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1-Heteroaromatic-Substituted Tetraphenylboroles: π–π Interactions Between Aromatic and Antiaromatic Rings Through a B–C Bond

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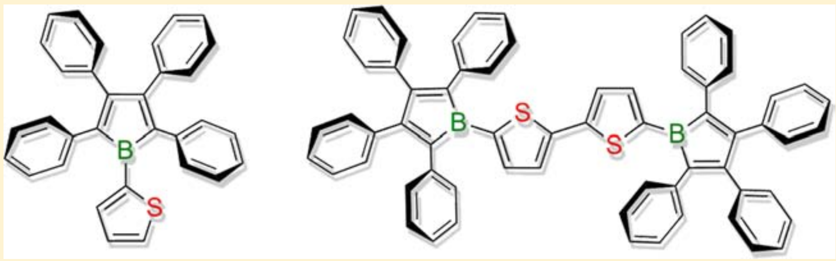
Ⓢ *Supporting Information*



ABSTRACT: A series of 2,3,4,5-tetraphenylboroles substituted with different aromatic heterocycles (thiophene, furan, pyrrole, and dithiophene) in the 1-position were synthesized and characterized by means of NMR, elemental analysis, and X-ray crystallography. In contrast to known 2,3,4,5-tetraphenylboroles, X-ray diffraction revealed a nearly coplanar arrangement of the aromatic heterocycles and the antiaromatic borole scaffold as a result of π-conjugation, which could be substantiated by DFT calculations. Furthermore, the 2,2′-dithiophene-bridged bisborole (**14**) exhibits a large bathochromic shift in the absorption spectrum, demonstrating the exceptional Lewis acidity of the nonannulated borolyl moiety.

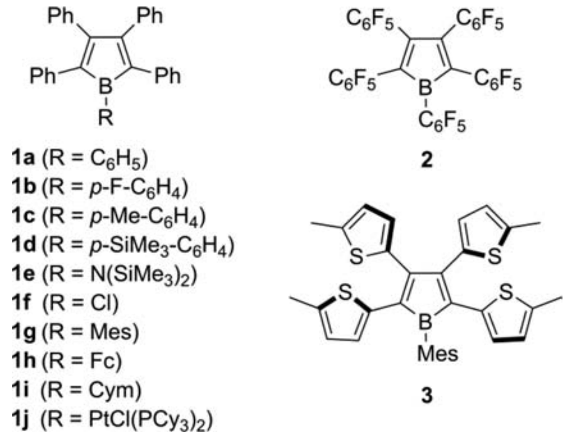
■ INTRODUCTION

Conjugated organic systems have been established as an important class of materials because of their interesting applications in a range of technological areas.[1] In particular, dimesitylboryl-substituted heterocyclic compounds reported by Marder, Lequan, and Shirota demonstrated the versatile properties of boron-modified π-conjugated systems, such as strong photoluminescence, electroluminescence, and nonlinear optical qualities.[2] With its empty p_z orbital, the three-coordinated boron atom is able to interact with organic π-systems leading to planar conjugated frameworks.[3,4] For instance, Jäkle and co-workers reported on diborylated 2,2′-dithiophenes with different aryl substituents on boron featuring a planarized geometry between the p_z orbital of boron and the organic spacer, enabling these compounds to display interesting electron transfer phenomena.[5] Investigations by Weber and co-workers on the synthesis and characterization of 1,3,2-diazaborolyl-functionalized thiophenes and dithiophenes revealed desirable electrochemical and optical properties for functional materials.[6]

Boroles are unsaturated, extremely electron-deficient, pentacyclic molecules with four π-electrons. Due to their photophysical characteristics and isoelectronic relationship to the cyclopentadienyl cation, boroles are of fundamental interest. Up to date, several differently substituted, nonannulated borole derivatives have been isolated and characterized by X-ray crystallography.[7] The substitution pattern of the C_4R_4 backbone is mainly limited to phenyl (**1a–i**),[8] but examples with perfluorophenyl (**2**)[9] or thienyl groups (**3**) are known.[10] In contrast, the substituent at the boron atom has been varied over a much wider range, including phenyl derivatives (**1a–d**, **1g**), halogens (**1f**), ferrocenyl (**1h**), cymantrenyl (**1i**), or platinum groups (**1j**) (Chart 1).

The metallocene-substituted boroles (**1h**, **1i**) display a boron–metal through-space interaction, which induces the π-

Chart 1. Several Nonannulated Boroles[a]



[a]Mes = 2,4,6-trimethylphenyl; Fc = ferrocenyl; Cym = cymantrenyl; Cy = cyclohexyl.

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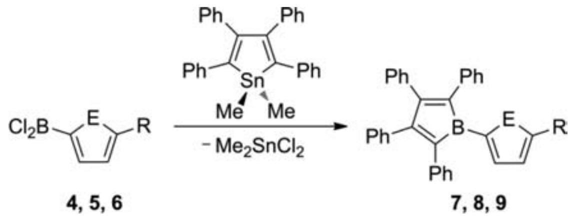
systems of the cyclopentadienyl and borole ring to lie in the same plane. In contrast, the metal-free boroles share as a common feature a propeller-like arrangement of the aryl substituents around the BC_4 scaffold. The phenyl substituent on boron in pentaphenylborole (**1a**) features a torsion angle of −32.9(2)°, thus not allowing an effective π-stabilization of the boron atom. Some degree of π-conjugation was suggested in tetrathienylborole (**3**), in which the thienyl groups in 2 and 5 position showed smaller dihedral angles (10.7° and 38.2°). However, direct conjugation between a nonannulated borolyl boron atom and an organic π-system has not been observed so far.

Given our interest in borole chemistry, we attempted to combine the highly Lewis acidic borolyl group (BC_4Ph_4) with heteroaromatic π-conjugated systems. Herein, we disclose the syntheses of the first 1-heteroaromatic-substituted 2,3,4,5-tetraphenylboroles (heterocycles: **7** = thiophene, **8** = 5-trimethylsilylthiophene, **9** = 5-methylfuran, **11** = *N*-methylpyrrole, **14** = 2,2′-dithiophene) and provide a rationale for the interactions between the two different types of five-membered rings.

■ RESULTS AND DISCUSSION

Two different routes to prepare 1-heteroaromatic-substituted boroles can be envisaged. The possible salt-elimination reaction of 1-chloroborole (**1f**) with the respective lithiated heterocycles was not followed, as the preparation and handling of **1f** is rather cumbersome. Instead, we used the established tin−boron exchange reaction to synthesize the target compounds. The boron dihalide precursors **4**, **5**, and **6** have been prepared via a silicon−boron exchange reaction by treating the corresponding trimethylsilyl-substituted compounds with neat BCl_3.[11] Hence, compounds **7**, **8**, and **9** were successfully obtained by reaction with 1,1-dimethyl-2,3,4,5-tetraphenylstannole and the respective boron dihalides (Scheme 1).

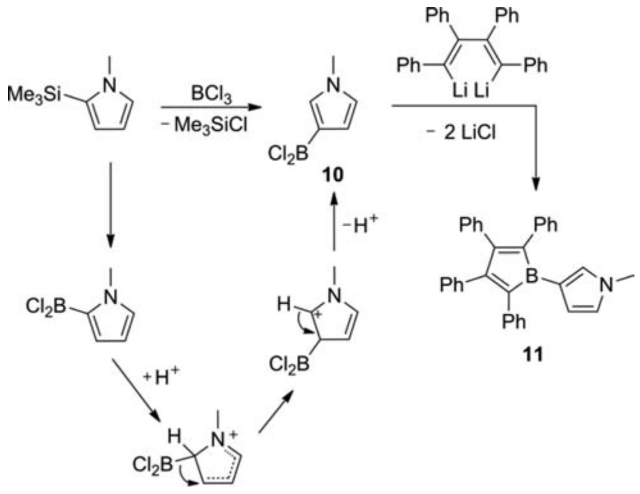
Scheme 1. Synthesis of Various 1-Heteroaromatic-Substituted 2,3,4,5-Tetraphenylboroles (4, 7 (E = S; R = H); 5, 8 (E = S; R = $SiMe_3$); 6, 9 (E = O; R = Me))



After workup and recrystallization from toluene, **7**, **8**, and **9** were isolated as air- and moisture-sensitive deep purple solids in moderate to good yields (**7**: 70%, **8**: 77%, and **9**: 39%). The identity of **7**, **8**, and **9** was confirmed by means of NMR spectroscopy and elemental analysis. The ^{11}B NMR resonances of **7** (58.2 ppm), **8** (58.1 ppm), and **9** (52.3 ppm) are, compared to the known pentaphenylborole (**1a**) (65.4 ppm), shifted to lower frequency, due to the higher π-donor strength of the heterocycles.[12]

Crystallization of **7** and **8** from CH_2Cl_2/hexane solutions yielded dark purple crystals that were suitable for X-ray analysis. In compound **7** (monoclinic, $P2_1/c$), two independet molecules were found in the unit cell, and the thiophene rings were disordered over two positions (occupancies: 85:15; 79:21). The unit cell of **8** (monoclinic, $P2_1/c$) contains two molecules and reveals no disorder in the thiophene unit due to the $SiMe_3$ substituent. In comparison to 1-aryl-2,3,4,5-tetraphenylboroles (**1a−d**), the most striking feature of the thiophene-functionalized boroles **7** and **8** is the nearly coplanar alignment of the two five-membered rings. Although **7** shows some disorder, the interplanar torsion angles are found in a range between 6.4(2)° and 13.0(2)°. In **8** we found a similar coplanar arrangement of the borolyl moiety and the 5-trimethylsilylthiophene ring with even smaller interplanar torsion angles (5.7(2)°, 10.1(2)°). This indicates that some degree of π-conjugation and electronic interaction is operative in these systems. With the exception of tetrathienyl-substituted borole (**3**), which features a π-interaction between two thienyl moieties and the borole scaffold,[10] all known nonannulated boroles display a propeller-like arrangement throughout all substituents.[7] The B1−C5 bond length of **8** (av. 1.527 Å) lies in the same range compared to other 1-aryl-2,3,4,5-tetraphenylboroles (**1c** = 1.537(7) Å, **1d** = 1.513(8) Å) but is shorter than the B1−C5 bond in **1g** (1.560(2) Å) or **3** (1.552(6) Å) with a sterically demanding mesityl group.[8d,m,10] Compound **9** was crystallized from a saturated benzene solution as dark purple needles. Similar to the solid state structures of **7** and **8**, the borolyl substituent and the aromatic furan ring in **9** are coplanar in the solid state, suggesting π-bonding interactions. The interplanar torsion angle of 17.4(2)° is slightly larger compared to the thiophene derivatives **7** and **8**. The B1−C5 bond length of **9** (1.515(4) Å) is comparable to those of **8** (Table 1).

Scheme 2. Synthesis of 11 via Salt Elimination and a Proposed Boryl Migration Mechanism



To extend this series of 2-borolyl heterocycles, we attempted the synthesis of 1-pyrrolyl-2,3,4,5-tetraphenylborole. However, the required dichloro-*N*-methylpyrrol-2-ylborane could not be isolated according to the literature procedure.[11] Instead, we found the selective formation of dichloro-*N*-methylpyrrol-3-ylborane (**10**) in good yields. Comparable migrations are known for 2-(arylsulfinyl)pyrroles and 2-(acyl)pyrroles, which are reported to be acid-induced transpositions.[13] Unlike the thiophene- and furan-substituted boroles, no reaction was observed by treatment of dihaloborane (**10**) with 1 equiv of 1,1-dimethyl-2,3,4,5-tetraphenylstannole even at elevated temperatures (50 °C). Accordingly, the synthesis could only be accomplished via a salt-elimination reaction of **10** with 1,4-dilithio-2,3,4,5-tetraphenylbuta-1,3-diene (Scheme 2). As ex-

Table 1. ^{11}B NMR Chemical Shifts δ [ppm], Bond Lengths [Å], and Interplanar Torsion Angles [°] of **7**, **8**, **9**, and **11**

	7^{b}	**8**^{b}	**9**	**11**
^{11}B [ppm]^{a}	58.2	58.1	52.3	57.5
B1−C1	1.576(3)/1.574(3)	1.577(3)/1.589(3)	1.587(4)	1.579(4)
B1−C4	1.576(3)/1.577(3)	1.587(3)/1.589(3)	1.574(4)	1.580(4)
B1−C5	__^{c}	1.528(3)/1.525(3)	1.515(4)	1.509(6)
C1═C2	1.352(3)/1.352(3)	1.353(3)/1.353(3)	1.358(4)	1.357(4)
C2−C3	1.535(3)/1.529(3)	1.532(3)/1.528(3)	1.521(4)	1.516(5)
C3═C4	1.361(3)/1.360(3)	1.347(3)/1.352(3)	1.352(4)	1.357(4)
borole/heterocycle [°]	__^{c}	10.1(2)/5.7(2)	17.4(2)	6.7(4)

^{a}Referenced against external [$Et_2O{\cdot}BF_3$]. ^{b}Two independent molecules in the unit cell. ^{c}Not discussed, due to disorder.

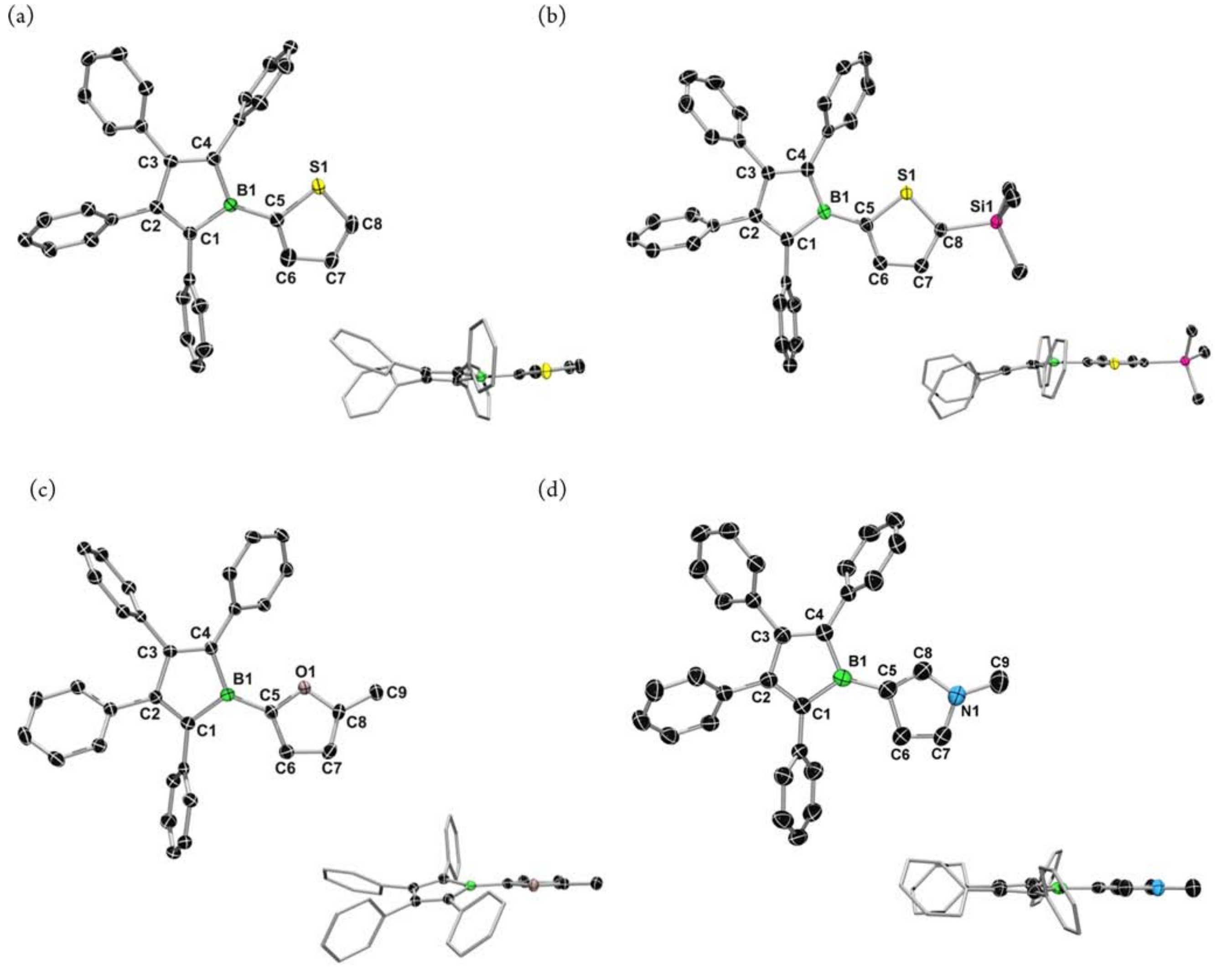


Figure 1. Molecular structures and side views of (a) **7**, (b) **8**, (c) **9**, and (d) **11**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at 50% probability.

pected, the ^{11}B NMR resonance of **11**, detected at 57.2 ppm, is comparable to those observed for the thiophene derivatives **7** and **8**.

Single crystals of **11** could be obtained from a saturated toluene solution as dark red crystals. Despite the fact that the borolyl group resides in the 3-position, the solid structure features a similar coplanar arrangement with torsion angles of 6.77(4)°. The B1−C5 distance of **11** (1.509(6) Å) is slightly shortened compared to **8** and **9**, which arises from the better π-donor ability of the nitrogen atom.[12] It is noteworthy that **7**, **8**, **9**, and **11** exhibit an intermolecular interaction between the boron atom of the borole and a phenyl group of a neighboring molecule as previously reported for related 1-aryl-2,3,4,5-tetraphenylboroles.[8b,d] Moreover, the enhanced π-conjugation in **7**, **8**, **9**, and **11** (Figure 1) does not affect the degree of bond alternation in the borolyl moiety (Table 1).

To finally isolate *N*-methylpyrrole with a borolyl group in the 2-position, we used 1-chloro-2,3,4,5-tetraphenylborole (**1f**) as a borole source since it is known that lithiation of *N*-methylpyrrole with one equivalent butyllithium in the presence

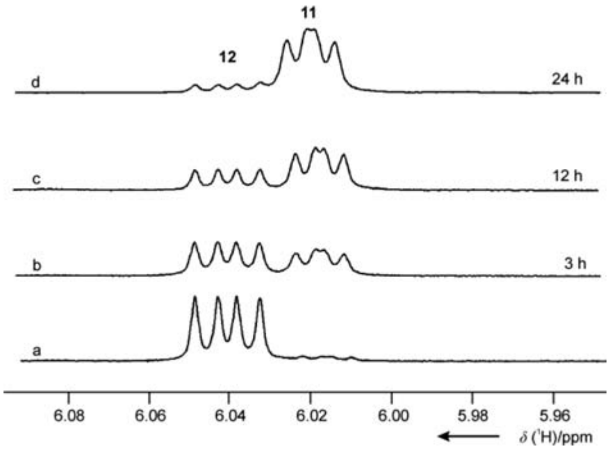
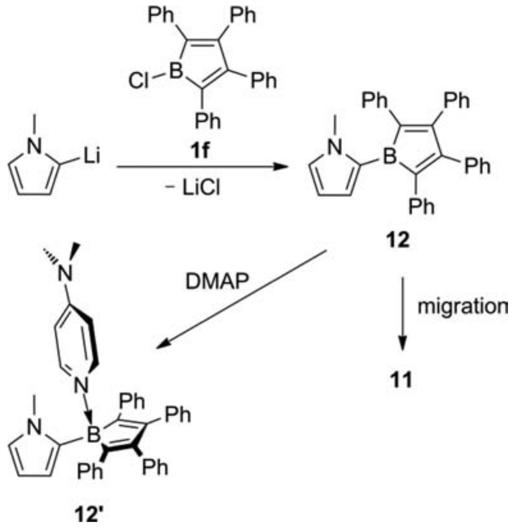


Figure 2. Migration of the borolyl moiety as followed by ^{1}H NMR spectroscopy for one characteristic doublet of doublets (a: reaction start; b: after 3 h; c: after 12 h; d: after 24 h).

Scheme 3. Synthesis of 12 by Direct Functionalization of the Chloroborole and Inhibition of the Migration Process by DMAP



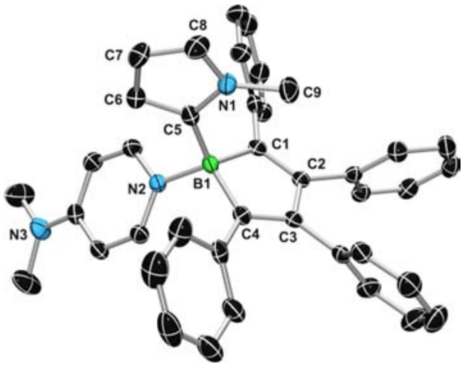


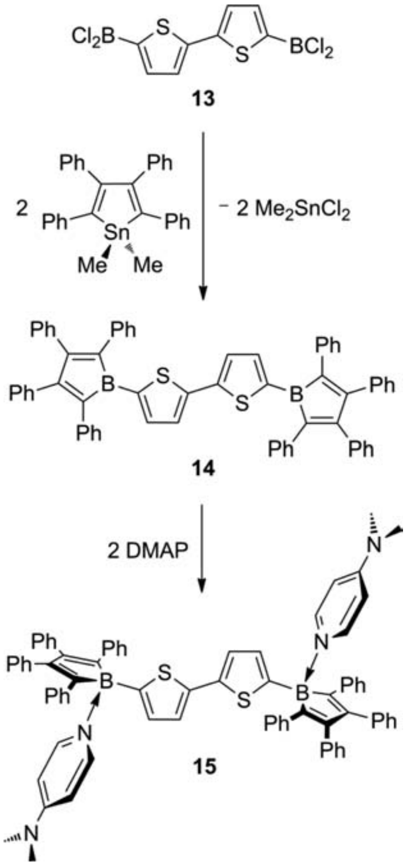
Figure 3. Molecular structure of **12′** in the solid state with hydrogen atoms and solvent molecules omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond distances [Å] and angles [°]: B1−C1 1.647(2), B1−C4 1.635(2), C1−C2 1.349(2), C2−C3 1.502(2), C3−C4 1.360(2), B1−N2 1.610(2), B1−C5 1.610(2), C5−C6 1.387(2), C6−C7 1.409(2), C7−C8 1.364(2), C8−N1 1.370(2), N1−C5 1.385(2), N1−C9 1.449(2); C1−B1−C4 99.3(1), C1−B1−C5 116.2(1), C1−B1−N2 108.3(1).

of tetramethylethylenediamine (TMEDA) occurs selectively in the 2-position.[14] Immediately after addition of the lithiated *N*-methylpyrrole to **1f** in benzene, two doublets of doublets at 6.04 (^3J = 4.00 Hz, ^3J = 2.24 Hz) and 6.78 ppm (^3J = 4.00 Hz, ^4J = 1.44 Hz) and one multiplet at 6.43 ppm were found in the ^{1}H NMR spectrum, for the three protons of the pyrrole ring. A comparison with literature data revealed that only pyrroles substituted in the 2-position show coupling constants between 3.8 and 4.0 Hz, suggesting the formation of **12.**[15] Surprisingly, we could observe a similar rearrangement reaction as found for the dihaloborane **10**. The migration of the borolyl moiety from the 2- to 3-position is slower compared to the migration of **10** and was followed by means of ^{1}H NMR spectroscopy. The ratio between **12** and **11** was determined to be 1:10 after one day in benzene at room temperature (Figure 2).

To prove the initial formation of **12**, we added the electron-rich base 4-dimethylaminopyridine (DMAP) to block the empty p_z-orbital of the boron atom and consequently inhibit the migration process (Scheme 3). After addition, the color of the reaction mixture turned from deep red to pale yellow, and the ^{11}B NMR resonance shifted to lower frequency (0.1 ppm).

Single crystals of **12′** were obtained from a saturated toluene solution. The solid state structure clearly confirms the initial formation of **12** since the boron atom (B1) is bonded to the carbon atom in the 2-position (C5) of the *N*-methylpyrrole (Figure 3). The borolyl moiety is planar, and the bond lengths within the C_4Ph_4 backbone correspond to those of an isolated diene system, such as *cis*,*cis*-1,2,3,4-tetraphenylbuta-1,3-diene.[16] The environment of the boron center shows a distorted

Scheme 4. Synthesis of 14 via Tin−Boron Exchange and Formation of the DMAP Adduct 15



tetrahedral geometry with a shorter B1−N2 distance (1.610(2) Å) as compared to the known Lewis acid−base adducts of boroles due to the electron-rich nature of DMAP.[8l,n]

To extend the concept of borolyl-substituted π-conjugated systems, we performed the synthesis of bisborole **14** with dithiophene as a spacer between two borolyl moieties. 5,5′-Bis(dichloroboryl)-2,2′-dithiophene (**13**) was prepared by reaction of 5,5′-bis(trimethylsilyl)-2,2′-dithiophene with an excess of BCl_3 via the silicon−boron exchange route. In a similar manner as for the boroles **7**, **8**, and **9**, compound **14** was obtained via a tin−boron exchange reaction and isolated in 75% yield as an orange-brown solid. The ^{11}B NMR resonance was observed as a broad signal (56.5 ppm) in a region of slightly higher frequency in comparison to 1-(thiophen-2-yl)-2,3,4,5-tetraphenylborole (**7**). Structural characterization was achieved as its DMAP adduct (Scheme 4). To this end, 2 equiv of DMAP was added to a solution of **14** in CH_2Cl_2. The color of the solution turned from orange to yellow, and the ^{11}B NMR resonance was found at 0.3 ppm, characteristic of four-coordinate boron. Single crystals of **15** were obtained from a saturated CH_2Cl_2/hexane solution. X-ray diffraction confirmed a distorted tetrahedral geometry at the boron center and the overall connectivity of the bisborole (Figure 4).

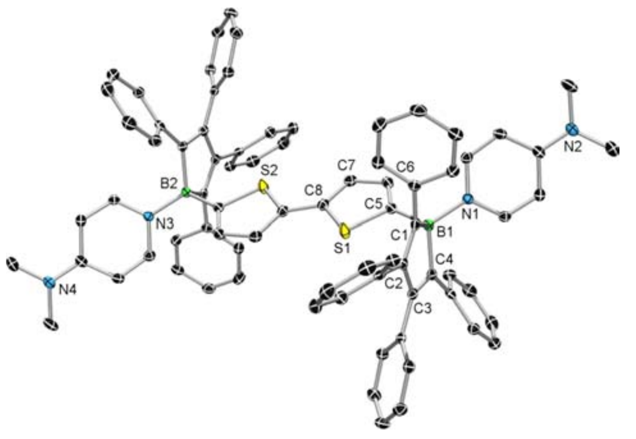


Figure 4. Molecular structure of **15** in the solid state with hydrogen atoms and solvent molecules omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond distances [Å]: B1−C1 1.625(3), B1−C4 1.615(4), C1−C2 1.358(3), C2−C3 1.504(3), C3−C4 1.354(3), B1−N2 1.588(3), B1−C5 1.631(4), C5−C6 1.370(4), C6−C7 1.424(4), C7−C8 1.363(4), C8−S1 1.732(3), C5−S1 1.742(2).

■ ELECTROCHEMICAL STUDIES

Cyclic voltammetry was used to investigate the reduction behavior of the different boroles **7**, **8**, **9**, and **14**. Similar to pentaphenylborole (**1a**), **7**, **8**, and **9** show a quasi-reversible one-electron reduction and a second irreversible one-electron reduction event in CH_2Cl_2 with $[nBu_4N]PF_6$ as the supporting electrolyte. As shown in our previous work, the two reduction events can be assigned to the formation of a paramagnetic 5π-electron radical anion and an aromatic 6π-electron dianion.[8l] As a representive example of the newly synthesized boroles, Figure 5 shows the cyclic voltammogramm of **7** with the quasi-reversible reduction event at $E^0_{1/2} = -1.63$ V, indicating the formation of a paramagnetic monoanion. The peak potential is in the same region as that found for 1-mesityl-2,3,4,5-tetrakis(2-methylthienyl)borole (**3**) ($E^0_{1/2} = -1.57$ V) or 1-mesityl-2,3,4,5-tetraphenylborole (**1g**) ($E^0_{1/2} = -1.69$ V) and anodically shifted compared to 1-ferrocenyl-2,3,4,5-tetraphenylborole (**1h**) ($E^0_{1/2} = -1.96$ V)[8h,l,10] The second irreversible reduction process is centered at −2.32 V and corresponds to the formation of the dianion.

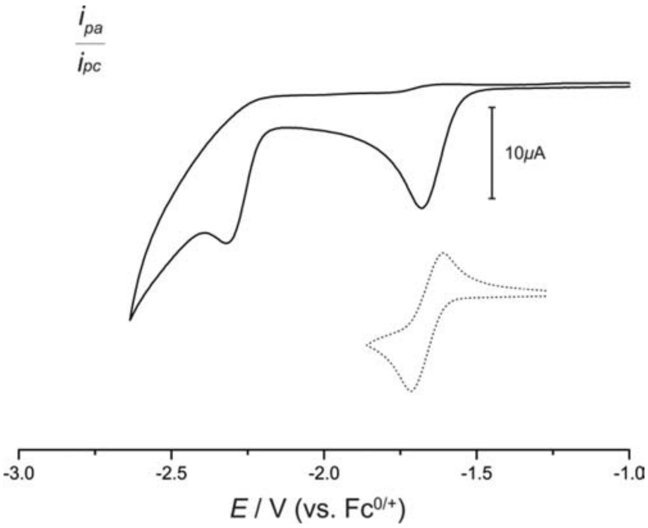


Figure 5. Cyclic voltammogram of **7** at room temperature in CH_2Cl_2. Scan rate 200 mVs^{-1}, Pt/$[nBu_4N][PF_6]$/Ag, quasi-reversible reduction wave upon one-electron reduction (dashed lines).

Bisborole **14** is able to accept up to four electrons. Therefore, one would expect four reduction events for a fully conjugated system. The cyclic voltammogram of **14**, however, shows only two broad irreversible reduction waves in THF ($E_{pa} = -2.35$ V, $E_{pa} = -2.97$ V) which could not be further resolved using square wave voltammetry. Due to the highly Lewis acidic boron atoms, THF readily forms a Lewis acid−base adduct with **14**, resulting in a significant cathodic shift of the redox potentials compared to the measurements in noncoordinating solvents (for details, see Supporting Information).

■ UV−VIS SPECTROSCOPY

The π-electron donation from the heterocycles to the boron atom is also evident in the electronic absorption spectra (Figure 6). The absorption maxima of the strongly colored boroles **7**

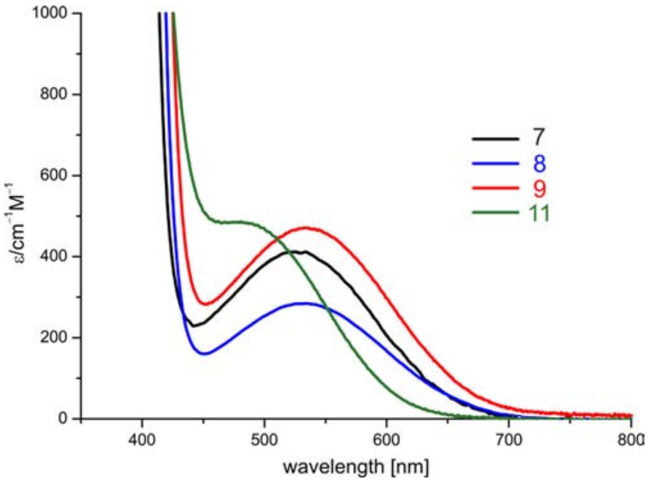


Figure 6. UV−visible spectra of compounds **7** (black), **8** (red), **9** (blue), and **11** (green) in CH_2Cl_2 at concentrations of 1 mmol L^{-1}.

(λ_{max} = 527 nm; ε = 384 L·mol^{-1}·cm^{-1}), **8** (λ_{max} = 522 nm; ε = 292 L·mol^{-1}·cm^{-1}), and **9** (λ_{max} = 530 nm; ε = 462 L·mol^{-1}·cm^{-1}) are blue-shifted compared to **1a** (λ_{max} = 567 nm; ε = 361 L·mol^{-1}·cm^{-1}). The lowest energy transition band is in the same region as the cationic 1-metalloborole (**1j**) (λ_{max} = 524 nm; ε = 813 L·mol^{-1}·cm^{-1}), previously prepared in our group.[8i] The considerable hypsochromic shift for **11** (λ_{max} = 470 nm; ε = 507 L·mol^{-1}·cm^{-1}) supports again the higher π-donor strength of the pyrrolyl substituent.[12] Calculated excitation energies for **7**, **8**, **9**, and **11** correlate well with the experimental findings and display the same hypsochromic shift for **11** (for details, see Supporting Information).

The bisborolyl-substituted bithiophene **14** exhibits an absorption band at 456 nm (ε = 53862 L·mol^{-1}·cm^{-1}) with a red-shifted shoulder (Figure 7). Interestingly, these data correlate well with the diborylated bithiophenes **16**, **17**, and **18** reported by Jäkle et al., who observed that the absorption bands of **16** (λ_{max} = 387 nm; ε = 23 890 L·mol^{-1}·cm^{-1}), **17** (λ_{max} = 396 nm; ε = 48 290 L·mol^{-1}·cm^{-1}), and **18** (λ_{max} = 413 nm; ε = 31 400 L·mol^{-1}·cm^{-1}) experience a bathochromic shift with increased Lewis acidity of the boryl substituents (Chart 2).[5b]

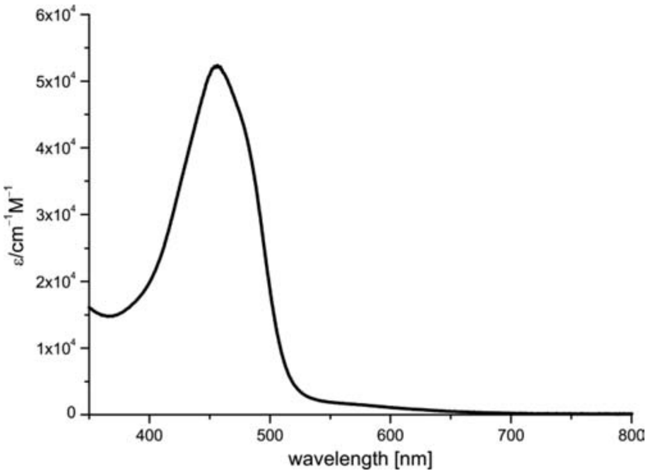
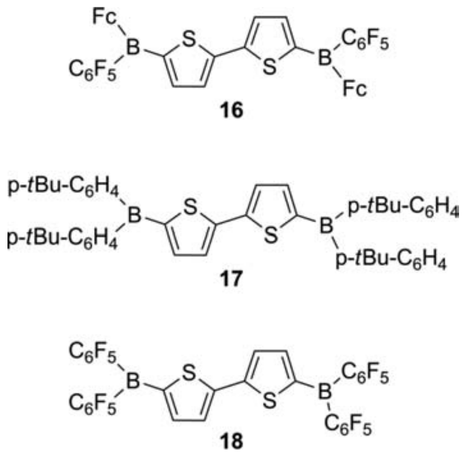


Figure 7. UV–visible spectra of **14** in CH_2Cl_2 at concentrations of 0.1 mmol·L^{-1}.

Chart 2. Various Diborylated Bithiophenes Reported by Jäkle et al



14 is distinctly red-shifted compared to **18**, which suggests a more pronounced Lewis acidity of the borolyl moiety in comparison to the $B(C_6F_5)_2$ group. Jäkle et al. performed DFT calculations and showed that the excitations for **17** and **18** arise from the HOMO → LUMO transitions. DFT calculations for **14** display that the HOMO is centered at the borole, and therefore the HOMO → LUMO energy separation gives rise to a very weak absorption at 509 nm. The much more pronounced calculated absorption at 507 nm is a consequence of the HOMO-2 → LUMO transition in **14**. This correlates well with the findings of Jäkle since the molecular orbital of the HOMO-2 in **14** resembles the HOMO of **17** and **18** (for details, see Supporting Information).

THEORY

DFT calculations were performed to gain further insight into a possible π-conjugation between the borolyl moiety and the heterocycles.[17] The calculated orbital plots for compounds **7**, **8**, **9**, and **11** display a certain amount of π-conjugation in the HOMO-2 along the B–C5 bond (Figure 8). For the larger system **14**, we found π-conjugation in the HOMO-4 (for details, see Supporting Information).

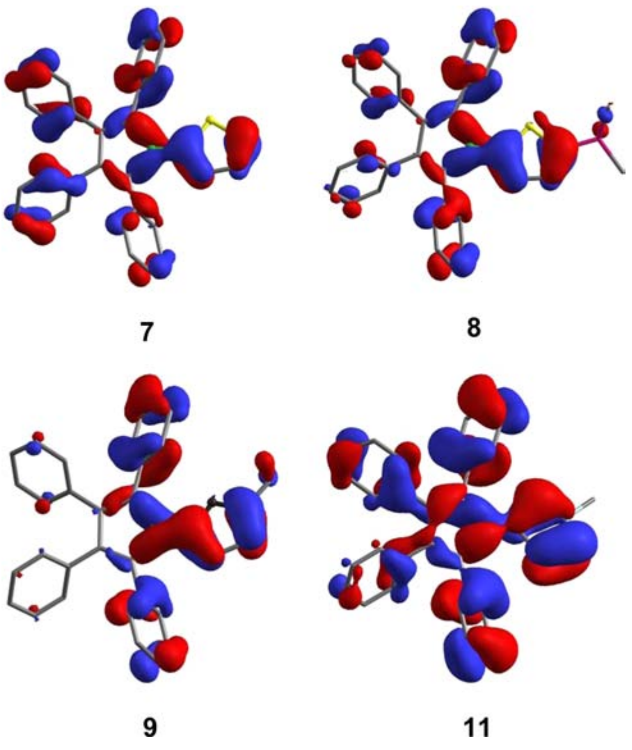
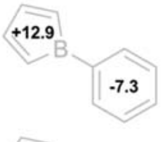
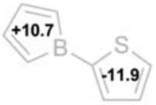
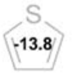
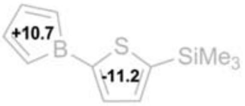
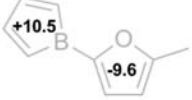
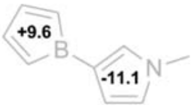
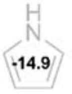


Figure 8. Molecular orbitals (isovalue = 0.03 au) related to π-conjugation found in the studied borole compounds calculated at the PBE0/6-31+G(d,p) level.

To gain a better understanding of the π-conjugation, we carried out energy decomposition analysis (EDA) for model systems of **7′**, **8′**, **9′**, and **11′** compared to a model of **1a′**. For the model compounds we ignored the phenyl substituents at the borolyl moiety, and only the conjugated core has been taken into account. The relative energy values for the π-conjugation percentage ΔE_π in the model systems **7′** (20.7%), **8′** (20.4%), **9′** (22.7%), and **11′** (20.5%) are significantly larger compared to **1a′** (18.2%) (see Supporting Information). In other words, the energy difference regarding the π-conjugation between these compounds relative to **9′**, which shows the highest degree of π-interaction, is 4.8 (**7′**), 5.1 (**8′**), 2.9 (**11′**), and 10.8 (**1a′**) kcal/mol, respectively. These results confirm the experimental findings and show that π-conjugation in 1-heteroaromatic-substituted boroles is much more pronounced compared to aryl-substituted tetraphenylboroles.

In addition, nucleus-independent chemical shift (NICS) calculations were conducted at the PBE0/6-31+g(d,p) level to evaluate the antiaromatic character of the borole ring and the aromatic nature of the heterocycles. The obtained NICS(0) values are listed in Table 2 and compared to literature data for the unsubstituted aromatic compounds.

Table 2. NICS(0) Values at the PBE0/6-31+g(d,p) Level[a]

	NICS values	Literature values[17,18]
(1a)		
(7)		
(8)		
(9)		
(11)		

[a]The phenyl groups around the borole moiety in the chemical drawings are omitted for clarity.

Interestingly, the comparison with literature NICS(0) values clearly displays a π-interaction of the heterocycles with the boron atom, which leads to a mutual compensation of aromaticity and antiaromaticity. While the aromaticity of the heterocycles is significantly reduced compared to literature data, the value for the benzene ring in pentaphenylborole (**1a**) remains unperturbed (C_6H_6: −7.2 ppm).[18,19] A similar behavior can be expected for boryl-substituted derivatives. In the case of borolyl substituents, however, the π-interaction of the aromatic heterocycle with the vacant p_z orbital on boron leads to a decrease in antiaromaticity of the borole ring. We believe that this effect is more pronounced in boroles **7**, **8**, **9**, and **11** than in pentaphenylborole (**1a**) (+12.9 ppm) as a result of the higher π-donating abilities of the heteroaromatic groups.[10,18]

The π-electrons of the dithiophene spacer in bisborole **14** are shared between the two borolyl moieties, which leads to an increased antiaromatic character (NICS(0): 12.1 ppm), in a region typical for pentaphenylborole **1a**.

■ CONCLUSION

In summary, the synthesis and structural characterization of the first 1-heteroaromatic-substituted-2,3,4,5-tetraphenylboroles and a dithiophene-spaced bis-2,3,4,5-tetraphenylborole was carried out. An interesting migration process could be elucidated for the *N*-methylpyrrole derivative. Absorption data for bisborole **14** correlate well with known dithiophene-bridged bisboryl compounds and underlines the high Lewis acidity of the 2,3,4,5-tetraphenylborolyl group. All investigations (i.e., X-ray, UV−vis, and cyclic voltammetry) support that a certain degree of π-conjugation is operative between the aromatic heterocycles and the antiaromatic borole. These findings were corroborated by DFT calculations and demonstrate that the coplanarity in these systems can be explained by an electronic interaction of the heterocycles with the empty p_z orbital of the boron atom. Studies to extend the concept of borolyl-based π-conjugated systems are currently underway.

■ EXPERIMENTAL DETAILS

General Information. All manipulations were performed under an inert atmosphere of dry argon using standard Schlenk techniques or in a glovebox (MBraun). Hexane, THF, and CH_2Cl_2 were dried by distillation over Na/K alloy (hexane, THF) or phosphorus pentoxide (CH_2Cl_2) under argon and stored over activated molecular sieves (4 Å). CD_2Cl_2 was degassed by several freeze−pump−thaw cycles and stored over molecular sieves. (*E,E*)-(1,2,3,4-Tetramethyl-1,3-butadien-1,4-ylidene)-dilithium, 1,1-dimethyl-2,3,4,5-tetraphenyl-stannole,[8a] 2,5-bistrimethylsilyl-thiophene,[14] dichlorothiophene-2-ylborane, and dichloro-5-methylfurane-2-ylborane[11] were prepared according to known methods. The NMR spectra were recorded on a Bruker AV 500 (^{1}H: 500.1 MHz, ^{13}C: 125.8 MHz, ^{11}B: 160.5 MHz, ^{29}Si: 99.4 MHz) FT-NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS via the residual protons of the solvent (^{1}H) or the solvent itself (^{13}C). ^{11}B{^{1}H} NMR spectra were referenced to [$BF_3 \cdot OEt_2$]. Microanalyses for C, H, and N were performed on a Leco CHNS-932 Elemental Analyzer. UV−vis spectra were measured on a JASCO V-660 UV−vis spectrometer.

Synthesis of 1-(Thien-2-yl)-2,3,4,5-tetraphenylborole (7). A solution of $Me_2SnC_4Ph_4$ (3.06 g, 6.06 mmol) in 30 mL of dichloromethane was treated dropwise with 0.60 mL of dichlorothiophene-2-ylborane (1.00 g, 6.07 mmol) at −40 °C. The reaction mixture was stirred for 3 h and subsequently allowed to warm to rt, resulting in a color change from yellow to red. All volatiles were removed in vacuo, and the side product Me_2SnCl_2 was removed quantitatively by sublimation at rt and 10^{-6} mbar within 5 h. The red residue was recrystallized from toluene/hexane to yield **7** (1.90 g, 4.22 mmol, 70%) as a purple red solid. ^{1}H NMR (500.1 MHz, CD_2Cl_2, 297 K): δ = 6.85 (m, 4H, *Ph*), 7.00−7.10 (m, 6H, *Ph*), 7.11 (m, 1H, *H*-thienyl), 7.17−7.27 (m, 10H, *Ph*), 7.44 (m, 1H, *H*-thienyl), 7.90 (m, 1H, *H*-thienyl). ^{13}C NMR (125.8 MHz, CD_2Cl_2, 297 K): δ = 126.13, 127.37, 127.43, 128.01 (*C*H), 129.12 (*C*-thienyl), 129.72, 130.19 (*C*H), 141.37, 145.43 (*C*-thienyl), 136.91, 140.91, 162.25 (C_q). ^{11}B NMR (160.5 MHz, CD_2Cl_2, 297 K): δ = 58.2 (br). Elemental analysis (%) calcd. for $C_{32}H_{23}BS$: C, 85.33; H, 5.15; S, 7.12. Found: C, 84.40; H, 5.48; S, 7.11.

Synthesis of Dichloro-5-trimethylsilylthien-2-ylborane (5). To a sample of neat BCl_3 (5.00 mL, 6.63 g, 56.6 mmol) was added 2,5-trimethylsilylthiophene (2.30 g, 10.1 mmol) at −50 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. All volatiles were removed in vacuo, and the residue was distilled (1.4 mbar, 65 °C) to give **5** as a colorless liquid (2.08 g, 8.78 mmol, 87%). ^{1}H NMR (500.1 MHz, C_6D_6, 297 K): δ = 0.13 (s, 9H, Si*Me*$_3$), 7.00 (d, $^3J_{H-H}$ = 3.54 Hz, 1H, *H*-thienyl), 7.83 (d, $^3J_{H-H}$ = 3.54 Hz, 1H, *H*-thienyl). ^{13}C NMR (125.8 MHz, C_6D_6, 297 K): δ = −0.59 ($SiMe_3$), 136.18, 143.91 (*C*H-thienyl), 158.64 (C_q). ^{29}Si NMR (99.4 MHz, CD_2Cl_2, 297 K): δ = −5.62. ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 47.8.

Synthesis of 1-(5-Trimethylsilylthien-2-yl)-2,3,4,5-tetraphenylborole (8). A solution of $Me_2SnC_4Ph_4$ (554 mg, 1.10 mmol) in 15 mL of dichloromethane was treated dropwise with a solution of dichloro-5-trimethyl-silylthiophene-2-ylborane (260 mg, 1.10 mmol) in 5 mL of dichloromethane at −40 °C. The reaction mixture was stirred for 3 h and subsequently allowed to warm to rt, resulting in a color change from yellow to red. All volatiles were removed in vacuo, and the side product Me_2SnCl_2 was removed quantitatively by sublimation at rt and 10^{-6} mbar within 5 h. The red residue was recrystallized from a mixture of toluene/hexane to yield **8** as a purple solid (440 mg, 0.84 mmol, 77%). ^{1}H NMR (500.1 MHz, CD_2Cl_2, 297 K): δ = 0.24 (s, 9H, $SiMe_3$), 6.83−6.86 (m, 4H, *Ph*), 6.99−7.08 (m, 6H, *Ph*), 7.14−7.16 (m, 4H, *Ph*), 7.18−7.26 (m, 7H, *Ph* & *H*-thienyl), 7.42 (d, $^3J_{H-H}$ = 3.55 Hz, 1H, *H*-thienyl). ^{13}C NMR (125.8 MHz, CD_2Cl_2, 297 K): δ = −0.32 ($SiMe_3$), 126.04, 127.27, 127.38, 127.89, 129.72, 130.18 (s, CH), 135.49, 145.62 (CH-thienyl), 136.99, 140.85 (C_q), 140.96 (C_q-thienyl), 146.59 (C_q), 159.23 (C_q-thienyl), 162.03 (C_q). ^{29}Si NMR (99.4 MHz, CD_2Cl_2, 297 K): δ = −5.61. ^{11}B NMR (160.5 MHz, CD_2Cl_2, 297 K): δ = 58.6 (br). Elemental analysis (%) calcd for $C_{35}H_{31}BSSi$: C, 80.44; H, 5.98; S, 6.14. Found: C, 80.06; H, 5.94; S, 5.71.

Synthesis of 1-(5-Methylfuran-2-yl)-2,3,4,5-tetraphenylborole (9). A solution of $Me_2SnC_4Ph_4$ (1.00 g, 1.98 mmol) in 15 mL of dichloromethane was treated dropwise with a solution of dichloro-5-methylfurane-2-ylborane (322 mg, 1.98 mmol) in 5 mL of dichloromethane at −60 °C. The reaction mixture was stirred for 16 h and subsequently allowed to warm to rt, resulting in a color change from yellow to red. All volatiles were removed in vacuo, and the side product Me_2SnCl_2 was removed quantitatively by sublimation at rt and 10^{-6} mbar within 5 h. The red residue was recrystallized from toluene at −30 °C to yield **9** as a purple solid (348 mg, 0.78 mmol, 39%). ^{1}H NMR (500.1 MHz, CD_2Cl_2, 297 K): δ = 2.66 (s, 3H, CH_3), 6.11 (dd, ^3J = 3.5 Hz, ^4J = 0.8 Hz, 1H, *H*-furanyl), 6.80−6.82 (m, 4H, *Ph*), 6.91 (dd, ^3J = 3.5 Hz, ^5J = 0.6 Hz, 1H, *H*-furanyl), 7.06−7.08 (m, 6H, *Ph*), 7.15−7.13 (m, 6H, *Ph*), 7.18−7.21 (m, 4H, *Ph*). ^{13}C NMR (125.8 MHz, CD_2Cl_2, 297 K): δ = 14.4 (CH_3), 110.2 (CH-furanyl), 125.7, 127.2, 127.4, 127.6, 129.9, 130.1 (CH), 138.3 (CH-furanyl), 137.2 (C_q), 140.6 (b, C_q), 140.9, 161.9, 164.7 (C_q). ^{11}B NMR (160.5 MHz, CD_2Cl_2, 297 K): δ = 52.3 (br). Elemental analysis (%) calcd for $C_{33}H_{25}BO$: C, 88.40; H, 5.62. Found: C, 88.31; H, 5.60.

Synthesis of 1-(*N*-Methylpyrrol-3-yl)-2,3,4,5-tetraphenylborole (11). A solution of dichloro-*N*-methylpyrrole-3-ylborane (0.20 g, 1.23 mmol) in 3 mL of benzene was treated dropwise with a suspension of (*E*,*E*)-(1,2,3,4-tetramethyl-1,3-butadien-1,4-ylidene)-dilithium (0.50 g, 1.23 mmol) in 10 mL of benzene at 0 °C. The reaction mixture was allowed to warm to rt, changing its color from light brown to dark red, and stirred for 12 h. Lithium chloride was filtered off, and all volatiles were removed in vacuo. The product was recrystallized from toluene, yielding **11** as red crystals (246 mg, 0.55 mmol, 45%). ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 3.50 (s, 3H, CH_3), 6.03 (dd, ^3J = 2.6 Hz, ^4J = 1.6 Hz, 1H, *H*-pyrrolyl), 6.49 (dd, ^3J = 2.6 Hz, ^4J = 1.9 Hz, 1H, *H*-pyrrolyl), 6.83−6.85 (m, 4H, *Ph*), 6.71 (m, 1H, *H*-pyrrolyl), 6.99−7.04 (m, 6H, *Ph*), 7.13−7.17 (m, 6H, *Ph*), 7.20−7.24 (m, 4H, *Ph*). ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = 36.54 (CH3), 118.55 (CH-pyrrolyl), 123.87 (CH-pyrrolyl), 125.51, 126.83, 127.31, 127.72, 129.80, 129.97 (CH), 137.54 (C_q), 139.10 (C_q-pyrrolyl), 141.57, 142.22, 160.11 (C_q). ^{11}B NMR (160.5 MHz, CD_2Cl_2): δ = 57.5 (br). Elemental analysis (%) calcd for $C_{33}H_{26}BN$: C, 88.59; H, 5.86; N, 3.13. Found: C, 88.39; H, 5.91; N, 3.30.

Synthesis of 1-(*N*-Methylpyrrol-2-yl)-2,3,4,5-tetraphenylborole-dimethylaminopyridine (12′). 2-Lithio-*N*-methylpyrrole (10.8 mg, 124 μmol) and 1-chloro-2,3,4,5-tetraphenylborole (50.0 mg, 124 μmol) were dissolved in 2 mL of benzene at rt. After 5 min, DMAP (15.2 mg, 124 μmol) was dissolved in 2 mL of benzene and added slowly, resulting in a color change from red to pale yellow. Lithium chloride was filtered off, and all volatiles were removed in vacuo. The residue was recrystallized from toluene, and **12′** was isolated as pale yellow solid (42 mg, 73.9 μmol, 60%). ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 3.02 (s, 6H, N(CH_3)$_2$), 3.83 (s, 3H, N−CH_3), 5.75 (dd, ^3J = 3.4 Hz, ^4J = 1.7 Hz, 1H, *H*-pyrrolyl), 6.04 (dd, ^3J = 3.4 Hz, ^4J = 2.4 Hz, 1H, *H*-pyrrolyl), 6.37−6.39 (m, 2H, NC_5H_4-4-NMe_2), 6.69−6.71 (m, 4H, *Ph*), 6.76−6.77 (m, 1H, *H*-pyrrolyl), 6.87−7.04 (m, 16H, *Ph*), 8.14 − 8.17 (m, 2H, NC_5H_4-4-NMe_2). ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = 35.23 (*N*-CH_3), 39.62 (N(CH_3)$_2$), 106.25 (NC_5H_4-4-NMe_2), 106.98, 113.98, 123.35 (CH-pyrrolyl), 124.56, 125.58, 127.47, 127.63, 129.23, 130.47 (CH), 145.40 (NC_5H_4-4-NMe_2), 141.13 (C_q), 143.76 (C_q, NC_5H_4-4-NMe_2), 150.66, 155.85 (C_q). ^{11}B NMR (160.5 MHz, CD_2Cl_2): δ = 0.08. Elemental analysis (%) calcd for $C_{40}H_{36}BN_3$: C, 84.35; H, 6.37; N, 7.38. Found: C, 83.66; H, 6.41; N, 6.79.

Synthesis of 5,5′-Bis(dichloroboryl)-2,2′-bithiophene (13). To a sample of neat BCl_3 (4.80 g, 3.62 mL, 40.9 mmol) was added a solution of 5,5′-bis(trimethylsilyl)-2,2′-bithiophene (1.92 g, 6.18 mmol) at −20 °C. The mixture was allowed to warm to room temperature and was stirred for 2 h. All volatiles were removed in vacuo, and the residue was recrystallized from toluene at −30 °C to yield **4** as a yellow solid (1.81 g, 5.52 mmol, 89%).

^{1}H NMR (500.1 MHz, C_6D_6, 297 K): δ = 6.78 (m, $^3J_{H-H}$ = 3.90 Hz, 2H, *H*-dithienyl), 7.43 (d, $^3J_{H-H}$ = 3.90 Hz, 2H, *H*-dithienyl). ^{13}C NMR (125.8 MHz, C_6D_6, 297 K): δ = 128.2 (CH-dithienyl), 144.1 (CH-dithienyl), 149.8 (C_q-dithienyl). ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 47.7. Elemental analysis (%) calcd for $C_8H_4B_2Cl_4S_2$: C, 29.32; H, 1.23; S, 19.57. Found: C, 29.81; H, 1.24; S, 19.39.

Synthesis of 5,5′-Bis-(2,3,4,5-tetraphenylborole)-2,2′-bithiophene (14). A solution of $Me_2SnC_4Ph_4$ (514 mg, 1.02 mmol) in 5 mL of dichloromethane was treated dropwise with a solution of 5,5′-bis(dichloroboryl)-2,2′-bithiophene (200 mg, 0.61 mmol) in 5 mL of dichloromethane at −50 °C. The reaction mixture was stirred for 3 h and subsequently allowed to warm to rt, resulting in a color change from yellow to orange. All volatiles were removed in vacuo, and the side product Me_2SnCl_2 was removed quantitatively by sublimation at rt and 10^{-6} mbar within 5 h. The red residue was recrystallized from toluene/hexane to yield **5** as a orange brown solid (415 mg, 4.61 mmol, 75%). ^{1}H NMR (500.1 MHz, CD_2Cl_2, 297 K): δ = 6.82−6.84 (m, 8H, *Ph*), 6.99−7.06 (m, 14H, *Ph*), 7.12−7.14 (m, 8H, *Ph* & *H*-dithienyl), 7.21−7.26 (m, 14H, *Ph* & *H*-dithienyl). ^{13}C NMR (125.8 MHz, CD_2Cl_2, 297 K): δ = 126.23, 127.41, 127.48, 128.01 (CH), 128.03 (CH-dithienyl), 129.68, 130.05 (CH), 146.26 (CH-dithienyl), 136.80, 140.60, 150.93, 162.14 (C_q). ^{11}B NMR (160.5 MHz, CD_2Cl_2, 297 K): δ = 56.5 (br). Elemental analysis (%) calcd $C_{64}H_{44}B_2S_2$: C, 85.52; H, 4.93; S, 7.14. Found: C, 84.59; H, 4.84; S, 6.76.

Synthesis of 5,5′-Bis-(2,3,4,5-tetraphenylborole)-2,2′-bithiophene-bis(dimethylaminopyridine) (15). To a solution of **5** (20 mg, 22.3 μmol) in 3 mL of dichloromethane was added DMAP (5.44 mg, 44.6 μmol), causing an immediate color change from dark orange to yellow. All volatiles were removed in vacuo, and the residue was recrystallized in CH_2Cl_2/hexane to give **12** (22.4 mg, 19.6 μmol, 88%) as yellow crystals. ^{1}H NMR (500.1 MHz, CD_2Cl_2, 297 K): δ = 3.10 (s, 12H, N*Me*$_2$), 6.55−6.58 (m, 4H, NC_5H_4-4-NMe_2), 6.66 (d, $^3J_{H-H}$ = 3.45 Hz, 2H, *H*-dithienyl), 6.73−6.76 (m, 8H, *Ph*), 6.87−7.04 (m, 34H, *Ph* & *H*-dithienyl), 8.24−8.27 (m, 4H, NC_5H_4-4-NMe_2). ^{13}C NMR (125.8 MHz, CD_2Cl_2, 297 K): δ = 39.77 (N*Me*$_2$), 106.99 (NC_5H_4-4-NMe_2), 123.31 (CH-dithienyl), 124.43, 125.52, 127.38, 127.43, 129.36, 130.68 (CH), 131.92 (CH-dithienyl), 145.12 (NC_5H_4-4-NMe_2), 139.18, 140.85, 143.51, 150.04, 155.95 (C_q). ^{11}B NMR (160.5 MHz, CD_2Cl_2, 297 K): δ = 0.29. Elemental analysis (%) calcd for $C_{78}H_{64}B_2N_4S_2\cdot 2(CH_2Cl_2)$: C, 73.18; H, 5.22; N, 4.27; S, 4.88. Found: C, 73.33; H, 5.29; N, 4.23; S, 4.81.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data of complexes **7**, **8**, **9**, **11**, **12′**, and **15** in cif format, cyclic voltammetry measurements, and details about DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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