Directed C-H Borylation for the Synthesis of Fused and Ladder Type Conjugated Oligomers and Polymers

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6.1 Summary

6.2 Further Work

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<th>Definition</th>
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<tbody>
<tr>
<td>ACQ</td>
<td>aggregation caused quenching</td>
</tr>
<tr>
<td>AIE</td>
<td>aggregation induced emission</td>
</tr>
<tr>
<td>BHJ</td>
<td>bulk heterojunction</td>
</tr>
<tr>
<td>BT</td>
<td>2,1,3-benzothiadiazole</td>
</tr>
<tr>
<td>D-A</td>
<td>donor-acceptor</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>DTBT</td>
<td>4,7-dithieno-2,1,3-benzothiadiazole</td>
</tr>
<tr>
<td>EML</td>
<td>emission layer</td>
</tr>
<tr>
<td>EMS</td>
<td>electromagnetic spectrum</td>
</tr>
<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
</tr>
<tr>
<td>F8</td>
<td>9,9-dioctylfluorene</td>
</tr>
<tr>
<td>Fc/Fc+</td>
<td>ferrocene/ferrocenium</td>
</tr>
<tr>
<td>FMO</td>
<td>frontier molecular orbital</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HRMS</td>
<td>high-resolution mass spectrometry</td>
</tr>
<tr>
<td>ICT</td>
<td>internal charge transfer</td>
</tr>
<tr>
<td>IQE</td>
<td>internal quantum efficiency</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>LA</td>
<td>Lewis acid</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MALDI-TOF</td>
<td>matrix assisted laser desorption/ionization time of flight</td>
</tr>
<tr>
<td>NIR</td>
<td>near infra-red</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>o-DCB</td>
<td>orthodichlorobenzene</td>
</tr>
<tr>
<td>OFET</td>
<td>organic field effect transistor</td>
</tr>
<tr>
<td>OLED</td>
<td>organic light emitting Device</td>
</tr>
<tr>
<td>OLET</td>
<td>organic light emitting transistor</td>
</tr>
<tr>
<td>OPV</td>
<td>organic photovoltaic</td>
</tr>
<tr>
<td>P3HT</td>
<td>poly(3-hexylthiophene-2,5-diyl)</td>
</tr>
<tr>
<td>PCBM</td>
<td>[6,6]-phenyl-C_{61}-butyric acid methyl ester</td>
</tr>
<tr>
<td>PCE</td>
<td>power conversion efficiency</td>
</tr>
</tbody>
</table>
PCM = polarizable continuum model
PF8-BT = poly(9,9-dioctylfluorene-alt-2,1,3-benzothiadiazole
PF8-TFB = poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-sec-butylphenyl)diphenylamine))]
PL = photoluminescence
PLQY = photoluminescence quantum yield
PPV = poly(p-phenylene vinylene)
$S_{E}Ar$ = electrophilic aromatic substitution
TADF = thermally activated delayed fluorescence
TBP = 2,4,6-tri-tbutylpyridine
TCTA = 4,4',4''-tri(N-carbazolyl)triphenylamine
THF = tetrahydrofuran
TPBi = 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)
TT = thieno[3,2-b]thiophene
UV-vis = ultraviolet-visible
$V_{oc}$ = open circuit voltage
Abstract

The synthesis, photophysical and electronic properties of a series of novel boron containing fused and ladder type donor–acceptor (D-A) oligomers and polymers are reported. The synthesis was achieved through coordination of the basic functionality of the ubiquitous benzothiadiazole acceptor unit onto a boron Lewis acid followed by an electrophilic aromatic borylation resulting in the formation of fused and ladder type structures (termed borylative fusion). The novel C,N-chelated borane structures disclosed herein are a new member of a large family of tetra-coordinate organoboron compounds that are used for the construction of highly emissive materials. Upon borylation large bathochromic shifts in the absorption and fluorescence spectra were observed, DFT and cyclic voltammetry demonstrate that this is a result of a significant reduction of the LUMO energy levels whilst the HOMO energy levels remains relatively unperturbed. These large bathochromic shifts lead to materials that show far red/NIR emission in the solid state with absolute quantum yields of up to 44%. Furthermore, the frontier molecular orbital energy levels of these fused structures can be modulated through judicious selection of the exocyclic boron substituents. These novel borocycles also proved stable to a range of cross-coupling conditions which facilitated further modulation of the frontier molecular orbitals and emissive properties. Borylative fusion was also applicable to D-A conjugated polymers, this represents a facile post-polymerisation functionalisation that is an effective method of modulating the photophysical properties of D-A conjugated polymers. Solution processed OLEDs with far red/NIR electroluminescence (EL) were fabricated from these materials. These devices showed good external quantum efficiency values (EQE) for the far red/NIR region of the electromagnetic spectrum (EQE >0.4 % for maximum EL >700 nm).
Acknowledgments

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Chapter 1

Introduction
1.1 Organic Semiconductors

Following the discovery that doped polyacetylene demonstrated high conductivity by Shirakawa, MacDiarmid and Heeger in 1977\(^1\) (for which they would be awarded the Nobel prize in Chemistry in 2000\(^2\)), organic \(\pi\)-conjugated materials have been the subject of intense scientific and industrial research due to their unique optical and semiconducting properties.\(^3,4\) These materials exhibit desirable characteristics such as solution processability, high tuneability of their photophysical properties and ambipolar charge transporting capabilities.\(^5-9\) The promising properties of organic \(\pi\)-conjugated materials hold potential for applications in organic thin-film transistors (OFETs), organic photovoltaic cells (OPV) and most conspicuously organic light-emitting diodes (OLEDs) which have reached commercial production.\(^10-19\) The function of these materials is not necessarily that of exceeding the level of performance achieved in silicon based technologies but to facilitate the fabrication of devices at reduced expense and/or enabling completely novel device functionalities such as mechanical flexibility which can be difficult to accomplish with traditional silicon technologies (Figure 1.1).\(^4,6,16\)

![Figure 1.1: Examples of commercially available OLED products.\(^20-22\)](image-url)
In organic $\pi$-conjugated materials the 2p$_z$ valance atomic orbitals of the carbon atoms combine into occupied $\pi$-bonding orbitals and unoccupied $\pi^*$-antibonding orbitals that are highly delocalised along the backbone of the material.\textsuperscript{23-27} The highest energy $\pi$-bonding orbital is referred to as the highest occupied molecular orbital (HOMO) and the lowest energy $\pi^*$-antibonding is referred to as the lowest unoccupied molecular orbital (LUMO) with the difference in energy between these orbitals referred to as the band-gap. In a conjugated polymer as the number of conjugated units is increased so does the density of $\pi$-bonding orbitals and the $\pi^*$-bonding states become closer in energy approaching a band structure analogous to the valence band and conduction band of inorganic semiconductors (Figure 1.2). Due to the Peierls distortion\textsuperscript{25} these bands will not overlap and the material will be a semiconductor rather than an intrinsic conductor.\textsuperscript{26-28}

![Figure 1.2: Evolution of molecular orbitals into discreet bands upon increasing the number of conjugated repeat units.](image-url)
For an undoped polymer in the ground state the valence band will be fully occupied and the conduction band empty thereby preventing the movement of charge. To achieve conductivity charge carriers must be induced by either removing an electron from the valance band or the generation of an electron in the conduction band, this can be achieved through doping or excitation (optical or electrical). Whilst the charge carriers can move freely throughout the conjugated backbone intermolecular charge transport is limited by charge hopping between adjacent molecules. As a result, the mobility of organic materials is usually orders of magnitude lower than the mobility of inorganic materials, such as crystalline silicon.

1.2 Band-Gap Modulation

1.2.1 Donor-Acceptor Conjugated Materials

The band-gap and relative energy levels of the frontier molecular orbitals (FMOs) of \( \pi \)-conjugated materials are key functional criteria in the realisation of semiconducting materials that meet the requirements for the specific applications. Therefore there has been considerable attention devoted to materials comprising of alternating donor (electron rich) and acceptor (electron poor) units as rational structural modification can lead to a large degree of control over a materials electronic and optical properties (Figure 1.3).
As the HOMO energy level of the material is highly influenced by the donor unit and the LUMO energy level by the acceptor unit, judicious selection of these units enables fine tuning of energy levels. Increasing the strength of the electron withdrawing groups on the acceptor unit reduces the band-gap by lowering the LUMO levels whereas; the introduction of a strong electron donating groups on the donor unit reduces band-gap by raising the HOMO energy levels (although a high HOMO energy level can lead to poor oxidative stability). The use of a Donor-Acceptor (D-A) system also facilitates enhanced intermolecular interactions through strong dipole interactions which can be beneficial for charge transport characteristics. A materials band-gap can be further reduced by strong orbital interactions between donor and acceptor units (Figure 1.4), the HOMO/LUMO of the donor unit will interact with the respective HOMO/LUMO of the acceptor unit to create four new orbitals. The new hybridized orbitals generated will result in higher HOMO and lower LUMO energy levels than those of the discrete donor or acceptor units leading to a narrowing of the optical bandgap. OPV applications especially require low band-gap polymers to enhance good light harvesting capabilities.
Figure 1.4: Molecular orbital interactions by hybridization of donor and acceptor units of D-A conjugated copolymers.

D-A polymers where the low band-gap has been obtained principally by reduction of the LUMO level are desirable as donor materials in photovoltaic applications. In bulk heterojunction (BHJ) photovoltaic cells the open circuit voltage ($V_{OC}$) is dependent on the energy gap between HOMO of the donor material and the LUMO of the acceptor material (most commonly 6,6-phenyl-C61-butyric acid methyl ester (PCBM)). Therefore, achieving a low band-gap by lowering the LUMO whilst maintaining a low HOMO in the donor material can results in higher efficiencies, as a larger percentage of the solar spectrum is available for absorbance, without reducing the $V_{OC}$ (Figure 1.5).
Figure 1.5: In a bulk heterojunction photovoltaic cell the open circuit voltage is proportional to the energy gap between HOMO of the donor polymer and the LUMO of the acceptor material.

Among the multitude of D-A conjugated materials, 2,1,3-benzothiadiazole (BT) and its derivatives are particularly prevalent as the acceptor unit. BT copolymers exhibit several desirable photophysical characteristics and have been widely exploited for application in OLEDs, photovoltaic cells, liquid crystals, dyes and OFET devices (Figure 1.3). BT is a ubiquitous acceptor unit in copolymers as the resulting materials show promising performance due high electron affinities, efficient fluorescence, strong internal charge transfer characteristics and the planar polarised nature of BT leads to increased intermolecular interactions such as heteroatom contacts and \( \pi-\pi \) interactions. However, in regards to their application as the donor materials in bulk heterojunction (BHJ) solar cells the band-gaps of common BT-based D-A conjugated polymers are approximately 1.7-1.9 eV, which are not optimal for efficient light harvesting. Therefore, to create materials with the optimal band-gap for solar cell applications a considerable effort has been put into the modification of the BT based acceptor units. Whilst current donor-acceptor polymer motifs show very promising results, there is still ongoing research in the modification of the donor and acceptor units to engineer materials that show superior performance.
1.2.2 Fused and Ladder Type $\pi$-Conjugation Structures

The degree of conjugation between the aromatic units of conjugated D-A materials also plays a significant role in the optoelectronic properties. Elongation of the effective conjugation length results in more delocalised FMOs resulting in a lower ionisation potential (higher HOMO) and higher electron affinity (lower LUMO). Therefore maximizing the $\pi$-conjugation within the conjugated materials can lead to a further lowering of the band-gap.\(^{47}\) Enhanced $\pi$-conjugation can be achieved through maintaining a coplanar arrangement between the materials neighbouring aromatic units as the interactions between parallel $\pi$-orbitals can increase $\pi$-electron delocalization and improve the materials properties (Figure 1.6).\(^{47}\)

![Fused and Ladder Type Structures](image)

**PTPTBT\(^{48}\)**  
**Photovoltaic Parameters**  
$J_{sc} = 11.2 \text{ mA cm}^{-2}$  
$V_{oc} = 0.85 \text{ V}$  
$FF = 67.2 \%$  
$PCE = 6.41 \%$

**BBL\(^{49}\)**  
**n-type OFET Parameters**  
Electron Mobility = 0.1 cm\(^2\) V\(^{-1}\) s\(^{-1}\)

Figure 1.6: Structures and device parameters of polymers with fused/ladder architectures.

Coplanarity can be enforced by the inhibition of monomer rotation through the formation of covalent linkages thereby creating fused and ladder type structures.\(^{47}\) For example, in highly substituted (to attain solubility) conjugated polymers without ladder linkages, the degree of extended conjugation is greatly diminished due to unfavourable steric interactions which reduce the coplanarity of the aromatic units.\(^{47}\) The increase in rigidity of the structures upon tethering repeat units coplanar can reduce the rotational disorder around interannular single bonds and lower the reorganization energy which can result in enhanced thermal stability, increased quantum yield values (due to decreases in non-radiative relaxation processes) and increased intrinsic
charge mobility by promoting $\pi$-$\pi$ stacking interactions.\textsuperscript{50-52} The advantageous characteristics derived from incorporating ladder type structures into organic electronic materials is evident by many of the highest performing OPV and OFET materials containing highly fused planar structures.\textsuperscript{50}

1.2.3 Lewis Acid Coordination

Whilst the D-A approach has yielded a myriad of interesting low band-gap materials, the required synthetic modifications of conjugated polymers to afford a fine control over their optical and electronic properties is often onerous. The C=N bond is a ubiquitous motif in acceptor units (such as BT) due to its strong electron withdrawing nature.\textsuperscript{44} One interesting band-gap modulation strategy demonstrated by Bazan \textit{et. al.}\textsuperscript{53} exploits the Lewis basic functionalities of the C=N motif within the D-A system. The binding of a main group Lewis acid (LA) to the Lewis basic nitrogen atoms of the imine unit of acceptor units (e.g. Scheme 1.1) results in a redistribution of electron density which can greatly modified the FMOs and concomitantly the band-gap of D-A materials.\textsuperscript{53}

Scheme 1.1: Binding of Lewis acids to basic functionalities within D-A system.\textsuperscript{53}
Figure 1.7: UV-vis absorption spectra demonstrating the reduction in band-gap upon the binding Lewis acids to basic functionalities in D-A system. (image modified from *J. Am. Chem. Soc.*, 2009, 131, 10802-10803).

This methodology revealed a progressively red shifted absorbance upon the binding of Lewis acids of increased Lewis acidity (Figure 1.7). This is due to the binding of Lewis acids to the less sterically unencumbered Lewis basic site of the benzothiadiazole unit resulting in an enhancement of its electron affinity as observed by a significant reduction in the LUMO energy level. A concomitant minor reduction in the HOMO is also observed which is attributed to a localisation of the HOMO upon binding the Lewis acid. This simple method produces a red shift of $\lambda_{\text{max}_{\text{abs}}}$ up to 178 nm upon LA binding, however, deficiencies in the stability of these materials has inhibited their wider application.

1.3 Far Red/Near *Infra*-red Emission

The development of organic lumiphores that show efficient emission in the solid state is of fundamental importance for numerous applications such as OLEDs, solid state lasers and fluorescent sensors. Recently, materials that show near *infra*-red (NIR) emission in the solid state have received increasing interest as they have potential for applications in night-vision displays, sensors,
optical communication and bio-imaging.\textsuperscript{54-63} However, the realisation of materials that show efficient NIR emission is impeded by the intrinsic limitations imposed by the energy-gap law\textsuperscript{64-67} (as the band-gap of a material decreases there is increased vibrational overlap between the ground and excited states which enhances non-radiative decay, Figure 1.18) in addition to the effects of the Einstein coefficient\textsuperscript{67} (the probability of a spontaneous radiative transition is proportional to the frequency cubed).

![Diagram](image)

Figure 1.8: Diagram representing the nuclear potential surfaces and decay processes of low band-gap molecules upon excitation.

Whist a large number of compounds show substantial NIR emission in solution these materials show severely decreased photoluminescence quantum yield (PLQY) values in the solid state due to aggregation caused quenching (ACQ).\textsuperscript{68-71} Extended $\pi$-systems such as perylene bisimides\textsuperscript{69}, are
often employed to achieve the required low band-gaps which concomitantly result in NIR emission. However, ACQ is severe in molecules such as perylene bisimides (Figure 1.9, left) as extended \( \pi \)-systems promote aggregation through extensive \( \pi-\pi \) stacking interactions, this decreases the separation between lumiphores which induces alternative non-radiative decay processes. Additionally, the NIR emission of low band-gap donor-acceptor systems can be inefficient (relative to emission in the visible region of the spectrum) due to increased localisation of FMOs observed in system containing strongly electron withdrawing/donating units, the reduced HOMO-LUMO spatial overlap results in a low radiative-transition rate. Therefore, it is intrinsically difficult to develop materials that show efficient far red/NIR emission in the solid state and innovative approaches are required to overcome these deficiencies.

![Figure 1.9](image)

**Figure 1.9:** Examples of fluorophores that exhibit aggregation caused quenching.

Recently, materials that exploited the phenomenon of aggregation-induced emission (AIE) have attracted considerable attention as this provides a means to circumvent problematic ACQ effects. Antithetical to ACQ, AIE results in an enhancement in the emission of a lumiphore in the solid state (relative to in solution) due to the physical restriction of intramolecular rotations and vibrations which lead to non-radiative relaxation when in solution. The development of far red/NIR lumiphores that show AIE properties is of particular interest as the solid state emission of these is particularly diminished by ACQ (relative to emission in the visible region of the spectrum) which limits their ability to find practical applications (Figure 1.10).
Figure 1.10: Examples of far red/NIR fluorophores that exhibit AIE.

Solid state NIR emissive materials are being developed for a range of applications, including OLEDs which is of most relevance to the work in this thesis, therefore a brief background to OLEDs is provided below.
1.4 Organic Light Emitting Diodes

Following the discovery of electroluminescence in the semiconducting conjugated polymer poly(\(p\)-phenylene vinylene) (PPV)\textsuperscript{77-82}, much scientific and industrial attention has been devoted to the development of organic light emitting diode (OLED) technology in an effort to realise light sources which are light weight, flexible, have low power consumption and can be solution processed to reduce manufacturing costs.\textsuperscript{77-82} Impressive progress in the efficiency of OLEDs over the last few decades has resulted in the technology becoming commercially viable and consumer products have reached large scale production.\textsuperscript{19-22}

![Diagram depicting the basic operating mechanism of an OLED.](image)

Figure 1.11: Diagram depicting the basic operating mechanism of an OLED.

The phenomenon of electroluminescence is the result of an emissive state being generated upon the application of an electric field.\textsuperscript{78} This emissive state is generated by the injection of free charge carriers (electrons from the cathode and holes from the anode) into the functional layers of a device which migrate through a hopping mechanism and recombine in the emissive layer to form a bound electron-hole pair referred to as an exciton (Figure 1.11).\textsuperscript{78-82} This exciton can then decay to the ground state by emitting a photon. The energy of this photon is a function of the HOMO-LUMO energy gap of the EML therefore tuning of the emission wavelength can be achieved \textit{via} rational modification of the band-gap.\textsuperscript{79} Whilst in principle an OLED can operate with only the EML deposited between two electrodes, in practice multi-layered devices show much
higher efficiencies as they are comprised of several charge injection and transport layers which are customised to the relevant work functions of the electrodes and the FMO energy levels of the EML.\textsuperscript{79-82}

It is important to note that when a hole and electron combine to form an exciton, spin statistics result in the formation of singlet and triplet excited states in a ratio of 1:3 (Figure 1.12).\textsuperscript{79-82} Therefore the efficiencies of OLEDs where the EML is comprised of conventional fluorescent materials (i.e. metal free) is limited by the fact that there is theoretical maximum internal quantum efficiency (IQE) of 25% as only the singlet state can undergo radiative decay.\textsuperscript{79-82} However, triplet-triplet annihilation (62.5% theoretical IQE) or the highly promising thermally activated delayed fluorescence (TADF) (100% theoretical IQE) are alternative strategies to realise improved efficiencies in fluorescent material based OLEDs by harvesting the otherwise unutilised electro-generated triplet excitons.\textsuperscript{58,73, 79-86}

![Exciton Formation Diagram](image)

Figure 1.12: Diagram depicting the population of singlet and triplet levels of organic molecules under electrical excitation.

The use of phosphorescent materials has proven to be an effective methodology in realising high efficiency OLEDs.\textsuperscript{82} Materials that show phosphorescence at room temperature usually comprise of chelated heavy-metals such as iridium or platinum.\textsuperscript{73,82,83} The heavy atom effect enhances spin-orbit coupling which facilitates an otherwise spin forbidden radiative transition from the triplet exciton to the ground state.\textsuperscript{81-83} Not only does this mean that the
phosphor can utilise the electro-generated triplet states, the heavy atom effect also enhances intersystem crossing from the singlet state which can result in a theoretical IQE value of 100 %.\textsuperscript{82-86} However, the reliance on the expensive noble metals and the efficiency roll-off generally observed at high current densities for Ir/Pt based materials (due to the long life times of triplet excitons) are limiting factors.\textsuperscript{73,83} Whist impressive progress has been made in OLED technology within the visible spectrum\textsuperscript{16,87}, the development of OLEDs that show emission at frequencies below the visible region of the spectrum have failed to reach comparable efficiencies (devices with a electroluminescence $\lambda_{\text{max}}$ ($\lambda_{\text{max}_{\text{EL}}}$) at $>700$ nm typically show maximum external quantum efficiency (EQE$_{\text{max}}$) values of $<1 \%$).\textsuperscript{55-58,63}

In the effort to realise efficient NIR OLEDs, phosphorescent platinum(II) complexes have proven to be promising candidates.\textsuperscript{55,87} Reynolds \textit{et. al.}\textsuperscript{55}, demonstrated a highly substituted (with tBu group) platinum(II) porphyrin (Pt-Ar$_4$TBP, Figure 1.13, left) that showed narrow emission centred around 773 nm with a EQE$_{\text{max}}$ value of 9.2 %. However, extremely high EQE values were only observed at an extremely low current density and severe EQE roll-off at higher current densities was observed due to the long lived triplet states.\textsuperscript{55} Other high performing platinum(II) complexes include those reported by M. Cocchi \textit{et. al.}\textsuperscript{88} (PtL$_2$Cl, Figure 1.13, right), in which emission is centred around 700 nm with an excellent EQE$_{\text{max}}$ value of 14.5 %. Additionally, significantly less EQE roll-off at higher current densities relative to Pt-Ar$_4$TBP is observed. This represents the most efficient OLED device for emission with a $\lambda_{\text{max}_{\text{EL}}}$ $\geq$700 nm. Whilst impressive EQE values can be achieved, the price and scarcity of platinum limits the potential for such complexes to be utilised in mainstream commercial products. Therefore, the development of noble-metal free NIR OLEDs is of significant interest.
Despite not currently achieving the same high EQE values as their phosphorescent counterparts, there has recently been encouraging progress made in the developments of NIR OLEDs based on fluorescent heavy-metal free D-A $\pi$-conjugated systems. Xue et al.\textsuperscript{57} reported the donor-acceptor-donor (D-A-D) system BEDOT-TQMe$_2$ (Figure 1.14, top), the OLED device fabricated from this oligomer demonstrated a good EQE$_{\max}$ value of 1.6 % at a $\lambda_{\max_{EL}}$ of 692 nm. Y. Ma et al.\textsuperscript{63} reported the D-A oligomer PTZ-BZP (Figure 1.14, middle) which showed similar performance to BEDOT-TQMe$_2$. Interestingly, a radiative exciton ratio of 48 % was measured for the device in which PTZ-BZP was the emissive layer which breaks the theoretical limit of 25%. This was attributed to a “hot-exciton” process in which a high lying triplet state ($T_3$) undergoes reverse intersystem crossing (RISC) to the singlet state therefore producing >25 % radiative excitons. Further advances in organic D-A NIR OLEDs were realised through the utilisation of an oligomer that demonstrated TADF. Y. Wang et al.\textsuperscript{58} reported a EQE$_{\max}$ value of 2.1 % at a $\lambda_{\max_{EL}}$ of 710 nm. This device showed a high efficiency as the electro-generated triplet state excitons (75 % of total excitons generated) could be harvested by undergoing RISC to the singlet state and subsequently undergoing radiative decay.
The emission layer of the aforementioned devices is comprised of small molecules that show good performance for far red/NIR OLEDs but these are fabricated using vacuum deposition rather than the more desirable solution processing methods. The development of the solution processed far red/NIR polymers OLEDs which show high efficiencies have remained challenging.\textsuperscript{89-92}

The copolymerisation of small quantities of low band-gap fluorophores into a wide band-gap semiconducting polymers has proven to be an effective strategy to realise long wavelength emission whilst minimising ACQ effects. Y.Coa \textit{et al.}\textsuperscript{89,90} exploited this strategy to realise solution processed polymer OLEDs that showed $\lambda_{\text{max}_{\text{EL}}}$ above >700 nm with moderate EQE values (PFO-SeBSe1 and PFO-DTTP5, Figure 1.15). Therefore, much research is still required in order to achieve efficient solution processed NIR polymer OLEDs.
1.5 Tetra-coordinate Organoboron Compounds

Tetra-coordinate organoboranes compounds have emerged as attractive materials for various applications such as optoelectronic devices\textsuperscript{93,94}, charge transport\textsuperscript{95}, sensors\textsuperscript{96}, biological imaging\textsuperscript{97} and as photoresponsive materials\textsuperscript{98}. Coordination from the Lewis basic site of the $\pi$-conjugated ligand to the vacant $p_z$ orbital of the boron atom redistributes electron density resulting in the $\pi$-conjugated ligand demonstrating an enhanced electron affinity.\textsuperscript{93} Additionally, tetra-coordinate organoboranes are often highly emissive as the boron acts as a light rigidifying atom that decreases non-radiative relaxation processes and results in enhanced quantum yields (relative to the free ligand).\textsuperscript{93,94} The development of nitrogen coordinated systems is particularly interesting as the B-N bond is isoelectronic and isosteric to a C-C bond although a strong dipole is present in the former.\textsuperscript{99}

1.5.1 N,N-Chelate Organoboron Compounds

N,N-chelates constitute the most widely studied class of tetra-coordinate organoboron compounds with boron dipyrrromethenes (BODIPYs) being the exemplar.\textsuperscript{100} BODIPYs and their derivatives have found widespread applications due to their many advantageous properties such as narrow and highly tunable absorption and emission bands, high molar extinction coefficients and they typically show excellent fluorescence quantum yields in solution.\textsuperscript{100-102} However, the presence of a rigid planar $\pi$-conjugated system encourages $\pi$-
stacking interactions which lead to ACQ and in generally BODIPYs show low Stokes shifts which leads to self-absorption. These factors result in the fluorescence of BODIPYs being severely quenched in the solid state (unless substituted with extremely bulky groups) which limits their applications as optoelectronic materials.

Several N,N-chelated organoboron compounds have been examined as emitters in OLED devices. Recently, P. Chou et al. demonstrated highly efficient OLED devices based on a pyridyl pyrrolide π-conjugated ligand which showed TADF characteristics (Figure 1.16). The LUMO of these compounds is mainly located on the pyridyl pyrrolide π-conjugated ligand and the HOMO is mainly located on the electron rich exocyclic substituents, this leads to the spatial separation of the FMOs and restriction of the HOMO-LUMO overlap. This limiting of the HOMO-LUMO overlap leads to a low energy-gap between singlet and triplet states which facilitates thermally activated RISC from triplet to singlet states. These materials showed solid state PLQY values of up to 60 % at ~520 nm when doped (8 wt. %) into the high triplet energy host 4,4',4''-tri(N-carbazolyl)triphenylamine (TCTA). Solution processed devices fabricated using the same as the EML exhibited extremely high EQE_{max} values of up to 13.5 % with ω_{max,EL} similar to their corresponding photoluminescence (PL) spectra.

![Figure 1.16: Structure and solution processed OLED device parameters of pyridyl pyrrolide based N,N-chelated organoboron compounds.]

<table>
<thead>
<tr>
<th>Compound</th>
<th>PL ( \lambda_{max} )</th>
<th>Solid State PLQY</th>
<th>EQE_{max}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrFPCz</td>
<td>522 nm</td>
<td>40 %</td>
<td>7.6 %</td>
</tr>
<tr>
<td>PrFCzP</td>
<td>505 nm</td>
<td>38 %</td>
<td>4.8 %</td>
</tr>
<tr>
<td>PrFTPA</td>
<td>520 nm</td>
<td>60 %</td>
<td>13.5 %</td>
</tr>
</tbody>
</table>

EML = 8 wt. % PrFPCz/PrFCzP/PrFTPA in TCTA
1.5.2 C,N-Chelate Organoboron Compounds

Tetra-coordinate C,N-chelate organoboron compounds were first developed by Yamaguchi et al.\textsuperscript{106} These B-N fused thienyl-thiazole boracycles (TTz-BMes\textsubscript{2}) displayed red-shifted absorption and fluorescence spectra in addition to a significantly lower LUMO energy level relative to the non-borylated precursor (TTz) (Figure 1.17, top).\textsuperscript{106} Recently, Liu et al.\textsuperscript{107} extended this approach to prepare fused B-N fused thienyl-thiazole containing conjugated polymers (P-BN-IID, Figure 1.17, bottom) which displayed high electron affinities. The low HOMO and LUMO energy levels displayed by these polymers lead to their evaluation as the accepter material in all polymer OPV devices. These devices showed excellent power conversion efficiency (PCE) of up to 5.04 %, this shows that the enhancement in electron affinity via the incorporation of the B-N unit is a promising strategy in developing acceptor polymers for all polymer OPV devices.\textsuperscript{107}

![TTz\textsuperscript{106}](TTz.png)  \( \lambda_{\text{max}}^{\text{abs}} = 313 \text{ nm} \)  \( \lambda_{\text{max}}^{\text{em}} = 373 \text{ nm} \)  \( E_{\text{pc vs Fc/Fc}^+} = 2.95 \text{ V} \)

![TTz-BMes\textsubscript{2}\textsuperscript{106}](TTz-BMes.png)  \( \lambda_{\text{max}}^{\text{abs}} = 333 \text{ nm} \)  \( \lambda_{\text{max}}^{\text{em}} = 452 \text{ nm} \)  \( E_{\text{pc vs Fc/Fc}^+} = 2.41 \text{ V} \)

**P-BN-IID Photovoltaic parameters\textsuperscript{107}**

- \( J_{\text{sc}} = 11.37 \text{ mA cm}^{-2} \)
- \( V_{\text{oc}} = 0.92 \text{ V} \)
- \( FF = 48 \% \)
- PCE = 5.04 %

Figure 1.17: Top: Structure, photophysical and electrochemical properties of B-N fused thienyl-thiazole. Bottom: All polymer OPV device parameters of B-N fused thienyl-thiazole containing materials.\textsuperscript{106,107}

H. Quo et al.\textsuperscript{108} demonstrated that incorporating tetra-coordinate C,N-chelate organoboron moieties into \( \pi \)-conjugated systems can have advantageous effects on the luminescence properties. Although only having a minor effect on the PL wavelength, the formation of the B-N fused phenyl-pyridyl boracyle leads to a significant enhancement in the solid state PLQY
values (Figure 1.18). Moreover, OLEDs fabricated from these materials demonstrated that significantly higher EQE values are achievable for the borylated materials relative to their unborylated precursors.\textsuperscript{107} These studied indicated that the incorporation of tetra-coordinate C,N-chelate organoboron moieties into $\pi$-conjugated systems can be an effective strategy in improving the EL properties of privileged fluorophores.\textsuperscript{75,108}

![Figure 1.18: Effect on the photophysical properties and OLED device performance upon incorporation of C,N-chelate organoboron moieties into $\pi$-conjugated systems.\textsuperscript{108}](image)

Others studies into tetra-coordinate C,N-chelate organoboron compounds by Wang \textit{et. al.} demonstrated that the B-N fused phenyl-pyridyl boracycle displayed photochromism when the boron atom is functionalised with mesity groups. Compound PPy-BMes$_2$ (Figure 1.19) could reversibly isomerise through the tetrahedral boron centre and a colour change was observed upon the formation/breaking of a C-C bond.\textsuperscript{109}
1.6 Summary and Scope of Thesis

As discussed in this chapter, donor-acceptor (D-A) $\pi$-conjugated systems have emerged as attractive materials for many applications such as organic thin-film transistors (OFETs), organic photovoltaic cells (OPV) and organic light-emitting diodes (OLEDs). Their synthetic flexibility enables the modulation of the frontier orbital energy levels resulting in the ability to fine tune the material’s properties. Whilst a plethora of fascinating donor-acceptor materials has been developed, there is still ongoing research into the modification of the donor and acceptor units to engineer materials that show superior performance. Furthermore, materials that show low lying LUMO energy levels are particularly desirable for use as n-type or ambipolar semi-conductors, acceptor materials in solar cells and for the generation of low band-gap materials. Moreover, low band-gaps are required in order to realise near infra-red emission (NIR) which is desirable for a range of applications although the development of efficient NIR emitters is impeded many factor including the intrinsic limitations imposed by the energy-gap law. Additionally, the incorporation of tetra-coordinate C,N-chelate organoboron moieties into $\pi$-conjugated systems has been shown to be an effective strategy to modulate the FMO energy levels of $\pi$-conjugated systems. This strategy results in an enchantment of the electron affinity has been shown to positively influence the emissive properties.

With these factors in mind, the ambition of this project was to study the effects of the incorporation of tetra-coordinate C,N-chelate organoboron moieties into well studied and ubiquitous benzothiadiazole containing donor-acceptor systems via a directed C-H borylation. This was intended to result in a lower LUMO energy level (enhanced electron affinity), concomitantly leading to
a narrower band-gap and red shifted emission. The Lewis basic imine functionality of the benzothiadiazole unit is utilised to direct borylation onto and enforce the planarity between a range common electron rich $\pi$-conjugated units such as thiophene, fluorene and carbazole (Figure 1.20). Furthermore, the effects that the exocyclic boron substituent has on the material properties are investigated.

\[
\begin{align*}
R^1 &= \text{alkyl or aryl} \\
R^2 &= \text{H or aryl} \\
R^3 &= \text{alkyl} \\
R^4 &= \text{H or BT}
\end{align*}
\]

Figure 1.20: Incorporation of tetra-coordinate C,N-chelated boron into benzothiadiazole containing donor-acceptor systems.

1.7 References


Chapter 2

Borylative Fusion of Thiophene-Benzothiadiazole Based Materials
2.1 Introduction

Thiophene is a 5-membered electron rich heteroaromatic containing an electron donating sulphur atom which contributes two electrons to the aromatic 6 \( \pi \)-electron system.\(^1\) Thiophene based polymers and copolymers are one of the most extensively studied class of organic semiconducting materials and have found applications in organic light emitting diodes (OLEDs), organic light emitting transistors (OLETs), organic field effect transistors (OFETs) and occur particularly prevalently in organic photovoltaic (OPV) devices.\(^1,2\) Poly(3-hexylthiophene-2,5-diyl) (P3HT) is by far the most studied donor material used in bulk heterojunction (BHJ) OPV applications due to its polycrystallinity which facilitates a high hole mobility (up to \( \sim 0.1 \) cm\(^2\) V\(^-1\) s\(^-1\)) and has resulted in impressive power conversion efficiencies (PCE) of up to 5 % for such a simple to synthesise polymer (other polymers give higher PCEs but often require extremely complex multistep monomer synthesis) (e.g., Figure 2.1, middle).\(^3\)

![Figure 2.1: Thiophene and thiophene based materials.](image)

P3HT has excellent morphological characteristics for a donor material in OPV applications but the suboptimal band-gap of 1.9 eV fails to utilise an high proportion of the terrestrial spectrum (only \( \sim 20 \) % of incident photons can be harvested).\(^4\) In an effort to improve OPV efficiencies research has been directed towards the synthesis of lower band-gap materials which show red shifted absorbance (relative to P3HT) and that can absorb a greater range of the terrestrial spectrum. This reduction in band-gap has to occur whilst maintaining appropriate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels to ensure efficient dissociation of excitons into free charge carriers in OPV devices.\(^5\) A highly effective methodology for creating low band-gap materials is through the previously
discussed formation of donor-acceptor (D-A) systems. A myriad of such low band-gap thiophene containing donor-acceptor polymers and small molecules have been synthesised and it is noteworthy that the dithienylbenzothiadiazole (DTBT) unit is particularly prevalent among some of the highest performing organic electronic materials.

The use of DTBT as the acceptor unit in D-A systems holds several advantages over using only benzothiadiazole (BT). The thiophene units act as \( \pi \)-conjugated bridges reducing the dihedral angle between the BT and donor unit allowing the D-A system to remain coplanar. Increased coplanarity results in an extension of the conjugation length further reducing the band-gap in addition to facilitating denser \( \pi \)-\( \pi \) stacking between the polymer/oligomer backbones potentially resulting in increased charge mobility and OPV performance. Due to these highly advantageous properties efforts have been made to ensure the retention of a coplanar arrangement. One strategy involves covalently tethering the thiophene units to the 5 and 6 positions of the central BT unit, e.g., by using a nitrogen atom and forming two pyrrole rings embedded in the DTBT structure (Figure 2.3). Whilst coplanarity and extended \( \pi \)-conjugation is achieved, the presence of the highly electron rich pyrrole rings in DTPBT serves to increase the HOMO energy level and concomitantly decrease

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**Photovoltaic parameters**

- \( J_{sc} = 11.0 \) mA cm\(^{-2} \)
- \( V_{oc} = 0.91 \) V
- FF = 61 %
- PCE = 6.1 %

**n-type OFET parameters**

- Electron mobility = 0.04 cm\(^2\) V\(^{-1}\) s\(^{-1}\)
- on/off = 1x10\(^{-5}\)
- Threshold Voltage = 39 V
the electron affinity of the benzothiadiazole resulting in a higher LUMO energy level relative to the unfused system.\textsuperscript{8}

Figure 2.3: Structure of DTPBT (Image modified from \textit{J. Org. Chem.}, \textbf{2012}, 77, 7595-7606).\textsuperscript{8}

An alternative approach from Yamaguchi \textit{et al.}\textsuperscript{12} achieved enforced coplanarity between a thiophene and the relatively weak acceptor unit thiazole\textsuperscript{13} in addition to a substantial enhancement in the electron affinity through the incorporation of a boryl group (Figure 2.4). The intramolecular coordination of the Lewis acidic boryl group to the basic functionality of the thiazole ring locks the \pi-conjugated framework planar (termed borylative fusion) and also results in a reduction in the energy of the LUMO by 0.54 eV relative to the unborylated counterpart. Other systems have been explored which accomplish fused structures by incorporation of a boryl group, although there is limited investigation on the effects this borylation has upon the frontier orbital energies.

Figure 2.4: Thiophene and thiazole units fused by boryl group.\textsuperscript{12}

This chapter presents a simple synthetic modification to lock thiophene and benzothiadiazole units coplanar in DTBT systems using boryl moieties. This involves a BT directed electrophilic C-H borylation which exploits the coordination of boron Lewis acids by the nucleophilic functionality (nitrogen atom) of the BT unit.\textsuperscript{14} Borylation locked the BT and thiophene units coplanar in a stable (to ambient conditions) C,N-chelated borane structure (Scheme 2.1). Whilst similar C,N-chelated boranes based on pyridine and thiazole acceptor
units are reported in the literature\textsuperscript{12,14,15}, to the best of our knowledge borylative fusion has not been applied to D-A materials containing the significantly less nucleophilic (relative to pyridyl) BT unit which is a good acceptor moiety ubiquitous in organic semiconducting materials.\textsuperscript{16}

Scheme 2.1: Proposed borylative fusion of DTBT compounds.

A series of substituents on the boron atom are accessible and the effect of these exocyclic boron substituents on the FMO energy levels is also examined, such studies for C,N-chelate boranes are limited in the literature.\textsuperscript{17} These studies demonstrated that extremely precise modulation of the FMO energy levels of the fused borylated system was possible through installing different exocyclic boron substituents.
2.2 Synthesis

2.2.1 Borylative Fusion of Thiophene D-A-D structures

Compound 2 was synthesised by using modified literature procedures.\(^1\) The addition of excess BX\(_3\) (X = Br or Cl) to a DCM solution of 2 in an open system under a dynamic flow of N\(_2\) resulted in coordination of boron to the basic nitrogen site on BT proceeded by electrophilic borylation to form 2-BX\(_2\) with the loss of HX (Scheme 2.2).

Scheme 2.2: Synthetic route towards compound 2-BX\(_2\).

Borylation of 2 proceeded in quantitative yields in an open system (by \textit{in-situ} \(^1\)H NMR spectroscopy (Figure 2.2)). An open system is necessary to ensure the loss of HX gas. In a closed system some HX remains in solution and broad resonances are observed in the \textit{in-situ} \(^1\)H NMR spectrum suggesting that borylation is reversible with protodeboronation reforming 2. Under these conditions addition of an equivalent of a sterically hindered Brønsted base (e.g. Hünig’s base) is required to drive borylation to completion by sequestering the protic by-product from S\(_{EAr}\).
Figure 2.2: $^1$H NMR spectra comparing open system borylation of 2 with BCl$_3$ (black), with closed system borylation (red) (S:CH$_2$Cl$_2$ with a d$_6$-DMSO capillary insert, 400 MHz, 298 K).

Importantly, addition of pyridine (a stronger Lewis base relative to BT) to 2-BX$_2$ resulted in no cleavage of the dative bond confirming the enhanced stability of the BT-BX$_2$ bond. The disparity between the reaction of 2 with BCl$_3$/BBr$_3$ (C-H borylation) and work published by Bazan and co-workers$^{14}$ (no C-H borylation) can be attributed to the presence of two proximate 2-ethylhexyl chains of the cyclopentadithiophene (CPDT) units in the latter which provide sufficient steric hindrance adjacent to the borylation site to prevent borylation (Scheme 2.3).

Scheme 2.3: The reactivity of 2 and a CPDT-BT-CPDT analogue towards BX$_3$.

The expected significant bathochromic shift in absorbance upon formation of the C,N-chelate was observed as a colour change (from orange to
dark blue). Whilst neither 2-BX₂ compounds were stable to moisture 2-BBr₂ was significantly more sensitive than 2-BCl₂. 2-BBr₂ was also less soluble in DCM than 2-BCl₂ as precipitation of 2-BBr₂ from the reaction mixture was observed. The precipitate of 2-BBr₂ could be redissolved by heating the reaction mixture to 60°C in a sealed tube and upon slow cooling material suitable for X-ray diffraction analysis was obtained.

Figure 2.3: Solid state structure of 2-BBr₂, thermal ellipsoids at 50 % probability level, hydrogens are omitted for clarity. Selected bond lengths (Å) = C3-B1 (1.577(7)), N1-B1 (1.578(6)), C6-N1 (1.333(6)), C10-N2 (1.323(6)), N1-S1 (1.654(4)), N2-S1 (1.600(4)). Selected angles (°) = C3-B1-N1 (108.0(4)), B1-N1-C6 (124.8(4)), C6-N1-S1 (107.3), S1-N2-C10 (110.1(3)).

Figure 2.4: Extended packing structure of 2-BBr₂ (hydrogens and octyl chains are omitted for clarity). Benzothiadiazole-thiophene centroid-centroid distance = 3.7 Å. Selected angles (°) = A-B-C (76.8), B-C-D (99.4), E-F-G (80.0), F-G-H (98.7).
This confirmed the expected connectivity with formation of an essentially planar six membered boracycle. The short distance between the planes of the fused aromatic cores of adjacent molecules (centroid to centroid distances 3.7 Å, Figure 2.4) in the extended structure of 2-BBr$_2$ indicates significant π-π interactions. There is a significant difference in the lengths of the two N-S bonds. The N-S bond associated with the borocycle (N1-S1) is significantly (>3σ) longer (1.654(4) Å) than that of the free N-S bond (N2-S1 = 1.600(4) Å). This is due to the donation of electron density from the N1 atom into the vacant p$_z$ orbital of the boron atom reducing the N2-S1 bond strength. The extended structure reveals a π-π stacking arrangement (Figure 2.4) with the fused thiophene of each molecule stacking atop a BT unit through dipolar interactions. The centre of the unfused thiophene stacking directly on top of one of the carbons of the C-C bond of the thiaadiazole ring giving an alternating, off-set structure.

Scheme 2.4: Reactivity of 2-BCl$_2$ with borocations.

Diborylation of 2 to generate the fully fused structure with both nitrogen atoms of the benzothiadiazole ring coordinating to boron (Scheme 2.4) proved unsuccessful under a range of conditions using BX$_3$. This is attributed to the initial borylation reducing the nucleophilicity of the remaining nitrogen in benzothiadiazole disfavouring coordination of a second boron Lewis acid.$^{19,20}$
Figure 2.5: $^1$H NMR spectra showing the formation of [2-BCl][AlCl$_4$] upon the addition of [DMT-BCl$_2$][AlCl$_4$] to 2-BCl$_2$ (*DMT-BCl$_3$/[DMT-BCl$_2$][AlCl$_4$] (S:CH$_2$Cl$_2$ with a d$_6$-DMSO capillary insert, 400 MHz, 298 K).

Attempts to form fused diborylated systems using highly electrophilic 3-coordinate borocations resulted instead in halide abstraction from 2-BCl$_2$ to form [2-BCl][AlCl$_4$]. (In-situ NMR spectroscopy showed formation of DMT-BCl$_3$ as a sharp singlet at 9.7 ppm in the $^{11}$B NMR spectrum and downfield shifts of the aromatic $^1$H resonances (Figure 2.5)). This $^1$H NMR spectrum is consistent with that observed from the independent synthesis of [2-BCl][AlCl$_4$] through the addition of AlCl$_3$ to 2-BCl$_2$ (Figure 2.4).

Borylation of 2 is not limited to the use of BX$_3$ as the electrophile, reaction of PhBCl$_2$ with 2 under the same reaction conditions used to form 2-BCl$_2$ also resulted in borylation to yield 2-B(Ph)Cl (not isolated). The reaction proceeded at a slower rate than with BCl$_3$ and resulted in lower yields due to the reduced Lewis acidity and electrophilicity of PhBCl$_2$ as a result of the interaction of the aromatic $\pi$-system with the empty $p_z$ orbital of the boron atom.$^{21}$ Upon addition of 2-(5-octyl-thiophene)BCl$_2$ (termed OTBCl$_2$) or bis(2-(5-octyl-thiophene)BCl (termed OT$_2$BCl) to compound 2 no borylation was observed. This is attributed to the more electron rich $\pi$-system of the thiophene groups further reducing the Lewis acidity/electrophilicity of the boron centre preventing electrophilic borylation.
2.2.2 Functionalisation of 2-BCl(Y)

The borylated dihalide species 2-BCl₂ is stable to non-protic Lewis bases (e.g., pyridine) but undergoes facile hydrolysis in wet solvent/ambient conditions. B-Cl hydrolysis is inferred from the observed colour change from dark blue to red upon stirring 2-BCl₂ for 16 hours in non-anhydrous THF ('wet THF'). This red product is assigned as 2-B(OH)₂ which could not be isolated as upon removal of the solvent, the reaction mixture changes colour to brown/black and the ¹H NMR spectrum shows a complex mixture of products. It is assumed that condensation of the proposed 2-B(OH)₂ to boroxines occurs in the condensed state. Stirring of a solution of the putative 2-B(OH)₂ with excess pinacol results in the formation of the significantly more stable 2-BPin in a high isolated yield (85%). The boron centre of 2-BPin is three coordinate with no significant N-B interaction as indicated by a signal in the ¹¹B NMR spectrum at 29 ppm which is consistent with a three coordinate ArylBPIN moiety. The formation of the pinacol boronate ester 2-BPin achieved by directed borylation at the 3-position could facilitate subsequent Suzuki-Miyura cross coupling. This opens up access to substitution patterns that are difficult to access by conventional/non-directed borylation methods.
Replacement of the halide substituents on boron (which are good leaving groups) with aryl/alkyl groups (poor leaving group) is necessary to achieve enhanced stability to ambient conditions. In addition to the vastly improved ambient stability, the exocyclic boron substituents can significantly modulate key optoelectronic properties including frontier orbital energies. A range of organometallic reagents were examined to find suitable reagents to functionalise \(2-BX_2\). Conventional organometallic reagents commonly used to transform B-halide to B-R/Ar (e.g., alkyl/aryl lithium and aryl(Grignard reagents) were not viable reagents and simply led to the decomposition of the borylated material; similar reactivity was observed by Murakami et al. in related borylated 2-phenyl-pyridine systems. Trialkylaluminium reagents, such as \(\text{AlMe}_3\), proved to be an effective reagent to exchange halide substituents for methyl groups. Exchanging chloride for methyl by treatment of \(2-\text{BCl}_2\) or \(2-\text{B(Ph)Cl}\) with excess \(\text{AlMe}_3\) resulted in the formation of \(2-\text{BMe}_2\) and \(2-\text{B(Ph)Me}\), respectively, which dramatically improved the borylated compounds stability to hydrolysis with these compounds showing excellent stability to protic media (e.g., \(2-\text{BMe}_2\) is stable in refluxing EtOH for at least 1 hour).
Scheme 2.6: Methylation of 2-BCl2 and 2-B(Ph)Cl.

Figure 2.6: Solid state structure of 2-BMe2, thermal ellipsoids at 50% probability level, hydrogens are omitted for clarity. Selected bond lengths (Å) = C3-B1 (1.611(6)), N1-B1 (1.659 (6)), C6-N1 (1.341(5)), C10-N2 (1.348(5)), N1-S1 (1.632(3)), N2-S1 (1.611(4)). Selected angles (°) = C3-B1-N1 (103.1(3)), B1-N1-C6 (124.1(3)), C6-N1-S1 (108.4(3)), S1-N2-C10 (108.0(3)).

Figure 2.7: Extended packing structure of 2-BMe2 (hydrogens and octyl chains are omitted for clarity). Benzothiadiazole-thiophene centroid-centroid distance = 3.8 Å. Selected angles (°) = A-B-C (106.5), B-C-D (69.7).
The solid state structure of 2-BMe₂ confirms the expected connectivity and possesses similar metrics and π-π stacking interactions to those observed for 2-BBr₂ (Figures 2.6 and 2.7). The addition of diarylzinc reagents (ZnPh₂/Zn(C₆F₅)₂) was also effective to functionalise 2-BCl₂ with aryl substituents in excellent yields (Scheme 2.7). Additionally, the use of pure (ethereal/alkali earth metal free) commercially available diarylzinc reagents reduces the workup to a simple filtration through silica providing ready access to compounds 2-BPh₂ and 2-B(C₆F₅)₂.

![Scheme 2.7: Functionalisation of 2-BCl₂ with aryl substituents.](image)

Figure 2.8: Solid state structure of 2-BPh₂, thermal ellipsoids at 50 % probability level, hydrogens are omitted for clarity. Selected bond lengths (Å) = C3-B1 (1.624(13)), N1-B1 (1.644(14)), C6-N1 (1.375(10)), C10-N2 (1.369(11)), N1-S1 (1.639(7)), N2-S1 (1.586(8)). Selected angles (°) = C3-B1-N1 (104.6(7)), B1-N1-C6 (124.9(7)), C6-N1-S1 (107.7(6)), S1-N2-C10 (109.5(6)), C2-C1-Cα1-Cβ1 (98(1)), C13-C14-Cα2-Cβ2 (3(2)).

The solid state structure of 2-BPh₂ demonstrated similar metrics and packing structure to that observed for 2-BMe₂ with the exception of a large twist (98(1)°) relative to the thiophene plane) in the alkyl chain of the borylated thiophene unit, this is in contrast to the linear conformation of the alkyl chain of the unborylated thiophene unit (3(2)°) (Figures 2.8 and 2.9) and is attributed to packing effects.
Figure 2.9: Extended structure of 2-BPh$_2$ (hydrogens are omitted for clarity). Benzothiadiazole-thiophene centroid-centroid distance = 3.8 Å. Selected angles (°) = A-B-C (102.5), B-C-D (70.6).

Whist 2 did not prove amenable to crystallisation the solid state structure of its methyl analogue MT-BT-MT was accessible. MT-BT-MT shows essentially the same packing structure as 2-BMe$_2$ and 2-BPh$_2$ (Figure 2.10) indicating that intermolecular interactions are dominated by $\pi$-stacking between the electron rich and poor heterocycles.

Figure 2.10: Extended structure of MeT-BT-MeT (hydrogens are omitted for clarity). Benzothiadiazole-thiophene centroid-centroid distance = 3.8 Å. Selected angles (°) = A-B-C (101.3), B-C-D (77.1).
All alkyl/aryl substituted compounds $2$-$\text{BR}_2$ have high moisture stability with no hydrolysis observed when exposed to moisture (9 months stored in solution or in the solid state) or upon reflux in ethanol (for at least 1 h). Whilst organozinc reagents are highly effective at transmetalating to tetra-coordinate boranes\textsuperscript{15}, these nucleophiles are highly sensitive to protic species (ROH) and the synthesis of organozinc reagents from ZnX$_2$ and ArLi/ArMgX often results in mixtures containing ionic species (termed zincates) and coordinated etherate solvent, which can complicate transmetalation (see Appendix). It therefore proved essential to ensure that the diarylzinc reagents used were ethereal/alkali earth metal salt free as the presence of these resulted in severely lower yields (13 \%) as observed in the synthesis of compound $2$-$\text{B(p-Tol)}_2$ (Scheme 2.8) which was synthesised from $2$-$\text{BCl}_2$ using the anionic Zincate A\textsuperscript{23,24} (Figure 2.11, synthesised by Dr. Jay Dunsford in pursuit of Zn(p-Tol)$_2$).

**Scheme 2.8:** Reaction of $2$-$\text{BCl}_2$ with Zincate A\textsuperscript{24}

![Scheme 2.8: Reaction of $2$-$\text{BCl}_2$ with Zincate A\textsuperscript{24}](image)

**Figure 2.11:** Solid state structure of Zincate A.\textsuperscript{24}

Due to difficulty in isolating etherate free diarylzinc reagents\textsuperscript{24}, a modular synthetic method for producing compounds with varied exocyclic substituents from readily synthesised, well defined and easy to handle reagents was desired. Arylstannane reagents meet these requirements and are extensively used in the functionalisation of tri-coordinate boron halides.\textsuperscript{25} Unlike tri-coordinate boron halides, tetra-coordinate boranes (including $2$-$\text{BCl}_2$) do not react with ArSnR$_3$
reagents to give tetra-coordinate aryl substituted boranes due to the Lewis acidity at boron being quenched by the dative bond (Scheme 2.9).\textsuperscript{15,23}

\[
\text{BCl}_3 + \text{ArSn}^{n}\text{Bu}_3 \rightarrow \text{Ar} - \text{B} - \text{Cl}_2
\]

Tri-coordinate borane

\[
\text{2-BCl}_2 \rightarrow \text{2-BClAr}
\]

Tetra-coordinate borane

Scheme 2.9: Reactivity of tri- and tetra-coordinate boranes to arylstannane reagents.

As discussed above, the borylated dihalide compound 2-BCl\textsubscript{2} readily undergoes chloride abstraction by a chlorophilic Lewis acid such as AlCl\textsubscript{3} to give [2-BCl][AlCl\textsubscript{4}] (Scheme 2.9) and it was hypothesised that this electrophilic borenium cation would undergo transmetalation with aryl-stannanes. The process is potentially catalytic in the AlCl\textsubscript{3} initiator as the by-product from transmetalation will act as a functional equivalent of [\textsuperscript{t}Bu\textsubscript{3}Sn\textsuperscript{+}] which can abstract a halide from boron to generate further equivalents of borenium cations for subsequent transmetalation steps (Scheme 2.10). This hitherto unknown reactivity was exploited to perform the catalytic functionalization of compound 2-BCl\textsubscript{2} with a range of aromatic groups (Scheme 2.10).

\[
\text{2-BCl}_2 + \text{ArSn}^{n}\text{Bu}_3 \rightarrow \text{2-BClAr}
\]

Surveyed: 2-B(MeT)\textsubscript{2} (51 %) Ar = \textsuperscript{1,2}N\textsubscript{2}S\textsubscript{2}Me

2-B(F\textsubscript{8})\textsubscript{2} (88 %) Ar = \textsuperscript{1,2}N\textsubscript{2}S\textsubscript{2}C\textsubscript{6}H\textsubscript{17}C\textsubscript{6}H\textsubscript{17}

\[
\text{2-BCl}_2 \rightarrow \text{2-BiarCl} + \text{ClSn}^{n}\text{Bu}_3
\]

Scheme 2.10: Proposed mechanism of boro-destannylation.
The addition of 2.2 equivalents of ArSnBu3 to 2-BCl2 resulted in no reaction, only upon the addition of ~5 mol % of AlCl3 was the reaction initiated and arylation (borodestannylation) observed. The rate of the reaction is dependent on the relative nucleophilicity of the arylstannane. Reactions with tri"butyl(5-methylthiophen-2-yl)stannane were completed rapidly (<10 minutes), whereas the reaction with tri"butyl(9,9-dioctyl-9H-fluoren-2-yl)stannane takes over 24 hours at 20°C to achieve appreciable conversion. It should be noted that 2-B(MeT)2 undergoes slow protodeboronation of the exocyclic thienyl groups on standing in wet solvents but it is stable in the solid state under ambient conditions for at least three months. The application of borenium cation mediated borodestannylation was expanded to other (C,N-chelate)BX2 compounds such as the extensively studied 2-phenylpyridyl derivatives (see Appendix).
2.3 Photophysical Properties

The photophysical characteristics of 2 and the borylated compounds 2-BMe₂, 2-B(Ph)Me, 2-BPh₂, 2-B(p-Tol)₂, 2-B(MeT)₂ and 2-B(C₆F₅)₂ were investigated by solution ultraviolet-visible (UV-vis) absorption spectroscopy in toluene (1 x 10⁻⁵ M).

Figure 2.12: UV-vis absorbance of 2, 2-BMe₂, 2-B(Ph)Me and 2-BPh₂ (1 x 10⁻⁵ M toluene solutions).

Table 2.1: Comparison of photophysical properties of 2, 2-BMe₂, 2-B(Ph)Me and 2-BPh₂.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ\text{max}_{\text{abs}} (nm)ᵃ</th>
<th>ε (M⁻¹ cm⁻¹)ᵃ</th>
<th>Optical Band-Gap (eV)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>471</td>
<td>15700</td>
<td>2.29</td>
</tr>
<tr>
<td>2-BMe₂</td>
<td>602</td>
<td>9700</td>
<td>1.73</td>
</tr>
<tr>
<td>2-B(Ph)Me</td>
<td>611</td>
<td>9800</td>
<td>1.72</td>
</tr>
<tr>
<td>2-BPh₂</td>
<td>617</td>
<td>12600</td>
<td>1.70</td>
</tr>
</tbody>
</table>

ᵃ1 x 10⁻⁵ M toluene solutions.ᵇBand-gap estimated from onset of absorption.
The absorption bands located at the higher energy part of the spectrum (300-400 nm) are attributed to localised $\pi-\pi^*$ transitions whereas the longer wavelength absorption bands are attributed to the internal charge transfer (ICT) from thiophene to the benzothiadiazole units. The expected large bathochromic shift in absorption relative to the absorption of 2 was observed upon borylation. The significant lowering of the band-gap (>0.5 eV) is mainly attributed to the significant reduction in the energy of the LUMO upon coordination of the Lewis acidic borane to the benzothiadiazole units (see subsequent voltammetry studies). The borylated compounds all show a decreased extinction coefficient relative to their parent unborylated compound although the absorption band is significantly broader. The borylated compounds 2-BMe$_2$, 2-B(Ph)Me and 2-BPh$_2$ showed similar absorption bands. The borylated compounds containing varying exocyclic aromatic units 2-BPh$_2$, 2-B(p-Tol)$_2$ and 2-B(MeT)$_2$ also showed approximately the same absorption bands. In contrast, the compound furnished with strongly electron withdrawing pentafluorophenyl substituents on boron, 2-B(C$_6$F$_5$)$_2$, showed an additional red shift in $\lambda_{\text{max}_{\text{abs}}}$ (>20 nm) and onset of absorption. This red shift for 2-B(C$_6$F$_5$)$_2$ is attributed to a further reduction in the LUMO energy level consistent with a more Lewis acid boron centre due to the strongly electron withdrawing pentafluorophenyl substituents leading to a greater N$\rightarrow$B $\sigma$-donation.
Figure 2.13: UV-vis absorbance of $2$, $2$-BPh$_2$, $2$-B(p-Tol)$_2$, $2$-B(MeT)$_2$ and $2$-B(C$_6$F$_5$)$_2$ ($1 \times 10^{-5}$ M toluene solutions).

Table 2.2: Comparison of photophysical properties of $2$, $2$-BPh$_2$, $2$-B(p-Tol)$_2$, $2$-B(MeT)$_2$ and $2$-B(C$_6$F$_5$)$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)$^{a}$</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)$^{a}$</th>
<th>Optical Band-Gap (eV)$^{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>471</td>
<td>15700</td>
<td>2.29</td>
</tr>
<tr>
<td>2-BPh$_2$</td>
<td>617</td>
<td>9700</td>
<td>1.70</td>
</tr>
<tr>
<td>2-B(p-Tol)$_2$</td>
<td>616</td>
<td>8500</td>
<td>1.70</td>
</tr>
<tr>
<td>2-B(MeT)$_2$</td>
<td>618</td>
<td>8500</td>
<td>1.70</td>
</tr>
<tr>
<td>2-B(C$_6$F$_5$)$_2$</td>
<td>641</td>
<td>7800</td>
<td>1.60</td>
</tr>
</tbody>
</table>

$^{a}$1x $10^{-5}$ M toluene solutions. $^{b}$Band-gap estimated from onset of absorption.

Whilst compound 2 is highly emissive in solution the borylated compounds derived from 2 are effectively non-emissive.

2.4 Redox Properties

Cyclic voltammetry was employed in order to gain further insight into the effects that borylation and installation of different exocyclic boron substituents has on the frontier molecular orbital energies. All the borylated compounds show a single fully reversible reduction process which is stable to at least 10 cycles in addition to multiple irreversible oxidation peaks.
Figure 2.14: Cyclic voltammetry plots of 2, 2-BMe$_2$, 2-B(Ph)Me and 2-BPh$_2$ (potential sweeps are offset by 40 µA for clarity), measured in DCM (1 mM) with [nBu$_4$N][PF$_6$] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV s$^{-1}$.

Table 2.3: Comparison of redox properties of 2, 2-BMe$_2$, 2-B(Ph)Me and 2-BPh$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{ox,onset}}$ (V)</th>
<th>$E_{\text{red,onset}}$ (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Electrochemical Band-Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.60</td>
<td>-1.66</td>
<td>-6.00</td>
<td>-3.73</td>
<td>2.27</td>
</tr>
<tr>
<td>2-BMe$_2$</td>
<td>0.46</td>
<td>-1.33</td>
<td>-5.85</td>
<td>-4.06</td>
<td>1.79</td>
</tr>
<tr>
<td>2-B(Ph)Me</td>
<td>0.52</td>
<td>-1.30</td>
<td>-5.91</td>
<td>-4.09</td>
<td>1.82</td>
</tr>
<tr>
<td>2-BPh$_2$</td>
<td>0.57</td>
<td>-1.24</td>
<td>-5.96</td>
<td>-4.15</td>
<td>1.81</td>
</tr>
</tbody>
</table>

Measured in DCM (1 mM) with [nBu$_4$N][PF$_6$] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV s$^{-1}$, potentials are given relative to the Fc/Fc$^+$ redox couple which is taken to be 5.39 eV below vacuum.$^{27}$

Compounds 2-BMe$_2$ and 2-B(Ph)Me that have alkyl substituents on boron produce the smallest reduction in the LUMO energy and the largest increase in the HOMO energy. This is consistent with an enhanced electron donation from methyl (relative to phenyl) to boron generating a boron centre that withdraws less electron density from the benzothiadiazole unit. The mixed phenyl-methyl derivative 2-B(Ph)Me has frontier orbital energies between 2-BPh$_2$ and 2-BMe$_2$ indicating a cumulative effect of exocyclic boron substituents.
Figure 2.15: Cyclic voltammetry plots of $2$, $2$-$\text{BPh}_2$, $2$-$\text{B(p-Tol)}_2$, $2$-$\text{B(MeT)}_2$ and $2$-$\text{B(C}_6\text{F}_5)_2$ (potential sweeps are offset by $30 \mu\text{A}$ for clarity), measured in DCM (1 mM) with $\left[^{\text{n}}\text{Bu}_4\text{N}\right][\text{PF}_6]$ (0.1 M) as the supporting electrolyte at a scan rate of $50 \text{ mV s}^{-1}$.

Table 2.4: Comparison of redox properties of $2$, $2$-$\text{BPh}_2$, $2$-$\text{B(p-Tol)}_2$, $2$-$\text{B(MeT)}_2$ and $2$-$\text{B(C}_6\text{F}_5)_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{ox}}^{\text{onset}}$ (V)</th>
<th>$E_{\text{red}}^{\text{onset}}$ (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Electrochemical Band-Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2$</td>
<td>0.60</td>
<td>-1.66</td>
<td>-6.00</td>
<td>-3.73</td>
<td>2.27</td>
</tr>
<tr>
<td>$2$-$\text{BPh}_2$</td>
<td>0.57</td>
<td>-1.24</td>
<td>-5.96</td>
<td>-4.15</td>
<td>1.81</td>
</tr>
<tr>
<td>$2$-$\text{B(p-Tol)}_2$</td>
<td>0.53</td>
<td>-1.24</td>
<td>-5.92</td>
<td>-4.15</td>
<td>1.77</td>
</tr>
<tr>
<td>$2$-$\text{B(MeT)}_2$</td>
<td>0.59</td>
<td>-1.17</td>
<td>-5.98</td>
<td>-4.22</td>
<td>1.76</td>
</tr>
<tr>
<td>$2$-$\text{B(C}_6\text{F}_5)_2$</td>
<td>0.67</td>
<td>-1.05</td>
<td>-6.07</td>
<td>-4.34</td>
<td>1.73</td>
</tr>
</tbody>
</table>

Measured in DCM (1 mM) with $\left[^{\text{n}}\text{Bu}_4\text{N}\right][\text{PF}_6]$ (0.1 M) as the supporting electrolyte at a scan rate of $50 \text{ mV s}^{-1}$, potentials are given relative to the $\text{Fc/Fc}^+$ redox couple which is taken to be $5.39 \text{ eV below vacuum.}^{27}$

Only subtle differences are observed comparing the aryl substituted compounds $2$-$\text{BPh}_2$, $2$-$\text{B(p-Tol)}_2$ and $2$-$\text{B(MeT)}_2$ with the exception of the strongly electron withdrawing C$_6$F$_5$ substituted analogue $2$-$\text{B(C}_6\text{F}_5)_2$. Compound $2$-$\text{B(C}_6\text{F}_5)_2$ demonstrated the largest reduction the LUMO energy level, lowering it by 0.61 eV, whilst only a relatively minor decrease in the HOMO energy level is observed (by 0.07 eV). This observed significant decrease in the LUMO energy level and lowering of the HOMO is attributed to a significant increase in the Lewis acidity of the boron centre relative to the other compounds in the series.
2.5 Conclusion

In this chapter a simple strategy for modifying the FMO energy levels of dithienylbenzothiadiazole (DTBT) by a directed electrophilic borylation to fuse the alternating donor-acceptor units coplanar is disclosed. Borylative fusion and subsequent arylation/alkylation at boron results in highly moisture stable compounds which show significantly decreased band-gaps (up to 0.69 eV) due to a substantially lowered LUMO energy level, whilst changes to the energy of the HOMO are minimal. A wide variety of exocyclic boron substituents can be installed starting from the dihalide functionalised material (2-BCl2) through facile synthetic methods. Cyclic voltammetry measurements show that exchange of the boron substituents fine tuning of the frontier orbital energies can be achieved. Whilst these molecules are effectively non-emissive precluding applications in OLED devices the small band-gap and extremely low LUMO energy levels suggest they and analogues discussed in later chapters have potential as the acceptor material in all-polymer OPVs and as ambipolar semiconductors.

2.6 Experimental

2.6.1 General Considerations

Unless otherwise indicated all reagents were purchased from commercial sources and were used without further purification. Trioctyl(5-octylthiophen-2-yl)stannane28, trimethyl(5-methylthiophen-2-yl)stannane28, trioctyl(9,9-dioctyl-9H-fluoren-2-yl)stannane28, MeT-BT-Me32 and Zincate A24 were prepared according to modified published procedures. All appropriate manipulations were performed using standard Schlenk techniques or in an argon-filled MBraun glovebox (O2 levels below 0.5 ppm). Glassware was dried in a hot oven overnight and heated under vacuum before use. Solvents and amines were distilled from NaK, CaH2, or K and degassed prior to use. Dichloromethane and THF were stored over activated 3Å molecular sieves while toluene was stored over a potassium mirror.

1H NMR and 13C{1H} NMR spectra were recorded using 400 or 500 MHz spectrometers with chemical shift values being reported in ppm relative to residual protio solvent (e.g. CHCl3 in CDCl3 \( \sigma \)H = 7.27 or \( \sigma \)C = 77.2) as internal standards. Other NMR spectra were recorded with a Bruker AV-400/500 spectrometer (400/500 MHz 1H, 101/126 MHz 13C{1H}, 128/160 MHz 11B; 104 MHz 19F).
MHz $^{27}$Al, 376 MHz $^{19}$F($^1$H}). The $^{19}$F($^1$H) NMR spectra were referenced to C$_6$F$_6$. $^{11}$B NMR spectra were referenced to external BF$_3$:Et$_2$O and $^{27}$Al to Al(NO$_3$)$_2$ in D$_2$O (Al(D$_2$O)$_6$)$^{3+}$. Unless otherwise stated all NMR spectra are recorded at 293 K. Broad features in the $^{11}$B NMR spectra are due to boron present in borosilicate glass whilst broad features in $^{27}$Al NMR spectra are due to aluminium materials used in the spectrometer probe. Carbon atoms directly bonded to boron are not always observed in the $^{13}$C($^1$H) NMR spectra due to quadrupolar relaxation leading to signal broadening. All CH$_2$ resonances were not distinctly observed due to similar chemical/magnetic environments. Coupling constants $J$ are given in Hertz (Hz) as positive values regardless of their real individual signs. The multiplicity of the signals are indicated as “s”, “d”, “t”, “quin”, “pent”, “sept” or “m” for singlet, doublet, triplet, quintet, pentet, septet, or multiplet, respectively. (br.) denotes a broad signal.

Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) and high-resolution mass spectrometry (HRMS) measurements was performed by the Mass Spectrometry Service, School of Chemistry, University of Manchester. MALDI-TOF analyses were performed using a Shimadzu Axima Confidence spectrometer using a 4k PPG as a calibration reference. 1 μL of a solution of dopant NaI in THF (10 mg mL$^{-1}$) was spotted onto a well of the MALDI plate and the solvent left to evaporate. Solutions were made up to 10 mg mL$^{-1}$ in DCM. A solution of matrix dithranol was made up to 10 mg mL$^{-1}$ in THF. 2 μL of sample solution and 20 μL of matrix solution were thoroughly mixed and 1 μL of this solution was spotted onto a well with no dopant and 1 μL spotted by a layered method with the NaI. The solvent was allowed to evaporate before being placed in the spectrometer. Samples were run in positive polarity mode in either linear or reflection mode. High resolution mass spectra (HRMS) were recorded on a Waters QTOF mass spectrometer. Accurate combustion data of the borylated compounds were not obtainable as consistently low %C content was observed; this is attributed to boron carbide formation and persisted even when V$_2$O$_5$ was used as an oxidant.

Data for compounds 2-BBr$_2$, 2-BMe$_2$ and 2-BPh$_2$ were recorded on a Bruker APEX-II diffractometer, with Cu Kα radiation (graphite monochromator, monochromator, λ = 1.5418 Å). The Bruker APEX2 software package was used
for data collection and the CrysAlisPro\textsuperscript{29} software package was used for cell refinement and data reduction.

Data for compounds \textbf{MeT-BT-MeT} was recorded on an Agilent Supernova diffractometer, with Mo K\textsubscript{\textalpha} radiation (mirror monochromator, $\lambda = 0.7107$ Å). The CrysAlisPro\textsuperscript{29} software package was used for data collection, cell refinement and data reduction. For all data sets the CrysAlisPro\textsuperscript{29} software package was used for empirical absorption corrections, which were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. All structures were solved using direct methods\textsuperscript{30} and refined against F\textsuperscript{2} using the Crystals\textsuperscript{31} software package. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all located in a difference map and repositioned geometrically. Experimental details are given in Table 2.5.

All UV-vis absorption spectra were recorded on a Varian Cary 5000 UV-vis-NIR at room temperature in spectroscopic grade solvents.

The Cyclic voltammetry measurements of compounds 2, 2-BMe\textsubscript{2} and 2-B(Ph)Me were performed by Dr. Aude Escande. Cyclic voltammetry was performed using a CH-Instrument 1110C Electrochemical/Analyzer potentiostat under a nitrogen flow. Measurements were made using a 1 mM analyte solution with 0.1 M tetra\textsuperscript{"}{"}butylammonium hexafluorophosphate (Fluka $\geq$99.0 %) as the supporting electrolyte in methylene chloride that had been degassed prior to use and obtained from a dry solvent system. A glassy carbon electrode served as the working electrode and a platinum wire as the counter electrode. An Ag/AgNO\textsubscript{3} non-aqueous reference electrode was used. All scans were calibrated against the ferrocene/ferrocnium (Fc/Fc\textsuperscript{+}) redox couple, which in this work is taken to be 5.39 eV below vacuum.\textsuperscript{27} The half-wave potential of the ferrocene/ferrocnium (Fc/Fc\textsuperscript{+}) redox couple ($E_{1/2, \text{Fc}, \text{Fc}^+}$) was estimated from $E_{1/2, \text{Fc}, \text{Fc}^+} = (E_{\text{ap}} + E_{\text{cp}})/2$, where $E_{\text{ap}}$ and $E_{\text{cp}}$ are the anodic and cathodic peak potentials, respectively.
2.6.2 Synthetic Procedures

Synthesis of 2

4,7-dibromobenzo[c][1,2,5]thiadiazole (2.00 g, 6.80 mmol), tri-n-butyl(5-octylthiophen-2-yl)stannane (7.26 g, 14.96 mmol) and PdCl$_2$(PPh$_3$)$_2$ (0.48 g, 0.68 mmol) were mixed in dry THF (60 ml) under an nitrogen atmosphere and stirred for 22 h at 80 °C under reflux. The mixture was cooled to room temperature and then diluted with DCM (200 mL). The reaction mixture was then washed with saturated NaHCO$_3$ solution (1 x 100 mL), brine (1 x 200 mL), water (1 x 200 mL) and then dried over MgSO$_4$. After evaporating the solvent, the residue was purified by column chromatography on silica gel [eluent: hexane:chloroform (4:1)] to afford 2 as an orange powder. (Yield 1.08 g, 30 %)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.94 (d, $^3$J$_{HH}$ = 3.6 Hz, 2 H$_a$), 7.79 (s, 2 H$_b$), 6.88 (d, $^3$J$_{HH}$ = 3.6 Hz, 2 H$_c$), 2.90 (t, $^3$J$_{HH}$ = 7.6, 4 H), 1.81 - 1.71 (m, 4 H), 1.47 - 1.22 (m, 20 H), 0.89 (t, $^3$J$_{HH}$ = 7.2, 6 H);

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$: aryl = 152.62, 147.80, 136.84, 127.32, 125.75, 125.22, 125.12, alkyl = 31.90, 31.70, 30.33, 29.39, 29.28, 29.20, 22.70, 14.16;

MALDI-TOF: calc. for C$_{36}$H$_{44}$BN$_2$S$_3^+$ [M]$^+$ = 524.2, found 523.9
Synthesis of 2-BCl₂

BCl₃ (1M solution in heptanes) (0.60 mL, 0.6 mmol) was added to a bright orange solution of 2 (0.312 g, 0.60 mmol) in DCM (10 mL) in a Schlenk flask resulting in a colour change to dark blue and the reaction mixture was stirred for 16 hours under the dynamic flow of N₂ (addition of a base was unnecessary as in the open system of a Schlenk flask gaseous HCl is lost from solution under the flow of nitrogen). The solvent was removed under reduced pressure and 2-BCl₂ was isolated as a dark blue powder. (Yields 322 mg, 89 %)

¹H NMR (400 MHz, C₆D₆) δ = 7.65 (d, ³J_HH = 3.8 Hz, 1 Hₐ), 7.54 (s, 1 Hₜ), 7.11 (d, ³J_HH = 7.6 Hz, 1 Hₚ), 6.97 (d, ³J_HH = 7.6 Hz, 1 Hₜ), 6.73 (d, ³J_HH = 3.8 Hz, 1 Hₚ), 2.69 (t, ³J_HH = 8.0 Hz, 2 H), 2.67 (t, ³J_HH = 8.0 Hz, 2 H), 1.72 - 1.52 (m, 4 H), 1.38 - 1.14 (m, 20 H), 0.92 (t, ³J_HH = 6.9 Hz, 6 H);

¹³C{¹H} NMR (101 MHz, C₆D₆) δ: aryl = 151.3, 150.8, 150.0, 145.0, 134.7, 131.7, 129.2, 128.8, 127.9, 126.2, 126.0, 125.7, 122.2, alkyl = 32.0, 31.7, 31.7, 30.6, 30.4, 29.4, 29.4, 29.2, 22.8, 14.0;

¹¹B NMR (128 MHz, C₆D₆) δ = ~3 (br.);

Due to the sensitivity of 2-BCl₂ mass spec. was not obtainable.
Synthesis of $[2\text{-BCl}]^+$

$$[\text{DMT-BCl}_2][\text{AlCl}_4]$$ (13 mg, 0.033 mmol) was added to a dark blue solution of $2\text{-BCl}_2$ (20 mg, 0.033 mmol) in DCM (0.70 mL). The solution turned a dark green colour and NMR spectroscopy showed a significant downfield shift in the NMR resonances relative to that of $2\text{-BCl}_2$. The formation of DMT-BCl$_3$ adduct was also confirmed by multinuclear NMR spectroscopy. These observations are consistent with the chloride abstraction from $2\text{-BCl}_2$ to form $[2\text{-BCl}]^+$.

$^1\text{H NMR}$ (400 MHz, CH$_2$Cl$_2$) $\delta = 8.65$ (d, $^3J_{HH} = 8.1$ Hz, 1 H$_a$), 8.37 (s, 1 H$_b$), 8.14 (d, $^3J_{HH} = 8.1$ Hz, 1 H$_c$), 7.54 (s, 1 H$_d$), 7.14 (s, 1 H$_e$), 3.13 - 2.87 (m, 4 H), 1.91 - 1.61 (m, 4 H), 1.48 - 1.19 (m, 20 H), 0.88 (t, $^3J_{HH} = 6.4$ Hz, 6 H);
Synthesis of \textit{2-BBr}_2

\[ \text{H}_1\text{C}_8 \text{S} \text{N} \text{S} \text{N-B-Br} \text{C}_8 \text{H}_{17} \]

BBR\textsubscript{3} (1M solution in heptanes) (0.20 mL, 0.20 mmol) was added to a bright orange solution of \textit{2} (26 mg, 0.05 mmol) in DCM (0.70 mL) in a J. Young’s NMR tube resulting in a colour change to dark blue and a blue precipitate was formed. 2,6-lutidine (0.011 mL, 0.10 mmol) was added and the reaction mixture was heated at 60°C to dissolve the precipitate. Upon cooling material suitable for X-ray diffraction crystallised from the reaction mixture.

\textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}) \( \delta = 7.64 \) (d, \( ^3J_{\text{HH}} = 3.2 \text{ Hz} \), 1 H\textsubscript{a}), 7.55 (s, 1 H\textsubscript{b}), 7.09 (d, \( ^3J_{\text{HH}} = 7.6 \text{ Hz} \), 1 H\textsubscript{c}), 6.94 (d, \( ^3J_{\text{HH}} = 7.6 \text{ Hz} \), 1 H\textsubscript{d}), 6.73 (d, \( ^3J_{\text{HH}} = 3.0 \text{ Hz} \), 1 H\textsubscript{e}), 2.69 (t, \( ^3J_{\text{HH}} = 7.57 \text{ Hz} \), 2 H\textsubscript{f}), 2.65 (t, \( ^3J_{\text{HH}} = 7.72 \text{ Hz} \), 2 H), 1.70 - 1.54 (m, 4 H), 1.37 - 1.18 (m, 20 H), 0.92 (t, \( ^3J_{\text{HH}} = 6.94 \text{ Hz} \), 6 H) ppm;

Due to the sensitivity of \textit{2-BBr}_2 mass spec. was not obtainable.
Synthesis of 2-BMe₂

A solution of AlMe₃ (2 M solution in heptanes) (0.4 mL, 0.80 mmol) in dry toluene (3 mL) was slowly added a stirred solution of 2-BCl₂ (200 mg, 0.33 mmol) in dry toluene (3 mL). After stirring for 20 minutes the excess AlMe₃ and solvent were removed under reduced pressure. Compound 2-BMe₂ was isolated as a dark blue/purple powder without further purification (Yield 178 mg, 96 %)

¹H NMR (400 MHz, C₆D₆) δ = 7.84 (d, 3 Jₕₕ = 3.8 Hz, 1 Hₐ), 7.35 (d, 3 Jₕₕ = 7.6 Hz, 1 Hₗ), 7.11 (s, 1 Hₑ), 7.05 (d, 3 Jₕₕ = 7.3 Hz, 1 Hₐ), 6.78 (d, 3 Jₕₕ = 3.5 Hz, 1 Hₑ), 2.81 (t, 3 Jₕₕ = 7.7 Hz, 2 H), 2.72 (t, 3 Jₕₕ = 7.6 Hz, 2 H), 1.76 - 1.61 (m, 4 H), 1.38 - 1.17 (m, 20 H), 0.92 (t, 3 Jₕₕ = 7.2, 3 H), 0.91 (t, 3 Jₕₕ = 7.2, 3 H), 0.72 (s, 6 H);

¹³C{¹H} NMR (101 MHz, C₆D₆) δ: aryl = 152.5, 149.5, 148.1, 147.6, 137.0, 130.8, 130.7, 130.2, 127.8, 127.7, 126.5, 126.0, 123.8, 120.6, alkyl = 32.6, 32.5, 32.4, 31.3, 30.9, 30.1, 30.0, 29.8, 23.4, 17.8, 14.7, 14.7;

¹¹B NMR (128 MHz, CDCl₃) δ = No ¹¹B NMR peak was observed at 20°C

MALDI-TOF: calc. for C₃₁H₄₂BN₂S₃⁺ [M - CH₃]⁺ = 549.7, found 549.6
Synthesis of 2-B(Ph)Me

PhBCl₂ (0.013 mL, 0.10 mmol) was added to a bright orange solution of 2 (0.52 g, 0.10 mmol) in DCM (0.7 mL) in a J. Young’s NMR tube resulting in a colour change to dark green and the reaction mixture was rotated for 16 hours. 2,6-lutidine (0.011 mL, 0.10 mmol) was added to the reaction mixture and after rotating for 16 hours the solvent was removed under reduced pressure to leave a dark blue/green residue. The residue was dissolved in benzene (0.7 mL) and AlMe₃ (2M solution in heptanes) (0.05 mL, 0.10 mmol) was added. After the reaction mixture had been rotated for 16 hours the excess AlMe₃ and solvent were removed under reduced pressure. The crude product was purified by chromatography on base treated silica gel (5 % NEt₃ in hexane) using hexane as eluent and 2-B(Ph)Me was isolated as a dark blue residue. (Yield 22 mg, 35 %)

¹H NMR (400 MHz, CDCl₃) δ = 7.83 (d, 3J_HH = 3.5 Hz, 1 Hₐ), 7.77 (d, 3J_HH = 7.6 Hz, 1 Hₚ), 7.46 (d, 3J_HH = 7.6 Hz, 1 Hₗ), 7.35 - 7.29 (m, 2 Hₜ), 7.23 (t, 3J_HH = 7.3 Hz, 2 Hₜ), 7.20 - 7.12 (m, 1 Hᵢ), 6.85 (d, 3J_HH = 3.5 Hz, 1 Hᵢ), 6.75 (s, 1 Hᵢ), 2.88 (t, 3J_HH = 7.6 Hz, 2 Hᵢ), 2.83 (t, 3J_HH = 7.7 Hz, 2 Hᵢ), 1.82 - 1.65 (m, 4 H), 1.50 - 1.22 (m, 20 H), 0.90 (t, 3J_HH = 7.2 Hz, 3 H), 0.90 (t, 3J_HH = 7.2 Hz, 3 H), 0.70 (s, 3 H);

¹³C{¹H} NMR (101 MHz, CDCl₃) δ: aryl = 151.9, 149.0, 147.7, 147.3, 135.5, 131.7, 130.2, 129.9, 128.2, 127.7, 127.1, 126.0, 125.4, 125.3, 123.5, 121.0, alkyl = 31.8, 31.6, 31.5, 30.9, 30.5, 30.2, 29.3, 29.3, 29.2, 29.1, 22.6, 14.1;

¹¹B NMR (128 MHz, CDCl₃) δ = No ¹¹B NMR peak was observed at 20°C

MALDI-TOF: calc. for C₃₆H₄₄BN₂S₃⁺ [M - CH₃⁺] = 611.8, found 611.8
Synthesis of 2-BPh₂

BCl₃ (1M solution in DCM) (0.12 mL, 0.12 mmol) was added to a bright orange solution of 2 (0.50 g, 0.10 mmol) in DCM (3 mL) in a Schlenk flask. The reaction mixture was stirred for 16 hours under a dynamic flow of nitrogen, where upon a colour change to dark blue was observed. The solvent and excess BCl₃ was removed under reduced pressure to yield a dark blue residue. The residue was dissolved in toluene and ZnPh₂ (50 mg, 0.23 mmol) was then added to the reaction mixture and stirred for 3 hours. The solution was then filtered through silica gel and the solvent was removed under reduced pressure to afford 2-BPh₂ as a dark blue residue. (Yield 46 mg, 69 %)

¹H NMR (400 MHz, CDCl₃) δ = 7.76 (d, ³J_HH = 3.7 Hz, 1 Hα), 7.65 (d, ³J_HH = 7.6 Hz, 1 Hb), 7.38 (d, ³J_HH = 7.7 Hz, 1 Hc), 7.31 - 7.14 (m, 10 Hd), 6.80 (s, 1 He), 6.81 (d, ³J_HH = 3.7 Hz, 1 Hf), 2.87 (t, ³J_HH = 7.6 Hz, 2 Hg), 2.81 (t, ³J_HH = 7.6 Hz, 2 H), 1.80 - 1.65 (m, 4 Hδ), 1.49 - 1.20 (m, 20 Hε), 0.92 (t, ³J_HH = 7.2 Hz, 3 H), 0.91 (t, ³J_HH = 7.2 Hz, 3 H);

¹³C{¹H} NMR (101 MHz, CDCl₃) δ: aryl = 160.7 (br.), 154.0 (br.), 151.5, 148.9, 147.8, 147.4, 135.4, 133.2, 130.9, 130.3, 127.9, 127.6, 127.3, 126.0, 125.4, 124.9, 123.6, 121.6, alkyl = 31.9, 31.8, 31.6, 31.5, 30.5, 30.2, 29.3, 29.3, 29.2, 29.2, 29.1, 22.7, 14.1;

¹¹B NMR (128 MHz, CDCl₃) δ = No ¹¹B NMR peak was observed at 20°C

MALDI-TOF: calc. for C₃₆H₄₄BN₂S₃⁺ [M - C₆H₅]⁺ = 611.8, found 612.0
Synthesis of 2-B(C₆F₅)₂

Zn(C₆F₅)₂ (152 mg, 0.4 mmol) was added to a toluene (5 mL) solution of 2-BCl₂ (115 mg, 0.19 mmol), the reaction mixture was stirred for 3 hours and then after the addition of wet toluene the solution was passed through a plug of silica. The solvent was removed under reduced pressure to afford a dark blue residue (Yield 151 mg, 92 %)

¹H NMR (400 MHz, CDCl₃) δ = 7.88 (d, ³JHH = 3.8 Hz, 1 Hₐ), 7.83 (d, ³JHH = 7.6 Hz, 1 Hₐ), 7.61 (d, ³JHH = 7.6 Hz, 1 Hₐ), 6.89 (d, ³JHH = 3.5 Hz, 1 Hₐ), 6.78 (s, 1 Hₐ), 2.89 (t, ³JHH = 7.6, 2 H), 2.82 (t, ³JHH = 7.6, 2 H), 1.81 - 1.64 (m, 4 H), 1.49 - 1.20 (m, 20 H), 0.89 (t, ³JHH = 6.8, 3 H), 0.88 (t, ³JHH = 6.8, 3 H);

¹³C{¹H} NMR (101 MHz, CDCl₃) δ: aryl = 150.4, 148.9, 147.8, 146.0, 133.8, 128.8, 127.0, 127.0, 124.6, 123.4, 122.7, 122.6, alkyl = 30.8, 30.8, 30.5, 30.5, 29.4, 29.3, 28.3, 28.3, 28.2, 28.1, 28.1, 21.6, 21.6, 13.0, 13.0;

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ = -132.43 (dd, ³JFF = 22.6, ⁴JFF = 7.9, 4F), -156.58 (t, ³JFF = 20.30, 2F), -162.40 (m, 4F);

¹¹B NMR (128 MHz, CDCl₃) δ = No ¹¹B NMR peak was observed at 20°C

MALDI-TOF: calc. for C₄₂H₃₉BN₂S₁₀⁺ [M]⁺ = 868.2, found 868.7
Synthesis of 2-B(MeT)$_2$

BCl$_3$ 1M in DCM (0.3 mL, 0.30 mmol) was added to a solution of 2 (95 mg, 0.18 mmol) in DCM (3 mL) and the solution was stirred overnight under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure. The resulting residue was dissolved in DCM (3 mL) and AlCl$_3$ (1 mg) was added to the solution. 2-methyl-5-tri$n$butylstannythiophene (154 mg, 0.40 mmol) was added to the reaction mixture which was then stirred overnight. The solvent was then removed under reduced pressure and the resulting residue was then purified via column chromatography on base treated silica gel (5% NEt$_3$ in hexane) [eluent DCM:hexane (1:9)] to afford a dark blue residue. (Yield 67 mg, 51%)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta = 7.71$ (d, $^3$J$_{HH} = 3.7$ Hz, 1 H$_a$), 7.58 (d, $^3$J$_{HH} = 7.6$ Hz, 1 H$_b$), 7.35 (d, $^3$J$_{HH} = 7.6$ Hz, 1 H$_c$), 6.90 (s, 1 H$_d$), 6.79 (d, $^3$J$_{HH} = 3.7$ Hz, 1 H$_e$), 6.76 (d, $^3$J$_{HH} = 3.2$ Hz, 2 H$_i$), 6.71 - 6.64 (m, 2 H$_g$), 2.87 (t, $^3$J$_{HH} = 7.1$ Hz, 4 H), 2.45 (s, 6 H$_h$), 1.83 - 1.68 (m, 4 H), 1.51 - 1.22 (m, 20 H), 1.00 - 0.82 (m, 6 H);

$^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$) $\delta$: aryl = 158.7 (br.), 153.8 (br.), 151.9, 149.4, 148.8, 147.0, 142.3, 135.8, 131.6, 131.3, 130.9, 128.1, 128.1, 126.4, 126.1, 124.5, 124.4, 122.8, alkyl = 32.5, 32.5, 32.2, 31.0, 30.8, 29.9, 29.9, 29.9, 29.8, 29.8, 23.3, 15.5, 14.5;

$^{11}$B NMR (128 MHz, CD$_2$Cl$_2$) $\delta = ~-2$ (br.);

HRMS (APCI) calc. for C$_{35}$H$_{44}$BN$_2$S$_4$ $^+$ [M - C$_5$H$_5$S]$^+$ = 631.2486, found 631.2477
Synthesis of 2-B(F8)2

BCl3 1M in DCM (0.10 mL, 0.10 mmol) was added to a solution of 2 (30 mg, 0.057 mmol) in DCM (3 mL) and the solution was stirred overnight under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure. The resulting residue was dissolved in DCM (3 mL) and AlCl3 (1 mg) was added to the solution. Tri tert-butyl(9,9-dioctyl-9H-fluoren-2-yl)stannane (85 mg, 0.125 mmol) was added to the reaction mixture which was then stirred overnight. The solvent was then removed under reduced pressure and the residue was dissolved in hexane and was passed through a short plug of base treated silica gel (5 % NEt3 in hexane) and only the dark blue coloured solution was retained. The solvent was removed to afford a blue residue. (Yield 66 mg, 88 %)

1H NMR (400 MHz, CDCl3) δ = 7.88 (d, 3J_HH = 3.7 Hz, 1 H_a), 7.84 (d, 3J_HH = 7.6 Hz, 1 H_b), 7.66 (dd, 3J_HH = 6.2, 4J_HH = 1.3 Hz, 2 H_c), 7.61 - 7.50 (m, 5 H), 7.37 - 7.22 (m, 6 H), 7.04 (dd, 3J_HH = 7.6, 4J_HH = 0.9 Hz, 2 H_d), 6.86 (d, 3J_HH = 3.7 Hz, 1 H_e), 6.79 (s, 1H_f), 2.89 (t, 3J_HH = 7.6 Hz, 2 H_g), 2.81 (t, 3J_HH = 7.7 Hz, 2 H), 2.07 - 1.85 (m, 8 H), 1.81 - 1.64 (m, 4 H), 1.42 - 0.98 (m, 60 H), 0.97 - 0.83 (m, 18 H), 0.68 (m, 8 H);

13C{1H} NMR (101 MHz, CDCl3) δ: aryl = 162.0 (br.), 153.3 (br.), 151.9, 150.9, 149.9, 149.0, 147.9, 147.6, 141.7, 139.3, 135.5, 132.0, 130.9, 130.2, 128.2, 127.4, 126.5, 126.4, 125.5, 125.2, 123.9, 122.8, 121.6, 119.3, 118.9, alkyl = 54.9, 40.5, 31.9, 31.9, 31.8, 31.6, 30.7, 30.3, 30.3, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.3, 29.2, 24.1, 24.1, 22.7, 22.7, 14.2, 14.2;

11B NMR (128 MHz, CDCl3) δ = No 11B NMR peak was observed at 20°C

HRMS (APCI) calc. for C_{88}H_{122}BN_{2}S_{3}^{+} [M + H]^{+} = 1313.8858, found 1313.8862
Synthesis of $2\text{-B(p-Tol)}_2$

BCl$_3$ 1M in DCM (0.35 mL, 0.35 mmol) was added to a solution of 2 (160 mg, 0.3 mmol) in DCM (10 mL) and the solution was stirred overnight under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure. The resulting residue was dissolved in toluene (10 mL) and Zincate A (270 mg, 0.28 mmol) was added to the stirred solution. After stirring for 3 hours the reaction mixture was filtered through a plug of base treated silica gel (5 % NEt$_3$ in hexane). The solvent was removed under reduced pressure and resulting residue was purified via column chromatography on silica gel [eluent DCM:hexane (2:8)] to afford the desired product as a blue residue. (Yield 28 mg, 13 %)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.82$ (d, $^3$J$_{HH} = 3.5$ Hz, 1 H$_a$), 7.76 (d, $^3$J$_{HH} = 7.6$ Hz, 1 H$_b$), 7.47 (d, $^3$J$_{HH} = 7.6$ Hz, 1 H$_c$), 7.17 (d, $^3$J$_{HH} = 8.1$ Hz, 4 H$_d$), 7.07 (d, $^3$J$_{HH} = 7.8$ Hz, 4 He), 6.85 (d, $^3$J$_{HH} = 3.8$ Hz, 1 H$_i$), 6.79 (s, 1 H$_g$), 2.88 (t, $^3$J$_{HH} = 7.6$ Hz, 2 H), 2.81 (t, $^3$J$_{HH} = 7.6$ Hz, 2 H), 2.32 (s, 6 H$_h$), 1.83 - 1.65 (m, 4 H), 1.47 - 1.25 (m, 20 H), 0.96 - 0.86 (m, 6 H);

$^{13}$C{${^1}$H} NMR (101 MHz, CDCl$_3$) $\delta$: aryl = 151.7, 150.8, 148.9, 147.8, 147.5, 135.4, 133.2, 131.0, 130.2, 128.4, 128.1, 127.2, 125.4, 125.0, 123.7, 121.5, alkyl = 31.8, 31.6, 31.5, 30.5, 30.3, 29.3, 29.2, 29.2, 29.1, 22.7, 22.7, 21.2, 14.1;

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta = No$ $^{11}$B NMR peak was observed at 20°C

HRMS (APCI) calc. for C$_{44}$H$_{54}$BN$_2$S$_3$ $^+ [M + H]^+ = 717.3537$, found 717.3533
Synthesis of 2-BPin

2-BCl₂ (83 mg, 0.14 mmol) was dissolved in ‘wet’ THF (5 mL) and the dark blue solution was stirred overnight at room temperature were upon the solution had changed colour to dark orange/red. Pinacol (77 mg, 0.65 mmol) was then added to the orange/red solution and the reaction mixture stirred overnight. The reaction mixture was then filtered through base treated (5 % NEt₃ in hexane) silica gel using hexane as eluent. The solvent was removed under reduced pressure to give 2-BPin as a dark orange residue (Yield 76 mg, 85 %).

^1H NMR (500 MHz, CDCl₃) δ = 7.98 (d, ³J_HH = 3.8 Hz, 1 H_a), 7.79 (d, ³J_HH = 7.6 Hz, 1 H_b), 7.73 (d, ³J_HH = 7.3 Hz, 1 H_c), 7.17 (s, 1 H_d), 6.90 (d, ³J_HH = 3.8 Hz, 1 H_e), 2.90 (t, ³J_HH = 7.7 Hz, 2 H), 2.88 (t, ³J_HH = 7.8 Hz, 2 H), 1.85 - 1.67 (m, 4 H), 1.47 - 1.23 (m, 20 H), 1.19 (s, 12 H), 0.99 - 0.80 (m, 6 H);

^13C{^1H} NMR (126 MHz, CDCl₃) δ: aryl = 154.4, 152.2, 147.8, 147.0, 145.4, 136.9, 130.9, 129.7, 127.5, 126.9, 126.7, 125.2, 124.6, alkyl = 83.3, 31.8, 31.6, 30.3, 29.9, 29.3, 29.2, 29.2, 29.1, 24.8, 22.6, 14.1;

^11B NMR (160 MHz, CDCl₃) δ = ~29 (br.);

MALDI-TOF: calc. for C₃₆H₅₁O₂BN₂S₃⁺ [M]^+ = 650.8, found 650.9
### 2.6.3 Crystallographic Details

Table 2.5: Summary of crystallography data for $2$-$\text{BBr}_2$, $2$-$\text{BMe}_2$, $2$-$\text{BPh}_2$ and $\text{MeT-BT-MeT}$.

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<th>$2$-$\text{BBr}_2$</th>
<th>$2$-$\text{BMe}_2$</th>
<th>$2$-$\text{BPh}_2$</th>
<th>$\text{MeT-BT-MeT}$</th>
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<td>1050963</td>
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<td>$\text{C}<em>{32}$-$\text{H}</em>{45}$-$\text{BN}_2$-$\text{S}_3$</td>
<td>$\text{C}<em>{42}$-$\text{H}</em>{49}$-$\text{B}$-$\text{N}_2$-$\text{S}_3$</td>
<td>$\text{C}<em>{16}$-$\text{H}</em>{12}$-$\text{N}_2$-$\text{S}_3$</td>
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<td><strong>Fw / g mol$^{-1}$</strong></td>
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<td>564.69</td>
<td>688.87</td>
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<td><strong>Crystal System, Space group</strong></td>
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<td>Triclinic, $P\text{-}1$</td>
<td>Triclinic, $P\text{-}1$</td>
<td>Monoclinic, $P\text{2}_1\text{/}n$</td>
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<td>100</td>
<td>220</td>
<td>100</td>
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<tr>
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<td>6.5240(6)</td>
<td>6.3487(6)</td>
<td>5.05783(2)</td>
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<td><strong>$b$ / Å</strong></td>
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<td>13.6675(11)</td>
<td>16.1168(15)</td>
<td>11.3455(4)</td>
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<tr>
<td><strong>$c$ / Å</strong></td>
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<td>18.0034(17)</td>
<td>19.3671(17)</td>
<td>24.6029(10)</td>
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<td>(3846)</td>
<td>(3194)</td>
<td>(2433)</td>
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2.7 References


Chapter 3

Borylative Fusion of Fluorene-Benzothiadiazole Based Materials
3.1 Introduction

Fluorene has proven to be an invaluable building block in the synthesis of π-conjugated materials for organic light emitting diode (OLED), organic Photovoltaics (OPV), organic field effect transistors (OFET) and organic light emitting transistor (OLET) applications.\textsuperscript{1-3} Fluorene can be considered as a special derivative of biphenyl in which the conjugation between the two phenyl units is enhanced by using a methylene bridge to lock the two phenyl units coplanar.\textsuperscript{4} The methylene bridge enhances the delocalisation of the π-electron system as a result of the planar arrangement of the molecule, this increased rigidity results in higher fluorescence quantum yields than those observed for biphenyl.\textsuperscript{4}

![Figure 3.1: Structures of biphenyl and fluorene.](image)

Polyfluorene and their derivatives have been found to show high thermal and chemical stability, deep highest occupied molecular orbital (HOMO) energy levels, good processability and good charge transport characteristics.\textsuperscript{4,5} Furthermore, functionalisation at the 9 position of fluorene allows the solubility and aggregation behaviour to be modified independently of its electronic properties.\textsuperscript{6} The efficient photoluminescence, relatively high bipolar charge transport, morphological stability and ease of processing all render fluorene based oligomers/polymers as attractive electroactive materials particularly for OLED and OLET applications.\textsuperscript{7} The large band-gap and low triplet energy (2.1 - 2.3 eV) of polyfluorene also make it a suitable OLED host material for lower band-gap emissive dopants particularly red emitting iridium dyes.\textsuperscript{8}

The use of fluorene as the electron donating unit in high performance donor-acceptor (D-A) π-conjugated materials is highly prevalent.\textsuperscript{7} There are many literature reports on tuning the wavelength of emission of fluorene-acceptor copolymers by varying the acceptor unit to achieve full colour emission (Figure 3.2).\textsuperscript{9}
Figure 3.2: Structures and solid state emission of fluorene-acceptor copolymers.

Whilst there exists a wide variety of high performing fluorene based co-oligomers and polymers, one particularly well studied D-A fluorene derivative is poly(9,9-dioctylfluorene-alt-2,1,3-benzothiadiazole) (PF8-BT). PF8-BT has been widely utilised for OLED applications in which it exhibits high quantum and power efficiencies as a green emitter (maximum external quantum efficiencies (EQE$_{\text{max}}$) up to 17.8%).$^2$ The modest electron affinity of the benzothiadiazole unit (BT) (lowest unoccupied molecular orbital (LUMO) energy = -3.3 eV) and the deep HOMO of the fluorene unit (-5.9 eV) leads to a relatively high band-gap of ~2.6 eV for PF8-BT based systems resulting in yellow-green emission ($\lambda_{\text{max}}^{\text{em}}$ ~550 nm in the solid state).$^7$ The ability to maintain the desirable qualities of a PF8-BT structure but modulate its frontier molecular orbital (FMO) energy levels by lowering of the LUMO energy to give a lower band-gap material is desirable. Within this context, this chapter focuses on the extension of the borylative fusion methodology discussed in Chapter 2 to fluorene based analogues to form a series of fused borylated F8-BT based donor-acceptor-donor (D-A-D) triads with the intention of decreasing the band-gap to create far red/near infra-red (NIR) emitting materials.
3.2 Synthesis

3.2.1 Synthesis and Borylative Fusion of Fluorene D-A-D Structures

Scheme 3.1: Synthesis and borylation of F8-BT-F8 system.

Compound 3 was synthesised by modified literature procedures. The borylation of 3 proceeded using the same conditions as developed for the borylation of 2 (see Chapter 2) but at a slower rate presumably due to the less nucleophilic π-system of fluorene relative to thiophene. The addition of excess BCl₃ to a DCM solution of 3 in an open system under N₂ resulted in coordination of boron to the basic nitrogen site on BT and successful C-H borylation to form 3-BCl₂ with the loss of HCl (Scheme 3.1). Borylation with BCl₃ was regioselective occurring exclusively at the less sterically hindered C3 position (Scheme 1), with no boration observed at the more hindered C1 position confirming the sensitivity of electrophilic borylation to the steric environment. This further confirms that the absence of borylation of CPDT-BT-CPDT (see Chapter 2, Figure 3.3) is due to steric reasons. The borylation of 3 proceeded quantitatively in an open system (by ¹H NMR spectroscopy). However, the exposure of compound 3 to BCl₂Ph in order to synthesise a monophenylated product, 3-BCl₂Ph, was unsuccessful. Whilst applicable to compound 2 (see Chapter 2), borylation of 3 with BCl₂Ph failed as BCl₂Ph is less Lewis acidic than BCl₃ and is therefore unable to undergo nucleophilic attack by the relatively (compared to thiophene) less nucleophilic fluorene (Scheme 2).
Scheme 3.2: Attempted synthesis of 3-B(Ph)Cl.

Diborylation of 3 to generate the fully fused structure with both nitrogens coordinating to boron (Scheme 3) proved unsuccessful under a range of conditions. This is partly attributed to the initial borylation reducing the nucleophilicity of the remaining nitrogen in benzothiadiazole disfavouring coordination of a second boron Lewis acid. For example, attempts to form a fused diborylated system using highly electrophilic three coordinate borocations resulted instead in halide abstraction from 3-BX₂ to form [3-BCl]⁺ (Scheme 3.3, Figure 3.3). The borocation [3-BCl]⁺ will be extremely electron withdrawing further reducing (compared to that in 3-BCl₂) the nucleophilicity of the second benzothiadiazole nitrogen precluding any subsequent borylation.

Scheme 3.3: Reactivity of 3-BCl₂ with borocations.
Figure 3.3: $^1$H NMR spectra showing the formation of [3-BCl][AlCl$_4$] upon the addition of [DMT-BCl$_2$][AlCl$_4$] to 3-BCl$_2$ (*[DMT-BCl$_3$], S:CH$_2$Cl$_2$ with a d$_6$-DMSO capillary insert, 400 MHz, 298 K).

A related D-A-D system F8-TTDz-F8 which incorporated the stronger electron withdrawing moiety thienothiadiazole (TTDz) did not undergo directed borylation under the same reaction conditions used for compound 3 (and even upon the addition of a hindered base (2,4,6-tri-$^1$butylpyridine (TBP))). This is attributed to the decreased nucleophilicity of the nitrogen atoms relative to BT no longer facilitating borylative fusion.

Scheme 3.4: Attempted synthesis of F8-TTDz-BPh$_2$-F8.
3.2.2 Functionalisation of 3-BCl₂

As demonstrated with the thienyl analogue 2-BCl₂ (Chapter 2), borylated dihalide species such as 3-BCl₂ are stable to non-protic Lewis bases but undergo facile hydrolysis in wet solvent/ambient conditions. In a similar procedure to that detailed in Chapter 2, 3-BCl₂ could be hydrolysed and then esterified with pinacol to give 3-BPin. The formation of the pinacol boronate ester by directed borylation at the 3-position could be used for subsequent Suzuki-Miyaura cross-coupling. This would facilitate access to 2,3-disubstituted fluorene structures of which literature precedence is extremely limited. ¹³

Scheme 3.5: Synthesis of 3-BPin.

Exchanging chloride for methyl substituents by treatment of 3-BCl₂ with excess AlMe₃ resulted in the quantitative (by in-situ NMR spectroscopy) formation of 3-BMe₂. This exchange dramatically improved the borylated compounds susceptibility to hydrolysis but 3-BMe₂ is not indefinitely stable under ambient conditions/in non-anhydrous solvents (though decomposition in the solid state is extremely slow e.g., ~50 % decomposition after 12 months in solid state).
The sensitivity of 3-BMe₂ to H₂O is in contrast to the thiényl analogue 2-BMe₂ (see Chapter 2) which shows excellent stability to protic media (e.g., stable to refluxing EtOH for at least 1 hour). This is a disparate stability trend to that observed for thiényl and fluorenyl boronic acids and boronate esters, in which the more electron rich thiényl congeners are generally more susceptible to C-B bond cleavage (protodeborylation).\textsuperscript{14,15} Insight into the origin of this stability trend was provided through computational calculations. Calculations were performed at the M06-2X/6-311G (d,p) level with PCM solvation (DCM) on simplified models of 2-BMe₂ and 3-BMe₂ (labelled 2'- and 3'-BMe₂, respectively), where C₈H₁₇ has been replaced for methyl groups and the non-borylated F₈/thienyl is omitted. The calculations revealed that borylative fusion planarises the aromatic units and leads to a short H-H distance in 3'-BMe₂ (Figure 3.4, H₁-H₂ = 2.03 Å) between a benzothiadiazole proton and a fluorene proton (H₁ and H₂, respectively). This presumably generates more force to twist the molecule non-planar thus weakens the B-N bond potentially resulting in decooordination of boron from N facilitating hydrolysis. B-N bond cleavage has previously been shown to be the initial step in the hydrolysis of related boracycles.\textsuperscript{16} No close H-H contacts are observed in the analogous calculated structure where fluorene has been replaced with thiophene (labelled 2'-BMe₂), as the sulphur atom is located in the position adjacent to the analogous benzothiadiazole C-H.
Figure 3.4: Calculated structures of 2'-BMe₂ and 3'-BMe₂. Selected bond lengths (Å) and angles (°) for 2'-BMe₂: B-N = 1.638, C-B = 1.614, N-B-C (endocyclic) = 103.729. For 3'-BMe₂: B-N = 1.618, C-B = 1.623, N-B-C (endocyclic) = 105.267.

The addition of diarylzinc reagents proved an effective method to functionalise 3-BCl₂ with aryl substituents in excellent yields (Scheme 7). The addition of commercially available diarylzinc reagents to 3-BCl₂ in DCM reduces the isolation procedure for the desired compounds to a simple filtration through silica (e.g., providing compound 3-BPh₂ in 99 % isolated yield). Again it proved important to ensure that the zinc reagents used were ethereal/alkali earth metal free as their presence resulted in lower yields as seen in the formation of compound 3-B(p-Tol)₂ which was synthesised using the Zincate A⁽¹⁷⁾ (Scheme 7) although the reduction in yield was not as severe as that observed with the thienyl analogue. The aryl substituted boranes, 3-BPh₂, 3-B(p-Tol)₂ and 3-B(C₆F₅)₂ have drastically improved moisture stability (relative to 3-BMe₂) due to greater kinetic stability provided by bulkier groups. These compounds show no hydrolysis when exposed to moisture after 9 months stored in solution or in the solid state under ambient atmosphere.

Scheme 3.7: Functionalisation of 3-BCl₂ with organozinc reagents.
The borenium cation mediated borodestannylation as described in Chapter 2 was applicable to the functionalisation of 3-BCl₂. Addition of 2.2 equivalents of (MeT)Sn³Bu₃ to 3-BCl₂ and ~5 mol % of AlCl₃ resulted in rapid borodestannylation at room temperature to give 3-B(MeT)₂ (scheme 8). Attempted extension of this methodology to PhSn^nBu₃ under the same reaction conditions shows limited transmetalation at room temperature due to the lower nucleophilicity of PhSn^nBu₃ compared to the 2-methylthiophene stannane congener. Compound 3-BPh₂ can be isolated in high yields from 3-BCl₂ and PhSn^nBu₃ upon heating at 60°C for 16 hours with 5 mol % AlCl₃.

Scheme 3.8: Reactivity of 3-BCl₂ with arylstannanes catalysed by AlCl₃.

The application of this methodology using arylsilane nucleophiles (which are also prevalent in halide-aryl group exchange reactions on boron¹⁸) is preferable over arylstannanes from a toxicity perspective. However, reacting PhSiMe₃ with 3-BCl₂ at a range of AlCl₃ loadings and temperatures (at 20 and 60°C) resulted in minimal transmetalation. It is well documented that silicon-boron exchange only proceeds with highly electrophilic boranes in contrast with tin-boron exchange reactions.¹⁸ This suggests that the borenium cation [3-BCl]⁺ is insufficiently electrophilic to boro-desilylate PhSiMe₃. It should be noted that 9,9-dimethyl-9H-9-silafluorene also shows no reactivity towards 3-BCl₂ even upon heating to 60°C with the addition of stoichiometric AlCl₃, unlike that observed with a related boron dihalide C-N chelate compound (PhPy-BCl₂) (see Appendix).¹⁹ A more nucleophilic silane, trimethyl(5-methylthiophen-2-yl)silane ((MeT)SiMe₃) was therefore utilised for the arylation of 3-BCl₂. The reaction of 3-BCl₂ with excess (2.2 eq.) (MeT)SiMe₃ was initiated by the addition of AlCl₃ (~5 mol %) leading to borodesilylation. Unlike the analogous tin reagent ((MeT)Sn^nBu₃), only one transmetalation per boron is observed using (MeT)SiMe₃ which produces 3-BCl(MeT) (Figure 3.5,
Scheme 9) and this reaction proceeds at a much slower rate (80 % conversion after 5 hours) owing to the decreased reactivity towards boron electrophiles of arylsilanes compared to arylstannanes.\textsuperscript{18,19}

Scheme 3.9: Synthesis of 3-B(MeT)(C\textsubscript{6}F\textsubscript{5}).

As the borenium cation [3-B(MeT)]\textsuperscript{+} formed after the first arylation contains a thienyl $\pi$-donor its Lewis acidity is presumably reduced relative to [3-BCl]\textsuperscript{+} disfavouring an additional boro-desilylation of (MeT)SiMe\textsubscript{3}. Analogous trends in Lewis acidity have been observed when comparing the Lewis acidity of [PhBCl(amine)]\textsuperscript{+} and [Cl\textsubscript{2}B(amine)]\textsuperscript{+} borocations.\textsuperscript{20}

The propensity of activated arylsilane reagents to only arylate once at boron allows for the creation of unsymmetrically functionalised borylated products (such as 3-B(MeT)(C\textsubscript{6}F\textsubscript{5}), Scheme 9) by arylation of 3-B(MeT)Cl with an organozinc reagent (in this case Zn(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}). The boron substituents can have a strong influence on packing/morphology and the FMO energies (both important for device applications)\textsuperscript{21}, therefore the ability to selectively install desired boron substituents will facilitate precise tuning of these properties.
Figure 3.5: $^1$H NMR spectra demonstrating only a single transmetalation occurs when using arylsilanes, (S:CH$_2$Cl$_2$, with a d$_6$-DMSO capillary insert, 400 MHz, 298 K).

3.3 Photophysical Properties

3.3.1 Solution Ultraviolet-Visible Absorbance and Photoluminescence Properties

The ultraviolet-visible (UV-vis) absorbance and photoluminescence (PL) characteristics of the moisture stable compounds 3, 3-BPh$_2$, 3-B(C$_6$F$_5$)$_2$, 3-B(p-Tol)$_2$ and 3-B(MeT)$_2$ were investigated in toluene (1 x 10$^{-5}$ M). The absorption bands located at the higher energy part of the spectrum (300-400 nm) are attributed to localised $\pi-\pi^*$ transitions whereas the longer wavelength absorption bands are attributed to the internal charge transfer (ICT) from fluorene to the BT units$^{22}$ which is consistent with the D-A character of these compounds.$^{2,3}$
Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

Table 3.1: Comparison of photophysical properties of 3, 3-BPh₂, 3-B(C₆F₅)₂, 3-B(p-Tol)₂ and 3-B(MeT)₂.

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<th>ε (M⁻¹ cm⁻¹)ᵃ</th>
<th>Optical Band-Gap (eV)ᵇ</th>
<th>λ_{max}^{em} (nm)ᵃ</th>
<th>Stokes shift (nm)</th>
<th>Φᵢ (%) ᶜ</th>
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<tr>
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<tr>
<td>3-B(MeT)₂</td>
<td>552</td>
<td>13400</td>
<td>1.92</td>
<td>702</td>
<td>150</td>
<td>4.1</td>
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ᵃ1x 10⁻⁵ M toluene solutions. ᵇBand-gap estimated from onset of absorption.
ᶜRelative fluorescence quantum yield, estimated by using cresyl violet as standard (Φᵢ = 54 % in methanol)²⁴, estimated error ± 20 %. Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

The expected large bathochromic shift in absorption relative to the absorption of 3 was observed upon borylation due to the coordination of the BT unit to a Lewis acidic boron centre. The borylated compounds all show a decreased extinction coefficient relative to their parent unborylated compound.
although the absorption band is significantly broader. Compounds $3\text{-BPh}_2$, $3\text{-B(p-Tol)}_2$ and $3\text{-B(MeT)}_2$ show approximately the same $\lambda_{\text{max}}^{\text{abs}}$ (552-559 nm) and $\lambda_{\text{onset}}$ of absorption in addition to large Stokes shifts in toluene (143-150 nm) with broad emission centred at $\lambda_{\text{max}} \sim 702$ nm but the emission continues significantly into the near infra-red region of the spectra ($\sim$700-850 nm). The solution quantum yield in toluene for $3\text{-BPh}_2$ and $3\text{-B(p-Tol)}_2$ are 10.0 and 10.2 % respectively, which are reasonable values for deep red/NIR emitters as molecules with low band-gaps have accelerated non-radiative excited state decay processes consistent with the energy gap law.\textsuperscript{25} Whereas the thienyl functionalised $3\text{-B(MeT)}_2$ shows a diminished quantum yield value of 4.1 %.

The only borylated compound that showed distinct photophysical properties relative to other $3\text{-B(Ar)}_2$ compounds was that bearing strongly electron withdrawing pentafluorophenyl substituents on the boron. Compounds $3\text{-B(C}_6\text{F}_5)_2$ showed a further red shift in $\lambda_{\text{max}}^{\text{abs}}$ ($\leq$20 nm) and $\lambda_{\text{onset}}$ of absorption with concomitant red shifted in emission, although with a reduced quantum yield (1.5 %). The absorption and emission of compounds $3\text{-BPh}_2$ and $3\text{-B(C}_6\text{F}_5)_2$ were investigated by solution UV-vis absorption and PL spectroscopy in different polarity solvents (all at $1 \times 10^{-5}$ M). Compounds $3\text{-BPh}_2$ and $3\text{-B(C}_6\text{F}_5)_2$ exhibited minor absorbance and major emission solvatochromism. The observed bathochromic shift of fluorescence wavelength with increasing solvent polarity (Figures 3.7 and 3.8) is indicative of emission from a photoinduced-excited state with strong intramolecular charge transfer character (ICT).\textsuperscript{26} This shift of fluorescence wavelength with increasing solvent polarity is due to fact that excitation ($S_0 \rightarrow S_1$) enhances the dipole moment relative to that in the ground state and this change in dipole moment is particularly large in molecules which show intramolecular charge transfer character. In solution, before the fluorophore undergoes radiative decay, the surrounding solvent molecules rearrange and interact with the excited molecule; the extent of this interaction is dependent on the polarity of the solvent. Solvents with a larger dipole moment can stabilise the excited-state to greater degree. This stabilisation results in a lower energy-gap between the $S_1$ and $S_0$ states and culminates in lower energy emission from the radiative $S_1 \rightarrow S_0$ transition. Therefore large
increases in Stokes shifts are expected with increasing solvent polarity for molecules which show a large degree of intramolecular charge transfer character.\textsuperscript{26}

![Graph showing absorbance and emission spectra of 3-BPh\textsubscript{2} and 3-B(C\textsubscript{6}F\textsubscript{5})\textsubscript{2} in solvents of varying polarity.](image)

Figure 3.7: Absorbance and emission spectra of 3-BPh\textsubscript{2} (top) and 3-B(C\textsubscript{6}F\textsubscript{5})\textsubscript{2} (bottom) in solvents of varying polarity (1 x 10\textsuperscript{-5} M). Fluorescence spectra were measured by exciting the solutions at their
absorption maxima.

Table 3.2: Comparison of the photophysical properties of 3-BPh$_2$ and 3-B(C$_6$F$_5$)$_2$ in solvents of varying polarity.

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<th>$\lambda_{\text{max}}_{\text{em}}$ (nm)</th>
<th>Stokes shift (nm)</th>
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<table>
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<th>Solvent</th>
<th>$\lambda_{\text{max}}_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{max}}_{\text{em}}$ (nm)</th>
<th>Stokes shift (nm)</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
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Absorption and fluorescence data of 3-BPh$_2$ and 3-B(C$_6$F$_5$)$_2$ in solvents of different polarity (1 x 10$^{-5}$ M). Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

Figure 3.8: Lippert-Mataga plots for compounds 3-BPh$_2$ and 3-B(C$_6$F$_5$)$_2$. $\Delta f=((\varepsilon-1)/(2\varepsilon+1))-(n^2-1)/(2n^2-1))$, where $\varepsilon$ and $n$ are the dielectric constant and the refractive index of the solvent, respectively.
3.3.2 Solid State Photoluminescence

As \(3\text{-BPh}_2\) was the most facile to synthesise (in highest yield) and was amongst the most emissive in solution, the solid state emission of this compound was investigated. The solid state emission and photoluminescence quantum yield (PLQY) of \(3\text{-BPh}_2\) was examined by preparing thin films from a 5 wt. % mixture of \(3\text{-BPh}_2\) dispersed in LUMATION™ 1300 Series green emitting polymer (L1300).\(^{27}\) Upon doping \(3\text{-BPh}_2\) into a L1300 host matrix and exciting at 400 nm complete quenching of the host occurs and a broad emission band to \(>800\) nm with a \(\lambda_{\text{max}}\text{em}\) at 697 nm (black, Figure 3.10) and a quantum yield of 24.0 % is observed which is good for this region of the electromagnetic spectrum. Compound \(3\text{-BPh}_2\) shows a short excited state life time (5.35 ns) whilst dispersed in L1300 confirming the emission is due to fluorescence (Figure 3.9).

![Figure 3.9: PL lifetime data of a thin film of a 5 wt. % mixture of 3-BPh2 dispersed in L1300 polymer, excited at 400 nm, estimated error \(±10\) %.]
Figure 3.10: Solid state PL of 3-BPh₂ 5 wt. % dispersed in L1300 (excited at 400 nm, black) and PF8-BT (excited at 468 nm, red).

Table 3.3: Summary of solid state PL data of 3-BPh₂

<table>
<thead>
<tr>
<th>Film</th>
<th>Transmittance (A.U)</th>
<th>λmax_em (nm)</th>
<th>Φ (%)</th>
<th>τ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1300:3-BPh₂ (95:5 wt. %)</td>
<td>0.32</td>
<td>697</td>
<td>24.0</td>
<td>5.35</td>
</tr>
<tr>
<td>PF8-BT:3-BPh₂ (95:5 wt. %)</td>
<td>0.36</td>
<td>696</td>
<td>32.9</td>
<td>-</td>
</tr>
</tbody>
</table>

*Excited at 400 nm. *Excited at 468 nm. *Absolute values, determined with an integrating sphere, estimated error ± 4.5 %. *Estimated error ± 10 %.

The solid state emission of a film of 3-BPh₂ 5 wt. % dispersed in PF8-BT showed a significantly improved quantum yield value relative to that dispersed in LUMATION 1300. On excitation at 468 nm compound 3-BPh₂ completely quenched the emission of the PF8-BT host polymer and showed emission at a λmax_em of 696 nm with an excellent (for deep red emitters) solid state quantum yield of 32.9 % (Table 3). The PL emission of the PF8-BT host overlaps extremely well with the ICT absorption band of 3-BPh₂ which suggests efficient Förster resonance energy transfer can be expected. The relative quantum yields suggest improved energy transfer between PF8-BT and the borylated dopant compared to L1300. The impressive solid state quantum yield values for the relevant region of the electromagnetic spectrum can be attributed to due to
high degree of rigidity of the borylated structure which minimises non-radiative decay processes due to rotations or vibrations of fluorophore, in addition to the two proximate quaternary-centres in $3$-$\text{BPh}_2$ that project considerable steric bulk above and below the conjugated backbone plane preventing aggregation induced quenching processes which are prevalent in highly fused, planar fluorophores.$^{26,29,30}$ State of the art solid state NIR emissive small molecules with similar fluorescence spectra to $3$-$\text{BPh}_2$ display less efficient photoluminescence (Figure 3.11).$^{26,30}$

![Diagram of structures](image)

**Figure 3.11**: Structures and solid state photoluminescence data of high performing solid state NIR emitters. TPBi = $2,2',2''$-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-$H$-benzimidazole).
3.4 Redox Properties

Cyclic voltammetry was employed in order to gain further insight into the effects that borylation and installation of different exocyclic boron substituents have on the frontier molecular orbital energies. Compounds 3, 3-BPh₂, 3-B(C₆F₅)₂, 3-B(p-Tol)₂ and 3-B(MeT)₂ all show a single fully reversible reduction process which is stable to at least 10 cycles. Compounds 3 and 3-B(C₆F₅)₂ show two reversible oxidation peaks which are stable to at least 10 cycles whilst 3-BPh₂, 3-B(p-Tol)₂ and 3-B(MeT)₂ show multiple irreversible oxidation peaks.

Figure 3.12: Cyclic voltammetry plots of 3, 3-BPh₂, 3-B(C₆F₅)₂, 3-B(p-Tol)₂ and 3-B(MeT)₂, measured in DCM (1 mM), with [nBu₄N][PF₆] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV s⁻¹.

<table>
<thead>
<tr>
<th>Compound</th>
<th>E_{ox}^{onset} (V)</th>
<th>E_{red}^{onset} (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Electrochemical Band-Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.88</td>
<td>-1.87</td>
<td>-6.27</td>
<td>-3.52</td>
<td>2.75</td>
</tr>
<tr>
<td>3-BPh₂</td>
<td>0.80</td>
<td>-1.28</td>
<td>-6.19</td>
<td>-4.11</td>
<td>2.08</td>
</tr>
<tr>
<td>3-B(C₆F₅)₂</td>
<td>0.85</td>
<td>-1.12</td>
<td>-6.24</td>
<td>-4.27</td>
<td>1.97</td>
</tr>
<tr>
<td>3-B(p-Tol)₂</td>
<td>0.77</td>
<td>-1.31</td>
<td>-6.16</td>
<td>-4.08</td>
<td>2.08</td>
</tr>
<tr>
<td>3-B(MeT)₂</td>
<td>0.79</td>
<td>-1.27</td>
<td>-6.18</td>
<td>-4.12</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Table 3.4: Comparison of redox properties of 3, 3-BPh₂, 3-B(C₆F₅)₂, 3-B(p-Tol)₂ and 3-B(MeT)₂.

Measured in DCM (1 mM) with [nBu₄N][PF₆] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV s⁻¹, potentials are given relative to the Fc/Fc⁺ redox couple which is taken to be 5.39 eV below vacuum.³¹
Similar trends to those seen in Chapter 2 were observed with all compounds showing a large decrease (up to 0.56 eV) in the energy of the LUMO and a minor increase (+0.03-0.11 eV) in the HOMO energy level. The measured reduction in electrochemical band-gap (up to 0.67 eV) upon borylation of 3 and installation of aryl substituents is in strong agreement with the optical band-gap from UV-vis absorbance spectra. Similar to that observed in Chapter 2, 3-BPh$_2$, 3-B(p-Tol)$_2$ and 3-B(MeT)$_2$ all show very similar oxidation and reduction potentials whilst cyclic voltammetry measurements showed that exchanging the exocyclic phenyl substituents for the more electron withdrawing pentafluorophenyl groups resulted in a further reduction (0.16 eV) of the LUMO energy level but a smaller modulation of the HOMO energy level (+0.05 eV) resulting in a lower electrochemical band-gap. This further reduction in the LUMO energy level of 3-B(C$_6$F$_5$)$_2$ is attributed to the coordination of the BT unit to a more Lewis acidic boron centre (due to the strongly electron withdrawing pentafluorophenyl substituents) which leads to a greater N→B σ-donation and a more electron deficient BT unit. This is in strong agreement with the UV-vis measurements as a distinctly lower optical band-gap is observed for 3-(BC$_6$F$_5$)$_2$. 

3.5 Computational Analysis

Computational analysis was performed at the M06-2x/6-311G (d,p) level with PCM solvation (DCM) for a model compound of 3-BPh$_2$ (termed 3'-BPh$_2$) where the C$_8$H$_{17}$ chains of the F8 unit were replaced by methyl (termed F1) to reduce calculation time. The ground state optimized geometry and the relevant HOMO and LUMO energy levels together with the molecular orbital contours for 3'-BPh$_2$ are depicted in Figure 3.13.

![Molecular orbital energy levels and molecular orbital contours](image)

**Figure 3.13:** Molecular orbital energy levels and molecular orbital contours (isovalue = 0.04) of the HOMO and LUMO of 3'-BPh$_2$.

The calculations reveal that the borylated F1 shows greater coplanarity with the BT unit of 3'-BPh$_2$ as can be seen by the reduced torsion angle between the BT and the borylated fluorene unit (4.68°) compared to the torsion angle between the BT and the unborylated F1 unit (39.01°). Analysis of the molecular orbital contour plots show that the LUMO is localised almost entirely on the BT unit whereas the HOMO is delocalised across all three units of the D-A-D structure with no FMO contribution from the peripheral phenyl substituents on boron. The high degree of
HOMO and LUMO character on the BT unit indicates the potential to achieve a high oscillator strength and may be a factor in explaining the high PLQY values observed for the related compound 3-BPh₂.

It is noteworthy that although delocalised there is significantly more HOMO character on the borylated F1 unit than on the unborylated F1 unit. This significant HOMO character on the borylated F1 unit can explain why the identity of the boron substituent can modulate the HOMO energy levels as seen in the cyclic voltammetry measurements (the boron substituents influence the Lewis acidity of the boron centre which modulates the HOMO energy level through an inductive effect from four coordinate boron through the B-C sigma bond). This high degree of HOMO character on the F1 unit, coupled with the planarization which increases the effective conjugation length is presumably why the HOMO energy is destabilised upon borylative fusion which is in contrast to the decrease in the HOMO energy level observed by Poverenov et al. in calculations of related systems upon coordination of boron Lewis acids to benzoselenodiazole (BSe).³⁰ In the absence of C-H borylation and enforced coplanarity, calculations showed that the coordination of the Lewis acidic BF₃ to the basic functionality of a BSe moiety in a D-A system also imparts a large degree of steric hindrance around that acceptor unit resulting in a decrease in coplanarity between the donor and BSe unit (Figure 3.14) which disrupt π-conjugation, stabilising the HOMO (by 0.58 eV).³²

![Figure 3.14: Steric effects of coordinating boron Lewis acids to the basic functionality of an acceptor unit in a D-A system.³²](image)

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³² The notation γ = 0° refers to coplanar orientation, while γ = 106° indicates decreased planarity.
3.6 OLED Devices

A series of solution processed OLED devices were fabricated to analyse the performance of 3-BPh$_2$ as a deep red/NIR emitter. The device architecture was as follows, ITO (45 nm)/Plexcore OC$^\circledR$ AQ1200 (65 nm)/PF8-TFB (poly[(9,9-diocylfluorenyl-2,7-diyl)-co-(4,4’-(N-(4-sec-butylphenyl)diphenyl amine))]) (22 nm)/emission layer (EML) (100 nm)/Ba (3.5 nm). In **Device 3.1** the EML was comprised of 5 wt. % of 3-BPh$_2$ in 80 wt. % PF8-BT and 15 wt. % PF8-TFB. The purpose of the PF8-TFB co-host was to improve hole mobility through the emission layer. An additional device was also fabricated, **Device 3.2**, which possessed the same device architecture only excluding the PF8-TFB co-host in the EML (EML = 5 wt. % 3-BPh$_2$:95 wt. % PF8-BT).

![Device 3.1 OLED architecture](image)

**Figure 3.15:** (a) **Device 3.1** OLED architecture (b) Relative energy level diagram of **Device 3.1**. (c) Structures of materials used in **Device 3.1** and 3.2.
The electroluminescence (EL) spectrum of **Device 3.1** showed a broad emission from 600 to >830 nm with a $\lambda_{\text{max}}^{\text{EL}}$ of 678 nm which is slightly hypsochromically shifted (by 16 nm) relative to the PL $\lambda_{\text{max}}$ of a film of 3-BPh$_2$ 5 wt. % dispersed in PF8-BT. Minor amounts of green emission (~500-580 nm) from the PF8-BT host was also observed. This device had a low turn on voltage (2.3 V) and a maximum external quantum efficiency (EQE$_{\text{max}}$) value of 0.46 % which is good for a solution processed device with a metal free fluorophore emitting in the deep red/NIR region of the electromagnetic spectrum.**Device 3.2** showed essentially the same electroluminescence as **Device 3.1** but with slightly reduced emission from the PF8-BT host. **Device 3.2** also showed a slightly improved EQE$_{\text{max}}$ of 0.48 % and a low turn-on voltage of 2.5 V.
Figure 3.17: **Device 3.1** and **3.2** (a) Electroluminescence spectra (b) Plot of EQE vs voltage (c) Plot of current density vs voltage.

Table 3.5: Summary of OLED device performance.

<table>
<thead>
<tr>
<th>Device</th>
<th>$\lambda_{\text{max}}^{\text{EL}}$ (nm)</th>
<th>$V_{\text{on}}^a$ (V)</th>
<th>$\text{EQE}_{\text{max}}^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>678</td>
<td>2.3</td>
<td>0.46</td>
</tr>
<tr>
<td>3.2</td>
<td>679</td>
<td>2.5</td>
<td>0.48</td>
</tr>
</tbody>
</table>

$^a$Turn-on voltage, $^b$Maximum external efficiency.

**Device 3.1** and **3.2** both showed low EQE roll off at high current densities (EQE at 200 mA cm$^{-2}$ = 83 % and 81 % of EqE$_{\text{max}}$, respectively). Whilst luminance is a commonly provided metric in the evaluation of OLED devices this is inappropriate for NIR emitting materials as a large proportion of the emission is beyond the visible region of the electro-magnetic spectrum. Similar devices were fabricated with L1300 as the host material (EML = 5 wt. % 3-BPh$_2$:95 wt. % L1300), the interlayer and low work-function cathode were comprised of CDT Ltd proprietary materials. These devices showed significantly reduced performance (EQE = 0.13 % at 50 mA cm$^{-2}$) relative to PF8-BT as host.
This decrease in efficiency is in agreement with the reduced solid state PLQY value observed when 3-BPh₂ is dispersed in L1300. The poor EQE values are attributed to poor energy/inefficient exciton transfer between host and guest due to a mismatch in frontier molecular orbital energy levels particularly that of the HOMO energies of the host/guest system (L1300 HOMO = 5.9 eV³², ΔE_HOMO >0.60 eV) presumably leading to poor hole injection onto the guest.

3.7 Conclusions

The directed C-H electrophilic borylative fusion methodology outlined in Chapter 2 was successfully extended to the ubiquitous fluorene donor unit. These compounds showed dramatically lowered band-gaps and the borylated compounds could be readily functionalised to install a variety of exocyclic aromatic substituents. Borylative fusion dramatically lowers the LUMO energy of these materials whilst changes to the energy of the HOMO are minimal with the choice of the exocyclic substituent facilitating fine tuning of the FMO energy levels. The borylated compounds with aryl substituents on boron were highly moisture stable and showed large bathochromic shifts in absorption (relative to the unborylated precursors) and far red/NIR fluorescence. The functionalised compounds were moderately emissive in solution with 3-BPh₂ demonstrating an excellent solid state PLQY for a deep red/NIR emitter of 32.9 %. A series of unoptimised OLED devices were fabricated which showed good maximum EQE values for solution processed far red/NIR fluorescent OLED devices.
3.8 Experimental

3.8.1 General Considerations

For general considerations see Chapter 2. Trimethyl(5-methylthiophen-2-yl)silane was synthesised by modified literature procedures.\textsuperscript{35} Solution emission spectra were recorded on a Varian Cary Eclipse Fluorimeter at room temperature in spectroscopic grade solvents, the solutions were excited at their relative absorbance maxima. Solid state fluorescence and absolute quantum yields were measured on spin coated films of polymer host / 5 wt. % emitter using a Hamamatsu C9920-02 Absolute quantum yield measurement system. The thin film lifetime measurements were performed in polymer host / 5 wt. % emitter using a Hamamatsu Picosecond Lifetime system C11200 using a Fianium UV power 343 nm fibre laser as excitation source. The OLED efficiency was measured using a Labsphere integrating sphere system (25 cm) equipped with CDS610 spectrometer. The J/V curves were measured on a Botest LIV system. Calculations were performed using the Gaussian09 suite of programmes.\textsuperscript{36} Structures 2'-BMe\textsubscript{2} and 3'-BMe\textsubscript{2} were pre-optimised by HF at 3-21G and structure 3'-BPh\textsubscript{2} was pre-optimised by DFT at B3LYP/6-31G level. These were followed by optimisation at the M06-2X/6-311G (d,p) level with inclusion of a PCM model for solvent correction (DCM).\textsuperscript{37} Structures were confirmed as minima by frequency analysis and the absence of imaginary frequencies.
3.8.2 Synthetic Procedures

Synthesis of 3

4,7-dibromobenzo[c][1,2,5]thiadiazole (1.36 g, 4.6 mmol), tri[tris(9,9'-dioctyl-9H-fluoren-2-yl)-stannane, (6.70 g, 10.2 mmol) and PdCl$_2$(PPh$_3$)$_2$ (0.33 g, 0.047 mmol) were mixed in dry THF (80 ml) under an nitrogen atmosphere and stirred for 36 h at 80 °C under reflux. The mixture was cooled to room temperature and then diluted with ethyl acetate (100 mL). The reaction mixture was then washed with brine (2 x 100 mL), water (2 x 200 mL) and then dried over MgSO$_4$. After evaporating the solvent, the residue was purified by column chromatography on silica gel [eluent: hexane:DCM (9:1)] to afford 3 as a yellow viscous oil which solidified upon standing. (Yield 1.73 g, 41%)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 7.96 (dd, $^3$J$_{HH}$ = 7.9, $^4$J$_{HH}$ = 1.6 Hz, 2 H$_a$), 7.88 (d, $^3$J$_{HH}$ = 1.3 Hz, 2 H$_b$), 7.90 (s, 2 H$_c$) 7.88 (d, $^3$J$_{HH}$ = 7.9 Hz, 2 H$_d$), 7.70 (dd, $^3$J$_{HH}$ = 6.3, $^4$J$_{HH}$ = 0.9 Hz, 2 H$_e$), 7.36 - 7.23 (m, 6 H), 1.86 - 2.05 (m, 8 H), 1.17 - 0.95 (m, 40 H), 0.78 - 0.62 (m, 20 H);

$^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$) $\delta$: aryl = 154.4, 151.3, 151.1, 141.3, 140.7, 136.2, 133.6, 128.1, 127.9, 127.2, 126.8, 123.9, 123.0, 119.9, 119.7, alkyl = 55.2, 40.3, 31.8, 30.1, 29.2, 29.2, 23.9, 22.6, 14.0;

MALDI-TOF: calc. for C$_{64}$H$_{84}$N$_2$S$^+$ = 913.4, found 913.4
Synthesis of 3-BCl₂

A 1M BCl₃ solution in DCM (0.15 mL, 0.12 mmol) was added to a bright yellow solution of 3 (0.078 g, 0.085 mmol) in DCM (3 mL) in a Schlenk flask. The reaction mixture was stirred for 16 hours under a dynamic flow of nitrogen (in a closed system some HCl remains in solution, thus borylation is reversible due to protodeboronation of 3-BCl₂ and an equivalent of Brønsted base is then required to drive borylation to completion by sequestering the protic by-product), where upon a colour change to dark blue was observed. The solvent and excess BCl₃ was removed under reduced pressure to yield 3-BCl₂ a dark blue residue. 3-BCl₂ was then used directly in subsequent reactions.

**¹H NMR** (500 MHz, CD₂Cl₂) δ = 8.61 (d, 3J_HH = 7.6 Hz, 1 Hₐ), 8.40 (s, 1 Hₖ), 8.16 (d, 3J_HH = 7.3 Hz, 1 Hₙ), 8.08 (s, 1 Hₖ), 8.06 - 7.99 (m, 2 H), 7.90 (d, 3J_HH = 6.9 Hz, 1 H), 7.96 - 7.88 (m, 2 H), 7.48 - 7.32 (m, 6 H), 2.21 - 1.99 (m, 8 H), 1.25 - 1.02 (m, 40 H), 0.81 (t, 3J_HH = 6.6 Hz, 6 H), 0.80 (t, 3J_HH = 6.6 Hz, 6 H), 0.74 (m, 8 H);

**¹³C{¹H} NMR** (126 MHz, CD₂Cl₂) δ: aryl = 155.4, 153.5, 153.4, 153.3, 153.3, 147.5, 145.2, 144.6, 142.3, 142.1, 135.7, 135.4, 132.9, 130.1, 129.9, 129.8, 129.6, 128.9, 128.9, 128.4, 126.9, 125.8, 125.1, 124.9, 122.5, 122.1, 122.0, 118.3, alkyl = 57.3, 57.1, 42.4, 42.1, 33.7, 32.0, 31.9, 31.1, 31.1, 25.9, 25.8, 24.5, 24.5, 15.7;

**¹¹B NMR** (160 MHz, CD₂Cl₂) δ = ~10.0;

Due to the sensitivity of 3-BCl₂ mass spec. was not obtainable
Synthesis of [3-BCl]⁺

[DMT-BCl₂][AlCl₄] (24 mg, 0.06 mmol) was added to a dark blue solution of 3-BCl₂ (60 mg, 0.06 mmol) in DCM. The solution turned a dark green colour and NMR spectroscopy showed a significant downfield shift in the NMR resonances relative to that of 3-BCl₂. The formation of DMT-BCl₃ adduct was also confirmed in solution by multinuclear NMR spectroscopy. These observations are consistent with the chloride abstraction from 3-BCl₂ to form [3-BCl]⁺.

^1H NMR (400 MHz, CH₂Cl₂) δ = 9.27 (d, ^3JHH = 7.8 Hz, 1 H), 8.81 (s, 1 H), 8.57 - 8.42 (m, 2 H), 8.20 - 8.12 (m, 2 H), 8.00 (d, ^3JHH = 7.8 Hz, 2 H), 7.85 (m, 1 H), 7.51 (m, 6 H), 2.31 - 2.02 (m, 8 H), 1.24 - 0.94 (m, 40 H), 0.79 (m, ^3JHH = 6.9 Hz, 20 H);
Synthesis of **3-BMe₂**

AlMe₃ 2M in heptanes (0.11 mL, 0.22 mmol) was added to a toluene (3 mL) solution of **3-BCl₂** (94 mg, 0.10 mmol). After 10 minutes the excess AlMe₃ was removed under reduced pressure. The reaction mixture was then filtered through base treated silica (5% NEt₃ in hexane) and the solvent was removed under reduced pressure to afford a dark purple residue.

**¹H NMR** (500 MHz, CH₂Cl₂) δ = 8.37 (d, ³J_HH = 7.9 Hz, 1 Hₐ), 8.10 - 7.98 (m, 4 H), 7.96 (s, 1 H), 7.90 (d, ³J_HH = 7.6 Hz, 1 H), 7.86 - 7.78 (m, 2 H), 7.46 - 7.30 (m, 6 H), 2.16 - 2.00 (m, 8 H), 1.04 - 1.24 (m, 40 H), 0.83 - 0.68 (m, 20 H), 0.47 (s, 6 Hₐ);

**¹³C{¹H} NMR** (101 MHz, CH₂Cl₂) δ: aryl = 154.3, 151.7, 151.5, 148.5, 148.3, 142.0, 141.9, 141.3, 140.6, 134.7, 131.9, 130.9, 129.4, 129.2, 128.0, 127.7, 127.3, 127.1, 126.9, 123.7, 123.2, 123.1, 123.1, 120.2, 120.0, 116.6, alkyl = 55.5, 54.9, 32.0, 30.3, 30.2, 29.4, 29.4, 24.2, 24.1, 22.8, 17.9, 14.0;

**¹¹B NMR** (128 MHz, CH₂Cl₂) δ = No ¹¹B NMR peak was observed at 20°C
Synthesis of 3-BPh$_2$ via ZnPh$_2$

Zn(Ph)$_2$ (110 mg, 0.5 mmol) was added to a DCM (5 mL) solution of 3-BCl$_2$ (212 mg, 0.213 mmol (made in-situ as described above)), the reaction was stirred for 3 hours and then the solution was filtered through silica gel and the solvent was removed under reduced pressure to afford 3-BPh$_2$ as a dark purple residue. (Yield 231 mg, 99 %)

via nBu$_3$SnPh

BCl$_3$ 1M in DCM (0.10 mL, 0.10 mmol) was added to a solution of 3 (50 mg, 0.055 mmol) in DCM (3 mL) and the solution was stirred overnight under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure. The resulting residue was dissolved in DCM (3 mL) and AlCl$_3$ (1 mg) was added to the solution. Tri$n$butylphenylstannane (40 mg, 0.121 mmol) was added to the solution and the reaction mixture was stirred and heated overnight at 60$^\circ$C. The solvent was then removed under reduced pressure and the residue was dissolved in hexane and was passed through a short plug of base treated silica gel (5 % NEt$_3$ in hexane) using hexane initially and then DCM:hexane (1:9) as eluent and only the purple coloured solution was retained. (Yield 53 mg, 89 %)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ = 8.52 (d, $^3$$J_{HH}$ = 7.8 Hz, 1 H$_a$), 8.18 (s, 1 H$_b$), 8.12 (d, $^3$$J_{HH}$ = 7.6 Hz, 1 H$_c$), 8.06 (d, $^4$$J_{HH}$ = 0.8 Hz 1 H$_d$), 8.01 (d, $^3$$J_{HH}$ = 7.9 Hz, 1 H$_e$), 7.95 (d, $^3$$J_{HH}$ = 8.0 Hz, 1 H$_f$), 7.95 (s, 1 H$_g$), 7.87 (m, 1 H), 7.76 - 7.68 (m, 1 H), 7.53 - 7.24 (m, 16 H), 2.27 - 2.03 (m, 8 H), 1.36 - 1.20 (m, 40 H), 1.00 - 0.76 (m, 20 H);

$^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$) $\delta$: aryl = 154.3, 153.0, 152.2, 151.3, 149.1, 147.8, 142.4, 140.7, 135.3, 133.6, 130.1, 128.9, 127.6, 127.4, 126.7, 126.1, 125.8, 123.5, 122.7, 120.6, 116.4, 110.5, alkyl = 54.8, 40.6, 31.7, 30.0, 29.2, 29.1, 23.9, 22.5, 14.0;

$^{11}$B NMR (128 MHz, CD$_2$Cl$_2$) $\delta$ = ~2.0 (br.);
Synthesis of 3-B(C₆F₅)₂

Zn(C₆F₅)₂ (97 mg, 0.24 mmol) was added to a toluene (5 mL) solution of 3-BCl₂ (110 mg, 0.11 mmol) made in-situ, the reaction mixture was stirred for 3 hours and then after the addition of ‘wet’ toluene (unpurified toluene used as received) to quench unreacted diarylzinc reagent the solution was purified via silica gel chromatography (5 % NEt₃ in hexane) [eluent : hexane:DCM (9:1)] to afford a dark purple residue. (Yield 131 mg, 94 %)

¹H NMR (400 MHz, CDCl₃) δ = 8.58 (d, ³J_HH = 8.1 Hz, 1 H), 8.21 - 8.07 (m, 2 H), 8.03 (s, 1 H), 7.94 (m, 2 H), 7.89 - 7.78 (m, 2 H), 7.74 (s, 1 H), 7.49 - 7.30 (m, 6 H), 2.11 (m, 8 H), 1.13 (m, 40 H), 0.89 - 0.66 (m, 20 H);

¹³C{¹H} NMR (101 MHz, CDCl₃) δ: aryl = 153.7, 151.5, 151.3, 151.3, 150.2, 147.8, 143.0, 142.4, 140.4, 140.2, 133.6, 133.0, 131.0, 128.1, 128.1, 127.9, 127.8, 127.7, 127.0, 126.9, 125.8, 124.3, 123.8, 123.0, 122.9, 120.4, 120.2, 120.1, 116.3, alkyl = 55.3, 55.0, 40.7, 40.3, 31.8, 30.1, 30.0, 29.2, 29.2, 29.2, 23.9, 23.8, 22.6, 22.6, 14.0, 14.0;

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ = -131.55 (dd, ³J_FF = 23.3, ⁴J_FF = 8.6 Hz, 4F), -156.65 (t, ³J_FF = 20.7 Hz, 2F), -162.62 (m, 4F);

¹¹B NMR (128 MHz, CDCl₃) δ = ~4.0 (br.);

MALDI-TOF: calc. for C₇₀H₈₅BF₅N₂S⁺ [M - C₆F₅]⁺ = 1090.3, found 1090.4
Synthesis of 3-BPin

A 1M BCl$_3$ solution in DCM (0.10 mL, 0.10 mmol) was added to a bright yellow solution of 3 (0.071 g, 0.078 mmol) in DCM (3 mL). The reaction mixture was stirred for 16 hours under a dynamic flow of nitrogen, where upon a colour change to dark blue was observed. The solvent and excess BCl$_3$ was removed under reduced pressure to yield a dark blue residue of 3-BCl$_2$. This residue was dissolved in 'wet' THF (5 mL) and stirred at room temperature for 16 hours where upon the solution had turned dark yellow. Pinacol (47 mg, 0.4 mmol) was then added and the reaction mixture was stirred for a further 16 hours. The solvent was removed under reduced pressure and the resulting residue was purified via base treated (5 % NEt$_3$ in hexane) preparative TLC plate using hexane as eluent. (Yield 35 mg, 43%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.31$ (s, 1 H$_a$), 8.12 - 8.06 (m, 1 H$_b$), 7.96 (s, 1 H$_c$), 7.94 - 7.83 (m, 3 H), 7.80 (d, $^3$$J_{HH} = 6.6$ Hz, 1 H$_d$), 7.75 (d, $^3$$J_{HH} = 7.2$ Hz, 1 H), 7.51 (s, 1 H$_e$), 7.45 - 7.30 (m, 6 H), 2.17 - 1.89 (m, 8 H), 1.25 - 1.05 (m, 40 H), 1.04 (s, 12 H$_f$), 0.82 (t, $^3$$J_{HH} = 7.0$ Hz, 20 H);

$^{13}$C ${^1}$H NMR (101 MHz, CDCl$_3$) $\delta$: aryl = 156.2, 153.7, 153.6, 151.3, 151.2, 150.9, 142.3, 141.2, 140.8, 140.7, 140.6, 136.6, 136.4, 133.3, 128.4, 128.1, 127.9, 127.3, 127.1, 126.9, 126.6, 124.7, 123.8, 123.0, 122.8, 120.2, 120.0, 119.7, alkyl = 83.3, 55.4, 55.2, 40.3, 31.9, 31.8, 30.1, 30.1, 29.3, 29.3, 29.2, 24.7, 23.9, 23.9, 22.7, 14.2;

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta = -30$ (b.);

MALDI-TOF: calc. for C$_{70}$H$_{83}$BO$_2$N$_2$S$^+$ [M + H]$^+ = 1039.7$, found 1039.7
Synthesis of 3-B(p-Tol)$_2$

BCl$_3$ 1M in DCM (0.25 mL, 0.25 mmol) was added to a solution of 3 (223 mg, 0.24 mmol) in DCM (10 mL) and the solution was stirred overnight under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure. The resulting residue was dissolved in toluene (10 mL) and Zincate A (240 mg, 0.26 mmol) was added to the stirred solution. After stirring for 3 hours the reaction mixture was filtered through a plug of base treated silica gel (5 % NEt$_3$ in hexane). The solvent was removed under reduced pressure and the resulting residue was purified via column chromatography on silica gel [eluent DCM:hexane (2:8)] to afford the desired product as a purple residue. (Yield 152 mg, 57 %)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 8.46 (d, $^3$J$_{HH}$ = 7.9 Hz, 1 H$_a$), 8.11 (s, 1 H$_b$), 8.06 (d, $^3$J$_{HH}$ = 7.6 Hz, 1 H$_c$), 7.99 (d, $^3$J$_{HH}$ = 1.3 Hz, 1 H$_d$), 7.96 (dd, $^3$J$_{HH}$ = 7.9, $^4$J$_{HH}$ = 1.6 Hz, 1 H$_e$), 7.91 (d, $^3$J$_{HH}$ = 7.9 Hz, 1 H$_f$), 7.88 (s, 1 H$_g$), 7.78 - 7.84 (m, 1 H), 7.68 - 7.65 (m, 1 H), 7.35 - 7.46 (m, 4 H), 7.26 - 7.34 (m, 6 H), 7.11 (d, $^3$J$_{HH}$ = 7.6 Hz, 4 H$_i$), 2.36 (s, 6 H$_j$), 2.16 - 1.99 (m, 8 H), 1.29 - 1.06 (m, 40 H), 0.95 - 0.71 (m, 20 H);

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$: aryl = 152.8, 151.3, 150.6, 150.3, 150.3, 147.9, 147.3, 141.0, 140.9, 140.1, 139.3, 134.3, 133.2, 132.8, 131.3, 129.7, 128.6, 128.2, 127.3, 126.7, 126.5, 126.1, 125.9, 125.6, 124.7, 122.7, 122.0, 121.7, 119.5, 119.0, 118.9, 115.2, alkyl = 54.2, 53.7, 39.6, 39.2, 30.8, 30.8, 29.1, 29.0, 28.2, 28.2, 22.9, 22.8, 22.6, 21.6, 20.1, 13.0, 13.0;

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ = No $^{11}$B NMR peak was observed at 20°C

MALDI-TOF: calc. for C$_{78}$H$_{97}$BN$_2$S$^+$ [M]$^+$ = 1104.8, found 1104.8
Synthesis of 3-B(MeT)$_2$

BCl$_3$ 1M in DCM (0.30 mL, 0.30 mmol) was added to a solution of 3 (95 mg, 0.10 mmol) in DCM (3 mL) and the solution was stirred overnight under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure. The resulting residue was dissolved in DCM (3 mL) and AlCl$_3$ (1 mg) was added to the solution. 2-methyl-5-trinbutylstannylthiophene (90 mg, 0.22 mmol) was added to the reaction mixture which was then stirred overnight. The solvent was then removed under reduced pressure, the residue was dissolved in hexane and was passed through a short plug of base treated silica gel (5 % NEt$_3$ in hexane) using hexane initially and then DCM:hexane (1:9) as eluent whilst only retaining the purple coloured solution. The solvent was removed under reduced pressure to afford 3-B(MeT)$_2$ as a purple residue. (Yield 78 mg, 67%)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$: = 8.50 (d, $^3$$J_{HH} = 7.7$ Hz, 1 H$_a$), 8.15 (s, 1 H$_b$), 8.09 (d, $^3$$J_{HH} = 7.6$ Hz, 1 H$_c$), 8.04 - 7.96 (m, 3 H), 7.90 (d, $^3$$J_{HH} = 7.9$ Hz, 1 H$_d$), 7.82 (m, 1 H), 7.76 - 7.69 (m, 1 H), 7.48 - 7.27 (m, 6 H), 6.82 (d, $^3$$J_{HH} = 3.3$ Hz, 2 H$_e$), 6.69 (d, $^3$$J_{HH} = 3.1$ Hz, 2 H$_f$), 2.44 (s, 6 H$_g$), 2.20 - 2.01 (m, 8 H), 1.27 - 1.04 (m, 40 H), 0.89 - 0.67 (m, 20 H);

$^{13}$C{$_^1$}H NMR (101 MHz, CD$_2$Cl$_2$) $\delta$: aryl = 155.1(br.), 154.4, 152.0, 151.9, 150.8 (br.), 150.1, 148.0, 142.5, 142.5, 142.2, 141.4, 140.9, 134.7, 133.2, 131.3, 131.2, 130.0, 128.7, 128.4, 128.2, 127.9, 127.5, 127.3, 126.3, 126.1, 125.2, 124.3, 123.6, 123.5, 120.9, 120.6, 120.5, 117.0, alkyl = 55.8, 55.5, 41.1, 40.7, 32.4, 32.4, 30.6, 30.6, 29.8, 29.8, 29.8, 24.5, 24.4, 23.2, 15.6, 14.4;

$^{11}$B NMR (128 MHz, CD$_2$Cl$_2$) $\delta = -2$ (br.);

HRMS (APCI) Calculated for C$_{74}$H$_{94}$BN$_2$S$_3$ $^+$ [M+H]$^+$ = 1117.6667, found 1117.6664
Synthesis of $3\text{-B(MeT)}(\text{C}_8\text{F}_5)$

AlCl$_3$ (1 mg) was added to a solution of $3\text{-BCl}_2$ (50 mg, 0.50 mmol) and trimethyl(5-methylthiophen-2-yl)silane (20 µL, 0.10 mmol) in DCM (0.70 mL). After inverting for 14 hours at room temperature NMR investigation showed only one arylation had occurred. The reaction mixture was then evaporated to dryness and the residue was dissolved in DCM (0.70 mL). Zn(C$_6$F$_5$)$_2$ (24 mg, 0.06 mmol) was added to the reaction mixture. After stirring for 3 hours the reaction mixture was filtered through a plug of base treated silica gel (5 % NEt$_3$ in hexane). The reaction mixture was then purified via column chromatography on base treated silica gel (5 % NEt$_3$ in hexane) [eluent DCM:hexane (1:9)] to afford a dark purple residue. (Yield 48 mg, 81 %)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta = 8.51$ (d, $^3J_{HH} = 7.7$ Hz, 1 H$_a$), 8.13 (s, 1 H$_b$), 8.10 (d, $^3J_{HH} = 7.6$ Hz, 1 H$_c$), 8.07 (s, 1 H$_d$), 8.01 (s, 1 H$_e$), 7.98 (d, $^3J_{HH} = 7.9$ Hz, 1 H$_f$), 7.90 (d, $^3J_{HH} = 7.8$ Hz, 1 H$_g$), 7.85 - 7.77 (m, 1 H), 7.74 (m, 1 H), 7.47 - 7.27 (m, 6 H), 6.78 (d, $^3J_{HH} = 3.2$ Hz, 1 H$_a$), 6.70 - 6.64 (m, 1 H), 2.44 (s, 3 H$_j$), 2.20 - 1.94 (m, 8 H), 1.26 - 1.01 (m, 40 H), 0.86 - 0.58 (m, 20 H);

$^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$) $\delta$: aryl = 154.4, 152.0, 151.9, 150.7, 148.1, 142.9, 142.7, 142.5, 141.2, 140.9, 134.6, 133.4, 131.3, 130.9, 130.1, 128.5, 128.5, 128.2, 128.1, 127.5, 127.4, 126.6, 125.8, 125.5, 124.4, 123.6, 123.6, 120.8, 120.6, 120.5, 117.2, alkyl = 55.9, 55.6, 41.1, 40.9, 40.8, 32.4, 32.4, 32.3, 30.6, 30.6, 30.6, 29.8, 29.8, 24.6, 24.6, 24.5, 24.5, 23.2, 23.1, 15.6, 14.4, 14.4;

$^{19}$F($^1$H) NMR (376 MHz, CD$_2$Cl$_2$) $\delta = -131.74$ (dd, $^3J_{FF} = 24.8$, $^4J_{FF} = 9.0$ Hz, 2 F), -158.63 (t, $^3J_{FF} = 20.7$ Hz, 1 F), -164.05 (m, 2 F);

$^{11}$B NMR (128 MHz, CD$_2$Cl$_2$) $\delta = -3$ (br.);

HRMS (APCI) Calculated for $C_{75}H_{89}BN_2S_2^+$ [M+H]$^+$ = 1187.6475, found 1187.6471
3.8.3 OLED Device Fabrication

Light-emitting diodes were prepared on glass/ITO substrates, which were cleaned using polar solvents. They were treated with oxygen plasma prior to the deposition of the organic layers. All organic layers were spin coated from toluene. The Plexcore OC® AQ1200 layer was annealed at 170°C for 15 mins, the PF8-TFB layer was annealed at 180°C for 60 mins and the emissive layer was annealed at 150°C for 10 mins. All annealing was conducted under an inert atmosphere. The top barium cathode was deposited via vacuum deposition.

3.9 References


Chapter 4

Cross-coupling Reactions of Borylated Fluorene-Benzothiadiazole Units
4.1 Introduction

One of the main advantages of organic semiconducting materials based on the alternating donor-acceptor (D-A) system is the large degree of control over the electronic and optical properties that is achievable through structural modification.\(^1\) As the highest occupied molecular orbital (HOMO) energy level of the material is mainly dependant on the donor unit and the lowest unoccupied molecular orbital (LUMO) energy level is mainly dependant on the acceptor unit, judicious selection of these units can facilitate the creation of materials with finely tuned frontier molecular orbital (FMO) energy levels to realise materials with tailored optical and electronic characteristics.\(^2,3\) For organic light emitting diode (OLED) and photovoltaic applications the HOMO-LUMO energy gap (band-gap) is a critical parameter as it determines the colour of the emitted light or range of the terrestrial spectrum absorbed.\(^4,5\) To construct D-A conjugated materials with a precisely defined molecular composition, the ability to effectively couple two \(sp^2\) hybridised carbon atoms of distinct aromatic units is of paramount importance.\(^6-9\) Transition metal catalysed cross-coupling is the most powerful and prevalent method of \(Csp^2-Csp^2\) single bond formation and has yielded a myriad of donor-acceptor conjugated materials with interminable structural variations (Figure 4.1).\(^6-13\) Stille and Suzuki-Miyaura cross-coupling reactions are the most utilised synthetic methodologies to achieve \(Csp^2-Csp^2\) cross-coupling due to their high versatility and reasonable functional group tolerance, although direct arylation, Negishi and other cross-coupling methods are applicable in certain cases.\(^14-17\)
The highly versatile and relatively facile ability to couple selected donor and acceptor units allows the effects that the respective units have on photophysical properties of the resulting materials to be explored through a modular approach. Examination of the materials produced through this modular approach reveals a high degree of tunability in photophysical properties. To illustrate, whilst keeping the acceptor moiety unchanged (as benzothiadiazole) the attachment of donor substituents of an increasing π-electron rich character results in an increase in the HOMO energy level (Figure 4.2). This results in a decrease in the optical band-gap and a concomitant red shift in emission which facilitates tuning of the emission from blue to red (Figure 4.2).
This chapter describes an investigation into the stability of bromine functionalised borylated compounds toward palladium catalysed cross-coupling reactions (Stille, Suzuki-Miyaura and Negishi) with the intention of incorporating discrete aromatic units into the conjugated backbone (Scheme 4.1). This will facilitate further modulation of the FMO energy levels and concomitantly realise emission further into the near infra-red (NIR) region of the electromagnetic spectrum than achieved in Chapter 3.

Figure 4.2: Emission wavelength tuning of benzothiadiazole based donor-acceptor-donor small molecules (Images modified from Chem. Mater. 2005, 17, 5238-5241).
4.2 Synthesis

4.2.1 Borylation of Bromine Functionalised Benzothiadiazole-Fluorene Unit

4Br was borylated to produce 4Br-BCl₂ (not isolated) using a similar procedure to that of compound 3-BCl₂ (see Chapter 3), although an excess of BCl₃ (3 eq.) and extended reaction times are necessary. The extended reaction time is due to competitive and reversible coordination (the steric bulk of the peripheral bromine atom ensures this coordination is reversible) of BCl₃ to N² (4Br-BCl₃ (2)), which significantly reduces the nucleophilicity of the remaining nitrogen N¹ (Scheme 4.2). N¹ is therefore prevented from coordinating and directing borylation at position C³ when BCl₃ is bound to N². The competitive binding of BCl₃ between the two Lewis basic sites (N¹ and N³) leads to the formation of 4Br-BCl₃ (1) at which point borylation can occur through the loss of HCl which is then removed from solution under the dynamic flow of nitrogen. BCl₃ is volatile (bp = 12.6°C) and is removed from the reaction mixture along with HCl gas under the dynamic flow of nitrogen so a large excess is required to maintain a sufficient solution concentration over the required reaction time to drive the reaction to completion.

Scheme 4.1: Synthetic overview of post-borylation cross-coupling reactions.
4.2.2 Functionalisation of Borylated Bromine Functionalised Benzothiadiazole-Fluorene Unit

Compound 4Br-BCl₂ can be functionalised by the same methodologies discussed in Chapters 2 and 3. The addition of commercially available organozinc reagents ZnPh₂ and Zn(C₆F₅)₂ to 4Br-BCl₂ resulted in the formation of compounds 4Br-BPh₂ and 4Br-B(C₆F₅)₂, respectively, in good to excellent isolated yields (72 and 96 % respectively).
4.2.3 Direct Borylation of Unsymmetrical 4,7-substituted Benzothiadiazole

The ability to perform cross-coupling on the post borylated bromine functionalised products $4\text{Br-BPh}_2$ and $4\text{Br-B(C}_6\text{F}_5)_2$ is essential in achieving $D^1$-$A$-$D^2$ materials (where $D^1$ and $D^2$ are discrete donor units) with complete selectivity over the position of borylation. Application of the borylation methodology to an unsymmetrically 4,7-substituted benzothiadiazole (MeT-4) results in a mixture of products (Scheme 4.4). Exposure of MeT-4 to BCl$_3$ followed by Zn(C$_6$F$_5$)$_2$ resulted in ~90% borylation of the 2-methyl thiophene unit (MeT-4*-B(C$_6$F$_5$)$_2$) and ~10% borylation of the fluorene unit (MeT-4-B(C$_6$F$_5$)$_2$) (by $^1$H and $^{19}$F{$^1$H} NMR spectroscopy). This is due to the 2-methylthiophene unit being much more electron rich than the fluorene unit and the higher nucleophilicity results in a significantly faster rate of borylation (the lower aromatic stabilisation energy of thiophene may also effect the relative rates of borylation). Due to their extremely similar structures MeT-4-B(C$_6$F$_5$)$_2$ and MeT-4*-B(C$_6$F$_5$)$_2$ were inseparable by chromatography in our hands.

![Scheme 4.4](image)

Scheme 4.4: Direct borylation of unsymmetrically substituted benzothiadiazole $D^1$-$A$-$D^2$ system.

4.2.4 Cross-Coupling Reactions

The $4\text{Br-BAr}_2$ compounds proved stable to the Stille and Negishi cross-coupling reaction conditions explored herein. This represents a method to selectively synthesise borylated $D^1$-$A$-$D^2$ system, including examples that are borylated on the least nucleophilic $\pi$-system, i.e. The major product observed in the direct borylation of unsymmetrical $D^1$-$A$-$D^2$ systems
This facilitated the synthesis of borylated fluorene based D^1-A-D^2 systems in which the peripheral donor unit can be a variety of different conjugated aromatic units. As the nature of the peripheral donor units can have a substantial effect on the FMO energy levels, this represents an additional methodology to achieve further tuning of the electronic band structures and emission wavelengths of the borylated compounds.18-21

4.2.4.1 Stille Cross-Coupling

Stille cross-coupling reactions involving 4Br-BPh2 proceeded with excellent yields (81-97 %) (Scheme 4.5). Cross-coupling of 4Br-BPh2 with 2-methyl-5-(tri-n-butylstannane)thiophene resulted in MeT-4-BPh2. This gives an unsymmetrically substituted benzothiadiazole exclusively borylated at the least nucleophilic donor unit (Scheme 4.4). The presence of the more electron rich thiophene unit should result in an increased HOMO energy level (relative to 3-BPh2) and lower band-gap with a concomitant red shift in emission.20

Scheme 4.5: Stille cross-coupling reactions of 4Br-BPh2.
This strategy can be further extended by the reaction of 4Br-BPh₂ with an aromatic unit with two cross-coupling functionalities such as 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene. This coupling links two of the borylated F8-BT units by a sterically unencumbered π-conjugated spacer (thieno[3,2-b]thiophene (TT)) to give TT-(4-BPh₂)₂ (Scheme 4.5). The advantages of the incorporation of a sterically unhindered π-conjugated spacer unit is that it can maintain good planarity between the two conjugated borylated aromatic frameworks extending the effective conjugation length. This strategy is highly exploited in the engineering of π-conjugated semi-conducting materials and typically results in a decrease in band-gap and redshifted emission. TT-(4-BPh₂)₂ did not prove amenable to crystallisation but crystals of its pentafluorophenyl boron substituted counterpart (made via an analogous approach) TT-(4-B(C₆F₅)₂)₂ were accessible (Scheme 4.6 and Figure 4.3).

Scheme 4.6: Stille cross-coupling reactions of 4Br-B(C₆F₅)₂.
The cross-coupling of 4Br-B(C₆F₅)₂ with 2,5-bis(tri^n-butylstannyl) thieno[3,2-b]thiophene resulted in the isolation of TT-(4-B(C₆F₅)₂)₂ in significantly poorer yields than those isolated for TT-(4-BPh₂)₂ which used a trimethyl substituted stannane (Scheme 4.6), this is due to the increased propensity of tri^n-butylstannyl substituted thieno[3,2-b]thiophene to undergo destannylation (protodestannylation) compared to trimethylstannyl substituted thieno[3,2-b]thiophene. These factors lead to a reduction in the yield of the doubly cross-coupled product and the isolation of the singularly cross-coupled product TT-4-B(C₆F₅)₂ from the reaction mixture as a significant by-product. The solid state structures of TT-(4-B(C₆F₅)₂)₂ and TT-4-B(C₆F₅)₂ demonstrated high co-planarity between the borylated unit and thieno[3,2-b]thiophene (Figure 4.3, angles between aromatic planes of 9.17° and 1.87°, respectively).

Figure 4.3: Solid state structures of TT-(4-B(C₆F₅)₂)₂ (left) and TT-4-B(C₆F₅)₂ (right), thermal ellipsoids at the 50 % probability level (hydrogens and octyl chains are omitted for clarity).

4.2.4.2 Negishi Cross-Coupling

Whilst cross coupling reactions using stannanes are highly prominent in the synthesis of conjugated systems due to their broad scope and reliability, several drawbacks exist such as the toxicity of organostannane compounds.¹⁴-¹⁶ From this point of view it may be preferential to employ a Negishi type cross-coupling that utilises non-toxic and highly nucleophilic
The impressive development of more efficient palladium catalysts for the cross-couplings of small molecules and the application of electron-rich ligands enables Negishi cross-coupling reactions to proceed involving otherwise inactive electrophiles with low catalyst loadings levels and under mild conditions.\textsuperscript{16}

Scheme 4.7: Synthesis of \textit{p-Tol-4-BPh}_2 by Negishi cross-coupling.

The application of a Negishi cross-coupling to \textit{4Br-BPh}_2 using a previously reported \textit{Zincate A}\textsuperscript{25} as the transmetalation reagent results in the formation of \textit{p-Tol-4-BPh}_2 in an excellent isolated yield (98 %) with the workup reduced to a simple filtration through silica gel (Scheme 4.7).

4.2.4.3 Suzuki-Miyaura Cross-Coupling

Suzuki-Miyaura cross-coupling is often preferable to either Stille or Negishi cross-coupling due to its many advantageous features which include air-stability of the transmetalation reagent, mild aqueous reaction conditions, high functional group tolerance and low toxicity of reaction by-products.\textsuperscript{14} In addition to these factors advances in direct arene borylation chemistry facilitates the generation of boronic esters required for Suzuki-Miyaura cross-coupling through direct methods precluding the need for halogenation and/or lithiation steps which are often a requirement in the
synthesis of stannane and organozinc compounds. \textsuperscript{26} The attempted synthesis of compound \textit{p-Tol-4-B(C_6F_5)_2} \textit{via} conventional Suzuki-Miyaura cross-coupling reaction conditions proved unsuccessful. To determine why this procedure was unsuccessful \(4\text{Br-B(C}_6\text{F}_5\text{)_2}\) was refluxed in etherate solvent in the presence of aqueous \(\text{K}_2\text{CO}_3\) or \(\text{CsF}\), which resulted in decomposition of \(4\text{Br-B(C}_6\text{F}_5\text{)_2}\) within 15 minutes. This was easily identifiable by the observed colour change from dark purple to yellow which implies proto-deborylation (confirmed by \(^1\text{H NMR}\) spectroscopy). This demonstrates the instability of the borylated materials to heating in the presence of a strong base or fluoride source. \(4\text{Br-B(C}_6\text{F}_5\text{)_2}\) shows some stability to ether/H\(_2\)O mixes in the absence of a strong base/fluoride source as 50 % of the starting material could be recovered after refluxing in dioxane with 22 equivalents of water for 16 hours whereas no starting material is recovered on heating in the presence of \(\text{K}_2\text{CO}_3\) or \(\text{CsF}\) (Scheme 4.8) under related conditions. This suggests that \(\text{K}_2\text{CO}_3\) or \(\text{CsF}\) in the presence of water leads to protodeborylation (presumably from reaction of water with \([\text{ArylB(Y)(C}_6\text{F}_5\text{)_2}]^+\), \(Y = \text{OH or F}\)) and that the unsuccessful cross-coupling is not due to the decomposition of \(4\text{Br-B(C}_6\text{F}_5\text{)_2}\) at high temperatures in the presence of protic species (H\(_2\)O). The observed decomposition of boryl group containing electrophiles under conventional Suzuki-Miyaura cross-coupling conditions is not unprecedented. \textsuperscript{27}
Scheme 4.8: Unsuccessful Suzuki-Miyaura cross-coupling reactions involving $4\text{Br-BPh}_2$.

The successful Suzuki-Miyaura cross-coupling of $4\text{Br-BPh}_2$ was achieved under milder conditions through the utilisation of a more active catalytic system. Hu et al.\textsuperscript{28} showed that polyfluorenes with high molecular weights and low polydispersity could be synthesised using Suzuki-Miyaura cross-coupling polymerisation with the highly active catalyst Pd(P$\text{tBu}_3$)$_2$ at room temperature and short reaction times (30 minutes). A similar methodology was applied to the cross-coupling of $4\text{Br-BPh}_2$ with F8(Bpin)$_2$ to synthesise F8-(4-BPh)$_2$ with an excellent yield of 84% (Scheme 4.9). This cross-coupling reaction gives access to F8-(4-BPh)$_2$ which represents an alternating F8-BT oligomer which is borylated purely on the peripheral fluorene units. This complete regio-selectivity of borylation would not be accessible through the direct borylation of its parent oligomer, F8-BT-F8-BT-F8, as a mixture of products would likely be formed due to some degree of borylation on the central F8 unit. This methodology was also used to synthesis TPA-4-BPh$_2$ (Scheme 4.9, Figure 4.4).
Scheme 4.9: Successful Suzuki-Miyaura cross-coupling of 4Br-BPh₂.

Figure 4.4: Solid state structure of TPA-4-BPh₂, thermal ellipsoids at the 50 % probability level (hydrogens and octyl chains are omitted for clarity).
4.3 Photophysical Properties

4.3.1 Solution Ultraviolet-Visible Absorbance and Emission Properties

4.3.1.1 Phenyl Substituted Borylated Compounds

The photophysical characteristics of MeT-4-BPh₂, TT-(4-BPh₂)₂ and F8-(4-BPh₂)₂ were investigated by solution ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectroscopy in toluene (1 x 10⁻⁵ M).

![Absorption and emission properties of MeT-4-BPh₂, TT-(4-BPh₂)₂, F8-(4-BPh₂)₂, TPA-4-BPh₂ and 3-BPh₂](image)

Figure 4.5: Absorption and emission properties of MeT-4-BPh₂, TT-(4-BPh₂)₂, F8-(4-BPh₂)₂, TPA-4-BPh₂ and 3-BPh₂ (1 x 10⁻⁵ M solutions in toluene). Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

Table 4.1: Comparison of photophysical properties of MeT-4-BPh₂, TT-(4-BPh₂)₂, F8-(4-BPh₂)₂, TPA-4-BPh₂ and 3-BPh₂ (1 x 10⁻⁵ M toluene solutions).

<table>
<thead>
<tr>
<th>Compound</th>
<th>λₘₐₓ(abs) (nm)ᵃ</th>
<th>ε (M⁻¹ cm⁻¹)</th>
<th>Optical Band-Gap (eV)ᵇ</th>
<th>λₘₐₓ(em) (nm)ᵃ</th>
<th>Stokes shift (nm)</th>
<th>Φᵣ %ᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeT-4-BPh₂</td>
<td>583</td>
<td>12400</td>
<td>1.83</td>
<td>721</td>
<td>137</td>
<td>1.8</td>
</tr>
<tr>
<td>TT-(4-BPh₂)₂</td>
<td>661</td>
<td>44500</td>
<td>1.68</td>
<td>765</td>
<td>104</td>
<td>1.5</td>
</tr>
<tr>
<td>F8-(4-BPh₂)₂</td>
<td>573</td>
<td>34400</td>
<td>1.91</td>
<td>704</td>
<td>131</td>
<td>12.6</td>
</tr>
<tr>
<td>TPA-4-BPh₂</td>
<td>584</td>
<td>13900</td>
<td>1.81</td>
<td>753</td>
<td>169</td>
<td>0.9</td>
</tr>
<tr>
<td>3-BPh₂</td>
<td>559</td>
<td>12400</td>
<td>1.92</td>
<td>702</td>
<td>143</td>
<td>10.0</td>
</tr>
</tbody>
</table>

ᵃ1x 10⁻⁵ M toluene solutions. ᵇBand-gap estimated from onset of absorption. ᵇRelative fluorescence quantum yield, estimated by using cresyl violet as standard (Φᵣ = 54 % in methanol)²⁹, estimated error ± 20 %. Fluorescence spectra were measured by exciting the solutions at their absorption maxima.
The absorption bands located at the higher energy part of the spectrum (350-450 nm) are attributed to localised \( \pi-\pi^* \) transitions whereas the longer wavelength absorption bands are attributed to the internal charge transfer (ICT) from the donor unit to the BT unit\(^{30}\) which is consistent with the D-A character of these compounds.\(^{31}\) The compounds that feature \( \pi- \) conjugated bridges \((TT-(4-BPh)_2)\) and \( F8-(4-BPh)_2 \) showed significantly increased extinction coefficients due to the fact they contain multiple chromophores (donor-acceptor units). Compounds \(\text{MeT-4-BPh}_2\) and \(\text{TPA-4-BPh}_2\) showed a red shifted \( \lambda_{\text{max}} \) \(\text{abs}\) (24 and 25 nm, respectively) and \( \lambda_{\text{max}} \) \(\text{em}\) (19 and 32 nm, respectively) relative to the fluorene substituted analogue \(\text{(3-BPh)}_2\). This is attributed to an increase in the HOMO energy level achieved by replacement of the moderately \( \pi \)-electron donating fluorene unit with the more electron rich methyl thiophene/triphenylamine unit which lowers the optical band-gap and concomitantly shifts the emission to a longer wavelength.

A substantial decrease in the optical band-gap and red shift in the emission relative to \(\text{MeT-4-BPh}_2\) is observed upon linking two of the borylated F8-BT units \(\text{via}\) a thieno[3,2-\( b \)]thiophene unit \((TT-(4-BPh)_2)\). The delocalisation of \( \pi \)-electron density from the thieno[3,2-\( b \)]thiophene unit into the conjugated backbone should be less favourable compared to 2-methylthiophene due to the larger resonance stabilisation energy and consequently a higher energy of the quinoidal form of thieno[3,2-\( b \)]thiophene.\(^{32}\)

The large decrease in optical band-gap is therefore attributed to a substantial increase in the HOMO energy level due to the thieno[3,2-\( b \)]thiophene \( \pi \)-electron bridge maintaining good planarity and increasing the effective conjugation length of the HOMO by facilitating \( \pi \)-orbital overlap between the borylated F8-BT units. This is consistent with literature reports\(^{23}\) of using thieno[3,2-\( b \)]thiophene as a \( \pi \)-electron bridge unit and these effects are further clarified through cyclic voltammetry measurements \((\text{vida infra})\). On the other hand, linking the borylated F8-BT units with a fluorene unit \((\text{F8-(4-BPh)}_2)\) leads to a small red shift in the \( \lambda_{\text{max}} \) \(\text{abs}\) value (14 nm) relative to \(3\)-\(\text{BPh}_2\) but demonstrates an essentially identical optical band-gap. The emission maximum of \(\text{F8-(4-BPh)}_2\) is
substantially blue shifted (61 nm) relative to TT-(4-BPh₂)₂ which is attributed to a reduced influence on the HOMO energy level as the fluorene unit is less electron rich compared to thieno[3,2-\(b\)]thiophene in addition to the increased torsion angle between the linking F8 unit and the borylated F8-BT units leading to a reduction in effective conjugation length. The toluene solution PLQY values of the longer wavelength emitting systems (MeT-4-BPh₂, TT-(4-BPh₂)₂ and TPA-4-BPh₂) are relatively low (<2 %) compared to the related fluorene substituted systems (≥10 %) (3-BPh₂ and F8-(4-BPh₂)₂). This could be due to a number of factors such as the energy-gap law\(^3\),\(^4\) in which the quantum yield of a fluorophore decreases with a reduction in band-gap.

4.3.1.2 Pentafluorophenyl Substituted Borylated Compounds

The photophysical characteristics of TT-4-(C₆F₅)₂ and TT-(4-(C₆F₅)₂)₂ were investigated by solution ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectroscopy in toluene (1 x 10⁻⁵ M).

Figure 4.6: Absorption and emission properties of 3-B(C₆F₅)₂, TT-4-B(C₆F₅)₂ and TT-(4-B(C₆F₅)₂)₂ (1x 10⁻⁵ M solutions in toluene). Fluorescence spectra were measured by exciting the solutions at their absorption maxima.
Table 4.2: Comparison of photophysical properties of 3-B(C₆F₅)₂, TT-4-B(C₆F₅)₂ and TT-(4-B(C₆F₅)₂)₂ (1x 10⁻⁵ M toluene solutions).

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{max}^{abs} (nm)</th>
<th>ε (M⁻¹ cm⁻¹)</th>
<th>Optical Band-Gap (eV)</th>
<th>λ_{max}^{em} (nm)</th>
<th>Stokes shift (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-B(C₆F₅)₂</td>
<td>579</td>
<td>9600</td>
<td>1.83</td>
<td>730</td>
<td>151</td>
</tr>
<tr>
<td>TT-4-B(C₆F₅)₂</td>
<td>619</td>
<td>15500</td>
<td>1.70</td>
<td>777</td>
<td>158</td>
</tr>
<tr>
<td>TT-(4-B(C₆F₅)₂)₂</td>
<td>685</td>
<td>34300</td>
<td>1.59</td>
<td>805</td>
<td>120</td>
</tr>
</tbody>
</table>

*aBand-gap estimated from onset of absorption. Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

The compounds furnished with pentafluorophenyl substituents on the boron atom displayed similar photophysical property trends to those of the phenyl substituted compounds, although significantly reduced emission intensities were observed. Compound TT-4-B(C₆F₅)₂ showed a red shifted λ_{max}^{abs} (40 nm) and λ_{max}^{em} (44 nm) relative to the fluorene substituted analogue (3-B(C₆F₅)₂). This is attributed to an increase in the HOMO energy level achieved by replacement of the moderately π-electron donating fluorene unit with the more electron rich thieno[3,2-b]thiophene unit which lowers the optical band-gap and concomitantly shifts the emission to a longer wavelength. A substantial decrease in the optical band-gap (by 0.11 eV) and red shift in the emission (by 28 nm) relative to TT-4-B(C₆F₅)₂ is observed upon linking two of the pentafluorophenyl substituted borylated F8-BT units via a thieno[3,2-b]thiophene unit (TT-(4-B(C₆F₅)₂)₂). This decrease in band-gap is attributed to the thieno[3,2-b]thiophene π-electron bridge maintaining good planarity and increasing the effective conjugation length of the FMOs by facilitating π-orbital overlap between the borylated F8-BT units. These effects are further clarified through cyclic voltammetry measurements (*vida infra*).
4.3.2 Solid State Emission Properties

The solid state emission properties of the longer wavelength emitting materials MeT-4-BPh₂, TT-(4-BPh₂)₂, F8-(4-BPh₂)₂ and TPA-4-BPh₂ were investigated by preparing thin films from a 5 wt. % mixture of the compounds dispersed in PF8-BT. These compounds showed low solution state quantum yields in toluene but as demonstrated in Chapter 3 the related 3-BPh₂ compound showed enhanced quantum yield values in the solid state when dispersed in PF8-BT (>3 times increase) (Tables 4.1 and 4.3).

![Solid state emission properties](image)

Figure 4.7: Solid state emission properties of MeT-4-BPh₂, TT-(4-BPh₂)₂, F8-(4-BPh₂)₂, TPA-4-BPh₂ and 3-BPh₂ (thin films comprising of a 5 wt. % of the relative guest compound dispersed in PF8-BT). Excited at 468 nm.
Table 4.3: Comparison of solid state emission properties of MeT-4-BPh$_2$, TT-(4-BPh)$_2$, F8-(4-BPh)$_2$, TPA-4-BPh$_2$ and 3-BPh$_2$ (thin films comprising of a 5 wt. % of the relative guest compound dispersed in PF8-BT).

<table>
<thead>
<tr>
<th>Film</th>
<th>Transmittance (A.U)</th>
<th>$\lambda_{\text{max,em}}$ (nm)</th>
<th>$\Phi_f$ %$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF8-BT:MeT-4-BPh$_2$ (95:5 wt. %)$^a$</td>
<td>0.30</td>
<td>737</td>
<td>8.8 (9.2)</td>
</tr>
<tr>
<td>PF8-BT:TT-(4-BPh)$_2$ (95:5 wt. %)$^a$</td>
<td>0.31</td>
<td>789</td>
<td>4.4 (4.7)</td>
</tr>
<tr>
<td>PF8-BT:F8-(4-BPh)$_2$ (95:5 wt. %)$^a$</td>
<td>0.35</td>
<td>702</td>
<td>37.4 (37.4)</td>
</tr>
<tr>
<td>PF8-BT:TPA-4-BPh$_2$ (95:5 wt. %)$^a$</td>
<td>0.34</td>
<td>749</td>
<td>8.9 (9.7)</td>
</tr>
<tr>
<td>PF8-BT:3-BPh$_2$ (95:5 wt. %)$^a$</td>
<td>0.36</td>
<td>696</td>
<td>32.9 (32.9)</td>
</tr>
</tbody>
</table>

$^a$Excited at 468 nm. $^b$Absolute values, determined with an integrating sphere, estimated error $\pm$ 4.5 %, $\Phi_f$ excluding emission from the PF8-BT host centred at ~550 nm (total PLQY in parentheses).

Unlike 3-BPh$_2$ and F8-(4-BPh)$_2$ the complete quenching of the host emission was not observed upon dispersing MeT-4-BPh$_2$, TT-(4-BPh)$_2$ and TPA-4-BPh$_2$ in PF8-BT. This incomplete energy transfer could be due to the PL of the PF8-BT host being less well matched with the red shifted ICT absorption band of MeT-4-BPh$_2$, TT-(4-BPh)$_2$ and TPA-4-BPh$_2$ resulting in less efficient Förster energy transfer to the guest compounds.$^{35}$ The solid state emission of MeT-4-BPh$_2$ and TT-(4-BPh)$_2$ are red shifted (16 and 24 nm, respectively) when distributed in the polymer films relative to that observed in dilute toluene solutions. Curiously, this is in contrast to what is observed for compounds 3-BPh$_2$ and F8-(4-BPh)$_2$ and TPA-4-BPh$_2$ in which a slight blue shift in emission is observed (by 6, 2 and 4 nm, respectively). Compounds F8-(4-BPh)$_2$ showed a slight red shift in emission compared to 3-BPh$_2$ ($\Delta = 6$ nm) with an outstanding (for solid state emission $>700$ nm) PLQY of 37.4 %. Compounds MeT-4-BPh$_2$, TT-(4-BPh)$_2$ and TPA-4-BPh$_2$ display solid state PLQY values of 8.8 %, 4.4 % and 8.9 % respectively (excluding emission from the PF8-BT host) which are reasonably high for solid state emission in the NIR regions of the electromagnetic spectrum.
4.4 Computational Analysis

Computational analysis was performed at the M06-2x/6-311G (d,p) level with PCM solvation (DCM) for model compounds of **3-BPh₂**, **MeT-4-BPh₂** and **TPA-4-BPh₂** (termed 3'-BPh₂, MeT-4'-BPh₂ and TPA-4'-BPh₂ respectively) where the C₈H₁₇ chains of the F8 unit were replaced by methyl (termed F1) to reduce calculation time. The ground state optimized geometry and the relevant HOMO and LUMO energy levels together with the molecular orbital contour plots for 3'-BPh₂, MeT-4'-BPh₂ and TPA-4'-BPh₂ are depicted in Figure 4.8.

![Molecular orbital energy levels and molecular orbital contours](image)

**Figure 4.8:** Molecular orbital energy levels and molecular orbital contours (isovalue = 0.04) of the HOMO and LUMO of 3'-BPh₂, MeT-4'-BPh₂ and TPA-4'-BPh₂.

The calculations reveal that exchanging the unborylated F1 unit for a 2-methylthiophene unit (MeT) results in an increase in the HOMO energy level (by 0.10 eV) due to the more electron rich nature of 2-methylthiophene and a slight lowering of the LUMO energy level (-0.06 eV). The molecular orbital contour plots of MeT-4'-BPh₂ show that the electron density of the HOMO is delocalised across all three of the aromatic units, whilst the LUMO is predominantly localised on the BT unit. The molecular orbital contour plots suggest a minor amount of LUMO density is located on the 2-methylthiophene unit which is in contrast to 3'-
BPh₂ in which the LUMO is effectively localised solely on the BT unit (Figure 4.8). This minor delocalisation could explain the slight stabilisation of the LUMO (by 0.06 eV) upon exchanging the unborylated F1 unit for a 2-methylthiophene unit. The calculations also show that by replacing the 2-methylthiophene group with the highly electron donating triphenylamine (TPA) group results in a further destabilisation of the HOMO (by 0.29 eV, relative to MeT-4’-BPh₂). The molecular orbital contour plots suggest that the HOMO is predominantly localised on the TPA group although a minor amount of HOMO density is located on the BT and F1 units. A slight increase (by 0.06 eV, relative to MeT-4’-BPh₂) in the LUMO energy is observed which is attributed to the localisation of the LUMO onto the BT unit. However, the calculation predicts a significantly reduction in band-gap (by 0.25 eV) upon exchanging the 2-methylthiophene group for a TPA unit which is not observed in the UV-vis measurements (Δ = 0.02 eV) (Figures 4.5 and 4.8).
4.5 Redox Properties

4.5.1 Phenyl Substituted Borylated Compounds

Cyclic voltammetry was employed in order to gain further insight into the effects different peripheral/bridging aromatic groups have on the frontier molecular orbital energies. MeT-4-BPh₂, F8-(4-BPh₂)₂ and TPA-4-BPh₂ show a single fully reversible reduction process which is stable for at least 10 cycles (at 50 mV s⁻¹), whereas TT-(4-BPh₂)₂ begins to show a second irreversible reduction peak at the limit of the potential sweep range of DCM. MeT-4-BPh₂, TT-(4-BPh₂)₂, F8-(4-BPh₂)₂ and TPA-4-BPh₂ all show multiple irreversible oxidation peaks.

Figure 4.9: Compounds related to Figure 4.10.
Figure 4.10: Cyclic voltammetry plots of MeT-4-BPh₂, TT-(4-BPh₂)₂, F8-(4-BPh₂)₂, TPA-4-BPh₂ and 3-BPh₂ (potential sweeps are offset by 50 μA for clarity). Measured in DCM (1 mM) with [nBu₄N][PF₆] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV s⁻¹.

Table 4.4: Comparison of redox properties of MeT-4-BPh₂, TT-(4-BPh₂)₂, F8-(4-BPh₂)₂ and 3-BPh₂.

<table>
<thead>
<tr>
<th>Compound</th>
<th>E_{ox}^{\text{onset}} (V)</th>
<th>E_{red}^{\text{onset}} (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Electrochemical Band-Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeT-4-BPh₂</td>
<td>0.69</td>
<td>-1.23</td>
<td>-6.08</td>
<td>-4.16</td>
<td>1.92</td>
</tr>
<tr>
<td>TT-(4-BPh₂)₂</td>
<td>0.59</td>
<td>-1.18</td>
<td>-5.98</td>
<td>-4.21</td>
<td>1.77</td>
</tr>
<tr>
<td>F8-(4-BPh₂)₂</td>
<td>0.73</td>
<td>-1.29</td>
<td>-6.12</td>
<td>-4.10</td>
<td>2.02</td>
</tr>
<tr>
<td>TPA-4-BPh₂</td>
<td>0.45</td>
<td>-1.29</td>
<td>-5.84</td>
<td>-4.10</td>
<td>1.74</td>
</tr>
<tr>
<td>3-BPh₂</td>
<td>0.80</td>
<td>-1.28</td>
<td>-6.19</td>
<td>-4.11</td>
<td>2.08</td>
</tr>
</tbody>
</table>

Measured in DCM, (1 mM), with [nBu₄N][PF₆] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV s⁻¹, potentials are given relative to Fc/Fc⁺ redox couple which is taken to be 5.39 eV below vacuum.³⁶

Cyclic voltammetry measurements reveal the anticipated increase in the HOMO energy level of compound MeT-4-BPh₂ (by 0.11 eV) and TPA-4-BPh₂ (by 0.35 eV) relative to that measured for 3-BPh₂ (Figure 4.10, Table 4.4). This is consistent with incorporation of the electron rich 2-methylthiophene/triphenylamine unit into the conjugated backbone and with strong agreement with the computational results for models of these compounds (Figure 4.8). A further increase in the HOMO energy level is observed for TT-(4-BPh₂)₂ (+0.21 eV relative to 3-BPh₂) which is
attributed to the aforementioned thieno[3,2-b]thiophene bridging unit facilitating the increase in \( \pi \)-orbital overlap between the borylated F8-BT units and thus extending the effective conjugation length. The measured HOMO energy level of the fluorene unit bridged compound \( \text{F8-(4-BPh}_2 \text{)}_2 \) is slightly raised (by 0.07 eV) relative to \( \text{3-BPh}_2 \). The increase in the energy of the HOMO is considerably lower than that observed in the analogous thieno[3,2-b]thiophene bridged compound due to the less electron rich nature of fluorene compared to the thienyl units in addition to the more sterically encumbered fluorene unit presumably having an increased torsion angle between the peripheral borylated units and the central \( \pi \)-conjugated F8 bridge unit which would result in less effective \( \pi \)-orbital overlap.

Figure 4.11: Relative energy level diagrams for \( \text{MeT-4-BPh}_2 \), \( \text{TT-(4-BPh}_2 \text{)}_2 \), \( \text{F8-(4-BPh}_2 \text{)}_2 \) and \( \text{3-BPh}_2 \) as measured by cyclic voltammetry.

Due to the more localised nature of the LUMO in these systems (Figure 4.8) the effect on the reduction potential resulting from incorporating different peripheral/bridging aromatic groups is more subtle. Compound \( \text{F8-(4-BPh}_2 \text{)}_2 \) has essentially the same LUMO energy level as \( \text{3-BPh}_2 \) (\( \Delta = 0.01 \text{ eV} \)) whereas a minor stabilisation of the LUMO energy levels is observed for the thienyl group incorporated compounds \( \text{MeT-4-BPh}_2 \) (-0.05 eV) and \( \text{TT-(4-BPh}_2 \text{)}_2 \) (-0.10 eV). The stabilisation of the LUMO
through replacing a fluorene for 2-methylthiophene is in strong agreement with the trends observed through computational analysis of models of 3-BPh$_2$ and MeT-4-BPh$_2$ (see Figure 4.8). The relative trends in the electrochemical band-gap are consistent with those observed in the UV-vis absorption spectra except for TPA-4-BPh$_2$ which shows a narrower electrochemical band-gap than expected from the UV-vis measurements (see Figure 4.5).
4.5.2 Pentafluorophenyl Substituted Borylated Compounds

Further insight into the modulation of the FMO energy level achieved through cross-coupling was gained through examination of the pentafluorophenyl substituted compounds.

Figure 4.12: Compounds related to Figure 4.13.

Figure 4.13: Cyclic voltammetry plots of TT-4-B(C₆F₅)₂, TT-(4-B(C₆F₅)₂)₂ and 3-B(C₆F₅)₂. Measured in DCM, (1 mM), with ["Bu₄N][PF₆] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV s⁻¹.
Table 4.5: Comparison of redox properties of TT-4-B(C₆F₅)₂, TT-(4-B(C₆F₅)₂)₂ and 3-B(C₆F₅)₂.

<table>
<thead>
<tr>
<th>Compound</th>
<th>E_{ox}^{onset} (V)</th>
<th>E_{red}^{onset} (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Electrochemical Band-Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-B(C₆F₅)₂</td>
<td>0.85</td>
<td>-1.12</td>
<td>-6.24</td>
<td>-4.27</td>
<td>1.97</td>
</tr>
<tr>
<td>TT-4-B(C₆F₅)₂</td>
<td>0.76</td>
<td>-1.03</td>
<td>-6.15</td>
<td>-4.36</td>
<td>1.79</td>
</tr>
<tr>
<td>TT-(4-B(C₆F₅)₂)₂</td>
<td>0.63</td>
<td>-0.95</td>
<td>-6.02</td>
<td>-4.44</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Measured in DCM (1 mM) with [nBu₄N][PF₆] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV s⁻¹, potentials are given relative to Fc/Fc⁺ redox couple which is taken to be 5.39 eV below vacuum.³⁶

Cyclic voltammetry measurements of the pentafluorophenyl substituted compounds TT-(4-B(C₆F₅)₂)₂ and 3-B(C₆F₅)₂ reveal similar trends to those of the phenyl substituted compounds. As observed with TT-(4-B(C₆F₅)₂)₂ the compounds that contain thieno[3,2-b]thiophene show a second irreversible reduction peak close to the limit of the potential sweep range of DCM which is assigned as a TT based process as it is not observed in any other borylated compounds discussed herein (Figure 4.12). Exchanging the unborylated fluorene unit of 3-B(C₆F₅)₂ with a thieno[3,2-b]thiophene unit (TT-4-B(C₆F₅)₂) results in an increase in the HOMO energy level due to the more electron rich nature of thieno[3,2-b]thiophene. This increase in the HOMO is accompanied by a decrease in the LUMO energy level (-0.09 eV). Compound TT-(4-B(C₆F₅)₂)₂ shows a further substantial increase in the HOMO and decrease in the LUMO relative to TT-4-B(C₆F₅)₂ (Table 4.5). As with the phenyl substituted analogues these effects are attributed to an increasing the effective conjugation length due to the thieno[3,2-b]thiophene bridge facilitating π-orbital overlap between the borylated F8-BT units. The relative decrease in the band-gap observed by cyclic voltammetry measurements is highly consistent with those observed in the UV-vis absorption spectra (see Figure 4.6).
Figure 4.14: Relative energy level diagrams for \( \text{TT-4-B(C}_6\text{F}_5)\text{)}_2 \), \( \text{TT-(4-B(C}_6\text{F}_5)\text{)}_2 \) and \( \text{3-B(C}_6\text{F}_5)\text{)}_2 \) as measured by cyclic voltammetry.

4.6 Conclusions

The bromine functionalised borylated compounds \( 4\text{Br-BPh}_2 \) and \( 4\text{Br-B(C}_6\text{F}_5)\text{)}_2 \) proved amenable to Stille, Suzuki-Miyaura and Negishii cross-coupling reactions. This facilitates the creation of borylated structures that would not be readily accessible through the direct borylation of the parent oligomers due to regio-selectivity being dominated by electronic effects during the borylation step. This stability towards cross-coupling reactions opens up a route to the modular synthesis of a vast array of structural motifs and provides an additional method to modulate the FMO energy levels and tailor the optical properties of the borylated compounds. The introduction of more electron rich units into the conjugated backbone of the borylated F8-BT unit resulted in materials that showed reasonable quantum yield values in the solid state with \( \lambda_{\text{max}} \text{em} \) values >700 nm.
4.7 Experimental

4.7.1 General Considerations

For general considerations see Chapters 2 and 3. F8(Bpin)2\(^{37}\) and 2,5-bis(tri"butylstannyl)thieno[3,2-b]thiophene\(^{38}\) were prepared according to modified published procedures. Pd(\(^{t}\)Bu\(_3\)P)\(_2\) was prepared by Josue Ayuso-Carrillo.

Crystallographic data for compound TT-4-B(C\(_6\)F\(_5\))\(_2\) was recorded on a Bruker APEX-II diffractometer, with Cu K\(\alpha\) radiation (graphite monochromator, monochromator, \(\lambda = 1.5418 \text{ Å}\)). The Bruker APEX2 software package was used for data collection and the CrysAlisPro\(^{39}\) software package was used for cell refinement and data reduction. For this data set CrysAlisPro\(^{40}\) software package was used for empirical absorption corrections, which were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. All structures were solved using direct methods\(^{40}\) and refined against F\(^2\) using the Crystals\(^{41}\) software package. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all located in a difference map and repositioned geometrically. X-ray data for compound TPA-4-BPh\(_2\) was collected using Mo-K\(\alpha\) radiation on an Agilent Supernova, equipped with an Oxford Cryosystems Cobra nitrogen flow gas system. The data was measured using CrysAlisPro suite of programs. Synchrotron X-ray data was collected at beamline I19 (\(\lambda = 0.6889 \text{ Å}\)) Diamond Light Source\(^{42}\) for compound TT-(4-B(C\(_6\)F\(_5\))\(_2\))\(_2\). The data was measured using the GDA suite of programs. The data for TPA-4-BPh\(_2\) and TT-(4-B(C\(_6\)F\(_5\))\(_2\))\(_2\) was processed and reduced using CrysAlisPro\(^{40}\) suite of programs. Absorption correction was performed using empirical methods (SADABS) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.\(^{43,44}\) All the atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. The structure was solved and refined against all F\(^2\) values using the SHELXTL and Olex 2 suite of programs.\(^{45}\) Experimental details are given in Table 4.6.
4.7.2 Synthetic Procedures

**Synthesis of 4Br**

4,7-Dibromobenzo[c][1,2,5]thiadazole (2.64 g, 9 mmol), 9,9-dioctylfluorene-2-boronic acid pinacol ester, (1.55 g, 3 mmol) and Pd(PtBu₃)₂ (0.09 g, 0.18 mmol) were mixed in dry THF (40 mL) under an inert atmosphere. K₃PO₄ (2M aq.) (7.5 mL, 15 mmol) was added to the reaction mixture which was stirred at room temperature for 3 hours. The reaction mixture was diluted with THF (50 mL) and then washed with brine (100 mL). The organic layer was then isolated using a separating funnel and dried over MgSO₄. The solvent was evaporated under reduced pressure and a hexane:toluene (8:2) mixture was added to the residue. The residue was filtered and washed with petroleum ether (100 mL). The resulting solid (unreacted 4,7-dibromobenzo[c][1,2,5]thiadazole) was discarded and the filtrate was then evaporated to dryness and the resulting residue was purified by column chromatography on silica gel [eluent: hexane:toluene (8:2)] to afford 4Br as a yellow viscous oil. (Yield 1.10 g, 61 %)

**¹H NMR** (400 MHz, CD₂Cl₂) δ = 7.91 - 7.98 (m, 3 H), 7.84 - 7.89 (m, 1 Hₐ), 7.76 - 7.82 (m, 1 Hₐ), 7.67 (d, 3 J_HH = 7.6 Hz, 1 Hₐ), 7.33 - 7.44 (m, 3 H), 1.97 - 2.14 (m, 4 H), 1.00 - 1.25 (m, 20 H), 0.80 (t, 3 J_HH = 7.0 Hz, 6 H), 0.67 - 0.78 (m, 4 H);

**¹³C{¹H} NMR** (101 MHz, CD₂Cl₂) δ: aryl = 154.5, 153.9, 151.9, 151.7, 142.3, 141.1, 135.9, 135.0, 132.9, 128.8, 128.5, 128.0, 127.5, 124.5, 123.6, 120.6, 120.2, 113.1, alkyl = 55.8, 40.8, 32.4, 30.6, 29.8, 29.8, 24.5, 23.2, 14.4;

MALDI-TOF: calc. for C₃₅H₄₃N₂SBr⁺ [M + H]⁺ = 604.7, found 604.7
Synthesis of 4Br-BPh$_2$

BCl$_3$ 1M solution in DCM (5 mL, 5 mmol) was added to a bright yellow solution of 4Br (500 mg, 0.83 mmol) in DCM (10 mL). The reaction mixture was stirred for 16 hours under the flow of nitrogen whereupon the colour changed from yellow to dark purple was observed. The solvent and unreacted BCl$_3$ were removed under reduced pressure to yield a dark purple residue. The reaction mixture was then dissolved in toluene (10 mL) and ZnPh$_2$ (400 mg, 1.82 mmol) was added to the reaction mixture. The reaction mixture was stirred for 2 hours, ‘wet’ toluene (unpurified toluene used as received) (10 mL) was then added to the reaction mixture which was then passed through a plug of silica. The resulting solution was purified via silica gel chromatography (5 % NEt$_3$ in hexane) [eluent: hexane:DCM (9:1)] to afford the desired product as a dark purple residue. (Yield 456 mg, 72 %)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.23 (d, $^3$$J_{HH}$ = 8.1 Hz, 1 H), 8.12 (s, 1 H), 8.08 (d, $^3$$J_{HH}$ = 7.8 Hz, 1 H), 7.94 (s, 1 H), 7.77 - 7.68 (m, 1 H), 7.47 - 7.43 (m, 1 H), 7.42 - 7.21 (m, 12 H), 2.15 (t, $^3$$J_{HH}$ = 8.3 Hz, 4 H), 1.36 - 1.10 (m, 20 H), 0.96 - 0.75 (m, 10 H);

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$: aryl = 154.3, 153.0, 152.2, 151.3, 149.1, 147.8, 142.4, 140.7, 135.3, 133.6, 130.1, 128.9, 127.6, 127.4, 126.7, 126.1, 125.8, 123.5, 122.7, 120.6, 116.4, 110.5, alkyl = 54.8, 40.6, 31.7, 30.0, 29.2, 29.1, 23.9, 22.5, 14.0;

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ = ~2 (br.);

HRMS (APCI) calc. for C$_{47}$H$_{53}$BBrN$_2$S$^+$ [M + H]$^+$ = 767.3200, found 767.3197
Synthesis of $4\text{Br-B(C}_6\text{F}_5)_2$

$\text{Br}$ $\text{C}_6\text{F}_5$ $\text{B}-\text{C}_6\text{F}_5$

BCl$_3$ 1M solution in DCM (3.3 mL, 3.3 mmol) was added to a bright yellow solution of 4Br (330 mg, 0.55 mmol) in DCM (10 mL) in a Schlenk flask. The reaction mixture was stirred for 16 hours during which time a colour change from yellow to dark purple was observed. The solvent and any reacted BCl$_3$ were removed under reduced pressure to yield a dark purple residue. The reaction mixture was then dissolved in DCM (10 mL) and Zn(C$_6$F$_5$)$_2$ (484 mg, 0.12 mmol) was added. The reaction mixture was stirred for 2 hours and then after the addition of wet DCM the solution was passed through a plug of silica. The solvent was removed under reduced pressure to afford a dark purple residue. (Yield 497 mg, 96 %)

$^1\text{H NMR}$ (400 MHz, CD$_2$Cl$_2$) $\delta = 8.32$ (d, $^3J_{HH} = 7.9$ Hz, 1 H$_a$), 8.17 (d, $^3J_{HH} = 7.8$ Hz, 1 H$_b$), 8.05 (s, 1 H$_c$), 7.76 (s, 1 H$_d$), 7.62 - 7.69 (m, 1 H$_e$), 7.25 - 7.41 (m, 3 H), 1.95 - 2.13 (m, 4 H), 1.00 - 1.22 (m, 20 H), 0.78 (t, $^3J_{HH} = 7.0$ Hz, 6 H), 0.58 - 0.74 (m, 4 H);

$^{13}\text{C}^{\text{1H}}$ NMR (101 MHz, CD$_2$Cl$_2$) $\delta$: aryl = 153.7, 152.0, 151.0, 148.0, 143.9, 140.8, 136.5, 129.6, 128.4, 128.2, 127.4, 126.3, 124.8, 123.6, 120.8, 117.3, 112.0, alkyl = 55.6, 41.0, 32.3, 30.5, 29.8, 29.7, 24.4, 23.1, 14.4;

$^{11}\text{B NMR}$ (128 MHz, CD$_2$Cl$_2$) $\delta = -5$ (br.);

$^{19}\text{F NMR}$ (376 MHz, CD$_2$Cl$_2$) $\delta = -131.91$ (dd, $^3J_{FF} = 20.2$, $^4J_{FF} = 8.3$, 4 F), -157.50 (d, $^3J_{FF} = 20.3$, 2 F), -163.47 (m, 4 F);

HRMS (APCI) calc. for C$_{47}$H$_{53}$BBrN$_2$S$^+ [M + K]^+ = 985.1817$, found 985.2341
Synthesis of MeT-4

4-bromo-7-(9,9-dioctyl-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazole (250 mg, 0.41 mmol), trimethyl(5-methylthiophen-2-yl)stannane (180 mg, 0.69 mmol) (CAUTION Me₃Sn-X by-product can be volatile and are highly toxic compounds) and Pd(PPh₃)₄ (23 mg, 0.04 mmol) were dissolved in THF (4 mL) and the reaction mixture was stirred at 90°C in a sealed ampule for 20 hours. The reaction mixture was allowed to cool and purified by column chromatography on silica gel [eluent: hexane/DCM (4/1)] to afford MeT-4 as a dark orange residue. (Yield 225 mg, 88 %)

¹H NMR (400 MHz, CDCl₃) δ = 8.07 - 7.93 (m, 3 H), 7.88 (d, ³J_HH = 7.7 Hz, 2 H), 7.80 (t, ³J_HH = 6.8 Hz, 2 H), 7.47 - 7.34 (m, 3 H), 6.90 (d, ³J_HH = 2.7 Hz, 1 H), 2.61 (s, 3 H), 2.19 - 1.95 (m, 4 H), 1.28 - 1.04 (m, 20 H), 0.90 - 0.72 (m, 10 H);

¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 154.0, 152.7, 151.2, 151.0, 141.5, 141.2, 140.6, 137.1, 135.9, 132.7, 128.0, 127.8, 127.5, 127.2, 126.8, 126.3, 126.2, 125.1, 123.7, 122.9, 119.9, 119.6, alkyl = 55.1, 40.2, 31.8, 30.0, 29.2, 29.2, 23.8, 22.6, 15.5, 14.1;

MALDI-TOF: calc. for C₄₀H₄₈N₂S₂⁺ [M⁺] = 620.3, found 620.9
Synthesis of MeT-4*-B(C₆F₅)₂

BCl₃ (1M solution in heptanes) (0.12 mL, 0.12 mmol) was added to an orange solution of MeT-4 dissolved in DCM (3 mL). The reaction mixture instantly changed colour from orange to blue. The reaction mixture was stirred for 16 hours. The solvent and excess BCl₃ were removed under reduced pressure and the residue was dissolved in toluene. Zn(C₆F₅)₂ (70 mg, 0.18 mmol) was added to the reaction mixture and after 2 hours the reaction mixture was filtered through silica. The solvent was removed under reduced pressure and ¹H and ¹⁹F{¹H} NMR analysis of the reaction mixture indicated that MeT-4*-B(C₆F₅)₂ was the major product (~90 %) with the minor product the other regio-isomer MeT-4-B(C₆F₅)₂ (~10 %).

NMR data below are listed for the major component only.

¹H NMR (400 MHz, CDCl₃) δ = 7.94 - 7.89 (m, 2 H), 7.87 (d, ³J_HH = 1.0 Hz, 2 H), 7.81 - 7.71 (m, 2 H), 7.42 - 7.34 (m, 3 H), 6.81 (s, 1 H), 2.55 (s, 3 H), 2.03 (m, 4H), 1.24 - 1.04 (m, 20 H), 0.80 (t, ³J_HH = 7.1 Hz, 6 H), 0.71 (m, 4 H);

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ = -131.43 (dd, ³J_FF = 24.3, ⁴J_FF = 8.7, 4 F), -156.54 (t, ³J_FF = 21.08, 2 F), -162.39 (m, 4 F);

¹¹B NMR (128 MHz, CDCl₃) δ = No ¹¹B NMR peak was observed at 20°C
Synthesis of MeT-4-BPh$_2$

4Br-BPh$_2$ (120 mg, 0.15 mmol), tri$n$butyl(5-methylthiophen-2-yl)stannane (75 mg, 0.195 mmol) and Pd(PPh$_3$)$_4$ were dissolved in THF (10 mL). The reaction mixture was heated at 75°C for 20 hours. After cooling to room temperature the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel [eluent: hexane followed by hexane:DCM (8:2)] to afford MeT-4-BPh$_2$ as a dark blue residue. (Yield 96 mg, 81 %)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.21 (d, $^3$J$_{HH}$ = 7.8 Hz, 1 H$_a$), 7.99 (s, 1 H$_b$), 7.91 - 7.75 (m, 3 H), 7.68 - 7.57 (m, 1 H$_c$), 7.39 - 7.09 (m, 13 H), 6.80 (dd, $^3$J$_{HH}$ = 3.5, $^4$J$_{HH}$ = 1.0 Hz, 1 H$_d$), 2.55 (s, 3 H$_e$), 2.04 (t, $^3$J$_{HH}$ = 8.3 Hz, 4 H), 1.24 - 0.97 (m, 20 H), 0.86 - 0.63 (m, 10 H);

$^{13}$C{$_^1$H} NMR (101 MHz, CDCl$_3$) $\delta$: aryl = 154.7, 152.0, 151.5, 151.3, 148.9, 148.0, 142.2, 141.9, 140.9, 135.5, 133.7, 129.6, 128.1, 128.1, 127.7, 127.5, 127.1, 126.8, 126.6, 125.9, 125.7, 125.2, 123.8, 122.7, 120.4, 116.0, 77.3, 76.7, alkyl = 54.7, 40.6, 31.8, 30.1, 29.2, 29.2, 23.9, 22.6, 15.5, 14.1;

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ = -2 (br.);

MALDI-TOF: calc. for C$_{46}$H$_{52}$BN$_2$S$_2^+$ [M - C$_6$H$_5$]$^+$ = 707.4, found 707.6
Synthesis of \( p \)-Tol-4-BPh₂

\[
\begin{array}{c}
\text{H₃C-} \\
\text{e} \\
\text{N} \\
\text{N-B-Ph} \\
\text{d} \\
\text{H₇C₆} \\
\text{C₈H₁₇} \\
\text{a} \\
\text{b} \\
\text{c} \\
\text{H} \\
\text{d} \\
\text{Ph} \\
\end{array}
\]

\( 4\text{Br-BPh₂} \) (50 mg, 0.065 mmol), Zincate A (75 mg, 0.078), \( \text{Pd₂(dba)}₃ \) (3.5 mg, 0.004 mmol) and S-Phos (5.3 mg, 0.013 mmol) were dissolved in THF (3 mL). The reaction mixture was heated at \( 70{\degree}\text{C} \) for 20 hours. After cooling to room temperature the solvent was removed under reduced pressure and the residue was dissolved in hexane and passed through a short plug of silica. A mixture of hexane:DCM (8:2) was then passed through the silica plug and only the purple coloured fractions were collected. Evaporation of the solvent gave the desired product as a dark purple residue. (Yield 50 mg, 98%)

\( ^{1}\text{H NMR} \) (400 MHz, CDCl₃) \( \delta = 8.44 \) (d, \( ^{3}J_{HH} = 7.7 \) Hz, 1 Hₐ), 8.10 (s, 1 Hₖ), 7.98 (d, \( ^{3}J_{HH} = 7.5 \) Hz, 1 Hₜ), 7.92 - 7.82 (m, 3 H), 7.70 - 7.62 (m, 1 Hₜ), 7.46 - 7.17 (m, 15 H), 2.51 (s, 3 Hₖ), 2.09 (t, \( ^{3}J_{HH} = 7.8 \) Hz, 4 H), 1.30 - 1.04 (m, 20 H), 0.91 - 0.67 (m, 10 H);

\( ^{13}\text{C}\{^{1}\text{H}\} \text{ NMR} \) (101 MHz, CDCl₃) \( \delta \): aryl = 154.7, 153.7, 151.8, 151.3, 149.0, 148.3, 142.0, 141.0, 139.0, 133.7, 132.8, 131.8, 130.6, 129.6, 129.2, 128.9, 128.8, 127.5, 127.1, 126.6, 125.9, 125.8, 123.8, 122.8, 120.5, 116.2, alkyl = 54.8, 40.6, 31.8, 30.1, 29.2, 23.9, 22.6, 21.3, 14.0;

\( ^{11}\text{B NMR} \) (128 MHz, CDCl₃) \( \delta = -2 \) (br.);

MALDI-TOF: calc. for \( \text{C}_{48}\text{H}_{54}\text{BN}_{2}\text{S}_{2} \)\(^{+}\) [M - C₆H₅]⁺ = 701.4, found 701.7
Synthesis of **TT-(4-BPh₂)₂**

4Br-BPh₂ (100 mg, 0.13 mmol), 2,5-bis(trimethylstanny)thieno[3,2-b]thiophene (28 mg, 0.06 mmol), Pd₂(dba)₃ (96 mg, 0.0065) and S-Phos (18 mg, 0.013) were dissolved in THF (3 mL). The reaction mixture was heated at 70°C for 20 hours during which time it had changed colour from dark purple to dark green. After cooling to room temperature the solvent was removed under reduced pressure and the residue was purified by column chromatography on base treated silica gel (5 % NEt₃ in hexane) [eluent: hexane followed by hexane:DCM (8:2)] to afford **TT-(4-BPh₂)₂** as a dark green residue. (Yield 88 mg, 97 %)

**¹H NMR** (400 MHz, CD₂Cl₂) δ = 8.40 (s, 2 Hₐ), 8.34 (d, ³J₉H = 7.9 Hz, 2 Hₗ), 8.12 (s, 2 Hₗ), 8.07 (d, ³J₉H = 7.8 Hz, 2 Hₗ), 7.85 (s, 2 Hₗ), 7.59 - 7.68 (m, 2 Hₗ), 7.43 - 7.13 ppm (m, 28 H), 1.95 - 2.23 (m, 8 H), 1.25 - 1.01 (m, 40 H), 0.64 - 0.94 (m, 20 H);

**¹³C{¹H} NMR** (101 MHz, CDCl₃) δ: aryl = 155.3, 152.9, 152.7, 152.1, 149.8, 148.8, 142.8, 141.8, 141.7, 141.3, 134.1, 130.2, 129.6, 129.2, 128.2, 128.0, 127.3, 126.6, 125.9, 125.6, 124.6, 123.5, 121.0, 120.9, 117.3, alkyl = 55.5, 41.1, 32.4, 30.7, 29.8, 29.8, 24.6, 23.2, 14.4;

**¹¹B NMR** (128 MHz, CDCl₃) δ = No **¹¹B NMR peak was observed at 20°C**

HRMS (APCI) calc. for C₁₀₀H₁₀₇B₂N₄S₂⁺ [M + H]⁺ = 1514.7593, found 1514.7600
Synthesis of $\text{F8-}(4\text{-BPh}_2)_2$

$4\text{Br-BPh}_2$ (100 mg, 0.13 mmol), 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (40 mg, 0.06 mmol) and Pd($t$Bu$_3$P)$_2$ (4 mg, 0.007 mmol) were dissolved in THF (3 mL). K$_3$PO$_4$ (2M aq.) (0.62 mL, 1.2 mmol) was added to the reaction mixture which was stirred at room temperature for 30 minutes. The solution was then diluted with THF (100 mL) and then washed with brine (100 mL). The organic layer was then isolated using a separating funnel and dried (MgSO$_4$). The solvent was evaporated under reduced pressure and the residue was purified by column chromatography [eluent: hexane followed by hexane:DCM (8:2)] to afford the desired product as a dark purple residue. (Yield 92 mg, 84 %)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta = 8.52$ (d, $^3$$J_{HH} = 7.9$ Hz, 2 H$_a$), 8.19 (s, 2 H$_b$), 8.14 (d, $^3$$J_{HH} = 7.6$ Hz, 2 H$_c$), 8.10 (s, 2 H$_d$), 8.06 - 8.01 (m, 2 H$_e$), 7.97 (d, $^3$$J_{HH} = 7.9$ Hz, 2 H$_f$), 7.89 (s, 2 H$_g$), 7.68 (m, 2 H$_h$), 7.46 - 7.38 (m, 2 H), 7.37 - 7.16 (m, 24 H), 2.23 - 2.04 (m, 12 H), 1.27 - 1.03 (m, 60 H), 0.93 - 0.71 (m, 30 H);

$^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$) $\delta$: aryl = 155.5, 154.3, 152.5, 152.0, 149.6, 148.8, 142.5, 141.7, 141.4, 135.4, 134.1, 132.8, 131.4, 130.3, 129.4, 128.6, 128.1, 127.9, 127.2, 126.5, 125.8, 124.8, 124.4, 123.5, 120.9, 120.8, 117.2, alkyl = 56.1, 55.4, 41.1, 40.7, 32.4, 30.6, 30.5, 29.8, 29.8, 24.6, 23.2, 14.4;

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta = No$ $^{11}$B NMR peak was observed at 20°C

HRMS (APCI) calc. for C$_{123}$H$_{145}$B$_2$N$_4$S$_2$ $^+$$[M + H]^+$ = 1765.1125, found 1765.1135
Synthesis of TPA-4-BPh₂

4Br-BPh₂ (129 mg, 0.17 mmol), 4-(diphenylamino)phenylboronic acid (68 mg, 0.24 mmol) and Pd(ηBu₃P)₂ (13 mg, 0.025 mmol) were dissolved in THF (5 mL). K₃PO₄ (2M aq.) (1 mL, 2 mmol) was added to the reaction mixture which was stirred at room temperature for 30 minutes. The solution was then diluted with THF (20 mL) and water (30 mL) was added. The reaction mixture was then washed with brine (2 x 100 mL). The organic layer was then isolated using a separating funnel and dried (MgSO₄). The solvent was evaporated under reduced pressure and the residue was purified by column chromatography [eluent: graduated petroleum ether:toluene (9:1 to 6:4)] to afford the desired product as a dark purple residue. (Yield 123 mg, 79 %)

¹H NMR (400 MHz, CD₂Cl₂) δ = 8.42 (d, ³J_HH = 7.8 Hz, 1 Hₐ), 8.12 (s, 1 Hₖ), 7.96 (d, ³J_HH = 7.8 Hz, 1 Hₐ), 7.89 (d, ³J_HH = 8.8 Hz, 2 Hₗₜ), 7.83 (s, 1 Hₐ), 7.65 (s, 1 Hₗₜ), 7.11 - 7.37 (m, 25 H), 2.05 - 2.18 (m, 4 H), 1.09 - 1.26 (m, 20 H), 0.72 - 0.95 (m, 10 H);

¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ: aryl = 155.5, 154.2, 152.4, 152.0, 149.7, 149.2, 148.9, 147.8, 142.4, 141.5, 134.2, 132.0, 130.4, 130.4, 130.3, 130.0, 129.3, 128.8, 128.1, 127.8, 127.3, 126.5, 125.8, 125.7, 124.9, 124.3, 123.5, 123.0, 120.8, 117.1, alkyl = 55.5, 41.2, 32.4, 30.7, 29.8, 29.8, 24.6, 23.2, 14.5;

¹¹B NMR (128 MHz, CDCl₃) δ = ~2 (br.);

MALDI-TOF: calc. for C₅₉H₆₁BN₃S⁺ [M - C₆H₅]⁺ = 855.0, found 854.7
Synthesis of TT-(4-B(C₆F₅)₂)₂

A mixture of compound 4Br-B(C₆F₅)₂ (150 mg, 0.16 mmol), 2,5-bis(tri"butylstanny"l)thieno[3,2-b]thiophene (56 mg, 0.08 mmol) and Pd(PPh₃)₄ (17 mg, 0.016 mmol) was dissolved in toluene (4 mL) and heated at 100°C for 40 hours. After evaporating the solvent, the residue was purified by column chromatography on silica gel [eluent: hexane:DCM (6:4)] to afford TT-(4-B(C₆F₅)₂)₂ as a dark green residue. (Yield 51 mg, 35 %)

¹H NMR (400 MHz, CDCl₃) δ = 8.53 - 8.43 (m, 4 H), 8.16 (d, ³JHH = 7.8 Hz, 2 Hₐ), 8.03 (s, 2 Hₖ), 7.78 (s, 2 Hₜ), 7.74 - 7.65 (m, 2 Hₜd), 7.40 - 7.29 (m, 6 H), 2.06 (t, ³JHH = 8.2 Hz, 8 H), 1.23 - 1.01 (m, 40 H), 0.85 - 0.62 (m, 20 H);

¹³C{¹H} NMR (400 MHz, CDCl₃) δ: aryl = An acceptable ¹³C NMR spectrum was not achievable for this compound due an insufficient amount of material

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ = -131.52 (dd, ³JFF = 24.1, 8.7, 8 F), -156.32 (t, ³JFF = 20.3, 4 F), -162.42 (m, 8 F);

MALDI-TOF: calc. for C₁₀₀H₈₆B₂N₄S₄⁺ [M]⁺ = 1872.6, found 1872.0
Synthesis of \( \text{TT-4-B(C}_6\text{F}_5\text{)}_2 \)

\( \text{TT-4-B(C}_6\text{F}_5\text{)}_2 \) was isolated as a dark blue solid from the reaction mixture of \( \text{TT-(4-B(C}_6\text{F}_5\text{)}_2 \). (Yield 19 mg, 24 %)

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \( \delta = 8.36 - 8.46 \text{ (m, 2 H), 8.08 (d, }^3\text{J}_\text{HH} = 7.8 \text{ Hz, 1 H}_a), 8.02 \text{ (s, 1 H}_b), 7.78 \text{ (s, 1 H}_c), 7.65 - 7.74 \text{ (m, 1 H}_d), 7.51 \text{ (d, }^3\text{J}_\text{HH} = 5.3 \text{ Hz, 1 H}_e), 7.30 - 7.42 \text{ (m, 4 H), 2.06 (t, }^3\text{J}_\text{HH} = 8.2 \text{ Hz, 4 H), 1.00 - 1.23 \text{ (m, 20 H), 0.56 - 0.85 \text{ (m, 10 H));}

\(^{13}\text{C}\{^1\text{H}\} \text{ NMR}\) (101 MHz, CDCl\(_3\)) \( \delta = 152.0, 151.3, 150.3, 147.7, 143.1, 140.6, 140.3, 140.1, 139.0, 129.5, 128.5, 128.0, 127.9, 127.7, 126.9, 125.9, 125.6, 124.3, 122.9, 121.0, 120.4, 119.6, 116.3, \text{ alkyl = 55.0, 40.6, 31.8, 30.0, 29.2, 29.1, 23.8, 22.5, 14.0;}

\(^{19}\text{F}\{^1\text{H}\} \text{ NMR}\) (376 MHz, CDCl\(_3\)) \( \delta: \text{ aryl = -131.51 (dd, }^3\text{J}_{\text{FF}} = 22.6, \text{ }^3\text{J}_{\text{FF}} = 8.7, 4\text{F), -156.46 (t, }^3\text{J}_{\text{FF}} = 20.30, 2\text{F), -162.49 (m, 4F);}

\(^{11}\text{B} \text{ NMR}\) (128 MHz, CDCl\(_3\)) \( \delta = \sim-6 \text{ (br.);}

MALDI-TOF: calc. for C\(_{53}\)H\(_{45}\)BF\(_{10}\)N\(_2\)S\(_3\)\(^+\) [M]\(^+\) = 1006.3, found 1006.4
### 4.7.3 Crystallographic Details

Table 4.6: Summary of crystallography data for TT-4-B(C$_6$F$_5$)$_2$, TT-(4-B(C$_6$F$_5$)$_2$)$_2$ and TPA-4-BPh$_2$.

<table>
<thead>
<tr>
<th>CCDC Reference</th>
<th>TT-4-B(C$_6$F$_5$)$_2$</th>
<th>TT-(4-B(C$_6$F$_5$)$_2$)$_2$</th>
<th>TPA-4-BPh$_2$</th>
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</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C$<em>{53}$H$</em>{44}$BF$_{10}$N$_2$S$_3$</td>
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<td></td>
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<tr>
<td>Fw / g mol$^{-1}$</td>
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<td></td>
<td></td>
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<tr>
<td>Crystal System, Space group</td>
<td>Orthorhombic, $Pnma$</td>
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<td></td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>$b$ / Å</td>
<td>18.0986(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c$ / Å</td>
<td>9.9254(4)</td>
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<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>$\beta$ / deg</td>
<td>90.000</td>
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<tr>
<td>$\gamma$ / deg</td>
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<tr>
<td>Vol / Å$^3$</td>
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<tr>
<td>Z</td>
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<tr>
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<tr>
<td>Radiation / Å</td>
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<td>$\lambda$ = 1.5418</td>
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<td></td>
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<tr>
<td>F(000)</td>
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<tr>
<td>$\theta$ range (deg)</td>
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<tr>
<td>No. of data / Restraints / Parameters</td>
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<tr>
<td>$R_{int}$</td>
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<td></td>
<td></td>
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<tr>
<td>No. of data / Restraints / Parameters</td>
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<td></td>
<td></td>
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<tr>
<td>$R$ (data with $</td>
<td>I^2 &gt; 2\sigma(I^2)$)](5591 (0.0591)</td>
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<tr>
<td>wR (all data)</td>
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<tr>
<td>$S$</td>
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<tr>
<td>$\Delta \rho_{max, min}$ / e·Å$^{-3}$</td>
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</table>

170
4.8 References


Chapter 5

Diborylated Ladder Type A-D-A Structures
5.1 Introduction

Ladder type compounds have many desirable attributes which make them attractive candidates as high performing materials in organic electronics. In ladder type structures the effective conjugation length is enhanced by completely locking the main chain aromatic units coplanar. The increased rigidity resulting from a fully fused, coplanar, polycyclic backbone can enhance thermal stability, quantum yields (due to decreases in non-radiative relaxation processes) and intrinsic charge mobility by suppression of rotational disorder around interannular single bonds promoting \( \pi-\pi \) stacking interactions.\(^1\)\(^,\)\(^2\) The advantageous characteristics derived from incorporating ladder type structures into organic electronic materials is evident by many of the highest performing OPV and OFET materials containing highly fused planar structures.\(^1\)

The incorporation of a tetra-coordinate boron centre to planarise the structure through coordination to the basic functionality of a \( \pi\)-conjugated ligand is a useful and elegant strategy utilised in many highly emissive ladder type structures, usually in the form of a N,N, O,N, or C,N-chelated BR\(_2\) system.\(^2\)\(^-\)\(^11\) In addition to the enhanced rigidity, incorporation of the electron deficient boron centre lowers the LUMO energy level which results in increased electron affinity/transport characteristics and red shifted emission relative to that of the unborylated precursor.\(^2\)\(^-\)\(^10\) These virtues make tetra-coordinate boron containing ladder systems particularly applicable as emitters for OLED applications, which is where the majority of research into this class of materials has been targeted.\(^9\)\(^,\)\(^10\)

![Structures of fused and ladder type C,N-chelates](image)

Figure 5.1: Structures of fused and ladder type C,N-chelates.
Table 5.1: Comparison of the fluorescence properties of fused and ladder type C,N-chelated boranes.\textsuperscript{11}

Kawashima et al.\textsuperscript{11} showed that through the double borylation and resulting rigidification of the non-emissive azobenzene (5i) the C,N-chelated borane ladder complex (5iiia) results in red shifted emission due to elongated $\pi$-conjugation and an increased quantum yield relative to that of the singly borylated fused structure (5ii).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R = \lambda_{\text{max}_\text{em}}$</th>
<th>$\Phi_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5ii</td>
<td>H</td>
<td>503</td>
</tr>
<tr>
<td>5iiia</td>
<td>H</td>
<td>572</td>
</tr>
<tr>
<td>5iiib</td>
<td>$^n$Bu</td>
<td>597</td>
</tr>
<tr>
<td>5iiic</td>
<td>Br</td>
<td>602</td>
</tr>
<tr>
<td>5iiid</td>
<td>$^n$Bu</td>
<td>663</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Measured in hexane.

Table 5.2: Comparison of substituent effects on the LUMO energy level of thiazolo[5,4-d]thiazole based ladder type C,N-chelates.\textsuperscript{4}

Zhang et al.\textsuperscript{4} also explored the effects of forming tetra-coordinate boron ladder structures through the extension of the thiazole C,N-chelated borane system developed by the Yamaguchi et al. to the thiazolo[5,4-d]thiazole acceptor unit (5iv) which contains two coordination sites. A significant decrease in the LUMO energy level by 0.5 eV was observed in addition to a red shift in absorbance and emission on borylation (Table 2). This demonstrates the enhancement in electron affinity upon double borylation and formation of a ladder system. The electronic and photophysical properties of these C,N-chelate ladder systems are also

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R = \lambda_{\text{max}_\text{abs}}$</th>
<th>$\lambda_{\text{max}_\text{em}}$</th>
<th>$\Phi_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5iv</td>
<td>H</td>
<td>N/A</td>
<td>-2.47</td>
</tr>
<tr>
<td>5v</td>
<td>H</td>
<td>Ph</td>
<td>-2.97</td>
</tr>
<tr>
<td>5vi</td>
<td>F</td>
<td>Ph</td>
<td>-3.07</td>
</tr>
<tr>
<td>5vii</td>
<td>H</td>
<td>Mes</td>
<td>-2.88</td>
</tr>
<tr>
<td>5viii</td>
<td>OMe</td>
<td>Mes</td>
<td>-2.91</td>
</tr>
</tbody>
</table>

Measured in CH$_2$Cl$_2$ (1 x 10$^{-5}$ M).
tuneable through the functionalisation of either the chelating thiazole or the exocyclic boron substituents although the latter approach is much less investigated.\textsuperscript{9,10} Attaching electron donating substituents to the peripheries of the ladder backbone generally resulted in emission at higher wavelengths (than unfunctionalised analogues) due to an increase HOMO energy level resulting in a decreased bandgap (5\textit{iii}a-d compound series, Table 5.1). Substituting the phenyl substituent in 5\textit{v} for the more electron donating mesityl group (5\textit{vii}) also resulted in a decreased bandgap and red shifted emission, despite an observed increase in the LUMO energy. In addition an increase in quantum yield was observed presumably due to the more bulky mesityl substituents reducing aggregation-induced quenching (Table 5.2, entry 5\textit{vii}).

Although possessing interesting photophysical properties, literature examples of C,N-chelated boron containing ladder molecules are scarce.\textsuperscript{4} This is presumably due to challenges synthesising these molecules which usually involves the lithiation of a selectively pre-halogenated compound at cryogenic temperatures followed by quenching with Aryl\textsubscript{2}BX.\textsuperscript{4,11} This chapter describes our efforts to expand the direct C-H borylative fusion methodology to form fully fused ladder structures. As previously discussed in earlier chapters the double borylation of D-A-D systems by coordinating both nitrogen atoms of a single BT unit to separate boron moieties to form a ladder structure is not possible as only one borylation per acceptor unit can occur. Fluorene/carbazole structures substituted with 2 BT units contain two viable coordination sites (one per BT unit) and two borylation sites (see Figure 5.3), therefore attention was directed toward the double borylation of fluorene and carbazole based A-D-A structures to synthesise fully fused ladder type structures. This double borylation is intended to have the additional benefits of increasing rigidity (resulting in higher quantum yield values) and increasing effective conjugation length (lowering the band-gap) relative to the single borylated D-A-D fused structures (see Chapter 2 and 3).
5.2 Synthesis

5.2.1 Synthesis and Borylative Fusion of Fluorene A-D-A Structures

Compound 5F was synthesized through Suzuki-Miyaura cross-coupling using a modified literature procedure (Scheme 1).\textsuperscript{13} The double borylation of the A-D-A structure 5F was attempted initially using the same methodology as utilised for compounds 2 and 3 (see Chapters 2 and 3).

Unlike the D-A-D structures compound 5F did not undergo borylation simply upon the addition of BCl\textsubscript{3} in an open system, rather a di-adduct between BCl\textsubscript{3} and the less sterically hindered peripheral nitrogen (N2, N2’ Scheme 2) atoms of the BT units was formed. The B-N bonds in this di-adduct could then be cleaved upon the addition of a stronger Lewis base (NEt\textsubscript{3} forming Et\textsubscript{3}N-BCl\textsubscript{3}). This reactivity is different to compounds 2 and 3 as coordination of BCl\textsubscript{3} at the peripheral nitrogen in 5F (N2, N2’) deactivates the internal nitrogen atoms (N1, N1’) towards coordination of BCl\textsubscript{3}. BCl\textsubscript{3} is therefore unable to undergo directed borylation onto the adjacent aromatic unit, whereas in the D-A-D structures (compounds 2
and 3) either nitrogen atom can direct borylation.

Scheme 5.2: Attempted Borylation of the A-D-A system 5F.

Addition of multiple equivalents (4 eq.) of BCl₃, a hindered base (2,4,6-triisobutylpyridine (TBP)) and heating to 60°C in DCM in a sealed tube (in an attempt to de-coordinate the boron from the peripheral nitrogen) resulted in no C-H borylation reaction. Similar reaction condition to those used by Murakami et al.¹⁴ to achieve C-H borylation of 2-phenylpyridine (Et(iPr)₂N/excess BBr₃) were applied but this also led to no C-H borylation. Double borylation can be achieved in quantitative conversion (by in-situ NMR spectroscopy) through the addition of a sterically hindered base (TBP) to sequester the protic by-products and AlCl₃ to abstract a halide. The exact mechanism and identity of the key boron electrophile in this process is unclear but the addition of 4 equivalents of AlCl₃ is required to ensure full conversion to the doubly borylated product [5F-(BCl)₂][AlCl₄]₂, as two equivalents of AlCl₃ are consumed in a competing halide abstraction reaction resulting in the formation of borenium cations (such as [5F-(BCl)₂]²⁺).
Scheme 5.3: Diborylation of 5F.

The C-H borylation of 5F proved to be rather slow and the optimised procedure involved adding 3 eq. of AlCl₃ and stirring for 16 hours followed by the addition a fourth equivalent and further stirring for 16 hours. This stepwise addition was necessary as addition of four equivalents at the start of the reaction failed to drive the reaction to completion (monitored via percentage of protonated TBP formed in-situ by ¹H NMR spectroscopy). Four equivalents of BCl₃ also proved necessary to accelerate the rate of reaction as borylations using stoichiometric (two equivalents) BCl₃ were slow and never went to completion (again monitored via percentage of protonated TBP formed by in-situ ¹H NMR spectroscopy). The dicationic borylated product, \([5F-(BCl)₂]^{2+}\) can be transformed to its neutral form \(5F-(BCl₂)_2\) through a salt metathesis reaction with \(N^\text{Bu}_4\text{Cl}\) with this resulting in a significant up-field shift of the aromatic ¹H resonances (Figure 5.4).
Figure 5.4: $^1$H NMR spectra comparing reactions detailed in Scheme 3. Reaction 1 (blue), Reaction 2 step 1 (green) and Reaction 2 step 2 (red), (S:CH$_2$Cl$_2$ with a d$_6$-DMSO capillary insert, 400 MHz, 298 K).

5.2.2 Synthesis and Borylative Fusion of Brominated Fluorene A-D-A Structures

The BT units of 5F were brominated to facilitate the subsequent attachment of other $\pi$-conjugated systems onto this molecule to further modulate photophysical properties. This double bromination proved highly selective simply through the addition of Br$_2$ to a solution of 5F in CHCl$_3$. Br$_2$ as brominating agent was necessary as the use of NBS resulted in no bromination.

Scheme 5.4: Synthesis of 5FBr$_2$. 

Borylation of compound 5FBr$_2$ occurs through the addition of multiple equivalents of BCl$_3$ (6 eq.) in an open system in the absence of base and AlCl$_3$. This reactivity is different to compound 5F as the increased steric bulk provided by bromine (relative to H) ensures reversible coordination of BCl$_3$ to N2/N2’ so N1/N1’ isn’t permanently deactivated towards
coordination of BCl$_3$ as is proposed to be occurring in 5F-(BCl$_3$)$_2$. This eliminates the need for the addition of a sterically hindered base and AlCl$_3$. The coordination of BCl$_3$ to 5FBr$_2$ is to N2 is labile enough for N1 to direct borylation onto the adjacent fluorene C-H position over extended reaction times (Scheme 5). Multiple equivalents of BCl$_3$ (6 eq.) are required as this accelerates the rate of reaction, in addition to ensuring a sufficiently high solution concentration of BCl$_3$ is maintained throughout the reaction as the application of a dynamic flow of N$_2$ results in the removal of both HCl and volatile BCl$_3$ (b.p = 12.6$^\circ$C) from the reaction mixture. 5FBr$_2$-(BCl$_2$)$_2$ was not isolated, the reaction mixture was degassed and then used directly in subsequent functionalisation reactions.

Scheme 5.5: Borylation of 5FBr$_2$.

5.2.3 Synthesis and Borylative Fusion of Carbazole A-D-A Structures

The N-(9-heptadecyl)-carbazole analogue of 5F was synthesised with the intention of creating an analogous system with a donor unit that has an increased HOMO energy level which would lead to a relatively smaller band-gap and a red shifted emission. Compound 5C was synthesised by a modified procedure to that used to synthesise 5F. Compound 5C could be borylated using essentially the same procedure to that used to borylate 5F (Scheme 6), although due to the carbazole unit being more electron rich (relative to fluorene) the borylation proceeded at a faster rate.
Scheme 5.6: Borylation of 5C.

5.2.4 Functionalisation of Diborylated Fluorene A-D-A Ladder Structures

5F-(BCl₂)₂ was functionalised without isolation as it proved intractable from the ionic by-products. The addition of organo-zinc reagents (ZnPh₂ or Zn(C₆F₅)₂) directly to the reaction mixture proved a moderately effective method to functionalise 5F-(BCl₂)₂ with aryl substituents.

Scheme 5.7: Synthesis of 5F-(BPh₂)₂ and 5F-(B(C₆F₅)₂)₂.
The presence of the ionic by-products from electrophilic borylation complicated trans-metalation and a mixture of products was observed so compounds $5F-(\text{BPh}_2)_2$ and $5F-(\text{B(C}_6\text{F}_5)_2)_2$ were isolated by column chromatography in moderate to good yields (53 and 71 %, respectively). $5F-(\text{BPh}_2)_2$ could also be synthesised directly from $[5F-(\text{BCl})_2][\text{AlCl}_4]_2$ using the previously discussed boro-destannylation reaction through the addition of excess (6 eq.) Ph$_3$Bu$_3$Sn although this afforded the desired product in a lower yield (32 %). Once isolated $5F-(\text{BPh}_2)_2$ and $5F-(\text{B(C}_6\text{F}_5)_2)_2$ have excellent moisture stability with both showing no hydrolysis when exposed to moisture in solution for at least 9 months.

Figure 5.5: Solid state structure of $5F$ (octyl chains are omitted for clarity). Thermal ellipsoids at 50 % probability level. Left: front view. Right: side view. Selected bond lengths (Å) = N1-S1 (1.617(3)), N2-S1 (1.614(2)), C1-N2 (1.350(3)). Selected angles (°) = C3-C2-C4-C5 (46.5(4)), C6-C7-C8-C9 (29.6(4)).

Figure 5.6: Solid state structure of $5F-(\text{BPh}_2)_2$ (octyl chains are omitted for clarity). Thermal ellipsoids at 50 % probability level. Top left: front view. Bottom left: side view. Right: Extended structure. Selected bond lengths (Å) = N1-S1 (1.597(4)), N2-S1 (1.644(3)), C1-N1 (1.354(5)), C6-N2 (1.339(5)), N2-B1 (1.622(5)), C9-B1 (1.619(6)), N3-S2 (1.589(4)), C18-B2 (1.623(6)), N4-B2 (1.623(5)), N4-S2 (1.656(3)), N3-C10 (1.348(5)), N4-C15 (1.345(5)). Selected angles (°) = C4-C5-C7-C8 (6.8(6)), C13-C16-C14-C13 (6.2(6)).
Both 5F-(BPh₂)₂ and 5F-(B(C₆F₅)₂)₂ proved amenable to crystallisation with both ladder structures possessing a slightly curved conjugated backbone. The angles between the benzothiadiazole planes and the plane of the central five membered ring of fluorene are 8.2° and 8.4° for 5F-(BPh₂)₂ and 15.5° and 11.2° for 5F-(B(C₆F₅)₂)₂ which is a significant decrease compared to the unborylated compound 5F (49.0° and 29.0°) demonstrating the enhanced coplanarity achieved through this double borylation (Figures 5.5 and 5.6). The slight non-planarity in the borylated ladder complexes arises from steric crowding as discussed in Chapter 3 which is supported by the non-zero torsion angles for C4-C5-C7-C8 = 6.80° and C13-C14-C16-C17 = 6.15° for 5F-(BPh₂)₂ (Figure 5.6). Compound 5F-(B(C₆F₅)₂)₂ shows slightly reduced torsion angles of C3-C2-C4-C5 = 3.74° and C10-C8-C9 = 1.79° (Figure 5.6). Compounds 5F-(BPh₂)₂ and 5F-(B(C₆F₅)₂)₂ have essentially planar six membered boracycles possessing similar structural metrics, excluding the B-N distances which are shorter in 5F-(B(C₆F₅)₂)₂ (B1-N1 = 1.604(5), N3-B2 = 1.603(5) Å) than in 5F-(BPh₂)₂ (B1-N1 = 1.622(5), N3-B2 = 1.623(5) Å). This is consistent with greater N-B σ-donation due to the increased Lewis acidity of the boron centre substituted with the electron withdrawing pentafluorophenyl groups (Figures 5.6 and 5.7). In the extended structure of 5F-(BPh₂)₂ there is no close π–π stacking interactions involving the fused conjugated backbones rather the extended structure of 5F-(BPh₂)₂ shows an packing structure involving close π–π stacking interactions between the fused conjugated backbone and the peripheral phenyl boron substituents (Figure 5.6, Right).
Figure 5.7: Solid state structure of 5F-(B(C₆F₅)₂)₂ (octyl chains are omitted for clarity). Thermal ellipsoids at 50 % probability level. Left: Front view. Right: Side view. Selected bond lengths (Å) = N1-S1 (1.602(3)), N2-S1 (1.654(3)), C1-N2 (1.358(5)), N2-B1 (1.604(5)), C6-B1 (1.620(5)), N3-S2 (1.651(3)), N4-S2 (1.594(3)), N3-C7 (1.345(5)), N3-B2 (1.603(5)), B2-C12 (1.614(5)). Selected angles (°) = C3-C2-C4-C5 (1.8(6)), C9-C10-C8-C9 (3.7(5)).

Figure 5.8: Left: Extended structure of 5F-(B(C₆F₅)₂)₂ front view. Right: Extended structure side view.

The extended structure of 5F-(B(C₆F₅)₂)₂ shows solid state packing dominated by C-F interactions of the peripheral C₆F₅ substituents (Figure 5.8, left), in addition to a close interaction (3.5 Å) between the bottom edges of the phenyl rings of the alternating BT units (Figure 5.8, right). The absence of multiple π-π close contacts between the backbone of adjacent molecules is in contrast to the borylated thiophene compounds (Chapter 2) and is presumably due to the three quaternary-centres present in 5F-(B(aryl)₂)₂ that project considerable bulk above and below...
the plane that prevents aggregation. The absence of any close $\pi-\pi$ contacts between the conjugated backbones is beneficial for enhancing solid state emission properties as it disfavour aggregation induced quenching.\footnote{15}

5.2.5 Functionalisation of Diborylated Dibrominated A-D-A Ladder Structures

Addition of commercial organozinc reagents ZnPh$_2$ or Zn(C$_6$F$_5$)$_2$ to the reaction mixture of 5FBr$_2$-(BCl)$_2$ led to the formation of 5FBr$_2$-(BPh)$_2$ and 5FBr$_2$-(B(C$_6$F$_5$)$_2$)$_2$. The desired products (5FBr$_2$-(BPh)$_2$ and 5FBr$_2$-(B(C$_6$F$_5$)$_2$)$_2$) could be isolated by column chromatography in moderate yields (58 and 30\%, respectively scheme 7). Compound 5FBr$_2$-(BPh)$_2$ also proved amenable to crystallisation with the brominated ladder structures possessing similar metrics to those of the non-brominated counterparts 5F-(BPh)$_2$ (Figure 5.9).

![Scheme 5.8: Functionalisation of 5FBr$_2$-(BCl)$_2$.](image1.png)

![Figure 5.9: Solid state structure of 5FBr$_2$-(BPh)$_2$.](image2.png)
5.2.6 Functionalisation of Diborylated Carbazole A-D-A Ladder Structures

The functionalisation of the borylated carbazole analogues proved more problematic than the fluorene analogues. Unlike 5F-(BCl₂)₂ which readily transmetalates in DCM at 20°C (within 3 hours) with organozinc reagents (ZnPh₂ or Zn(C₆F₅)₂), 5C-(BCl₂)₂ is extremely slow to transmetalate under these conditions.

It proved necessary to perform the trans-metalation of 5C-(BCl₂)₂ in toluene at 60°C as reactions in DCM at 20-60°C resulted in only trace amounts of the desired product. The desired products 5C-(BPh₂)₂ and 5C-(B(C₆F₅)₂)₂ were isolated via column chromatography in poor yields (15 and 23 %, respectively). As the only structural modification is the replacement of a CR₂ in fluorene with a NR group in carbazole, this could indicate that the disparity in reaction rate is due to an association between the carbazole nitrogen lone pair and the highly Lewis acidic zinc centre. Monitoring the trans-metalation of 5C-(BCl₂)₂ using 4 equivalents of Zn(C₆F₅)₂ by in-situ ¹⁹F{¹H} NMR spectroscopy showed an up-field shift and substantial broadening of the p-fluorine resonances of the pentafluorophenyl group (-153.96 ppm) immediately upon addition to the 5C-(BCl₂)₂ reaction mixture, consistent with R₃N-Zn(aryl)₂ adduct formation. Over time and upon heating to 60°C (for 16 hours) the resonances associated with the transmetalated product (resonances at -131.92, -156.80, -136.83 ppm) emerge but the majority of the 5C-(BCl₂)₂ remains unreacted and heating at longer reaction times and higher temperatures (100°C) only resulted in decomposition of 5C-(BCl₂)₂ to unidentified products.
Figure 5.10: In-situ $^{19}$F($^1$H) NMR spectra monitoring the transmetalation of 5C-(BCl$_2$)$_2$ with Zn(C$_6$F$_5$)$_2$. ($^{19}$F($^1$H) NMR in toluene with a d$_6$-DMSO capillary insert, 376 MHz, 298 K).

As the addition of organozinc reagents to 5C-(BCl)$_2$ was relatively low yielding, the synthesis of 5C-(BPh)$_2$ was attempted via a boro-destannylation reaction. This procedure did not result in an improved yield rather the addition of excess (6 eq.) Ph$^n$Bu$_3$Sn to the reaction mixture of [5C-(BCl)$_2$][AlCl$_4$]$_2$ only resulted in the formation of trace amounts of the desired product.

5.3 Photophysical Properties of Diborylated Fluorene A-D-A Ladder Structures

5.3.1 Solution Ultraviolet-Visible Absorbance and Photoluminescence Properties

The photophysical characteristics of the moisture stable borylated ladder compounds 5F-(BPh)$_2$ and 5F-(B(C$_6$F$_5$)$_2$ were investigated by solution ultraviolet-visible absorption (UV-vis) and photoluminescence (PL) spectroscopy in toluene (1 x 10$^{-5}$ M).
Figure 5.11: UV-vis absorbance of 5F, 5F-(BPh$_2$)$_2$ and 5F-(B(C$_6$F$_5$)$_2$)$_2$ (1 x 10$^{-5}$ M toluene solutions). Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

Table 5.3: Comparison of the photophysical properties of 5F, 5F-(BPh$_2$)$_2$ and 5F-(B(C$_6$F$_5$)$_2$)$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$$_{\text{abs}}$ (nm)</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>Optical Band Gap (eV)</th>
<th>$\lambda_{\text{max}}$$_{\text{em}}$ (nm)</th>
<th>Stokes shift (nm)</th>
<th>$\Phi_f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5F</td>
<td>394</td>
<td>25200</td>
<td>2.82</td>
<td>477</td>
<td>83</td>
<td>-</td>
</tr>
<tr>
<td>5F-(BPh$_2$)$_2$</td>
<td>538</td>
<td>19500</td>
<td>2.02</td>
<td>636</td>
<td>98</td>
<td>17.9</td>
</tr>
<tr>
<td>5F-(B(C$_6$F$_5$)$_2$)$_2$</td>
<td>540</td>
<td>14700</td>
<td>2.00</td>
<td>645</td>
<td>105</td>
<td>11.5</td>
</tr>
</tbody>
</table>

*1x 10$^{-5}$M toluene solutions. *Band-gap estimated from onset of absorption.
*Relative fluorescence quantum yield, estimated by using cresyl violet as a standard ($\Phi_f$ = 54 % in methanol)$^{16}$, estimated error ± 20 %. Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

The absorption and emission of 5F, 5F-(BPh$_2$)$_2$ and 5F-(B(C$_6$F$_5$)$_2$)$_2$ were recorded in toluene (1 x 10$^{-5}$ M). The absorption bands located at the higher energy part of the spectrum (300-400nm) are attributed to localised $\pi$-$\pi^*$ transitions whereas the longer wavelength absorption bands are attributed to the internal charge transfer (ICT) from fluorene to the BT units$^{17}$ which is consistent with the D-A character of these compounds.$^{18}$ The expected large bathochromic shift in the absorption of 5F-(BPh$_2$)$_2$ ($\lambda_{\text{max}}$$_{\text{abs}}$ = 538 nm) and 5F-(B(C$_6$F$_5$)$_2$)$_2$ ($\lambda_{\text{max}}$$_{\text{abs}}$ = 540 nm) relative to 5F ($\lambda_{\text{max}}$$_{\text{abs}}$ = 394 nm) was observed upon borylation. This significant lowering of the band-gap (~0.8 eV) is mainly
attributed to a significant reduction in the energy of the LUMO upon coordination of the Lewis acidic boron atoms to the BT units (see subsequent cyclic voltammetry section). The borylated compounds all show a decreased extinction coefficient relative to their parent unborylated compound although the absorption bands are significantly broader post borylation.

It would be expected that the more electron withdrawing C₆F₅ exocyclic boron substituent would result in a greater red shifted absorbance due to a larger reduction in the LUMO energy level relative to the phenyl congener as seen in Chapters 2 and 3. Interestingly, the λmaxabs and λonsetabs of 5F-(BPh₂)₂ and 5F-(B(C₆F₅)₂)₂ are only marginally different. This implies that the effect of exchanging C₆F₅ for phenyl substituents modulates both the HOMO and LUMO to a similar degree (see subsequent cyclic voltammetry section for further discussion). 5F-(BPh₂)₂ and 5F-(B(C₆F₅)₂)₂ displayed broad emission (from 600-800 nm) with the λmaxabs of 5F-(B(C₆F₅)₂)₂ showing a slightly red shifted emission relative to 5F-(BPh₂)₂. Compound 5F-(BPh₂)₂ exhibits a reasonable solution quantum yields of 17.5 % for a red emitting material with 5F-(B(C₆F₅)₂)₂ showing a lower quantum yield of 11.5 % due to the presence C₆F₅ substituents, which is consistent with the trend observed in related compounds in Chapter 3. The absorption and emission of compounds 5F-(BPh₂)₂ and 5F-(BPh₂)₂ were investigated by solution UV-vis absorption and PL spectroscopy in a range of different polarity solvents (all at 1 x 10⁻⁵ M). 5F-(BPh₂)₂ and 5F-(BPh₂)₂ exhibited minor absorbance and major emission solvatochromism with the observed bathochromic shift of fluorescence increasing with increased solvent polarity characteristic of emission from a photoinduced-excited state with strong intramolecular charge transfer character (Figures 5.12, 5.13 and 5.14).¹⁹ This is fully analogous to that discussed in Chapter 3 and is not therefore discussed further here.
Figure 5.12: Absorbance and emission spectra of $\text{5F-}(\text{BPh}_2)_2$ in solvents of varying polarity ($1 \times 10^{-5}$ M). Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

Figure 5.13: Absorbance and emission spectra of $\text{5F-B(C}_6\text{F}_5)_2)_2$ in solvents of varying polarity ($1 \times 10^{-5}$ M). Fluorescence spectra were measured by exciting the solutions at their absorption maxima.
**Figure 5.14:** Lippert-Mataga plots for compounds $5\text{F}-(\text{BPh}_2)_2$ and $5\text{F}-(\text{B(C}_6\text{F}_5)_2)_2$.

**Table 5.4:** Comparison of the photophysical properties of $5\text{F}-(\text{BPh}_2)_2$ and $5\text{F}-(\text{B(C}_6\text{F}_5)_2)_2$ in solvents of varying polarity.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}_{\text{abs}}}$ (nm)</th>
<th>$\lambda_{\text{max}_{\text{em}}}$ (nm)</th>
<th>Stokes shift (nm)</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>553</td>
<td>609</td>
<td>56</td>
<td>19800</td>
</tr>
<tr>
<td>Toluene</td>
<td>538</td>
<td>636</td>
<td>98</td>
<td>19500</td>
</tr>
<tr>
<td>DCM</td>
<td>541</td>
<td>708</td>
<td>167</td>
<td>17600</td>
</tr>
<tr>
<td>Acetone</td>
<td>525</td>
<td>717</td>
<td>192</td>
<td>16500</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}_{\text{abs}}}$ (nm)</th>
<th>$\lambda_{\text{max}_{\text{em}}}$ (nm)</th>
<th>Stokes shift (nm)</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>551</td>
<td>623</td>
<td>72</td>
<td>14900</td>
</tr>
<tr>
<td>Toluene</td>
<td>540</td>
<td>645</td>
<td>105</td>
<td>14700</td>
</tr>
<tr>
<td>DCM</td>
<td>541</td>
<td>721</td>
<td>180</td>
<td>13500</td>
</tr>
<tr>
<td>Acetone</td>
<td>522</td>
<td>732</td>
<td>210</td>
<td>12100</td>
</tr>
</tbody>
</table>

Absorption and fluorescence data of $5\text{F}-(\text{BPh}_2)_2$ and $5\text{F}-(\text{B(C}_6\text{F}_5)_2)_2$ in solvents of different polarity ($1 \times 10^{-5}$ M). Fluorescence spectra were measured by exciting the solutions at their absorption maxima.
5.3.2 Solid State Photoluminescence Properties

The solid state structures of $5\text{F}-(\text{BPh}_2)_2$ and $5\text{F}-(\text{B(C}_6\text{F}_5)_2)_2$ display only minimal intermolecular $\pi-\pi$ stacking interactions involving the conjugated backbones, which should result in reduced aggregation induced fluorescence quenching processes. The solid state emission properties of $5\text{F}-(\text{BPh}_2)_2$ and $5\text{F}-(\text{B(C}_6\text{F}_5)_2)_2$ were examined by preparing thin films from a 5 wt. % mixture of each compound dispersed in LUMATION™ 1300 Series green emitting polymer (L1300). Upon doping $5\text{F}-(\text{BPh}_2)_2$ into a L1300 host matrix and exciting at 400 nm (the L1300 host polymer $\lambda_{\text{max}}$abs), complete quenching of the host emission is observed and broad emission stretching past 800 nm with a $\lambda_{\text{max}}$em at 657 nm and quantum yield of 15.8 % is observed which is moderate for solid state emission in this region of the electromagnetic spectrum. $5\text{F}-(\text{B(C}_6\text{F}_5)_2)_2$ on the other hand failed to fully quench the emission from L1300 and showed emission at $\lambda_{\text{max}}$em at 659 nm with a much lower quantum yield (3.2 %). The low quantum yield value results in very poor signal to noise ratio of the normalised emission spectrum (Figure 5.15). The low quantum yield value for $5\text{F}-(\text{B(C}_6\text{F}_5)_2)_2$ is attributed to poor energy transfer between host and dopant. $5\text{F}-(\text{BPh}_2)_2$ and $5\text{F}-(\text{B(C}_6\text{F}_5)_2)_2$ shows short excited state life times when dispersed in L1300 (5-6 ns) confirming that emission is due to fluorescence.

![Figure 5.15: PL spectra of thin films from a 5 wt. % mixture of compounds 5F-(BPh2)_2 and 5F-(B(C6F5)_2)_2 dispersed in 95 wt. % L1300 polymer spin coated from toluene, excited at 400 nm.](image-url)
Table 5.5 Summary of thin films PL data of compounds \(5\text{F-}(\text{BPh}_2)_2\) and \(5\text{F-}(\text{B(C}_6\text{F}_5)_2)_2\) dispersed in L1300.

<table>
<thead>
<tr>
<th>Film</th>
<th>Transmittance (A.U)</th>
<th>(\lambda_{\text{max}}^\text{em}) (nm)</th>
<th>(\Phi_f^b)</th>
<th>(\tau^c) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1300: (5\text{F-}(\text{BPh}_2)_2) (95:5 wt. %)(^a)</td>
<td>0.32</td>
<td>657</td>
<td>15.8</td>
<td>5.65</td>
</tr>
<tr>
<td>L1300: (5\text{F-}(\text{B(C}_6\text{F}_5)_2)_2) (95:5 wt. %)(^a)</td>
<td>0.32</td>
<td>659</td>
<td>3.2</td>
<td>5.06</td>
</tr>
</tbody>
</table>

\(^a\)Excited at 400 nm. \(^b\)Absolute values, determined with an integrating sphere, estimated error ± 4.5 %. \(^c\)Estimated error ± 10 %.

The solid state emission of \(5\text{F-}(\text{BPh}_2)_2\) and \(5\text{F-}(\text{B(C}_6\text{F}_5)_2)_2\) films formed from 5 wt. % dispersed in poly[(9,9-di-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (PF8-BT) spin coated from toluene showed significantly improved quantum yield values. On excitation at 468 nm (the PF8-BT host polymer \(\lambda_{\text{max}}^\text{abs}\)) compounds \(5\text{F-}(\text{BPh}_2)_2\) and \(5\text{F-}(\text{B(C}_6\text{F}_5)_2)_2\) completely quenched the emission of the host and showed emission at a \(\lambda_{\text{max}}\) of 651 and 673 nm with good (for deep red emitters) solid state quantum yields of 33.5 and 19.9 %, respectively (Table 5.6). These values suggest improved energy transfer between PF8-BT and the borylated dopants compared to films with L1300 as discussed earlier.

Figure 5.16: (a) The solid state emission spectra of \(5\text{F-}(\text{BPh}_2)_2\) and \(5\text{F-}(\text{B(C}_6\text{F}_5)_2)_2\), 5 wt. % dispersed in PF8-BT. (b) The solid state emission of \(5\text{F}\) and \(5\text{F-}(\text{BPh}_2)_2\) films drop cast from DCM under UV irradiation.
Table 5.6: Summary of thin films PL data of compounds 5F-(BPh\(_2\))\(_2\) and 5F-(B(C\(_6\)F\(_5\))\(_2\))\(_2\) dispersed in PF8-BT.

<table>
<thead>
<tr>
<th>Film</th>
<th>Transmittance (A.U)</th>
<th>(\lambda_{\text{max}_{\text{em}}}) (nm)</th>
<th>(\Phi_f)%(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF8-BT: 5F-(BPh(_2))(_2) (95:5 wt. %)(^a)</td>
<td>0.36</td>
<td>659</td>
<td>33.5</td>
</tr>
<tr>
<td>PF8-BT: 5F-(B(C(_6)F(_5))(_2))(_2) (95:5 wt. %)(^a)</td>
<td>0.36</td>
<td>673</td>
<td>19.9</td>
</tr>
</tbody>
</table>

\(^a\)Excited at 468 nm, \(^b\)Absolute values, determined with an integrating sphere, estimated error ± 4.5 %.

5.4 Redox Properties of Diborylated Fluorene A-D-A Ladder Structures

Cyclic voltammetry was employed in order to gain further insight into the effects that double borylation and installation of different exocyclic boron substituents have on the frontier molecular orbital energies. 5F, 5F-(BPh\(_2\))\(_2\) and 5F-(B(C\(_6\)F\(_5\))\(_2\))\(_2\) all show a single fully reversible reduction process which is stable for at least 10 cycles. 5F and 5F-(B(C\(_6\)F\(_5\))\(_2\))\(_2\) both show a single reversible oxidation peak which is stable to at least 10 cycles whilst the phenyl substituted 5F-(BPh\(_2\))\(_2\) shows a single irreversible oxidation peak (Figure 5.17).

Figure 5.17: Cyclic voltammograms of 5F, 5F-(BPh\(_2\))\(_2\) and 5F-(B(C\(_6\)F\(_5\))\(_2\))\(_2\), measured in DCM (1 mM) with [\(\text{Bu}_4\)N][PF\(_6\)] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV/s, relative to the Fc/Fc\(^+\) redox couple.
Table 5.7: Comparison of redox properties of 5F, 5F-(BPh$_2$)$_2$ and 5F-(B(C$_6$F$_5$)$_2$)$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{ox,onset}}$ (V)</th>
<th>$E_{\text{red,onset}}$ (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Electrochemical Band-Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5F</td>
<td>0.95</td>
<td>-1.87</td>
<td>-6.34</td>
<td>-3.52</td>
<td>2.82</td>
</tr>
<tr>
<td>5F-(BPh$_2$)$_2$</td>
<td>0.72</td>
<td>-1.28</td>
<td>-6.11</td>
<td>-4.11</td>
<td>2.00</td>
</tr>
<tr>
<td>5F-(B(C$_6$F$_5$)$_2$)$_2$</td>
<td>0.94</td>
<td>-1.07</td>
<td>-6.33</td>
<td>-4.32</td>
<td>2.01</td>
</tr>
</tbody>
</table>

Measured in DCM (1 mM) with $[t^6\text{Bu}_4\text{N}][\text{PF}_6]$ (0.1 M) as the supporting electrolyte at a scan rate of 50 mV s$^{-1}$, potentials are given relative to the Fc/Fc$^+$ redox couple which is taken to be 5.39 eV below vacuum.$^{21}$

Similar trends to those seen in Chapters 2 and 3 were observed with compound 5F-(BPh$_2$)$_2$ showing a large decrease (by 0.59 eV) in the energy of the LUMO and a moderate increase (by 0.23 eV) in the HOMO energy level. The measured reduction in electrochemical band-gap upon diborylation of 5F and installation of phenyl substituents on the boron is in good agreement with the UV-vis spectra. Similar to trends observed in Chapters 2 and 3 cyclic voltammetry measurements showed that exchanging the exocyclic phenyl boron substituents for the more electron withdrawing C$_6$F$_5$ groups (in 5F-(B(C$_6$F$_5$)$_2$)$_2$) resulted in a further reduction (by 0.21 eV) of the LUMO energy level in addition to a reduction in the HOMO energy level by approximately the same magnitude (by 0.22 eV) relative to 5F-(BPh$_2$)$_2$. This effect results in 5F-(BPh$_2$)$_2$ and 5F-(B(C$_6$F$_5$)$_2$)$_2$ demonstrating essentially identical electrochemical band-gaps. This is also in strong agreement with the optical band-gap estimated by the onset of absorbance in the UV-vis spectra. The HOMO of 5F-(B(C$_6$F$_5$)$_2$)$_2$ is effectively unchanged in energy relative to the unborylated precursor 5F ($\Delta V = 0.01$) so double borylation and functionalisation with C$_6$F$_5$ substituents therefore represents an effective methodology to dramatically reduce the LUMO energy level whilst having minimal effect on the HOMO energy level. The cyclic voltammetry measurements indicate that after diborylation and functionalisation with Ph the increase in the HOMO energy (0.23 eV) is more than double that observed for a single borylation of the related D-A-D structure (0.08 eV for 3-BPh$_2$, see Chapter 3). This suggests that the HOMO energy level of the diborylated ladder system is more sensitive to the effects imparted by the identity of the boron substituents.
5.5 Computational Analysis of Diborylated Fluorene A-D-A Ladder Structures

Computational analysis was performed (at the M06-2x/6-311g (d,p) level with PCM solvation (DCM)) for model compounds of 5F and 5F-(BPh₂)₂ which are termed 5F' and 5F'-(BPh₂)₂ (where the C₈H₁₇ chains of the F8 unit are replaced for methyl (termed F1) to reduce calculation time). The ground state optimized geometry structures and relevant HOMO and LUMO energy levels together with the molecular orbital contours for the model compounds are depicted in Figure 5.18 (calculations were performed by Dr. Ewan Clark).

![Molecular orbital energy levels and molecular orbital contours](image)

**Figure 5.18:** Molecular orbital energy levels and molecular orbital contours (isovalue = 0.04) of the HOMO and LUMO of 5F’ and 5F’-(BPh₂)₂.

The calculations reveal that upon diborylation and formation of the ladder structure a considerable reduction in the torsion angle from 38.7° (5F') to 5.2° (5F’-(BPh₂)₂) between the F1 and BT units of the model
compounds is observed. This is consistent with the angles observed in the solid state structures of 5F and 5F-(BPh₂)₂. The molecular orbital contour plots show that for both 5F’ and 5F’-(BPh₂)₂ the electron density of the HOMO orbital is delocalised across both the F1 and the BT units, whilst the electron density of the LUMO is localised on the BT units with no FMO contribution from the peripheral phenyl substituents on boron. The molecular orbital contour representation suggests no additional delocalisation present from locking the π-conjugated system of the A-D-A units coplanar. The calculations indicate a stabilisation in the LUMO energy level by 0.67 eV and a destabilisation in the HOMO energy level by 0.21 eV upon borylation which is consistent with the large reduction in band-gap observed by UV-vis spectrometry (by 0.80 eV) and cyclic voltammetry (by 0.82 eV). Comparison with 3’-BPh₂ indicates the HOMO is less delocalised onto the BT moiety in 5F’-(BPh₂)₂ than in 3’-BPh₂. This may be the origin of the larger increase in the HOMO energy observed for 5F after borylation. Lower HOMO character on the BT moiety will result in this orbital being less stabilised (lowered in energy) by Lewis acid coordination to nitrogen.

5.6 OLED Devices

As compounds 5F-(BPh₂)₂ and 5F-(B(C₆F₅)₂)₂ showed good solid state PLQY values a number of solution processed OLED devices were fabricated to analyse the performance of these compounds as deep red emitters. OLEDs fabricated using 5 wt. % 5F-(BPh₂)₂ or 5F-(B(C₆F₅)₂)₂ doped in LUMATION™ 1300 series green emitting polymer (L1300) as the emission layer (EML) resulted in devices which showed extremely poor external quantum efficiency (EQE) values (~0.02 %) with emission dominated by green emission from the host. The poor EQE values are attributed to inefficient exciton transfer between host and dopant due to a mismatch in frontier molecular orbital energy levels particularly the HOMO energies of the host/dopant system (ΔE >0.50 eV) leading to poor hole injection onto the dopants. In agreement with the superior solid state quantum yield values, solution processed devices fabricated using PF8-BT as host resulted in superior performance relative to devices with L1300 as host. The device architecture was as follows, ITO (45
nm)/Plexcore OC® AQ1200 (65nm)/PF8-TFB (poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4’-(N-(4-sec-butylphenyl) diphenylamine))]) (22 nm)/EML (100 nm)/Ba (3.5 nm). The emission layer (EML) comprised 5 wt. % of 5F-(BPh2)2 (Device 5.1) or 5F-(B(C6F5)2)2 (Device 5.2) in 80 wt. % PF8-BT and 15 wt. % PF8-TFB. The purpose of the PF8-TFB co-host is to improve hole mobility through the emission layer (Figure 5.19).

![Diagram of Device 5.1 and 5.2 OLED architectures.](image)

Device 5.1  \( X = 5F-(BPh_2)_2 \)
Device 5.2  \( X = 5F-(B(C_6F_5)_2)_2 \)

**Figure 5.19:** Device 5.1 and 5.2 OLED architectures.

![Relative energy level diagrams for Device 5.1 and 5.2.](image)

**Figure 5.20:** Relative energy level diagrams for Device 5.1 and 5.2.
The EL spectrum of **Device 5.1** showed a hypsochromic shift in EL relative to the solid state PL of a film of 5 wt. % 5F-(BPh$_2$)$_2$ dispersed in PF8-BT with significant green emission (~500-560 nm) observed from the PF8-BT host. **Device 5.2** showed a greater hypsochromic shift in the EL relative to the PL of a film of 5 wt. % 5F-(B(C$_6$F$_5$)$_2$)$_2$ dispersed in PF8-BT but showed minimal green emission from the PF8-BT host. Both devices showed low turn on voltages (2.1-2.2 V) but the EQE values (0.13-0.14 %) are low considering the high solid state PLQY values of PF8-BT host/guest films and the good performance of similar devices using 3-BPh$_2$ as dopant (see Chapter 3).

Figure 5.21: **Device 1 and 2** (a) Electroluminescence (b) Plot of EQE vs voltage (c) Plot of Current density vs voltage.
Table 5.8: Summary of OLED device performance.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Device</th>
<th>EL $\lambda$max (nm)</th>
<th>$V_{on}^{a}$ (V)</th>
<th>EQE$_{max}^{b}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5F-(BPh)$_2$</td>
<td>5.1</td>
<td>634</td>
<td>2.1</td>
<td>0.14</td>
</tr>
<tr>
<td>5F-(B(C$_6$F$_5$)$_2$)$_2$</td>
<td>5.2</td>
<td>643</td>
<td>2.2</td>
<td>0.13</td>
</tr>
</tbody>
</table>

$^a$Turn-on voltage, $^b$Maximum external quantum efficiency.

5.7 Photophysical Properties of Diborylated Carbazole A-D-A Ladder Structures

Compounds 5C, 5C-(BPh)$_2$ and 5C-(B(C$_6$F$_5$)$_2$)$_2$ were investigated by solution ultraviolet-visible spectroscopy and photoluminescence (PL) spectroscopy in toluene (1 x 10$^{-5}$ M).

![Figure 5.22: UV-vis absorbance of 5C, 5C-(BPh)$_2$ and 5C-(B(C$_6$F$_5$)$_2$)$_2$ (1 x 10$^{-5}$ M toluene solutions). Fluorescence spectra were measured by exciting the solutions at their absorption maxima.](image)

Table 5.9: Comparison of the photophysical properties of 5C, 5C-(BPh)$_2$ and 5C-(B(C$_6$F$_5$)$_2$)$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{max}^{abs}$ (nm)$^{a}$</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)$^{a}$</th>
<th>Optical Band Gap (eV)$^{b}$</th>
<th>$\lambda_{max}^{em}$ (nm)$^{b}$</th>
<th>Stokes shift (nm)</th>
<th>$\Phi_f$ $^{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5C</td>
<td>401</td>
<td>24600</td>
<td>2.74</td>
<td>491</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>5C-(BPh)$_2$</td>
<td>540</td>
<td>17000</td>
<td>1.98</td>
<td>727</td>
<td>187</td>
<td>0.3</td>
</tr>
<tr>
<td>5C-(B(C$_6$F$_5$)$_2$)$_2$</td>
<td>548</td>
<td>15200</td>
<td>1.95</td>
<td>719</td>
<td>171</td>
<td>0.3</td>
</tr>
</tbody>
</table>

$^a$1x 10$^{-5}$ M solution in toluene. $^b$Band-gap estimated from onset of absorption.

$^c$Relative fluorescence quantum yield, estimated by using cresyl violet as standard ($\Phi_f = 54 \%$ in methanol)$^{16}$, estimated error $\pm 20 \%$. Fluorescence spectra were measured by exciting the solutions at their absorption maxima.
The absorption spectra of the carbazole containing compounds were remarkably similar to those of the fluorene containing series. Considering the more electron rich nature of carbazole a noticeable red shift in absorbance correlating to a decreased band-gap would be expected due to an increased HOMO energy level relative to the fluorene congeners. Only a minor red shift in $\lambda_{\text{max,abs}}$ and the onset on absorption relative to the fluorene analogues is observed although a red shift to longer wavelength emission (>700 nm) is observed due to the carbazole compounds showing increased Stokes shift values. Unlike their fluorene containing analogues toluene solutions of 5C-(BPh$_2$)$_2$ and 5C-(B(C$_6$F$_5$)$_2$)$_2$ display extremely low fluorescence quantum yield values (<0.5 %). Computational analysis on models of these compounds was performed to gain insight into the possible origin of the observed low fluorescence quantum yield values (see subsequent discussion).

5.8 Redox Properties of Diborylated Carbazole A-D-A Ladder Structures

Cyclic voltammetry was employed in order to gain further insight into the effects double borylation and different exocyclic boron substituents have on the frontier molecular orbital energies. In general, very strong parallels with the trends on double borylation and installation of different exocyclic boron substituents for the corresponding fluorene containing compounds were observed. The expected large decrease in the LUMO energy level was observed upon borylation and functionalisation with phenyl substituents to form 5C-(BPh$_2$)$_2$ with a concomitant increase in the HOMO energy level (by 0.19 eV). Exchanging the exocyclic phenyl boron substituents for the more electron withdrawing C$_6$F$_5$ groups (5C-(B(C$_6$F$_5$)$_2$)$_2$) resulted in a further reduction (by 0.18 eV) of the LUMO energy level in addition to a reduction in the HOMO energy level by approximately the same magnitude (0.17 eV) relative to 5C-(BPh$_2$)$_2$. This effect results in 5C-(BPh$_2$)$_2$ and 5C-(B(C$_6$F$_5$)$_2$)$_2$ demonstrating essentially identical electrochemical band-gaps. These trends are in strong agreement with the UV-vis absorbance spectra. The electrochemical band-gaps are ~0.2 eV smaller than the fluorene analogues due to higher energy HOMO as originally hypothesised when these molecules were selected for synthesis.
Figure 5.23: Cyclic voltammetry plots for 5C, 5C-(BPh₂)₂ and 5C-(B(C₆F₅)₂)₂, measured in DCM (1 mM) with [nBu₄N][PF₆] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV s⁻¹.

Table 5.10: Comparison of redox properties of 5C, 5C-(BPh₂)₂ and 5C-(B(C₆F₅)₂)₂.

<table>
<thead>
<tr>
<th>Compound</th>
<th>E₉ₓ_{onset} (V)</th>
<th>E₉ₓ_{onset} (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Electrochemical Band-Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5C</td>
<td>0.75</td>
<td>-1.87</td>
<td>-6.18</td>
<td>-3.50</td>
<td>2.68</td>
</tr>
<tr>
<td>5C-(BPh₂)₂</td>
<td>0.50</td>
<td>-1.31</td>
<td>-5.89</td>
<td>-4.08</td>
<td>1.81</td>
</tr>
<tr>
<td>5C-(B(C₆F₅)₂)₂</td>
<td>0.67</td>
<td>-1.13</td>
<td>-6.06</td>
<td>-4.26</td>
<td>1.80</td>
</tr>
</tbody>
</table>

Measured in DCM (1 mM) with [nBu₄N][PF₆] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV s⁻¹, potentials are given relative to the Fc/Fc⁺ redox couple which is taken to be 5.39 eV below vacuum.²¹

5.9 Computational Analysis of Diborylated Carbazole A-D-A Ladder Structures

Computational analysis was performed (at the M06-2x/6-311g (d,p) level with PCM solvation (DCM)) for model compounds of 5C, 5C-(BPh₂)₂ and 5C-(B(C₆F₅)₂)₂ which are termed 5C', 5C'-(BPh₂)₂ and 5C'-,(B(C₆F₅)₂)₂ (where C₁₇H₃₅ of the carbazole unit is replaced with methyl (termed C1) to reduce calculation time). The ground state optimized geometry and relevant HOMO
and LUMO energy levels together with the molecular orbital contours for the model compounds are depicted in Figure 5.24.

Figure 5.24: Molecular orbital energy levels and molecular orbital contours (isovalue = 0.04) of the HOMO and LUMO of 5C’, 5C’-(BPh₂)₂ and 5C’-(B(C₆F₅)₂)₂.

Upon diborylation a considerable reduction in the torsion angle from 46.3° (5C’) to 3.0° (5C’-(BPh₂)₂) and 2.0° (5C’-(B(C₆F₅)₂)₂) between the C1 and BT units of the model compounds is observed. The calculations show the expected large reduction in the band-gap mainly due to a reduction in the LUMO and slightly raised HOMO energy levels. The energy levels of the HOMO and LUMO are reduced a further 0.21 and 0.22 eV upon exchanging phenyl boron substituents for pentafluorophenyl to give approximately the same band-gap. This is consistent with the similar band-gaps observed by UV-vis spectroscopy in addition to the photophysical and electrochemical trends observed for the fluorene congeners. The molecular orbital contours of 5C’ are similar to that of 5F’ in that both show the electron density of the HOMO is delocalised across both the donor unit (F1 and C1) and BT units, whilst the electron density of the LUMO is localised purely on the BT units. Unlike 5F’-
the HOMO of \(5C'-(BPh)_2\) and \(5C'-(B(C_6F_5)_2)\) has reduced delocalisation and no significant character on the BT units. This results in \(5C'-(BPh)_2\) and \(5C'-(B(C_6F_5)_2)\) showing no spatial HOMO–LUMO overlap as the LUMO is still highly localised on the BT units. This dearth of any spatial HOMO–LUMO overlap can explain the observed low quantum yield values as some degree of HOMO–LUMO spatial overlap is required to achieve a high oscillator strength which is essential for achieving a high radiative transition rate which leads to a high fluorescence quantum yield.\(^{22}\) The lack of any HOMO character on the BT unit also suggests the increase in the energy of the HOMO of \(5C\) upon borylation (observed by cyclic voltammetry) is not due to an enhanced conjugation length as a result from enforced planarity but rather an inductive effect from the BPh\(_2\) group. This also explains the decrease in the HOMO and LUMO upon exchanging the phenyl boron substituents for the more electron withdrawing \(C_6F_5\) substituents. This simultaneous reduction in both the HOMO and LUMO upon exchanging aromatic boron substituents for their perfluorinated analogues is not unprecedented.\(^{23}\)

5.10 Conclusions

The direct electrophilic borylative fusion methodology was successfully expanded to synthesise fully fused ladder-type structures based on fluorene and carbazole donor units. Solid state structures determined by X-ray diffraction analysis demonstrate that bulky aryl substituents on the boron centres prevent \(\pi\)-stacking of the conjugated backbones. These molecules show large bathochromic shifts in the absorption, far red/NIR fluorescence, large Stokes shifts and in some cases excellent solid state quantum yield values post borylation. Calculations and electrochemical measurements confirm the energy of the LUMO energy level is substantially decreased upon borylation, whilst only moderately affecting the HOMO energy level. The effect on the HOMO energy level is minimised with exocyclic \(C_6F_5\) substituents on boron. This demonstrates that the synthetic modification described herein is an effective method to lower the LUMO, reduce the band-gap and increase the rigidity of \(\pi\)-conjugated D-A systems. Unoptimised solution processed OLED devices of the ladder compounds were fabricated but these showed lower maximum EQE values at shorter wavelengths than those observed for the singularly borylated fused structures in Chapter 3. Exchange of the fluorene donor unit with a carbazole
unit generated materials with poor emissive properties due to spatial separation of frontier orbitals leading to low quantum yield values.

5.11 Experimental

5.11.1 General Considerations

For general considerations see Chapters 2, 3 and 4. Heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole was synthesised by modified literature procedures.\textsuperscript{24} 5C and 5C-(B(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}) were synthesised with the assistance of Rosanne Goh. Data for compounds 5F, 5F-(BPh\textsubscript{2}), 5F-(B(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}) and 5FB\textsubscript{r}\textsubscript{2}-(BPh\textsubscript{2})\textsubscript{2} were recorded on an Agilent Supernova diffractometer with Mo K\textsubscript{\alpha} radiation (mirror monochromator, \(\lambda = 0.7107 \text{ Å}\)). The CrysAlisPro\textsuperscript{25} software package was used for data collection, cell refinement and data reduction. Data for compound 5FB\textsubscript{r}\textsubscript{2}-(BPh\textsubscript{2})\textsubscript{2} was recorded on a Bruker APEX-II diffractometer, with Cu K\textsubscript{\alpha} radiation (graphite monochromator, \(\lambda = 1.5418 \text{ Å}\)). The Bruker APEX2 software package was used for data collection and the OLEX 2\textsuperscript{26} software package was used for cell refinement and data reduction. Structures 5F\textsuperscript{-} and 5F\textsuperscript{-}-(BPh\textsubscript{2})\textsubscript{2} were pre-optimised by HF at 3-21G and structure 5C\textsuperscript{-}, 5C\textsuperscript{-}-(BPh\textsubscript{2})\textsubscript{2} and 5\textsuperscript{-}B((C\textsubscript{6}F\textsubscript{5})\textsubscript{2})\textsubscript{2} were pre-optimised by DFT at the B3LYP/6-31G level. These were followed by optimisation at the M06-2X/6-311G (d,p) level with inclusion of a PCM model for solvent correction (DCM).\textsuperscript{27} Structures were confirmed as minima by frequency analysis and the absence of imaginary frequencies.
5.11.2 Synthetic Procedures

**Synthesis of 5F**

![Image of 5F molecule]

4-bromo-2,1,3-benzothiadiazole (3.90 g, 1.84 mmol), 9,9-dioctylfluorene-2,7-diboronic acid (4.00 g, 8.36 mmol), K$_3$PO$_4$ (10.65 g, 5.016 mmol), Pd$_2$(dba)$_3$ (0.38 g, 0.042 mmol) and S-Phos (0.168 mmol) were dissolved in THF (120 mL) and heated at 70ºC for 24 hours. The reaction mixture was then allowed to cool, filtered (to remove excess K$_3$PO$_4$), dissolved in EtOAc (200 mL) and washed with water (3 x 100 mL) and then with brine (1 x 100 mL), dried (MgSO$_4$) and evaporated to dryness. After evaporating the solvent, the residue was purified by column chromatography on silica gel [eluent: hexane:EtOAc (1:0 to 97:3)] and subsequent recrystallisation by slow evaporation of the eluent afforded 5F as yellow needles. (Yield 3.40 g, 62%)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.08 - 7.98 (m, 4 H), 7.98 - 7.87 (m, 4 H), 7.85 - 7.66 (m, 4 H), 2.17 - 2.06 (m, 4 H), 1.24 - 1.06 (m, 20 H), 0.88 (m, 4 H), 0.78 (t, $^3$J$_{HH}$ = 6.9 Hz, 6 H);

$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$: aryl = 155.7, 153.7, 151.7, 140.9, 136.3, 135.0, 129.7, 128.3, 127.5, 124.0, 120.3, 120.0, alkyl = 55.4, 40.2, 31.8, 30.1, 29.2, 24.0, 22.6, 14.0;

MALDI-TOF: calc. for C$_{41}$H$_{46}$BN$_4$S$_2$ [M]$^+$ = 658.3, found 658.7

The spectra of 5F are consistent with that previously reported$^{13}$
Synthesis of 5F-(BCl$_2$)$_2$

BCl$_3$ (1M solution in DCM) (0.40 mL, 0.40 mmol) was added to a bright yellow solution of 3 (66 mg, 0.10 mmol) in DCM (0.7 mL) in a J. Young's NMR tube. The solution instantly changed colour to a dark red. 2,4,6-tri$^3$butylpyridine (50 mg, 0.2 mmol) and AlCl$_3$ (40 mg, 0.3 mmol) were added as solids to the reaction mixture. After rotating for 16 hours, an additional portion of AlCl$_3$ (14 mg, 0.1 mmol) was added as a solid and the solution was rotated for a further 16 hours whereupon the solution had turned dark green. N$^n$Bu$_4$Cl (48 mg, 0.2 mmol) was then added to the reaction mixture and the solution turned dark purple. $^1$H NMR spectroscopy indicated full conversion to the desired product 5F-(BCl$_2$)$_2$ and this reaction mixture was used directly in subsequent steps.

$^1$H NMR (400 MHz, CH$_2$Cl$_2$) $\delta$: aryl = 8.64 (d, $^3$J$_{HH}$ = 7.1 Hz, 2 H$_a$), 8.47 (s, 2 H$_b$), 8.44 - 8.36 (m, 2 H$_c$), 8.31 (d, $^3$J$_{HH}$ = 8.8 Hz, 2 H$_d$), 8.12 (s, 2 H$_e$), 2.19 (m, 4 H), 1.04 (m, 20 H), 0.72 (m, 10 H);

$^{11}$B NMR (128 MHz, CH$_2$Cl$_2$) $\delta$ = ~10.0 (br.);

Due to the sensitivity of 5F-(BCl$_2$)$_2$ mass spec were not obtainable.
Synthesis of 5F-(BPh₂)₂ via ZnPh₂

A reaction mixture containing 5F-(BCl₂)₂ (0.45 mmol) and the ionic by-products from borylation (e.g., ammonium[AlCl₄]) was dissolved in DCM (15 mL) and ZnPh₂ (400 mg, 1.82 mmol) was added. The reaction mixture was then stirred for 16 hours after which it was passed through a plug of silica. The solvent was then removed under reduced pressure and the product was isolated by column chromatography on base treated (5 % NEt₃ in hexane) silica gel [eluent: hexane:DCM (8:2)] to afford 5F-(BPh₂)₂ as a purple residue. (Yield 236 mg, 53%)

via nBu₃SnPh

BCl₃ (1M solution in DCM) (0.30 mL, 0.3 mmol), 2,4,6-tri⁷butylpyridine (38 mg, 0.16 mmol) were added to a bright yellow solution of 5F (50 mg, 0.08 mmol) in DCM (3 mL). The solution instantly changed colour to a dark red. AlCl₃ (20 mg, 0.15 mmol) was then added to the reaction mixture. After rotating for 16 hours, an additional portion of AlCl₃ (20 mg, 0.15 mmol) was added to the reaction mixture. The solution was rotated for a further 16 hours whereupon the solution had turned dark green. The DCM was removed under reduced pressure and the reaction mixture was dissolved in o-DCB (4 mL). Tri⁷butylphenylstannane (0.15 mL, 0.46 mmol) was added to the reaction mixture which was then stirred at 20°C for 48 hours followed by heating at 40°C for 16 hours. NMe₄Cl (50 mg, 0.46 mmol) was added to the reaction mixture and after 1 hour the solvent was then removed under reduced pressure. The resulting residue was then purified via column chromatography on base treated (5 % NEt₃ in hexane) silica gel [eluent chloroform:hexane (2:8)] to afford 5F-(BPh₂)₂ as a purple residue. (Yield 24 mg, 32%)

¹H NMR (400 MHz, CD₂Cl₂) δ = 8.39 (d, ³J_HH = 7.1 Hz, 2 Ha), 8.18 (s, 2 Hb), 7.90 - 7.77 (m, 6 H), 7.31 - 7.15 (m, 20 H), 2.32 - 2.13 (m, 4 H), 1.18 (m, 20 H), 0.97 (m., 4 H), 0.82 (t, ³J_HH = 6.7 Hz, 6 H);
$^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$) $\delta$: aryl = 155.8, 155.3, 152.7, 150.4, 148.2, 142.4, 134.0, 133.7, 131.0, 130.4, 128.1, 126.5, 126.4, 123.9, 119.5, 117.3, alkyl = 55.1, 41.3, 32.4, 30.7, 29.8, 24.7, 23.2, 14.4;

$^{11}$B NMR (128 MHz, CD$_2$Cl$_2$) $\delta = \sim 2.0$ (br.);

MALDI-TOF: calc. for C$_{59}$H$_{55}$B$_2$N$_4$S$_2$ $^+$ [M - C$_6$H$_5$]$^+$ = 909.9, found 910.0

Synthesis of 5F-(B(C$_6$F$_5$)$_2$)$_2$

A reaction mixture of 5F-(BCl)$_2$ (0.45 mmol) also containing the ionic by-products from borylation (e.g., ammonium[AlCl$_4$]) was dissolved in DCM (15 mL) and Zn(C$_6$F$_5$)$_2$ (728 mg, 1.82 mmol) was added. The reaction mixture was then stirred for 16 hours after which it was passed through a plug of silica. The solvent was then removed under reduced pressure and the product was isolated by column chromatography on base treated (5 % NEt$_3$ in hexane) silica gel [eluent: hexane:DCM (8:2)] to afford 5F-(B(C$_6$F$_5$)$_2$)$_2$ as a dark purple residue. (Yield 435 mg, 71%)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta = 8.48$ (d, $^3$J$_{HH}$ = 6.8 Hz, 2 Ha), 8.10 (s, 2 Hb), 8.02 - 7.85 (m, 4 H), 7.67 (s, 2 Hc), 2.25 - 2.05 (m, 4 H), 1.20 - 1.00 (m, 20 H), 0.78 - 0.68 (m, 10 H);

$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$: aryl = 154.9, 150.7, 147.0, 142.2, 133.5, 129.7, 128.7, 125.0, 125.0, 119.4, 116.5, alkyl = 55.0, 40.9, 31.8, 30.0, 29.2, 29.1, 22.5, 14.0;

$^{19}$F{$^1$H} NMR (376 MHz, CDCl$_3$) $\delta = -132.23$ (dd, $^3$J$_{FF}$ = 22.6, $^4$J$_{FF}$ = 8.3, 8 F), -157.83 (t, $^3$J$_{FF}$ = 20.7, 4 F), -163.77 (m, 8 F);

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta = \sim 3.0$ (br.);

MALDI-TOF: calc. for C$_{59}$H$_{44}$B$_2$F$_{15}$N$_4$S$_2$ $^+$ [M - C$_6$F$_5$]$^+$ = 1179.8, found 1179.7
Synthesis of 5FBr₂

5F (512 mg, 0.78 mmol) was dissolved in chloroform (5 mL) and bromine (0.9 mL, 1.7 mmol) was added. The reaction mixture was then stirred for 18 hours after which the reaction mixture was quenched with Na₂S₂O₃ solution (10 mL), washed with brine (50 mL) then water (50 mL) and dried (MgSO₄). The crude product was then purified via silica gel chromatography [eluent: hexane:EtOAc (98:2)] to afford 5FBr₂ as a yellow solid. (Yield 612 mg, 97%)

¹H NMR (400 MHz, CDCl₃) δ = 8.05 - 7.84 (m, 8 H), 7.65 (d, ³J_HH = 7.6 Hz, 2 H), 2.25 - 1.98 (m, 4 H), 1.22 – 1.02 (m, 20 H), 1.00 - 0.82 (m, 4 H), 0.76 (t, ³J_HH = 6.7 Hz, 6 H);

¹³C{¹H} NMR (101 MHz, CDCl₃) δ: aryl = 153.7, 153.0, 151.6, 140.9, 135.4, 134.1, 132.1, 128.2, 127.8, 123.8, 120.1, 112.6, alkyl = 55.3, 40.0, 31.6, 29.9, 29.1, 23.9, 22.5, 22.5, 14.0;

MALDI-TOF: calc. for C₄₁H₄₄Br₂N₄S₂⁺ [M]⁺ = 814.1, found 814.0
Synthesis of 5FBr₂-(BPh₂)₂

BCl₃ (1M in DCM) (4.5 mL, 4.5 mmol) was added to a solution of 5F-Br₂ (430 mg, 0.53 mmol) in DCM (5 mL). The reaction was stirred under a dynamic flow of N₂ for 20 hours after which it was degassed and the solvent was removed under reduced pressure. The residue was dissolved in DCM (5 mL), ZnPh₂ (574 mg, 2.61 mmol) was then added to the reaction mixture. The reaction mixture was left to stir for 4 hours after which it was diluted with DCM (5 mL) and the solution was passed through a plug of silica. The solvent was then removed under reduced pressure and the product was isolated by column chromatography on silica gel [eluent: chloroform:hexane (7:3)] to afford 5FBr₂-(BPh₂)₂ as a dark purple solid. (Yield 347 mg, 58%)

¹H NMR (400 MHz, CDCl₃) δ = 8.22 (d, 3 JHH = 8.0 Hz, 2 Hₐ), 8.08 (d, 3 JHH = 7.9 Hz, 2 Hₖ), 8.05 (s, 2 Hc), 7.76 (s, 2 Hₐ), 7.15 - 7.32 (m, 20 H), 2.04 - 2.20 (m, 4 H), 1.14 - 0.94 (m, 20 H), 1.00 - 0.86 (m, 4 H), 0.83 (t, 3 JHH = 6.7 Hz, 6 H);

¹³C{¹H} NMR (101 MHz, CDCl₃) δ: aryl = 154.3, 153.0, 152.1, 149.9, 147.7, 142.2, 135.3, 133.5, 130.0, 129.2, 127.6, 126.6, 126.1, 123.6, 116.4, 110.6, alkyl = 54.3, 40.8, 31.8, 30.1, 29.2, 29.2, 24.1, 22.6, 14.1;

¹¹B NMR (128 MHz, CDCl₃): δ = ~2.0 (br.);

MALDI-TOF: calc. for C₆₅H₆₂Br₂N₄NaS₂ [M + Na]⁺ = 1167.3, found 1167.0
Synthesis of $5\text{FBr}_2(\text{B(C}_6\text{F}_5)_2)\text{Br}_2$

BCl$_3$ (1M in DCM) (0.6 mL, 0.6 mmol) was added to a solution of $5\text{F-Br}_2$ (82 mg, 0.1 mmol) in DCM (3 mL). The reaction was stirred under a dynamic flow of nitrogen for 20 hours after which it was degassed and the solvent was removed under reduced pressure. The residue was dissolved in DCM (5 mL), Zn(C$_6$F$_5$)$_2$ (200 mg, 0.5 mmol) was then added to the reaction mixture. The reaction mixture was left to stir for 4 hours after which time it was diluted with DCM (5 mL) and the solution was passed through a plug of silica. The solvent was then removed under reduced pressure and the product was isolated by column chromatography on silica gel [eluent: DCM:hexane (3:7)] to afford $5\text{FBr}_2(\text{B(C}_6\text{F}_5)_2)\text{Br}_2$ as a dark purple solid. (Yield 44 mg, 30%)

$^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ = 8.41 - 8.28 (d, $^3J_{HH} = 7.9$ Hz, 2 H$_a$), 8.19 - 8.09 (d, $^3J_{HH} = 7.8$ Hz, 2 H$_b$), 8.02 (s, 2 H$_c$), 7.64 (s, 2 H$_d$), 2.21 - 2.01 (m, 4 H), 1.19 - 1.04 (m, 20 H), 0.77 (m, 10 H);

$^{13}\text{C\{}^{1}\text{H}\}$ NMR (101 MHz, CDCl$_3$) $\delta$: aryl = 152.9, 150.9, 147.2, 145.5, 142.3, 135.8, 128.9, 128.4, 125.7, 125.0, 116.5, 111.7, alkyl = 55.1, 40.8, 31.7, 30.0, 29.2, 29.1, 23.8, 22.5, 14.0;

$^{19}\text{F\{}^{1}\text{H}\}$ NMR (376 MHz, CDCl$_3$) $\delta$ = -131.63 (dd, $^3J_{FF} = 24.1$, $^4J_{FF} = 7.9$ Hz, 8 F), -155.9 (t, $^3J_{FF} = 22.2$, 4 F), -162.8 (m, 8 F);

$^{11}\text{B NMR}$ (128 MHz, CDCl$_3$) $\delta$ = ~-4.0 (br.);

MALDI-TOF: calc. for C$_{65}$H$_{42}$B$_2$Br$_2$F$_{20}$NaS$_2$ $[\text{M + Na}]^+ = 1525.1$, found 1525.2

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**Synthesis of 5C**

Heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (0.62 g, 0.94 mmol), 4-bromo-2,1,3-benzothiadiazole (0.46 g, 2.1 mmol), K$_3$PO$_4$.H$_2$O (1.30 g, 5.62 mmol), degassed deionised water (1.35 mL), Pd$_2$(dba)$_3$ (42.9 mg, 0.05 mmol) and S-PHOS (38.5 mg, 0.01 mmol) were dissolved in THF (10 mL). The reaction mixture was stirred at 70°C for 24 hours. The cooled mixture was extracted with DCM (100 mL), washed with brine (1 x 100 mL), then water (1 x 100 mL) and dried with MgSO$_4$. After evaporation of solvents, the resulting orange residue was purified on base treated silica gel (5 % NEt$_3$ in hexane) column chromatography [eluent: chloroform:hexane (0:1 followed by 2:8)]. The desired product was obtained as a yellow solid. (Yield 0.48 g, 77 %)

**$^1$H NMR** (400 MHz, CD$_2$Cl$_2$) $\delta =$ 8.42 - 8.21 (m, 3 H), 8.10 (s, 1 H), 8.04 (dd, $^3$J$_{HH} = 8.7$, 0.9 Hz, 2 H), 7.92 - 7.68 (m, 6 H), 4.76 (sept, $^3$J$_{HH} = 4.8$, 1 H), 2.57 - 2.39 (m, 2 H), 2.10 - 1.94 (m, 2 H), 1.41 - 1.04 (m, 24 H), 0.79 (t, $^3$J$_{HH} = 6.9$ Hz, 6 H);

**$^{13}$C{$^1$H} NMR** (101 MHz, CDCl$_3$) $\delta$: aryl = 155.7, 153.7, 142.8, 139.3, 135.5, 135.4, 134.9, 134.3, 129.6, 127.7, 127.7, 123.6, 122.3, 120.5, 120.2, 120.1, 113.0, 110.2, 77.3, 76.7, alkyl = 56.4, 33.8, 31.7, 29.4, 29.3, 29.1, 26.8, 22.5, 13.9;

**MALDI-TOF**: calc. for C$_{41}$H$_{47}$N$_5$S$_2$$^+$ [M]$^+$ = 673.3, found 673.8
Synthesis of 5C-(BPh$_2$)$_2$

BCl$_3$ 1M in DCM (0.38 mL, 0.38 mmol) was added to a stirred solution of 5C (64 mg, 0.095 mmol) and 2,4,6-tri$^t$butylpyridine (48 mg, 0.19 mmol) in DCM (3 mL). AlCl$_3$ (26 mg, 0.19 mmol) was added to the reaction mixture which was then stirred for 2 hours at room temperature. An additional quantity of AlCl$_3$ (26 mg, 0.19 mmol) was added and the reaction mixture was stirred for 2 hours whereupon the reaction mixture had turned blue. The reaction mixture was evaporated to dryness and the residue was then dissolved in DCM (5 mL) and NMe$_4$Cl (41 mg, 0.38 mmol) was added to the solution which instantly turned pink. After the removal of the solvent under reduced pressure, the reaction mixture was dissolved in toluene (20 mL) and ZnPh$_2$ (105 mg, 0.49 mmol) was added to the reaction mixture. The reaction was stirred at 60°C for 2 hours which resulted in a purple solution. After the solvent was removed under reduced pressure, the desired product was purified by base treated (5 % NEt$_3$ in hexane) preparative TLC [eluent: DCM:hexane (7:3)] to afford a purple solid. (Yield 16 mg, 17 %).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.37$ (d, $^3J_{HH} = 6.3$ Hz, 2 H), 8.32 (d, $^3J_{HH} = 6.8$ Hz, 2 H), 8.21 (s, 1 H), 8.12 (d, $^3J_{HH} = 6.8$ Hz, 2 H), 8.03 (s, 1 H), 7.96 - 7.78 (m, 4 H), 7.13 - 7.31 (m, 20 H), 4.70 (sept, $^3J_{HH} = 4.8$ Hz, 1 H), 2.44 (m, 2 H), 2.09 (m, 2 H), 1.43 - 1.08 (m, 24 H), 0.79 (t, $^3J_{HH} = 6.80$, 6 H);

$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$: aryl = 155.2, 155.1, 147.7, 142.8, 142.6, 139.4, 133.5, 133.0, 131.2, 128.6, 128.2, 127.5, 127.0, 126.7, 125.8, 124.6, 122.9, 118.7, 104.3, 101.6, alkyl = 56.1, 33.9, 31.9, 31.7, 31.6, 29.7, 29.6, 29.3, 29.2, 27.1, 22.5, 14.0;

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta = -3.0$ (br.);

MALDI-TOF: calc. for C$_{59}$H$_{60}$B$_2$N$_6$S$_2$ $^+$ [M - C$_6$H$_5$]$^+$ = 924.4, found 924.6
Synthesis of 5C-(B(C₆F₅)₂)₂

BCl₃ 1M in DCM (0.6 mL, 1M) was added to a stirred solution of 5C (100 mg, 0.15 mmol) and 2,4,6-tri­butylpyridine (73 mg, 0.30 mmol) in DCM (3 mL). AlCl₃ (40 mg, 0.30 mmol) was then added to the reaction mixture which was then stirred for 2 hours at room temperature. An additional quantity of AlCl₃ (40 mg, 0.30 mmol) was added and the reaction mixture was stirred for 2 hours whereupon the reaction mixture had turned blue. The reaction mixture was evaporated to dryness and the reaction mixture was then dissolved in DCM (5 mL) and NMe₄Cl (32 mg, 0.30 mmol) was added to the solution which instantly turned pink. After the removal of the solvent under reduced pressure, the reaction mixture was dissolved in toluene (20 mL) and Zn(C₆F₅)₂ (237 mg, 0.59 mmol) was added to the reaction mixture. The reaction was left to stir overnight at 60°C which resulted in a purple solution. After the solvent was removed under reduced pressure, the desired product was purified by base treated (5% NEt₃ in hexane) preparative TLC [eluent: DCM:hexane (7:3)] to afford a purple solid. (Yield 48 mg, 24%)

¹H NMR (400 MHz, CDCl₃) δ = 8.50 (d, 3JₜH = 6.7 Hz, 1 H), 8.54 (d, 3JₜH = 6.7 Hz, 1H) 8.20 (s, 1 H), 8.09 - 7.87 (m, 7 H), 4.69 (sept, 3JₜH = 5.0 Hz, 1 H), 2.46 - 2.35 (m, 2 H), 2.15 - 2.04 (m, 2 H), 1.40 - 1.07 (m, 24 H), 0.79 - 0.73 (t, 3JₜH = 6.8 Hz, 6 H);

¹³C{¹H} NMR (101 MHz, CDCl₃) δ: aryl = 155.2, 155.1, 147.7, 142.8, 142.6, 139.4, 133.5, 133.0, 131.2, 128.6, 128.2, 127.5, 127.0, 126.7, 125.8, 124.6, 122.9, 118.7, 104.3, 101.6, alkyl = 56.1, 33.9, 31.9, 31.7, 31.6, 29.7, 29.6, 29.3, 29.2, 27.1, 22.5, 14.0;

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ = -131.89 (m, 8 F), -156.7 (m, 4 F), -162.80 (m, 8 F);

¹¹B NMR (128 MHz, CDCl₃) δ = ~-4.0 (br.);

MALDI-TOF: calc. for C₅₉H₄₅B₂N₅F₁₅S₂⁺ [M - C₆F₅]⁺ = 1194.3, found 1194.0
## 5.11.3 Crystallographic Details

Table 5.11: Summary of crystallography data for 5F, 5F-(BPh$_2)_2$ and 5F-(B(C$_6$F$_5)_2)_2.

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<th>5F</th>
<th>5F-(B(C$_6$F$_5)_2)$_2$</th>
<th>5F-(BPh$_2)_2$</th>
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<tr>
<td><strong>CCDC reference</strong></td>
<td>1050921</td>
<td>1050923</td>
<td>1050922</td>
</tr>
<tr>
<td><strong>Empirical Formula</strong></td>
<td>C$<em>{41}$H$</em>{46}$N$_4$S$_2$</td>
<td>C$<em>{65}$H$</em>{44}$B$<em>2$F$</em>{20}$N$_4$S$_2$, 2(CH$_3$CO)</td>
<td>C$<em>{65}$H$</em>{64}$B$_2$N$_4$S$_2$, 0.5(C$<em>6$H$</em>{14}$)</td>
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<td><strong>Fw / g mol$^{-1}$</strong></td>
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<td>1585.56</td>
<td>1030.09</td>
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<tr>
<td><strong>Crystal system, space group</strong></td>
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<td>Monoclinic P 2$_1$/c</td>
<td>Tetragonal I 4$_1$/a</td>
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<td><strong>T / K</strong></td>
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<td>150</td>
<td>150</td>
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<tr>
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<td><strong>$b$ / Å</strong></td>
<td>18.1370(7)</td>
<td>22.7422(8)</td>
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<td><strong>$c$ / Å</strong></td>
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<tr>
<td><strong>$\alpha$ / deg</strong></td>
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<td>90</td>
<td>90</td>
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<tr>
<td><strong>$\beta$ / deg</strong></td>
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<td>96.749(3)</td>
<td>90</td>
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<tr>
<td><strong>$\gamma$ / deg</strong></td>
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<td>90</td>
<td>90</td>
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<tr>
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<td>6613.2(4)</td>
<td>22735.2(12)</td>
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<tr>
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<td>4</td>
<td>16</td>
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<tr>
<td><strong>calc. density (Mg m$^{-3}$)</strong></td>
<td>1.242</td>
<td>1.592</td>
<td>1.204</td>
</tr>
<tr>
<td><strong>radiation</strong></td>
<td>Mo K$_\alpha$</td>
<td>Mo K$_\alpha$</td>
<td>Mo K$_\alpha$</td>
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<tr>
<td><strong>$\lambda$ / Å</strong></td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
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<tr>
<td><strong>abs. coeff.(mm$^{-1}$)</strong></td>
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<td>0.427</td>
<td>0.139</td>
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<td>8784</td>
</tr>
<tr>
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<tr>
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<td>16576 / 9431</td>
<td>31516 / 6933</td>
</tr>
<tr>
<td><strong>collected / unique</strong></td>
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<td>0.031</td>
<td>0.038</td>
</tr>
<tr>
<td><strong>$R_{int}$</strong></td>
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<td>0.055</td>
<td>0.038</td>
</tr>
<tr>
<td><strong>no. of data / restraints / parameters</strong></td>
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<td>9402 / 0 / 910</td>
<td>6906 / 83 / 768</td>
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<tr>
<td><strong>R (data with $I^2 &gt; 2\sigma(I^2)$)</strong></td>
<td>0.0613 (5781)</td>
<td>0.0644 (6044)</td>
<td>0.0595 (5402)</td>
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<td><strong>wR (all data)</strong></td>
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<td>0.1752</td>
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<td><strong>S</strong></td>
<td>0.9999</td>
<td>0.9618</td>
<td>1.0014</td>
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<td><strong>$\Delta \rho_{\text{max}, \text{min}} / e \cdot \text{Å}^3$</strong></td>
<td>0.54, -0.58</td>
<td>1.02, -0.79</td>
<td>0.68, -0.47</td>
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Table 5.12: Summary of crystallography data for 5FBr$_2$-(BPh$_2$)$_2$

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<tr>
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<th>5FBr$_2$-(BPh$_2$)$_2$</th>
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<tr>
<td>CCDC reference</td>
<td>1468920</td>
</tr>
<tr>
<td>Empirical Formula</td>
<td>C$<em>{65}$H$</em>{62}$B$_2$Br$_2$N$_4$S$_2$</td>
</tr>
<tr>
<td>Fw / g mol$^{-1}$</td>
<td>1144.74</td>
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<td>Crystal system, space group</td>
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<td>a / Å</td>
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<td>b / Å</td>
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<td>c / Å</td>
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<td>β / deg</td>
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<td>γ / deg</td>
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<tr>
<td>Vol / Å$^3$</td>
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<tr>
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</tr>
<tr>
<td>calc. density (Mg m$^{-3}$)</td>
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</tr>
<tr>
<td>λ</td>
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</tr>
<tr>
<td>abs. coeff.(mm$^{-1}$)</td>
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</tr>
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<td>θ range (deg)</td>
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<td>no. of reflns</td>
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<td>collected / unique</td>
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<td>R (data with $</td>
<td>I^2</td>
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<td>wR (all data)</td>
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<td>Δρ max, min / e·Å$^{-3}$</td>
<td>0.69, -0.74</td>
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5.12 References


Chapter 6

Borylated PF8-BT
6.1 Introduction

Small molecule based organic π-conjugated materials have many desirable properties such as ease of purification, highly defined molecular structures, high solubility and high batch reproducibility.\(^1\) Conversely, conjugated polymers can provide several advantages including facile processing, light weight, good film forming qualities and mechanical flexibility.\(^1\) Importantly, polymeric semiconducting materials have the potential to be solution processed and printed which precludes conventional processing and patterning methodologies such as vacuum deposition and photolithography which is essential in achieving large area printed electronics at minimal expense.\(^4\)

Impressive advances in the field of polymer organic electronics have been driven by an improved understanding of the physics of charge transport and detailed structure-property relationships. This has now led to organic semiconducting polymers that can outperform amorphous silicon semiconductors.\(^5\) A key structural feature in many high performing semiconducting polymers is the utilisation of fused polycyclic aromatic units in donor-acceptor (D-A) polymers. This enforced planarity can result in an enhancement in π-electron delocalization and also reduces rotational disorder which can encourage intermolecular π-stacking interactions.\(^6\) These intermolecular interactions can lead to more highly ordered polymer films that can facilitate charge transport but that can also negatively impact a polymers solubility and emissive properties.\(^7\)

Chemical modification a polymer’s repeat units represents a highly effective methodology to modulate a materials photophysical and morphological characteristics but these often require onerous synthetic procedures. Alternatively, Bazan and co-workers\(^8\) demonstrated a methodology of reversibly modulating the photophysical and conductive properties post-polymerisation through the coordination of Lewis acids to basic functionalities of conjugated polymers (Scheme 6.1).
Scheme 6.1: Coordination of B(C₆F₅)₃ to the Lewis basic site of a donor-acceptor conjugated polymer.

Application of this post polymerisation modification to PF8-Py by incremental addition of the Lewis acid B(C₆F₅)₃ results in a progressive red-shift in the PL_max from 424 to >500 nm. This represents emission from a lower band-gap system due to a significant stabilisation of the LUMO energy level in addition to a concomitant minor stabilisation of the HOMO energy level. OLED devices fabricated from these Lewis adduct polymers demonstrated that the electroluminescence maximum wavelength (λ_max_EL) of PF8-Py could be controllably tuned from 426 nm in the pristine polymer up to 509 nm upon addition of 0.01-0.10 eq. of B(C₆F₅)₃. Additionally, Bazan and co-workers showed that the addition of 0.02 eq. B(C₆F₅)₃ to PDTS-Py (scheme 6.2) effectively p-dopes the polymer and results in an enhancement in charge carrier mobility from 3.2 x 10⁻⁵ cm² V⁻¹ s⁻¹ in the pristine polymer to 2.5 x 10⁻³ cm² V⁻¹ s⁻¹ in the doped polymer (after addition of 0.02 eq. B(C₆F₅)₃). Whist oxidative doping by chemical or electrochemical methods is well studied; this doping effect without the need for formation of a formally charged species (non-oxidative) is less investigated. The Lewis acid doping shows a negative effect on the charge carrier mobility upon increasing the concentration of B(C₆F₅)₃ beyond 0.02 eq., this was attributed to the coordination of the bulky B(C₆F₅)₃ causing a twisting of neighbouring aromatic units. This twisting reduces coplanarity and disrupts the effective conjugation length which results in the observed reduction in charge carrier mobility. A similar effect was
demonstrated by E. Poverenov et al.\textsuperscript{10} in which the conductivity of a benzothiadiazole-\textit{alt}-EDOT polymer (PBT-EDOT) was increased by several orders of magnitude upon the addition of BF\textsubscript{3} (Scheme 6.2).

\begin{equation}
EH = 2\text{-ethylhexyl}
\end{equation}

\begin{equation}
\text{m Eq. } B(C_6F_5)_3
\end{equation}

\begin{equation}
\text{PDTS-Py(B(C_6F_5)_3)} \times m\% \quad m = 0.01, 0.02, 0.05, 0.1 \text{ or } 0.25
\end{equation}

Scheme 6.2: Structures of polymers doped with boron based Lewis acids.\textsuperscript{9,10}

PF8-BT (Fig. 6.1) is a particularly well studied polymer which contains a weakly Lewis basic benzothiadiazole functionality and is highly relevant to this work (see previous chapters). This polymer has been investigated for OFET, OLET and OPV applications but particularly emphasis has been placed on OLED applications due to its high quantum and power efficiencies as a green emitter.\textsuperscript{11}

Figure 6.1: Structure of PF8-BT.
In addition to the impressive emissive properties one of the most interesting characteristics of PF8-BT is the ability to form a liquid crystalline phase which leads to an increase in the carrier mobility in the alignment direction.\(^{12}\) An efficient ambipolar field-effect mobility of \(7-8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) is observed which potentially leads to OLET applications although a LUMO energy level of \(\sim 3.3 \text{ eV}\) is above the threshold (3.7 eV) for air stable n-channel conductivity.\(^{13,14}\) The reasonable electron affinity (\(\sim 3.3 \text{ eV}\)) and large ionization potential (\(\sim 5.9 \text{ eV}\)) leads to PF8-BT being utilised as either the active electron donating or accepting material in polymer/polymer solar cells. However, PF8-BT based systems have yellow-green emission due to the relatively high band-gap of 2.6 eV\(^{11}\), which results in its absorption spectrum failing to cover a large portion of the terrestrial spectrum which is sub optimum for OPV applications.\(^{15-17}\) These factors show the promise of F8-alt-BT polymer based systems for organic electronic applications but also provide a clear rationale for reducing the LUMO level to achieve air stable n-channel behaviour and lower band-gap derivatives.

Whilst impressive progress has been made in polymer OLED technology within the visible spectrum\(^{18}\), the development of efficient polymer OLED devices that show emission in the NIR region of the spectrum has proven more challenging.\(^{19-22}\) Recently heavy-metal free vacuum deposited small molecule NIR OLED devices have shown external quantum efficiency values of >1 \%, although solution processed polymer OLEDs with emission maxima >700 nm have failed to reach comparable external quantum efficiency (EQE) values.\(^{23-27}\) Moreover, even polymers demonstrating substantial NIR (\(\lambda_{\text{max,em}} >700 \text{ nm}\)) photoluminescence (PL) in the solid state are sparsely reported.\(^{19-30}\) The provenance of these deficiencies is attributed to an increased severity of aggregation caused quenching (ACQ) and the energy-gap law.\(^{19-30}\)

Considering these factors, this chapter focuses on the extrapolation of the borylative fusion methodology to the conjugated polymer PF8-BT. This post-polymerisation modification is utilised to borylate varying percentages of the repeat units of PF8-BT (~10 to 100 \%) and results in a reduction in the materials band-gap with a concomitant red shift in emission into the NIR region of the electromagnetic spectrum (EMS).
6.2 Synthesis

PF8-BT (Mₙ 93 kDa, M_w 276 kDa) was provided by CDT Ltd. and was used as received. Post-polymerisation borylative fusion was achieved through a similar methodology to that utilised for compound 3 (see Chapter 3). Various molar equivalents of BCl₃ (0.2 M) (0.10, 0.15, 0.25 eq. with respect to the repeat unit) in DCM and 2,4,6-tri-t-butylpyridine (TBP) were added to a DCM solution of PF8-BT in a closed system (sealed J.Young’s tube) to borylate varying percentages of the repeat units of PF8-BT (10 to 25%, Scheme 6.3). As BCl₃ is volatile (bp = 12.6°C), a closed system is necessary to ensure it remains within the reaction mixture at the desired molar ratio. A closed system also requires the addition of TBP to act as a non-coordinating Brønsted base to sequester the resultant HCl that is produced (and which otherwise makes borylation reversible).

Scheme 6.3: Synthesis of 6-BPh₂-10%, 6-BPh₂-15% and 6-BPh₂-25%.
After stirring overnight, the reaction mixture was treated with the necessary quantity of ZnPh$_2$. The reaction mixture was then filtered through silica gel to remove any inorganic by-products (boron or zinc species) and precipitated in methanol. The polymers were then subjected to Soxhlet extraction with methanol, acetone and hexane, dried (under vacuum) and the polymers were recovered in excellent yields (≥95 %). The percentage of repeat units that had been borylated was estimated by the integration of the $^1$H proton resonances attributed to the Ph boron substituents (7.10 – 7.61 ppm) against the remaining aromatic resonances (7.61 - 7.65 ppm) (Figure 6.2). Attempts to assess loading level using combustion analysis consistently gave materials low in carbon (possibly due to incomplete combustion and boron carbide formation as previously documented).

Maximum borylation (6-BPh$_2$-RI-Max) of PF8-BT could be achieved through the addition of 3 eq. of BCl$_3$ to a DCM solution of PF8-BT with the reaction mixture stirred under the dynamic flow of nitrogen for 16 hours (Scheme 6.4). TBP is unnecessary as the resultant HCl is removed from solution under these conditions. The solution was degassed (reaction mixture was bubbled with N$_2$) to remove excess BCl$_3$ and then ZnPh$_2$ was added to the
reaction mixture. Polymer 6-BPh$_2$-RI-Max was then subjected to identical work up conditions as the 6-BPh$_2$-m\% series polymers.

Scheme 6.4: Synthesis of 6-BPh$_2$-RI-Max.

The maximum level borylated polymer functionalised with C$_6$F$_5$ substituents on the boron atom (6-B(C$_6$F$_5$)$_2$-RI-Max) was synthesised from the high molecular weight PF8-BT (M$_n$ 93 kDa, M$_w$ 276 kDa) but this material proved essentially insoluble in common organic solvents. The synthesis of 6-B(C$_6$F$_5$)$_2$-RI-Max from lower molecular weight PF8-BT (M$_n$ 32 kDa, M$_w$ 100 kDa) produced a significantly more soluble material.

The post-polymerisation borylative fusion produces a regio-irregular polymer as there is no regio control over the borylation site. A regio-regular analogue of the maximum level borylated polymer 6-BPh$_2$-RR-Max can be achieved through polymerisation of the pre-borylated monomer unit 5FBr$_2$-(BPh)$_2$ (see Chapter 5). Polymer 6-BPh$_2$-RR-Max was synthesised by a Suzuki-Miyaura cross-coupling of 5FBr$_2$-(BPh)$_2$ with F8(Bpin)$_2$ (Scheme 6.5) using the optimised method for Suzuki-Miyaura cross-coupling of the borylated compounds discussed in Chapter 4. The reaction mixture was washed with water and 10 wt. \% sodium diethyldithiocarbamate aq. solution (to remove palladium species). Polymer 6-BPh$_2$-RR-Max was then subjected to identical work up conditions as 6-BPh$_2$-RI-Max. This yielded a polymer with a Mn of 19.5 kDa and Mw 40.0 kDa and a unimodal distribution by gel permeation chromatography (GPC) (Figure 6.3). The $^1$H NMR spectrum for 6-BPh$_2$-RR-Max displayed an integral ratio of 16.7:24 for the aromatic backbone hydrogen resonances vs the BPh$_2$ hydrogen moieties confirming minimal deboronation of the borylated units during polymerisation.
Figure 6.3: GPC trace of 6-BPh$_2$-RR-Max.

Scheme 6.5: Synthesis of 6-BPh$_2$-RR-Max.

F8(BPin)$_2$ + 5FBr$_2$-(BPh)$_2$

S: THF
0.24 eq. Pd(P$^t$Bu)$_3$$_2$
10 eq. K$_3$PO$_4$ (2M aq.)

6-BPh$_2$-RR-Max (63 %)

Mn = 19.5 kDa
Mw = 40.0 kDa
PDI = 2.05
Comparison of the $^1$H NMR spectra of the maximum borylated polymers showed that the resonances of the regio-regular polymer 6-BPh$_2$-RR-Max are much more resolved relative to 6-BPh$_2$-RI-Max (Figure 6.4). This is attributed to the lower variation in the magnetic environments of the repeat units in 6-BPh$_2$-RR-Max as 50% of the fluorene contains no boryl substituents and the other 50% contain 2 boryl substituents. In polymer 6-BPh$_2$-RI-Max each fluorene unit may be functionalised with 0, 1 or 2 boryl substituents in an unknown ratio (Figure 6.5) although the regio-irregular polymer has a significantly greater average molecular weight ($M_n$) which may also contribute to the resonance broadening. It is noteworthy that there is no resonance overlap in the $^1$H NMR between the main chain and exo-cyclic phenyl boron substituents. This can be deduced from the absence of any resonances between 7.5 and 7.0 ppm in the $^1$H NMR of 6-B(C$_6$F$_5$)$_2$-RI-Max (Figure 6.4).
Figure 6.5: Examples of possible borylated structures within 6-BPh₂-Rl-Max.

The thermal stability of the polymers was investigated by thermal gravimetric analysis (TGA) which revealed that all materials were stable up to at least 300°C (Figure 6.6, Table 6.1).

![TGA plots of 6-BPh₂-10%, 6-BPh₂-15%, 6-BPh₂-25%, 6-BPh₂-Rl-Max and 6-BPh₂-RR-Max.](image)

Table 6.1: Temperature at 5 % mass loss of 6-BPh₂-10%, 6-BPh₂-15%, 6-BPh₂-25%, 6-BPh₂-Rl-Max and 6-BPh₂-RR-Max.

<table>
<thead>
<tr>
<th>Polymer 6-BPh₂</th>
<th>10%</th>
<th>15%</th>
<th>25%</th>
<th>RI-Max</th>
<th>RR-Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C) at 5 % mass loss</td>
<td>417</td>
<td>347</td>
<td>304</td>
<td>314</td>
<td>337</td>
</tr>
</tbody>
</table>
Post polymerisation borylative fusion was also applicable to the thienyl containing polymer PF8-TBTT (Scheme 6.6). Borylative fusion of this polymer to synthesis PF8-TBTT-BMe₂ resulted in a substantial decrease in the optical band-gap of this polymer. Further details will not be given here as this is the scope of another project.

Scheme 6.6: Borylative fusion of PF8-TBTT.
6.3 Photophysical Properties of Borylated PF8-BT

6.3.1 Solution Ultraviolet-Visible Absorbance and Photoluminescence Properties

The solution state absorbance properties of 6-BPh₂-10%, 6-BPh₂-15%, 6-BPh₂-25%, 6-BPh₂-RL-Max, and 6-BPh₂-RR-Max were investigated by solution ultraviolet-visible absorption (UV-vis) and photoluminescence (PL) spectroscopy in toluene (1 x 10⁻⁵ M). Toluene was selected based on solubility and due to previous studies on small molecules where this solvent led to optical properties in solution that most closely resembled that in the solid state.

![UV-Vis absorbance and photoluminescence spectra](image)

Figure 6.7: UV-vis absorbance and photoluminescence of 6-BPh₂-10%, 6-BPh₂-15% and 6-BPh₂-25% (1 x 10⁻⁵ M toluene solutions).
Table 6.2: Comparison of the solution state photophysical properties of 6-BPh₂-10%, 6-BPh₂-15% and 6-BPh₂-25%.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>λmax_abs (nm)</th>
<th>ε (M⁻¹cm⁻¹)</th>
<th>Optical Band-Gap (eV)</th>
<th>λmax_em (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF8-BT</td>
<td>456</td>
<td>29200</td>
<td>2.48</td>
<td>526</td>
</tr>
<tr>
<td>6-BPh₂-10%</td>
<td>456</td>
<td>26100</td>
<td>2.48</td>
<td>523</td>
</tr>
<tr>
<td>6-BPh₂-15%</td>
<td>455, 562</td>
<td>25000, 1200</td>
<td>1.90</td>
<td>527, 706</td>
</tr>
<tr>
<td>6-BPh₂-25%</td>
<td>454, 564</td>
<td>18900, 2800</td>
<td>1.89</td>
<td>527, 710</td>
</tr>
</tbody>
</table>

1x 10⁻⁵ M solution in toluene. b Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

The absorption bands located at the higher energy part of the spectrum (300-400nm) are attributed to localised π-π* transitions whereas the longer wavelength absorption bands are attributed to the internal charge transfer (ICT) from fluorene to the BT units. The absorbance spectra of 6-BPh₂-10%, 6-BPh₂-15% and 6-BPh₂-25% show intense ICT absorption bands (~370-510 nm) associated with the unborylated F8-BT units, the intensity of which decreases as borylation level increases. Polymer 6-BPh₂-10% demonstrates essentially identical absorbance and emission spectra in toluene solution to that of PF8-BT (Figure 6.7). No noticeable ICT absorbance band or fluorescence associated with the borylated F8-BT units is observed. Polymer 6-BPh₂-15% demonstrates a low intensity absorbance band (ε =1200 M⁻¹ cm⁻¹) associated with the borylated PF8-BT units (520 to 650 nm) and 6-BPh₂-25% shows a relative increase in absorption intensity (ε =2800 M⁻¹ cm⁻¹) in this region due to the increased proportion of borylated chromophores. Upon exciting the ICT band of the unborylated F8-BT units (λ_ex = 468 nm) of 6-BPh₂-15%, the observed emission is majorly from the unborylated F8-BT units with a minor amount of emission from the lower band-gap borylated units. Polymer 6-BPh₂-25% shows the inverse relative emission that of 6-BPh₂-15% as the emission from the F8-BT unit is exceeded in intensity by the lower band-gap borylated unit. This is attributed to the higher concentration of borylated units in the polymer chain increasing the probability of the intramolecular photo-generated exciton migrating to the lower band-gap borylated unit before radiative decay. This results in an increase in the intensity of emission in the NIR region although due to the large overlap between the emission of the F8-BT units and the...
absorbance of the borylated F8-BT units, reabsorption may also be a contributing factor.

Figure 6.8: UV-vis absorbance and photoluminescence of 6-BPh$_2$-RI-Max and 6-BPh$_2$-RR-Max (1 x 10$^{-5}$ M toluene solutions). Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

Table 6.3: Comparison of the solution state photophysical properties of 6-BPh$_2$-RI-Max and 6-BPh$_2$-RR-Max.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max,abs}}$ (nm)$^a$</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)$^a$</th>
<th>Optical Band-Gap (eV)$^b$</th>
<th>$\lambda_{\text{max,em}}$ (nm)$^a$</th>
<th>Stokes shift (nm)</th>
<th>$\Phi_f$ %$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-BPh$_2$-RI-Max</td>
<td>609</td>
<td>12100</td>
<td>1.85</td>
<td>702</td>
<td>93</td>
<td>11.9</td>
</tr>
<tr>
<td>6-BPh$_2$-RR-Max</td>
<td>613</td>
<td>37900</td>
<td>1.85</td>
<td>703</td>
<td>90</td>
<td>15.2</td>
</tr>
</tbody>
</table>

$^a$1 x 10$^{-5}$ M solution in toluene. $^b$Band-gap estimated from onset of absorption. $^c$Relative fluorescence quantum yield estimated by using cresyl violet as standard (QY = 54% in methanol)$^{32}$, estimated error $\pm$ 20 %. Fluorescence spectra were measured by exciting the solutions at their absorption maxima.

The solution UV-vis absorbance and fluorescence spectra of 6-BPh$_2$-RI-Max and 6-BPh$_2$-RR-Max are almost identical although 6-BPh$_2$-RR-Max possesses an additional fine structure in the localised $\pi-\pi^*$ transitions absorption band. Polymer 6-BPh$_2$-RR-Max has a considerably greater extinction coefficient relative to 6-BPh$_2$-RI-Max due to a combination of the
borylated ladder unit having an increased extinction coefficient relative to the singularly borylated unit (see Chapters 3 and 5) in addition to the relative molecular mass of the repeat unit being double that of the singularly borylated unit (double the number of F8 and BT units present for solutions of the same concentration). Both polymers show broad emission into the NIR region (620-850 nm) with reasonably high solution quantum yield values for the respective region of the electromagnetic spectrum (Figure 6.8, Table 6.3).  

6.3.2 Solid State Ultraviolet-Visible Absorbance Properties of Borylated Polymer Thin Films

The solid state ultraviolet-visible absorption (UV-vis) characteristics of the borylated polymers $6\text{-BPh}_2\text{-10\%}$, $6\text{-BPh}_2\text{-15\%}$, $6\text{-BPh}_2\text{-25\%}$, $6\text{-BPh}_2\text{-RI-Max}$ and $6\text{-BPh}_2\text{-RR-Max}$ were examined by preparing thin films on glass slides.

![Solid state UV-vis absorbance of thin films of $6\text{-BPh}_2\text{-10\%}$, $6\text{-BPh}_2\text{-15\%}$, $6\text{-BPh}_2\text{-25\%}$, $6\text{-BPh}_2\text{-RI-Max}$ and $6\text{-BPh}_2\text{-RR-Max}$.](image)

Figure 6.9: Solid state UV-vis absorbance of thin films of $6\text{-BPh}_2\text{-10\%}$, $6\text{-BPh}_2\text{-15\%}$, $6\text{-BPh}_2\text{-25\%}$, $6\text{-BPh}_2\text{-RI-Max}$ and $6\text{-BPh}_2\text{-RR-Max}$.

The solid state absorbance spectra of the polymers show very similar trends to those observed in dilute toluene solutions. The absorption bands located at the higher energy part of the spectrum are attributed to localised $\pi-\pi^*$ transitions whereas the longer wavelength absorption bands are attributed to
the internal charge transfer (ICT) from fluorene to the BT units. All absorption peaks are red shifted relative to those measured in dilute toluene solution which is a commonly observed property of conjugated polymers in the aggregated state and is attributed to $\pi-\pi$ stacking interactions between polymer chains. Unlike in solution 6-BPh$_2$-10% shows absorption intensity associated with the borylated F8-BT units (weak feature centred around 600 nm) with 6-BPh$_2$-15% and 6-BPh$_2$-25% showing an increase in intensity in this region due to an increase in number of borylated F8-BT units. Polymers 6-BPh$_2$-RI-Max and 6-BPh$_2$-RR-Max show almost identical absorbance features in the solid state with the exception of 6-BPh$_2$-RR-Max possessing an additional feature in the localised $\pi-\pi^*$ transitions absorption band which is also observed in solution (Figure 6.9).

Table 6.4: Comparison of the solid state photophysical properties of 6-BPh$_2$-10%, 6-BPh$_2$-15%, 6-BPh$_2$-25%, 6-BPh$_2$-RI-Max and 6-BPh$_2$-RR-Max.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max,abs}}$ (nm)$^a$</th>
<th>Absorbance (A.U)$^b$</th>
<th>Optical Band-Gap (eV)$^c$</th>
<th>Film Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF8-BT</td>
<td>468</td>
<td>0.18</td>
<td>2.38</td>
<td>56</td>
</tr>
<tr>
<td>6-BPh$_2$-10%</td>
<td>468</td>
<td>0.30</td>
<td>2.33</td>
<td>52</td>
</tr>
<tr>
<td>6-BPh$_2$-15%</td>
<td>468</td>
<td>0.28</td>
<td>2.33</td>
<td>49</td>
</tr>
<tr>
<td>6-BPh$_2$-25%</td>
<td>464, 587</td>
<td>0.18, 0.04</td>
<td>1.79</td>
<td>43</td>
</tr>
<tr>
<td>6-BPh$_2$-RI-Max</td>
<td>626</td>
<td>0.16</td>
<td>1.75</td>
<td>47</td>
</tr>
<tr>
<td>6-BPh$_2$-RR-Max</td>
<td>632</td>
<td>0.11</td>
<td>1.75</td>
<td>30</td>
</tr>
</tbody>
</table>

$^a$Spin-cast from 5 mg mL$^{-1}$ polymer solutions in toluene, 1000 rpm for 60 s. $^b$At $\lambda_{\text{max,abs}}$. $^c$Band-gap estimated from onset of absorption.
6.3.3 Solid State Photoluminescence Properties of Borylated Polymer Thin Films

The solid state emission and photoluminescence quantum yield (PLQY) of $6\text{-BPh}_2\text{-}10\%$, $6\text{-BPh}_2\text{-}15\%$, $6\text{-BPh}_2\text{-}25\%$, $6\text{-BPh}_2\text{-RI-Max}$ and $6\text{-BPh}_2\text{-RR-Max}$ were examined by preparing thin films on quartz disks from $10$ mg mL$^{-1}$ polymer solutions in toluene.

![Figure 6.10: Solid state PL of neat films of $6\text{-BPh}_2\text{-}10\%$, $6\text{-BPh}_2\text{-}15\%$, $6\text{-BPh}_2\text{-}25\%$, $6\text{-BPh}_2\text{-RI-Max}$ and $6\text{-BPh}_2\text{-RR-Max}$.](image)

The solid state emission spectra of the borylated polymers differed drastically from that observed in the dilute toluene solution. The PL emission of the F8-BT units overlaps extremely well with the ICT absorption band of the borylated units which suggests that efficient Förster resonance energy transfer to the lower band-gap borylated units can be expected. On excitation of $6\text{-BPh}_2\text{-}10\%$ at $468$ nm the emission from the F8-BT unit is almost completely quenched ($\sim5\%$ of the PL intensity from $500$-$610$ nm) and emission at a $\lambda_{\text{max,em}}$ of $700$ nm with an exceptionally high (for deep red/NIR emitters) solid state total PLQY of $44.4\%$ is observed (Figure 6.10, Table 6.5). The minor emission from the unborylated F8-BT units is completely quenched upon increasing the borylation level above $10\%$ due to an increase in the
concentration of low band-gap units in the polymer chain leading to a greater probability of energy transfer. A progressive red shift in emission upon increasing the borylation level was observed from a $\lambda_{\text{max}_{\text{em}}}$ of 700 nm for 6-BPh$_2$-10% to 730 nm for 6-BPh$_2$-25% with a concomitant decrease in quantum yield values. Whist the observed solid state quantum yield values are remarkably high for their relative region of the electromagnetic spectrum the decrease in quantum yield values with increasing emission wavelength is consistent with the energy-gap law.$^{34}$ The maximum level borylated polymers 6-BPh$_2$-RI-Max and 6-BPh$_2$-RR-Max were excited at 626 nm as only weak absorption at 468 nm is observed. Similar emission spectra for 6-BPh$_2$-RI-Max and 6-BPh$_2$-RR-Max were observed ($\lambda_{\text{max}_{\text{em}}}$ of 757 and 764 nm, respectively). These emission maxima are red shift in the solid state by $>200$ nm when compared to PF8-BT. The PLQY values for 6-BPh$_2$-RI-Max and 6-BPh$_2$-RR-Max (11.4 and 12.1 % respectively) are substantial for solid state fluorophores with a $\lambda_{\text{max}_{\text{em}}}$ $>$750 nm.$^{19,21,26,29}$

Table 6.5: Summary of solid state PL data of 6-BPh$_2$-10%, 6-BPh$_2$-15%, 6-BPh$_2$-25%, 6-BPh$_2$-RI-Max and 6-BPh$_2$-RR-Max.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Transmittance (A.U)</th>
<th>$\lambda_{\text{max}_{\text{em}}}$ (nm)</th>
<th>$\Phi_\text{f}$ %$^c$</th>
<th>$\tau$ [$\sigma^2$] (ns)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF8-BT</td>
<td>0.39</td>
<td>547$^a$</td>
<td>77.4$^a$</td>
<td>1.8$^{35}$</td>
</tr>
<tr>
<td>6-BPh$_2$-10%</td>
<td>0.32</td>
<td>547$^a$ [5 %], 700$^a$ [95 %]</td>
<td>44.4$^a$</td>
<td>5.24$^b$ [0.03]</td>
</tr>
<tr>
<td>6-BPh$_2$-15%</td>
<td>0.34</td>
<td>710$^a$</td>
<td>31.9$^a$</td>
<td>4.04$^e$ [0.02]</td>
</tr>
<tr>
<td>6-BPh$_2$-25%</td>
<td>0.39</td>
<td>731$^a$</td>
<td>23.4$^a$</td>
<td>3.26$^a$ [0.03]</td>
</tr>
<tr>
<td>6-BPh$_2$-RI-Max</td>
<td>0.38</td>
<td>757$^b$</td>
<td>11.4$^b$</td>
<td>1.53$^f$ [0.02], 7.03$^f$ [1.87]</td>
</tr>
<tr>
<td>6-BPh$_2$-RR-Max</td>
<td>0.38</td>
<td>764$^b$</td>
<td>12.1$^b$</td>
<td>1.65$^f$ [0.03], 5.72$^f$ [1.40]</td>
</tr>
</tbody>
</table>

$^a$Excited at 468 nm. $^b$Excited at 626 nm. $^c$Absolute values determined with an integrating sphere. $^d$Recorded on samples prepared for solid state absorbance measurements (see section 6.2.2.2), the lifetime data is recorded at $\lambda_{\text{max}_{\text{em}}}$, estimated error $\pm$ 10 %. $^e$Excited at 405.4 nm, $^f$Excited at 636.6 nm.
Lifetime measurements on neat films of the borylated polymers showed a general decrease in emission lifetime with increasing borylation level. The percentage borylated polymers (6-BPh₂-10%, 6-BPh₂-15% and 6-BPh₂-25%) can be fitted with a single exponential function. The emission lifetimes for the maximum level borylated polymer are essentially identical and are best fitted with two exponential functions (Figure 6.11, Table 6.5).

![Figure 6.11: PL lifetime data of thin films of 6-BPh₂-10%, 6-BPh₂-15%, 6-BPh₂-25%, 6-BPh₂-RI-Max and 6-BPh₂-RR-Max.](image)

As PF8-BT was used as a host polymer in our previous solid state emission studies the properties of the borylated polymers 6-BPh₂-15%, 6-BPh₂-25%, 6-BPh₂-RI-Max and 6-BPh₂-RR-Max blended with PF8-BT were examined. The ratio of borylated polymer to PF8-BT host was designed to maintain ~10 wt. % borylated units in the blend. Polymer 6-BPh₂-10% was therefore omitted as it already contained this loading of borylated units. The 6-BPh₂-15%, 6-BPh₂-25% and 6-BPh₂-RR-Max all showed very similar emission spectra and similar PLQY values ($\lambda_{\text{max}_{\text{em}}} = \sim 715$ nm and PLQY = ~33 %) with the exception of 6-BPh₂-RI-Max which contained a large component of emission from the PF8-BT host (Figure 6.12). The poor energy transfer from PF8-BT and the red shifted emission relative to the other borylated polymers (8-9 nm) was attributed to a phase separation of 6-BPh₂-RI-Max and PF8-BT upon spin-casting.
Figure 6.12: Solid state PL of $6$-$BPh_2$-10%, $6$-$BPh_2$-15%, $6$-$BPh_2$-25%, $6$-$BPh_2$-RI-Max and $6$-$BPh_2$-RR-Max blended with PF8-BT.

Table 6.6: Summary of solid state PL data of $6$-$BPh_2$-10%, $6$-$BPh_2$-15%, $6$-$BPh_2$-25%, $6$-$BPh_2$-RI-Max and $6$-$BPh_2$-RR-Max blended with PF8-BT.

<table>
<thead>
<tr>
<th>Film</th>
<th>Transmittance (A.U)</th>
<th>$\lambda_{\text{max}_{\text{em}}}$ (nm)</th>
<th>$\Phi_t$ %\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>33 wt. % PF8-BT/67 wt. % $6$-$BPh_2$-15%\textsuperscript{a}</td>
<td>0.32</td>
<td>716</td>
<td>34.8</td>
</tr>
<tr>
<td>60 wt. % PF8-BT/40 wt. % $6$-$BPh_2$-25%\textsuperscript{a}</td>
<td>0.34</td>
<td>715</td>
<td>31.8</td>
</tr>
<tr>
<td>90 wt. % PF8-BT/10 wt. % $6$-$BPh_2$-RI Max\textsuperscript{a}</td>
<td>0.38</td>
<td>542 [minor], 724 [major]</td>
<td>36.8\textsuperscript{c}, 21.3\textsuperscript{d}</td>
</tr>
<tr>
<td>90 wt. % PF8-BT/10 wt. % $6$-$BPh_2$-RR Max\textsuperscript{a}</td>
<td>0.37</td>
<td>715</td>
<td>33.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Excited at 468 nm. \textsuperscript{b}Absolute values determined with an integrating sphere. \textsuperscript{c}Total $\Phi_t$ %. \textsuperscript{d}$\Phi_t$ % excluding emission from PF8-BT host (<650 nm).
6.4 Redox Properties

Cyclic voltammetry was employed in order to gain further insight into the effects of borylation level on the FMO energies of the polymers. Polymers $6$-$\text{BPh}_2$-10%, $6$-$\text{BPh}_2$-15% and $6$-$\text{BPh}_2$-25% show two reduction processes which are stable to at least 10 cycles (at a scan rate of 25 mV s$^{-1}$) in addition to multiple broad irreversible oxidation peaks. Polymers $6$-$\text{BPh}_2$-$\text{RI}$-$\text{Max}$ and $6$-$\text{BPh}_2$-$\text{RR}$-$\text{Max}$ show a single fully reversible reduction process which is stable to at least 10 cycles in addition to multiple broad irreversible oxidation peaks.

![Figure 6.13: Negative potential sweep plots of PF8-BT, 6-$\text{BPh}_2$-10%, 6-$\text{BPh}_2$-15% and 6-$\text{BPh}_2$-25% (potential sweeps are offset by 8 $\mu$A for clarity), measured in DCM (1 mM) with $\left[\text{^nBu}_4\text{N}\right]\left[\text{PF}_6\right]$ (0.1 M) as the supporting electrolyte at a scan rate of 25 mV s$^{-1}$.](image-url)
Figure 6.14: Isolated first reduction peaks of 6-BPh$_2$-10%, 6-BPh$_2$-15% and 6-BPh$_2$-25% measured in DCM (1 mM) with $[\text{tBuN}][\text{PF}_6]$ (0.1 M) as the supporting electrolyte at a scan rate of 25 mV s$^{-1}$.

The negative potential sweeps of 6-BPh$_2$-10%, 6-BPh$_2$-15% and 6-BPh$_2$-25% show 2 reductions peaks. The most negative ($E_{\text{onset}}^{\text{red}}$ all at $\sim$-1.8 V) and intense reduction peak is associated with the unborylated F8-BT units and the least negative reduction peak is associated with the borylated F8-BT units (Figure 6.13). Due to the low intensity of the reduction peaks associated with the borylated unit there is a large error when estimating the onset of reduction ($E_{\text{onset}}^{\text{red}}$). Therefore the $E_{\text{onset}}^{\text{red}}$ for all reduction peaks associated with the borylated F8-BT unit were estimated to be $\sim$-1.2 V (Figures 6.13 and 6.14). As expected the reduction peak associated with the borylated F8-BT units increase in intensity with an increase in borylation level (Figure 6.13 and 6.14). The polymers 6-BPh$_2$-10%, 6-BPh$_2$-15% and 6-BPh$_2$-25% all show similar broad oxidation peaks with approximately the same onset of $E_{\text{onset}}^{\text{ox}}$ (all at $\sim$-6.16 V) (Figure 6.15, Table 6.7).
Figure 6.15: Positive potential sweep plots of PF8-BT, 6-BPh$_2$-10%, 6-BPh$_2$-15% and 6-BPh$_2$-25% (potential sweeps are offset by 30 μA for clarity), measured in DCM (1 mM) with [nBu$_4$N][PF$_6$] (0.1 M) as the supporting electrolyte at a scan rate of 25 mV s$^{-1}$.

Table 6.7: Comparison of the redox properties of PF8-BT, 6-BPh$_2$-10%, 6-BPh$_2$-15% and 6-BPh$_2$-25%.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{\text{ox onset}}$ (V)</th>
<th>$E_{\text{red onset}}$ (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Electrochemical Band-Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF8-BT</td>
<td>0.75</td>
<td>-1.82</td>
<td>-6.14</td>
<td>-3.57</td>
<td>2.57</td>
</tr>
<tr>
<td>6-BPh$_2$-10%</td>
<td>0.77</td>
<td>-1.83, -1.2</td>
<td>-6.16</td>
<td>-3.56, -4.19</td>
<td>2.60, 1.97</td>
</tr>
<tr>
<td>6-BPh$_2$-15%</td>
<td>0.79</td>
<td>-1.85, -1.2</td>
<td>-6.18</td>
<td>-3.54, -4.19</td>
<td>2.64, 1.99</td>
</tr>
<tr>
<td>6-BPh$_2$-25%</td>
<td>0.77</td>
<td>-1.79, -1.2</td>
<td>-6.16</td>
<td>-3.60, -4.19</td>
<td>2.56, 2.97</td>
</tr>
</tbody>
</table>

Measured in DCM, (1 mM), with [nBu$_4$N][PF$_6$] (0.1 M) as the supporting electrolyte at a scan rate of 25 mV s$^{-1}$, potentials are given relative to the Fc/Fc$^+$ redox couple which is taken to be 5.39 eV below vacuum.$^{36}$
Figure 6.16: Relative energy level diagrams for polymers PF8-BT, 6-BPh₂-10%, 6-BPh₂-15% and 6-BPh₂-25%.

Unlike the percentage borylated polymers (6-BPh₂-10%, 6-BPh₂-15% and 6-BPh₂-25%) the maximum level borylated polymers (6-BPh₂-RI-Max and 6-BPh₂-RR-Max) show only one observable reduction peak due to the absence of unborylated F8-BT units (Figure 6.17). The onset of this reduction peak is at a significantly less negative potential than observed in PF8-BT ($\Delta V \approx 0.56$ V) due to a significantly lower LUMO energy as a result of borylation (Table 6.8). Both 6-BPh₂-RI-Max and 6-BPh₂-RR-Max show essentially identical redox properties with identical electrochemical band-gaps in strong agreement with UV-vis absorbance measurements.
Figure 6.17: Cyclic voltammetry plots of PF8-BT, 6-BPh$_2$-RI-Max and 6-BPh$_2$-RR-Max (potential sweeps are offset by 40 µA for clarity), measured in DCM (1 mM), with [$^n$Bu$_4$N][PF$_6$] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV s$^{-1}$.

Table 6.8: Comparison of the redox properties of PF8-BT, 6-BPh$_2$-RI-Max and 6-BPh$_2$-RR-Max.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{ox}$ onset (V)</th>
<th>$E_{red}$ onset (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Electrochemical Band-Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF8-BT</td>
<td>0.75</td>
<td>-1.82</td>
<td>-6.14</td>
<td>-3.57</td>
<td>2.57</td>
</tr>
<tr>
<td>6-BPh$_2$-RI-Max</td>
<td>0.67</td>
<td>-1.27</td>
<td>-6.06</td>
<td>-4.12</td>
<td>1.94</td>
</tr>
<tr>
<td>6-BPh$_2$-RR-Max</td>
<td>0.68</td>
<td>-1.26</td>
<td>-6.07</td>
<td>-4.13</td>
<td>1.94</td>
</tr>
<tr>
<td>PC$_{60}$BM</td>
<td>1.06</td>
<td>-1.06</td>
<td>-6.45</td>
<td>-4.33</td>
<td>2.12</td>
</tr>
</tbody>
</table>

Measured in DCM, (1 mM), with [$^n$Bu$_4$N][PF$_6$] (0.1 M) as the supporting electrolyte at a scan rate of 50 mV s$^{-1}$, potentials are given relative to the Fc/Fc$^+$ redox couple which is taken to be 5.39 eV below vacuum. The redox potentials for PC$_{60}$BM are provided for reference.
Figure 6.18: Relative energy level diagrams for polymers PF8-BT, 6-BPh$_2$-RI-Max, 6-BPh$_2$ RR-Max and PC$_{60}$BM.

6.5 OLED Devices

Solution processed OLED devices were fabricated to analyse the performance of the borylated polymers as deep red/NIR emitters. The device architecture was as follows, ITO (45 nm)/Plexcore OC® AQ1200 (65 nm)/PF8-TFB (poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-[(4,4’-(N-(4-sec-butylphenyl)diphenylamine)]) (22 nm)/emission layer (EML) (100 nm)/Ba (3.5 nm). The EML for Device 6.1 and Device 6.2 was comprised of neat films of 6-BPh$_2$-10% and 6-BPh$_2$-25% respectively. The EML for Device 6.3, Device 6.4 and Device 6.5 comprised of the borylated polymers blended with PF8-BT.

Device 6.1 EML = 6-BPh$_2$-10%
Device 6.2 EML = 6-BPh$_2$-15%
Device 6.3 EML = 33 wt. % PF8-BT/ 67 wt. % 6-BPh$_2$-15%
Device 6.4 EML = 60 wt. % PF8-BT/ 40 wt. % 6-BPh$_2$-25%
Device 6.5 EML = 90 wt. % PF8-BT/ 10 wt. % 6-BPh$_2$-RR-Max

Figure 6.19: Architectures of Device 6.1-6.5.
Figure 6.20: **Device 6.1** and **6.2** (a) Electroluminescence (b) Plot of EQE vs voltage (c) Plot of current density vs voltage.

The device in which the emission layer (EML) consisted of a neat film of **6-BPh_2-10% (Device 6.1)** showed a $\lambda_{\text{max}}^{\text{EL}}$ of 688 nm and a maximum EQE of 0.18 % with low EQE roll-off at high current densities (EQE at 171 mA cm$^{-2}$ = 94 % of EQE$_{\text{max}}$). Only a minor amount of green emission from unborylated PF8-BT units (500-600 nm) was observed (Figure 6.20). The $\lambda_{\text{max}}^{\text{EL}}$ of **6-BPh_2-10%** was slightly blue-shifted (by 12 nm) relative to the solid state PL. The device in which the EML consisted of a neat film of **6-BPh_2-25% (Device 6.2)** showed a $\lambda_{\text{max}}^{\text{EL}}$ of 716 nm and a maximum EQE of 0.41 %. This EQE$_{\text{max}}$ value is high for a solution processed OLED with a $\lambda_{\text{max}}^{\text{EL}}$ above 700 nm with such a simple device structure.$^{19-21}$ Although this device showed a substantially increased EQE$_{\text{max}}$ relative to **Device 6.1** a substantial amount of EQE roll-off at high current densities (EQE at 194 mA cm$^{-2}$ = 46 % of EQE$_{\text{max}}$) was observed. The $\lambda_{\text{max}}^{\text{EL}}$ of **6-BPh_2-25%** was blue-shifted (by 14 nm) relative to the solid state $\lambda_{\text{max}}^{\text{em}}$ of **6-BPh_2-25%**. The EL was red shifted relative to the EL of **Device 6.1** which is consistent with the effects on the emission wavelength upon increasing the borylation level. The increase in borylation level also resulted in a reduced turn-on voltage (Table 6.9).
Table 6.9: Summary of OLED performance of Device 6.1 and 6.2.

<table>
<thead>
<tr>
<th>Device</th>
<th>EML</th>
<th>$\lambda_{\text{max}_{\text{EL}}}$ (nm)</th>
<th>$V_{\text{on}}$ (^a) (V)</th>
<th>$\text{EQE}_{\text{max}}$ (^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>6-BPh(_2)-10%</td>
<td>688</td>
<td>3.3</td>
<td>0.18</td>
</tr>
<tr>
<td>6.2</td>
<td>6-BPh(_2)-25%</td>
<td>716</td>
<td>1.8</td>
<td>0.41</td>
</tr>
</tbody>
</table>

\(^a\)Turn-on voltage, \(^b\)Maximum external efficiency.

Devices were also fabricated in which the EML was comprised of the borylated polymers blended with PF8-BT. The ratio of borylated polymer to PF8-BT host was designed to maintain ~10 wt. % borylated units in the blend. As observed with the devices fabricated using neat borylated polymer films the EQE values of the higher borylation level polymers exceed those of the lower borylation level polymers in addition to showing lower turn-on voltages. Only a minor amount of green emission from unborylated PF8-BT units (500-600 nm) was observed in these devices (Figure 6.21). Device 6.3 (EML = 33 wt. % PF8-BT/67 wt. % 6-BPh\(_2\)-15\%) showed the worst performance with an $\text{EQE}_{\text{max}}$ value of 0.08 % with a $\lambda_{\text{max}_{\text{EL}}}$ of 697 nm. Device 6.4 (EML = 60 wt. % PF8-BT/40 wt. % 6-BPh\(_2\)-25\%) showed an improved $\text{EQE}_{\text{max}}$ value of 0.14 % (relative to Device 6.3) with a $\lambda_{\text{max}_{\text{EL}}}$ of 712 nm. This device showed a substantial amount of EQE roll-off at high current densities (EQE at 76 mA cm\(^{-2}\) = 60 % of $\text{EQE}_{\text{max}}$). Among the borylated polymer blends the EL of this device most closely matches its PL properties. Device 6.5 (EML = 90 wt. % PF8-BT/10 wt. % 6-BPh\(_2\)-RR\(-\text{Max}\)) was the most efficient of the blended emission layer devices (Table 6.10). This device showed an $\text{EQE}_{\text{max}}$ value of 0.22 % at a $\lambda_{\text{max}_{\text{EL}}}$ of 701 nm although a substantial amount of EQE roll-off at high current densities (EQE at 161 mA cm\(^{-2}\) = 51 % of $\text{EQE}_{\text{max}}$). Although none of the devices discussed in this chapter show superior $\text{EQE}_{\text{max}}$ values to those described in Chapter 3, all show longer wavelength emission (by up to 37 nm).
Figure 6.21: **Device 6.3, 6.4 and 6.5** (a) Electroluminescence (b) Plot of EQE vs voltage (c) Plot of current density vs voltage.

Table 6.10: Summary of OLED performance of **Device 6.3, 6.4 and 6.5**.

<table>
<thead>
<tr>
<th>Device</th>
<th>EML</th>
<th>$\lambda_{\text{max}}^{\text{EL}}$ (nm)</th>
<th>$V_{\text{on}}^a$ (V)</th>
<th>EQE$_{\text{max}}^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>33 wt. % PF8-BT/67 wt. % 6-BPh$_2$-15%</td>
<td>697</td>
<td>3.0</td>
<td>0.08</td>
</tr>
<tr>
<td>6.4</td>
<td>60 wt. % PF8-BT/40 wt. % 6-BPh$_2$-25%</td>
<td>712</td>
<td>2.6</td>
<td>0.14</td>
</tr>
<tr>
<td>6.5</td>
<td>90 wt. % PF8-BT/10 wt. % 6-BPh$_2$-RR-Max</td>
<td>701</td>
<td>1.6</td>
<td>0.22</td>
</tr>
</tbody>
</table>

$^a$Turn-on voltage, $^b$Maximum external efficiency.
6.6 Conclusions

The directed C-H electrophilic borylative fusion methodology proved applicable to conjugated polymers. This post-polymerisation functionalisation methodology was utilised to borylate varying percentages of the repeat units of PF8-BT (~10 to ~100 %). This modification introduced lower band-gap chromophores into the polymer chain and red shifted the solid state emission by >150 nm relative to the pristine polymer. These polymers exhibited extremely strong photoluminescence in the solid state (absolute PLQY up to 44.4 %) in the far red/NIR region of the electromagnetic spectrum. The post-polymerisation borylative fusion produces a regio-irregular borylated polymer, as the dibrominated ladder unit $5\text{FBr}_2\text{-(BPh}_2\text{)}_2$ proved amenable to a Suzuki-Miyaura polymerisation reaction the regio-regular analogue could be synthesised. Both maximum level borylated polymers $6\text{-BPh}_2\text{-RI-Max}$ and $6\text{-BPh}_2\text{-RR-Max}$ showed almost identical photophysical and electrochemical properties. Unoptimised OLED devices were fabricated with the emission layer comprised of neat films of the borylated polymers in addition to devices where the emission layer consisted of the borylated polymers blended with PF8-BT. These polymers showed good EQE$_\text{max}$ values for simple solution processed devices in the NIR region of the electromagnetic spectrum although these devices suffered from a substantial efficiency roll-off at high current densities. The borylated polymers are currently being studied for other applications (e.g., ambipolar OFETs).
6.7 Experimental

6.7.1 General Considerations

For general considerations see previous chapters. PF8-BT (Mₙ 93 kDa, Mₘ 276 kDa) and PF8-BT (Mₙ 32 kDa, Mₘ 100 kDa) was provided by CDT Ltd. and was used as received.

Gel permeation chromatography (GPC) analyses was performed in THF (~1 mg mL⁻¹) at 35 °C using a Viscotex GPCmax VE2001 solvent/sample module with 2 × PL gel 10 μm mixed-B and a PL gel 500 A column, and equipped with a Viscotex VE3580 RI detector employing narrow polydispersity polystyrene standards (Agilent Technologies) as a calibration reference. The sample was filtered through an Acrodisc CR 13 mm syringe filter with 0.45 μm PTFE membrane before injection and the experiment was carried out with an injection volume of 100 μL, with a flow rate of 1 mL min⁻¹. The result was analysed using Malvern Omnisec 4.7 software.

The solid state UV-vis spectra and lifetime measurements were performed on thin films of the borylated polymer which were spin-cast onto glass slides. The glass slides were cleaned by sonication in isopropanol, acetone and methanol for 10 min each, followed by drying with a N₂ stream and 20 minutes UV/Ozone. Thin films were spun from toluene at 1500 rpm for 60 sec. The resulting film thicknesses were determined by scratching across the film and measuring the resulting depth with a Dektak profilometer.

The Lifetime measurements were recorded on an Edinburgh Instruments FP920 Phosphorescence Lifetime Spectrometer. Lifetime data were recorded following excitation with either an Edinburgh Instruments model EPL 405 (405.4 nm) or EPL 640 (636.6 nm) picosecond pulsed diode laser. Lifetimes were obtained by tail fit on the data obtained, and quality of fit judged by minimization of reduced χ² and residuals squared.

Thermal gravimetric analysis (TGA) was carried out on a TA TGA Q5000 at a heating at 20 °C min⁻¹ from 25-800 °C (platinum pan) under an atmosphere of nitrogen (sample purge flow = 10 mL min⁻¹).
6.7.2 Synthetic Procedures

General procedure for the synthesis of 6-BPh₂⁻m%

\[ \text{6-BPh}_2⁻m\% \]
\[ m = 10, 15 \text{ or } 25 \]

m% molar equivalents (with respect to the repeat unit mass) of BCl₃ (0.2 M in DCM) and m% equivalents 2,4,6-tri-‘butylpyridine (TBP) were added to a PF8-BT (250 mg, 0.476 mmol (with respect to the repeat unit mass)) solution in DCM (~40 mL) in a closed J.Young’s tube. After stirring overnight, the reaction mixture was treated with 3 x m% equivalents of ZnP₂ after stirring for 3 hours at room temperature. The reaction mixture was then filtered through silica gel to remove any inorganic by-products (boron or zinc species), concentrated and precipitated in methanol. The polymer was then subjected to Soxhlet extraction with methanol, acetone and hexane followed by drying under reduced pressure.

6-BPh₂⁻10% (Yield 248mg, 96 %)

6-BPh₂⁻15% (Yield 254mg, 97 %)

6-BPh₂⁻25% (Yield 255mg, 95 %)

Synthesis of 6-BPh₂⁻RI-Max

BCl₃ (1M in DCM) (1.7 mL, 1.7 mmol) was added to a PF8-BT (300 mg, 0.57 mmol (with respect to the repeat unit mass)) solution in DCM (~50 mL). The reaction mixture was stirred overnight under the flow of nitrogen and a colour change from yellow to dark blue was observed. N₂ was bubbled through the solution to remove excess BCl₃/HCl and ZnPh₂ (376 mg, 1.7 mmol) was added to the reaction mixture. This was then stirred for 3 hours at room temperature. The reaction mixture was then filtered through silica gel to remove any inorganic
by-products (boron or zinc species), concentrated and precipitated in methanol. The polymer was then subjected to Soxhlet extraction with methanol, acetone and hexane followed by drying under reduced pressure. (Yield 351 mg, 98 %)

**Synthesis of 6-B(C₆F₅)₂-Rl-Max**

![Chemical structure image]

BCl₃ (1M in DCM) (5.1 mL, 5.1 mmol) was added to a PF8-BT (850 mg, 1.62 mmol (with respect to the repeat unit mass)) solution in DCM (~150 mL). The reaction mixture was stirred overnight under the flow of nitrogen and a colour change from yellow to dark blue was observed. N₂ was bubbled through the solution to remove excess BCl₃/HCl and Zn(C₆F₅)₂ (1.70 mg, 4.25 mmol) was added to the reaction mixture. This was then stirred for 4 hours at room temperature. The reaction mixture was then filtered through silica gel to remove any inorganic by-products (boron or zinc species), concentrated and precipitated in methanol. The polymer was then washed with methanol and subjected to Soxhlet extraction with acetone and hexane followed by drying under reduced pressure. (Yield 982 mg, 70 %)

**Synthesis of 6-BPh₂-RR-Max**

![Chemical structure image]

5FBr₂-(BPh₂)₂ (125 mg, 0.109 mmol), F₈(BPin)₂ (70 mg, 0.109 mmol) and Pd(Bu₃P)₂ (14 mg, 0.026 mmol) were dissolved in THF (10 mL). K₃PO₄ (2M aq.) (1.1 mL, 2.2 mmol) was added to the solution and the reaction mixture was stirred for 30 minutes at room temperature. The solution was then diluted with THF (20 mL) and then the reaction mixture was washed with 10 wt. % sodium diethylthiocarbamate (aq.) solution (2 x 50 mL) and then with water (50 mL). The organic layer was then isolated using a separating funnel and dried (MgSO₄). The solvent was then removed under reduced pressure. The resulting
residue was dissolved in DCM and filtered through silica gel, concentrated and precipitated in methanol. The polymer was then subjected to Soxhlet extraction with methanol, acetone and hexane followed by drying under reduced pressure. (Yield 97 mg, 64 %)

### 6.8 References


Chapter 7

Summary and Further Work
7.1 Summary

This thesis describes the synthesis and photophysical properties of tetra-coordinate C,N-chelated donor-acceptor organoboron compounds.

Chapter 2 describes a simple strategy to modify the frontier molecular orbital (FMO) energy levels of the ubiquitous dithienylbenzothiadiazole (DTBT) unit via a benzothiadiazole directed electrophilic borylation. This directed borylation acts to lock the neighbouring aromatic units coplanar (termed borylative fusion). Borylative fusion dramatically lowers the LUMO energy of these materials whilst changes to the energy of the HOMO are minimal with the choice of the exocyclic substituent facilitating fine tuning of the FMO energy levels. Additionally, an efficient and versatile synthetic route to arylate (C,N-chelate)BX₂ complexes utilizing a catalytic borenium mediated boro-desilylation/destannylation reaction was developed (see appendix).

Chapter 3 describes the extension of the benzothiadiazole directed C-H electrophilic borylative fusion to the ubiquitous fluorene donor unit. These materials were moderately emissive in solution with 3-BPh₂ demonstrating an excellent solid state PLQY for a deep red/NIR emitter of 32.9 %. A series of unoptimised OLED devices were fabricated which showed good maximum EQE values for solution processed far red/NIR fluorescent OLED devices.

Chapter 4 describes the cross-coupling of bromine functionalised borylated benzothiadiazole-fluorene (BT-F8) units. This facilitates the creation of borylated structures that would not be readily accessible through the direct borylation of the parent oligomers due to regioselectivity being dominated by electronic effects during the borylation step. The introduction of more electron rich units into the conjugated backbone of the borylated F8-BT unit resulted in materials that showed reasonable quantum yield values in the solid state with λ_max_em values >700 nm.

Chapter 5 describes the synthesis of fully fused ladder-type structures based on fluorene and carbazole donor units via a diborylation. The fluorene based borylated ladder molecules show large bathochromic shifts, far red/NIR fluorescence, large Stokes shifts and in some cases excellent solid state quantum yield values. Electrochemical measurements confirm the energy of the
LUMO energy level is substantially decreased upon borylation, whilst only moderately affecting the HOMO energy level. The effect on the HOMO energy level is minimised with exocyclic C₆F₅ substituents on boron. This demonstrates that the diborylation acts to lower the LUMO, reduce the band-gap and increase the rigidity of π-conjugated D-A systems. Exchange of the fluorene donor unit with a carbazole unit generated materials with red shifted emission but these were poorly emissive due to spatial separation of frontier orbitals leading to low quantum yield values.

Chapter 6 the directed C-H electrophilic borylative fusion methodology proved applicable to conjugated polymers. This post-polymerisation functionalisation methodology was utilised to borylate varying percentages of the repeat units of PF8-BT (~10 to ~100 %). These polymers exhibited extremely strong photoluminescence in the solid state (absolute PLQY up to 44.4 %) in the far red/NIR region of the electromagnetic spectrum. The post-polymerisation borylative fusion produces a regio-irregular borylated polymer. The regio-regular analogue of the fully borylated regio-irregular polymer could be synthesised via a Suzuki-Miyaura cross-coupling polymerisation. Unoptimised OLED devices were fabricated with the emission layer comprised of neat films of the borylated polymers in addition to devices were the emission layer consisted of the borylated polymers blended with PF8-BT. These polymers showed good EQE_{max} values for simple solution processed devices in the NIR region of the electromagnetic spectrum although these devices suffered from a substantial efficiency roll-off at high current densities.
7.2 Further Work

Further work will focus on the expansion of the directed borylative fusion methodology utilising a range of acceptors other than benzothiadiazole in addition to further investigation of the effects of exchanging the exocyclic aromatic groups (Figure 7.1).

![Chemical Structures]

Figure 7.1: Additional acceptor units that will be investigated as tetra-coordinate C,N-chelated donor-acceptor organoboron compounds.

As the borylated polymer demonstrate extremely high solid state quantum yields values in the far-red/NIR region of the electromagnetic spectrum, conjugated polymer nanoparticle will be synthesised from these materials and they will be investigated for bioimaging applications.
Appendix
Facile Arylation of Four-Coordinate Boron Halides by Borenium Cation Mediated Boro-desilylation and -destannylation

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Supporting Information

ABSTRACT: The addition of AlCl3 to four-coordinate boranes of the general formula (C–N-chelate)BCl3 results in halide abstraction and formation of three-coordinate borenium cations of the general formula [(C–N-chelate)BCl]+. The latter react with both arylstannanes and arylsilanes by boro-destannylation and -destannylation, respectively, to form arylated boranes. Catalytic quantities of AlCl3 were sufficient to effect high-yielding arylation of (C–N-chelate)BCl3. Boro-destannylation is more rapid than boro-desilylation and leads to double arylation at the boron center, whereas in reactions with arylsilanes either single or double arylation occurs dependent on the nucleophilicity of the arylsilane and on the electrophilicity of the borenium cation. The electrophilicity of the borenium cation derived from 2-phenylpyridine was greater than that of the benzothiazole analogues, enabling the boro-desilylation of less nucleophilic silanes and the direct electrophilic borylation of 2-methylthiophene.

INTRODUCTION

Four-coordinate boron compounds containing a chelating π-conjugated C/N donor and two exocyclic aromatic moieties, termed (C–N-chelate)BAR3 (e.g., 1-BAR3 right Scheme 1), have been extensively studied for application in optoelectronic devices.1-3 Changing the exocyclic aryl groups in 1-BAR3 significantly modulates the key optoelectronic properties including the frontier orbital energies and the photoluminescence quantum yield.2,4 Therefore, efficient and versatile routes to libraries of these compounds are important to optimize the materials properties and deliver improved device performance. A particularly attractive approach is the arylation of (C–N-chelate)BAR3 groups (e.g., 1-BAr3, X = Cl or Br) to form a wide range of (C–N-chelate)BAR3 compounds, as the starting compounds are readily accessed by electrophilic C–H borylation (Scheme 1).5-7

Installation of aromatic moieties at three-coordinate boric species is generally achieved by reaction with either aryllithium or aryl Grignard reagents.2 However, reaction of these reagents with Lewis base adducts of boranes often gives the desired product in poor yield.1 Instead functionalization of borane-Lewis adducts such as (2-phenylpyridyl)BBAr (1-BBAr, Scheme 1) requires organozinc or organoaluminum reagents to achieve high-yielding transmetallation.1,4 Unfortunately these nucleophiles are highly sensitive to protic species (ROH), and the synthesis of organozinc reagents often results in mixtures containing ionic species (term zincates) and coordinated etherate solvent, which can complicate transmetallation.8 Alternative nucleophiles are required that are readily synthesized, are well-defined, can be handled in air, and enable the boron-containing products to be easily isolated, preferably without column chromatography. Arylstannanes and arylstannanes meet these criteria; however, while three-coordinate boranes (e.g., Ar3BBAr) undergo transmetallation with arylstannanes and arylstannanes, four-coordinate boranes do not due to the Lewis acidity at boron being effectively quenched by the dative bond.9 We hypothesized that conversion of (C–N-chelate)BAR3 into borenium cations, [(C–N-chelate)BAR+]+, using a halophilic Lewis acid (e.g., AlCl3) will enable transmetallation using arylstannanes and arylsilanes. The process is potentially catalytic in the halophile, as the byproduct from transmetallation will react as a functional equivalent of [R3Si]+ or [R3Sn]+, abstracting halide to generate further equivalents of borenium cations for subsequent transmetallation (Scheme 2). Related, albeit stoichiometric in halophile, approaches have been
reported for activating chloro-boron sulphonylchlorane and F-B-dipyromethene toward substitution of B–X with chalcogen-based nucleophiles. In contrast, the use of borenium cations in boro-desilylation has extremely limited precedence, while their use in boro-destannylation has not been reported to date to the best of our knowledge. Herein is reported catalytic (in AlCl₃ activator) borenium cation mediated borylation as a simple method to functionalize (C–N-olate)-BCl₂ species based on benzoindiolato (BT) and pyridyl with aryl and heteroaryl groups.

RESULTS AND DISCUSSION

Our initial attempts to access new 2-BAr₂ compounds used an isolated organoazinc reagent synthesized from ZnBr₂ and p-tolylMgBr in THF, but this led to low yields of the desired arylated product. The low conversion was attributed to the "Zn[p-tolyl]₂" formed under these conditions actually being the zizicate [Mg(THF)₆]₂(μ-Br)₂(Zn(p-tolyl)₂). Due to the significant challenge presented in forming ether-free arylating reagents, ArylSiMe₃, and ArylSnBu₃ nucleophiles were investigated for expanding the exocyclic boron substituents.

Mixing 2-BCl (readily formed from the unbolystyrene precursor 2 (F₄-BS-Pt) and BCl₃), with 2 equiv of PhSnBu₃, in CH₂Cl₂ at room temperature led to no reaction until catalytic (ca. 5 mol %) AlCl₃ was added to the reaction mixture. Compound 2-BCl then slowly transformed into diphenylated 2-BPF₃ at 20 °C (Scheme 3). Heating of the reaction resulted in a more rapid reaction and good conversion to 2-BPF₃ (89% isolated yield after 16 h at 60 °C in CH₂Cl₂ in a sealed tube). The addition of AlCl₃ results in chloride abstraction from 2-BCl and borenium cation formation (indicated by downfield shifts in the 1H NMR spectrum and formation of [AlCl₃]⁻ in the 27Al NMR spectrum), consistent with previous studies on related compounds. The borenium cation [2-BCl]⁺ is then sufficiently electrophilic to boro-destannylation PhSnBu₃. An alternative mechanism where AlCl₃ and PhSnBu₃ react to form AlPh₂ species (which have been previously reported to transmetalate to four-coordinate boron halides) is precluded based on previous work where the combination of these reagents (in the absence of 2-BCl) in halalkane solvents (such as CH₂Cl₂) leads to solvent activation via C–Cl=AlCl₂ interactions (Friedel–Crafts-type reactivity) and carbosubstitution to form R₂C·Ph. Friedel–Crafts products are not observed in the reaction with 2-BCl, which is attributed to AlCl₃ reacting rapidly to form the borenium cation, thus disfavoring solvent activation. The ability to form 2-BPF₃ in high conversion using catalytic AlCl₃ confirmed that the electrophilic [Bu₃Sn]+ (or a functional equivalent thereof) byproduct can react with further 2-BCl₂ directly or via initial reaction with [AlCl₃]⁻, to provide access to additional equivalents of borenium cations.

The installation of boron of heteraryl substituents using S-Bu₃Sn-2-Me-thiophene, 3 (prepared by lithiation of 2-methylthiophene and quenching with Bu₃SnCl) was also explored. Mixing 2-BCl with 2.2 equiv of 3 gave no reaction, but addition of catalytic AlCl₃ (ca. 5 mol %) resulted in rapid arylation at 20 °C (complete within 10 min), and facile isolation simply by filtration through silica allowed 2-B(Me(T))- to be isolated in 67% yield. It is noteworthy that arylation using 3 is considerably more rapid at 20 °C than reactions with PhSnBu₃, consistent with the enhanced nucleophilicity of the thienylstannane. Furthermore, the use of 3 indicates that transmetalation occurs via direct boro-destannylation, as the α C-Me in 3 precludes an alternative mechanism involving C–H borylation followed by proto-destannylation, as determined by Jäkle and co-workers for the borylation of a stannylated ferrocene.

Borenium cation mediated transmetalation with organostannanes is effective for tetraarylation of [4-(BCl)₂]²⁺. The diborenium cation [4-(BCl)₂]²⁻ (Scheme 4) is produced by double borylative fusion of the unbolystyrene precursor 4 (BT-F₈-BT) as previously reported. With a slight excess of PhSnBu₃ (4.2 equiv) [4-(BCl)₂]²⁻ forms the previously characterized tetra-aryl borylated product 4 (BP₂)₂ with the major boron-containing complex after 72 h at 20 °C or 24 h at 60 °C (by multinuclear NMR spectroscopy) in 1,2,4-C₃H₃(CHT₄), Transmetlation with ZnP₂ to form 4-(BP₂)₂ required prior conversion of [4-(BCl)₂]²⁻ to neutral 4-(BCl)₂ by addition of NMe₃Cl for acceptable conversion. In contrast, the boro-destannylation methodology requires the borenium for transmetalation; therefore it proceeds directly from [4-(BCl)₂]²⁻.

The thiophene analogue of 2-BCl 5-BCl, Scheme 5, can be readily prepared from the unbolystyrene precursor 5 as previously reported. Again while arylation with ethere-free diaryl zinc reagents proceeds with high fidelity, the addition of [Mg(THF)₆]₂(μ-Br)₂(Zn(p-tolyl)₂)₂ to 2-BCl led to an extremely low conversion to 5-B[p-tolyl]₂ (isolated in only 13% yield). Analogous to the fluorene conjugated 2-BCl, the addition of stoichiometric AlCl₃ to 5-BCl resulted in halide abstraction and formation of the borenium cation [5-BCl]-[AlCl₃] (based on the significant downfield chemical shift of aryl 1H NMR resonances and the observation of [AlCl₃]⁻ in the 27Al NMR spectrum), indicating the feasibility of borenium-mediated transmetalation with organostannanes. The addition of stannane 3 to 5-BCl again resulted in no reaction until addition of catalytic AlCl₃ (ca. 5 mol %), at which point double arylation proceeded rapidly (complete within 10 min at 20 °C) to form 5-B(Me(T)₂)₂. This product could be isolated by column chromatography in 51% yield (Scheme 5). It should be noted that both 2-B(Me(T)₂)₂ and 5-B(Me(T)₂)₂ undergo slow protodeboronation of the exocyclic thienyl groups on standing in wet solvents but are stable in the solid state under ambient conditions.
atmosphere for at least three months. An alternative synthesis of 5-B(MeT) by electrolytic C–H borylation was explored based on our previous success using PhBCl₂ to form 5-B(PhCl) directly from 5. However, 5-(2-methylthiophene)-BCl₂ (MeT-BCl₂) does not react with 5 (Scheme 5, right), presumably due to the reduced Lewis acidity at boron (relative to BCl₂ and PhBCl₂). Furthermore, MeT-BCl₂ also fails to borylate 5. Thus, C–H borylation using BCl₂ followed by transmetalation is necessary to access this compound.

The boro-destannylation reaction was extended to 2-Bu₂Sn-9,9-dimethylfluorene (6), synthesized by standard procedures. The reaction of 5-BCl₂ with 2.2 equiv of 6 and catalytic AlCl₃ (ca. 5 mol %) proceeded at room temperature, but required 18 h for formation of 5-(F8₁₂), in high conversion. The longer reaction time compared to transmetalation with 3 is attributable to the variation in arene nucleophilicity. Attempts to selectively form the monoaoylated product by addition of 1 equiv of 6 to 5-BCl₂ (with catalytic AlCl₃) led to a mixture of 5-BCl₂(5-BCl₂(5-F8₁₂) and 5-F(B8₁₂), 5-F(B8₁₂) also can be synthesized from 5 in a two-step, one-pot reaction without the use of a glovebox in 88% yield. Compound 5-BCl₂ is prepared by reaction of 5 with BCl₂, followed by degassing (removing excess BCl₂ and the HCl byproduct from C–H borylation) and subsequent addition of catalytic AlCl₃ and 2.2 equiv of 6 (both weighed and handled under anhydrous atmosphere). The product, 5-BCl₂, is then simply isolated by filtering through silica.

The use of arylsilanes in place of arylstannanes is preferable from a toxicity perspective. However, reacting PhSiMe₃ and 2-BCl₂ with a range of AlCl₃ loadings and reaction conditions (at 20 and 60 °C) consistently resulted in minimal transmetalation. It was well documented that silicon–boron exchange only proceeds with highly electrophilic boranes, in contrast with tin–boron exchange. This suggests that the borenium cation [2-BCl₂]⁺ is insufficiently electrophilic to effect boro-desilylation of PhSiMe₃. A more nucleophilic silane, 2-Me₅-SiMe₃, was therefore utilized. Compound 2-BCl₂ was combined with an excess (2.2 equiv) of 7, resulting in no reaction. Addition of AlCl₃ (ca. 5 mol %) to the reaction mixture initiated transmetalation, leading to only one transmetalation per boron, producing 2-BCl₂(MeT) (Scheme 6), even after long reaction times. As the borenium cation [2-B(PhCl)₂]⁺ formed after the first transmetalation and subsequent halide abstraction contains a thienyl α donor, its Lewis acidity is presumably reduced relative to [2-BCl₂]⁺, disfavoring boro-desilylation of 7. Analogous trends have been previously observed when comparing the Lewis acidity of [PhBCl₂(amine)]⁺ and [Cl₃B(amine)]⁺ borocations. Compound 2-BCl₂(MeT) can then be further arylated using other organometallic reagents; for example reaction with Zn(C₆F₅)₂ gave the mixed arylated complex 2-B(PhMe)₂(C₆F₅)₂ (in 81% isolated yield). This provides a simple route to mixed arylated compounds, (C–N-aryl)BArF (ArF = C₆F₅). It is notable that current routes to unsymmetrically substituted borane derivatives are challenging and require multiple steps and purifications. This is due to the formation of Ar₃Ar₃BN (for reaction with inactivated C–N precursors), often leading to mixtures generally necessitating purification by fractional distillation.

(C–N-aryl)BArF compounds based on 2-arylpyridyls and derivatives have been more extensively studied than the benzothiadiazole systems for a range of optoelectronic applications. Therefore, the borenium cation mediated boro-destannylation/boro-desilylation reactions of these species were explored. 2-Phenylnaphthoquinone, 8, was readily borylated by a modification of a literature method using BCl₂, 2,6-tri-tert-butylpyridine (TBP), and AlCl₃ to form 1-BCl₂. Compound 1-BCl₂ was stable to ambient conditions and could be readily isolated in air simply by sequential washing with H₂O/MeOH and pentane. In contrast BT derivatives (e.g., 2-BCl₂) are sensitive to water and column chromatography. The enhanced stability of 1-BCl₂ is attributed to a stronger N–B dative bond in the pyridyl congener. The addition of an equivalent of AlCl₃ to 1-BCl₂ led to formation of the borenium salt 1-[1-BCl₂][AlCl₃], as indicated by a signal at +39.0 ppm in the ¹B NMR spectrum and further confirmed by X-ray diffraction studies (crystallized by cooling a saturated CH₂Cl₂ solution to 4 °C, Figure 1).

The solid-state structure of [1-BCl₂][AlCl₃] reveals a planarized trigycyclic structure and a trigonal planar environment at boron (Σ = 359.8°). Although two [AlCl₃]⁻ anions are proximal, the four Al–Cl (two participating in Al–Cl–B bridges and two not) distances are all identical (within 3%), suggesting that these close contacts are principally due to electrostatic forces and packing effects. The ability of the borenium cation [1-BCl₂]⁺ to mediate boro-desilylation was investigated. Addition of 2.2 equiv of PhSiMe₃ to 1-BCl₂ resulted in no reaction until addition of ca. 5 mol % of AlCl₃, which resulted in rapid boro-destannylation at 20 °C to form 1-Bp₂. This compound has been previously synthesized by Murakami and co-workers via 1-BB₄ and AlCl₃. The synthesis of 1-Bp₂ in one pot in two steps from 2-
phenylpyridine via electrophilic C–H borylation and subsequent AlCl₃-catalyzed boro-desilylation can be performed without use of a glovebox in high conversion (72% isolated yield).

The rapid room-temperature double boro-desilylation observed on combination of 1-BCl₃, catalytic AlCl₃, and PhSnBu₃ is in contrast to the BT congener 2-BCl₃ (which requires heating to 60 °C). This suggests an enhanced electrophilicity of the boron center in [1-B⁺]⁺ (V = Cl and Ph) relative to that in [2-B⁺]⁺. This was confirmed by the observation that addition of 2.2 equiv of Ph₃SiMe₂ to 1-BCl₃ in the presence of catalytic (ca. 5 mol%) AlCl₃ rapidly led to monoarylation (<10 min) and complete double arylation of boron within 10 h at 20 °C to form 1-BPh₂. Thus, with 1-BCl₃, double transmetallation is possible using the less toxic arylsilane reagent. This methodology can also be performed without the aid of a glovebox with no significant loss in yield, and the doubly arylated products can be isolated simply by filtration through a short plug of silica followed by drying in vacuo. The electronically deactivated silane (meta-Br-C₆H₄)LiMe₂ was also a viable reagent for transmetallation to boron; however, at 20 °C this led only to a single arylation of 1-BCl₃ (using ca. 5 mol% AlCl₃), with no further arylation proceeding at 20 °C (Scheme 7). Double arylation of 1-BCl₃ can be realized with (meta-Br-C₆H₄)LiMe₂ by heating 1-BCl₃/catalytic AlCl₃ in 1,2,3-C₆H₃H₂. The change in solvent is essential, as in this case heating a mixture of AlCl₃, CH₂Cl₂, and an arylsilane for prolonged periods of time led to Friedel–Crafts alkylation reactions.⁶ Analogous conditions enabled the synthesis of the spiro complex 1-B(biphenyl) (Scheme 7, bottom) in good yield (82%) from the commercially available 99-dimethyl-α,β-unsaturated silane. Spiro complexes such as 1-B(biphenyl) have been extensively explored as electron transport materials in electro-luminescent devices.¹⁰ It is notable that attempts to make the analogous spiro compound from 2-BCl₃ using catalytic AlCl₃ failed with no reaction observed at 20 or 60 °C, again indicating the lower electrophilicity of the [2-B⁺]⁺ borenium cation relative to [1-B⁺]⁺.

\[
[X,\text{BL}]^+ + [\text{HBB}]^- \xrightarrow{\text{AlCl}_3} X_{3}\text{HBL} + \text{BET}_3
\]

The greater reactivity of [1-BCl⁺]⁺ relative to [2-B⁺]⁺ suggested an enhanced electrophilicity at boron; to assess if this was due to the change in the aromatic moiety (i.e., thiienyl/fluorenyl vs phenyl), calculations comparing [1-B⁺]⁺ with the model BT analogue [8-B⁺]⁺ were performed at the M06-2X/6311G(d,p) (PCM DCM) level (Figure 2). The optimized structure of [1-BCl⁺]⁺ was in excellent agreement with the solidsate structure of [1-BCl⁺][AlCl₃]. Using a previously reported approach the hydride ion affinity (HIA, eq 1)¹¹ relative to BET₃ was assessed and found to be 6.7 kcal mol⁻¹ greater for [1-B⁺]⁺ compared to [8-B⁺]⁺. This indicates a greater Lewis acidity for the pyridyl congener toward soft nucleophiles (such as π systems) consistent with the relative reactivity observed. The nitrogen sites in BT are weakly basic relative to that in pyridyl; however examination of the calculated structure of [8-B⁺]⁺ indicates a greater N→B π donation than in [1-B⁺]⁺ (B–N in [8-B⁺]⁺ = 1.474 Å; B–N in [1-B⁺]⁺ = 1.514 Å). Furthermore, the N–S distances in [8-B⁺]⁺ are different with a longer S–N bond involving the nitrogen bound to boron (N₁–S = 1.69 vs N₁–S = 1.59 Å, Scheme 8). Natural bond orbital analysis also indicates a significant positive charge on sulfur (+1.073e) and a greater negative charge on N₁ in [8-B⁺]⁺ (−0.757e for N₁ vs −0.511e for N₁) relative to that of the nitrogen in [1-B⁺]⁺ (−0.588e). This indicates a significant contribution from a resonance form where sulfur is formally in the +4 oxidation state for [8-B⁺]⁺ (Scheme 8, right). Presumably this effect combined with the preference for the...
Scheme 8. Resonance Structures of [8-BCl]⁺

![Diagram](image)

five-membered boracyle to pyramidal relative to the six-membered boracyle (N—B—C angles of 104.8° in [1-BCl]⁺ and 115.7° in [8-BCl]⁺) leads to the observed Lewis acidity and reactivity trend.

The significant electrophilicity of [1-BCl]⁺ suggested it may be sufficiently reactive to directly boracyle C—H bonds of activated arenes. This would require the removal for pre-installation of R=E—groups on the desired aryl moiety. The addition of 1 equiv of 2-methylthiophene and TBP (to sequester the proton) to [1-BCl][AlCl₄] (generated in situ) resulted in full consumption of [1-BCl][AlCl₄] to form two new resonances in the ¹¹B NMR spectrum. However, multinuclear NMR spectroscopy showed that ca. 0.6 equiv of 2-methylthiophene and 0.5 equiv of TBP and 1-BCl were present in the reaction mixture. The observations are consistent with the second new boron resonance being [1-B(MeT)]⁺. Minor variations in starting stoichiometry (between 1-BCl and AlCl₃) led to the new ¹¹B NMR resonance varying between 18 and 40 ppm. This is attributed to a fast exchange between differing quantities of [1-B(MeT)][AlCl₄] and 1-B(MeT)Cl (Scheme 9). [1-B(MeT)]⁺ does not react with further 2-


![Diagram](image)
methylthiophene (presumably due to insufficient Lewis acidity) and is less chlorohphoric than [1-BCl]⁺, resulting in the consumption of 0.5 equiv of the latter by rapid halide transfer from the expected initial product 1-B(MeT)Cl. The addition of a second equivalent of AlCl₃ to this reaction mixture led to consumption of all 1-BCl and full conversion to [1-B(MeT)]⁺ (45 ppm in ¹¹B NMR spectrum, Scheme 9). With only a single C—H borylation of 2-methyl thiophene possible using the 2-phenylpyridyl-chelated borenium cation double arylation at boron requires addition of an organometallic nucleophile, e.g., an arylsilane or arylsilane reagent. Alternatively, conversion of [1-B(MeT)]⁺ to form 1-BCl(MeT) is achieved by addition of a halide source to form 1-BCl(MeT).

### EXPERIMENTAL SECTION

Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques under argon or in a MBraun Unilab glovebox under an atmosphere of argon (<0.1 ppm of O₂/H₂O). Unless otherwise indicated, solvents were distilled from appropriate drying agents: tetrahydrofuran (p-toluene sulfonic acid), toluene (potassium), n-hexane (NaK), and dichloromethane (CaH₂). Tetrahydrofuran and dichloromethane were stored over activated 3 Å molecular sieves, while toluene and n-hexane were stored over potassium mirrors. 2-BCl₄, 8, 2-methyl-5-tert-butylthiophene, trimethyl(5-methyl thiophen-2-yl)silane, tris(dimethyl(5-methyl thiophen-2-yl)phosphinyl)borane, and [Mg(THF)(μ-Br)₃(Zn(p-tolyl)₃)] were prepared according to previously published procedures. All other compounds were purchased from commercial sources and used as received. NMR spectra were recorded on Bruker AvanceIII 400 or Bruker Ascend–400 spectrometers. Chemical shifts are reported as dimensionless δ values and are referenced relative to residual proto-imidazoles in the NMR solvents for [H] and [¹³C] [¹[H], respectively. While ²B and [¹⁷F] shifts are referenced relative to external BF₃·etherate and benzaldehyde, respectively. Coupling constants J are given in Hz (Hertz) as positive values regardless of their real individual signs. The multiplicities of the signals are indicated as ‘s’, ‘d’, ‘t’, ‘q’, ‘p’, ‘m’ for singlet, doublet, triplet, quartet, or multiplet, respectively. Carbon atoms directly bonded to boron are not always observed in the [¹³C] [¹[H] NMR spectra due to quinupolar relaxation leading to considerable signal broadening. In a number of compounds individual carbon resonances are not observed for all inequivalent protons (particularly in the acyl chains) due to resonance coincidence. High-resolution mass spectra (HRMS) were recorded on a Waters QTOF mass spectrometer. Microanalysis was performed by Stephen Boyer at the London Metropolitan University microanalytical service. For the aryldoped compounds accurate combustion data were not obtained with consistently low %C content observed. This is attributed to boron carbyne formation and persisted even when V₂O₅ was used as an oxidant. For these compounds NMR spectra are included in the SI to support compound purity.

Synthesis of 2-B(MeT)BCl₄: 1 M to DCM (0.3 mL, 0.3 mmol), was added to a solution of 2 (95 mg, 0.10 mmol) in DCM (5 mL), and the solution was stirred overnight under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure. The resulting residue was dissolved in DCM (3 mL), and AlCl₃ (1 mmol) was added to the solution. 2-Methyl-5-triisobutylthiophene (90 mg, 0.22 mmol) was added to the reaction mixture, which was then stirred overnight. The solvent was then removed under reduced pressure, and the purification was performed under ambient atmosphere using non-purified solvents thereon. The residue was dissolved in hexane and was passed through (using hexane initially and then 10% DCM/90% hexane as eluent) a short plug of base-treated silica gel (pretreated with 5% NHaBr,hexane), and only the purple-colored solution was retained. The solvent was removed to afford a purple residue. Yield: 78%.

¹¹B NMR (400 MHz, CDCl₃, δ): 8.50 (d, J = 7.7 Hz, 1 H), 8.35 (s, 1 H), 8.09 (d, J = 6.7 Hz, 1 H), 8.04—7.96 (m, 3 H), 7.93—7.87 (m, 1 H), 7.82 (d, J = 2.3 Hz, 1 H), 7.76—7.69 (m, 1 H), 7.48—7.27 (m, 6 H), 6.82 (d, J = 3.3 Hz, 2 H), 6.69 (d, J = 3.1 Hz, 2 H), 2.44 (s, 6 H), 2.20—2.01 (m, 8 H), 1.27—1.04 (m, 40 H), 0.89—0.67 (20 H) ppm.

¹³C NMR (101 MHz, CDCl₃, δ): 155.1 (br), 154.4, 152.0, 151.9, 150.8 (br), 150.1, 149.0, 142.5, 142.2, 141.4, 140.9, 134.7, 133.2.
Organometallics

131.3, 131.2, 130.0, 128.7, 128.4, 128.2, 127.9, 127.5, 127.3, 126.3, 126.1, 125.2, 124.3, 123.6, 123.5, 120.9, 120.6, 120.5, 117.0, 58.5, 55.5, 41.1, 40.7, 32.4, 32.0, 30.6, 29.8, 29.8, 29.5, 24.5, 24.4, 23.2, 15.6, 14.4 ppm. 1H NMR (128 MHz, CDCl3): δ = –2 ppm (v br). HRMS (APCI): caleđ for \( \text{C}_{9}\text{H}_{16}\text{BiN}_{3}\text{S}_{7} (M + H)^{+} \left[ 1173.6667 \right] \) found 1173.6664.

Synthesis of 2-BPb, BCl3 1 M in DCM (0.1 mL, 0.1 mmol) was added to a solution of 3 (20 mg, 0.055 mmol) in DCM (3 mL), and the solution was stirred under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure. The resulting residue was dissolven in DCM (3 mL), and AlCl3 (1 mg) was added to the solution. Tributylphenylstannane (40 mg, 0.121 mmol) was added to the solution, and the reaction mixture was stirred and heated overnight at 60 °C. The solvent was then removed under reduced pressure, and the purification was performed under ambient atmosphere using unpurified solvents thereon. The residue was dissolved in hexane and was passed through a short plug of base-treated silica gel (5% NMe3/Sephax, and only the dark blue colored solution was retained. The solvent was removed to afford a purple residue. Yield: 53 mg, 89%. The spectra agree with that previously reported.

Synthesis of 4-BPb, BCl3 1 M in solution in DCM (0.30 mL, 0.3 mmol), was added to a bright yellow solution of 4 (50 mg, 0.076 mmol) and 2,4,6-tri-t-butylpyridine (38 mg, 0.154 mmol) in DCM (3 mL). The solution rapidly changed color to a dark red. AlCl3 (20 mg, 0.151 mmol) was then added to the AgBF4 (16 h), an additional portion of AlCl3 (20 mg, 0.151 mmol) was added to the reaction mixture. The solution was rotated for a further 16 h, whereupon the solution turned dark green. The DCM was removed under reduced pressure, and the reaction mixture was dissolved in ODCM (4 mL). Tributylphenylstannane (0.15 mL, 0.456 mmol) was added to the reaction mixture, which was then stirred at 20 °C for 48 h and heated at 40 °C for 16 h. NMe3Cl (50 mg, 0.456 mmol) was added to the reaction mixture, and after 1 h the solvent was removed under reduced pressure. The purification was performed under ambient atmosphere using unpurified solvents thereon. The residue was purified via column chromatography on base-treated silica gel (5% NMe3/hexane) [elemental chromaform/hexane (2:8)] to afford a purple residue. Yield: 24 mg, 32%. The spectra agree with that previously reported.

Synthesis of 5-B(Me2)2, BCl3 1 M in DCM (0.2 mL, 0.20 mmol), was added to a solution of 5 (95 mg, 0.18 mmol) in DCM (3 mL), and the solution was stirred overnight under the dynamic flow of nitrogen. The solvent was then removed under reduced pressure. The resulting residue was dissolved in DCM (3 mL), and AlCl3 (1 mg) was added to the solution. 2-Methyl-5-tributylstannylithiophene (154 mg, 0.40 mmol) was added to the reaction mixture, which was then stirred overnight. The solvent was then removed under reduced pressure, and the purification was performed under ambient atmosphere using unpurified solvents thereon. The residue was purified via column chromatography on base-treated silica gel (5% NMe3/hexane) [elemental chromaform/hexane (19:1)] to afford a dark blue residue. Yield: 67 mg, 51%.

1H NMR (400 MHz, CDCl3): δ = 7.71 (d, J = 3.7 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 6.94–6.83 (m, 6H), 6.82–6.77 (m, 1H), 6.70 (d, J = 3.2 Hz, 2H), 6.71–6.64 (m, 2H), 2.87 (q, J = 7.1 Hz, 4H), 2.45 (s, 6H), 1.83–1.68 (m, 4H), 1.51–1.22 (m, 20H), 1.00–0.82 (m, 6H), 6.4 ppm. 1C NMR (100 MHz, CDCl3): δ = 158.7 (br), 153.8 (br), 151.0, 149.4, 148.8, 147.0, 142.3, 135.8, 131.6, 131.3, 130.9, 128.1, 128.1, 126.1, 126.1, 124.5, 124.4, 122.8, 122.5, 32.5, 32.2, 31.0, 30.8, 29.9, 29.9, 29.8, 29.8, 23.3, 15.5, 14.5 ppm. 13B NMR (128 MHz, CDCl3): δ = –2 ppm (v br). HRMS (APCI): caleđ for \( \text{C}_{9}\text{H}_{16}\text{BiN}_{3}\text{S}_{7} (M + H)^{+} \left[ 1173.6688 \right] \) found 1173.6688.

Synthesis of 1-BCl2, BCl3 1 M in DCM (4.0 mL, 4 mmol), 2,4,6-tri-t-butylpyridine (0.8 g, 3.2 mmol), and 2-phenylpyridine (0.5 g, 3.2 mmol) were dissolved in DCM (40 mL). AlCl3 (0.854 mmg, 6.4 mmol) was added to the reaction mixture, whereupon a color change from colorless to yellow was observed. After stirring for 4 h the reaction mixture was degassed under vacuum and NMe3Cl (0.351 g, 3.2 mmol) was added, whereupon the reaction mixture changed color from yellow to colorless. The reaction mixture was evaporated to dryness and washed with water (3 × 100 mL) and hexane (100 mL). The resulting white powder was dried under reduced pressure. Yield: 0.584 g, 77%.

1H NMR (400 MHz, CDCl3): δ = 8.82 (d, J = 5.8 Hz, 1H), 8.18 (d, J = 15.7, 8 Hz, 1H), 7.98–7.91 (m, 1H), 7.86 (d, J = 7.3 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.62–7.53 (m, 2H), 7.47–7.39 (m, 1H). Carbon NMR data are not reported due to the extremely low solubility of the product in a range of common organic solvents. 13B NMR (138 MHz, CDCl3): δ = 7 (v br) ppm. Anal. Caled for \( \text{C}_{9}\text{H}_{16}\text{BiN}_{3}\text{C}_{2} \): C, 56.0; H, 5.94. Found: C, 56.09; H, 5.32. N, 8.8.

Synthesis of 1-BCl2[AlCl3], AlCl3 (57 mg, 0.42 mmol) was added to a suspension of 1-BCl2 (100 mg, 0.42 mmol) in DCM (10 mL). This was stirred overnight, whereupon all the 1-BCl2 had dissolved and the reaction mixture had changed color from colorless to yellow. The reaction mixture was then concentrated to a saturated

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solution (~4 mL), which was then filtered via cannula, and the solution transferred to a 10 mL Young’s ampule. The sample was then held at 2 °C for 16 h, whereupon amber-colored crystals formed. The crystals were isolated via filtration. Yield: 93% m/v.

1H NMR (400 MHz, CDCl₃): δ = 8.43 (d, J = 5.7 Hz, 1 H), 8.13–8.00 (m, 2 H), 7.98 (dd, J = 7.6 Hz, 1 H), 7.69 (d, J = 7.3 Hz, 1 H), 7.42 (t, J = 7.3 Hz, 1 H), 7.40 (m, 2 H), 7.32 (t, J = 7.3 Hz, 2 H), 7.09 (d, J = 7.6 Hz, 2 H). 13C NMR (101 MHz, CDCl₃): δ = 161.3 (br), 158.4, 153.2, 143.8, 144.1, 135.8, 135.2, 131.6, 130.6, 129.3, 128.9, 126.5, 122.6, 122.3, 121.9, 118.5. *B* NMR (128 MHz, CDCl₃): δ = 3 (v br) ppm. HRMS (APCI): calcd for C₅H₅N⁺: (M + H) 79.1447, found 79.1446.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo...557.

Full experimental procedures, compound characterization data, copies of NMR spectra, and coordinates for all calculations (PDF)

Crystallographic data (CCDC 1429268) (CIF)

Crystallographic data (CCDC 1429269) (CIF)

Structure model (XYZ)

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Notes

The authors declare no competing financial interest.

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