Highly Stable, Readily Reducible, Fluorescent, Trifluoromethylated 9-Borafluorenes

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Abstract: Three different perfluoroalkylated borafluorenes (FBf) were prepared and their electronic and photophysical properties were investigated. The systems have four trifluoromethyl moieties on the borafluorene moiety as well as two trifluoromethyl groups at the ortho positions of their exo-aryl moieties. They differ with regard to the para substituents on their exo-aryl moieties, being a proton (XylBF, Xyl: 2,6-bis(trifluoromethyl)phenyl), a trifluoromethyl group (MesBF, Mes: 2,4,6-tris(trifluoromethyl)phenyl) or a dimethylamino group (pNMe2XylBF, p-NMe2-Xyl: 4-(dimethylamino)-2,6-bis(trifluoromethyl)phenyl), respectively. All derivatives exhibit extraordinarily low reduction potentials, comparable to those of perynediimidic. The most electron-deficient derivative MesBF was also chemically reduced and its radical anion isolated and characterized. Furthermore, all compounds exhibit very long fluorescent lifetimes of about 250 ns up to 1.6 μs; however, the underlying mechanisms responsible for this differ. The donor-substituted derivative pNMe2XylBF exhibits thermally activated delayed fluorescence (TADF) from a charge-transfer (CT) state, whereas the MesBF and XylBF borafluorenes exhibit only weakly allowed locally excited (LE) transitions due to their symmetry and low transition-dipole moments.

Introduction

Boron-containing organic π-systems, especially triaryboranes[1–13] and, more recently, boron-containing polyaromatics are of much current interest.[10-16] Three-coordinate boron is isoelectronic with a carbonium ion, having an unoccupied p-orbital, making it inherently electron deficient and Lewis acidic. Thus, three-coordinate boranes can be employed as π-acceptors, single-electron or electron-pair acceptors. Such boranes have been used in linear[21-40] and non-linear[41-53] optical materials, anion sensors,[54-56] frustrated Lewis pairs (FLPs),[57–71] as well as in organic light-emitting diodes (OLEDs).[72–81] There are numerous examples, both aromatic and antiaromatic, of boron-containing conjugated cyclic π-systems.[16,20] The subclass of boroles is of special interest.[17,57-82] They are isoelectronic with the antiaromatic cyclopentadiene[83-86] and, therefore, are highly reactive towards nucleophiles and thereby unsuitable for many applications. Steric shielding, which works well for triaryboranes,[83,84] only stabilizes boroles to a certain degree.[87-89] Through benzannulation, the stability of boroles can be greatly increased,[86,89] but the anti-aromatic character is significantly decreased due to delocalization of π-electron density over the biphenylene backbone. This leads to a stabilization of the HOMO as well as a destabilization of the LUMO resulting in a larger HOMO–LUMO gap and loss of the characteristic strong color of boroles. This also results in a lower Lewis acidity and, subsequently, significantly more stable systems.[16,77] Detailed studies by Martin and co-workers demonstrate, however, that sterically less hindered derivatives, in particular, retain characteristic borole reactivity.[90–94] Compared with their triarylborate derivatives, borafluorenes are usually more Lewis acidic and exhibit more positive reduction potentials.[95] The stability of these systems can be further improved by sterically shielding[87,88] or electronically saturating the boron center[86] through direct n→π conjugation or indirect F–B interaction (Figure 2).

Yamaguchi and co-workers reported air and moisture-stable borafluorene derivatives employing either Tip (2,4,6-tris(trisopropylphenyl) or the even bulkier Mes* (2,4,6-tris(tert-butyl)phenyl) substituents.[96,97] It was found that the Tip derivatives could be used as turn-on type fluoride sensors, whereas the
Mes⁺ compounds showed no reaction with fluoride. Recently, Rupar and co-workers have studied these effects in detail. They found that although Tip-substituted derivatives still decompose slowly (<10% decomp. over 24 h) in wet solvents, the corresponding FMes derivatives exhibit higher stability (5% decomp. over 24 h). Derivatives containing π-bonding moieties were found to be much more sensitive towards moisture (iPrN₂: 50% decomp. over 1 h; tBuO: 10% decomp. over 1 h). ortho-Trifluoromethyl-substituted aryls exhibit a strong stabilizing effect on boranes. In addition to the steric effect, a direct interaction of the lone pairs of the fluorine atoms with the empty p orbital of the boron center is observed. This is supported by B−F distances which are much shorter than the sum of their van der Waals radii (3.39 Å) in crystal structures. The electronic properties of borafluorenes can be easily tuned to fit different applications by the introduction of different substitution patterns on the biphenyl backbone (Figure 2, right). The introduction of methoxy groups at the 6 and 12 positions leads to a small hypsochromic shift of both the absorption and emission wavelength, whereas elongation of the π-system with electron-rich conjugated systems attached at the 5 and 13 positions leads to a bathochromic shift of both the absorption and emission wavelength. The photophysical properties of borafluorenes can also be modified by coordination of Lewis bases. Both Yamaguchi and co-workers and Rivard and co-workers observed turn-on fluorescence upon adduct formation. Wilson and Gillard and co-workers observed turn-off fluorescence of a borafluorenium cation upon coordination of a Lewis base at low temperature, resulting in thermochromism. Piers and co-workers investigated the properties of a highly electron-deficient perfluorinated borafluorene. Although they only observed a reduction corresponding to the perfluoroaryl in the cyclic voltammogram, a reaction with the relatively mild reducing agent CoCp₂ (CoCp₂/CoCp₂⁺: −1.3 vs.Fc/Fc⁺) was observed, underlining the electron-deficient nature of the compound. In competition experiments with the strong Lewis acid B(C₆F₅)₃, preference towards the borafluorene derivative was observed, especially
Results and Discussion

Synthesis

In order to maximize the stability of the trifluoromethylated borafluorenes (3\textsuperscript{BF}) we chose three different meta-fluoroxylylene (1,3-bis(trifluoromethyl)benzene) derivatives as the exo-aryl moieties. To examine the influence of the exo-aryl and, specifically, substituents at the para position, we chose 2,6-bis(trifluoromethyl)phenyl (\textsuperscript{Xyl}), 2,4,6-tris(trifluoromethyl)phenyl (\textsuperscript{Mes}) and 4-(dimethylamino)-2,6-bis(trifluoromethyl)phenyl (p-NMe\textsubscript{2}-Xyl) groups (Scheme 1).

Biphenyl derivative 2 was synthesized through regioselective C–H borylation of 1\textsuperscript{[106,107]} ortho to the bromine and a subsequent copper-catalyzed oxidative homocoupling. For the last step, 2 was dehalogenated and subsequently reacted with the appropriate Ar-BF\textsubscript{3}K salt. Attempts to synthesize the haloborafluorenes with different BX\textsubscript{3} (X = F, Cl, Br) sources failed. Attempts to use aryl boronates in place of the Ar-BF\textsubscript{3}K salt were also unsuccessful. The use of aryltrifluoroborate salts as boron source was previously reported by our group for the synthesis of boroles with enhanced stability\textsuperscript{[79]} and applied by others in the synthesis of boron polyaromatic hydrocarbons (PAHs)\textsuperscript{[108,109]} and aryl borates.\textsuperscript{[110,111]} Organic trifluoroborate salts are widely employed in cross-coupling reactions as they are readily accessible and very stable.\textsuperscript{[112,113]} During the synthesis we observed that adding LiBr greatly improves the reactivity of the Ar-BF\textsubscript{3}K salts. It is possible that a cation-exchange reaction generates the more reactive Ar-BF\textsubscript{3}Li salt. The increased reactivity of the Ar-BF\textsubscript{3}Li salt is due to the thermodynamically favorable LiF elimination. It is also possible that LiBr stabilizes the aryllithium species towards decomposition in ethereal solvents. This decomposition also explains the low yields of isolated material. It is important to note that the corresponding ortho-trifluoromethylarylboron halides (X = Cl, Br) are not stable due to halide exchange.\textsuperscript{[114]} This might also explain why the synthesis of the haloborafluorenes was not possible. The compounds \textsuperscript{1}Mes\textsuperscript{BF}, \textsuperscript{Xyl}\textsuperscript{BF}, and p-NMe\textsubscript{2}-Xyl\textsuperscript{BF} were obtained after purification through sublimation and recrystallization. Both \textsuperscript{1}Mes\textsuperscript{BF} and \textsuperscript{Xyl}\textsuperscript{BF} are bright-green solids. In contrast, p-NMe\textsubscript{2}-Xyl\textsuperscript{BF} is a red solid. All compounds exhibit \textsuperscript{1}H NMR and \textsuperscript{13}C\{\textsuperscript{1}H\} NMR signals consistent with their proposed structures. The \textsuperscript{13}B\{\textsuperscript{1}H\} NMR shifts for all three borafluorene derivatives are around 64 ppm and differ only slightly. The \textsuperscript{19}F\{\textsuperscript{1}H\} NMR spectra display singlets and septets, the latter with a \textit{J}_{\text{BF}} coupling constant of 3–4 Hz (Table 1).

The singlets at about $\delta = -63.5$ ppm correspond to the two freely rotating para CF\textsubscript{3} groups on the borafluorene core. For \textsuperscript{1}Mes\textsuperscript{BF}, another singlet corresponding to the para CF\textsubscript{3} group on the exo-aryl is observed. The CF\textsubscript{3} groups ortho to the boron center display a complex coupling pattern of two septets with small coupling constants ($\textit{J}_{\text{BF}} = 4$ Hz). This can be attributed to through-space F–F coupling as previously observed at low temperature (243 K) for \textsuperscript{1}Mes\textsubscript{2}BF compounds.\textsuperscript{[102]} The fact that the borafluorenes exhibit this phenomenon at room temperature is an indicator of the high rigidity of the systems.

Table 1. \textsuperscript{13}B\{\textsuperscript{1}H\} and \textsuperscript{19}F\{\textsuperscript{1}H\} NMR shifts of \textsuperscript{1}Mes\textsuperscript{BF}, \textsuperscript{Xyl}\textsuperscript{BF}, and p-NMe\textsubscript{2}-Xyl\textsuperscript{BF} recorded in C\textsubscript{6}D\textsubscript{6}.

|          | \textsuperscript{1}Mes\textsuperscript{BF} | \textsuperscript{Xyl}\textsuperscript{BF} | p-NMe\textsubscript{2}-Xyl\textsuperscript{BF} |
|----------|---------------------------------|---------------------------------|---------------------------------|
| \textsuperscript{13}B\{\textsuperscript{1}H\} NMR (ppm) | 63.2 | 64.1 | 64.7 |
| \textsuperscript{19}F\{\textsuperscript{1}H\} NMR (ppm) singlet | -63.4 | -62.0 | -63.5 | -63.4 |
| \textsuperscript{19}F\{\textsuperscript{1}H\} NMR (ppm) septets | -58.2 ($\textit{J}_{\text{BF}} = 4$ Hz) | -58.4 ($\textit{J}_{\text{BF}} = 4$ Hz) | -58.1 ($\textit{J}_{\text{BF}} = 4$ Hz) |

\textsuperscript{1}B\{\textsuperscript{1}H\} NMR and \textsuperscript{19}F\{\textsuperscript{1}H\} NMR shifts of \textsuperscript{1}Mes\textsuperscript{BF}, \textsuperscript{Xyl}\textsuperscript{BF}, and p-NMe\textsubscript{2}-Xyl\textsuperscript{BF} recorded in C\textsubscript{6}D\textsubscript{6}.

\[ \text{Scheme 1. Synthesis of } \textsuperscript{1}Mes\textsuperscript{BF}, \textsuperscript{Xyl}\textsuperscript{BF} \text{ and p-NMe\textsubscript{2}-Xyl\textsuperscript{BF}}. \]
All three compounds are stable in the solid state and can be stored under ambient conditions without decomposition. In wet CDCl₃ (1.5 equiv. H₂O per borafluorene) at room temperature, no decomposition of either ¹MesBF or ¹XylBF was observed over 4 days by NMR spectroscopy. This is surprising given that for ¹MesBF and TipBF, both less electron-deficient compounds, decomposition rates of 5 and 10% respectively in wet solvents over 24 h were reported.[88] This indicates that the CF₃-groups ortho to the boron center on the borafluorene core have a stabilizing effect, likely due to steric shielding. However, p-NMe₂-²XylBF shows very rapid decomposition when exposed to wet solvents. It is likely that the dimethylamine moiety is protonated first, thereby further increasing the electrophilicity of the boron center and decreasing its stability towards nucleophilic attack. The reaction with H₂O leads to cleavage of one B–C bond of the borafluorene core, resulting in a BOH and CH moiety. The same reactivity towards water and other E–H bonds (E = N, O, S) was previously observed by Martin and co-workers.[94] Likely due to less steric hinderance in their system, a second borafluorene reacts with the decomposition product to form a B-O-B motif. The product of the hydrolysis of p-NMe₂-²XylBF was isolated and studied by X-ray diffraction (compound D in Figure S41, Supporting Information). All three compounds are slightly soluble in non-polar solvents such as hexane or toluene and soluble in polar non-coordinating solvents such as CH₂Cl₂ and THF. Dissolving ¹MesBF in acetonitrile gives a colorless solution. Investigation of the solution using ¹⁹F NMR spectroscopy revealed the formation of an acetonitrile adduct, which is consistent with previous studies by Martin and co-workers for less sterically hindered borafluorenes.[91] The para-CF₃ groups, both on the borafluorene backbone as well as the exo-aryl moiety, are influenced only weakly by the coordination of acetonitrile, because both singlets in the ¹⁹F NMR spectrum shift only slightly to lower field. The signals corresponding to the ortho CF₃-groups, however, change dramatically. Instead of two septets as observed for ¹MesBF, one septet at −51.9 ppm (JFF = 10 Hz), one broad singlet at −56.2, and a quartet at −60.7 ppm (JFF = 10 Hz), are observed (Figure 3, middle).

This suggests that only one exo-aryl trifluoromethyl moiety is coupling to the ortho trifluoromethyl groups on the borafluorene backbone. After evaporation of the acetonitrile and dissolution in C₆D₆, only the borafluorene was observed through ¹⁹F NMR spectroscopy. Thus, the formation of the adduct with acetonitrile is completely reversible.

Crystal and molecular structures

Single crystals of the three borafluorenes as well as the acetonitrile adduct of ¹MesBF (¹MesBF·MeCN) suitable for X-ray studies were obtained (Figure 4) and selected bond lengths, angles, torsion angles and short B–F contacts are listed in Table 2. The single crystals of ¹MesBF and p-NMe₂-²XylBF were obtained from a saturated hexane solution at −30 °C, that of ¹XylBF was obtained by evaporation of a saturated CH₂Cl₂ solution and that of ¹MesBF·MeCN was obtained from a saturated acetonitrile solution at −30 °C.

A comparison of the crystal structures of the three target compounds shows the following. Although all three B–C bond lengths are in a similar range for ¹MesBF (1.579(3)–1.591(3) Å), the B–C₁₋ₓ distances to the ³Xyl groups of ³XylBF and p-NMe₂-³XylBF (B–C = 1.570(3) Å) are slightly shorter than the respective B–C₂ and B–C₃ bonds (1.591(3)–1.595(3) Å) within the borole moieties (Table 2). The boron atoms have a nearly ideal trigonal-planar configuration with the sum of the C-B-C angles being 359.74(16)–359.99(16)°. In all three compounds, the C₂-B-C₃ angle (102.94(14)–103.95(15)) within the borole moiety is much smaller than the other two C-B-C angles. The borole

Figure 3. ¹⁹F NMR spectra (188 MHz, 298 K) of ¹MesBF in C₆D₆ (top), in CH₂CN (middle) and in C₆D₆ after removal of all volatiles (bottom).
moiety shows similar bond lengths and angles in all three compounds. The angles increase from C–B–C to B–C–C (106.57(16)–107.52(15)°) and to C–C–C (110.98(17)–111.41(15)°). The C2–C and C3–C bond lengths (1.408(3)–1.410(2) Å) are typical for aromatic bonds, whereas the C–C–C bond (1.474(2)–1.482(2) Å) that is opposite to the boron atom has significant single-bond character. The interplanar angle between the borafluorene (BC,C) and the exo-aryl substituent is close to 90° in all three compounds (88.69(5)–89.54(6)°). This is due to the large steric demand of the CF3 groups in the ortho positions of both the exo-aryl moiety as well as the borafluorene core. In all three compounds, two B–F distances, each in the range of 2.366(2)–2.440(3) Å, are observed, which are significantly shorter than the sum of the van der Waals radii for boron and fluoride (3.39 Å).[100] This was previously observed in boranes and boroles with ortho-CF3 ary moieties.[31,79,100,114,115] Given that the two respective fluorine atoms are directly above and below the boron center, it is most likely that the lone pair electrons of these fluorine atoms interact with the empty p-orbital of the boron center. The torsion angle Cendo⋅C2endo⋅B–Clendo with the endo carbon atoms belonging to the borole moiety deviates slightly from 180° (171.28(16)–178.83(17)°). This shows that the B–C1 bond to the exocyclic moiety is tilted slightly out of the borafluorene plane. The out-of-plane tilt increases from p-NMe2XYlBF (1.17(17)°) to XYlBF (3.55(16)°) and MesBF (8.72(16)°). The magnitude of the tilt is related to the molecular packing, which is similar in all three crystal structures because the borafluorene moieties are arranged in pairs, which are related by inversion symmetry and form weak intermolecular π···π interactions between the borafluorene backbones. The strongest π···π interaction is observed in MesBF, which shows the smallest centroid–distance, interplanar sepa-

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Figure 4. Molecular structures of 1MesBF (top left), 2MesBF (top right), p-NMe2XYlBF (bottom left) and 1MesBF-MeCN (bottom right) determined by single-crystal X-ray diffraction at 100 K. All ellipsoids are drawn at the 50% probability level, and H atoms and solvent molecules are omitted for clarity.

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Table 2. Selected bond lengths [Å] and angles [°] in 1MesBF, 2XYlBF, p-NMe2XYlBF and 1MesBF-MeCN. Atom labels for the respective molecular structures are shown in Figure 4.

|                  | 1MesBF | 2XYlBF | p-NMe2XYlBF | 1MesBF-MeCN |
|------------------|--------|--------|-------------|-------------|
| B–C1             | 1.579(3) | 1.570(2) | 1.570(3) | 1.652(3) |
| B–C2             | 1.581(3) | 1.591(3) | 1.595(3) | 1.645(3) |
| B–C3             | 1.591(3) | 1.591(3) | 1.591(3) | 1.645(3) |
| B–N              |        |        | 1.591(3) |             |
| C3–C19/C18/C20   | 1.408(3) | 1.410(2) | 1.409(2) | 1.401(3) |
| C2–C18/C17/C19   | 1.410(2) | 1.409(2) | 1.408(2) | 1.410(3) |
| C18/C17/C19–C19/C18/C20 | 1.481(3) | 1.474(2) | 1.482(2) | 1.475(3) |
| α, BC3–Ar                       | 89.32(7) | 89.84(8) | 89.27(6) |             |
| β, BC3–Ar                        | 89.43(6) | 89.54(6) | 88.69(5) | 82.12(6) |
| torsion of Arout of borafluorene plane | 171.28(16) | 176.45(16) | 178.83(17) | 137.6(2) |
| α, C1–B–C2–C18/C17/C19 |        |        |             |             |
| S-ring, c, C2BC3          | 103.95(15) | 103.07(13) | 102.94(14) | 99.74(18) |
| Sum, C, CBC               | 359.74(16) | 359.90(15) | 359.99(16) | 338.43(18) |
| sum, c, CNC                |        |        | 359.84(19) |             |
| shortest B–F contact(s)    | 2.392(3) | 2.440(3) | 2.379(2) | 2.366(2) |

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ration, and offset shift (Table S3, Supporting Information). Hence, these pairs of molecules are closest in \(^{1}\text{Mes}'\text{Bf}\), and the exocyclic \(^{1}\text{Mes}\) moiety is tilted out of the plane the most, away from the center of the pair in order to avoid close F···F contacts between the two molecules. In the crystal structure of the acetonitrile adduct of \(^{1}\text{Mes}'\text{Bf}\), as the hybridization at the boron is now sp\(^2\) rather than sp\(^2\), all of the B–C bonds are elongated. The C2-B1-C3 angle of the borole ring (99.74(18)\(^\circ\)) is decreased compared to \(^{1}\text{Mes}\text{Bf}\) (103.95(15)\(^\circ\)). The torsion angle of the exo-aryl towards the borafluorene backbone is decreased (82.12(6)\(^\circ\)) and the bending of the exo-aryl out of the plane of the borafluorene moiety (137.6(2)\(^\circ\)) deviates significantly from 180\(^\circ\). In the adduct, there is only one short B···F contact (F3···B1 = 2.853(3)\(\text{Å}\)) that is elongated compared to \(^{1}\text{Mes}\text{Bf}\), but still shorter than the sum of the van der Waals radii. The B···N bond length is 1.591(3)\(\text{Å}\), which is significantly shorter than that in the acetonitrile adduct of B(C\(_6\)F\(_6\))\(_3\) (1.616(3)\(\text{Å}\)).[116] The N···C bond (1.129(3)\(\text{Å}\)) is also shorter than that in the acetonitrile adduct of B(C\(_6\)F\(_6\))\(_3\) (1.141(2)\(\text{Å}\)) and very similar to that in PhBF·MeCN (1.128(4)\(\text{Å}\)).

**Electrochemistry**

Cyclic voltammograms of the three borafluorenes were recorded in dichloromethane with [nBu4N][PF\(_6\)] as the electrolyte and a scan rate of 250 mV s\(^{-1}\) (Figure 5) in order to determine their reduction potentials. All measurements were referenced to the ferrocene/ferrocenium redox couple (Fc/Fc\(^{+}\)). The most electron-deficient borafluorene, \(^{1}\text{Mes}'\text{Bf}\), exhibits a reversible reduction at \(-1.13\) V and an irreversible reduction at \(-2.04\) V. For the slightly less electron-deficient \(^{1}\text{Xyl}'\text{Bf}\), a reversible reduction at \(-1.21\) V and an irreversible reduction at \(-2.12\) V are observed. Interestingly, \(^{p}\text{NMe}_{2}'\text{Xyl}'\text{Bf}\) shows a reversible reduction at \(-1.28\) V, an irreversible reduction at \(-2.15\) V and a partially reversible oxidation at 0.95 V.

The three borafluorenes exhibit much higher reduction potentials \((^{1}\text{Mes}'\text{Bf} = -1.13\) V; \(^{1}\text{Xyl}'\text{Bf} = -1.21\) V and \(^{p}\text{NMe}_{2}'\text{Xyl}'\text{Bf} = -1.28\) V) than any of the previously reported borafluorenes and boroles or triarylboranes (Table 3). The substitution patterns of compounds \(^{1}\text{MesBC}_{4}\text{Ph}_{4}\) (\(E_1 = 2\) V) and \(^{1}\text{MesBF}\) (\(E_1 = 1.52\) V) allows a direct comparison of the fluorinated borafluorene backbone (\(^{1}\text{BF}\)) with the unsubstituted borafluorene backbone (BF) and the non-annulated borole.[88] The strong anodic shift of the \(^{1}\text{Mes}'\text{Bf}\) as compared to \(^{1}\text{MesBC}_{4}\text{Ph}_{4}\) and \(^{1}\text{MesBF}\) demonstrates the strong electron-withdrawing effect of the CF\(_3\) groups on the borafluorene.
Table 3. Tabulated first reduction potential values of various three-coordinate boron species.

| Compound          | First reduction potential $E_{1/2}$ [V] vs. Fc/Fc$^+$ this work |
|-------------------|---------------------------------------------------------------|
| FMesFBfa          | $-1.13$                                                       |
| FMesFBfa          | $-1.21$                                                       |
| p-NMe2CFxFFBfa     | $-1.28$                                                       |
| Mes+BF$_2$        | $-2.28^{[27]}$                                               |
| TipBF$_2$         | $-2.14^{[28]}$                                               |
| $^1$MesBF$_2$     | $-1.82^{[28]}$                                               |
| $^1$MesBF$_2$a    | $-1.98^{[10]}$                                               |
| $^1$MesBF$_2$b    | $-1.84^{[15]}$                                               |
| $^1$MesBF$_2$c    | $-1.38^{[15]}$                                               |
| B(Mes)$_3$        | $-2.73^{[31]}$                                               |
| B(Mes)$_3$(C,F$_2$) | $-2.10^{[21]}$                                               |
| B(Mes)$_3$(C,F$_3$) | $-1.72^{[21]}$                                               |
| B(C,F$_3$)$_4$     | $-1.97^{[21]}$                                               |

Measurement conditions: [a] Platinum electrode, CH$_3$Cl$_2$ (solvent), [nBu$_4$N][PF$_6$] (electrolyte); [b] Platinum electrode, THF (solvent), [nBu$_4$N][B(C,F$_2$)$_2$]$_2$ (electrolyte); [c] Glassy carbon electrode, CH$_3$Cl$_2$ (solvent), [nBu$_4$N][B(C,F$_3$)$_2$]$_2$ (electrolyte); [d] Glassy carbon electrode, THF (solvent), [nBu$_4$N][ClO$_4$] (electrolyte); [e] Glassy carbon electrode, CH$_3$Cl$_2$ (solvent), [nBu$_4$N][PF$_6$] (electrolyte); [f] Glassy carbon electrode, THF (solvent), [nBu$_4$N][PF$_6$] (electrolyte); [g] Platinum electrode, THF (solvent), [nBu$_4$N][PF$_6$] (electrolyte).

backbone. This is likely due to the planar geometry as well as the fact that the ortho CF$_3$-groups of the borafluorene backbone do not display B–F interactions, and thus do not increase electron density at the boron atom. The reduction potentials of the trifluoromethylated borafluorenes do not differ strongly from one another. This indicates that the para substituent on the exo-cyclic aryl moiety does not have a significant influence on the electron accepting properties of these borafluorenes. This is best illustrated by the fact that the π-donating dimethylamino group only leads to a cathodic shift of 0.15 V compared to a trifluoromethyl group. This is likely due to the nearly perpendicular arrangement of the exo-aryl group with respect to the borafluorene backbone, that limits π-conjugation leaving only inductive effects of the exo-aryl moiety on the borafluorene core and the boron center. To investigate further the electronic properties of borafluorene $^1$MesBF$_2$, CoCp$_2$ was chosen as a reducing agent ($E^{0}$(CoCp$_2$) = $-1.3$ V vs. Fc/Fc$^+$). Thus, after addition of CoCp$_2$, the yellowish THF solution of $^1$MesBF$_2$ turned dark purple and an ESR measurement confirmed the presence of the borafluorene radical anion $[^1$MesBF$_2]^-$(Figure 6).

A THF solution of the radical anion $[^1$MesBF$_2]^-$ shows a complex EPR signal centered at $g_{ee}$ = 2.004 consisting of hyperfine splittings to boron ($a^{[1]}$B) = 3.3 G; see non-annulated borole derivatives ($a^{[1]}$B) = 3.4–3.7 G$^{[35,123]}$, the CF$_3$ fluorine atoms ($a^{[3]}$F) = 11.3 and 6.0 G) and the hydrogen atoms ($a^{[1]}$H) = 6.1 and 2.9 G) of the borafluorene core. The relatively small boron hyperfine coupling together with the relatively large proton and fluorine hyperfine couplings indicate significant spin de-
localization onto the benzene rings, to a greater extent than in other singly reduced borafluorenes.\[87\]

Crystals of the radical anion suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated THF solution (Figure 7). Upon reduction, a variety of changes in the structure are observed. As there are two independent molecules in the unit cell for the radical anion, both molecules are taken into account for comparison (Table S2, Supporting Information). The negative charge is apparently localized on the borafluorene core, as the exo-aryl moiety is only slightly influenced, with almost all changes in bond length being within 3 esd’s. Although the B–C1 bond length is slightly increased (ΔB–C1 = +0.008 and +0.015 Å), both borole fluorine B–C bonds (B–C2 and B–C3) are shortened (ΔB–C2 = −0.034 and −0.025 Å; ΔB–C3 = −0.043 and −0.040 Å). The neighboring borole C–C bonds are elongated (ΔC3–C19 = +0.030 and +0.027 Å; ΔC2–C18 = +0.019 and +0.022 Å) and the C–C bond connecting the two borole aryls is shortened (ΔC18–C19 = −0.024 Å). In summary, the bond lengths within the five-membered heterocycle equalize. This behavior was previously observed in the structures of borole radical anions and dianions.\[85\] The one-electron reduction also influences the shortest B-F distances which are elongated (mean ΔB–F = +0.278 Å).

Photophysical properties

To obtain further insight into the electronic structure of the borafluorenes, absorption and emission spectra as well as quantum yields and excited-state lifetimes were measured in hexane (Figure 8 and Table 4). Furthermore, \[^{7}\text{Mes}^{5}\text{BF}\] was also studied in CH\(_2\)Cl\(_2\) and in the solid state. Solvatochromic studies of \(p\-\text{NMe}_2\-\text{Xyl}\-\text{BF}\) could not be carried out, because no emission was detected in more polar solvents. This is most likely due to a further redshift of the emission, which in turn results in increased non-radiative decay processes and thus a much lower quantum yield. A photophysical investigation of \[^{7}\text{Mes}^{5}\text{BF}-\text{MeCN}\] is included in the Supporting Information (see also Figure S50 and Table S5).

![Figure 7. The solid-state molecular structure of \[^{7}\text{Mes}^{5}\text{BF}]\([\text{CoCp}_2]\) determined by single-crystal X-ray diffraction at 100 K. All ellipsoids are drawn at the 50% probability level. H atoms and THF solvent molecules are omitted for clarity. Only half of the symmetrically non-equivalent molecules are shown. One of the CF\(_3\) groups on the borafluorene core is rotationally disordered and only the part with the higher occupancy (64%) is shown here (left). The relevant changes in bond lengths of \[^{7}\text{Mes}^{5}\text{BF}\] compared to the neutral starting material are shown at the right.](image)

![Figure 8. Absorption (black) and emission spectra (red) in hexane of \[^{7}\text{Mes}^{5}\text{BF}\] (top left), \[^{5}\text{Xyl}^{7}\text{BF}\] (top right) and \(p\-\text{NMe}_2\-\text{Xyl}^{7}\text{BF}\) (bottom left). For comparison, the emission spectra are plotted together (bottom right; \[^{7}\text{Mes}^{5}\text{BF}\] (black), \[^{5}\text{Xyl}^{7}\text{BF}\] (blue), \(p\-\text{NMe}_2\-\text{Xyl}^{7}\text{BF}\) (red).](image)
All borafluorenes exhibit very small extinction coefficients for their lowest-energy absorption (ε = 300–400 M⁻¹ cm⁻¹; log ε = 2.48–2.60) which can be classified as weakly allowed transitions, similar to those in previously reported boroles and borafluorenes. The lowest-energy absorption of 1XylBF (λ_max = 386 nm) appears to be slightly hypsochromically shifted compared to 1MesBF (λ_max = 400 nm) and p-NMe₂-XylBF (λ_max = 396 nm) but, due to the broad absorption bands, this is difficult to determine accurately. All three borafluorenes exhibit broad, structureless emission bands. The emission maximum of 1MesBF (Φ_e = 0.37; hexane) and 1XylBF (Φ_e = 0.30; hexane) are higher than most of the reported borafluorenes (ca. 0.1). In contrast, p-NMe₂-XylBF exhibits a very low quantum yield (Φ_e = 0.03; hexane). To our surprise, 1MesBF and 1XylBF exhibit very long fluorescent lifetimes in solution (1MesBF: τ = 224 ns (hexane); τ = 151 ns (CH₂Cl₂); 1XylBF: τ = 249 ns (hexane)) as well as in the solid state (1MesBF: τ = 173 ns). Similar fluorescence lifetimes (116–150 ns) of borafluorenes with bulky exo-aryl moieties were previously observed by Rupar and co-workers. This results in exceptionally long natural lifetimes, τ₀, uncommon for organic molecules, for which fluorescence usually takes place on a nanosecond timescale. There are, however, some exceptions such as pyrene. This indicates a forbidden process. It is very interesting that even though the radiative rate constants are small for organic chromophores, the non-radiative rate constants are of the same order, resulting in moderate quantum yields. This is likely a result of the high rigidity of the systems. In contrast, p-NMe₂-XylBF exhibits two different radiative decay processes, a prompt (τ = 9.2 ns) and a delayed (τ = 1.6 µs) one. This can be caused by different processes namely TTA (triplet–triplet annihilation) or TADF (thermally activated delayed fluorescence). Due to the low concentrations (≤ 10⁻⁴ M) of the compound employed, the lack of dependence on the concentration and the temperature dependence of the lifetime, we can attribute the observed behavior to TADF. The mechanism for TADF is based on a reverse intersystem crossing process (rISC) between the lowest-energy triplet state (T₁) and excited singlet state (S₂) of a molecule. In order for this to occur, the energy difference between S₁ and T₁ (∆E_S₂) has to be sufficiently small. The most common structures to exhibit this phenomenon are twisted dipolar systems with spatially separated HOMO and LUMO such as D(donor)–π–A(acceptor) compounds. This structural motif is also found in p-NMe₂-XylBF. The singlet–triplet gap (∆E_S₂) can be easily determined experimentally if phosphorescence can be observed. However, for p-NMe₂-XylBF, even at 77 K in a frozen glass matrix of 2-MeTHF, no phosphorescence was observed. However, ∆E_S₂ can also be calculated once the rate constant of the rISC process (k_rISC) is obtained, which is given by the Arrhenius Equation (1), or Equation (2) as derived by Dias et al.

\[ k_{\text{rISC}} = A \exp \left( -\frac{\Delta E_{S_2}}{kT} \right) \]  

(1)

\[ k_{\text{rISC}} = \frac{\Phi_{\text{PF}} + \Phi_{\text{PS}}}{\tau_{\text{PF}}} \]  

(2)

with \( \Phi_{\text{PF}} \) and \( \Phi_{\text{PS}} \) being the quantum yields of the delayed and prompt fluorescence and the reverse intersystem crossing, respectively. Given that no phosphorescence was observed at 77 K, but delayed fluorescence was, it can be assumed that ∆E_S₂ is small and, as such, the rate of reverse intersystem crossing is very high, i.e.,

\[ \Phi_{\text{rISC}} = \frac{k_{\text{rISC}}}{k_{\text{rISC}} + k_{\text{PF}}} \approx 1 \]

and, thus, Equation (2) can be modified to give Equation (3).

\[ k_{\text{rISC}} = \frac{1}{\tau_{\text{PF}}} \left( \frac{\Phi_{\text{PF}} + \Phi_{\text{PS}}}{\Phi_{\text{PF}}} \right) = \frac{1}{\tau_{\text{PF}}} \left( 1 + \frac{\Phi_{\text{PS}}}{\Phi_{\text{PF}}} \right) = \frac{1}{\tau_{\text{PF}}} + \frac{\Phi_{\text{PS}}}{\Phi_{\text{PF}}} \]  

(3)

The ratio \( \Phi_{\text{PS}}/\Phi_{\text{PF}} \) can be ascertained from time-resolved measurements via Equation (4),

\[ \frac{\Phi_{\text{PF}}}{\Phi_{\text{PS}}} = \frac{B_{\text{PF}}}{B_{\text{PS}}} + \frac{T_{\text{PF}} T_{\text{PS}}}{T_{\text{PF}} T_{\text{PS}}} \]  

(4)

| Table 4. Photophysical data for borafluorenes 1MesBF, 1XylBF, and p-NMe₂-XylBF. |
|-----------------|---------------------------------|-----------------|-----------------|
| Compound        | Solvent | \( \lambda_{\text{em}} \) [nm] | \( \lambda_{\text{em}} \) Apparent Stokes shift [10⁻³ cm⁻¹] | \( \phi_{\text{rISC}} \) |
| ----------------|---------|-------------------------------|-----------------|-----------------|
| 1MesBF          | hexane  | 299 (2.9; 3.46), 321 (0.8; 2.90), 400 (0.3; 2.48) | 521 | 5.8 | 0.37 | \( 224 \) | 605 | 0.3 | 0.2 |
| 1MesBF          | CH₂Cl₂ | 395 | 540 | 6.8 | \( 0.18 \) | \( 151 \) | 835 | 0.1 | 0.005 |
| 1MesBF          | solid   | 405 | 527 | 6.0 | \( 0.06 \) | \( 173 \) | 2557 | 0.5 | 0.04 |
| 1XylBF          | hexane  | 256 (54.2; 4.73), 290 (2.9; 3.46), 386 (0.4; 2.60) | 510 | 6.3 | \( 0.30 \) | \( 249 \) | 820 | 0.3 | 0.1 |
| p-NMe₂-XylBF    | hexane  | 268 (32.3; 4.51), 326 (2.7; 3.43), 396 (0.3; 2.48) | 627 | 9.3 | \( 0.03 \) | \( 9.2 (64\%) \) | – | – | – |

[a] Excited at the respective \( \lambda_{\text{abs max}} \) of the \( S_1 \to S_0 \) transition. [b] The non-radiative rate constants were calculated from \( k_{\text{nr}} = (1 - \phi_{\text{rISC}}) / \tau \). [c] The radiative rate constants were calculated from \( k_{\text{rISC}} = \phi_{\text{rISC}} / \tau \).
with $B_{\text{ex}}$ and $B_{\text{of}}$ being the pre-exponential fitting parameters of the time-resolved fluorescence lifetime measurements. As such, equation (1) can be written as Equation (5) where all parameters can be obtained from the time-resolved fluorescence decay.

$$k_{\text{sec}} = A\exp\left(\frac{-\Delta E_{s,T}}{kT}\right) = \frac{1}{\tau_{\text{of}}} + \frac{1}{\tau_{\text{of}}} A_{\text{ex}} T_{\text{of}}$$

(5)

Lifetime were obtained between 300 K and 230 K in methylcyclohexane. From the slope of a plot of $\ln(k_{\text{sec}})$ versus $1/T$ (Figure 9), we obtain $\Delta E_{s,T} = 15 \text{ meV}$, which is comparable to values previously reported for TADF emitters.[145]

![Figure 9. Arrhenius plot of $\ln(k_{\text{sec}})$ of $\pi$-NMe$_2$-XylBf (determined from temperature-dependent lifetime measurements) vs. $1/T$.](image)

**DFT and time-dependent (TD)-DFT studies**

Using the crystal structures as the starting geometries, the ground-state (GS) structures were optimized using DFT calculations at the B3LYP/6-31G+(d) level of theory. For $^{1}$Mes$^\text{Bf}$ and $^{1}$Xyl$^\text{Bf}$, the optimized ground-state structures exhibit $C\text{v}_{s}$ and $C\text{v}_{u}$ symmetries, respectively. For $\pi$-NMe$_2$-Xyl$^\text{Bf}$, optimization of the GS structure with $C\text{v}_{s}$ symmetry did not lead to a global minimum but rather to a saddle point (1 imaginary frequency remained). However, given that the $C\text{v}_{s}$ structure is very close to the $C\text{v}_{u}$ symmetry one, in both geometry and energy, and exhibits almost the same transition dipole moments, the symmetry descriptors will be used as it simplifies the discussion. The optimized structures reproduce the geometries, bond lengths, angles, and shortest $B$–$F$ contacts of the crystal structures reasonably well. However, as compared to the crystal structures, the optimized structures do not exhibit bending of the exo-aryl out of the plane of the borafluorene backbone. Given that this torsion arises from solid-state interactions, this is to be expected. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies increase from $^{1}$Mes$^\text{Bf}$ to $^{1}$Xyl$^\text{Bf}$ to $\pi$-NMe$_2$-Xyl$^\text{Bf}$ (Figure 10 and Table 5). The calculated LUMO energies fit well with the LUMO energies estimated from the redox potentials obtained through cyclic voltammetry. Due to the very broad nature of the lowest-energy absorption band, the HOMO energies of $^{1}$Mes$^\text{Bf}$ and $^{1}$Xyl$^\text{Bf}$ were not calculated from the experimental data.

The LUMOs are all localized on the borafluorene moieties with their largest components on boron, and the energies differ by only 0.2–0.4 eV. For $^{1}$Mes$^\text{Bf}$ and $^{1}$Xyl$^\text{Bf}$ the HOMOs are also localized on the borafluorene moieties with boron lying on a nodal plane, and are energetically similar ($\Delta E = 0.16 \text{ eV}$). The HOMO of $\pi$-NMe$_2$-Xyl$^\text{Bf}$ is localized on the exo-aryl moiety and lies about 1.4 eV higher in energy than the HOMOs of $^{1}$Mes$^\text{Bf}$ and $^{1}$Xyl$^\text{Bf}$. This is due to the electron-donating effect of the para-dimethylamino-group that increases the energy of the exo-aryl fragment MO thereby raising it above the borafluorene-centered orbital which is now HOMO–1. For both $^{1}$Mes$^\text{Bf}$ and $^{1}$Xyl$^\text{Bf}$, HOMO–1 is localized on the exo-aryl moiety; however, due to the para-CF$_3$ group, the HOMO–1 of $^{1}$Mes$^\text{Bf}$ is about 0.5 eV lower. Based on the optimized ground-state structures the nucleus-independent chemical shift (NICS) values of the borafluorenes were calculated (Table 6).

It is apparent that the perfluoroalkylated borafluorenes exhibit lower NICS(1)$_{zz}$ values as compared to that of the borafluorene TipBF which does not contain CF$_3$ groups. This suggests a higher degree of delocalization of the electron density over the borafluorene backbone in our compounds. Thus, the aromatic character is less than in non-trifluoromethylated borafluorenes. The optimized structures were then used for TD-DFT calculations to simulate the absorption spectra. Time-dependent DFT calculations on $^{1}$Mes$^\text{Bf}$ and $^{1}$Xyl$^\text{Bf}$ were carried out at the B3LYP/6-31+G(d) level of theory whereas for the donor substituted $\pi$-NMe$_2$-Xyl$^\text{Bf}$ the Coulomb-attenuated functional CAM-B3LYP was employed using the same basis set (Table 7), because CAM-B3LYP is better suited to systems involving charge transfer.[146,147] Furthermore, the optimized $S_{1}$-state geometries of $^{1}$Mes$^\text{Bf}$ and $^{1}$Xyl$^\text{Bf}$ were obtained. In order to characterize the nature of the transition the overlap coefficients ($\beta$) were determined.[146] The calculated lowest-n
energy absorptions of the borafluorenes fit well with the experimental values. For all compounds, the lowest-energy transitions are predominantly of HOMO to LUMO character.

For both 1MesBF and 1XylBF these can be classified as locally excited (LE) transitions (A ≈ 0.65) as both HOMO and LUMO are localized on the borafluorene backbone. This is surprising, as LE transitions usually exhibit high extinction coefficients and the symmetries of the frontier molecular orbitals it is possible to determine whether these transitions are forbidden by symmetry. The symmetries of the HOMOs of 1MesBF (C3v) and 1XylBF (C2v) are A1 and B1, respectively, and the LUMO symmetries are A1 and B2. Transitions are allowed by symmetry if the initial and final states multiplied by the x, y, and z-characters of the electronic dipole operator contain the totally symmetric irreducible representation (C1: A1 and C2v: A1). For 1MesBF (C3v), the lowest-energy transition is forbidden in the z-direction, whereas x and y are allowed, making the transition an allowed transition. For 1XylBF (C2v), the x- and z-directions are forbidden, whereas the y-direction is allowed, making the transition an allowed transition. However, for both molecules, the dipole moment is oriented along the z-axis, resulting in a very small transition dipole moment in the x- and y-directions.

Table 6. NICS(1)z values of the borole moiety of 1MesBF, 1XylBF, p-NMe2-XylBF, and TipBF calculated at the B3LYP/6–31+G(d) level.

| Compound       | calcd | Lit. |
|----------------|-------|------|
| 1MesBF         | 20.7  |      |
| 1XylBF         | 20.2  |      |
| p-NMe2-1XylBF  | 20.0  |      |
| TipBF          | 24.3  | 24.5 |

Table 7. Lowest-energy and highest oscillator-strength absorptions and emissions of 1MesBF and 1XylBF calculated at the B3LYP/6–31+G(d) level of theory and lowest-energy absorptions of p-NMe2-XylBF calculated at the CAM-B3LYP/6–31+G(d) level of theory.

| Compound       | State | E [eV] | λ [nm] | λmax [nm] | f | Symmetry | Major contributions | A |
|----------------|-------|--------|--------|-----------|---|----------|---------------------|---|
| 1MesBF (C3v)   | S1→S0 | 3.05   | 406    | 400       | 0.0005 | A1       | HOMO→LUMO (99%)     | 0.65|
| S2→S0          | 3.90   | 318    | 0      | A*        |      |          | HOMO→LUMO (99%)     | 0.25|
| S2→S0          | 4.80   | 258    | 257    | 0.8133    | A1 |          | HOMO→LUMO (24%), HOMO→LUMO+1 (70%) | 0.73|
| 1MesBF (C2v)   | S1→S0 | 2.22   | 559    | 521       | 0.0038 | A1       | H-SOMO→L-SOMO (99%) | 0.06|
| S2→S0          | 3.64   | 340    | 0      | A1        |      |          | HOMO→LUMO (99%)     | 0.23|
| S2→S0          | 4.81   | 258    | 256    | 0.8143    | B1 |          | HOMO→LUMO (28%), HOMO→LUMO+1 (68%) | 0.74|
| 1MesBF (C2v)   | S1→S0 | 2.34   | 531    | 510       | 0.0030 | A         | H-SOMO→L-SOMO (99%) | 0.06|
| p-NMe2-1XylBF  | S1→S0 | 3.25   | 382    | 396       | 0    | A        | HOMO→LUMO (92%)     | 0.15|
| S2→S0          | 3.46   | 358    | 326    | 0.0006    | A1 |          | HOMO→LUMO (97%)     | 0.67|
| S2→S0          | 4.25   | 292    | 270    | 0.0491    | A1 |          | HOMO→L+2 (70%), HOMO→L+3 (24%) | 0.49|
| S4→S0          | 5.11   | 243    | 256    | 0.6022    | A1 |          | HOMO→L+4 (86%)      | 0.71|

Figure 10. Frontier molecular orbitals of 1MesBF (left), 1XylBF (middle), and p-NMe2-XylBF (right) calculated at the B3LYP/6–31+G(d) level of theory.
which results in very low oscillator strengths. So, the lowest-energy transitions are allowed, but exhibit only small changes in dipole moment resulting in weak absorptions. This can be, in part, attributed to the boron center, because its contribution to the LUMO gives the transition a π–n character. The $S_1$–$S_0$ transitions, in both cases, are predominantly HOMO–1 to LUMO transitions. The HOMO–1 of $\text{Mes}^\text{S}\text{BF}$ and $\text{Xyl}^\text{S}\text{BF}$ are of $A'$ and $B_2$ symmetry, respectively, and, thus, are symmetry forbidden. Both $\text{Mes}^\text{S}\text{BF}$ and $\text{Xyl}^\text{S}\text{BF}$ exhibit large oscillator strengths for their $S_0$–$S_0$ and $S_1$–$S_0$ transitions, respectively. In both cases, these transitions have predominantly HOMO to LUMO–1 character. Both HOMO and LUMO–1 are delocalized over the borafluorene backbone without contributions from the boron center. The optimized $S_0$ geometries of $\text{Mes}^\text{S}\text{BF}$ and $\text{Xyl}^\text{S}\text{BF}$ differ only slightly from their ground-state structures (Figure 11).

In comparison, in the $S_1$ structure of $\text{Mes}^\text{S}\text{BF}$, only the $\text{para}$-CF$_2$ groups on the borafluorene backbone are rotated and in both $\text{Mes}^\text{S}\text{BF}$ and $\text{Xyl}^\text{S}\text{BF}$ the $\text{ortho}$-CF$_2$ groups on the $\text{exo}$-aryl are slightly bent away from the boron center. The calculated emission maxima of $\text{Mes}^\text{S}\text{BF}$ and $\text{Xyl}^\text{S}\text{BF}$ fit the experimental data in hexane and also exhibit very low oscillator strengths. Even though the optimized structures do not exhibit a higher symmetry it can be assumed that a similar phenomenon as for the absorption takes place and is the reason for the observed long lifetimes. Interestingly, as previously discussed, the reasonably high quantum yields observed are due to extremely slow non-radiative decay processes.

The photophysical properties of $\text{p-NMe}_2\text{Xyl}^\text{S}\text{BF}$ differ strongly from those of $\text{Mes}^\text{S}\text{BF}$ and $\text{Xyl}^\text{S}\text{BF}$. This is, in part, due to the fact that the nature of the lowest-energy absorption has CT rather than LE character ($\lambda = 0.15$). This is not surprising, given that $\text{p-NMe}_2\text{Xyl}^\text{S}\text{BF}$ is a donor–acceptor system. The $S_1$–$S_0$ transition of $\text{p-NMe}_2\text{Xyl}^\text{S}\text{BF}$ exhibits an oscillator strength of 0. Using the optimized structure of $C_2$, symmetry as an approximation, it becomes apparent that this transition is symmetry forbidden and, furthermore, the overlap between HOMO and LUMO is minuscule due to the nearly perpendicular arrangement of the $\text{exo}$-aryl group with respect to the borafluorene core. The HOMO is of $B_1$ symmetry and the LUMO has $B_1$ symmetry. This is the same as for the $S_2$–$S_0$ transitions of $\text{Mes}^\text{S}\text{BF}$ and $\text{Xyl}^\text{S}\text{BF}$, because the HOMO and HOMO–1 are inverted compared to those of $\text{p-NMe}_2\text{Xyl}^\text{S}\text{BF}$. For $\text{p-NMe}_2\text{Xyl}^\text{S}\text{BF}$, however, the $S_2$–$S_0$ transition is allowed, but analogously to the $\text{Mes}^\text{S}\text{BF}$ and $\text{Xyl}^\text{S}\text{BF}$ cases, exhibits a very low oscillator strength. This explains the low extinction coefficient observed for the lowest-energy absorption of $\text{p-NMe}_2\text{Xyl}^\text{S}\text{BF}$. Furthermore, we optimized the $S_0$ structure of $\text{p-NMe}_2\text{Xyl}^\text{S}\text{BF}$ as well as its $T_1$ structure in order to calculate the $S_1$–$T_1$ energy gap. Both optimizations were carried out using the PCM solvent-correction model due to the charge-transfer nature of the transitions and the high dipole moment of both $S_1$ and $T_1$. Comparing the energies of both structures results in $\Delta E_{S_1:T_1} = 423$ meV which is almost 30 times higher than the experimentally determined gap. It is noteworthy that the experimental determination of the gap is highly flawed due to approximations as well as unpredictable solvent effects at lower temperature. However, this should still give a good estimate, but the calculations fail to match the experimental value at this level of theory, illustrating the difficulty of predicting phenomena such as TADF accurately.

Conclusions

Herein, we reported the synthesis and properties of three trifluoromethylated borafluoranes $\text{Mes}^\text{S}\text{BF}$, $\text{Xyl}^\text{S}\text{BF}$, and $\text{p-NMe}_2\text{Xyl}^\text{S}\text{BF}$. The copper-catalyzed homocoupling of boronate esters provides a convenient route to 2,2’-dibromobiphenyl derivatives, which can be lithiated and then reacted with stable and accessible ary1-BF$_2$K salts for the synthesis of borafluoranes. All of the borafluoranes exhibit a rigid geometry with the $\text{exo}$-aryl group lying perpendicular to the borafluorene plane. All three borafluoranes exhibit exceptionally positively shifted reduction potentials, emphasizing the electron-withdrawing nature of the CF$_2$ groups. This allowed us to use a mild reducing agent (CoCp$_2$, $E^\theta = -1.3$ eV vs. Fc/Fc$^+$) to reduce the most anodically shifted borafluorene $\text{Mes}^\text{S}\text{BF}$. The resulting radical cation of $\text{Mes}^\text{S}\text{BF}$ exhibits a strong delocalization of the additional electron over the borafluorene backbone as evidenced by EPR spectroscopy and its solid-state structure. The trifluoromethylated borafluoranes exhibit unusually long excited-state lifetimes and weakly allowed lowest-energy transitions. For $\text{Mes}^\text{S}\text{BF}$ and $\text{Xyl}^\text{S}\text{BF}$, this is the result of the transitions being forbidden in the $z$-direction which coincides with the dipole moment and the transition dipole moment being negligible in the $x$- and $y$-directions. The same is apparently true for their emissions, as both compounds exhibit fluorescence lifetimes of $\tau > 200$ ns in hexane. Even with small oscillator strengths, the two compounds exhibit fluorescence quantum yields of 0.37 and 0.30, respectively, because their rigidity results in exceptionally slow non-radiative decay. In contrast, the twisted donor–acceptor system $\text{p-NMe}_2\text{Xyl}^\text{S}\text{BF}$ has a symmetry forbidden lowest-energy transition and exhibits TADF, with a singlet-triplet energy gap $\Delta E_{S,T}$ experimentally determined to be only 15 meV. The compounds $\text{Mes}^\text{S}\text{BF}$ and $\text{Xyl}^\text{S}\text{BF}$ are highly stable towards hydrolysis, which makes them interesting potential building blocks for organic materials.
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Conflict of interest

The authors declare no conflict of interest.

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