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The role of borole in a fully conjugated electron-rich system

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Received (in Cambridge, UK) 29th September 2003, Accepted 23rd October 2003
First published as an Advance Article on the web 3rd November 2003

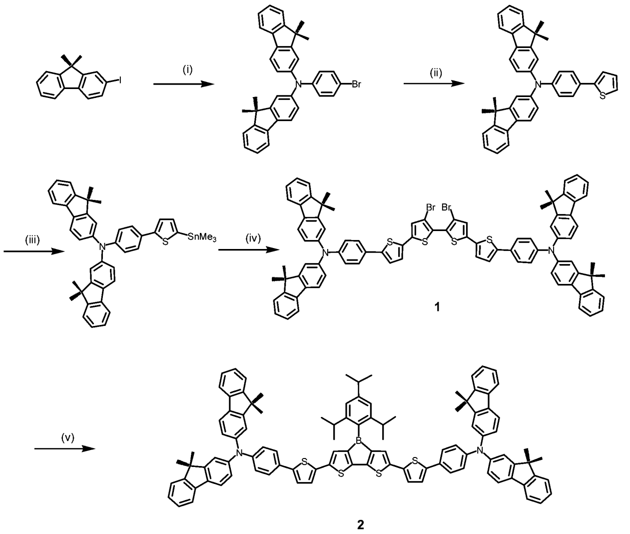
The reaction of the 3,3′-dilithiobithieno complex with Tip-B(OMe)$_2$ affords a borole with an extended conjugated electron-rich π-electron system; the electronic perturbation by the introduction of push–pull substituents is described.

Interest in the chemistry of borirenes,[1] borepines,[2] and boroles[3] stems from the concept of π-electron aromatic and antiaromatic character, and conjugation across the sp^2-hybridized boron. Boroles, the most representative example of this class of compounds, have recently attracted increasing attention as potent Lewis acids for ethylene polymerization[4] and a new type of fluorescent sensor for a specific anion.[5] Several borole catalysts have been designed that are based on the substituent effects on the aryl rings. Less attention has been focused on how the perturbation of the π-electron systems influences the photophysical properties[6] and Lewis acidity. One promising way is the control of the p_π–π* conjugation by removal of the boron p-orbital from conjugation in the borole ring. Another potential way may be to take advantage of the bipolar character by the incorporation of the triphenylamine and boryl moieties, which are π-conjugated through the electron-rich thiophene ring.[7] It should be noted that such push–pull types of π-electron systems have been well documented as potent nonlinear optical materials[8] or emitting compounds.[7] In this communication, we present the first example of controlling the photophysical properties and Lewis acidity by the introduction of a fully conjugated electron-rich unit into the borole.

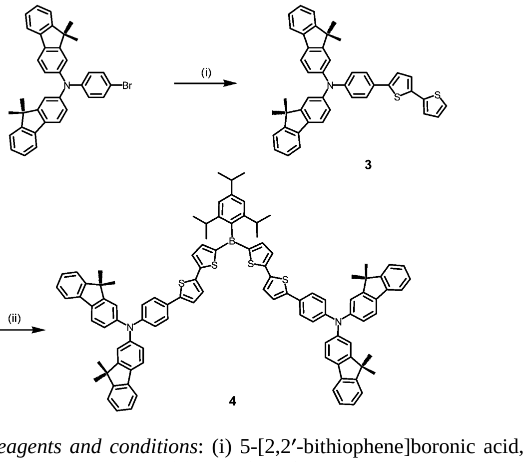
To examine this perturbation, we employed a borole having extended π-conjugated thienyl substituents. The introduction of 9,9-dimethylfluorenyl, amine, boryl, and π-electron bridge units into the borole is intended to provide amorphous glass, electron-donating, electron-accepting, control of the HOMO–LUMO gap and charge-carrier transport, respectively. A bulky 2,4,6-triisopropylphenyl (Tip) unit is introduced at a boron atom for kinetic stabilization.

Our synthesis of bis{2-[4-(bis(9,9-dimethylfluorenyl)amino)-phenyl]-5-thienyl}dithienoborole (**2**), starting from the 3,3′-dibromobithieno compound (**1**), was prepared by the metalation of **1** with TipB(OMe)$_2$ in THF under a nitrogen atmosphere (Scheme 1).† The compound **2** is air- and moisture-stable and was identified by various spectroscopic methods, mass spectrometry, and elemental analysis. A key feature in the ^{11}B NMR spectrum of **2** occurs at δ_B −16.2, about 60 ppm and 10 ppm upfield of the resonance for the fluorinated 9-borafluorene, and tris(9-anthryl) fluoroborate·K$^+$·[2.2.2] cryptand,[9] respectively. This remarkable property strongly suggests the existence of strong electronic interactions between the boron and fully conjugated electron-rich groups along the chain, resulting in charge donation from the π-electron systems toward the boron atom. Further support for this interaction is provided by the similar property of the conjugated borane **4** prepared by the reaction of lithiated 2-[*N*,*N*-bis(9,9-dimethylfluoren-2-yl)aminophenyl]-5,5′-bithienyl with TipB(OMe)$_2$ (Scheme 2).‡ The borane **4** is a pale yellow solid exhibiting ^{11}B NMR resonance at δ_B −8.6. Such an abnormal upfield shift of the resonance was observed in the unsaturated polymers containing the boron and thiophenyl units.[10]

Compounds **2** and **4** are bright green and greenish-blue emitters in THF, respectively and in the solid state when irradiated by UV light. Compound **2** exhibits an absorption band at 369 nm attributed to the π–π* transition of the π-electron unit and an intense band at 438 nm. Compound **2** displays a green fluorescence at 534 nm in THF. The positions of the absorption and fluorescence bands in **2** are independent of the solvents (Table 1). The somewhat large Stokes shift (100 nm) suggests a significant contribution of the boron vacant p-orbital to the photophysical properties. In contrast to the fluorescence band of **2**, that of **4** is solvent dependent. When the solvent is changed from hexane or THF to DMF, the emission maximum shifts to a longer wavelength (Fig. 1). The shift is about 30 nm for THF and ~50 nm for hexane. The solvatochromism exhibited in **4** is attributable to the relatively easy removal of the



Scheme 1 *Reagents and conditions*: (i) 4-bromoaniline, CuCl, 1,10-phenanthroline, KOH in toluene at 125 °C for 12 h, (ii) 2-thiophene boronic acid, Pd(PPh$_3$)$_4$, K$_2$CO$_3$ in THF at rt for 12–16 h, (iii) n-BuLi, Me$_3$SnCl in THF at 0 °C→rt, (iv) 3,3′-5,5′-tetrabromo-2,2′-bithiophene, PdCl$_2$(PPh$_3$)$_2$, LiCl in toluene at 125 °C, (v) TipB(OMe)$_2$, n-BuLi, THF.



Scheme 2 *Reagents and conditions*: (i) 5-[2,2′-bithiophene]boronic acid, Pd(PPh$_3$)$_4$, K$_2$CO$_3$ in THF at rt, (ii) TipB(OMe)$_2$, n-BuLi, THF.

DOI: 10.1039/b312028g

boron p-orbital from conjugation relative to the borole compound **2** by coordinating the donor solvent to the boron atom.

To evaluate the electron-donating and -accepting properties, cyclic voltammograms for compounds **1**, **2**, and **4** were recorded. Compound **2** undergoes a reversible anodic oxidation. No oxidation counterpart corresponding to the anodic peak was observed in spite of the presence of the boryl unit. This observation is presumably due to the fact that Lewis acidity in **2** no longer exists. Both compounds **1** and **4** exhibited two sequential cathodic and the corresponding anodic waves. The first half-wave oxidation potentials ($E_{1/2}^{\text{oxid}}$) of **2** and **4** were almost the same irrespective of the difference in the geometric configuration of the borole and borane, being 0.44 V *vs.* Ag/Ag$^+$. The oxidation potential is comparable to or lower than that for the π-electron rich bithienyl complexes such as bis(triarylamines) based on 3,3′-diphenyl-2,2′-bithiophene[11] and 2,5-bis{4-[bis(4-methylphenyl)amino]phenyl}thiophene.[12]

In order to obtain the characteristic features of the electronic structure, molecular orbital calculations of **2** were performed with the B3LYP/3-21G*. The HOMO is delocalized over the π-conjugated systems *via* the boron vacant p-orbital (Fig. 2). On the other hand, the LUMO is localized on a boron with a dithienyl unit. Examination of the HOMO and the LUMO of **2** indicates that photoexcitation results in a net charge transfer from the conjugated π-electron system to the borole ring.

In summary, we have disclosed the synthesis of a fully conjugated electron-rich borole. The perturbation of the π-electron systems by introducing amine and boryl moieties influences the photophysical properties and Lewis acidity. The extremely upfield shift of the resonance in the ^{11}B NMR spectrum of **2** may be attributable to the charge donation from the π-electron systems to the boron atom. This intrinsic property should be considered in the design of compounds targeted for specific applications.

We are grateful to BK21(2003) for generous financial support.

Table 1 Photophysical and electrochemical data of **2** and **4**

Compound	Solvent	Absorption ($\lambda_{\max}$/nm)	Fluorescence[a] ($\lambda_{\max}$/nm)	First oxidation potential/V *vs.* Ag/Ag^{+b}
2	DMF	369, 438	541	0.45
	THF	370, 436	534	
	Hexane	370, 433	438, 518	
4	DMF	376	511	0.43
	THF	375	481	
	Hexane	373	440, 463	

[a] Excited at the longest absorption maximum wavelengths. [b] Peak potential measured on a 1 mM solution in dichloromethane containing 100 mM of TBAP using Pt electrode and Pt plate as working and counter electrodes at a scan rate of 20 mV s^{-1}.

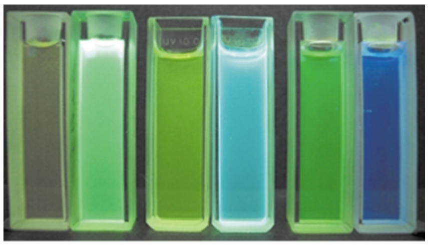


Fig. 1 Photograph of **2** and **4** solutions under UV irradiation (365 nm). From left to right: **2**, **4** in DMF, **2**, **4** in THF, **2**, **4** in hexane (*ca.* 10^{-6} M).

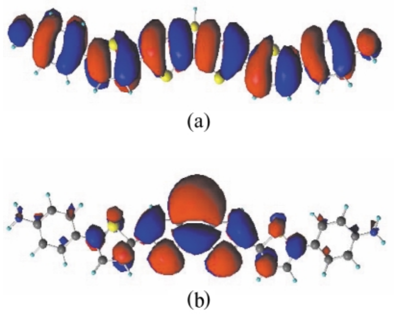


Fig. 2 Representation of (a) HOMO and (b) LUMO of **2** based on the B3LYP/3-21G* calculation.

Notes and references

† *Experimental procedure* for **2**: To a stirred THF solution (30 mL) of **1** (0.95 g, 0.67 mmol) was added n-BuLi (1 ml of 1.6 M solution in hexane, 1.6 mmol) at 0 °C. The solution was warmed to room temperature and continually stirred for 2 h at that temperature. The THF solution (5 mL) of TipB(OMe)$_2$ (0.22 g, 0.8 mmol) was slowly added to the solution at 0 °C and then the mixture was warmed to room temperature. The solution was stirred for 12 h. The product was extracted with methylene chloride and washed with hexane (5 mL × 3) to afford **2** in 71% yield. ^{1}H NMR (CDCl$_3$): δ 7.65 (d, 4H, J = 7.5 Hz), 7.61 (d, 4H, J = 8.1 Hz), 7.49 (d, 4H, J = 8.4 Hz), 7.39 (d, 4H, J = 7.5 Hz), 7.32–7.24 (m, 16H), 7.18 (d, 2H, J = 8.1 Hz), 7.15 (d, 2H, J = 4.8 Hz), 7.12 (d, 4H, J = 8.1 Hz), 7.08 (s, 2H), 6.91 (s, 2H), 2.87 (m, 2H), 2.65 (m, 1H), 1.42 (s, 24H), 1.24 (m, 18H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 155.2, 153.6, 147.6, 147.1, 142.9, 130.9, 136.1, 134.6, 134.5, 128.2, 127.1, 126.7, 126.4, 126.2, 125.3, 124.5, 124.1, 123.7, 123.2, 122.8, 122.3, 122.0, 121.0, 120.5, 119.3, 118.4, 47.0, 35.8, 35.4, 34.2, 33.7, 27.3. ^{11}B NMR: δ −16.2. MS:*m/z* 1494 [M$^+$].

‡ *Experimental procedure* for **4**: Compound **4** was prepared using the same procedure as that described for **2**. ^{1}H NMR (CDCl$_3$): δ 7.68 (d, 4H, J = 7.5 Hz), 7.64 (d, 4H, J = 8.1 Hz), 7.52 (d, 4H, J = 8.1 Hz), 7.42 (d, 4H, J = 7.2 Hz), 7.35–7.25 (m, 10H), 7.23–7.14 (m, 16H), 7.04 (d, 2H, J = 4.2 Hz), 6.95 (s, 2H), 2.91 (m, 2H), 2.70 (m, 1H), 1.45 (s, 24H), 1.30 (m, 18H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 155.2, 153.6, 147.6, 147.1, 143.1, 130.9, 137.7, 135.9, 134.5, 128.8, 128.2, 127.8, 127.4, 127.1, 126.7, 126.3, 125.3, 124.8, 124.1, 123.7, 123.2, 122.9, 122.3, 120.9, 120.6, 119.7, 119.4, 119.1, 46.9, 35.2, 34.8, 34.0, 33.6, 27.1. ^{11}B NMR: δ −8.6. MS: *m/z* 1496 [M$^+$].

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