Thiophene-Fused Borepins As Directly Functionalizable Boron-Containing π-Electron Systems

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S *Supporting Information*

ABSTRACT: Synthetic protocols were developed for the gram-scale preparation of two isomeric dithienoborepins (DTBs), boron-containing polycyclic aromatics featuring the fusion of borepin and thiophene rings. DTBs exhibit reversible cathodic electrochemistry and boron-centered Lewis acidity in addition to enhanced electronic delocalization relative to benzo-fused analogues. Boron's precise position within the conjugation pathway of DTBs significantly affected electronic structure, most clearly demonstrated by the variation in

spectroscopic responses of each isomer to fluoride ion binding. In addition to excellent stability in the presence of air and moisture, DTBs could also be subjected to electrophilic aromatic substitution and metalation chemistry, the latter enabling the direct, regiospecific functionalization of the unsubstituted thiophene rings. Subsequent tuning of molecular properties was achieved through installation of donor and acceptor π-substituents, leading to compounds featuring multistep electrochemical reductions and polarizable electronic structures. As rare examples of directly functionalizable, π-conjugated, boron-containing polycyclic aromatics, DTBs are promising building blocks for the next generation of organoboron π-electron materials whose development will demand broad scope for molecular diversification in addition to chemical robustness.
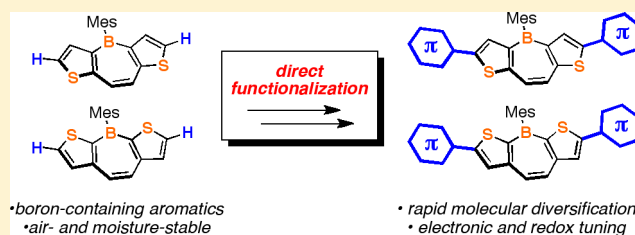
I. INTRODUCTION

Embedding main group elements within rigidly planar polycyclic aromatic molecules has emerged as a promising strategy to construct organic materials with unique and desirable optoelectronic properties.[1] For example, in addition to modulating frontier molecular orbital levels, exotic main group elements (such as B,[2] Si,[3] P,[4] Se,[5] and Te[6]) provide opportunities for reversible heteroatom coordination number change[7] and irreversible covalent modification (e.g., via heteroatom oxidation[8] or functionalization[9]) as gateways to dynamic or permanent property tuning. This has allowed for the continued evolution of more traditional materials derived from polycyclic aromatics based on the elements C, N, O, and S.[10] A remarkably broad scope of function has been demonstrated by the main group π-electron family of compounds: planar, boron-doped nanographenes[11] exhibit high electron-accepting ability and emission extending into the near-IR; stimulus-responsive "phosphole-lipids"[12] self-assemble into organogels demonstrating efficient solid state and solution FRET; and compounds containing azaborine motifs take advantage of C–C/B–N isosterism to act broadly as either enzyme-inhibitory benzene mimics[13] or as hole carriers in p-type OFET devices.[14] Replacement of carbon centers with main group atoms in π-conjugated systems also provides many opportunities to glean new fundamental chemical insight. For example, this approach has deepened our understanding of aromaticity and antiaromaticity in modified benzenoid and nonbenzenoid systems.[15]

To fully realize the potential of organo-main group heterocycles as candidates for functional materials, it is critical to develop streamlined procedures for their synthesis as well as their incorporation into more complex, extended π-conjugated systems. This presents a particular challenge in the context of compounds containing tricoordinate boron centers, which are inherently sensitive to oxygen, moisture, and many typical reaction conditions.[16] Therefore, despite elegant synthetic preparation and intriguing molecular properties, many unique, cutting-edge π-conjugated organoboron architectures are reported as final targets without mention of continued chemical tailoring.

Interest has recently re-emerged in polycyclic π-electron compounds featuring borepin rings,[17] charge-neutral, boron-containing heteroaromatic analogues of the tropylium cation.[18] In contrast to prevailing synthetic precedent at the time, a key component of our contribution to borepin research was to achieve molecular and polymeric functionalization of benzo-fused borepins[17e–h] via transition-metal-catalyzed cross-coupling chemistry, a general approach which has drawn increasing attention as a route to a variety of functionalized organoboron heterocycles.[19] However, this strategy has typically relied upon the *preinstallation* of transformable functional groups (generally a halogen or its equivalent) onto molecular precursors in order
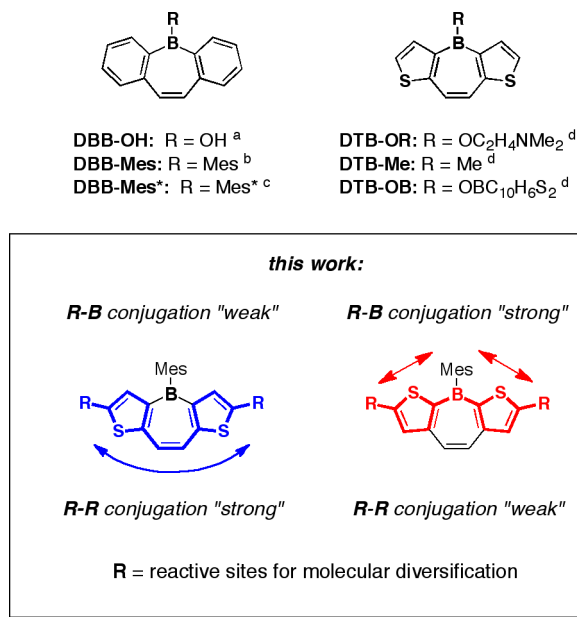
to later carry out the desired reactions on the fully constructed boron-containing species.

We now report the synthesis, characterization, and chemical reactivity of two structurally isomeric *B*-mesityl (Mes; 2,4,6-trimethylphenyl) dithienoborepins (DTBs; Chart 1, "this

Chart 1. Structures of Dibenzo- and Dithieno-Fused Borepins

DBB-OH: R = OH [a]
DBB-Mes: R = Mes [b]
DBB-Mes*: R = Mes* [c]

DTB-OR: R = OC$_2$H$_4$NMe$_2$ [d]
DTB-Me: R = Me [d]
DTB-OB: R = OBC$_{10}$H$_6$S$_2$ [d]

this work:

R-B conjugation "weak"

R-B conjugation "strong"

R-R conjugation "strong"

R-R conjugation "weak"

R = reactive sites for molecular diversification

[a] Reference 17a. [b] Reference 17d. [c] Reference 17e, f. [d] Reference 21.

work"). These molecules were prepared on gram scales in a straightforward manner and exhibited excellent tolerance for moisture and oxygen while preserving the important Lewis acidic character of boron. The precise position of boron within isomeric DTB scaffolds leads to key differences in electronic structure, strongly influencing molecular properties. The chemically robust nature of DTBs allows the use of standard thiophene synthetic chemistry, thus enabling *direct, late-stage molecular diversification of the parent systems* for rapid tuning of electronic and redox properties.

II. RESULTS AND DISCUSSION

Design Considerations. The key structural feature of these molecules is the fusion of two thiophene rings to the *b*- and *f*-positions of a central borepin core. This pattern of ring fusion has been employed in the context of dibenzo-fused borepins [such as **DBB-OH**,[17a] **DBB-Mes**,[17d] and **DBB-Mes***[17e,f] (Mes* = 2,4,6-tri-*tert*-butylphenyl); Chart 1] to obtain compounds which possess greater degrees of stability than unfused borepin systems and, with appropriate steric shielding for boron, can be rendered highly robust toward air and moisture. Inspired by analogous dithienotropylium cations,[20] Gronowitz and co-workers demonstrated over 40 years ago that replacement of the benzo rings in dibenzoborepins with thieno rings[21,22] (as in **DTB-OR, DTB-Me,** and **DTB-OB**; Chart 1) lent additional stability to the borepin substructure. However, it was reported soon thereafter that **DTB-OB** decomposed upon further attempted synthetic manipulation.[23] We envisioned that installation of an appropriate boron-protecting group (such as Mes) might provide compounds with sufficiently robust character to allow the use of well-established thiophene

chemistry[24] to functionalize the unsubstituted DTB cores (thieno "R" sites, Chart 1).

Annelation of borepin and thiophene presents a choice with respect to the orientation of the fused rings. Altering the fusion motif leads to different structural isomers with unique conjugation pathways. Based on our previous studies of *meta*- and *para*- substituted DBBs,[17e−h] we speculated this could provide a basis for molecular property tuning. Therefore, we targeted DTBs possessing clear differences in the electronic relationship between boron and the extended π-system (Chart 1, "this work"). Because the dominant pathway for electron delocalization involving thiophene rings typically extends outward from the α-positions (Chart 1, blue and red conjugation pathways), these model compounds can be thought of as possessing thiophene R-substituents with weak (left) or strong (right) conjugation to the boron center. At the same time, R−R electronic communication should be more effective when the thiophene rings are α-conjugated to one another via the olefinic borepin bridge (Chart 1, R−R conjugation "strong") than when cross-conjugated to one another via the boron center (Chart 1, R−R conjugation "weak").

Synthesis of DTBs. We prepared the parent *B*-Mes DTBs **1** and **2** by employing a synthetic strategy based on the condensation of dimetalated (*Z*)-dithienylethenes[25] with a mesityl boronic ester (Scheme 1). Lithium−bromine exchange

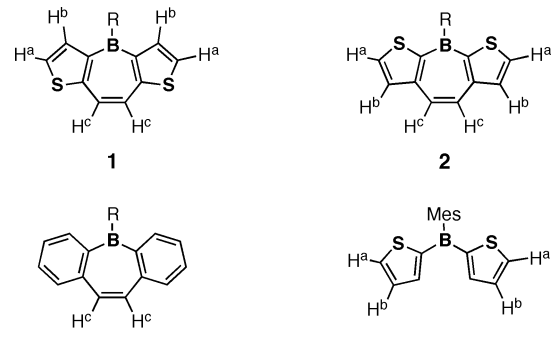**Scheme 1. Synthesis of Parent *B*-Mes DTBs**
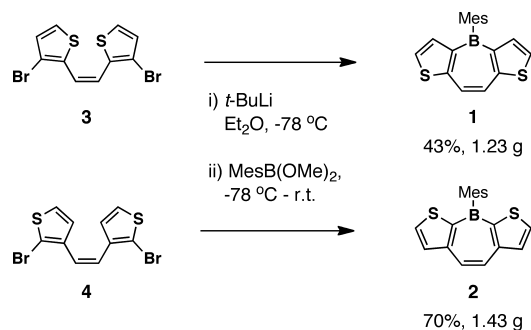
of **3**[26] and **4**[21a] with *tert*-butyllithium (*t*-BuLi), followed by treatment with MesB(OMe)$_2$, provided DTBs **1** and **2** in 43% and 70% yields, respectively. This straightforward preparative method is more step-economic than the stannocyclization/tin−boron exchange routes commonly used to construct doubly fused borepin rings[17d−h] and avoids the toxic organotin reagents and boron halides associated with the latter protocol. Importantly, this procedure enabled the synthesis of **1** and **2** on gram scales.

DTBs exhibited excellent tolerance for oxygen, moisture, and silica gel, allowing for aqueous reaction workup and purification by chromatography under ambient laboratory conditions.[27] Additionally, both compounds could be stored under air for several months without showing any signs of decomposition as indicated by NMR and UV−vis spectroscopy. This is quite notable given that the *B*-Mes bond of **DBB-Mes** is hydrolyzed by atmospheric water over the course of several hours to form the B−O−B anhydride,[17d] requiring the use of the bulkier *B*-Mes* protective group to impart prolonged stability.[17e] Thus, the high degree of robustness exhibited by DTBs suggests a special stability conferred by thiophene-borepin ring fusion.

Characterization of DTBs. The identity and purity of the parent DTBs were confirmed with NMR spectroscopy (^{1}H, [11]B, ^{13}C) and high-resolution mass spectrometry in conjunction with unambiguous structural determination via X-ray crystallography. UV−vis and photoluminescence (PL) spectroscopy were utilized to elucidate electronic properties, and electrochemical properties were examined by cyclic voltammetry (CV). Theoretical calculations were carried out to obtain optimized geometries, molecular orbital surfaces/energies, optical transitions, and nucleus-independent chemical shift (NICS)[28] values. For comparison, we reference data for **DBB-Mes** as reported by Piers[17d] and bis(2-thienyl)mesitylborane (**BTMB**) as reported by Kawashima.[29]

^{11}B NMR spectra of DTBs show broad peaks near 50 ppm, which are shielded by 12−15 ppm relative to **DBB-Mes** (Table 1). This suggests that thieno-ring fusion substantially enhances

Table 1. Selected ^{1}H NMR, ^{11}B NMR, and NICS(1) Data for 1, 2, DBB-Mes, and BTMB

	1	2	DBB-Mes	BTMB
[11]B (δ, ppm)[a]	51.9	48.7	64.3[c]	54.9[d]
[1]H^a (δ, ppm)[a]	7.47	7.95	−	7.81[d]
[1]H^b (δ, ppm)[a]	7.38	7.70	−	7.29[d]
[1]H^c (δ, ppm)[a]	7.69	7.74	7.37[c]	−
NICS(1)$_{borepin}$[b]	−4.93	−4.90	−2.90	−

[a]R = Mes; spectra collected in CDCl$_3$ solution. [b]R = H; GIAO method, DFT, B3LYP/6-31+G*. [c]Reference 17d. [d]Reference 29.

the π-electron density at boron relative to benzo-fusion. The rigidly planar geometry provided by the centrally fused borepin rings also appears to promote effective π-electron delocalization to boron; relative to the unconstrained (yet similarly thiophene-conjugated) congener **BTMB**, the boron center of **2** is shielded by 6.2 ppm. The two DTB isomers also show substantial differences in the magnetic environments of their polycyclic core protons. Thieno protons (H^a, H^b; Table 1) in **2** are noticeably deshielded relative to **1**, presumably due to the stronger electron-withdrawing effect of the α-conjugated boron center. On the other hand, chemical shifts for the "olefinic" borepin ring protons (H^c, Table 1) in both DTBs are quite close in value, yet are deshielded by over 0.3 ppm compared to **DBB-Mes**.

The [11]B and [1]H^c chemical shift values suggested a possible difference in aromatic character between the dibenzo-fused and dithieno-fused borepins. To gain further insight regarding the contribution of borepin-centered ring currents to the observed NMR shifts, we carried out NICS calculations on simplified models of **1**, **2**, and DBB-Mes, replacing the Mes groups with H (Table 1). While NICS(1) values for the borepin rings

featuring thieno fusions ($\sim$ −4.9 ppm) are consistent with weak aromaticity (as has been reported for other hetero-annelated borepins),[30] the values for the dibenzo-fused borepin model (−2.90 ppm) indicated even less aromatic character. These results correlate well with the stronger deshielding of borepin rings protons (H^c) in DTBs compared to **DBB-Mes**, as well as crystallographic data (vide infra) showing considerably reduced borepin C−C bond length alternation in DTBs (**1**: 0.078 Å; **2**: 0.088 Å) compared to **DBB-Mes** (0.111 Å). The enhancement in aromaticity of borepin rings in DTBs compared to DBB can be rationalized in terms of the weaker localization of aromatic π-electron sextets within fused thieno rings relative to benzo rings, allowing greater diatropic ring currents to circulate within the central borepin substructures of the DTB systems.

Single crystals suitable for X-ray structure determination were grown by slow diffusion of MeOH into concentrated solutions of **1**/CHCl$_3$ and **2**/CH$_2$Cl$_2$ (Figure 1). All C−B−C
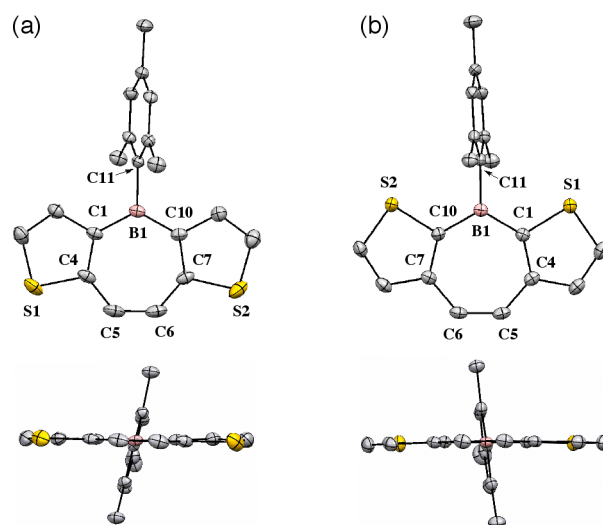

Figure 1. Displacement ellipsoid plots for (a) **1** and (b) **2** at 110(2) K (50% probability level) with views perpendicular (top) and parallel to (bottom) the polycyclic planes. Selected bond lengths (Å), **1**: B1−C1 = 1.533(2), B1−C10 = 1.538(2), B1−C11 = 1.581(2), C1−C4 = 1.409(2), C4−C5 = 1.426(2), C5−C6 = 1.348(2), C6−C7 = 1.426(2), C7−C10 = 1.404(2); **2**: B1−C1 = 1.522(2), B1−C10 = 1.521(2), B1−C11 = 1.583(2), C1−C4 = 1.406(2), C4−C5 = 1.440(2), C5−C6 = 1.353(2), C6−C7 = 1.441(2), C7−C10 = 1.403(2).

bond angles fall within the range 118.5°−123.0°, confirming sp^2 hybridization of the boron centers. The DTB backbones possess highly planar geometries [angle between thiophene (Th) mean planes: **1**$_{Th−Th}$ = 2.4°, **2**$_{Th−Th}$ = 3.0°] with the pendant Mes groups oriented in near-perpendicular fashion to the polycyclic core [borepin-Mes dihedral angles: **1** = 76.6(2)°, **2** = 82.5(2)°]. These solid-state molecular geometries were well-reproduced by DFT calculations (B3LYP/6-31G*, Supporting Information). The planarity of the DTBs differentiates them from **DBB-Mes**, which shows a slightly bowed borepin ring in the solid state.[17d] Despite the planar X-ray structures of **1** and **2**, we did not observe extensive intermolecular π-stacking in the crystal lattices (Supporting Information), likely due to the steric hindrance of the Mes groups.

B−C bond lengths (Figure 1) can be used to gauge boron's participation within the delocalized DTB π-electron networks.

Borepin B−C bonds (1.52−1.53 Å) are much shorter than B−C bonds to the exocyclic Mes groups (∼1.58 Å), revealing substantial boron−carbon π-bonding within the fused, planarized portions of the molecules. The enhancement of B−C π-bonding due to ring fusion is highlighted by the fact that **2** has 0.02−0.03 Å shorter B−C$_{thieno}$ bonds than unfused **BTMB** [1.544(4), 1.549(6) Å],[29] despite the otherwise similar connectivities between boron and the thiophene rings. We also observe considerable shortening of the borepin B−C bonds (0.03−0.04 Å) in DTBs relative to **DBB-Mes** [1.563(3), 1.564(3) Å],[17d] demonstrating that more efficient boron-π-overlap is achieved through the polarizable electronic structures of the thiophene-fused arrays relative to the benzo-fused analogue.

UV−vis spectra indicate a slight bathochromic shift in absorption onset for **1** (390 nm) relative to **2** (378 nm) (Figure 2a, c). This is consistent with a smaller calculated HOMO−
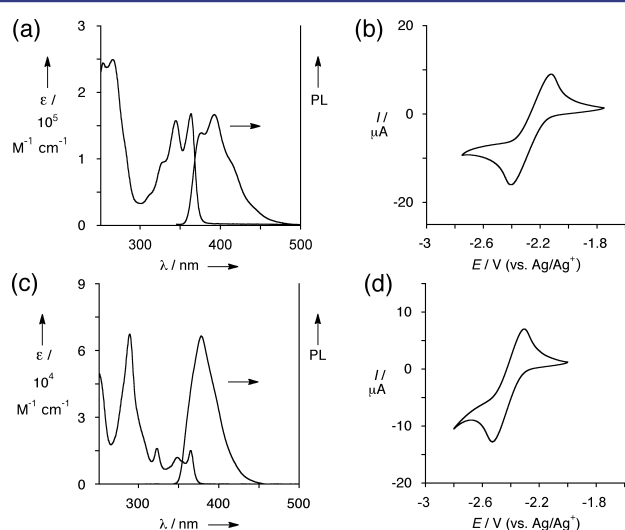

Figure 2. Photophysical and electrochemical data for **1** (a, b) and **2** (c,d). UV−vis/PL spectra obtained in CHCl$_3$ solution. CV scans obtained in 0.1 M n-Bu$_4$NPF$_6$/THF.

LUMO gap for the former (Supporting Information) and reflects the notion that **1** possesses greater electron delocalization owing to a longer effective conjugation pathway (via the olefinic bridge of the borepin, Chart 1). In the low-energy spectral region (310−380 nm), **1** shows much greater absorption intensity than **2**, in agreement with TD-DFT calculated transitions revealing oscillator strengths an order of magnitude larger for the former (Supporting Information). DTBs were luminescent under 365 nm light both as solids and in solution; however, solution state PL quantum yields for **1** (Φ_{PL} = 0.06) and **2** (Φ_{PL} = 0.05) were low in comparison to **DBB-Mes** (Φ_{PL} = 0.70).

CV showed single, reversible electrochemical reductions for both DTBs in THF ($E_{1/2\ red}$ **1** = −2.26 V, $E_{1/2\ red}$ **2** = −2.42 V vs Ag/Ag$^+$; Figure 2b, 2d). The slightly more difficult reduction of isomer **2** is in qualitative agreement with a higher calculated LUMO level (Supporting Information) and can be ascribed to mitigation of boron's electron-deficient character by strong conjugation with the thiophene rings. Interestingly, the reversible reduction of **DBB-Mes** ($E_{1/2\ red}$ = −2.36 vs Ag/Ag$^+$)[31] is observed at a similar potential to DTBs, indicating that replacement of benzo rings with more electron-rich thiophene rings does not significantly diminish the electron-

accepting character of these systems. Despite the presence of terminal thieno moieties in DTBs, we were unable to observe anodic CV waves or other follow-up electrochemical processes (such as electropolymerization) within the THF solvent window (<0.90 V).

DTB Reactivity. Noting the high stability of the DTBs toward air and water exposure, we were curious to see if they could withstand reaction conditions required for continued synthetic modification. Thus, we subjected **1** and **2** to typical reactions used to functionalize unsubstituted thiophene rings: electrophilic aromatic substitution (S$_E$Ar) and metalation/electrophile quench (Scheme 2).

Scheme 2. Reactivity of Parent DTBs: S$_E$Ar and Direct Metalation Chemistry[a]
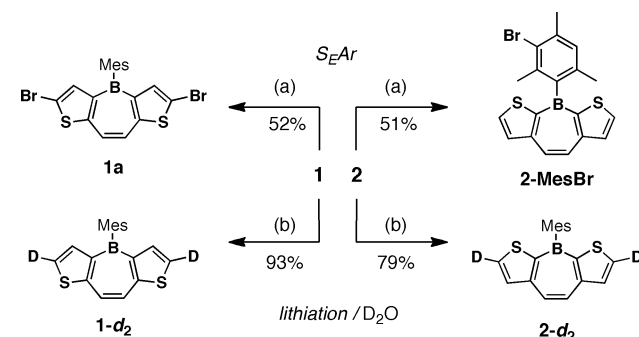
[a]Reaction conditions: (a) NBS (2.0 equiv), DMF, rt, dark. (b) (i) t-BuLi (2.2 equiv), Et$_2$O, −78 °C; (ii) D$_2$O.

S$_E$Ar reactions demonstrated that bromine substituents could be installed electrophilically onto DTBs without causing decomposition of the boron-containing cores (Scheme 2, condition a).[32] Unexpectedly, we found the site selectivity of bromination to be isomer-dependent. Upon treatment of **1** with 2 equiv of N-bromosuccinimide (NBS), bromine incorporation was observed at the typical thiophene α-positions to give dibrominated **1a** in 52% yield and a lesser amount (∼30%) of a singly thieno-brominated product. However, subjecting **2** to identical reaction conditions led instead to bromination of the pendant mesityl ring, giving **2-Mes-Br** in 51% yield in addition to recovered starting material. It appears that strong conjugation between boron and the thiophene rings in **2** deactivates the latter toward S$_E$Ar chemistry, leading to a preference for mesityl bromination. The protection afforded to boron by the B-Mes group appears to be critical for the stability of the DTB core during bromination, since Párkányi reported **DTB-OB** to undergo B−C bond cleavage upon treatment with a brominating agent.[23]

Despite the fact that S$_E$Ar preferentially occurred at the mesityl group of **2**, we found direct metalation with organolithium reagents to be a very effective method for exclusive α-thieno-functionalization of both DTB isomers. Treatment of **1** or **2** with t-BuLi followed by addition of D$_2$O provided deuterated DTBs **1-d$_2$** and **2-d$_2$** in 93% and 79% yields, respectively (Scheme 2). ^{1}H NOE spectra of the deuterated products confirmed the regiospecific nature of the metalation process (Supporting Information). The high yields obtained are evidence of the impressive stability of DTB cores toward strongly basic reagents without the requirement for very severe steric shielding of boron (such as found in B-Mes*[19b,17e−h] or BMes$_2$[33] functional groups). Importantly, in

Scheme 3. Molecular Diversification of DTBs via Direct Functionalization[a]
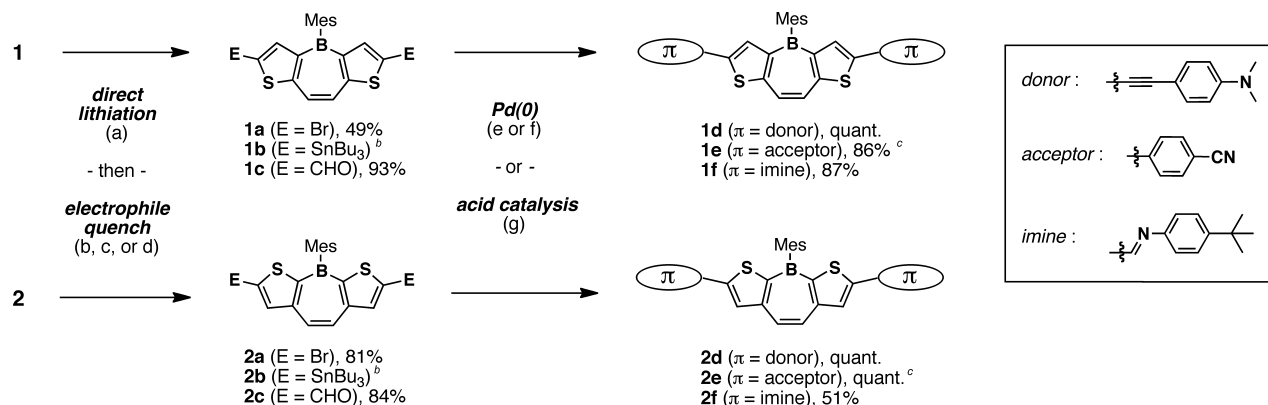
[a]Reaction conditions: (a) t-BuLi (2.5 equiv), Et₂O, −78 °C. (b) For **1a/2a**: Br₂ (2.4 equiv), hexanes. (c) For **1b/2b**: n-Bu₃SnCl (3.0 equiv). (d) For **1c/2c**: DMF (3.2 equiv); (e) For **1a → 1d/2a → 2d**: 4-ethynyl-N,N-dimethylaniline (2.4 equiv), Pd[P(t-Bu)₃]₂ (0.1 equiv), CuI (0.08 equiv), i-Pr₂NH (2.4 equiv), toluene, rt; (f) For **1b → 1e/2b → 2e**: 4-bromobenzonitrile (2.2 equiv), Pd(PPh₃)₄ (0.05 equiv), 1,4-dioxane, reflux. (g) For **1c → 1f/2c → 2f**: 4-tert-butylaniline (2.1 equiv), TFA (cat.), CHCl₃, 60 °C. [b] Used without purification. [c] Yield given over two steps.

addition to D₂O, dilithio-DTBs were found to react with other synthetically relevant electrophiles (*vide infra*).

Stability in the presence of t-BuLi provoked another question: could the tricoordinate boron centers of DTBs still kinetically function as Lewis acids? Indeed, the ability of tricoordinate boron to bind with anions is the key functional property upon which organoboron-based sensing and catalysis schemes rely.[34] Previously, we were unable to observe such interactions in **DBB-Mes***, presumably due to the extreme steric bulk presented by the B-Mes* groups. However, the less demanding steric environment in DTBs suggested that they might be able to show anion binding behavior. In fact, addition of increasing amounts of tetrabutylammonium fluoride (TBAF) to NMR samples of **1** and **2** in CDCl₃ led to the gradual disappearance of the native ¹¹B NMR signals near 50 ppm, accompanied by the appearance of new peaks at 2.8 and 2.1 ppm, respectively (Supporting Information). These spectral shifts are characteristic of coordinative saturation of triarylboranes to form tetracoordinate fluoroborates, confirming that the Lewis acidity of boron in DTBs remains intact.

Notably, fluoride binding had quite different effects on the electronics of the two DTB isomers (Figure 3). While TBAF addition to **1** led only to very subtle changes in the UV−vis profile (Figure 3a), **2** was dramatically impacted as key bands were strongly hypsochromically shifted or suppressed entirely (Figure 3b). This further supports the notion that the degree of boron−π interaction varies according to the specific nature of the available conjugation pathways in each DTB; though
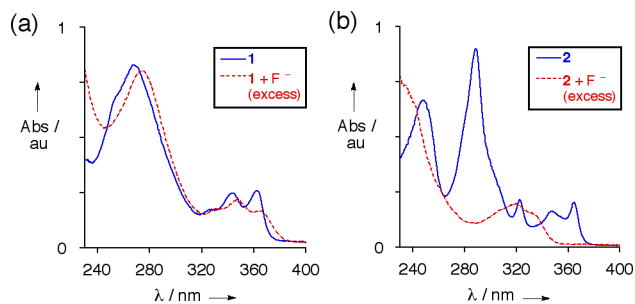
isomeric variation has been shown to lead to changes in anion-binding-induced electronic responses in vinyl side-chain borylated materials,[35] to our knowledge DTBs represent the only examples of such phenomena being caused by structural isomerism within a boron-conjugated main chain.

Molecular Diversification. Regiospecific lithiation of DTBs provided a robust method to synthesize functionalized analogues directly from the unsubstituted parent compounds (Scheme 3).[36] Thus, treatment of dilithio-DTBs with molecular bromine, tri-n-butylstannyl chloride, or DMF furnished dibromide (**1a**, **2a**), distannane (**1b**, **2b**), and dialdehyde (**1c**, **2c**) derivatives, respectively. The bromides and stannanes were employed in subsequent Pd-catalyzed cross-couplings: Sonogashira[37] cross-couplings between **1a/2a** and 4-ethynyl-N,N-dimethylaniline and Stille[38] cross-couplings between **1b/2b** and 4-bromobenzonitrile were used to prepare DTBs with donor- (**1d**, **2d**) and acceptor-type (**1e**, **2e**) π-conjugated substituents, respectively. The flexibility to employ DTBs as either electrophilic (**1a**, **2a**) or nucleophilic (**1b**, **2b**) cross-coupling partners suggests that a wide scope of functionalized DTBs should be accessible via Pd-catalyzed methods.

To demonstrate an alternative approach toward DTB functionalization, we carried out trifluoroacetic acid (TFA)-catalyzed condensations between 4-tert-butylaniline and DTB dialdehydes **1c** and **2c** to give conjugated imines **1f** and **2f**. In addition to demonstrating the compatibility of DTBs with a strong Brønsted acid, these reactions suggest that reversible, self-correcting imine bond formation[39] could offer opportunities to access structurally and functionally complex π-conjugated DTB-based organoboron architectures via dynamic covalent chemistry.[40]

Properties of π-Functionalized DTBs. Characterization of π-donor and π-acceptor substituted DTBs confirmed that functionalization could be used to tune electrochemical and photophysical properties (Figure 4). CV revealed that extending π-conjugation with either donor or acceptor substituents led to earlier electrochemical reduction onsets (Figure 4a, 4b), in agreement with lower calculated LUMO levels for substituted DTBs relative to the unsubstituted parent systems (Supporting Information). Donor-substituted DTBs **1d** and **2d** showed strong second irreversible reductions following the first reversible processes (Figure 4a). However,
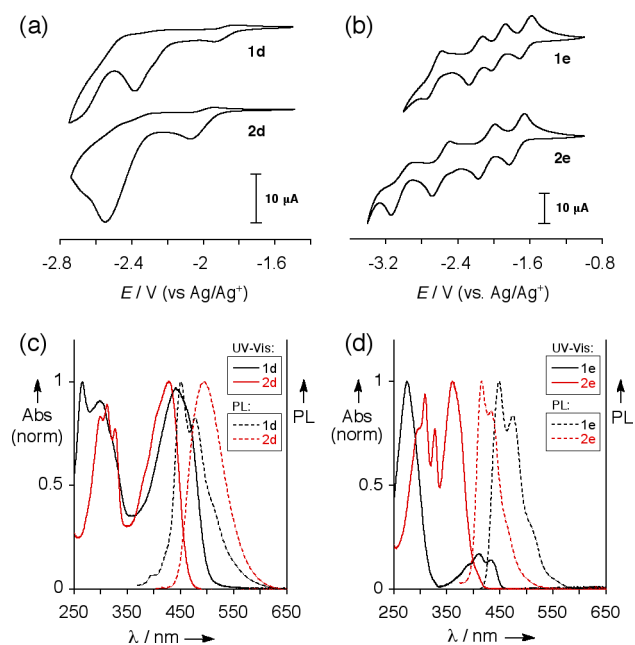

Figure 3. UV/vis spectra of (a) **1** and (b) **2** before and after addition of excess fluoride (TBAF).

Figure 4. Electrochemical and photophysical data for donor- (**1d**, **2d**) and acceptor-functionalized (**1e**, **2e**) DTBs: CV scans of (a) **1d** and **2d** and (b) **1e** and **2e** in 0.1 M n-Bu$_4$NPF$_6$/THF. Normalized UV–vis and PL spectra of (c) **1d** and **2d** and (d) **1e** and **2e** in CHCl$_3$ solution.

acceptor-functionalized DTBs **1e** and **2e** exhibited up to four separate reversible reduction waves within a comparable electrochemical window (Figure 4b), a phenomenon we attribute to the high electron-accepting capacity of the boryl and PhCN groups. The ability shown by acceptor-functionalized DTBs to reversibly attain stable tetraanionic states in a stepwise fashion is quite rare in the realm of small organic molecules and suggests that such compounds could be of interest as capacitive elements for multistate switching[41] in n-type logic or memory devices.[42]

Electronic spectra of π-functionalized DTBs in CHCl$_3$ showed clear bathochromic shifts in absorption and emission onsets relative to the parent DTBs (Figure 4c, 4d), consistent with DFT calculations indicating narrowed HOMO–LUMO gaps for the functionalized DTB analogues (Supporting Information). This demonstrates that DTB effective conjugation lengths are efficiently extended by installation of π-substituents. As found for the parent systems, the absorption onsets for π-extended derivatives of **1** were bathochromically shifted from the corresponding derivatives of **2**. Structured, bimodal emission spectra with low-energy shoulders were observed for compounds **1d**, **1e**, and **2e**; however, donor-functionalized DTB **2d** exhibited a broad, featureless emission spectrum with a much larger Stokes shift than the isomeric donor-substituted **1d**. These features are consistent with optically induced intramolecular charge transfer between boryl moieties and the strongly conjugated donor groups.[43] To further investigate the polarizable character of donor-functionalized DTBs, we collected two-photon absorption (TPA) data for **1d** and **2d**, obtaining TPA cross section values of 63 and 75 GM in THF, respectively (excitation at 780 nm, Supporting Information). While the values are small compared to performance-oriented nonlinear optical chromophores,[44] the flexibility of DTB functionalization chemistry should offer many options to optimize these properties through molecular tailoring.

The donor–acceptor character of **1d** and **2d** suggested that fluoride binding (to give putative DTB fluoroborates **1d-F$^-$** and **2d-F$^-$**, Figure 5a, d) could provoke even more dramatic
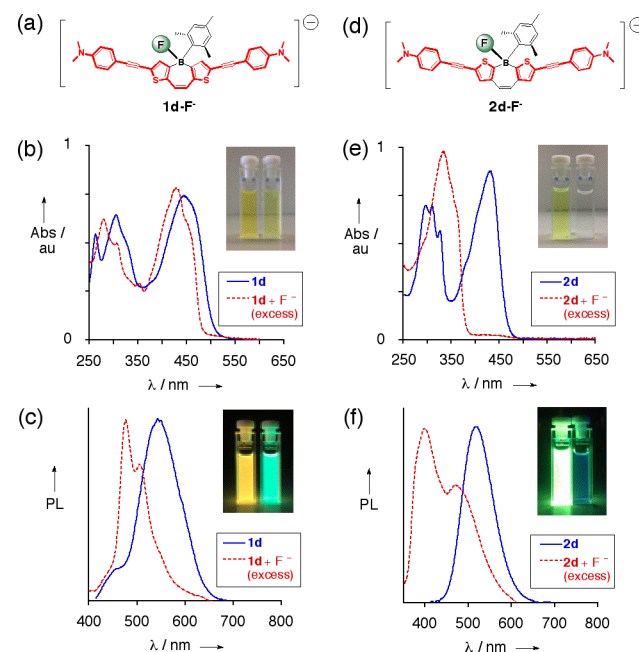

Figure 5. Photophysical responses upon fluoride addition to **1d** and **2d** in THF. PL spectra are normalized for clarity and do not reflect emission intensity quenching after F$^-$ addition. (a) Representation of fluoride bound **1d-F$^-$**, with unbroken major conjugation pathway in red. (b) UV–vis and (c) normalized PL spectra before and after TBAF addition to **1d**. (d) Representation of fluoride-bound **2d-F$^-$** with broken major conjugation pathway in red. (e) UV–vis spectra and (f) normalized PL spectra before and after TBAF addition. Photo insets illustrate sample appearance before (left cuvette) and after (right cuvette) addition of fluoride under ambient light (b, e) and 365 nm irradiation (c, f).

electronic structure changes than those observed in **1** and **2** (*vide supra*). In fact, upon treatment with TBAF, samples of **1d** and **2d** underwent significant electronic changes that were observable both spectroscopically and with the naked eye (Figure 5). As with the parent DTBs, the degree of change observed here was isomer-dependent. In the UV–vis spectrum of compound **1d** (with the boron center weakly conjugated to the peripheral donor groups), only small hypsochromic shifts of the main spectral bands occurred upon TBAF addition (Figure 5b), along with a subtle color change of the sample (Figure 5b, photo inset). In the emission spectra, a $\lambda_{PL\ max}$ hypsochromic shift of 66 nm was evident (Figure 5c), and a visually detectable emission color change could be seen under 365 nm irradiation (Figure 5c, photo inset).

The response of DTB **2d** (in which boron is strongly conjugated to the donor groups) to fluoride treatment was much more dramatic. A large hypsochromic shift of 95 nm for the $\lambda_{Abs\ max}$ was accompanied by a visible color change of the sample from yellow to completely colorless (Figure 5e). This was accompanied by a hypsochromic shift of 118 nm for the $\lambda_{PL\ max}$ along with a strong quenching of emission intensity (Figure 5f). These changes were visually apparent as "on–off" switching of sample luminescence (Figure 5f, photo inset). The distinct differences in electronic responses of **1d** and **2d** to fluoride binding can be rationalized in terms of the impact on

π-conjugation in the two isomers (Figure 5a, d, red pathways): fluoride binding leaves the all-carbon major conjugation pathway of **1d** relatively unaffected (Figure 5a) while **2d**'s intramolecular charge-transfer pathway is instead shut down due to occupation of the boron p-orbital (Figure 5d). These observations should prove useful in the rational design of new DTBs or other organoboron-based sensor materials which not only consider the placement of boron within the "main chain" or "side chain" but also take into account the strength of conjugation between boron and the extended π-electron system to provide additional opportunities for electronic property tuning.

III. CONCLUSION

We have reported the synthesis of two new isomeric *B*-Mes dithienoborepins (DTBs), air- and moisture-stable boron-containing polycyclic aromatics featuring the fusion of thiophene and borepin rings. These compounds could be prepared on gram scales and exhibit the desirable properties characteristic of typical boron-containing π-electron materials, such as polarizable electronic structures, reversible electrochemical reductions, and fluoride-binding ability. We have shown that DTB isomerism, by virtue of the innate differences in electronic structure between **1** and **2**, can be used as a design motif to tune electronic properties, most clearly highlighted by the strongly isomer-dependent electronic responses to fluoride binding. This strategy should prove generally useful for maximizing the tunability of other boron-embedded π-electron systems.

Most remarkably, DTBs survive demanding synthetic transformations—including bromination and metalation of the organic scaffold—allowing for their direct functionalization without causing B−C bond cleavage or other decomposition. The ability to achieve molecular diversification of boron-containing π-conjugated heterocycles without relying on preinstalled synthetic handles is particularly rare and offers a promising approach for streamlining the synthesis of complex π-conjugated organoboron systems. In this spirit we have employed regiospecific DTB metalation/functionalization chemistry coupled with follow-up molecular tailoring to quickly access a diverse array of π-extended derivatives whose electrochemical and photophysical properties could be tuned through judicious substituent choice. The resulting functionalized systems displayed strongly polarizable electronic structures (**1d**, **2d**) and the capacity to achieve stable, polyreduced states (**1e**, **2e**). The combination of excellent chemical stability, broad prospects for molecular diversification, and facile property tuning situate DTBs as promising platforms upon which to build the next generation of π-conjugated organoboron materials.

ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental methods, full details for the synthesis of all DTB compounds and precursors, NMR spectra, UV−vis and PL data, electrochemical data, X-ray crystallographic data, and theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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