Development of a general route to periphery-functionalized azaborines and ladder-type azaborines by using common intermediates†

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Received (in Cambridge, UK) 27th April 2007, Accepted 26th June 2007
First published as an Advance Article on the web 5th July 2007
DOI: 10.1039/b706418g

Azaborines and ladder-type azaborines bearing various functional groups can be synthesized starting from common dibromo derivative intermediates, and among several substituents, the carbazol-9-yl group was shown to enhance the photo-luminescence quantum yield of the azaborines up to a value of unity.

Recently, π-conjugated molecules bearing main group elements have attracted much attention, because electronic interactions between the π-orbitals and main group elements can change the electronic state of the parent π-systems by raising the HOMO or lowering the LUMO,[1] and these molecules can have various interesting and useful properties, such as electro-luminescence.[2] Among the many main group elements that can be used, boron occupies a special position,[3] because the electronic interaction between the vacant 2p orbital of boron and the π* orbital is favorable due to the efficient overlapping of these orbitals, and boron exhibits a strong electron-withdrawing characteristic, substantially lowering the energy level of a LUMO.

The construction of a widespread library of emissive materials covering the full color range is an important issue for their application in devices, such as electro-luminescence devices. The introduction of electron donors or acceptors to a π-conjugated framework is an efficient way to modulate the electronic and optical properties of organic materials, such as the HOMO–LUMO energy gap and emission color, and by following such a strategy, π-conjugated molecules exhibiting various properties can be obtained easily when starting from a common synthetic intermediate. Because boranes are potentially strong electron acceptors, several donor–acceptor or acceptor–acceptor hybrid molecules using the borane functionality as an acceptor moiety have been investigated.[2a,2b,3,4]

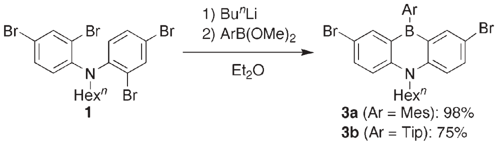
Recently, we reported on the synthesis and properties of heteraborins, which are π-conjugated molecules bearing two main group elements in a 9,10-dihydroanthracene framework.[5,6] The structure and properties of heteraborins varied according to the main group element.[7] We have also synthesized ladder-type molecules based on an azaborine functionality (ladder-type azaborines), which exhibited reduced HOMO–LUMO energy gaps and had strong fluorescence emissions.[8]

However, to tune the electronic and optical properties of azaborines using this previous synthetic method, the synthesis of different precursors for each new azaborine is necessary, and such shortcomings in synthetic generalities have hampered the screening of azaborine-based optical materials, and an alternative diversity-oriented synthetic strategy needs to be developed. In this communication, we describe a general synthetic method for the preparation of various azaborines from common starting materials. This new strategy was successfully applied to the synthesis of periphery-functionalized azaborines and ladder-type azaborines. In particular, amino-functionalized azaborines exhibited red-shifted absorption and emission spectra, and carbazol-9-yl substituted azaborines showed an increased photo-luminescence yield that was nearly equal to a value of unity.

Bromo derivatives show potential as common intermediates for functionalized azaborines due to their diverse reactivity in many types of reaction. Direct bromination of azaborines is difficult due to the low tolerance of the boron moiety against oxidation. Alternatively, the dibromo derivatives **3a** and **3b** were prepared from bis(2,4-dibromophenyl)hexylamine (**1**) and $ArB(OMe)_2$ (Ar = Mes (**2a**) or Tip (**2b**)) taking advantage of the *ortho*-selective dilithiation of **1** (Scheme 1).[9]

We first investigated palladium-catalyzed coupling reactions utilizing the bromo functionality, selecting the Hartwig–Buchwald amination, because amino groups can work as efficient donor groups and can decrease the HOMO–LUMO energy gap (Scheme 2).[10] After screening various amines, Hex^nNH_2 and Ph_2NH were coupled with **3a** or **3b** using a standard amination condition ($Pd(dba)_2$–BINAP) without affecting the boron centers. Carbazole, a less reactive amine, could be also introduced by taking advantage of a more powerful catalyst system ($Pd(dba)_2$–PBu^t_2(2-Biph)). In contrast, coupling with cyclic dialkylamines (pyrrole, morpholine and piperazine), which have been reported to be efficient coupling partners for various aryl halides,[11] gave complex mixtures. Although the reason for this is unclear, much more basic and nucleophilic dialkylamines can attack boron centers and can degrade an azaborine framework.

To examine the generality of the coupling reactions, the introduction of carbon-functional groups was investigated, and



Scheme 1

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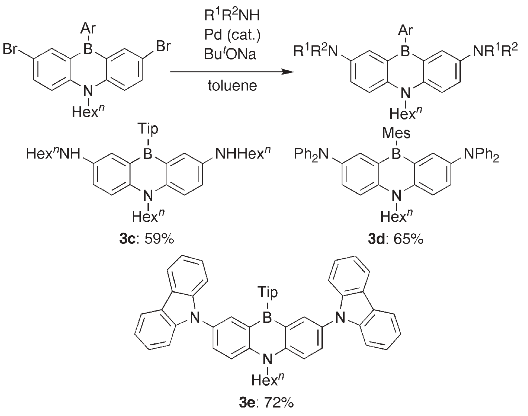
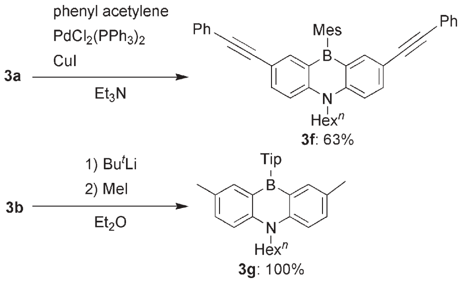
† Electronic supplementary information (ESI) available: Synthesis of the compounds and details of the theoretical calculations. See DOI: 10.1039/b706418g



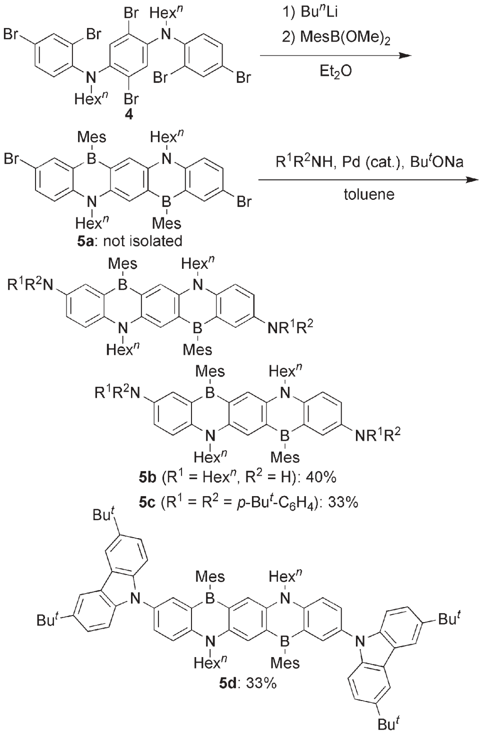
Scheme 2



Scheme 3

the preliminary results are shown in Scheme 3. The Sonogashira coupling with phenyl acetylene proceeded well, indicating that alkyne substituted azaborine oligomers or azaborine–alkyne co-polymers can be obtained using the Sonogashira coupling protocol. In addition, halogen–lithium exchange reaction could be carried out without affecting the triarylborane moiety,[12] and the generated di-lithio derivative reacted with MeI to give dimethyl derivative **3g** quantitatively. Such a result shows that other functional groups, including $B(OR)_2$ and SnR_3 groups, can be introduced into the azaborine framework.

Because the azaborine functionality was shown to tolerate coupling conditions, the expansion of this protocol to more extended molecules, such as ladder-type azaborines, was then investigated. The common precursor, dibromo-derivative **5a**, was prepared from hexabromide **4**. Surprisingly, the halogen–lithium exchange of **4** proceeded in an *ortho*-selective fashion, similar to the case of **1**, and the generated tetralithio derivative reacted with $MesB(OMe)_2$ to give an orange precipitate that was insoluble in ordinary solvents. Although the crude product contained **5a** as the major component, judging from the ^1H NMR spectrum and the FAB-MS spectrum, the isolation of **5a** was difficult due to its low solubility. We tried amination reactions using the crude material without further purification. Amino-substituted pentacene-type azaborines **5b–d** could be obtained following the optimized conditions for the amination of **3a** and **3b** (Scheme 4). These extended azaborines had a high solubility in ordinary organic solvents, and could be purified using GPC and recrystallization.[13] These results show that the common precursor strategy using dibromo derivatives is applicable in general for various azaborine-based materials.



Scheme 4

Table 1 Optical data of the azaborines

	$\lambda_{max}{}^a$/nm (log ε)	$\lambda_{em}{}^a$/nm (Φ)	ΔE^b/cm^{-1}	$\lambda_{em}{}^c$/nm
3c	453 (3.77)	501 (0.51)^e	1500	530
3d	466 (3.80)	494 (0.49)^e	1800	519
3e	400 (3.86)	443 (1.00)^d	2400	448
3h	405 (4.02)	421 (0.48)^d	940	456

[a] In cyclohexane at rt. [b] $\Delta E = 1/\lambda_{max} - 1/\lambda_{em}$. [c] In the solid state. [d] Determined by using 9,10-diphenylanthracene in cyclohexane (Φ 1.00) as a standard. [e] Determined by using fluorescein in 0.1 M aq. NaOH (Φ 0.85) as a standard.

Electronic and fluorescence spectra of the substituted azaborines were recorded in cyclohexane at room temperature, and the optical data are summarized in Table 1. The absorption wavelength of **3e** was close to that of the reference compound, dimethyl derivative **3h** (Fig. 1), indicating a weak electronic effect of the carbazolyl group. On the other hand, azaborines bearing more electron-donating amino groups (Ph_2N or HexⁿNH) showed red-shifted absorptions. Such a difference in absorption wavelength indicated that electron-donating groups at the *para*-positions to the nitrogen

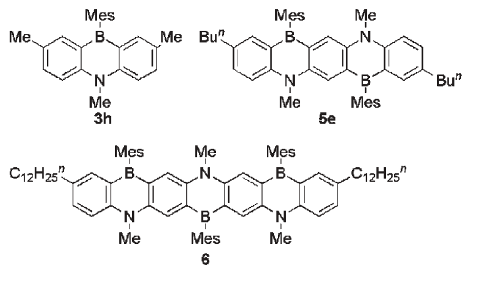


Fig. 1 The structures of reference azaborine and ladder-type azaborines.

Table 2 Optical data of the ladder-type azaborines

	$\lambda_{max}{}^{a}$/nm (log ε)	$\lambda_{em}{}^{a,b}$/nm (Φ)	ΔE^{c}/cm^{-1}	$\lambda_{em}{}^{d}$/nm
5b	580 (4.14)	603 (0.12)	660	620
5c	568 (3.99)	592 (0.20)	620	636
5d	529 (4.14)	546 (0.98)	590	570
5e	523 (4.23)	534 (0.69)	390	599
6	609 (4.28)	626 (0.55)	450	683

[a] In cyclohexane at rt. [b] Determined by using rhodamine B in EtOH (Φ 0.61) as a standard. [c] $\Delta E = 1/\lambda_{max} - 1/\lambda_{em}$. [d] In the solid state.

atom of azaborine decreased the HOMO–LUMO energy gap by elevating the HOMO energy level. Theoretical calculations on model azaborines support this conclusion, with the electron-donating groups elevating the HOMO, while the energy level of the LUMO does not change much on substitution.[14]

The azaborines exhibited strong fluorescence emissions in solution. In particular, the introduction of a carbazol-9-yl group enhanced the fluorescence quantum yield of azaborines dramatically, probably due to the molecular rigidity of both the azaborine and carbazole frameworks. In addition, irradiation of the absorption bands of carbazole (**3e**) or Ph_2N (**3d**) groups (*ca.* 300 nm) resulted in an emission from the azaborine moiety with the same quantum yield, indicating an efficient energy transfer from the amino groups. The emission wavelengths of the azaborines in the solid state are also summarized in Table 1. Irradiation by UV-lamp (254 nm or 366 nm) of these compounds showed a strong emission that varied from blue (**3e** and **3h**) to green (**3c** and **3d**), which was probably due to the prevention of intermolecular interactions by the bulky Mes or Tip groups on the boron atoms.

The optical data of ladder-type azaborines in cyclohexane are summarized in Table 2. Similar to the azaborines, the absorption maxima of the ladder-type azaborines were shifted to longer wavelengths in accordance with the increase in the electron-donating capability of the amino group, *i.e.*, carbazolyl derivative **5d** showed an absorption maximum that was close to that of the reference compound, butyl derivative **5e**, but Ar_2N- or Hex^{n}NH-substituted molecules **5b** or **5c** exhibited absorption spectra that were more red-shifted, reflecting their enhanced donating capability.

Fluorescence spectra of the ladder-type azaborines were recorded in cyclohexane at room temperature. The emission color of **5d** (green) was almost the same as that of **5e**, but the fluorescence quantum yield of **5d** increased up to a value close to unity, like **3e**, and thus, the carbazol-9-yl group was shown to work as an enhancer of the photo-luminescence emission of azaborines without affecting the HOMO–LUMO energy gap. Although the fluorescence quantum yield was not very high, **5b** and **5c** exhibited a red emission, as heptacene-type azaborine **6** does.[8] The Stokes shift of these ladder-type molecules was smaller than that of the azaborines, probably due to the rigid framework. On irradiation using a UV-lamp (254 or 366 nm), the ladder-type molecules showed photo-luminescence in the solid-state that could be observed by the naked eye. The luminescence color varied from yellow to red, in accordance with the absorption and emission wavelength in solution.

In summary, we have developed a new and general synthetic method to introduce various functional groups on the periphery of azaborines and ladder-type azaborines. This methodology will enable the construction of organic functional materials, such as luminescent polymers. In addition, by screening the electronic effect of amino groups, the carbazol-9-yl group was revealed to enhance the photo-luminescence quantum yield of azaborines and ladder-type azaborines substantially without affecting the HOMO–LUMO energy gap, and thus, these amino groups can work as pure photo-luminescence enhancers.

This work was supported by Grants-in-Aid for The 21st COE Program for Frontiers in Fundamental Chemistry and for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan (T.K.) and Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists (T.A.). We thank Tosoh Finechem Corp. for the generous gift of alkyllithiums.

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12. If Bu^{n}Li was used instead of Bu^{t}Li, **3b** was recovered in 65% yield. Coordination of a butyl group to the boron center may prevent the halogen–lithium exchange reaction.
13. When Ph_2NH or carbazole was used as a coupling partner instead of Ar_2NH or di-Bu^t-carbazole, respectively, the generated amino-substituted ladder-type azaborine could not be isolated due to low solubility.
14. The results of the theoretical calculations are included in Electronic Supplementary Information.