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Syntheses, Structure, and Optical Properties of Ladder-Type Fused Azaborines

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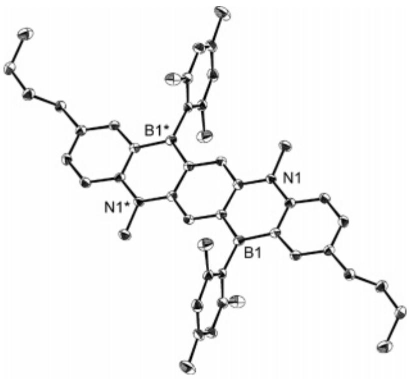
ABSTRACT



λ_{max} 523 nm, λ_{em} 534 nm (Φ 0.69)

Ladder-type fused azaborines were synthesized. X-ray crystallographic analysis of a pentacene-type molecule shown here revealed the planarity of a fused azaborine. It was revealed by UV–vis and fluorescence spectra that such fused molecular structures are efficient for the extension of π-conjugated systems containing main group elements.

Organic light-emitting devices (OLEDs) have been studied extensively as alternative devices to conventional cathode ray tube or liquid crystalline displays. They have many advantages over the conventional devices, such as improved brightness and color purity, as well as lower drive voltages.[1] π-Conjugated small molecules and polymers are used for the constituents of OLEDs, and π-conjugated molecules bearing main group elements are one of the latest targets in this research area.

In these molecules, the main framework consists of a π-conjugated hydrocarbon backbone and main group elements because the electronic interactions between the π-orbitals and the donor/acceptor orbitals can substantially decrease the HOMO−LUMO energy gap. Group 15 and 16 elements, which have lone pairs, usually act as electron donors, and group 13 and 14 elements have acceptor orbitals and can behave as acceptors. Many main group element compounds have been investigated as electron acceptors in π-conjugated systems, and extensive research on heteracyclopentadienes (heteroles) has revealed that π-conjugated molecules substituted by boron, silicon, and phosphorus show good optical and electronic properties.[2]

Boron is a unique element among such electron acceptors.[3] A vacant 2p orbital provides the electron-withdrawing property, and the acceptor property can be switched revers-

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ibly when Lewis bases coordinate to the vacant orbital and diminish acceptor ability. Boron-containing π-systems possess two interesting properties: (1) small HOMO−LUMO gaps due to the strong acceptor property; and (2) dynamic control of the electronic state and molecular structure by external stimuli (Lewis bases). From such a viewpoint, much attention has been paid to boron-containing π-conjugated molecules.

Dibenzoheteraborins are π-conjugated molecules bearing one or more main group elements with boron atoms on the framework, and the electronic state can be tuned by the exchange of the main group elements. Optical properties and some reactivities of dibenzoazaborine including a nitrogen atom have been reported by several researchers.[4] We also reported the syntheses of dibenzophosphaborins, π-conjugated molecules containing phosphorus atoms as electron donors.[5] Although dibenzophosphaborins showed UV−vis absorption similar to that of dibenzoazaborine, their photoluminescence properties are inferior in terms of broadening of emission peaks and quantum yields.

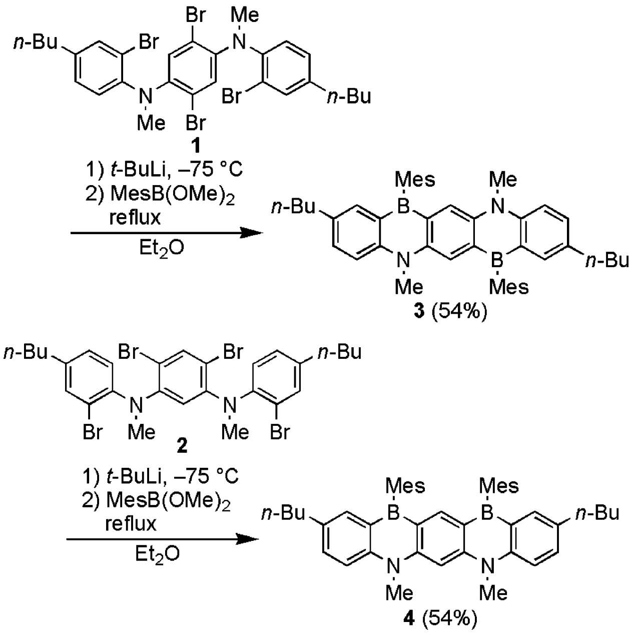
Ladder-type and planar π-conjugated molecular architectures bearing main group elements on main chains or the periphery are current topics in material chemistry because the rigid and planar framework of ladder molecules is expected to improve several of the properties important for applications, including the degree of π-conjugation as well as photo- and electroluminescence quantum yields. For example, silicon-bridged phenylene−vinylene oligomers have been synthesized via an efficient intramolecular cyclization, and these compounds exhibited good optical properties (small HOMO−LUMO gaps and strong light emission).[6]

If π-conjugated oligomers or polymers bearing boron atoms in the main chains are fixed into planar ladder-type structures, such molecules will be among the best candidates for OLEDs because of the substantially decreased HOMO−LUMO energy gaps and strong emissive properties of triarylboranes.[7] The boron-containing ladder molecules, however, have not been reported yet, despite their desirable properties.

In this paper, we report the syntheses of new planar π-conjugated molecules having a fused azaborine framework. These ladder-type molecules have boron and nitrogen atoms in the main chains as electron acceptors and donors, respectively. The ladder-type molecules showed decreased HOMO−LUMO gaps, because of the two main group elements, as well as efficient π-conjugation because of the molecular planarity, judging from X-ray crystallographic analysis, UV−vis spectroscopy, and fluorescence spectroscopy. The ladder molecules emitted strong fluorescence with a small Stokes shift because of their rigid molecular structures.

p-Phenylenediamine **1** and *m*-phenylenediamine **2** were synthesized from 2-bromo-4-butylaniline and 1,4-dibromo-2,5-diiodobenzene or 1,3-dibromo-4,6-diiodobenzene via palladium-catalyzed amination.[8] Pentacene-type ladder molecules **3** and **4** were synthesized by the reaction of MesB(OMe)$_2$ with tetralithio derivatives prepared from **1** and **2** under reflux conditions (Scheme 1). Para-type compound **3** was obtained as a red solid, and meta-type compound **4** was obtained as a yellow solid. Both compounds are stable against air and moisture because of steric protection of the boron atoms by the bulky mesityl groups and rigid structure.

Scheme 1. Syntheses of Ladder Molecules **3** and **4**



To synthesize a precursor for an extended ladder molecule, a sequential palladium-catalyzed amination protocol was employed. Benzophenone imine, an ammonia synthon, was coupled with iodide **5**, and subsequent deprotection gave amine **6**.[9] The precursor **7** for a longer ladder molecule was obtained by coupling of **5** and **6** followed by methylation at the central nitrogen atom. Heptacene-type ladder molecule **8** was synthesized from **7** and MesB(OMe)$_2$ by the same procedure described above (Scheme 2). **8** was obtained as a violet solid that was stable against air and moisture.

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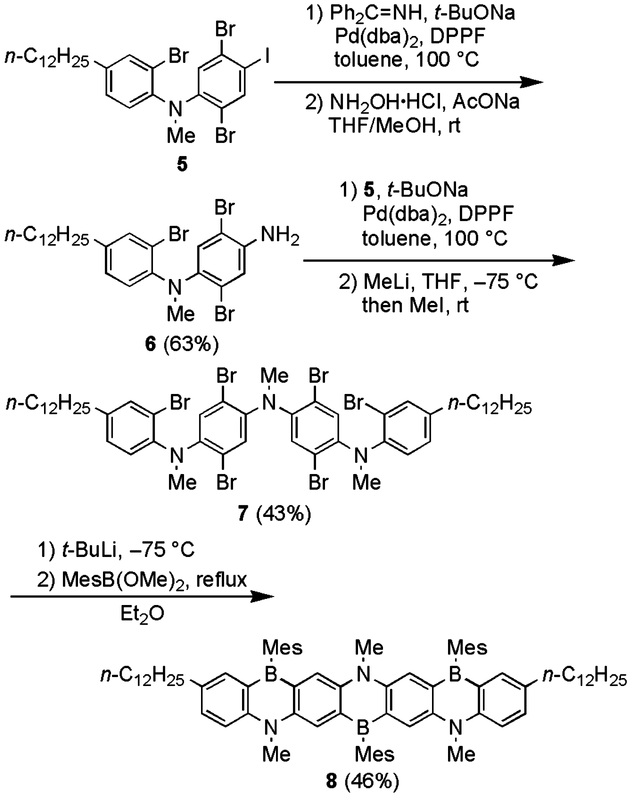
Scheme 2. Synthesis of Ladder Molecule **8**



Single crystals of **3** suitable for X-ray crystallographic analysis were obtained by recrystallization from $CHCl_3$/EtOH solution (Figure 1).[10,11] The diazadiborapentacene framework is nearly planar, judging from the dihedral angles between the peripheral benzene rings and the azaborine rings. **3** does not show any significant intermolecular interactions such as $\pi-\pi$ stacking or CH$-\pi$ interaction in the crystalline state, despite its extended planar π-conjugated systems. Such intermolecular interaction might be prevented by the bulky substituents on the boron atoms.

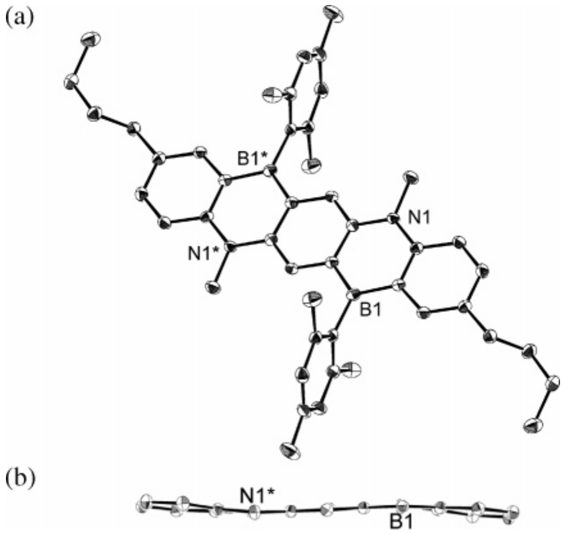


Figure 1. ORTEP drawings of pentacene-type ladder molecule **3** with a thermal ellipsoid plot (50% probability). H atoms are omitted for clarity. (a) Top view. (b) Side view. Mesityl, *n*-butyl, and methyl groups are not shown in the side-view drawing.

The UV$-$vis spectra of the ladder molecules, as well as those of parent dibenzoazaborine **9**, are shown in Figure 2. Para-type ladder molecules **3** and **8** showed red-shifted absorption maxima compared to that of **9**, exhibiting extended π-conjugation by ladder-type frameworks. The longest absorption band of meta-type ladder molecule **4**, however, stays at almost the same wavelength as **9**, indicating weak or no π-conjugation between the two neighboring azaborine units in the meta-type connection mode.

The steady-state fluorescence spectra of the ladder molecules and **9** are shown in Figure 3, and the photophysical data are listed in Table 1.

These compounds exhibited small Stokes shifts ($\Delta\lambda$ < 20 nm) because the rigid framework restricts structural deformation upon photoexcitation. Para-type ladder molecules **3** and **8** showed higher quantum yields than **9**, but the meta-type ladder molecule **4** gave only a low quantum yield. The energy transfer may occur between two neighboring mesityl groups

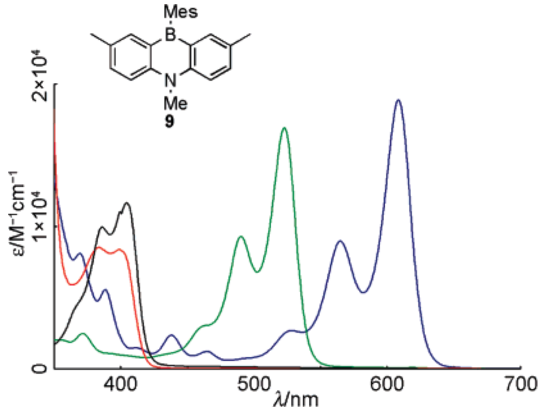


Figure 2. UV$-$vis spectra of the ladder molecules in cyclohexane at 298 K. Green: **3**. Red: **4**. Blue: **8**. Black: **9**.

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[10] Crystallographic data for **3**: $C_{46}H_{54}B_2N_2$, red cube, monoclinic, space group P_{21}/n, a = 11.654(3) Å, b = 10.754(3) Å, c = 15.597(4) Å, β = 107.3673(11)°, V = 1865.6(9) Å^3, Z = 2, $F(000)$ = 708, crystal size 0.20 × 0.20 × 0.20 mm^3, 6.42 ≤ 2Θ ≤ 55.00. In total, 10052 reflections were collected, of which 2844 were independent (R_{int} = 0.0168) and employed for refinement: 231 parameters, 0 restraints, $R1$ ($I > 2\sigma(I)$) = 0.0377, w$R2$ (all data) = 0.0961. The intensities of reflections were collected at 120 K on a RIGAKU MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) using CrystalClear (Rigaku Corp.). The structure was solved by direct methods (SHELXS) and expanded using Fourier techniques. The structure was refined by full-matrix least-squares methods on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factor calculations. CCDC-298596 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax: (+44) 1223−336−033 or deposit@ccdc.cam.ac.uk).

[11] Sheldrick, G. M. *SHELXL-97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

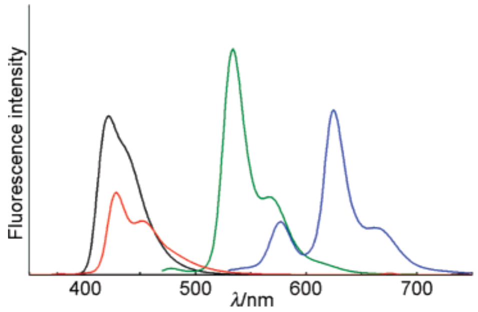

Figure 3. Fluorescence spectra of the ladder molecules in cyclohexane at 298 K. Green: **3**. Red: **4**. Blue: **8**. Black: **9**.

Table 1. Photophysical Data of the Ladder Compounds[a]

	λ_{max}/nm (log ϵ)	λ_{em}/nm	Φ
3	523 (4.23)	534	0.69
4	415 (3.94)	428	0.21
8	608 (4.28)	625	0.55
9	405 (4.02)	421	0.48

[a] The UV−vis absorption spectra and the fluorescence spectra were recorded in cyclohexane at 298 K. The fluorescence quatum yields were determined using anthracene in EtOH (Φ 0.27), fluorescein in 0.1 M aqueous NaOH (Φ 0.85), or rhodamine B in EtOH (Φ 0.71) as standards.

in the excited state of **4**. These data suggest that para-type connections between main group elements in the ladder molecules are efficient for light-emitting devices.

Longer ladder molecule **8** showed two emission maxima, unlike the other compounds. The peak shape observed around 608 nm is similar to those of the other ladder compounds, but the other emission was observed around 580 nm. The origin of this peak remains unclear, and further investigation on this fluorescence is now underway.

In summary, three new π-conjugated ladder-type molecules featuring azaborine have been synthesized via palladium-catalyzed amination reactions as key steps. These are the first examples for boron-containing π-conjugated ladder molecules. The X-ray crystallographic analysis revealed the planar molecular structure that is important for the extension of π-conjugation. The para-type ladder molecules showed red-shifted absorption maxima and fluorescence according to the molecular length. These results indicate that para-type ladder molecules are good candidates for novel π-conjugated molecules, taking advantage of electronic characteristics of main group elements.

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Supporting Information Available: Experimental procedures for the syntheses of all the compounds and the X-ray crystallographic data in CIF format for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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