

1,3,2-Diazaborolyl-functionalized thiophenes and dithiophenes: synthesis, structure, electrochemistry and luminescence†

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Reaction of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (**1**) with equimolar amounts of thienyl lithium or 2,2'-dithienyl lithium led to the generation of benzodiazaboroles **2** and **3** which are functionalized at the boron atom by a 2-thienyl or a 5-(2,2'-dithienyl) unit. Similarly 2-bromo-1,3-diethyl-1,3,2-naphthodiazaborole (**4**) and thienyl lithium or 2,2'-dithienyl lithium afforded the naphthoborolyl-substituted thiophene **5** or dithiophene **6**. Treatment of 2,5-bis(dibromoboryl)-thiophene **7** with 2 eq. of *t*BuN=CH–CH=N*t*Bu in *n*-hexane followed by sodium amalgam reduction of the obtained bis(diazaborolium) salt **8** gave the 2,5-bis(diazaborolyl)thiophene **9**. The 2,5-bis(diazaborolidinyl)-thiophene **10** resulted from the cyclocondensation of **7** with 2 eq. of *N,N'*-di-*tert*-butylethylenediamine in the presence of NEt₃. Analogously, cyclocondensation of **7** with *N,N'*-diethylphenylenediamine gave the bis(benzodiazaborolyl) functionalized thiophene **11**. The novel compounds were characterized by elemental analysis and spectroscopy (¹H-, ¹¹B-, ¹³C-NMR, MS and UV-VIS). The molecular structure of **3** was elucidated by X-ray diffraction. Cyclovoltammograms show an irreversible oxidation wave at 298–598 vs. Fc/Fc⁺. The borolylated thiophenes and dithienyls show intense blue luminescence with Stokes shifts of 30–107 nm.

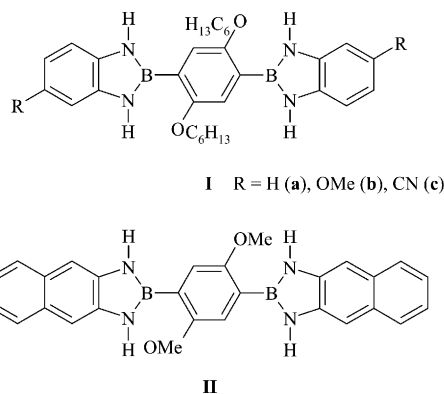
Introduction

Three-coordinate luminescent organoboron compounds are an important class of molecules because of their potential applications in advanced materials. Conjugation of the vacant 2p_z-orbital on the boron center with the π*-orbital of the attached organic π-system proved to be responsible for some outstanding properties such as unique absorption and emission characteristics, a low reduction potential susceptible to doping as well as high electron-transporting abilities.¹

In the past, heavily substituted triarylboranes have been investigated for this purpose.^{2,3} Previously compounds **Ia–c** and **II** were synthesized by the reaction of 2,5-bis(hexyloxy)-1,4-phenylene diboronic acid with 1,2-phenylenediamine derivatives or 2,3-diaminonaphthalene.

Solutions of the molecules **Ia–c** in DMF showed absorption peaks around 350 nm. Compounds **Ia** and **Ic** exhibited violet emission (**Ia**: λ_{em}/nm = 370, 389, 405; **Ic**: 378, 389) using 340 nm as an excitation wavelength. Interestingly the emission maximum of **Ib** was observed around 438 nm which corresponds to the blue region.⁴

In the course of our investigations of the chemical and physicochemical properties of 1,3,2-diazaboroles^{5–7} we were interested in the electrochemical and optical characteristics of thiophene-functionalized derivatives thereof.



Results and discussion

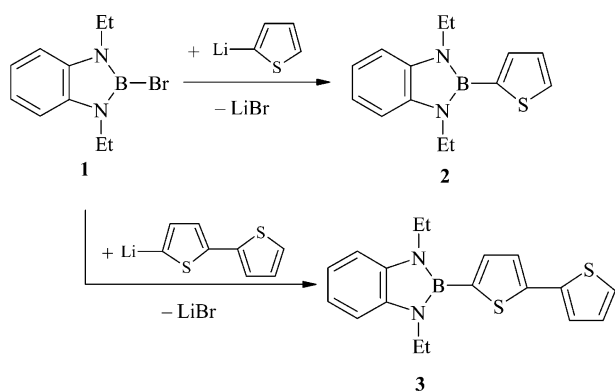
Reaction of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (**1**)⁸ with equimolar amounts of *in situ* generated thienyl lithium or 2,2'-dithienyl lithium in mixtures of diethyl ether and hexane at room temperature and in the absence of light led to the generation of benzodiazaboroles **2** and **3** which are functionalized by a 2-thienyl- or a 5-(2,2'-dithienyl)-unit at the boron atom (Scheme 1).

Products were isolated by distillation as colorless microcrystalline solids in 62 or 57% yield, respectively. They can be stored at –5 °C under an argon atmosphere for several weeks without decomposition.

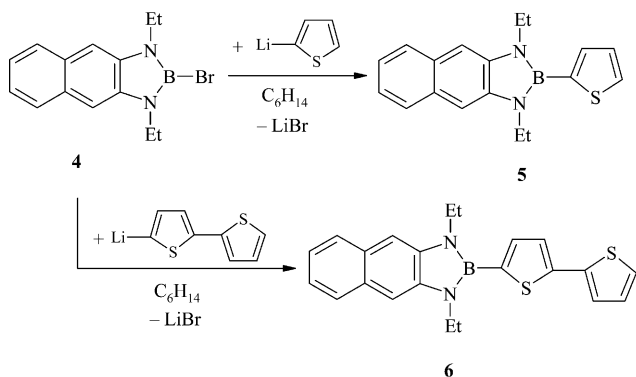
Similarly, reaction of equimolar amounts of 2-bromo-1,3,2-naphthodiazaborole **4** and thienyl lithium in hexane at ambient temperature afforded compound **5** as colorless needles in 57% yield (Scheme 2).

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† The HTML version of this article has been enhanced with additional colour images.



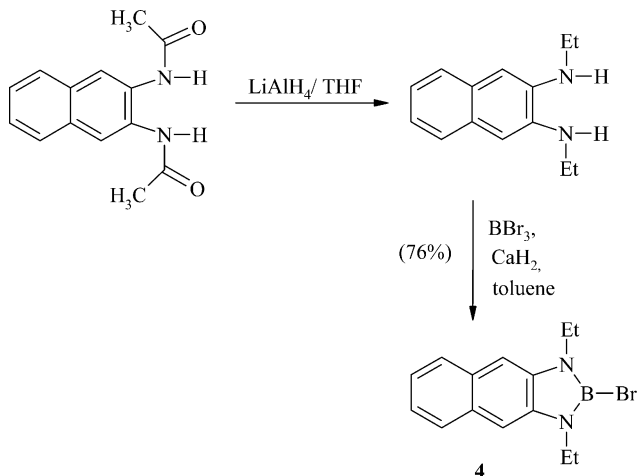
Scheme 1 Synthesis of benzodiazaborole derivatives **2** and **3**.



Scheme 2 Synthesis of compounds **5** and **6**.

In contrast to this, the reaction of **4** with 2-dithienyl lithium under comparable conditions afforded only a few crystals (<1% yield) of pure **6** after crystallizing the crude product from acetonitrile (Scheme 2).

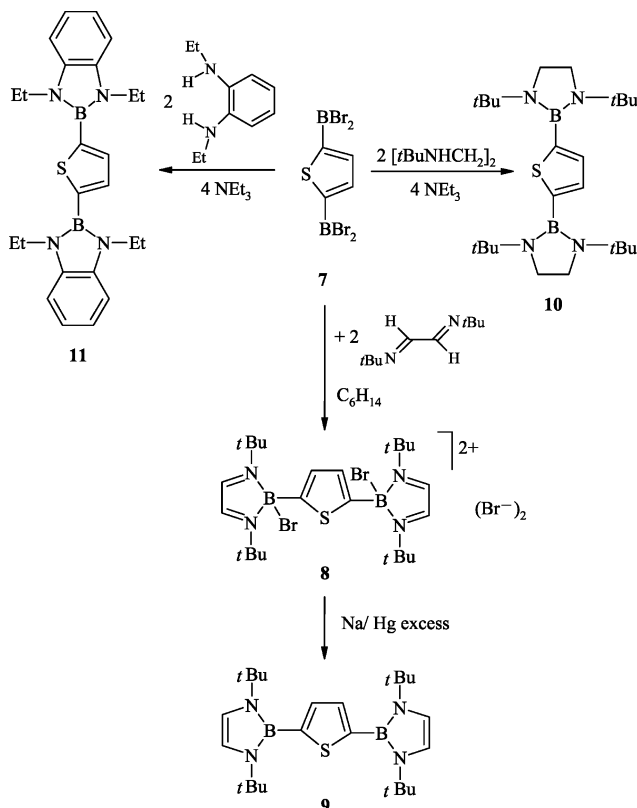
The required starting material **4** was synthesized analogously to the preparation of **1** from *N,N*-diacetyl-2,3-diaminonaphthalene⁹ and LiAlH₄ and the subsequent cyclocondensation of the resulting *N,N*-diethyl-2,3-diaminonaphthalene with BBr₃ in the presence of CaH₂ as a base (68% overall yield) (Scheme 3).



Scheme 3 Preparation of 2-bromo-1,3,2-naphthodiazaborole **4**.

Treatment of 2,5-bis(dibromoboryl)thiophene (**7**) with 2 eq. of *t*BuN=CH-CH=N-*t*Bu in hexane gave the bright yellow

bis(diazaborolium) salt **8**, which was subsequently reduced by an excess of sodium amalgam to yield crystalline **9** (84% yield) (Scheme 4). Stirring a mixture of **7**, 2 eq. of *N,N*-di-*tert*-butylethylenediamine and 4 eq. of NEt₃ in boiling *n*-hexane for 3 h led to the formation of 2,5-bis(1',3',2'-diazaborolidinyl)thiophene **10** as colorless crystals in 89% after crystallization from pentane at -30 °C.



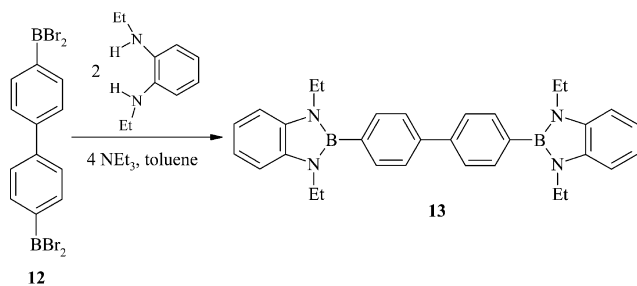
Scheme 4 Preparation of **9**–**11**.

Combination of 2 eq. of *N,N*'-diethyl-1,2-diaminobenzene with the mixture of **7** and 4 eq. of NEt₃ in hexane and boiling the mixture for 3 h afforded product **11** as light-brown crystals (55% yield) (Scheme 4).

In the ¹¹B{¹H} NMR spectra of the 1,3,2-benzodiazaborole derivatives **2**, **3** and **11** singlets are observed at δ = 26.2–26.6 ppm, which is close to the ¹¹B NMR resonances of 2-phenyl-1,3-dimethyl-1,3,2-diazaborole (δ = 25.6 ppm)¹⁰ and 2-phenyl-1,3-di-*tert*-butyl-1,3,2-diazaborole (δ = 26.4 ppm).¹¹ The annulation of a second benzogroup to give the 1,3,2-naphthodiazaboroles **5** and **6** leads to a slight deshielding (**5**: δ = 28.1; **6**: 27.8 ppm). The same trend is evident in the ¹¹B{¹H} NMR spectra of the precursors **1** (δ = 22.8 ppm) and **4** (δ = 25.4 ppm). In the 2,5-bis(diazaborolyl)thiophene **9** and the saturated analogue **10** ¹¹B NMR signals are observed at δ = 23.5 and 30.5 ppm, respectively.

Previously we have found that biphenyl featuring diazaborolyl- and diazaborolidinyl functions in their *para*-position exhibit a bright blue luminescence.¹² At this point it was interesting to compare the optical properties of biphenyl-functionalized with thienyl-functionalized 1,3,2-diazaboroles. For this purpose compound **13** was prepared by the cyclocondensation of 4,4'-bis(dibromoboryl)biphenyl¹³ with two equivalents of

N,N'-diethylphenylenediamine in the presence of an excess of NEt_3 in toluene at 60–80 °C. The product was isolated as colorless crystals in 58% yield (Scheme 5).



Scheme 5 Preparation of **13**.

X-Ray structural analysis of **3**

Single crystals of compound **3** were grown from a hexane solution overnight at room temperature. In the unit cell are two pairs of independent molecules, the bonding parameters of which are identical within the threefold standard deviation. Thus only the structure of molecule **1** is discussed in detail (Fig. 1, Table 3).

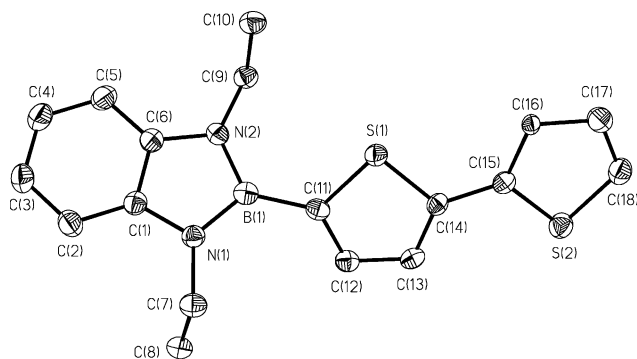
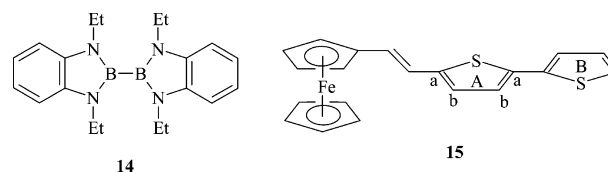


Fig. 1 Molecular structure of **3** in the crystal. Selected bond lengths [Å] and angles [°]: B(1)–N(1) 1.431(5), B(1)–N(2) 1.440(4), N(1)–C(1) 1.397(4), N(2)–C(6) 1.392(4), C(1)–C(6) 1.413(5), N(1)–C(7) 1.464(4), N(2)–C(9) 1.465(4), B(1)–C(11) 1.547(5), S(1)–C(11) 1.736(3), S(1)–C(14) 1.730(3), C(11)–C(12) 1.379(4), C(12)–C(13) 1.403(5), C(13)–C(14) 1.375(4), C(14)–C(15) 1.457(4), S(2)–C(15) 1.728(3), S(2)–C(18) 1.705(4), C(15)–C(16) 1.410(4), C(16)–C(17) 1.437(4), C(17)–C(18) 1.358(5); N(1)–B(1)–N(2) 106.1(3), B(1)–N(1)–C(1) 108.9(3), B(1)–N(2)–C(6) 108.2(3), N(1)–C(1)–C(6) 107.9(3), N(2)–C(6)–C(1) 108.9(3), N(1)–B(1)–C(11) 126.9(3), N(2)–B(1)–C(11) 127.0(3), B(1)–N(1)–C(7) 130.0(3), B(1)–N(2)–C(9) 131.0(3), C(1)–N(1)–C(7) 120.9(3), C(6)–N(2)–C(9) 120.7(3), B(1)–C(11)–S(1) 121.2(2), B(1)–C(11)–C(12) 129.5(3), C(11)–S(1)–C(14) 93.0(2), S(1)–C(14)–C(13) 110.2(2), C(12)–C(13)–C(14) 113.3(3), C(11)–C(12)–C(13) 114.4(3), S(1)–C(11)–C(12) 109.2(2), S(1)–C(14)–C(15) 120.1(2), C(13)–C(14)–C(15) 129.7(3), C(14)–C(15)–S(2) 120.7(2), C(14)–C(15)–C(16) 127.8(3), C(15)–S(2)–C(18) 92.0(2), S(2)–C(15)–C(16) 111.5(2), C(15)–C(16)–C(17) 110.3(2), C(16)–C(17)–C(18) 113.5(3), S(2)–C(18)–C(17) 112.7(3).

The molecule features a planar 1,3,2-benzodiazaborole unit which is linked to the α -carbon atom of the dithienyl fragment by a BC-single bond of 1.547(5) Å. Both rings of the dithienyl group are present in an *anti*-conformation enclosing interplanar angles of 137.5° and 133.7° with the plane of the B–N-heterocycle.

The dihedral angle between both thienyl units is 7°. The BN bond lengths [1.431(5); 1.440(4) Å] are at the upper end of such values in monocyclic 1,3,2-diazaboroles [1.395(4)–1.450(2) Å].^{14–19} All other bond lengths and angles within the benzoborole fragment are similar to those in compound **14** and deserve no more comment.⁸



Bond lengths and endocyclic bond angles of the thiophene group at atom B(1) closely resemble those of thiophene ring A in complex **15** [$\text{S}–\text{C}_a$]av = 1.733(3) Å; $\text{C}_a–\text{C}_b$]av = 1.359(4) Å; $\text{C}_b–\text{C}_b$ = 1.408(4) Å; $\text{C}–\text{S}–\text{C}$ = 92.2(3)°; $\text{S}–\text{C}–\text{C}$]av = 110.3(2); $\text{C}–\text{C}–\text{C}$ = 113.7(3)°.²⁰ It is remarkable that the exocyclic angles B(1)–C(11)–S(1) [121.2(2)°] and B(1)–C(11)–C(12) [129.5(3)°] differ significantly. Similar observations are made with angles S(1)–C(14)–C(15) [120.1(2)°] and C(13)–C(14)–C(15) [129.7(3)°]. Ring B is significantly more distorted than ring A, which is evident from bond lengths C(15)–C(16) [1.410(4) Å] and C(18)–C(17) [1.358(5) Å] in comparison to C(11)–C(12) [1.379(4) Å] and C(13)–C(14) [1.375(4) Å]. The C–C bonds opposite the sulfur atoms are also markedly different in ring A [1.403(5) Å] and ring B [1.437(4) Å].

UV-VIS, luminescence and electrochemical data

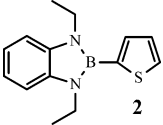
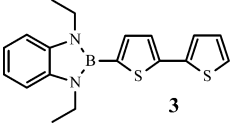
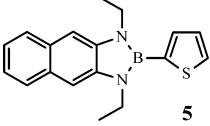
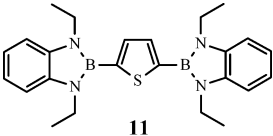
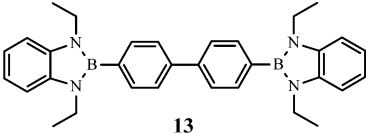
The selected molecules given below show interesting aspects of their fluorescence properties. They all exhibit blue luminescence under ultraviolet radiation (Table 1). The absorption maxima range from 296 nm (**2**) to 341 nm (**5**), and the emission maxima from 371 nm to 433 nm. As expected, the molecule with the smallest π -conjugated system **2** exhibits maximum absorption at the shortest wavelength compared to the other systems. Enlargement of the π -system at the backbone of the benzodiazaborole leads only to a bathochromic shift of the maximum absorption but not that of emission. This fact leads to the extremely small Stokes-shift of compound **5** (30 nm) in comparison to **2** (86 nm). Extending the π -system by using dithiophene instead of thiophene as a substituent at the boron atom leads to a bathochromic shift of the maximum absorption from 296 nm to 326 nm as well as that of the emission from 382 nm to 433 nm. The optical behavior of the bis(diazaboroles) **11**, **13** is more pronounced. They show absorption maxima at 316 nm and 304 nm and emission maxima at 404 nm and 427 nm. Both of them show quantum yields higher than the standard coumarin 120.

It is a matter of common knowledge that the vacant p_z -orbital of boron makes conjugation with organic π -systems possible. Recent investigations have shown that three-coordinate boron can serve as a fluoride-sensor simply by the fact that the fluoride ion occupies the vacant p_z -orbital. If our systems possess a fully-conjugated π -system which includes the p_z -orbital of the boron, fluoridation should lead to a change in absorption and emission properties.

For our investigations we chose the compounds **2** and **3**. Normally these compounds show a clear blue fluorescence under UV-radiation (Fig. 2).

As a fluoride donor we selected $n\text{-Bu}_4\text{NF} \cdot \text{BF}_3 \cdot \text{OEt}_2$ was chosen for the interception of the fluoride to test the reversibility of the reaction (Scheme 6).

Table 1 Photophysical data of the thienylboroles (**2**, **3**, **5**) and the bis(diazaboroles) **11** and **13**

Compound	$\lambda_{\text{max(abs)}}$ /nm (THF)	$\lambda_{\text{max(em)}}$ /nm (THF)	$\Phi_{\text{f,abs}}$ (%) (THF)	Stokes-shift/nm (THF)
 2	296	382	—	86
 3	326	433	29	107
 5	341	371	18	30
 11	316	404	59	88
 13	304	427	52	123

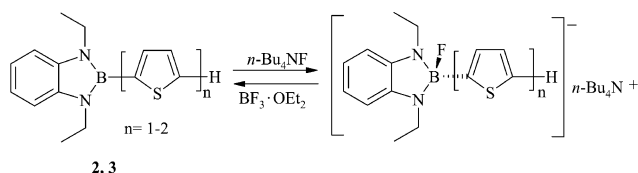
**Fig. 2** Thienylborole **2** (in THF) under UV-radiation (355 nm).**Scheme 6** Fluoridation of **2**, **3**.

Fig. 3a and 3b show the emission bands of **2** and **3** in THF. After addition of $n\text{-Bu}_4\text{NF}$ the emission bands of both compounds decrease drastically. The $^{11}\text{B}\{^1\text{H}\}$ NMR signal of the F^- -adduct of **2** appears at $\delta = 3.4$ ppm, and the ^{19}F NMR resonance at

$\delta = -132.1$ ppm. The corresponding data for the F^- -adduct of **3** are $\delta^{11}\text{B} = 3.3$ ppm and $\delta^{19}\text{F} = -132.2$ ppm. For the equilibrium constant of adduct formation between **2** and tetrabutylammonium fluoride in CDCl_3 at 20°C a value of $5.2 \times 10^{-4} \text{ mol L}^{-1}$ was determined by ^{19}F NMR spectroscopy. Removal of fluoride by the addition of $\text{BF}_3 \cdot \text{OEt}_2$ leads to an increase in intensity of the bands nearly to the original values.

This experiment confirms that the vacant p_z -orbital of the boron-atom has great importance for the emission-properties of the here synthesized molecules. Thus it is possible to “switch on” or “switch off” the fluorescence of these compounds by changing the coordination number of the boron atom.

The mono- and dithienyl-substituted 1,3,2-diazaboroles (**2**, **3**) as well as the thienyl- and the biphenyl-bridged bis(diazaboroles) (**11**, **13**) were oxidized by cyclovoltammetry. The poor solubility of **5** in dichloromethane or acetonitrile prevented an electrochemical study of this compound. The purpose of the electrochemical investigations was to find out how the oxidation potentials are influenced by the substitution pattern at the boron atom, and whether or not these species give rise to reversible cyclovoltammograms.

The oxidation potentials E°_{ox} (Table 2) were taken from square wave voltammetry and vary from 435 mV (**2**) to 867 mV (**13**), versus the ferrocene/ferrocinium couple as standard.

All cyclovoltammograms show a clean, irreversible wave. Even with high scan rates of 850 mV s^{-1} , no quasi-reversibility could be observed.

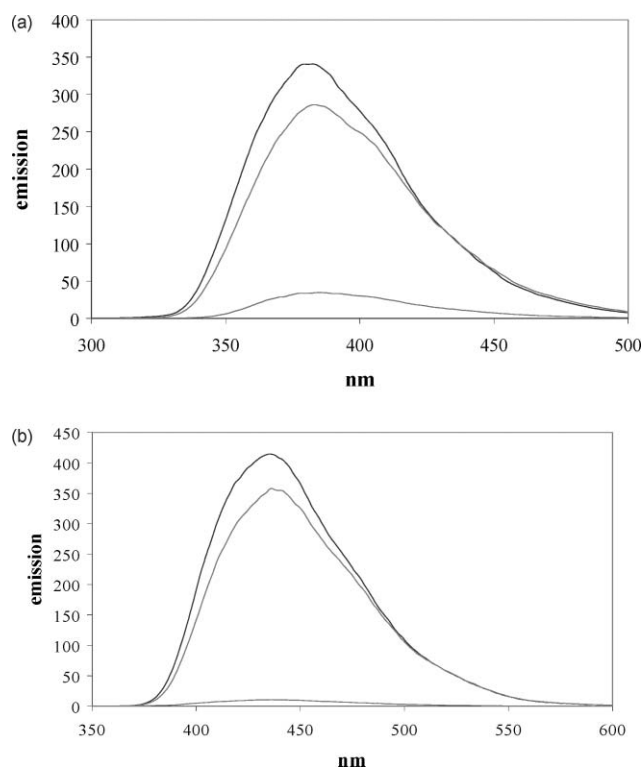


Fig. 3 Emission spectra of **2** (a) and **3** (b) in THF (radiation wavelength 300 nm, $c = 1 \times 10^{-5}$ mol L $^{-1}$). Top trace: compound **2/3** in THF. Bottom trace: compound **2/3** in THF after addition of $n\text{-Bu}_4\text{NF}$. Middle trace: compound **2/3** in THF after addition of $\text{BF}_3 \cdot \text{OEt}_2$.

Table 2 Oxidation potentials E°_{ox} of the thienylboroles (**2,3**) and the bis(diazaboroles) **11** and **13**

Compound	2	3	11	13
$E^\circ_{\text{ox}}/\text{mV}$	435	510	598	867

Conclusion

We have extended the methodologies for the synthesis of 1,3,2-benzodiazaboroles to the construction of 2-thienyl- and 5-(2,2')-dithienyl functionalized benzo- and naphthodiazaboroles with extended π -systems including the vacant $2p_z$ -orbital of the boron atom. All new derivatives exhibit an intense blue luminescence, which can reversibly be extinguished by fluoride ions or $\text{BF}_3 \cdot \text{OEt}_2$, respectively.

Experimental

All manipulations were performed under an atmosphere of dry, oxygen-free argon using standard Schlenk techniques. All solvents were dried by standard methods and freshly distilled prior to use. The compounds 2-bromo-1,3,2-diethyl-1,3,2-benzodiazaborole **1**,⁸ N,N' -diacetyl-2,3-diamino-naphthalene,⁹ 4,4'-bis(dibromoboryl)biphenyl,¹³ dithiophene and $t\text{BuN}=\text{CH}-\text{CH}=\text{N}t\text{Bu}$ were prepared according to literature methods. Thiophene, $t\text{BuN}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{H})t\text{Bu}$, BBr_3 and 2,5-bis(trimethylsilyl)thiophene were purchased from commercial sources. NMR spectra were recorded at room temperature on a Bruker AM Avance DRX 500 spectrometer (^1H , ^{11}B , ^{13}C)

using SiMe_4 and $\text{BF}_3 \cdot \text{OEt}_2$ as external standards. Mass spectra were taken with a VG Autospec sector field mass spectrometer (Micromass). The UV-VIS spectra were recorded on a Perkin Elmer UV Win Lab spectrometer and the emission spectra on a Perkin Elmer Luminescence spectrometer. The quantum yields are determined against coumarin 120 ($\phi = 50\%$) as a standard. The electrochemical experiments were performed with a PAR Model 270A instrument and the relevant software (Model 270). A system of microelectrodes with a three-electrode array was used. A platinum wire (1.5 cm length, 0.5 mm diameter) served as the working electrode which was formed into a helix around the counter electrode. A silver wire (1.5 cm length, 1 mm diameter) served as the pseudo-reference electrode. All experiments were conducted in a glass device, which was flame dried prior to use and filled with dry argon. The determinations were performed at 20 °C in 0.1 M solutions of TBAPF in CH_2Cl_2 with analyte concentrations of 1×10^{-4} mol L $^{-1}$. The cyclic voltammograms were recorded with scan rates of 5–700 mV s $^{-1}$, whereby the results presented here were obtained with scan rates 10, 20, 50 and 100 mV s $^{-1}$. All published potentials were confirmed by square-wave-voltammetry (frequency: 5 Hz). The oxidation potentials were referenced *versus* the ferrocene/ferrocenium couple ($E_{\text{ox}} = 0.0$ eV).

(2'-Thienyl)-1,3-diethyl-1,3,2-benzodiazaborole (**2**)

A chilled solution (-78 °C) of thiophene (1.38 g, 16.4 mmol) in diethyl ether (50 mL) was treated with a 2.5 M solution of n -butyllithium in hexane (6.9 mL, 16.5 mmol). After warming to ambient temperature it was stirred for 2 h. A solution of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole **1** (4.15 g, 16.4 mmol) in hexane (20 mL) was added dropwise to the solution of 2-thienyl lithium. The red solution was stirred overnight at room temperature in the absence of light. The resulting brown solution was concentrated, and filtered from the precipitate of LiBr. The solvent and volatile components were removed from the filtrate *in vacuo* affording a solid residue, which was subsequently distilled at 10^{-3} bar. Product **2** was collected as colorless solid (2.62 g, 62%). Found C, 66.16; H, 6.80; N, 10.84%; $\text{C}_{14}\text{H}_{17}\text{BN}_2\text{S}$ requires C, 65.64; H, 6.69; N, 10.94%. ^1H NMR (CDCl_3): $\delta = 1.40$ (t, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_3), 3.96 (q, $^3J_{\text{HH}} = 7.3$ Hz, 4H, CH_2), 7.07 (m, 2H, H-aryl), 7.14 (m, 2H, H-aryl), 7.33 (m, 1H, 4-H-thiophene), 7.37 (d, $^3J_{\text{HH}} = 3.1$ Hz, 1H, 3-H-thiophene), 7.49 (d, $^3J_{\text{HH}} = 5.0$ Hz, 1H, 5-H-thiophene). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 16.2$ (s, CH_3), 37.8 (s, CH_2), 108.8 (s, CH-aryl), 118.8 (s, CH-aryl), 128.2 (s, CH-thiophene), 129.8 (s, CH-thiophene), 133.7 (s, C-4,5-diazaborole). $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 26.6$ s. MS/EI: $m/z = 256$ (M^+). UV-VIS: $\lambda_{\text{max, abs}}$ 296 nm (THF) (297 nm (hexane)); $\lambda_{\text{max, em}}$ 382 nm (THF) (374 nm (hexane)). CV: $E_{\text{ox}} = 510$ mV.

(5'-2',2''-Dithienyl)-1,3-diethyl-1,3,2-benzodiazaborole (**3**)

A solution of 7.7 mL of a 2.5 M n -butyllithium solution in hexane was added dropwise to a chilled solution (-78 °C) of 2,2'-dithienyl (3.04 g, 18.3 mmol) in diethyl ether (50 mL). Warming to room temperature was followed by 2 h of stirring. Then a solution of **1** (4.63 g, 18.3 mmol) in hexane (20 mL) was added dropwise, whereby a red brownish color occurred. The reaction mixture was stirred overnight at room temperature in the absence of light. The

brown solution was concentrated and freed from a precipitate of LiBr. The filtrate was evaporated to dryness. The solid residue was distilled at 10^{-3} bar and $240\text{ }^{\circ}\text{C}$ to afford product **3** (3.54 g, 57%) as a colorless solid. Found C, 64.36; H, 6.12; N, 7.88; $\text{C}_{18}\text{H}_{19}\text{BN}_2\text{S}_2$ requires C, 63.91; H, 5.66; N, 8.28%. $^1\text{H NMR}$ (CDCl_3): $\delta = 1.38$ (t, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_3), 3.95 (q, $^3J_{\text{HH}} = 7.2$ Hz, 4H, CH_2), 7.05 (m, 3H, 2H-aryl, 1H-dithienyl), 7.11 (m, 2H, H-aryl), 7.26 (d, $^3J_{\text{HH}} = 1\text{H}$, H-dithienyl), 7.24 (d, $^3J_{\text{HH}} = 3.8$ Hz, 1H, H-dithienyl), 7.34 (m, 2H, H-dithienyl). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 16.3$ (s, CH_3), 37.9 (s, CH_2), 108.8 (s, C-aryl), 118.9 (s, C-aryl), 124.0 (s, C-dithienyl), 124.6 (s, C-dithienyl), 125.1 (s, C-dithienyl), 127.9 (s, C-3,4-diazaborole), 134.6 (s, C-dithienyl), 137.1 (s, C-dithienyl). $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 26.2$ s. MS/EI: $m/z = 338$ (M^+). UV-VIS: $\lambda_{\text{max,abs}}$ 326 nm (THF) (331 nm (hexane)); $\lambda_{\text{max,em}}$ 433 nm (THF) (411 nm (hexane)), $\phi = 29\%$. CV: $E_{\text{ox}} = 435$ mV.

2-Bromo-1,3-diethyl-1,3,2-naphthodiazaborole (4)

Step a. A sample of *N,N'*-diacetyl-2,3-diaminonaphthalene (3.00 g, 12.4 mmol) was slowly added to the slurry of LiAlH_4 (0.94 g, 24.7 mmol) in 120 mL of THF. The mixture was stirred for 12 h at ambient temperature, then cooled to $0\text{ }^{\circ}\text{C}$ and combined with an excess of crushed ice. The precipitate was filtered off and the filter-cake was washed with THF (2×10 mL). The combined organic phases were dried (MgSO_4), and then evaporated to dryness. The residue was distilled at 1×10^{-6} bar to afford 2.4 g (90%) of *N,N'*-diethyl-2,3-diaminonaphthalene **4** as a colorless solid. $^1\text{H NMR}$ (CDCl_3): $\delta = 1.37$ (t, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_3CH_2), 3.25 (q, $^3J_{\text{HH}} = 7.2$ Hz, 4H, CH_3CH_2), 3.41 (s, br, 2H, NH), 6.89 (s, 2H, $\text{NH}-\text{C}=\text{CH}$), 7.20 (m, 2H, H-aryl), 7.59 (m, 2H, H-aryl). MS/EI: $m/z = 214$ (M^+).

Step b. Solutions of *N,N'*-diethyl-2,3-diaminonaphthalene (2.40 g, 11.2 mmol) and boron tribromide (3.0 g, 12.0 mmol), each in toluene (30 mL) were added simultaneously to the slurry of CaH_2 (0.70 g, 16.0 mmol) in 50 mL of chilled toluene ($0\text{ }^{\circ}\text{C}$). The mixture was stirred at room temperature (12 h) and then filtered. The filtercake was washed with toluene (2×10 mL). The combined toluene phases were freed from solvents and the residue was distilled at 10^{-6} bar to give 2.58 g (76%) of product **4** as colorless crystals. Found C, 54.53; H, 5.54; N, 9.17; $\text{C}_{14}\text{H}_{16}\text{BBrN}_2$ requires 55.49; H, 5.32; N, 9.24%. $^1\text{H NMR}$ (CDCl_3): $\delta = 1.38$ (t, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_2CH_3), 3.90 (q, $^3J_{\text{HH}} = 7.2$ Hz, 4H, CH_2CH_3), 7.36 (m, 4H, H-aryl), 7.83 (m, 2H, H-aryl). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 15.1$ (s, CH_2CH_3), 37.9 (s, CH_2CH_3), 104.4 (s, $\text{N}-\text{C}=\text{CH}$), 123.2 (s, C-aryl), 127.8 (s, C-aryl), 137.6 (s, $\text{N}-\text{C}=\text{CH}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 25.4$ s. MS/EI: $m/z = 303$ (M^+).

(2'-Thienyl)-1,3-diethyl-1,3,2-naphthodiazaborole (5)

A chilled solution of ($-78\text{ }^{\circ}\text{C}$) of thiophene (0.58 g, 6.9 mmol) in hexane (30 mL) was combined with 2.9 mL of a 2.5 M solution of *n*-butyllithium (7.25 mmol) in hexane. After warming to room temperature stirring was continued for 1 h. Then a solution of **4** (2.11 g, 6.9 mmol) in 20 mL of hexane was added dropwise to the mixture whereby a red color occurred. After stirring for 12 h at room temperature precipitated LiBr was filtered off, and the filtrate was freed from solvent and volatile components *in vacuo*. The residue was distilled by means of a heat gun (*ca.* $360\text{ }^{\circ}\text{C}$, 10^{-6}

bar) to afford 1.29 g (57%) of **5** as colorless needles. Found C, 69.45; H, 6.87; N, 8.83; $\text{C}_{18}\text{H}_{19}\text{BN}_2\text{S}$ requires 70.60; H, 6.25; N, 9.15%. $^1\text{H NMR}$ (CDCl_3): $\delta = 1.44$ (t, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_2CH_3), 4.01 (q, $^3J_{\text{HH}} = 7.1$ Hz, 4H, CH_2CH_3), 7.34 (m, 2H, H-aryl), 7.38 (dd, $^3J_{\text{HH}} = 3.8, 4.4$ Hz, 4-H-thiophene), 7.39 (s, 2H, $\text{NC}=\text{CH}$), 7.54 (d, $^3J_{\text{HH}} = 3\text{-H-thiophene}$), 7.70 (d, $^3J_{\text{HH}} = 4.6$ Hz, 5-H-thiophene), 7.84 (m, 2H, H-aryl). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 15.8$ (s, CH_2CH_3), 38.0 (s, CH_2CH_3), 104.2 (s, $\text{N}-\text{C}=\text{CH}$), 122.8 (s, C-aryl), 126.8 (s, C-aryl), 128.4 (s, 3-C-thiophene), 128.9 (s, C-aryl), 130.3 (s, 2-C-thiophene), 134.2 (s, 5-C-thiophene), 138.7 (s, C-aryl). $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 28.1$ s. MS/EI: $m/z = 306.2$ (M^+). UV-VIS: $\lambda_{\text{max,abs}}$ 341 nm (THF); $\lambda_{\text{max,em}}$ 371 nm (THF); $\phi = 18\%$.

(5',2',2''-Dithienyl)-1,3-diethyl-1,3,2-naphthodiazaborole (6)

A chilled solution ($-78\text{ }^{\circ}\text{C}$) of 2,2'-dithiophene (0.40 g, 2.4 mmol) in hexane (15 mL) was combined with 1.0 mL of a 2.5 M solution of *n*-butyllithium (2.5 mmol) in hexane. It was warmed to room temperature and stirred for another hour. Then a solution of **4** (0.76 g, 2.5 mmol) in 20 mL of hexane was added dropwise whereby the color of the mixture changed to orange. After stirring for 12 h at room temperature it was filtered. The filtrate was evaporated to dryness. The residue was triturated with acetonitrile (10 mL). Storage of the solution at $-4\text{ }^{\circ}\text{C}$ for 3 d afforded a few colorless crystals of **6**. Elemental analyses could not be obtained due to the lack of material. $^1\text{H NMR}$ (CDCl_3): $\delta = 1.45$ (t, $^3J_{\text{HH}} = 7.0$ Hz, 6H, CH_2CH_3), 4.04 (q, $^3J_{\text{HH}} = 7.0$ Hz, 4H, CH_2CH_3), 7.06 (dd, $^3J_{\text{HH}} = 3.8, 4.4$ Hz, 1H, H-4''), 7.26 (d, $^3J_{\text{HH}} = 4.4$ Hz, 1H, H-3''), 7.29 (d, $^3J_{\text{HH}} = 3.8$ Hz, 1H, H-5''), 7.33 (m, 2H, H-aryl), 7.37 (d, $^3J_{\text{HH}} = 3.8$ Hz, 1H, H-3'), 7.40 (s, 2H, $\text{NC}=\text{CH}$), 7.42 (d, $^3J_{\text{HH}} = 3.8$ Hz, H-4'), 7.85 (m, 2H, H-aryl). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 15.9$ (s, CH_2CH_3), 38.1 (s, CH_2CH_3), 104.2 (s, $\text{N}-\text{C}=\text{CH}$), 122.8 (s, C-aryl), 124.2 (s, 4'-C-dithienyl), 124.8 (s, 3'-C-dithienyl), 125.1 (s, 3''-C-dithienyl), 126.9 (s, C-aryl), 127.9 (s, 5''-C-dithienyl), 128.9 (s, C-aryl), 135.1 (s, 4''-C-dithienyl), 137.0 (s, 5'-dithienyl), 138.6 (s, $\text{BNC}=\text{}$), 142.4 (s, 2''-C-dithienyl). $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 27.8$ s.

2,5-Bis(dibromoboryl)thiophene (7)

A sample of neat boron tribromide (19.41 g, 78.0 mmol) was added to a solution of 2,5-bis(trimethylsilyl)thiophene in 70 mL of toluene. The mixture was heated under reflux for 3 h, then cooled to room temperature and concentrated until the onset of crystallization. The solution was stored for 12 h at $4\text{ }^{\circ}\text{C}$ which led to the separation of 11.42 g (87%) of colorless microcrystalline **7**. This was filtered off and the filtercake was washed with cold hexane (3×10 mL). Found C, 11.35; H, 0.48; $\text{C}_4\text{H}_2\text{B}_2\text{Br}_2\text{S}$ requires C, 11.35; H, 0.58%. $^1\text{H NMR}$ (C_6D_6): $\delta = 7.49$ (s, 2H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 143.4$ (s, C-3,4). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 49.7$ s. MS/EI: $m/z = 423$ (M^+).

2,5-Bis(1,3-di-*tert*-butyl-2'-1',3',2'-diazaboroly)thiophene (9)

Solutions of equimolar amounts of 2,5-bis(dibromoboryl)thiophene (**7**) (2.00 g, 4.63 mmol) and 1,2-*tert*-butyliminoethane (1.56 g, 9.26 mmol), each in hexane (30 mL) were added dropwise and simultaneously into a flask containing 50 mL of hexane. Diazaborolium salt **8** is spontaneously formed as a bright yellow

solid. To a slurry of the latter in 150 mL of hexane an excess of 1% sodium amalgam (from 0.7 g Na and 70 g Hg) was added. The resulting mixture was vigorously stirred for 12 h. The supernatant yellow solution was decanted and concentrated *in vacuo* to the onset of crystallization. Storage of the mixture for 2 d at $-30\text{ }^{\circ}\text{C}$ afforded 1.70 g (84%) of analytically pure **9**. Found C, 71.89; H, 9.49; N, 9.89; $\text{C}_{24}\text{H}_{42}\text{B}_2\text{N}_4\text{S}$ requires C, 71.51; H, 9.56; N, 9.40%. $^1\text{H NMR}$ (C_6D_6): $\delta = 1.31$ (s, 36H, *t*Bu), 6.48 (s, 4H, NCH), 7.19 (s, 2H, SCCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 32.6$ [s, $\text{C}(\text{CH}_3)_3$], 53.7 [s, $\text{C}(\text{CH}_3)_3$], 112.9 (s, NCH), 131.5 (s, SCCH). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 23.5$ s. MS/EI: $m/z = 440$ (M^+). CV: $E_{\text{ox}} = 298$ mV.

2,5-Bis(1,3-di-*tert*-butyl-2'-1',3',2'-diazaborolidinyl)thiophene (10)

A solution of **7** (2.00 g, 4.63 mmol) in hexane (30 mL) was added dropwise to a chilled solution ($0\text{ }^{\circ}\text{C}$) of NEt_3 (1.78 g, 18.52 mmol) in 40 mL of hexane, whereby a white precipitate separated. After warming to ambient temperature a sample of neat *N,N'*-di-*tert*-butyl-ethylenediamine (1.60 g, 9.26 mmol) was added and the resulting mixture was heated under reflux for 3 h. The slurry was filtered and the filtrate was evaporated to dryness. The pale yellow residue was crystallized from pentane at $-30\text{ }^{\circ}\text{C}$ to afford 1.78 g (89%) of **10** as colorless crystals. Found C, 64.74; H, 12.49; N, 10.44; $\text{C}_{24}\text{H}_{46}\text{B}_2\text{N}_4\text{S}$ requires C, 64.87; H, 12.61; N, 10.43%. $^1\text{H NMR}$ (C_6D_6): $\delta = 1.03$ (s, 36H, *t*Bu), 3.28 (s, 8H, NCH_2), 6.92 (s, 2H, SCCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 30.6$ [s, $\text{C}(\text{CH}_3)_3$], 45.2 (s, NCH_2), 53.6 [s, $\text{C}(\text{CH}_3)_3$], 131.4 (s, SCCH). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 30.5$ s. MS/EI: $m/z = 444$ (M^+ , 7%), 429 ($\text{M}^+ - \text{CH}_3$, 100%). CV: $E_{\text{ox}} = 641$ mV.

2,5-Bis(1',3'-diethyl-1',3',2'-benzodiazaboroly)thiophene (11)

A solution of 2,5-bis(dibromoboryl)thiophene (2.30 g, 5.40 mmol) in hexane (50 mL) was added to a chilled solution ($0\text{ }^{\circ}\text{C}$) of NEt_3 (2.20 g, 21.7 mmol) in hexane (50 mL). The solution was stirred for 30 min at room temperature and then slowly combined with *N,N'*-diethyl-1,2-diaminobenzene (1.78 g, 10.9 mmol). The mixture was heated under reflux for 3 h, and there after stirring was continued at room temperature for 12 h. It was filtered and the filtercake was washed with hexane (2×20 mL). The combined organic phases were concentrated to the onset of crystallization and then stored at $-30\text{ }^{\circ}\text{C}$ for 3 d. Product **11** separated as brownish crystals (1.27 g, 55%). Found C, 67.33; H, 7.15; N, 13.16; $\text{C}_{24}\text{H}_{30}\text{B}_2\text{N}_4\text{S}$ requires C, 67.32; H, 7.06; N, 13.08%. $^1\text{H NMR}$ (CD_2Cl_2): $\delta = 1.49$ (t, $J_{\text{HH}} = 7.2$ Hz, CH_2CH_3), 4.08 (q, $J_{\text{HH}} = 7.2$ Hz, CH_2CH_3), 7.12 (m, 4H, H-aryl), 7.22 (m, 4H, H-aryl), 7.77 (s, 2H, 3,4-H-thiophene). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 16.5$ (s, CH_2CH_3), 38.3 (s, CH_2CH_3), 109.2 (s, CH-aryl), 119.3 (s, CH-aryl), 135.5 (s, $\text{BC}=\text{CH}$), 137.6 (s, N_2C_2). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 26.6$ s. MS/EI: $m/z = 428$ (M^+). UV-VIS: $\lambda_{\text{max,abs}} = 316$ nm (THF); $\lambda_{\text{max,em}} = 404$ nm (THF); $\phi = 59\%$. CV: $E_{\text{ox}} = 598$ mV.

4,4'-Bis(1'',3''-diethyl-1'',3'',2''-benzodiazaboroly)-1,1'-biphenyl (13)

A solution of 3.00 g (6.08 mmol) of **12** in toluene (80 mL) was added dropwise to a chilled solution ($0\text{ }^{\circ}\text{C}$) of triethylamine (2.50 g, 24.4 mmol) in toluene (100 mL). The mixture was warmed to ambient temperature and then combined with neat *N,N'*-diethylphenylenediamine (2.00 g, 12.2 mmol). It was heated at $60\text{--}80\text{ }^{\circ}\text{C}$ for 3 h. Then stirring was continued overnight at $20\text{ }^{\circ}\text{C}$. After

Table 3 Crystal data and collection parameters for compound **3**

Empirical formula	$\text{C}_{18}\text{H}_{19}\text{BN}_2\text{S}_2$
$M_r/\text{g mol}^{-1}$	338.28
Crystal dimensions/mm	$0.23 \times 0.22 \times 0.02$
Crystal system	Triclinic
Space group	$P\bar{1}$
$a/\text{\AA}$	9.6520(4)
$b/\text{\AA}$	9.7290(3)
$c/\text{\AA}$	18.4350(7)
$\alpha/^\circ$	95.045(2)
$\beta/^\circ$	94.163(2)
$\gamma/^\circ$	102.149(2)
$V/\text{\AA}^3$	1678.41(11)
Z	4
$\rho_{\text{calc.}}/\text{Mg m}^{-3}$	1.339
μ/mm^{-1}	0.317
$F(000)$	712
$\theta/^\circ$	2.91–25
No. refl. collected	27183
No. refl. unique	5882
$R(\text{int})$	0.073
No. refl. [$I > 2\sigma(I)$]	4345
Refined parameters	419
GOF	1.048
R_f [$I > 2\sigma(I)$]	0.0510
wR_f^2 [all data]	0.1323
$\Delta\rho_{\text{max,min}}/e\text{\AA}^{-3}$	0.348, -0.384

filtration the filtrate was concentrated *in vacuo* to the onset of crystallization. Storing overnight at $-18\text{ }^{\circ}\text{C}$ furnished colorless crystalline **13**. Found C, 77.19; H, 7.31; N, 11.06; $\text{C}_{32}\text{H}_{36}\text{B}_2\text{N}_4$ requires C, 77.06; H, 7.22; N, 11.23%. $^1\text{H NMR}$ (C_6D_6): $\delta = 1.11$ (t, $^3J_{\text{HH}} = 6.9$ Hz, 12H, CH_2CH_3), 3.61 (q, $^3J_{\text{HH}} = 5.9$ Hz, 8H CH_2CH_3), 7.04 (q, $^3J_{\text{HH}} = 3.2$ Hz, 4H, $\text{C}_6\text{H}_4\text{N}_2$), 7.18 (q, $^3J_{\text{HH}} = 3.2$ Hz, 4H, $\text{C}_6\text{H}_4\text{N}_2$), 7.66 (d, $^3J_{\text{HH}} = 8.0$ Hz, 4H, biphenyl), 7.74 (d, $^3J_{\text{HH}} = 8.1$ Hz, 4H, biphenyl). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 16.4$ (s, CH_2CH_3), 38.0 (s, CH_2CH_3), 109.2 (s, $\text{N}-\text{C}-\text{CH}=\text{CH}$), 119.0 (s, $\text{N}-\text{C}-\text{CH}=\text{CH}$), 126.9 (s, $\text{C}-2,2'-6,6'$), 134.5 (s, $\text{C}-3,3'-5,5'$), 137.5 (s, $\text{C}-1,1'$), 141.4 (s, $\text{N}-\text{C}=\text{C}-\text{N}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 28.6$ s. MS/EI: $m/z = 498.2$ (100%, M^+). UV-VIS: $\lambda_{\text{max,abs}} = 304$ nm (THF); $\lambda_{\text{max,em}} = 427$ nm (THF); $\phi = 52\%$. CV: $E_{\text{ox}} = 867$ mV.

X-Ray crystallography

Crystal data were measured on a Nonius Kappa CCD-diffractometer and are given in Table 3.

CCDC reference number 296130.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603365b

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