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On the Ambiguity of 1,3,2-Benzodiazaboroles as Donor/Acceptor Functionalities in Luminescent Molecules

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Keywords: Boron / Diazaboroles / Perfluoroaryls / Photophysics

Summary:

A series of 1,3-bis(perfluoroaryl)-2-(hetero)aryl-1,3,2-benzodiazaboroles, 1,3-$^{F}Ar_2$-2-Ar-1,3-2-$N_2BC_6H_4$ (Ar = Ph, $^{F}Ar = C_6F_5$ **5**; Ar = Ph, ^{F}Ar = 4-C_5F_4N **6**; Ar = Ph, ^{F}Ar = 4-NCC_6F_4 **7**; Ar = 2-C_4H_3S, $^{F}Ar = C_6F_5$ **8**; Ar = 2-C_4H_3S, ^{F}Ar = 4-C_5F_4N **9**; Ar = 2-C_4H_3S, ^{F}Ar = 4-NCC_6F_4 **10**), were synthesised by cyclocondensation of the adducts $PhBBr_2{\cdot}PPh_3$ or 2-thienyl $BBr_2{\cdot}PPh_3$ with *N,N′*-bis(perfluoroaryl)-*o*-phenylenediamines in the presence of 2,2,6,6-tetramethylpiperidine. Similar treatments of the PPh_3 adducts of 4-(1′,3′-diethyl-1′,3′,2′-benzodiazaborolyl)-phenyldibromoborane with the corresponding diamines gave rise to the push-pull compounds, $C_6H_4(NEt)_2$B-1,4-C_6H_4-B($N^{F}Ar)_2C_6H_4$ ($^{F}Ar = C_6F_5$ **11**; 4-C_5F_4N **12**) and $C_6H_4(NEt)_2$B-2,5-C_4H_2S-B($N^{F}Ar)_2C_6H_4$ ($^{F}Ar = C_6F_5$ **13**; 4-C_5F_4N **14**). The X-ray structures of **8**, **11**, **12** and **13** were determined. Electronic structure calculations reveal that the LUMOs are located at the perfluoroaryl groups in **5-14** thus the fluorinated benzodiazaborolyl groups are considered as electron-withdrawing moieties. These moieties differ from alkylated benzodiazaborolyl groups which are regarded as donors. The emission spectra for **5-14** show charge transfer bands with significant solvatochromism and large Stokes shifts (6100-12500 cm^{-1} in cyclohexane and 8900-15900 cm^{-1} in CH_2Cl_2). The emissions of the benzodiazaboroles, **5-10**, arise from a different charge transfer (CT) process to the local charge transfer (LCT) process typically found in many fluorescent benzodiazaboroles. This novel remote charge transfer (RCT) process involving the perfluoroaryl groups is supported by CAM-B3LYP computations. The push-pull systems **11-14** here give fluorescent emissions with moderate to high fluorescence quantum yields (65-97%) that arise from the usual LCT process only.

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Electronic supplementary information (ESI) available: Lippert-Mataga analyses on **11**-**14**, table comparing experimental and computed geometrical parameters for **11**-**13**, cartesian coordinates for optimised geometries of **5**, **11** and **20** and figures of MOs involved in the transitions of parent benzodiazaborole and model of the push pull system **22**.

Introduction:

The chemistry of fluorescent organoboranes for potential application in electrooptical devices has attracted considerable interest. The most prominent three-coordinate boron substituent in these systems is the dimesitylboryl group ($BMes_2$, Mes = 2,4,6-$Me_3C_6H_2$) which functions as a π-electron acceptor due its vacant p-orbital at the boron centre.[1] These compounds can display sizable second and third-order nonlinear optical (NLO) properties, [2] wherein the $BMes_2$ acceptor strength is usually somewhere between that of NO_2 and CN. They can also exhibit large two-photon absorption (TPA) cross-sections and strong two-photon excited fluorescence (TPEF). [3] Such electron deficient compounds have low LUMO energies and have thus been shown to be efficient electron-transporting and/or emitting layers in organic light emitting diodes (OLEDs). [4] Compounds with $BMes_2$ groups are often strongly colored and/or luminescent,[5] and thus have potential for use as colorimetric or luminescent sensors for anions, particularly fluoride ions. [6] Conjugated molecules with boryl side groups have recently been shown to display very large Stokes shifts and high quantum yields both in solution and the solid state, properties which were attributed to the lack of close packing caused by the bulky mesityl groups. [7] Besides those with $BMes_2$ groups, optically interesting materials based on three-coordinate boron compounds have been reported recently including vinyleneboranes,[8] diboraanthracenes,[9] borataanthracene anions,[10] boracyclophanes,[11] fluoreneboranes[12] and aminoboranes.[13]

In the past decade, the chemistry of 1,3,2-diazaboroles rapidly developed[14-16] and some of these three-coordinate boron compounds are strongly luminescent.[17-24] Calculations on 2-arylethynyl-1,3-diethyl-1,3,2-benzodiazaboroles disclosed that the diazaborolyl unit did not function as a π-acceptor as anticipated, but instead behaved as a π-donor substituent.[19] It was experimentally confirmed that the π-donor capacity of the 1,3-diethyl-1,3,2-benzodiazaborolyl group towards the $BMes_2$-acceptor is between those of

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methoxy- and dimethylamino-groups.[20] Benzodiazaboroles are also efficient donors when linked to the carbon atoms of carborane clusters.[25,26]

In a recent paper, we reported on a series of carbazolylphenyl- and carbazolylthienyl-derivatives of benzodiazaboroles, **1**-**4**, (Chart 1) where both *N*-atoms were substituted by electron-withdrawing pentafluorophenyl or tetrafluoropyridyl groups.[27] Here, the benzodiazaboroles served as π-acceptors towards the π-donating *N*-carbazolyl unit. These compounds are luminescent with Stokes shifts between 1200 and 5000 cm^{-1} in cyclohexane and between 4800 and 6300 cm^{-1} in dichloromethane solutions. To understand the interaction of the fluoroarylated diazaborolyl units with phenyl- or thienyl groups, the parent derivatives, **5**-**10**, were targeted. The next logical step in the quest for novel push-pull molecules with tuneable photophysical properties was the construction of π-conducting scaffolds, **11**-**14,** with both the novel electron-withdrawing fluoroaryl-functionalised benzodiazaborolyl groups and the familiar 1,3-diethyl-1,3,2-benzodiazaborolyl donor, as terminal substituents.

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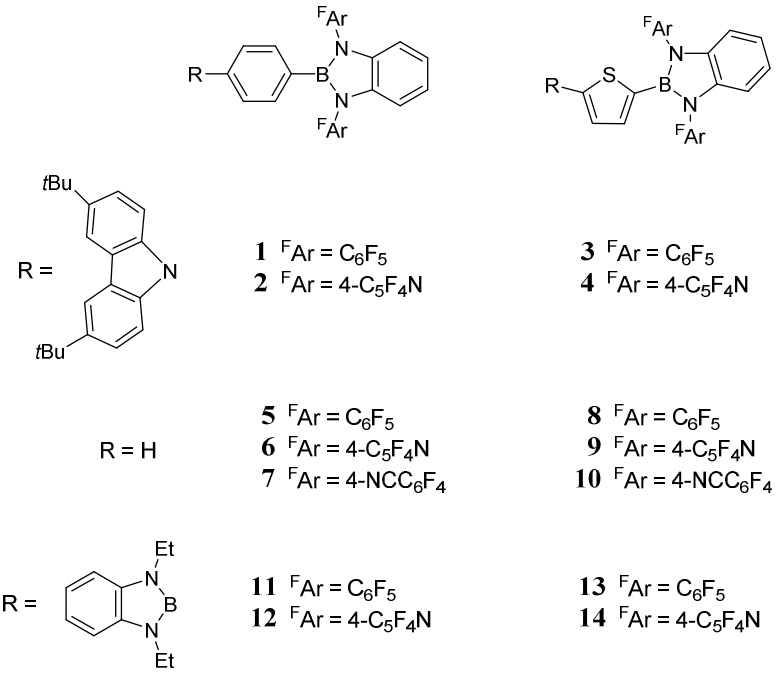

Chart 1. Fluoroaryl benzodiazaboroles **1-14** discussed in this study.

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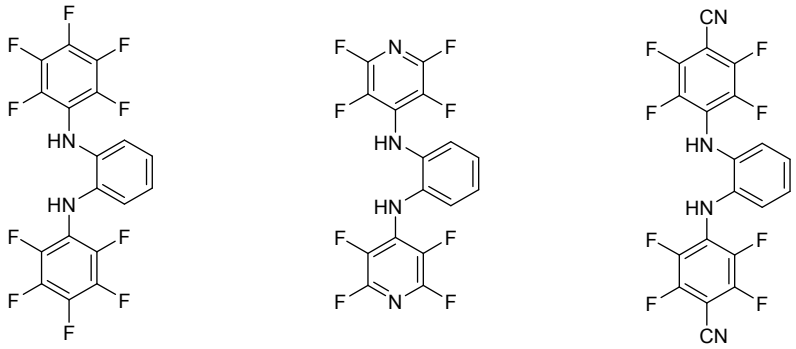
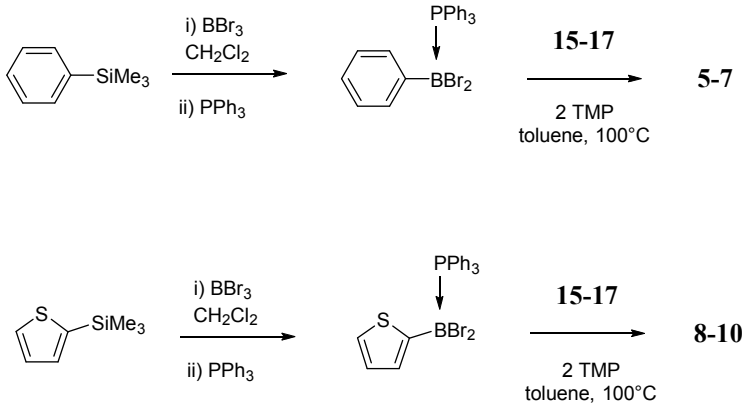
Results and Discussion

The reported synthetic method leading to the diamine precursors, *N,N′*-bis(perfluoroaryl)-*ortho*-phenylenediamines **15** and **16**, was also applied here in the synthesis of the new diamine **17** from pentafluorobenzonitrile and lithiated *ortho*-phenylenediamine (Scheme 1).[27] These diamines were reacted with appropriate aryldibromoborane-triphenylphosphine adducts to generate the fluoroaryl-functionalised benzodiazaboroles, **1-10** here and elsewhere.[27]



15 **16** **17**



Scheme 1. Syntheses of fluorinated benzodiazaboroles **5-10**.

Aryldibromoboranes were produced by the treatment of trimethylsilylaryls with boron tribromide and combined with an excess of triphenylphosphine in dichloromethane to afford the corresponding adducts. These mixtures were subsequently freed from solvent *in vacuo* to give colourless solid residues. Toluene solutions of the adducts were reacted with phenylenediamines **15-17** in the presence of 2,2,6,6-tetramethylpiperidine (TMP) at 100 °C.

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Under these conditions, the cyclocondensations were completed in 24-60 h. After removal of the piperidinium salts, the filtrates were evaporated to dryness. Sublimation at ca. 100°C was applied to remove excess PPh_3 from **5**, **6**, **8** and **9**. The crude products were crystallised from *n*-hexane (**5**, **9**), toluene (**6**) or *n*-hexane/CH_2Cl_2 mixtures (**8**) to give colourless crystals in 55-69% yields. In the case of crude compounds **7** and **10**, featuring nitrile substituents, purification was effected by crystallisation from *n*-hexane (**7**) or a *n*-hexane/CH_2Cl_2 2:1 mixture (**10**) to give yellow crystals in 14 and 36% yield respectively.

In contrast to other non-fluorinated 2-aryl-1,3-bis(alkyl/aryl)benzodiazaboroles compounds **5**-**10** are not affected by contact with air and moisture, and thus may be stored in air for months. The pentafluorophenyl derivatives **5** and **8** can be worked up in the presence of water whereas compounds **6**, **7**, **9** and **10** are hydrolysed to phenylene diamines. Diazaboroles **5**, **6**, **8** and **9** are well soluble in the common aprotic organic solvents, and may be recrystallised from alkanes at low temperatures. Derivatives **7** and **10** are poorly soluble in alkanes.

The reaction of freshly prepared 4-trimethylsilylphenyllithium with an equimolar amount of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole[28] in diethyl ether in the temperature range between -78 and 20°C led to the formation of 1-diazaborolyl-4-trimethylsilyl benzene **18** as colourless needles in 50% yield (Scheme 2).

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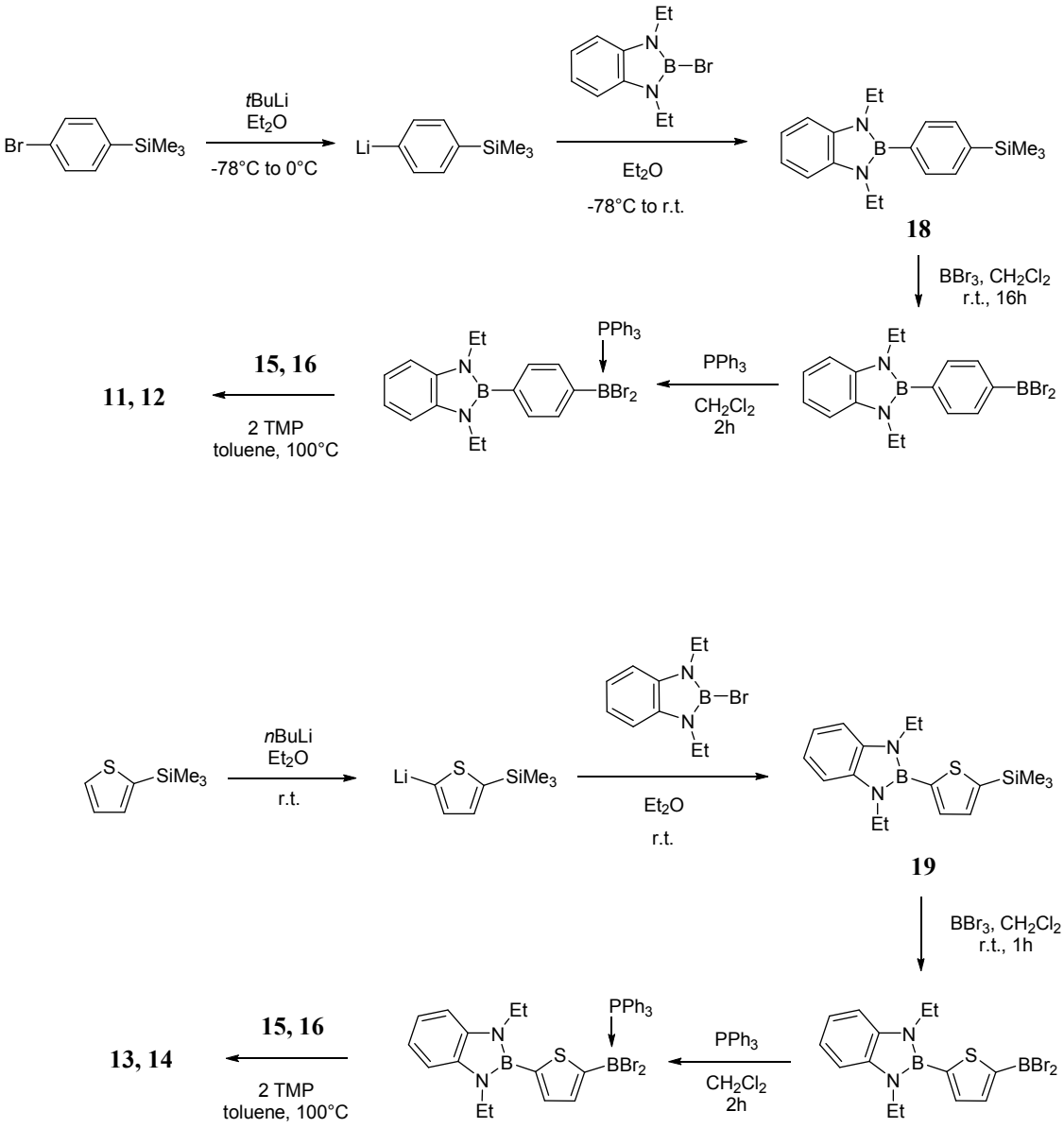

Scheme 2. Syntheses of push-pull systems, **11-14.**

The solution of **18** in CH_2Cl_2 was treated at room temperature with 1 equiv. of boron tribromide over a period of 16 h and then combined with 1 equiv. of triphenylphosphine. The obtained adduct was allowed to react with the *ortho*-phenylenediamine derivatives **15** or **16** in hot toluene (100°C) in the presence of 2 equiv. of 2,2,6,6-tetramethylpiperidine (TMP) to afford products **11** and **12** as colourless solids in 32% and 23% yield respectively.

Similar protocols were applied to the preparation of the thiophene-2,5-diyl-bridged benzodiazaboroles **13** and **14** (Scheme 3). Thus, *ortho*-lithiated 2-trimethylsilylthiophene was

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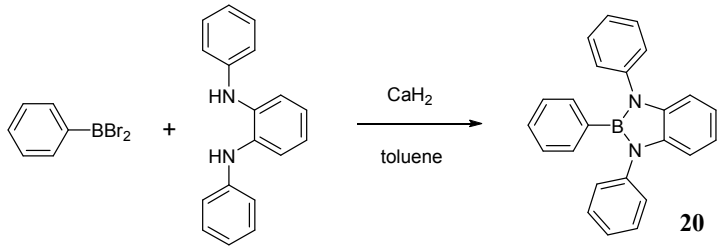
coupled with 1 equiv. of the bromoborole in diethyl ether at 20°C to give 2-thienyldiazaborole **19** as a pale yellow oil after distillation (yield 81%). The reaction of **19** with boron tribromide was completed after 1 h, and the product was subsequently converted into its triphenylphosphine adduct. Base-assisted cyclocondensation of the adduct with phenylene diamines **15** and **16** gave rise to the formation of colourless solids **13** and **14,** in 46% and 21% yield, respectively.

Unlike **5-10**, compounds **11-14** are air and moisture sensitive. Under an argon atmosphere they can be stored for months without decomposition. The pentafluorophenyl derivatives, **11** and **13**, are well soluble in the common aprotic organic solvents, whereas the tetrafluoropyridyl functionalised systems **12** and **14** are poorly soluble in alkanes.

To compare with the fluorinated derivative **5**, the non-fluorinated analogue **20** was made in 80% yield using *N,N´*-diphenyl-*ortho*-phenylenediamine as the diamine precursor (Scheme 3).



Scheme 3. Synthesis of **20**.

The $^{11}B\{^1H\}$ NMR spectra of **5-7** show singlets at δ = 30.4-30.9 ppm, which in comparison to derivative **20** (δ = 28.3 ppm) are slightly deshielded reflecting the electron-withdrawing character of the heterocycle. Similarly, the $^{11}B\{^1H\}$ NMR spectra of **8-10** (δ = 27.4-28.5 ppm) are downfield shifted with respect to **19** (δ = 26.7 ppm). The $^{11}B\{^1H\}$ NMR spectra of the 1,4-phenylene-bridged products **11** and **12** are characterised by broad singlets at δ = 29.3 and 28.7 ppm, respectively. The 2,5-thiophene-bridged derivatives **13** and **14** show broad resonances at δ = 26.2 and 26.4 ppm, respectively. Thus, the ^{11}B NMR spectra of the novel compounds are well comparable with other 2-phenyl- or 2-thienyl-1,3,2-benzodiazaboroles regardless of the substituents at the ring nitrogen atoms.[20-23]

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X-ray crystallography

Single crystals of **8** were grown from a 5:1 mixture of *n*-hexane and CH_2Cl_2 at 4°C (Figure 1). The compound crystallised as meroedric twins in the orthorhombic space group $P2_12_12_1$. Due to the poor quality of the crystals and disordering of the thiophene rings, a detailed discussion of the bonding parameters is meaningless. Here it should be mentioned, however, that the thiophene ring and the BN heterocycle are close to coplanar ($\phi = 11.9°$), whereas the C_6F_5-rings and the benzodiazaborole core enclose interplanar angles of 69.1 and 69.3°. For the related compound **3**, the angle ϕ between the central thiophene ring and the diazaborole plane was determined to 10.1°, whereas the C_6F_5 rings and the BN heterocycle enclose interplanar angles of 65.2 and 87.6°.[27]

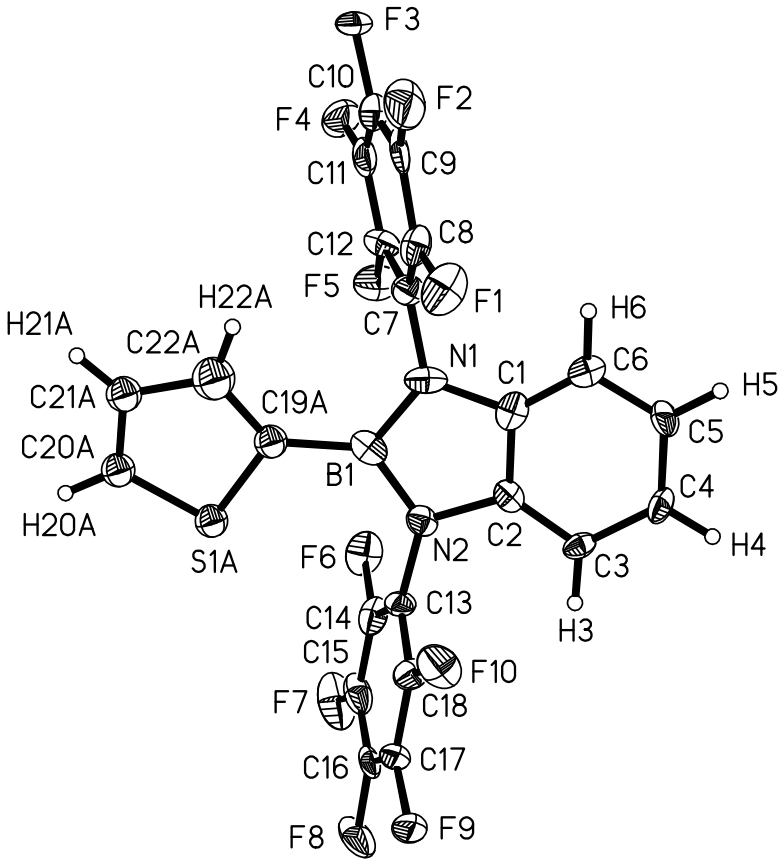

Figure 1. Molecular structure of **8**.

Molecular structures were determined for the two phenylene-bridged bis(benzodiazaboroles) **11** and **12** as well as for the thiophene-2,5-diyl derivative **13** (Figure 2). Single crystals of **11** and **13** were grown from *n*-hexane whereas crystallisation of **12** was achieved from a 10:1 mixture of *n*-hexane and dichloromethane at -20°C. Derivatives **11** and

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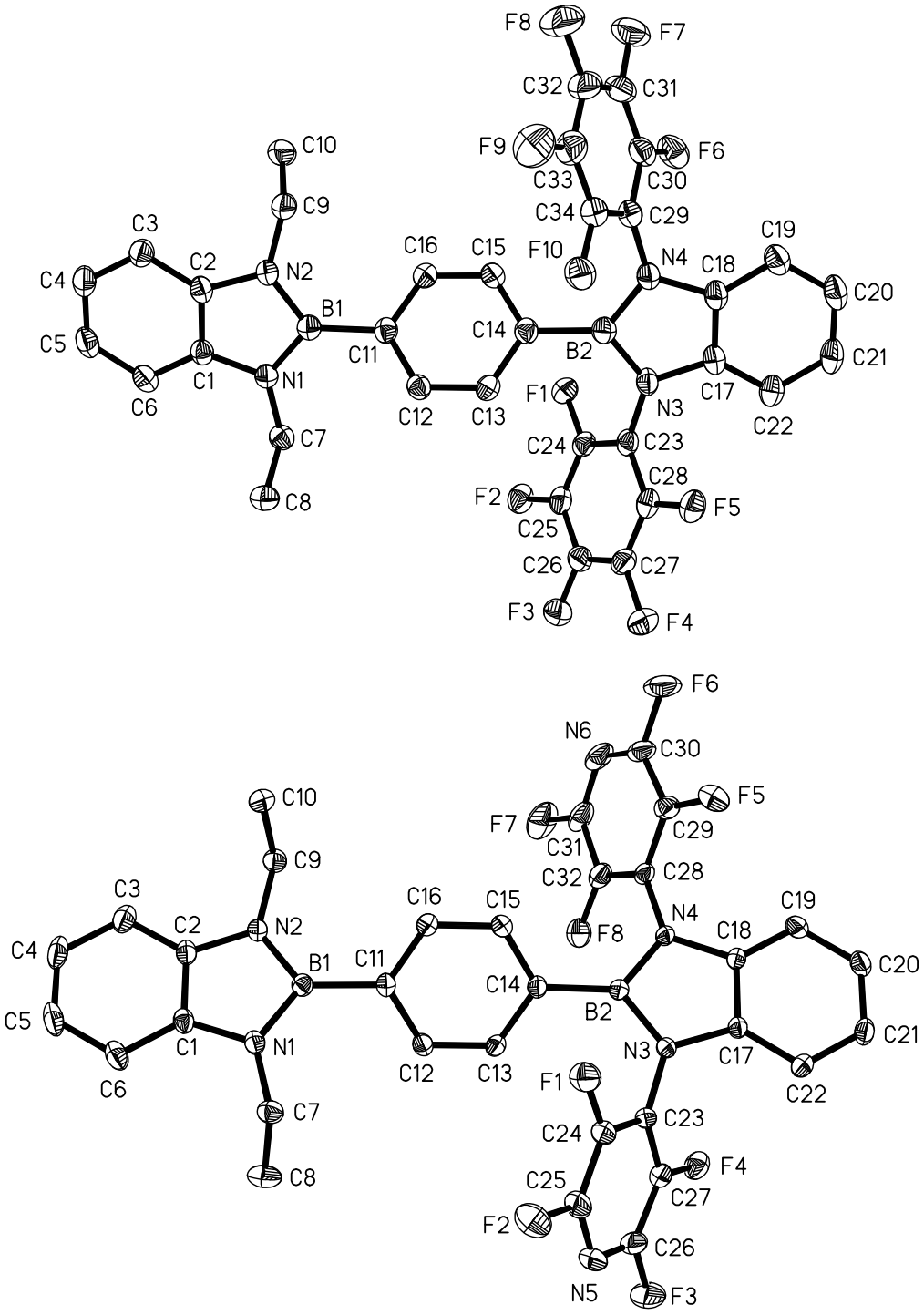
13 featuring pentafluorophenyl substituents crystallise in the triclinic space group P_1, whereas the monoclinic space group $P2_1$ was determined for the tetrafluoropyridyl derivative **12**. The asymmetric units of **12** and **13** contain two independent molecules with virtually identical bond lengths and endocyclic bond angles.



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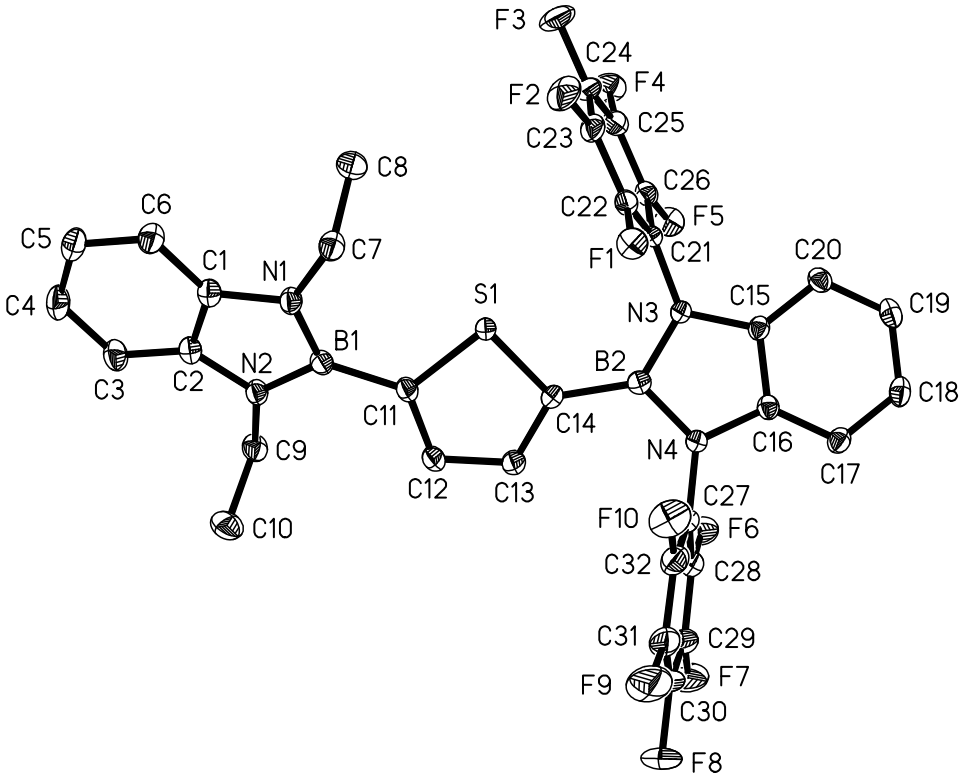

Figure 2. Molecular structures of **11** (top), **12** (middle) and **13** (bottom). Hydrogen atoms are omitted for clarity.

The bond lengths within both benzodiazaborolyl parts of the molecules in **11**-**13** are unexceptional with B-N, N-C_{ring}, and C-C bonds of 1.44, 1.40 and 1.40 Å. As expected the exocyclic bonds N(1)-C(7) and N(2)-C(9) [ca. 1.46 Å] are significantly longer as compared with bonds N(3)-C(23) and N(4)-C(28) [ca. 1.40 Å] in **11** and **12** or N(3)-C(21) and N(4)-C(27) [ca. 1.41 Å] in **13** to the differing hybridisation at the carbon atoms.

Significant differences are found for the C-B bond lengths and the mutual orientations of the three ring systems as well as for the fluoroaryl substituents at the nitrogen atoms in **11**-**13** (Figure 2). These parameters, summarised in Table 1, are of particular interest as a better overlap between the π-orbitals on boron and on the carbon atom attached to boron would occur if the arene moiety and the diazaborolyl functions are coplanar. The coplanarity between thiophene and the B/N heterocycle is more favourable (4.9-45.8°, av. 24.6°) in **13** than for the diazaborole-benzene combination (41.4-45.3°, av. 43.3°) in **11** and **12** in the solid state as found in related systems elsewhere.[20,21,23] The B-C bond lengths involving the

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alkylated heterocycle are longer than those involving the fluoroarylated benzodiazaborolyl groups which may be attributed to the electron-withdrawing character of the aryl groups as observed in similar systems.[25,26]

It is noted that the *para*-phenylene ring in compound **11** contains two C-C bonds at 1.386(1) and 1.388(1) Å where the C atoms are unsubstituted and four C-C bonds at 1.401(1)-1.404(1) Å indicating a small degree of quinoid character. This degree of quinoid character is also found in the closely related structure of **11** with ethyl groups in place of fluoroaryl groups.[21] However, in derivative **12** changes in the C-C bond lengths in the bridge are not significant within 3 esds.

Table 1. Selected geometric parameters of **11-13**. Two independent molecules are present in the crystal structures of **12** and **13**. Et_2BDB = 1,3-diethyl-1,3,2-benzodiazaborolyl group, $^{F}Ar_2BDB$ = 1,3-difluoroaryl-1,3,2-benzodiazaborolyl group.

	11	**12A**	**12B**	**13A**	**13B**
B-C bond length					
At Et_2BDB group	1.565(1) Å	1.556(2) Å	1.553(2) Å	1.548(2) Å	1.551(2) Å
At $^{F}Ar_2BDB$ group	1.551(1) Å	1.542(2) Å	1.537(2) Å	1.537(2) Å	1.540(2) Å
Ring orientation					
Et_2BDB – bridge	N(1)-B(1)-C(11)-C(12) -45.3(1)°	N(1)-B(1)-C(11)-C(12) 44.1(2)°	N(7)-B(3)-C(43)-C(44) -42.5(2)°	N(1)-B(1)-C(11)-S(1) 26.3(2)°	N(5)-B(3)-C(43)-S(2) -45.8(2)°
$^{F}Ar_2BDB$ – bridge	N(3)-B(2)-C(14)-C(13) 43.5(1)°	N(3)-B(2)-C(14)-C(13) -41.4(2)°	N(9)-B(4)-C(46)-C(45) 42.9(2)°	N(3)-B(2)-C(14)-S(1) 21.1(2)°	N(7)-B(4)-C(46)-S(2) 4.9(2)°
^{F}Ar-BDB	B(2)-N(3)-C(23)-C(24) 56.0(1)°	B(2)-N(3)-C(23)-C(24) 60.1(2)°	B(4)-N(9)-C(55)-C(56) 57.6(2)°	B(2)-N(3)-C(21)-C(22) 67.9(2)°	B(4)-N(7)-C(53)-C(54) 58.2(2)°
	B(2)-N(4)-C(29)-C(34) 56.1(1)°	B(2)-N(4)-C(28)-C(32) 54.4(2)°	B(4)-N(10)-C(60)-C(64) 57.2(2)°	B(2)-N(4)-C(27)-C(32) -69.0(2)°	B(4)-N(8)-C(59)-C(64) -60.5(2)°

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Photophysics

Photophysical data for compounds **1**-**14** and **20** in cyclohexane and CH_2Cl_2 solutions are listed in Table 2. Absorption and emission spectra are shown in Figures S1-3. As no emissions from solids of **1**-**14** under UV radiation were visible to the naked eye, no solid-state photophysical measurements were carried out. The absorption maxima for the reported[27] compounds **1**-**4** containing the carbazolyl groups are at λ_{max} = 340-344 nm whereas for compounds **5**-**12** and **20** they occur at λ_{max} = 271-295 nm with little solvatochromism. While the lowest energy bands in **1**-**4** arise from $\pi > \pi^*$ transitions involving the π-bridge and carbazolyl groups,[27] the $\pi > \pi^*$ transitions for compounds **5**-**12** and **20** are likely to involve the benzodiazaborolyl groups. The absorption maxima for the thienylene 'push-pull' systems **13** and **14** are at 322-330 nm suggesting that the thiophene unit contributes significantly to the $\pi > \pi^*$ transitions.

Emission maxima of the new compounds **5**-**12** showed very large Stokes shifts of between 6100 and 15900 cm^{-1} in contrast to the carbazolyl boroles **1**-**4** with values between 1200 and 6100 cm^{-1}. A large Stokes shift indicates that the solvated species goes through a significant geometry rearrangement under excitation.

Many known organic π-systems containing 1,3-diethyl- and 1,3-diphenyl-1,3,2-benzodiazaborolyl groups have Stokes shifts in the region of 5000-10000 cm^{-1} such as the non-fluorinated analogue **20** here at 5200-6400 cm^{-1} and high quantum yields.[18-24] Such emissions from these reported systems arise from the $S_0 < S_1$ transitions involving the π^*(organic π-system) and π(benzodiazaborolyl) orbitals (*vide infra*). In **20**, the π^*(organic π-system) orbital would be at the phenyl group attached to the boron atom (*vide infra*). These emissions are considered to be charge transfer (CT) due to evidence of significant solvatochromism as reflected in the solvatochromic shifts (Table 2). However, the boron atom of the diazaborolyl unit is involved in both orbitals according to computations (*vide infra*) so there is a degree of local excitation (LE) involved which may explain the remarkable fluorescence properties of benzodiazaborolyl groups in organic π-systems.[18-24]

As compounds **5** and **20** differ only in the fluorines instead of hydrogens at the phenyl groups attached to the nitrogens of the benzodiazaborole moiety, it is logical to compare their photophysical data. Compound **20** has a Stokes shift of 5200 cm^{-1} and a quantum yield of 41% whereas compound **5** has the corresponding values of 10600 cm^{-1} and 2% respectively. In addition, the emission band for compound **5** has a more significant solvatochromic shift of 4300 cm^{-1} on going from cyclohexane to dichloromethane compared to **20**

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with a solvatochromic shift of 1200 cm^{-1}. Thus, compounds with 1,3-difluoroaryl-1,3,2-benzodiazaborolyl groups have more significant excited state geometry rearrangements than compounds with non-fluorinated benzodiazaborolyl groups suggesting a different charge transfer (CT) process. This process involves the fluorinated aryl groups and, since the fluorinated aryl orbitals (*vide infra*) involved in this process do not have contributions from the boron atom in the benzodiazaborolyl unit, are considered to be genuine charge transfer.

To distinguish these two CT processes on the basis of the Stokes shifts, the transition involved in the emission of **20** is denoted local charge transfer (LCT) whereas the transition in the emission of **5** is remote charge transfer (RCT). If this assumption is applied to compounds **6**-**10** then all emissions with large Stokes shifts in cyclohexane or dichloromethane are RCT except for emissions with smaller Stokes shifts of compounds **8** and **9** in cyclohexane which are LCT.(Table 2) These CT assignments are supported by the larger solvatochromic shifts found for RCT. The emission spectrum in dichloromethane for compound **8** contains two distinct bands at 362 nm and 503 nm which are assigned LCT and RCT respectively. The dual emission[25,26,29] in **8** has lifetimes of *ca* 0.2 ns at 362 nm and 1.05 ns at 503 nm which shows that two independent excited states are formed.

The fluorescence quantum yields, Φ_F, for the compounds **1**-**14** clearly depend on the nature of the substituent at the boron atom of the fluorinated benzodiazaborole. Low Φ_F values are observed with phenyl or thienyl groups (**5**-**10** with Φ_F up to 8%) and generally high Φ_F values with the 2-(1,3-diethyl-1,3,2-benzodiazaborolyl)aryl groups (**11**-**14** with Φ_F up to 97%).

The quantum yields differ considerably in the case of compounds with the tetrafluoropyridyl groups (**2**, **4**, **12, 14**) where the values are lower in dichloromethane than in cyclohexane. Non-radiative processes are thus dominant in more polar solvents where the excited states involve the tetrafluoropyridyl groups. By contrast, the effect of solvent on the quantum yields is not obvious for compounds containing the pentafluorophenyl and cyanotetrafluorophenyl groups.

Lippert-Mataga analyses carried out on **11**-**14** with four different solvents reveal that the transition dipole moments $\Delta\mu$ are 15.8 D for **11**, 23.0 D for **13** and 18.3 D for **14** which support the charge transfer nature of their emissions.(Figures S4-S7, Tables S2-S5) Values of 14.8 – 19.7 D have been determined for similar benzodiazaboroles with LCT emissions.[22] The $\Delta\mu$ value for **12** could not be determined as there is no linear fit in the Lippert-Mataga

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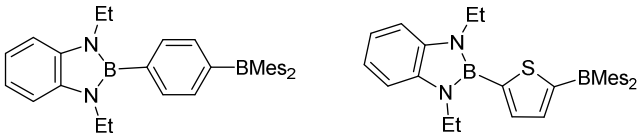
plot for **12**. It is possible that either LCT or RCT emission takes place in different solvents for **12**.

The push-pull systems, **21** and **22** (Chart 2),[20] which differ from **11**-**14** by virtue of the electron-withdrawing $BMes_2$ group instead of the fluoroaryl diazaborolyl group, have similar emission data to **11**-**14**. In cyclohexane solutions, the Stokes shifts are 8800 cm^{-1} and 6070 cm^{-1} and the quantum yields are 90% and 99% for **11** and **21** respectively. Similarly, the thiophene analogues have values of 6300 cm^{-1} and 6210 cm^{-1} and 59% and 81% for **13** and **22** respectively. It may be concluded here that the emissions of the push-pull systems **11**-**14** are LCT like for many other reported organic **π**-systems with benzodiazaborolyl groups.[18-24]



21 **22**

Chart 2. Push-pull systems, **21** and **22**.

Table 2. Photophysical data for the benzodiazaboroles 2-Ar-1,3-Ar_2-$BN_2C_6H_4$, **1-14** and **20**. Cz = 4,7-*t*Bu_2-carbazolyl group; BDB = 1,3-Et_2-benzodiazaborolyl group.

	2-Ar	1/3-Ar	Solvent	$\lambda_{max,Abs}$ [nm]	$\tilde{\nu}_{max,Abs}$ [cm^{-1}]	ε [$Lmol^{-1}cm^{-1}$]	$\lambda_{max,Em}$ [nm]	$\tilde{\nu}_{max,Em}$ [cm^{-1}]	Stokes shift [cm^{-1}]	Φ_{fl} [%]	Solvatochromic shift [cm^{-1}]
1	CzC_6H_4	C_6F_5	*c*-C_6H_{12}	344	29100	17700	358	27900	1200	79	
			CH_2Cl_2	344	29100	10000	407	24600	4500	26	3300
2	CzC_6H_4	4-C_5F_4N	*c*-C_6H_{12}	344	29100	11600	377	26200	2900	47	
			CH_2Cl_2	344	29100	10400	414	23800	5300		2400
3	CzC_4H_2S	C_6F_5	*c*-C_6H_{12}	340	29400	15600	394	25400	4000	14	
			CH_2Cl_2	340	29400	12000	411	24300	5100	18	1100
4	CzC_4H_2S	4-C_5F_4N	*c*-C_6H_{12}	340	29400	11600	410	24400	5000	16	
			CH_2Cl_2	341	29300	15900	431	23200	6100	2	1100
5	C_6H_5	C_6F_5	*c*-C_6H_{12}	283	35300	11350	405	24270	10600	3	
			CH_2Cl_2	283	35300	6960	489	20500	14900	<1	4300
6	C_6H_5	4-C_5F_4N	*c*-C_6H_{12}	275	36400	18420	419	23900	12500	1	
			CH_2Cl_2	271	36900	20400	477	21000	15900	<1	3400
7	C_6H_5	4-NCC_6F_4	*c*-C_6H_{12}	287	34800	7800	417	24000	10800	3	
			CH_2Cl_2	281	35600	18370	472	21200	14400	5	3600
8	C_4H_3S	C_6F_5	*c*-C_6H_{12}	291	34400	10430	353	28300	6100	8	
			CH_2Cl_2	292	34200	16340	362	27600	6600	<1	500
							503	19900	14300		8200
9	C_4H_3S	4-C_5F_4N	*c*-C_6H_{12}	281	35600	12260	363	27400	8100	1	
			CH_2Cl_2	280	35700	2130	464	21600	14100	<1	6000
10	C_4H_3S	4-NCC_6F_4	*c*-C_6H_{12}	289	34600	7110	408	24500	10100	1	
			CH_2Cl_2	290	34500	24110	483	20700	13800	2	3700
11	$BDBC_6H_4$	C_6F_5	*c*-C_6H_{12}	293	34100	15080	395	25300	8800	90	
			CH_2Cl_2	295	33900	22150	428	23400	11300	97	2500
12	$BDBC_6H_4$	4-C_5F_4N	*c*-C_6H_{12}	286	35000	26040	408	24500	10500	95	
			CH_2Cl_2	289	34600	21930	447	22400	12200	2	1700
13	$BDBC_4H_2S$	C_6F_5	*c*-C_6H_{12}	322	31100	18780	404	24800	6300	59	
			CH_2Cl_2	320	31300	21710	446	22400	8900	65	2600
14	$BDBC_4H_2S$	4-C_5F_4N	*c*-C_6H_{12}	330	30300	10030	418	23900	6400	78	
			CH_2Cl_2	325	30800	9990	464	21600	9200	46	2800
20	C_6H_5	C_6H_5	*c*-C_6H_{12}	295	33900	6670	349	28700	5200	41	
			CH_2Cl_2	295	33900	6440	364	27500	6400	38	1200

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Computations

Ground state geometry optimisations of **5**-**14** and **20** were computed at the B3LYP/6-31G* level of theory. A very good agreement was found between the optimised S_0 geometries and the X-ray data of **11**-**13** (Table S6). However, the relative orientations between the benzodiazaborolyl plane and the planes of the bridge and fluoroaryl groups are somewhat more twisted in the computed geometries than in the experimental geometries. It is not possible to rotate the fluoroaryl groups attached to the nitrogen atoms in the benzodiazaboroles about the N-C bond. Geometries where both the benzodiazaborole unit and one of the fluoroaryl groups are coplanar could not be located due to the obvious steric barriers between these moieties. The sterics can be visualised by adjusting the fluoroaryl group containing F1 for **8** in Figure 1 to be coplanar with the benzodiazaborole unit resulting in the F1 atom occupying the space where the H6 atom is. However, the aryl or thienyl group attached to the boron atom can be rotated about the B-C bond with estimated energy barriers of only 3.8 and 1.1 kcal mol^{-1} for **5** and **8**, respectively.

Molecular Orbitals

The frontier orbitals in the parent benzodiazaborole are the π and π* orbitals on the 1,3,2-$N_2BC_6H_4$ system (Figure S8). When a π–organic substituent is attached to boron, the HOMO is generally on the benzodiazaborolyl group whereas the LUMO is typically on the π–system attached to boron with some boron atom character. A π–organic substituent at nitrogen would also result in a HOMO on the benzodiazaborolyl group and in a LUMO on the substituent itself. Thus, if two π–organic substituents are attached to N and B like the systems discussed in this study, the LUMO may be located at either the substituent at N or at B, whereas the HOMO would be located on the benzodiazaborolyl moiety.

For the non-fluorinated system, 1,2,3-Ph_3-1,3,2-$N_2BC_6H_4$ **20**, the LUMO is at the phenyl group attached to B. For the fluorinated system, 1,3-$(C_6F_5)_2$-2-Ph-1,3,2-$N_2BC_6H_4$ **5**, however, the LUMO resides at the C_6F_5 group (Figure 7). The same picture exists for compounds **6**-**10** where the LUMOs are also located on the aryl groups attached to the nitrogen atoms of the diazaborole. The molecules with a thiophene unit have considerable contributions from the thiophene in both frontier orbitals. Each push-pull system (**11**-**14**) has the HOMO located at the *N*,*N*-diethyl benzodiazaborolyl group and the LUMO at the aryl groups in the *N*,*N*-diaryl benzodiazaborolyl group.

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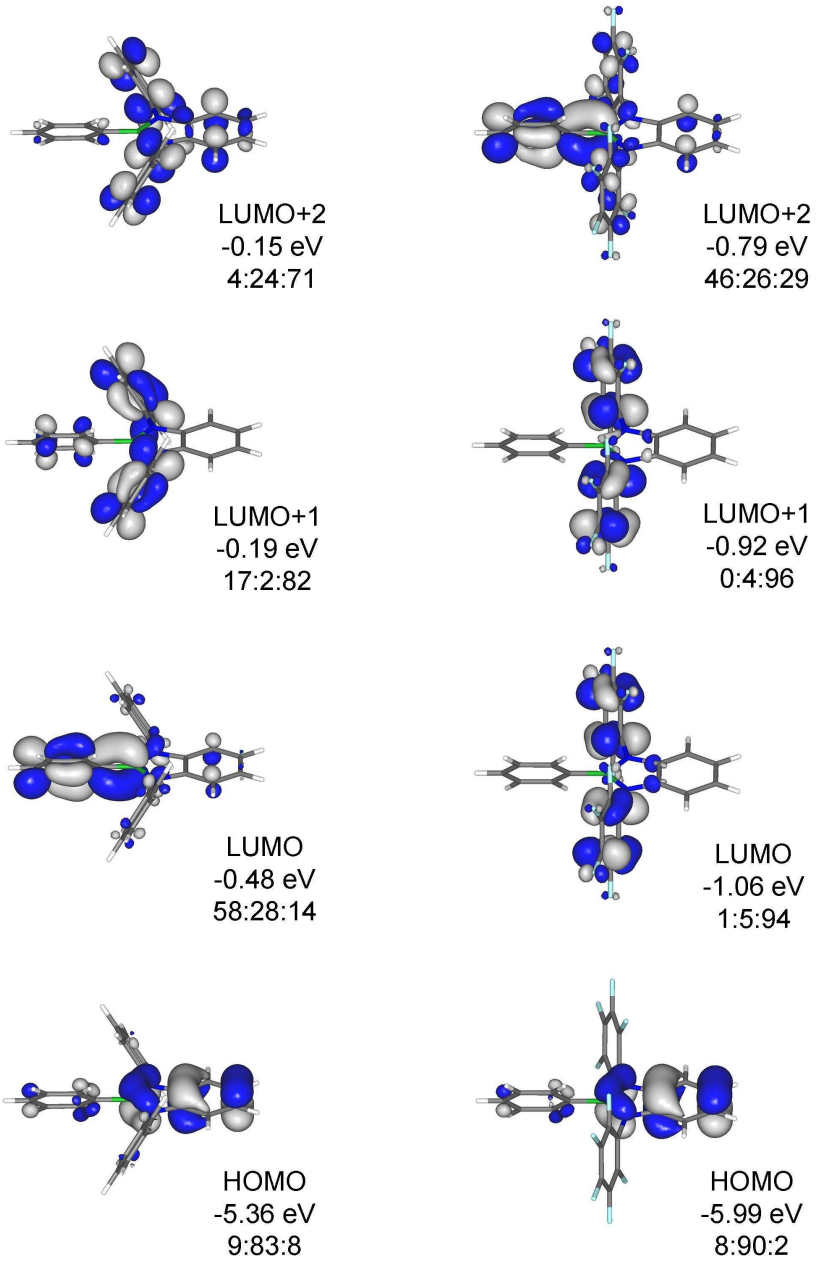

Figure 7. Molecular orbitals in the optimised ground state (S_0) geometries for 1,2,3-Ph_3-1,3,2-$N_2BC_6H_4$ **20** (left column) and 1,3-$(C_6F_5)_2$-2-Ph-1,3,2-$N_2BC_6H_4$ **5** (right column). The MO contribution ratio of the three groups, Ph (at B) : $N_2BC_6H_4$: Ar (at N), are given.

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TD-DFT computations

The hybrid functional CAM-B3LYP is used to compute charge transfer transitions as it has the necessary physics to model charge contributions more correctly than the widely used B3LYP functional.[20] The data summarised in Table 3 show very good agreement between the observed absorption maxima of the strong bands and the computed maxima with predicted strong bands. However, bands with lower oscillator strengths are predicted at lower energies for **6**, **7**, **9** and **10**. These weak bands are from transitions from the fluorinated rings to the benzodiazaborole unit (i.e. RCT). While the predicted weak bands for the tetrafluoropyridyl compounds **6** and **9** are not observed due to the strong bands, the weak bands for the cyano compounds **7** and **10** are present as shoulder bands. Based on Gaussian deconvolution analyses, these bands are 314 nm (**7**) and 318 nm (**10**) in cyclohexane and 316 nm (**7**) and 322 nm (**10**) in dichloromethane. This has implications in determining the Stokes shifts – a Stokes shift is generally regarded as the energy difference between the lowest energy absorption band ($S_0 > S_1$) and the highest energy emission band ($S_0 < S_1$). Nevertheless, using the computed $S_0 > S_1$ absorption data and observed emission data, the Stokes shifts remain large with values between 4300 and 10600 cm^{-1}.

All the strong absorption bands for **5-14** and **20** are assigned as arising from π-benzodiazaborolyl > π*-B-aryl transitions. As described earlier, they are defined as local charge transfers (LCTs), these are not strictly local π > π* or charge transfer (CT) transitions as both orbitals contain some boron atom character. Compounds with thiophene units have considerable thiophene character in both frontier orbitals and therefore have thiophene character in the important transitions.[20] Transitions at lower energies are predicted for compounds **6**, **7**, **9** and **10** on going from the benzodiazaborolyl HOMO to the fluorinated aryl group LUMO and defined as remote charge transfers (RCTs).

Table 3. Comparison between observed and computed absorption data for the benzodiazaboroles, **5**-**14** and **20**.

	λ_{max}, Abs. Obs.[a] [nm]	λ_{max}, Abs. Calc.[b] [nm]	Osc. Str.[c] Calc.	Transition Type	$S_0 > S_1$ Abs. Calc.[d] [nm]	Osc. Str. Calc.	Transition Type	Observed Stokes shift [cm^{-1}]	Calculated Stokes shift[e] λ_{max} [cm^{-1}]
5	283	283	0.2206	HOMO > LUMO+2 π-borolyl > π*-BPh				10600	10600
6	275	283	0.1934	HOMO > LUMO+2 π-borolyl > π*-BPh	307	0.0236	HOMO > LUMO π-borolyl > π*- ^{F}Ar	12500	11500
7	287	281	0.1778	mixed	333	0.0369	HOMO > LUMO π-borolyl > π*- ^{F}Ar	10800	11600
8	291	298	0.2941	HOMO > LUMO π-borolyl /Th > π*-BTh/^{F}Ar				6100	5200
9	281	290	0.2730	HOMO > LUMO+2 π-borolyl /Th > π*-BTh/^{F}Ar	314	0.0293	HOMO > LUMO π-borolyl/Th > π*- ^{F}Ar	8100	6900
10	289	293	0.2985	HOMO > LUMO+2 π-borolyl /Th > π*-BTh/^{F}Ar	337	0.0027	HOMO > LUMO π-borolyl > π*- ^{F}Ar	10100	9600
11	293	306	0.6368	HOMO > LUMO+1 π-Et_2borolyl > π*-BC_6H_4B				8800	7400
12	286	308	0.4535	HOMO > LUMO+2 π-Et_2borolyl > π*-BC_6H_4B				10500	8000
13	322	335	0.7578	HOMO > LUMO π-Et_2borolyl/Th > π*-BThB				6300	5100
14	330	341	0.6116	HOMO > LUMO, HOMO > LUMO+2 π-Et_2borolyl/Th > π*-BThB/^{F}Ar				6400	5400
20	295	295	0.2667	HOMO > LUMO π-borolyl > π*-BPh				5200	5200

[a] in cyclohexane
[b] maxima with highest oscillator strength.
[c] oscillator strength.
[d] for calculated $S_0 > S_1$ transitions that are not also maxima with highest oscillator strengths.
[e] energy difference between computed absorption maxima and observed emission data.

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Excited state calculations

The parent benzodiazaborole where only local $\pi > \pi^*$ and $\pi < \pi^*$ transitions within the fused heterocycle are possible has a computed Stokes shift of 2000 cm^{-1} based on calculated transitions from its S_0 and S_1 optimised geometries (Figure S8). This value agrees well with the observed Stokes shift of ca 2000 cm^{-1} for the related alkyl derivative, 2-*t*Bu-1,3-Et_2-1,3,2-$N_2BC_6H_4$. [24,26] For the benzodiazaboroles **5-14** and **20** here, the Stokes shifts are in the region of 5200-13400 cm^{-1} as listed in Table 3. As the observed Stokes shifts are large, the S_1 excited state geometries must be significantly different to the S_0 ground state geometries.

Two distinct excited state optimised geometries were located for **5**, **8** and **9** and are denoted LCT and RCT. The LCT geometry involves changes within the diazaborolyl and B-aryl groups as reported elsewhere,[20] whereas the RCT geometry involves a highly distorted aryl group at N as shown in Figure 8 for **5**. The Stokes shifts based on TD-DFT data from S_0 and S_1(RCT) are generally larger than those from S_0 and LCT as shown in Table 4.

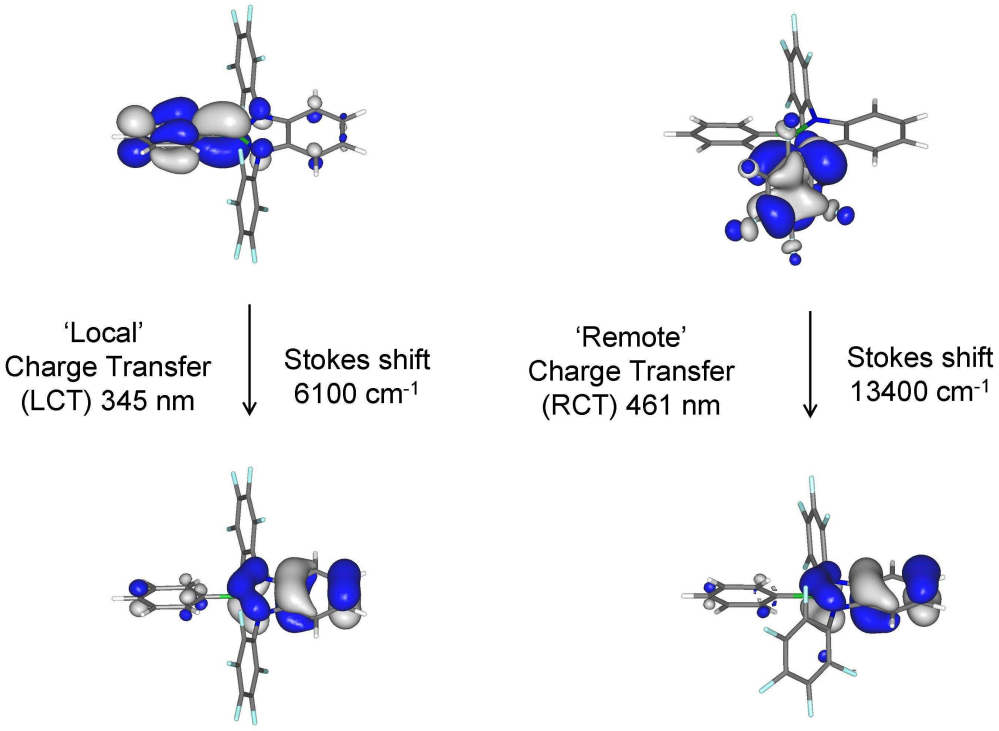

Figure 8. Molecular orbitals involved in the emissions for the two distinct excited state geometries of **5**, LCT and RCT with calculated values

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From Table 4, a comparison between the observed emission data in cyclohexane solutions and the computed emission data indicates that RCT emissions take place for compounds **5**, **6**, **7** and **10** and LCT emissions take place for the other systems. RCT emissions are likely to take place for compounds **8** and **9** in the more polar dichloromethane solutions as solvatochromic shifts of 8200 and 6000 cm^{-1} on going from cyclohexane to CH_2Cl_2 are too large for LCT emissions to take place in both solvents. Two emission bands are observed in CH_2Cl_2 for **8** which may be assigned as LCT and RCT emissions for the high and low energy bands, respectively.

For compounds **11-14,** the calculated and observed emission maxima based on LCT are in good agreement (Table 4). The orbitals involved in the LCT emission for **11** are shown in Figure 9. They closely resemble the orbitals involved in the LCT emission of the related push-pull system, **21** (Figure S9) reported previously.[20]

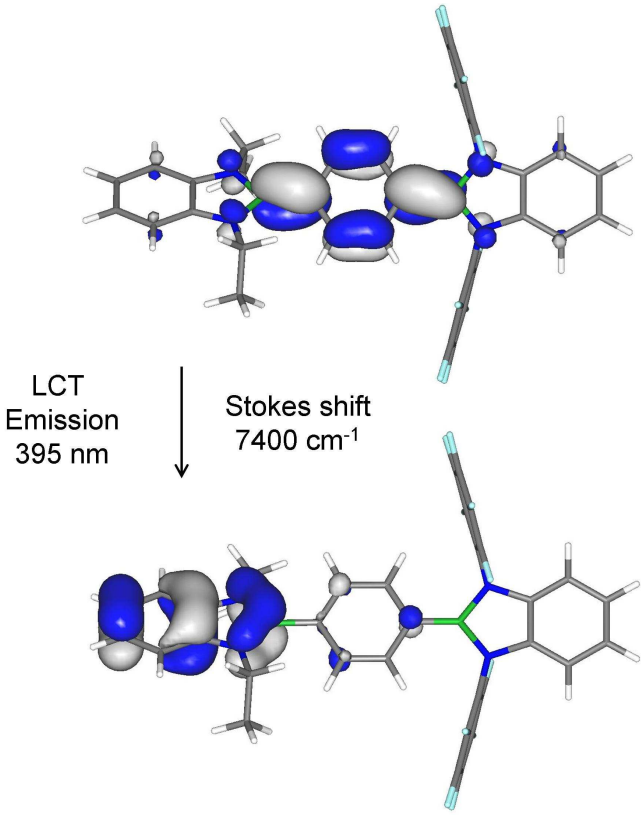

Figure 9. Molecular orbitals involved in the emission for the excited state LCT geometry of **11**. Emission and Stokes shift values are calculated.

Table 4. Comparison between observed and computed emission data for the benzodiazaboroles, **5**-**14** and **20**. The optimised LCT and RCT excited state geometries are used to compute the emission data.

	λ_{max}, Em Obs, cyclohexane [nm]	λ_{max}, Em (LCT) Calc [nm]	Stokes shift[a] (LCT) Calc [cm^{-1}]	$S_0 < S_1$ Transition Type[b]	λ_{max}, Em (RCT) Calc [nm]	Stokes shift[a] (RCT) Calc [cm^{-1}]	$S_0 < S_1$ Transition Type[b]	Emission Assignment, cyclohexane
5	405	345	6100	π-borolyl < π*-BPh	461	13400	π-borolyl < π*- ^{F}Ar	RCT
6	419	-[c]			486	12000	π-borolyl < π*- ^{F}Ar	RCT
7	417	-[c]			484	9300	π-borolyl < π*- ^{F}Ar	RCT
8	353	395	8300	π-borolyl/Th < π*-BTh	473	12500	π-borolyl/Th < π*- ^{F}Ar	LCT
9	363	406	7200	π-borolyl/Th < π*-BTh	505	12000	π-borolyl/Th < π*- ^{F}Ar	LCT
10	408	-[c]			511	10100	π-borolyl/Th < π*- ^{F}Ar	RCT
11	395	395	7400	π-borolyl < π*-BC_6H_4B	-[d]			LCT
12	408	418	8600	π-borolyl < π*-BC_6H_4B	487	11900	π-borolyl/Th < π*- ^{F}Ar	LCT
13	404	436	7000	π-borolyl/Th < π*-BThB	-[d]			LCT
14	418	448	7000	π-borolyl/Th < π*-BThB	-[d]			LCT
20	349	372	7000	π-borolyl < π*-BPh	-[d]			LCT

[a] Energy difference between computed absorption maxima (Table 3) and computed emission data.
[b] From molecular orbital calculations on the optimised excited state geometries where the LUMO is assumed to be the highest occupied spin orbital and the HOMO is assumed as the second highest occupied spin orbital.
[c] Optimised LCT geometry could not be located.
[d] Optimised RCT geometry could not be located.

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Conclusions

Ten new compounds, **5**-**14**, containing the electron-withdrawing bis(perfluoroaryl)benzodiazaborolyl groups were synthesised to examine the influence of the fluorinated rings on the photophysical properties of benzodiazaboroles. The benzodiazaboroles **5**-**10** exhibit weak fluorescence emissions with pronounced Stokes shifts up to 15900 cm^{-1} which arise from charge transfer of the excited states involving the perfluoroaryl groups. This unusual CT process is supported by excited state geometries located computationally and differs from the emission process involving many highly fluorescent organic systems with benzodiazaborolyl groups. The push-pull systems **11**-**14**, containing fluorinated benzodiazaborolyl groups as acceptors and alkylated benzodiazaborolyl groups as donors, did not result in pure charge transfer emissions between the two groups. The photophysical and computational data for these push-pull systems resemble other push-pull benzodiazaboroles where the $BMes_2$ group is used as the acceptor. Thus, the π-donor or π-acceptor character of a benzodiazaborole unit may easily be tailored by the choice of the substituents at the nitrogens of the heterocycle.

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Experimental Section

All manipulations were performed under an atmosphere of dry, oxygen-free argon by using Schlenk techniques. All solvents were dried by standard methods and freshly distilled prior to use. The compounds 1,2-(HN-4′-pyridyl)$_2$C$_6$H$_4$,[27] 1,2-(HNPh)$_2$C$_6$H$_4$,[27] 1,2-(HNC$_6$F$_5$)$_2$C$_6$H$_4$,[30] 1-Br-4-Me$_3$Si-C$_6$H$_4$,[31] 2-Me$_3$Si-C$_4$H$_3$S[32] and 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole[28] were prepared according to literature methods. Boron tribromide, 2,2,6,6-tetramethylpiperidine, triphenylphosphine, *n*- and *tert*-butyllithium were purchased commercially.

NMR spectra were recorded at room temperature in C_6D_6 or $CDCl_3$ on a Bruker Avance III 300 (^{1}H: 300, ^{11}B: 96, ^{13}C: 75, ^{19}F: 282 MHz) or a Bruker Avance III 500 spectrometer (^{1}H: 500, ^{11}B: 160, ^{13}C: 125, ^{19}F: 470, ^{31}P: 202 MHz) with $SiMe_4$ (^{1}H, ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), $CFCl_3$ (^{19}F) and 85% H_3PO_4 (^{31}P) as external standards. Some expected ^{13}C peaks corresponding to the boron-bound carbon atoms were not detected above the noise level while some ^{13}C peaks corresponding to carbon atoms of the ^{F}Ar groups were obscured by other peaks in the same region. Mass spectra were obtained with a VG autospec sector field mass spectrometer (Micromass). In some cases, the C-mass fractions in the elemental analyses were too low, which may be rationalized by incomplete combustion of boron carbides formed in this process.

2-Phenyl-1,3-bis(pentafluorophenyl)-1,3,2-benzodiazaborole (**5**)

A sample of boron tribromide (0.526 g, 2.1 mmol) was added at 20°C to a solution of phenyltrimethylsilane (0.330 g, 2.2 mmol) in dichloromethane (30 mL). The mixture was stirred for 16 h before a solution of triphenylphosphine (0.655 g, 2.5 mmol) in dichloromethane (10 mL) was added. After 2 h of stirring at room temperature volatiles were removed *in vacuo*, and NMR spectra were taken from the colourless solid residue (δ^{11}B (C_6D_6) = -4.7 (s), δ^{31}P (C_6D_6) = -3.9 (s) ppm). This adduct and *N,N′*-bis(pentafluorophenyl)phenylenediamine **15** (0.924 g, 2.1 mmol) were dissolved in toluene (70 mL) and 2,2,6,6-tetramethylpiperidine was added (0.636 g, 4.5 mmol). The mixture was heated at 100°C for 24 h and then cooled to 20°C. It was filtered and the filtrate was evaporated to dryness. The residue was freed from triphenylphosphine by sublimation *in vacuo* at 90-100°C. The residue was crystallised from *n*-hexane to yield 0.640 g (1.16 mmol, 55%) of **5**.

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^{1}H NMR (C_6D_6): δ= 6.66 (m, 2H, C<u>H</u>=CHCH=C<u>H</u>), 7.00 (m, 3H, *m*, *p*-Ph-H), 7.05 (m, 2H, CH=C<u>H</u>C<u>H</u>=CH), 7.34 (m, 2H, *o*-Ph-H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ=110.8 (s, <u>C</u>H=CHCH=<u>C</u>H), 122.3 (s, CH=<u>C</u>H<u>C</u>H=CH), 128.5, 130.5, 132.4 (3s, BC-<u>C</u>H-<u>C</u>H-<u>C</u>H), 136.1 (s, N_2C_2), 138.0 (dm, $^{1}J_{C,F}$=255 Hz, C_6F_5), 140.6 (dm, $^{1}J_{C,F}$=255 Hz, C_6F_5), 144.2 (dm, $^{1}J_{C,F}$=255 Hz, C_6F_5) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ= 30.7 (s) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ= -161.3 (m, 4F, *m*-F), -154.3 (t, $^{1}J_{F,F}$=22 Hz, 2F, *p*-F), -146.1 (m, 4F, *o*-F) ppm. MS/EI (m/z): 526.1 (100%) [M^+]. $C_{24}H_9BF_{10}N_2$ (526.14): calcd.: C: 54.79, H: 1.72, N: 5.32; found: C: 54.62, H: 1.85, N: 5.23.

<u>2-Phenyl-1,3-bis(2′,3′,5′,6′-tetrafluoropyridyl)-1,3,2-benzodiazaborole (**6**)</u>

According to the protocol for **5** 2.1 mmol of adduct $PhBBr_2{\cdot}PPh_3$ was reacted with an equimolar amount of *N,N′*-bis(tetrafluoropyridyl)-*ortho*-phenylenediamine **16** (0.853 g) and 4.5 mmol (0.636 g) of 2,2,6,6-tetramethylpiperidine in toluene at 100°C for 24 h. After filtration and evaporation of the filtrate to dryness triphenylphosphine was sublimed off at 90°C *in vacuo*. The residue was crystallised from toluene at -20°C to give product **6** (0.710 g, 69%).

^{1}H NMR (C_6D_6): δ= 6.52 (m, 2H, C<u>H</u>=CHCH=C<u>H</u>), 6.90 (t, 2H, $^{3}J_{H,H}$=7.1 Hz, *m*-Ph-H), 6.99 (m, 3H, CH=C<u>H</u>C<u>H</u>=CH and *p*-Ph-H), 7.10 (d, 2H, $^{3}J_{H,H}$=7.0 Hz, *o*-Ph-H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ= 111.2 (s, <u>C</u>H=CHCH=<u>C</u>H), 122.7 (s, CH=<u>C</u>H<u>C</u>H=CH), 128.5, 130.7, 131.9 (3s, BC-CH-CH-CH), 134.4 (s, N_2C_2), 138.6 (dm, $^{1}J_{C,F}$=263 Hz, C_5F_4N), 144.0 (dm, $^{1}J_{C,F}$=245 Hz, C_5F_4N) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ= 30.4 (s) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ= -145.31 (m, 4F, *o*-F), -88.01 (m, 4F, *m*-F) ppm. MS/EI (m/z): 492.0 (100%) [M^+], 472.0 (10%) [M^+ –HF]. HRMS-EI ($C_{22}H_9BF_8N_4$): calcd.: 492.07870; found: 492.07953.

<u>*N,N′*-*ortho*-Bis(2,3,5,6-tetrafluoro-4-cyanophenyl)-phenylenediamine (**17**)</u>

A chilled solution (-78°C) of *n*-butyllithium in *n*-hexane (116 mL, 186 mmol) was combined portionwise with hexamethyldisilazane (30.0 g, 186 mmol). The mixture was transferred into chilled (-78°C) dropping funnel and then added during 60-70 min to a cold (-78°C) solution of *ortho*-phenylenediamine (5.0 g, 46.0 mmol) in THF (150 mL). The dark violet reaction mixture was warmed to 0°C, and then re-cooled to -78°C before a sample of pentafluoro-benzonitrile (17.8 mL, 92.2 mmol) was added. The mixture was warmed to ambient temperature within 16 h, and subsequently combined with water (80 mL) and THF (50 mL). The organic phase was separated and washed with brine (2x50 mL). The combined aqueous phases were extracted with THF (3x50 mL). Then the combined THF phases were dried with

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Na_2SO_4 and filtered. The filtrate was evaporated to dryness. The brown solid reaction residue was suspended in toluene (250 mL). The obtained solid which contained the product was filtered off and dried. This extraction procedure was repeated three times. Purification of the crude product was effected by crystallisation from dichloromethane (350 mL). *N,N′-ortho*-Bis(2,3,5,6-tetrafluoro-4-cyanophenyl)-phenylenediamine **17** was obtained as pale pink crystals (12.5 g, 27.5 mmol, 60%).^{1}H NMR ($CDCl_3$): δ= 6.08 (s, br, 2H, NH), 7.05 (m, 2H, CH=CHCH=CH), 7.23 (m, 2H, CH=CHCH=CH) ppm. ^{13}C-{^{1}H}-NMR (CD_2Cl_2): δ= 83.2 (m, C_5F_4CCN), 108.7 (s, C_6F_4CN) 122.4 (s, CH=CHCH=CH), 126.4 (s, CH=CHCH=CH), 132.9 (s, N_2C_2), 138.6 (dm, $^1J_{C,F}$ = 246Hz, C_6F_4CN), 148.5 (dm, $^1J_{C,F}$ = 261Hz, C_6F_4CN) ppm. ^{19}F{^{1}H}-NMR ($CDCl_3$): δ= -150.6 (m, 4F, *o*-F), -133.1 (m, 4F, *m*-F) ppm. MS/EI (m/z): 454.0 (100 %) [M^+], 434.0 (52%) [M^+ -HF].$C_{20}H_6F_8N_4$ (454.28): calcd.: C: 52.88, H: 1.33, N: 12.33; found: C: 52.91, H: 2.70, N: 12.31.

2-Phenyl-1,3-bis(2′,3′,5′,6′-tetrafluoro-4′-cyanophenyl)-1,3,2-benzodiazaborole (**7**)

Analogously to the synthesis of **5** the adduct of $PhBBr_2{\cdot}PPh_3$ (2.1 mmol) was reacted with 2.1 mmol (0.954 g) of *N,N′-ortho*-bis(2,3,5,6-tetrafluoro-4-cyanophenyl)-phenylenediamine **17** and 2,2,6,6-tetramethyl-piperidine (0.636 g, 4.5 mmol) in toluene at 100°C for 60 h. The solid residue from the filtrated reaction mixture was dissolved in a mixture of CH_2Cl_2 (10 mL) and *n*-hexane (25 mL) and stored at -20°C, whereby PPh_3 and unreacted *ortho*-phenylenediamine precipitated. This mixture was filtered and the filtrate was freed from solvent. The residue was dissolved in *n*-hexane and stored at -20°C for a few days. By this large yellow orange crystals of **7** (162 mg, 0.30 mmol, 14%) were obtained. ^{1}H NMR (C_6D_6): δ= 6.63 (m, 2H, CH=CHCH=CH), 6.99 (m, 3H, *m,p*-Ph-H), 7.03 (m, 2H, CH=CHCH=CH), 7.22 (m, 2H, *o*-Ph-H) ppm. ^{13}C-{^{1}H} NMR (C_6D_6): δ=111.0 (s, CH=CHCH=CH), 122.7 (s, CH=CHCH=CH), 128.5, 130.7, 131.9, (3s, BC-CH-CH-CH), 135.0 (s, N_2C_2), 143.2 (dm, $^1J_{C,F}$=260 Hz, C_6F_4CN), 147.1 (dm, $^1J_{C,F}$=264 Hz, C_6F_4CN) ppm. ^{11}B-{^{1}H} NMR (C_6D_6): δ= 30.9 (s) ppm. ^{19}F-{^{1}H} NMR (C_6D_6): δ= -142.7 (m, 4F, *o*-F), -131.7 (m, 4F, *m*-F) ppm. MS/EI (m/z): 540.1 (100%) [M^+], 520.1 (5%) [M^+ -HF]. HRMS-EI ($C_{26}H_9BF_8N_4$): calcd.: 540.07870; found: 540.07957.

2-Thienyl-1,3-bis(pentafluorophenyl)-1,3,2-benzodiazaborole (**8**)

Following the same protocol, 2-trimethylsilylthiophene (0.343 g, 2.2 mmol) was reacted with 0.526 g (2.1 mmol) of BBr_3 in 30 mL of CH_2Cl_2 for 2 h. After the addition of PPh_3 (0.655 g, 2.5 mmol) the adduct was isolated from the solution (δ^{11}B (C_6D_6) = -7.1 (s), δ^{31}P (C_6D_6) = -

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4.5 (s) ppm) and dissolved in toluene (70 mL) together with *N,N′*-bis(pentafluorophenyl)-*ortho*-phenylenediamine **15** (0.924 g, 2.1 mmol) and 0.636 g (4.5 mmol) of 2,2,6,6-tetramethyl-piperidine. The mixture was heated at 100°C for 16 h, cooled to room temperature and filtered. After evaporation of the filtrate, the dry residue was first sublimed *in vacuo* at 90-100°C to remove the phosphine and crystallised from an *n*-hexane/CH_2Cl_2 mixture (25/5 mL) at 4°C to afford compound **8** (0.750 g, 1.41 mmol, 67%) as colourless crystals. ^{1}H NMR (C_6D_6): δ= 6.75 (m, 2H, C<u>H</u>=CHCH=C<u>H</u>), 6.81 (t, $^3J_{H,H}$=4.1 Hz, 1H, 4-H-thiophene), 7.09 (d, $^3J_{H,H}$=4.0 Hz, 1H, 3-H-thiophene), 7.15 (m, 2H, CH=C<u>H</u>C<u>H</u>=CH), 7.64 (d, $^3J_{H,H}$=4.1 Hz ,1H, 5-H-thiophene) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ= 110.4 (s, <u>C</u>H=CHCH=<u>C</u>H), 122.1 (s, CH=<u>C</u>H<u>C</u>H=CH), 128.5, 131.9, 134.8 (3s, BC<u>C</u>H<u>C</u>H<u>C</u>HS), 136.1 (s, N_2C_2), 138.0 (dm, $^1J_{C,F}$=252 Hz, C_6F_5), 140.8 (dm, $^1J_{C,F}$=255 Hz, C_6F_5), 144.5 (dm, $^1J_{C,F}$=252 Hz, C_6F_5) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ= 27.8 (s) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ= -160.9 (m, 4F, *m*-F), -153.8 (t, $^1J_{F,F}$=22 Hz, 2F, *p*-F), -145.2 (m, 4F, *o*-F) ppm. MS/EI (m/z): 531.9 (100%) [M^+], 511.9 (6%) [M^+ -HF]. $C_{22}H_7BF_{10}N_2S$ (532.16): calcd.: C: 49.65, H: 1.33, N: 5.26; found: C: 48.88, H: 1.13, N: 5.15.

<u>2-Thienyl-1,3-bis(2′,3′,5′,6′-tetrafluoropyridyl)-1,3,2-benzodiazaborole (**9**)</u>

The adduct of 2-Br_2B-C_4H_3S and PPh_3 (1.084 g, 2.1 mmol), was prepared as described before and treated with 1 equiv. of *N,N′*-bis(tetrafluoropyridyl)-*ortho*-phenylenediamine **16** (0.853 g) and 0.636 g (4.5 mmol) of 2,2,6,6-tetramethylpiperidine in toluene at 100°C for 16 h. After an analogous work up the reaction residue was sublimed *in vacuo* at 90°C to remove PPh_3 and then at 140°C, whereby product **9** separated as a colourless solid. The latter fraction was purified by crystallisation from *n*-hexane to yield 0.650 g of product (1.30 mmol, 62%). ^{1}H NMR ($CDCl_3$): δ= 6.94 (m, 2H, C<u>H</u>=CHCH=C<u>H</u>), 7.10 (d, $^3J_{H,H}$=3.4 Hz, 1H, 3-H-thiophene), 7.17 (t, $^3J_{H,H}$=3.6 Hz, 1H, 4-H-thiophene), 7.24 (m, 2H, CH=C<u>H</u>C<u>H</u>=CH), 7.64 (d, $^3J_{H,H}$=4.0 Hz, 1H, 5-H-thiophene) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ= 110.9 (s, <u>C</u>H=CHCH=<u>C</u>H), 119.9 (s, CH=<u>C</u>H<u>C</u>H=CH), 128.9, 132.5, 135.3 (3s, BC-<u>C</u>H-<u>C</u>H-C<u>H</u>-S), 134.7 (s, N_2C_2), 138.6 (dm, $^1J_{C,F}$=265 Hz, C_5F_4N), 144.1 (dm, $^1J_{C,F}$=248 Hz, C_5F_4N) ppm. ^{11}B{^{1}H} NMR ($CDCl_3$): δ= 27.4 (s) ppm. ^{19}F{^{1}H} NMR ($CDCl_3$): δ= -144.3 (m, 4F, *o*-F), -87.4 (m, 4F, *m*-F) ppm. MS/EI (m/z): 498.1 (100%) [M^+], 478.1 (10%) [M^+ -HF]. $C_{20}H_7BF_8N_4S$ (498.16): calcd.: C: 48.22, H: 1.42, N: 11.25; found: C: 47.10, H: 1.55, N: 10.80.

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2-Thienyl-1,3-bis(2′,3′,5′,6′-tetrafluoro-4-cyanophenyl)-1,3,2-benzodiazaborole (**10**)

By analogy to the protocol above the adduct from 2-Br_2B-C_4H_3S and PPh_3 (1.084 g, 2.1 mmol) was treated with 1 equiv. of *N,N′-ortho*-bis(2,3,5,6-tetrafluoro-4-cyanophenyl)phenylenediamine **17** (0.954 g) and 0.636 g (4.5 mmol) of 2,2,6,6-tetramethyl-piperidine in 100 mL of toluene (100°C) for 60 h. The reaction mixture was freed from solvent by evaporation, and the solid residue was washed with *n*-hexane (2 x 50 mL). Crystallisation from a 2:1 mixture of *n*-hexane/CH_2Cl_2 at -30°C afforded **10** as yellow crystals (yield 0.412 g, 0.75 mmol, 36%). ^{1}H NMR (C_6D_6): δ= 6.60 (m, 2H, C<u>H</u>=CHCH=C<u>H</u>), 6.69 (t, $^3J_{H,H}$=4.3 Hz, 1H, 4-H-thiophene), 6.90 (d, $^3J_{H,H}$=4.0 Hz, 1H, 3-H-thiophene), 6.97 (d, $^3J_{H,H}$=4.3 Hz, 1H, 5-H-thiophene), 7.01 (m, 2H, CH=C<u>H</u>C<u>H</u>=CH) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ=110.8 (s, <u>C</u>H=CHCH=<u>C</u>H), 122.7 (s, CH=<u>C</u>H<u>C</u>H=CH), 128.5, 130.7, 131.9 (3s, BC-<u>C</u>H-<u>C</u>H-<u>C</u>H-S), 135.0 (s, N_2C_2),143.0 (dm, $^1J_{C,F}$=260 Hz, C_6F_4CN), 147.4 (dm, $^1J_{C,F}$=264 Hz, C_6F_4CN) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ= 28.5 (s) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ= -142.1 (m, 4F, *o*-F) -131.4 (m, 4F, *m*-F) ppm. MS/EI (m/z): 545.9 (100%) [M^+], 525.9 (7%) [M^+ -HF]. HRMS-EI ($C_{24}H_7BF_8N_4S$): calcd.: 546.03512; found: 546.03462.

1,3-Diethyl-2-(4′-trimethylsilyl-1′-phenyl)-1,3,2-benzodiazaborole (**18**)

A chilled solution (-78°C) of 1-bromo-4-trimethylsilylbenzene (2.07 g, 9.03 mmol) in diethyl ether (50 mL) was dropwise combined with a *n*-pentane solution of *tert*-butyllithium (1.6 M, 29 mL, 18.1 mmol). The solution was warmed to 0°C and then re-cooled to -78°C before solid 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (2.27 g, 9.00 mmol) was added. During 16 h the mixture was allowed to reach room temperature. Solvent was removed in *vacuo*, and the residue was distilled (bath temperature 170°C 10^{-6} bar) to afford a colourless oil. The oil was completely dissolved in *n*-hexane. Storage of the solution at -20°C for two days furnished colourless crystals of **18** (1.45 g, 4.5 mmol, 50%). ^{1}H NMR (C_6D_6): δ=0.26 (s, 9H, $SiMe_3$), 1.08 (t, $^3J_{H,H}$ =7.2 Hz, 6H, $NCH_2C\underline{H}_3$), 3.57 (q, $^3J_{H,H}$=7.2 Hz, 4H, $NC\underline{H}_2CH_3$), 7.01 (m, 2H, C<u>H</u>=CHCH=C<u>H</u>), 7.14 (m, 2H, CH=C<u>H</u>C<u>H</u>=CH), 7.60 (s, 4H, Ph-H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ=0.0 (s, Si(<u>C</u>H_3)$_3$), 17.4 (s, <u>C</u>H_3CH_2N), 38.8 (s, CH_3<u>C</u>H_2N), 110.5 (s, <u>C</u>H=CHCH=<u>C</u>H), 120.4 (s, CH=<u>C</u>H<u>C</u>H=CH), 134.2, 134.4 (2s, <u>C</u>-Ph), 138.7 (s, N_2C_2), 141.7 (s, Si-<u>C</u>-Ph) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ= 29.3 (s) ppm. MS/EI (m/z): 322.2 (100%) [M^+], 307.2 (21%) [M^+ -CH_3], 233.1 (25%) [M^+ -Et, -4CH_3].$C_{19}H_{27}BN_2Si$ (322.33): calcd.: C: 70.80, H: 8.44, N: 8.69; found: C: 70.09, H: 8.87, N: 8.56.

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1-(1′,3′-Bis(pentafluorophenyl)-1,3,2-benzodiazaborolyl)-4-(1′′,3′′-diethyl-1′′,3′′,2′′-benzodiazaborolyl)-benzene (**11**)

A solution of **18** (0.644 g, 2.0 mmol) in CH_2Cl_2 (30 mL) was treated at 20°C with boron tribromide (0.501 g, 2.0 mmol). After a period of 16 h a solution of triphenylphosphine (0.577 g, 2.2 mmol) in CH_2Cl_2 (10 mL) was added. After 2 h of stirring volatile compounds were removed *in vacuo* and NMR spectra of the residue were recorded ($\delta^{11}B$ (C_6D_6) = -4.3 (s), $\delta^{31}P$ (C_6D_6) = -4.0 (s) ppm). A slurry of the adduct in toluene (60 mL) was combined with *N,N′*-bis(pentafluorophenyl)phenylenediamine **15** (0.792 g, 1.8 mmol) and 2,2,6,6-tetramethyl-piperidine (0.636 g, 4.5 mmol), and heated for 16 h at 100°C. The resulting mixture was evaporated to dryness and triphenylphosphine was removed by sublimation at 90-100°C and 10^{-6} bar. The residue was stirred in *n*-hexane (40 mL) and the slurry was filtered. Storing of the filtrate at -20°C for a few days afforded product **11** (0.400 g, 0.57 mmol, 32%) as colourless crystals. ^{1}H NMR (C_6D_6): δ= 0.88 (t, $^3J_{H,H}$ =7.0 Hz, 6H, $NCH_2C\underline{H}_3$), 3.36 (q, $^3J_{H,H}$=7.0 Hz, 4H, $NC\underline{H}_2CH_3$), 6.68 (m, 2H, C<u>H</u>=CHCH=C<u>H</u>-$BN_2(C_6F_5)_2$), 6.90 (m, 2H, C<u>H</u>=CHCH=C<u>H</u>-BN_2Et_2), 7.07 (m, 4H, CH=C<u>H</u>C<u>H</u>=CH-$BN_2(C_6F_5)_2$ and -BN_2Et_2), 7.47 (d, $^3J_{H,H}$=8.0 Hz, 2H, Ph-H), 7.57 (d, $^3J_{H,H}$=8.0 Hz, 2H, Ph-H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ=15.8 (s, $\underline{C}H_3CH_2N$), 37.4 (s, $CH_3\underline{C}H_2N$), 109.2 (s, <u>C</u>H=CHCH=<u>C</u>HBN_2Et_2), 110.7 (s, <u>C</u>H=CHCH=<u>C</u>H-$BN_2(C_6F_5)_2$), 119.1 (s, CH=<u>C</u>H<u>C</u>H=CHBN_2Et_2), 122.3 (s, CH=<u>C</u>H<u>C</u>H=CH-$BN_2(C_6F_5)_2$), 132.0, 133.6 (2s, Ph-<u>C</u>H) 136.2, 137.1 (2s, N_2C_2), 137.9 (dm, $^1J_{C,F}$=254 Hz, C_6F_5), 140.6 (dm, $^1J_{C,F}$=255 Hz, C_6F_5), 144.2 (dm, $^1J_{C,F}$=251 Hz, C_6F_5) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6): δ= 29.3 (s) ppm. $^{19}F\{^1H\}$ NMR (C_6D_6): δ= -161.3 (m, 4F, *m*-F) , -154.2 (t, $^1J_{F,F}$=22 Hz, 2F, *p*-F), -146.1 (m, 4F, *o*-F) ppm. MS/EI (m/z): 698.2 (100%) [M^+], 683.2 (29%) [M^+ -CH_3]. HRMS-EI ($C_{34}H_{22}B_2F_{10}N_4$): calcd.:698.18654; found: 698.18756.

1-(1′,3′-Bis(2′′,3′′,5′′,6′′-tetrafluoropyridyl)-1,3,2-benzodiazaborolyl)-4-(1′′′,3′′′-diethyl-1′′′,3′′′,2′′′-benzodiazaborolyl)-benzene (**12**)

Compound **18** (0.644 g, 2.0 mmol) was reacted with BBr_3 (0.501, 2.0 mmol) and subsequently PPh_3 (0.577 g, 2.2 mmol)was added to the dichloromethane mixture as described before in protocol for **11**. The obtained dibromoboryl-triphenylphosphine adduct (1.376 g, 2.0 mmol) was combined with *N,N′*-bis(tetrafluoropyridyl)-*ortho*-phenylenediamine **16** (0.731 g, 1.8 mmol) and 2,2,6,6-tetramethylpiperidine (0.636 g, 4.5 mmol) were reacted in toluene at 100°C for 24 h. It was filtered, and the solid was crystallised from a mixture of *n*-hexane/CH_2Cl_2 (40/4 mL) whereby colourless crystals of **12** were obtained (0.280 g,

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0.42 mmol, 23%). ^{1}H NMR (C_6D_6): δ= 0.93(t, $^{3}J_{H,H}$ =7.1 Hz, 6H, $NCH_2C\underline{H}_3$), 3.37 (q, $^{3}J_{H,H}$=7.1 Hz, 4H, $NC\underline{H}_2CH_3$), 6.53 (m, 2H, C<u>H</u>=CHCH=C<u>H</u>-$BN_2(C_5F_4N)_2$), 6.93 (m, 2H, C<u>H</u>=CHCH=C<u>H</u>-BN_2Et_2), 7.00 (m, 2H, CH=C<u>H</u>C<u>H</u>=CH-$BN_2(C_5F_4N)_2$), 7.10 (m, 2H, CH=C<u>H</u>C<u>H</u>=CH-BN_2Et_2), 7.31 (d, $^{3}J_{H,H}$=7.8 Hz, 2H, Ph-H), 7.38 (d, $^{3}J_{H,H}$=7.8 Hz, 2H, Ph-H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ= 15.9 (s, $NCH_2\underline{C}H_3$), 37.4 (s, $N\underline{C}H_2CH_3$), 109.2 (s, <u>C</u>H=CHCH=<u>C</u>HBN_2Et_2), 111.3 (s, <u>C</u>H=CHCH=<u>C</u>H-$BN_2(C_5F_4N)_2$), 119.2 (s, CH=<u>C</u>H<u>C</u>H=CHBN_2Et_2), 122.9 (s, CH=<u>C</u>H<u>C</u>H=CH-$BN_2(C_5F_4N)_2$), 134.6, 137.1 (2s, Ph-<u>C</u>H), 131.6, 133.6 (2s, N_2C_2), 138.8 (dm, $^{1}J_{C,F}$=262 Hz, C_5F_4N), 144.0 (dm, $^{1}J_{C,F}$=248 Hz, C_5F_4N) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ= 28.7 (s) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ= -87.9 (m, 4F, *m*-F), -145.1 (m, 4F, *o*-F) ppm. MS/EI (m/z): 664.2 (100%) [M^+], 649.2 (35%) [M^+ –CH_3], 620.2 (20%) [M^+ -CH_2CH_3, -CH_3]. HRMS-EI ($C_{32}H_{22}B_2F_8N_6$): calcd.: 664.19588; found: 664.19727.

<u>1,3-Diethyl-2-(5´-trimethylsilyl-thien-2´-yl)-1,3,2-benzodiazaborole (**19**)</u>

A solution of 2-trimethylsilylthiophene (2.1 g, 13.4 mmol) in diethyl ether (50 mL) was treated at room temperature with an *n*-hexane solution of *n*-butyllithium (1.6 M, 8.4 mL, 13.4 mmol). After 1 h of stirring a sample of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (3.38 g, 13.4 mmol) was added, and stirring was continued over night. Solvent was removed in vacuo, and the residue was distilled (bath temperature 180°C, 10^{-6} bar) to yield 3.57 g (10.9 mmol, 81%) of product **19**. ^{1}H NMR (C_6D_6): δ= 0.32 (s, 9H, $SiMe_3$), 1.14 (t, $^{3}J_{H,H}$ =7.0 Hz, 6H, $NCH_2C\underline{H}_3$), 3.73 (q, $^{3}J_{H,H}$=7.0 Hz, 4H, $NC\underline{H}_2CH_3$), 6.99 (m, 2H, C<u>H</u>=CHCH=C<u>H</u>), 7.13 (m, 2H, CH=C<u>H</u>C<u>H</u>=CH), 7.40 (d, $^{3}J_{H,H}$=3.2 Hz, 1H, thiophene-H), 7.51(d, $^{3}J_{H,H}$=3.2 Hz, 1H, thiophene-H) ppm. ^{13}C-{^{1}H}-NMR (C_6D_6): δ= 0.00 (s, $Si(\underline{C}H_3)_3$), 16.1 (s, $\underline{C}H_3CH_2N$), 37.8 (s, $CH_3\underline{C}H_2N$), 109.2 (s, <u>C</u>H=CHCH=<u>C</u>H), 119.3 (s, CH=<u>C</u>H<u>C</u>H=CH), 135.1 (s, N_2C_2), 135.6, 137.5 (2s, thiophene-<u>C</u>H) 144.9 (s, thiophen-<u>C</u>-Si) ppm. ^{11}B-{^{1}H}-NMR (C_6D_6): δ= 26.7 (s) ppm. MS/EI (m/z): 328.2 (100 %) [M^+], 313.1 (15%) [M^+ –CH_3].$C_{17}H_{25}BN_2SSi$ (328.36): calcd.: C: 62.18, H: 7.67, N: 8.53; found: C: 61.86, H: 7.71, N: 8.47.

<u>2-(1´,3´-Bis(pentafluorophenyl)-1,3,2-benzodiazaborolyl)-5-(1´´,3´´-diethyl-1´´,3´´,2´´-benzodiazaborolyl)-thiophene (**13**)</u>

The solution of **19** (0.656 g, 2.0 mmol) in CH_2Cl_2 (30 mL) was reacted at 20°C with boron tribromide (0.501 g, 2.0 mmol). After 1 h the solution of 0.577 g (2.2 mmol) of PPh_3 in CH_2Cl_2 (10 mL) was added. After 2 h of stirring the mixture was liberated from solvents, and

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NMR spectra were taken from the residue (δ^{11}B (C_6D_6) = -5.9 (s), δ^{31}P (C_6D_6) = -4.2 (s) ppm). The adduct was combined with *N,N′*-bis(pentafluorophenyl)phenylenediamine **15** (0.792 g, 1.8 mmol) and 2,2,6,6-tetramethylpiperidine (0.636 g, 4.5 mmol) in toluene (70 mL) and the mixture was heated for 16 h at 100°C. After cooling to 20°C and filtration, the filtrate was evaporated to dryness. Triphenylphosphine was separated by sublimation at 90°C (10^{-6} bar) before the residue was crystallised from *n*-hexane. The product **13** was obtained as colourless crystals (yield 0.580 g, 0.82 mmol, 46%). ^{1}H NMR (C_6D_6): δ= 1.01 (t, $^3J_{H,H}$ =7.2 Hz, 6H, $NCH_2C\underline{H}_3$), 3.49 (q, $^3J_{H,H}$=7.1 Hz, 4H, $NC\underline{H}_2CH_3$), 6.69 (m, 2H, $C\underline{H}$=CHCH=C$\underline{H}$-$BN_2(C_6F_5)_2$), 6.89 (m, 2H, $C\underline{H}$=CHCH=C$\underline{H}$-BN_2Et_2), 7.07 (m, 4H, CH=C$\underline{H}$C$\underline{H}$=CH-$BN_2(C_6F_5)_2$ and -BN_2Et_2), 7.24 (s, 2H, thiophene-H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ= 15.7 (s, $\underline{C}H_3CH_2N$), 37.6 (s, $CH_3\underline{C}H_2N$), 109.1 (s, $\underline{C}$H=CHCH=$\underline{C}$HBN_2Et_2), 110.4 (s, $\underline{C}$H=CHCH=$\underline{C}$H-$BN_2(C_6F_5)_2$), 119.3 (s, CH=$\underline{C}$H$\underline{C}$H=CHBN_2Et_2), 122.1 (s, CH=$\underline{C}$H$\underline{C}$H=CH-$BN_2(C_6F_5)_2$), 134.8, 137.0 (2s, thiophene-$\underline{C}$H), 136.0, 136.2 (2s, N_2C_2), 137.7 (dm, $^1J_{C,F}$=255 Hz, C_6F_5), 140.9 (dm, $^1J_{C,F}$=256 Hz, C_6F_5), 144.8 (dm, $^1J_{C,F}$=255 Hz, C_6F_5) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ= 26.6 (s) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ= -161.1 (m, 4F, *m*-F) , -154.1 (t, $^1J_{F,F}$=22 Hz, 2F, *p*-F), -145.1 (m, 4F, *o*-F) ppm. MS/EI (m/z): 704.1 (100%) [M^+], 689.1 (43%) [M^+ -Me]. $C_{32}H_{20}B_2F_{10}N_4S$ (704.20): calcd.: C: 54.58, H: 2.86, N: 7.96; found: C: 54.32, H: 3.06, N: 7.75.

2-(1′,3′-Bis(2′,3′,5′,6′-tetrafluoropyridyl)-1,3,2-benzodiazaborolyl)-5-(1′′,3′′-diethyl-1′′,3′′,2′′-benzodiazaborolyl)-thiophene (**14**)

The dibromoboryl-triphenylphosphine adduct (1.445 g, 2.1 mmol) obtained by the reaction of **19** (0.656 g, 2.0 mmol) with BBr_3 (0.501 g, 2.0 mmol) and the addition of PPh_3 (0.577 g, 2.2 mmol) analogue to protocol for **13**, was reacted with *ortho*-phenylenediamine **16** (0.731 g, 1.8 mmol) and 2,2,6,6-tetramethylpiperidine (0.636 g, 4.5 mmol) in toluene (70 mL) at 100°C for 30 h. After filtration, the filtrate was evaporated to dryness, and the residue was stirred in *n*-hexane (40 mL) and then filtered again. The filtrate was discarded, and the filtercake was washed with 10 mL of pentafluorobutane. The product **14** was isolated as yellow solid (0.250 g, 0.37 mmol, 21%). ^{1}H NMR (C_6D_6): δ= 1.01 (t, $^3J_{H,H}$ =7.1 Hz, 6H, $NCH_2C\underline{H}_3$), 3.46 (q, $^3J_{H,H}$=7.1 Hz, 4H, $NC\underline{H}_2CH_3$), 6.49 (m, 2H, $C\underline{H}$=CHCH=C$\underline{H}$-$BN_2(C_5F_4N)_2$), 6.88 (m, 2H, $C\underline{H}$=CHCH=C$\underline{H}$-BN_2Et_2), 6.98 (m, 2H, CH=C$\underline{H}$C$\underline{H}$=CH-$BN_2(C_5F_4N)_2$), 7.10 (m, 2H, CH=C$\underline{H}$C$\underline{H}$=CH-BN_2Et_2), 7.14 (s, 2H, thiophene-H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ= 15.9 (s, $\underline{C}H_3CH_2N$), 37.5 (s, $CH_3\underline{C}H_2N$), 109.1 (s, $\underline{C}$H=CHCH=$\underline{C}$HBN_2Et_2), 110.9 (s, $\underline{C}$H=CHCH=$\underline{C}$H-$BN_2(C_5F_4N)_2$), 119.4 (s,

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CH=CHCH=CHBN$_2$Et$_2$), 122.8 (s, CH=CHCH=CH-BN$_2$(C$_5$F$_4$N)$_2$), 134.6, 135.0 (2s, thiophene-CH), 136.2, 136.9 (2s, N$_2$C$_2$), 138.9 (dm, $^1J_{C,F}$=265 Hz, C$_5$F$_4$N), 144.0 (dm, $^1J_{C,F}$=246 Hz, C$_5$F$_4$N) ppm. ^{11}B{^{1}H} NMR (C$_6$D$_6$): δ= 26.2 (s) ppm. ^{19}F{^{1}H} NMR (C$_6$D$_6$): δ= -144.7 (m, 4F, *o*-F), -87.7 (m, 4F, *m*-F) ppm. MS/EI (m/z): 670.1 (100%) [M$^+$], 655.1 (43%) [M$^+$ -Me]. HRMS-EI (C$_{30}$H$_{20}$B$_2$F$_8$N$_6$S): calcd.: 670.15230; found: 670.15298.

1,2,3-Triphenyl-1,3,2-benzodiazaborole (**20**)

Two separate solutions of *N,N′*-diphenyl-*ortho*-phenylenediamine (1.20 g, 4.6 mmol) and phenyldibromoborane (1.14 g, 4.6 mmol), each in 15 mL of toluene, were added dropwise to a well stirred slurry of CaH$_2$ (1.00 g, 23.8 mmol) in 30 mL of cold toluene (0°C). After 0.5 h of stirring at 0°C the slurry continued at room temperature for another 24 h. It was filtered and the flitrate was liberated from solvent. Recrystallisation of the residue afforded **20** (1.27 g, 80%) as light yellow crystals. ^{1}H NMR (CDCl$_3$): δ=7.03 (m, 2H, CH=CHCH=CH), 7.10 (m, 4H, CH=CHCH=CH and 2-H-Ph), 7.14 (d, $^3J_{H,H}$ = 6.6 Hz, 2H, 2-H-BPh), 7.21 (t, $^3J_{H,H}$ = 7.2 Hz, 1H, *p*-H-BPh), 7.33 (m, 6H, H-NPh), 7.42 (t, $^3J_{H,H}$ = 7.5 Hz, 4H, H-NPh) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ= 110.0 (s, CH=CHCH=CH), 120.0 (s, CH=CHCH=CH), 126.3 (3s, C-BPh), 127.3 (s, C-NPh), 127.8 (s, C-NPh), 128.6 (s, *p*-C-BPh), 129.3 (s, C-NPh), 134.4 (s, C-BPh), 137.8(s, C-NPh), 140.4 (s, N$_2$C$_2$) ppm. ^{11}B{^{1}H} NMR (C$_6$D$_6$): δ= 28.3 (s) ppm. MS/EI (m/z): 346.2 [M$^+$], 268.1 [M$^+$ -Ph-H].C$_{24}$H$_{19}$BN$_2$ (346.23): calcd.: C: 83.3, H: 5.5, N: 8.1; found: C: 82.3, H: 5.5, N: 7.6.

Photophysical measurements

For all solution state measurements, samples were placed in quartz cuvettes of 10 × 10 mm (Hellma type 111-QS, suprasil, optical precision). Cyclohexane was used as received from commercial sources (p. a. quality), the other solvents were dried by standard methods prior to use. Concentrations varied from 20 to 70 µM according to their optical density. Absorption was measured with a UV/VIS double-beam spectrometer (Shimadzu UV-2550), using the solvent as a reference.

The output of a continuous Xe-lamp (75 W, LOT Oriel) was wavelength-separated by a first monochromator (Spectra Pro ARC-175, 1800 l/mm grating, Blaze 250 nm) and then used to irradiate a sample. The fluorescence was collected by mirror optics at right angles and imaged on the entrance slit of a second spectrometer while compensating astigmatism at the same time. The signal was detected by a back-thinned CCD camera (RoperScientific, 1024 \ 256 pixels) in the exit plane of the spectrometer. The resulting images were spatially and

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spectrally resolved. As the next step, an averaged fluorescence spectrum was calculated from the raw images and stored in the computer. This process was repeated for different excitation wavelengths. The result is a two-dimensional fluorescence pattern with the *y*-axis corresponding to the excitation, and the *x*-axis to the emission wavelength. The wavelength range is λ_{ex} = 230-430 nm (in 1 nm increments) for the UV light and λ_{em} = 305-894 nm for the detector. The time to acquire a complete EES is typically less than 15 min. Post-processing of the EES includes subtraction of the dark current background, conversion of pixel to wavelength scales, and multiplication with a reference file to take the varying lamp intensity as well as grating and detection efficiency into account. The quantum yields were determined against POPOP (*p*-bis-5-phenyl-oxazolyl(2)-benzene) (Φ_F = 0.93) as the standard. The Lippert-Mataga studies on **11**-**14** are described in detail on pages S3-S5.

Fluorescence lifetimes were measured with a time correlated single photon counting experiment. Pulses (3 ps) from a Ti:sapphire laser (Spektra Physics, *Tsunami*) were frequency tripled to get pulses with a wavelength of 297 nm. The resulting laser beam was used to excite the sample and the fluorescence was detected in the right angle with a MCP-PMT (Hamamatsu). The time dependence of the fluorescence photons was analysed with a picosecond-time-analyzer (PTA, Ortec), one discriminator creates the start signal from the detected fluorescence photons and the other creates the stop signal from the laser signal on a photodiode (Hamamatsu). The resulting decay curves were deconvoluted with the laser puls signal and then a monoexponential fit was used to determine the fluorescence lifetime.

Crystallographic data

Crystallographic data were collected at 100 K. Crystallographic programmes used for structure solution and refinement were from SHELX-97.[33] CCDC 961427-961429, and 924348 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

	8	**11**	**12**	**13**
Measurment device	Nonius KappaCCD	Bruker AXS X8 Prospector Ultra with APEX II	Bruker KAPPA APEX II	Bruker KAPPA APEX II
λ [Å]	0.71073	1.54178	0.71073	0.71073
Empirical formula	C22 H7 B F10 N2 S	C34 H22 B2 F10 N4	C32 H22 B2 F8 N6	C32 H20 B2 F10 N4 S
M_r [g mol^{-1}]	532.17	698.18	664.18	704.20
Crystal dimensions[mm]	0.22 x 0.19 x 0.12	0.30 x 0.26 x 0.11	0.24 x 0.17 x 0.14	0.29 x 0.21 x 0.13
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group	P $2_12_12_1$	$P\bar{1}$	$P2_1$	$P\bar{1}$
a[Å]	11.234(2)	8.6356(3)	8.4303(6)	13.5530(8)
b[Å]	15.755(9)	12.0927(5)	20.4508(14)	15.9823(10)
c[Å]	22.977(7)	15.2734(5)	17.5857(12)	16.9069(10)
α[°]	90	102.8230(17)	90	106.763(3)
β[°]	90	91.6271(13)	94.393(4)	106.383(3)
γ[°]	90	93.3910(15)	90	107.713(3)
V[Å^3]	4067(3)	1551.05(10)	3023.0(4)	3053.5(3)
Z	8	2	4	4
ρ_{calc} [g cm^{-3}]	1.738	1.495	1.459	1.532
μ [mm^{-1}]	0.266	1.138	0.122	0.199
F (000)	2112	708	1352	1424
Θ[°]	2-25	2.97-67.00	2.62-30.00	2.68-27.50
No. refl. collected	32223	14335	103885	121751
No. refl. unique	6853	11776	17618	14001
R (int)	0.0686	0.0000	0.0360	0.0318
No. refl. *[I* > 2σ(*I*)]	5310	11033	15046	11528
Refined parameter	635	540	869	887
GOF	1.103	1.048	1.011	1.017
R_F [I > 2 σ (I)]	0.0745	0.0344	0.0384	0.0335
w R_{F2} (all data)	0.1753	0.0989	0.0974	0.0882
$\Delta\rho_{max/min}$ [e Å^{-3}]	0.620/-0.376	0.261/-0.232	0.349/-0.247	0.381/-0.307
Remarks	Disorder of both thiophene rings on two positions (55:45, 56:44). They were restrained to be same and refined isotropically, all other non-hydrogen atoms were refined anisotropically. meroedric twin	twinned crystal, BASF 0.45135, reflections of both domains were used (HKLF 5) Rotated from first domain by 2.5 degrees about reciprocal axis -0.055 1.000 0.130 and real axis 0.002 1.000 0.249 Hydrogens were refined isotropically.		
CCDC-No.	961427	961428	961429	924348

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Computational data

All computations were carried out with the Gaussian 09 package.[34] The S_0 model geometries were fully optimised with the B3LYP functional[35] with no symmetry constraints using the 6-31G* basis set[36] for all atoms. Frequency calculations on these optimised geometries (**5 – 14, 20**) revealed no imaginary frequencies. Computed absorption data were obtained from TD-DFT[37] calculations on S_0 geometries whereas computed TD-DFT emission data were from the fully optimised S_1 geometries using the CAM-B3LYP functional.[38] As the CAM-B3LYP functional generally overestimates the transition energies, compared to that of experimental and B3LYP data, a scaling factor of 0.85 was applied. The two distinct excited states LCT and RCT were located from different starting geometries using TD-DFT optimisations. Both states are defined computationally as S_1 states even though they are different in energies. The MO diagrams were generated with the Gabedit package[39] and the %MO contributions were obtained using the GaussSum software.[40]

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