Kinetically stabilized dibenzoborole as an electron-accepting building unit†‡

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Received (in Cambridge, UK) 18th October 2007, Accepted 16th November 2007
First published as an Advance Article on the web 23rd November 2007
DOI: 10.1039/b716107g

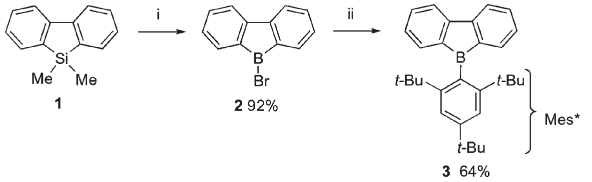
A synthetic route to a dibenzoborole, kinetically stabilized by the 2,4,6-tri-*tert*-butylphenyl group, was developed, and a series of π-extended derivatives were synthesized, which show orange-red emissions and stable electrochemical redox properties.

In boron-containing π-conjugated molecules, the p_{π}–π^* conjugation through a vacant p orbital of the boron atom endows them with intriguing photophysical and electronic properties, and makes them attractive materials for organic (opto)electronics.[1,2] As a representative core skeleton, dibenzoborole (9-borafluorene) is of particular interest. While its carbon and nitrogen congeners, fluorene and carbazole, have been widely used as the core skeleton for emissive and hole-transporting materials, respectively, the dibenzoborole would have significant potential as an electron-accepting building unit, since the perpendicular arrangement of the vacant p orbital of the boron to the biphenyl plane in this skeleton promises an effective p_{π}–π^* conjugation.[3] However, this chemistry is still in its infancy, mainly due to the inaccessibility of a kinetically well-stabilized dibenzoborole skeleton. For example, we previously reported the synthesis of dibenzoborole derivatives having a 2,4,6-triisopropylphenyl (Tip) group on the boron atom, which showed dramatic photoluminescence changes upon treatment with DMF or fluoride ions.[4] These changes resulted from the coordination of the donor species to the boron atom, causing interruption of the p_{π}–π^* conjugation.[4,5] While these results suggest their potential use as sensory materials for anionic analytes, from another viewpoint, the steric protection by Tip is still not sufficient for kinetic stabilization. To utilize the dibenzoborole skeleton for electronic device applications, the first issue to overcome is to establish a synthetic route for introducing a bulkier group on the boron atom. In this context, we now report the synthesis of dibenzoborole-based π-electron systems having a 2,4,6-tri-*tert*-butylphenyl (supermesityl, Mes*) group on the boron atom. Their photophysical and electrochemical properties were also studied to unveil the potential of the dibenzoborole skeleton as a π-electron-accepting building unit.

In a previous study, the Tip-substituted dibenzoborole derivatives were prepared by the reaction of $TipB(OMe)_2$ with 2,2′-dimetalated biphenyls.[4,6,7] In this study, whereas we first used Mes^*BF_2 in place of $TipB(OMe)_2$, all the attempts resulted in forming a monoborylbiphenyl derivative. Therefore, we adopted an alternative route through *B*-halodibenzoborole as a key precursor, as shown in Scheme 1. Thus, bromodibenzoborole **2** was obtained in 92% yield by the treatment of dimethyldibenzosilole **1** with BBr_3[8] without solvent at 50 °C, followed by distillation. Compound **2** was further reacted with Mes*Li in toluene to produce the Mes*-substituted dibenzoborole **3** in 64% yield. For this transformation, toluene is crucial. The use of ether or THF as solvents only resulted in forming complex mixtures. The produced **3** was stable enough in air and water to purify by column chromatography on silica gel.

A straightforward synthetic route to the extended π-conjugated systems is to use 3,7-dihalodibenzoborole as the precursor. However, all attempts of the direct halogenation of **3** with several kinds of reagents such as Br_2, NBS, and ICl resulted in no reaction or the formation of complex mixtures, most likely due to deactivation by the boryl group toward the aromatic electrophilic substitution reactions. Therefore, we chose another route that was the preparation of 3,7-diiododibenzoborole **8** from 4,4′-diamino-2,2′-dibromobiphenyl **4** in 4 steps, as shown in Scheme 2. Thus, **4** was first converted into the bis(triazenyl) derivative **5** and its dilithiation with *t*-BuLi followed by reaction with Bu_2SnCl_2 gave 3,7-bis(triazenyl)dibenzostannole **6**. Diiodination of **6** was conducted with MeI at 100 °C to give the diiododibenzostannole **7** in 45% yield.[9] The transformation from dibenzostannole to dibenzoborole **8** was accomplished by treatment with BCl_3 followed by reaction with Mes*Li in toluene in 62% yield. In this sequence of reactions, when Me_2SiCl_2 was employed in place of Bu_2SnCl_2, the transmetalation from the corresponding dibenzosilole with BBr_3 did not give **8**, due to the low reactivity of the diiodo derivative.

With diiodide **8** in hand, further cross-coupling reactions can produce the extended π-conjugated compounds. Thus, the reaction of **8** with bithienylzinc chloride or 4-(diphenylamino)phenylzinc chloride in the presence of a $Pd_2(dba)_3{\cdot}CHCl_3$–$P(furyl)_3$ catalyst system gave the corresponding π-extended dibenzoboroles **9** and **10** as orange solids in 60% and 77% yields, respectively. These



Scheme 1 *Reagents and conditions*: (i) BBr_3, neat, 50 °C, 48 h; (ii) Mes*Li, toluene, rt, 22 h. Mes* = 2,4,6-tri-*tert*-butylphenyl.

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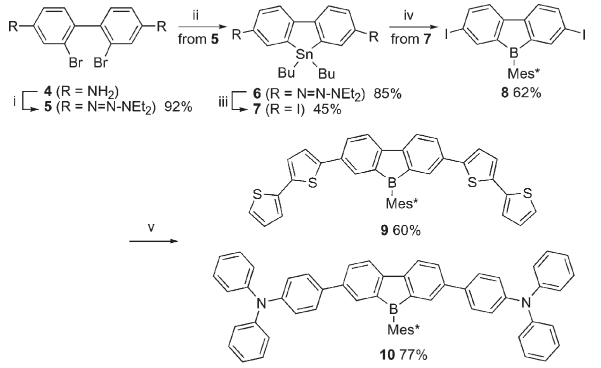
† Dedicated to the late Prof. Yoshihiko Ito.

‡ Electronic supplementary information (ESI) available: Synthetic procedures and analytical data, X-ray analysis, UV-vis and FL, and theoretical calculations. See DOI: 10.1039/b716107g



Scheme 2 *Reagents and conditions*: (i) (1) *t*-BuONO, $BF_3{\cdot}OEt_2$, THF, −10 °C, (2) Et_2NH, K_2CO_3, CH_2Cl_2, 0 °C; (ii) (1) *n*-BuLi, THF, −78 °C, (2) Bu_2SnCl_2; (iii) MeI, neat, 100 °C; (iv) (1) BCl_3, toluene, −78 °C to rt, (2) Mes*Li, rt; (v) ArZnCl (Ar = bithienyl (**9**), *p*-$(Ph_2N)C_6H_4$– (**10**)), $Pd_2(dba)_3{\cdot}CHCl_3$–4P(furyl)$_3$, THF, 40 °C, 12 h.

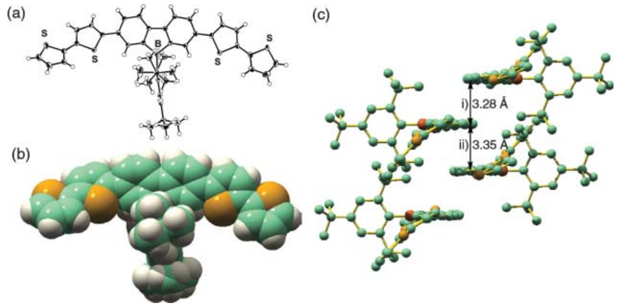


Fig. 1 Crystal structure of **9**: (a) ORTEP drawing (50% probability for thermal ellipsoids), (b) space filling model, and (c) packing structure.

compounds **9** and **10** could be purified by column chromatography on silica gel.

The X-ray crystallographic analysis of **9** revealed that the boron is sufficiently covered with the bulky Mes* group, as shown in Fig. 1.§ The π-conjugated framework takes a banana-shaped planar conformation. The dihedral angles between the dibenzoborole plane and inner thiophene ring and between the terminal and inner thiophene rings are 5.4°, 31.5° and 16.5°, 17.8°, respectively. In the packing structure, molecules are arranged in an offset face-to-face π-stacking array with intermolecular distances of *ca.* 3.3 Å (Fig. 1c, see ESI‡).

The photophysical properties for compound **3** and extended compounds **9** and **10** were measured (Table 1). We were particularly interested in how the solvent or presence of fluoride ions affects the fluorescence, in order to prove the effect of the steric protection by the Mes* group.

Table 1 Photophysical data for π-extended dibenzoborole derivatives

Compd	Solvent	Absorption λ_{max}/nm (log ε)	Fluorescence[a] λ_{max}/nm (Φ_F)[b]
3	Cyclohexane	331 (2.79), 397 (2.41)	495 (0.54)
	THF	333 (2.85), 397 (2.42)	501 (0.35)
	DMF	333 (2.89), 397 (2.39)	505 (0.29)
9	Cyclohexane	383 (4.66), 466 (3.88)	590 (0.26)
	THF	388 (4.75), 470 (4.06)	608 (0.24)
	DMF	390 (4.79), 470 (4.09)	622 (0.23)
10	Cyclohexane	366 (4.60), 453 (3.65)	569 (0.65)
	THF	366 (4.75), 457 (3.80)	600 (0.48)
	DMF	368 (4.73), 460 (3.90)	634 (0.25)

[a] Excited at 360 nm. [b] Absolute quantum yield determined by a calibrated integrating sphere system.

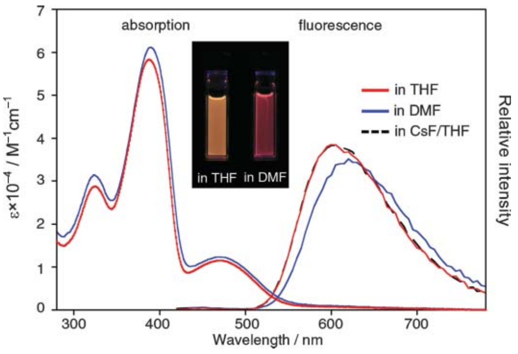


Fig. 2 Absorption and fluorescence spectra of **9**: red line in THF; blue line in DMF; dashed line in THF (8.1×10^{-6} M) with CsF (0.01 M).

In the UV-vis absorption spectra, **3** showed a weak absorption band at 397 nm. The extended compounds **9** and **10** showed intense absorption bands around 366–390 nm and weak absorption bands around 453–470 nm (Table 1 and Fig. 2). According to calculations on **9** and **10** at the B3LYP/6-31G(d) level of theory, in both cases, while the HOMO is spread over the entire π-conjugated framework, the LUMO is mainly localized on the dibenzoborole moiety with a large contribution from the vacant p orbital of the boron atom, and the LUMO+1 is the π* orbital delocalized over the whole π-conjugated skeleton. The TD-DFT calculations (B3LYP/6-31+G(d)) indicate that the absorption bands observed at the shorter and longer wavelengths can be assigned to the HOMO–LUMO+1 (π–π*) transition and the HOMO–LUMO (π–(p_π–π*)) transition, respectively (see ESI‡).

In the fluorescence spectra in THF, **3** showed a blue-green emission at 501 nm, while **9** and **10** showed orange-red emissions with the maxima around 600 nm. The notable common feature is their much higher fluorescence quantum yields compared to those of the previously reported Tip-substituted derivatives.[4a] This difference is most likely attributed to the restricted rotation of the Mes* group due to steric hindrance. When the nonpolar solvent cyclohexane (**3**: 495 nm, **9**: 590 nm, **10**: 569 nm) was replaced with the polar DMF (**3**: 505 nm, **9**: 622 nm, **10**: 634 nm), the emission bands shifted to a longer wavelength, while only subtle changes were observed in the absorption spectra. The degree of the red shift in the fluorescence increases in the order of **3**, **9**, and **10**, which corresponds to the order of the π-donating ability. These results confirm that the dibenzoborole framework acts as a π-electron accepting unit only in the excited state, and the enhancement in the charge transfer character in the excited state results in the large red shift in the emission. More importantly, upon addition of an excess amount of fluoride ions (CsF or *n*-Bu_4NF) in the THF solutions of **9** and **10**, the emission bands did not change at all. These results clearly indicate that the Mes* group effectively protects the boron atom and prevents the coordination of DMF or a fluoride ion. This is in sharp contrast to the result obtained for the Tip-substituted dibenzoborole, which showed significant blue shifts in emission due to the coordination of DMF or a fluoride ion to the boron center.[4]

In order to obtain insights into the electrochemical properties of the dibenzoborole systems, the cyclic voltammograms of **3**, **9**, and

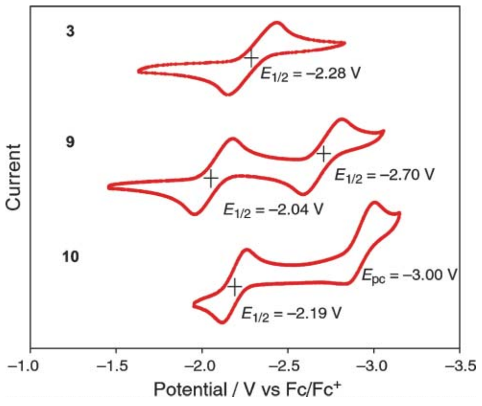


Fig. 3 Cyclic voltammograms of **3**, **9**, and **10**. Measurement conditions: sample 1 mM in THF with n-Bu_4NClO_4 (0.1 M); scan rate 0.10 V s^{-1}.

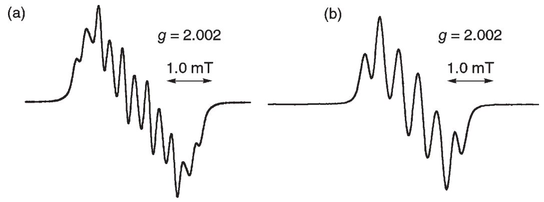


Fig. 4 ESR spectra of (a) $\mathbf{3}^{\bullet-}\cdot K^+$ and (b) $\mathbf{9}^{\bullet-}\cdot K^+$ obtained in THF.

10 were measured in THF (Fig. 3). Dibenzoborole **3** exhibited a reversible reduction wave at −2.28 V *vs.* Fc/Fc$^+$, demonstrating the high electron affinity of the dibenzoborole framework. The second reduction wave was not observed even when swept to −3.2 V. The extension of π-conjugation by two bithiophene units in **9** not only shifted the first reduction wave to a less negative potential ($E_{1/2}$ = −2.04 V) by 0.24 V compared with **3**, but also exhibited a reversible second reduction wave at −2.70 V (*vs.* Fc/Fc$^+$), indicative of the generation of the stable radical anion and dianion under these conditions. On the other hand, the electron-donating (diphenylamino)phenyl-substituted **10** exhibited two reversible oxidation waves at +0.29 V and +0.51 V (*vs.* Fc/Fc$^+$), in addition to two reduction waves at $E_{1/2}$ = −2.19 V and E_{pc} = −3.00 V, which indicates the potential use of **10** as an ambipolar carrier transporting material (see ESI‡).

While the dianions of the dibenzoborole derivatives have been reported by several groups,[10] the properties of the radical anion are still not well understood. We conducted a chemical reduction of the dibenzoboroles. The reaction of **3** with potassium in THF under vacuum at room temperature gave a dark red solution. The ESR measurement of the resulting solution of $\mathbf{3}^{\bullet-}$ exhibited an eleven-line signal (g = 2.002), as shown in Fig. 4a, which is assignable to the coupling with boron (^{11}B: I = 3/2, 80.20%; ^{10}B: I = 3, 19.80%) and proton. According to the simulated ESR signal using the coupling constants of 0.55 mT for boron, 0.35 mT for two equivalent protons and 0.21 mT for two equivalent protons (see ESI‡), the spin density on boron is estimated as 0.21. In a similar manner, the reduction of **9** with potassium was conducted in THF. The ESR spectrum of the resulting dark green solution exhibited a six-line signal (g = 2.002), as shown in Fig. 4b. The simulation using the coupling constants of 0.45 mT for boron and 0.31 mT for two equivalent protons (see ESI‡) indicates that the spin density on boron is estimated to be 0.18. The decrease in the spin density on the boron atom in $\mathbf{9}^{\bullet-}$ (0.18) from $\mathbf{3}^{\bullet-}$ (0.21) suggests delocalization of the spin density to the bithiophene skeleton.

In summary, dibenzoborole-based π-conjugated systems with the bulky Mes* group on the boron atoms were synthesized using 3,7-diiododibenzoborole **8** as a key precursor. The Mes* group is bulky enough to protect the boron atom and hence the molecules showed identical fluorescence spectra even upon addition of fluoride ions and showed stable electrochemical redox properties. In addition, a study on the radical anions $\mathbf{3}^{\bullet-}$ and $\mathbf{9}^{\bullet-}$, produced by chemical reduction, suggests spin distribution over the π framework, which may be informative for considering their potential use as electron-transporting materials. Further study along this line is now in progress in our laboratory.

We thank Professor Kunio Awaga and Dr. Hirofumi Yoshikawa of Nagoya University for use of the ESR spectrometer. This work was supported by a Grant-in-Aid (No. 19685004) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, and SORST, Japan Science and Technology Agency.

Notes and references

§ Crystal data for **9** (from CH_2Cl_2–CH_3CN): $C_{46}H_{45}BS_4\cdot0.5(CH_2Cl_2)\cdot0.5(CH_3CN)$, M = 799.86, triclinic $P\bar{1}$ (no. 2), a = 9.353(2), b = 13.047(2), c = 18.255(4) Å, α = 69.849(6), β = 87.420(8), γ = 81.615(7)°, V = 2068.9(7) $Å^3$, T = 100 K, Z = 2, D_c = 1.284 g cm^{-1}, 13 893 reflections measured, 7146 unique (R_{int} = 0.0231). $R1$ = 0.0613, w$R2$ = 0.1479, GOF = 1.065 ($I > 2\sigma(I)$). CCDC 665414. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b716107g

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