulting red solids were extracted with CHCl$_3$, and the solvent was evaporated. The crude product was subjected to GPLC to give **4** as yellow solids (88 mg, 48%). M.p. 210–212°C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.86$ (t, $J = 7.4$ Hz, 6H), 1.29 (sext, $J = 7.4$ Hz, 4H), 1.52 (q, $J = 7.7$ Hz, 4H), 1.95 (s, 12H), 2.45 (2, 6H), 2.58 (t, $J = 7.8$ Hz, 4H), 6.71 (s, 4H), 7.46 (dd, $J = 8.2$, 2.0 Hz, 2H), 7.65 (d, $J = 8.2$ Hz, 2H), 7.71 (d, $J = 2.0$ Hz, 2H), 7.98 (s, 1H), 8.05 ppm (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 13.9$, 21.4, 22.3, 22.7, 34.0, 35.2, 119.4, 125.3, 126.5, 128.8, 129.9, 130.9, 133.2, 136.3, 138.2, 139.3, 139.9, 140.2, 147.8, 153.7 ppm; ^{11}B NMR (128 MHz, CDCl$_3$): $\delta = 57.5$ ppm ($h_{1/2} = 1900$ Hz); UV/Vis (cyclohexane): λ_{max} (log ε): 399 (3.81), 384 (3.81), 339 (4.60), 266 nm (4.58); HRMS (FAB$^+$, *m*NBA, PEG600): m/z: calcd for $^{12}C_{44}H_{48}{}^{32}S_2{}^{10}B^{11}B$: 661.3419; found: 661.3434; elemental analysis calcd (%) for $C_{44}H_{48}B_2S_2 \cdot 2.2\,H_2O$: C 75.26, H 7.52; found: C 75.06, H 7.49.

1,4-Dibromo-2-(2-bromo-4-butylphenylsulfanyl)-5-iodobenzene (11): A mixture of 2-bromo-4-butylbenzenethiol (11 g, 45 mmol), 1,4-dibromo-2,5-diiodobenzene (22 g, 45 mmol), NaO*t*Bu (6.5 g, 68 mmol), [Pd(dba)$_2$] (1.3 g, 2.3 mmol), DPPF (1.3 g, 2.3 mmol), and toluene (200 mL) was stirred at 100°C for 14 h. The reaction was quenched by the addition of aqueous NH$_4$Cl, and the aqueous layer was extracted with Et$_2$O. The organic layer was washed with water and dried with Na$_2$SO$_4$, and the solvents were evaporated. The crude product was separated by column chromatography (SiO$_2$, eluent: hexane) to give **11** as colorless oil (9.1 g, 33%) and **9** (5.3 g, 33%). ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 0.93$ (t, $J = 7.4$ Hz, 3H), 1.36 (sext, $J = 7.4$ Hz, 2H), 1.61 (quint, $J = 7.6$ Hz, 2H), 2.62 (t, $J = 7.7$ Hz, 2H), 6.90 (s, 1H), 7.15 (dd, $J = 7.9$, 1.6 Hz, 1H), 7.35 (d, $J = 7.9$ Hz, 1H), 7.55 (d, $J = 1.6$ Hz, 1H), 7.98 ppm (s, 1H); ^{13}C NMR (126 MHz, CDCl$_3$): $\delta = 13.90$, 22.26, 33.00, 34.96, 97.70, 121.20, 128.69, 128.86, 128.92, 129.19, 131.37, 133.96, 135.54, 140.11, 142.79, 146.63 ppm; HRMS (FAB$^+$): m/z: calcd for $C_{16}H_{14}{}^{79}Br_3SI$: 601.7411; found: 601.7420.

Bis[2,5-dibromo-4-(2-bromo-4-butylphenylsulfanyl)phenyl] sulfide (12):[28] To a mixture of **11** (1.0 g, 1.7 mmol), [Pd(dba)$_2$] (50 mg, 87 µmol), DPPF (50 mg, 87 µmol), and toluene (20 mL) was added TIPS-SLi prepared from TIPS-SH (0.44 mL, 2.1 mmol) (TIPS-SH = triisopropylsilanethiol) and *n*BuLi (1.6 M in hexane, 1.2 mL, 1.9 mmol) in THF (10 mL), and the mixture was stirred at 80°C for 12 h. The reaction was quenched by the addition of aqueous NH$_4$Cl, and the aqueous layer was extracted with Et$_2$O. The combined organic layer was dried over Na$_2$SO$_4$, and the solvents were removed under reduced pressure. The crude product was subjected to GPLC to give **12** as colorless solids (0.50 g, 60%). M.p. 152–154°C; ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 0.93$ (t, $J = 7.3$ Hz, 6H), 1.35 (sext, $J = 7.4$ Hz, 4H), 1.61 (quint, $J = 7.7$ Hz, 4H), 2.62 (t, $J = 7.7$ Hz, 4H), 6.97 (s, 2H), 7.16 (dd, $J = 7.9$, 1.9 Hz, 2H), 7.28 (s, 2H), 7.37 (d, $J = 7.9$ Hz, 2H), 7.55 ppm (d, $J = 1.9$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): $\delta = 13.89$, 22.28, 33.05, 34.99, 121.81, 124.93, 128.53, 138.97, 129.10, 132.61, 133.62, 134.02, 135.43, 135.48, 139.65, 146.63 ppm; LRMS (FAB$^+$): m/z: 982 [M^+]; elemental analysis calcd (%) for $C_{32}H_{28}Br_6S_3$: C 38.89, H 2.86; found: C 38.76, H 2.95.

2,12-Dibutyl-7,14,18-trimesityl-7,18-dihydro-14*H*-5,9,16-trithia-7,14,18-triboraheptacene (6): To a Et$_2$O solution (300 mL) of **12** (0.20 g, 0.20 mmol) at −75°C was added *t*BuLi (2.2 M in pentane, 1.2 mL, 2.6 mmol), and the mixture was stirred for 20 min. To this mixture was added MesB(OMe)$_2$ (0.19 mL, 0.92 mmol) at −75°C. The resulting mixture was refluxed for 1 h, and the solvents were removed under reduced pressure. The resulting solids were extracted with C$_6$H$_6$, and the solution was filtered over Celite pad, then the solvents were evaporated. The crude product was subjected to GPLC to give **6** as red solids (63 mg, 35%) and **13** (see below) as yellow solids (41 mg, 22%).

6: Red solids. Decomposed above 250°C. ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 0.88$ (t, $J = 7.4$ Hz, 6H), 1.29 (sext, $J = 7.4$ Hz, 4H), 1.53 (quint, $J = 7.6$ Hz, 4H), 1.93 (s, 12H), 2.00 (s, 6H), 2.43 (s, 6H), 2.49 (s, 3H), 2.60 (t, $J = 7.7$ Hz, 4H), 6.94 (s, 4H), 7.03 (s, 2H), 7.47 (dd, $J = 8.3$, 1.2 Hz, 2H), 7.67 (d, $J = 8.3$ Hz, 2H), 7.74 (d, $J = 1.2$ Hz, 2H), 8.15 (s, 2H), 8.30 ppm (s, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): $\delta = 13.89$, 21.31, 21.38, 22.22, 22.98, 23.18, 33.91, 35.16, 125.35, 127.15, 127.37, 129.07, 133.38, 133.69, 136.12, 136.51, 137.00, 137.25, 137.40, 138.57, 138.72, 138.88, 139.01, 139.35, 139.51, 142.16 ppm; ^{11}B NMR (128 MHz, CDCl$_3$): $\delta = 56.2$ ppm ($h_{1/2} = 3700$ Hz); HRMS (FAB$^+$): m/z: calcd for $C_{59}H_{61}S_3{}^{10}B^{11}B_2$: 897.4250; found: 897.4247; elemental analysis calcd (%) for $C_{59}H_{61}H_3S_3 \cdot H_2O$: C 77.30, H 6.93; found: C 77.77, H 6.97.



13

13: Yellow solids. M.p. 257–259°C; ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 0.88$ (t, $J = 7.4$ Hz, 6H), 1.30 (sext, $J = 7.4$ Hz, 4H), 1.54 (quint, $J = 7.6$ Hz, 4H), 1.95 (s, 12H), 2.45 (s, 6H), 2.61 (t, $J = 7.7$ Hz, 4H), 6.98 (s, 4H), 7.50 (dd, $J = 8.2$, 1.2 Hz, 2H), 7.68 (d, $J = 1.2$ Hz, 2H), 7.76 (d, $J = 8.2$ Hz, 2H), 8.31 (s, 2H), 8.66 ppm (s, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): $\delta = 13.91$, 21.36, 22.21, 22.97, 33.90, 35.18, 118.71, 125.10, 127,12, 133.31, 133.38, 133.80, 133.94, 136.87, 137.63, 137.77, 138.82, 139.23, 139.36, 139.82, 140.18, 141.42 ppm; HRMS (FAB$^+$): m/z: calcd for $C_{50}H_{50}S_3{}^{11}B_2$: 768.3261; found: 768.3308.

X-ray crystallographic analyses of 2 and 8: Crystallographic data for **2**: $C_{44}H_{48}B_2S_2$, yellow plate, monoclinic, space group $P2_1/n$, $a = 15.995(5)$ $b = 10.582(3)$ $c = 22.316(7)$ Å, $\beta = 106.6961(13)°$, $V = 3617.9(18)$ Å^3, $Z = 4$, $F(000) = 1416$, crystal size $0.20 \times 0.20 \times 0.01$ mm^3, $6.40 = 2\Theta = 54.96$. In total, 27500 reflections were collected, of which 8299 were independent ($R_{int} = 0.0382$) and employed for refinement: 441 parameters, 0 restraints, Goodness of fit on $F^2 = 0.982$, R_1 [$I > 2\sigma(I)$] = 0.0549, wR_2 (all data) = 0.1653. Crystallographic data for **8**: $C_{21}H_{19}BS$, pale-yellow cube, monoclinic, space group $P2_1/n$, $a = 9.0261(11)$ $b = 21.984(3)$ $c = 9.2912(11)$ Å, $\beta = 113.4148(15)°$, $V = 1691.8(4)$ Å^3, $Z = 4$, $F(000) = 664$, crystal size $0.20 \times 0.20 \times 0.20$ mm^3, $6.04 = 2\Theta = 54.94$. In total, 12779 reflections were collected, of which 3835 were independent ($R_{int} = 0.0275$) and employed for refinement: 221 parameters, 0 restraints, Goodness of fit on $F^2 = 1.060$, R_1

$[I>2\sigma(I)]=0.0638$, wR_2 (all data) $=0.1366$. The intensities of reflections were collected at 120 K by using a RIGAKU MSC Mercury CCD diffractometer with a graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71070$ Å) by using CrystalClear (Rigaku Corp.). The structure was solved by direct methods (SHELXS) and expanded by using Fourier techniques. The structure was refined by full-matrix least-squares methods on F^2 (SHELXL-97).[29] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure-factor calculations. CCDC-299490 and CCDC-635514 contain the supplementary crystallographic data for **2** and **8**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data/request/cif.

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