Angewandte
International Edition Chemie

Lewis Acids

DOI: 10.1002/anie.201403700

Highly Electron-Deficient and Air-Stable Conjugated Thienylboranes**

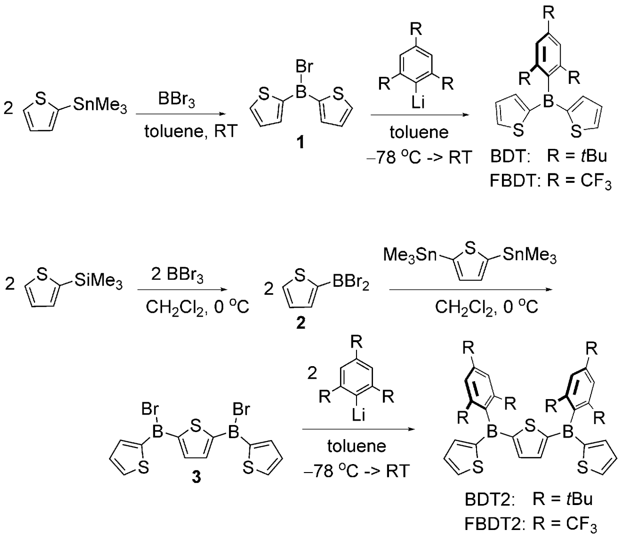
Xiaodong Yin, Jiawei Chen, Roger A. Lalancette, Todd B. Marder, and Frieder Jäkle**

***Abstract:** Introduced herein is a series of conjugated thienylboranes, which are inert to air and moisture, and even resist acids and strong bases. X-ray analyses reveal a coplanar arrangement of the thiophene rings, an arrangement which facilitates p–π conjugation through the boron atoms despite the presence of highly bulky 2,4,6-tri-tert-butylphenyl (Mes*) or 2,4,6-tris(trifluoromethyl)phenyl (^{F}Mes) groups. Short B···F contacts, which lead to a pseudotrigonal bipyramidal geometry in the ^{F}Mes species, have been further studied by DFT and AIM analysis. In contrast to the Mes* groups, the highly electron-withdrawing ^{F}Mes groups do not diminish the Lewis acidity of boron toward F^- anions. These compounds can be lithiated or iodinated under electrophilic conditions without decomposition, thus offering a promising route to larger conjugated structures with electron-acceptor character.*

In recent years, main-group elements have been successfully incorporated into the backbone of conjugated organic oligomers and polymers, commonly resulting in unusual properties and improved performance.[1] Among these conjugated hybrids, boron-containing materials have attracted considerable attention.[2] As a result of interactions between the empty p orbital of boron and π-conjugated systems, desirable optical and electronic properties are achieved, which in turn enable applications in optoelectronics and sensory materials.[3] Two mesityl groups are generally sufficient to stabilize three-coordinate aryl or vinyl boron compounds with respect to attack by air, water, and most nucleophiles.[3f–n] However, a significant drawback remains the susceptibility to degradation upon attack by nucleophiles in other systems, especially in the case of conjugated organoboranes with high Lewis acidity.[4] The apparent dichotomy that higher electron deficiency is desirable for application purposes, but also tends to induce degradation, has become an obstacle to further progress.

Several strategies have been explored to stabilize organoboranes while still promoting effective p–π conjugation. Bulky groups, such as 2,4,6-tri-isopropylphenyl (Tip)[5] and 2,4,6-tri-*tert*-butylphenyl (Mes*)[6] have been successfully utilized to sterically protect the boron atom from attack by nucleophiles. In an alternative approach, tricoordinate boranes have been embedded into cyclic and extended planar conjugated structures.[6,7] For applications in organic electronics and sensing schemes, however, it is desirable not only to increase the stability, but also to maximize the electron-acceptor properties. A promising strategy in this respect is the use of ^{F}Mes groups,[8] which combine steric hindrance with strongly electron-withdrawing character. Theoretical studies by Marder and Weber et al. showed that replacement of Mes with ^{F}Mes groups in 5,5′-bis(dimesitylboryl)-2,2′-bithiophene significantly lowers the LUMO energy.[9] We introduce herein a new series of conjugated organoboranes with Mes* and ^{F}Mes groups. The influence of the ^{F}Mes moiety is clearly demonstrated, and the organoboranes serve as promising building blocks for conjugated oligomers and polymers. To facilitate p–π conjugation with boron we utilize thiophene moieties, because their small ring size should favor adoption of a coplanar structure. Another advantage is the high reactivity of the thiophene α position which lends itself to further derivatization.

The compound **1** was readily prepared starting from 2-(trimethylstannyl)thiophene by Sn–B exchange and then treatment with a bulky aryl lithium reagent, Mes*Li or ^{F}MesLi, to give the borane monomers BDT and FBDT in an overall yield of 44% and 43%, respectively (Scheme 1).



Scheme 1. Synthesis of sterically shielded (oligo)thienylboranes.

---

[*] Dr. X. Yin, J. Chen, Prof. R. A. Lalancette, Prof. Dr. F. Jäkle
Department of Chemistry, Rutgers University - Newark
73 Warren Street, Newark, NJ 07102 (USA)
E-mail: fjaekle@rutgers.edu
Homepage: http://chemistry.rutgers.edu/fjaekle
Prof. Dr. T. B. Marder
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
E-mail: todd.marder@uni-wuerzburg.de

[**] This material is based upon work supported by the National Science Foundation under Grant No. CHE-1112195.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201403700.

Using similar methods, we also synthesized the corresponding dimeric species BDT2 and FBDT2 from 2,5-bis(trimethylstannyl thiophene) with the expectation that they would allow assessment of the degree of extended conjugation in the presence of the Mes* or ^{F}Mes groups. All of the products proved to be perfectly air and moisture stable and were easily purified by silica-gel column chromatography without any precautions. Remarkably, they proved to be resistant to oxidants, acids, and strong bases, such as halogens, acetic acid, and *n*-butyl lithium, respectively, thus enabling facile functionalization.

Single crystals of BDT and FBDT were obtained by recrystallization from hexanes and the structure plots are shown in Figure 1 a,b. Metrical parameters of a second independent molecule in the unit cell of FBDT are provided within parentheses in the following discussions. Rotation about the B1–C1 and B1–C5 bonds results in disorder of the thiophene rings, but the conformations in which the S atoms point away from the Mes*/^{F}Mes group are dominant.[10] The Mes*/^{F}Mes groups adopt orientations almost orthogonal to the thiophene rings with dihedral angles of 85.4° and 85.8° for BDT and 84.4° and 88.2° (86.1° and 89.2°) for FBDT.

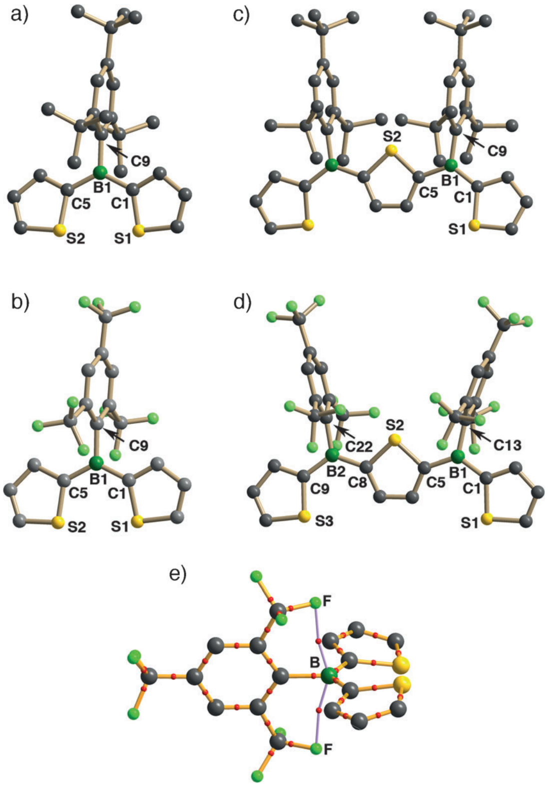


Figure 1. X-ray structure plots of a) BDT, b) FBDT, c) BDT2, d) FBDT2, and e) atoms-in-molecules (AIM) analysis of FBDT, showing B⋯F bond paths (purple lines) and bond critical points (BCP, red points).

Importantly, the thiophenes and the boron atom form a quasiplanar structure. The small torsion angle, between the thiophene rings, of 19.0° for BDT and 16.3° (5.7°) for FBDT is ideal for promoting π conjugation along the main chain through the empty p orbital on boron. The B–C bonds to the thiophene rings are 1.541(7) and 1.526(6) Å [1.546(7) and 1.518(11) Å)] for FBDT, and on average are significantly shorter than those in BDT [1.589(6) and 1.568(4) Å], and could indicate stronger p–π conjugation between boron and the thiophenes in the more-electron-deficient FBDT. Indeed, the B–C distances in FBDT are close to those in related pentafluorophenyl-substituted thienylboranes, for example, $(C_6F_5)_2$B-$(Th)_2$-B$(C_6F_5)_2$ 1.507(3)[11] and $(C_6F_5)_2$B-$(Th)_2$-NPh$_2$ 1.502(3).[4b] Similar conformations are observed in the molecular structures of BDT2 and FBDT2 (Figure 1 c,d) with small torsion angles of 10.6 (BDT2) and 4.8 (Th_{S1}-Th_{S2})/16.5° (Th_{S2}-Th_{S3}) (FBDT2).[12] We also note that the Mes* rings in BDT2 adopt an almost coplanar conformation, but the ^{F}Mes rings in FBDT2 are oriented so that the space between them is enlarged. This orientation turns out to be related to an unusual chainlike supramolecular structure of FBDT2, in which the terminal thiophene ring of a neighboring molecule is captured in a sandwich-like arrangement between the ^{F}Mes groups (see Figure S3 in the Supporting Information).

Another very interesting aspect is the observation of short B⋯F contacts in the structures of FBDT and FBDT2. The B–F distances of 2.66 and 2.49 Å (2.60 and 2.89 Å) for FBDT and 2.55, 2.56, 2.57, and 2.61 Å for FBDT2 are all much shorter than the sum of the B and F van der Waals radii[13] of 3.39 Å.[14] The slight variations in the distances are related to rotation of the CF_3 group. To develop a better understanding of the nature of these (weak) interactions, we performed full geometry optimization at the B3LYP/6-31+G* level of theory, starting from the crystal structure parameters.[15] In the optimized structure of FBDT, the B⋯F distances are identical at 2.64 Å, which is comparable to the experimental distances. Atoms-in-molecules (AIM) analysis revealed the presence of bond paths between B and the neighboring F atoms, thus resulting in a pentacoordinate geometry (Figure 1 e).[16] The electron density (ρ) and its Laplacian ($\nabla^2\rho$) at the bond critical points (BCPs) for FBDT were computed to be $0.014\,e\,a_0^{-3}$ (a_0 is the Bohr radius) and $0.050\,e\,a_0^{-5}$, respectively. The corresponding values for FBDT2 proved to be similar with average values of $0.015\,e\,a_0^{-3}$ and $0.050\,e\,a_0^{-5}$. The relatively lower electron density for FBDT and FBDT2 in comparison to that reported by Yamaguchi for related B⋯Cl[17] and by Yamashita for B⋯O contacts[18] is likely a result of the smaller atomic radii and higher electronegativity of fluorine.

The electron acceptor properties were studied by cyclic voltammetry (CV; Figure 2). Single reversible reduction waves were observed at $E_{1/2} = -2.58$ (BDT) and -2.22 V (FBDT, vs $Fc^{+/0}$), which unequivocally demonstrates that the ^{F}Mes group strongly decreases the LUMO energy level. Results from DFT calculations[15] further confirm this phenomenon. The LUMOs of both compounds show strong overlap of the empty p orbital on B with the thiophene orbitals, thus resulting in an effective conjugation path (Table 1 and Figure 3). However, there are significant differences in that the Mes* group strongly contributes to the HOMO and even more so the HOMO-1 of BDT, whereas in FBDT the ^{F}Mes group contributes to the LUMO and makes up almost exclusively the LUMO+1 (see Figure S5 in the Supporting Information). Importantly, both the HOMO and

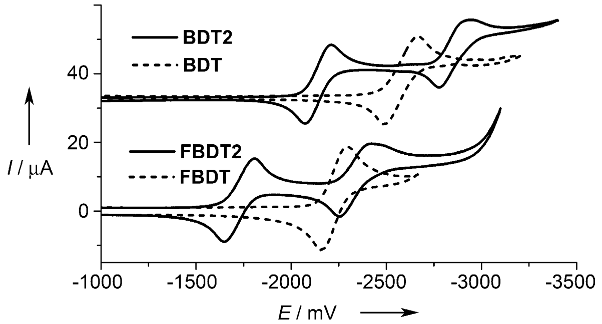


Figure 2. Comparison of cyclic voltammograms in THF/0.1 M $Bu_4N[PF_6]$ (1×10^{-3} mol L^{-1}; vs. Fc$^{0/+}$, $\nu = 100$ mV s^{-1}).

Table 1: Comparison of experimental and calculated LUMO energy levels.

	BDT	FBDT	BDT2	FBDT2
LUMO (exp)[a]/eV	−2.22	−2.58	−2.66	−3.07
LUMO (calcd)[b]/eV	−2.27	−2.59	−2.54	−3.12

[a] Determined using the equation $E_{\text{LUMO}} = -(4.8+E_{\text{vs.Fc}})$; [b] Calculated orbital energies (DFT, B3PW91/6-311+G*; see Ref. [15])

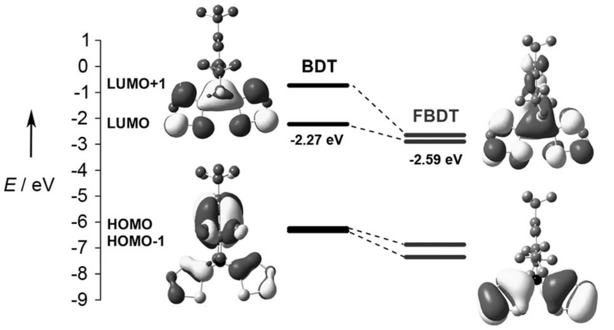


Figure 3. Calculated frontier orbital energy levels and HOMO/LUMO orbital plots of BDT and FBDT (DFT, B3PW91/6-311+G*; see Ref. [15]).

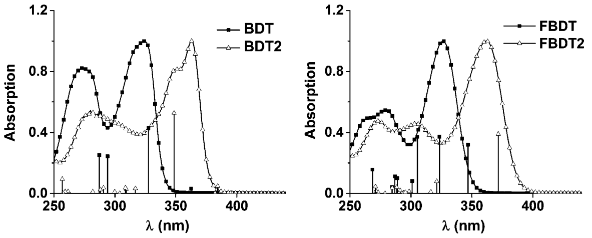


Figure 4. Comparison of UV-Vis spectra in THF. Vertical lines correspond to calculated excitations (TD-DFT, B3LYP/6-31+G*; see Ref. [15]).

the LUMO energy levels of FBDT are significantly lowered. The former facilitates reduction, while the latter is expected to be beneficial for the oxidative stability.

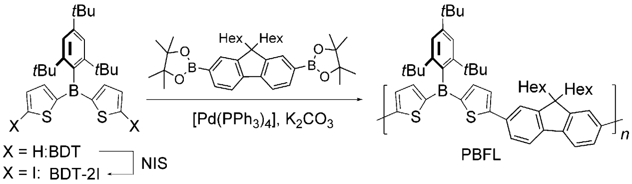
For the dimeric compounds BDT2 and FBDT2, two reversible redox waves are observed in the CV (Figure 2), and they correspond to stepwise reduction of the individual borane moieties. In comparison to the monoboron analogues, the first reduction potentials (BDT2: $E_{1/2} = -2.14$ V; FBDT2: $E_{1/2} = -1.73$ V) show a pronounced anodic shift, which is a result of strong electronic communication between the boron atoms. Indeed, the LUMO orbital plots (Figure S5) display clear evidence of overlap of the two boron p orbitals and the central thiophene moiety. The second redox processes of BDT2 ($E_{1/2} = -2.84$ V) and FBDT2 ($E_{1/2} = -2.34$ V) are shifted to more negative potentials because of the electronic interactions between the boron radical anion ($B^{-\bullet}$) and neutral boron.[19] Remarkably large splittings of $\Delta E = 700$ (**BDT2**) and 610 mV (FBDT2) further demonstrate that the very bulky groups do not interfere with, but likely even enhance, electronic communication as a result of the rigidification of the Th-B-Th-B-Th skeleton.[20]

The simultaneous decrease of both the HOMO and LUMO orbital energies of FBDT relative to BDT leads to similar absorption characteristics of these compounds. As shown in Figure 4, BDT features two main absorption bands with maxima at $\lambda = 324$ and 270 nm in THF solution, while a slight bathochromic shift to $\lambda = 326$ and 280 nm is observed for FBDT. The origin of these electronic transitions was verified by TD-DFT calculations (B3LYP/6-31+G*).[15] The lowest energy transition to the S_1 state of BDT corresponds to charge transfer from the Mes* group (HOMO, HOMO−1) to the dithienylborane moiety (LUMO), but this transition is very weak. Instead, the absorption bands of BDT at $\lambda = 325$ and 275 nm are mainly due to excitation from lower energy thiophene-centered orbitals to the LUMO (see Table S4 and Figure S5 in the Supporting Information). Differently, for FBDT the longest wavelength excitation is predominantly HOMO to LUMO, where the HOMO is localized on the thiophene rings and the LUMO is delocalized over the dithienylborane moiety with a pronounced contribution from the boron p orbital. The coplanar structure in BDT2 and FBDT2 allows for effective extension of π conjugation and, as a consequence, the UV-Vis absorptions are strongly red-shifted compared to that of the monoboron analogues ($\lambda =$ 360 nm; Figure 4). We note that BDT, FBDT, and BDT2 are essentially non-emissive in THF solution, while for FBDT2 only a very weak blue fluorescence with a quantum yield of 0.8 % is observed.[21]

To explore whether these compounds are still capable of acting as typical Lewis acids we performed binding studies with F^- as a small and powerful Lewis base.[22] For BDT or BDT2, even the exposure to a very large excess of $[Bu_4N]F$ (> 20 equivs) did not lead to any detectable changes in the NMR signatures ($CDCl_3$) or the absorption characteristics (THF).[23] In contrast, FBDT and FBDT2 respond readily to small amounts of F^-. As shown in Figure S16 in the Supporting Information, the absorption of FBDT at $\lambda =$ 320 nm decreases rapidly with increasing amounts of added F^- (lg $\beta = 7.2$). Since p–π conjugation is blocked in the resulting borate $[\text{FBDT-F}]^-$, only weak absorptions are observed in the range of $\lambda = 250$–350 nm, and are a result of charge transfer from thiophene to ^{F}Mes (see Table S5 in the Supporting Information).[24] For FBDT2, the absorption at $\lambda = 370$ nm decreases and is slightly blue-shifted to about $\lambda =$

350 nm upon formation of the monoborate species (lg $\beta_{11}=7.8$). In the presence of an excess F^-, the new band at $\lambda = 350$ nm only very gradually disappears (lg β_{12} ca. 3.7), thus indicating a much more severe steric strain when two tetrahedral fluoroborate moieties are generated in close proximity to one another (see Scheme S2 in the Supporting Information).

To demonstrate the general utility of our approach we also explored the derivatization of BDT and FBDT with halogens. For BDT, iodination with NIS in chloroform in the presence of acetic acid occurred readily and with excellent selectivity for the α-position (Scheme 2). However, the more-electron-deficient FBDT did not react under similar reaction conditions and attempted bromination with NBS in DMF resulted only in low yields of the monobrominated product. In contrast, lithiation of FBDT with *n*BuLi in THF at −78 °C proceeded readily, and subsequent quenching with iodine led to the bis(iodinated) product in good yield (see Scheme S1 in the Supporting Information). In a preliminary study on the formation of conjugated polymers, BDT-2I was reacted with a diboronated fluorene by Suzuki–Miyaura cross-coupling to obtain PBFL ($M_n = 8.4$ kDa; 61 % yield), which is orange in color and displays a strong blue luminescence in solution [($\varphi = 31 \pm 3$) %] and as thin film [($\varphi = 3.2 \pm 1$) %; see Figure S9 b in the Supporting Information]. NMR studies indicate that the polymer is comprised of fluorene and BDT in the expected approximate 1:1 ratio, and a broad peak in the ^{11}B NMR spectrum confirms that the borane building block remained intact.



Scheme 2. Synthesis of a conjugated polymer from BDT-2I.

In conclusion, crystal structures of BDT and FBDT, and the corresponding dimers reveal an almost perfectly coplanar arrangement of the thienylborane skeleton. The highly bulky Mes* and ^{F}Mes groups actually facilitate extended π conjugation as they lock in the coplanar structure. This conjugation is reflected in strong red shifts in the absorptions of the dimers and large redox splittings in the CVs. The bulky groups greatly increase the stability, thus making the borane species inert to air, moisture, and even acids and bases. The ^{F}Mes derivatives exhibit not only excellent stability, but at the same time high Lewis acidity because of the strongly electron-withdrawing character of the ^{F}Mes groups. The facile functionalization by iodination enables C−C coupling chemistries and promises broad utility as electron-deficient building blocks in organic electronics and sensing applications.

Received: March 25, 2014

Keywords: boron · conjugation · fluoride · heterocycles · Lewis acids

---

[1] a) M. A. Brook, *Silicon in organic, organometallic, and polymer chemistry*, Wiley-VCH, New York, **2000**; b) N. R. Neale, T. D. Tilley, *J. Am. Chem. Soc.* **2002**, *124*, 3802–3803; c) R. C. Smith, J. D. Protasiewicz, *J. Am. Chem. Soc.* **2004**, *126*, 2268–2269; d) V. A. Wright, B. O. Patrick, C. Schneider, D. P. Gates, *J. Am. Chem. Soc.* **2006**, *128*, 8836–8844; e) T. Baumgartner, R. Reau, *Chem. Rev.* **2006**, *106*, 4681–4727; f) M. Heeney, W. Zhang, D. J. Crouch, M. L. Chabinyc, S. Gordeyev, R. Hamilton, S. J. Higgins, I. McCulloch, P. J. Skabara, D. Sparrowe, S. Tierney, *Chem. Commun.* **2007**, 5061–5063; g) A. A. Jahnke, D. S. Seferos, *Macromol. Rapid Commun.* **2011**, *32*, 943–951; h) X. M. He, T. Baumgartner, *RSC Adv.* **2013**, *3*, 11334–11350; i) G. He, L. Kang, W. T. Delgado, O. Shynkaruk, M. J. Ferguson, R. McDonald, E. Rivard, *J. Am. Chem. Soc.* **2013**, *135*, 5360–5363.

[2] A. Doshi, F. Jäkle, *Comprehensive Inorganic Chemistry II*, *Vol. 1* (Eds.: J. Reedijk, K. Poeppelmeier), Elsevier, Oxford, **2013**, pp. 861–891.

[3] a) C. D. Entwistle, T. B. Marder, *Angew. Chem.* **2002**, *114*, 3051–3056; *Angew. Chem. Int. Ed.* **2002**, *41*, 2927–2931; b) C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, *16*, 4574–4585; c) N. Matsumi, Y. Chujo, *Polym. J.* **2008**, *40*, 77–89; d) F. Jäkle, *Chem. Rev.* **2010**, *110*, 3985–4022; e) A. Lorbach, A. Huebner, M. Wagner, *Dalton Trans.* **2012**, *41*, 6048–6063; f) J. C. Doty, B. Babb, P. J. Grisdale, M. E. Glogowski, J. L. R. Williams, *J. Organomet. Chem.* **1972**, *38*, 229–236; g) Z. Yuan, N. J. Taylor, R. Ramachandran, T. B. Marder, *Appl. Organomet. Chem.* **1996**, *10*, 305–316; h) J. C. Collings, S.-Y. Poon, C. Le Droumaguet, M. Charlot, C. Katan, L. O. Palsson, A. Beeby, J. A. Mosely, H. M. Kaiser, D. E. Kaufmann, W.-Y. Wong, M. Blanchard-Desce, T. B. Marder, *Chem. Eur. J.* **2009**, *15*, 198–208; i) M. Lequan, R. M. Lequan, K. Chane-Ching, *J. Mater. Chem.* **1991**, *1*, 997–999; j) T. Noda, Y. Shirota, *J. Am. Chem. Soc.* **1998**, *120*, 9714–9715; k) W.-L. Jia, D.-R. Bai, T. McCormick, Q.-D. Liu, M. Motala, R.-Y. Wang, C. Seward, Y. Tao, S. Wang, *Chem. Eur. J.* **2004**, *10*, 994–1006; l) M. Varlan, B. A. Blight, S. Wang, *Chem. Commun.* **2012**, *48*, 12059–12061; m) H. Li, A. Sundararaman, K. Venkatasubbaiah, F. Jäkle, *J. Am. Chem. Soc.* **2007**, *129*, 5792–5793; n) Y. Kim, H. Zhao, F. P. Gabbaï, *Angew. Chem.* **2009**, *121*, 5057–5060; *Angew. Chem. Int. Ed.* **2009**, *48*, 4957–4960.

[4] a) A. Sundararaman, M. Victor, R. Varughese, F. Jäkle, *J. Am. Chem. Soc.* **2005**, *127*, 13748–13749; b) A. Sundararaman, R. Varughese, H. Y. Li, L. N. Zakharov, A. L. Rheingold, F. Jäkle, *Organometallics* **2007**, *26*, 6126–6131; c) A. E. Ashley, T. J. Herrington, G. G. Wildgoose, H. Zaher, A. L. Thompson, N. H. Rees, T. Kramer, D. O'Hare, *J. Am. Chem. Soc.* **2011**, *133*, 14727–14740.

[5] a) A. Nagai, T. Murakami, Y. Nagata, K. Kokado, Y. Chujo, *Macromolecules* **2009**, *42*, 7217–7220; b) P. Chen, R. A. Lalancette, F. Jäkle, *J. Am. Chem. Soc.* **2011**, *133*, 8802–8805; c) P. Chen, F. Jäkle, *J. Am. Chem. Soc.* **2011**, *133*, 20142–20145; d) J. F. Araneda, B. Neue, W. E. Piers, M. Parvez, *Angew. Chem.* **2012**, *124*, 8674–8678; *Angew. Chem. Int. Ed.* **2012**, *51*, 8546–8550.

[6] a) A. Wakamiya, K. Mishima, K. Ekawa, S. Yamaguchi, *Chem. Commun.* **2008**, 579–581; b) D. R. Levine, A. Caruso, M. A. Siegler, J. D. Tovar, *Chem. Commun.* **2012**, *48*, 6256–6258; c) D. R. Levine, M. A. Siegler, J. D. Tovar, *J. Am. Chem. Soc.* **2014**, *136*, 7132–7139.

[7] a) S. Saito, K. Matsuo, S. Yamaguchi, *J. Am. Chem. Soc.* **2012**, *134*, 9130–9133; b) J. F. Araneda, B. Neue, W. E. Piers, *Angew. Chem.* **2012**, *124*, 10117–10119; *Angew. Chem. Int. Ed.* **2012**, *51*, 9977–9979; c) C. Reus, S. Weidlich, M. Bolte, H.-W. Lerner, M. Wagner, *J. Am. Chem. Soc.* **2013**, *135*, 12892–12907.

[8] a) S. M. Cornet, K. B. Dillon, C. D. Entwistle, M. A. Fox, A. E. Goeta, H. P. Goodwin, T. B. Marder, A. L. Thompson, *Dalton Trans.* **2003**, 4395–4405; b) A. E. J. Broomsgrove, D. A. Addy, A. Di Paolo, I. R. Morgan, C. Bresner, V. Chislett, I. A. Fallis, A. L. Thompson, D. Vidovic, S. Aldridge, *Inorg. Chem.* **2010**, *49*, 157–173; c) Z. Lu, Z. Cheng, Z. Chen, L. Weng, Z. H. Li, H. Wang, *Angew. Chem.* **2011**, *123*, 12435–12439; *Angew. Chem. Int. Ed.* **2011**, *50*, 12227–12231; d) T. Taniguchi, J. Wang, S. Irle, S. Yamaguchi, *Dalton Trans.* **2013**, *42*, 620–624.

[9] L. Weber, V. Werner, M. A. Fox, T. B. Marder, S. Schwedler, A. Brockhinke, H. G. Stammler, B. Neumann, *Dalton Trans.* **2009**, 1339–1351.

[10] BDT: 63% occupation of S1 and 78% of S2; FBDT: 72% occupation of S1 and 82% of S2 (73% for S3, 50% for S4; see Figure S1 in the Supporting Information).

[11] A. Sundararaman, K. Venkatasubbaiah, M. Victor, L. N. Zakharov, A. L. Rheingold, F. Jäkle, *J. Am. Chem. Soc.* **2006**, *128*, 16554–16565.

[12] The plane Th_{S1} is defined by C1-C2-C3-C4-S1, Th_{S2} by C5-C6-C7-C8-S2, and Th_{S3} by C9-C10-C11-C12-S3.

[13] M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. A* **2009**, *113*, 5806–5812.

[14] The ^{11}B NMR chemical shifts of FBDT ($\delta = 51.5$) and FBDT2 ($\delta = 52.2$) are smaller than those of BDT ($\delta = 53.5$) and BDT2 ($\delta = 53.9$), which might further substantiate the presence of B–F interactions as a more downfield shifted B signal would be expected for the compounds with the more electron withdrawing aryl groups. However, a stronger B–C(thiophene)interaction in the fluorinated species could also result in an upfield shift of the ^{11}B NMR resonances.

[15] All calculations were performed using the Gaussian 09 suite of programs (Gaussian 09 (Revision B.01), M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, **2010**). For details on the selection of functionals and basis sets, see the Supporting Information.

[16] Short C···B and H···B distances are also observed in BDT, but no bond path was evident from AIM analysis.

[17] C. D. Dou, S. Saito, S. Yamaguchi, *J. Am. Chem. Soc.* **2013**, *135*, 9346–9349.

[18] M. Yamashita, Y. Yamamoto, K. Y. Akiba, D. Hashizume, F. Iwasaki, N. Takagi, S. Nagase, *J. Am. Chem. Soc.* **2005**, *127*, 4354–4371.

[19] The first and second reduction potentials of BDT2 and FBDT2 are much lower than those reported for 2,5-bis(borolyl)thiophene ($E_{pc} = -2.53$ V and -3.08 V; H. Braunschweig, V. Dyakonov, B. Engels, Z. Falk, C. Hörl, J. H. Klein, T. Kramer, H. Kraus, I. Krummenacher, C. Lambert, C. Walter, *Angew. Chem.* **2013**, *125*, 13088–13092; *Angew. Chem. Int. Ed.* **2013**, *52*, 12852–12855), because THF does not coordinate to the electron-deficient, but sterically protected borane moieties in our compounds.

[20] The redox splitting of 700 mV for BDT2 is comparable to that of Kaim's 1,4-bis(dimesitylboryl)benzene (690 mV): A. Schulz, W. Kaim, *Chem. Ber.* **1989**, *122*, 1863–1868.

[21] Almost identical UV-Vis absorption and fluorescence data are observed in the solid state. A thin film of FBDT2 shows a slightly enhanced fluorescence with a quantum yield of 1.8% (see Figure S9a in the Supporting Information).

[22] C. R. Wade, A. E. J. Broomsgrove, S. Aldridge, F. P. Gabbai, *Chem. Rev.* **2010**, *110*, 3958–3984.

[23] This finding is consistent with earlier results by Yamaguchi et al. See Ref. [6a].

[24] The binding process was also monitored by NMR titrations (see Figures S10–12 in the Supporting Information), and the reversibility confirmed by treatment with a large amount of water (see Figure S13 in the Supporting Information).