A Donor−Acceptor Dyad with a Highly Lewis Acidic Boryl Group

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A donor−π−acceptor dyad with a highly electron-deficient $B(C_6F_5)_2$ group as the acceptor has been prepared. 5-Diphenylamino-5′-bis(pentafluorophenyl)boryl-2,2′-bithiophene (**3**) was fully characterized by multinuclear NMR spectroscopy, mass spectrometry, and X-ray crystallography. The solid-state structure of **3** shows the presence of multiple π-stacking interactions rather than Lewis acid−base bonding between boron and nitrogen. Cocrystallized benzene molecules are incorporated into a channel-like framework of **3**. The electronic structure and photophysical properties were investigated by UV−visible absorption and emission spectroscopy and DFT calculations. The absorption and emission maxima experience a strong bathochromic shift relative to the non-fluorinated analogues, the origin of which has been further examined by DFT calculations.

Introduction

The electron-deficient nature of triorganoboranes provides for intriguing properties including their ability to act as efficient optoelectronic device materials and sensors for nucleophiles.[1] A key feature that enables these applications is the overlap between the empty p_π orbital on boron and an organic π-system of one (or more) of the substituents. Among these conjugated organoboranes, donor−π−acceptor dyads (D−π−A) represent a unique class of compounds. These push−pull systems, in which typically a dimesitylboryl group acts as the acceptor that is separated from a donor group such as an amine, a phosphine, a ferrocene moiety, or other electron-rich groups through a π-conjugated bridge, have been shown to display interesting linear and nonlinear optical properties, including large hyperpolarizabilities and two-photon excited fluorescence (TPEF).[2,3] Changes in the optical properties upon binding of nucleophiles to the empty p_π orbital on boron have recently been exploited in fluoride anion recognition.[4] Suitably substituted donor−π−acceptor organoborane derivatives have also been studied as bipolar materials for organic light emitting devices (OLEDs) and photovoltaic applications.[5,6]

In all of these intriguing applications, the nature of the donor and the effect of different conjugated bridging groups have been studied thoroughly.[2] However, the nature of the boryl group and, in particular, the effect of electron-donating or electron-withdrawing substituents on boron have not been examined in detail. Indeed, one of the general features of donor−bridge−acceptor compounds that have been previously studied is the use of bulky mesityl groups to sterically stabilize the boron center.

We have recently examined the effect of the electronic structure of aryl groups attached to boron on the photophysical and nucleophile binding properties of symmetric diboranes such as compounds **A** (Ar = 4-^{t}BuC_6H_4, C_6F_5, Fc/C_6F_5), in which two highly Lewis acidic boryl groups are connected via a conjugated bithiophene bridge.[7,8] We have also reported several

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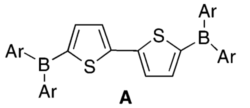
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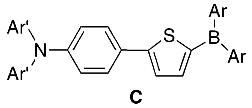
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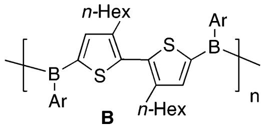
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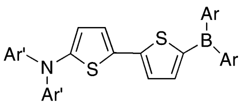
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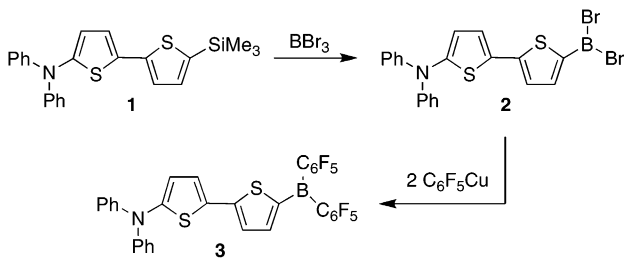
related main chain organoboron polymers **B** (Ar = 4-^{i}PrC$_6$H$_4$, C$_6$F$_5$, Fc) and studied their behavior as polymeric Lewis acids in the binding of amines.[9] In this Article, we explore how the relative Lewis acidity of boron affects the properties of a D−π−A dyad. Specifically, we discuss the synthesis and properties of a new D−π−A compound that features a bis(pentafluorophenyl)boryl group as the acceptor moiety and a diphenylamino group as the donor that is separated by a bithiophene bridge. In comparison to previously studied compounds that feature mesityl (Mes) groups on boron, such as the bipolar emitting OLED material **C** (Ar = mesityl, Ar′ = *p*-tolyl)[5] and the bithiophene-bridged compound **D** (Ar = mesityl/4-^{t}BuC$_6$H$_4$, Ar′ = Ph),[10] the strongly electron-withdrawing nature of the pentafluorophenyl groups was expected to enhance the Lewis acidity of boron, thereby possibly leading to greater electronic interaction through the bithiophene linker.[11]

Results and Discussion

Synthesis and Characterization. Lithiation of the free 5′-position of 5-diphenylamino-2,2′-bithiophene and subsequent treatment with Me$_3$SiCl gave 5-trimethylsilyl-5′-diphenylamino-2,2′-bithiophene (**1**) as a pale yellow solid in 82% yield. The 5′-borylated diphenylaminobithiophene **2** was obtained readily via silicon−boron exchange with BBr$_3$. The progress of the reaction can be conveniently monitored by a change of the color from pale yellow to dark red. The intermediate **2** was isolated in 66% yield upon repeated recrystallization from toluene, and its structure was established by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy. Treatment of **2** with 2 equiv of pentafluorophenyl copper[12−14] at −35 °C resulted in selective transfer of two pentafluorophenyl groups to boron (Scheme 1). Repeated recrystallization of the product from small amounts of toluene/hexanes gave **3** as dark red crystals in 75% yield. Compound **3** is highly sensitive to air and moisture as evident from an instantaneous color change from dark red to colorless upon exposure to air and therefore has to be handled and stored under nitrogen. This new D−π−A system was fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy and high-resolution MALDI-TOF-TOF mass spectrometry, and elemental analysis.

Scheme 1. Synthesis of the Donor−π−Acceptor Dyad 3



The ^{11}B NMR spectrum of **3** displays a resonance in the expected region for triarylboranes at δ 50.5, which indicates that there is no significant intermolecular interaction between nitrogen and the Lewis acidic boryl group. In the ^{1}H NMR spectra, the presence of four doublets for the bithiophene linker confirms the unsymmetric substitution pattern at the 5,5′-positions of bithiophene. For **3**, these signals appear in the region from 7.45 to 6.20 ppm in C$_6$D$_6$, and some of the resonances are partially overlapping with the phenyl resonances. The attachment of the bis(pentafluorophenyl)boryl group in **3** is reflected in the ^{19}F NMR spectrum, which shows a set of three resonances at δ −131.1 (F$_o$), −151.0 (F$_p$), −161.9 (F$_m$), where the separation of the *meta*- and *para*-fluorine atoms of $\Delta\delta_{m,p}$ = 10.9 is considerably smaller than that in B(C$_6$F$_5$)$_3$ ($\Delta\delta_{m,p}$ = 18.4)[14] as may be expected due to more effective π-overlap of the p$_\pi$ orbital on boron with the bithiophene π-system. The chemical shift difference is similar to that of PhB(C$_6$F$_5$)$_2$ with $\Delta\delta_{m,p}$ = 12.6.[14]

Dark red rodlike single crystals of **3** suitable for X-ray analysis were obtained by slow solvent evaporation from deuterated benzene, which is also incorporated into the solid. The X-ray structure of **3** confirms the tri-coordinate environment of boron and nitrogen and reveals a nearly coplanar arrangement of the central thiophene rings with a small angle of 11.7° between the S1,C1−C4 and S2,C5−C8 average planes (Figure 1). Selected bond distances and angles are included in Table 1. The sum of the C−B−C angles of 360.0° and that of the C−N−C angles of 359.8° demonstrate that the environments at boron and nitrogen are trigonal planar. The bond distances and bond angles of **3** are similar to those of the symmetric bifunctional Lewis acid (C$_6$F$_5$)$_2$B−Th−Th−B(C$_6$F$_5$)$_2$ (**A**).[7] For

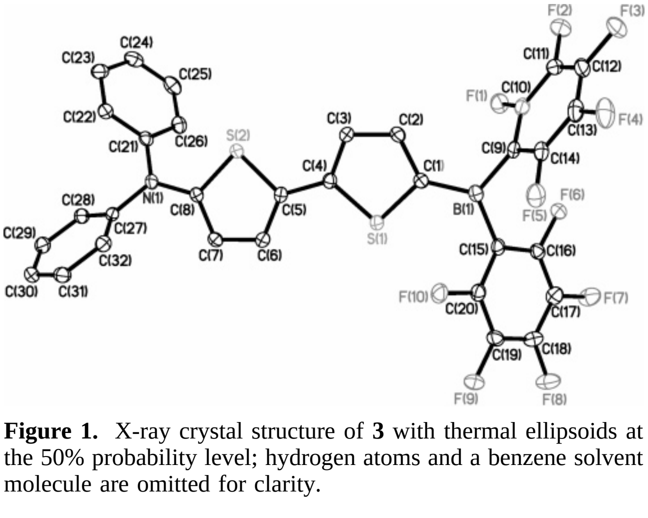


Figure 1. X-ray crystal structure of **3** with thermal ellipsoids at the 50% probability level; hydrogen atoms and a benzene solvent molecule are omitted for clarity.

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[8] Related diborylated bithiophene and terthiophene derivatives that feature mesityl groups on boron (**A**, Ar = 2,4,6-trimethylphenyl) have been studied by Shirota and co-workers as organic light emitting device (OLED) materials. See: (a) Noda, T.; Shirota, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9714−9715. (b) Noda, T.; Ogawa, H.; Shirota, Y. *Adv. Mater.* **1999**, *11*, 283−285.

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[11] It is interesting to note that a D−π−A system with a highly Lewis acidic B(C$_6$F$_5$)$_2$ moiety that is linked to a PMes$_2$ group through a short C$_6$F$_4$ bridge has recently been reported by Stephan to reversibly bind dihydrogen: (a) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124−1126. A related *ortho*-substituted system 1-(NPh$_2$)-2-[B(C$_6$F$_5$)$_2$]C$_6$H$_4$ has been reported by Roesler and Piers: (b) Roesler, R.; Piers, W. E.; Parvez, M. *J. Organomet. Chem.* **2003**, *680*, 218−222.

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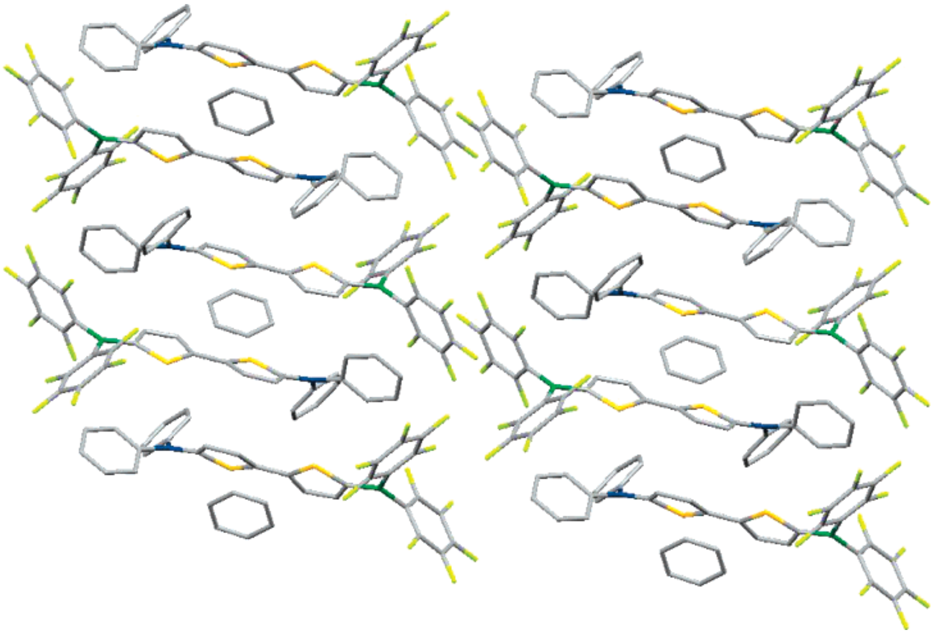

Figure 2. Plot illustrating the extended structure of **3** (view along the crystallographic *b*-axis); color code: blue (N), yellow (S), dark green (B), light green (F).

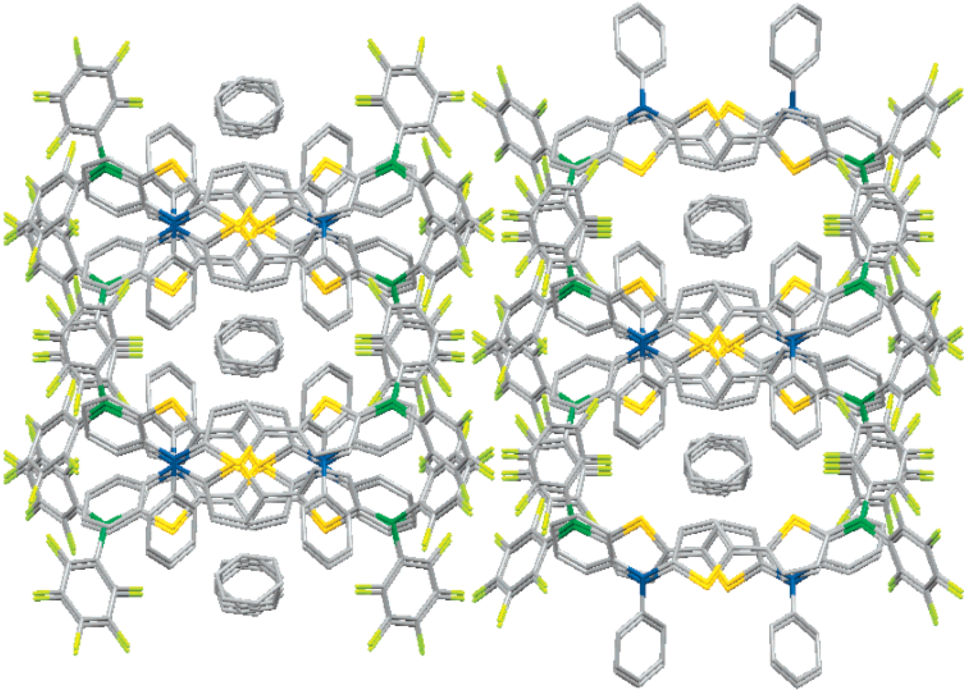

Figure 3. Plot illustrating the incorporation of C_6D_6 in channels of **3** (view along the crystallographic *c*-axis); color code: blue (N), yellow (S), dark green (B), light green (F).

instance, the distance between the two adjacent thiophene rings amounts to C(4)−C(5) = 1.438(3) Å for **3**, which is comparable to 1.445(7) Å for **A**. The B−C(thiophene) distance of 1.502(3) Å is also essentially identical to that of **A** (1.507(3) Å).

Extended Structure. As shown in Figure 2, adjacent molecules in the crystal lattice are oriented in a parallel and head-to-tail manner, such that the amine nitrogen is in proximity to the boron-bound thiophene ring (shortest distances C4(*x*,*y*,*z*)···N1(2 − *x*,*y*,0.5 − *z*) = 4.212 Å). Moreover, the nitrogen-attached thiophene rings are at a distance that suggests the presence of π-stacking interactions with the shortest intermolecular contact being C6(*x*,*y*,*z*)···C6(2 − *x*,*y*,0.5 − *z*) = 3.357 Å; however, the thiophene rings are oriented at a significant angle of 29.4° with respect to each other. π-Stacking between C_6F_5 moieties of adjacent molecules is also evident from the extended structure plot in Figure 2.

Intriguingly, the inclusion of one molecule of benzene for every two main molecules in the unit cell results in a channel-like extended structure. The diphenylaminobithiophene moieties form a highly symmetric framework that allows for inclusion of the benzene molecules (Figure 3). The shortest H···H distances between thiophene hydrogens across the channels are ca. 6.0 Å, and the F···F distances across the channels are ca. 11.1 Å. However, the phenyl rings of the diphenylamino groups extend far into the channels, thus limiting the effective channel diameters significantly. The exterior channel walls are decorated

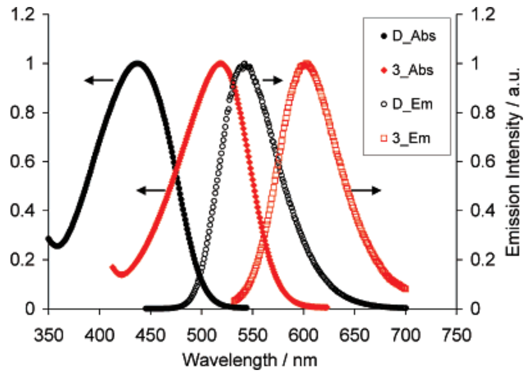

Figure 4. Comparison of the absorption and emission spectra of **3** with those of the non-fluorinated analogue (^{t}BuPh)MesB−ThTh−NPh$_2$ (**D**) in CH_2Cl_2.

with C_6F_5 moieties that show multiple short intermolecular F···F contacts ranging from 2.718 to 2.754 Å (Σ_{vdW} = 2.94 Å).

Photophysical Properties. Compound **3** is dark red colored due to a strong absorption at λ_{max} = 520 nm (lg ϵ = 4.0) in CH_2Cl_2 solution (Figure 4). This band is red-shifted by ca. 80 nm relative to the lowest energy absorption of the symmetric diboron analog **A** with λ_{max} = 413, 437(sh) nm. The band is attributed to charge transfer from the amino group to the highly Lewis acidic boron center. Upon excitation at 520 nm in CH_2Cl_2 solution, **3** emits red light with a fluorescence maximum at $\lambda_{em,max}$ = 620 nm. In comparison, the bithiophene-bridged species (^{t}BuPh)MesB−Th−Th−NPh$_2$ (**D**)[10] has a $\lambda_{max,abs}$ = 436 nm (lg ϵ = 4.6) and emits green light at $\lambda_{max,em}$ = 540 nm in CH_2Cl_2 solution. Thus, the absorption and emission bands for **3** are clearly red-shifted as a result of substitution of boron with electron-withdrawing C_6F_5 groups.[15] As expected for charge-transfer bands in donor−π−acceptor systems, a pronounced solvatochromic effect is observed. The absorption and to an even larger extent the emission maximum are significantly blue-shifted in hexanes ($\lambda_{max,abs}$ = 513 nm and $\lambda_{max,em}$ = 558 nm). More polar, coordinating solvents such as pyridine, MeCN, DMF, or DMSO bind to boron as evident from the spontaneous discoloration of the red solution. For instance, addition of excess pyridine to **3** in CH_2Cl_2 leads to a colorless solution with $\lambda_{max,abs}$ = 369 nm that shows, similar to the non-borylated diphenylaminobithiophene, an intense blue luminescence. The quantum efficiency of 2% for compound **3** in CH_2Cl_2 is low in comparison to related mesityl-substituted donor−acceptor dyads (e.g., 74% for (^{t}BuPh)MesB−Th−Th−NPh$_2$ (**D**)[10]), but not unlike the 3% found for the symmetric C_6F_5-substituted diboron analogue (**B**). The solid-state emission of **3** (635 nm) is further red-shifted by about 15 nm relative to that in CH_2Cl_2 solution, likely as a result of favorable π-stacking interactions in the solid state as evident from the crystal structure analysis.

DFT Calculations. To gain further insight into the origin of the observed bathochromic shift of the absorption and emission of fluorinated **3** in comparison to donor−acceptor dyads with mesityl or phenyl substituents on boron, we optimized the structure of **3** and of the non-fluorinated analogue **4** (Figure 5) using DFT calculations and determined for both compounds the vertical transition energies using TD-DFT calculations (Gaussian 2003, B3LYP).[16]

Table 1. Comparison of Selected Bond Lengths [Å] from X-ray Analysis of 3 with Data from DFT Calculations on 3 and Ph$_2$B−Th−Th−NPh$_2$ (4)

	3 (X-ray)	**3** (DFT)	**4** (DFT)
B(1)−C(1)	1.502(3)	1.5116	1.5442
B(1)−C(9)	1.583(3)	1.5824	1.5716
B(1)−C(15)	1.572(3)	1.5837	1.5707
S(1)−C(1)	1.734(2)	1.7643	1.7640
S(1)−C(4)	1.710(2)	1.7418	1.7455
C(1)−C(2)	1.387(3)	1.3959	1.3900
C(2)−C(3)	1.392(3)	1.3998	1.4094
C(3)−C(4)	1.385(3)	1.3961	1.3878
N(1)−C(8)	1.392(3)	1.3874	1.3947
N(1)−C(21)	1.425(3)	1.4296	1.4261
N(1)−C(27)	1.427(3)	1.4302	1.4273
S(2)−C(5)	1.734(2)	1.7633	1.7601
S(2)−C(8)	1.735(2)	1.7627	1.7659
C(5)−C(6)	1.360(3)	1.3821	1.3799
C(6)−C(7)	1.400(3)	1.4121	1.4168
C(7)−C(8)	1.360(3)	1.3822	1.3767
C(4)−C(5)	1.438(3)	1.4378	1.4448

Table 2. Calculated Electronic Transitions from TD-DFT Calculations

compound	transition	MO contributions	excitation energy eV (nm)	oscillator strength/f
3	$S_0 \rightarrow S_1$	HOMO→LUMO	2.44 (508)	0.8857
	$S_0 \rightarrow S_2$	HOMO−1→LUMO HOMO→LUMO+1	3.52 (352)	0.3450
	$S_0 \rightarrow S_3$	HOMO−2→LUMO	3.63 (341)	0.0011
4	$S_0 \rightarrow S_1$	HOMO→LUMO	2.65 (468)	0.7679
	$S_0 \rightarrow S_2$	HOMO→LUMO+1	3.59 (345)	0.1369
	$S_0 \rightarrow S_3$	HOMO−1→LUMO	3.66 (339)	0.2540

The calculated bond lengths for **3** correlate well with those obtained from X-ray diffraction analysis (Table 1). Importantly, the comparatively short B−C distance to the bithiophene bridge of 1.502(3) Å is well reproduced in the calculations (1.5116 Å). Similarly, an unusually small degree of bond alternation in the thiophene ring that is attached to boron is found from both the X-ray and the computed structure (X-ray, C−C distances from 1.385(3) to 1.392(3) Å; DFT, C−C distances from 1.396 to 1.400 Å). Most revealing is a comparison with the data computed for the non-fluorinated derivative **4**. The B−C distance for **4** is considerably longer with 1.5442 Å and the bond alternation more pronounced (C−C distances of 1.388−1.409 Å). These observations suggest enhanced electronic delocalization between boron and the thiophene ring with increasing Lewis acidity at boron. In this context, it is also interesting to note that a higher Mulliken charge of +0.220 is calculated for B in **3** than in **4** (+0.092).

Orbital plots for compounds **3** and **4** are displayed in Figure 5. The most obvious difference in the frontier orbitals is found for the HOMO level, where a significantly stronger contribution of the boron empty p-orbital leads to enhanced overlap with the organic π-system in **3**. The orbital energies for both the HOMO and the LUMO are lower in **3** in comparison to **4** as a

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(15) The absorption maximum for 1-(NPh$_2$)-2-[B(C_6F_5)$_2$]C_6H_4 (λ_{max} = 517 nm in CH_2Cl_2) is observed at similar energy. See ref 11b.

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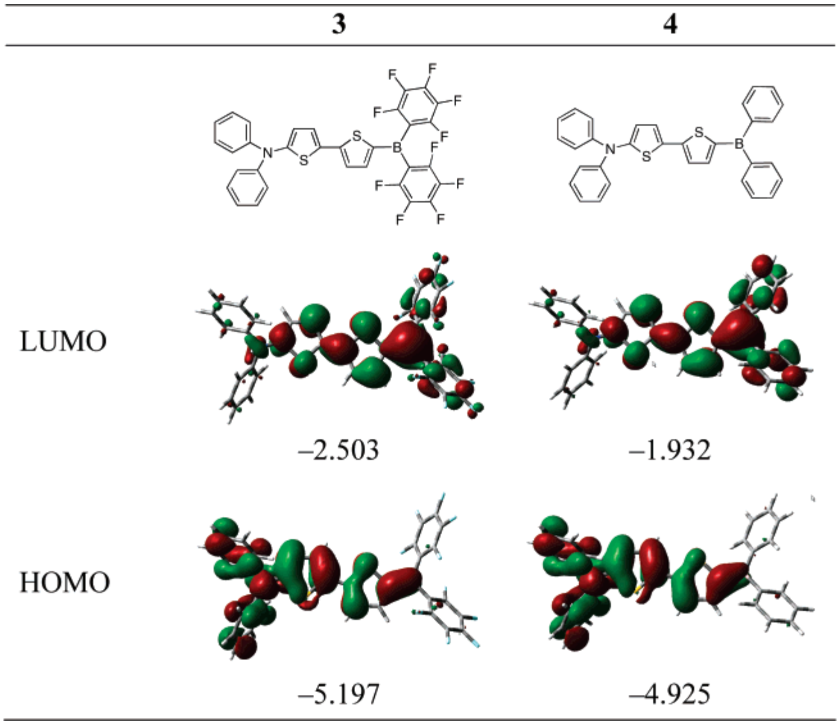

Figure 5. Computed contour plots and orbital energies (eV) of the frontier orbitals for **3** and **4** (isovalue = 0.02).

result of fluorination of the phenyl rings (Figure 5). However, the difference is considerably less pronounced for the HOMO than the LUMO level, which ultimately results in a smaller HOMO−LUMO gap of 2.694 eV for **3** in comparison to 2.993 eV for **4**. We next calculated the vertical electronic transitions for **3** and **4**, which are summarized in Table 2. For both compounds, the lowest energy transition corresponds to a high probability excitation from the HOMO to the LUMO level. The calculated excitation energy of 508 nm for **3** is in excellent agreement with the experimentally determined absorption maximum of 520 nm. Moreover, the lowest energy absorption for non-fluorinated **4** is much higher in energy (468 nm) and in a range similar to that of experimental data reported for (^{t}BuPh)-MesB−Th−Th−NPh$_2$ (**D**).[10]

Conclusions

The donor−π−acceptor dyad (**3**) with a highly electron-deficient bis(pentafluorophenyl)boryl group as the acceptor is readily prepared through successive treatment of 5-trimethylsilyl-5′-diphenylamino-2,2′-bithiophene with BBr$_3$ and the mild aryl transfer reagent (CuC$_6$F$_5$)$_4$. Because of the front strain exerted by the diphenylamino group, Lewis acid−base complexation is observed neither in solution nor in the solid state. However, multiple π-stacking interactions give rise to a channel-like structure that leads to inclusion of benzene solvent molecules. Most intriguing is the distinct bathochromic shift of both the absorption and the emission maxima for **3** in comparison to related non-fluorinated donor−acceptor species with diarylborane moieties as the acceptor functionality. The origin of this shift can be traced back to a considerably smaller HOMO−LUMO gap in **3**, which is a result of the different impact of fluorination on the energy of these frontier orbitals.

Experimental Section

Materials and General Methods. Me$_3$SiCl and ^{n}BuLi (1.6 M in hexanes) were purchased from Acros, and BBr$_3$ was from Aldrich. BBr$_3$ was distilled under high vacuum prior to use. 2-Diphenylamino-5,5′-bithiophene[17] and (C$_6$F$_5$Cu)$_4$[13,14] were prepared according to literature procedures, and 2-diphenylamino-2′-trimethylsilyl-5,5′-bithiophene was synthesized in analogy to the preparation of 2-diphenylamino-2′-tributylstannyl-5,5′-bithiophene.[18] All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Innovative Technologies). Ether solvents were distilled from Na/benzophenone prior to use. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies; alumina/copper columns for hydrocarbon solvents), and the chlorinated solvents were subsequently distilled from CaH$_2$ and degassed via several freeze pump thaw cycles.

Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

All 499.9 MHz ^{1}H, 125.7 MHz ^{13}C, 160.4 MHz ^{11}B, 470.2 MHz ^{19}F, and 79.45 MHz ^{29}Si NMR spectra were recorded at room temperature on a Varian INOVA spectrometer equipped with a boron-free 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). Solution ^{1}H and ^{13}C NMR spectra were referenced internally to solvent signals. ^{11}B NMR spectra were referenced externally to BF$_3$·Et$_2$O (δ = 0), ^{19}F NMR spectra to α,α',α''-trifluorotoluene (0.05% in C$_6$D$_6$; $\delta = -63.73$), and ^{29}Si NMR spectra to SiMe$_4$ (δ = 0). ^{11}B NMR spectra were acquired with boron-free quartz NMR tubes. The abbreviations Th (thiophene), Pf (2,3,4,5,6-pentafluorophenyl), and pst (pseudotriplet) were used for peak assignments.

UV−visible absorption data were acquired on a Varian Cary 500 UV−vis/NIR spectrophotometer. The fluorescence data and quantum yields were measured on a Varian Cary Eclipse fluorescence spectrophotometer. Anthracene was used as the standard for determination of the quantum yields. The quantum yield of anthracene was adopted from the Handbook of Photochemistry.[19]

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Sample solutions were prepared using a microbalance (±0.1 mg) and volumetric glassware.

The MALDI TOF/TOF measurement was performed on an Applied Biosystems 4700 Proteomics Analyzer in reflectron (+)-mode with delayed extraction. Benzo[*a*]pyrene was used as the matrix (10 mg/mL toluene). The sample was dissolved in toluene (10 mg/mL), mixed with the matrix in a 1:10 ratio, and then spotted on the wells of a sample plate inside a glovebox. Peptides were used for calibration (Des-Arg-Bradykinin (904.4681), Angiotensin I (1296.6853), Glu-Fibrinopeptide B (1570.6774), ACTH (clip 1−17) (2093.0867), ACTH (clip 18−39) (2465.1989), and ACTH (clip 7−38) (3657.9294)) with α-hydroxy-4-cyanocinnamic acid as the matrix.

X-ray diffraction intensities for **3** were collected on a Bruker SMART APEX CCD diffractometer at $T = 100(2)$ K using Mo Kα ($\lambda = 0.71073$ Å) radiation. Crystallographic data and details of the X-ray diffraction experiment and crystal structure refinement are given in Table S1. SADABS[20] absorption correction was applied, and the structure was solved using direct methods and completed by subsequent difference Fourier syntheses and refined by full matrix least-squares procedures on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. All software and sources scattering factors are contained in the SHELXTL (5.10) program package.[21] Crystallographic data for **3** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-657125. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

DFT calculations were performed with the Gaussian 03 program.[16,22] Geometries and orbital energies were calculated by means of the hybrid density functional B3LYP with the basis set of 6-31G(d). The input files and orbital representations were generated with Gaussview (isovalue of 0.02). Excitation data were determined using TD-DFT (B3LYP) calculations.

Caution! BBr_3 is toxic and highly corrosive and should be handled appropriately with great care. Fluorinated grease was used for ground glass joints in reactions involving BBr_3.

Synthesis of 2-Diphenylamino-2′-trimethylsilyl-5,5′-bithiophene (1). A solution of ^{n}BuLi in hexanes (5.6 mL, 1.6 M in hexanes, 9.0 mmol) was added dropwise to a solution of diphenylamino-bithiophene (2.50 g, 7.50 mmol) in THF (150 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and kept stirring for 3 h. The mixture was cooled back to −78 °C, Me_3SiCl (1.20 mL, 9.30 mmol) was added dropwise, and the mixture was then allowed to warm to room temperature overnight. The crude product was loaded on an alumina column and eluted with 5% diethyl ether/hexanes mixture. The product was obtained as a colorless solid upon removal of the solvents. Yield: 2.50 g (82%). ^{1}H NMR ($CDCl_3$, 499.893 MHz): $\delta = 7.33$ (pst, $^3J = 7.5$ Hz, 4H, Ph−H_m), 7.24 (d, $^3J = 8.0$ Hz, 4H, Ph−H_o), 7.16 (br, 2H, Th−H7,8), 7.10 (t, $^3J = 7.0$ Hz, 2H, Ph−H_p), 7.02 (d, $^3J = 3.5$ Hz, 1H, Th−H4), 6.64 (d, $^3J = 3.5$ Hz, 1H, Th−H3), 0.39 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$, 125.7 MHz): $\delta = 150.7$ (Th−C), 147.8 (Ph−C_i), 143.1 (Th−C), 139.2 (Th−C), 134.9 (Th−C), 131.6 (Th−C), 129.4 (Ph−C_m), 124.3 (Th−C), 123.4 (Ph−C_p), 122.9 (Ph−C_o), 122.5 (Th−C), 121.4 (Th−C), 0.1 ($SiMe_3$). ^{29}Si NMR ($CDCl_3$, 99.3 MHz): $\delta = -6.3$. Anal. Calcd for $C_{23}H_{23}NS_2Si$ (405.65): C, 68.10; H, 5.71; N, 3.45. Found: C, 68.02; H, 5.57; N, 3.41.

Reaction of 1 with BBr_3. Synthesis of 2. A solution of BBr_3 (1.02 g, 4.08 mmol) in toluene (10 mL) was added at −78 °C to a solution of **1** (1.65 g, 4.07 mmol) in toluene (40 mL). The reaction mixture was allowed to slowly warm to room temperature and left stirring overnight. All volatile components were removed under high vacuum, and the crude red material was recrystallized twice from toluene/hexanes mixture at −35 °C. Isolated yield: 1.35 g (66%). ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.90$ (d, $^3J = 4.0$ Hz, 1H, Th−H8), 7.32 (pst, $^3J = 7.0$ Hz, 4H, Ph−H_m), 7.22 (m, 5H, Ph−H_o, Th−H4/7), 7.19 (d, $^3J = 4.0$ Hz, 1H, Th−H4/7), 7.13 (t, $^3J = 8.0$ Hz, 2H, Ph−H_p), 6.55 (d, $^3J = 4.0$ Hz, 1H, Th−H3). ^{13}C NMR ($CDCl_3$, 125.7 MHz): $\delta = 155.1$ (Th−C), 154.9 (Th−C), 147.3 (Ph−C_i), 145.3 (Th−C), 129.7 (Ph−C_m), 127.5 (Th−C), 126.1 (Th−C), 125.1 (Th−C), 124.5 (Ph−C_p), 124.0 (Ph−C_o), 118.7 (Th−C), Th−C9 not observed. ^{11}B NMR ($CDCl_3$, 160.7 MHz): $\delta = 45.7$ ($w_{1/2} = 600$ Hz). Anal. Calcd for $C_{20}H_{14}BBr_2NS_2$ (503.08): C, 47.75; H, 2.80; N, 2.78. Found: C, 47.55; H, 2.59; N, 2.72.

Reaction of 2 with 2 equiv of C_6F_5Cu: Synthesis of 3. A solution of "C_6F_5Cu" (0.46 g, 1.99 mmol) in toluene (10 mL) was cooled to −35 °C and then added dropwise to a solution of **2** (0.50 g, 0.99 mmol) in toluene (10 mL) at −35 °C. The reaction mixture was allowed to slowly warm to room temperature and left stirring for 1 h. The mixture was then filtered through a fritted glass funnel, and all volatile components were removed under high vacuum. The product was obtained upon recrystallization from a fairly concentrated solution in a toluene/hexanes mixture at −35 °C. Isolated yield: 0.50 g (75%). ^{1}H NMR (C_6D_6, 500 MHz): $\delta = 7.45$ (d, $^3J = 4.0$ Hz, 1H, Th−H), 7.06 (d, $^3J = 7.5$ Hz, 4H, Ph−H_o), 7.01 (pst, $^3J = 8.0$ Hz, 4H, Ph−H_m), 6.88−6.85 (m, 4H, Ph−H_p and Th−H), 6.20 (d, $^3J = 4.0$ Hz, 1H, Th−H). ^{19}F NMR (C_6D_6, 470.2 MHz): $\delta = -131.1$ (m, 4F, Pf−F_o), −151.0 (t, $^3J_{FF} = 20$ Hz, 2F, Pf−F_p), −161.9 (m, 4F, Pf−F_m). ^{13}C NMR (C_6D_6, 125.7 MHz): $\delta = 159.1$ (Th−C), 157.3 (Th−C), 149.1 (Ph−C_i), 147.6 (Th−C), 146.2 (dm, $^1J_{CF} = 244$ Hz, Pf−C_o), 142.9 (dm, $^1J_{CF} = 256$ Hz, Pf−C_p), 141.5 (Th−C9), 138.1 (dm, $^1J_{CF} = 252$ Hz, Pf−C_m), 130.3 (Ph−C_m), 126.5 (Th−C), 125.9 (Th−C), 125.4 (Ph−C_p), 124.8 (Ph−C_o), 117.9 (Th−C), 114.3 (t, $^2J_{CF} = 33$ Hz, Pf−C_i). ^{11}B NMR ($CDCl_3$, 160.7 MHz): $\delta = 50.5$ ($w_{1/2} = 1200$ Hz). UV−vis (CH_2Cl_2, 4.7×10^{-5} M), $\lambda_{max} = 520$ nm (lg $\epsilon = 4.0$) and 350 (lg $\epsilon = 4.0$); fluorescence (CH_2Cl_2, 4.7×10^{-5} M), $\lambda_{em,max} = 620$ nm, $\Phi = 0.02$ ($\lambda_{exc} = 520$ nm); UV−vis/fluorescence in hexanes, $\lambda_{max} = 513$ nm, $\lambda_{em,max} = 558$ nm, $\Phi = 0.09$ ($\lambda_{exc} = 513$ nm); fluorescence of solid, $\lambda_{em,max} = 635$ nm ($\lambda_{exc} = 515$ nm). High-resolution MALDI TOF/TOF: $m/z = 677.0212$ (calcd for $^{12}C_{32}{}^1H_{14}{}^{11}B^{19}F_{10}{}^{14}N^{32}S_2$ 677.0501). Anal. Calcd for $C_{32}H_{14}BF_{10}NS_2$ (677.39): C, 56.74; H, 2.08; N, 2.07. Found: C, 56.80; H, 1.94; N, 2.11.

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Supporting Information Available: Crystallographic data for compound **3** including tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters. Computed contour plots of selected molecular orbitals for **3** and **4** and calculated orbital energies (eV) from DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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