Synthesis and Structure of Diboraporphyrinogenes

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Dedicated to Prof. Dr. Robert Corriu

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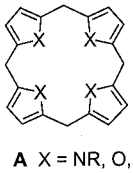
Reactions of 5,5′-dilithiated 1,1-bis(2-thienyl)ethane (**3**) with different substituted dichloroboranes led to the novel 5,15-diboraporphyrinogenes **5**–**8**, in good yields. Amino groups at the boron atoms stabilize the macrocycles **5**–**7**, whereas the first organyl-stabilized diboraporphyrinogene **8** contains the 2,3,5,6-tetramethylphenyl substituent at the boron atoms. A [3+1] approach yields the 5,10-diboraporphyrinogene **13** by treating 2,5-bis[1-(5-lithio-2-thienyl)ethyl]thiophene (**4**) with the 2,5-diborylthiophene derivative **9**. Analogously, the mixed 5,10-diboraporphyrinogenes **15** and **16** are formed from **4** and 2,5-diborylfuran **11** and 2,5-diboryl-*N*-methylpyrrole **12**, respectively. The constituents of the new compounds follow from spectroscopic and structural data.

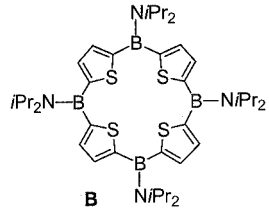
Introduction

Different syntheses for porphyrins are known: 5,10,15,20-Tetraphenylporphyrin is formed in a one-pot reaction of pyrrole with benzaldehyde in the presence of a catalyst.[1] The [2+2] approach uses dipyrromethanes[2] or dipyrromethenes.[3] In a [3+1] formation of porphyrin a 2,5-difunctionalized pyrrole reacts with a tripyrrolic species to produce the macrocycle.[4] The latter two types of porphyrin formation are used for the synthesis of diboraporphyrinogenes.

The chemistry of porphyrinogenes containing thiophene, furan and *N*-protected pyrrole instead of pyrrole has been studied intensely since the isolation of the first chalcogen porphyrinogene by Johnson et al. in 1971.[5] The heteroatom analogs **A** of the porphyrin may be regarded as bridged [20]annulenes having a paratropic ring current.[6] They are oxidized to yield dicationic aromatic compounds having diatropic ring currents.[7]



A X = NR, O, S

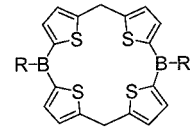


B

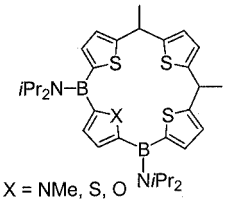
Different boron-containing porphyrins and porphyrinogenes have been synthesized. Recently, Corriu, Douglas, Siebert et al.[8] reported the first tetraboratetrathiaporphyrinogene **B**, and porphyrins with boron atoms in side chains have been used for BNCT (boron neutron capture therapy) studies.[9] Boryl and diborane(4)-diyl groups bridging the nitrogen atoms[10] have been incorporated into porphyrins.

The tetraboratetrathiaporphyrinogene **B** is nonplanar in the solid and has no delocalized electrons in the macrocycle. In solution a magnetic ring current or an electronic interaction of the thiophene units through the boron atoms can be ruled out. Compound **B** exhibits an ^{11}B NMR signal at δ = 40 ppm, which is expected for diaryl(dialkylamino)boranes. Attempts to reduce **B** to the dianion $\mathbf{B}^{2-}$ and to form metal complexes of the macrocycle have not been successful.

We are interested in the synthesis and characterization of diboraporphyrins, in their electronic structures and in the ligand properties of the diboraporphyrinogenes **C** and **D**, which formally derive from **A** by exchange of two *meso*-carbon atoms for two boron atoms. The empty p_z orbitals of the boron atoms may allow macrocyclic conjugation when **C** and **D** are deprotonated to give dianions. The formation of silyl- and stannyl-bridged macrocycles has been reported.[11]



C



D X = NMe, S, O

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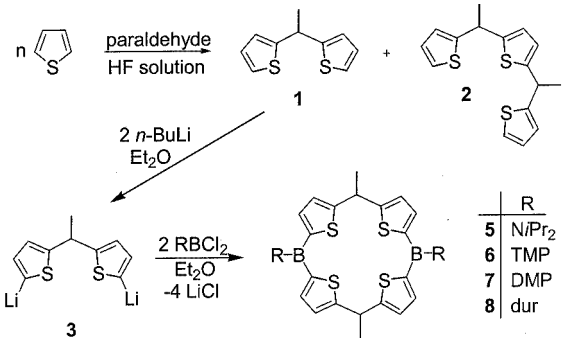
Results and Discussion

Synthesis of Diboraporphyrinogenes

Liquid 1,1-bis(2-thienyl)ethane (**1**) is formed[12] in 39% yield by treating thiophene and paraldehyde with a solution of 40% HF. After distillation of **1**, a dark residue is obtained, probably a mixture of thiophene and the aldehyde condensation products (Scheme 1). Under the same conditions we obtained a mixture of **1** and **2** in a ratio of 5:7; 28.3% of thiophene reacted to give **1** and **2** in 42 and 58% yield, respectively. Deprotonation of **1** with butyllithium in diethyl ether at room temperature leads to 1,1-bis(5-lithio-2-thienyl)ethane (**3**). Under these conditions it is not necessary to use a solvent mixture of hexane and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) as proposed.[8,13] Due to its high reactivity **3** is prepared in situ for the synthesis of the macrocycles **5**−**8**.



Scheme 1

Reaction of **3** with iPr_2N-BCl_2 leads to the yellow, air- and moisture-sensitive tetrathiadiboraporphyrinogene **5** in 95% yield. Its composition follows from spectroscopic data and its structure is confirmed by an X-ray diffraction analysis. In the solid **5** has a center of inversion and is nonplanar, which may prevent possible electron delocalization. The observed B−C distances of 1.58(2) Å are in the range expected for B−C single bonds (1.56−1.60 Å). The short B−N distance of 1.40(1) Å results from the donor effect of the nitrogen atom. In the thienyl ring the bond lengths C1−C2, C3−C4, C5−C6 and C7−C8 are smaller than C2−C3 and C6−C7, which may indicate a localized π system[14] and no electronic interaction between the thiophene units across the boron atoms (Figure 1).

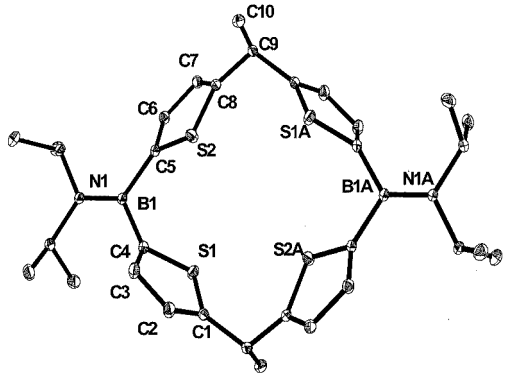


Figure 1. Molecular structure of **5** in the crystal, selected bond lengths [Å] and angles [°]: C1−C2 1.358(2), C2−C3 1.426(2), C4−B1 1.584(2), B1−N1 1.401(1), B1−C5 1.575(2); C4−B1−N1 124.56(10), C5−B1−N1 122.23(10), C5−B1−C4 113.20(9)

The ^1H NMR spectrum of **5** exhibits the expected doublet and septuplet of the isopropyl substituent, the doublet and quadruplet of the bridging $HCCH_3$ group and the two doublets of the thiophene protons at δ = 6.78 and 6.84 ppm, shifted high-field by 0.4 ppm relative to those of **1**. Similar shifts have been explained by a π interaction of the heterocycle with the boryl substituent.[15] In the ^{11}B NMR spectrum a broad signal appears at δ = 35 ppm, indicating a B−N π interaction. The ^{13}C NMR spectrum shows signals for the $HCCH_3$ groups at δ = 14.5 and 50.3 ppm, the signals of the isopropylamino substituents appear at δ = 25.3 and 37.1 ppm. For the thienyl rings three sharp and one broad signal for the *ipso*-carbon atoms are observed.

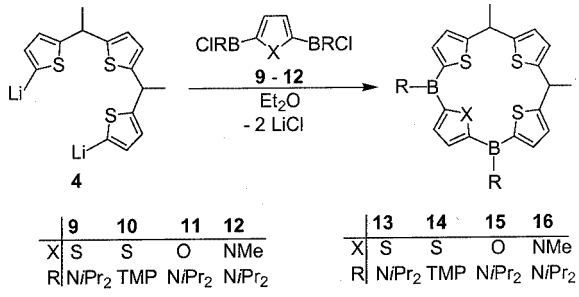
Attempts to replace the diisopropylamino substituents in **5** with $AlMe_3$ and MeOH were not successful; instead cleavage of the macrocycle occurred. We could not obtain any metal complexes of **5** with rhodium, ruthenium and silver reagents.

Treatment of **3** with dichloro(2,2′,6,6′-tetramethylpiperidyl)borane and dichloro(2,6-dimethylpiperidyl)borane yielded the yellow 5,15-diboraporphyrinogenes **6** and **7** in 51 and 60% yield, respectively. As for **5** and **8** (see below), the macrocycles **6** and **7** are air- and moisture-sensitive. Their ^{11}B NMR spectra exhibit broad signals at δ = 43 ppm (**6**) and δ = 42 ppm (**7**), which appear in the same region as that of the tetrathiatetraboraporphyrinogene **B**.[8] Because of the amino substituents at the boron atoms, the tetrathia-5,15-diboraporphyrinogenes **5**−**7** are electronically saturated due to the π interactions with the nitrogen atoms.

In order to obtain a sterically rather than an electronically stabilized macrocycle we prepared the first aryl-stabilized tetrathia-5,15-diboraporphyrinogene **8**, in 45% yield by treating **3** with dichloro(2,3,5,6-tetramethylphenyl)borane. In yellow **8** the boron atoms are sterically protected by the duryl substituents (dur), because the ring planes are perpendicular to the plane of the trigonal-planar arranged boryl groups [^{11}B NMR: δ = 70 (br)]. Compound **8** is an interesting molecule for deprotonation of the 10,20-positions. If we could deprotonate **8** to obtain the dianion $[\mathbf{8} - 2\ H^+]^{2-}$, we may create a conjugated π system in the macrocycle.

Deprotonation of **2**, analogously to **1**, forms the dilithio compound **4** as a red solution which reacts with the 2,5-bis(boryl)thiophenes **9**[16] and **10** at low temperature to give the tetrathia-5,10-diboraporphyrinogenes **13** and **14** as yellow solids in 61 and 62% yield, respectively (Scheme 2). Applying the [3+1] method for the synthesis of porphyrins it is possible to prepare mixed porphyrinogenes. The reaction of **4** with the 2,5-bis(boryl)furan **11** and 2,5-bis(boryl)-*N*-methylpyrrole **12** in diethyl ether leads to the formation of **15** and **16** in 40 and 47% yield, respectively. Their ^{11}B NMR

signals appear in the expected region (δ = 39, 43 ppm) as (amino)dithienylboranes (δ = 38 ppm).[17]



Scheme 2

The 5,10-diboraporphyrinogenes **13**−**16** are yellow solids, sensitive to air and moisture. They show similar properties to those of the 5,15-diboraporphyrinogenes **5**−**8**. It was not possible to replace the boron substituent with $AlMe_3$ or MeOH without destruction of the macrocycles. Furthermore, attempts to obtain metal complexes with ruthenium, rhodium or silver reagents were unsuccessful. Treatment of **13**−**16** with tricarbonyltris(acetonitrile)-chromium did not lead to a macrocyclic tricarbonyl(thiophene)chromium complex.

Conclusion

The synthesis of 5,15- (**5**−**7**) and 5,10-diboraporphyrinogenes **13**−**16** is possible when electron-donating amino substituents like diisopropylamino, dimethylpiperidyl and tetramethylpiperidyl reduce the Lewis acidity of the boron atoms. Despite this electronic stabilization, the yellow macrocycles are sensitive to moisture and air. The sterically active 2,3,5,6-tetramethylphenyl substituents protect the boron atoms in yellow **8**, which after deprotonation to the dianion may have better ligand properties towards transition metals than that of **5**.

Experimental Section

General: Reactions were carried out under dry nitrogen using standard Schlenk techniques. Solvents and chemicals were dried, distilled, and saturated with nitrogen. Glassware was dried with a heat-gun under high vacuum. ^1H, ^{11}B, ^{13}C NMR: Bruker DRX 200 spectrometer, NMR references are $(CH_3)_4Si$ and $BF_3{\cdot}Et_2O$. Mass spectra were obtained with a Joel JMS-700 spectrometer, using EI, CI and FAB techniques. Melting points (uncorrected) were measured with a Büchi apparatus, using a capillary, which was filled under nitrogen and sealed. Cl_2BNiPr_2,[14] Cl_2BTMP,[18] Cl_2BDMP,[19] Cl_2Bdur,[20] 2,5-bis[chlorobis(diisopropylamino)boryl]thiophene,[16] 1,1-bis(2-thienyl)ethane[12] were prepared according to literature procedures.

1 and 2: A solution of paraldehyde (52.8 g, 0.4 mol) in thiophene (101 g, 1.2 mol) was placed in a 1-L plastic flask. The flask was immersed in an ice-bath and 50 g of 40% hydrofluoric acid was added with stirring as follows: 5 g at the beginning, 10 g after 1.5 h and the rest after 3 h. Stirring was continued for 4 h at 0 °C and 3 d at room temperature. Distilled water (300 mL) and diethyl ether (200 mL) were added to the reaction mixture. After separating the organic layer, it was washed twice with a solution of NaOH (0.1 N) and dried with Na_2SO_4. Distillation gave **1** (10.3 g, 0.055 mol, 42%), b.p. 90 °C/1.0 mbar and **2** (23.5 g, 0.077 mol, 58%) as a brown, oily residue. **1:** ^1H NMR (CD_2Cl_2, 200.1 MHz): δ = 1.87 (d, $^3J_{H,H}$ = 7 Hz, 1 H, $CHCH_3$), 4.74 (q, $^3J_{H,H}$ = 7 Hz, 3 H, $CHCH_3$), 7.03 (m, 4 H, CH), 7.24 (d, 2 H, CH) ppm. ^{13}C NMR (CD_2Cl_2, 50.3 MHz): δ = 24.9 ($CHCH_3$), 36.6 ($CHCH_3$), 124.1, 127.0, 150.6 (CH) ppm. EI-MS: *m*/*z* (%) = 194 (75) $[M]^+$, 179 (100) $[M - CH_3]^+$. **2:** ^1H NMR (CD_2Cl_2, 200.1 MHz): δ = 1.75 (d, $^3J_{H,H}$ = 7 Hz, 6 H, $CHCH_3$), 4.60 (q, $^3J_{H,H}$ = 7 Hz, 2 H, $CHCH_3$), 6.80 (m, 3 H, CH), 6.90 (m, 3 H, CH), 7.15 (d, 2 H, CH) ppm. ^{13}C NMR (CD_2Cl_2, 50.3 MHz): δ = 24.4 ($CHCH_3$), 36.7 ($CHCH_3$), 124.2, 125.4, 127.3, 148.5, 150.5 (CH) ppm. EI-MS: *m*/*z* (%) = 304 (70) $[M]^+$; 289 (100) $[M - CH_3]^+$.

5: To a stirred solution of 1,1-bis(2-thienyl)ethane (**1**) (1.0 g, 5.2 mmol) in diethyl ether (20 mL), a 2.5 M solution of butyllithium in hexane (4.2 mL) was added dropwise at room temp. The colorless solution turned red within 30 min. After cooling to −30 °C, Cl_2BNiPr_2 (1.0 g, 5.5 mmol) was added dropwise and stirred for 14 h at 20 °C. The solid was then filtered and washed with diethyl ether and the solvent was removed under vacuum to give a yellow solid which was washed twice with pentane. Yield: 1.50 g (2.5 mmol, 95%) of yellow **5**, m.p. 175 °C (decomp.). ^1H NMR ($CDCl_3$, 200.1 MHz): δ = 1.20 [d, $^3J_{H,H}$ = 7 Hz, 24 H, $CH(CH_3)_2$], 1.71 (d, $^3J_{H,H}$ = 7 Hz, 3 H, $CHCH_3$), 4.03 [s, $^3J_{H,H}$ = 7 Hz, 4 H, $CH(CH_3)_2$], 4.57 (q, $^3J_{H,H}$ = 7 Hz, 2 H, $CHCH_3$), 6.76 (d, $^3J_{H,H}$ = 4.0 Hz, 4 H, H_{ar}), 6.84 (d, $^3J_{H,H}$ = 4.0 Hz, 4 H, H_{ar}) ppm. ^{11}B NMR ($CDCl_3$, 64.1 MHz): δ = 35.0 ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 14.5 ($CHCH_3$), 25.3 [$CH(CH_3)_2$], 37.1 [$CH(CH_3)_2$], 50.3 ($CHCH_3$), 125.0, 134.0, 154.8 (C_{ar}), 143 (br, CB) ppm. FAB-MS: *m*/*z* (%) = 606 (90) $[M]^+$, 591 (43) $[M - CH_3]^+$, 507 (49) $[M - NiPr_2]^+$. HR-FAB-MS: *m*/*z* (%) = $C_{32}H_{44}N_2S_4{}^{11}B_2$ $[M]^+$ calcd. 606.2575; found 606.2615; Δ*m* = 4.0 mmu.

6: The compound was prepared, analogously to **5**, from **1** (0.95 g, 4.9 mmol), *n*-butyllithium (4.2 mL) and dichloro(2,2′,6,6′-tetramethylpiperidyl)borane (1.1 g, 4.98 mmol). Yield: 0.86 g (1.3 mmol, 51%) of yellow **6**, m.p. 185 °C (decomp.). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.43 [s, 24 H, $C(CH_3)_2$], 1.68 (m, 12 H, CH_2), 1.77 (d, $^3J_{H,H}$ = 7 Hz, 6 H, $CHCH_3$), 4.63 (q, $^3J_{H,H}$ = 7 Hz, 2 H, $CHCH_3$), 6.87 (m, 8 H, H_{ar}) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 43.3 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.0 ($CHCH_3$), 24.5 [$C(CH_3)_2$], 32.1 (CH_2), 36.1 (CH_2), 55.4 [$CH(CH_3)$], 123.6; 126.5; 150.0 (C_{ar}) ppm, CB signal not detected. CI-MS: *m*/*z* (%) = 743 (10) [M + C_4H_8 gas], 687 (15) $[M]^+$, 672 (13) $[M - CH_3]^+$. HR-FAB-MS: $C_{38}H_{52}N_2S_4{}^{11}B_2$ $[M]^+$ calcd. 686.3200; found 686.3220; Δ*m* = 2.0 mmu.

7: The compound was prepared analogously to **5**, from 1,1-bis(2-thienyl)ethane (1.82 g, 9.4 mmol), *n*-butyllithium (8.3 mL) and dichloro(2,6-dimethylpiperidyl)borane (1.83 g, 9.6 mmol). Yield: 1.78 g (2.8 mmol, 60%) of yellow **7**, m.p. 185 °C (decomp.). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.36−1.87 (m, 28 H, H_{dmp} and $CHCH_3$), 4.35 (q, $^3J_{H,H}$ = 7 Hz, 2 H, CH_3HC_{dmp}), 4.47 (q, $^3J_{H,H}$ = 7 Hz, 2 H, CH_3HC_{dmp}), 4.67 (q, $^3J_{H,H}$ = 7 Hz, 2 H, $CHCH_3$), 6.93−7.06 (m, H_{ar}) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 42.3 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.1 (H_3CHC_{dmp}

and $CHCH_3$), 23.1, 24.3, 26.2, 28.5, 31.6, 34.1 (CH_2), 36.2 ($CHCH_3$), 48.0, 49.1, 49.9, 52.5 (CH_3HC_{dmp}), 124.4, 134.5, 152.6 (C_{ar}), 142 (br, C−B) ppm. EI-MS: *m*/*z* (%) = 630 (15) $[M]^+$, 615 (7) $[M - CH_3]^+$. HR-EI-MS: $C_{40}H_{44}N_2S_4{}^{11}B_2$ $[M]^+$ calcd. 630.2574; found 630.2609; Δm = 3.5 mmu.

8: The compound was prepared analogously to **5**, from **1** (1.2 g, 6.2 mmol), *n*-butyllithium (5.4 mL) and dichloro(2,3,5,6-tetramethylphenyl)borane (1.3 g, 6.2 mmol). Yield: 0.92 g (1.4 mmol, 45%) of yellow **8**, m.p. 180 °C (decomp.). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.79 (d, $^3J_{H,H}$ = 7 Hz, 6 H, $CHCH_3$), 1.95 (s, 9 H, CH_{3dur}), 2.19 (s, 15 H, H_3C_{dur}), 4.68 (q, $^3J_{H,H}$ = 7 Hz, 2 H, $CHCH_3$), 6.95 (m, 8 H, H_{ar}), 7.57 (s, 2 H, HC_{dur}) ppm. ^{11}B NMR ($CDCl_3$, 64.2 MHz): δ = 70 (br) (special parameters have been used: *SW* = 1000 ppm, *TD* = 8 k, *NS* = 1 k) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 19.8, 20.1 (H_3C_{dur}), 24.3 ($CHCH_3$), 37.2 ($CHCH_3$), 124.2, 127.0 (C_{ar}), 131.2, 133.0, 134.0, 134.5 (C_{dur}), 142.6 (C_{dur}), 163 (br, B−C_{ar}) ppm. FAB-MS: *m*/*z* (%) = 673 (5) $[M + H]^+$; 540 (6) $[M - dur]^+$. HR-FAB-MS: $C_{40}H_{42}B_2S_4$ $[M]^+$ calcd. 672.2355; found 672.2377; Δm = 2.2 mmu.

13: To a solution of 2,5-bis[1(2-thienyl)ethyl]thiophene (**2**) (1.0 g, 3.3 mmol) in diethyl ether (20 mL), a 2.5 M solution of butyllithium (3 mL) was added slowly. After stirring for 30 min at room temp., the red solution was cooled to −30 °C and 2,5-bis[chlorobis(diisopropylamino)boryl]thiophene (**9**) (1.23 g, 3.3 mmol) was added slowly. The solution was warmed to 20 °C over 14 h, LiCl was filtered off, and the solvent was evaporated under vacuum to give a residue, which was extracted with pentane. Evaporation of the solvent gave yellow **13**, m.p. 178 °C (decomp.), yield: 1.22 g (2.0 mmol, 61%). ^{1}H NMR ($CDCl_3$, 200.1 MHz): δ = 1.26 [d, $^3J_{H,H}$ = 7 Hz, 24 H, $CH(CH_3)_2$], 1.70 (d, $^3J_{H,H}$ = 7 Hz, 6 H, $CHCH_3$), 4.09 [sept, $^3J_{H,H}$ = 7 Hz, 4 H, $CH(CH_3)_2$], 4.53 (q, $^3J_{H,H}$ = 7 Hz, 2 H, $CHCH_3$), 6.64−6.90 (m, 6 H, H_{ar}), 7.08 (m, 2 H, H_{ar}) ppm. ^{11}B NMR ($CDCl_3$, 64.2 MHz): δ = 36.5 ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 14.3 ($CHCH_3$), 23.3, 23.7 [$CH(CH_3)_2$], 36.6 [$CH(CH_3)_2$], 47.2 ($CHCH_3$), 123.2, 124.0, 124.3, 124.5, 129.1, 131.2 (C_{ar}), 149 (br, CB) ppm. EI-MS: *m*/*z* (%) = 606 (15) $[M]^+$, 591 (10) $[M - CH_3]^+$, 507 (20) $[M - NiPr_2]^+$.

14: The compound was prepared analogously to **13**, from **2** (0.17 g, 0.4 mmol), *n*-butyllithium (0.4 mL) and 2,5-bis[chloro(2,2′,6,6′-tetramethylpiperidyl)boryl]thiophene (**10**) (0.19 g, 0.42 mmol). Yield: 0.19 g (0.3 mmol, 62%) yellow **14**, m.p. 185 °C (decomp.). ^{1}H NMR ($CDCl_3$, 200.1 MHz): δ = 1.29 [s, 24 H, $C(CH_3)_2$], 1.62 (d, 6 H, $CHCH_3$), 1.72−1.91 (m, 12 H, CH_2), 4.54 (q, 2 H, $CHCH_3$), 6.67 (s, 2 H, CH_{thio}), 6.89−7.01 (m, 4 H, CH_{thio}), 7.16−7.27 (m, 2 H, CH_{thio}) ppm. ^{11}B NMR ($CDCl_3$, 64.2 MHz): δ = 40 (br) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 14.4 [$CH(CH_3)$], 30.0 [$C(CH_3)_2$], 32.2 (CH_2), 36.6 (CH_2), 46.6 [$CH(CH_3)$], 122.9; 123.8; 126.7 (C_{ar}), 148.4 (br, CB) ppm. EI-MS: *m*/*z* (%) = 684 (20) $[M - H_2]^+$, 604 (10) $[M -$ thiophene$]^+$.

15: The compound was prepared analogously to **13**, from **2** (0.30 g, 0.1 mmol), *n*-butyllithium (0.9 mL) and 2,5-bis[chlorobis(diisopropylamino)boryl]furan (**11**) (0.33 g, 1.0 mmol). Yield: 0.24 g (0.4 mmol, 40%) of yellow **15**, m.p. 187 °C (decomp.). ^{1}H NMR ($CDCl_3$, 200.1 MHz): δ = 1.27 [d, 24 H, $^3J_{H,H}$ = 5.0 Hz, $CH(CH_3)_2$], 1.49 [d, 6 H, $^3J_{H,H}$ = 4.8 Hz, $CH(CH_3)_2$], 4.01 [sept, 4 H, $^3J_{H,H}$ = 5.0 Hz, $CH(CH_3)_2$], 4.56 [q, 2 H, $^3J_{H,H}$ = 4.8 Hz, $CH(CH_3)_2$], 6.68(m, 2 H, H_{ar}), 6.87−6.93 (m, 3 H, H_{ar}), 7.14−7.23 (m, 3 H, H_{ar}) ppm. ^{11}B NMR ($CDCl_3$, 64.2 MHz): δ = 39.0 ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 14.4 ($CHCH_3$), 23.6, 24.2 [$CH(CH_3)_2$], 36.5 [$CH(CH_3)_2$], 47.0 ($CHCH_3$), 123.3; 123.8; 123.9; 124.3; 125.4(C_{ar}), 150 (br, CB) ppm. EI-MS: *m*/*z* (%) = 590 (5) $[M]^+$, 490 (12) $[M - NiPr_2]^+$.

16: The compound was prepared analogously to **13**, from **2** (0.55 g, 1.8 mmol), *n*-butyllithium (1.6 mL) and 2,5-bis[chlorobis(diisopropylamino)boryl]-*N*-methylpyrrole (**12**) (0.67 g, 1.8 mmol). Yield: 0.51 g (0.85 mmol, 47%) of yellow **16**, m.p. 190 °C (decomp.). ^{1}H NMR ($CDCl_3$, 200.1 MHz): δ = 1.35 [d, 24 H, $^3J_{H,H}$ = 5.0 Hz, $CH(CH_3)_2$], 1.73 [d, 6 H, $^3J_{H,H}$ = 4.8 Hz, $CH(CH_3)_2$], 3.27 (s, 3 H, NCH_3), 3.75 [sept, 4 H, $^3J_{H,H}$ = 5.0 Hz, $CH(CH_3)_2$], 4.54 [q, 2 H, $^3J_{H,H}$ = 4.8 Hz, $CH(CH_3)_2$], 6.21 (m, 2 H, H_{py}), 6.63−6.68 (m, 3 H, H_{thio}), 6.83−7.11 (m, 3 H, H_{thio}) ppm. ^{11}B NMR ($CDCl_3$, 64.2 MHz): δ = 43.9 ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 14.1 ($CHCH_3$), 23.0; 25.3 [$CH(CH_3)_2$], 36.2 [$CH(CH_3)_2$], 47.2 ($CHCH_3$), 50.7 (NCH_3), 107.1; 114.1 ($C_{ar,py}$), 122.9; 124.1; 124.8 ($C_{ar,thio}$), 148 (br, CB) ppm. CI-MS: *m*/*z* (%) = 661 (20) $[M + H + C_4H_8]^+$, 604 (45) $[M + H]^+$, 581 (8) $[M + H - Me]^+$, 524 (15) [M + H − *N*-methylpyrrole].

Crystal Structure Determination of 5: Intensity data were collected with a Bruker AXS SMART 1000 area detector (Mo-K_α radiation, λ = 0.71073, ω-scans, *T* = −83 °C). All calculations were performed using SHELXLT 5.1.[21] Non-hydrogen atoms were refined with anisotropic displacement factors. Hydrogen atoms were located in a difference Fourier synthesis and refined with isotropic displacement factors. Crystal data and details of the structure determination are given in Table 1. CCDC-175313 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **5**

Empirical formula	$C_{34}H_{48}B_2Cl_4N_2S_4$
Formula mass	776.40
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell	
a [Å]	10.438(2)
b [Å]	10.865(2)
c [Å]	10.999(2)
α [°]	72.911(3)
β [°]	65.324(2)
γ [°]	64.731(3)
V [Å^3]	1014.8(2)
Z	1
Calcd. density [g/cm^3]	1.27
Adsorption coeff. [mm^{-1}]	0.524
F(000)	408
Crystal size [mm]	0.54 × 0.28 × 0.17
Θ_{max} [°]	30
Index ranges	−13/+15, −15/+15, 0/+16
Number of reflections unique	6767
Observed [$I > 2\sigma(I)$]	5628
Parameters	313
Final *R* indices	
R1 [$I > 2\sigma(I)$]	0.0361
*wR*2	0.1025
Max. diff. peak/hole [e/Å^3]	+0.755/−0.573

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