Dithiophene-Fused Oxadiborepins and Azadiborepins: A New Class of Highly Fluorescent Heteroaromatics
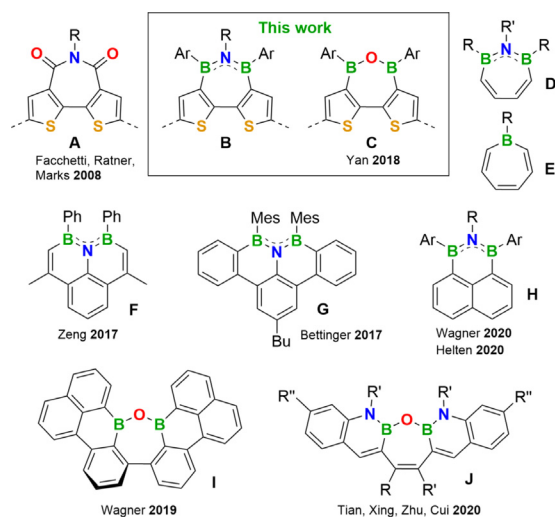
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Dedicated to Professor Ian Manners on the occasion of his 60th birthday

Abstract: *Access to dithiophene-fused oxadiborepins and the first azadiborepins attained via a modular synthesis route are presented. The new compounds emit intense blue light, some of which demonstrate fluorescence quantum yields close to unity. Cyclic voltammetry (CV) revealed electrochemically reversible one-electron reduction processes. The weak aromatic character of the novel 1,2,7-azadiborepin ring is demonstrated with in-depth theoretical investigations using nucleus-independent chemical shift (NICS) scans and anisotropy of the induced current density (ACID) calculations.*

*I*n the past decades, π-conjugated organic materials have received tremendous attention due to applications thereof in organic (opto)electronics, sensors, and biomedicine.[1] The current focus in the design of new materials for such purposes has shifted towards electron-deficient building blocks, which, in the past, have been markedly less well developed compared with their electron-rich counterparts.[2] The doping of π-conjugated frameworks with trivalent boron has recently emerged as a powerful tool for producing strongly electron-accepting materials; a result of the incorporation of the vacant p orbital of boron in the π system.[3]

2,2′-Bithiophene-3,3′-dicarboximide (BTI, **A**, Figure 1) is a representative example of an electron-deficient polycyclic organic building block that has been successfully used in electron-transporting materials.[4–6] It features the effectively π-accepting imide moiety [-C(=O)-NR-C(=O)-].[7] Borylene groups (>B-R) share some common features with carbonyl groups (>C=O): both of them constitute a trigonal-planar linking site with bond angles of approximately 120°, and they

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Figure 1. 2,2′-Bithiophene-3,3′-dicarboximide (BTI, **A**), dithieno[3,2-*c*:2′,3′-*e*][1,2,7]azadiborepin (**B**), and dithieno[3,2-*c*:2′,3′-*e*]-[1,2,7]oxadiborepin building blocks (**C**); the parent 1,2,7-azadiborepin (**D**) and borepin (**E**) ring systems; BNB-doped PAHs (**F–H**), and oxadiborepin-containing PAHs (**I** and **J**).

both have pronounced π-acceptor character. Considering this analogy, we decided to target the dithiophene-fused azadiborepin system **B**, which is formally derived from **A** by substitution of the C=O with B-Ar units. The latter should offer the additional opportunity of fine-tuning of the compound's properties through the variable aryl group (Ar). The substance class **B** is unknown thus far, and so is the parent seven-membered azadiborepin ring system **D**. It contains six π electrons in the cycle and is therefore potentially aromatic. Heteroaromaticity in boron-containing heterocycles has fascinated experimental and theoretical researchers for a long time.[8,9] Borepin (**E**), for example, comprises a seven-membered ring with one boron atom and six π electrons. It has been ascribed substantial aromaticity.[9] Replacing one or more C=C pairs in mono- or polycyclic aromatic hydrocarbons (PAHs) by their isoelectronic and isosteric B=N units has brought about a wide range of novel heteroaromatic compounds, many of which show intriguing properties and functions.[10,11] Surprisingly, PAHs comprising 3-center 2-π-electron B-N-B moieties have been explored rather scarcely thus far.[12–15] Zeng et al. recently presented the BNB-phenalenyl analogue **F**.[12] Steric congestion between the two *B*-bonded phenyl groups causes significant distortion of its

tricyclic scaffold from planarity. Detailed theoretical investigations revealed that the NBC_4 rings in **F** are weakly aromatic. Bettinger and co-workers reported the π-extended BNB-doped PAH **G**.[13] Computations on this species showed that its BN-containing rings are nonaromatic, while aromatic character is confined to the three peripheral carbonaceous rings (also here, the two *B*-Mes groups induce some distortion of the PAH plane). Wagner's group and ours independently explored the BNB-doped phenalenyl system **H**, wherein such steric stress is effectively prevented.[14,15] Via in-depth theoretical studies using nucleus-independent chemical shift (NICS) scans and anisotropy of the induced current density (ACID) calculations, we showed that the B_2NC_3-ring in **H** is slightly aromatic.[15]

Recently, Yan et al. reported the synthesis of dithiophene-fused oxadiborepin derivatives **C**.[16] The tricyclic compound with Ar = FMes (2,4,6-tris(trifluoromethyl)phenyl) was serendipitously obtained in an attempt to prepare a dithienoborole from 3,3′-dilithio-2,2′-bithiophene and BCl_3 and subsequent reaction with FMesLi. The unexpected product **C** formed through hydrolysis during the workup procedure. Only few further examples of compounds featuring oxadiborepin as a substructure have been reported in the literature.[17–20] The first one, described by Wagner and co-workers in 2011, was a bisboronic acid anhydride.[17] Recently, they presented the BOB-doped PAH **I**.[18] Due to steric congestion between the annulated benzene rings, this species deviates significantly from planarity. Tian, Xing, Zhu, Cui et al. recently presented BNO-doped PAHs **J**,[20] which feature a planar framework. This system is actually described as a bis-BN-naphthalene-fused oxepin.

Herein, we present the systematic synthesis of dithiophene-fused oxadiborepins and the first azadiborepin derivatives from a common precursor. Extensive theoretical investigations aid in elucidating the aromatic character of the individual rings of these strongly blue light emitting species.

As we were unable to obtain a selective reaction towards the desired products if the bithiophene starting material was unsubstituted in the positions 5 and 5′, we decided to block these positions with methyl groups. Selective 5,5′-dilithiation of 3,3′,5,5′-tetrabromo-2,2′-bithiophene (**1**) was accomplished with *n*BuLi in Et_2O, and subsequent reaction with MeI afforded compound **2** in nearly quantitative yield (Scheme 1). Treating **2** with two equivalents of *n*BuLi, followed by addition of Me_3SiCl, resulted in formation of the disilylated compound **3**, which served as the precursor for all further transformations. Bisborylation of **3** with BCl_3 and mono-arylation of both introduced dichloroboryl groups with ArLi (Ar = Tip, FMes; Tip = 2,4,6-triisopropylphenyl) was performed sequentially without isolating the intermediates. Further in situ reaction of **4Tip** and **4FMes** with H_2O gave dithienooxadiborepins **5Tip** and **5FMes** in 75% yield each. For the synthesis of dithienoazadiborepins **6Tip**, **6FMes**, and **7Tip**, toluene solutions of **4Tip** and **4FMes** were treated with $HN(SiMe_3)_2$ or $MeN(SiMe_3)_2$, respectively; CH_2Cl_2 was added to increase the polarity, and refluxing the resulting mixtures for about one day gave the novel dithienoazadiborepins **6Tip**, **6FMes**, and **7Tip** in moderate yields. All products
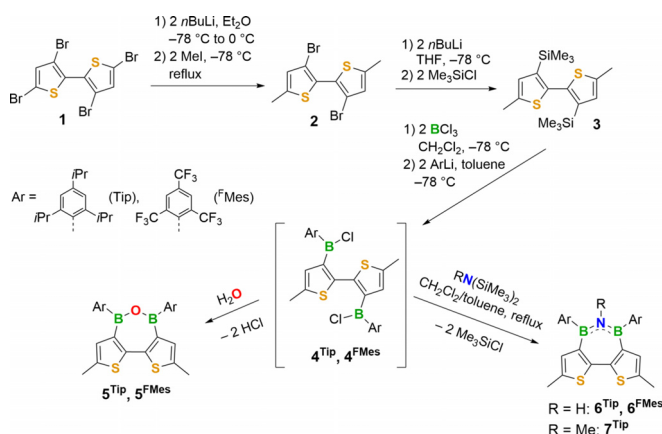

Scheme 1. Synthesis of dithienooxa- and -azadiborepins **5**, **6**, and **7**.

proved to be fully stable towards air and moisture and could be purified by column chromatography at standard ambient conditions. They were unambiguously identified by multi-nuclear NMR spectroscopy and mass spectrometry, and elemental analyses gave satisfactory results. Compounds **5Tip** and **7Tip** were additionally characterized by single-crystal X-ray diffractometry (Figure 2).
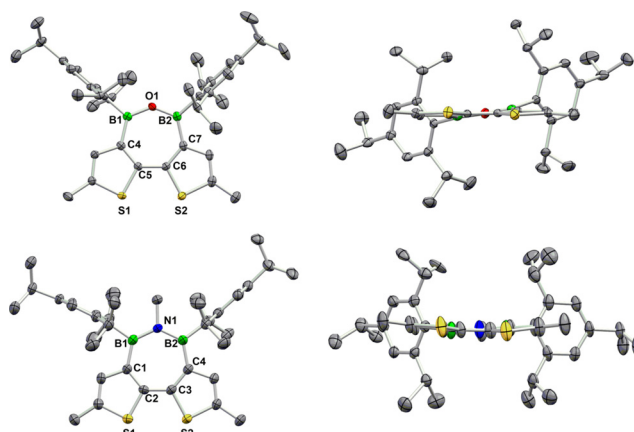
Figure 2. Molecular structures of **5Tip** and **7Tip** (with views perpendicular and parallel to the polycyclic plane) in the solid state by single-crystal X-ray diffraction (H-atoms and disorder of a Tip group in **7Tip** omitted for clarity).

In the solid-state structure, both species feature a quasi-planar tricycle, with the Tip groups being almost perpendicularly oriented to that plane. The seven-membered rings are close to planar, as suggested by the sums of their interior angles, which are 898.1° (**5Tip**) and 899.3° (**7Tip**), respectively. The oxadiborepin shows a slight twist of 7.2(3)° between the B-O-B moiety and the best plane through the ring carbon atoms C(4)-C(5)-C(6)-C(7). The B-O-B bond angle in **5Tip** amounts to 137.05(17)° (cf. 134.8(10)° in **I**),[18] and is much larger than the B-N-B angle in **7Tip** (129.7(3)°). This is accompanied by a slightly shorter distance between the thiophene units in the latter [C(2)−C(3), 1.432(5) Å in **7Tip** vs. C(5)−C(6), 1.449(3) Å in **5Tip**]. The twist angles between the thiophene rings are 7.00(10) (**5Tip**) and 11.4(2)° (**7Tip**), respec-
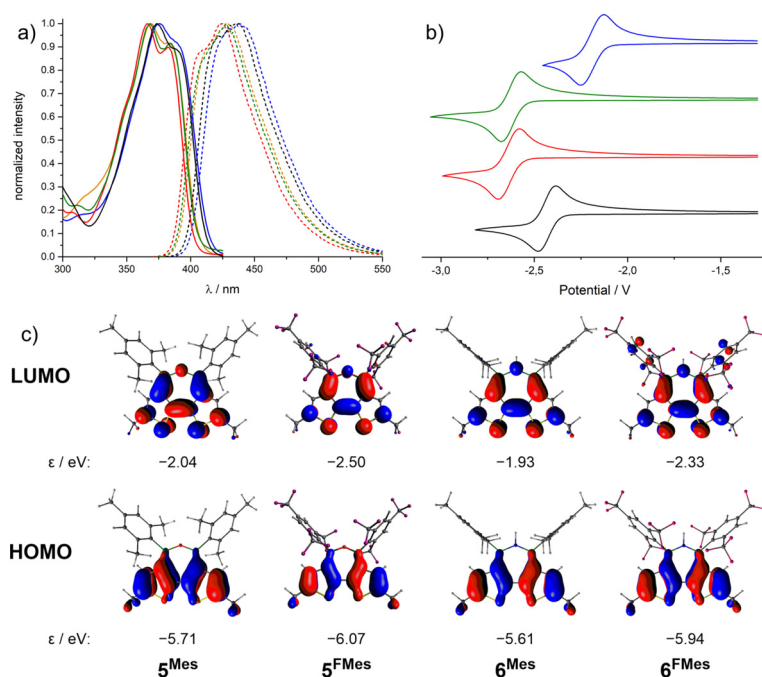
Figure 3. a) UV-vis absorption (solid lines) and fluorescence (dashed lines) spectra of **5^{Tip}** (black), **6^{Tip}** (red), **7^{Tip}** (green), **5^{FMes}** (blue), and **6^{FMes}** (orange) in CH$_2$Cl$_2$. b) Cyclic voltammograms of **5^{Tip}** (black), **6^{Tip}** (red), **7^{Tip}** (green), and **5^{FMes}** (blue) in THF (vs. [Cp$_2$Fe]$^{0/+}$, scan rate: 250 mVs^{-1}). c) B3LYP-D3(BJ)/def2-SV(P) calculated frontier orbitals of **5^{Mes}**, **5^{FMes}**, **6^{Mes}**, and **6^{FMes}** (isovalue 0.035).

tively. The B−N bond lengths in **7^{Tip}** are 1.434(5) and 1.445(5) Å, which is in the same range with those in derivatives of **H**[14,15] and typical BN aromatics,[10] but shorter than in **F** (1.463(1) Å)[12] and **G** (1.46 Å).[13]

The UV-vis absorption spectra for **5^{Tip}**, **6^{Tip}**, **7^{Tip}**, **5^{FMes}**, and **6^{FMes}** in CH$_2$Cl$_2$ display one structured low-energy band each with a maximum at 366–376 nm (Figure 3a, Table 1). According to our TD-DFT calculations (level: B3LYP-D3(BJ)/def2-SV(P)), this is assigned to a π–π* transition involving the HOMO and the LUMO of the molecules (Figure 3c). Both orbitals are fully delocalized over the tricyclic plane, and both include the two boron centers. The O or N atoms contribute to the LUMOs, while in the HOMOs there is a nodal plane at the same position. The calculated excitation wavelengths are in excellent agreement with the experimental data. These

Table 1: Photophysical data for **5^{Tip}**, **6^{Tip}**, **7^{Tip}**, **5^{FMes}**, and **6^{FMes}**.[a]

Compound	λ_{abs} [nm][b] (calcd[c])	λ_{em} [nm][b,d]	Φ_{fl}[e]
5^{Tip}	374, 391[f] (365)[g]	421,[f] 436	0.92
6^{Tip}	366, 382 (360)[g]	410,[f] 424	0.96
7^{Tip}	368, 384 (364)[g]	413,[f] 428	0.94
5^{FMes}	376, 392[f] (373)	428,[f] 439	0.70
6^{FMes}	369, 383 (370)	417,[f] 429	0.80

[a] In CH$_2$Cl$_2$. [b] Highest absorption and emission maxima underlined. [c] Data from TD-DFT calculations in parentheses. [d] Excited at the wavelength of the respective absorption maximum. [e] Fluorescence quantum yield determined absolutely with an integrating sphere. [f] Shoulder. [g] *B*-Mes- instead of Tip-substituted derivatives were calculated for computational convenience.

show a marginal bathochromic shift of the absorption maximum (by 6–8 nm) upon exchanging N(H/Me) by O (cf. **5^{Tip}** vs. **6^{Tip}**/**7^{Tip}**, and **5^{FMes}** vs. **6^{FMes}**). Our calculations reveal that this modification results in a decrease of the frontier orbital energies to a similar extent. Exchange of Tip by ^{F}Mes leads to virtually no shift of the absorption wavelength. This substitution causes an even more pronounced lowering of the energies of both frontier orbitals, to approximately the same extent. All compounds show intense blue fluorescence with exceptionally high quantum efficiencies. Especially in the series of Tip-substituted derivatives, the quantum yields are close to unity. The Φ_{fl} values for the azadiborepin species are slightly higher than those for their respective oxadiborepin congeners (by 4% for **5^{Tip}** vs. **6^{Tip}**, and by 10% for **5^{FMes}** vs. **6^{FMes}**).

To the best of our knowledge, it has not been reported if the parent 2,2′-bithiophene-3,3′-dicarboximide (BTI) or the corresponding anhydride show any luminescence; absorption data are available for *N*-substituted derivatives.[4a] In order to get an estimate of how the optoelectronic properties of our new diborepins compare with those of their organic congeners, we performed TD-DFT calculations additionally for the latter. This revealed that the excitations for BTI and its anhydride are blue-shifted compared to those of **5–7** (by 16–29 nm). Their frontier orbital energies are slightly lower, but those of the *B*-^{F}Mes derivatives **5^{FMes}** and **6^{FMes}** fall roughly in the same range (cf. Supporting Information, Table S2, Figures S40 and S41).
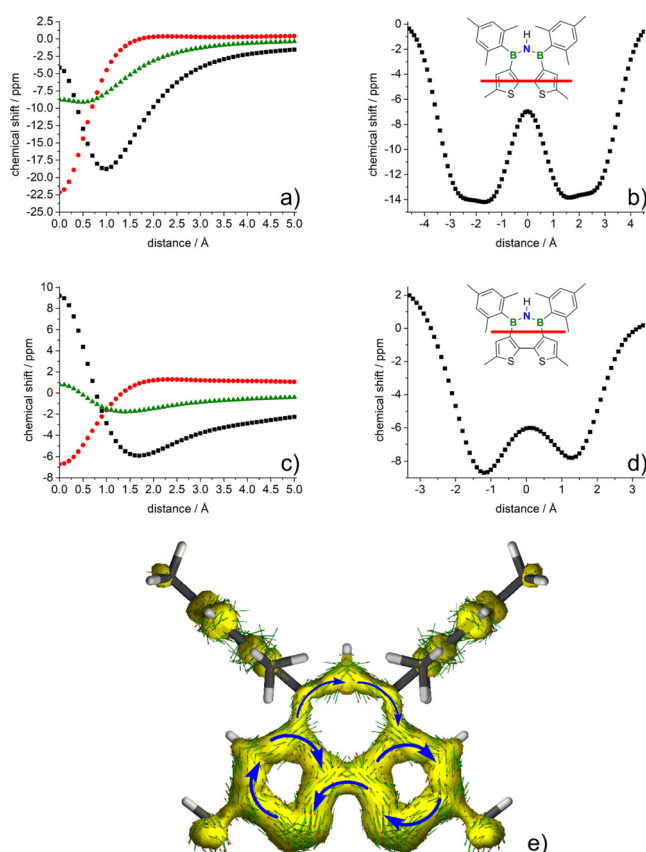
Cyclic voltammetry (CV) in THF (Figure 3b) using [nBu$_4$N][PF$_6$] as the supporting electrolyte revealed for compounds **5^{Tip}**, **6^{Tip}**, **7^{Tip}**, and **5^{FMes}** one reversible one-electron reduction wave each [$E_{1/2} = -2.43$ (**5^{Tip}**), -2.63 (**6^{Tip}**), -2.62 (**7^{Tip}**), -2.19 V (**5^{FMes}**)], whereas **6^{FMes}** undergoes an irreversible reduction at $E_{pc} = -2.50$ V. All compounds also show a second reduction process [$E_{pc} = -3.10$ (**5^{Tip}**), -3.32 (**6^{Tip}**), -3.34 (**7^{Tip}**), -2.91 (**5^{FMes}**), and -2.87 V (**6^{FMes}**)], which, however, is irreversible (Supporting Information, Figures S34–S38). Consistent with our MO calculations mentioned above, the reduction waves show an anodic shift upon the transition from N(H/Me) to O (**5^{Tip}** vs. **6^{Tip}**/**7^{Tip}**) and an even stronger shift upon exchanging Tip through ^{F}Mes (cf. **5^{FMes}** vs. **5^{Tip}**).

Of special interest was to assess the aromatic character of the novel azadiborepin ring system. First evidence comes from ^{1}H NMR spectroscopy. The resonance for the NH proton of **6^{Tip}** and **6^{FMes}** was detected at 7.11 and 6.67 ppm, respectively, which is at relatively low field, thus pointing to some degree of aromaticity in this ring. For comparison, the NH proton of the weakly aromatic BNB-phenalenyl **H** with R = H and Ar = Mes by Wagner et al. (Figure 1) resonated at 6.15 ppm.[14]

To gain deeper insight, we performed NICS-scans[21a] through the centers of the constituent ring systems (perpendicular to the resp. ring, from its center up to 5 Å above the

plane; Figure 4a,c) as well as NICS-*X*-scans[21b] (at 1.7 Å above the rings, along the red lines drawn in the respective formulae in Figure 4b,d). Such calculations provide more detailed information than NICS(0)/NICS(1) values alone. For computational convenience, we used a model compound, **6**[Mes], that carries mesityl (Mes) instead of Tip or [F]Mes substituents. The plot for the NICS-scan through one of the thiophene rings of **6**[Mes] (Figure 4a) shows the typical shape of an aromatic system. The isotropic chemical shift is mainly controlled by the out-of-plane component, and both curves show a clear minimum. The NICS-*X*-scan through the bithiophene subunit (Figure 4b) shows negative chemical shifts throughout the scan. The local maximum at the center results from the C−C-bond connecting the two thiophene rings.

Indeed, the corresponding graphs for the azadiborepin ring show similar shapes. In the NICS-scan through this ring (Figure 4c), the isotropic value is also mainly controlled by the out-of-plane component, and both curves show a distinct minimum. In this case, the minima are shallower than in the plot for the thiophene ring, and the values are overall less negative. Also in the NICS-*X*-scan (Figure 4d), the chemical shifts are negative throughout.[22] Overall, these results suggest that the azadiborepin system is weakly aromatic. This interpretation is further substantiated by ACID calculations.[21c,d] The plot for **6**[Mes] (Figure 4e) shows an overall

diatropic ring current, which is somewhat more pronounced in the bithiophene subunit.

To learn more about the electronic situation of the novel azadiborepin and the oxadiborepin system, we additionally performed analogous calculations on the parental heterocycles without dithiophene fused. This revealed that these rings are slightly aromatic as such, though the conjugation between boron and carbon is somewhat less effective compared to the dithiophene-fused systems (Supporting Information, Figures S49–S54). As anticipated, the aromaticity is more pronounced in the azadiborepin than in the oxadiborepin system (cf. Figure S49 vs. Figure S52). For borepin (**E**, R = Mes; Figure 1), our calculations indicate significantly stronger aromaticity (Supporting Information, Figures S55–S57), consistent with previous studies on this ring system.[9]

In conclusion, we have devised a modular synthesis of highly fluorescent dithienooxa- and -azadiborepins from a common precursor. Our calculations show that the novel azadiborepin ring system exhibits weak aromatic character. Currently, we are working on the incorporation of the new heterocycles into π-extended materials and we are exploring the potential of such materials for use in optoelectronic and related applications.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

Keywords: aromaticity · BN compounds · boron · isoelectronic analogues · polycycles

Figure 4. NICS-scans: a) thiophene ring, c) azadiborepin ring; out-of-plane (black), in-plane (red) component, and isotropic chemical shift (green). NICS-*X*-scans: b) bithiophene, d) azadiborepin ring, and e) ACID plot (isovalue 0.02) of **6**[Mes].

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