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Highly stable, readily reducible, fluorescent, trifluoromethylated 9-borafluorenes

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Abstract: Three different perfluoroalkylated borafluorenes 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 (^FXyl^FBf), a trifluoromethyl group (^FMes^FBf) or a dimethylamino group (*p*-NMe₂-^FXyl^FBf), respectively. All derivatives exhibit extraordinarily low reduction potentials, comparable to those of perylenediimides. The most electron deficient derivative ^FMes^FBf was also chemically reduced and its radical anion isolated and characterized. Furthermore, all compounds exhibit very long fluorescent lifetimes of ca. 250 ns up to 1.6 μs; however, the underlying mechanisms responsible for this differ. The donor substituted derivative *p*-NMe₂-^FXyl^FBf exhibits thermally activated delayed fluorescence (TADF) from a charge transfer (CT) state, while the ^FMes^FBf and ^FXyl^FBf 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 triarylboranes^[1-13] and, more recently, boron-containing polyaromatics are of much current interest.^[3, 10, 14-20] 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,^[8, 54-56] frustrated Lewis pairs (FLPs),^[57-63] as well as in organic light emitting diodes (OLEDs).^[64-66] 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.^[3, 18, 67-82] They are isoelectronic with the antiaromatic cyclopentadiene cation, having 4 π electrons; however, the introduction of the boron vertex lowers the symmetry. This leads to a singlet ground state with a small HOMO-LUMO gap, resulting in the intense color of boroles, even though the molar extinction coefficient (ϵ) is quite small for their S₁←S₀ transitions.

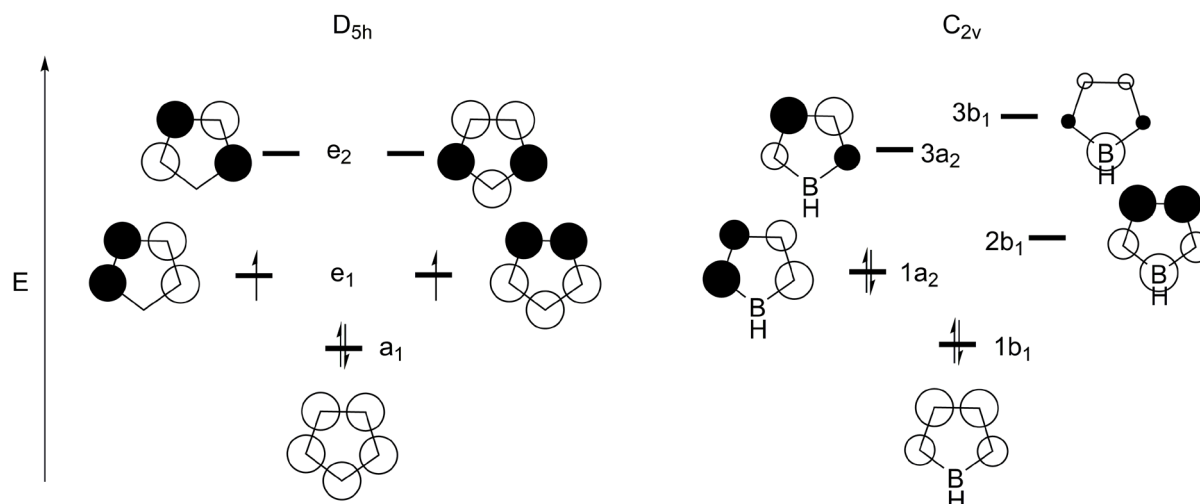


Figure 1: Frontier orbitals of the cyclopentadienyl cation (left) and borole (right).

Because of that, they are highly reactive towards nucleophiles and thereby unsuitable for many applications. Steric shielding, which works well for triarylboranes,^[33, 83, 84] only stabilizes boroles to a certain degree.^[79, 85] Via 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 triarylborane 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 to p conjugation or indirect F–B interaction (Figure 2).

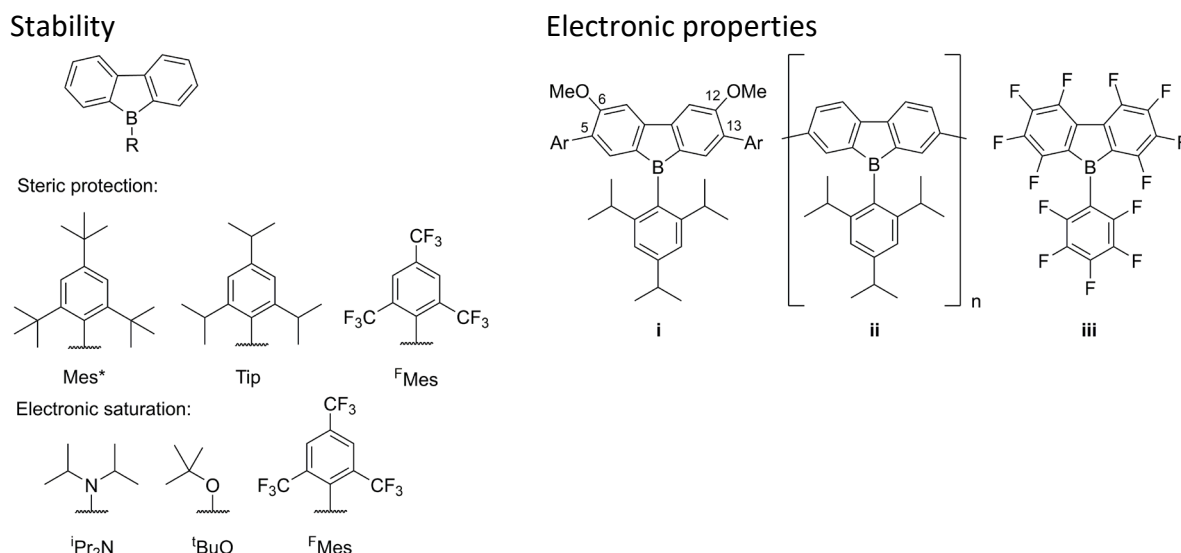


Figure 2: Selected examples of borafluorenes. A variety of *exo*-aryl substituents and the nature of their respective influence on the stability of the borafluorene (left).^[87, 88] It is important to note, that *ortho*-trifluoromethyl substituted aryls provide both steric as well as electronic stabilization. Examples of the functionalization of the borafluorene backbone to tune the electronic properties (right).^[86, 95-97]

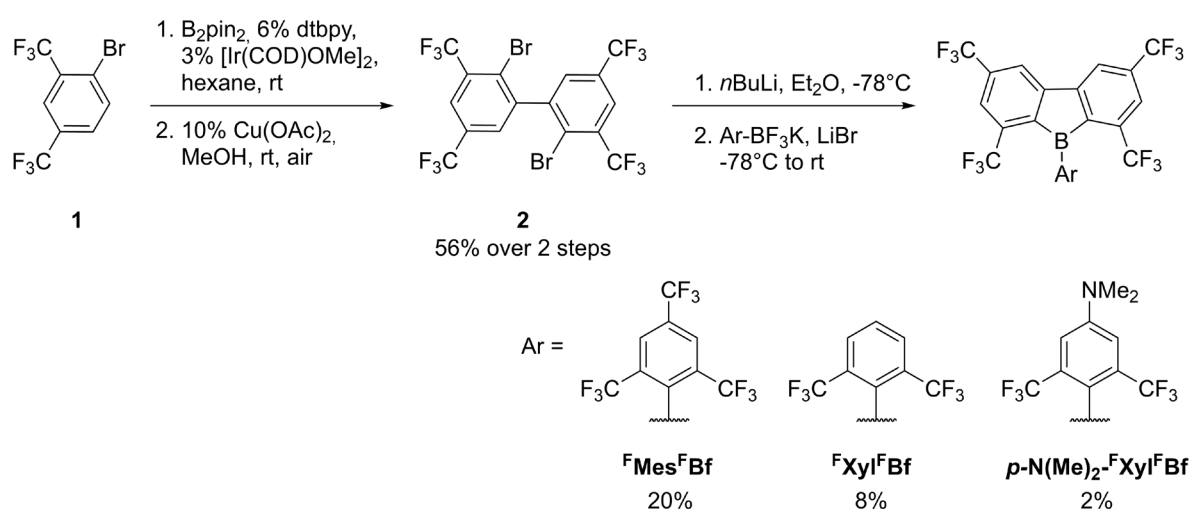
Yamaguchi and co-workers reported air and moisture stable borafluorene derivatives employing either Tip or the even bulkier Mes* substituents.^[86, 87] It was found that the Tip derivatives could be used as turn on type fluoride sensors, whereas the Mes* compounds showed no reaction with fluoride. Recently, Rugar and co-workers have studied these effects in detail.^[88] They found that while 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 (ⁱPr₂N: 50% decomp. over 1 h; ^tBuO: 10% decomp. over 1 h). *Ortho* trifluoromethyl substituted aryls exhibit a strong stabilizing effect on boranes.^[33, 79, 98-102] 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)^[103] 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,^[86] 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.^[87] 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.^[86, 104] Wilson and Gillard and co-workers observed turn-off fluorescence of a borafluorene cation upon coordination of a Lewis base at low temperature, resulting in thermochromism.^[105] Piers and co-workers investigated the properties of a highly electron deficient perfluorinated borafluorene **iii**.^[95, 96] While they only observed a reduction corresponding to the perfluoroaryls 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 $B(C_6F_5)_3$, preference towards the borafluorene derivative was observed, especially with sterically-demanding Lewis bases. The (sp^2 -C)–F bonds in this compound, however, are still reactive towards nucleophiles. In contrast, perfluoroalkyl groups are inert towards nucleophiles, provide a strong inductive electron withdrawing effect and have been previously employed in the synthesis of electron deficient triarylboranes.^[102] To the best of our knowledge, there have been no photophysical studies of borafluorenes with electron deficient biphenyl backbones. We envisioned that judicious incorporation of trifluoromethyl groups both in the biphenyl core and at the *exo*-aryl moiety would provide a significant stability enhancement while retaining the low-lying LUMO typical of non-annulated boroles.

Results and discussion

Synthesis

In order to maximize the stability of the trifluoromethylated borafluorenes (**F₃Bf**) we chose three different *meta*-fluoroxylene (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 (**F₃Xyl**), 2,4,6-tris(trifluoromethyl)phenyl (**F₃Mes**) and 4-(dimethylamino)-2,6-bis(trifluoromethyl)phenyl (**p-N(Me)₂-F₃Xyl**) groups.



Scheme 1: Synthesis of **F₃Mes^FBf**, **F₃Xyl^FBf** and **p-NMe₂-F₃Xyl^FBf**.

Biphenyl derivative **2** was synthesized via regioselective C–H borylation of **1**^[106, 107] *ortho* to the bromine and a subsequent copper-catalyzed oxidative homocoupling. For the last step, **2** was dilithiated and subsequently reacted with the appropriate Ar-BF₃K salt. Attempts to synthesize the haloborafluorene with different BX₃ (X = F, Cl, Br) sources failed. Attempts to use aryl-boronates in place of the Ar-BF₃K 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,^[79] and applied by others in the synthesis of boron PAHs^[108, 109] and aryl-borates.^[110, 111] Organic trifluoroborate salts are widely employed in cross-coupling reactions as they are readily accessible and very stable.^[112, 113] During the

synthesis we observed that adding LiBr greatly improves the reactivity of the Ar-BF₃K salts. It is possible that a cation exchange reaction generates the more reactive Ar-BF₃Li salt. The increased reactivity of the Ar-BF₃Li 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 isolated yields. It is important to note that the corresponding *ortho*-trifluoromethylarylboron halides (X = Cl, Br) are not stable due to halide exchange.^[114] This might also explain why the synthesis of the haloborafluorenes was not possible. The compounds ^FMes^FBf, ^FXyl^FBf and *p*-NMe₂-^FXyl^FBf were obtained after purification via sublimation and recrystallization. Both ^FMes^FBf and ^FXyl^FBf are bright green solids. In contrast, *p*-NMe₂-^FXyl^FBf is a red solid. All compounds exhibit ¹H NMR and ¹³C{¹H} NMR signals consistent with their proposed structures. The ¹¹B{¹H} NMR shifts for all three borafluorene derivatives are around 64 ppm and differ only slightly. The ¹⁹F{¹H} NMR spectra display singlets and septets, the latter with a J_{FF} coupling constant of 3 – 4 Hz. (Table 1)

Table 1: ¹¹B{¹H} and ¹⁹F{¹H} NMR shifts of ^FMes^FBf, ^FXyl^FBf, and *p*-NMe₂-^FXyl^FBf recorded in C₆D₆.

	^F Xyl ^F Bf	^F Mes ^F Bf	<i>p</i> -NMe ₂ - ^F Xyl ^F Bf
¹¹ B{ ¹ H} NMR (ppm)	63.2	64.1	64.7
¹⁹ F{ ¹ H} NMR (ppm) singlet	-63.4	-62.0; -63.5	-63.4
¹⁹ F{ ¹ H} NMR (ppm) septets	-58.2 (J _{FF} = 4 Hz)	-58.4 (J _{FF} = 4 Hz)	-58.1 (J _{FF} = 4 Hz)
	-59.6 (J _{FF} = 4 Hz)	-59.6 (J _{FF} = 4 Hz)	-59.5 (J _{FF} = 4 Hz)

The singlets at ca. $\delta = -63.5$ ppm correspond to the two freely rotating *para* CF₃-groups on the borafluorene core. For ^FMes^FBf, another singlet corresponding to the *para* CF₃-group on the *exo*-aryl is observed. The CF₃-groups *ortho* to the boron center display a complex coupling pattern of two septets with small coupling constants (J_{FF} = 4 Hz). This can be attributed to through-space F–F coupling as previously observed at low temperature (243 K) for (^FMes)₂BAR compounds.^[100] The fact that the borafluorenes exhibit this phenomenon at room temperature is an indicator of the high rigidity of the systems.

All three compounds are stable in the solid-state and can be stored under ambient conditions without decomposition. In wet CDCl₃ (1.5 eq. H₂O/borafluorene) at room temperature, no decomposition of either ^FMes^FBf or ^FXyl^FBf was observed over 4 d by NMR spectroscopy. This is surprising as for ^FMesBf 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-^FXyl^FBf 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-^FXyl^FBf was isolated and studied by X-ray diffraction (compound **D** in Figure S41). 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 ^FMes^FBf in acetonitrile gives a colorless solution. Investigation of the solution via 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, as 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 ^FMes^FBf, one septet at –51.9 ppm (*J*_{FF} = 10 Hz) one broad singlet at –56.2 ppm and a quartet at –60.7 ppm (*J*_{FF} = 10 Hz), are observed (Figure 3, middle).

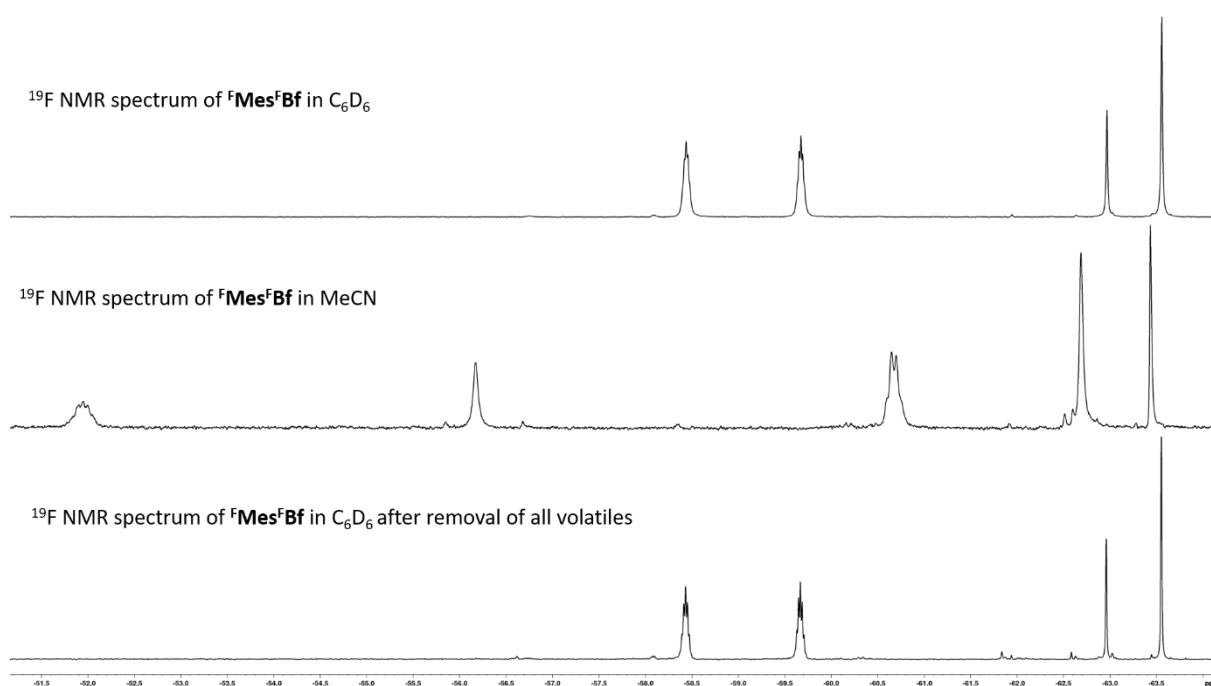


Figure 3: ¹⁹F NMR spectra (188 MHz, 298 K) of ^FMes^FBf in C₆D₆ (top), in CH₃CN (middle) and in C₆D₆ after removal of all volatiles (bottom).

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 via 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 ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ (${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}\cdot\text{MeCN}$) 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 ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ and $p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ were obtained from a saturated hexane solution at $-30\text{ }^{\circ}\text{C}$, that of ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ was obtained by evaporation of a saturated DCM solution and that of ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}\cdot\text{MeCN}$ was obtained from a saturated acetonitrile solution at $-30\text{ }^{\circ}\text{C}$.

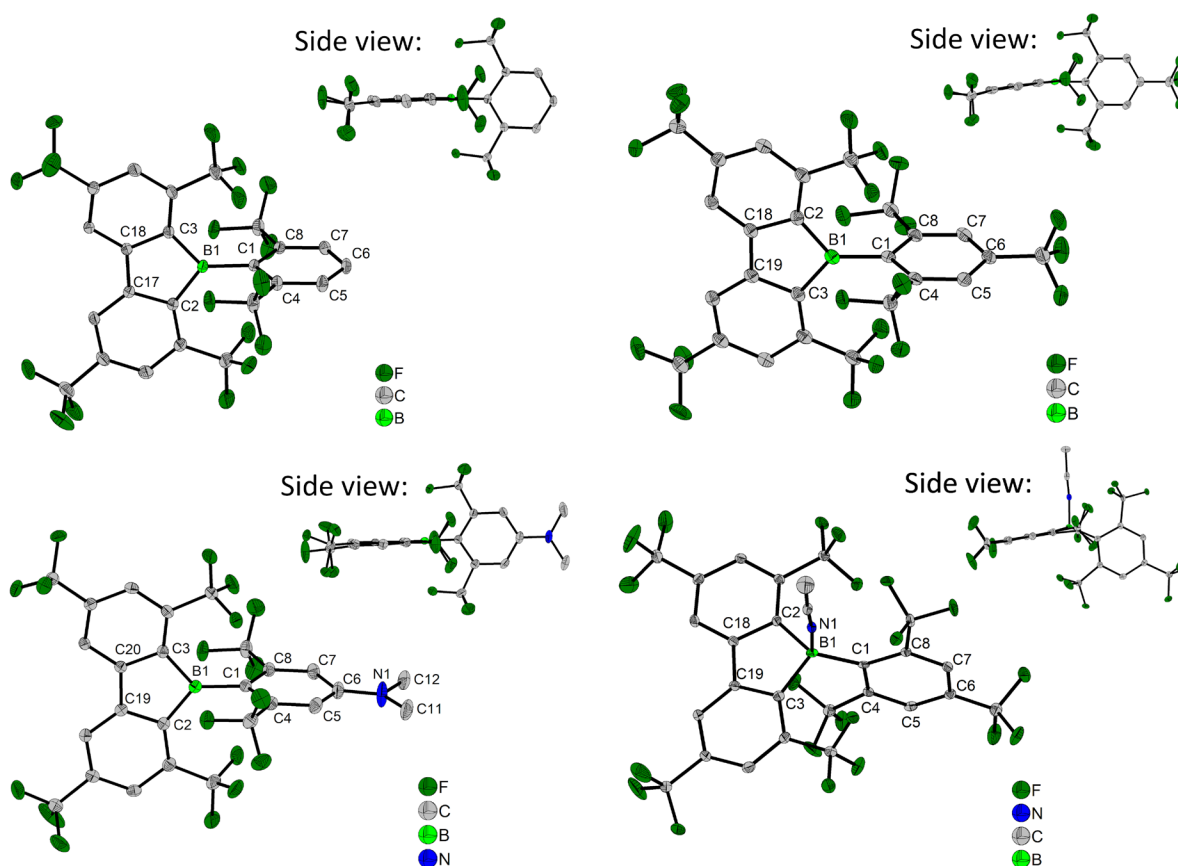


Figure 4: Molecular structures of ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ (top left), ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ (top right), $p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ (bottom left) and ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}\cdot\text{MeCN}$ (bottom 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.

Table 2: Selected bond lengths [Å] and angles [°] in ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$, ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$, $p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ and ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}\cdot\text{MeCN}$. Atom labels for the respective molecular structures are shown in Figure 4.

	${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$	${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$	$p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$	${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}\cdot\text{MeCN}$
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)
$\angle \text{BC}_3\text{-Aryl}_{\text{exo}}$	89.32(7)	89.84(8)	89.27(6)	
$\angle \text{BC}_{12}\text{-Aryl}_{\text{exo}}$	89.43(6)	89.54(6)	88.69(5)	82.12(6)
Torsion of Ar_{exo} out of borafluorene plane $\angle \text{C1-B-C2-C18/C17/C19}$	171.28(16)	176.45(16)	178.83(17)	137.6(2)
5-ring: $\angle \text{C2BC3}$	103.95(15)	103.07(13)	102.94(14)	99.74(18)
Sum $\angle \text{CBC}$	359.74(16)	359.90(15)	359.99(16)	338.43(18)
Sum $\angle \text{CNC}$			359.84(19)	
Shortest B–F contact(s)	2.392(3) 2.440(3)	2.379(2) 2.390(3)	2.366(2) 2.434(2)	2.853(3)

A comparison of the crystal structures of the three target compounds shows the following. While all three B–C bond distances are in a similar range for ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ (1.579(3)–1.591(3) Å), the B–C1_{exo} distances to the ${}^{\text{F}}\text{Xyl}^{\text{F}}$ groups of ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ and $p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ (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 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, while the 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 (BC₁₂) 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 on 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 fluorine (3.39 Å).^[103] This was previously observed in boranes and boroles with *ortho*-CF₃ aryl moieties.^[33, 79, 102, 114, 115] As 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 C_{endo}–C2_{endo}–B–C1_{exo} with the endo carbon atoms belonging to the

borole moiety deviates slightly from 180° ($171.28(16)$ – $178.83(17)^\circ$). 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*-NMe₂-^FXyl^FBf ($1.17(17)^\circ$) to ^FXyl^FBf ($3.55(16)^\circ$) and ^FMes^FBf ($8.72(16)^\circ$). The magnitude of the tilt is related to the molecular packing, which is similar in all three crystal structures as the borafluorene moieties are arranged in pairs, which are related by inversion symmetry and form weak intermolecular $\pi\cdots\pi$ interactions between the borafluorene backbones. The strongest $\pi\cdots\pi$ interaction is observed in ^FMes^FBf, which shows the smallest centroid-centroid distance, interplanar separation, and offset shift (Table S3). Hence, these pairs of molecules are closest in ^FMes^FBf, and the exocyclic ^FMes moiety is tilted out of the plane the most, away from the center of the pair in order to avoid close F \cdots F contacts between the two molecules. In the crystal structure of the acetonitrile adduct of ^FMes^FBf, as the hybridization at the boron is now sp³ rather than sp², all of the B–C bonds are elongated. The C2–B1–C3 angle of the borole ring ($99.74(18)^\circ$) is decreased compared with ^FMes^FBf ($103.95(15)^\circ$). 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° . In the adduct, there is only one short B–F contact (F3–B1 = $2.853(3)$ Å) that is elongated compared to ^FMes^FBf, but still shorter than the sum of the van der Waals radii. The B–N bond length is $1.591(3)$ Å, which is significantly shorter than that in the acetonitrile adduct of B(C₆F₆)₃ ($1.616(3)$ Å),^[116] but similar to that in the previously reported MeCN adduct of PhBf (PhBf•MeCN) ($1.598(4)$ Å).^[91] The N≡C bond ($1.129(3)$ Å) is also shorter than that in the acetonitrile adduct of B(C₆F₆)₃ ($1.141(2)$ Å) and very similar to that in PhBf•MeCN ($1.128(4)$ Å).

Electrochemistry

Cyclic voltammograms of the three borafluorenes were recorded in dichloromethane with $[n\text{Bu}_4\text{N}][\text{PF}_6]$ as the electrolyte and a scan rate of 250 mVs^{-1} (Figure 5) in order to determine their reduction potentials.

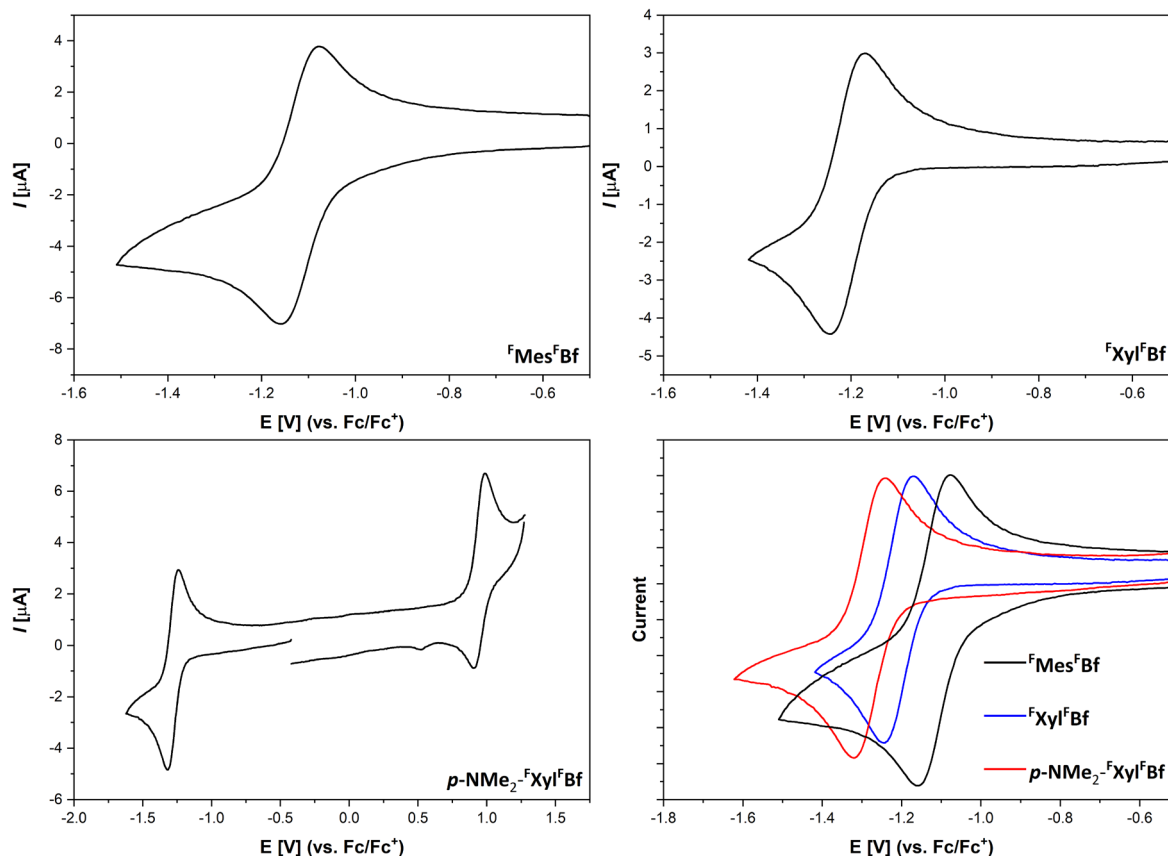
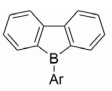
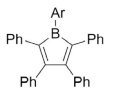
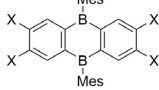
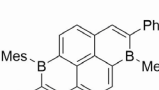
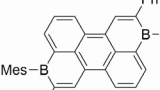


Figure 5: Cyclic voltammograms of the reversible redox events of $\text{F}^{\text{Mes}}\text{Fbf}$ (top left), $\text{F}^{\text{Xyl}}\text{Fbf}$ (top right) and $p\text{-NMe}_2\text{-F}^{\text{Xyl}}\text{Fbf}$ (bottom left). All samples are referenced against the Fc/Fc^+ ion couple. For better comparison, the reduction waves are plotted together (bottom right; $\text{F}^{\text{Mes}}\text{Fbf}$ (black), $\text{F}^{\text{Xyl}}\text{Fbf}$ (blue), $p\text{-NMe}_2\text{-F}^{\text{Xyl}}\text{Fbf}$ (red)).

All measurements were referenced to the ferrocene/ferrocenium redox couple (Fc/Fc^+). The most electron deficient borafluorene, $\text{F}^{\text{Mes}}\text{Fbf}$, exhibits a reversible reduction at -1.13 V and an irreversible reduction at -2.04 V . For the slightly less electron deficient $\text{F}^{\text{Xyl}}\text{Fbf}$, a reversible reduction at -1.21 V and an irreversible reduction at -2.12 V are observed. Interestingly, $p\text{-NMe}_2\text{-F}^{\text{Xyl}}\text{Fbf}$ shows a reversible reduction at -1.28 V , an irreversible reduction at -2.15 V and a partially reversible oxidation at 0.95 V .

Table 3: Tabulated 1st reduction potential values of various three-coordinate boron species.

compound	1 st reduction potential E _{1/2} in [V] vs. Fc/Fc ⁺	compound	1 st reduction potential E _{1/2} in [V] vs. Fc/Fc ⁺
Borafluorenes		Free boroles	
			
Mes [*] Bf: Ar = Mes [*] ; TipBf: Ar = Tip; ^F MesBf: Ar = ^F Mes		PhBC ₄ Ph ₄ : Ar = Ph; MesBC ₄ Ph ₄ : Ar = Mes; ^F MesBC ₄ Ph ₄ : Ar = ^F Mes	
This work			
^F Mes ^F Bf ^a	-1.13	PhBC ₄ Ph ₄ ^a	-1.61 ^[117]
^F Mes ^F Bf ^a	-1.21	MesBC ₄ Ph ₄ ^a	-1.69 ^[85, 117, 118]
<i>p</i> -NMe ₂ - ^F Xyl ^F Bf ^a	-1.28	^F MesBC ₄ Ph ₄ ^a	-1.52 ^[79]
Mes [*] Bf ^d	-2.28 ^[87]		
TipBf ^e	-2.14 ^[88]		
^F MesBf ^e	-1.82 ^[88]		
a ^f	-1.98 ^[119]		
Diboraanthracene		Boron PAHs	
			
b: X = H; c: X = Cl			
b ^g	-1.84 ^[115]	d ^a	-1.15 ^[120]
c ^g	-1.38 ^[121]	e ^a	-1.07 ^[120]
Triaryl boranes			
B(Mes) ₃ ^b	-2.73 ^[122]	B(3,5-(CF ₃) ₂ C ₆ H ₃) ₃ ^c	-1.61 ^[102]
B(Mes) ₂ (C ₆ F ₅) ₂ ^b	-2.10 ^[122]	B(2,4-(CF ₃) ₂ C ₆ H ₃) ₃ ^c	-1.79 ^[102]
B(Mes)(C ₆ F ₅) ₂ ^b	-1.72 ^[122]	B(2,5-(CF ₃) ₂ C ₆ H ₃) ₃ ^c	-1.85 ^[102]
B(C ₆ F ₅) ₃ ^a	-1.97 ^[77]		

^a Measured using a platinum electrode in CH₂Cl₂ using [nBu₄N][PF₆] as the electrolyte; ^b Measured using a platinum electrode in THF with [nBu₄N][B(C₆F₅)₄] as the electrolyte; ^c Measured using a glassy carbon electrode in CH₂Cl₂ with [nBu₄N][B(C₆F₅)₄] as the electrolyte; ^d Measured using a glassy carbon electrode in THF with [nBu₄N][ClO₄] as the electrolyte; ^e Measured using a glassy carbon electrode in CH₂Cl₂ with [nBu₄N][PF₆] as the electrolyte; ^f Measured using a glassy carbon electrode in THF with [nBu₄N][PF₆] as the electrolyte; ^g Measured using a platinum electrode in THF with [nBu₄N][PF₆] as the electrolyte.

The three borafluorenes exhibit much higher reduction potentials (^FMes^FBf = -1.13 V; ^FXyl^FBf = -1.21 V and *p*-NMe₂-^FXyl^FBf = -1.28 V) than any of the previously reported borafluorenes and boroles or triarylboranes (Table 3). The substitution patterns of compounds ^FMesBC₄Ph₄ (E_{1/2} = -1.52 V) and ^FMesBf (E_{1/2} = -1.82 eV) allows a direct comparison of the fluorinated borafluorene backbone (^FBf) with the unsubstituted borafluorene backbone (Bf) and the non-annulated borole.^[88] The strong anodic shift of the ^FMes^FBf as compared to ^FMesBC₄Ph₄ and ^FMesBf demonstrates the strong electron withdrawing effect of the CF₃-groups on the borafluorene backbone. This is likely due to the planar geometry as well as the fact that the *ortho* CF₃-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 *exocyclic* 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 **FMes^FBf**, CoCp₂ was chosen as a reducing agent ($E^0(\text{CoCp}_2) = -1.3 \text{ V vs. Fc/Fc}^+$).^[123] Thus, after addition of CoCp₂, the yellowish THF solution of **FMes^FBf** turned dark purple and an ESR measurement confirmed the presence of the borafluorene radical anion [**FMes^FBf**]⁻ (Figure 6).

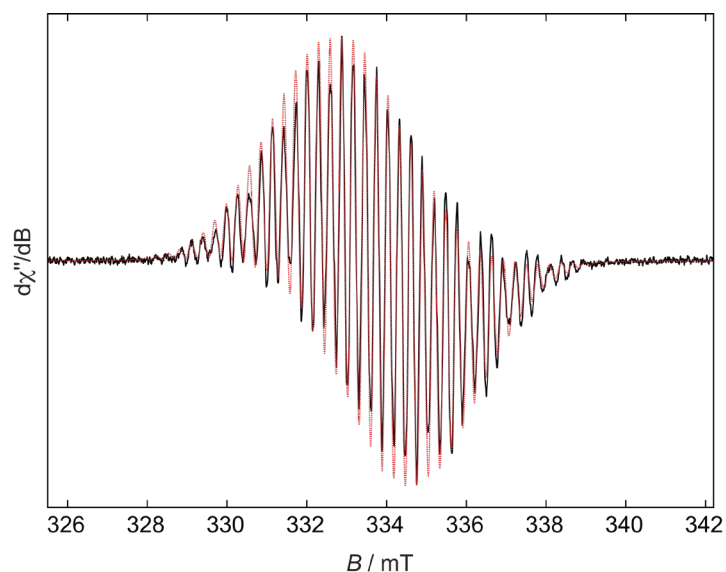


Figure 6: Experimental (black solid line) and simulated (red dashed line) continuous-wave X-band EPR spectra of [**FMes^FBf**]⁻ in a THF solution at room temperature.

A THF solution of the radical anion [**FMes^FBf**]⁻ shows a complex EPR signal centered at $g_{\text{iso}} = 2.004$ consisting of hyperfine splittings to boron ($a(^{11}\text{B}) = 3.3 \text{ G}$; cf. non-annulated borole derivatives ($a(^{11}\text{B}) = 3.4 - 3.7 \text{ G}$)^[85, 124]), the CF₃ fluorines ($a(^{19}\text{F}) = 11.3 \text{ G}$ and 6.0 G) and the hydrogen atoms ($a(^1\text{H}) = 6.1 \text{ G}$ 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 delocalization 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).

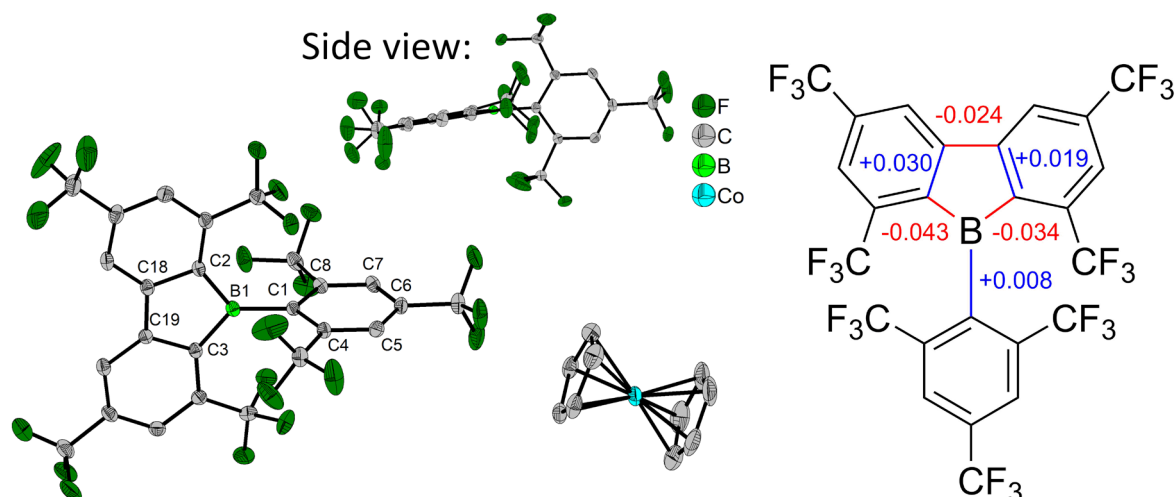


Figure 7: The solid-state molecular structure of $[\text{F}^{\text{Mes}}\text{Fbf}][\text{CoCp}_2]$ determined by single-crystal X-ray diffraction at 100 K. All ellipsoids are drawn at the 50% probability level. H atoms and THF solvent molecules are omitted for clarity. Only half of the symmetrically 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 $[\text{F}^{\text{Mes}}\text{Fbf}]^{\bullet-}$ compared to the neutral starting material are shown at the right.

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). 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. While the B–C1 bond length is slightly increased ($\Delta(\text{B}–\text{C}1) = +0.008$ and $+0.015$ Å), both borafluorene B–C bonds (B–C2 and B–C3) are shortened ($\Delta(\text{B}–\text{C}2) = -0.034$ and -0.025 Å; $\Delta(\text{B}–\text{C}3) = -0.043$ and -0.040 Å). The neighboring borafluorene C–C bonds are elongated ($\Delta(\text{C}3–\text{C}19) = +0.030$ and 0.027 Å; $\Delta(\text{C}2–\text{C}18) = +0.019$ and 0.022 Å) and the C–C bond connecting the two borafluorene aryls is shortened ($\Delta(\text{C}18–\text{C}19) = -0.024$ 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 $\Delta(\text{B}–\text{F}) = -0.278$ Å).

Photophysical properties

In order 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, $^{\text{F}}\text{Mes}^{\text{F}}\text{bf}$ was also studied in CH_2Cl_2 and in the solid state. Solvatochromic studies of $p\text{-NMe}_2\text{-}^{\text{F}}\text{Xyl}^{\text{F}}\text{bf}$ could not be carried out, as no emission was detected in more polar solvents. This is most likely due to a further red shift of the emission, which in turn results in increased non-radiative decay processes and thus a much lower quantum yield. A photophysical investigation of $^{\text{F}}\text{Mes}^{\text{F}}\text{bf}\cdot\text{MeCN}$ is included in the Supporting Information (see also Figure S50 and Table S5).

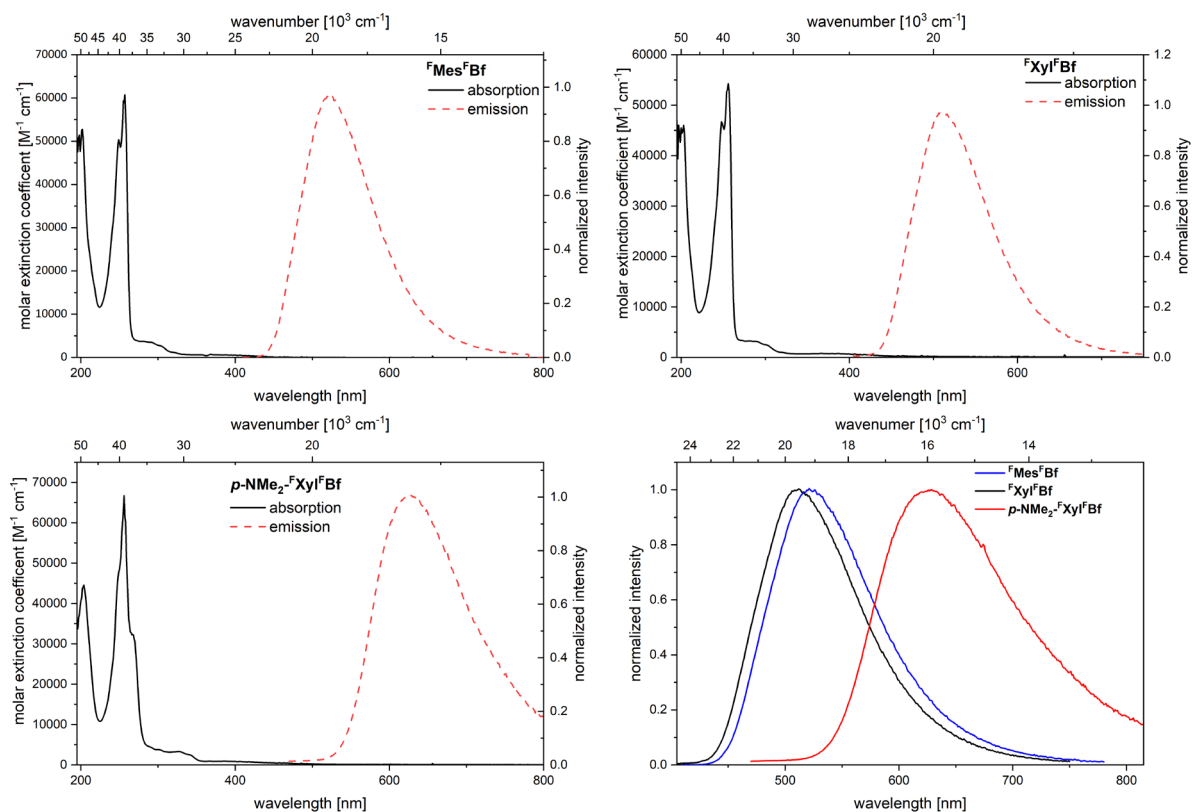


Figure 8: Absorption (black) and emission spectra (red) in hexane of ${}^F\text{Mes}^F\text{Bf}$ (top left), ${}^F\text{Xyl}^F\text{Bf}$ (top right) and $p\text{-NMe}_2\text{-}{}^F\text{Xyl}^F\text{Bf}$ (bottom left). For comparison, the emission spectra are plotted together (bottom right; ${}^F\text{Mes}^F\text{Bf}$ (black), ${}^F\text{Xyl}^F\text{Bf}$ (blue), $p\text{-NMe}_2\text{-}{}^F\text{Xyl}^F\text{Bf}$ (red)).

Table 4: Photophysical data for borafluorenes ${}^F\text{Mes}^F\text{Bf}$, ${}^F\text{Xyl}^F\text{Bf}$, and $p\text{-NMe}_2\text{-}{}^F\text{Xyl}^F\text{Bf}$.

Compound	solvent	λ_{abs} [nm] (ϵ [$10^3 \text{ M}^{-1} \text{ cm}^{-1}$]; $\log \epsilon$)	λ_{em} [nm] ^[a]	apparent Stokes shift (10^3 cm^{-1})	Φ_{fl}	τ [ns] (rel%)	τ_0 [ns]	k_{nr} [10^7 s^{-1}] ^[b]	k_{r} [10^7 s^{-1}] ^[c]
${}^F\text{Mes}^F\text{Bf}$	hexane	290 (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
	CH_2Cl_2	395	540	6.8	0.18	151	835	0.1	0.005
	solid	405	527	6.0	0.06	173	2557	0.5	0.04
${}^F\text{Xyl}^F\text{Bf}$	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
$p\text{-NMe}_2\text{-}{}^F\text{Xyl}^F\text{Bf}$	hexane	268 (32.3; 4.51), 326 (2.7; 3.43), 396 (0.3; 2.48)	627	9.3	0.03	9.2 (64%), 1626 (36%)	-	-	-

[a] Excited at the respective $\lambda_{\text{abs,max}}$ of the $S_1 \leftarrow S_0$ transition. [b] The non-radiative rate constants were calculated from $k_{\text{nr}} = (1 - \Phi_{\text{fl}})/\tau$. [c] The radiative rate constants were calculated from $k_{\text{r}} = \Phi_{\text{fl}}/\tau$.

All borafluorenes exhibit very small extinction coefficients for their lowest energy absorption ($\epsilon = 300 - 400 \text{ M}^{-1} \text{ cm}^{-1}$; $\log \epsilon = 2.48 - 2.60$) which can be classified as weakly allowed transitions,^[125] similar to those in previously reported boroles and borafluorenes. The lowest energy absorption of **FXyl^FBf** ($\lambda_{\text{abs, max}} = 386 \text{ nm}$) appears to be slightly hypsochromically shifted compared to **FMes^FBf** ($\lambda_{\text{abs, max}} = 400 \text{ nm}$) and **p-NMe₂-FXyl^FBf** ($\lambda_{\text{abs, max}} = 396 \text{ nm}$) 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 **p-NMe₂-FXyl^FBf** is strongly bathochromically shifted ($\lambda_{\text{em, max}} = 627 \text{ nm}$) compared to the two non-donor-substituted borafluorene derivatives (**FMes^FBf**: $\lambda_{\text{em, max}} = 521 \text{ nm}$; **FXyl^FBf**: $\lambda_{\text{em, max}} = 510 \text{ nm}$), which indicates that the emission arises from an intramolecular charge transfer (ICT) transition. The quantum yields of **FMes^FBf** ($\Phi_{\text{fl}} = 0.37$; hexane) and **FXyl^FBf** ($\Phi_{\text{fl}} = 0.30$; hexane) are higher than most of the reported borafluorenes (ca. 0.1). In contrast, **p-NMe₂-FXyl^FBf** exhibits a very low quantum yield ($\Phi_{\text{fl}} = 0.03$; hexane). To our surprise, **FMes^FBf** and **FXyl^FBf** exhibit very long fluorescent lifetimes in solution (**FMes^FBf**: $\tau = 224 \text{ ns}$ (hexane); $\tau = 151 \text{ ns}$ (CH₂Cl₂); **FXyl^FBf**: $\tau = 249 \text{ ns}$ (hexane)) as well as in the solid state (**FMes^FBf**: $\tau = 173 \text{ ns}$). Similar fluorescence lifetimes (116 – 150 ns) of borafluorenes with bulky exo-aryl moieties were previously observed by Rupar and co-workers.^[89] This results in exceptionally long natural lifetimes, τ_0 , uncommon for organic molecules, for which fluorescence usually takes place on a ns timescale. There are, however, some exceptions such as pyrene.^[36, 126, 127] 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-FXyl^FBf** exhibits two different radiative decay processes, a prompt ($\tau = 9.2 \text{ ns}$) and a delayed ($\tau = 1.6 \mu\text{s}$) one. This can be caused by different processes namely TTA (triplet-triplet annihilation)^[128] or TADF (thermally activated delayed fluorescence).^[66, 129-143] Due to the low concentrations ($\leq 10^{-5} \text{ M}$) 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 (T_1) and excited singlet state (S_1) of a molecule. In order for this to occur, the energy difference between S_1 and T_1 (ΔE_{S-T}) 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-FXyl^FBf**. The singlet-triplet gap (ΔE_{S-T}) can be easily determined experimentally if phosphorescence can be observed. However, for **p-NMe₂-FXyl^FBf**, even at 77 K in a frozen glass matrix of 2-MeTHF, no phosphorescence was observed. However, ΔE_{S-T} 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.*^[144]

$$k_{\text{rISC}} = A \exp\left(-\frac{\Delta E_{S-T}}{kT}\right). \quad (1)$$

$$k_{\text{rISC}} = \frac{\Phi_{\text{rISC}}}{\tau_{\text{DF}}} \left(\frac{\Phi_{\text{PF}} + \Phi_{\text{DF}}}{\Phi_{\text{PF}}}\right). \quad (2)$$

with Φ_{DF} , Φ_{PF} and Φ_{rISC} being the quantum yields of the delayed and prompt fluorescence and the reverse intersystem crossing, respectively. As no phosphorescence was observed at 77 K, but delayed fluorescence was, it can be assumed that ΔE_{S-T} is small and, as such, the rate of reverse intersystem crossing is very high, i.e., $\Phi_{rISC} = \frac{k_{rISC}}{k_{rISC} + k_{IC}^T + k_{PH}} \approx 1$ and, thus, equation (2) can be modified to give equation (3).

$$k_{rISC} = \frac{1}{\tau_{DF}} \left(\frac{\Phi_{PF} + \Phi_{DF}}{\Phi_{PF}} \right) = \frac{1}{\tau_{DF}} \left(1 + \frac{\Phi_{DF}}{\Phi_{PF}} \right) = \frac{1}{\tau_{DF}} + \frac{1}{\tau_{DF}} * \frac{\Phi_{DF}}{\Phi_{PF}}. \quad (3)$$

The ratio Φ_{DF}/Φ_{PF} can be ascertained from time-resolved measurements via equation (4),

$$\frac{\Phi_{DF}}{\Phi_{PF}} = \frac{B_{DF}\tau_{DF}}{B_{PF}\tau_{DF}}. \quad (4)$$

with B_{DF} and B_{PF} 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.

$$k_{rISC} = A \exp\left(-\frac{\Delta E_{S-T}}{kT}\right) = \frac{1}{\tau_{DF}} + \frac{1}{\tau_{DF}} \frac{A_{DF}\tau_{DF}}{A_{PF}\tau_{DF}}. \quad (5)$$

Lifetimes were obtained at temperatures between 300 K and 230 K in methylcyclohexane. From the slope of a plot of $\ln(k_{rISC})$ vs. $1/T$ (Figure 9), we obtain $\Delta E_{S-T} = 15$ meV, which is comparable to values previously reported for TADF emitters.^[144]

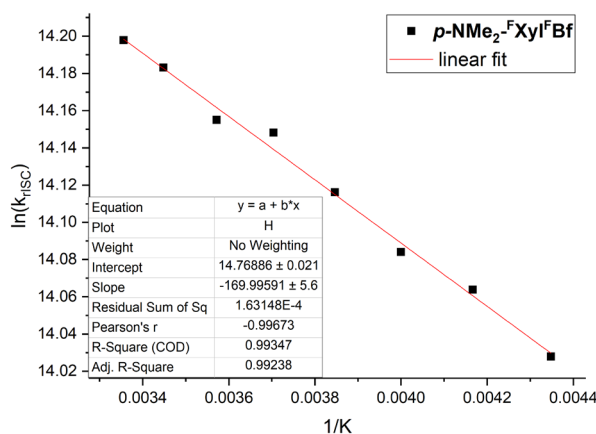


Figure 9: Arrhenius plot of $\ln(k_{rISC})$ of $p\text{-NMe}_2\text{-}^F\text{Xyl}^F\text{Bf}$ (determined from temperature-dependent lifetime measurements) vs. $1/T$.

DFT and TD-DFT studies

Using the crystal structures as the starting geometries, the ground state structures were optimized via DFT calculations at the B3LYP/6-31G+(d) level of theory. For $^F\text{Mes}^F\text{Bf}$ and $^F\text{Xyl}^F\text{Bf}$, the optimized ground state structures exhibit C_s and C_{2v} symmetries, respectively. For $p\text{-NMe}_2\text{-}^F\text{Xyl}^F\text{Bf}$, optimization of the GS structure with C_{2v} symmetry did not lead to a global minimum but rather to a saddle point (1 imaginary frequency remained). However, as the C_1 structure is very close to the C_{2v} 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. As 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 ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ to ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ to $p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ (Figure 10 and Table 5). The calculated LUMO energies fit well with the LUMO energies estimated from the reduction potentials obtained via cyclic voltammetry. Due to the very broad nature of the lowest energy absorption band, the HOMO energies of ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ and ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ were not calculated from the experimental data.

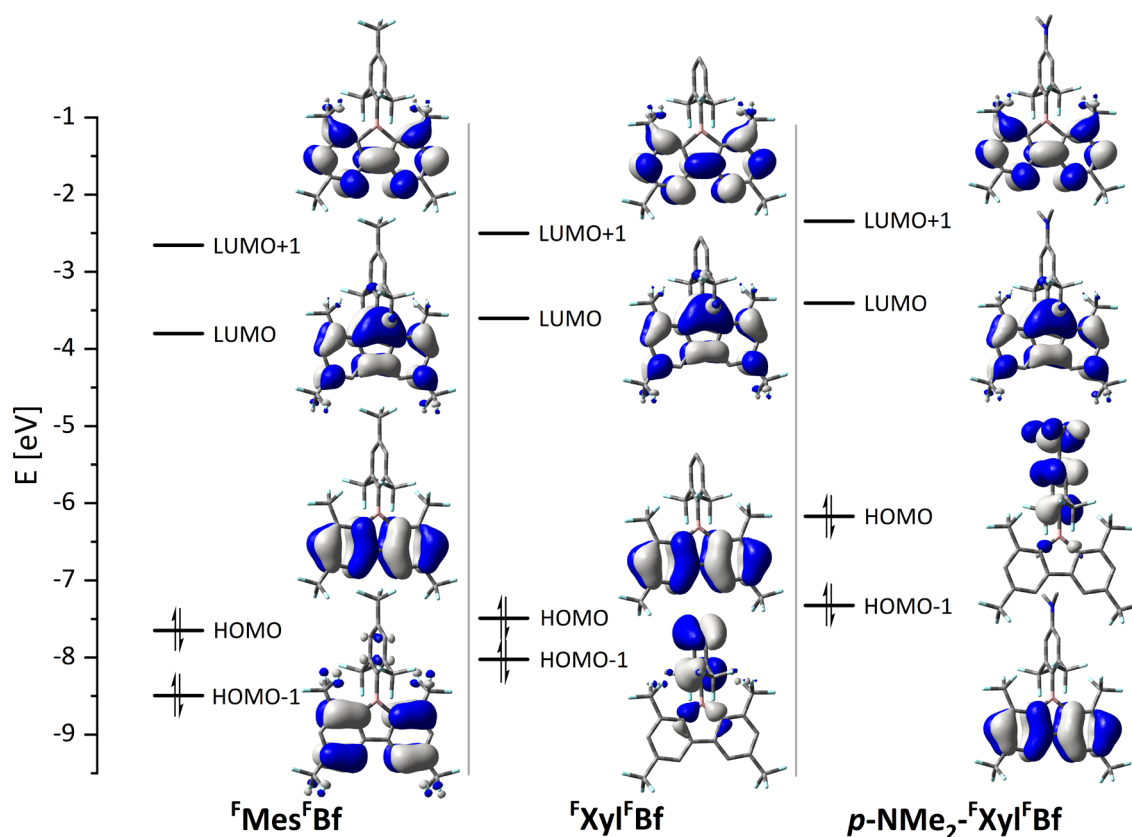


Figure 10: Frontier molecular orbitals of ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ (left), ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ (middle), and $p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ (right) calculated at the B3LYP/6-31+G(d) level.

Table 5: Frontier molecular p orbital energies [eV] and symmetries of ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$, ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$, and $p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ calculated at the B3LYP/6-31+G(d) level.

Symmetry	${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$		${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$		$p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$		
	C_s		C_{2v}		C_1	C_{2v}	
	calc.	exp. ^a	calc.	exp. ^a	calc.	calc.	exp. ^a
LUMO+1 [eV]	-2.66 (A'')		-2.50 (B_1)		-2.34 (A_1)	-2.32 (B_1)	
LUMO [eV]	-3.80 (A'')	-4.02	-3.60 (B_1)	-3.95	-3.41 (A_1)	-3.42 (B_1)	-3.88
HOMO [eV]	-7.65 (A'')		-7.49 (A_2)		-6.17 (A_1)	-6.16 (B_2)	-6.11
HOMO-1 [eV]	-8.49 (A')		-8.03 (B_2)		-7.32 (A_1)	-7.41 (A_2)	

^a Determined from the half wave potentials: HOMO = $-(5.16 + E_{1/2,ox})$ eV, LUMO = $-(5.16 + E_{1/2,red})$ eV.^[123, 145, 146]

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 ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ and ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ the HOMOs are also localized on the borafluorene moieties with boron lying on a nodal plane, and are energetically similar ($\Delta E = 0.16$ eV). The HOMO of $p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ is localized on the *exo*-aryl moiety and lies about 1.4 eV higher in energy than the HOMOs of ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ and ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$. 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 ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ and ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$, HOMO-1 is localized on the *exo*-aryl moiety; however, due to the *para*-CF₃-group, the HOMO-1 of ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ is about 0.5 eV lower in energy. Based on the optimized ground state structures the nucleus-independent chemical shift (NICS) values of the borafluorenes were calculated (Table 6).

Table 6: NICS(1)_{zz} values of the borole moiety of ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$, ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$, $p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$, and $\text{TipBf}^{[125]}$ calculated at the B3LYP/6-311+G(d) level.

Compound	NICS(1) _{zz}	
	Calc.	Lit.
${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$	20.7	
${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$	20.2	
$p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$	20.0	
TipBf	24.3	24.5 ^[119]

It is apparent that the perfluoroalkylated borafluorenes exhibit lower NICS(1)_{zz} values as compared to that of the borafluorene TripBf which does not contain CF₃-groups. This suggests a higher degree of delocalization of the electron density over the borafluorene backbone in our compounds. Thus, the antiaromatic 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 ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ and ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ were carried out at the B3LYP/6-31+G(d) level of theory whereas for the donor substituted $p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ the Coulomb-attenuated functional CAM-B3LYP was employed using the same basis set (Table 7), as CAM-B3LYP is better suited to systems involving charge transfer.^[147, 148] Furthermore, the optimized S₁-state geometries of ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ and ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ were obtained. In order to characterize the nature of the transition the overlap coefficients (Λ) were determined.^[147] The calculated lowest 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.

Table 7: Lowest energy and highest oscillator strength absorptions and emissions of ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ and ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ calculated at the B3LYP/6-31+G(d) level of theory and lowest energy absorptions of $p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ calculated at the CAM-B3LYP/6-31+G(d) level of theory.

Compound	State	E [eV]	λ [nm]	λ_{exp} [nm]	f	Symmetry	Major contributions	Λ
${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ (C_s)	$S_1 \leftarrow S_0$	3.05	406	400	0.0005	A'	HOMO \rightarrow LUMO (99%)	0.65
	$S_2 \leftarrow S_0$	3.90	318		0	A''	HOMO-1 \rightarrow LUMO (99%)	0.25
	$S_7 \leftarrow S_0$	4.80	258	257	0.8333	A'	HOMO-2 \rightarrow LUMO (24%), HOMO \rightarrow LUMO+1 (70%)	0.73
	$S_1 \rightarrow S_0$	2.22	559	521	0.0038	A	H-SOMO \leftarrow L-SOMO (99%)	
${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ (C_{2v})	$S_1 \leftarrow S_0$	3.09	401	385	0.0006	B ₂	HOMO \rightarrow LUMO (99%)	0.66
	$S_2 \leftarrow S_0$	3.64	340		0	A ₂	HOMO-1 \rightarrow LUMO (99%)	0.23
	$S_6 \leftarrow S_0$	4.81	258	256	0.8413	B ₂	HOMO-3 \rightarrow LUMO (28%), HOMO \rightarrow LUMO+1 (68%)	0.74
	$S_1 \rightarrow S_0$	2.34	531	510	0.0030	A	H-SOMO \leftarrow L-SOMO (99%)	
$p\text{-NMe}_2\text{-}{}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ (C_1)	$S_1 \leftarrow S_0$	3.25	382	396	0	A	HOMO \rightarrow LUMO (92%)	0.15
	$S_2 \leftarrow S_0$	3.46	358	326	0.0006	A	HOMO-1 \rightarrow LUMO (97%)	0.67
	$S_3 \leftarrow S_0$	4.25	292	270	0.0491	A	HOMO \rightarrow L+2 (70%), HOMO \rightarrow L+3 (24%)	0.49
	$S_8 \leftarrow S_0$	5.11	243	256	0.6022	A	HOMO \rightarrow L+4 (86%)	0.71

For both ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ and ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ these can be classified as locally excited (LE) transitions ($\Lambda \approx 0.65$) as both HOMO and LUMO are localized on the borafluorene backbone. This is surprising, as LE transitions usually exhibit high extinction coefficients and ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ and ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ exhibit weakly allowed lowest energy absorptions. However, the calculated oscillator strengths of the $S_1 \leftarrow S_0$ transitions of ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ and ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ are also very small. From 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 ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ (C_s) and ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ (C_{2v}) are A'' and A₂, respectively, and the LUMO symmetries are A'' and B₁. 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 (C_s : A' and C_{2v} : A₁). For ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ (C_s), the lowest energy transition is forbidden in the z-direction, while x and y are allowed, making the transition an allowed transition. For ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ (C_{2v}), the x- and z-directions are forbidden, while 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, 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, as its contribution to the LUMO gives the transition a π -n character. The $S_2 \leftarrow S_0$ transitions, in both cases, are predominantly HOMO-1 to LUMO transitions. The HOMO-1 of ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ and ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$ are of A' and B₂ symmetry, respectively, and, thus, are symmetry-forbidden. Both ${}^{\text{F}}\text{Mes}^{\text{F}}\text{Bf}$ and ${}^{\text{F}}\text{Xyl}^{\text{F}}\text{Bf}$, exhibit large oscillator strengths for their $S_7 \leftarrow S_0$ and $S_6 \leftarrow S_0$ 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_1 geometries of ${}^1\text{Mes}^{\text{Bf}}$ and ${}^1\text{Xyl}^{\text{Bf}}$ differ only slightly from their ground state structures (Figure 11).

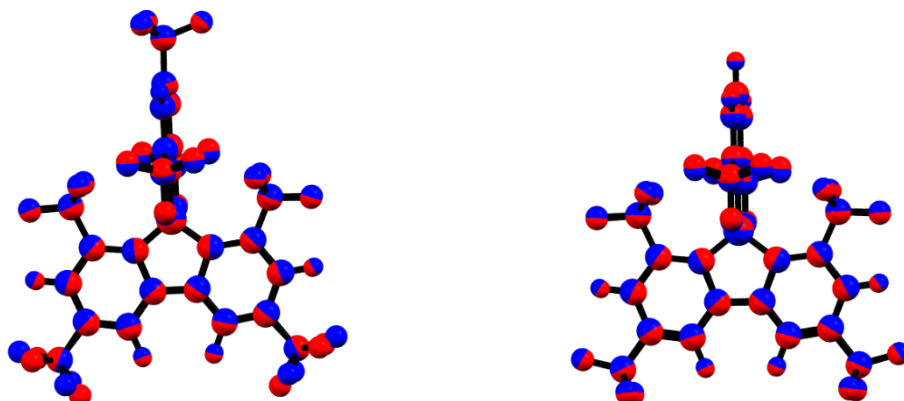


Figure 11: Overlap of the optimized ground state (blue) and S_1 (red) geometries of ${}^1\text{Mes}^{\text{Bf}}$ (left) and ${}^1\text{Xyl}^{\text{Bf}}$ (right).

In comparison, in the S_1 structure of ${}^1\text{Mes}^{\text{Bf}}$, only the *para* CF_3 -groups on the borafluorene backbone are rotated and in both ${}^1\text{Mes}^{\text{Bf}}$ and ${}^1\text{Xyl}^{\text{Bf}}$ the *ortho* CF_3 -groups on the *exo*-aryl are slightly bent away from the boron center. The calculated emission maxima of ${}^1\text{Mes}^{\text{Bf}}$ and ${}^1\text{Xyl}^{\text{Bf}}$ 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 $p\text{-NMe}_2\text{-}{}^1\text{Xyl}^{\text{Bf}}$ differ strongly from those of ${}^1\text{Mes}^{\text{Bf}}$ and ${}^1\text{Xyl}^{\text{Bf}}$. 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, as $p\text{-NMe}_2\text{-}{}^1\text{Xyl}^{\text{Bf}}$ is a donor-acceptor system. The $S_1 \leftarrow S_0$ transition of $p\text{-NMe}_2\text{-}{}^1\text{Xyl}^{\text{Bf}}$ exhibits an oscillator strength of 0. Using the optimized structure of C_{2v} 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 *exo*-aryl group with respect to the borafluorene core. The HOMO is of B_2 symmetry and the LUMO has B_1 symmetry. This is the same as for the $S_2 \leftarrow S_0$ transitions of ${}^1\text{Mes}^{\text{Bf}}$ and ${}^1\text{Xyl}^{\text{Bf}}$, as the HOMO and HOMO-1 are inverted compared to those of $p\text{-NMe}_2\text{-}{}^1\text{Xyl}^{\text{Bf}}$. For $p\text{-NMe}_2\text{-}{}^1\text{Xyl}^{\text{Bf}}$, however, the $S_2 \leftarrow S_0$ transition is allowed, but analogously to the ${}^1\text{Mes}^{\text{Bf}}$ and ${}^1\text{Xyl}^{\text{Bf}}$ cases, exhibits a very low oscillator strength. This explains the low extinction coefficient observed for the lowest energy absorption of $p\text{-NMe}_2\text{-}{}^1\text{Xyl}^{\text{Bf}}$. Furthermore, we optimized the S_1 structure of $p\text{-NMe}_2\text{-}{}^1\text{Xyl}^{\text{Bf}}$ 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.

Conclusion

Herein, we report the synthesis and properties of three trifluoromethylated borafluorenes **^FMes^FBf**, **^FXyl^FBf**, and ***p*-NMe₂-^FXyl^FBf**. 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 aryl-BF₃K salts for the synthesis of borafluorenes. All of the borafluorenes exhibit a rigid geometry with the *exo*-aryl group lying perpendicular to the borafluorene plane. All three borafluorenes exhibit exceptionally positively shifted reduction potentials, emphasizing the electron withdrawing nature of the CF₃-groups. This allowed us to use a mild reducing agent (CoCp₂ E⁰ = -1.3 eV vs. Fc/Fc⁺) to reduce the most anodically shifted borafluorene **^FMes^FBf**. The resulting radical anion of **^FMes^FBf** exhibits a strong delocalization of the additional electron over the borafluorene backbone as evidenced by EPR spectroscopy and its solid-state structure. The trifluoromethylated borafluorenes exhibit unusually long excited state lifetimes and weakly allowed lowest energy transitions. For **^FMes^FBf** and **^FXyl^FBf**, 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 τ > 200 ns in hexane. Even with small oscillator strengths, the two compounds exhibit fluorescence quantum yields of 0.37 and 0.30, respectively, as their rigidity results in exceptionally slow non-radiative decay. In contrast, the twisted donor-acceptor system ***p*-NMe₂-^FXyl^FBf** has a symmetry-forbidden lowest energy transition and exhibits TADF, with a singlet-triplet energy gap ΔE_{S-T} experimentally determined to be only 15 meV. **^FMes^FBf** and **^FXyl^FBf** are highly stable towards hydrolysis, which makes them interesting potential building blocks for organic materials.

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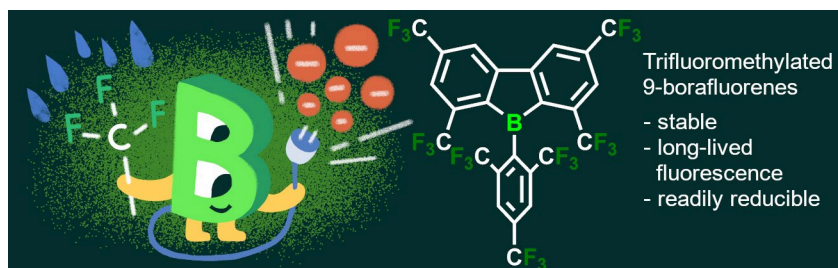
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Having your cake and eating it too: Functionalization of 9-borafluorenes with trifluoromethyl groups makes them exceptionally easy to reduce while maintaining excellent stability towards hydrolysis. The systems also exhibit long-lived fluorescence or thermally activated delayed fluorescence (TADF) depending on the *exo-aryl para*-substituent.