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**Fluorescence**

**D-π-A Triarylboron Compounds with Tunable Push-Pull Character Achieved by Modification of Both the Donor and Acceptor Moieties**


**Abstract:** The push-pull character of a series of donor-bithiptyl-acceptor compounds has been tuned by adopting triphenylamine or 1,1,7,7-tetramethyljulolidine as a donor and B(2,6-Mes-4-R-C_{6}H_{4})_{2} (R = Me, CF_{3} or 3,5-(CF_{3})_{2}C_{6}H_{4}) or B(2,4,6-(CF_{3})_{3}C_{6}H_{2})_{2} as an acceptor. Ir-catalyzed C–H borylation was utilized in the derivatization of the boryl acceptors and the tetramethyljulolidine donor. The donor and acceptor strengths were evaluated by electrochemical and photophysical measurements. In solution, the compound with the strongest acceptor, B(2,4,6-(CF_{3})_{3}C_{6}H_{2})_{2} ((FMes)_{2}B), has strongly quenched emission, while all other compounds show efficient green to red (Φ<sub>e</sub> 0.80–1.00) or NIR (Φ<sub>e</sub> 0.27–0.48) emission, depending on solvent. Notably, this study presents the first examples of efficient NIR emission from three-coordinate boron compounds. Efficient solid-state red emission was observed for some derivatives, and interesting aggregation-induced emission of the (FMes)_{2}B-containing compound was studied. Moreover, each compound showed a strong and clearly visible response to fluoride addition, with either a large emission-color change or turn-on fluorescence.

**Introduction**

Three-coordinate organoboron compounds are an important class of materials for optical and optoelectronic applications.[1-7] In particular, donor-(π-spacer)-acceptor (D-π-A) organoboron systems with an aromatic amine donor group and a boryl acceptor group have attracted tremendous research interest.[8-11] Such push-pull systems usually show strong intramolecular charge-transfer (ICT) emission, which make them promising materials for applications in nonlinear optics (NLO),[9] organic light-emitting diodes (OLEDs),[10] and anion sensing.[11] Modification of each of the donor, π-spacer, or acceptor groups has been shown to be effective for tuning the properties of the materials.[8-11] Considering the ‘push-pull’ structure and the ICT character of the excited states of these D-π-A compounds, the incorporation of strong donor and/or acceptor groups is important for improving some of the properties of this type of boron compounds: 1) higher HOMO and lower LUMO energies arising from stronger donors and acceptors, respectively, can enhance the carrier-injecting properties of the materials in OLEDs,[12] which may improve device performance; 2) smaller HOMO-LUMO gaps may lead to red/near-infrared (NIR) emissive materials, which are rare for three-coordinate boron-based systems, particularly in the solid state,[3i,13] 3) red-shifted emission, caused by a stronger acceptor, may increase the difference in emission color before and after fluoride or cyanide coordination to the boron center and, thus, facilitate naked-eye detection of these important analytes.[4c] Therefore, we were motivated to develop organoboron compounds with strong push-pull character by strengthening the acceptor and/or donor groups. Up until now, many different donors have been employed in this type of compound:[8-11] however, the boryl acceptor is still quite limited, with the group bis(mesityl)boryl ((FMes)_{2}B) typically used, in which the sterically bulky mesityl substituents decrease the reactivity of the boron center towards nucleophiles, providing air stability. Although a few attempts to tune the boryl acceptors have been reported,[14] most of the modified boryl groups do not provide sufficient air-stability for the boron compounds, due to a lack of steric protection of the boron center.[4d,14a-d]

Recently, we introduced the strongly electron-accepting bis(5-fluoromesityl)boryl ((FMes)_{2}B) group into D-π-A systems.[15] In the present study, we modified the Mes_{2}B group through substitution of the methyl substituents para to the boron atom by electron-withdrawing perfluorophenyl and 3,5-bis(trifluoromethyl)phenyl substituents, to produce the acceptor groups (Pfp)_{2}B and (Tfp)_{2}B, respectively (Scheme 1). To allow comparison of the acceptor strength of the known Mes_{2}B and (FMes)_{2}B groups with the newly obtained (Pfp)_{2}B and (Tfp)_{2}B...
groups, as well as to systematically study their influence on material properties, compounds 1–4 with the same triphenylamine (Tpa) donor group and each of these acceptors have been synthesized. Furthermore, to elucidate the influence of enhanced push-pull character, 5 and 6 have been prepared, which are analogues of 2 and 3 with a stronger 1,1,7,7-tetramethyljulolidine (Tmjul) donor group in conjunction with the (Pfp)B and (Tfp)B acceptor groups. In all of these compounds, 5,5′-substituted 2,2′-bithienyl was chosen as the π-spacer, because its electron-rich character and often close-to-coplanar structure were expected to facilitate long-wavelength emission.[14]

![Scheme 1. Molecular structures of 1–6.](image)

Results and Discussion

Synthesis

The procedures used to synthesize compounds 1–6 are summarized in Scheme 2. 1–6 were obtained by reactions between the appropriate Tpa/Tmjul–bithienyl–Li and R₂BF precursors in an adaptation of the typical method for synthesizing three-coordinate organoboron compounds.[15] The Tpa/Tmjul–bithienyl–Li reagents were prepared by lithiation of the products of the Suzuki–Miyaura cross-coupling reactions of Tpa–Br with [(2,2′-bithiophene)-5,5′-]boring acid or Tmjul–Bpin with 5-ido-2,2′-bithiophene. The Tmjul–Bpin was obtained in high yield (88%) by regioselective iridium-catalyzed C–H borylation[17] of Tmjul–H on a multi-gram scale in hexane with a simple workup of filtration followed by washing with cold solvents (the crystal structure is shown in Figure S1). The C–H borylation of Tmjul–H is stericly controlled and, consequently, highly selective, leading to exclusive borylation at the 9-position, i.e. para to the nitrogen atom. This provides a facile and rapid route to the complementary nucleophilic coupling partner to 9-bromojulolidine, a compound that is widely used in the construction of D–π–A chromophores.[18]

Furthermore, we note that simple adaptation of the method might also be expected to expedite the synthesis of related Bpin-substituted planarized triphenylamines[19] and 2,6-substituted anilines[20] of pharmaceutical relevance, both of which otherwise require a two-step procedure of bromination and Pd-catalyzed Miyaura borylation. Key precursors Br–Pfp and Br–Tfp, required for modifying the boryl moiety, were prepared by Ir-catalyzed C–H borylation of 2,6-dimethylbromobenzene at the 4-position in 95% yield on a multi-gram scale, and subsequent Suzuki–Miyaura cross coupling with pentafluoriodobenzene or 3,5-bis(trifluoromethyl)iodobenzene in 79–80% yield; notably, the borylation reaction was regiospecific and was, therefore, pivotal to ensuring high isolated yields of the products. The Grignard reagents prepared from these two precursors were reacted with BF₂OEt₂ to produce the R₂BF precursors for the synthesis of 2, 3, 5 and 6. These compounds were characterized by multinuclear NMR spectroscopy, mass spectrometry, and elemental analysis. The room temperature [19F]{¹H} NMR spectrum of 4 shows three broad peaks at –50.4, –52.1 and –56.5 ppm (1:1:2) for the four CF₃ groups of the FMes moieties that are in positions ortho to the boron atom and one singlet at –63.4 ppm for the two CF₃ groups at the para-positions (Figure S4), which indicates restricted rotation of the boron-bonded aryl rings. A similar phenomenon has been observed in our studies of Ar–B(FMes)₂ compounds.[15]

At 223 K, the signals for the six CF₃ groups are fully separated, resulting in four quartets (two pairs, J = 11 and 13 Hz, respectively) and two singlets for the ortho- and para-CF₃ groups, respectively (Figure S4). This is different from the behavior of Tpa–B(FMes)₂[15] which only displays two quartets and one singlet at 223 K for the ortho- and para-CF₃ groups, respectively. The loss of the C₂ symmetry along the B–C(thiényl) bond in compound 4, accompanied by restricted rotation, is responsible for the complete inequity of the six CF₃ groups at low temperature, and the observed splitting of the signals into quartets for the ortho-CF₃ groups is due to through-space [19F]–[19F] coupling.[15]

Crystal Structures

To confirm the molecular structures and to investigate the influence of different donors and acceptors on the molecular conformations, single crystals of these compounds were grown and their structures were determined by X-ray diffraction. Single crystals of 2 were obtained by cooling the seeded melt and those of 4 were grown by crystalization from hexane solution at –30 °C. The crystal structures are shown in Figure 1, and selected bond lengths and dihedral angles are given in Table 1. The boron
atoms in both structures have a nearly perfect trigonal planar configuration, with the sum of the three C–B–C angles close to 360°. In 4, the B1–C1 (1.605(4) Å) and B1–C9 (1.601(4) Å) bonds in the boryl group are significantly longer than the B1–C17 bond (1.518(4) Å), while the corresponding differences between the two types of B–C bonds in 2 are smaller (ca. 0.03–0.05 Å). It has been observed previously that replacement of (Mes)2B, for example, by more electron-withdrawing boryl groups, such as (C6F5)2B[14a,b] and (FMes)2B, [15] leads to an increase in such bond-length differences. Therefore, the large bond-length difference in 4 reflects the stronger acceptor strength of (FMes)2B than (Pfp)2B. In 2, the dihedral angles between the BC3 plane and the 2,4,6-trisubstituted phenyl rings (P1 and P2) are similar to each other (57.8(2)° and 57.7(2)°) and to the analogous dihedral angles (ca. 57–59°) in the compound 4-Me3N-C6H4–CH=CH–2′,5′-thienyl–B(Mes)2[15] (Figure 1). In compound 4, the two thienyl rings (T1 and T2) are 19.0(2)° and 12.7(2)° in 2 and 4, respectively, allowing good conjugation. The dithienyl H-system is also relatively planar with respect to the adjacent BC3 plane and the diphenylamine-substituted phenyl ring (P3), exhibiting dihedral angles of 15.8(2)° in 2 and 19.1(2)° in 4 between T1 and the BC3 plane and 25.5(2)° in 2 and 18.6(1)° in 4 between T2 and P3. In compound 2, the two C6F5 groups (P4 and P5) and the adjacent phenyl rings (P1 and P2, respectively) exhibit dihedral angles of 51.6(3)° and 61.8(2)° and are, thus, expected to be relatively poorly conjugated in the solid-state.

Table 1. Selected bond lengths (Å) and dihedral angles (°) for 2 and 4, as obtained by single-crystal X-ray diffraction.

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1–C1</td>
<td>1.584(9)</td>
<td>1.605(4)</td>
</tr>
<tr>
<td>B1–C15/B1–C9</td>
<td>1.565(9)</td>
<td>1.601(4)</td>
</tr>
<tr>
<td>B1–C29/B1–C17</td>
<td>1.532(9)</td>
<td>1.518(4)</td>
</tr>
<tr>
<td>∠P1–BC3 plane</td>
<td>59.9(3)</td>
<td>67.5(2)</td>
</tr>
<tr>
<td>∠P2–BC3 plane</td>
<td>57.8(2)</td>
<td>43.9(2)</td>
</tr>
<tr>
<td>∠T1–BC3 plane</td>
<td>15.8(2)</td>
<td>19.1(2)</td>
</tr>
<tr>
<td>∠T1–T2</td>
<td>19.0(2)</td>
<td>12.7(2)</td>
</tr>
<tr>
<td>∠T2–P3</td>
<td>25.5(2)</td>
<td>18.6(1)</td>
</tr>
<tr>
<td>∠P1–P4</td>
<td>51.6(3)</td>
<td>-</td>
</tr>
<tr>
<td>∠P2–P5</td>
<td>61.8(2)</td>
<td>-</td>
</tr>
</tbody>
</table>

Absorption Spectra

In toluene, all compounds show a broad and structureless lowest-energy absorption band with large molecular extinction coefficients ranging from 32 000 to 42 000 M⁻¹ cm⁻¹ (Figure 2). Considering the push-pull structures of these compounds, their absorption bands are assigned as ICT transitions. The absorption maxima (λabs) of 1–3 are located at 433, 452 and 457 nm, respectively (Table 2). The very close values of λabs for 2 and 3 indicates that (Pfp)2B and (Tfp)2B have similar acceptor strengths. A spectral red shift of ca. 20 nm (1000 cm⁻¹) from 1 to 2 and 3 shows the effect of increased acceptor strength; however, the absorption maximum of 4 is significantly red shifted to 507 nm (a further 2200 cm⁻¹), indicating that (FMes)2B is a much stronger acceptor than Mes2B, (Pfp)2B, and (Tfp)2B. By enhancing the donor strength, the λabs of 5 (484 nm) and 6 (487 nm) are red shifted by ca. 30 nm (1400 cm⁻¹) compared to those of the corresponding Tpa-substituted analogues, 2 and 3, but still not to the same extent as 4. The λabs of these compounds are slightly dependent on the solvent polarities: from toluene to CH3CN, a negative shift of 5–23 nm was observed.

Figure 1. Molecular structures of 2 (top) and 4 (bottom) from single-crystal X-ray diffraction. Hydrogen atoms are omitted for clarity. The phenyl rings related to the discussion are labeled P1–P5, and the thienyl rings are labeled T1 and T2. Element (color): carbon (gray), nitrogen (blue), sulfur (yellow), boron (orange) and fluorine (green).

Figure 2. UV-visible absorption spectra of 1–6 in toluene.
DFT and TD-DFT Calculations

To understand further the electronic structures of these compounds, and to examine the orbitals involved in the electronic transitions, we carried out DFT (B3LYP/6-31G(d)) and TD-DFT (CAM-B3LYP/6-31G(d)) calculations for 1, 2, 4 and 5. Considering the quite similar profiles and peak wavelengths of the absorption spectra of 2 and 3, and 5 and 6, the electronic structures of 3 and 6 are expected to be similar to those of 2 and 5, respectively. TD-DFT calculations show that the S\(_1\) ← S\(_0\) transitions of these compounds have large oscillator strengths, greater than or equal to 1.466, and the excitation wavelengths for the S\(_1\) ← S\(_0\) transitions are 392, 405, 424 and 410 nm for 1, 2, 4 and 5, respectively (Table 3). These calculated values overestimate the experimental \(\lambda_{\text{abs}}\) values by 0.30–0.46 eV, which is not untypical for such systems\(^{[6,15]}\). Importantly, the results reproduce the variation in observed values of \(\lambda_{\text{abs}}\). According to the calculations, for all three compounds, the S\(_1\) ← S\(_0\) transitions are predominantly LUMO ← HOMO with a small contribution from LUMO ← HOMO–1. As can be seen from Figure 3, the HOMO and HOMO–1 are distributed on the donor and the bithienyl-spacer for all compounds, while the LUMO is mainly distributed on the acceptor and the bithienyl-spacer. Therefore, these transitions possess ICT character, which is consistent with our assignment of the experimental lowest-energy absorption bands as being due to ICT.

<table>
<thead>
<tr>
<th>Transition</th>
<th>(E) / eV(^{[4]})</th>
<th>(\lambda) / nm(^{[4]})</th>
<th>Dominant Components(^{[1]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S(_1) ← S(_0) (1.618)</td>
<td>3.16 (2.86)</td>
<td>392 (433)</td>
</tr>
<tr>
<td>2</td>
<td>S(_1) ← S(_0) (1.676)</td>
<td>3.06 (2.74)</td>
<td>405 (452)</td>
</tr>
<tr>
<td>3</td>
<td>S(_1) ← S(_0) (1.470)</td>
<td>2.93 (2.50)</td>
<td>424 (507)</td>
</tr>
<tr>
<td>4</td>
<td>S(_1) ← S(_0) (1.466)</td>
<td>3.02 (2.56)</td>
<td>410 (484)</td>
</tr>
<tr>
<td>5</td>
<td>S(_1) ← S(_0) (1.466)</td>
<td>3.02 (2.56)</td>
<td>410 (484)</td>
</tr>
</tbody>
</table>

[a] Values in parentheses are experimental longest-wavelength absorption maxima in toluene. [b] Components with greater than 10% contribution shown. Percentage contribution approximated by \(2 \times (c)^2 \times 100\%\), where \(c\) is the coefficient for the particular orbital rotation.
Figure 3. DFT (B3LYP/6-31G(d)) calculated frontier orbitals for 1, 2, 4 and 5. Surface isovalue: ± 0.02 [e a.u.].

Figure 4. Cyclic voltammograms of 1–6. Oxidation and reduction processes were measured in CH₂Cl₂ and THF, respectively.

Table 4. Cyclic voltammetric data[a] and experimental HOMO and LUMO energies.

<table>
<thead>
<tr>
<th></th>
<th>E_{ox} [V]</th>
<th>E_{red} [V]</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
<th>E_g [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+0.39</td>
<td>–2.23</td>
<td>–5.19</td>
<td>–2.57</td>
<td>2.62</td>
</tr>
<tr>
<td>2</td>
<td>+0.41</td>
<td>–2.04</td>
<td>–5.21</td>
<td>–2.76</td>
<td>2.45</td>
</tr>
<tr>
<td>3</td>
<td>+0.41</td>
<td>–2.04</td>
<td>–5.21</td>
<td>–2.76</td>
<td>2.45</td>
</tr>
<tr>
<td>4</td>
<td>+0.43</td>
<td>–1.61</td>
<td>–5.23</td>
<td>–3.19</td>
<td>2.04</td>
</tr>
<tr>
<td>5</td>
<td>+0.04</td>
<td>–2.10</td>
<td>–4.84</td>
<td>–2.70</td>
<td>2.14</td>
</tr>
<tr>
<td>6</td>
<td>+0.04</td>
<td>–2.11</td>
<td>–4.84</td>
<td>–2.69</td>
<td>2.15</td>
</tr>
</tbody>
</table>

[a] Potentials are given vs. ferrocene/ferrocenium (Fc/Fc⁺). [b] Measured in CH₂Cl₂. [c] Measured in THF. [d] Estimated assuming that the HOMO of Fc lies 4.8 eV below the vacuum level. [e] Values in parentheses are optical band gaps calculated from the low-energy edge of the absorption spectra in toluene.

Electrochemistry

Electrochemical measurements were carried out to evaluate further the acceptor strength and to confirm experimentally the influence of different donors and acceptors on the HOMO and LUMO levels and energy gaps. Cyclic voltammetry measurements (Figure 4 and Table 4) show that both the reduction and oxidation processes of these compounds are reversible, indicating their bipolar character. Compared to 1 (E_{ox} = –2.23 V), compounds 2 (E_{ox} = –2.04 V) and 3 (E_{ox} = –2.04 V) are more easily reduced with reduction potentials positively shifted by ca. 0.2 V. The reduction of 4 (E_{ox} = –1.61 V) is much easier than that of 2 or 3, exhibiting an E_{ox} positively shifted by ca. 0.4 V. These results confirm an increased acceptor strength in the order of (Mes)₂B < (Pfp)₂B ≈ (Tp)₂B << (FMes)₂B. The oxidation potentials of 1–4 are very similar, exhibiting little increase with enhanced acceptor strength and, thus, the donor and acceptor groups are relatively electronically decoupled in the ground state. The stronger Tmj donor groups of 5 and 6 make their oxidation (E_{ox} = +0.04 V) much easier than that of either 2 or 3 (E_{ox} = +0.41 V) bearing triarylamine donors. The increased donor strength also has a slight influence on E_{ox}, making the reduction of 5 and 6 slightly more difficult than that of either 2 or 3 by ca. 0.06 eV. From the electrochemical data, the HOMO and LUMO energy levels and energy gaps were calculated (Table 4). Compared to 1, the LUMOs of 2 and 3 are stabilized by 0.19 eV, while their HOMO levels are stabilized by only 0.02 eV, resulting in reduced HOMO-LUMO gaps. Moving from 2 and 3 to 5 and 6, the HOMOs are strongly elevated while LUMO levels are only slightly raised, further leading to reduced energy gaps. The extremely strong acceptor in 4 results in a significantly stabilized LUMO level, which serves as a key factor leading to its small energy gap, the smallest amongst the compounds presented here. Therefore, the energy gaps obtained from electrochemical measurements show the same trend as the optical band gaps.

Photoluminescence

In solution, the emission wavelengths and observed emission colors of these compounds strongly depend on the solvent (Figure 5 and Table 2). With increased solvent polarity, the emission spectra of all of the compounds broaden and exhibit a significant red shift. This is attributed to a highly polarized ICT excited state, which is typical for D-π-A compounds. From toluene to CH₂CN, the emission maxima (λ_em) of 1 shifts from 504 to 599 nm (3100 cm⁻¹), and the color of the emission varies from green to orange. With its increased acceptor strength, 2 shows red-shifted emission in every solvent compared to 1, exhibiting emission ranging from yellow-green to red with λ_em shifting from 530 to 638 nm. It is notable that compounds 1 and 2 show very high Ph values (0.92–1.00), even for the orange/red emission in polar solvents, which is remarkable and uncommon for push-pull systems, since emission from ICT states is usually quenched in more polar solvents. Only a few D-π-A type organoboron compounds showing solvent-independent Ph values close to unity have been reported.[65] The emission spectra of 3 are similar to those of 2 in each solvent, consistent with their similar absorption
spectra, as discussed above. Compound 3 also has high \( \Phi_F \) (0.85–0.96) values in all three solvents used; however, the emission is somewhat more easily quenched by polar CH\(_2\)CN compared to 1 and 2. Compound 4, with the strongest acceptor, displays a huge spectral red shift in toluene (\( \lambda_{em} = 644 \) nm) of 109–140 nm (3200–4300 cm\(^{-1}\)) compared to 1–3. However, the emission of 4 in toluene is too weak to obtain a reliable value of \( \Phi_F \), and in more polar solvents, 4 is almost nonemissive. 5 and 6 have close \( \lambda_{em} \), similar to the case of 2 and 3, but their emission spectra are red-shifted and more sensitive toward solvents in relation to those of 2 and 3, resulting from their stronger donors. These compounds show efficient orange (\( \lambda_{em} = ca. 585 \) nm) and red (\( \lambda_{em} = ca. 664 \) nm) emission in toluene and THF, respectively, with \( \Phi_F \) ranging from 0.80–0.95. It is notable that these compounds display NIR (\( \lambda_{em} > 700 \) nm) emission in CH\(_2\)CN solution; this emission is somewhat quenched relative to that in less polar solvents (Table 2), but the \( \Phi_F \) values are still good to high: 0.48 for 5 and 0.27 for 6. As far as we are aware, these two compounds represent the first examples of three-coordinate boron compounds showing efficient NIR emission. We note, however, that a (Mes)\(_2\)B-containing iridium complex with two emission bands, one in the visible and one in the NIR region, was reported previously,\(^{[23]}\) but this compound had a very low emission quantum yield of 5.7 \( \times 10^{-4}\). Moreover, recently, a borondipyrromethane derivative with (Mes)\(_2\)B-containing substituents was reported to show NIR emission; however, \( \Phi_F \) was not mentioned.\(^{[24]}\) In addition, in our previous work, we observed that Tpa–B(FMes)\(_2\) displays NIR emission in THF; however, the \( \Phi_F \) could not be determined because the emission was weak.\(^{[15]}\) As compounds exhibiting NIR emission normally have relatively small \( \Phi_F \) values, the quantum yield of 5 is among the highest reported,\(^{[25]}\) to the best of our knowledge. In addition, our new NIR-emitting compounds also possess sizeable Stokes shifts of over 7000 cm\(^{-1}\) (ca. 270 nm) in CH\(_2\)CN. To understand the factors influencing the \( \Phi_F \) values of the present systems, the \( \Phi_F \) and fluorescence lifetimes (\( \tau_F \)) of 1–3, 5 and 6 were measured in all three solvents and the radiative (\( k_r \)) and nonradiative (\( k_{nr} \)) rate constants were calculated from these data. Due to its very weak emission, related data could not be obtained for 4. The \( k_r \) values of these compounds show the following trends: 1) independent of solvent, \( k_r \) becomes smaller in the order of 1 > 2 = 3 > 5 = 6, due to enhanced push-pull character; and 2) for each compound, \( k_r \) decreases with increased solvent polarity. The \( k_{nr} \) values of 1–3 are very small and do not show obvious changes between the three solvents, which results in high and solvent-independent \( \Phi_F \) values for these compounds. In contrast, both 5 and 6 possess obviously increased \( k_{nr} \) values upon changing from toluene to CH\(_2\)CN solutions, with a more significant increase for 6. The combined decrease in \( k_r \) and increase in \( k_{nr} \), with increasing solvent polarity leads to the relatively low \( \Phi_F \) values of 5 and 6 in polar solvents, while the lower value of \( \Phi_F \) for 6 in CH\(_2\)CN compared to 5 is attributed to the larger increase of \( k_{nr} \). As for compound 4, with the strongest push-pull character, as deduced from its significantly red-shifted absorption and emission spectra, the very weak emission is possibly related to a fairly small \( k_{nr} \) value, caused by a twisted ICT (TICT) excited state, which could restrict the radiative deactivation of the S\(_1\) state. Our previous study of Tpa–B(FMes)\(_2\) showed that this compound has a highly twisted geometry in the S\(_1\) excited state with a large deformation of the B(FMes)\(_2\) group, which forms even in the gas phase.\(^{[15]}\) To investigate whether the same process occurs for compound 4 of the present study, the excited-state (S\(_1\)) structure of this compound has been calculated using TD-DFT optimization (CAM-B3LYP/6-31G(d)). In the relaxation process from the S\(_1\) Franck-Condon state following absorption, one FMes group rotates towards a more planar conformation (50.7 to 24.8\(^\circ\)), while the second FMes group rotates somewhat and the bithienyl unit rotates to a significantly larger dihedral angle with respect to the BC plane (63.8 to 74.9\(^\circ\)) and 19.3 to 76.7\(^\circ\), respectively. Figure S5); therefore, the S\(_1\) state of 4 is described as a TICT state and is analogous to that observed for Tpa–B(FMes)\(_2\). In the TICT state, there is electronic decoupling between the molecular orbitals involved in the emission (S\(_1\) \( \rightarrow \) S\(_0\)) process (Figure S6), leading to a small oscillator strength of 0.035, consistent with the observed weak emission from this state in solution. This is in contrast to the allowed S\(_1\) \( \rightarrow \) S\(_0\)) transition at the more planar ground-state geometry, which has a large oscillator strength of 1.470.

![Figure 5. Emission spectra of 1–6 in toluene (red), THF (blue) and CH\(_2\)CN (green).](image-url)

Because binding of anions to the Lewis acidic boron atom in the acceptor group occupies the previously vacant \( p_x \)-orbital thus destroying its accepting ability, this can be used to confirm the
ICT nature of the optical transitions. The different push-pull strengths of these compounds lead to different changes in emission color upon treatment with fluoride in THF. As can be seen from Figure 6, after an excess of fluoride was added to the solution, the emission of 1, 2 and 5 changed from yellow-green to blue, yellow-orange to blue, and red to blue, respectively. A $^{19}$F NMR study of 2 in CD$_2$Cl$_2$ confirmed that a 1:1 complex between the compound and fluoride was formed and that complete recovery of 2 can be achieved by washing with water (Figure S7). These results clearly confirmed that the original emission of these compounds come from an ICT state. The gradually larger color difference upon fluoride binding from 1 to 2 to 5 can be easily understood: initially, the enhanced push-pull character from 1 to 2 to 5 leads to red-shifted ICT emission; after fluoride is bound to the boron atom of the acceptor, the original ICT state cannot be formed; therefore, bright blue emission arising from the electronic transition within the donor-spacer moiety is observed. The emission-color change from red to blue for 5 is particularly remarkable. Such a large color difference has not been observed in sensing studies of three-coordinate-boron systems to the best of our knowledge. The distinct color change and the bright emission of both free and bound states facilitates naked-eye recognition. Considering the similar photophysical properties of 2 and 3 and of 5 and 6 in THF, compounds 3 and 6 are expected to have responses similar to 2 and 5, respectively. Compound 4 is non-emissive in THF; however, bright blue emission is observed after fluoride binding (Figure 7). Such a "turn-on" response behavior is quite different from the case of the other compounds. The elimination of the non-emissive ICT state of 4 upon fluoride binding and the generation of an emissive state similar to those observed for fluoride-bound 1, 2 and 5 reasonably explains the "turn-on" response behavior. Following fluoride binding, 4 could not be recovered by washing with water; instead, excess BF$_3$·OEt$_2$ was used to extract the more strongly bound fluoride, which further demonstrates the enhanced Lewis acidity of 4 compared to 2 (Figure S8). We suggest that the binding of fluoride used herein to confirm our interpretation of the photophysical studies could possibly be applied to the development of efficient fluoride probes, but we note that this is already a very mature area.[19b-d,14a-c,5a-e,6,11,14a]

As solid powders, 1–3 show yellow emission, while 4–6 show red emission. The emission maxima are located at 548, 545, 563, 646, 635 and 618 nm for 1–6, respectively (Figure 8). The solid-state $\Phi_e$ values of 1–3, 5 and 6 are 0.30, 0.46, 0.27, 0.23 and 0.05, respectively, which, although still moderate, are much lower than those of their solutions (Table 2). Such aggregation-induced quenching of fluorophores is commonly observed in the solid state. Interestingly, compound 4 shows the opposite behavior, exhibiting a much higher $\Phi_e$ value (0.31) in the solid state than in solution: such behavior is known as aggregation-induced emission (AIE).[26a,27] but has rarely been observed for three-coordinate boron compounds.[28] Several studies indicate that the AIE phenomenon of compounds possessing donor and acceptor subunits may be caused by restricted formation of a TICT state,[28] which is likely the reason for the AIE of 4. As discussed in regard to the solution photophysics, the nonemissive nature of 4 in solution should be related to a highly twisted ICT excited state geometry with a low S$_1 \rightarrow$ S$_0$ oscillator strength. However, as disclosed in the crystal structure of 4, the NC$_1$-Ph-dithienyl-BC$_3$ moiety is relatively planar with small interplanar dihedral angles in the ground state, close to the optimized S$_0$ structure. Once the compound is excited in the solid state, the rigid environment restricts the formation of the TICT state; therefore, more efficient

![Figure 6](image6.png) Emmission spectra of 1 (black), 2 (red) and 5 (blue) before (solid line) and after (dashed line) excess F$^-$ (> 5 eq.) is added to the THF solution. The inset shows the emission-color changes of 1 (left), 2 (middle) and 5 (right) following F$^-$ binding in THF under 365 nm UV-light irradiation.

![Figure 7](image7.png) Emission spectra of 4 before (black line) and after (red line) excess F$^-$ (> 5 eq.) is added to the THF solution. The inset shows the "turn-on" of fluorescence after F$^-$ binding under 365 nm UV irradiation.

![Figure 8](image8.png) Emission spectra of solid (powder) samples of 1–6.
emission might be expected from this geometry. The low-
temperature (77 K) emission spectrum of 4 in frozen toluene (\(\text{\(\lambda_{em} = 597\) nm}\)) shows a significant blue shift of 47 nm (1200 cm\(^{-1}\)) compared to the solution spectrum in toluene (Figure 9), which is similar to the behavior of Tpa–B(FMes)\(_2\) and consistent with the lack of formation of a TICT state in a rigid environment.\(^{[15]}\) In addition, the emission in frozen toluene solution shows significantly increased intensity, similar to the case in the rigid solid and consistent with our hypothesis of an efficient emission from a more planar excited-state conformation. We note that \(\lambda_{em}\) of 4 in the solid-state is red-shifted compared to that in frozen toluene by 49 nm (1300 cm\(^{-1}\)), which may be related to aggregation in the solid state. Compounds 4 (\(\Phi_T = 0.23\)) and 5 (\(\Phi_T = 0.31\)), with their efficient red emission in the solid state, are especially interesting, given the lack of efficient red emitters based on organoboron compounds.

Figure 9. Emission spectra of 4 in toluene at different temperatures. Inset: Normalized spectra showing the blue-shift upon cooling.

Conclusion

A series of donor-bithiophen-acceptor compounds containing Ar2B
acceptor and arylamine donor groups was synthesized. The acceptor strength was systematically tuned by varying Ar2B, namely by using Ar = mesityl ([Mes]2B), 2,6-dimethyl-4-pentafluoropenylbenzene ([Pfp]2B), 2,6-dimethyl-4-(3,5-bis(trifluoromethyl)phenyl)benzene ([Tfp]2B) and 2,4,6-tris(trifluoromethyl)benzene ([PFm]2B). Tuning the donor strength by exchange of a triphenylamine donor for a stronger 1,1,7,7-tetramethyljulolidine donor gave further fine control over the optoelectronic properties. The key to the high-yield syntheses of these compounds was the use of iridium-catalyzed C–H borylation, which was successfully employed in the process of derivatizing both the boryl acceptors and the tetramethyljulolidine donor.

The acceptor groups were evaluated using a complementary combination of crystallographic, photophysical, electrochemical and theoretical studies, which established that the order of increasing strength is [Mes]2B < [Pfp]2B < [Tfp]2B << (FMes)2B. In CH\(_3\)CN, near-infrared emission with quantum yields of 0.27–0.48 was obtained for derivatives containing the moderately strong ([Pfp]2B and [Tfp]2B acceptors and tetramethyljulolidine donors, which is the first time such efficient low-energy emission has been observed from a three-coordinate organoboron system. A compound containing the strongest acceptor, (FMes)2B, and a triphenylamine donor suffers from strongly quenched emission in solution, while the analogous derivatives containing (Pfp)2B and (Tfp)2B, have near-unity quantum yields, even in polar CH\(_3\)CN solution, making them particularly attractive for practical applications. Although very high quantum yields (>0.80) were obtained for (Pfp)2B- and (Tfp)2B-containing compounds with tetramethyljulolidine donors in toluene and THF, reduced values of \(k_e\) and increased values of \(k_i\) led to quantum yields in CH\(_3\)CN solution being decreased by a factor of approximately two to three. Thus, our systematic studies suggest that employing donors and acceptors of medium strength is essential for achieving efficient emission in polar solvents, insight that should facilitate the future design of bright, organoboron-based NIR emitters. Efficient solid-state red emission was observed for some derivatives and interesting aggregation-induced emission of 4 containing the (FMes)2B group was studied. Moreover, each compound showed a strong and clearly visible response to the addition of fluoride, with either a large emission-color change, e.g. from red to blue or turn-on fluorescence.

Experimental Section

General Information

(FMes)\(_2\)BF\(_4\), (bis([fluoromesityl]boron fluoride))\(_2\), (2,2'-bithiophen)-5-yboronic acid,\(^{[25]}\), 5-ido-2,2'-bithiophene\(^{[26]}\) and [(rp-OMe(COD)]\(_2\))\(_2\) were prepared according to literature procedures. All other starting materials were purchased from commercial sources and were used without further purification. The organic solvents are for reactions were performed in an Innovative Technology Inc. Pure-Solv Solvent Purification System and deoxygenated using the freeze-pump-thaw method. All synthetic reactions were performed in an Innovative Technology Inc. glovebox under an argon atmosphere using standard Schlenk techniques. \(\text{H}, \text{C}(\text{H})\) and \(\text{B} NMR\) spectra were measured on either a Bruker Avance 500 \(\text{H}, 500\) MHz, \(\text{C}, 125\) MHz; \(\text{B}, 160\) MHz or Bruker Avance 300 \(\text{H}, 300\) MHz; \(\text{C}, 75\) MHz; \(\text{B}, 96\) MHz NMR spectrometer. \(\text{^{13}F}(\text{H})\) and \(\text{^{19}F} NMR\) spectra were measured on either a Bruker Avance 200 \(\text{^{13}F}, 188\) MHz or Bruker Avance 500 \(\text{^{19}F}, 470\) MHz NMR spectrometer. The abbreviation \(\text{dpm}\) stands for doublet of multiplets. Mass spectra were recorded on an Agilent 7890A/5975C Inert GC/MS or Varian 320MS-GC/MS systems operating in EI mode. Elemental analyses were performed on a Leco CHNS-932 Elemental Analyzer.

Single-Crystal X-ray Diffraction

Crystals suitable for single-crystal X-ray diffraction were selected, coated in paraffinpolyethylene oil, and mounted on MITEGen sample holders. Diffraction data of 1,3,5-trimethylbenzene and 2 were collected on a Bruker D8 Quest three-circle diffractometer utilizing mirror-monochromated Mo K\(_\alpha\) radiation \((\lambda = 0.71073\) Å) from an \(\mu\)s microfocus sealed X-ray tube (Incoatec, Germany) operated at 50 kV and 1 mA, and equipped with a Photon area detector. Diffraction data of 4 were collected on a Nonius Kappa three-circle diffractometer utilizing graphite monochromated Mo K\(_\alpha\) radiation \((\lambda = 0.71073\) Å) from a rotating anode tube run at 50 kV and 30 mA, equipped with an APEX2 area detector. Both instruments were operated with an open-flow N\(_2\) Cryoflex II (Bruker) device and measurements were performed at 100 K. For data reduction, the Bruker Apex2 software suite (Bruker AXS) was used. Subsequently, utilizing Olex2\(^{[27]}\), the structures were solved using the Olex2.solve charge-flipping algorithm, and were subsequently refined with Olex2.refine using Gauss-Newton minimization. All non-hydrogen atom positions were located from the Fourier maps and refined anisotropically. Hydrogen atom positions were calculated using a riding model in geometric positions and refined isotropically.
Fluorescence Quantum Yield Measurements

The fluorescence quantum yields of solutions and powders were measured using a calibrated integrating sphere (150 mm inner diameter) from Edinburgh Instruments combined with the FLSP920 spectrometer described above. For solution-state measurements, the longest-wavelength absorption maximum of the compound in the respective solvent was chosen as the excitation wavelength, while for solid-state (powder) measurements, the longest-wavelength absorption maximum in toluene was selected.

Fluorescence Lifetime Measurements

Fluorescence lifetimes were recorded using the time-correlated single-photon counting (TCSPC) method using an Edinburgh Instruments FL5980 spectrometer equipped with a high speed photomultiplier tube positioned after a single emission monochromator. Measurements were made in right-angle geometry mode, and the emission was collected through a polarizer set to the horizontal polarization. All solutions used in photophysical measurements had a concentration lower than $10^{-5}$ M.

Synthesis

5-(4-Bisphenylaminophenyl)-2,2'-bithiophene (Tpa–Th) was synthesized by the reaction of 2,2'-bithiophene-5-sulfonyl acid (500 mg, 2.38 mmol), Na$_2$CO$_3$ (1.26 g, 11.9 mmol), [Pd(PPh)$_3$]$_2$ (110 mg, 0.10 mmol), THF (35 mL), and degassed H$_2$O (6 mL) were added to a flask. The mixture was heated at reflux for 24 h and then cooled to r.t. Water and diethyl ether were added to the mixture for extraction. The organic phase was washed with cold hexane (80 mL) and dried in vacuum to provide the title compound as a yellow solid (695 mg, 71%).

$1^H$ NMR (500 MHz, DMSO-d$_6$, ppm) 5.7-6.6, 6.3-7.2 (m, 7 H), 6.99 (s, 1 H). [Clyl]NMR (125 MHz, THF-d$_8$, ppm): 148.5, 148.4, 143.8, 138.3, 131.2, 129.7, 128.6, 127.1, 125.3 (2 C, overlapped), 125.1, 124.5, 124.2, 124.0, 123.8. MS (EI) $m/z$: 409 [M$^+$]. Anal. Calcd (%) for C$_{37}H$_$_2$_8N$_4$: C, 76.25; H, 4.86; N, 3.52; S, 15.66. Found: C, 76.91; H, 4.81; N, 3.46; S, 15.90.

5,1,1',7-Tetramethyl-9-(31G(d))boronic acid pinacol ester (Tmj–Bpin)

5,1,1'-Tetramethyl-9-(31G(d))boronic acid (8.20 g, 26.2 mmol), bis(pinacolato)diboron (Bpin$_2$, 8.65 g, 34.1 mmol), [Ir(μ-OMe)(COD)]$_2$ (174 mg, 0.26 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (dtbbpy) (138 mg, 0.51 mmol) and hexane (36 mL) were added to a flask. The reaction mixture was heated at 80 °C for 48 h, then cooled to r.t. and then further cooled in ice-water to crystallize the product. The mixture was filtered, and the solid product was washed with cold hexane (80 mL) and dried in vacuum to provide the title compound as an off-white solid (8.22 g, 88%).

$1^H$ NMR (300 MHz, CD$_2$Cl$_2$, ppm): 6.05 (s, 2 H), 2.86 (t, J = 8 Hz, 4 H), 1.50 (t, J = 6 Hz, 4 H), 1.20 (s, 12 H), 1.19 (s, 12 H). [Clyl]NMR (125 MHz, CD$_2$Cl$_2$, ppm): 5 143.3, 130.8, 129.5, 11.43 (br), 83.3, 47.1, 37.1, 32.4, 31.2, 25.1. [B] NMR (360 MHz, CD$_2$Cl$_2$, ppm): 3.31 (s, 1 B). MS (EI) $m/z$: 355 [M$^+$]. Anal. Calcld (%) for C$_{37}H$_$_2$_8N$_4$: C, 74.73; H, 6.94; N, 3.94. Found: C, 74.23; H, 9.58; N, 3.96.

4-Bromo-3,5-dimethylthiophen-2-carboxylic acid pinacol ester (4-(Br)-3,5-Me$_2$Ph-Bpin)

2,6-Dimethylthiobenzene (185 g, 1.50 mmol), B$_2$pin$_2$ (33.4 g, 130 mmol), [Ir(μ-OMe)(COD)]$_2$ (333 mg, 0.50 mmol), dtbbpy (403 mg, 1.50 mmol) and hexane (116 mL) were added to a flask. The reaction mixture was heated at 80 °C for 65 h, cooled to r.t. and then filtered through a short silica-gel pad. The obtained solution was evaporated to give a oil, which was purified by column chromatography (silica gel, hexane). The obtained oily product solidified under vacuum to give the title compound as a white solid (29.5 g, 95%).

$1^H$ NMR (500 MHz, CD$_2$Cl$_2$, ppm): 7.26 (s, 2 H), 7.24 (dd, J = 5, 1 Hz, 1 H), 7.19 (d, J = 4 Hz, 1 H), 7.03 (d, J = 4 Hz, 1 H), 6.98 (dd, J = 5, 4 Hz, 1 H), 3.20-3.18 (m, 4 H), 1.77-1.74 (m, 4 H), 1.30 (s, 12 H). [Clyl]NMR (125 MHz, THF-d$_8$, ppm): 6 146.2, 141.1, 138.7, 134.3, 131.1, 128.3, 124.9, 124.1, 123.2, 122.2, 121.1, 42.7, 37.6, 32.8, 31.3. MS (EI) $m/z$: 393 [M$^+$]. Anal. Calcld (%) for C$_{37}H$_$_2$_8N$_4$: C, 72.33; H, 6.91; N, 3.56; S, 16.29. Found: C, 72.05; H, 6.85; N, 3.56; S, 16.05.

4-Perfluorophen-2,6-dimethylbenzobenzene (Pfp–Br)

4-Br-3,5-Me$_2$Ph-Bpin (8.00 g, 25.8 mmol), CF$_3$I (12.9 g, 43.9 mmol), Ag$_2$CO$_3$ (17.8 g, 64.5 mmol), [Pd(PPh)$_3$$_2$] (1.48 g, 2.18 mmol) and THF (120 mL) were added to a flask. The mixture was heated at reflux for 25 h, cooled to r.t. and then filtered. The filtrate was evaporated to dryness, and the residue was purified by column chromatography (silica gel, hexane) to provide the title compound as a white solid.
solid (7.25 g, 80%). 1H NMR (500 MHz, CDCl3, ppm): δ 7.15 (s, 2 H), 2.49 (s, 6 H). 13C NMR (126 MHz, CDCl3, ppm): δ 144.2 (dm, 1J = 248 Hz), 139.8 (s), 130.0 (dm, 1J = 162 Hz), 129.7 (s), 129.1 (10 m), 115.4 (s, 1J ≈ 17 Hz, 4 J, 124 Hz), 24.0. 19F NMR (188 MHz, CDCl3, ppm): δ -142.9 (dd, J = 23, 8 Hz, 2 F), -153.3 (J, J = 21 Hz, 1 F), -162.0 to -162.2 (2 m, 2 F). MS (EI)* m/z 350 [M]. Anal. Calcld. (%) for C13H18BrF6: C, 47.89; H, 1.46.

4-(3,5-Bis[(trifluoromethyl)phen-2-yl]-6-dimethylbenzobenzene (TpBr-Br, 4). Br-3,5-Me2-Ph-Bpin (3.10 g, 10.0 mmol, 3.5-bis[(trifluoromethyl)iodobenzene (5.78 g, 17.0 mmol), AgCO3 (6.9 g, 25.0 mmol), [Pd(PPh3)4] (577 mg, 0.50 mmol) and THF (45 mL) were added to a flask. The mixture was heated at reflux for 21 h, cooled to r.t. and then filtered. The filtrate was evaporated to dryness, and the residue was purified by column chromatography (silica gel, hexane) and subsequent crystallization from methanol to provide the title compound as a white solid (3.11 g, 79%). 1H NMR (500 MHz, CDCl3, ppm): δ 8.05 (m, 2 H), 7.91 (m, 1 H), 7.35 (m, 2 H), 2.51 (m, 6 H). 13C NMR (126 MHz, CDCl3, ppm): δ 142.9, 139.9, 137.0, 132.5 (q, 1J ≈ 33 Hz), 128.9, 127.5 (m), 127.2, 124.0 (J, 1J ≈ 273 Hz), 121.5 (septet, 1J ≈ 4 Hz), 24.2. 19F NMR (188 MHz, CDCl3, ppm): δ -61.4 (6 s, F). MS (EI)* m/z 396 [M]+. Anal. Calcld. (%) for C13H11BrF6: C, 48.39; H, 2.79. Found: C, 48.83; H, 2.79.

Tpa-TH-Th-B(Mes)2 (1). nBuLi (2.5 M in hexane, 0.23 mL, 0.58 mmol) was added to a THF (5 mL) solution of Tpa-Th (216 mg, 0.53 mmol) at −78 °C, and the mixture was stirred at this temperature for 1 h. After the THF (2 mL) solution of Mes2Br (170 mg, 0.63 mmol) was added, the mixture was slowly warmed to r.t. and stirred for 2 h. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, 4:1 hexane/CH2Cl2) and subsequent precipitation from dichloromethane by addition of methanol to provide 1 as a yellow solid (303 mg, 67%). 1H NMR (500 MHz, THF-d8, ppm): 7.57 (d, J = 4 Hz, 2 H), 7.39 (d, J = 4 Hz, 1 H), 7.33–7.32 (m, 2 H), 7.27–7.23 (m, 5 H), 7.09–7.07 (m, 4 H), 7.03–7.00 (m, 4 H), 6.81 (s, 4 H), 2.27 (s, 6 H), 2.13 (s, 12 H). 13C NMR (126 MHz, CDCl3, ppm): δ 150.4, 149.1 (br), 148.2, 147.8, 145.1, 142.2, 141.5 (br), 141.2, 139.0, 135.8, 129.8, 128.9, 127.8, 126.8, 126.5, 125.9, 125.1, 123.8, 123.6, 123.5, 23.6, 21.4. 19F NMR (160 MHz, CDCl3, ppm): δ 6.4 (s, br). MS (EI)* m/z 658 [M]+. Anal. Calcld. (%) for C13H15BrF2N2S2: C, 30.85; H, 6.13; N, 2.13; S, 9.75. Found: C, 30.85; H, 6.15; N, 1.94; S, 9.72.

Tpa-TH-Th-B(p-P) (2). 4H NMR (500 MHz, CDCl3, ppm): 7.51 (s, J = 4 Hz, 1 H), 7.48 (d, J = 4 Hz, 2 H), 7.41 (d, J = 4 Hz, 1 H), 7.33 (d, J = 4 Hz, 1 H), 7.30–7.27 (m, 4 H), 7.20 (d, J = 4 Hz, 1 H), 7.14 (s, 4 H), 7.13–7.11 (m, 4 H), 7.08–7.04 (m, 4 H), 2.31 (s, 12 H). 13C NMR (126 MHz, CDCl3, ppm): δ 152.1, 149.3, 148.7, 147.4 (br), 145.8, 143.1, 142.5 (br), 141.5, 139.0, 135.9, 132.9, 129.8, 128.7, 126.9, 126.5, 125.2, 125.1, 123.8, 123.6, 123.5, 23.6, 21.4. 19F NMR (160 MHz, CDCl3, ppm): δ 6.4 (s, br). MS (EI)* m/z 658 [M]+. Anal. Calcld. (%) for C13H15BrF2N2S2: C, 30.85; H, 6.13; N, 2.13; S, 9.75. Found: C, 30.85; H, 6.15; N, 1.94; S, 9.72.

Tpa-TH-Th-B(THF) (3). 1H NMR (500 MHz, CDCl3, ppm): 7.51 (s, J = 4 Hz, 1 H), 7.48 (d, J = 4 Hz, 2 H), 7.41 (d, J = 4 Hz, 1 H), 7.33 (d, J = 4 Hz, 1 H), 7.30–7.27 (m, 4 H), 7.20 (d, J = 4 Hz, 1 H), 7.14 (s, 4 H), 7.13–7.11 (m, 4 H), 7.08–7.04 (m, 4 H), 2.31 (s, 12 H). 13C NMR (126 MHz, CDCl3, ppm): δ 150.4 (s), 149.1 (s), 148.2, 147.8, 145.1, 142.5 (br), 141.5, 139.0, 135.9, 132.9, 129.8, 128.7, 126.9, 126.5, 125.2, 125.1, 123.8, 123.6, 123.5, 23.6, 21.4. 19F NMR (160 MHz, CDCl3, ppm): δ 61.6 (s). MS (EI)* m/z 962 [M]+. Anal. Calcld. (%) for C13H20BrF6N2: C, 78.21; H, 3.94; N, 2.13; S, 9.04. Found: C, 78.28; H, 3.81; N, 2.13; S, 9.04.
C, and the mixture was stirred at this temperature for 1 h. A solution of (3B/5B) in THF (5 mL) prepared in the same batch as that used in the synthesis of 3, was added to the to the lithium reagent. The mixture was warmed to r.t. and stirred overnight. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, 3:1 hexane/CHCl₃) and subsequent precipitation from CHCl₃ by addition of methanol to provide compound 6 as a red solid (330 mg, 50% based on Tmj⁻⁻⁻⁻–Th⁻⁻⁻⁻⁻⁻–Th⁻–Th). ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.15 (s, 4 H), 7.09 (s, 2 H), 7.47 (d, J = 4 Hz, 1 H), 7.38 (d, J = 4 Hz, 1 H), 7.36 (s, 4 H), 7.29 (d, J = 4 Hz, 1 H), 7.27 (s, 2 H), 7.08 (s, 1 H), 3.21 (s, 2 H), 2.35 (s, 12 H), 1.76 (t, J = 4 Hz, 4 H), 1.30 (s, 12 H). ¹³C NMR (126 MHz, THF-d₈, ppm): δ 153.7, 149.1, 147.4, 145.4, 144.6, 144.0, 142.8 (br), 141.7, 139.3, 133.2, 131.2 (q, JCF = 33 Hz), 131.3, 128.2 (m), 127.6, 121.7, 125.9, 124.7 (q, JCF = 273 Hz), 122.3, 121.9, 121.7, 121.6 (m). 1H NMR (160 MHz, THF-d₈, ppm): δ -63.2 (s, 12 F). ¹³B NMR (160 MHz, THF-d₈, ppm): ca. 165 (weak and broad). MS (EI) m/z: 1038 [M⁺]. Anal. Calcd (%) for C₄H₆B₂F₄: C: 64.6; H: 4.6; N: 3.5; S: 6.18; Found: C: 65.2; H: 4.8; N: 1.55; S: 6.09.

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Layout 1:

FULL PAPER

D-π-A organoboron compounds with tunable push-pull character have been prepared by varying the donor and acceptor groups. Efficient green to NIR emission has been achieved from these compounds in solution. Aggregation-induced emission was observed for one compound. Each compound showed a strong and clearly visible response to fluoride addition, with either a large emission-color change or turn-on fluorescence.

Fluorescence
Zuolin Zhang, Robert M. Edkins, Jörn Nitsch, Katharina Fucve, Antonius Eichhorn, Andreas Steffen, Yue Wang, and Todd B. Marder*