Thienyl- and Furylborane Oligomers, Polymers, and Macrocycles – Development of a Catalytic Si/B Exchange Reaction As a Novel B–C Bond Formation Method

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der RWTH Aachen University zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften genehmigte Dissertation

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Within a cooperation with the University of Kassel, I had the pleasure to work with Denis Kargin and Stefan Isenberg, two of my former fellow students, and Prof. Rudolf Pietschnig, one of my former professors.
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Contributions

Each section is self-contained and is in the form of a publication for the open literature. The content of Section 3.1 has been published in the *Journal of the American Chemical Society*. Sections 3.2–3.5 are intended to be submitted for publication. A manuscript containing the content of Section 3.6 has been submitted for publication.

*Section 3.1:* Within their master theses, Lars Müller and Lars Fritze worked on the development of the presented catalytic route. This comprised synthetic and analytical procedures. The content of this section is adapted with permission from Artur Lik, Lars Fritze, Lars Müller, and Dr. Holger Helten, *J. Am. Chem. Soc.* 2017, 139, 5692. Copyright (2017) American Chemical Society.

*Section 3.2:* In addition to Lars Müller and Lars Fritze, Sangeth Kevin Jenthra performed the synthesis of the mixed monodisperse oligomers presented. Khai-Nghi Truong was responsible for the solution and refinement processes of the single crystal X-ray diffraction experiments carried out. For this section, a manuscript is in preparation.

*Section 3.5:* Within his internship, Nicolas Riensch performed reactions and analytical measurements on the synthesis of the presented tetrathiatetraboraporphyrinogen.

*Section 3.6:* During a cooperation with the University of Kassel, Denis Kargin synthesized the starting materials for the synthesis of a PBP bridged [3]ferrocenophane. The electrochemical measurements were performed by Stefan Isenberg. The content of this section has been submitted for publication.
## List of Abbreviations

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<thead>
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<th>Full Form</th>
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<tbody>
<tr>
<td>Å</td>
<td>Angström</td>
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<tr>
<td>a.u.</td>
<td>arbitrary units</td>
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<tr>
<td>abs</td>
<td>absorbance</td>
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<tr>
<td>anal.</td>
<td>analysis</td>
</tr>
<tr>
<td>Ar</td>
<td>aromatic ring</td>
</tr>
<tr>
<td>b.p.</td>
<td>boiling point</td>
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<tr>
<td>BBr₂</td>
<td>dibromoboryl</td>
</tr>
<tr>
<td>BBr₃</td>
<td>tribromoborane</td>
</tr>
<tr>
<td>BCl₂</td>
<td>dichloroboryl</td>
</tr>
<tr>
<td>BCl₃</td>
<td>trichloroborane</td>
</tr>
<tr>
<td>BF₃•OEt₂</td>
<td>trifluoroborane etherate</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>C₆D₆</td>
<td>deuterated benzene</td>
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<tr>
<td>CaH₂</td>
<td>calcium hydride</td>
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<tr>
<td>cat.</td>
<td>catalyst</td>
</tr>
<tr>
<td>CD₂Cl₂</td>
<td>deuterated dichloromethane</td>
</tr>
<tr>
<td>CDCl₃</td>
<td>deuterated chloroform</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>dichloromethane</td>
</tr>
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</table>
Cl₂BNiPr₂  dichloro-di(iso-propyl)aminoborane

cm  centimeter

Compd.  compound

Cp  cyclopentadienyl

CTP  catalyst transfer polymerization

CV  cyclo voltammetry

d  doublet

DCB  dichlorobenzene

DCM-D₂  deuterated dichloromethane

dd  doublet of doublet

DPA  diphenylanthracene

DPₙ  average degree of polymerization

e.g.  exempli gratia

ECL  effective conjugation length

EI  electron ionization

elem.  elemental

em  emission

equiv  equivalents

Et₂O  diethylether

eV  electron Volt
<table>
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<tr>
<th>Abbreviation</th>
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<tbody>
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<td>ex</td>
<td>extinction</td>
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<tr>
<td>Fc/Fc⁺</td>
<td>ferrocen/ferrocenium cation</td>
</tr>
<tr>
<td>FET</td>
<td>field-effect transistor</td>
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<tr>
<td>F'Mes</td>
<td>2,4,6-tris(trifluoro)methylbenzene</td>
</tr>
<tr>
<td>Fur</td>
<td>furan</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width half maximum</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
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<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
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<tr>
<td>GRIM</td>
<td>Grignard metathesis</td>
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<td>head-to-head</td>
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<td>highest occupied molecular orbital</td>
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<td>HT</td>
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<td>Hz</td>
<td>Hertz</td>
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<tr>
<td>J</td>
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<td>liter</td>
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<td><strong>LED</strong></td>
<td>light-emitting diode</td>
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<td>------------------</td>
<td>-------------------------------</td>
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<tr>
<td><strong>LUMO</strong></td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td><strong>M</strong></td>
<td>mol per liter</td>
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<td><strong>m</strong></td>
<td>multiplet</td>
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<tr>
<td><strong>m.p.</strong></td>
<td>melting point</td>
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<td>mass per charge</td>
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<td>maximum</td>
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<tr>
<td><strong>mbar</strong></td>
<td>millibar</td>
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<td>trimethylsilyl bromide</td>
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<tr>
<td><strong>Me$_3$SiNTf$_2$</strong></td>
<td>trimethylsilyl bis(trifluoromethylsulfonyl)imide</td>
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<td><strong>MesCu</strong></td>
<td>mesityl copper</td>
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<td>Abbreviation</td>
<td>Description</td>
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<td>--------------------------------------------------</td>
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<tr>
<td>mg</td>
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<td>MHz</td>
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<td>min</td>
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<td>number average molar mass</td>
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<tr>
<td>MS</td>
<td>mass spectrometry</td>
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<tr>
<td>$M_v$</td>
<td>volume average molar mass</td>
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<td>mV</td>
<td>millivolt</td>
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<td>$M_w$</td>
<td>mass average molar mass</td>
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<td>centrifugation average molar mass</td>
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<tr>
<td>NaOMe</td>
<td>sodium methanolate</td>
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<tr>
<td>NBO</td>
<td>natural bond orbitals</td>
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<td>NBu$_4$PF$_6$</td>
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<td>NEt$_2$</td>
<td>diethylamin</td>
</tr>
<tr>
<td>nm</td>
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<td>NMR</td>
<td>nuclear magnetic resonance</td>
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<tr>
<td>norm.</td>
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<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>o</td>
<td>ortho</td>
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<tr>
<td>OFET</td>
<td>organic field-effect transistor</td>
</tr>
<tr>
<td>OLED</td>
<td>organic light-emitting diode</td>
</tr>
<tr>
<td>OPV</td>
<td>organic photovoltaics</td>
</tr>
<tr>
<td>p</td>
<td>para</td>
</tr>
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<td>PDI</td>
<td>Polydispersity index</td>
</tr>
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<td>Ph</td>
<td>phenyl</td>
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<tr>
<td>PhBBBr₂</td>
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<tr>
<td>PhSiMe₃</td>
<td>trimethylsilyl benzene</td>
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<tr>
<td>PLED</td>
<td>polymeric light-emitting diode</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
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<tr>
<td>R</td>
<td>organic rest</td>
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<td>r.t.</td>
<td>room temperature</td>
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<td>RI</td>
<td>refractive index</td>
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<td>ROP</td>
<td>ring-opening polymerization</td>
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<td>RRDE</td>
<td>rotating ring-disk electrode</td>
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<tr>
<td>SiMe₃</td>
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<td>SIMS</td>
<td>secondary ion mass spectrometry</td>
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<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>SR</td>
<td>standard reaction</td>
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<tr>
<td>t</td>
<td>tert</td>
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<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
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<tr>
<td>TBACl</td>
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<td>tetrabutylammonium fluoride</td>
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<tr>
<td>t-Bu</td>
<td>tert-butyl</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>time-dependent discrete fourier transformation</td>
</tr>
<tr>
<td>Tf</td>
<td>bis(trifluoromethyl)sulfonyl</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>Thi</td>
<td>thiophene</td>
</tr>
<tr>
<td>Tip</td>
<td>2,4,6-tri-iso-propylphenyl</td>
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<td>TipB(OMe)$_2$</td>
<td>2,4,6-tri-iso-propylphenyl-dimethoxyborane</td>
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<td>TMEDA</td>
<td>tetramethylethylene diamin</td>
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<td>TMS</td>
<td>trimethylsilyl</td>
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<td>TMSBr</td>
<td>trimethylsilyl bromide</td>
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<td>TMSNTf$_2$</td>
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</tr>
<tr>
<td>TOF</td>
<td>turn over frequency</td>
</tr>
<tr>
<td>TT</td>
<td>teal-to-tail</td>
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</tbody>
</table>
UV \quad \text{ultra-violet}

V \quad \text{Volt}

\text{vis} \quad \text{visible}

\text{vs} \quad \text{versus}

\Phi_F \quad \text{fluorescence quantum yield}

\delta \quad \text{chemical shift}

\varepsilon \quad \text{extinction coefficient}

\lambda \quad \text{wavelength}

\tau \quad \text{lifetime}
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1. Abstract

The synthesis of new functional materials with tailored optical and (electro)chemical properties is of considerable interest in current research. State-of-the-art inorganic-based devices rely on available resources and are limited by poor processability. Due to the better processability and potential use in light-weight devices, organic materials have emerged as a very promising alternative to currently used inorganic materials. Organic polymers have been the subject of tremendous research activity in the last decades. They found application in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaics (OPVs). An effective way to tune the optical and electronic properties of these materials beyond that is based on the incorporation of electron-acceptor and electron-donor moieties into organic structures, thus, giving rise to $\pi$ interactions between them. Based upon its inherent electron deficiency, incorporation of boron into organic $\pi$ systems inherits the possibility of obtaining materials with unique and improved properties compared to their purely organic congeners.

In this thesis, a novel, environmental benign and highly efficient synthetic method for the formation of $\text{B}–\text{C}$ bonds via $\text{Si}/\text{B}$ exchange is presented. The catalytic reaction proceeds smoothly and selectively at ambient temperature, affording poly(2-thienyl)- and poly(2-furyl)boranes amongst other (hetero)arylboranes. In order to investigate the optical properties upon extension of the $\pi$ system, the new synthetic protocol has been employed on the synthesis of monomeric, dimeric and trimeric model compounds. This allowed to determine the effective conjugation wavelength of the thiophene- and furan-based materials. In addition, suitable organoborane (macro)molecules can serve as potent chemical sensors for the selective detection of fluoride anions. We performed first mechanistic studies on this catalytic approach, which reveal a linear relation between the reaction rate and the amount of catalyst applied and the total concentration of the reaction mixture. The dependency of the reaction progression on the nature of the starting materials was found to be complex. This is presumably a result of two different reaction paths leading to the desired product. The influence of the kinetically stabilizing aryl group (which provides stability to the Lewis acidic boron
center towards air and moisture) and the substitution pattern at the 5,5’-positions of di(2-thienyl)arylboranes on the structure in the solid-state has been verified. Furthermore, a novel tetrathiatetraboraporphyrinogen was successfully synthesized, which is formally derived from the porphyrin framework by substitution of pyrrole with thiophene and the meso carbon atoms by boron. The resulting 16 π electron species comprises a fully delocalized system with unique absorption and emission behavior, compared to its linear congener. Upon addition of fluoride anions, its UV–vis absorption and fluorescence emission characteristics are influenced significantly. Therefore, it also serves as a potent chemical sensor. Finally, the first P–B–P bridged [3]ferrocenophane with a redox trigger has been synthesized. An intramolecular electron transfer process from the bridge to the ferrocenium backbone in the mono-oxidized state is supported by electrochemical investigations.
2. Introduction

2.1 Semiconducting materials

In the last decades (semi)conducting materials have emerged as a prosperous field of research. Due to their applications in useful devices such as light-emitting diodes (LEDs) or field effect transistors (FETs), (semi)conducting materials have been the subject of tremendous research activity. Current materials used for industrial purposes consist of inorganic solids. Replacement of established inorganic components with organic macromolecules offers the possibility of reducing production costs, due to the facile processability, and the possibility to obtain light-weight materials.\(^\text{[1]}\) This leads to potential usage of such materials in flexible optoelectronic devices,\(^\text{[2-4]}\) bioimaging, drug delivery,\(^\text{[5]}\) and chemical sensing.\(^\text{[6]}\) For this purpose a variety of organic polymers have been synthesized, characterized, and investigated with respect to their possible industrial applications. Besides polythiophenes 1, polyfurans 2, polyselenophenes 3 and polytellurophenes 4 (Figure 1) play a significant role in this context.

![Figure 1. Organic polymers. From left to right: polythiophene, -furan, -selenophene, and -tellurophene.](image)

Polythiophenes are by far one of the most important and best-studied class of conjugated organic polymers.\(^\text{[7]}\) A large number of different thiophene-containing (macro)molecules has been synthesized, characterized and studied.\(^\text{[8]}\) In polythiophenes, the heteroaromatic rings are linked by C–C coupling \(\alpha\) to the heteroatom to give cyclolinear polymers. These systems show p-channel charge transport characteristics and are used in plastic electronic devices (e.g. organic field-effect transistors (OFETs)).\(^\text{[1]}\) Instead of pure thiophene-containing polymers, copolymers with thiophene building blocks have been synthesized, where thiophene serves as an electron-rich moiety. The 2,5-coupled polythiophenes show high conductivity, especially upon oxidative doping, but are mostly insoluble in common solvents. In order to enhance the solubility of these compounds and obtain
materials that can be processed from solution, flexible side chains can be introduced at the 3-position (e.g. \textit{n}-hexyl, \textit{n}-octyl, \textit{n}-dodecyl). However, a possible drawback of this substitution is that the resulting macromolecules have three different ways of undergoing the C–C coupling reaction, with respect to the positions at the heteroaromatic ring (Figure 2).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Top: Possible coupling between 3-alkyl substituted thiophene moieties. Bottom: Regioregular and regioirregular coupling products of 3-alkyl substituted polythiophenes.}
\end{figure}

Whereas in head-to-tail (HT) coupled polymers the highest degree of coplanarity (heteroaromatic rings relative to each other) is provided (regioregular polymers), partial head-to-head (HH) and tail-to-tail (TT) coupling leads to regioirregular polymers with significantly reduced coplanarity, due to the steric repulsion of the side chains in the backbone (Figure 2).\textsuperscript{[1]} Coplanarity is a significant factor, if transport characteristics and \(\pi\) conjugation is of major interest. The resulting torsion of the thiophene rings in HH and TT polythiophenes renders these molecules to less attractive targets in polymer chemistry. In contrast to regioirregular polythiophenes, regioregular polythiophenes form highly ordered, self-assembled solid-state structures. This leads to a favorable effect on inter- and intra-chain charge carrier mobilities of these materials.\textsuperscript{[9]} Since polythiophenes are well-established systems, various different strategies for their synthesis are known.\textsuperscript{[10-16]} McCullough and co-workers performed a method which proceeds
via Grignard metathesis reaction (GRIM).[14] After reaction of 2,5-dibromothiophene 5 with a suitable Grignard reagent, the polymerization is mediated by a Ni-based Kumada cross coupling reaction (Scheme 1; equation (1)). With this route a high selectivity, with respect to the formation of HT polythiophenes, is achieved (>99%). A related route was presented by Rieke et al. They used a zinc reagent instead of a Grignard reagent. The subsequent polymerization reaction follows a Kumada-type reaction as well (Scheme 1; equation (2)).[11] Barker and Bidan used a third approach based on Palladium-catalyzed Suzuki-Miyaura or Stille coupling.[12,13]

Scheme 1. Polymerization of 5 using a Grignard reagent (1) or Rieke-zinc (2).
Replacing thiophene with selenium or tellurium, respectively, offers certain advantages. Due to the larger size of these atoms, compared to sulfur, and greater polarizability, these structures inherit a better capability of charge stability upon doping. Therefore, they are of growing interest.[17] Computational studies show, that the incorporation of sulfur in cyclopentadiene has an influence on the lowest unoccupied molecular orbital (LUMO), but not on the highest occupied molecular orbital (HOMO). Based on the lower ionization potential of selenium compared to sulfur, the LUMO energy in selenophene is further decreased (LUMO (thiophene): ~ 1.6 eV; LUMO (selenophene): ~ 1.3 eV), whereas the HOMO is not influenced (~ –4.8 eV). The decrease of the band gap was experimentally verified by Tierney and co-workers.[18] This effect is even more pronounced in polytellurophenes 4. Synthetic strategies for obtaining polyselenophenes 3 and polytellurophenes 4 are the same as for polythiophenes 1, with congruent results in selectivity.
Bendikov and Gidron performed a variety of experiments and computational studies to verify the influence of different heteroatoms in cyclolinear chalcogenophene-containing macromolecules. Whereas the band gap decreases when heavier analogues of thiophene (selenophene, tellurophene) are incorporated into macromolecules as adjacent organic building blocks, the band gap increases if furan is incorporated.\textsuperscript{[19]} This is a result of the lower aromaticity in conjugated furan rings, compared to non-conjugated ones, and was further verified by determination of the respective resonance energies.\textsuperscript{[20]} However, polyfurans show increased conjugation, stronger luminescence, better solubility and can be derived from biomass.\textsuperscript{[21]} The smaller atomic size of oxygen, compared to sulfur, selenium and tellurium, leads to a shorter O–C2(5) bond in furan. As a result, the angle between C5–O–C2 is smaller than in its higher analogues.\textsuperscript{[22]} Therefore, the furan rings in polyfuran are more likely to adopt a planar arrangement than the thiophene rings in polythiophene (steric effect).\textsuperscript{[23e]} In addition, the quiniodal resonance form has a larger contribution to the properties of oligofuran than the aromatic resonance form (Figure 3). This effect is pronounced less in oligothiophene.\textsuperscript{[23d,24]}

Figure 3. Aromatic and quiniodal structure of polyfuran.

A further difference between oligofurans and oligothiophenes is the more rigid structure of the first. Due to the higher rigidity, trifuran shows more intense fluorescence than trithiophene (quantum yields: 78 % for trifuran; 6 % for trithiophene).\textsuperscript{[23c]} However, a possible reason for polyfurans to have received comparatively less attention is their intrinsic instability. This results in a decomposition tendency in the presence of light and oxygen. Syntheses and subsequent processes have to be carried out in the dark, which is a major drawback with respect to the practicability compared to thiophene.

The better solubility of α-hexafurans compared to α-hexathiophenes (0.7 mg/L in CHCl₃ vs. < 0.05 mg/L in CHCl₃)\textsuperscript{[23d]} has two reasons. First, the higher electronegativity of oxygen (and higher dipole moment of furan) results in a better solubility in polar solvents. Second, solid-state
interactions are reduced and solubility is improved.\cite{23e} Single crystal X-ray diffraction studies show that the inter-ring C–C bonds in \( \alpha \)-polyfurans are shorter than in \( \alpha \)-polythiophenes. In addition, the smaller atomic size of the oxygen atom in furan favors the quinoidal structure even more.\cite{23d} As a result, \( \alpha \)-polyfurans reveal a more rigid structure compared to their thiophene-containing congeners. The furan rings in HH-3-hexylfurans still remain remarkably planar.\cite{23a} Based on the increased band gap (~ 0.3–0.4 eV higher relative to polythiophene) in polyfurans, the absorption is blue-shifted. However, polyfurans show a more intense fluorescence and a smaller Stokes shift.\cite{21} Presumably, the more intense fluorescence is a result of the lack of a heavy atom and, therefore, less inter-system crossing can occur. In addition, the small Stokes shift is probably based on the more rigid structure of polyfurans compared to polythiophenes. Syntheses of polyfurans are very similar to those of polythiophenes. However, some modifications have to be considered. As mentioned before, exposure to light has to be reduced to a minimum or eliminated completely. Also, an acidic environment is not favorable, because this may lead to decomposition of the compound. Nemes \textit{et al.} have synthesized 3-alkylsubstituted polyfurans\cite{25} either via 2,5-dibromo-3-alkylfuran with Rieke zinc in the presence of a Ni-containing transition metal complex or with a Pd-containing transition metal complex. Both these approaches belong to the class of catalyst-transfer polymerization reactions (CTP). Whereas, the Ni-catalyzed reaction results in regioregular HT-polyfurans, the Pd-catalyzed reaction leads to regioirregular compounds. The syntheses of copolymerized materials are also very similar to those of thiophene\cite{26} and proceed e.g. via Stille coupling.\cite{27} The major advantage of furan compared to thiophene lies within the possibility of furan to be derived from biorenewable resources.\cite{23c} Furan is obtained by the decarbonylation of furfural, which is derived from agricultural by-products.\cite{28}

2.2 Organic macrocycles

For monodisperse linear oligothiophenes the physical properties are well correlated to the structural parameters (e.g. conjugation length).\cite{8} However, for smaller chain lengths undesirable effects (perturbing end effects) can influence these properties.\cite{29} In order to rule out these
effects, the synthesis and characterization of fully $\pi$-conjugated, shape-persistent macrocycles is a promising way. They serve as model systems because no end group effects are present, but they resemble structurally well-defined oligomers.\[^8\] Because of the ring strain, the number of repeating units in a macrocycle that are formed through $\alpha$-C–C coupling is limited. For a purely thiophene-containing oligomer $\alpha$-coupling is necessary, in order to obtain fully conjugated systems. The importance of fully $\alpha$-conjugated cyclothiophene was supported by theoretical calculations presented by Tol \textit{et al.} The cyclo[12]thiophene 6 and its dication 7 showed a nearly non-strained coplanar structure, with all-\textit{syn} conformation (Figure 4).\[^{30}\]

![Figure 4. Uncharged 6 and radical dicationic congeners 7.](image)

Computational studies revealed an interesting effect. If 6 is singly oxidized, the charge of the resulting radical cation is delocalized only on half of the semicircle. Upon a second oxidation step, the two charges are delocalized separately each on one of the halfs of 7.\[^{30}\] Subsequent to these computational studies, the cyclo[12]thiophene, cyclo[16]thiophene, and cyclo[18]thiophene have been synthesized in the working group of Bäuerle.\[^8\] These annulenes consist of alternating thiophene units, either unsubstituted at the 3- and 4-position or substituted with two butyl chains. These annulenes have to be considered as antiaromatic (4n) $\pi$ annulenes based on the classification of Hückel. Indeed, no ring currents were observed. The annulenes reveal a benzoid rather than an annulenoid character.\[^8\] For the synthesis of macrocyclic oligothiophenes the same protocols are used as for their linear congeners. Moore and Müllen, amongst others, have improved the yields by template-assisted synthesis.\[^{31-36}\] In order to reduce the ring strain present, smaller macrocycles (e.g. trimers 8, tetramers 9) have been synthesized by Lewis \textit{et al.} through
introduction of vinylene-bridges between the thiophene rings (Scheme 2).[37]

Scheme 2. Synthesis of vinylene-bridged trimeric and tetrameric cyclathiophene.

Detailed single crystal X-ray structure analysis revealed that the thiophene rings are not planar and twisted out of plane. Therefore, no significant ring current is present and no additional aromaticity (in addition to the aromaticity of thiophene) is evidenced by NMR spectroscopy. The trimer may be viewed as a combination of independent thiophene and vinylene units, rather than a conjugated system.[8] The amount of vinylene units can be reduced by usage of α-coupled bithiophene moieties. However, again no ring current is present, the molecule is non-planar and an oxidation process to the aromatic $18\pi$ dication was not successful.[8] Based upon these results, porphyrins with bridged thiophene groups should resemble structural variants of fully aromatic [18]annulenes. Vogel and co-workers have successfully synthesized and characterized tetrathia- 10, tetraoxo- 11 and tetraselenoporphyrin dications 12, which were among the first representatives of this particular class of molecules (Scheme 3).[38,39]
Scheme 3. Syntheses of neutral and dicationic chalcogen-containing porphyrins.

The synthesis proceeds in three steps (except for 11; only two steps are required) starting from furfuryl alcohol. Single crystal X-ray structure analysis showed nonplanarity of the thiophene-containing dication with a distortion angle of ~23°. Despite this distortion the dication is aromatic and shows a diatropic ring current. The UV-vis spectrum of this compound revealed an absorption maximum at 700 nm. This low-energy transition refers to a band gap decrease, due to pronounced $\pi$ conjugation in the system. Therefore, it can be regarded as an 18 $\pi$ annulene. Whereas the 16 $\pi$ annulene-precursor molecules show intrinsic instability, the dications are perfectly stable colorful solids. Besides the symmetric systems consisting of one type of five-membered heteroaromatic rings, also mixed variants (different types) with deviating numbers of $\pi$ electrons are accessible.\[^8\]

2.3 Boron-containing cyclolinear (macro)molecules

A general strategy to tune electronic and optical properties of conjugated macromolecules is the utilization of electron-acceptor and electron-donor units.\[^1\] These units may consist of purely organic building blocks or inorganic compounds. Through incorporation of inorganic elements in well-established organic macromolecules, it is possible to obtain various novel hybrid macromolecules with unique
properties, which are not achievable with purely organic compounds.\textsuperscript{[40,41]} By far the most widely used strategy for the synthesis of such compounds involves polycondensation reactions. Usually they proceed via a step-growth mechanism, although chain-growth mechanisms are also known.\textsuperscript{[1]} Other synthetic protocols include ring-opening polymerization (ROP) and polyaddition polymerization. The coupling reaction can either proceed via C–C or E–C bond formation, where E is a heteroelement (Figure 5). The electron-donor moiety is often represented by an electron-rich arene (e.g. thiophene, furan). Whereas for the synthesis of hybrid macromolecules via C–C coupling established methods are used, E–C coupling procedures are element-specific. For example, Stille or Suzuki-Miyaura coupling reactions, which are catalyzed by transition metal complexes, play a significant role.\textsuperscript{[1]}

\begin{equation} a) \quad X - R - X + Y - R' - E - R' - Y \xrightarrow{-XY} \left[ R - R' - E - R' \right]_n \end{equation}

\begin{equation} b) \quad X - R - E - R' - Y \xrightarrow{-XY} \left[ R - E - R' \right]_n \end{equation}

\begin{equation} c) \quad X - R - X + Y - E - R' - E - Y \xrightarrow{-XY} \left[ E - R' - E \right]_n \end{equation}

\begin{equation} d) \quad X - R - X + Y - E - Y \xrightarrow{-XY} \left[ E - Y \right]_n \end{equation}

\begin{equation} e) \quad X - R - E - Y \xrightarrow{-XY} \left[ E \right]_n \end{equation}

Figure 5. Polycondensation reactions (a)-e)). R: organic building block; E: main-group element; X,Y: complementary leaving groups.

In equation a) a main-group element containing compound reacts with an organic building block in an AA/BB type reaction procedure. Both starting materials have two complementary leaving groups. In this reaction, exact stoichiometry is of crucial importance, if high molecular weights are of particular interest. An A/B type reaction (equation b)) is not dependent on an exact stoichiometry. Both leaving groups are positioned at the starting material (monomer unit) and polymerization is either initiated by elevated temperature or by addition of a suitable
catalyst. These considerations are also valid for E–C coupling reactions (equations (c) – (e)).

As a group 13 element, trivalent boron has an inherent electron deficiency, which renders it attractive for the incorporation into extended \( \pi \) conjugated macromolecules. The resulting macromolecules represent interesting species with intriguing electronic and optical properties. However, the electrophilic nature of boron makes synthesis challenging with respect to stability towards air and moisture. Yamaguchi and co-workers were able to provide sufficient stability of trivalent boron towards air, moisture and amines by structural constraint.\[42\] Noticeably, no steric protection in the vertical direction with respect to the B atom was required.\[42a\] Furthermore, by substitution of the boron center with sterically demanding aryl substituents, it is possible to increase the stability of these compounds. Kinetically stabilizing arene groups are amongst others anthracenyl,\[43\] mesityl\[44\] (Mes = 2,4,6-trimethylbenzene), tripyl\[45\] (Tip = 2,4,6-tri-iso-propylbenzene), and supermesityl\[46\] (Mes* = 2,4,6-tri-tert-butylbenzene). Because of the empty p orbital of boron and its possible participation in \( \pi \) conjugated systems, it has a unique position, potentially leading to n-type semiconducting materials.\[1\] As a result, there is growing interest in the synthesis and characterization of organoboron based conjugated materials for applications in organic electronics and optoelectronics, for bioimaging, and as chemosensors.\[47-52\]

Since the discovery of borazine 13 (Figure 6) in 1926, it is known, that B–N bonds are isoelectronic and isosteric to C=C double bonds. Therefore, borazine has been termed “inorganic benzene”. Replacement of CC units with BN units is a viable strategy to obtain novel materials with similar structural properties but different electronic and optical properties. This approach led to BN doped polycyclic hydrocarbons with tailored properties.\[53\]
Jäkle et al. have prepared a poly(1,2-azaborinine) 14 (Figure 6), which was the first example for a BN containing macromolecule polymerized in an A/B type polycondensation reaction. The 2,4,6-trimethylphenyl substituent (Mes) serves as a kinetically stabilizing group, which renders the product stable against water and nucleophiles. The heterocycles adopt all-syn conformation and are almost perfectly coplanar. Comparison of the model compound with the polymer reveals a significant bathochromic shift. This is a result of the effective extended conjugation in the polymer. The electronic structure is better resembled by poly(cyclohexadiene) than poly(β-phenylene). This behavior is due to the low contribution of the BN units to the frontier orbitals of the polymer. The first polythiophene-type polymers with BN units consisted of azaborinine units incorporated in thiophene-fused polycycles (15) and were synthesized by Pei and co-workers via Stille coupling (Figure 6). The band gap is similar to that of poly-3-hexylthiophene, but the HOMO level is lower in energy. The azaborinine-based polymer shows favorable p-channel charge transport characteristics and, with respect to its monomeric building block, it revealed improved performance.

1,3,2-Benzodiazaboroline was used as another building block for hybrid macromolecules by Sato et al. Polymerizations by its benzocore proceed via a Stille coupling reaction procedure (16) (Figure 6). Other reactions include polycondensation with 3,3′-diaminobenzidine, electropolymerization with thiophene units, and polymer modification processes with fluorene derivatives.
The obtained materials also revealed low participation of the BN units to the \( \pi \) conjugation. In order to improve the contribution of the BN units to the conjugation, a strategy was to incorporate them into the polymer main chain along the conjugation path. A versatile route for this purpose was the silicon/boron exchange polycondensation under ambient conditions recently presented by Helten et al. (Scheme 4).\(^{[61]}\)

![Scheme 4](image_url)

**Scheme 4.** Silicon/boron exchange reaction for the synthesis of polymers with a BN unit incorporated into the main chain.

Polymer 17 consists of \( p \)-phenylene building blocks, which are linked by NBN moieties. Although a slight twist of the phenylene units relative to each other, caused by \( E,Z \)-configuration, is present, some \( \pi \) conjugation across the NBN units was evidenced by photophysical investigations. Comparison of model compounds with the polymer revealed bathochromic shift in the absorption. Time-dependent DFT calculations suggest \( \pi-\pi^* \) transitions. Synthesis and characterization of B–H substituted derivatives revealed the analogous trends.\(^{[61,62]}\) In polymer 18, an all-trans conformation is present, which improves \( \pi \) conjugation.\(^{[63]}\) Complete replacement of CC units by BN units in the main chain leads to polyiminoboranes (19), which are analogues of polyacetylenes.\(^{[64]}\) In order to prevent cyclization reactions to borazine derivatives, an ethylene bridge was introduced in the backbone (Scheme 4).
In addition to polymers with B–N linkages, polymers with B–C linkages are also known. One possible way was described by Chujo and co-workers. It is based on the formation of B–vinylene linkages through hydroboration. In this synthetic approach suitable boron-containing molecules (e.g. MesBH₂, TipBH₂) are coupled with aromatic (hetero)diynes (20; Scheme 5).[65-69]

![Scheme 5. Synthetic procedures for the formation of B–C linkages in organic-inorganic hybrid polymers.](image)

Photophysical measurements revealed highly effective π conjugation in these systems, evidenced by a large bathochromic shift (monomer: 336 nm; polymer: 440 nm). This effect is enhanced by substitution of the organic spacer with electron-donating substituents. The reason for this behavior is an improved charge transfer process from the organic building block to the boron center. Haloboration-phenylboration reactions are also known.[70] Syntheses of B–aryl coupled polymers (21, 22) generally proceed via polycondensation reactions. As mentioned for the B–C linkages in general, these reactions may occur by C–C coupling or B–C coupling in an AA/BB type manner. Usually, a suitable organodimetallic species is reacted with a dihaloborane under elimination of an insoluble inorganic salt. Thereby, poly(p-phenylene)boranes (21),[71] and poly(ethynylene p-phenylene ethynylene)boranes[72] have been obtained (Scheme 5).

The dimetallic species (Grignard or dilitio compound) reacts with an aryldimethoxyborane to give the polymeric product. A drawback of this method is the limitation to coordinating solvents, which is necessary for the generation of the dimetallic species, but may lead to undesirable side-reactions with the boron-containing compound. This is especially
the case, if halogen substituted boranes serve as starting materials. Through introduction of bis-stannyl substituted compounds Jäkle et al. were able to eliminate this problem, as non-coordinating solvents (e.g. pentane, dichloromethane) can be employed. Tin/boron exchange reactions have been used for the reaction of bis-stannyl compounds with either bifunctional haloboranes[73,74] or bis-haloboryl compounds ([22]; Scheme 5).[75,76] Although such reactions are very successful for the synthesis of polymeric compounds, a major drawback of these routes is the toxicity of the starting materials (bis-stannyl compounds) as well as the by-products (trialkylstannyl halogenide) formed during the reaction. The optical properties of these materials are further tunable by the kinetically stabilizing aryl substituent.[46,73,77] If the kinetic stability is sufficiently low, the Lewis acidity of the boron centers is high enough to (reversibly) bind pyridine and/or fluoride and, therefore, an application as chemosensors is possible. Photophysical measurements reveal a significant influence of the “binding partner”, which is shown in quenched absorption, “turned off” fluorescence, or both. Instead of introducing the kinetically stabilizing aryl substituent before polymerization occurs, Jäkle and co-workers have introduced a variety of different aryl substituents after the polycondensation via polymer-modification reactions (Scheme 6; left).[75]

![Scheme 6](image_url)

**Scheme 6.** Left: Synthesis of a fluorene-based polymer 23 and polymer-modification reactions with different aryl substituents to yield polymers 24 and 25. Right: Synthesis of polymers with varying numbers of thiophene units as \( \pi \) spacers.
Jäkle et al. have presented the synthesis of a fluorene-based molecule 23, which served as a starting material for the polymers 24 and 25 (Scheme 6). The synthesized polymers revealed significant stability towards air and moisture, except for the Mes-stabilized 24, which decomposed slowly in several weeks. This proves that for these systems a Tip group has to be introduced, in order to provide sufficient stability. Furthermore, they have synthesized polymers 26, 27, and 28, which consist of alternating supermesityl (2,4,6-tri-tert-butylbenzene) stabilized boron moieties and thiophene-based π spacer blocks (Scheme 6; right). The syntheses proceed smoothly at ambient temperature in a Stille coupling reaction procedure under microwave-irradiation. Finally, Jäkle et al. have prepared a copolymer 29, in which a supermesityl stabilized boron-containing moiety reacted with a fluorene-based building block (Scheme 7).

![Scheme 7. Synthesis of copolymer 29 by Jäkle et al.[46]](image)

2.4 Boron-containing macrocycles

As the mentioned representatives of cyclic tetrameric oligothiophenes with CH₂-bridges are known,[38,39] silicon-bridged,[78a] tin-bridged,[78b] and phosphorus-bridged tetra[2]porphyrins have been synthesized and well characterized by König et al. The incorporation of boron has been first performed by Siebert and co-workers. The incorporation may be complete (all meso-positions) or partially (two of four meso-positions). The interaction of the Lewis-basic sulfur and the Lewis-acidic boron leads to molecules with potentially interesting properties, the so-called tetraboratetraphiaporphyrinogens (33; Scheme 8).[79]
First evidence for the formation of 33 was found in the mass spectrum of a reaction mixture of a dialkylamino substituted dichloroborane 30 with 2,5-dilithiothiophene 31 (a); Scheme 8). However, the obtained yields were low. Yields have been improved by performing a reaction of 30 with a di(lithiothienyl)borane 32 (b); Scheme 8). Using single crystal X-ray structure analysis it was shown that the macrocyclic products reveal non-planarity of the thiophene groups and the boron atoms are twisted out of plane. This is not the case for their carbon- and silicon-bridged congeners.\textsuperscript{[38,78a]} Due to the twisted conformation, no ring current and, therefore, no delocalization of $\pi$ electrons is present. The B–C bond lengths (1.57 Å) are in the range of B–C single bonds.\textsuperscript{[80]} Presumably, the macrocycles are antiaromatic 16 $\pi$ electron species. Reduction should lead to dicationic 18 $\pi$ macrocyclic species, where the $\pi$ electrons are delocalized. Unfortunately, such compounds remained elusive because the performed reductions were not successful. The synthesis of the corresponding furyl derivatives were not successful as well.\textsuperscript{[81]} Due to the higher intrinsic instability of furyl derivatives of known thiophene-containing structures, syntheses are challenging. In diboratetrathiaporphyrinogens (34, 35), two meso carbon atoms are replaced by boron (Figure 7).

Figure 7. Diboratetrathiaporphyrinogens 34 and 35.
If these compounds are "formally" deprotonated twice, the empty p orbital of boron should provide the possibility of macrocyclic $\pi$ conjugation. The reaction occurs via dilithiation of 1,1-di(2-thienyl)ethane with a dialkylamino substituted dichloroborane or a duryl (2,3,5,6-tetramethylbenzene) substituted dichloroborane. Whereas the dialkylamino substituted products were stable against moisture and air, the duryl substituted products were unstable in the presence of water. The introduction of an aryl substituent at the boron atom, instead of a dialkylamino substituent, provides kinetic stabilization rather than electronic stabilization. Thus, a subsequent deprotonation of the molecule and the ability of the boron atom to contribute to macrocyclic conjugation should be improved. Currently, there is no example for a successful reduction (tetraboraporphyrinogen) or deprotonation (diboraporphyrinogen) known. Presumably, reducing the electronic stabilization through incorporation of kinetically stabilizing aryl substituents (high steric demand) will lead to macrocyclic molecules with stability towards air and moisture and possible formation of charged species, if suitable reagents are applied.

Recently, Jäkle and co-workers have synthesized different macrocycles (36-39) with differing structural motifs and sizes (Figure 8). Macrocycle 36 has been synthesized analogously to the mentioned linear congener 24. However, the reaction has been performed under high-dilution conditions to reduce the formation of cyclolinear oligomers. The resulting macrocycle 36 with six boron units proved to be an effective anion binding moiety (fluoride and cyanide) and the optical behavior differs significantly from its linear counterpart. Furthermore, they presented a macrocycle 37 with ambipolar nature. The replacement of fluorene spacers by phenylene units reduces the ring strain, compared to 36. Through incorporation of a nitrogen-containing building block, an electron-acceptor (boron group) and electron-donor (nitrogen group) are neighboring each other, which leads to improved conjugation in the system. Therefore, this macrocycle can be termed as a $\pi$ expanded borazine.
Figure 8. Four different macrocycles (36-39) synthesized by Jäkle and co-workers.

Redox processes of 37 revealed its ambipolar character and, furthermore, it shows strong blue fluorescence. The latter property is in contrast to its cyclolinear congener. Since the ring strain is a major drawback in macrocyclization reactions, due to the thermodynamically unfavored bonding situations in small macrocycles, building blocks with desirable structural parameters have to be employed. Based upon this, the fluorene groups in 36 have been partially replaced by carbazole units (38, 39; Figure 8). Substitution of carbazole in 3,6-position reduced the preferred angle dramatically compared to the 2,7-substituted fluorene.\textsuperscript{[85]} Therefore, it was possible to synthesize smaller boron-containing macrocycles with less ring strain and good stability towards air and moisture.

2.5 Outline of this thesis

In Section 3.1 a novel catalytic approach for the formation of B–C bonds via Si/B exchange is detailed. Usage of this route allowed the synthesis of different boron-containing (macro)molecules, including the first poly- and oligofurans.\textsuperscript{[45]}
In *Section 3.2* the extension of the catalytic route to synthesize symmetrically substituted monodisperse oligomers (monomers, dimers, and trimers), as well as mixed substituted congeners thereof is presented.\[^{86}\]

In *Section 3.3*, first mechanistic studies on the catalytic Si/B exchange are shown. The dependencies of the reaction rate on the total concentration of the starting materials, and on the concentration of the catalyst are presented. In addition, the rate-determining steps are discussed.\[^{87}\]

In *Section 3.4*, the synthesis of difunctionalized triarylboranes and the influence of the kinetically stabilizing aryl substituent as well as the electronic influence of the substituents at the 5,5´-positions on the structure in the solid-state are detailed.\[^{88}\]

In *Section 3.5*, the results on the synthesis of the first kinetically stabilized water- and air-stable tetraboratetrahiaoporphyrinogen are presented. Kinetic stabilization has been achieved by substitution with the sterically demanding Tip substituent. The cyclic compound reveals a markedly different optical behavior than its cyclolinear analogue.\[^{89}\]

In *Section 3.6*, a diphospha substituted ferrocene was reacted with dibromo-mesitylborane to give the first PBP-bridged [3]ferrocenophane. The product was thoroughly characterized and theoretical calculations were carried out. Electrochemical investigations reveal a reversible redox process, if the measurements are performed with increased scan rates.\[^{90}\]

2.6 References


[90] Lik, A., Kargin, D., Isenberg, S., Kelemen, Z., Pietschnig, R., Helten H. submitted for publication.
3. Results and Discussion

3.1 Catalytic B–C Coupling by Si/B Exchange: A Versatile Route to \(\pi\)-Conjugated Organoborane Molecules, Oligomers, and Polymers

**Abstract:** Extended conjugated organoboranes have emerged as an important class of organic–inorganic hybrid in materials science. Herein, a highly efficient, environmentally benign catalytic B–C bond formation method is presented that uses organosilicon compounds, dibromoboranes, and the metal-free organocatalyst \(\text{Me}_3\text{SiNTf}_2\). This Si/B exchange approach has been successfully applied to the synthesis of conjugated triarylboranes 4a-c, oligomers 8a,b, and polymers 8a,b'. Photophysical investigations, supported by TD-DFT calculations, reveal highly effective extension of \(\pi\)-conjugation in thienyl- and furylborane species; the latter were found to be highly emissive.

\(\pi\)-Conjugated organoboranes have emerged as an important class of organic–inorganic hybrid compounds in materials science.\(^{[1,2]}\) Intriguing optical and electronic features result from the incorporation of the vacant p orbital of boron into extended \(\pi\)-systems, thus often leading to highly emissive and/or electron-transporting (\(n\)-channel semiconducting) materials.\(^{[1,2]}\) This has enabled applications in organic electronic and optoelectronic devices (OFETs, OLEDs, photovoltaic cells)\(^{[1]}\) or as chemosensors for certain anions or amines.\(^{[1,3]}\) In recent years, donor–acceptor type conjugated oligomers and polymers that contain trivalent boron centers as the electron-deficient component alternating with electron-rich \(\pi\)-systems came into the focus of intense research activity.\(^{[1a,d,f,4-11]}\) Rational synthetic routes to extended cyclolinear species that feature B–C\(_{\text{aryl}}\) linkages follow one of the general polycondensation strategies a–e (Figure 1).\(^{[4]}\)

The types a and b utilize transition metal-catalyzed C–C coupling reactions of preformed organoborane (co)monomers.\(^{[5,10b,11]}\) For this, the boron center of the reactant borane has to be particularly kinetically stabilized to survive the cross-coupling conditions employed. Very
recently, Liu and Jäkle and co-workers applied for the first time an AB type procedure (type b, i.e. using a single monomer containing both complementary functional groups required for condensation) to synthesize a π-conjugated boron-containing (azaborine) polymer by Suzuki–Miyaura coupling methods.\cite{5e} Routes c–e, on the other hand, make use of B–C bond forming processes. Different organometallic metathesis reactions have been adopted for this purpose.\cite{6-8} The currently most sophisticated method available, which was developed by Jäkle and co-workers, uses distannyl compounds ($X = \text{SnMe}_3$) in combination with diboryl species (c) or boranes (d) with $Y = \text{Br}$.\cite{7} Polycondensations via such Sn/B exchange reactions generally proceed under mild conditions—often at room temperature or below—which is advantageous for the controlled construction of extended architectures.

![Figure 1](image_url) General strategies for the synthesis of arylborane oligomers and polymers ($\text{Ar, Ar'} = \text{arenes; R} = \text{organic substituent; X, Y} = \text{complementary leaving groups}$).

A major drawback of the use of organotin compounds, however, is their pronounced toxicity. This prompted us to seek for an appropriate, environmentally benign alternative. We considered organosilicon compounds as the ideal candidates. Compared to Sn/B exchange processes, analogous Si/B exchange reactions are significantly slower. The method is well-established for the introduction of $\text{BCl}_2$ or $\text{BBr}_2$ groups on arenes. For instance, $\text{PhSiMe}_3$ and $\text{BBr}_3$ react smoothly at room temperature to give PhBBR$_2$. However, subsequent replacement of the second bromine on boron by a phenyl group using
PhSiMe$_3$ to give Ph$_2$BBr requires harsh reaction conditions, i. e., heating of the neat reactants at 180 °C in a sealed ampule for 24 h.$^{[12]}$ Certainly, such conditions are not suitable for controlled polymerizations, but we speculated that such processes might be induced by a strong reagent under significantly milder conditions.

Herein, we demonstrate the use of Si/B exchange as a new route to conjugated organoborane molecules, oligomers, and polymers.$^{[13]}$ Our studies revealed that Si/B exchange condensations are effectively initiated at ambient temperature with the electrophilic silyl reagents Me$_3$SiOTf and, especially, Me$_3$SiNTf$_2$ (Tf = SO$_2$CF$_3$). The reactions can be performed in catalytic fashion, and, in some cases, AB type monomers can be generated and subsequently oligomerized through this approach in a controlled manner.

We started our investigations with the reaction between 2-(trimethylsilyl)thiophene (1a) and 2-(dibromoboryl)thiophene (2a) to give bromo-bis(thien-2-yl)borane (3a;$^{[5c]}$ Figure 2). In fact, 1a and 2a in CH$_2$Cl$_2$ showed some condensation at ambient temperature already without an initiator added. However, $^1$H NMR spectroscopic reaction monitoring showed that the conversion leveled off at an early stage and did not go to completion within 12 d (Figure 3, and Experimental Section, Figure S3). We anticipated that the reaction could be accelerated by adding a halogen-abstracting reagent. For this, we chose the electrophilic trimethylsilyl reagents Me$_3$SiOTf and Me$_3$SiNTf$_2$, and applied them in substoichiometric amounts (5 mol%). Me$_3$SiOTf, indeed, yielded significant rate acceleration with 95% conversion after 5 d. Finally, the stronger electrophilic species Me$_3$SiNTf$_2$ proved to be a highly efficient catalyst: complete and selective conversion to 3a was observed within 72 min. The volatile condensation by-product, Me$_3$SiBr, was easily removed with the solvent at reduced pressure. Subsequent derivatization of 3a with TipLi (Tip = 2,4,6-trisopropylphenyl) afforded dithienylborane 4a as an air- and moisture-stable product.
Figure 2. Catalytic B–C coupling and subsequent derivatization to give diarylboranes 4a-c.

Figure 3. Consumption of 1a (by $^1$H NMR spectroscopy) during the reaction with 2a to give 3a, without catalyst (red), with 5 mol% of Me$_3$SiOTf (blue), and with 5 mol% of Me$_3$SiNTf$_2$ (green).

Next, we aimed at the synthesis of a difurylborane. The general value of furan-based materials for organic electronics has been recognized only quite recently, although such materials show several favorable features and are in some respect complementary to their well-established thiophene congeners. Notably, different from most other components of organic electronic materials, furan rings are biodegradable, and they can be obtained from entirely renewable resources.$^{[14]}$ Furan-containing organoborane oligomers and polymers, however, are unknown, so far. We reacted 2-(trimethylsilyl)furan (1b) with 2-(dibromoboryl)furan (2b) in CH$_2$Cl$_2$ and in the presence of 5 mol% of Me$_3$SiNTf$_2$. This yielded full conversion to 3b within less than 2 h at ambient temperature. After derivatization with Mes*Li (Mes* = 2,4,6-tri-tert-butylphenyl) the triarylborane 4b was
formed, which was isolated via column chromatography. The bulky Mes* group was chosen in this case because this substituent was also effective in stabilizing a furylborane polymer (8b'; see below).

In order to investigate the substrate scope of our catalytic process, we additionally considered as reactants the less activated phenyl species 1c and 2c. Condensation thereof proceeded significantly slower and required an increased substrate concentration (4 M) and higher catalyst loadings (25 mol% Me3SiNTf2). Nevertheless, under these conditions the reaction was fully selective, showing 95 % conversion to 3c after 3 d at room temperature. In this case, the product obtained upon terminal reaction with Mes*Li, compound 4c, turned out to be air-sensitive. However, we succeeded in isolating it via double re-crystallization. The constitutions of 4a-c were unambiguously ascertained by multinuclear NMR spectroscopy and mass spectrometry (MS).

The solid state structures of 4b and 4c were determined by single crystal X-ray diffraction (Figure 4). The asymmetric unit of 4b contains two independent molecules with similar metrical data. In both 4b and 4c the aryl plane of the Mes* group is nearly perpendicular oriented to the respective BC3 plane [dihedral angles: 87.0° and 82.9° (4b) and 83.4° (4c)]. The furan rings of 4b adopt anti-conformation and are almost perfectly coplanar. The interplanar angle between these rings is only 4.9° or 7.8°, respectively, which is even smaller than that between the thiophene (Thi) rings in Mes*B(Thi)2 (19.0°).[5c] This parallels observations made for oligofurans, which also showed greater planarity than analogous thiophene oligomers.[14] The twist angle between the phenyl groups in 4c, on the other hand, amounts to 43.8°. The furan derivative 4b also shows the shortest B–C bond lengths: 1.550(6), 1.542(6), 1.515(6), and 1.542(6) Å (to the furan substituents). The B–Cphenyl bonds of 4c are significantly longer (1.579(3) and 1.581(3) Å), i.e. in the same range with the B–Cthienyl bonds of Mes*B(Thi)2 (1.589(6) and 1.568(4) Å).[5c]
Compounds 4a and 4b show similar UV–vis absorption characteristics in THF (Figure 5 and Table 1). Their spectra display a major band, which is, according to our TD-DFT calculations (B3LYP-D3(BJ)/def2-SV(P)), assigned to a $\pi\rightarrow\pi^*$ transition. While the HOMO\rightarrow LUMO excitation is of low probability, the strong absorption band observed arises from an excitation from the HOMO–2 to the LUMO in both cases (Figure 6). The HOMO–2 is a $\pi$ orbital basically delocalized over the hetaryl rings, and the LUMO shows significant contribution from the $p_\pi$ orbital on boron. Therefore, the excitation process is associated with intramolecular charge transfer (ICT) from the hetaryl groups to the boron center. When going from the thiophene (4a) to the furan system (4b\textsuperscript{Tip}), the energy levels of the relevant molecular orbitals are increased to approximately the same degree, which results in similar excitation energies. This correlates with the more electron-rich nature of furan vs. thiophene. The absorption band of compound 4c appears at significantly higher energy. While 4c is basically non-emissive, compound 4a shows weak fluorescence, and the difurylborane 4b shows intense fluorescence emission in solution.
Figure 5. UV–vis absorption spectra of 4a and 8a’ (left) and 4b and 8b’ (right) in THF.

Figure 6. Frontier orbital energy levels and plots of LUMO and HOMO–2 (isovalue: 0.04 a.u.) of 4a and 4b\textsuperscript{Tip}. 

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**Table 1.** Photophysical data\(^a\) for 4a-c, 8a,b, and 8a,b′, and GPC data\(^b\) for 8a,b and 8a,b′

<table>
<thead>
<tr>
<th>Compd.</th>
<th>(\lambda_{\text{abs, max}} / \text{nm})</th>
<th>(\lambda_{\text{em, max}} / \text{nm})</th>
<th>(\Phi_f / %)</th>
<th>(M_n)</th>
<th>(M_w)</th>
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<td>325</td>
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<td>3.1</td>
<td>–</td>
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<td>–</td>
</tr>
<tr>
<td>4b</td>
<td>315</td>
<td>345</td>
<td>24.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
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<td>271</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
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<td>1,550</td>
<td>1,760</td>
<td>4</td>
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<td>10</td>
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<tr>
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<td>5</td>
</tr>
<tr>
<td>8b′</td>
<td>411</td>
<td>426</td>
<td>71.1</td>
<td>3,260</td>
<td>5,220</td>
<td>9</td>
</tr>
</tbody>
</table>

\(^a\)In THF, except for 4c (in CH\(_2\)Cl\(_2\)). \(^b\)In THF, vs. polystyrene standards.

We then attempted polycondensation reactions using our catalytic Si/B exchange approach (Figure 7, Route A). Careful addition of BBr\(_3\) (1 equiv.) to disilyl compounds 5a,b in \(n\)-pentane at \(-78^\circ\text{C}\) and subsequent warming to 0 °C selectively yielded the AB monomers 6a and 6b, which were obtained in considerable purity after removing the volatiles in vacuo (see Appendix; Figures A1.28-33). In the case of 6a, minor by-products were removed by filtration at \(-40^\circ\text{C}\). Catalytic polycondensation of 6a and 6b was then performed in CH\(_2\)Cl\(_2\) at
ambient temperature. Subsequent substitution of the B–Br bonds of 7a with TipLi gave 8a, which was purified by precipitation with ethanol. As the product obtained upon treating 7b with TipLi was found to be unstable towards ethanol and water, we employed Mes*Li for derivatization in this case. After workup this yielded 8b, which proved to be perfectly stable in air and towards moisture. The NMR spectra of 8a,b are consistent with the proposed linear structures. The SiMe₃ end groups, detected by ¹H and ¹³C NMR spectroscopy, were partially cleaved off, giving rise to a new signal in the aromatic region. Analysis of 8a,b by gel permeation chromatography (GPC) revealed that these species were oligomeric and almost monodisperse, featuring on average 4 or 5 repeat units, respectively (Table 1). A plausible reason for this is the observed precipitation of 7a,b at some point during the polycondensation process, thus inhibiting further chain growth. The products 8a,b, obtained after incorporation of the Tip or Mes* side groups, however, were readily soluble in solvents such as CH₂Cl₂, THF, and even n-pentane. In view of this solubilizing effect of the Tip and Mes* substituents, we decided to explore polymerizations starting from 9a,b, in which the growing polymer chain, 10a,b, carries one of these groups on every second boron atom and should, therefore, show increased solubility (Route B). For the reaction of 9a, we also changed the solvent to the more polar o-dichlorobenzene (o-DCB), from which we anticipated further enhancement of the solubility of the macromolecular intermediate 10a. After 2 d, precipitation of 10a was observed, which was separated by centrifugation and decantation prior to derivatization with TipLi to 8a′. In an attempt to adopt analogous conditions for the synthesis of 8b′, the primary product 10b underwent decomposition during the centrifugation process. Therefore, the polymerization was repeated in CH₂Cl₂, which gave 8b′ after derivatization. The GPC analyses revealed that 8a,b′ were of significantly increased molecular weight.
In the UV–vis spectra of \(8a,b\) and \(8a,b'\) the \(\pi-\pi^*\) absorption band appears significantly red-shifted from that of their respective small molecule congeners, \(4a,b\) (Figure 5). The shift is in a similar range with that of a recently reported Mes*-substituted poly(thienylborane)[5f] with respect to Mes*B(Thi)\(_2\)[5c] and evidences highly effective extension of \(\pi\)-conjugation with chain elongation. The extended furylborane species \(8b\) and \(8b'\) showed intense blue fluorescence.

In conclusion, we have developed a highly efficient, environmentally benign catalytic B–C bond formation method and demonstrated its application for the synthesis of conjugated organoborane molecules, oligomers, and polymers. Thereby, we applied a catalytic B–C coupling\(^{[16]}\) process for a polycondensation for the first time. The use of organosilicon compounds with this method offers several advantages. Silyl groups are chemically robust and can be introduced into organic substrates by many facile and general methods. The reactants used are less toxic than those employed in previous routes. Notably, the condensation by-product, Me\(_3\)SiBr, is less harmful and
easily separated. As the formation of B–C bonds is fundamental for the construction of organoboron compounds in general, and the latest advances have shown that the significance of organoboron compounds extends well beyond their role in Suzuki–Miyaura cross-coupling reactions, we believe that our new method will be useful in various fields of chemical research.

3.1.1 Experimental Section

General procedures. All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques or in an MBraun glovebox. Solvents (dichloromethane, n-pentane, diethyl ether, toluene, and tetrahydrofuran) were dried and degassed by means of a MBraun SPS-800 solvent purification system. o-Dichlorobenzene was dried over CaH₂ and distilled prior to use. Deuterated solvents for NMR spectroscopy were dried and degassed at reflux over Na (C₆D₆) or CaH₂ (CDCl₃ and CD₂Cl₂) and freshly distilled prior to use. Solvents for aqueous work-up (dichloromethane, ethanol, n-hexane, n-pentane), 2-bromothiophene, tribromoborane, lithium bis(trifluoromethylsulfonyl)imide, bromobenzene, sulfuric acid, and magnesium turnings were purchased from commercial sources and used as received. Solutions of n-butyllithium (1.6 M in hexane and 2.5 M in hexane, respectively) and t-butyllithium (1.7 M in pentane) were purchased from Sigma Aldrich and used as received as well. Chlorotrimethylsilane, 2-bromo-1,3,5-triisopropylbenzene, thiophene and furan were commercially purchased and freshly distilled prior to use. 2-Bromofuran,[17] 2,5-dibromofuran,[17] trimethylsilyl bis(trifluoromethylsulfonyl)imide,[18] 2,4,6-triisopropylphenyllithium,[19] 2-bromo-1,3,5-tri-tert-butylbenzene[20] and 2,4,6-tri-tert-butylphenyllithium[5c] were prepared according to methods described in the literature. NMR spectra were recorded at 25 °C on a Bruker Avance II-400 spectrometer or on a Bruker Avance III HD spectrometer operating at 400 MHz. Chemical shifts were referenced to residual protic impurities in the solvent (¹H) or the deuterio solvent itself (¹³C) and reported relative to external SiMe₄ (¹H, ¹³C) or BF₃·OEt₂ (¹¹B) standards. Mass spectra were obtained with the use of a Finnigan MAT95 spectrometer employing electron ionization (EI) using a 70 eV electron impact ionization source or secondary ionization (SIMS).
Elemental analysis was performed with a CHN-O-Rapid VarioEL by Heraeus. UV-vis spectra were obtained using a Jasco V-630 spectrophotometer. Fluorescence spectra were obtained with a Jasco FP-6500 spectrofluorometer. Fluorescence quantum yields were determined against commercially available standards (4a, 4b and 4c against diphenylanthracene (DPA), 8a and 8b against perylene). Melting points (uncorrected) were obtained using a SMP3 melting point apparatus by Stuart in 0.5 mm (o.d.) glass capillaries, which were sealed under argon. GPC chromatograms were recorded on an Agilent 1100 Series, equipped with two SDV linear N columns of 8x300 mm and 8x600 mm measures and 5 mm pore size at 30 °C against a polystyrene standard. Detection was carried out via UV signal (λ = 250 nm) and refractive index (RI), respectively.

**Synthesis of 1a.** To a solution of 2-bromothiophene (8.15 g, 50 mmol) in n-pentane (120 mL) was added n-butyllithium (2.5 M, 20 mL, 50 mmol) via dropping funnel at 0 °C. After the resulting mixture had been stirred for 3 h at ambient temperature, chlorotrimethylsilane (5.40 g, 50 mmol) was slowly added, and the mixture was stirred over night. The colorless precipitate formed was removed by filtration. All volatiles were removed under reduced pressure (20 mbar, r.t.). The crude product was further purified by distillation to yield 1a\(^{[21]}\) as a colorless liquid (b.p. 65 °C/20 mbar). Yield: 5.20 g (33.3 mmol, 67 %); \(^1\)H NMR (400 MHz, CDCl\(_3\), δ): 7.61 (dd, \(^3\)J = 4.8 Hz, \(^4\)J = 0.8 Hz, 1H, Th-\(\text{H}_1\)), 7.28 (dd, \(^3\)J = 3.5 Hz, \(^4\)J = 0.8 Hz, 1H, Th-\(\text{H}_2\)), 7.21 (dd, \(^3\)J = 3.5, 4.8 Hz, 1H, Th-\(\text{H}_3\)), 0.35 (s, 9H, Si(CH\(_3\))\(_3\)).

**Synthesis of 1b.** To a solution of n-butyllithium (2.5 M, 44 mL, 110 mmol) in diethyl ether (300 mL) was added 2-bromofuran (14.71 g, 100 mmol) dropwise at 0 °C, and the mixture was stirred for 20 min at that temperature, followed by 3 h at ambient temperature. Chlorotrimethylsilane (11.95 g, 110 mmol) was slowly added at 0 °C and the resulting mixture was stirred over night. The colorless precipitate was removed by filtration. All volatiles were removed under reduced pressure (20 mbar, r.t.). The crude product was further purified by distillation to yield 1b\(^{[22]}\) as a colorless liquid (b.p. 55 °C/20
mbar). Yield: 7.11 g (50.7 mmol, 51 %); $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.66 (dd, $^3$J = 1.7 Hz, $^4$J = 0.6 Hz, 1H, Fur-H$_2$), 6.64 (dd, $^3$J = 3.2 Hz, $^4$J = 0.6 Hz, 1H, Fur-H$_2$), 6.39 (dd, $^3$J = 3.2, 1.7 Hz, 1H, Fur-H$_2$), 0.28 (s, 9H, Si(CH$_3$)$_3$).

**Synthesis of 1c.** To a solution of n-butyllithium (2.5 M, 40 mL, 60.0 mmol) in diethyl ether (80 mL) was added bromobenzene (9.42 g, 60.0 mmol) dropwise at 0 °C, and the mixture was stirred for 30 min at that temperature. Chlorotrimethylsilane (6.50 g, 60.0 mmol) was slowly added at 0 °C and the resulting mixture was stirred over night. The colorless precipitate was removed by filtration. All volatiles were removed under reduced pressure (20 mbar, r.t.). The crude product was further purified by distillation to yield 1d$^{[23]}$ as a colorless liquid (b.p. 60 °C/20 mbar). Yield: 6.20 g (41.3 mmol, 69 %); $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.55–7.57 (m, 2H, Ph-H$_2$), 7.37–7.39 (m, 3H, Ph-H$_3$), 0.30 (s, 9H, Si(CH$_3$)$_3$).

**Synthesis of 2a.** To a solution of tribromoborane (1.84 g, 7.35 mmol) in dichloromethane (10 mL) was slowly added 1a (1.09 g, 7.00 mmol) at 0 °C. After the mixture had been stirred over night at ambient temperature, all volatiles were removed in vacuo, and the crude product was distilled under reduced pressure, which gave 2a$^{[5c]}$ as a pale yellow liquid (b.p. 91 °C/15 mbar). Yield: 1.35 g (5.31 mmol, 76 %); $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.11 (dd, $^3$J = 4.7 Hz, $^4$J = 1.0 Hz, 1H, Th-H$_2$), 8.08 (dd, $^3$J = 3.7 Hz, $^4$J = 1.0 Hz, 1H, Th-H$_2$), 7.36 (dd, $^3$J = 3.7, 4.7 Hz, 1H, Th-H$_2$); $^{11}$B[${^1}$H] NMR (128 MHz, CDCl$_3$, $\delta$): = 47.7 (s).

**Synthesis of 2c.** To a solution of tribromoborane (5.26 g, 21.0 mmol) in dichloromethane (20 mL) was slowly added 1d (3.06 g, 20.0 mmol) at 0 °C. After the mixture had been stirred over night at ambient temperature, all volatiles were removed in vacuo, and the crude product was distilled under reduced pressure, which gave 2c$^{[12]}$ as a colorless solid (b.p. 85 °C/15 mbar). Yield: 3.18 g (12.8 mmol, 76 %); $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.24 (d, $J$ = 7.53 Hz, 2H, Ph-H$_2$), 7.69
(m, 1H, Ph-H), 7.49 (m, 2H, Ph-H); \(^{11}\)B(\(^{1}\)H) NMR (128 MHz, CDCl\(_3\), \(\delta\)): = 57.1 (s).

**Synthesis of 4a.** To a solution of 1a (156 mg, 1.00 mmol) and TMS-N\(_2\)F\(_2\) (17.6 mg, 0.05 mmol, 5 mol%) in dichloromethane (0.5 mL) was added a solution of 2a (256 mg, 1.01 mmol) in dichloromethane (0.5 mL) at ambient temperature, and the mixture was stirred overnight. After the reaction was complete (monitoring by \(^{1}\)H and \(^{11}\)B(\(^{1}\)H) NMR spectroscopy (1.2 h), 3a: \(^{1}\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 8.22 (dd, \(3J = 3.8\) Hz, \(4J = 1.0\) Hz, 2H, Th-H), 8.02 (dd, \(3J = 4.8\) Hz, \(4J = 1.0\) Hz, 2H, Th-H), 7.38 (dd, \(3J = 3.8\), \(4J = 4.8\) Hz, 2H, Th-H); \(^{11}\)B(\(^{1}\)H) NMR (128 MHz, CDCl\(_3\), \(\delta\)): 49.7 (s)), the solvent was removed in vacuo, and the solid residue was re-dispersed in toluene (3 mL). A solution of TipLi (210 mg, 1.00 mmol) in toluene (3 mL) was added dropwise at ambient temperature, and the mixture was stirred overnight. The resulting suspension was diluted with \(n\)-pentane (10 mL) and quenched by adding water (80 mL). The organic phase was washed with brine (2×80 mL), dried over MgSO\(_4\), and the solvent was removed in vacuo. The crude product was recrystallized from \(n\)-hexane at –30 °C, which afforded 4a as a pale colorless crystalline solid (m.p. 141 °C). Yield: 261 mg (0.69 mmol, 69 %); \(^{1}\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 7.93 (dd, \(3J = 4.8\) Hz, \(4J = 1.0\) Hz, 2H, Th-H), 7.89 (dd, \(3J = 3.5\) Hz, \(4J = 1.0\) Hz, 2H, Th-H), 7.31 (dd, \(3J = 3.5\), \(4J = 4.8\) Hz, 2H, Th-H), 7.06 (s, 2H, Tip-H), 3.00 (sept, \(3J = 7.0\) Hz, 1H, \(p-i\)-Pr-CH), 2.56 (sept, \(3J = 6.8\) Hz, 2H, \(o-i\)-Pr-CH), 1.37 (d, \(3J = 7.0\) Hz, 6H, \(p-i\)-Pr-CH\(_3\)), 1.09 (d, \(3J = 6.8\) Hz, 12H, \(o-i\)-Pr-CH\(_3\)), \(^{13}\)C(\(^{1}\)H) NMR (101 MHz, CDCl\(_3\), \(\delta\)): 149.6 (Tip-C-\(o\)-i-Pr), 148.6 (Tip-C-\(p\)-i-Pr), 145.1 (br, Th-C-B), 142.1 (Th-CH), 139.2 (br, Tip-C-B), 137.2 (Th-CH), 128.9 (Th-CH), 120.0 (Tip-CH), 35.2 (\(o-i\)-Pr-CH), 34.2 (\(p-i\)-Pr-CH), 24.2 (\(o-i\)-Pr-CH\(_3\)), 24.1 (\(p-i\)-Pr-CH\(_3\)); MS (EI, 70 eV): m/z (%) = 380.2 (M\(^{+}\), 80), 296.2 ([BThTip]\(^{+}\), 39), 253.2 ([BTh(Ph-(i-Pr))\(^{2}\)]\(^{+}\), 211.2 ([BTh(Ph-(i-Pr))]\(^{+}\), 55), 177.1 ([B(Th)]\(^{2}\), 21); elem. anal. calcd (%) for C\(_{23}\)H\(_{29}\)BS\(_2\): C 72.62, H 7.68; found: C 72.77, H 7.71; UV–vis (THF): \(\lambda_{\text{abs,max}} = 263\) (\(\varepsilon = 7254\) L mol\(^{-1}\) cm\(^{-1}\)), 275 (\(\varepsilon = 8643\) L mol\(^{-1}\) cm\(^{-1}\)), 325 nm (\(\varepsilon = 24227\) L mol\(^{-1}\) cm\(^{-1}\)); fluorescence (THF): \(\lambda_{\text{em,max}} (\lambda_{\text{ex}} = 325\) nm\) = 410 nm (\(\Phi = 3.1\) %).
Synthesis of 4b. To a solution of tribromoborane (626.3 mg, 2.50 mmol) in dichloromethane (2 mL) was added 1b (350.6 mg, 2.50 mmol) at 0 °C and stirred for 2 h. The generation of dibromo(fur-2-yl)borane 2b was evidenced by $^{11}$B$\{^1$H$\}$ NMR spectroscopy ($\delta = 45.0$). Then, a solution of 1b (350.6 mg, 2.50 mmol) and TMSNTf$_2$ (44.2 mg, 0.13 mmol, 5 mol%) in dichloromethane (1 mL) was added. After the reaction was complete (monitoring by $^1$H and $^{11}$B$\{^1$H$\}$ NMR spectroscopy (2 h), 3b: $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.94 (dd, $^3$J = 1.0 Hz, $^4$J = 0.5 Hz, 2H, Fur-H), 7.82 (dd, $^3$J = 3.0 Hz, $^4$J = 0.5 Hz, 2H, Fur-H), 6.64 (dd, $^3$J = 1.0, 3.0 Hz, 2H, Fur-H); $^{11}$B$\{^1$H$\}$ NMR (128 MHz, CDCl$_3$, $\delta$): 42.2 (s)), the solvent was removed in vacuo, and the solid residue was re-dispersed in toluene (8 mL). Mes*Li (1.01 g, 4.00 mmol) in toluene (8 mL) was added, and the mixture was stirred for 48 h at ambient temperature. The resulting suspension was diluted with n-pentane (20 mL) and quenched by adding water (100 mL). The organic phase was washed with brine (2x 100 mL), dried over MgSO$_4$, and the solvent was removed in vacuo. The brownish, solid crude product was subjected to column chromatography (silica; n-hexane) to give 4b as a colorless solid (m.p. 103 °C). Yield: 367.3 mg (0.94 mmol, 38 %); $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.79 (dd, $^3$J = 1.6, $^4$J = 0.6 Hz, 2H, Fur-H), 7.45 (s, 2H, Mes*H), 7.29 (br, 2H, Fur-H), 6.52 (dd, $^3$J = 3.4, $^4$J = 1.6 Hz, 2H, Fur-H), 1.39 (s, 9H, $p$-t-Bu), 1.18 (s, 18H, $o$-t-Bu); $^{11}$B$\{^1$H$\}$ NMR (128 MHz, CDCl$_3$, $\delta$): 47.7 (s); $^{13}$C$\{^1$H$\}$ NMR (101 MHz, CDCl$_3$, $\delta$): 164.0 (Fur-C-B), 152.0 (Mes*-C- o-t-Bu), 148.4 (Mes*-C- p-t-Bu), 148.0 (Fur-CH), 132.3 (Mes*-C-B), 127.9 (Fur-CH), 122.0 (Mes*-CH), 111.5 (Fur-CH), 38.2 (o-t-Bu-C-CH$_3$), 34.7 (p-t-Bu-C-CH$_3$), 34.1 (o-t-Bu-CH$_3$), 31.4 (p-t-Bu-CH$_3$); MS (EI, 70 eV): m/z (%) = 390.5 (M$^+$, 81), 257.4 (BMes*); HRMS calcd for C$_{26}$H$_{35}$BO$_2$: 390.2740, found: 390.2727, UV–vis (THF): $\lambda_{abs,max} = 315$ ($\varepsilon = 25676$ L mol$^{-1}$ cm$^{-1}$); fluorescence (THF): $\lambda_{em,max} (\lambda_{ex} = 308$ nm) = 400 nm ($\phi = 24.0$ %).

Synthesis of 4c. To a solution of 1c (150 mg, 1.00 mmol) and TMSNTf$_2$ (88.3 mg, 0.25 mmol, 25 mol%) in dichloromethane (0.25 mL) was added a solution of 2c (247 mg, 1.00 mmol) in dichloromethane (0.10 mL) at ambient temperature, and the mixture was stirred for 3 d. The
conversion of the reaction was 95 % (monitoring by $^1$H and $^{11}$B{$^1$H}) NMR spectroscopy, 3c: $^1$H NMR (400 MHz, CDCl$_3$, δ): 7.99 (m, 4H, Ph-H), 7.60-7.64 (m, 2H, Ph-H), 7.48-7.52 (m, 4H, Ph-H); $^{11}$B{$^1$H}) NMR (128 MHz, CDCl$_3$, δ): 66.5 (s)). The solvent was removed in vacuo, and the solid residue was re-dispersed in toluene (2.5 mL). A suspension of Mes$^*$Li (328 mg, 1.3 mmol) in toluene (2.5 mL) was added dropwise at ambient temperature, and the mixture was stirred over night. The resulting suspension was filtered, washed two times with toluene (4 mL) and the combined organic phases evaporated to dryness. The crude product was recrystallized twice from n-hexane at –40 °C, which afforded 4c as a colorless crystalline solid (m.p. 153°C). Yield: 143 mg (0.35 mmol, 35 %); $^1$H NMR (400 MHz, CDCl$_3$, δ): 7.90 (dd, $^3$J = 6.5, $^4$J = 1.5 Hz, 4H, Ph-H), 7.38-7.47 (m, 6H, Ph-H), 7.45 (s, 2H, Mes$^*$-H), 1.42 (s, 9H, p-tBu-CH$_3$), 1.09 (s, 18H, o-tBu-C$_3$H$_3$); $^{11}$B{$^1$H}) NMR (128 MHz, CDCl$_3$, δ): 67.6 (s); $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$, δ): 151.5 (Mes$^*$-C-o-t-Bu), 148.6 (Mes$^*$-C-p-t-Bu), 143.5 (br, Ph-C–B), 139.0 (Ph-CH), 136.8 (br, Mes$^*$-C–B), 130.5 (Ph-CH), 127.3 (Ph-CH), 121.9 (Mes$^*$-CH), 38.1 (o-t-Bu-C(CH$_3$)$_3$), 34.8 (p-t-Bu-C(CH$_3$)$_3$), 34.8 (p-t-Bu-C(CH$_3$)$_3$), 31.5 (o-t-Bu-C(CH$_3$)$_3$); MS (EI, 70 eV): m/z (%) = 410.2 (M$^+$, 29), 231.2 ([BH$_2$(Ph-i-Pr-(t-Bu)$_2$])$^+$, 100); HRMS: calcd for C$_{30}$H$_{39}$B: 410.3139, found: 410.3148; UV–vis (CH$_2$Cl$_2$): $\lambda_{\text{abs,max}}$ = 251 (ε = 17383 L mol$^{-1}$ cm$^{-1}$), 271 (ε = 19437 L mol$^{-1}$ cm$^{-1}$); fluorescence (CH$_2$Cl$_2$): non-emissive.

**Synthesis of 5a.** Dilithiation of thiophene was carried out according to a literature procedure.$^{[24]}$ To a solution of 2,5-dilithiothiophene was added chlorotrimethylsilane (2.97 g, 27.3 mmol, 2.2 equiv.) at 0 °C. After the mixture was stirred overnight, it was washed with brine (3x150 mL), dried over MgSO$_4$, and the solvent was removed via rotary evaporator. The resulting orange oil was distilled under reduced pressure to give 5a$^{[25]}$ as a colorless liquid (b.p. 92 °C/20 mbar), which crystallized upon cooling in a refrigerator (5 °C). Yield: 2.28 g (9.98 mmol, 80 %); $^1$H NMR (400 MHz, CDCl$_3$, δ): 7.34 (s, 2H, Th-H), 0.34 (s, 18H, Si(CH$_3$)$_3$).
Synthesis of 5b. To a solution of 2,5-dibromofuran (6.78 g, 30 mmol) in THF (120 mL) was added n-butyllithium (2.5 M, 25.2 mL, 63 mmol) at −50 °C. After the mixture had been stirred for 30 min at 0 °C, chlorotrimethylsilane (6.84 g, 63 mmol) was added, and the resulting mixture was first stirred for another 3 h at −50 °C, and then over night at ambient temperature. The organic phase was washed with brine (3x200 mL), dried over MgSO₄, and the solvent was removed in vacuo. The crude product was further purified by distillation to yield 5b[26] as a colorless liquid (b.p. 84 °C/20 mbar). Yield: 4.52 g (21.3 mmol, 71 %); ¹H NMR (400 MHz, CDCl₃, δ): 6.61 (s, 2H, Fur-H), 0.27 (s, 18H, Si(CH₃)₃).

Synthesis of 8a. To a solution of 5a (457 mg, 2.00 mmol) in n-pentane (4 mL) was added BBr₃ (489 mg, 1.95 mmol) at −78 °C, and the resulting suspension was stirred for 2 h maintaining −78 °C. Then, the mixture was warmed to 0 °C and was stirred until a solution was formed (15 min). All volatiles were removed in vacuo at 0 °C. Addition of n-pentane (5 mL), storage over night at −30 °C, filtration at −40 °C, and removing the volatiles under reduced pressure yielded 6a as a yellow oil (843 mg, 85 %). ¹H NMR (400 MHz, CDCl₃, δ): 7.90 (d, ³J = 3.5 Hz, 1H, Th-H), 7.02 (d, ³J = 3.5 Hz, 1H, Th-H), 0.11 (s, 9H, Si(CH₃)₃); ¹¹B{¹H} NMR (128 MHz, CDCl₃): 47.6 (s). Subsequently, 6a was dissolved in dichloromethane (3 mL) and TMSNTf₂ (35.3 mg, 0.10 mmol, 5 mol%) was added. After 3 d, the solvent was removed in vacuo, and the solid residue was re-dispersed in toluene (9 mL). TipLi (526 mg, 2.50 mmol) toluene (9 mL) was added to the suspension. The mixture was stirred for 3 d and quenched by adding water (50 mL). After aqueous work-up, 8a was obtained as a pale yellow solid by precipitation in n-pentane/ethanol. Yield: 254 mg (0.17 mmol, 35 %), ¹H NMR (400 MHz, CDCl₃, δ): 7.95–7.87 (br, 8H, Th-H), 7.42 (d, br, 1H, from partial cleavage of the silyl end group), 6.99 (br, 10H, Tip-H), 2.93 (br, 5H, p-i-Pr-CH₂), 2.50 (br, 9H o-i-Pr-CH₂), 1.31 (br, 30H p-i-Pr-CH₃), 1.03 (br, 54H, o-i-Pr-CH₃), 0.36 (s, 9H, Si(CH₃)₃ end group); ¹¹B{¹H} NMR (128 MHz, CDCl₃): no signal detectable; ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 156.9 (br, Th-C), 149.4 (Tip-C-o-i-Pr), 148.6 (Tip-C-p-i-Pr), 143.3, 142.3 (Th-C), 141.9, 139.1 (br, Tip-C-B), 135.6 (Th-C), 122.1, 120.1 (Tip-C-H), 35.8 (o-i-Pr-CH₂), 34.2 (p-i-Pr-CH₂), 24.1 (i-Pr-
\( \text{C}_3\text{H}_3\), \(-0.1\) (Si(CH\(_3\))\(_3\)); \(^{29}\text{Si}\{^1\text{H}\}\) NMR (79.5 MHz, CDCl\(_3\), \(\delta\)): \(-6.02\); UV–vis (THF): \(\lambda_{\text{abs,max}} = 409\ \text{nm} \ (\varepsilon = 160180\ \text{L}\ \text{mol}^{-1}\ \text{cm}^{-1})\); fluorescence (THF): \(\lambda_{\text{em,max}}\ (\lambda_{\text{ex}} = 411\ \text{nm}) = 421\ \text{nm} \ (\phi = 0.6\ %)\).

**Synthesis of 8b.** To a solution of 5b (425 mg, 2.00 mmol) in \(n\)-pentane (2 mL) was added BBr\(_3\) (489 mg, 1.95 mmol) at \(-78\ °C\) and the mixture was stirred for 2 h maintaining \(-78\ °C\). Then, the resulting suspension was warmed to 0 °C, and was stirred until a solution was formed (15 min). All volatiles were removed in vacuo at 0 °C, which yielded 6b as a brownish solid. \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\), \(\delta\)): 7.67 (d, \(^3\text{J} = 3.6\ \text{Hz}, 1\text{H, Fur-}H\)), 6.79 (d, \(^3\text{J} = 3.6\ \text{Hz}, 1\text{H, Fur-}H\)), 0.35 (s, 9H, Si(CH\(_3\))\(_3\)); \(^{11}\text{B}\{^1\text{H}\}\) NMR (128 MHz, CDCl\(_3\)): 45.0 (s). Subsequently, 6b was dissolved in dichloromethane (2 mL) and TMSNTf\(_2\) (35 mg, 0.1 mmol, 5 mol\%) was added at ambient temperature. After 3 d, the solvent was removed in vacuo, and the solid residue was re-dispersed in toluene (6 mL). Mes*Li (631 mg, 2.50 mmol) in toluene (6 mL) was added to the suspension. The mixture was stirred for 3 d and quenched by adding water (30 mL). After aqueous work-up, 8b was further purified by precipitation from \(n\)-pentane/ethanol to give 8b as a brown solid. Yield: 96 mg (0.05 mmol, 13 %) \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\), \(\delta\)): 7.36 (br, Mes*H), 7.25 (s, Fur-H, from partial cleavage of the silyl end group), 6.95 (br, Fur-H), 1.35–1.32 (br, \(p-t\)-Bu-CH\(_3\)), 1.05 (br, \(o-t\)-Bu-CH\(_3\)), 0.20 (br, Si(CH\(_3\))\(_3\)); \(^{13}\text{C}\{^1\text{H}\}\) NMR (101 MHz, CDCl\(_3\), \(\delta\)): 168.8 (br, Fur-C-B), 152.1 (Mes*–C–(CH\(_3\))\(_3\)), 149.9 (Fur-C), 148.4, 132.4, 127.6 (br, Mes*-C-B), 121.6 (Mes*-C-H), 119.5 (Fur-C), 38.2, 34.3 (\(o-t\)-Bu-C-CH\(_3\)), 31.5 (\(p-t\)-Bu-C-CH\(_3\)), 1.7 (Si(CH\(_3\))\(_3\)); \(^{29}\text{Si}\{^1\text{H}\}\) NMR (79.5 MHz, CDCl\(_3\), \(\delta\)): no signal detectable; UV–vis (THF): \(\lambda_{\text{abs,max}} = 407\ \text{nm} \ (\varepsilon = 73340\ \text{L}\ \text{mol}^{-1}\ \text{cm}^{-1})\); fluorescence (THF): \(\lambda_{\text{em,max}}\ (\lambda_{\text{ex}} = 412\ \text{nm}) = 422\ \text{nm} \ (\phi = 70.3\ %)\).

**Synthesis of 9a.** To a solution of 4a (380 mg, 1.00 mmol) dissolved in Et\(_2\)O (7.5 mL) was added \(t\)-butyllithium (1.7 M, 1.24 mL, 2.1 mmol) at \(-78\ °C\), and the reaction mixture was stirred at this temperature for 4 h. After complete lithiation, chlorotrimethylsilane (240 mg, 2.2 mmol) was added. The cooling bath was removed, and the reaction mixture
was stirred over night at room temperature. The colorless precipitate was removed by filtration and extracted with Et$_2$O (5mL). All volatiles were removed in vacuo, and the obtained dark violet solid was purified by recrystallization from $n$-hexane/CH$_2$Cl$_2$. Compound 9a was obtained as a colorless crystalline solid (m.p. 191 °C). Yield: 443 mg (0.84 mmol, 84 %); $^1$H-NMR (400 MHz, CDCl$_3$, $\delta$): 7.88 (d, $^3J$ = 3.5 Hz, 2H, Th-H), 7.44 (d, $^3J$ = 3.5 Hz, 2H, Th-H), 7.05 (s, 2H, Tip-H), 3.01 (sept, $^3J$ = 7.0 Hz, 1H, p-i-Pr-H), 2.50 (sept, $^3J$ = 6.8 Hz, 2H, o-i-Pr-H), 1.39 (d, $^3J$ = 7.0 Hz, 6H, p-i-Pr-CH$_3$), 1.10 (d, $^3J$ = 6.8 Hz, 12H, o-i-Pr-CH$_3$), 0.42 (s, 18H, Si(CH$_3$)$_3$). $^{11}$B$[^1$H$]$ NMR (128 MHz, CDCl$_3$, $\delta$): 55.6 (s); $^{13}$C$[^1$H$]$ NMR (101 MHz, CDCl$_3$, $\delta$): 154.5 (Th-C-Si(CH$_3$)$_3$), 151.0 (br, Th-C–B), 149.9 (Tip-C-o-i-Pr), 148.6 (Tip-C–p-i-Pr), 143.3 (Th-CH), 140.0 (br, Tip-C–B), 135.7 (Th-CH), 120.2 (Tip-CH), 35.5 (o-i-Pr-CH), 34.5 (p-i-Pr-CH), 24.6 (o-i-Pr-CH$_3$), 24.5 (p-i-Pr-CH$_3$), 0.3 (Si(CH$_3$)$_3$); MS (EI, 70 eV): m/z (%) = 524.4 ([M$^+$, 22], 368.4 ([BThSiMe$_3$Tip, 28]$^+$, 294.3 ([BTh(Ph-(i-Pr)$_2$), 100]$^+$, 147.2 ([BTh(Ph-(i-Pr)$_2$)]$^+$, 27); elem. anal. calcld (%) for C$_{28}$H$_{45}$BS$_2$Si$_2$: C 66.37, H 8.64, found: C 65.49, H 8.81, UV–vis (THF): $\lambda_{abs,max} = 296$ nm ($\varepsilon = 10334$ L mol$^{-1}$ cm$^{-1}$), 341 nm ($\varepsilon = 35233$ L mol$^{-1}$ cm$^{-1}$); fluorescence (THF): non- emissive.

**Synthesis of 9b.** To a solution of 4b (390.4 mg, 1.00 mmol) dissolved in Et$_2$O (7.5 mL) was added tert-butyllithium (1.7 M, 1.21 mL, 2.05 mmol) at −78 °C, and the reaction mixture was stirred at this temperature for 2 h, followed by 30 min at 0 °C. After complete lithiation, chlorotrimethylsilane (222.5 mg, 2.05 mmol) was added at −78 °C. The cooling bath was removed, and the reaction mixture was stirred over night at room temperature. The colorless precipitate was removed by filtration. All volatiles were removed in vacuo and the brownish crude product was subjected to column chromatography (silica; $n$-hexane) to give 9b as a colorless solid (m.p. 112 °C). Yield: 334.1 mg (0.62 mmol, 62 %); $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.41 (s, 2H, Mes$^*$H), 7.21 (br, 2H, Fur-H), 6.72 (d, $^3J$ = 3.3 Hz, 2H, Fur-H), 1.40 (s, 9H p-t-Bu-CH$_3$), 1.15 (s, 18H, o-t-Bu-CH$_3$), 0.29 (s, 18H, Si(CH$_3$)$_3$); $^{11}$B$[^1$H$]$ NMR (128 MHz, CDCl$_3$, $\delta$): 47.8 (s); $^{13}$C$[^1$H$]$ NMR (101 MHz, CDCl$_3$, $\delta$): 168.3 (Fur-C-B), 166.5 (Fur-C-Si), 152.1 (Mes$^*$$\equiv$$-$C–o-t-Bu), 148.0 (Mes$^*$$\equiv$$-$C–p-t-Bu), 133.5 (Mes$^*$$\equiv$C-B), 127.4 (Fur-CH), 121.3 (Mes$^*$$\equiv$-CH)
120.7 (Fur-CH), 38.1 (o-t-Bu-C-CH₃), 34.7 (p-t-Bu-C-CH₃), -1.6 (Si(CH₃)₃); MS (EI, 70 eV): m/z (%) = 534.6 ([M⁺, 81], 379.5 ([BFurSiMe₃ Ph-(t-Bu)2(i-Pr)], 53)⁺, 231.4 ([BH₂(Ph-i-Pr-(t-Bu)₂), 74]⁺, 147.2 ([BTh(Ph-(i-Pr)₂])¹⁺, 81); HRMS (EI, 70 eV): calcd for C₃₁H₅₁BO₂Si₂: 543.3517, found: 543.3518; UV–vis (THF): λₚₑₑₚ₃₃₁ nm (ε = 26195 L mol⁻¹ cm⁻¹); fluorescence (THF): non-emissive.

Synthesis of 8a´. To a suspension of 9a (262 mg, 0.5 mmol) in n-pentane (5 mL) was added BBr₃ (126 mg, 0.5 mmol) at −78 °C, and the reaction mixture was stirred for 30 min maintaining −78 °C. The mixture was warmed to room temperature and stirred for another 30 min. Dichloromethane (2 mL) was added and the resulting clear solution was stirred for 1 h. All volatiles were removed in vacuo and the obtained yellow solid was dissolved in o-dichlorobenzene (1 mL). After addition of TMS-NTf₂ (8.8 mg, 0.025 mmol, 5 mol%) the reaction was stirred for 3 d at ambient temperature. Afterwards the solvent was removed in vacuo at 60 °C, and the obtained solid was redispersed in toluene (1.5 mL). TipLi (1.25 equiv.) was dissolved in toluene (1.5 mL) and added dropwise to the suspension. The mixture was stirred for 3 d and quenched by adding water. After aqueous work-up the compound was purified by precipitation in n-pentane/ethanol. Yield: 182 mg (0.34 mmol, 68 %); UV-vis (THF): λₚₑₑₚ₃₃₁ nm (ε = 299291 L mol⁻¹ cm⁻¹); fluorescence (THF): λₑₑₑₚ₃₅₅ nm (λₑₑₑ = 420 nm) = 455 nm (Φₑₑₑ = 0.8 %).

Synthesis of 8b´. To a solution of 9b (535 mg, 1.0 mmol) in n-pentane (10 mL) was added BBr₃ (251 mg, 1.0 mmol) at −78 °C, and the reaction mixture was stirred for 30 min maintaining −78 °C. The mixture was warmed to room temperature and stirred for another 30 min. Dichloromethane (2 mL) was added and the resulting clear solution was stirred for 1 h. All volatiles were removed in vacuo at 0 °C and the obtained yellow solid was dissolved in dichloromethane (1 mL). After addition of TMS-NTf₂ (17.6 mg, 0.05 mmol, 5 mol%) the reaction had been stirred for 3 d at ambient temperature. Afterwards the solvent was removed in vacuo at 0 °C, and the obtained solid was redispersed in
toluene (1.5 mL). Mes*Li (316 mg, 1.25 mmol) was suspended in toluene (1.5 mL) and added to the suspension. The mixture was stirred for three days and quenched by adding water. After aqueous work-up the compound was purified by precipitation in dichloromethane/ethanol. Yield: 100 mg (0.31 mmol, 31%); UV-vis (THF): \( \lambda_{\text{abs,\text{max}}} = 411 \text{ nm} \) (\( \varepsilon = 178043 \text{ L mol}^{-1} \text{ cm}^{-1} \)); fluorescence (THF): \( \lambda_{\text{em,\text{max}}} \) (\( \lambda_{\text{ex}} = 413 \text{ nm} \)) = 426 nm (\( \Phi = 71.1 \% \)).

**X-ray crystallographic analysis of 4b,c.** Suitable colorless single crystals of 4b,c were obtained by slow evaporation of hexane at ambient temperature. Data were collected on a Bruker SMART APEX CCD detector on a D8 goniometer equipped with an Oxford Cryostream 700 temperature controller at 100(2) K using graphite monochromated Mo-K\( \alpha \) radiation (\( \lambda = 0.71073 \text{ Å} \)). An absorption correction was carried out semi-empirically using SADABS\(^{[27]} \) (min./max. transmissions = 0.5287/0.7453 (4b; CCDC number: 1533828), 0.6045/0.7454 (4c; CCDC number: 1533827)). The structure was solved with Olex2\(^{[28]} \) using Direct Methods (ShelXS\(^{[29a]} \)) and refined with the ShelXL\(^{[29b]} \) refinement package by full-matrix least squares on \( F^2 \). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included isotropically and treated as riding. The structure of 4b shows two molecules in the unit cell.

**Table S1.** Crystal structure and refinement data for 4b,c.

<table>
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<th>No.</th>
<th>4b</th>
<th>4c</th>
</tr>
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<td>Color, habit</td>
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<td>colorless block</td>
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<tr>
<td>Size/ mm</td>
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<tr>
<td>Empirical Formula</td>
<td>C(<em>{26})H(</em>{35})BO(_2)</td>
<td>C(<em>{30})H(</em>{39})B</td>
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<tr>
<td>M</td>
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<td>monoclinic</td>
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<td>Space group</td>
<td>C2/c</td>
<td>(P2_1/n)</td>
</tr>
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<td>Parameter</td>
<td>Value 1</td>
<td>Value 2</td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>a/Å</td>
<td>53.471(9)</td>
<td>8.978 (2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>10.4165(18)</td>
<td>10.200 (3)</td>
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<tr>
<td>c/Å</td>
<td>18.028(3)</td>
<td>27.625 (7)</td>
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<tr>
<td>α/°</td>
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<td>90.00</td>
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<tr>
<td>β/°</td>
<td>109.305(3)</td>
<td>93.447 (4)</td>
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<tr>
<td>γ/°</td>
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<td>90.00</td>
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<tr>
<td>V/Å³</td>
<td>9477(3)</td>
<td>2527.9 (11)</td>
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<tr>
<td>Z</td>
<td>16</td>
<td>4</td>
</tr>
<tr>
<td>μ/Åmm⁻¹</td>
<td>0.066</td>
<td>0.059</td>
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<tr>
<td>T/K</td>
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<td>100</td>
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<tr>
<td>θmin,max</td>
<td>2.30, 15.99</td>
<td>2.34, 19.65</td>
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<tr>
<td>Completeness</td>
<td>1.00 to θ = 51.36</td>
<td>1.00 to θ = 52.86</td>
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<tr>
<td>Reflections: total/independent</td>
<td>39914/8968</td>
<td>29863/5175</td>
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<tr>
<td>Rint</td>
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<td>0.0858</td>
</tr>
<tr>
<td>Final R1 and wR2</td>
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<td>0.0533, 0.1503</td>
</tr>
<tr>
<td>Largest peak, hole/Å⁻³</td>
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<td>0.24, −0.24</td>
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<tr>
<td>ρcalc/g cm⁻³</td>
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<td>1.0780</td>
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</table>
Figure S1. Molecular structure of 4b in the solid state with thermal ellipsoids set at 50 % probability (hydrogen atoms omitted for clarity).
Figure S2. Molecular structure of 4c in the solid state with thermal ellipsoids set at 50 % probability (hydrogen atoms omitted for clarity).
**Figure S3.** Consumption of 1a (by $^1$H NMR spectroscopy) during the reaction with 2a to give 3a with TMSOTf (black) and without catalyst (red).

**Gel permeation chromatography (GPC)**

**Figure S4.** GPC trace of 8a (green line: detection by UV signal; red line: detection by RI signal).
**Table S2:** Data of the GPC analysis of 8a.

<table>
<thead>
<tr>
<th></th>
<th>UV</th>
<th>RI</th>
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<tr>
<td>$M_n$</td>
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<td>1580 g/mol</td>
</tr>
<tr>
<td>$M_w$</td>
<td>1762 g/mol</td>
<td>1789 g/mol</td>
</tr>
<tr>
<td>$M_z$</td>
<td>2081 g/mol</td>
<td>2103 g/mol</td>
</tr>
<tr>
<td>$M_v$</td>
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<td>1789 g/mol</td>
</tr>
<tr>
<td>PDI</td>
<td>1.11</td>
<td>1.10</td>
</tr>
</tbody>
</table>

**Figure S5.** GPC trace of 8b (green line: detection by UV signal; red line: detection by RI signal).

**Table S3:** Data of the GPC analysis of 8b.

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<th>RI</th>
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<tbody>
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<td>1982 g/mol</td>
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<tr>
<td>$M_w$</td>
<td>2891 g/mol</td>
<td>3088 g/mol</td>
</tr>
<tr>
<td>$M_z$</td>
<td>4218 g/mol</td>
<td>4925 g/mol</td>
</tr>
</tbody>
</table>
\[ M_n \quad 2891 \text{ g/mol} \quad 3088 \text{ g/mol} \]

\[ PDI \quad 1.54 \quad 1.56 \]

---

**Figure S6.** GPC trace of 8a⁺ (detection by UV signal failed due to technical reasons; red line: detection by RI signal).

**Table S4:** Data of the GPC analysis of 8a⁺.

<table>
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<tr>
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</thead>
<tbody>
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<td>( M_n )</td>
<td>3274 g/mol</td>
</tr>
<tr>
<td>( M_w )</td>
<td>4095 g/mol</td>
</tr>
<tr>
<td>( M_z )</td>
<td>5159 g/mol</td>
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<td>( M_\nu )</td>
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<tr>
<td>PDI</td>
<td>1.25</td>
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</tbody>
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Figure S7. GPC trace of $8b'$ (green line: detection by UV signal; red line: detection by RI signal).

Table S5: Data of the GPC analysis of $8b'$.

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<thead>
<tr>
<th></th>
<th>UV</th>
<th>RI</th>
</tr>
</thead>
<tbody>
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<td>2983 g/mol</td>
</tr>
<tr>
<td>$M_w$</td>
<td>5219 g/mol</td>
<td>4910 g/mol</td>
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<tr>
<td>$M_z$</td>
<td>8370 g/mol</td>
<td>7959 g/mol</td>
</tr>
<tr>
<td>$M_v$</td>
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<tr>
<td>PDI</td>
<td>1.60</td>
<td>1.65</td>
</tr>
</tbody>
</table>

3.1.2 Computational Information

DFT calculations were carried out with the TURBOMOLE V7.0.1 program package.[30] Optimizations were performed with Becke’s three parameter exchange-correlation hybrid functional B3LYP[31] in combination with the valence-double-$\zeta$ basis set def2-SV(P).[32] The empirical dispersion correction DFT-D3 by Grimme was used including
the three-body term and with Becke-Johnson (BJ) damping.[33] The stationary points were characterized as minima by analytical vibrational frequency calculations,[34] which revealed the absence of imaginary frequencies. Vertical singlet excitations were calculated by means of time-dependent DFT[35] using the same density functional–basis set combination as specified above.

**Table S6.** Results from TD-DFT calculations.

<p>| Compound | λ / nm | Oscillator strength f | Orbital contributions | |c|^2 / % |
|----------|--------|------------------------|-----------------------|-----------------------------|
| 4a       | 368.3  | 0.0007                 | HOMO → LUMO           | 96.5                        |
|          | 351.3  | 0.0051                 | HOMO–1 → LUMO         | 94.4                        |
|          | 313.3  | 0.3277                 | HOMO–2 → LUMO         | 93.9                        |
|          | 285.5  | 0.0186                 | HOMO–3 → LUMO         | 96.9                        |
| 4bTip    | 357.9  | 0.0001                 | HOMO → LUMO           | 96.8                        |
|          | 339.4  | 0.0040                 | HOMO–1 → LUMO         | 79.8                        |
|          |        |                        | HOMO–2 → LUMO         | 17.9                        |</p>
<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Weight (a.u.)</th>
<th>Orbital Transition</th>
<th>Ionization Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.1</td>
<td>0.4455</td>
<td>HOMO–2 → LUMO</td>
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<tr>
<td></td>
<td></td>
<td>HOMO–1 → LUMO</td>
<td>17.3</td>
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<tr>
<td>261.9</td>
<td>0.1483</td>
<td>HOMO–3 → LUMO</td>
<td>93.0</td>
</tr>
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</table>

**Figure S8.** Calculated frontier orbitals (isovalue 0.04 a.u.) of 4a.
**Figure S9.** Calculated frontier orbitals (isovalue 0.04 a.u.) of 4b\textsuperscript{Tip}.

### 3.1.3 References


[15] For better comparison with 4a, the furylborane congener was also calculated with Ar’ = Tip, denoted as 4bTip.


[27] SADABS: Area-Detector Absorption Correction; Siemens Industrial Automation, Inc.: Madison, WI, **1996**.


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3.2 From Monodisperse Thienyl- and Furylborane Oligomers to Polymers – Modulating the Optical Properties Through the Hetarene Ratio

Abstract: The incorporation of trivalent boron into conjugated organic frameworks has emerged as a powerful tool to access novel organic–inorganic hybrid materials with interesting properties and functions. Herein, the application of our newly developed B–C bond formation method by catalytic Si/B exchange is demonstrated for the synthesis of a series of triarylboranes (1), monodisperse thienyl- and furylborane dimers (2) and trimers (10) as well as extended oligomers (3) and polymers (3'); mixed (oligo)thienyl-/furylborane species have also been prepared. This allowed us to determine the effective conjugation lengths (ECL) of poly(thienylborane)s and poly(furylborane)s, which gave \( \text{ECL} = 9 \) for both classes of compounds, corresponding to absorption wavelengths of \( \lambda_\infty = 414 \) and 412 nm, respectively, for polymers of infinite chain length. Through variation of the furan-to-thiophene ratio, the optical properties of these materials are effectively modulated. Significantly, higher furan contents lead to considerably increased fluorescence intensities. The structures of 1aa\textsuperscript{Tip}, 1bb\textsuperscript{Tip}, and 2bbb\textsuperscript{Mes\*} have been determined by single crystal X-ray diffraction. This revealed largely coplanar hetarene rings and BR\textsubscript{3} environments, being most pronounced in the furylborane species 1bb\textsuperscript{Tip} and 2bbb\textsuperscript{Mes\*}. Compounds 1aa\textsuperscript{Tip}, 1bb\textsuperscript{Tip} and 3a\textsuperscript{Tip} showed the ability to bind fluoride anions, signaled by a distinct change in their optical absorption characteristics, which renders these compounds attractive targets for chemical sensory applications.

3.2.1 Introduction

In the last few decades, \( \pi \)-conjugated materials have been the subject of tremendous research activity,\textsuperscript{[1]} driven mainly by applications in electronic and optoelectronic devices such as (polymer-based) organic light-emitting diodes (OLEDs/PLEDs),\textsuperscript{[2]} field-effect transistors (OFETs),\textsuperscript{[3]} and organic photovoltaic cells (OPVs),\textsuperscript{[4,3b]} as well as biomedical\textsuperscript{[5]} and sensory applications.\textsuperscript{[6]} In recent years, organic–inorganic hybrid materials generated by doping of \( \pi \) systems with inorganic main group elements have emerged as versatile alternatives
with special features. Conjugated organoboranes and organoborane polymers have attracted particular attention. The interaction of the vacant p orbital on boron with an adjacent π system causes intriguing optical and electronic properties, thus enabling applications for organic (opto)electronics, anion or amine sensing, and bioimaging. The combination of inherently electron-deficient trivalent borane moieties with electron-rich organic π systems results in the formation of donor–acceptor arrays. Thiophene, a ubiquitous building block of organic electronic materials in general, has proved particularly useful for this purpose. For instance, Jäkle and Marder and co-workers presented dithienylboranes and bisboranes, which feature extended conjugated π systems involving the largely coplanar thiophene rings and the boron centers (Figure 1). The bulky aromatic side groups, 2,4,6-tri-tert-butylphenyl (supermesityl, Mes*; R = tBu) and 2,4,6-tris(trifluoromethyl)phenyl (fluoromesityl, FMes; R = CF₃), adopt a nearly perpendicular arrangement to this π plane and provide kinetic stabilization, thus making these species chemically very robust. Compounds and also the B-mesityl substituted derivative (R = Me) by Miyasaka, Kobayashi, and Kawashima are able to bind and detect fluoride anions via an optical response. Recently, Jäkle et al. reported the synthesis of poly(thienylborane) and related polymers comprising oligothiophene building blocks by Sn/B exchange or Stille cross-coupling polycondensation, respectively.

Figure 1. Dithienylboranes 1aaMes*, 1aaFMes, thienylborane dimers 2aaaMes*, 2aaaFMes, and poly(thienylborane) 3aMes*.

In contrast to thiophene, the use of furan as a component of π-conjugated materials is significantly less well explored. The general value of furan-based materials for organic electronics has been
recognized only quite recently, although such compounds show several favorable features and they are in some respect complementary to their well-established thiophene congeners.[20,21] Significantly, different from most other components of organic electronic materials, furan rings are biodegradable and can be obtained from entirely renewable resources. The combination of boron with furan moieties, however, has been largely unexplored so far.[11,22] Recently, we communicated the development of a highly efficient, environmentally benign method for the formation of B–C bonds using a novel catalytic Si/B exchange condensation approach and demonstrated its application to the synthesis of arylborane molecules, oligomers, and polymers, including the first oligo- and poly(furylborane).[23,24] Herein, we report full details of these studies and an extension thereof to longer monodisperse oligomers, i.e., dimers and trimers, as well as mixed thienyl-/furylborane oligomers prepared by modular synthesis. This allowed us to determine the effective conjugation lengths of these classes of compounds, and we demonstrate that their optoelectronic properties can be effectively modulated through the heterocycle ratio. We also investigate the effect of the aromatic side group on the photophysical properties of the new materials and their ability to bind and detect F−.

3.2.2 Results and Discussion

**Synthesis of triarylboranes.** As outlined in our preliminary communication,[23] in the first step of our investigations we explored the reaction between 2-(dibromoboryl)thiophene (4a) and 2-(trimethylsilyl)thiophene (5a) to give bromo-bis(thien-2-yl)borane 6aa (Scheme 1). Some condensation was observed by 1H NMR spectroscopy in a 1 M CH₂Cl₂ solution at ambient temperature already without an initiator added. However, the reaction did not go to completion within 12 d. Addition of catalytic amounts (5 mol%) of Me₃SiOTf yielded significant rate acceleration with 95 % conversion after 5 d. The stronger electrophilic species Me₃SiNTf₂, finally, proved to be a highly efficient catalyst: complete and selective conversion to 6aa was observed with 5 mol% of Me₃SiNTf₂ at ambient temperature within 72 min. Analogous conditions were adopted to generate 6bb and the new, mixed-substituted derivative 6ab. Both reactions proceeded quantitatively (by 1H NMR spectroscopy) within less than 2
h as well. The formation of the phenyl derivative 6cc was considerably slower, and it required increased substrate concentration (4 M) and higher catalyst loading (25 mol%). Nevertheless, this reaction was fully selective, too, and afforded 95% conversion within 3 days at room temperature.

Scheme 1. Synthesis of triarylboranes via catalytic B–C coupling.

After the formation of the respective bromodiarylborane 6 was complete (or almost complete, in the case of 6cc), the reaction mixture was evaporated to dryness, the crude product was re-dissolved in toluene and treated with a solution or suspension of the appropriate aryllithium reagent to furnish the kinetically stabilized triarylboranes 1. In the cases of 6aa and 6bb, TipLi (Tip = 2,4,6-trisopropylphenyl) was used, which afforded the air- and moisture-stable products 1aaTip and 1bbTip. As our further investigations revealed that longer furylborane oligomers were water-sensitive despite having the sterically demanding Tip group attached to the boron center (see below), we additionally derivatized 6bb with the even bulkier Mes*Li to obtain 1bbMes*. Also the mixed-substituted species 6ab was derivatized with Mes*Li to give the stabilized triarylborane 1abMes*. Only the diphenyl derivative 1ccMes* was found to be air- and moisture-sensitive in spite of the Mes* group at boron. However, we succeeded in isolating 1ccMes* in pure form by re-crystallization.

All other triarylboranes 1 were purified by column chromatography on silica and isolated in moderate to good yields (35–69%) as colorless crystalline solids. Their constitution was unambiguously ascertained by 1H, 11B, and 13C NMR spectroscopy, mass spectrometry, and single crystal X-ray diffraction. In the case of 1abMes*, however, the quality of the X-ray data obtained was too poor to allow the discussion of
structural parameters. The $^{11}\text{B}$ NMR resonance of compound $1\text{ab}^{\text{Mes}^*}$ appears at a chemical shift of 50.2 ppm, which is intermediate between that of $1\text{aa}^{\text{Tip}}$ (56.1 ppm) and $1\text{bb}^{\text{Mes}^*}$ (47.7 ppm) or $1\text{bb}^{\text{Tip}}$ (48.6 ppm), respectively. Compared to that of $1\text{cc}^{\text{Mes}^*}$ (67.6 ppm), these signals are at significantly higher field, indicating more effective $\pi$-electron donation from the heteroaromatic rings to the vacant $p_\pi$ orbital on boron. The $^1\text{H}$ NMR spectrum of $1\text{bb}^{\text{Mes}^*}$ showed broad resonances for the protons at the furan rings (Figure A2.20, Appendix). This was not observed for $1\text{bb}^{\text{Tip}}$ (Figure A2.23, Appendix). Presumably, this is a result of the hindered rotation of the furan rings in $1\text{bb}^{\text{Mes}^*}$ in solution at ambient temperature, in contrast to $1\text{bb}^{\text{Tip}}$.

**Synthesis of monodisperse oligomers.** In order to systematically investigate the effect of chain elongation on the photophysical properties of linear extended thienyl- and furylboranes and also mixed species, we prepared a series of monodisperse oligomers (Scheme 2). The bisboranes 2, which can be regarded as hetarylborane “dimers”, were synthesized by the reaction of a 2,5-bis(trimethylsilyl)hetarene 7a or 7b with two equivalents of either 4a or 4b in CH$_2$Cl$_2$ at room temperature in the presence of 5 mol% of Me$_3$SiNTf$_2$, and subsequent post-modification with TipLi or Mes$^*$Li in toluene, respectively. The products, $2\text{aaa}^{\text{Tip}}$, $2\text{bbb}^{\text{Mes}^*}$, $2\text{aab}^{\text{Mes}^*}$, and $2\text{abb}^{\text{Mes}^*}$, were isolated by column chromatography on silica, and their identity was unambiguously ascertained by multinuclear NMR spectroscopy and mass spectrometry. The structure of $2\text{bbb}^{\text{Mes}^*}$ in the solid-state was additionally determined by a single crystal X-ray diffraction study. The $^{11}\text{B}$/$^1\text{H}$ resonances of $2\text{aaa}^{\text{Tip}}$ (58 ppm) and $2\text{bbb}^{\text{Mes}^*}$ (49 ppm) appeared in the same range as those of their respective monoborane congeners, $1\text{aa}^{\text{Tip}}$ and $1\text{bb}^{\text{Mes}^*}$, however, the signals were significantly broadened (FWHM = 2978 (2aaa$^{\text{Tip}}$) and 2120 Hz (2bbb$^{\text{Mes}^*}$)). Although the mixed derivatives $2\text{aab}^{\text{Mes}^*}$ and $2\text{abb}^{\text{Mes}^*}$ both contain two boron atoms in distinct chemical environment, they each show only one signal in their $^{11}\text{B}$/$^1\text{H}$ NMR spectrum ($\delta_B = 51$ ($2\text{aab}^{\text{Mes}^*}$) and 49 ppm ($2\text{abb}^{\text{Mes}^*}$)), obviously a result of the broadened signal patterns. Furthermore, an overall increase in the ratio of furan to thiophene rings leads to a slight highfield shift of the $^{11}\text{B}$ signal (from $2\text{aab}^{\text{Mes}^*}$ to $2\text{abb}^{\text{Mes}^*}$ by ca. 2 ppm).
Scheme 2. Synthesis of monodisperse hetarylborane oligomers.

The synthesis of the “trimers” 10 required prior preparation of disilylated compounds 9. This was done via dilithiation of the appropriate triarylborane 1 and subsequent reaction with Me₃SiCl (2 equiv.). Compounds 9 were then treated with two equivalents of 4 at ambient temperature in a catalytic reaction using Me₃SiNTf₂ (Scheme 3). Post-modification with TipLi or Mes*Li afforded 10. The derivatives 10aaaTip and 10aabbMes⁺ were isolated by column chromatography, and their constitution was unambiguously ascertained by NMR spectroscopy and mass spectrometry. The ¹¹B{¹H} resonance of 10aaaTip (57 ppm) was in the expected range and further broadened (FWHM = 3053 Hz) compared to those of the “dimers” and “monomers”; for 10aabbMes⁺ the resonance was not detected. The formation of 10babbMes⁺ was evidenced by mass spectrometry (m/z = 1051.1; see Appendix, Figure A2.118), however, the product suffered from decomposition during the chromatographic work-up.[25]

Polycondensation reactions. As communicated recently,[23] we performed polycondensation reactions leading to oligo- and poly(thienyl/furylborane)s via two different routes (Scheme 3).[23]

**Route A:** Reactions of 7a and 7b with one equivalent of BBr₃ at −78 °C selectively yielded the AB monomers 11a,b, which contain both functional groups required for polycondensation (SiMe₃ and BBr₂) in one molecule. Addition of 5 mol% of Me₃SiNTf₂ to CH₂Cl₂ solutions of
11a,b initiated polycondensation thereof to give the intermediates 12a,b. The latter were subsequently derivatized with TipLi (12a) or Mes*Li (12b). After aqueous work-up and purification by precipitation with ethanol this afforded the air- and moisture-stable products 3aTip and 3bMes*. Gel permeation chromatography (GPC), however, suggested that they were of relatively low molecular weight with narrow polydispersity (Table 1). We assume that this is a result from the observed precipitation of the intermediates 12a,b at some point during the polycondensation process. Route B: As we found that the Tip and Mes* side groups impart pronounced solubility, in the next step, we decided to employ the Tip/Mes*-containing disilyl compounds 9aaTip and 9bbMes* as the monomers in combination with BBr3 in analogous catalytic reactions. In the case of 9aaTip we furthermore changed the solvent to the more polar 1,2-dichlorobenzene (o-DCB). Apparently due to the improved solubility of the macromolecular intermediates 13aTip and 13bMes*, the products 3aTip and 3bMes* were obtained with significantly increased molecular weights, corresponding to number average degrees of polymerization of 10 and 9, respectively.

Scheme 3. Polycondensation reactions.
Table 1. GPC data\textsuperscript{a} for 3a\textsuperscript{Tip}, 3a\textsuperscript{′Tip}, 3b\textsuperscript{Mes*}, and 3b\textsuperscript{′Mes*}.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PDI</th>
<th>DP\textsubscript{n}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a\textsuperscript{Tip}</td>
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<td>1760</td>
<td>1.1</td>
<td>4</td>
</tr>
<tr>
<td>3a\textsuperscript{′Tip}</td>
<td>3270</td>
<td>4100</td>
<td>1.3</td>
<td>10</td>
</tr>
<tr>
<td>3b\textsuperscript{Mes*}</td>
<td>1880</td>
<td>2890</td>
<td>1.5</td>
<td>5</td>
</tr>
<tr>
<td>3b\textsuperscript{′Mes*}</td>
<td>3260</td>
<td>5220</td>
<td>1.6</td>
<td>9</td>
</tr>
</tbody>
</table>

\textsuperscript{a}In THF, vs polystyrene standards.

**Structural studies.** The solid-state structures of 1\textsuperscript{aa}\textsuperscript{Tip}, 1\textsuperscript{bb}\textsuperscript{Tip}, 1\textsuperscript{bb}\textsuperscript{Mes*}, 1\textsuperscript{cc}\textsuperscript{Mes*}, and the furylborane dimer 2\textsuperscript{bbb}\textsuperscript{Mes*} have been determined by single crystal X-ray diffraction (Figure 2; the molecular structures of 1\textsuperscript{bb}\textsuperscript{Mes*} and 1\textsuperscript{cc}\textsuperscript{Mes} have been displayed in our previous communication\textsuperscript{[23]}). In each of these compounds the boron centers are trigonal-planar coordinated (sums of the bond angles around boron, $\Sigma$(BC$_3$), ca. 360° each). The Tip/Mes* substituents are nearly perpendicular to the respective BC$_3$ plane, thus ruling out any possible $\pi$ interaction between this aromatic system and the vacant $p$ orbital on boron. Interestingly, the two Mes* substituents of 2\textsuperscript{bbb}\textsuperscript{Mes*} point into opposite directions, which is different from the thienylborane dimers 2\textsuperscript{aaa}\textsuperscript{Mes*} and 2\textsuperscript{aaa}\textsuperscript{FMes} (with $^{\text{F}}\text{Mes} = 2,4,6$-(CF$_3$)$_3$C$_6$H$_2$) recently described by Jäkle and Marder wherein the aryl side groups are on the same side of the molecule.\textsuperscript{[14]} The orientation of the hetaryl rings with respect to the BC$_3$ moiety, on the other hand, and to lesser extent also that of the phenyl rings in 1\textsuperscript{cc}\textsuperscript{Mes*}, indicate potential $\pi$ conjugation between these groups over the boron center. In 1\textsuperscript{aa}\textsuperscript{Tip} both thiophene rings are disordered by rotation about the B–C bonds, while in the furyl derivatives 1\textsuperscript{bb}\textsuperscript{Tip}, 1\textsuperscript{bb}\textsuperscript{Mes*}, and 2\textsuperscript{bbb}\textsuperscript{Mes*} the heterocycles consistently adopt all-\textit{anti} conformation in the solid-state. It is noteworthy that the most pronounced coplanarity of the rings is observed in the furyl derivatives 1\textsuperscript{bb}\textsuperscript{Tip}, 1\textsuperscript{bb}\textsuperscript{Mes*}, and 2\textsuperscript{bbb}\textsuperscript{Mes*}. The interplanar angles are 5 – 8° only. The mean twist angle between the thiophene (Thi) planes in 1\textsuperscript{aa}\textsuperscript{Tip} is 30.2°, which is somewhat larger compared to those in Mes*B(Thi)$_2$ (19.0°),\textsuperscript{[14]} $^{\text{F}}$MesB(Thi)$_2$ (16.3°),\textsuperscript{[14]} and MesB(Thi)$_2$ (8.4 and 4.2°).\textsuperscript{[11]} The observation that the furylboranes show greater planarity than their thienylborane congeners parallels the trend found
for oligofurans vs. analogous thiophene oligomers.\textsuperscript{[21]} The torsion angle between the phenyl groups in 1cc\textsuperscript{Mes} is 43.8°. The lengths of the B–C bonds to the thiophene or furan substituents, respectively, in 1aa\textsuperscript{Tip}, 1bb\textsuperscript{Tip}, 1bb\textsuperscript{Mes*}, and 2bbb\textsuperscript{Mes*} are roughly in the same range, and also in the same range with those of MesB(Thi)\textsubscript{2} (averaged: 1.548 Å\textsuperscript{[11]} and F\textsuperscript{Mes}B(Thi)\textsubscript{2} (1.541(7) and 1.526(6) Å),\textsuperscript{[14]} but significantly shorter than in Mes*B(Thi)\textsubscript{2} (1.589(6) and 1.568(4) Å).\textsuperscript{[14]}

![Figure 2. Molecular structures of 1aa\textsuperscript{Tip}, 1bb\textsuperscript{Tip}, and 2bbb\textsuperscript{Mes*} in the solid state (H atoms omitted for clarity).]

Table 2. Selected structural data for triarylboranes 1 and dimer 2bbb\textsuperscript{Mes*}.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>Interplanar angle BC\textsubscript{Tip}/Mes* / °</th>
<th>Interplanar angle (het)aryl/(het)aryl / °</th>
<th>B–C1 bond length / Å</th>
<th>B–C5 bond length / Å</th>
</tr>
</thead>
</table>

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Table 3. Photophysical data\textsuperscript{a} for triarylboranes 1, dimers 2, trimers 10, oligomers 3, and polymers 3'.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>$\lambda_{\text{abs,max}}$/ nm</th>
<th>$\varepsilon_{\text{max}}$/ (L mol$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{em,max}}$/ nm</th>
<th>$\Phi_F$/ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1aa$^{\text{Tip}}$</td>
<td>325</td>
<td>24227</td>
<td>410</td>
<td>3</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Taken from ref. [23]. \textsuperscript{b}The asymmetric unit of 1bb$^{\text{Mes}}$ contains two independent molecules. \textsuperscript{c}Mean value from the four different relative conformations of the disordered rings. \textsuperscript{d}B2–C27. \textsuperscript{e}B2–C31. \textsuperscript{f}B2–C9. \textsuperscript{g}B2–C8.

**Photophysical studies.** All monomers 1, dimers 2, trimers 10, oligomers 3, and polymers 3' presented were studied by UV–vis absorption and fluorescence emission spectroscopy in THF solution (Table 2). Comparison of the data for 1bb$^{\text{Tip}}$ and 1bb$^{\text{Mes}}$ reveals a significant effect of changing the stabilizing aryl substituent from Tip to Mes*. This causes a decrease in the wavelength of the lowest-energy absorption maximum, which we assign to a $\pi$–$\pi^*$ process,\textsuperscript{[23]} by 9 nm (315 vs. 324 nm). On the other hand, the emissivity is significantly enhanced through the substituent change. Whereas 1bb$^{\text{Tip}}$ was found to be basically non-emissive in THF, compound 1bb$^{\text{Mes}}$ showed relatively strong blue fluorescence with a quantum yield of 24 %. Presumably, this is associated with the increased rigidity of the molecules of 1bb$^{\text{Mes}}$ compared to 1bb$^{\text{Tip}}$ due to the hindered rotation of the furan rings in the former, as evidenced by $^1$H NMR spectroscopy (vide supra), thus favoring radiative decay processes.
In THF, except for $\text{1cc}^{\text{Mes*}}$ (in CH$_2$Cl$_2$). $b$Taken from ref. [23]. $c$Taken from ref. [14]. $d$Not reported.

In the case of the couple $\text{1aa}^{\text{Mes*}} / \text{1aa}^{\text{Mes*}}$, on the other hand, variation of the bulky aryl substituent has negligible influence on the absorption and emission characteristics of the compounds. The maximum of the lowest-energy absorption band for both derivatives appears at virtually identical wavelength. Notable fluorescence was observed for neither of them. While $\text{1aa}^{\text{Mes*}}$ was described as non-emissive in THF,[14] compound $\text{1aa}^{\text{Tip}}$ showed weak fluorescence with a quantum yield of only 3 %.

Within the series of triarylboranes 1 having the same bulky aryl substituent (Mes*), the UV–vis spectra reveal a clear trend depending on nature of the conjugated aryl groups (Figure 3; due to the similarity of the spectra of $\text{1aa}^{\text{Tip}}$ and $\text{1aa}^{\text{Mes*}}$, it seems appropriate to include the spectrum of $\text{1aa}^{\text{Tip}}$ in the graphical comparison). Here, the wavelength
of the absorption maximum increases in the order: phenyl << furyl < thienyl. The absorption band of $1cc_{\text{Mes}^*}$ appears at relatively high energy, evidencing rather weak conjugation between the phenyl groups, as indicated also by their orientation in the solid-state structure of $1cc_{\text{Mes}^*}$ (vide supra). The bands of the hetaryl-substituted compounds are considerably bathochromic shifted, with the maximum of the mixed-substituted derivative $1ab_{\text{Mes}^*}$ being right in the middle between those of $1aa_{\text{Tip}}/1aa_{\text{Mes}^*}$ and $1bb_{\text{Mes}^*}$. However, these bands are in a quite similar range, thus pointing to comparably strong conjugation between the thienyl and the furyl groups over the boron center. The fluorescence quantum yield of 10 % for the mixed derivative $1ab_{\text{Mes}^*}$ fits within the trend of increasing emission intensity with increasing ratio of furan rings.

![Figure 3. UV–vis absorption spectra of triarylboranes 1.](image)

Also within the series of dimeric compounds, the thienylborane derivative $2aaa_{\text{Tip}}$ absorbs at the longest wavelength ($\lambda_{\text{abs,max}} = 370$ nm). However, the band of its Mes$^*$ congener $2aaa_{\text{Mes}^*}$ is slightly blue-shifted ($\lambda_{\text{abs,max}} = 360$ nm),$^{[14]}$ which correlates with the trend observed for the couple $1bb_{\text{Tip}} / 1bb_{\text{Mes}^*}$. The mixed dimers $2aab_{\text{Mes}^*}$ and $2abb_{\text{Mes}^*}$ and the pure furylborane derivative $2bbb_{\text{Mes}^*}$ have very similar absorption characteristics with maxima at around 360 nm. Only the latter shows some fluorescence in solution.

One conclusion that can be drawn from our studies is that the furylborane species generally show significantly enhanced fluorescence compared to their thiophene congeners. Similar
observations have been made for oligofurans vs. oligothiophenes as well. This is thought to be a result of lower probability for intersystem crossing due to the lack of a heavier atom (such as sulfur) in the former.\[21\] Within our series of investigated compounds, the oligo- and poly(furylborane)s $3b^{\text{Mes}^*}$ and $3b^{\text{Mes}^*}'$ showed the strongest fluorescence intensities. Presumably, two effects contribute to this observation: the effect of i) the incorporation of furan rings and ii) the incorporation of Mes$^*$ rather than Tip as the side group.

Comparison of the UV–vis spectra for species of different chain length within each series of comparable compounds reveals considerable bathochromic shifts with increasing number of repeat units (Figure 4). This provides unequivocal evidence for effective $\pi$ conjugation along the thiienylborane and furylborane backbones and also that of mixed species. With the series $1\text{aa}^{\text{Tip}} < 2\text{aaa}^{\text{Tip}} < 10\text{aaaa}^{\text{Tip}} < 3\text{a}^{\text{Tip}} < 3\text{a}^{\text{Tip}}'$ and $1\text{bb}^{\text{Mes}^*} < 2\text{bbb}^{\text{Mes}^*} < 3\text{b}^{\text{Mes}^*} < 3\text{b}^{\text{Mes}^*}'$ at hand we were able to determine the effective conjugation lengths (ECL) of both pure oligo(thienylborane)s and oligo(furylborane)s by extrapolation of an exponential fit of the maximum absorption wavelengths plotted against the number of repeat units (Figure 4).\[27\] This gave an $n_{\text{ECL}}$ of 9 repeat units for both classes of compounds. For an infinite thiienylborane polymer chain our study predicts an absorption wavelength of $\lambda_\infty = 414$ nm, and for the limiting value of the infinite poly(furylborane) we obtain $\lambda_\infty = 412$ nm. Consequently, the effective conjugation lengths for both classes of polymers have been reached with $3\text{a}^{\text{Tip}}$ and $3\text{b}^{\text{Mes}^*}'$, respectively.
Figure 4. UV–vis absorption spectra and plots of the maximum absorption wavelengths against the number of repeat units and exponential fits thereof to determine the effective conjugation lengths (ECL) of oligo(thienylborane)s (top) and oligo(furylborane)s (bottom).

The UV–vis spectra of the mixed compounds show significant red-shifts with increasing chain lengths as well, as shown for the series $1ab^{\text{Mes}^*} < 2aba^{\text{Mes}^*} \approx 2bab^{\text{Mes}^*} < 10aaba^{\text{Mes}^*}$ (Figure 5). This demonstrates effective $\pi$ conjugation in these species between the different hetarenes and including the boron centers.
Fluoride sensing experiments. In order to explore the ability of our thienyl- and furylboranes to bind and detect fluoride anions, we performed reactions of the monomers $1\text{aa}_{\text{Tip}}$, $1\text{bb}_{\text{Tip}}$, and $1\text{bb}_{\text{Mes}^*}$ with tetra-$n$-butylammonium fluoride (TBAF) in THF. First, we monitored the reactions by NMR spectroscopy. Whereas the $^{11}$B NMR spectrum of $1\text{bb}_{\text{Mes}^*}$ remained unchanged in the presence of $F^-\,$, in the spectra of $1\text{aa}_{\text{Tip}}$ and $1\text{bb}_{\text{Tip}}$, new resonances appeared that are characteristic of four-coordinate boron species ($\delta_B \sim 2$ ppm ($1\text{aa}_{\text{Tip}}$), Appendix Figure A2.15; $\delta_B \sim 0$ ppm ($1\text{bb}_{\text{Tip}}$), Appendix Figure A2.25). Encouraged by these results, we then explored the possibility to follow the putative fluoride binding processes by UV–vis spectroscopy (Figure 6a,b). Indeed, upon titration of $1\text{aa}_{\text{Tip}}$ and $1\text{bb}_{\text{Tip}}$ in THF with TBAF, the absorption band at $\lambda_{\text{abs,max}} = 325$ nm ($1\text{aa}_{\text{Tip}}$) and 324 nm ($1\text{bb}_{\text{Tip}}$), respectively, was continuously quenched. After the addition of about two equivalents of TBAF the $\pi-\pi^*$ absorption band was quenched completely. This is consistent with the interpretation that facile binding of fluoride to the boron center occurs, thus leading to the formation of a borate species (see Figure 6, bottom right). Through this process, $\pi$ conjugation over the boron center is effectively disrupted, hence, the corresponding $\pi-\pi^*$ absorption band vanishes.
Figure 6. UV–vis absorption spectra recorded during the titration of 1aaTip (a), 1bbTip (b), and 3aTip (c) with TBAF.

We then aimed at transferring these results to the use of thienyl- and furylborane polymers 3aTip and 3bMes*. As in the case of the monomers, the Mes*-substituted derivative 3bMes* showed no evidence of fluoride binding ability. Upon addition of TBAF to a solution of 3aTip, on the other hand, the 11B NMR spectrum displayed a new resonance at 0.2 ppm assigned to a borate boron center (Appendix, Figure A2.64). The $\pi-\pi^*$ absorption band in the UV–vis spectrum of 3aTip ($\lambda_{\text{abs, max}} = 409$ nm) continuously decreased in intensity during fluoride titration and was fully quenched when four equivalents of TBAF had been added (Figure 6c). Concomitantly, two new bands emerged at $\lambda_{\text{abs, max}} = 294$ and 369 nm.

3.2.3 Summary
We have presented a systematic study of cyclolinear extended thienyl- and furylboranes and related species of mixed composition. Monodisperse monomers, dimers, and trimers have been prepared by
modular synthesis using our newly developed catalytic Si/B exchange condensation method. Polycondensation reactions via this approach led to higher oligomers and polymers. Having extensive series of oligo(thienylborane)s and oligo(furylborane)s of varying chain length at hand, allowed us to determine the effective conjugation lengths (ECL) of both classes of compounds. This revealed pronounced \(\pi\)-electron delocalization over the hetarene backbones including the boron centers. Our photophysical investigations further showed that the absorption and emission characteristics of such species are effectively modulated by the ratio of furan to thiophene rings incorporated. Significantly, higher furan ratios lead to considerably increased fluorescence intensities of the materials. Compounds 1aa\textsuperscript{TIP}, 1bb\textsuperscript{TIP} and 3a\textsuperscript{TIP} furthermore showed the ability to bind and detect fluoride anions, associated with a distinct change in their optical absorption characteristics. The possibility to easily monitor the binding processes by UV–vis spectroscopy demonstrates the potential use of our new materials for sensory applications. This study demonstrates the versatile application of our catalytic B–C bond formation method for the synthesis of conjugated organoborane oligomers and polymers. Currently, we are further extending this approach to access a broad range of new materials with tailored properties and functions, and we aim to elucidate mechanistic details of their formation.

### 3.2.4 Experimental Section

**General procedures.** All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques or in an MBraun glovebox. Solvents (dichloromethane, \(n\)-pentane, diethylether, toluene, and tetrahydrofuran) were dried and degassed by means of a MBraun SPS-800 solvent purification system. \(o\)-Dichlorobenzene was dried over CaH\(_2\) and distilled prior to use. Deuterated solvents for NMR spectroscopy were dried and degassed at reflux over Na (C\(_6\)D\(_6\)) or CaH\(_2\) (CDCl\(_3\) and CD\(_2\)Cl\(_2\)) and freshly distilled prior to use. Solvents for aqueous work-up (dichloromethane, ethanol, \(n\)-hexane, \(n\)-pentane), 2-bromothiophene, tribromoborane,
lithium bis(trifluoromethylsulfonyl)imide, bromobenzene, sulfuric acid, and magnesium turnings were purchased from commercial sources and used as received. Solutions of n-butyllithium (1.6 M in hexane and 2.5 M in hexane, respectively) and t-butyllithium (1.7 M in pentane) were purchased from Sigma Aldrich and used as received as well. Chlorotrimethylsilane, 2-bromo-1,3,5-triisopropylbenzene, thiophene and furan were commercially purchased and freshly distilled prior to use. 2-Bromofuran,[28] trimethylsilyl bis(trifluoromethylsulfonyl)imide,[29] 2,4,6-triisopropylphenyllithium,[30] 2-bromo-1,3,5-tri-tert-butylbenzene[31] and 2,4,6-tri-tert-butylphenyllithium[14] were prepared according to methods described in the literature. Compounds 5a, 5b, 5c, 4a, 4b, 4c, 7a, and 7b were prepared according to a procedure previously described by our group.[23] NMR spectra were recorded at 25 °C on a Bruker Avance II-400 spectrometer or on a Bruker Avance III HD spectrometer operating at 400 MHz. Chemical shifts were referenced to residual protic impurities in the solvent (1H) or the deuterio solvent itself (13C) and reported relative to external SiMe4 (1H, 13C) or BF3·OEt2 (11B) standards. Mass spectra were obtained with the use of a Finnigan MAT95 spectrometer employing electron ionization (EI) using a 70 eV electron impact ionization source or secondary ionization (SIMS). Elemental analysis was performed with a CHN-O-Rapid VarioEL by Heraeus. UV-vis spectra were obtained using a Jasco V-630 spectrophotometer. For fluoride titration experiments a solution of tetrabutylammonium fluoride (TBAF) in THF (1 M) was diluted to yield a solution with equivalent concentration with respect to 1aaTip, 1bbTip and 3aTip. Within a glass cuvette different equivalents of TBAF were mixed with a solution of the corresponding boron-containing compound in THF (c = 1.5 × 10^{-5} mol/L (1aaTip, 1bbMes^*); c = 5.1 × 10^{-6} mol/L (3aTip)) and the reaction was monitored by determination of the UV–vis absorption spectra. Fluorescence spectra were obtained with a Jasco FP-6500 spectrofluorometer. Fluorescence quantum yields were determined against commercially available standards (1abMes^* against diphenylanthracene (DPA), 3aTip and 3bMes^* against perylene). Melting points (uncorrected) were obtained using a SMP3 melting point apparatus by Stuart in 0.5 mm (o.d.) glass capillaries, which were sealed under argon. GPC chromatograms were recorded on an Agilent 1100 Series, equipped with two SDV linear N columns of 8x300 mm and 8x600 mm measures and 5 mm pore size at 30 °C against a
polystyrene standard. Detection was carried out via UV signal (λ = 250 nm) and refractive index (RI), respectively.

Monomeric compounds 1

General procedure for the synthesis of 1. To a solution of 5 (1 mmol) in dichloromethane (1 mL) was added TMS-NTf₂ (5 mol %) at room temperature. A solution of 4 (1 mmol) dissolved in dichloromethane (1 mL) was added and the reaction process was monitored using ¹H NMR spectroscopy. The resulting solution was evaporated to dryness to yield crude 6, which was subsequently redissolved in toluene (1.5 mL). To this solution a solution (TipLi) or a suspension (Mes*Li) of the lithiated arene (1.1 mmol) in toluene (1.5 mL) was added at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred over night. The resulting suspension was diluted with n-pentane and quenched by adding water. The organic phase was washed with brine, dried over MgSO₄, and the solvent was removed in vacuo. The triarylborane 1ccMes was purified by two re-crystallizations from n-hexane at −40 °C. The other solid crude products were subjected to column chromatography (silica; n-hexane) to give 1 as a colorless solid.

6aa: ¹H NMR (400 MHz, CDCl₃, δ): 8.22 (dd, ³J = 3.8 Hz, ⁴J = 1.0 Hz, 2H, Th-H), 8.02 (dd, ³J = 4.8 Hz, ⁴J = 1.0 Hz, 2H, Th-H), 7.38 (dd, ³J = 3.8, 4.8 Hz, 2H, Th-H); ¹¹B{¹H} NMR (128 MHz, CDCl₃, δ): 49.7 (s).

6ab: ¹H NMR (400 MHz, CDCl₃, δ): 8.36 (dd, ³J = 3.8 Hz, ⁴J = 1.0 Hz, 1H, Th-H), 8.04 (dd, ³J = 4.8 Hz, ⁴J = 1.0 Hz, 1H, Th-H), 7.98 (m, 1H, Fur-H), 7.74 (dd, ³J = 3.5 Hz, ⁴J = 0.8 Hz, 1H, Fur-H), 7.37 (dd, ³J = 3.8, 4.8 Hz, 1H, Th-H), 6.64 (dd, ³J = 1.5, 3.5 Hz, 1H, Fur-H); ¹¹B{¹H} NMR (128 MHz, CDCl₃, δ): 45.5 (s).
6bb: \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 7.94 (dd, \(3^J = 1.0\) Hz, \(4^J = 0.5\) Hz, 2H, Fur-\(H\)), 7.82 (dd, \(3^J = 3.0\) Hz, \(4^J = 0.5\) Hz, 2H, Fur-\(H\)), 6.64 (dd, \(3^J = 1.0\), 3.0 Hz, 2H, Fur-\(H\)); \(^{11}\)B\(^{\{\text{H}\}}\) NMR (128 MHz, CDCl\(_3\), \(\delta\)): 42.2 (s).

6cc: \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 8.00 (m, 4H, Ph-\(H\)), 7.60–7.64 (m, 2H, Ph-\(H\)), 7.48–7.52 (m, 4H, Ph-\(H\)); \(^{11}\)B\(^{\{\text{H}\}}\) NMR (128 MHz, CDCl\(_3\), \(\delta\)): 66.5 (s).

1aa\(^{\text{Tip}}\): Yield: 69%; m.p. 141 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 7.94 (dd, \(3^J = 4.8\) Hz, \(4^J = 1.0\) Hz, 2H, Th-\(H\)), 7.90 (dd, \(3^J = 3.5\) Hz, \(4^J = 1.0\) Hz, 2H, Th-\(H\)), 7.32 (dd, \(3^J = 3.5\), 4.8 Hz, 2H, Th-\(H\)), 7.06 (s, 2H, Tip-\(H\)), 3.00 (sept, \(3^J = 7.0\) Hz, 1H, \(p\)-\(i\)-Pr-\(CH\)), 2.56 (sept, \(3^J = 6.8\) Hz, 2H, \(o\)-\(i\)-Pr-\(CH\)), 1.38 (d, \(3^J = 7.0\) Hz, 6H, \(p\)-\(i\)-Pr-\(CH_3\)), 1.10 (d, \(3^J = 6.8\) Hz, 12H, \(o\)-\(i\)-Pr-\(CH_3\)); \(^{11}\)B\(^{\{\text{H}\}}\) NMR (128 MHz, CDCl\(_3\), \(\delta\)): 56.1 (s); \(^{13}\)C\(^{\{\text{H}\}}\) NMR (101 MHz, CDCl\(_3\), \(\delta\)): 149.6 (Tip-\(C\)-\(o\)-\(i\)-Pr), 148.6 (Tip-\(C\)-\(p\)-\(i\)-Pr), 145.1 (br, Th-\(C\)-\(B\)), 142.1 (Th-\(CH\)), 139.2 (br, Tip-\(C\)-\(B\)), 137.2 (Th-\(CH\)), 128.9 (Th-\(CH\)), 120.0 (Tip-\(CH\)), 35.2 (\(o\)-\(i\)-Pr-\(CH\)), 34.2 (\(p\)-\(i\)-Pr-\(CH\)), 24.2 (\(o\)-\(i\)-Pr-\(CH_3\)), 24.1 (\(p\)-\(i\)-Pr-\(CH_3\)); MS (EI, 70 eV): \(m/z\) (%): 380.2 (M\(^{\ast}\), 80), 296.2 ([BThTip\(^{\ast}\), 39), 253.2 ([BTh(Ph-\(i\)-Pr)\(^{\ast}\), 211.2 ([BTh(Ph-\(i\)-Pr)]\(^{\ast}\), 55), 177.1 ([B(Th)\(^{2}\)\(^{\ast}\), 21); elem. anal. calcd (%) for C\(_{23}\)H\(_{29}\)BS\(_2\): C 72.62, H 7.68, found: C 72.77, H 7.71; UV–vis (THF): \(\lambda_{\text{abs},\text{max}} = 263\) (\(\varepsilon = 7254\) L mol\(^{-1}\) cm\(^{-1}\)), 275 (\(\varepsilon = 8643\) L mol\(^{-1}\) cm\(^{-1}\)), 325 nm (\(\varepsilon = 24227\) L mol\(^{-1}\) cm\(^{-1}\)); fluorescence (THF): \(\lambda_{\text{em},\text{max}} (\lambda_{\text{ex}} = 325\) nm) = 410 nm (\(\varphi_t = 3.1\) %).

1ab\(^{\text{Mes}}\): Yield: 54%; m.p. 133 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 7.84 (dd, \(3^J = 1.5\), \(4^J = 0.5\) Hz, 1H, Fur-\(H\)), 7.84 (dd, \(3^J = 4.8\), \(4^J = 1.0\) Hz, 1H, Th-\(H\)), 7.71 (br, 1H, Th-\(H\)), 7.44 (s, 2H, Mes\(^{\ast}\)-\(H\)), 7.19 (dd, \(3^J = 3.8\), 4.8 Hz, 1H, Thi-\(H\)), 7.17 (br, 1H, Fur-\(H\)), 6.53 (dd, \(3^J = 1.5\), 3.5 Hz, 1H, Fur-\(H\)), 1.40 (s, 9H, \(p\)-\(t\)Bu-\(CH_3\)), 1.17 (s, 18 H, \(o\)-\(t\)Bu-\(CH_3\)); \(^{11}\)B\(^{\{\text{H}\}}\) NMR (128 MHz, CDCl\(_3\), \(\delta\)): 50.2 (s); \(^{13}\)C\(^{\{\text{H}\}}\) NMR (101 MHz, CDCl\(_3\), \(\delta\)): 165.1 (br, Fur-\(C\)-\(B\)), 151.9 (Mes\(^{\ast}\)-\(C\)-\(o\)-\(t\)Bu), 148.5 (Mes\(^{\ast}\)-\(C\)-\(p\)-\(t\)Bu), 147.9 (Fur-\(CH\)), 146.8 (br, Th-\(C\)-\(B\)), 141.6 (Th-\(C\)-\(H\)), 135.9 (Th-\(CH\)), 133.6 (br, Mes\(^{\ast}\)-\(C\)-\(B\)), 128.3 (Th-\(CH\)), 127.7 (Fur-\(CH\)), 122.3 (Mes\(^{\ast}\)-
CH), 111.5 (Fur-C-H) 38.5 (tBu -C(CH3)3), 34.6 (o-tBu-C(CH3)3), 31.4 (p-tBu-C(CH3)3); MS (EI, 70 eV): m/z (%) = 406.2 (M⁺, 75), 323.2 ([BFurMes*], 30), 281.2 ([BFur(Ph(i-Pr)3)]24), 231.2 ([Ph-(t-Bu)2- (i-Pr)], 100); HRMS: calcd for C26H35BOS: 406.2502, found: 406.2500; UV–vis (THF): λabs,max = 320 nm (ε = 19954 L mol⁻¹ cm⁻¹); fluorescence (THF): λem,max (λex = 342 nm) = 366 nm (φ = 9.8 %).

1bbTip: Yield: 21 %; m.p. 112 °C; ¹H NMR (400 MHz, CDCl₃, δ): 7.89 (dd, 3J = 1.8, 4J = 0.8 Hz, 2H, Fur-H), 7.45 (d (br), 2H, Fur-H), 7.04 (s, 2H, Tip-H), 6.58 (dd, 3J = 3.3, 4J = 1.5 Hz, 2H, Fur-H), 2.97 (sept, 3J = 6.8 Hz, 1H, p-i-Pr-CH₂), 2.54 (sept, 3J = 6.5 Hz, 2H, o-i-Pr-CH₂), 1.35 (d, 3J = 6.8 Hz, 6H, p-i-Pr-CH₃), 1.10 (d, 3J = 6.8 Hz, 12H, o-i-Pr-CH₃); ¹³B{¹H} NMR (128 MHz, CDCl₃, δ): 48.6 (s); ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 163.5 (br, Fur-C-B), 150.0 (Tip-C-o-i-Pr), 149.9 (Tip-C-p-i-Pr), 148.3 (Fur-CH), 135.7 (br, Tip-C-B), 131.1 (Fur-CH), 119.9 (Tip-CH), 111.7 (Fur-CH), 35.3 (o-i-Pr-CH₃), 34.2 (p-i-Pr-CH₃), 24.2 (o-i-Pr-CH₃), 24.1 (p-i-Pr-CH₃); MS (EI, 70 eV): m/z (%) = 348.1 (M⁺, 84), 237.1 ([BFur₂(Ph-(i-Pr₂)]+₁), 100; elem. anal. calcd (%) for C₂₃H₂₉BO₂: C 79.32, H 8.39, found: C 79.26, H 8.28; UV–vis (THF): λabs,max = 269 (ε = 16244 L mol⁻¹ cm⁻¹), 324 nm (ε = 40920 L mol⁻¹ cm⁻¹); fluorescence (THF): non-emissive.

1bbMes*: Yield: 38 %; m.p. 103 °C; ¹H NMR (400 MHz, CDCl₃, δ): 7.79 (dd, 3J = 1.6, 4J = 0.6 Hz, 2H, Fur-H), 7.45 (s, 2H, Mes*H), 7.29 (br, 2H, Fur-H), 6.53 (dd, 3J = 3.4, 4J = 1.6 Hz, 2H, Fur-H), 1.39 (s, 9H, p-t-Bu-CH₃), 1.18 (s, 18H, o-t-Bu-CH₃); ¹¹B{¹H} NMR (128 MHz, CDCl₃, δ): 47.7 (s); ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 164.0 (br, Fur-C-B), 152.0 (Mes*-C-o-t-Bu), 148.4 (Mes*-C-p-t-Bu), 148.0 (Fur-CH), 132.3 (br, Mes*-C-B), 127.9 (Fur-CH), 122.0 (Mes*-CH), 111.5 (Fur-CH), 38.2 (o-t-Bu-C-CH₃), 34.7 (p-t-Bu-C-CH₃), 34.1 (o-t-Bu-CH₃), 31.4 (p-t-Bu-CH₃); MS (EI, 70 eV): m/z (%) = 390.5 (M⁺, 81), 257.4 (BMes*); HRMS calcd for C₂₆H₃₅BO₂: 390.2740, found: 390.2727; UV–vis (THF): λabs,max = 315 (ε = 25676 L mol⁻¹ cm⁻¹); fluorescence (THF): λem,max (λex = 308 nm) = 400 nm (φ = 24.0 %).
\textbf{1cc}^{\text{Mes*}}: Yield: 35 \%; m.p. 153 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, \delta): 7.91 (dd, \textit{J} = 6.5, \textit{J} = 1.5 Hz, 4H, Ph-\textit{H}), 7.38–7.47 (m, 6H, Ph-\textit{H}), 7.45 (s, 2H, Mes*-\textit{H}), 1.42 (s, 9H, \textit{p}-tBu-CH\textsubscript{3}), 1.09 (s, 18H, \textit{o}-tBu-CH\textsubscript{3}); \textsuperscript{11}B\{\textsuperscript{1}H\} NMR (128 MHz, CDCl\textsubscript{3}, \delta): 67.6 (s); \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (101 MHz, CDCl\textsubscript{3}, \delta): 151.5 (Mes*-C-\textit{o}-t-Bu), 148.6 (Mes*-C-\textit{p}-t-Bu), 143.5 (br, Ph-\textit{C}=\textit{B}), 139.0 (Ph-CH), 136.8 (br, Mes*-\textit{C}=\textit{B}), 131.0 (Ph-\textit{C}H), 127.3 (Ph-\textit{C}H), 121.9 (Mes*-CH), 38.1 (\textit{p}-t-Bu-C(CH\textsubscript{3})\textsubscript{3}), 34.8 (\textit{p}-t-Bu-C(CH\textsubscript{3})\textsubscript{3}), 31.5 (\textit{o}-t-Bu-C(CH\textsubscript{3})\textsubscript{3}); MS (EI, 70 eV): \textit{m}/\textit{z} (%) = 410.2 (M\textsuperscript{+}, 29), 231.2 (\textit{[BH\textsubscript{2}(Ph-\textit{i}-Pr-(t-Bu)\textsubscript{2})]}\textsuperscript{+}, 100); HRMS: calcd for C\textsubscript{30}H\textsubscript{39}B: 410.3139, found: 410.3148; UV–vis (CH\textsubscript{2}Cl\textsubscript{2}): \textit{\lambda}_{\text{abs, max}} = 251 (\varepsilon = 17383 L \text{ mol}^{-1} \text{ cm}^{-1}), 271 (\varepsilon = 19437 L \text{ mol}^{-1} \text{ cm}^{-1}); fluorescence (CH\textsubscript{2}Cl\textsubscript{2}): non-emissive.

Dimeric compounds 2

\textbf{General procedure for the synthesis of 2.} To a solution of \textbf{7} (1 mmol) in dichloromethane (1 mL) was added TMS-NTf\textsubscript{2} (10 mol \%) at room temperature. A solution of \textbf{4} (1 mmol) dissolved in dichloromethane (1 mL) was added and stirred over night. The resulting solution was evaporated to dryness and subsequently redissolved in toluene (1.5 mL). To this solution a solution (TipLi) or a suspension (Mes*Li) of the lithiated arene (1.1 mmol) in toluene (1.5 mL) was added at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred over night. The resulting suspension was diluted with \textit{n}-pentane and quenched by adding water. The organic phase was washed with brine, dried over MgSO\textsubscript{4}, and the solvent was removed in vacuo. The solid crude product was subjected to column chromatography (silica; \textit{n}-hexane) to give \textbf{2} as a colorless solid.

\textbf{2aaa}^{\text{Tip}}: Yield: 46 \%; m.p. 173 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, \delta): 7.98 (dd, \textit{J} = 4.5 Hz, \textit{J} = 1.0 Hz, 2H, Th-\textit{H}), 7.95 (dd, \textit{J} = 3.5 Hz, \textit{J} = 1.0 Hz, 2H, Th-\textit{H}), 7.86 (s, 2H, Th-\textit{H}), 7.34 (dd, \textit{J} = 3.5, 4.5 Hz, 2H, Th-\textit{H}), 7.03 (s, 4H, Tip-\textit{H}), 2.97 (sept, \textit{J} = 6.8 Hz, 2H, \textit{p}-i-Pr-CH\textit{H}), 2.55 (sept, \textit{J} = 6.8 Hz, 4H, \textit{o}-i-Pr-CH\textit{H}), 1.34 (d, \textit{J} = 6.8 Hz, 12H, \textit{p}-i-Pr-CH\textit{H}), 1.05–1.09 (m, \textit{J} = 6.8 Hz, 24H, \textit{o}-i-Pr-CH\textit{H}); \textsuperscript{11}B\{\textsuperscript{1}H\} NMR
(128 MHz, CDCl₃, δ): 58 (s); \(^{13}\text{C}[^1\text{H}]\) NMR (101 MHz, CDCl₃, δ): 155.9 (br, Th-C-B), 149.5 (Tip-C-o-i-Pr), 148.7 (Tip-C-p-i-Pr), 145.4 (br, Th-C-B), 142.6 (Th-CH), 142.1 (Th-CH), 139.1 (br, Tip-C-B), 138.1 (Th-CH), 129.1 (Th-CH), 120.0 (Tip-CH), 35.5 (o-i-Pr-CH), 34.2 (p-i-Pr-CH), 24.2 (o-i-Pr-CH₃), 24.1 (p-i-Pr-CH₃); MS (SIMS, 70 eV): m/z (%): 676.0 (M⁺, 100); elem. anal. calcd (%) for C_{23}H_{29}B_{2}S_{2}: C 74.47, H 8.68; UV–vis (THF): λ_{abs,max} = 330 (ε = 19366 L mol⁻¹ cm⁻¹), 370 (ε = 23931 L mol⁻¹ cm⁻¹); fluorescence (THF): non-emissive.

\[2\text{aba}^{\text{Mes*}}\]: Yield: 20%; m.p. 257 °C; \(^1\text{H}\) NMR (400 MHz, CDCl₃, δ): 7.76 (d (br), \(^3\text{J} = 4.5\) Hz, 2H, Th-H), 7.71 (br, 2H, Fur-H), 7.45 (s, 4H, Mes*-H), 7.28 (br, 2H, Th-H), 7.12 (t (br), \(^3\text{J} = 4.0\) Hz, 2H, Th-H), 1.41 (s, 18H, p-tBu-CH₃), 1.15 (s, 36H, o-tBu-CH₃); \(^{11}\text{B}[^1\text{H}]\) NMR (128 MHz, CDCl₃, δ): 51.0 (br); \(^{13}\text{C}[^1\text{H}]\) NMR (101 MHz, CDCl₃, δ): 169.4 (Fur-C-B), 151.9 (Mes*-C-o-tBu), 148.4 (Mes*-C-p-tBu), 146.9 (br, Th-C-B), 141.8 (Fur-CH), 136.0 (Th-CH), 133.7 (br, Mes*-C-B), 128.3 (Th-CH), 126.9 (Th-CH), 122.2 (Mes*-CH), 38.5 (tBu-C(CH₃)₃), 34.7 (o-tBu-C(CH₃)₃), 31.5 (p-tBu-C(CH₃)₃); MS (EI, 70 eV): m/z (%): 744.3 (M⁺, 98), 370.2 ([([BH]₂Fur(Ph₂-(i-Pr)])], 57), 323.2 (BFur-Mes*), 271.2 ([([BH]₂Fur(Ph₂-(CH=CH₃)])], 43), 231.2 ([Ph-(i-Bu)₂-(i-Pr)]⁻), 100); HRMS: calcd for C₄₈H₆₆B₂OS₂: 744.4754, found: 744.4752; UV–vis (THF): λ_{abs,max} = 298 (ε = 16427 L mol⁻¹ cm⁻¹), 306 (ε = 16466 L mol⁻¹ cm⁻¹), 346 (ε = 30261 L mol⁻¹ cm⁻¹); fluorescence (THF): non-emissive.

\[2\text{bab}^{\text{Mes*}}\]: Yield: 20%; m.p. 196 °C; \(^1\text{H}\) NMR (400 MHz, CDCl₃, δ): 7.85 (d (br), \(^3\text{J} = 1.3\) Hz, 2H, Fur-H), 7.64 (br, 2H, Th-H), 7.41 (s, 4H, Mes*-H), 7.26 (s, 2H, Fur-H), 6.55 (dd, \(^3\text{J} = 1.5, 3.3\) Hz, 2H, Fur-H), 1.37 (s, 18H, p-tBu-CH₃), 1.11 (s, 36H, o-tBu-CH₃); \(^{11}\text{B}[^1\text{H}]\) NMR (128 MHz, CDCl₃, δ): 48.6 (s); \(^{13}\text{C}[^1\text{H}]\) NMR (101 MHz, CDCl₃, δ): 165.0 (br, Fur-C-B), 151.9 (Mes*-C-o-tBu), 156.6 (br, Th-C-B), 148.5 (Mes*-C-p-tBu), 148.2 (Fur-CH), 142.1 (Th-CH), 133.8 (br, Mes*-C-B), 128.0 (Fur-CH), 122.2 (Mes*-CH), 111.6 (Fur-CH), 38.4 (tBu-C(CH₃)₃), 34.5 (o-tBu-C(CH₃)₃), 31.2 (p-tBu-C(CH₃)₃); MS (EI, 70 eV): m/z (%): 728.3 (M⁺, 100), 406.2 ([BFur-θi-Mes*],
24), 323.2 (BFur-Mes*, 16), 307.2 ([BFurThi- (Ph- (i-Pr)-(CH-CH3)]}, 33), 281.2 ([BHFur(Ph-(i-Pr3)]; 19), 231.2 ([Ph- (t-Bu)-(i-Pr)]; 67); HRMS: calcd for C48H66B2O2S: 728.4977, found: 728.4976; UV–vis (THF): $\lambda_{abs,max} = 302$ ($\varepsilon = 17140$ L mol$^{-1}$ cm$^{-1}$), 348 ($\varepsilon = 31350$ L mol$^{-1}$ cm$^{-1}$), 361 ($\varepsilon = 38738$ L mol$^{-1}$ cm$^{-1}$); fluorescence (THF): non-emissive.

2bbbMes*: Yield: 14 %; m.p. 202 °C; $^1$H NMR (400 MHz, DCM-D2, $\delta$): 7.76 (br, 2H, Fur-H), 7.47 (s, 4H, Mes*-H), 7.21 (br, 2H, Fur-H), 7.17 (br, 2H, Fur-H), 6.47 (br, 2H, Fur-H), 1.41 (s, 18H, p-t-Bu-CH3), 1.13 (s, 36H, o-t-Bu-CH3); $^{11}$B{$^1$H} NMR (128 MHz, CDCl3, $\delta$): 49 (s); $^{13}$C{$^1$H} NMR (101 MHz, DCM-D2, $\delta$): 169.2 (br, Fur-C), 164.2 (br, Fur-C), 152.9 (Mes*-C-o-t-Bu), 149.4 (Mes*-C-p-t-Bu), 148.7 (Fur-C), 133.3 (Mes*-C-B), 128.1 (Fur-C), 122.6 (Mes*-CH), 112.4 (Fur-C), 38.7 (o-t-Bu-C-CH3), 35.3 (p-t-Bu-C-CH3), 34.5 (o-t-Bu-C-CH3), 31.8 (p-t-Bu-C-CH3); MS (EI, 70 eV): m/z (%) = 712.8 (M$^+$, 67), 231.4 ([BFur(Ph-(t-Bu)2CCH3)]; HRMS calcd (%) for C48H66B2O3: 712.5198, found:712.5194, UV–vis (THF): $\lambda_{abs,max} = 359$ ($\varepsilon = 40492$ L mol$^{-1}$ cm$^{-1}$); fluorescence (THF): $\lambda_{em,max}$ ($\lambda_{ex} = 360$ nm) = 385 nm ($\phi_\ell = 3$ %).

Trimeric compounds 10

**Synthesis of 9aaTip.** To a solution of 1aaTip (380 mg, 1.00 mmol) dissolved in Et2O (7.5 mL) was added t-butyllithium (1.7 M, 1.24 mL, 2.10 mmol) at −78 °C, and the reaction mixture was stirred at this temperature for 4 h. After complete lithiation, chlorotrimethylsilane (240 mg, 2.2 mmol) was added. The cooling bath was removed, and the reaction mixture was stirred overnight at room temperature. The colorless precipitate was removed by filtration and extracted with Et2O (5mL). All volatiles were removed in vacuo, and the obtained dark violet solid was purified by recrystallization from n-hexane/CH2Cl2. Compound 9aaTip was obtained as a colorless crystalline solid (m.p. 191 °C). Yield: 443 mg (0.84 mmol, 84 %); $^1$H-NMR (400 MHz, CDCl3, $\delta$): 7.88 (d, $^3$J = 3.5 Hz, 2H, Th-H), 7.45 (d, $^3$J = 3.5 Hz, 2H, Th-H), 7.05
(s, 2H, Tip-H), 3.01 (sept, 3J = 7.0 Hz, 1H, p-i-Pr-H), 2.50 (sept, 3J = 6.8 Hz, 2H, o-i-Pr-H), 1.40 (d, 3J = 7.0 Hz, 6H, p-i-Pr-CH3), 1.10 (d, 3J = 6.8 Hz, 12H, o-i-Pr-CH3), 0.42 (s, 18H, Si(CH3)3). 11B[1H] NMR (128 MHz, CDCl3, δ): 55.6 (s); 13C[1H] NMR (101 MHz, CDCl3, δ): 154.5 (Th-C-Si(CH3)3), 151.0 (br, Th-C-B), 149.9 (Tip-C-o-i-Pr), 148.6 (Tip-C-p-i-Pr), 143.3 (Th-CH), 140.0 (br, Tip-C-B), 135.7 (Th-CH), 120.2 (Tip-CH), 35.5 (o-i-Pr-CH3), 34.5 (p-i-Pr-CH3), 24.6 (o-i-Pr-CH3), 24.5 (p-i-Pr-CH3), 0.3 (Si(CH3)3); MS (El, 70 eV): m/z (%): 524.4 ([M+22], 368.4 ([BTh(Ph2(THi)(TMS)]2+)+, 294.3 ([BTh(Ph-(i-Pr)])2+, 147.2 ([BTh(Ph-(i-Pr)])2+, 27); elem. anal. calcd (%) for C29H45BS2Si2: C 66.37, H 8.64, found: C 65.49, H 8.81, UV–vis (THF): λabs,max = 296 nm (ε = 10334 L mol⁻¹ cm⁻¹), 341 nm (ε = 35233 L mol⁻¹ cm⁻¹); fluorescence (THF): non-emissive.

Synthesis of 9abMes⁺. To a solution of 1abMes⁺ (2.32 g, 5.75 mmol) dissolved in Et₂O (44 mL) was added t-butyllithium (1.7 M, 6.95 mL, 11.80 mmol) via dropping funnel at -78 °C. After the resulting mixture had been stirred for 2 h at -78 °C and 30 min at 0 °C, chlorotrimethylsilane (1.28 g, 11.80 mmol) was slowly added at -78 °C and the mixture was stirred over night at ambient temperature. The colorless precipitate was removed by filtration. All volatiles were removed in vacuo and the crude product was purified by column chromatography (silica, n-hexane), which gave 9abMes⁺ as a colorless crystalline solid (m.p. 124 °C). Yield: 2.95 g (5.35 mmol, 93%); 1H NMR (400 MHz, CDCl3, δ): 7.69 (br, 1H, Th-CH), 7.44 (s, 2H, Mes*-H), 7.30 (d, 3J = 3.5, 1H, Th-CH), 7.11 (d (br), 1H, Fur-CH), 6.72 (d, 3J = 3.3, 1H, Fur-CH), 1.42 (s, 9H, p-tBu-CH3), 0.17 (s, 18H, o-tBu-CH3), 0.38 (s, 9H, Th-Si(CH3)3), 0.36 (s, 9H, Fur-Si(CH3)3), 11B[1H] NMR (128 MHz, CDCl3, δ): 49.6 (s); 13C[1H] NMR (101 MHz, CDCl3, δ): 169.2 (br, Fur-C-B), 166.6 (Fur-C-Si), 152.7 (br, Th-C-B), 152.1 (Th-C-Si), 151.9 (Mes*-C-o-tBu), 148.1 (Mes*-C-p-tBu), 142.2 (Th-CH), 134.7 (Th-CH), 134.3 (br, Mes*-C-B), 127.4 (Th-CH), 122.0 (Mes*-CH), 120.7 (Fur-CH), 38.5 (tBu -C(CH3)3), 34.6 (o-tBu-C(CH3)3), 31.5 (p-tBu-C(CH3)3), 0.0 (Th-Si(CH3)3), −1.5 (Fur-Si(CH3)3), MS (El, 70 eV): m/z (%): 550.3 (M+, 100), 535.3 ([BFurThi(TMS)][(Ph-(t-Bu)2-(i-Pr)]), 31), 493.2 ([BFurThi(TMS)]2-(Ph-(t-Bu)2-(i-Pr)]2, 26), 379.2 ([BFurThiTMS-(Ph-(i-Pr)-(CH-CH3)]), 36), 231.2 ([Ph-(t-Bu)2-(i-Pr)], 55); HRMS:
Synthesis of 9bb$^{\text{Mes}^*}$. To a solution of 1bb$^{\text{Mes}^*}$ (390 mg, 1.00 mmol) dissolved in Et$_2$O (7.5 mL) was added $t$-butyllithium (1.7 M, 1.21 mL, 2.05 mmol) at $-78^\circ$C, and the reaction mixture was stirred at this temperature for 2 h, followed by 30 min at 0 °C. After complete lithiation, chlorotrimethylsilane (223 mg, 2.05 mmol) was added at $-78^\circ$C. The cooling bath was removed, and the reaction mixture was stirred over night at room temperature. The colorless precipitate was removed by filtration. All volatiles were removed in vacuo and the brownish crude product was subjected to column chromatography (silica; n-hexane) to give 9bb$^{\text{Mes}^*}$ as a colorless solid (m.p. 112 °C).

Yield: 334 mg (0.62 mmol, 62 %); $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.41 (s, 2H, Mes$^*$H), 7.21 (br, 2H, Fur-H), 6.72 (d, $^3$J = 3.3 Hz, 2H, Fur-H), 1.40 (s, 9H $p$-t-Bu-C$_3$H$_3$), 1.15 (s, 18H, $o$-t-Bu-C$_3$H$_3$), 0.29 (s, 18H, Si($\text{C}_3$H$_3$)$_3$); $^{11}$B($^1$H) NMR (128 MHz, CDCl$_3$, $\delta$): 47.8 (s); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, $\delta$): 168.3 (Fur-C), 166.5 (Fur-Si), 152.1 (Mes$^*$-C-$o$-t-Bu), 148.0 (Mes$^*$-C-$p$-t-Bu), 133.5 (Mes$^*$-C-B), 127.4 (Fur-C), 121.3 (Mes$^*$-CH), 120.7 (Fur-CH), 38.1 ($o$-t-Bu-C-C$_3$H$_3$), 34.7 ($p$-t-Bu-C-C$_3$H$_3$), 34.0 ($o$-t-Bu-C$_3$H$_3$), 31.5 ($p$-t-Bu-C$_3$H$_3$), $-1.6$ (Si(CH$_3$)$_3$); MS (EI, 70 eV): m/z (%) = 534.6 ([M$^+$, 81], 379.5 ([BFurSiMe$_3$ Ph-($t$-Bu)$_2$($i$-Pr)], 53), 231.4 ([BH$_2$Ph-($i$-Pr)-($t$-Bu)$_2$], 74), 147.2 ([BTh(Ph-($i$-Pr)$_2$)]$^+$, 81); HRMS (EI, 70 eV): calcd for C$_{31}$H$_{51}$BO$_2$Si$_2$: 543.3517, found: 543.3518; UV–vis (THF): $\lambda_{\text{abs,max}}$ 331 nm ($\varepsilon = 26195$ L mol$^{-1}$ cm$^{-1}$); fluorescence (THF): non-emissive.

General procedure for the synthesis of 10. To a solution of 9 (1 mmol) in dichloromethane (1 mL) was added TMS-NTf$_2$ (10 mol %) at room temperature. A solution of 4 (1 mmol) dissolved in dichloromethane (1 mL) was added and stirred over night. The resulting solution was evaporated to dryness and was subsequently redissolved in toluene (1.5 mL). To this solution a solution (TipLi) or a suspension (Mes$^*$Li) of the lithiated arene (1.1 mmol) in toluene (1.5 mL) was added at $-78^\circ$C. The reaction mixture was slowly warmed to
room temperature and stirred over night. The resulting suspension was
diluted with n-pentane and quenched by adding water. The organic
phase was washed with brine, dried over MgSO₄, and the solvent was
removed in vacuo. The solid crude product was subjected to column
chromatography (silica; n-hexane) to give 10 as a slight yellow powder.

10aaaa¹H NMR (400 MHz, CDCl₃, δ): 7.85–7.97 (m, 8H, Th-H), 7.33 (dd, 3J = 3.8, 4.8 Hz, 2H, Th-H), 7.01 (s, 4H, Tip-H), 7.00 (s, 2H, Tip-H), 2.95 (m, 3H, p-i-Pr-CH₂), 2.52 (m, 6H, o-i-Pr-CH₂), 1.32–1.34 (m, 18H, p-i-Pr-CH₃), 1.03–1.08 (m, 36H, o-
i-Pr-CH₃); ¹³B{¹H} NMR (128 MHz, CDCl₃, δ): 57 (br); ¹³C{¹H} NMR
(101 MHz, CDCl₃, δ): 156.8 (br, Th-C-B), 155.9 (br, Th-C-B), 149.5 (Tip-C-o-i-Pr), 149.4 (Tip-C-o-i-Pr), 148.7 (Tip-C-p-i-Pr), 145.4 (br, Th-
C-B), 142.6 (Th-CH), 142.0 (Th-CH), 139.0 (br, Tip-C-B), 138.2 (Th-
CH), 138.1 (Th-CH), 129.1 (Th-CH), 120.1 (Tip-CH), 120.0 (Tip-CH),
35.7 (o-i-Pr-CH), 35.5 (o-i-Pr-CH), 34.2 (p-i-Pr-CH), 24.1–24.2 (o-i-Pr-
CH₃, p-i-Pr-CH₃); MS (SIMS, 70 eV): m/z (%) = 972.8 (M⁺, 100); elem.
anal. calcd (%) for C₂₃H₂₉BS₂: C 74.30, H 8.18, found: C 74.28, H 8.19;
UV–vis (THF): λabs,max = 301 (ε = 18015 L mol⁻¹ cm⁻¹), 337 (ε = 21762
L mol⁻¹ cm⁻¹), 372 (ε = 34908 L mol⁻¹ cm⁻¹), 387 (ε = 35783 L mol⁻¹
cm⁻¹); fluorescence (THF): non-emissive.

10aaab¹H NMR (400 MHz, CDCl₃, δ): 7.61–7.90 (m, 6H, Th-H, Fur-H), 7.46 (s, 4H, Mes*-H), 7.43 (s, 2H, Mes*-H), 7.21 (dd, 3J = 3.8, 4.8 Hz, 2H, Th-H), 7.18 (br, 1H, Th-H),
7.07 (t (br), 3J = 3.8 Hz, 2H, Th-H), 1.38–1.43 (s, 27H, p-tBu-CH₃), 1.16–
1.18 (s, 54 H, o-tBu-CH₃); ¹³B{¹H} NMR (128 MHz, CDCl₃, δ): no signal
detectable; ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 169.2 (Fur-C-B), 157.7
(br, Th-C-B), 156.8 (br, Th-C-B), 151.7–152.0 (Mes*-C-o-tBu), 148.5
(Mes*-C-p-tBu), 148.2 (br, Th-C-B), 142.0 (br, Fur-C-H), 141.3 (br,
Fur-C-H), 136.3 (br, Th-CH), 135.9 (Th-CH), 135.2 (br, Mes*-C-B),
134.0 (br, Mes*-C-B), 133.6 (br, Mes*-C-B), 128.3 (Th-CH), 122.1–
122.5 (Mes*-CH), 38.4–38.5 (tBu-CH(CH₃)₃), 34.7–34.9 (o-tBu-C(CH₃)₃),
31.4–31.5 (p-tBu-C(CH₃)₃); MS (SIMS, 70 eV): m/z (%) = 1083.2 (M⁺,
100); elem. anal. calcd (%) for C₇₀H₉₇B₃OS₃: C 77.62, H 9.03, found:
C 77.38, H 9.09; UV–vis (THF): $\lambda_{\text{abs,max}} = 366$ ($\varepsilon = 32313$ L mol$^{-1}$ cm$^{-1}$), 381 ($\varepsilon = 42516$ L mol$^{-1}$ cm$^{-1}$); fluorescence (THF): non-emissive.

Attempted synthesis of $10\text{babb}^{\text{Mes}^*}$: MS (SIMS, 70 eV): $m/z$ (%) = 1051.1 ($M^+$, 100)

**Polymeric compounds 3**

**General procedure for the synthesis of 3 (Route A).** To a solution of 7 (1 mmol) in pentane (2 mL) was added BBr$_3$ (1 mmol) at −78 °C. The resulting suspension was stirred for 2 h maintaining −78 °C. Then, the mixture was warmed to 0 °C and was stirred until a solution was formed (15 min). All volatiles were removed in vacuo at 0 °C to yield crude 8, which was subsequently redissolved in dichloromethane (2 mL). TMS-NTf$_2$ (5 mol%) was added and the reaction had been stirred for 3 d at room temperature. After evaporating to dryness, the resulting solid residue was dispersed in toluene (3 mL). To this dispersion a solution (TipLi) or a suspension (Mes*Li) of the lithiated arene (1.25 mmol) in toluene (3 mL) was added at room temperature. The reaction mixture had been stirred for 3 d at room temperature. The resulting suspension was diluted with $n$-pentane and quenched by adding water. The organic phase was washed with brine, dried over MgSO$_4$, and the solvent was removed in vacuo. The solid crude product was purified by precipitation in pentane/ethanol to yield 3 as a slight yellow ($3a^{\text{Tip}}$) or brown ($3b^{\text{Mes}^*}$) solid.

$8a$: $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.90 (d, $^3J = 3.5$ Hz, 1H, Th-H)$^i$, 7.02 (d, $^3J = 3.5$ Hz, 1H, Th-H)$^i$, 0.11 (s, 9H, Si(CH$_3$)$_3$); $^{11}$B$^{[1]}$H$^i$ NMR (128 MHz, CDCl$_3$): 47.6 (s).
8b: $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.67 (d, $^3J = 3.6$ Hz, 1H, Fur-H), 6.79 (d, $^3J = 3.6$ Hz, 1H, Fur-H), 0.35 (s, 9H, Si(CH$_3$)$_3$); $^{11}$B($^1$H) NMR (128 MHz, CDCl$_3$): 45.0 (s).

General procedure for the synthesis of 3’ (Route B). To a solution of 9 (1 mmol) in pentane (10 mL) was added BBr$_3$ (1 mmol) at $-78$ °C. The cooling bath was removed and the reaction had been stirred for 30 min at room temperature. After addition of dichloromethane (4 mL) the reaction had been stirred for another hour at room temperature. The resulting solution was evaporated to dryness and was subsequently redissolved in dichloromethane (b) or o-dichlorobenzene (a) (2 mL). TMS-NTf$_2$ (5 mol%) was added and the reaction had been stirred for 3 d at room temperature. After evaporating to dryness the resulting solid residue was dispersed in toluene (3 mL). To this dispersion a solution (TipLi) or a suspension (Mes*Li) of the lithiated arene (1.25 mmol) in toluene (3 mL) was added at room temperature. The reaction mixture had been stirred for 3 d at room temperature. The resulting suspension was diluted with $n$-pentane and quenched by adding water. The organic phase was washed with brine, dried over MgSO$_4$, and the solvent was removed in vacuo. The solid crude product was purified by precipitation in pentane/ethanol to yield 3’ as a slight yellow (3a'^Tip) or brown (3b'^Mes') solid.

3a'^Tip: Yield: 35 %, $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.95–7.87 (br, 8H, Th-H), 7.42 (d, br, 1H, from partial cleavage of the silyl end group), 6.99 (br, 10H, Tip-H), 2.93 (br, 5H, $p$-i-Pr-CH$_3$), 2.50 (br, 9H $o$-i-Pr-CH$_3$), 1.31 (br, 30H $p$-i-Pr-CH$_3$), 1.03 (br, 54H, $o$-i-Pr-CH$_3$), 0.36 (s, 9H, Si(CH$_3$)$_3$ end group); $^{11}$B($^1$H) NMR (128 MHz, CDCl$_3$): no signal detectable; $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, $\delta$): 156.9 (br, Th-C-B), 149.4 (Tip-C-$o$-i-Pr), 148.6 (Tip-C-$p$-i-Pr), 143.3, 142.3 (Th-C), 141.9, 139.1 (br, Tip-C-B), 135.6 (Th-C), 122.1, 120.1 (Tip-C-H), 35.8 ($o$-i-Pr-C-H), 34.2 ($p$-i-Pr-C-H), 24.1 ($i$-Pr-CH$_3$), −0.1 (Si(CH$_3$)$_3$); $^{29}$Si($^1$H) NMR (79.5 MHz, CDCl$_3$, $\delta$): $-6.02$; UV–vis (THF): $\lambda_{abs,max} = 409$ nm ($\varepsilon = 160180$ L mol$^{-1}$ cm$^{-1}$); fluorescence (THF): $\lambda_{em,max}$ ($\lambda_{ex} = 411$ nm) = 421 nm ($\Phi_f = 0.6$ %).

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3a**Tip**: Yield: 68 %; \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 7.86–7.93 (br, 14H, Tip-H), 6.96 (br, 20H, Tip-H), 2.91 (br, 10H, \(p\)-i-Pr-C\(\_\)H), 2.48 (br, 20H \(o\)-i-Pr-C\(\_\)H), 1.30 (br, 60H \(p\)-i-Pr-C\(\_\)H\(_3\)), 1.00 (br, 106H, \(o\)-i-Pr-C\(\_\)H\(_3\)), 0.35 (s, 9H, Si(CH\(_3\))\(_3\) end group); \(^{11}\)B[\(^1\)H] NMR (128 MHz, CDCl\(_3\)): no signal detectable; \(^{13}\)C[\(^1\)H] NMR (101 MHz, CDCl\(_3\), \(\delta\)): 156.9 (br, Th-C), 149.4 (Tip-C-\(o\)-i-Pr), 148.6 (Tip-C-\(p\)-i-Pr), 143.3, 142.3 (Th-C), 141.9, 139.1 (br, Tip-C-B), 135.6 (Th-C), 122.1, 120.1 (Tip-C-H), 35.8 (\(o\)-i-Pr-C-H), 34.2 (\(p\)-i-Pr-C-H), 24.1 (\(i\)-Pr-C\(\_\)H\(_3\)), -0.1 (Si(CH\(_3\))\(_3\)); \(^{29}\)Si[\(^1\)H] NMR (79.5 MHz, CDCl\(_3\), \(\delta\)): -6.02; UV–vis (THF): \(\lambda_{\text{abs,max}} = 412\) nm (\(\varepsilon = 299291\) L mol\(^{-1}\) cm\(^{-1}\)); fluorescence (THF): \(\lambda_{\text{em,max}} (\lambda_{\text{ex}} = 420\) nm) = 455 nm (\(\Phi_t = 0.8\) %).

3b**Mes**: Yield: 13 % \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 7.36 (br, Mes\(^*\)H), 7.25 (s, Fur-H, from partial cleavage of the silyl end group), 6.95 (br, Fur-H), 1.35–1.32 (br, \(p\)-t-Bu-C\(\_\)H\(_3\)), 1.05 (br, \(o\)-t-Bu-C\(\_\)H\(_3\)), 0.20 (br, Si(CH\(_3\))\(_3\)); \(^{11}\)B[\(^1\)H] NMR (128 MHz, CDCl\(_3\)): no signal detectable; \(^{13}\)C[\(^1\)H] NMR (101 MHz, CDCl\(_3\), \(\delta\)): 168.8 (br, Fur-C-B), 152.1 (Mes\(^*\)-C-(CH\(_3\))\(_3\)), 149.9 (Fur-C), 148.4, 132.4, 127.6 (br, Mes\(^*\)-C-B), 121.6 (Mes\(^*\)-C-H), 119.5 (Fur-C), 38.2, 34.3 (\(o\)-t-Bu-C-CH\(_3\)), 31.5 (\(p\)-t-Bu-C-CH\(_3\)), 1.7 (Si(CH\(_3\))\(_3\)); \(^{29}\)Si[\(^1\)H] NMR (79.5 MHz, CDCl\(_3\), \(\delta\)): no signal detectable; UV–vis (THF): \(\lambda_{\text{abs,max}} = 407\) nm (\(\varepsilon = 73340\) L mol\(^{-1}\) cm\(^{-1}\)); fluorescence (THF): \(\lambda_{\text{em,max}} (\lambda_{\text{ex}} = 412\) nm) = 422 nm (\(\Phi_t = 70.3\) %).

3b**'Mes**: Yield: 31%; \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 7.31-7.46 (br, 2H, Mes\(^*\)H), 6.92 (br, 2H, Fur-H), 1.27–1.50 (br, 9H, \(p\)-t-Bu-C\(\_\)H\(_3\)), 0.87-1.16 (br, 17H, \(o\)-t-Bu-C\(\_\)H\(_3\)), 0.20 (br, Si(CH\(_3\))\(_3\)); \(^{11}\)B[\(^1\)H] NMR (128 MHz, CDCl\(_3\)): no signal detectable; \(^{13}\)C[\(^1\)H] NMR (101 MHz, CDCl\(_3\), \(\delta\)): 168.8 (br, Fur-C-B), 152.1 (Mes\(^*\)-C-(CH\(_3\))\(_3\)), 149.9 (Fur-C), 148.4, 132.4, 127.6 (br, Mes\(^*\)-C-B), 121.6 (Mes\(^*\)-C-H), 119.5 (Fur-C), 38.2, 34.3 (\(o\)-t-Bu-C-CH\(_3\)), 31.5 (\(p\)-t-Bu-C-CH\(_3\)), 1.7 (Si(CH\(_3\))\(_3\)); \(^{29}\)Si[\(^1\)H] NMR (79.5 MHz, CDCl\(_3\), \(\delta\)): no signal detectable; UV–vis (THF): \(\lambda_{\text{abs,max}} = 411\) nm (\(\varepsilon = 178043\) L mol\(^{-1}\) cm\(^{-1}\)); fluorescence (THF): \(\lambda_{\text{em,max}} (\lambda_{\text{ex}} = 413\) nm) = 426 nm (\(\Phi_t = 71.1\) %).
X-ray crystallographic analysis of $1\text{aa}^{\text{tip}}$, $1\text{bb}^{\text{tip}}$ and $2\text{bbb}^{\text{Mes}^*}$.

Suitable colorless single crystals of $1\text{aa}^{\text{tip}}$, $1\text{bb}^{\text{tip}}$ and $2\text{bbb}^{\text{Mes}^*}$ were obtained by slow evaporation of hexane at ambient temperature. Data were collected on a Bruker SMART APEX CCD detector on a D8 goniometer equipped with an Oxford Cryostream 700 temperature controller at 100(2) K using graphite monochromated Mo-$K_\alpha$ radiation ($\lambda = 0.71073$ Å). An absorption correction was carried out semi-empirically using SADABS$^{[32]}$ (min./max. transmissions = 0.4052/0.7446 ($1\text{aa}^{\text{tip}}$), 0.4324/0.7451 ($1\text{bb}^{\text{tip}}$), 0.5925/0.7452 ($2\text{bbb}^{\text{Mes}^*}$)). The structure was solved with Olex2$^{[33]}$ using Direct Methods (ShelXS$^{[34a]}$) and refined with the ShelXL$^{[34b]}$ refinement package by full-matrix least squares on $F^2$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included isotropically and treated as riding. The thiophene rings in $1\text{aa}^{\text{tip}}$ are splitted. Two molecules of hexane are cocrystallized in the structure of $2\text{bbb}^{\text{Mes}^*}$.

**Table S1.** Crystal structure and refinement data for $1\text{aa}^{\text{tip}}$, $1\text{bb}^{\text{tip}}$ and $2\text{bbb}^{\text{Mes}^*}$.

<table>
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<th>No.</th>
<th>$1\text{aa}^{\text{tip}}$</th>
<th>$2\text{bbb}^{\text{Mes}^*}$</th>
<th>$1\text{bb}^{\text{tip}}$</th>
</tr>
</thead>
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<tr>
<td>Color, habit</td>
<td>colorless block</td>
<td>colorless block</td>
<td>colorless block</td>
</tr>
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<td>Size/ mm</td>
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<td>$0.24 \times 0.23 \times 0.2$</td>
<td>$0.27 \times 0.27 \times 0.34$</td>
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<td>Empirical Formula</td>
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<td>$\text{C}<em>{48}\text{H}</em>{66}\text{B}_2\text{O}_3$</td>
<td>$\text{C}<em>{23}\text{H}</em>{29}\text{BO}_2$</td>
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<td>9.566(3)</td>
<td>8.692(2)</td>
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<td>Value</td>
<td>Value</td>
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<td>-----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>b/Å</td>
<td>9.0985(12)</td>
<td>15.464(5)</td>
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<td>c/Å</td>
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<td>γ/°</td>
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<td>1028.3(5)</td>
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<td>Completeness</td>
<td>1.00 to θ = 56.66</td>
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<td>Reflections: total/independent</td>
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<td>28287/9177</td>
<td>10688/3404</td>
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<td>R_int</td>
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<td>Final R1 and wR2</td>
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<td>Largest peak, hole/eÅ⁻³</td>
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<td>ρ_calculated/g cm⁻³</td>
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<td>1.125</td>
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Gel permeation chromatography (GPC)

Figure S1. GPC trace of 3a\textsuperscript{TIP} (green line: detection by UV signal; red line: detection by RI signal).

Table S2: Data of the GPC analysis of 3a\textsuperscript{TIP}.

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<td>$M_w$</td>
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<td>$M_z$</td>
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<td>2103 g/mol</td>
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<tr>
<td>$M_v$</td>
<td>1762 g/mol</td>
<td>1789 g/mol</td>
</tr>
<tr>
<td>PDI</td>
<td>1.11</td>
<td>1.10</td>
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</table>
Figure S2. GPC trace of $3\text{b}^{\text{Mes}^*}$ (green line: detection by UV signal; red line: detection by RI signal).

Table S3: Data of the GPC analysis of $3\text{b}^{\text{Mes}^*}$.

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</tr>
<tr>
<td>$M_w$</td>
<td>2891 g/mol</td>
<td>3088 g/mol</td>
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<td>$M_z$</td>
<td>4218 g/mol</td>
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<td>$M_v$</td>
<td>2891 g/mol</td>
<td>3088 g/mol</td>
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<td>PDI</td>
<td>1.54</td>
<td>1.56</td>
</tr>
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</table>
**Figure S3.** GPC trace of 3a^{Tip} (detection by UV signal failed due to technical reasons; red line: detection by RI signal).

**Table S4:** Data of the GPC analysis of 3a^{Tip}.

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<td>$M_v$</td>
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<td>PDI</td>
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Figure S4. GPC trace of 3b′\textsuperscript{Mes*} (green line: detection by UV signal; red line: detection by RI signal).

Table S5: Data of the GPC analysis of 3b′\textsuperscript{Mes*}.

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<td>PDI</td>
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</tbody>
</table>

3.2.5 References


[17] For polymers with boron-containing conjugated side groups, see, e. g.: a) Reitzenstein, D., Lambert, C. Macromolecules 2009, 42, 773; b) Nagai, A., Kokado, K., Miyake, J., Chujo, Y. Macromolecules 2009,


[25] We also attempted the synthesis of a furylborane trimer (10bbbb), which was not successful, probably due to decomposition of the intermediate formed during the catalytic reaction.

[26] In this case Mes*Li was used rather than TipLi because we found that the derivative 3bTip was unstable towards ethanol.


3.3 Mechanistic studies on the formation of diarylbromoboranes by catalytic Si/B exchange

Abstract: The development of environmental benign and selective routes for the synthesis of boron-containing functional materials is a challenging task. A well-established method for the introduction of a (hetero)aromatic ring in aryldibromoboranes 2 to yield diarylbromoboranes 3 uses tin-boron exchange reactions. However, organotin compounds and the by-product (Me₃SnBr) show pronounced toxicity. We recently presented a method to facilitate silicon-boron exchange reactions at ambient temperature, which uses the organocatalyst TMSNTf₂. Herein, we present our first studies on the mechanism of this reaction through investigations on its kinetics, and syntheses of mixed-substituted triarylborane derivatives 4. The molecular structures in the solid-state and the optical properties of the new compounds are also discussed.

(Semi)conducting materials have been the target of tremendous research activity in the last decades. Most of the materials currently used in, for example, light-emitting devices (LEDs) or field-effect transistors (FETs) are purely inorganic. The usage of organic (macro)molecules (e.g. polythiophenes) represents a reasonable and advantageous alternative in a number of applications such as organic light-emitting diodes (OLEDs, PLEDs),¹⁰ organic field-effect transistors (OFETs)² and organic photovoltaics (OPVs).³ Furthermore, organic polymers are capable of performing drug delivery⁴ and chemical sensoring.⁵ The electronic and optical properties of these compounds can be significantly altered by incorporation of inorganic atoms into the main chain.⁶ In the last few years, boron has emerged as an interesting component of π conjugated materials. Through incorporation of boron, the optical properties of organic polymers (e.g. polythiophenes and polyfurans) are changed dramatically, leading to novel compounds with desirable behavior⁷ (e.g. altered optical properties due to the lowered band gap between HOMO and LUMO).⁶ The synthesis of these compounds is, however, often challenging because of the sensitivity of the starting materials, intermediate
products and sometimes the final products, towards moisture and air. Sufficient stability of the electron-deficient boron atom can be obtained by e.g. the introduction of sterically demanding aryl substituents\textsuperscript{[8-11]} or by structural constraint.\textsuperscript{[12]}

Well-established reactions for the generation of polythiophenes, and -furans respectively, proceed via Grignard metathesis reaction or with Rieke zinc (both Kumada cross-coupling procedures\textsuperscript{[13]}) and palladium-catalyzed Suzuki-Miyaura coupling.\textsuperscript{[14]} Whereas these routes have been thoroughly studied, reactions leading to the incorporation of boron in organic polymers are poorly understood so far.

Kawashima \textit{et al.} showed that 2,4,6-trimethylphenyldi(2-thienyl)borane (I) is obtained if 2,4,6-trimethylphenyldimethoxyborane is treated with two equivalents of \textit{in situ} generated 2-thienyllithium (Scheme 1).\textsuperscript{[9]} However, this approach requires a preceding synthetic step, in which the kinetically stabilizing arene group (2,4,6-trimethylphenyl = mesityl) is introduced. Therefore, the synthesis of molecules with varying kinetically stabilizing aryl substituents requires the prior synthesis of a suitable dimethoxyborane.

\begin{equation}
\text{Scheme 1. Different methods for the introduction of heteroaromatic moieties in boron-containing molecules. Top: Kawashima \textit{et al.}\textsuperscript{[9]; Bottom: Jäkle \textit{et al.}\textsuperscript{[10]}}}
\end{equation}

A different synthetic protocol was presented by Jäkle \textit{et al.}\textsuperscript{[10]} They used boron tribromide which reacts first with 2-trimethylsilylthiophene to yield compound 2a. Silicon-boron exchange reactions represent a versatile method for the introduction of (hetero)aryl groups (e.g. phenyl, 2-thienyl, 2-furyl, etc.), but also amino groups, by substitution of the first halogen in BBr\textsubscript{3} or BCl\textsubscript{3}, respectively. They often proceed smoothly under mild conditions in a selective manner. For the introduction of a further (hetero)aryl substituent, the reactivity of trimethylsilyl substituted (hetero)arenes is insufficient at ambient temperature. In the case of phenyl, high reaction temperatures and a
sealed Young vessel are required.\textsuperscript{[15]} Jäkle \textit{et al.} used tin-boron exchange for the preparation of Mes\textsuperscript{*} stabilized boron moieties in (macro)molecules (Scheme 1). Although the reaction proceeds smoothly at ambient temperature, the major drawback of this route is the toxicity of the applied organotin compound (II) and the organotin by-product (Me\textsubscript{3}SnBr).

Recently, we presented a method in which a metal-free catalyst was used in a homogenous catalytic reaction.\textsuperscript{[11]} In this reaction, a trimethylsilyl substituted thiophene \textbf{1a}, furan \textbf{1b}, or benzene \textbf{1c} is used to introduce a second aryl group in the corresponding (hetero)aryldibromoborane compounds \textbf{2} (Scheme 2). The reaction to yield the symmetric thiophene compound \textbf{3aa} occurs at ambient temperature and is complete within 72 min. The volatile by-product, Me\textsubscript{3}SiBr, is easily removed under reduced pressure and the toxicity of the starting materials and the by-product is low in comparison to the organotin compounds.

Herein, we present our first investigations on the kinetics of the reaction of 2-trimethylsilylthiophene \textbf{1a} with the dibromo(2-thienyl)borane \textbf{2a} to give the di(2-thienyl)bromoborane \textbf{3aa} under catalytic conditions, using TMSNTf\textsubscript{2} as a potent catalyst. The dependence of the reaction rate on the total concentration, catalyst loading and the respective starting materials is discussed. Furthermore, two new mixed-substituted compounds \textbf{3ac} and \textbf{3bc} as well as their kinetically stabilized 2,4,6-tri-\textit{tert}-butylphenyl substituted derivatives are characterized (by means of NMR spectroscopy, single crystal X-ray diffraction and UV-vis spectroscopy).

The kinetic reactions were carried out at ambient temperature, with a total concentration of 1 M and a catalyst loading of 5 mol\% (standard reaction conditions; see Scheme 2).
Scheme 2: Overview of the catalytic formation of 3.

The kinetic measurements were carried out on the catalytic formation of 3aa. For this purpose, different parameters (total concentration, amount of catalyst, stoichiometry) of the standard reaction were changed in order to determine certain dependencies of the reaction rate, which were investigated using reaction progress analysis as detailed by Blackmond.\(^{[16]}\)

Monitoring the reaction of 1a with 2a using \(^1\)H NMR spectroscopy revealed a selective reaction to the desired product within 72 min.\(^{[11]}\) The only by-product in this reaction was TMSBr, of which the \(^1\)H NMR signal served as a reference to determine the conversion of the starting materials. First, we varied the total concentration of the reactants to find out whether or not product inhibition occurs. After monitoring with \(^1\)H NMR spectroscopy, it was found, that doubling the concentration resulted in a shortened reaction time (by the factor of two). After determination of the reaction rates (for the standard reaction (SR) and the reaction with a total concentration of 2 M), we plotted the reaction rates against the concentration of 1a (Figure 1). The slope of regression for SR is 1.293 and for the 2 M reaction 1.295. This demonstrates, that the catalytic reaction is 1\(^{st}\) order in the concentration and no product inhibition occurs.\(^{[16]}\)

The next dependence, which was investigated, was the amount of catalyst applied. Three different catalyst loadings were used (2.5 mol\%, 5 mol\% (SR), and 15 mol\%). After monitoring with \(^1\)H NMR spectroscopy, the reaction rate was determined and plotted against the concentration.
Figure 1. Plot of the reaction rate against the concentration for the standard reaction (1 M, 5 mol% catalyst) (left) and the reaction with a concentration of 2 M (right). Regression fitted mathematically and displayed as a red line.

After normalizing these results with the catalyst concentration, the turn over frequency (TOF) was correlated with the total concentration (Figure 2).

Figure 2: Plot of the turn over frequencies of the catalytic reactions of 1a with 2a to give 3aa with different concentrations of the catalyst against the concentration of 1a.

The regression lines are almost parallel to each other, with slopes of 1.307 (catalyst loading: 2.5 mol%), 1.293 (catalyst loading: 5 mol%),
and 1.320 (catalyst loading: 15 mol%). The slopes of the reaction with 2.5 mol% of catalyst and 15 mol% catalyst only show a small deviation from that for the standard reaction. This emphasizes, that the dependence of the catalytic reaction on the catalyst loading is also 1st order and, consequently, the catalyst is not desactivated in the course of the reaction.\textsuperscript{[16]}

Furthermore, we attempted to identify the reaction order with respect to the two starting materials 1a and 2a. However, our investigations did not afford an integer reaction order for either one of them. In this context, it is important to note that the \textsuperscript{1}H NMR spectra of the reaction solutions displayed an additional signal at 0.47 ppm that cannot be assigned to neither the product nor the reactants (Figure 3). The \textsuperscript{1}H NMR spectrum showed three high-field signals. The signal at 0.66 ppm was assigned to TMSBr formed during the catalytic reaction. The protons of the trimethylsilyl group of 1a show a resonance at 0.40 ppm. In order to identify the signal at 0.47 ppm, first experiments were carried out involving the mixture of either 2a or 1a with the catalyst. Neither of these two mixtures showed a similar nor identical resonance in the \textsuperscript{1}H NMR spectrum. Only if all three components (1a, 2a, and catalyst) are present, this species is formed. Efforts to isolate it failed, though. It decomposed upon removal of the solvent or varying the temperature. Even when the reaction mixture was kept at room temperature without any manipulation carried out, it reacted further within 6 hours to the desired product 3aa and TMSBr (no other signals are present at the end). Therefore, we assume that this species is an intermediate of the reaction between 1a and 2a.
Figure 3: $^1$H NMR spectrum of the standard reaction after 15 min. Detail of the resonances provided by the protons of the trimethylsilyl substituents.

We believe that the catalytic reaction solely proceeds via Si/B-exchange, but a reaction via C–H-activation at the 5-position might occur to some extent in addition. In this case, a second product (3aa$^{\text{'}}$) is formed (Scheme 3).
Scheme 3. Two different reaction paths in the catalytic reaction between 1a and 2a to form 3aa. Left: Reaction via C–H-activation. Right: Reaction via Si/B exchange.

The resonance in the $^1$H NMR spectrum of the standard reaction after 15 min (Figure 3) at 0.47 ppm might be assigned to 3aa’. The electron-withdrawing effect of the substituted boron moiety should result in a down-field shift of the protons of the trimethylsilyl substituent at the 5-position of the thiophene ring in 3aa’, compared to 1a. At the end of the reaction, 3aa’ reacts with HNTf$_2$, formed in situ, to 3aa. Since the isolation of 3aa’ was not achieved from catalytic reactions of 1a with 2a, a reaction between 2,5-bis(trimethylsilyl)-thiophene (5a) and 2a was carried out. 5a does not inherit the possibility of undergoing a reaction via C–H-activation and, therefore, 3aa’ should be the only product at the end of the reaction (Scheme 4).

Scheme 4. Catalytic reaction of 2a with 5a to obtain 3aa’.

In fact, this reaction proceeded smoothly and the $^1$H NMR spectrum of the completed reaction displayed a high-field signal at 0.46 ppm (Figure 4). This resonance we assign to the protons of the trimethylsilyl substituent at the 5-position of the thiophene ring in 3aa’. After derivatization with Mes*Li, aqueous work-up and subjecting the crude product to column chromatography, 4aa’ was obtained as a colorless solid. We analyzed the product using NMR spectroscopy ($^1$H, $^{11}$B, $^{13}$C, $^{29}$Si), elemental analysis and mass spectrometry (EI).
Figure 4. $^1$H NMR spectrum of the reaction of 5a with 2a (5 mol% of TMSNTf$_2$).

In order to get a better understanding of the process, TMSNTf$_2$ (5 mol%) was added to a solution of 2a in DCM-D$_2$ at room temperature. This mixture was then analyzed by $^1$H and $^{11}$B NMR spectroscopy (Figure 5).

Figure 5. Reaction of 2a with 5 mol% TMSNTf$_2$. $^{11}$B NMR spectrum (main) and detail of the $^1$H NMR spectrum (inlet).
Besides the signal at 47.6 ppm, assigned to $2a$, there is an additional signal in the $^{11}\text{B}$ NMR spectrum at 40.5 ppm, which might be assigned to $2a'$. The corresponding $^1\text{H}$ NMR spectrum shows two signals in the highfield-region (0.62 ppm: TMSNTf$_2$; 0.60 ppm: TMSBr) with almost equal intensity. It is noticeable that the generation of TMSBr occurs over an extended period of time. After 30 min, no change in intensities was observed. Based upon these results it is likely that the first reaction is an equilibrium where the catalyst reacts with $2a$ under substitution of a bromide with NTf$_2^-$ to give species $2a'$ (Scheme 3). NTf$_2^-$ is a weakly coordinating anion and $2a'$ shows a reactivity similar to borinium cations. Therefore, $2a'$ can be classified as a “masked” borinium cation.

In the next step, $1a$ was added to the same vessel and the catalytic reaction to form $3aa$ was monitored by NMR spectroscopy. The $^{11}\text{B}$$\{^1\text{H}\}$ NMR spectrum of the substitution of a bromide by NTf$_2^-$ and the subsequent addition of $1a$ differed in their signal pattern (Figure 6).

![Figure 6. $^{11}\text{B}$$\{^1\text{H}\}$ NMR spectrum of a mixture of $2a$ and TMSNTf$_2$ before (bottom) and after (top) addition of $1a$.](image)

The signal previously detected at 40.7 ppm disappeared and a signal at 31.6 ppm arised after the addition of $1a$. Therefore, we assume that
this new signal is assigned to an intermediate of the catalytic reaction. After addition of 1a the “masked” borinium cation reacts under formation of the final product 3aa and the catalyst is regained (Scheme 5).

![Scheme 5. Proposed catalytic cycle for the formation of 3aa.](image)

Although we were neither able to identify nor isolate the putative intermediate, we found that its formation occurs more readily and faster than the substitution of a bromide in 2a by NTf$_2^-$ (from TMSNTf$_2$). Our investigations, so far, have shown that the reaction is dependent on both starting materials, therefore, it is not possible to easily conclude which reaction step is the rate-determining one. Presumably, this is a result of the two possible reaction paths leading to 3aa. The “excess” concentration is defined as the concentration difference of the two starting materials in a non-stoichiometric reaction. Using reaction progress analysis,[16] no congruence between the regression lines of the standard reaction and the reactions with different “excess” concentrations was found for neither of the two starting materials 1a
and 2a. In order to verify which reaction step is the slower one, we performed experiments where we either used less electron-rich aryl substituents at the dibromo(hetero)arylboration 2, or more as well as less electron-rich aryl substituents at 1 (Scheme 2). The results obtained by monitoring with 1H NMR spectroscopy are summarized in table 1.

Table 1. Observed reaction times for the formation of corresponding 3.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound 1</th>
<th>Compound 2</th>
<th>Total reaction time under standard reaction conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>2a</td>
<td>72 min</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>2c</td>
<td>54 min</td>
</tr>
<tr>
<td>3</td>
<td>1c</td>
<td>2a</td>
<td>a</td>
</tr>
<tr>
<td>4</td>
<td>1b</td>
<td>2c</td>
<td>≤7 min (^b)</td>
</tr>
<tr>
<td>5</td>
<td>1c</td>
<td>2c</td>
<td>3 d (^c)</td>
</tr>
</tbody>
</table>

\(^a\)After 1 d the reaction was stopped at 33% conversion. \(^b\)7 min is the time between preparation and first NMR measurement. \(^c\)95% conversion with 25 mol% catalyst and a total concentration of 4 M.

The first entry in the table represents the standard reaction for the formation of 3aa. In the following entry, the dibromoborane was changed to dibromophenylborane 2c. In comparison to thiophene, the phenyl substituent in 2c is less electron-rich. Therefore, the boron atom is more Lewis acidic and more readily undergoes reactions with a nucleophile. The reaction time was reduced from entry 1 to entry 2. This demonstrates the influence of the Lewis acidity on the reaction time and led us to the conclusion that the catalyst first reacts with 2 under formation of a Lewis-acid-base adduct with subsequent elimination of TMSBr. While the influence of compound 2 was remarkable, the influence of compound 1 on the reaction time was even larger. The complementary reaction using 1c and 2a (instead of
1a and 2c), with a less electron-rich aryl substituent (phenyl), was significantly slower. This catalytic reaction showed a conversion of 33% to 3ac after one day. The use of the more electron-rich furan in 1b, compared to thiophene in 1a, accelerates the reaction dramatically (entry 4; table 1). In fact, the reaction was complete in less than 7 minutes. It was not possible to determine the exact reaction time because the time between preparation of the experiment and the NMR measurement could not be shortened any further. Compounds 3ac and 3bc were subsequently reacted with Mes*Li in toluene to yield the mixed substituted species 4ac and 4bc (Scheme 6).

![Scheme 6: Post-modification of 3 with Mes*Li to form 4.](image)

The reaction occurs readily at room temperature over night. After filtration from insoluble inorganic salts and evaporation of the solvent to dryness, the crude reaction products were subjected to column chromatography on silica to yield 4ac and 4bc as colorless solids. The constitution of 4ac and 4bc was ascertained by $^1$H, $^{11}$B, $^{13}$C NMR spectroscopy, mass spectrometry (EI and high resolution), UV-vis spectroscopy and single crystal X-ray diffraction (Figure 7). The $^{11}$B NMR spectra showed a resonance at 61.2 ppm (4ac) and 56.4 ppm (4bc), respectively (Appendix; Figure A3.17 and A3.20). Both compounds show a downfield shift compared to the previously described dithienyl and difuryl compounds Thi₂BTip (Thi = 2-thienyl; Tip = 2,4,6-tri-iso-propylphenyl) and Fur₂BMes* (Fur = 2-furyl; Mes* = 2,4,6-tri-tert-butylphenyl),[11] which can be explained by the less electron-rich phenyl substituent in 4ac and 4bc. The single crystal X-
ray diffraction data obtained for 4ac, however, were poor and the structure could not be sufficiently refined. N, it was possible to confirm the constitution via powder diffraction analysis.

**Figure 7.** Ortep plot of the molecular structure of 4ac (right) and 4bc (left) in the solid state with ellipsoids drawn at 50 % probability level (hydrogen atoms omitted for clarity).

Comparing the structures of 4ac and 4bc with the previously described structures of Ph₂BMes⁺ (4cc) (Ph = phenyl) and Fur₂BMes⁺,[11] as well as the dithienyl compound (Thi₂BMes⁺) described by Jäkle et al.[10] revealed significant differences in the coplanarity between the heteroaryl substituents. The interplanar angle of 4ac is 31.3° (14.4° for 4bc), which is significantly larger than in the corresponding Thi₂BMes⁺ (19.0°). However, it is lower than in the diphenyl species 4cc (43.8°).

This indicates a better π interaction, which results in a red-shift of the absorption maximum relative to 4cc (Figure 8). The trend that the interplanar angle increases upon substitution of a heteroaromatic ring by a phenyl group, also becomes apparent in 4bc in comparison to the difurfyl species.[11] The sterically demanding aryl substituent and the BC₃ plane show an almost perpendicular arrangement (4ac: 88.4°; 4bc: 87.7°), similar to the symmetrical compounds (Fur₂BMes⁺, Ph₂BMes⁺, and Thi₂BMes⁺).[10,11]
The absorption maximum of 4cc is shifted to lower wavelength relative to 4aa, 4ac, and 4bc. For 4ac and 4bc only a small difference of about 5 nm was observed. In comparison, the absorption maximum of 4aa lies at 325 nm. As already mentioned, the incorporation of different aryl substituents at the boron centers has a strong influence on the optical properties of the compounds. This results in the possibility of synthesizing conjugated organoboron materials with tailored properties.

In conclusion, our investigations revealed that the reaction kinetics to form 3aa is more complex than it appears on the first sight. Nevertheless, we were able to determine the order of the reaction with respect to the amount of catalyst applied (1st order) and the total concentration of the solution (1st order). However, it was not possible to determine the reaction order with respect to the two starting materials. The reason for this behavior, presumably, lies in the formation of an intermediate species, which either facilitates the reaction or reacts on a different way to form 3aa.

By using 2c in reactions with 1a and 1b, we clarified that the nature of the arenes has a significant impact on the reaction rate. The silylated compounds substituted with electron-rich arenes reacted more readily to form the corresponding compound 3 than their congeners with
electron-poor arenes. However, electron-poor aryl substituents at the dibromoborane species also accelerated the reaction, leading to the conclusion that the catalyst and the borane form a Lewis-acid-base adduct in the first step of the reaction.

The incorporation of benzene, instead of furan or thiophene, changed the optical behavior of the products significantly. This should lead to materials with tailored properties. Our preliminary kinetic investigations provide first insight into the mechanism of the B–C bond formation process via catalytic Si/B exchange. Furthermore, they will build the basis for the development of further, more sophisticated catalytic approaches using even less harmful starting materials (e.g. BCl₃) and yielding less harmful by-products (TMSCl). Current investigations using a different catalyst seem promising.

3.3.1 Experimental Section

**General procedures.** All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques or in an MBraun glovebox. Solvents (dichloromethane, n-pentane, diethylether, toluene, and) were dried and degassed by means of a MBraun SPS-800 solvent purification system. Deuterated solvents for NMR spectroscopy were dried and degassed at reflux over CaH₂ (CDCl₃ and CD₂Cl₂) and freshly distilled prior to use. Solvents for aqueous work-up (n-hexane, n-pentane), 2-bromothiophene, tribromoborane, lithium bis(trifluoromethylsulfonyl)imide, bromobenzene, sulfuric acid, and magnesium turnings were purchased from commercial sources and used as received. Solutions of n-butyllithium (1.6 M in hexane and 2.5 M in hexane, respectively) were purchased from Sigma Aldrich and used as received as well. Chlorotrimethylsilane, 2-bromo-1,3,5-triisopropylbenzene and furan were commercially purchased and freshly distilled prior to use. 2-Bromofuran,[¹⁷] trimethylsilyl bis(trifluoromethylsulfonyl)imide,[¹⁸] 2,4,6-triisopropylphenyllithium,[¹⁹] 2-bromo-1,3,5-tri-tert-butylnzene[²⁰] and 2,4,6-tri-tert-butyphenyllithium[¹⁰] were prepared according to methods described in the literature. Compounds 1a, 1b, 1c, 2a, 2c, were prepared according to a procedure previously described by our
Kinetical measurements were carried out according to a method described in the literature¹⁶ using NMR spectroscopy. NMR spectra were recorded at 25 °C on a Bruker Avance II-400 spectrometer or on a Bruker Avance III HD spectrometer operating at 400 MHz. Chemical shifts were referenced to residual protic impurities in the solvent (¹H) or the deuterio solvent itself (¹³C) and reported relative to external SiMe₄ (¹H, ¹³C) or BF₃·OEt₂ (¹¹B) standards. Mass spectra were obtained with the use of a Finnigan MAT95 spectrometer employing electron ionization (EI) using a 70 eV electron impact ionization source or secondary ionization (SIMS). Elemental analysis was performed with a CHN-O-Rapid VarioEL by Heraeus. UV-vis spectra were obtained using a Jasco V-630 spectrophotometer. Melting points (uncorrected) were obtained using a SMP3 melting point apparatus by Stuart in 0.5 mm (o.d.) glass capillaries, which were sealed under argon.

**General procedure for the synthesis of 4.** To a solution of 1 (1 mmol) in dichloromethane (1 mL) was added TMS-NTf₂ (5 mol %) at room temperature. A solution of 2 (1 mmol) dissolved in dichloromethane (1 mL) was added and the reaction process was monitored using ¹H NMR spectroscopy. The resulting solution was evaporated to dryness to yield crude 3, which was subsequently redissolved in toluene (1.5 mL). To this solution a solution (TipLi) or a suspension (Mes*Li) of the lithiated arene (1.1 mmol) in toluene (1.5 mL) was added at –78 °C. The reaction mixture was slowly warmed to room temperature and stirred over night. The resulting suspension was diluted with n-pentane and quenched by adding water. The organic phase was washed with brine, dried over MgSO₄, and the solvent was removed in vacuo. The solid crude product was subjected to column chromatography (silica; n-hexane) to give 4 as a colorless solid.

₃aa: ¹H NMR (400 MHz, CDCl₃, δ): 8.22 (dd, ³J = 3.8 Hz, ⁴J = 1.0 Hz, 2H, Th-H), 8.02 (dd, ³J = 4.8 Hz, ⁴J = 1.0 Hz, 2H, Th-H), 7.38 (dd, ³J = 3.8, 4.8 Hz, 2H, Th-H); ¹¹B(¹H) NMR (128 MHz, CDCl₃, δ): 49.7 (s).
3ac: $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.07–8.11 (m, 4H, (Ph-H (2H), Th-H (2H)), 7.58–7.63 (m, 1H, Ph-H), 7.48–7.52 (m, 2H, Ph-H), 7.39 (dd, $^3J = 3.8$, 4.5 Hz, 1H, Th-H); $^{11}$B$[^1]$H NMR (128 MHz, CDCl$_3$, $\delta$): 57.6 (s).

3bc: $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.34 (m, 2H, Ph-H), 8.01 (m, 1H, Fur-H), 7.78 (m, 1H, Fur-H), 7.58–7.63 (m, 1H, Ph-H), 7.47–7.52 (m, 2H, Ph-H), 6.65 (dd, $^3J = 1.5$, 3.5 Hz, 1H, Fur-H); $^{11}$B$[^1]$H NMR (128 MHz, CDCl$_3$, $\delta$): 53.2 (s).

4aa: Yield: 69%; m.p. 141 °C; $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.94 (dd, $^3J = 4.8$ Hz, $^4J = 1.0$ Hz, 2H, Th-H), 7.90 (dd, $^3J = 3.5$ Hz, $^4J = 1.0$ Hz, 2H, Th-H), 7.32 (dd, $^3J = 3.5$, 4.8 Hz, 2H, Th-H), 7.06 (s, 2H, Tip-H), 3.00 (sept, $^3J = 7.0$ Hz, 1H, $p$-i-Pr-CH$_2$), 2.56 (sept, $^3J = 6.8$ Hz, 2H, $o$-i-Pr-CH$_2$), 1.38 (d, $^3J = 7.0$ Hz, 6H, $p$-i-Pr-CH$_3$), 1.10 (d, $^3J = 6.8$ Hz, 12H, $o$-i-Pr-CH$_3$); $^{11}$B$[^1]$H NMR (128 MHz, CDCl$_3$, $\delta$): 56.1 (s); $^{13}$C$[^1]$H NMR (101 MHz, CDCl$_3$, $\delta$): 149.6 (Tip-C-0-i-Pr), 148.6 (Tip-C-p-i-Pr), 145.1 (br, Th-C-B), 142.1 (Th-CH), 139.2 (br, Tip-C-B), 137.2 (Th-CH), 128.9 (Th-CH), 120.0 (Tip-CH), 35.2 (o-i-Pr-CH), 34.2 (p-i-Pr-CH), 24.2 (o-i-Pr-CH$_3$), 24.1 (p-i-Pr-CH$_3$); MS (EI, 70 eV): $m/z$ (%) = 380.2 (M$^+$, 80), 296.2 ([BThTIP]$^+$, 39), 253.2 ([BTh(Ph-0-i-Pr)$_2$]$^+$, 211.2 ([BTh(Ph-0-i-Pr)]$^+$, 55), 177.1 ([BTh(Ph-0-i-Pr)]$^+$, 21); elem. anal. calcd (%) for C$_{23}$H$_{29}$BS$_2$: C 72.62, H 7.68, found: C 72.77, H 7.71; UV–vis (THF): $\lambda_{abs,max} = 263$ ($\varepsilon = 7254$ L mol$^{-1}$ cm$^{-1}$), 275 ($\varepsilon = 8643$ L mol$^{-1}$ cm$^{-1}$), 325 nm ($\varepsilon = 24227$ L mol$^{-1}$ cm$^{-1}$); fluorescence (THF): $\lambda_{em,max}$ ($\lambda_{ex} = 325$ nm) = 410 nm ($\phi = 3.1$ %).

4ac: Yield: 36%; m.p. 164 °C; $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.12 (br, 2H, Ph-H), 7.85 (dd, $^3J = 4.7$, $^4J = 1.0$ Hz, 1H, Th-H), 7.64 (d, $^3J = 3.6$, $^4J = 1.0$ Hz, 1H, Th-H), 7.40–7.48 (m, 3H, Ph-H), 7.45 (s, 2H, Mes*-H), 7.21 (dd, $^3J = 4.7$, 3.6 Hz, 1H, Th-H), 1.41 (s, 9H, $p$-tBu-CH$_3$), 1.13 (s, 18 H, $o$-tBu-CH$_3$); $^{11}$B$[^1]$H NMR (128 MHz, CDCl$_3$, $\delta$): 61.2 (s); $^{13}$C$[^1]$H NMR (101 MHz, CDCl$_3$, $\delta$): 151.5 (Mes*-C-0-tBu), 148.5 (Mes*-C-p-tBu), 147.9 (br, Th-C-B), 143.6 (br, Ph-C-B), 141.9 (Th-CH), 138.0 (Ph-
CH), 136.3 (br, Mes*-C-B), 135.6 (Th-CH), 130.8 (Ph-CH), 128.2 (Ph-CH), 127.7 (Ph-CH), 122.3 (Mes*-CH), 38.4 (tBu-C(CH₃)₃), 34.9 (o-tBu-C(CH₃)₃), 31.4 (p-tBu-C(CH₃)₃); MS (EI, 70 eV): m/z (%) = 416.2 (M⁺, 100), 317.2 ([BThiPh(Ph-(i-Pr)-(CH-CH₃))]+, 62), 247.2 ([BThiPh₂], 96), 231.2 ([Ph-(t-Bu)₂-(i-Pr)], 40); HRMS: calcd for C₂₈H₃₇BS: 416.2704, found: 416.2712; UV–vis (THF): λ_{abs,max} = 303 nm (ε = 14089 L mol⁻¹ cm⁻¹); fluorescence (THF): non-emissive.

4bc: Yield: 36%; m.p. 152 °C; ¹H NMR (400 MHz, CDCl₃, δ): 8.11 (br, 2H, Ph-H), 7.85 (dd, ³J = 1.5, ⁴J = 0.5 Hz, 1H, Fur-H), 7.38–7.48 (m, 3H, Ph-H), 7.45 (s, 2H, Mes*-H), 7.07 (d, ³J = 3.3 Hz, 1H, Fur-H), 6.52 (dd, ³J = 1.5, 3.3 Hz, 1H, Fur-H), 1.41 (s, 9H, p-tBu-C(CH₃)₃), 1.13 (s, 18 H, o-tBu-C(CH₃)₃); ¹¹B{¹H} NMR (128 MHz, CDCl₃, δ): 56.4 (s); ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 165.6 (br, Fur-C), 151.7 (Mes*-C-O-tBu), 148.4 (Mes*-C-p-tBu), 148.0 (Fur-C), 143.1 (br, Ph-C), 138.2 (Ph-C), 134.8 (Mes*-C-B), 130.9 (Ph-C), 128.8 (Fur-C), 127.6 (Ph-C), 122.1 (Mes*-CH), 111.3 (Fur-C), 38.3 (tBu-C(CH₃)₃), 34.5 (o-tBu-C(CH₃)₃), 31.5 (p-tBu-C(CH₃)₃); MS (EI, 70 eV): m/z (%) = 400.2 (M⁺, 100), 385.2 ([BFurPh(Ph-(i-Pr)-(CH-CH₃))]), 32), 281.2 ([BFur(Ph-(i-Pr))]), 44), 231.2 ([Ph-(t-Bu)₂-(i-Pr)]), 40); HRMS: calcd for C₂₈H₃₇BO: 400.2932, found: 400.2933; UV–vis (THF): λ_{abs,max} = 298 nm (ε = 19052 L mol⁻¹ cm⁻¹); fluorescence (THF): non-emissive.

X-ray crystallographic analysis of 4ac and 4bc. Suitable colorless single crystals of 4ac and 4bc were obtained by slow evaporation of hexane at ambient temperature. Data were collected on a Bruker SMART APEX CCD detector on a D8 goniometer equipped with an Oxford Cryostream 700 temperature controller at 100(2) K using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). An absorption correction was carried out semi-empirically using SADABS[21] (min./max. transmissions = 0.5960/0.7445 (4b), 0.6404/0.7454 (4c)) The structure was solved with Olex2[22] using Direct Methods (ShelXS[23a]) and refined with the ShelXL[23b] refinement package by full-matrix least squares on F². All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included isotropically and treated as riding.
**Table S1.** Crystal structure and refinement data for **4ac** and **4bc**.

<table>
<thead>
<tr>
<th>No.</th>
<th><strong>4ac</strong></th>
<th><strong>4bc</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Color, habit</td>
<td>colorless block</td>
<td>colorless rod</td>
</tr>
<tr>
<td>Size/ mm</td>
<td>$0.28 \times 0.25 \times 0.19$</td>
<td>$0.31 \times 0.17 \times 0.16$</td>
</tr>
<tr>
<td>Empirical Formula</td>
<td>$C_{28}H_{37}BS$</td>
<td>$C_{28}H_{37}BO$</td>
</tr>
<tr>
<td>M</td>
<td>416.45</td>
<td>400.39</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/n$</td>
<td>$P2_1/n$</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>8.971 (4)</td>
<td>8.9375 (19)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>10.004 (5)</td>
<td>10.055 (2)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>27.418 (13)</td>
<td>26.850 (6)</td>
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<tr>
<td>$\alpha$/°</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>$\beta$/°</td>
<td>90.078 (9)</td>
<td>91.115 (4)</td>
</tr>
<tr>
<td>$\gamma$/°</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>V/Å³</td>
<td>2461 (2)</td>
<td>2412.4 (9)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$\mu$/mm⁻¹</td>
<td>0.144</td>
<td>0.064</td>
</tr>
<tr>
<td>T/K</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$\theta_{\text{min, max}}$</td>
<td>2.17, 17.42</td>
<td>2.16, 18.79</td>
</tr>
<tr>
<td>Completeness</td>
<td>1.00 to $\theta = 41.76$</td>
<td>0.99 to $\theta = 52.98$</td>
</tr>
<tr>
<td>Reflections: total/independent</td>
<td>17130/2593</td>
<td>28717/4956</td>
</tr>
</tbody>
</table>
\begin{table}
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{R_{int}} & 0.0865 & 0.0767 \\
\hline
\textbf{Final } \textit{R1} \text{ and } w\textit{R2} & 0.0812, 0.2287 & 0.0599, 0.1688 \\
\hline
\textbf{Largest peak, } \text{hole/eÅ}^{-3} & 1.32, –0.45 & 0.41, –0.25 \\
\hline
\textbf{\(\rho_{calc}\)/g cm}^{-3} & 1.124 & 1.102 \\
\hline
\end{tabular}
\caption{}
\end{table}

3.3.2 Kinetical Measurements

**General procedure for the kinetical analysis of 3aa.** To a solution of 1a (78.2 mg; 0.5 mmol) in deuterated dichloromethane (0.25 mL) was added TMSNTf2 (8.8 mg; 0.025 mmol) at ambient temperature. This solution was transferred into a NMR tube. A second solution of 2a (126.9 mg; 0.5 mmol) in deuterated dichloromethane (0.25 mL) was added and the reaction progress of the resulting solution had been monitored using \(^1\)H NMR spectroscopy. The conversion to the desired product was determined by the decreasing intensity of the trimethylsilyl signal of 1a and further verified by the increasing intensity of the resulting trimethylbromosilane signal.
Different catalyst concentrations

2.5 mol%

**Figure S1.** Plot of the concentration of 1a against time (catalyst concentration = 0.024 M).

**Figure S2.** Plot of the reaction rate against time (catalyst concentration = 0.024 M).
Figure S3. Plot of the reaction rate against the concentration of 1a (catalyst concentration = 0.024 M).

5 mol%

Figure S4. Plot of the concentration of 1a against time (catalyst concentration = 0.048 M).
Figure S5. Plot of the reaction rate against time (catalyst concentration = 0.048 M).

Figure S6. Plot of the reaction rate against the concentration of 1a (catalyst concentration = 0.048 M).
15 mol%

**Figure S7.** Plot of the concentration of 1a against time (catalyst concentration = 0.154 M).

**Figure S8.** Plot of the reaction rate against time (catalyst concentration = 0.154 M).
Figure S9. Plot of the reaction rate against the concentration of 1a (catalyst concentration = 0.154 M).

Figure S10. Plot of the normalized turn over frequency (TOF) against the concentration of 1a. The different linear fits exhibit parallelity.
Table S2. Slope of the linear fits for the different catalytic concentrations applied.

<table>
<thead>
<tr>
<th>Amount of catalyst / %</th>
<th>Slope of the linear fit / mol L$^{-1}$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>1.307</td>
</tr>
<tr>
<td>5</td>
<td>1.293</td>
</tr>
<tr>
<td>15</td>
<td>1.330</td>
</tr>
</tbody>
</table>

5 mol% (overall concentration 2 mol L$^{-1}$)

Figure S11. Plot of the concentration of 1a against time (catalyst concentration = 0.088 M).
Figure S12. Plot of the reaction rate against time (catalyst concentration = 0.088 M).

Figure S13. Plot of the reaction rate against the concentration of 1a (catalyst concentration = 0.088 M). Normalized slope of regression = 1.295 mol L$^{-1}$ min$^{-1}$.
3.3.3 References


3.4 Electronic and Steric Effects that Govern the Structures of Aryl(dithienyl)boranes in the Solid State

**Abstract:** The incorporation of boron in extended $\pi$ conjugated materials is a promising way to obtain new materials with interesting optical properties. In ArB(Thi)$_2$ ($Ar = Mes$, Tip) two thienyl substituents (Thi) are in conjugation over a boron atom. The sterically demanding aryl substituent ($Ar$) serves the purpose of kinetically stabilizing the compounds against moisture and air. So far, only little is known about the influence of such kinetically stabilizing aryl substituents on the structures of such compounds in the solid state. Herein, the influence of 2,4,6-trimethylphenyl (Mes) and 2,4,6-triisopropylphenyl (Tip) as kinetically stabilizing aryl substituents is demonstrated. Furthermore, a versatile synthetic protocol for the introduction of trimethylsilyl and iodine as substituents in the 5-position at the thiophene rings is presented.

The synthesis of functional materials with incorporated boron moieties has developed as a promising way to obtain materials with unique and tunable optical and electrochemical properties.$^{[1]}$ The Lewis acidity of boron modifies the properties of such materials by interaction of the empty $p_\pi$ orbital with $\pi$ electron density provided by (hetero)aromatic ring systems through delocalization.$^{[2]}$ In order to yield macromolecular systems, it is necessary to develop new synthetic protocols for the preparation of functionalized precursor molecules. For that purpose, it is crucial to design materials that are stable towards air and moisture. Generally, stability against moisture and air can be achieved by introduction of kinetically stabilizing arene groups.$^{[3]}$ By substitution with a Mes (2,4,6-trimethylphenyl), Tip (2,4,6-triisopropylphenyl), or Mes* (2,4,6-tri-tert-butylphenyl) group, the boron center is often shielded sufficiently.

Jäkle and co-workers have presented (macro)molecules, in which boron moieties stabilized with Mes* are bridged by organic building blocks (Scheme 1).$^{[3b]}$ For the synthesis of such polymeric materials, a substitution of the 5,5'-positions of the starting materials is required (Scheme 1). For example, 5,5'-diiodo-2,2'-dithienyl-(2,4,6-tri-tert-butylphenyl)borane 3b$^{[3b]}$ can undergo subsequent Suzuki-Miyaura
coupling\textsuperscript{[\textdegree]} with a suitable reactant to yield polymers with exciting properties (Scheme 1). Also, the substitution with trimethylsilyl groups inherits the possibility of different further manipulations.\textsuperscript{[\textdegree]\text{c}} Both substituents are of significant interest, since they are easy to introduce, chemically robust, and the resulting polycondensation by-products are easily removed to afford pure products.

\textbf{Scheme 1}: Suzuki-Miyaura coupling reaction presented by Jäkle \textit{et al.}\textsuperscript{[\textdegree]b}

Herein, we present a general synthetic protocol for the introduction of iodine and trimethylsilyl groups as possible leaving groups in up-following reactions. Furthermore, we performed first investigations on the influence of the sterically demanding aryl group, as well as the substitution at the 5,5\textsuperscript{-}-positions on the structural properties of Mes- and Tip-substituted triarylboranes in the solid state, using single crystal X-ray diffraction experiments.

The synthesis of 2,4,6-trimethylphenyl-di(2-thienyl)borane\textsuperscript{[\textdegree]a} (MesBThi\textsubscript{2}, 1), 2,4,6-triisopropylphenyl-dithienylborane\textsuperscript{[\textdegree]c} (TipBThi\textsubscript{2}, 2), and 2,4,6-tri-\textit{tert}-butylphenyl-dithienylborane\textsuperscript{[\textdegree]b} (Mes\textsuperscript{\textit{\texttt{*}}}BThi\textsubscript{2}, 3) are described in the literature and will not be discussed in this work. These molecules serve as starting materials for more complex materials, in which organoborane units are incorporated in \textit{\pi} conjugated systems. For this, it is necessary to introduce potent functional groups. We focused our research on the introduction of trimethylsilyl (TMS) and iodide groups to obtain difunctional compounds, which can be used for subsequent reactions (e.g. silicon-boron exchange or Suzuki-Miyaura coupling reactions).

The introduction of TMS and iodide started with the dilithiation of 1 and 2. Whereas the dilithiation of 3 readily occured when \textit{n}-butyllithium was used in diethylether,\textsuperscript{[\textdegree]a} the less sterically demanding substituents Mes and Tip are not shielding the boron atom sufficiently from nucleophilic attack of \textit{n}-butyllithium. Therefore, we used the sterically more
demanding t-butyllithium as a suitable deprotonating reagent (Scheme 2).

**Scheme 2.** Dilithiation and derivatization of 1 and 2 by usage of iodine and trimethylsilyl chloride.

First, 1 or 2 were dissolved in diethylether at room temperature. After cooling to –78 °C, t-butyllithium was added and the reaction mixture was stirred for 4 hours maintaining the temperature. A constant temperature is crucial during this process because of possible decomposition of the dilithiated species via self-attack. In the course of the reaction, the initially clear solution changed its color from yellow to green and precipitation was observed. The precipitate presumably corresponds to the dilithiated species 1–Li and 2–Li, respectively. In the next step, the reaction mixture was either treated with trimethylsilyl chloride (a) or iodine (b). For the reaction with elemental iodine, the reactivity was increased by dissolving iodine in THF prior to the addition. After stirring for 24 h (a) and 22 h (b), respectively, the mixtures were subjected to aqueous work-up and the product was purified by column chromatography (silica; n-hexane). The pure products were obtained as colorless (1a, 2a) or yellow (1b, 2b) crystalline solids.

We analyzed the compounds via 1H, 11B, 13C NMR spectroscopy, mass spectrometry, elemental analysis and single crystal X-ray diffraction. The disilylated compounds 1a and 2a show a set of two doublets for the aromatic thiophene protons in the 1H NMR spectrum. They differ by a chemical shift of approximately 0.5 ppm. On the other hand, the compounds 1b and 2b show a multiplet in the aromatic region (Figure 1).
Figure 1. Detail of the aromatic region in the $^1$H NMR spectrum of $2b$. Apparently, the substitution of a thiophene ring with iodine at the 5-position has comparable influence on the resonance of the protons at the 4-position as the substitution by the boron moiety on the resonance of the protons at the 3-position. This leads to an overlap of the two signals. This effect is even stronger in $1b$, which shows only one broad signal with two small shoulders. Furthermore, by increasing the steric demand of the aryl substituent (Mes → Tip → Mes*[^3b]) the signals are separated slightly from each other.

The $^{11}$B NMR spectra of the compounds $1a$, $1b$, $2a$ and $2b$ show resonances at 55.4 ($1a$); 53.5 ($1b$); 55.6 ($2a$) and 54.2 ($2b$) ppm. Comparing $1a$ with $2a$ does not reveal any substantial differences. The same behavior was observed for $1b$ vs. $2b$. However, a comparison of the $^{11}$B NMR spectra of the compounds with different substitution pattern (iodine vs. TMS) revealed more significant differences. Whereas the disilylated compounds have a chemical shift of ~ 55 ppm, the diiodinated compounds are slightly down-field shifted with resonances at 53.5 ppm ($1b$) and 54.2 ppm ($2b$). This effect clearly results from the ability of iodine to withdraw electron density from the thiophene rings and, therefore, resulting in a lower electron density at the boron center. The effect, however, is quite weak, which can be rationalized by the low difference in the electronegativities of iodine and carbon, and by the opposing +M-effect of iodine. In Figure 2 the molecular structures of $1a$,$b$ and $2a$,$b$ in the solid state are depicted.
A significant difference between the structures is the conformation of the thiophene rings. Whereas in 1a and 2a they have a syn arrangement, the thiophene rings in 1b and 2b show an anti arrangement. Furthermore, in 1a they adopt an arrangement with the sulfur atoms oriented towards the mesityl substituent. In 2a the sulfur atoms are directed away from the Tip group. This might be either a result of the repulsion of the iodine substituents and the Tip group or different packing effects of the structure of 2a in the solid-state compared to 1a. Compound 1a shows a dihedral angle between the benzene core of the Mes substituent to the respective BC$_3$ plane of about 80.4°, which is the lowest of the four compounds, but still large enough that the relative orientation can be regarded as almost perpendicular. Substitution with Tip leads to an increase of the dihedral angle (84.6°), clearly evidencing the steric influence of the bulkier Tip group. The B–C bond lengths also differ depending on the substitution pattern. The B–C$_{Thi}$ bond length in 1a is 1.539 Å, which is slightly larger.
than in 2a (1.533 Å, and 1.532 Å, respectively). On the other hand the B–C<sub>Tip</sub> bond length in 2a (1.587 Å) is larger than the B–C<sub>Mes</sub> bond in 1a (1.581 Å). The interplanar angles between the thiophene rings of 1a and 2a reveal significant differences. In general, the interplanar angle between the conjugated moieties serves as a good indicator for the prediction of the optical properties of the compound, since π delocalization should be favored if the angle between the planes of the thienyl substituents is small. The interplanar angle in 1a is 47.4° and, therefore, significantly larger than in 2a (10.8°). The distinct difference results from the different steric demand of the aryl group. By enhancing the sterical demand at the boron center, a direct influence on the planarity of the thiophene rings was observed, which then changes the possible optical and chemical properties.

Changing the substitution in 5,5’-position from trimethylsilyl to iodine does not significantly affect the dihedral angle between the benzene core of the aryl substituent to the respective BC<sub>3</sub> plane (1b: 81.5°, 2b: 82.4°) or B–C<sub>Mes,Tip</sub> bond lengths (1b: 1.582 Å, 2b: 1.587 Å). However, the B–C<sub>Thi</sub> bond lengths in 1b and 2b are different than in 1a and 2a. In 1b they are shortened by approximately 0.01 Å (1a: 1.539 Å, 1b: 1.529 Å). Whereas the B–C<sub>Thi</sub> bond lengths in 1b are shorter than in 1a, they are longer in 2b (1.554 Å and 1.539 Å, respectively) compared to the corresponding 2a (1.533 Å and 1.532 Å, respectively). In 1b the interplanar angle is 1.0°, meaning the thiophene rings are almost coplanar and differ dramatically from 1a (47.4°). However, the interplanar angle in 2b (7.6°) is larger than in 1b. The possible reason for such a behavior lies probably within the repulsion effect of the iodine and the Tip group. It seems that the steric influence prohibits a shorter B–C<sub>Thi</sub> bond length and favors a larger interplanar angle in the structure in the solid-state. Selected structural parameters are summarized in table 1.

Table 1. Bond lengths and interplanar angles for 1a-2b.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>Dihedral angle [°]</th>
<th>B–C&lt;sub&gt;Thi&lt;/sub&gt; [Å]</th>
<th>B–C&lt;sub&gt;Mes,Tip&lt;/sub&gt; [Å]</th>
<th>Interplanar angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>80.4</td>
<td>1.539</td>
<td>1.587</td>
<td>47.4</td>
</tr>
<tr>
<td>1b</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
We also characterized **1a-2b** by UV-vis spectroscopy. The wavelength of the maximum absorption of **1a** (342 nm) and **2a** (341 nm) (**1b** (358 nm) and **2b** (357 nm)) did not differ significantly from each other. Although the interplanar angle of these compounds showed dramatic differences (table 1), their optical properties are remarkably similar. It should be noted that the photophysical data were acquired in solution and not in the solid-state. Unequivocally, rotation of the thiophene rings is not hindered in solution at ambient temperature, which has been ascertained using $^1$H NMR spectroscopy (Appendix; Figures A4.1, A4.4, A4.7, A4.10). As a result, the interplanar angle does not serve as a reliable indicator for the optical properties of these compounds. Whereas the substitution with different kinetically stabilizing aryl groups led to similar optical behavior, varying substitution at the 5,5´-positions resulted in considerable differences (Figure 3).

![Figure 3. UV-vis spectrum of 1a (blue) and 1b (red).](image)
The UV-vis spectrum of 1b is red-shifted (16 nm) compared to 1a. Furthermore, neither the bis-trimethylsilyl substituted compounds, nor the diiodo substituted compounds showed any sign of fluorescence. In conclusion, we have presented a synthetic protocol to obtain 5,5´-difunctionalized Mes- and Tip-substituted di(2-thienyl)boranes, which are stable towards moisture and air. Via dilithiation and subsequent derivatization we succeeded in synthesizing compounds that are suitable precursors for the construction of extended conjugated materials (e.g. via Suzuki-Miyaura coupling; when trialkyltin is used instead, Stille coupling should be possible as well). The influence of the stericly demanding aryl group and the substitution pattern has been pointed out. We believe that these results will be helpful to understand the correlation of different substituents at the boron center with varying substitution pattern at the thiophene rings and, therefore, may lead to a possible prediction of the optical behavior of different boron-containing π conjugated materials.

3.4.1 Experimental Section

**General procedures.** All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques or in an MBraun glovebox. Solvents (dichloromethane, n-pentane, diethylether, toluene, and tetrahydrofuran) were dried and degassed by means of a MBraun SPS-800 solvent purification system. Deuterated solvents for NMR spectroscopy were dried and degassed at reflux over Na (C₆D₆) or CaH₂ (CDC₃ and CD₂Cl₂) and freshly distilled prior to use. Solvent for aqueous work-up (n-hexane) and iodine were purchased from commercial sources and used as received. A solution of t-butyllithium (1.7 M in pentane) was purchased from Sigma Aldrich and used as received as well. Chlorotrimethylsilane was commercially purchased and freshly distilled prior to use. 1,[3a] and 2[3b] were prepared according to methods described in the literature. NMR spectra were recorded at 25 °C on a Bruker Avance II-400 spectrometer or on a Bruker Avance III HD spectrometer operating at 400 MHz. Chemical shifts were referenced to residual protic impurities in the solvent (¹H) or the deuterio solvent itself (¹³C) and reported
relative to external SiMe₄ (¹H, ¹³C) or BF₃·OEt₂ (¹¹B) standards. Mass spectra were obtained with the use of a Finnigan MAT95 spectrometer employing electron ionization (EI) using a 70 eV electron impact ionization source. Elemental analysis was performed with a CHN-O-Rapid VarioEL by Heraeus. UV-vis spectra were obtained using a Jasco V-630 spectrophotometer.

**Synthesis of 1a.** To a solution of 1 (592 mg, 2.0 mmol) in diethyl ether (20 mL) was added a solution of t-butyllithium (1.7 M, 2.4 mL, 4.2 mmol) at −78 °C. After maintaining the reaction temperature for 4 h, the resulting suspension was treated with chlorotrimethylsilane (478 mg, 4.4 mmol) at −78 °C. The reaction was slowly warmed to ambient temperature and had been stirred over night. After filtration from insoluble material and extraction twice with diethyl ether (2 x 10 mL) the combined organic phases were evaporated to dryness. The crude product was subjected to column chromatography (silica; n-hexane) to yield 1a as a colorless crystalline solid. Yield: 310 mg (0.7 mmol, 35 %); m.p. 108 °C; ¹H-NMR (400 MHz, CDCl₃, δ): 7.91 (d, ³J = 3.3 Hz, 2H, Th-H), 7.45 (d, ³J = 3.3 Hz, 2H, Th-H), 6.92 (s, 2H, Mes-H), 2.41 (s, 3H, p-CH₃), 2.12 (s, 6H, o-CH₃), 0.41 (s, 18H, Si(CH₃)₃); ¹¹B{¹H} NMR (128 MHz, CDCl₃, δ): 55.4 (s); ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 154.8 (Th-C–Si(CH₃)₃), 149.5 (br, Th-C–B), 142.6 (Th-CH), 142.0 (br, Mes-C–B), 138.3 (Mes-C-ο-CH₃), 136.8 (Mes-C-ρ-CH₃), 135.7 (Th-CH), 126.9 (Mes-CH), 22.8 (Mes-C-ο-CH₃), 21.5 (Mes-C-ρ-CH₃), −0.1 (Si(CH₃)₃); MS (EI, 70 eV): m/z (%) = 439.8 (M⁺, 26), 367.8 ([BTh₂TMSMes]⁺, 44), 283.9 ([BTh₂(PhMe₂)]⁺, 53), 211.9 ([BThMes]⁺, 72), 73.1 ([TMS]⁺, 100); elem. anal. calcd (%) for C₂₉H₄₅BS₂Si₂: C 62.69, H 7.55, found: C 62.52, H 7.47, UV–vis (THF): λabs,max = 276 nm (ε = 13712 L mol⁻¹ cm⁻¹), 284 nm (ε = 13121 L mol⁻¹ cm⁻¹), 342 (ε = 29443 L mol⁻¹ cm⁻¹); fluorescence (THF): non-emissive.

**Synthesis of 1b.** To a solution of 1 (2.96 g, 10 mmol) in diethyl ether (100 mL) was added a solution of t-butyllithium (1.7 M, 12 mL, 21 mmol) at −78 °C. After maintaining the reaction temperature for 4 h, the resulting suspension was treated with elemental iodine (5.63 g, 22 mmol) dissolved in tetrahydrofuran (15 mL) at −78 °C. The reaction
was slowly warmed to ambient temperature and had been stirred overnight. The brown reaction mixture was evaporated to dryness and the solid residue was extracted with n-pentane (3 x 50 mL). The combined organic phases were evaporated to dryness and the crude product was subjected to column chromatography (silica; n-hexane). After recrystallization in diethylether at −30 °C, 1b was obtained as a yellow crystalline solid. Yield: 2.36 g (4.3 mmol, 43 %); m.p. 115 °C; 1H-NMR (400 MHz, CDCl3, δ): 7.43 (m, 4H, Th-H), 6.86 (s, 2H, Mes-H), 2.36 (s, 3H, p-CH3), 2.06 (s, 6H, o-CH3); 11B{1H} NMR (128 MHz, CDCl3, δ): 53.5 (s); 13C{1H} NMR (101 MHz, CDCl3, δ): 150.7 (br, Th-C–B), 143.0 (Th-C), 140.0 (br, Mes-C–B), 139.5 (Th-C), 138.5 (Mes-C-o-CH3), 137.7 (Mes-C-p-CH3), 127.1 (Mes-C), 89.4 (Th–C–I), 22.6 (Mes-C-o-CH3), 21.3 (Mes-C-p-CH3); MS (El, 70 eV): m/z (%) = 547.4 (M+, 11), 417.4 ([Th2]2+, 70), 283.9 ([Th–I]2+, 100), 105.0 ([PhMe2]3, 54); elem. anal. calcd (%) for C29H45BS2Si2: C 37.26, H 2.76, found: C 37.78, H 3.04. UV–vis (THF): λabs,max = 278 nm (ε = 17614 L mol⁻¹ cm⁻¹), 347 nm (ε = 24229 L mol⁻¹ cm⁻¹); fluorescence (THF): non-emissive.

**Synthesis of 2a.** To a solution of 2 (380 mg, 1.00 mmol) in diethylether (7.5 mL) was added t-butyllithium (1.7 M, 1.24 mL, 2.10 mmol) at −78 °C, and the reaction mixture was stirred at this temperature for 4 h. After complete lithiation, chlorotrimethylsilane (240 mg, 2.2 mmol) was added. The cooling bath was removed, and the reaction mixture was stirred over night at room temperature. The colorless precipitate was removed by filtration and extracted with Et₂O (5mL). All volatiles were removed in vacuo, and the obtained dark violet solid was purified by recrystallization from n-hexane/CH₂Cl₂. Compound 2a was obtained as a colorless crystalline solid. Yield: 443 mg (0.84 mmol, 84 %); m.p. 191 °C; 1H-NMR (400 MHz, CDCl3, δ): 7.88 (d, 3J = 3.5 Hz, 2H, Th-H), 7.45 (d, 3J = 3.5 Hz, 2H, Th-H), 7.05 (s, 2H, Tip-H), 3.01 (sept, 3J = 7.0 Hz, 1H, p-i-Pr-H), 2.50 (sept, 3J = 6.8 Hz, 2H, o-i-Pr-H), 1.40 (d, 3J = 7.0 Hz, 6H, p-i-Pr-CH3), 1.10 (d, 3J = 6.8 Hz, 12H, o-i-Pr-CH3), 0.42 (s, 18H, Si(CH3)3). 11B{1H} NMR (128 MHz, CDCl3, δ): 55.6 (s); 13C{1H} NMR (101 MHz, CDCl3, δ): 154.5 (Th-C–Si(CH3)3), 151.0 (br, Th-C–B), 149.9 (Tip-C-o-i-Pr), 148.6 (Tip-C-p-i-Pr), 143.3 (Th-CH), 140.0 (br, Tip-C–B), 135.7 (Th-CH), 120.2 (Tip-CH), 35.5 (o-i-Pr-CH), 157
34.5 (p-i-Pr-CH), 24.6 (o-i-Pr-CH₃), 24.5 (p-i-Pr-CH₂), 0.3 (Si(CH₃)₃); MS (EI, 70 eV): m/z (%) = 524.4 (M⁺, 22), 368.4 ([BThSiMe₃Tip]⁺, 28), 294.3 ([BTh(Ph-(i-Pr)₂)]⁺, 100), 147.2 ([BTh(Ph-(i-Pr)₂)]²⁺, 27); elem. anal. calcd (%) for C₂₉H₄₅SiMe₃Tip: C 66.37, H 8.64, found: C 65.49, H 8.81. UV–vis (THF): λₐₙₙ = 296 nm (ε = 10334 L mol⁻¹ cm⁻¹), 341 nm (ε = 35233 L mol⁻¹ cm⁻¹); fluorescence (THF): non-emissive.

**Synthesis of 2b.** To a solution of 2 (380 mg, 1.00 mmol) in diethylether (10 mL) was added a solution of t-butyllithium (1.7 M, 1.2 mL, 2.10 mmol) at –78 °C. After maintaining the reaction temperature for 4 h, the resulting suspension was treated with elemental iodine (5.63 g, 22 mmol) dissolved in tetrahydrofuran (1.5 mL) at –78 °C. The reaction was slowly warmed to ambient temperature and had been stirred over night. The brown reaction mixture was evaporated to dryness and the solid residue was extracted with n-pentane (3 x 5 mL). The combined organic phases were evaporated to dryness and the crude product was subjected to column chromatography (silica; n-hexane). After recrystallization in n-hexane at –30 °C, 2b was obtained as a yellow crystalline solid. Yield: 367 mg (0.58 mmol, 58 %); m.p. 188 °C; ¹H-NMR (400 MHz, CDCl₃, δ): 7.43 (m, 4H, Th-H), 7.01 (s, 2H, Tip-H), 2.96 (sept, ³J = 7.0 Hz, 1H, p-i-Pr-H), 2.46 (sept, ³J = 6.8 Hz, 2H, o-i-Pr-H), 1.33 (d, ³J = 7.0 Hz, 6H, p-i-Pr-CH₂), 1.07 (d, ³J = 6.8 Hz, 12H, o-i-Pr-CH₃). ¹¹B[¹H] NMR (128 MHz, CDCl₃, δ): 54.2 (s); ¹³C[¹H] NMR (101 MHz, CDCl₃, δ): 151.9 (br, Th-C–B), 149.8 (Tip-C-o-i-Pr), 149.1 (Tip-C-p-i-Pr), 143.2 (Th-CH), 139.2 (br, Tip-C–B), 137.5 (Th-CH), 120.2 (Tip-CH), 88.9 (Th-C–I), 35.3 (o-i-Pr-CH), 34.2 (p-i-Pr-CH), 24.3 (o-i-Pr-CH₂), 24.1 (p-i-Pr-CH₂); MS (EI, 70 eV): m/z (%) = 632.1 ([M⁺, 59), 422.2 ([TipBThl]⁺, 32), 295.3 ([TipBTh⁺, 100), 213.3 ([TipB⁺, 20); elem. anal. calcd (%) for C₂₉H₄₅Bl₂S₂: C 43.70, H 4.30, found: C 44.06, H 4.94. UV–vis (THF): λₐₙₙ = 284 nm (ε = 16273 L mol⁻¹ cm⁻¹), 294 nm (ε = 13460 L mol⁻¹ cm⁻¹), 357 (ε = 39310 L mol⁻¹ cm⁻¹); fluorescence (THF): non-emissive.

**X-ray crystallographic analysis of 1a, 1b, 2a and 2b.** Suitable single crystals of 1a, 1b, 2a, and 2b were obtained by slow evaporation of hexane at ambient temperature. Data were collected on a Bruker SMART APEX CCD detector on a D8 goniometer equipped with an
Oxford Cryostream 700 temperature controller at 100(2) K using graphite monochromated Mo-\(K_{\alpha}\) radiation (\(\lambda = 0.71073 \text{ Å}\)). An absorption correction was carried out semi-empirically using SADABS\textsuperscript{[5]} (min./max. transmissions = 0.5970/0.7461 (1a), 0.5734/0.7452 (1b), 0.5960/0.7445 (2a), 0.2574/0.7461 (2b)). The structures were solved with Olex2\textsuperscript{[6]} using Direct Methods (ShelXS\textsuperscript{[7a]}) and refined with the ShelXL\textsuperscript{[7b]} refinement package by full-matrix least squares on \(F^2\). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included isotropically and treated as riding. The structure of 1a is sitting on a symmetry element and 1b displays three molecules within the asymmetric unit.

**Table S1.** Crystal structure and refinement data for 1a, 1b, 2a and 2b.

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<th>No.</th>
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<td>colorless block</td>
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### 3.4.2 References


3.5 A 16 \pi Electron Conjugated Boron-Doped Porphyrinogen

Abstract: The structural motif of porphyrin, comprising a system of 18 macrocyclic conjugated \pi electrons, is ubiquitous in nature and relevant for numerous biologically and technologically important processes. Herein, the synthesis and characterization of the unprecedented boron-bridged tetrathiaporphyrinogen 6b is presented. Despite the fact, that it contains only 16 \pi electrons, UV-vis and fluorescence spectroscopy, supported by TD-DFT calculations and computationally predicted structural features, unambiguously demonstrate that the macrocycle is fully \pi-conjugated. Two-electron reduction produced the short-lived dianion 6b^{2−}, which is presumably an 18 \pi-electron aromatic porphyrinoid.

The structural motif of porphyrin (Por, Figure 1) plays the key role in many essential processes of living organisms, for instance, the binding and transport of O_2 or the conversion of light into usable energy. Porphyrins and related macrocycles also have various important technological applications. In recent years, there has been an increasing interest in the use of such species as artificial light-harvesting antennae in organic photovoltaic (OPV) cells.\cite{1} As the efficiencies of organic solar cells are still severely limited, mainly due to insufficient light-harvesting abilities of the employed dyes, the design of novel organic materials with specifically tailored optical and electronic properties is an important field of current research.\cite{1}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{Structural motif of porphyrin (Por, the parent derivative, porphin) and two resonance forms of boron-bridged tetrathiaporphyrinogens 1a,b.\cite{7a,b}}
\end{figure}
\(\pi\)-Conjugated organoboranes\(^{[2,3]}\) and organoborane polymers\(^{[2,4]}\) have become important classes of organic–inorganic hybrid materials. The interaction of the vacant \(p_\pi\) orbital on boron with an adjacent organic \(\pi\) system leads to intriguing optical and electronic properties, thus enabling applications in organic electronics and optoelectronics as well as for sensory or imaging applications.\(^{[2-6]}\) Recently, Jäkle and co-workers presented a luminescent \(\pi\)-conjugated organoboron macrocycle containing six Lewis acidic boron centers, which was used as a fluorescent sensor for fluoride and cyanide ions.\(^{[5a,6]}\) Subsequently, they presented a series of ambipolar \(\pi\)-conjugated macrocycles with two, three, or four boron centers.\(^{[5b,c]}\)

In 1998, Corriu, Douglas, Siebert et al. reported the synthesis of the boron-bridged tetrathiaporphyrinogen \(1a.\)\(^{[7a,8,9]}\) Siebert and co-workers, subsequently, added the derivative \(1b.\)\(^{[7b]}\) among some further related macrocycles.\(^{[7b,c]}\) Although these species comprise a closed cycle of \(sp^2\) hybridized C and B atoms, the colorless compounds showed no evidence of macrocyclic \(\pi\) conjugation. In the solid state, the constituent thiophene rings were heavily twisted out of the plane that comprises the four boron atoms (e.g., by 62–66° in \(1b.\)\(^{[7b]}\)). Further crystallographic and spectroscopic data clearly supported the conclusion that any appreciable ring current or communication between the thiophene \(\pi\) systems through the boron atoms must be ruled out.\(^{[7a,b]}\)

Compounds \(1a,b\) are 16 \(\pi\) electron species, thus, with \(4n\) (\(n = 4\)) electrons potentially antiaromatic.\(^{[10]}\) It has also been noted, that the stabilizing amino groups limit, if not compromise, the Lewis acidity of the boron centers of \(1.\)\(^{[6]}\) It is well-known that the BN bonds in aminoboranes can have significant double bond character,\(^{[11]}\) as represented in resonance structure \(B\) for \(1\) in Figure 1. Therefore, it seems plausible that this exocyclic \(\pi\) bonding contribution also largely suppresses any possible \(\pi\) electron delocalization within the macrocycle across the boron atoms. We anticipated that macrocyclic conjugation should be favored if a non-\(\pi\)-donating substituent was attached to boron.

Herein, we present the synthesis and characterization of the first fully \(\pi\)-conjugated boron-bridged tetrathiaporphyrinogen. Despite the fact that the macrocycle contains 16 \(\pi\) electrons, spectroscopic and
computationally predicted structural features unambiguously evidence \( \pi \) electron delocalization over the entire macrocyclic system.

The first target of our study was a boron-bridged tetrathiaporphyrinogen with mesityl (2,4,6-trimethylphenyl, Mes) as the exocyclic substituent on boron. Various previous examples have demonstrated that this group attached to boron provides kinetic stabilization that is often sufficient to impart air and moisture stability to the organoboron compound while, at the same time, maintaining the Lewis acidity and the \( \pi \)-acceptor property of the boron center.\(^{[2-4]} \) The starting point of our synthetic route was di-2-thienyl(mesityl)borane\(^{[12]} \) (2a, Figure 2). As the archetypal synthesis of 1a had involved a [2+2] cyclization between 5,5'-dilithio-\( N,N \)-diisopropyl-1,1-di-2-thienylboranamine and \( \text{Cl}_2 \text{BN}{\text{iPr}}_2 \), we first decided to adopt this approach for our purpose. In order to verify the selective dilithiation in 5,5'-position of 2a, we reacted it with \( t\text{-BuLi} \) in \( \text{Et}_2\text{O} \) at \(-78^\circ\text{C} \) and subsequently quenched the putative dilithio species with \( \text{Me}_3\text{SiCl} \) (2 equiv). This selectively yielded the 5,5'-disilyl compound 3a. This result encouraged us to attempt the direct synthesis of the desired macrocycle 6a through a 1:1 reaction (a [2+2] cyclization) of the dilithio species with MesBCl\(_2 \). This, however, in our hands yielded a complex, inseparable mixture of products. The same was true when MesB(OMe)\(_2 \) was used instead. Therefore, we decided to apply a stepwise procedure.
Figure 2. Attempted synthesis of boron-bridged tetrathiaporphyrinogen 6a.

After dilithiation of 2a, two equiv. of MesB(OMe)\(_2\) were added. This afforded 4a in moderate yield, contaminated with ca. 1 % of residual MesB(OMe)\(_2\) which could not be separated. Nevertheless, we then attempted a cyclization of 4a with dilithiated 2a in Et\(_2\)O at −78 °C. The \(^{11}\)B{\(^1\)H} NMR spectrum of the reaction mixture showed two signals, one at 55 ppm and one at about 0 ppm (Appendix, Figure A5.7). The chemical shift of the former is identical with that of 2a and that of the central boron nucleus in 4a. A similar shift should also be expected for the desired macrocycle, 6a, as well as for the tri-coordinate boron atoms of the possible intermediate of its formation, 5a, in which the methoxide leaving groups are still coordinated to the other two boron centers. The resonance at 0 ppm is characteristic of tetra-coordinate...
boron. This is consistent with the formation of 5a. However, the $^1$H NMR spectrum of the obtained residue indicated the presence of further cyclic and/or linear oligomeric species of similar constitution as 5a.

Upon treating this crude product mixture with anhydrous HCl in diethylether, an $^{11}$B{$^1$H} NMR spectrum showed one broad signal at about 55 ppm; no resonance at around 0 ppm was detected (Appendix, Figure A5.8). This indicates that the B-bonded methoxide groups in species such as 5a were cleaved off with formation of tri-coordinate borane groups. The $^1$H NMR spectrum revealed a complex product mixture. However, as the peak of the molecular ion of the desired macrocycle, 6a, with correct isotope pattern was detected by secondary-ion mass spectrometry (SIMS) at m/z = 848.3 (Appendix, Figure A5.28), we subjected the mixture to aqueous work-up, followed by column chromatography to separate the macrocycle. This, however, was unsuccessful, and 6a was no longer detected by any analytical means. This led us to the conclusion it might be unstable towards water and/or silica, which was used as the stationary phase on the column, although, for comparison, compound 2a is perfectly air- and moisture-stable and can be readily purified by column chromatography on silica.\textsuperscript{[12]}
Figure 3. Synthesis of boron-bridged tetrathiaporphyrinogen 6b.

These findings led us to target the tetraboratetraphiaporphyrinogen 6b having 2,4,6-triisopropylphenyl (Tip) groups on boron, which should provide even better steric protection than mesityl[2-4] (Figure 3). Selective dilitiation of 2b[4] followed by a clean reaction with Me₃SiCl afforded 3b[4] in good yield (84%). Unfortunately, direct synthesis of the building block 4b via dilitiation of 2b and reaction with 2 equiv. of TipB(OMe)₂ did not afford a clean sample. The reaction seemed to require the presence of an excess of TipB(OMe)₂ to go to completion, and we did not succeed in separation of unreacted TipB(OMe)₂ from 4b at the final stage. Therefore, we chose a stepwise procedure for the synthesis of 4b via 3b. Two boryl groups were easily introduced at 3b by twofold silicon/boron exchange with BBr₃ to give 7b in a virtually quantitative reaction. Upon subsequent treatment of the latter with 2
equiv. of TipLi, selective mono-substitution occurred at each boryl group to yield 8b. As our attempts to access the macrocycle 6b through the reaction of 8b with dilithiated 2b were unsuccessful, 8b was first transformed into 4b by metathesis with NaOMe. Finally, the desired macrocycle 6b was obtained from the reaction of 8b with dilithiated 2b in diethyl ether at −78 °C. An intermediate analogous to 5a was not observed in this case. Nevertheless, addition of HCl in the last step proved to be advantageous for separation of the by-products. The tetraboratetraethiaporphyrinogen 8b was isolated by column chromatography and repeated precipitation with ethanol as a yellow solid in 24 % yield. Its constitution was unambiguously ascertained by NMR spectroscopy and mass spectrometry; elemental analysis yielded satisfactory results. It was further characterized by UV–vis and fluorescence spectroscopy as well as cyclic voltammetry (CV).

Figure 4. UV–vis absorption spectra of 2b and 6b and fluorescence spectrum of 6b in THF (excited at 418 nm).

As in the case of linear thienylborane oligomers and polymers of analogous constitution,[4] no 11B NMR signal could be detected for 6b. The 1H NMR spectrum showed a single resonance for the eight thiophene protons at 7.95 ppm. This is in the normal range of thiophene-C3/4-bonded protons, hence, any appreciable dia- or paratropic ring current that exceeds the influence of isolated thiophene aromatic systems can be ruled out. The optical spectroscopic data, however, clearly indicate π conjugation across the boron centers within the macrocycle. The UV–vis spectrum of 6b displayed an absorption
band at $\lambda_{\text{max,abs}} = 417$ nm with a shoulder at about 397 nm and a long tail in the visible region (Figure 4). This is a bathochromic shift by 92 nm with respect to the absorption band of 2b ($\lambda_{\text{max,abs}} = 325$ nm), which constitutes one structural unit of the macrocycle. The shift is even slightly more pronounced than that of the corresponding thienylborane oligomer ($\lambda_{\text{max,abs}} = 409$ nm) and the polymer ($\lambda_{\text{max,abs}} = 412$ nm).\[4j\] Compound 6b showed blue fluorescence in solution (Figure 4) with a maximum at $\lambda_{\text{max,em}} = 488$ nm. Interestingly, the fluorescence of 6b showed both a larger Stokes shift ($\Delta \nu \approx 3500$ cm$^{-1}$) and a higher fluorescence quantum yield ($\Phi_f = 5.9 \%$) than that of the oligomer ($\Delta \nu = 700$ cm$^{-1}$, $\Phi_f = 0.6 \%$) and the polymer ($\Delta \nu = 2300$ cm$^{-1}$, $\Phi_f = 0.8 \%$).[\[4j\]] Moreover, the fluorescence quantum yield of 6b is approximately twice as that of 2b ($\Phi_f = 3.1 \%$).[\[4j\]]

We performed halogen titration experiments using either tetrabutylammonium fluoride (TBAF) or tetrabutylammonium chloride (TBACl) (see Experimental Section for more details) and analyzed the received aliquots using UV-vis spectroscopy (Figure 5).

![Figure 5](image)

**Figure 5.** UV-vis spectra for the titration experiments of 6b (left: TBAF; right: TBACl).

The titration of 6b with TBAF afforded UV-vis spectra in which the tendency of fluorid binding is clearly depicted by the decrease of the UV-vis absorption maximum (417 nm) with increasing amount of TBAF. It seems, that four equivalents of TBAF are sufficient to eliminate the former absorption behavior. While the former absorption maximum decreases (417 nm), rise is given to a new absorption maximum (367 nm). Furthermore, the fluorescence of 6b is changed as well. The former yellow-green emission turns orange-red (Figure 6).
Figure 6. Emission of 6b in THF. Left: Without TBAF. Right: With four equivalents TBAF.

The process of fluorid binding seems rather selective, because with TBACL no reaction is observed. Also, no change in fluorescence emission is witnessed.

The cyclic voltammogram of 6b revealed two closely spaced irreversible reduction waves between −1.5 and −3.0 V vs the ferrocenium/ferrocene couple (Experimental Section, Figure S1). The dianion of 6b that is formed upon reduction might be an aromatic species with 18 macrocyclic conjugated π electrons. However, it is obviously unstable and prone to follow-up reactivity, resulting in irreversible redox behavior.

In order to elucidate the nature of 6b and its dianion, we calculated the B-Mes derivatives (6a and 6a^{2−}, as suitable and computationally convenient models for 6b and 6b^{2−}) of both species by means of DFT calculations (B3LYP-D3(BJ)/def2-SV(P)), Figure 7). The structural features of computed 6a corroborate our conclusions drawn from the spectroscopic data of 6b. The thiophene rings are slightly twisted out of the plane of the four boron atoms in relative 1,2-anti conformation as in 1a^{[7a]} and 1b^{[7b]} but to a much lesser extent than in the latter. The torsion angle between the thiophene rings and the adjacent BR_{3} units is only 24.2°. This points to possible π conjugation across the boron centers in 6a,b. The B–C_{thienyl} bonds are relatively short (1.553 Å on average) and in the same range with those of compound 3b (1.525(13) and 1.540(13) Å), in which the two thienyl groups and the boron center form an extended π-conjugated system^{[4l]} The C_{α}–C_{β} bonds (1.398 Å) are slightly shorter than the C_{β}–C_{β}′ bonds (1.414 Å). This indicates that the conjugative effects in 6a are not as strong as in macrocyclic
aromatic systems such as porphyrins, in which the constituent rings often show a quinoidal distortion. This effect is actually observed in $6a^{2-}$. As anticipated, the dianion $6a^{2-}$ represents an 18 $\pi$ electron aromatic species. Notably, its central macrocycle is completely planar.

![Image of calculated structures of 6a and 6a$^{2-}$](image)

**Figure 7.** Calculated structures of 6a (left) and 6a$^{2-}$ (right) (each in top and side view).

We additionally calculated vertical singlet excitations of 6a using time-dependent DFT. This lent further support for the assumption that the thiophene rings and the boron centers in 6a,b form an extended $\pi$-conjugated system. The HOMO−2 → LUMO and HOMO−3 → LUMO transitions are of charge transfer character from the exocyclic Mes substituents to boron (Figure 8). They are of medium probability, and they are presumably the origin of the long tail of the UV–vis spectrum of 6b in the visible region. The stronger absorbing processes involve transitions from the nearly degenerate orbitals HOMO−10 and HOMO−11 to the LUMO or to the nearly degenerate LUMO+1 and LUMO+2, which are all unambiguously characterized as $\pi$ orbitals. Note that the LUMO has significant contribution from the p$_\pi$ orbital of boron.
In conclusion, we succeeded in the synthesis of the unprecedented boron-bridged tetrathiaporphyrinogen 6b having kinetically stabilizing Tip groups on boron that do not compromise the \( \pi \)-acceptor strength of the boron centers. 6b shows interesting sensorical behavior when different halogens are applied. It reacts selectively with fluoride, leading to a dramatic change in its absorption and emission behavior, but does not react with chloride at all. Despite the fact that the macrocycle contains 16 \( \pi \) (i.e. \( 4n \) with \( n = 4 \)) electrons, it comprises a fully \( \pi \)-conjugated system. Two-electron reduction produces the

**Figure 8.** Calculated molecular orbitals of 6a (isovalue: 0.04 a.u., B3LYP-D3(BJ)/def2-SV(P)).
dianion 6b$^{2-}$, which is presumably an 18 $\pi$-electron aromatic porphyrinoid. The novel macrocycle 6b is also a suitable model system for linear thienylborane polymers.$^{[2g,4c,g,h,j]}$ Currently, we are investigating the coordination behavior of 6b and its usability for organic electronic applications.

3.5.1 Experimental Section

**General procedures.** All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques or in an MBraun glovebox. Solvents (dichloromethane, $n$-pentane, diethylether, toluene, and tetrahydrofuran) were dried and degassed by means of a MBraun SPS-800 solvent purification system. Deuterated solvents for NMR spectroscopy were dried and degassed at reflux over Na (C$_6$D$_6$) or CaH$_2$ (CDCl$_3$ and CD$_2$Cl$_2$) and freshly distilled prior to use. Solvents for aqueous work-up (ethyl acetate, ethanol, $n$-hexane), 2-bromothiophene, tribromoborane, sodium methanolate, and magnesium turnings were purchased from commercial sources and used as received. Solutions of $n$-butyllithium (1.6 M in hexane and 2.5 M in hexane, respectively), $t$-butyllithium (1.7 M in pentane), and hydrogenchloride (2 M in diethyl ether) were purchased from Sigma Aldrich and used as received as well. Chlorotrimethylsilane, 2-bromo-1,3,5-triisopropylbenzene were commercially purchased and freshly distilled prior to use. MesB(OMe)$_2$, TipB(OMe)$_2$, 2,4,6-triisoproplyphenyllithium, 2b$^{[4j]}$ and 3b$^{[4j]}$ were prepared according to methods described in the literature. NMR spectra were recorded at 25 °C on a Bruker Avance II-400 spectrometer or on a Bruker Avance III HD spectrometer operating at 400 MHz. Chemical shifts were referenced to residual protic impurities in the solvent ($^1$H) or the deuterio solvent itself ($^{13}$C) and reported relative to external SiMe$_4$ ($^1$H, $^{13}$C) or BF$_3$·OEt$_2$ ($^{11}$B) standards. Mass spectra were obtained with the use of a Finnigan MAT95 spectrometer employing electron ionization (EI) using a 70 eV electron impact ionization source or secondary ionization (SIMS). Elemental analysis was performed with a CHN-O-Rapid VarioEL by Heraeus. UV-vis spectra were obtained using a Jasco V-630 spectrophotometer. For fluoride titration experiments a solution of
tetrabutylammonium fluoride (TBAF) in THF (1 M) was diluted to yield a solution with equivalent concentration with respect to 6a. Within a glass cuvette different equivalents of TBAF were mixed with a solution of 6a in THF (c = 5.1 x 10^{-6}) and the reaction was monitored by determination of the UV–vis absorption spectra. Fluorescence spectra were obtained with a Jasco FP-6500 spectrofluorometer. Fluorescence quantum yields were determined against commercially available standards (6a against perylene). Cyclic voltammetric studies were carried out in a 20 mL scintillation vial with electrodes fixed in position by a rubber stopper. A platinum disc working electrode, a platinum-wire reference electrode and a silver-wire pseudo-reference electrode all purchased from CH Instruments were used. Cyclic voltammograms were acquired with a Metrohm Autolab PGSTAT101 potentiostat and recorded with Metrohm Autolab NOVA software with data processing on Origin. Melting points (uncorrected) were obtained using a SMP3 melting point apparatus by Stuart in 0.5 mm (o.d.) glass capillaries, which were sealed under argon.

**Synthesis of 2a.** To a solution of n-butyllithium (2.5 M, 40 mL, 100 mmol) in toluene (240 mL) was added 2-bromothiophene (16.30 g, 100 mmol) dropwise at room temperature. After stirring for 3 h at ambient temperature, the resulting white suspension was cooled to 0 °C and MesB(OMe)₂ (9.60 g, 50 mmol) was added dropwise. The mixture had been stirred over night at room temperature and subsequently quenched by adding HCl in diethylether (2 M, 50 mL, 100 mmol). After filtration of the inorganic precipitate, all volatiles were removed under reduced pressure. The crude product was purified by recrystallization from n-hexane (−30 °C) to give 2a[12] as a colorless crystalline solid. Yield: 8.86 g (29.9 mmol, 60 %); ¹H NMR (400 MHz, CDCl₃, δ): 7.94 (dd, ³J = 4.5 Hz, ⁴J = 0.8 Hz, 2H, Th-H), 7.85 (dd, ³J = 3.5 Hz, ⁴J = 0.8 Hz, 2H, Th-H), 7.30 (dd, ³J = 3.5, 4.5 Hz, 2H, Th-H), 6.87 (s, 2H, Mes-H), 2.37 (s, 3H, p-C₃H₃), 2.07 (s, 6H, o-C₃H₃); ¹¹B{¹H} NMR (128 MHz, CDCl₃, δ): 55.4 (s).

**Synthesis of 3a.** To a solution of 2a (296 mg, 1.00 mmol) dissolved in diethylether (7.5 mL) was added t-butyllithium (1.7 M, 1.24 mL, 2.10 mmol) at −78 °C. After the reaction mixture had been stirred at this temperature for 4 h, chlorotrimethylsilane (240 mg, 2.2 mmol) was
added. Then, the cooling bath was removed, and the reaction mixture was stirred overnight at room temperature. The colorless precipitate was removed by filtration and extracted with Et₂O (5mL). All volatiles were removed in vacuo, and the crude product solid was purified by column chromatography (silica; n-hexane). Compound 3a was obtained as a light yellow crystalline solid. Yield: 154 mg (0.35 mmol, 35 %); ¹H-NMR (400 MHz, CDCl₃, δ): 7.91 (d, 3J = 3.3 Hz, 2H, Th-H), 7.45 (d, 3J = 3.3 Hz, 2H, Th-H), 6.92 (s, 2H, Mes-H), 2.41 (s, 3H, p-CH₃), 2.12 (s, 6H, o-CH₃), 0.41 (s, 18H, Si(CH₃)₃); ¹¹B{¹H} NMR (128 MHz, CDCl₃, δ): 55.4 (s, Ar₃B), 45.6 (s, Ar₂BOMe); ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 154.8 (Th-C-Si(CH₃)₃), 149.5 (br, Th-C-B), 142.6 (Th-CH), 142.0 (br, Mes-C-B), 138.3 (Mes-C-o-CH₃), 136.8 (Mes-C-p-CH₃), 135.7 (Th-C), 126.9 (Mes-CH), 22.8 (Mes-C-o-CH₃), 21.5 (Mes-C-p-CH₃), 0.1 (Si(CH₃)₃); MS (El, 70 eV): m/z (%) = 439.8 (M⁺, 26), 367.8 ([BTh₂TMSMes⁺], 44), 283.9 ([BTh₂(PhMe₂)⁺], 53), 211.9 ([BThMes⁺], 72), 73.1 ([TMS⁺], 100); elem. anal. calcd (%) for C₂₉H₄₅BS₂Si₂: C 62.69, H 7.55, found: C 62.52, H 7.47.

**Synthesis of 4a.** To a solution of 2a (296 mg, 1.00 mmol) dissolved in diethylether (7.5 mL) was added t-butyllithium (1.7 M, 1.24 mL, 2.10 mmol) at −78 °C. After the reaction mixture had been stirred at this temperature for 4 h, MesB(OMe)₂ (432 mg, 2.2 mmol) was added. The cooling bath was removed, and the reaction mixture was stirred overnight at room temperature. Then, it was evaporated to dryness and extracted twice with pentane (20 mL). After filtration and removal of the solvent, the crude solid product was purified by recrystallization from diethylether at −40 °C. Compound 4a was obtained (with slight impurities (~ 1 %) of MesB(OMe)₂) as a light yellow crystalline solid. Yield: 351 mg (0.57 mmol, 57 %); ¹H-NMR (400 MHz, CDCl₃, δ): 7.85 (d, 3J = 3.5 Hz, 2H, Th-H), 7.45 (d, 3J = 3.5 Hz, 2H, Th-H), 6.90 (s, 4H, Mes-H), 6.87 (s, 2H, Mes-H), 3.77 (s, 6H, O-CH₃), 2.36 (s, 9H, p-CH₃), 2.23 (s, 12H, o-CH₃), 2.09 (s, 6H, o-CH₃); ¹¹B{¹H} NMR (128 MHz, CDCl₃, δ): 55.2 (s, Ar₃B), 45.6 (s, Ar₂BOMe); ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 152.8 (br, Th-C-B), 151.6 (br, Th-C-B), 142.5 (Th-CH), 141.8 (br, Mes-C-B), 139.7 (Th-CH), 138.7 (Mes-C-o-CH₃), 138.2 (Mes-C-o-CH₃), 138.0 (Mes-C-p-CH₃), 137.0 (Mes-C-p-CH₃), 134.4 (br, Mes-C-B), 127.1 (Mes-CH), 126.9 (Mes-CH), 55.3 (O-CH₃), 22.8
(Mes-C-ο-CH₃), 21.9 (Mes-C-ο-CH₃), 21.5 (Mes-C-p-CH₃); MS (EI, 70 eV): m/z (%) = 615.8 ([M⁺], 2), 455.8 ([MesBTh(MesBThOMe)]⁺, 9), 371.9 ([MesB(MesBThOMe)]⁺, 3), 161.0 ([MesBOMe]⁺, 100); elem. anal. calcd (%) for C₂₉H₄₅BS₂Si₂: C 72.11, H 7.03, found: C 71.85, H 7.12.

Attempted synthesis of 6a. To a solution of 2a (1.19 g, 4.00 mmol) in diethyl ether (30 mL) was added a solution of t-butyllithium (1.7 M, 4.82 mL, 8.20 mmol) dropwise at −78 °C. The mixture was stirred for 4 hours maintaining −78 °C. Subsequently, diethyl ether (50 mL) and a solution of 4a (2.47 g, 4.00 mmol) in diethyl ether (40 mL) were added slowly to the resulting suspension. The mixture was slowly warmed to room temperature over night. From this crude reaction mixture an aliquot was taken and analyzed by $^{11}$B{$^1$H} NMR spectroscopy and mass spectrometry. Subsequent quenching with HCl in diethyl ether (2 M, 4.1 mL, 8.20 mmol) resulted in the formation of a yellow solution over a colorless precipitate. The insoluble salts were filtered off and washed twice with Et₂O (40 mL). After evaporation to dryness, the crude solid was analyzed by NMR spectroscopy and mass spectrometry (SIMS). Neither compound 6a nor its fragments could be detected any longer.

Synthesis of 7b. To a solution of 3b (17.68 g, 33.7 mmol) in dichloromethane (135 mL) was added BBr₃ (21.09 g, 84.2 mmol) dropwise at 0 °C. The mixture was stirred for 2 h at that temperature. Subsequent evaporation of the solvent yielded almost pure 7b in quantitative yield. Slight impurities by residual BBr₃ were removed by washing the product twice with pentane (50 mL) to give 7b as a yellow solid (m.p. 156 °C). Yield: 21.8 g (30.3 mmol, 90 %); $^1$H-NMR (400 MHz, CDCl₃, $\delta$): 8.17 (d, $^3J = 3.7$ Hz, 2H, Th-H), 8.00 (d, $^3J = 3.7$ Hz, 2H, Th-H), 7.05 (s, 2H, Tip-H), 2.98 (sept, $^3J = 7.0$ Hz, 1H, p-i-Pr-H), 2.38 (sept, $^3J = 6.6$ Hz, 2H, o-i-Pr-H), 1.35 (d, $^3J = 7.0$ Hz, 6H, o-i-Pr-CH₃), 1.08 (d, $^3J = 6.6$ Hz, 12H, o-i-Pr-CH₃); $^{11}$B{$^1$H} NMR (128 MHz, CDCl₃, $\delta$): 56.8 (br, Ar₃B), 49.5 (ArBBr₂); $^{13}$C{$^1$H} NMR (101 MHz, CDCl₃, $\delta$): 159.2 (br, Th-C-BBr₂) 154.5 (br, Th-C–B), 149.8 (Tip-C-ο-iPr), 149.6 (Tip-C-p-iPr), 143.7 (Th-CH), 143.1 (Th-CH), 143.0 (Th-CH), 142.0 (Th-CH), 138.7 (Th-CH), 135.0 (Th-CH), 133.4 (Th-CH), 131.4 (Th-CH), 129.9 (Th-CH), 128.3 (Th-CH), 125.7 (Th-CH), 122.2 (Th-CH), 121.9 (Th-CH).
Synthesis of 4b. To a suspension of NaOMe (1.19 g, 22.0 mmol) in dichloromethane (45 mL) was added a solution of 8b (10.63 g, 11.0 mmol) in dichloromethane (45 mL) dropwise at −78 °C. The reaction mixture was slowly warmed to room temperature over night. After filtration from insoluble material and extraction with toluene (3 x 60 mL), the combined organic phases were evaporated to dryness. The crude product revealed slight impurities by 1,3,5-

Synthesis of 8b. To a suspension of 7b (6.48 g, 9.0 mmol) in n-pentane (90 mL) was added a solution of TipLi (3.79 g, 18.0 mmol) in pentane/toluene (1:1, 90 mL) dropwise at −78 °C. The reaction mixture was slowly warmed to room temperature over night. After filtration from insoluble material and extraction with toluene (3 x 60 mL), the combined organic phases were evaporated to dryness. The crude product revealed slight impurities by 1,3,5-triisopropylbenzene and residual toluene. After multiple recrystallizations, compound 4a (contaminated with ca. 5 % of TipH) was obtained as a slightly yellow solid (m.p. 143 °C). Yield: 7.13 g (7.4 mmol, 82 %); 1H-NMR (400 MHz, CDCl3, δ): 8.08 (d, 3J = 3.8 Hz, 2H, Th-H), 7.96 (d, 3J = 3.7 Hz, 2H, Th-H), 7.03 (s, 4H, Tip-H), 7.02 (s, 2H, Tip-H), 2.96 (m, 3H, p-i-Pr-H), 2.66 (sept, 3J = 6.7 Hz, 4H, o-i-Pr-H), 2.43 (sept, 3J = 6.6 Hz, 2H, o-i-Pr-H), 1.34 (m, 18H, p-i-Pr-CH3), 1.29 (d, 3J = 6.9 Hz, 12H, o-i-Pr-CH3), 1.14 (d, 3J = 6.6 Hz, 12H, o-i-Pr-CH3), 1.05 (d, 3J = 6.7 Hz, 12H, o-i-Pr-CH3); 11B[1H] NMR (128 MHz, CDCl3, δ): 61.4 (Ar2BBr), Ar3B: signal not detectable; 13C[1H] NMR (101 MHz, CDCl3, δ): 158.8 (br, Th-C-BBr) 156.0 (br, Th-C-B), 150.3 (Tip-C-o-iPr), 149.5 (Tip-C-p-iPr), 149.4 (Tip-C-p-iPr), 149.0 (Tip-C-o-iPr), 143.1 (Th-CH), 142.5 (Th-CH), 138.1 (br, Tip-C-B), 136.5 (br, Tip-C-B), 120.7 (Tip-CH), 120.4 (Tip-CH), 35.9 (p-i-Pr-CH3), 35.7 (o-i-Pr-CH3), 34.3 (o-i-Pr-CH), 34.2 (p-i-Pr-CH), 23.9-24.3 (i-Pr-CH3); elem. anal. calcld (%) for C39H59Cl2Si2Br2 (+ 5 % TipH): C 66.98, H 7.82, found: C 67.39, H 7.69; UV-vis (CH2Cl2): λabs,max = 281 (ε = 17658 L mol⁻¹ cm⁻¹), 348 nm (ε = 41914 L mol⁻¹ cm⁻¹); fluorescence (CH2Cl2): non-emissive.
mixture was slowly warmed to room temperature over night. After filtration from insoluble material and extraction with dichloromethane (2 x 30 mL), the combined organic phases were evaporated to dryness. The product was recrystallized from n-pentane to afford almost pure 4b as a colorless solid (impurities result from residual solvent) (m.p. 105 °C). Yield: 3.53 g (4.1 mmol, 37 %). 

1H-NMR (400 MHz, CDCl3, \( \delta \)):
7.81 (d, \( \delta J = 3.5 \) Hz, 2H, Th-H), 7.46 (d, \( \delta J = 3.8 \) Hz, 2H, Th-H), 7.01 (s, 4H, Tip-H), 6.96 (s, 2H, Tip-H), 3.79 (s, 6H, O–CH3), 2.93 (m, 3H, p-i-Pr-H), 2.62 (sept, \( \delta J = 6.8 \) Hz, 4H, o-i-Pr-H), 2.48 (sept, \( \delta J = 6.8 \) Hz, 2H, o-i-Pr-H), 1.31 (m, 18H, p-i-Pr-C), 1.26 (d (br), \( \delta J = 5.5 \) Hz, 12H, o-i-Pr-C), 1.07 (d (br), \( \delta J = 6.8 \) Hz, 12H, o-i-Pr-C), 1.01 (d, \( \delta J = 6.8 \) Hz, 12H, o-i-Pr-C); 

11B{1H} NMR (128 MHz, CDCl3, \( \delta \)):
45.2 (Ar2BOMe), Ar3B: signal not detectable; 

13C{1H} NMR (101 MHz, CDCl3, \( \delta \)):
153.7 (br, Th-C-BOMe) 152.7 (br, Th-C–B), 150.1 (Tip-B–o-Pr), 149.5 (Tip-C-p-Pr), 149.4 (Tip-C-p-Pr), 142.3 (Tip-CH), 139.6 (br, Tip-C–B), 139.4 (Th-CH), 132.7 (br, Tip-C–B), 120.3 (Tip-CH), 120.0 (Tip-CH), 56.0 (O-CH3), 35.4 (p-i-Pr-CH), 35.2 (o-i-Pr-CH), 34.3 (o-i-Pr-CH), 34.2 (p-i-Pr-CH), 24.0-24.6 (i-Pr-CH3); MS (EI, 70 eV): m/z (%): 869.2 ([M+2], 2), 624.9 ([TipBTh(TipBThOMe)]+, 1), 497.8 ([Ph(i-Pr)2BTh(TipBThOMe)]+, 1), 244.5 ([TipBOMe]+, 35), 189.5 ([Ph(i-Pr)Et]+, 100); elem. anal. calcd (%) for C55H79B3O2S2: C 76.04, H 9.17, found: C 75.42, H 9.21; UV–vis (THF): \( \lambda_{abs,max} = 303 (\varepsilon = 14486 \text{ L mol}^{-1} \text{ cm}^{-1}) \), 351 nm (\( \varepsilon = 40262 \text{ L mol}^{-1} \text{ cm}^{-1} \)); fluorescence (THF): non-emissive.

**Synthesis of 6b.** To a solution of 2b (1.52 g, 4.00 mmol) in diethyl ether (30 mL) was added a solution of t-butyllithium (1.7 M, 4.82 mL, 8.20 mmol) dropwise at –78 °C. The reaction mixture was stirred for 4 h maintaining –78 °C. Subsequently, diethyl ether (50 mL) and a solution of 4b in diethyl ether (40 mL) were added slowly to the resulting suspension. The mixture was slowly warmed to room temperature over night and quenched by the addition of HCl in diethyl ether (2 M, 4.1 mL, 8.20 mmol). The insoluble salts were filtered off and washed twice with diethyl ether (40 mL). After evaporation to dryness, the crude solid product was subjected to column chromatography (silica; n-hexane). The obtained product still contained 1,3,5-triisopropylbenzene as an impurity. Therefore, it was further purified by dissolving in
dichloromethane and subsequent addition of ethanol (1:1). After evaporation of dichloromethane the product precipitated from ethanol to give 6b as a yellow solid (m.p. 214 °C). Yield: 1.14 g (0.96 mmol, 24 %). $^1\text{H}$-NMR (400 MHz, CDCl$_3$, $\delta$): 7.95 (s (br), 8H, Th-H), 6.99 (s (br), 8H, Tip-H), 2.94 (m, 4H, $p$-i-Pr-H), 2.50 (m, 8H, o-i-Pr-H), 1.32 (m, 24H, $p$-i-Pr-CH$_3$), 1.03 (m, 48H, o-i-Pr-CH$_3$); $^{11}\text{B}$$^1\text{H}$ NMR (128 MHz, CDCl$_3$, $\delta$): signal not detectable; $^{13}\text{C}$$^1\text{H}$ NMR (101 MHz, CDCl$_3$, $\delta$): 156.8 (br, Th-C) 149.4 (Tip-C-o-Pr), 148.9 (Tip-C-p-Pr), 142.3 (Th-CH), 138.9 (br, Tip-C–B), 120.1 (Tip-CH), 35.8 (o-i-Pr-CH), 34.2 ($p$-i-Pr-CH), 24.2 (o-i-Pr-CH$_3$), 24.1 ($p$-i-Pr-CH$_3$); MS (SIMS, 70 eV): $m/z$ (%) = 1185.5 ([M$^+$], 88), 972.5 ([Tip$_2$B$_3$Th$_4$]$^+$, 52), 676.7 ([Tip$_2$B$_2$Th$_3$]$^+$, 100), 380.4 7 ([TipBTh$_2$]$^+$, 30); elem. anal. calcd (%) for C$_{76}$H$_{100}$B$_4$S$_4$: C 77.03, H 8.51, found: C 76.73, H 8.65; UV–vis (THF): $\lambda_{\text{abs, max}}$ = 295 ($\varepsilon$ = 20170 L mol$^{-1}$ cm$^{-1}$), 397 nm ($\varepsilon$ = 42466 L mol$^{-1}$ cm$^{-1}$) 417 nm ($\varepsilon$ = 59660 L mol$^{-1}$ cm$^{-1}$); fluorescence (THF): $\lambda_{\text{em, max}}$ ($\lambda_{\text{ex}}$ = 418 nm) = 488 nm ($\Phi$ = 5.9 %).

Figure S1. CV measurement of 6b (in THF; scan rate: 100 mV s$^{-1}$).
### 3.5.2 Computational Information

**Computational methods.** DFT calculations were carried out with the TURBOMOLE V7.0.1 program package.\[^{19}\] Optimizations were performed with Becke’s three parameter exchange-correlation hybrid functional B3LYP\[^{20}\] in combination with the valence-double-\(\zeta\) basis set def2-SV(P).\[^{21}\] The empirical dispersion correction DFT-D3 by Grimme was used including the three-body term and with Becke-Johnson (BJ) damping.\[^{22}\] The stationary points were characterized as minima by analytical vibrational frequency calculations,\[^{23}\] which revealed the absence of imaginary frequencies. Vertical singlet excitations were calculated by means of time-dependent DFT\[^{24}\] using the same density functional–basis set combination as specified above.

### 3.5.3 References


[9] Compounds 1a,b are formally derived from isophlorins by exchange of the meso-carbon atoms by boron atoms. See [7c].


3.6 PBP Bridged [3]Ferrocenophane: A Bisphosphanoborane with a Redox Trigger

Abstract: BP units started to emerge as attractive functional building blocks capable of stimulating unique electronic features in organic materials. Herein, the unprecedented P–B–P bridged [3]ferrocenophane Fe(C₅H₄PтBu)₂BMes (3) is presented, which combines a bisphosphanoborane fragment, formally analogous to the allylic anion system, with an electro-active ferrocene unit. Two synthetic routes were explored, both of which proceeded stereospecifically to give 3 as the rac diastereomer. Structural and spectroscopic data along with quantum chemical calculations are in agreement with moderate $\pi$ interaction within the P–B–P unit. Electrochemical investigations provide evidence for a short-lived primary oxidation product, the lifetime of which has been determined in solution. For this cation DFT calculations suggest a shift of spin-density from Fe to P upon pyramidal inversion.

In the last decades, BN-doped $\pi$-conjugated materials derived from unsaturated organic compounds through isoelectronic replacement of CC by BN units have attracted considerable attention, mainly due to electronic and biomedical applications.⁴ On the other hand, the incorporation of BP units,⁵ which are valence isoelectronic with BN and CC, into organic materials has been less-well studied, though their potential for electronic applications⁶ has been recognized quite recently⁷-⁸. Owing to the higher s-character of the lone pair, the phosphorus center in unhindered isolated phosphanoboranes, $R_2PBR_2^2$, is usually pyramidal, while the nitrogen atom in their amino-borane congeners, $R_2NBR_2^2$, is commonly in a trigonal-planar environment.⁹ This results in weaker $\pi$ bonding in the former and causes small phosphanoboranes to associate via intermolecular $\sigma$ bonding between B and P in the condensed phase as (mutual) Lewis pairs. However, this can often be suppressed by kinetic stabilization through the attachment of sterically demanding substituents, which results in enhanced $\pi$ bonding of the B–P unit.⁴,⁵,¹⁰ The nature of the B–P bond is further significantly influenced through incorporation into a cyclic system¹⁰ or interaction with Lewis acids or bases.¹¹
1,2-Phosphaborinines such as I (Scheme 1), which became accessible not until 2015 through work by Martin and co-workers, exhibit a planar, moderately aromatic BPC$_4$ ring.\textsuperscript{[7]} The previously reported dibenzo-1,4-phosphaborinines II with disconnected BP substitution are non-planar in the ground state, but show intramolecular charge transfer from the phosphorus to the boron atom upon photoexcitation.\textsuperscript{[5]} Tokitoh and Sasamori et al. presented 1-phospha-2-boraacenaphthenes III, which have interesting electrochemical and photochemical properties, associated with the intrinsic nature of the B–P bond in combination with the rigid structure of the fused tricyclic system.\textsuperscript{[6]} The P–B–P moiety in bisphosphanoboranes is valence isoelectronic with the allylic anion. However, except for reports on some structurally characterized monomeric bisphosphanoborane derivatives by Karsch\textsuperscript{[12]} and Power\textsuperscript{[13]} in the late 1980s, this functional group has received little attention,\textsuperscript{[14]} which contrasts their lighter boron–nitrogen analogues.\textsuperscript{[15,16]} Very recently, the use of N–B–N units as functional building blocks in conjugated polymers such as IV\textsuperscript{[2a]} as well as a synthetic access to a series of P–E–P bridged [3]ferrocenophanes with E = SiXY (V)\textsuperscript{[17]} and E = PX (VI)\textsuperscript{[18,19]} have been demonstrated by us.

Herein, we combine both approaches in the synthesis of an unprecedented [3]ferrocenophane with a P–B–P bridge via two different synthetic routes which allows to probe the $\pi$-electron
delocalization as well as the electrochemical interaction between the P–B–P unit and the ferrocenium moiety in the mono-oxidized state supported by quantum chemical calculations.

We first applied the common salt elimination reaction to form the B–P bonds\(^3\) in the synthesis of [3]ferrocenophane 3 (Scheme 2, Route A). Dilithiation of 1 with \(n\)-BuLi in the presence of TMEDA yielded 2, in which both prochiral phosphorus centers are symmetrically bridged by two Li atoms in solution, as previously shown.\(^{17}\) Subsequent addition of MesBBr\(_2\) at \(-78 \, ^\circ\mathrm{C}\) afforded 3, which was isolated by recrystallization in 28 % yield.

![Scheme 2. Synthesis of PBP bridged [3]ferrocenophane 3.](image)

While silyl exchange reactions have been well-developed into a mild and efficient method for the formation of B–N,\(^{1e,f,2}\) P–Si,\(^{17}\) and B–C\(^{20}\) bonds, its applicability for B–P coupling under mild conditions\(^{21}\) was demonstrated only very recently.\(^{3c,22}\) This encouraged us to explore the reaction between previously reported bis(silylphosphane) 4\(^{17}\) and MesBBr\(_2\) in CH\(_2\)Cl\(_2\) (Route B). Monitoring of the reaction by \(^{11}\)B\(_{\{1\}H}\) and \(^{31}\)P\(_{\{1\}H}\) NMR spectroscopy revealed selective and complete formation of 3 after 16 h. From this reaction, 3 was obtained in 70 % isolated yield. The constitution of 3 was unambiguously ascertained by multinuclear NMR spectroscopy, MS, elemental analysis, and single crystal X-ray diffraction (Figure 1). The NMR data showed that the
products obtained via both synthetic routes were virtually identical with stereospecific formation of 3 as a single diastereomer, although Route B started from rac/meso-4. The \(^{11}\text{B}\{^1\text{H}\}\) NMR spectrum of 3 showed a broad resonance at \(\delta_{\text{B}} = 78\ \text{ppm}\) (FWHM = 760 Hz), which is characteristic of tricoordinate boron, thus, confirming that the molecules of 3 are not associated in solution. The \(^{31}\text{P}\{^1\text{H}\}\) NMR signal at \(\delta_{\text{P}} = 12.4\ \text{ppm}\) is downfield-shifted from that of III (\(\delta_{\text{P}} = -28.2\ \text{ppm}\))\(^6\) and also Mes\(_2\)B(PPh\(_2\))\(_2\) (\(\delta_{\text{P}} = -0.01\ \text{ppm}\))\(^{13a}\) but slightly upfield from the resonances of the phosphanoboranes Mes\(_2\)BPMes\(_2\) (\(\delta_{\text{P}} = 27.4\ \text{ppm}\))\(^{9a}\) and Mes\(_2\)BPPh\(_2\) (\(\delta_{\text{P}} = 26.7\ \text{ppm}\))\(^{9a}\) that have strong B=P \(\pi\) bonding. With respect to the resonances of the bisphosphano-dihalosilyl bridged [3]ferrocenophanes \(\text{V} (XY = \text{Cl}_2, \text{Br}_2, \text{I}_2, \delta_{\text{P}} = -38.8/-30.8/-18.4\ \text{ppm})\),\(^{17}\) the \(^{31}\text{P}\) signal of 3 is significantly deshielded, however, in a similar range as those of the triphosphanylethyldene bridged [3]ferrocenophanes \(\text{VI} (X = \text{F, Cl, Br, I, H, NEt}_2, \text{fBu})\), which resonate between \(\delta_{\text{P}} = 15\) to 19 ppm.\(^{18}\)

The molecular structure of 3 in the solid state confirms the trigonal-planar coordination geometry of the boron center (\(\Sigma_\alpha = 360.0^\circ\)). The mesityl ring is nearly perpendicular to the plane containing the BP\(_2\)C(19) fragment (interplanar angle: 73.39(6)^\circ). At the pyramidal phosphorus atoms the sums of the angles are 332.5 (P1) and 328.8° (P2), respectively, which is significantly larger than in MesB(PPh\(_2\))\(_2\) (322.7°, average value)\(^{13a}\) and, on average, slightly larger than that of III (328.4(3)^\circ).\(^6\) The B–P bond lengths of 3 are 1.884(2) (B1–P1) and 1.896(2) Å (B1–P2), i.e. in the same range with those of MesB(PPh\(_2\))\(_2\) (1.901(2) and 1.879(2) Å)\(^{13a}\) and III (1.889(3) Å),\(^6\) but somewhat longer than that in Mes\(_2\)BPMes\(_2\) (1.839(8) Å)\(^{9a}\) and Mes\(_2\)BPPh\(_2\) (1.859(3) Å).\(^{9a}\) According to Pringle’s classification of B–P vs. B=P character, compound 3 is right in between both extremes, close to the arbitrarily chosen line at a B–P distance of 1.88 Å and an anglesum around phosphorus of 330°.\(^{3c}\)
To gain deeper insight into the bonding situation of 3, DFT calculations were performed. Second order perturbation theory analysis on the NBO basis verified a relatively strong donor-acceptor interaction (37.3 and 37.6 kcal mol\(^{-1}\)) between the lone pairs of the P atoms and the empty \(p_z\) orbital of the boron center. However, established bond order measures and the rather small ellipticity values (0.05) of the electron density in the B–P bond critical point suggest predominantly single bond character (table S1 in Computational Information).

The solid-state molecular structure of 3 further revealed a trans configuration of the \(t\)Bu groups on phosphorus, i.e., the rac isomer. This is completely different from the situation in V and VI, for which cis configuration of these groups was found in each of the derivatives prepared.\(^{[17,18]}\) Our DFT calculations (B3LYP/6-311+G**) showed that the observed trans-3 is more stable by 2.8 kcal mol\(^{-1}\) than the cis isomer (Figure S6) with a low inversion barrier of the phosphorus atom (5.0 kcal mol\(^{-1}\)) which is in good agreement with previously published values for phosphaneboranes.\(^{[13a,23,24]}\) Furthermore, the Cp rings in 3 are slightly tilted towards the P–B–P bridge with an interplanar angle of 6.91°, while in V and VI, they are slightly tilted away from the respective ansa bridge (the largest interplanar angle was found for V with \(X = Cl, 3.52(6)^\circ\)). A further difference between the structures of 3 and V and VI is that the ferrocene backbone of the latter adopts an eclipsed (V) or nearly eclipsed (VI) conformation, while in 3 a staggered conformation was found, similar to the analogous P–P–P bridged Fe(CpP\(_{\text{tBu}}\))\(_2\)P\(_{\text{tBu}}\).\(^{[18]}\)
The UV–vis spectrum of 3 showed a broad band at $\lambda_{\text{max}} = 347$ nm. Our TD-DFT calculations (B3LYP/6-311+G**; table S2, Computational Information) predict four close lying transitions, which involve an admixture of the excitations from the HOMO-X ($X=0,1,2,3$) to the LUMO. While in the case of the HOMO-X ($X=0,1,2,3$), the iron center (and in the case of the HOMO, HOMO-2, and HOMO-3, the phosphorus atoms as well) has significant contribution, the LUMO is localized only at the atoms of the PBP bridge (Figure 2). Therefore, the excitation is, to some extent, accompanied with charge transfer from the Fe center to the PBP bridging unit.

![Figure 2. UV–vis spectrum of 3 in CH$_2$Cl$_2$ (left) and selected Kohn-Sham orbitals of 3 (right) which are involved in the electronic transitions.](image)

Our cyclic voltammetry studies revealed two irreversible electrochemical responses for the oxidation of 3 in CH$_2$Cl$_2$ (scan rate: 250 mV s$^{-1}$; $E_p = +0.29(1)$ V and +0.82(1) V vs. Fc/Fc$^+$; Figure 3a) before reaching a broad irreversible downstream process at ca. +1 V, which indicates several similar follow-up oxidations (black line). Reversing the potential sweep after the first oxidation process, which is assigned to oxidation of the ferrocene backbone, leads to a “more reversible” redox response for this particular process (red line). With increasing scan rate up to 1 V s$^{-1}$ the oxidation behavior finally turns into quasi-reversible for the first oxidation process (blue line). This behavior demonstrates a consecutive reaction after initial oxidation of the ferrocene backbone. It is known that monocations of substituted
ferrocenes can exhibit low stability. Increased scan rates may overcome the decomposition of the corresponding ferrocenium species, as was observed for derivatives of VI.\[18\]

**Figure 3.** (a) Overlay of cyclic voltammetric measurements. Black: Overview at 250 mV s\(^{-1}\). Red: CV curve at 250 mV s\(^{-1}\) returning after the first oxidation. Blue: Quasi-reversible oxidation behavior at 1000 mV s\(^{-1}\). (b) Anodic disk and cathodic ring current in dual electrode experiments at different rotation speeds of the electrodes.

To get deeper insight in the electron transfer mechanism of the follow-up reaction, we extended our investigations to dual electrode methods using a rotating ring-disk electrode (RRDE) which is an established method for the determination of transient species in solution,\[26\] but has rarely been applied to organometallic compounds. Using this methodology, we determined the ratio of the anodic limiting disc current and the cathodic limiting ring current. From this, the collection efficiency and ultimately the rate constant \(k\) of the irreversible transformation of mono oxidized 3 was derived to 3.2(4) s\(^{-1}\) (Figure 3b), corresponding to an average lifetime of the primary oxidized intermediate of \(\tau = 0.31(4)\) s.\[27\]

Unrestricted DFT calculations on the radical cation 3\(^+\) revealed that the spin density is located at the ferrocene unit (Figure S8), in agreement with the observed quasi-reversible nature of the primary oxidation process. Similar to neutral 3, the computed inversion barrier at phosphorus is low, only 5.7 kcal mol\(^{-1}\) for 3\(^+\) using B3LYP/6-31G*, and
the corresponding cis isomer is less stable by 5.1 kcal mol$^{-1}$ at the same level of theory (table S4 in Computational Information). Owing to this low barrier and the small energy difference between the two isomers, a thermally activated dynamic inversion can be anticipated at room temperature, which furthermore affects the shape and the order of the orbitals in the frontier orbital region (Figure S7). In contrast to $3^+$, the spin density of the cis isomer is localised at the phosphorus atoms (Figure S8), which could be subject to irreversible follow up reactions. Thus, we hypothesize a shift of spin density from Fe to P triggered by inversion at phosphorus limiting the lifetime of $3^+$, which agrees well with the results of our electrochemical measurements.

In summary, we successfully synthesized the unprecedented P–B–P bridged [3]ferrocenophane 3, in which a bisphosphanoborane fragment with moderate $\pi$ interaction, formally analogous to the allylic anion, is combined with a redox-active ferrocene unit. Of the two synthetic routes applied, Si/B exchange condensation afforded 3 in significantly higher yield. Both reactions proceeded stereospecifically to give 3 as the rac diastereomer, contrasting the situation found for other P–E–P bridged [3]ferrocenophanes with E = SiXY or PX (V and VI). Electrochemical investigations support an intramolecular electron transfer process from the P–B–P bridge to the ferrocenium moiety in the mono-oxidized state for which the rate constant in solution has been determined. According to quantum chemical calculations, the radical center of monooxidized $3^+$ is localized at the Fe center, but in the cis isomer of $3^+$ it shifts to the adjacent P centers. We are currently exploring redox-switching and radical formation in related [3]ferrocenophanes.

### 3.6.1 Experimental Section

**General procedures.** All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques or in an MBraun glovebox. Solvents (dichloromethane, $n$-pentane, and toluene) were dried and degassed by means of an MBraun SPS-800 solvent purification system. Deuterated solvent for NMR spectroscopy
was dried and degassed at reflux over CaH$_2$ (CDCl$_3$) and freshly distilled prior to use. Boron tribromide, 1-bromo-2,4,6-trimethylbenzene, magnesium turnings and solutions of n-butyllithium (1.6 M in hexane and 2.5 M in hexane, respectively) were commercially purchased and used as received. Chlorotrimethylsilane was distilled prior to use and Cu(I)Cl was purified according to literature procedure.$^{[28]}$ MesCu,$^{[29]}$ MesBB$_2,$$^{[30]}$ 1,$^{[17]}$ 2,$^{[4]}$ and 4$^{[17]}$ were prepared according to methods described in the literature. NMR spectra were recorded at 25 °C on a Bruker AVANCE II-400 spectrometer or on a Bruker Advance III HD spectrometer operating at 400 MHz. Chemical shifts were referenced to residual protic impurities in the solvent ($^1$H) or the deuterio solvent itself ($^{13}$C) and reported relative to external SiMe$_4$ ($^1$H, $^{13}$C) or BF$_3$·OEt$_2$ ($^1$B) standards. Mass spectra were obtained with the use of a Finnigan MAT95 spectrometer employing electron ionisation (EI) using a 70 eV electron impact ionisation source. Elemental analysis was performed with a HEKAtech Euro EA CHNS elemental analyzer. Samples were prepared in a Sn cup and analyzed with added V$_2$O$_5$ to ensure complete combustion. UV-vis spectra were obtained using a Shimadzu UV mini1240 spectrophotometer. Melting points (uncorrected) were obtained using a Shimadzu UV mini1240 spectrophotometer. Melting points (uncorrected) were obtained using a SMP3 melting point apparatus by Stuart in 0.5 mm (o.d.) glass capillaries, which were sealed under argon. X-ray crystallographic data were collected on a Bruker SMART APEX CCD detector on a D8 goniometer equipped with an Oxford Cryostream 700 temperature controller at 100(2) K using graphite monochromated Mo-$K_{\alpha}$ radiation ($\lambda = 0.71073$ Å). An absorption correction was carried out semi-empirically using SADABS$^{[31]}$ (min./max. transmissions = 0.6725/0.7461 (3)). The structure was solved with Olex2$^{[32]}$ using Direct Methods (ShelXS$^{[33]}$a) and refined with the ShelXL$^{[33]}$b refinement package by full-matrix least squares on $F^2$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included isotropically and treated as riding. Cyclic voltammetric, chronoamperometric and dual electrode measurements were carried out in an MBraun acrylic glovebox GB2202-C-VAC under inert argon atmosphere. All samples were measured in dichloromethane, which was dried over CaH$_2$, distilled and stored over molecular sieves (3 Å) under argon atmosphere. Tetrabutylammonium hexafluorophosphate ([NBu$_4$][PF$_6$]) served as supporting electrolyte with a concentration of 0.1 mol L$^{-1}$. The sample concentration during the measurements was set to 0.1 mmol L$^{-1}$. For
cyclic voltammetric measurements the setup consisted of a three-electrode cell with a platinum disk as working electrode, a silver spiral as counter electrode and a silver pseudo reference electrode. Dual electrode voltammetry experiments as well as chronoamperometric measurements were carried out with a Modulated Speed Rotator ring-disk system from Pine Research Instrumentation including a mirror polished glassy carbon 5.0 mm OD disk insert and a 6.5 (ID)/7.5 (OD) mm platinum ring. The sweep rate was always 100 mV s\(^{-1}\), the disk electrode potential was driven from 0 to 900 resp. 1000 mV and the ring electrode potential held at 0 mV. While the potential was driven on the WaveDriver 20 Bipotentiostat from Pine Research Instrumentation, electrochemical data were recorded via AfterMath (Ver. 1.2.5966; Pine Instruments). The half wave potentials of the redox processes, which were referenced using decamethyl ferrocene, and current data of the dual electrode measurements were evaluated with OriginPro (Ver. 8.6.0; OriginLab Corporation). To calculate the rate constant \( k \) of the consecutive reaction the diffusion coefficient \( D = 1.9(2) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1} \) was determined by chronoamperometric measurements at 700 mV for 30 s and evaluation via Cottrell-Plot.\(^{[34]}\) Furthermore, the kinematic viscosity \( \nu \) was calculated on the supposition that the volume of the solvent and its dynamic viscosity does not change with the addition of supporting electrolyte.

**Synthesis of 3.**

**Route A:**

To a solution of 1 (181.1 mg, 0.50 mmol) in toluene (2.5 mL) was added a solution of \( n \)-butyllithium (2.5 M, 1.05 mmol, 0.42 mL) dropwise at 0 °C. The mixture was stirred for 12 h resulting in the formation of the dilithiated species 2 suspended in toluene. After cooling to −78 °C, MesBBr\(_2\) (144.9 mg, 0.50 mmol) was added dropwise. The reaction mixture was slowly warmed to room temperature and stirred overnight. After filtration and extraction of the solid residue twice with toluene (5 mL), the combined organic phases were evaporated to dryness. The product was purified by recrystallization from \( n \)-pentane/dichloromethane (5:1) at −40 °C to yield 3 as orange crystals (m.p. 191 °C). Yield: 68.7 mg (0.35 mmol, 28 %). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 6.81 \)
Route B:

To a solution of 4 (260.8 mg, 0.50 mmol) in dichloromethane (2.5 mL) was added MesBBr$_2$ (144.9 mg, 0.50 mmol) dropwise at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. All volatiles were removed in vacuo and the crude product was purified by recrystallization from n-pentane/dichloromethane (5:1) at −40 °C to yield 3 as orange crystals. Yield: 172.1 mg (0.35 mmol, 70 %).

X-ray crystallographic analysis of 3. Suitable colorless single crystals of 3 (C$_{27}$H$_{37}$BFeP$_2$, $M = 490.17$ g mol$^{-1}$) were obtained from a concentrated n-hexane solution by cooling to −40 °C. Crystal size 0.12 x 0.11 x 0.11 mm, monoclinic, P2$_1$/c, a = 9.9177(4), b = 11.5650(5), c = 22.0296(9) Å, V = 2520.82(18) Å$^3$, Z = 4, $\rho_{calc} = 1.292$ Mg ∙ m$^{-3}$, 3.7° ≤ 2θ ≤ 61.86°, collected (independent) reflections = 37814 (74 98), $R_{int} = 0.0364$, $\mu = 0.738$ mm$^{-1}$, 362 refined parameters, 0 restraints, $R_1 (I > 2\sigma(I)) = 0.0349$, $R_1$ (all data) = 0.0426, $wR_2 (I > 2\sigma(I)) = 0.1106$, $wR_2$ (all data) = 0.1217, residual electron density = 0.56/−0.39 e ∙ Å$^{-3}$. CCDC-1574232 contains the supplementary crystallographic data for the structure of 3. This data can be obtained free of charge from The
Figure S1. Molecular structure of 3 in the solid state with thermal ellipsoids set at 50 % probability (hydrogen atoms omitted for clarity).

Electrochemical measurements

Our cyclic voltammetric studies of 3 reveal two irreversible electrochemical responses for the oxidation in dichloromethane (scan rate: 250 mV s\(^{-1}\); with peak potentials \(E_p = +0.29(1) \text{ V and } +0.82(1) \text{ V vs. Fc/Fc}^+\); Figure S2) before reaching a broad irreversible downstream process at around +1 V (vs. Fc/Fc\(^+\)) which indicates several similar follow up oxidations (black line; Figure S2). Reversing the potential sweep after the first oxidation process, which is assigned to oxidation of the ferrocene backbone, leads to a “more reversible” redox response for this particular process (red line; Figure S2). With increasing scan rate up to 1 V s\(^{-1}\), leaving the system less time to react, the oxidation behavior finally turns into quasi reversible (blue line; Figure S2). This behavior demonstrates the presence of a consecutive reaction after oxidation of the ferrocene backbone. It is known from literature that monocations of substituted ferrocenes can exhibit less stability.\(^{[25]}\) Increased scan rates may overcome the decomposition of the corresponding ferrocenium species. Recently, a similar phenomenon was observed for PPP congeners of 3, i.e. compounds VI (cf. Scheme 1 in the main article).\(^{[18]}\)

To get deeper insight in the electron transfer mechanism of the follow up reaction, we extended our investigations using dual electrode methods. The established rotating ring-disk electrode (RRDE) system
produces a flux of analyte towards the central disk electrode. Radial components of the stream transport the primary oxidation product, generated at the disk, to the outer ring electrode. In transit, it may undergo follow up reactions whose products can be electrochemically analyzed at the ring. Due to diffusion effects, even without consecutive reactions only a small proportion of generated intermediates reach the ring electrode. The collection efficiency depends on the electrode geometry and is defined as

\[ N = \frac{nI_R}{qI_D} \]

with \( n \) resp. \( q \) electrons, ring current \( I_R \) and disk current \( I_D \).

For non-reversible oxidations the collection efficiency \( N_k \) shows dependencies from both the electrode geometry and the rotation rate \( \omega \). Ring and disk current increase with increasing rotational speed (see Figure S3). From the deviation of the measured \( N_k \) values and the undisturbed \( N \) value (taken from reversible oxidized ferrocene) it was possible to calculate the rate constant \( k \) of the consecutive reaction.

According to Albery and Hitchman\[27\] a simple correlation to \( k \) is obtained using following equation:

\[ \frac{1}{N_k} = \frac{I_D}{I_R} = \frac{1}{N} + \frac{1,28}{N} \left( \frac{\nu}{D} \right)^{1/3} \frac{k}{\omega} \]

with the kinematic viscosity \( \nu \) and the diffusion coefficient \( D \).

From the slope of the linear plot (\( 1/N_k \) over \( 1/\omega \); see Figure S4) the rate constant \( k \) was assigned to \( 3.2(4) \) s\(^{-1} \), corresponding to an average lifetime \( \tau \) of the oxidized intermediate of \( 0.31(4) \) s.
Figure S2. Overlay of cyclic voltammetric measurements. Black: Overview at 250 mV s$^{-1}$. Red: “More reversible” oxidation behavior at 250 mV s$^{-1}$ returning after the first oxidation. Blue: Quasi reversible oxidation behavior at high sweep rates (1000 mV s$^{-1}$).

Figure S3. Disk (positive values) and ring (negative values) current in dual electrode experiments at different rotation speeds of the electrodes.
3.6.2 Computational Information

All calculations were carried out with the Gaussian 09 program package.\cite{35} Full geometry optimization calculations were performed. Harmonic vibrational frequencies were calculated at that level, which was used for the optimization to establish the nature of the stationary points obtained, as characterized by none or a single negative eigenvalue of the Hessian for minima and transition structures, respectively. It should be noted in some cases calculation at different level of theory were also performed (Figure S7, Table S3), which gave similar results to the results at B3LYP/6-311+G** level of theory, which was earlier used for ferrocene containing systems.\cite{17,27} For the radical cations, unrestricted B3LYP/6-311+G** calculations were carried out. The $<S_2>$ values (see Table S3) of these systems were close to the theoretical 0.75, which suggests that they do not have significant multireference character. We also carried out single point calculations using the BPE0 method, which was successfully applied for ferrocene containing radical systems\cite{36} and gave similar results to our
calculations at B3LYP/6-311+G** level of theory. Bond orders and bond critical points and their properties were calculated with Multiwfn program.\footnote{37} For the visualization of the molecular structures and the molecular orbitals the MOLDEN\footnote{38} and Gaussview program\footnote{39} were used.

**Bonding situation of 3**

To understand the bonding situation of 3, different reference compounds (Figure S5) were also calculated and compared the properties of the B-P bond of them (Table S1). In case of D and E the related cis isomers (Dcis and Ecis) were also computed and although the energy difference between them are small (ED-EDcis=-0.5 kcal/mol EE-EEcis=1.0 kcal/mol) only the trans isomers were in more details investigated, since the observed 3 exhibits trans configuration.

While the calculated two B–P bond lengths in 3 are very close to each other (at B3LYP/6-311+G** level of theory) – similar to the parent HB(PH$_2$)$_2$ and D – in case B, C and E compounds the two B-P bonds differ significantly. Both phosphorus atoms in 3 exhibit high pyramidal character, in good agreement with the donor-acceptor interaction between the phosphorus lone pairs and the boron center, which is 37.3 and 37.6 kcal mol$^{-1}$ according to our second order perturbation analysis of the Fock matrix in NBO basis. For the better comparison of the interactions between the different compounds it is worth to sum up the interaction energies between the lone pairs of phosphorus and boron center (\(\Sigma E_{E-P}\)). As we can see in Table S1, 3 has one of the largest \(\Sigma E_{E-P}\) value among the investigated systems. The increased \(\Sigma E_{E-P}\) value of 3 can be explained by the ferrocene backbone which behaves as a spacer between the two phosphorus atoms and increases the bond angles around the phosphorus. Similar statement can be established in case of the six-membered ring containing E compound.

The NBO calculation and the planar phosphorus atoms indicate a strong interaction between the phosphorus and the boron center, thus suggesting double bond character. Established measures for bond
orders (see in Table S1, Mayer, Wiberg) are smaller for 3 than for the other reference compounds. The single bond character was also verified by the small ellipticity of the electron density in the B-P bond critical point.

![Chemical structures](image)

**Figure S5.** Reference compounds for the comparison of the bonding situation of 3.

**Table S1.** Different properties of the B-P bond in case of 3 and A-E compounds.

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<th>C</th>
<th>D</th>
<th>E</th>
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<td>\sum E_{E-P}</td>
<td>74.9</td>
<td>31.6</td>
<td>63.8</td>
<td>62.4</td>
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</tr>
<tr>
<td>Mayer bond order B-P(1)</td>
<td>1.53</td>
<td>1.25</td>
<td>1.84</td>
<td>2.26</td>
<td>2.24</td>
<td>2.31</td>
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<tr>
<td></td>
<td>1.54</td>
<td>1.25</td>
<td>1.72</td>
<td>1.85</td>
<td>2.21</td>
<td>2.92</td>
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<tr>
<td>Wiberg bond order B-P(1)</td>
<td>1.18</td>
<td>1.47</td>
<td>1.18</td>
<td>1.30</td>
<td>1.20</td>
<td>1.27</td>
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<tr>
<td></td>
<td>1.18</td>
<td>1.47</td>
<td>1.15</td>
<td>1.13</td>
<td>1.20</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>B-P(1)</td>
<td>0.140</td>
<td>0.146</td>
<td>0.139</td>
<td>0.142</td>
<td>0.142</td>
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</table>
Table 1. Electrostatic potential in the B-P bond critical point

<table>
<thead>
<tr>
<th></th>
<th>B-P(1)</th>
<th>B-P(2)</th>
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</thead>
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<tr>
<td>Ellipticity of</td>
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<td>0.05</td>
</tr>
<tr>
<td>Electrostatic</td>
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<td>0.01</td>
</tr>
<tr>
<td>Bond Critical</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>Point</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

**Figure S6.** The inversion barrier of 3 and the less stable 3’ isomer, which was not observed, at B3LYP/6-311+G** level of theory (at ωB97X-D/6-311+G** level of theory in brackets) and in kcal mol⁻¹ unit.

**TD-DFT calculations**

TD-DFT calculations at B3LYP/6-311+G** level of theory suggest four close lying transitions, which involve the (admixture of the) excitations from the HOMO-X (X=0,1,2,3) to the LUMO (Table S2).
Table S2. TD-DFT results.

<table>
<thead>
<tr>
<th>Experimental $\lambda_{\text{abs}}$ (nm)</th>
<th>Theoretical $\lambda_{\text{abs}}$ (nm)</th>
<th>Intensity</th>
<th>Transition</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>347</td>
<td>352</td>
<td>0.0215</td>
<td>HOMO-3- $\rightarrow$ LUMO</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HOMO-1- $\rightarrow$ LUMO</td>
<td>0.69</td>
</tr>
<tr>
<td>348</td>
<td>348</td>
<td>0.0286</td>
<td>HOMO-2- $\rightarrow$ LUMO</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>HOMO- $\rightarrow$ LUMO</td>
<td>0.57</td>
</tr>
<tr>
<td>332</td>
<td>332</td>
<td>0.0177</td>
<td>HOMO-3- $\rightarrow$ LUMO</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HOMO-1- $\rightarrow$ LUMO</td>
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<tr>
<td>329</td>
<td>329</td>
<td>0.1201</td>
<td>HOMO-2- $\rightarrow$ LUMO</td>
<td>0.57</td>
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<td></td>
<td></td>
<td></td>
<td>HOMO-1- $\rightarrow$ LUMO</td>
<td>-0.40</td>
</tr>
</tbody>
</table>
Figure S7. Selected Kohn-Sham orbitals at B3LYP/6-311+G** level of theory of 3, 3^+ and the cis isomer of 3^+ (3_{cis}^+).

Table S3. The <S2> values of 3^+ and 3_{cis}^+ at different level of theory.

<table>
<thead>
<tr>
<th>level of theory</th>
<th>3^+</th>
<th>3_{cis}^+</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-311+G**</td>
<td>0.787</td>
<td>0.775</td>
</tr>
<tr>
<td>B3LYP/6-31G**//B3LYP/6-311+G**</td>
<td>0.783</td>
<td>0.774</td>
</tr>
<tr>
<td>B3LYP/cc-pVTZ//B3LYP/6-311+G**</td>
<td>0.787</td>
<td>0.776</td>
</tr>
<tr>
<td>M06-2X/6-311+G**//B3LYP/6-311+G**</td>
<td>0.817</td>
<td>0.775</td>
</tr>
<tr>
<td>PBE0/6-311+G**//B3LYP/6-311+G**</td>
<td>0.798</td>
<td>0.789</td>
</tr>
</tbody>
</table>
Figure S8. Spin density maps of $3^+$ and $3_{\text{cis}}^+$.  

Table S4. The energy differences between 3 and $3_{\text{cis}}$ ($\Delta E(3-3_{\text{cis}})$) and between $3^+$ and $3_{\text{cis}}^+$ ($\Delta E(3^+-3_{\text{cis}}^+)$) and the related inversion barriers ($T_{\text{invers}}$). Our attempts to localize the transition state of the inversion of the phosphorus in case of $3^+$ at B3LYP/6-311+G** level of theory failed, due to convergence problems. On the other hand the results at B3LYP/6-31G* are similar to the results at B3LYP/6-311+G** level of theory.

<table>
<thead>
<tr>
<th>level of theory</th>
<th>$\Delta E(3-3_{\text{cis}})$</th>
<th>$T_{\text{invers}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-311+G**</td>
<td>-2.8</td>
<td>5.0</td>
</tr>
<tr>
<td>B3LYP/6-31G*</td>
<td>-3.3</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>$\Delta E(3^+-3_{\text{cis}}^+)$</td>
<td>$T_{\text{invers}}$</td>
</tr>
<tr>
<td>B3LYP/6-311+G**</td>
<td>-3.6</td>
<td>-</td>
</tr>
<tr>
<td>B3LYP/6-31G*</td>
<td>-5.1</td>
<td>5.7</td>
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</tbody>
</table>
Figure S9. The electrostatic potential map of $3^+$ and $3_{\text{cis}}^+$ (red <0.10, yellow 0.12, green 0.15, light blue 0.18, deep blue >0.20). While in case of $3^+$ the positive charge is rather localized at the ferrocene unit, in case of $3_{\text{cis}}^+$ the phosphorus atoms have partial positive charge.

3.6.3 References


[24] Low temperature NMR down to −40 °C showed no signal splitting.


4. Conclusion

In conclusion, a novel, highly effective and environmental benign method for the formation of B–C bonds via Si/B exchange has been presented. The reaction of a dibromo(hetero)arylborane 2 with a trimethylsilyl substituted (hetero)arene 1 proceeds catalytically with the metal-free organocatalyst TMSNTf$_2$ and affords the di(hetero)arylboronoboranes 3 (Scheme 1).

\[
\text{Ar}^1\text{TMS} + \text{Ar}^2\text{Br}_2 \xrightarrow{\text{DCM, r.t., TMSNTf}_2} \text{Ar}^1\text{B}^\text{Ar}^2 \xrightarrow{\text{Ar}^3\text{Li, toluene, r.t.}} \text{Ar}^1\text{B}^\text{Ar}^2 \text{Ar}^3
\]

Except the formation of 3cc, which requires a prolonged reaction time (3 d) and higher catalyst loading (25 mol%), the catalytic reactions proceed smoothly at ambient temperature with 5 mol% of TMSNTf$_2$ within less than 2 hours. The diarylbromoboranes 3 are formed selectively, with TMSBr as the only, volatile by-product. Significantly, with this method, toxic organotin compounds used in the previous state-of-the-art approach are excluded. Post-modification with a suitable aryllithium reagent (Tip: 2,4,6-triisopropylphenyl; Mes*: 2,4,6-tri-tert-butylphenyl) leads to kinetically stabilized triarylboronoboranes 4 (Scheme 1).

These products (except for 4cc) are perfectly stable against moisture and air. Furthermore, the catalytic reaction was applicable to the synthesis of oligo- and polythiophenes, and -furans, respectively (Scheme 2). The latter were the first examples of polyfurans with incorporated boron atoms. The absorption and emission behavior was thoroughly studied, revealing a significant difference between thiophene-based and furan-based compounds. $4bb$ and $6b^\prime$ are highly emissive, with quantum yields of 24 % for $4bb$ and 71 % for $6b^\prime$. 
whereas, the thiophene congeners were found to be weakly or non-emitting molecules. In addition, the synthesis of higher analogues comprising either thiophene and furan moieties (dimers 7, trimers 8) and mixed derivatives was successful as well (Figure 1).


Figure 1. Thiophene and furan containing dimers 7 and trimers 8.

With synthesis of the higher oligomers it could be demonstrated that an extension of the chain length leads to a red-shift of the absorption maximum. Furthermore, the mixed derivatives 7aba, 7bab and 8aaba showed different absorption characteristics compared to their symmetrical congeners. This gives rise to tailorable and tunable optical properties, depending on the heterocycle ratio applied. The synthesized model compounds as well as the oligo- and polymers were used to determine the effective conjugation wavelength (ECL). The result was that the ECL for the thiophene and furan systems is 9.

Compounds 4aa, 4bb' and 6a showed binding of fluoride under ambient conditions. Upon addition of tetrabutylammonium fluoride (TBAF), the UV-vis absorption behavior changed dramatically. Whereas 6a was capable of performing fluoride binding, 6b did not show similar properties. Presumably, this is a result of the higher steric
demand provided by Mes* compared to Tip. This is further corroborated by the different properties of 4bb’ and 4bb.

First kinetic studies revealed that the dependencies of the rate of the reaction to yield 3aa on the total concentration and the amount of catalyst applied are 1\textsuperscript{st} order. The dependency of the progression of the catalytic reaction on the nature of both starting materials proved to be complex. Presumably, the reason for this behavior lies within a second reaction path leading to 3aa as well. In addition to the desilylation reaction, C–H activation furnishes a product 3aa’, which is transformed subsequently to 3aa by post-desilylation \textit{in situ} (Scheme 3).

**Scheme 3.** Two possible pathways for the formation of 3aa.

Presumably, the \textit{in situ} formed strong acid HNTf\textsubscript{2} reacts with 3aa’ to form 3aa. First specific desilylation experiments with a Mes* substituted derivative of 3aa’ seem to confirm this hypothesis.

Furthermore, the influence of the sterically demanding aryl substituent and the substitution at the 5,5´-positions at the thiophene rings in 9 and 10 (Figure 2) on their structures in the solid-state was investigated.
Figure 2. Mes and Tip stabilized triarylboranes with different substituents at the 5,5´ positions.

The structures of 9 and 10 differ significantly from each other in the solid-state with respect to the B–C\textsubscript{Thi} bonds and the interplanar angle between the thiophene rings.

The first kinetically stabilized tetrathiatetraboraporphyrinogen 11 (Figure 3) has been successfully prepared. The macrocycle 11 was synthesized in a modular approach starting from 4aa.

Figure 3. B-Tip substituted tetrathiatetraboraporphyrinogen 11 and synthesis of boron-bridged [3]ferrocenophane 12.

\(^1\)H NMR spectroscopy ascertained that no additional aromaticity, other than the aromaticity provided by the thiophene rings, is present in the system, hence, no ring current was observed. However, although 11 consists of 16 \(\pi\) electrons, and, therefore, represents an antiaromatic species according to Hückel, it comprises a fully delocalized aromatic species. Despite the fact, that the boron atoms are kinetically stabilized by Tip groups, they maintain their Lewis acidic character. As a result,
11 is capable of binding fluoride anions selectively. This effect can be monitored either using UV-vis spectroscopy or by fluorescence detection. The lowest-energy absorption band (417 nm) was continuously quenched upon titration with fluoride. Furthermore, the fluorescence emission (quantum yield: 5.9 %) was visually altered after addition of four equivalents of TBAF (former green-yellow emission turned orange). Therefore, compound 11 can serve as a potent chemical sensor.

Finally, the first boron-bridged [3]ferrocenophane 12 having P–B bonds was synthesized (Figure 3). The reaction via Si/B exchange turned out to be more efficient than salt elimination via a dilithiated species. Formation of 12 proceeds selectively, with TMSBr as the only by-product, in good yields. In contrast to other P–E–P bridged [3]ferrocenophanes (E = SiXY, PX), 12 is formed steroespecifically as its rac diastereomer. Electrochemical investigations support an intramolecular electron transfer process from the P–B–P bridge to the ferrocenium moiety in the mono-oxidized state.
5. Outlook

Since the syntheses of thiophene- and furan-containing (macro)molecules by a catalytic Si/B exchange approach were successful, an extension of the reaction to the higher analogues of thiophene and furan (selenophene, tellurophene, Figure 1) seems to be a promising possibility to further tune the optical properties of boron-containing (macro)molecules. Based on the lower band gap of selenophene- and tellurophene-based compounds compared to thiophene and furan, polymers 1 and 2 might be attractive synthetic targets. Also the incorporation of electron-poor organic building blocks (e.g. fluorinated benzene) is an interesting way to render the electronic and optical properties in boron-containing (macro)molecules (Figure 1).

Polymer 3 might reveal improved anion binding properties, due to the increased Lewis acidity of the boron atoms in 3. The catalytic reaction of dibromo(hetero)arylboranes using TMSNTf₂ could possibly be extended to dichloro(hetero)arylboranes. The advantage of this extension would be the use of even less harmful starting materials and the lower toxicity of the resulting by-product trimethylsilyl chloride (TMSCl). To achieve this goal, presumably a stronger catalyst is required, as preliminary investigations revealed that the reactivity of TMSNTf₂ was not sufficient to enable the reaction between a dichloro(2-thienyl)borane and a trimethylsilyl substituted thiophene.

Further research on 11 should involve the attempt to reduce the tetrathiatetraaborapophyrinogen to an 18 π electron system and perform subsequent experiments with suitable transition metal complex precursor molecules.
In addition to the tetrathiatetraboraporphyrinogen, its tetrafuran congener 4 (Figure 2) represents a further attractive synthetic target. Due to the higher tendency of furan rings to adopt coplanarity, delocalization of \( \pi \) electrons should be improved compared to the thiophene compound. As a result, the tetraoxatetraboraporphyrinogen could exhibit intriguing optical and electronic properties. Furthermore, the smaller atom size of oxygen compared to sulfur, presumably, leads to a larger cavity in the center of the ring. Therefore, it might be possible to complex metals in this cavity without a previous reduction. Nonetheless, the corresponding reduced species having 18 \( \pi \) electrons might lead to improved performance with respect to complexation reactions.

\[ \text{Figure 2. Tetraoxatetraboraporphyrinogen 4 and [3]ferrocenophane 5 (substituted by Tip or Mes\(^*\)).} \]

Since only a low degree of delocalization was observed in the synthesized P–B–P bridged [3]ferrocenophane 5, introduction of a sterically more demanding aryl substituent (e.g. Tip or Mes\(^*\)) at the boron atom or at the phosphorous centers, possibly leads to a more planar conformation of the P–B–P plane. The resulting rigidity may be expected to result in improved \( \pi \) delocalization.
6. Appendix

6.1 Catalytic B–C Coupling by Si/B Exchange: A Versatile Route to $\pi$-Conjugated Organoborane Molecules, Oligomers, and Polymers

NMR spectra

Figure A1.1. $^1$H NMR spectrum of 1a (400 MHz, in CDCl$_3$).
Figure A1.2. $^1$H NMR spectrum of 1b (400 MHz, in CDCl$_3$).

Figure A1.3. $^1$H NMR spectrum of 1c (400 MHz, in CDCl$_3$).
Figure A1.4. $^1$H NMR spectrum of 2a (400 MHz, in CDCl$_3$).

Figure A1.5. $^{11}$B($^1$H) NMR spectrum of 2a (128 MHz, in CDCl$_3$).
Figure A1.6. $^1$H NMR spectrum of 2c (400 MHz, in CDCl$_3$).

Figure A1.7. $^{11}$B($^1$H) NMR spectrum of 2c (128 MHz, in CDCl$_3$).
Figure A1.8. $^1$H NMR spectrum of crude 3a (400 MHz, in CDCl$_3$).

Figure A1.9. $^1$H NMR spectrum of crude 3a (detail of aromatic region) (400 MHz, in CDCl$_3$).
**Figure A1.10.** $^{11}$B$^1$H NMR spectrum of crude 3a (128 MHz, in CDCl$_3$).

**Figure A1.11.** $^1$H NMR spectrum of 4a (400 MHz, in CDCl$_3$).
Figure A1.12. $^{11}$B($^1$H) NMR spectrum of 4a (128 MHz, in CDCl$_3$).

Figure A1.13. $^{13}$C NMR spectrum of 4a (101 MHz, in CDCl$_3$).
**Figure A1.14.** $^1$H NMR spectrum of crude 3b (400 MHz, in CDCl$_3$).

**Figure A1.15.** $^1$H NMR spectrum of crude 3b (detail of aromatic region) (400 MHz, in CDCl$_3$).
Figure A1.16. $^{11}$B$^{[1]}$H NMR spectrum of crude 3b (128 MHz, in CDCl$_3$).

Figure A1.17. $^1$H NMR spectrum of 4b (400 MHz, in CDCl$_3$).
Figure A1.18. $^{11}$B($^1$H) NMR spectrum of 4b (128 MHz, in CDCl$_3$).

Figure A1.19. $^{13}$C NMR spectrum of 4b (101 MHz, in CDCl$_3$).
Figure A1.20. $^1$H NMR spectrum of crude 3c (400 MHz, in CDCl$_3$).

Figure A1.21. $^1$H NMR spectrum of crude 3c (detail of aromatic region) (400 MHz, in CDCl$_3$).
Figure A1.22. $^{11}$B$^{1}$H) NMR spectrum of crude 3c (128 MHz, in CDCl$_3$).

Figure A1.23. $^1$H NMR spectrum of 4c (400 MHz, in CDCl$_3$).
Figure A1.24. $^{11}$B$^1$H NMR spectrum of 4c (128 MHz, in CDCl$_3$).

Figure A1.25. $^{13}$C NMR spectrum of 4c (101 MHz, in CDCl$_3$).
Figure A1.26. $^{1}$H NMR spectrum of 5a (400 MHz, in C$_6$D$_6$).

Figure A1.27. $^{1}$H NMR spectrum of 5b (400 MHz, in CDCl$_3$).
Figure A1.28. $^1$H NMR spectrum of 6a (400 MHz, in C$_6$D$_6$).

Figure A1.29. $^1$H NMR spectrum of 6a (detail of aromatic region) (400 MHz, in C$_6$D$_6$).
Figure A1.30. $^{11}$B$^{1}$H NMR spectrum of 6a (128 MHz, in CDCl$_3$).

Figure A1.31. $^1$H NMR spectrum of 6b (400 MHz, in CDCl$_3$; * = pentane; # = TMSBr).
Figure A1.32. $^1$H NMR spectrum of 6b (detail of aromatic region) (400 MHz, in CDCl$_3$).

Figure A1.33. $^{11}$B($^1$H) NMR spectrum of 6b (128 MHz, in CDCl$_3$).
Figure A1.34. $^1H$ NMR spectrum of $3a^{\text{Tip}}$ (400 MHz, in CDCl$_3$).

Figure A1.35. $^{11}$B($^1$H) NMR spectrum of $3a^{\text{Tip}}$ (128 MHz, in CDCl$_3$).
Figure A1.36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $3\text{a}^{\text{TIP}}$ (101 MHz, in CDCl$_3$).

Figure A1.37. $^{29}\text{Si}$ NMR spectrum of $3\text{a}^{\text{TIP}}$ (79.5 MHz, in CDCl$_3$).
Figure A1.38. $^1$H NMR spectrum of $3b_{\text{Mes}^*}$ (400 MHz, in CDCl$_3$).

Figure A1.39. $^{11}$B$[^1]$H NMR spectrum of $3b_{\text{Mes}^*}$ (128 MHz, in CDCl$_3$).
Figure A1.40. $^{13}\text{C}[^1\text{H}]$ NMR spectrum of $3b^{\text{Mes}^*}$ (101 MHz, in CDCl$_3$).

Figure A1.41. $^1\text{H}$ NMR spectrum of $9a$ (400 MHz, in CDCl$_3$).
Figure A1.42. $^{11}$B$^1$H NMR spectrum of 9a (128 MHz, in CDCl$_3$).

Figure A1.43. $^{13}$C NMR spectrum of 9a (101 MHz, in CDCl$_3$).
Figure A1.44. $^1$H NMR spectrum of 9b (400 MHz, in CDCl$_3$).

Figure A1.45. $^{11}$B($^1$H) NMR spectrum of 9b (128 MHz, in CDCl$_3$).
Figure A1.46. $^{13}$C NMR spectrum of 9b (101 MHz, in CDCl$_3$).

Figure A1.47. $^1$H NMR spectrum of 3a$^{^1}$Tip (400 MHz, in CDCl$_3$).
Figure A1.48. $^{11}$B($^1$H) NMR spectrum of 3a$^{11}$Tip (128 MHz, in CDCl$_3$).

Figure A1.49. $^1$H NMR spectrum of 3b$^{18}$Mes* (400 MHz, in CDCl$_3$).
Figure A1.50. $^{11}\text{B}^{(1)}\text{H}$ NMR spectrum of $3b^{\text{Mes}^*}$ (128 MHz, in CDCl$_3$).

Figure A1.51. $^{13}\text{C}^{(1)}\text{H}$ NMR spectrum of $3b^{\text{Mes}^*}$ (101 MHz, in CDCl$_3$).
UV–vis spectra

**Figure A1.52.** UV–vis spectrum of 4a (in THF).

**Figure A1.53.** UV-vis spectrum of 4b (in THF).
Figure A1.54. UV–vis spectrum of 4c (in CH₂Cl₂).

Figure A1.55. UV–vis spectrum of 8a (in THF).
Figure A1.56. UV–vis spectrum of 8b (in THF).

Figure A1.57. UV–vis spectrum of 9a (in THF).
Figure A1.58. UV–vis spectrum of 9b (in THF).

Figure A1.59. UV–vis spectrum of 8a’ (in THF).
Figure A1.60. UV–vis spectrum of 8b' (in THF).

Fluorescence spectra

Figure A1.61. Fluorescence spectrum of 4a (in CH$_2$Cl$_2$, $\lambda_{ex} = 325$ nm).
Figure A1.62. Fluorescence spectrum of 4b (in THF, $\lambda_{ex} = 308$ nm).

Figure A1.63. Fluorescence spectrum of 8a (in THF, $\lambda_{ex} = 380$ nm).
**Figure A1.64.** Fluorescence spectrum of 8b (in THF, $\lambda_{ex} = 380$ nm).

**Figure A1.65.** Fluorescence spectrum of 8a′ (in THF, $\lambda_{ex} = 380$ nm).
Figure A1.66. Fluorescence spectrum of $8b'$ (in THF, $\lambda_{ex} = 400$ nm).

**Mass spectra**

Figure A1.67. EI mass spectrum of 4a.
Figure A1.68. EI mass spectrum of 4b.

Figure A1.69. EI mass spectrum of 4c.
Figure A1.70. EI mass spectrum of 9a.

Figure A1.71. EI mass spectrum of 9b.
6.2 From Monodisperse Thienyl- and Furylborane Oligomers to Polymers – Modulating the Optical Properties Through the Hetarene Ratio

NMR spectra

Figure A2.1. $^1$H NMR spectrum of crude 6aa (400 MHz, in CDCl$_3$).
Figure A2.2. $^1$H NMR spectrum of crude 6aa (detail of aromatic region) (400 MHz, in CDCl$_3$).

Figure A2.3. $^{11}$B($^1$H) NMR spectrum of crude 6aa (128 MHz, in CDCl$_3$).
Figure A2.4. $^1$H NMR spectrum of crude 6ab (400 MHz, in CDCl$_3$).

Figure A2.5. $^1$H NMR spectrum of crude 6ab (detail of aromatic region) (400 MHz, in CDCl$_3$).
Figure A2.6. $^{11}$B($^1$H) NMR spectrum of crude 6ab (128 MHz, in CDCl$_3$).

Figure A2.7. $^1$H NMR spectrum of crude 6bb (400 MHz, in CDCl$_3$).
Figure A2.8. $^1$H NMR spectrum of crude 6bb (detail of aromatic region) (400 MHz, in CDCl$_3$).

Figure A2.9. $^{11}$B($^1$H) NMR spectrum of crude 6bb (128 MHz, in CDCl$_3$).
Figure A2.10. $^1$H NMR spectrum of crude 6cc (400 MHz, in CDCl$_3$).

Figure A2.11. $^1$H NMR spectrum of crude 6cc (detail of aromatic region) (400 MHz, in CDCl$_3$).
Figure A2.12. $^{11}$B($^1$H) NMR spectrum of crude 6cc (128 MHz, in CDCl$_3$).

Figure A2.13. $^1$H NMR spectrum of 1aa$^{\text{Tip}}$ (400 MHz, in CDCl$_3$).
**Figure A2.14.** $^{11}$B($^1$H) NMR spectrum of $1aa^\text{TIP}$ (128 MHz, in CDCl$_3$).

**Figure A2.15.** $^{11}$B($^1$H) NMR spectrum of $1aa^\text{TIP}$ treated with one eq. of TBAF (128 MHz, in CDCl$_3$).
Figure A2.16. $^{13}$C($^1$H) NMR spectrum of 1aa$^{TIP}$ (101 MHz, in CDCl$_3$).

Figure A2.17. $^1$H NMR spectrum of 1ab$^{Mes^*}$ (400 MHz, in CDCl$_3$).
Figure A2.18. $^{11}\text{B}(^1\text{H})$ NMR spectrum of $\text{1ab}^{\text{Mes}}$ (128 MHz, in CDCl$_3$).

Figure A2.19. $^{13}\text{C}(^1\text{H})$ NMR spectrum of $\text{1ab}^{\text{Mes}}$ (101 MHz, in CDCl$_3$).
Figure A2.20. $^1$H NMR spectrum of $\text{1bb}^{\text{Mes}^*}$ (400 MHz, in CDCl$_3$).

Figure A2.21. $^{11}\text{B}(^1\text{H})$ NMR spectrum of $\text{1bb}^{\text{Mes}^*}$ (128 MHz, in CDCl$_3$).
Figure A2.22. $^{13}$C($^1$H) NMR spectrum of $1bb^{\text{Mes}^*}$ (101 MHz, in CDCl$_3$).

Figure A2.23. $^1$H NMR spectrum of $1bb^{\text{Tip}^*}$ (400 MHz, in CDCl$_3$).
Figure A2.24. $^{11}\text{B}^1\text{H}$ NMR spectrum of $1\text{bb}^{\text{TIP}}$ (128 MHz, in CDCl$_3$).

Figure A2.25. $^{11}\text{B}^1\text{H}$ NMR spectrum of $1\text{bb}^{\text{TIP}}$ treated with one eq. of TBAF (128 MHz, in CDCl$_3$).
Figure A2.26. $^{13}$C($^1$H) NMR spectrum of $1\text{bb}^{\text{TP}}$ (101 MHz, in CDCl$_3$).

Figure A2.27. $^1$H NMR spectrum of $1\text{cc}^{\text{Mes}^*}$ (400 MHz, in CDCl$_3$).
Figure A2.28. $^{11}$B$^{(1}\text{H})$ NMR spectrum of $1\text{cc}^{\text{Mes}^*}$ (128 MHz, in CDCl$_3$).

Figure A2.29. $^{13}$C$^{(1}\text{H})$ NMR spectrum of $1\text{cc}^{\text{Mes}^*}$ (101 MHz, in CDCl$_3$).
Figure A2.30. $^1$H NMR spectrum of 2aaa$^{TIP}$ (400 MHz, in CDCl$_3$).

Figure A2.31. $^{11}$B($^1$H) NMR spectrum of 2aaa$^{TIP}$ (128 MHz, in CDCl$_3$).
Figure A2.32. $^{13}$C($^1$H) NMR spectrum of 2aaa$^{\text{Tip}}$ (101 MHz, in CDCl$_3$).

Figure A2.33. $^1$H NMR spectrum of 2aba$^{\text{Mes}^*}$ (400 MHz, in CDCl$_3$).
Figure A2.34. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of $2aba^\text{Mes}^*$ (128 MHz, in CDCl$_3$).

Figure A2.35. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $2aba^\text{Mes}^*$ (101 MHz, in CDCl$_3$).
Figure A2.36. $^1$H NMR spectrum of 2bab$^{\text{Mes}^*}$ (400 MHz, in CDCl$_3$).

Figure A2.37. $^{11}$B$^{(1)}$H NMR spectrum of 2bab$^{\text{Mes}^*}$ (128 MHz, in CDCl$_3$).
Figure A2.38. $^{13}$C($^1$H) NMR spectrum of $2\text{bab}^\text{Mes}^*$ (101 MHz, in CDCl$_3$).

Figure A2.39. $^1$H NMR spectrum of $2\text{bbb}^\text{Mes}^*$ (400 MHz, in CDCl$_3$).
Figure A2.40. $^{11}$B($^1$H) NMR spectrum of $2\text{bb}^{\text{Mes}^*}$ (128 MHz, in CDCl$_3$).

Figure A2.41. $^{13}$C($^1$H) NMR spectrum of $2\text{bb}^{\text{Mes}^*}$ (101 MHz, in DCM-D2).
Figure A2.42. $^1$H NMR spectrum of 9aa$^{Tip}$ (400 MHz, in CDCl$_3$).

Figure A2.43. $^{11}$B($^1$H) NMR spectrum of 9aa$^{Tip}$ (128 MHz, in CDCl$_3$).
Figure A2.44. $^{13}\text{C}(^1\text{H})$ NMR spectrum of $9\text{aa}^{\text{Tip}}$ (101 MHz, in CDCl$_3$).

Figure A2.45. $^1\text{H}$ NMR spectrum of $9\text{ab}^{\text{Mes}^*}$ (400 MHz, in CDCl$_3$).
Figure A2.46. $^{11}$B($^1$H) NMR spectrum of $9ab^{Mes}$ (128 MHz, in CDCl$_3$).

Figure A2.47. $^{13}$C($^1$H) NMR spectrum of $9ab^{Mes}$ (101 MHz, in CDCl$_3$).
Figure A2.48. $^1$H NMR spectrum of $9bb^{\text{Mes}}$ (400 MHz, in CDCl$_3$).

Figure A2.49. $^{11}$B$^{(1)}$H NMR spectrum of $9bb^{\text{Mes}}$ (128 MHz, in CDCl$_3$).
Figure A2.50. $^{13}$C($^1$H) NMR spectrum of $9bb^{Mes^5}$ (101 MHz, in CDCl$_3$).

Figure A2.51. $^1$H NMR spectrum of $10aaaa^{Tip}$ (400 MHz, in CDCl$_3$).
Figure A2.52. $^{11}$B($^1$H) NMR spectrum of 10aaaa$^{T_6}$ (128 MHz, in CDCl$_3$).

Figure A2.53. $^{13}$C($^1$H) NMR spectrum of 10aaaa$^{T_6}$ (101 MHz, in CDCl$_3$).
Figure A2.54. $^1$H NMR spectrum of 10aaba$^{\text{Mes}^*}$ (400 MHz, in CDCl$_3$).

Figure A2.55. $^{13}$C($^1$H) NMR spectrum of 10aaba$^{\text{Mes}^*}$ (101 MHz, in CDCl$_3$).
Figure A2.56. $^1$H NMR spectrum of 8a (400 MHz, in C$_6$D$_6$).

Figure A2.57. $^1$H NMR spectrum of 8a (detail of aromatic region) (400 MHz, in C$_6$D$_6$).
Figure A2.58. $^{11}$B{$^1$H} NMR spectrum of 8a (128 MHz, in CDCl$_3$).

Figure A2.59. $^1$H NMR spectrum of 8b (400 MHz, in CDCl$_3$; * = pentane; # = TMSBr).
Figure A2.60. $^1$H NMR spectrum of 8b (detail of aromatic region) (400 MHz, in CDCl$_3$).

Figure A2.61. $^{11}$B($^1$H) NMR spectrum of 8b (128 MHz, in CDCl$_3$).
Figure A2.62. $^1$H NMR spectrum of 3a$^{\text{Tip}}$ (400 MHz, in CDCl$_3$).

Figure A2.63. $^{11}$B$[^1]$H NMR spectrum of 3a$^{\text{Tip}}$ (128 MHz, in CDCl$_3$).
Figure A2.64. $^{11}$B{$^1$H} NMR spectrum of 3a$^{\text{Tip}}$ treated with four eq. of TBAF (128 MHz, in CDCl$_3$).

Figure A2.65. $^{13}$C{$^1$H} NMR spectrum of 3a$^{\text{Tip}}$ (101 MHz, in CDCl$_3$).
Figure A2.66. $^{29}$Si NMR spectrum of $3a^\text{Tip}$ (79.5 MHz, in CDCl$_3$).

Figure A2.67. $^1$H NMR spectrum of $3b^\text{Mes}$* (400 MHz, in CDCl$_3$).
Figure A2.68. $^{11}$B($^1$H) NMR spectrum of $3b^{\text{Mes}^*}$ (128 MHz, in CDCl$_3$).

Figure A2.69. $^{13}$C($^1$H) NMR spectrum of $3b^{\text{Mes}^*}$ (101 MHz, in CDCl$_3$).
Figure A2.70. $^1$H NMR spectrum of 3a\textsuperscript{TIP} (400 MHz, in CDCl\textsubscript{3}).

Figure A2.71. $^{11}$B($^1$H) NMR spectrum of 3a\textsuperscript{TIP} (128 MHz, in CDCl\textsubscript{3}).
Figure A2.72. $^1$H NMR spectrum of 3b$^{\text{Mes}}$ (400 MHz, in CDCl$_3$).

Figure A2.73. $^{11}$B($^1$H) NMR spectrum of 3b$^{\text{Mes}}$ (128 MHz, in CDCl$_3$).
Figure A2.74. $^{13}$C($^1$H) NMR spectrum of $3b^{\text{Mes}}$ (101 MHz, in CDCl$_3$).

UV–vis spectra

Figure A2.75. UV–vis spectrum of $1aa^{\text{Tip}}$ (in THF).
Figure A2.76. UV–vis spectrum of $1_{ab}^{\text{Mes}^*}$ (in THF).

Figure A2.77. UV-vis spectrum of $1_{bb}^{\text{Mes}^*}$ (in THF).
Figure A2.78. UV-vis spectrum of $1bb^{tip}$ (in THF).

Figure A2.79. UV–vis spectrum of $1cc^{Mes^*}$ (in $\text{CH}_2\text{Cl}_2$).
Figure A2.80. UV-vis spectrum of $2\text{aaa}^{\text{Tip}}$ (in THF).

Figure A2.81. UV-vis spectrum of $2\text{aba}^{\text{Mes}}^+$ (in THF).
Figure A2.82. UV-vis spectrum of $2\text{bab}^{\text{Mes}^*}$ (in THF).

Figure A2.83. UV-vis spectrum of $2\text{bbb}^{\text{Mes}^*}$ (in THF).
Figure A2.84. UV–vis spectrum of $9aa^{\text{Tip}}$ (in THF).

Figure A2.85. UV–vis spectrum of $9ab^{\text{Mes}^*}$ (in THF).
Figure A2.86. UV–vis spectrum of \(9\text{bb}^{\text{Mes}^*}\) (in THF).

Figure A2.87. UV–vis spectrum of \(10\text{aaaa}^{\text{Tlp}}\) (in THF).
Figure A2.88. UV-vis spectrum of $10aaba_{\text{Mes}^*}$ (in THF).

Figure A2.89. UV-vis spectrum of $3a_{\text{Tip}}$ (in THF).
Figure A2.90. UV-vis spectrum of 3b\textsuperscript{Mes} (in THF).

Figure A2.91. UV–vis spectrum of 3a\textsuperscript{Tip} (in THF).
Figure A2.92. UV–vis spectrum of $3b^\text{Mes}$ (in THF).

Figure A2.93. UV-vis spectra of the fluoride titration of $1\text{aa}^{\text{Tlp}}$ with different equivalents of TBAF.
Figure A2.94. UV-vis spectra of the fluoride titration of $1bb^{\text{TIP}}$ with different equivalents of TBAF.

Figure A2.95 UV-vis spectra of the fluoride titration of $3a^{\text{TIP}}$ with different equivalents of TBAF.
Fluorescence spectra

Figure A2.96. Fluorescence spectrum of $1\text{aa}^{\text{TIP}}$ (in THF, $\lambda_{ex} = 325$ nm).

Figure A2.97. Fluorescence spectrum of $1\text{ab}^{\text{Mes}^*}$ (in THF, $\lambda_{ex} = 324$ nm).
Figure A2.98. Fluorescence spectrum of $1bb^{\text{Mes}^*}$ (in THF, $\lambda_{\text{ex}} = 308 \text{ nm}$).

Figure A2.99. Fluorescence spectrum of $2bb^{\text{Mes}^*}$ (in THF, $\lambda_{\text{ex}} = 360 \text{ nm}$).
Figure A2.100. Fluorescence spectrum of 3aTip (in THF, $\lambda_{ex} = 380 \text{ nm}$).

Figure A2.101. Fluorescence spectrum of 3bTip (in THF, $\lambda_{ex} = 380 \text{ nm}$).
Figure A2.102. Fluorescence spectrum of $3a^\text{Tip}$ (in THF, $\lambda_{\text{ex}} = 380$ nm).

Figure A2.103. Fluorescence spectrum of $3b^\text{Mes}$* (in THF, $\lambda_{\text{ex}} = 400$ nm).
Mass spectra

Figure A2.104. EI mass spectrum of $1\text{aa}^{\text{TIP}}$.

Figure A2.105. EI mass spectrum of $1\text{ab}^{\text{Mes}^*}$. 
Figure A2.106. ESI mass spectrum of 1bb\textsuperscript{Mes}.

Figure A2.107. ESI mass spectrum of 1bb\textsuperscript{TIP}.
Figure A2.108. EI mass spectrum of $1cc^{\text{Mes}}$.

Figure A2.109. SIMS mass spectrum of $2\text{aaa}^{\text{Tip}}$. 
Figure A2.110. EI mass spectrum of $2aba^{\text{Mes}^{*}}$.

Figure A2.111. EI mass spectrum of $2bab^{\text{Mes}^{*}}$. 
Figure A2.112. EI mass spectrum of $2bbb^{\text{Mes}^+}$.

Figure A2.113. EI mass spectrum of $9aa^{\text{Tip}}$. 
Figure A2.114. EI mass spectrum of $9ab^{\text{Mes}^*}$.

Figure A2.115. EI mass spectrum of $9bb^{\text{Mes}^*}$. 
Figure A2.116. SIMS mass spectrum of $^{10\text{aaaa}}_{\text{Tip}}$.

Figure A2.117. SIMS mass spectrum of $^{10\text{aba}}_{\text{Mes}^*}$. 
Figure A2.118. SIMS mass spectrum of $^{10}$babb$^{\text{Mes}^+}$. 
6.3 Mechanistic studies on the formation of diarylbromoboranes by catalytic Si/B exchange

**NMR spectra**

Figure A3.1. $^1$H NMR spectrum of crude 3aa (400 MHz, in CDCl$_3$).
Figure A3.2. $^1$H NMR spectrum of crude 3aa (detail of aromatic region) (400 MHz, in CDCl$_3$).

Figure A3.3. $^{11}$B($^1$H) NMR spectrum of crude 3aa (128 MHz, in CDCl$_3$).
Figure A3.4. $^1$H NMR spectrum of crude 3ac (400 MHz, in CDCl$_3$).

Figure A3.5. $^1$H NMR spectrum of crude 3ac (detail of aromatic region) (400 MHz, in CDCl$_3$).
Figure A3.6. $^{11}$B($^1$H) NMR spectrum of crude 3ac (128 MHz, in CDCl$_3$).

Figure A3.7. $^1$H NMR spectrum of crude 3bc (400 MHz, in CDCl$_3$).
**Figure A3.8.** $^1$H NMR spectrum of crude 3bc (detail of aromatic region) (400 MHz, in CDCl$_3$).

**Figure A3.9.** $^{11}$B($^1$H) NMR spectrum of crude 3bc (128 MHz, in CDCl$_3$).
Figure A3.10. $^1$H NMR spectrum of 4aa (400 MHz, in CDCl$_3$).

Figure A3.11. $^{11}$B($^1$H) NMR spectrum of 4aa (128 MHz, in CDCl$_3$).
Figure A3.12. $^{13}\text{C}(^1\text{H})$ NMR spectrum of 4aa (101 MHz, in CDCl$_3$).

Figure A3.13. $^1\text{H}$ NMR spectrum of 4aa$^-$ (400 MHz, in CDCl$_3$).
**Figure A3.14.** $^{11}B\{^1H\}$ NMR spectrum of 4aa$^-$ (128 MHz, in CDCl$_3$).

**Figure A3.15.** $^{13}C\{^1H\}$ NMR spectrum of 4aa$^-$ (101 MHz, in CDCl$_3$).
Figure A3.16. $^1$H NMR spectrum of 4ac (400 MHz, in CDCl$_3$).

Figure A3.17. $^{11}$B($^1$H) NMR spectrum of 4ac (128 MHz, in CDCl$_3$).
Figure A3.18. $^{13}$C$^{1}{\text{H}}$ NMR spectrum of 4ac (101 MHz, in CDCl$_3$).

Figure A3.19. $^1$H NMR spectrum of 4bc (400 MHz, in CDCl$_3$).
Figure A3.20. $^{11}$B{$^1$H} NMR spectrum of 4bc (128 MHz, in CDCl$_3$).

Figure A3.21. $^{13}$C{$^1$H} NMR spectrum of 4bc (101 MHz, in CDCl$_3$).
UV–vis spectra

**Figure A3.22.** UV–vis spectrum of 4aa (in THF).

**Figure A3.23.** UV–vis spectrum of 4aa' (in THF).
Figure A3.24. UV–vis spectrum of 4ac (in THF).

Figure A3.25. UV-vis spectrum of 4bc (in THF).
Mass spectra

Figure A3.26 EI mass spectrum of 4aa.

Figure A3.27 EI mass spectrum of 4aa'.
Figure A3.28. EI mass spectrum of 4ac.

Figure A3.29. EI mass spectrum of 4bc.
6.4 Electronic and Steric Effects that Govern the Structures of Aryl(dithienyl)boranes in the Solid State

NMR spectra

Figure A4.1. $^1$H NMR spectrum of 1a (400 MHz, in CDCl$_3$).
Figure A4.2. $^{11}$B($^1$H) NMR spectrum of 1a (128 MHz, in CDCl$_3$).

Figure A4.3. $^{13}$C($^1$H) NMR spectrum of 1a (101 MHz, in CDCl$_3$).
Figure A4.4. $^1$H NMR spectrum of 1b (400 MHz, in CDCl$_3$).

Figure A4.5. $^{11}$B($^1$H) NMR spectrum of 1b (128 MHz, in CDCl$_3$).
Figure A4.6. $^{13}$C($^1$H) NMR spectrum of 1b (101 MHz, in CDCl$_3$).

Figure A4.7. $^1$H NMR spectrum of 2a (400 MHz, in CDCl$_3$).
Figure A4.8. $^{11}$B\{H\} NMR spectrum of 2a (128 MHz, in CDCl$_3$).

Figure A4.9. $^{13}$C NMR spectrum of 2a (101 MHz, in CDCl$_3$).
Figure A4.10. $^1$H NMR spectrum of 2b (400 MHz, in CDCl$_3$).

Figure A4.11. $^{11}$B($^1$H) NMR spectrum of 2b (128 MHz, in CDCl$_3$).
Figure A4.12. $^{13}$C NMR spectrum of 2b (101 MHz, in CDCl$_3$).

UV–vis spectra

Figure A4.13. UV–vis spectrum of 1a (in THF).
Figure A4.14. UV–vis spectrum of 1b (in THF).

Figure A4.15. UV–vis spectrum of 2a (in THF).
Figure A4.16. UV–vis spectrum of 2b (in THF).

Mass spectra

Figure A4.17. EI mass spectrum of 1a.
Figure A4.18. EI mass spectrum of 1b.

Figure A4.19. EI mass spectrum of 2a.
Figure A4.20. El mass spectrum of 2b.
6.5 A 16 $\pi$ Electron Conjugated Boron-Doped Porphyrinogen

NMR spectra

Figure A5.1. $^1$H NMR spectrum of 3a (400 MHz, in CDCl$_3$).
Figure A5.2. $^{11}$B($^1$H) NMR spectrum of 3a (128 MHz, in CDCl$_3$).

Figure A5.3. $^{13}$C($^1$H) NMR spectrum of 3a (101 MHz, in CDCl$_3$).
Figure A5.4. $^1$H NMR spectrum of 4a (400 MHz, in CDCl$_3$).

Figure A5.5. $^{11}$B($^1$H) NMR spectrum of 4a (128 MHz, in CDCl$_3$).
Figure A5.6. $^{13}\text{C}(^1\text{H})$ NMR spectrum of 4a (101 MHz, in CDCl$_3$).

Figure A5.7. $^{11}\text{B}(^1\text{H})$ NMR spectrum of the crude product mixture obtained from the reaction between dilithiated 2a and 4a (128 MHz, in CDCl$_3$).
Figure A5.8. $^{11}$B($^1$H) NMR spectrum of the mixture obtained from the reaction between dilithiated 2a and 4a after the addition of HCl (128 MHz, in CDCl$_3$).

Figure A5.9. $^1$H NMR spectrum of 7b (400 MHz, in CDCl$_3$).
Figure A5.10. $^{11}\text{B}^{(1)}\text{H}$ NMR spectrum of 7b (128 MHz, in CDCl$_3$).

Figure A5.11. $^{13}\text{C}^{(1)}\text{H}$ NMR spectrum of 7b (101 MHz, in CDCl$_3$).
Figure A5.12. $^1$H NMR spectrum of 8b (400 MHz, in CDCl$_3$).

Figure A5.13. $^{11}$B($^1$H) NMR spectrum of 8b (128 MHz, in CDCl$_3$).
Figure A5.14. $^{13}$C($^1$H) NMR spectrum of 8b (101 MHz, in CDCl$_3$).

Figure A5.15. $^1$H NMR spectrum of 4b (400 MHz, in CDCl$_3$).
Figure A5.16. $^{11}$B($^1$H) NMR spectrum of 4b (128 MHz, in CDCl$_3$).

Figure A5.17. $^{13}$C($^1$H) NMR spectrum of 4b (101 MHz, in CDCl$_3$).
Figure A5.18. $^1$H NMR spectrum of 6b (400 MHz, in CDCl$_3$).

Figure A5.19. $^{11}$B($^1$H) NMR spectrum of 6b (128 MHz, in CDCl$_3$).
Figure A5.20. $^{13}$C($^1$H) NMR spectrum of 6b (101 MHz, in CDCl$_3$).

UV–vis spectra

Figure A5.21. UV–vis spectrum of 7b (in CH$_2$Cl$_2$).
Figure A5.22. UV–vis spectrum of 8b (in CH$_2$Cl$_2$).

Figure A5.23. UV–vis spectrum of 4b (in THF).
Figure A5.24. UV–vis spectrum of 6b (in THF).

Fluorescence spectrum of 6b

Figure A5.25. Fluorescence spectrum of 6b (in THF, $\lambda_{ex} = 418$ nm).
Figure A5.26. EI mass spectrum of 3a.

Figure A5.27. EI mass spectrum of 4a.
Figure A5.28. SIMS of 6a.

Figure A5.29. EI mass spectrum of 4b.
Figure A5.30. SIMS of 6b.
6.6 PBP Bridged [3]Ferrocenophane: A Bisphosphanoborane with a Redox Trigger

NMR spectra

Figure A6.1. $^1$H NMR spectrum of 3 (400 MHz, in CDCl$_3$).
Figure A6.2. $^1$H NMR spectrum of 3 (detail of tBu-signal) (400 MHz, in CDCl$_3$).

Figure A6.3. $^{11}$B($^1$H) NMR spectrum of 3 (128 MHz, in CDCl$_3$).
Figure A6.4. $^{13}\text{C}(\text{H})$ NMR spectrum of 3 (101 MHz, in CDCl$_3$).

Figure A6.5. $^{31}\text{P}(\text{H})$ NMR spectrum of 3 (162 MHz, in CDCl$_3$).
UV–vis spectrum

![UV–vis spectrum of 3 (in CH₂Cl₂).](image1)

**Figure A6.6.** UV–vis spectrum of 3 (in CH₂Cl₂).

Mass spectrum

![EI mass spectrum of 3.](image2)

**Figure A6.7.** EI mass spectrum of 3.