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Extended conjugated borenium dimers via late stage functionalization of air-stable borepinium ions

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Applications of highly electron-deficient organoborenium ions in conjugated materials remain scarce due to their low stability toward air and moisture. We report here the preparation of benzo[*d*]dithieno[*b,f*]borepinium ions as air-stable π -conjugated heterocycles and their conversion into the first dimeric borenium cations, which exhibit very low lying LUMOs and enhanced fluorescence as a result of extended conjugation.

Tricoordinate organoboranes feature an empty p-orbital, giving rise to their characteristic strong Lewis acidity, which has in turn widely been exploited in catalysis and the recognition of anions and other Lewis basic compounds. In addition, an interaction between the p-orbital of boron with adjacent π^* -orbitals effectively lowers the LUMO level of organic π -conjugated materials. Hence, tricoordinate boron-containing conjugated systems have received much attention as n-type semiconducting, emissive, and photovoltaic materials.¹ Various approaches have been pursued to further enhance the electron-deficient character of tricoordinate organoboranes, most notably the attachment of fluorinated substituents,² embedding into antiaromatic scaffolds,³ and incorporation into oligomers or polymers⁴ such that multiple electron-deficient boranes mutually interact and reinforce the acceptor character. A conceptually different approach is to impose a positive charge in the form a borenium ion, a cationic tricoordinate borane. Taking advantage of their enhanced Lewis acidity, borenium ions have been extensively utilized as catalysts and in stoichiometric organic transformation.⁵ The expected enhanced p- π^* interaction in conjugated organoborenium ions also suggests great promise as powerful new building blocks for optoelectronic and sensing applications. However, the high Lewis acidity of borenium ions tends to impact their chemical stability. Because most isolated borenium cations are air-

sensitive,⁶ studies on their photophysical properties are rare and applications in organic electronics have yet to be pursued. Only very recently, the Gilliard group reported the isolation of dibenzo[*b,f*]borepinium (**A**, Chart 1) and borafluorenum ions.^{6d} These benzo-fused borenium ions are thermally stable, show interesting optical properties, and undergo reversible reduction to the respective neutral radical species.^{6e} When endowed with pendent OMe groups they also exhibit thermochromic behavior due to reversibly binding of the OMe group to the boron cation.^{6d} Despite the promising properties, and in great contrast to extensive studies on neutral triorganoboranes,^{1,4} conjugated oligomeric or polymeric materials that incorporate borenium cations have yet to be developed. An obstacle has been that the conjugated borenium ions developed thus far are sensitive to air and have to be handled in an inert atmosphere. We introduce here a new class of borenium ions that can be isolated and handled in air and are readily converted to conjugated dimers that display very low-lying LUMO levels and strongly enhanced emissions in the visible region, as a result of effective extension of conjugation involving two distinct borenium cation centers.

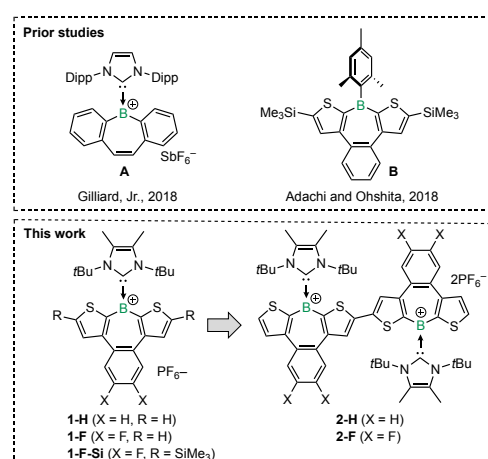


Chart 1 π -Conjugated fused borepins/borepinium ions.

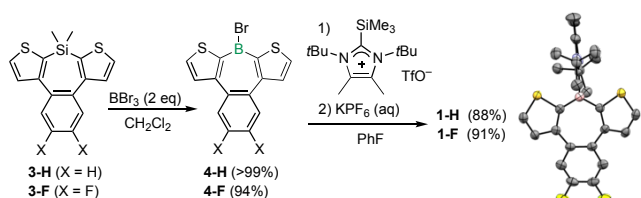
In our pursuit of extended conjugated borenium ion oligomers we focused on fused benzo[*d*]dithieno[*b,f*]borepin as a scaffold (**B**, Chart 1),^{8b} because (1) embedding boron into the

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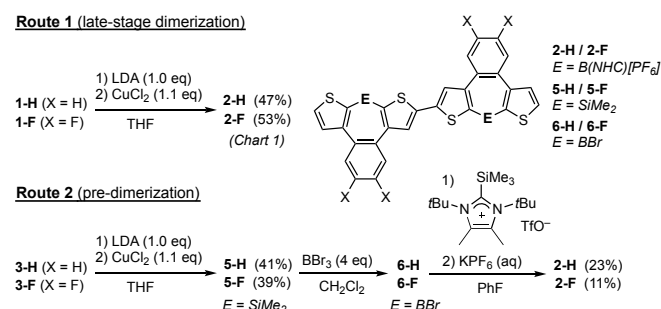
7-membered π -system results in aromatic stabilization and (2) fusion with thiophene further stabilizes borepins, while at the same time providing a handle for facile functionalization and integration into larger conjugated π -systems. Although over the past decade many stable borepins fused with aromatic rings have been synthesized,^{7,8} thiophene fusion at *b* and *f* positions has been reported to more effectively stabilize the borepins compared to benzene fusion and to result in lower HOMO-LUMO gaps than other regioisomers.^{8a,8c} Indeed, thiophene-fused benzo[*d*]dithieno[*b,f*]borepins, such as **B**,^{8g} proved to be highly stable in air due to the aromaticity of the borepin ring and the kinetic stabilization from a mesityl group on the boron center. In addition, the unique photophysical properties, including a reddish emission in the crystal state of **B**, indicate strong potential for applications as optoelectronic materials. We anticipated benzo[*d*]dithieno[*b,f*]borepinium ions **1** (Chart 1) to be even more electron-deficient than **B**, but still stable in air, and to be amenable to late stage functionalization for incorporation into extended conjugated π -systems such as **2** (Chart 1). To our knowledge, the latter represent the first examples of multiple conjugated borepinium ions embedded into larger conjugated π -systems.



Scheme 1 Synthesis of benzo[*d*]dithieno[*b,f*]borepinium ions and X-ray crystal structure of **1-F** (counterions, solvent omitted).

The synthesis of the borepinium ions was performed according to Tamm's method^{6c} for the preparation of borepinium ions. As a stabilizing bulky Lewis base, we employed an *N*-*tert*-butyl substituted *N*-heterocyclic carbene (NHC) with methyl groups in the 4,5-positions to prevent side reactions at the back of the NHC ring,^{9,10} and to achieve sufficient kinetic stabilization from placing the two *tert*-butyl groups very close to the boron center. In addition to the unsubstituted parent compound, borepins that are fluorinated on the fused benzene ring were also prepared, expecting further enhancement of the electron-deficient property. To achieve complete conversion, the boron-silicon exchange reaction of the silepin precursors **3-H** and **3-F** was conducted with two equivalents of BBr_3 , affording the bromoborepins **4-H** and **4-F** in nearly quantitative yields. The subsequent transmetalation with trimethylsilylated imidazolium triflate yielded the targeted NHC-stabilized borepinium ions **1-H** and **1-F**. The obtained borepinium ions are stable toward air and moisture both in solution and as solids. No decomposition of solid samples of **1-H** and **1-F** was observed even after storage in air for 2 months. The ^1H NMR spectral changes were monitored to check the stability in water-saturated CDCl_3 solution at room temperature. As shown in Fig. S1 and S2, only very little degradation (less than 5%) was observed for both borepinium ions after two days. Therefore, the crude products could be subjected to aqueous workup and purified by reprecipitation with undried solvents. The counter anion was exchanged from triflate to the weakly coordinating hexafluorophosphate anion by addition to a saturated KPF_6

aqueous solution. After purification, **1-H** and **1-F** were obtained as light yellow and white powder, respectively. Both compounds are well soluble in CH_2Cl_2 and acetonitrile, while insoluble in non-polar solvents such as toluene and ether. The structures of the borepinium ions were confirmed by NMR and HR-MS analysis. The ^{11}B NMR signals of **1-H** and **1-F** were observed around 42 ppm in CD_2Cl_2 , indicating the tricoordinate boron structure. The chemical shift of the broad signal did not change in coordinating deuterated solvents such as $\text{THF-}d_8$ and acetonitrile- d_3 , which suggests weak Lewis acidity of the borepinium cations. This is likely due to the steric bulkiness of the NHC ligand, and consistent with the high chemical stability of **1-H** and **1-F**. A crystal structure of **1-F** confirmed the molecular connectivity of the NHC-stabilized borepinium cation (Scheme 1 and Fig. S6). The B-C_{NHC} distance of 1.613(5) Å is in the typical range (A: 1.618(2) Å).^{6c,6d} The NHC and borepin rings are oriented nearly perpendicularly (90.6° , 95.2°), which is different from the conformation found for **A** (65.8° , 79.0°). This perpendicular orientation of **1-F** supports the efficient kinetic stabilization of the boron center by the bulky *tert*-butyl groups. The borepin ring plane deviates slightly from planarity, similar to the case of **B**^{8g}. The extended packing structure revealed π - π interactions between the difluorobenzene moieties of neighboring molecules (Fig. S7).



Scheme 2 Synthesis of conjugated borepinium dimers.

Next, we attempted the late-stage functionalization of **1-H** and **1-F**. Notably, **1-H** and **1-F** could be dilithiated selectively at the 5,5'-thienyl positions with 2.5 eq. of lithium diisopropylamide (LDA) in THF at -78°C . While the lithiation of dithienylboranes is well established,^{4a,8g} this is a remarkable accomplishment, considering the presence of not only highly electron-deficient borepinium ions but also of counter anions that may be prone to nucleophilic attack. The formation of the dilithiated borepinium ions was confirmed by ^1H NMR after quenching with D_2O (Fig. S3-S4). As a representative example of a nucleophilic substitution reaction that further demonstrates the synthetic utility, we treated the lithiated **1-F** with trimethylsilyl chloride to give the corresponding disilylated product **1-F-Si** in 68% yield (Chart 1). Importantly, the lithiation method also provides access to extended π -conjugated materials. Monolithiation of **1-H** and **1-F** with one equivalent of LDA and subsequent oxidative coupling in the presence of CuCl_2 produced the dimers **2-H** and **2-F** (Chart 1) in 47% and 53% yield (Scheme 2, *Route 1*). Using an alternate route, the borepinium dimers could also be obtained by generating first the silepin dimers that were then converted to the bis-borepinium products (Scheme 2, *Route 2*). As shown in Fig. S5, the ^1H NMR spectroscopic data for the dimers prepared via the two different synthetic routes are identical. However, the yield for **2-H/2-F** in *Route 2* (23%/11%) was significantly lower, possibly due to the

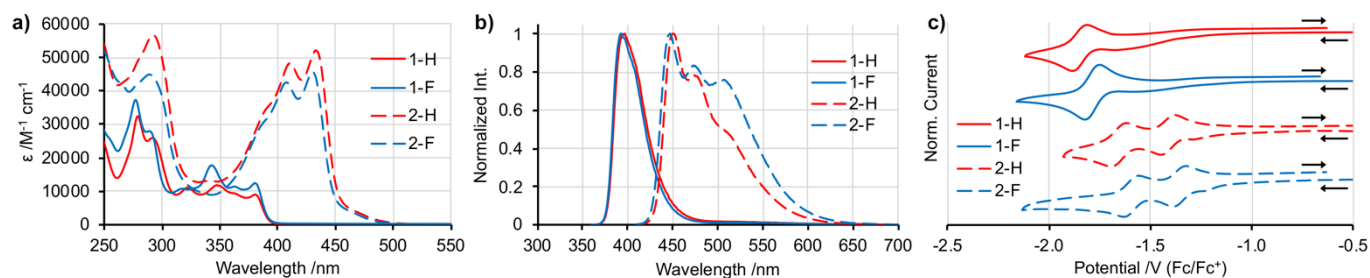


Fig. 1 a) Absorption and b) fluorescence spectra of monomeric and dimeric borepinium ions in dichloromethane at room temperature; c) cyclic voltammetry data (reductive waves) in acetonitrile containing 0.1 M Bu_4NPF_6 at a scan rate of 100 mV s^{-1} .

poor solubility of the bis(bromoborane) intermediates **6-H/6-F**. This further demonstrates the importance of late-stage functionalization for the preparation of borepinium ion systems with extended conjugation. The dimers are well soluble in acetonitrile and CH_2Cl_2 , but nearly insoluble in CHCl_3 . Their structures were confirmed by NMR and HR-MS analysis.

Having both the monomeric and extended conjugated dimeric borepinium ions in hand, we set out to investigate their optical properties. The absorption spectra in CH_2Cl_2 are shown in Fig. 1a. The absorption wavelengths and the absorption coefficients of the monomers are similar to those of mesityl-substituted **B**.^{8g} Compared to **A**,^{6d} the monomer absorptions are slightly blue-shifted, which could be due to a relatively lower lying HOMO with the phenylene in comparison to the vinylene bridge. On the other hand, the absorptions of the dimers are observed in the visible region, red-shifted by approximately 50 nm and greatly intensified relative to those of the monomers. This is consistent with significant extension of the conjugation.¹¹ The prominent role of the borepinium structure on the extension of conjugation was confirmed by DFT calculations (*vide infra*).¹² The fluorescence maxima of the dimers are also red-shifted from those of the monomers (Fig. 1b). Those of the fluorinated and non-fluorinated borepinium ions are comparable to each other (**1-H/1-F** and **2-H/2-F**), which implies that the HOMO–LUMO energy gaps are similar. The solid state emissions of powder samples of the borepinium ions are red-shifted from those in solution, but a reddish emission as observed for **B**^{8g} was not detected. For the monomers, the quantum yields are very low (<2%), similar to that of **B**^{8g} and other thiophene-fused borepins.^{8a,8c} However, for the dimers not only are the emission red-shifted into the visible, they are also markedly enhanced, both in solution (up to 9%) and as solids.¹³ In stark contrast to the reported behavior of **A**,^{6d} the optical properties were unchanged in Lewis basic solvents such as acetonitrile and DMF, consistent with the weak Lewis acidity and excellent stability of the highly shielded borepinium ions.

To verify the electron acceptor properties and to examine the electronic communication between borepinium ions in the π -conjugated dimers we carried out cyclic voltammetry measurements. A single reversible reduction wave was observed for the monomers **1-H** and **1-F** (Fig. 1c). The redox potential ($E_{1/2}^{\text{red1}} = -1.86 \text{ V}$) of **1-H** is more positive than that of **B** ($E_{\text{red onset}} = -2.08 \text{ V}$),^{8g} whereas the reduction of **A**^{6d} was reported to be irreversible due to THF coordination. Our observations reflect the highly electron poor yet robust nature of the cationic system. The $E_{1/2}^{\text{red1}}$ of **1-F** was further shifted to more positive potential due to the electronegative fluorine atoms (Table 1). The extended dimers **2-H** and **2-F** exhibited two reversible waves, and the first reduction potentials are much more positive relative to those of the corresponding monomers.

Thus, although the HOMO energies, estimated using the optical gaps, are nearly identical for all the compounds, the LUMO energies are dramatically lowered in the dimers relative to the monomers. These results again indicate that the borepinium cations are capable of very effective π - π^* conjugation and engage in strong electronic communication in the dimeric systems. The first reduction $E_{1/2}^{\text{red1}}$ of **2-F** at -1.36 V corresponds to an estimated LUMO level of -3.44 eV . This value is close to that of a typical n-type semiconducting material PC[60]BM (ca. -3.8 eV)¹⁴ and of triarylboranes that incorporate additional strong organic acceptors (-3.5 to -3.7 eV).^{4e,15}

Table 1 Summary of electrochemical data of borepinium ions.

| | $E_{1/2}^{\text{red1}}$ ^a | $E_{1/2}^{\text{red2}}$ ^a | LUMO ^b | E_g^{opt} ^c | HOMO ^d | E_g^{calc} ^e |
|------------|--------------------------------------|--------------------------------------|-------------------|---------------------------------|-------------------|----------------------------------|
| | /V($\text{Fc}^{0/+}$) | /V($\text{Fc}^{0/+}$) | /eV | /eV | /eV | /eV |
| 1-H | -1.86 | - | -2.94 | 3.18 | -6.12 | 3.90 |
| 1-F | -1.79 | - | -3.01 | 3.18 | -6.19 | 3.80 |
| 2-H | -1.39 | -1.76 | -3.41 | 2.73 | -6.14 | 3.20 |
| 2-F | -1.36 | -1.59 | -3.44 | 2.77 | -6.21 | 3.25 |

^a $E_{\text{red}} = 0.5 (E_{\text{pc}} + E_{\text{pa}})$; ^b Determined as $-(4.8 - E_{\text{red1}})$; ^c Obtained from the absorption onset in acetonitrile; ^d Determined as $\text{LUMO} - E_g^{\text{opt}}$; ^e Estimated from DFT calculations (B3LYP/6-31g(d,p)) for compounds without PF_6^- .

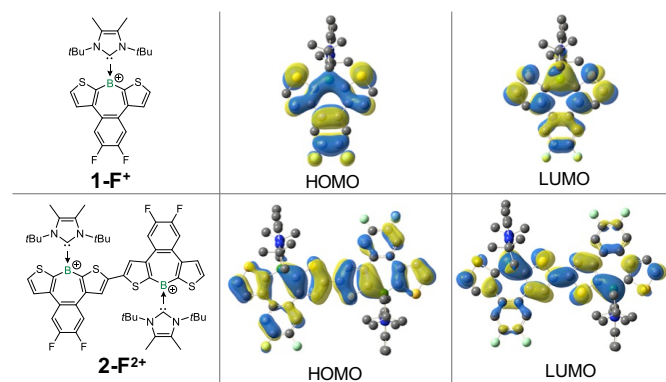


Fig. 2 Calculated HOMO/LUMO plots of **1-F⁺** and **2-F²⁺** (B3LYP/6-31g(d,p) level of theory).

Finally, to gain further insights into the electronic structures, density functional theory (DFT) calculations were performed without the PF_6^- anion at the B3LYP/6-31G(d,p) level of theory. Orbital profiles of monomers **1-H⁺** / **1-F⁺** and dimers **2-H²⁺** / **2-F²⁺** closely resemble each other (Fig. 2 and S13). The NHC ligand neither contributes to the HOMOs nor the LUMOs. For **1-H⁺** and **1-F⁺** the boron p-orbital overlaps strongly with the π/π^* -orbitals in both the HOMOs and LUMOs, suggesting a pronounced participation of the borepin entity in the conjugation. For the dimers **2-H²⁺** and **2-F²⁺**, although the HOMOs and LUMOs are distributed over the entire molecules, the boron p-orbital

participates much more effectively in the LUMOs. As a result of the electronic delocalization in the LUMO, the calculated HOMO-LUMO energy gaps of the dimers are much smaller than those of the monomers (Table 1), which is in good agreement with the experimental data. The HOMO and LUMO energy levels of the fluorinated borepinium ions **1-F⁺** and **2-F²⁺** are slightly lowered relative to those of the corresponding borepinium ions **1-H⁺** and **2-H²⁺**. For the dimeric species the difference is less, most likely as a result of a stronger localization of the orbitals on the conjugated main chain as seen in the orbital depictions in Figure 2. The aromaticity of the central borepin ring in **1-H⁺** and **1-F⁺** was affirmed by nucleus-independent chemical shifts (NICS) calculations. The calculated NICS(1) values of the borepinium cations are comparable to that of **A**,^{8g} indicating the existence of modest aromaticity (Table S2).

In conclusion, we have prepared highly robust borepinium ions, which are stabilized sterically by a bulky NHC ligand and electronically by the borepin aromaticity. The high chemical stability enabled the late-stage functionalization via lithiation and the following nucleophilic substitution and homocoupling reactions. The conjugated dimers exhibit strong redox coupling, as well as absorption and fluorescence bands that are shifted into the visible region and greatly enhanced. The cationic charges result in low LUMO levels, and that of **2-F** in particular is in the range required of effective n-type semiconducting materials. The extension of conjugation and enhanced electron-deficient nature of the dimers indicate potential applications as optoelectronic materials. The mild lithiation route is expected to provide access to a plethora of new functional conjugated materials composed of borepinium ion building blocks.

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Conflicts of interest

There are no conflicts to declare.

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- A comparison of the absorption spectra for the dimers prepared via the different synthetic routes is shown in Fig. S8. The main spectral shapes are identical, however, weak shoulder peaks are observed at longer wavelengths for the dimers prepared via *Route 1*. This is presumably due to the presence of a very small amount of higher oligomers. Therefore, for all the photophysical measurements, we used the dimers prepared via *Route 2* (pre-dimerization).
- The experimental absorption matches the TD-DFT results, and the lowest energy absorptions were assigned to a HOMO-LUMO transition for all the borepinium cations (Fig. S14-S17).
- Solvatochromic effects were not detected for any of the borepinium ions (Fig. S9-S12, Table S1), indicating a modest change in polarity in the excited relative to the ground state.
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TOC ENTRY

Conjugated dimeric borenium ions exhibit red-shifted absorptions, enhanced emission, and dramatically lower LUMO energies.

