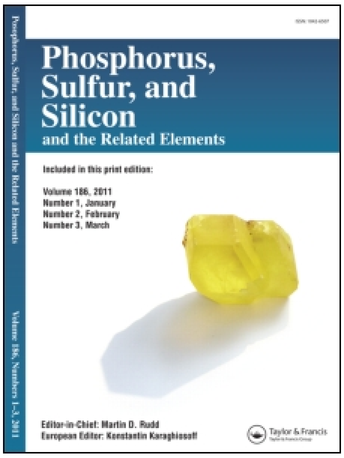

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SYNTHESIS AND OPTICAL PROPERTIES OF A BIS(BENZOTHIABORINO)CARBAZOLE, A THIABORIN-CARBAZOLE MIXED LADDER-TYPE π-CONJUGATED MOLECULE

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A ladder-type π-conjugated molecule containing both thiaborin and carbazole units exhibited strong light absorption and emission like other ladder-type π-conjugated molecules based on heteraborins.

Keywords Carbazole; ladder-type π-conjugated molecule; optical properties; thiaborin

INTRODUCTION

Ladder-type π-conjugated compounds are promising candidates for organic functional materials, including electron- or hole-transporting materials and light emitting materials. Their planar structures can enhance delocalization of π-orbitals and decrease HOMO–LUMO energy gaps, resulting in high electron or hole affinity. In addition, as the π-conjugated structures are fixed tightly by the rigid framework, intramolecular motions that are related to nonradiation decay of the excited state are suppressed, and thus photoluminescence properties of the ladder-type compounds are improved.[1] Recently, the introduction of various main group elements into ladder-type conjugated molecules proved to be a very effective way to develop new characteristics of π-conjugated molecules.[2]

In previous reports, we have described the optical properties of ladder-type azaborines and thiaborins.[3] However, their analogues containing both azaborine and thiaborin units have not been synthesized yet, and thus the effect of the mixing of these two different heteraborins in one molecule is still unclear. In this article, we report the attempted synthesis of a mixed-type, ladder-type heteraborin bearing azaborine and thiaborin units in a hexahydroheptacene framework, which resulted in the formation of a bis(benzothiaborino)carbazole instead of the expected ladder-type heteraborin (Figure 1).

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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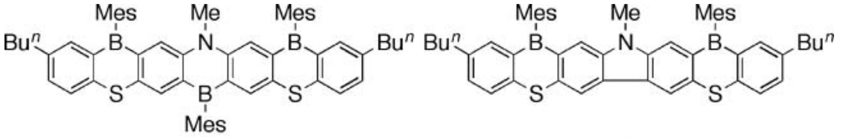


1

2

Figure 1 Ladder-type mixed heteraborin **1** and bis(benzothiaborino)carbazole **2**.

RESULTS AND DISCUSSION

Synthesis

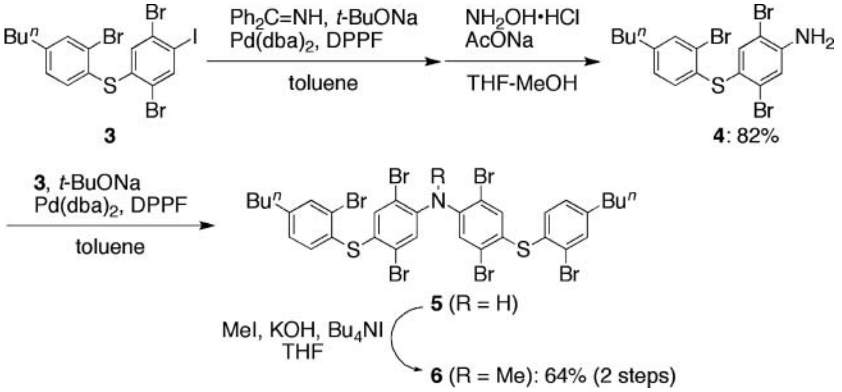
The synthesis of hexabromide **6** was accomplished by taking advantage of Buchwald–Hartwig amination protocols (Scheme 1).[4,5]

The synthesis of mixed ladder-type heteraborin **1** was attempted. However, instead of **1**, bis(benzothiaborino)carbazole **2** was obtained. A similar reaction using the corresponding sulfide gave bis(benzothiaborino)dibenzothiophene **7**, a sulfur analogue of **2**, together with the desired **8** (Figure 2).[3a] On the other hand, in the case of the synthesis of ladder-type azaborines, carbazole derivative was not obtained at all.[3b,3c] Therefore, terminal thiaborins formed by a twofold ring closure should be essential for these oxidative C–C coupling reactions. In fact, an electron transfer from lithio-derivatives to the thiaborin moiety may occur to give **2** or **7**, because the thiaborin has a LUMO of lower energy compared to that of the azaborine, as revealed by theoretical calculations on heteraborins by us,[3a] and seems to act as a one-electron oxidant (Scheme 2).[6]

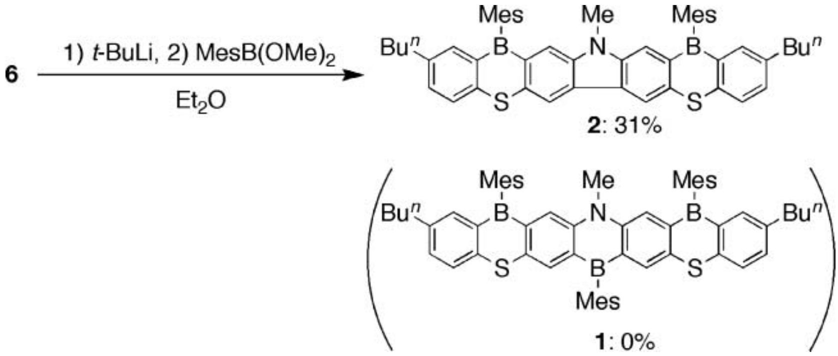
Optical Properties

The optical data for **2** as well as for other thiaborins are summarized in Table I.

The absorption maximum at longest wavelength of **2** lies between those of **7** and **8**. The electronic effect of the insertion of a carbazole moiety is weaker as compared with that of the insertion of a dibenzothiaborin ring. Compared to **7**, compound **2** showed red-shifted absorption maxima, probably due to the higher electron-donating ability of the nitrogen atom.



Scheme 1 The synthesis of hexabromide **6**.

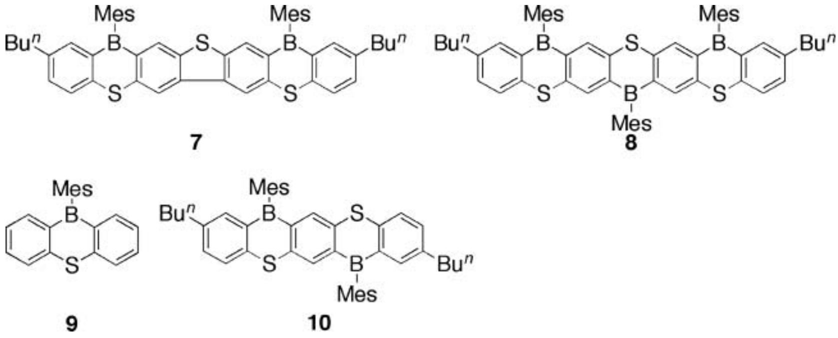


Scheme 2 The formation of bis(benzothiaborino)carbazole **2**.

Compound **2** exhibited green-colored photoluminescence with small Stokes shift, indicating that it maintains a planar and rigid framework upon photo-excitation, just like the other heteraborin-based ladder-type molecules. In addition, compound **2** can emit a green-colored luminescence also in the solid state due to the inhibition of intermolecular interaction by bulky mesityl groups, and thus a carbazole-thiaborin mixed ladder-type structure will be useful to develop strong light-emissive materials.

EXPERIMENTAL

Generally chemicals were used as received. For optical measurements, commercial spectrochemical- or fluorometric-grade solvents were used as received. All manipulations were performed under argon atmosphere using standard Schlenck technique. Dry solvents (THF, Et_2O, hexane, and toluene) were purchased from Kanto Chemicals and further purified by an MBRAUN MB-SPS system equipped with activated alumina and molecular sieve columns before use. Column chromatography was carried out with Kanto Silica Gel 60N. Gel permeation liquid chromatography was performed using Japan Analytical Industry LC-918 and LC-908 with JAIGEL 1H+2H columns and chloroform as a solvent. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DRX-500 spectrometer. Low resolution mass spectra were measured with a JEOL JMS-700P (FAB). High resolution mass spectra were obtained with a JEOL JMS-700P. UV-vis spectra were recorded with a JASCO V-670



7 **8** **9** **10**

Figure 2 Thiaborin and ladder-type thiaborins.

Table I Optical properties of bis(benzothiaborino)carbazole **2** and ladder-type thiaborins **7**–**10** in cyclohexane

	λ_{max}/nm (log ε)	λ_{em}/nm	Stokes shift[c]/cm^{-1}
2	521 (3.79)	540	6.8×10^2
7[b]	482 (3.60)	495	5.4×10^2
8[a]	558 (3.95)	580	6.8×10^2
9[a]	387 (3.94)	403	1.0×10^3
10[a]	499 (4.28)	517	7.0×10^2

[a] Ref. 1.

[b] Unpublished result.

[c] Stokes shift = $1/\lambda_{max}$—$1/\lambda_{em}$.

spectrophotometer, and fluorescence spectra were measured with a JASCO FP-6500 fluorescence spectrophotometer. All melting points were determined on a Yanaco MP-S3 micro melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, University of Tokyo. The preparation of (2-bromo-4-butylphenyl) (2,5-dibromo-4-iodophenyl) sulfide (**3**) was already reported.[3a]

Synthesis of 2,5-Dibromo-4-(2-bromo-4-butylphenylthio)aniline (4)

A mixture of **3** (2.0 g, 3.3 mmol), $Ph_2C=NH$ (0.61 mL, 3.6 mmol), $Pd(dba)_2$ (0.10 g, 0.17 mmol), 1,1′-bis(diphenylphophino)ferrocene (DPPF) (0.10 g, 0.17 mmol), *t*-BuONa (0.50 g, 5.2 mmol), and toluene (50 mL) was stirred at 100°C for 45 h.[4] To the mixture, aq. NH_4Cl was added, and the mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, and the solvents were removed under reduced pressure. The crude material was dissolved in THF (10 mL) and MeOH (40 mL), and to this mixture $NH_2OH{\cdot}HCl$ (5.0 g, 72 mmol) and AcONa (9.0 g, 0.11 mol) were added. The mixture was stirred at room temperature for 19 h, and the solvent was removed under reduced pressure. The resulting material was extracted with Et_2O and the organic layer was dried over Na_2SO_4. The solvent was evaporated, and the crude material was chromatographed (Al_2O_3, $CHCl_3$) and further purified by GPLC to give **4** as colorless viscous oil (1.3 g, 82%). **4**: colorless oil. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 7.3$ Hz, 3H), 1.32 (sext, $J = 7.5$ Hz, 2H), 1.55 (quint, $J = 7.7$ Hz, 2H), 2.53 (t, $J = 7.7$ Hz, 2H), 6.72 (d, $J = 8.1$ Hz, 1H), 6.98 (dd, $J = 8.1$, 1.6 Hz, 1H), 7.18 (s, 1H), 7.38 (d, $J = 1.6$ Hz, 1H), 7.49 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 13.9$, 22.2, 33.2, 34.7, 119.3, 121.5, 122.0, 128.1, 129.4, 129.5, 129.7, 132.9, 134.8, 139.5, 142.4, 145.8; HRMS (FAB^+) *m/z* calcd. for $C_{16}H_{16}N^{79}Br_3S$: 490.8553; found: 490.8534.

Synthesis of 2,5-Dibromo-4-(2-bromo-4-butylphenylthio)-*N*-[2,5-dibromo-4-(2-bromo-4-butylphenylthio)phenyl]-*N*-methylaniline (6)

A mixture of **4** (1.3 g, 2.7 mmol), **3** (1.8 g, 3.0 mmol), $Pd(dba)_2$ (0.10 g, 0.17 mmol), DPPF (0.10 g, 0.17 mmol), *t*-BuONa (0.43 g, 4.5 mmol), and toluene (30 mL) was stirred at 100°C for 13 h, and the reaction was quenched by the addition of aq. NH_4Cl. The mixture was extracted with Et_2O, and the organic layer was dried over Na_2SO_4. The solvents were removed under reduced pressure, and the crude material was chromatographed (SiO_2, $CHCl_3$) to give bis(2,5-dibromo-4-(2-bromo-4-butylphenyl-thio)phenyl)amine (**5**) as colorless solid. This material was dissolved in THF (20 mL), and to this solution MeI (0.16

mL, 2.6 mmol), KOH (1.1 g, 20 mmol), and Bu_4NI (0.18 g, 0.49 mmol) were added. The mixture was stirred at 40°C for 10.5 h, and the reaction was quenched by aq. NH_4Cl. The mixture was extracted with Et_2O and the organic layer dried over Na_2SO_4. The solvents were evaporated, and the crude material was subjected to column chromatography (SiO_2, hexane/$CHCl_3$ = 4:1) to give **6** as colorless solid (1.7 g, 64%). **6**: colorless solid, mp 140–142°C. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.92$ (t, $J = 7.3$ Hz, 6H), 1.34 (sext, $J = 7.4$ Hz, 4H), 1.59 (quint, $J = 7.6$ Hz, 4H), 2.58 (t, $J = 7.7$ Hz, 4H), 3.20 (s, 3H), 7.08–7.13 (m, 4H), 7.20 (s, 2H), 7.22 (s, 2H), 7.48 (d, $J = 1.4$ Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta =$ 13.9, 22.3, 33.1, 34.9, 41.5, 119.2, 124.4, 126.3, 128.0, 128.6, 130.0, 131.3, 133.0, 133.6, 136.4, 145.1, 147.4; LRMS (FAB+) *m/z* 983 (M^+). Anal. Calcd. for $C_{33}H_{31}Br_6NS_2$: C, 40.23; H, 3.17; N, 2.85. Found: C, 40.45; H, 3.34; N, 2.57.

Synthesis of Bis(benzothiaborino)carbazole (2)

To an Et_2O (500 mL) solution of **6** (0.50 g, 0.51 mmol), *t*-BuLi (2.2 M in pentane, 3.0 mL, 6.6 mmol) was added at –75°C, and the mixture was stirred for 20 min. To this mixture, $MesB(OMe)_2$ (0.37 mL, 1.8 mmol) was added, and the mixture was refluxed for 2 h. The solvent was evaporated, and the crude material was suspended in benzene. The suspension was filtered, and the solvent was removed under reduced pressure. $CHCl_3$ was added until all of the solid was dissolved, and the solution was concentrated to give a red precipitate. The precipitate was subjected to GPLC to give **2** as an orange solid (0.12 g, 31%). **2**: orange solid, mp 160–161°C (dec.). ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 7.3$ Hz, 6H), 1.30 (sext, $J = 7.5$ Hz, 4H), 1.54 (quint, $J = 7.6$ Hz, 4H), 1.96 (s, 12H), 2.46 (s, 6H), 2.60 (t, $J = 7.7$ Hz, 4H), 3.95 (s, 3H), 6.98 (s, 4H), 7.47 (dd, $J = 8.2, 2.0$ Hz, 2H), 7.63 (d, $J = 2.0$ Hz, 2H), 7.75 (d, $J = 8.2$ Hz, 2H), 7.84 (s, 2H), 8.60 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 13.9$, 21.4, 22.2, 23.0, 29.5, 33.9, 35.2, 117.3, 118.1, 124.9, 126.0, 127.0, 132.9, 133.1, 133.3, 133.6, 136.5, 138.7, 138.8, 139.0, 140.7, 140.9, 141.9; HRMS (FAB^+) *m/z* calcd for $C_{51}H_{53}{}^{11}B_2N^{32}S_2$: 765.3806; found: 765.3799.

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