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Synthesis, Structure, and Cyclic Voltammetry of 4,6-Bis(dimesitylboryl)dibenzofuran: Isolation of 4,6-Dilithiobenzofuran and 4,5-Dilithio-9,9-dimethylxanthene as tmeda Adducts

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The reaction of dibenzofuran and 9,9-dimethylxanthene with sec-BuLi and n-BuLi, respectively, in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) in hexane followed by storage at −20 °C results in the precipitation of 4,6-dilithiodibenzofuran-1.5-(tmeda) (**1**) and 4,5-dilithio-9,9-dimethylxanthene-1.5(tmeda) (**2**). Both of these adducts form tetranuclear dimers with the lithium atoms bridging the deprotonated aromatic ligands. The reaction of **1** with dimesitylboronfluoride affords 4,6-bis(dimesitylboryl)dibenzofuran (**3**), which has been fully characterized. Cyclic voltammetry of compound **3** shows two reduction waves at $E_{1/2}$ −2.45 and −2.81 V (vs Fc/Fc$^+$), which substantiates significant electronic coupling of the two boron centers. Computational studies show that the p-orbital of the two boron centers participates equally to the LUMO, thus providing grounds for the observed electronic coupling.

Introduction

Polyfunctional boranes have been widely investigated as polydentate Lewis acids. Following the pioneering work of Shriver and Biallas, who showed that methoxide anions are effectively chelated by 1,2-bis(difluoroborylethane),[1] a number of bidentate boranes in which the boron centers are linked by a rigid spacer have been prepared.[2] In this research, much effort has focused on the chemistry of 1,8-diborylnaphthalenes[2,3−8] and 1,2-diborylbenzenes.[2,9−16] Owing to the preorganization and proximity of the Lewis acidic centers, such derivatives are powerful complexing agents for small anions and form chelate complexes with fluoride and hydroxide ions.[3,4,7,14] The reduction chemistry of some of these derivatives has also been studied. In particular, we showed that the reduction of 1,8-bis(diphenylboryl)-naphthalene yields a radical anion that features a boron−boron one-electron σ-bond whose formation is facilitated by the short boron−boron separation enforced by the naphthalene backbone.[17] It occurred to us that a different set of both Lewis acidic and redox properties might be observed in diboranes featuring an increased separation between the Lewis acidic centers. In this contribution, we report the synthesis and structures of 4,6-dilithiodibenzofuran-1.5(tmeda), 4,5-dilithio-9,9-dimethylxanthene-1.5(tmeda), and 4,6-bis(dimesitylboryl)dibenzofuran,[18] as well as the redox properties of the latter.

Results and Discussion

The dilithiation of dibenzofuran by reaction with sec-BuLi has been previously reported, but the resulting dilithium salt has not been isolated.[19−21] We found that the reaction of dibenzofuran with 3 equiv of sec-BuLi and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) in hexane followed by storage at −20 °C for 24 h resulted in the precipitation of 4,6-dilithiodibenzofuran-1.5-(tmeda) (**1**) in the form of dark brown crystals (Scheme

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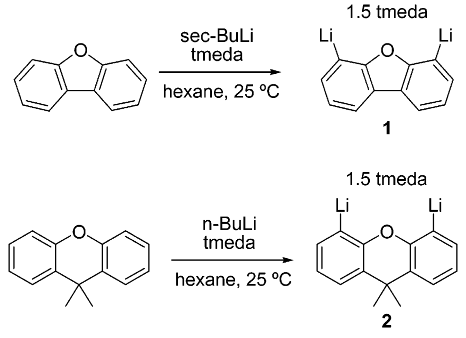
Scheme 1



1). Encouraged by these results, we decided to attempt the isolation of 4,5-dilithio-9,9-dimethylxanthene.[22] This objective was successfully achieved by treatment of 9,9-dimethylxanthene with n-BuLi and tmeda in hexane, which, upon cooling, resulted in the precipitation of 4,5-dilithio-9,9-dimethylxanthene-1.5(tmeda) (**2**) as a pink crystalline solid (Scheme 1). Compounds **1** and **2** are extremely air sensitive and ignite when exposed to air. The ^{1}H NMR spectra of **1** (in pyridine-d_5) and **2** (in benzene-d_6) are in agreement with the dimetalation of the backbone.

Compound **1** crystallizes in the $P2_1$ space group and forms a coordination polymer (Figure 1).[23] This coordination polymer consists of dimeric units of 4,6-dilithiodibenzofuran that are linked by a bridging tmeda molecule. In each dimeric unit, the dibenzofuran-4,6-diyl moieties are bridged by four lithium atoms that are coordinated to the deprotonated 4- and 6-positions of the organic backbone. The resulting C−Li bond distances observed in **1** range from 2.16 to 2.33 Å and are similar to those found in the structure of other aryllithium derivatives such as phenyllithium-tmeda (av C−Li = 2.21 Å).[24,25] Similarly to the situation encountered in the structure of phenyllithium-tmeda, the lithium atoms Li(1) and Li(2) are chelated by tmeda molecules and are tetracoordinated. Owing to positional disorder affecting the tmeda ligands, the Li−N bond distances are somewhat unreliable. The lithium atoms Li(3) and Li(4) are coordinated to a single nitrogen atom provided by the bridging tmeda ligand. As a result, these two lithium atoms are tricoordinated, as sometimes observed in the structure of bulky aryllithium derivatives.[26,27] While the Li(4) atom adopts a trigonal planar arrangement ($\sum_{\text{angles}} = 358.7°$), the coordination geometry of the Li(3) atom is distinctly pyramidal ($\sum_{\text{angles}} = 326.0°$), which is unusual but not unprecedented in sterically crowded systems.[28,29] Compound **2** crystallizes in the P_{bcn} space group and forms a C_2 symmetrical dimer in which the two doubly deprotonated 9,9-dimethylxanthenes are linked by four lithium atoms (Figure 2).[23] The Li(1) atom, which bridges the C(4) and C(5A) carbon atoms (Li(1)−C(4) = 2.209(3) Å and Li(1)−C(5A) = 2.402(3) Å), is also chelated by a tmeda molecule (Li(1)−N(1) = 2.120(3) Å, Li(1)−N(2) = 2.254(3) Å). As a result, its coordination geometry resembles that encountered in phenyllithium-tmeda. As indicated by the relatively short Li(2)−O (2.045(3) Å), Li(2)−C(10) (2.394(3) Å), and Li(2)−C(4) (2.274(3) Å) distances, one of the 9,9-dimethylxanthene-4,5-diyl groups acts as a η^3-ligand for the Li(2) atom. The coordination sphere of this lithium atom is completed by a deprotonated carbon atom (Li(2)−C(5A) = 2.142(3) Å) provided by another 9,9-dimethylxanthene-4,5-diyl ligand and a nitrogen atom of a bridging tmeda molecule (Li(2)−N(3) = 2.184(3) Å). All Li−C and Li−N distances observed in **2** fall within the expected range for such linkages.[24,25]

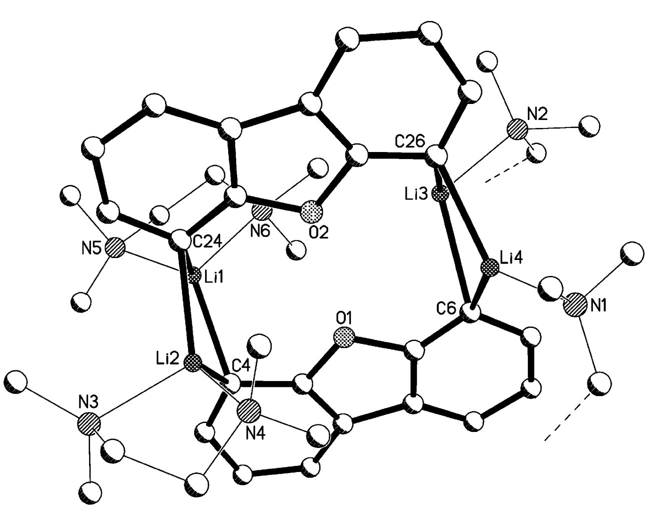


Figure 1. Stick and ball representation of **1**. H atoms omitted for clarity. Only one conformation of the disordered tmeda ligand is shown. Selected bond lengths (Å) and angles (deg): Li(1)−N(5) 2.076(18), Li(1)−N(6) 2.154(17), Li(1)−C(4) 2.229(16), Li(1)−C(24) 2.280(17),), Li(2)−N(3) 2.23(3), Li(2)−N(4) 2.21(2), Li(2)−C(4) 2.226(17), Li(2)−C(24) 2.235(17), Li(3)−N(2) 2.167(15), Li(3)−C(6) 2.333(14), Li(3)−C(26) 2.361(15), Li(4)−N(1) 2.022(16), Li(4)−C(6) 2.157(15), Li(4)−C(26) 2.231(14); N(5)−Li(1)−N(6) 91.4(7), C(4)−Li(1)−C(26) 108.9(7), N(4)−Li(2)−N(3) 84.7(8), C(4)−Li(2)−C(24) 110.7(7), N(2)−Li(3)−C(6) 112.0(6), N(2)−Li(3)−C(24) 106.8(6), C(6)−Li(3)−C(26) 107.2(6), N(1)−Li(4)−C(6) 124.7(7), N(1)−Li(4)−C(26) 115.2(6), C(6)−Li(4)−C(26) 118.8(7).

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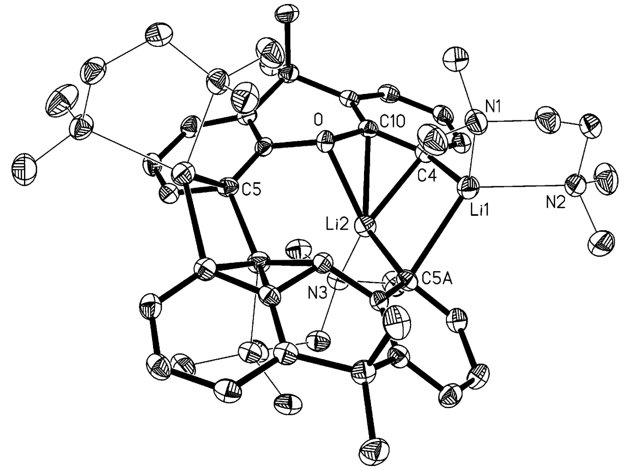
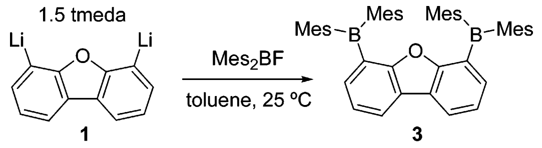


Figure 2. ORTEP view of **2**. Ellipsoids are drawn at the 50% probability level. H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Li(1)−N(1) 2.130(3), Li(1)−C(4) 2.209(3), Li(1)−N(2) 2.254(3), Li(1)−C(5A) 2.402(3), Li(2)−O 2.045(3), Li(2)−C(5A) 2.142(3), Li(2)−N(3) 2.184(3), Li(2)−C(4) 2.247(3), Li(2)−C(10) 2.394(3), N(1)−Li(1)−C(4) 117.67(13), N(1)−Li(1)−N(2) 83.08(10), C(4)−Li(1)−N(2) 117.49(13), N(1)−Li(1)−C(5A) 110.17(12), C(4)−Li(1)−C(5A) 105.31(11), N(2)−Li(1)−C(5A) 122.23(12), O−Li(2)−C(5A) 129.71(13), O−Li(2)−N(3) 114.18(12), C(5A)−Li(2)−N(3) 112.85(12), O−Li(2)−C(4) 66.53(9), C(5A)−Li(2)−C(4) 113.33(12), N(3)−Li(2)−C(4) 108.47(12), O−Li(2)−C(10) 36.41(6), C(5A)−Li(2)−C(10) 140.82(13), N(3)−Li(2)−C(10) 102.16(11), C(4)−Li(2)−C(10) 34.85(6).

Scheme 2



Adduct **1** reacts with 2 equiv of dimesitylboronfluoride to afford 4,6-bis(dimesitylboryl)dibenzofuran (**3**), which was isolated in a pure form by recrystallization from toluene (Scheme 2). Despite repeated efforts, attempts to synthesize and isolate 4,5-bis(dimesitylboryl)-9,9-dimethylxanthene by reaction of **2** with dimesitylboronfluoride have not been successful.[30] The ^{1}H and ^{13}C NMR spectra of **3** feature the expected resonances for a 4,6-disubstituted dibenzofuran derivative and also confirm the presence of the mesityl ligands. The ^{11}B NMR spectrum of **3** features a resonance at 74 ppm, comparable to that observed in other dimesitylarylboron derivatives.[31]

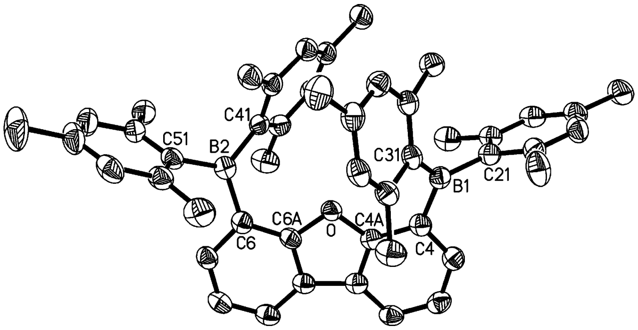


Figure 3. ORTEP view of **3**. Ellipsoids are drawn at the 50% probability level. H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): B(1)−C(31) 1.572(6), B(1)−C(21) 1.576(5), B(1)−C(4) 1.592(6), B(2)−C(41) 1.577(6), B(2)−C(6) 1.580(6), B(2)−C(51) 1.578(6), C(31)−B(1)−C(21) 122.2(4), C(31)−B(1)−C(4) 121.5(3), C(21)−B(1)−C(4) 116.2(4), C(41)−B(2)−C(6) 118.6(3), C(41)−B(2)−C(51) 122.7(4), C(6)−B(2)−C(51) 118.7(4), C(4A)−C(4)−B(1) 125.9(4), C(6A)−C(6)−B(2) 125.7(4).

Compound **3** crystallizes in the $P2_1/c$ space group with one interstitial molecule of toluene (Figure 3).[23] As indicated by the C(4A)−C(4)−B(1) (125.9(4)°) and C(6A)−C(6)−B(2) (125.7(4)°) angles, which deviate from the ideal value of 120° (Figure 3), the structure of **3** is sterically crowded. Each boron center adopts a trigonal planar arrangement ($\Sigma_{\text{angles}} = 359.9°$ at B(1) and B(2)). All carbon−boron distances in **3** are comparable to those found in the structure of other triarylboranes such as triphenylboron (av 1.58 Å).[32] Interestingly, each of the trigonal coordination planes of the B(1) and B(2) centers, respectively, forms a moderate dihedral angle of 35.7° and 34.0° with the plane containing the dibenzofuran-4,6-diyl backbone. The moderate values of these angles suggest the operative conjugation of the boron empty p-orbital with the π-system of the dibenzofuran-4,6-diyl backbone. In fact, the dihedral angles that each of the trigonal coordination planes of the B(1) and B(2) centers forms with the plane containing the aromatic core of the mesityl ligands (59.4°, 39.0°, 48.4°, 60.1°) are distinctly larger. Finally, the boron centers are separated by 5.79 Å.

The structure of this derivative was computationally optimized using density functional theory (DFT) (B3LYP, 6-31+G* for the boron centers, 6-31G for all other atoms).[33] The fully optimized geometry is close to that observed in the solid state, and all bond distances correspond accurately to those experimentally observed (av B−C: obs 1.579 Å, calc 1.578 Å) (Figure 4). It is also important to note that the dihedral angles formed by the trigonal coordination planes of each boron center and the plane of the aromatic ligands are also in reasonable agreement (dihedral angles formed between the boron trigonal planes and (i) the plane of the dibenzofuran backbone for B(1): obs 35.7°, calc 38.7°; for B(2) obs 34.0°, calc 38.8°; (ii) the plane of the mesityl subsiutents: av values for B(1) and B(2): obs 51.7°, calc 51.8°). Examination of the B3LYP orbitals indicates that the LUMO of **3** bears a large contribution from the p-orbitals of the two boron centers and the π-system of the dibenzofuran-4,6-diyl backbone (Figure 4).

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(30) Evidence for the formation of this diborane has been obtained, but its isolation in a pure form has failed.

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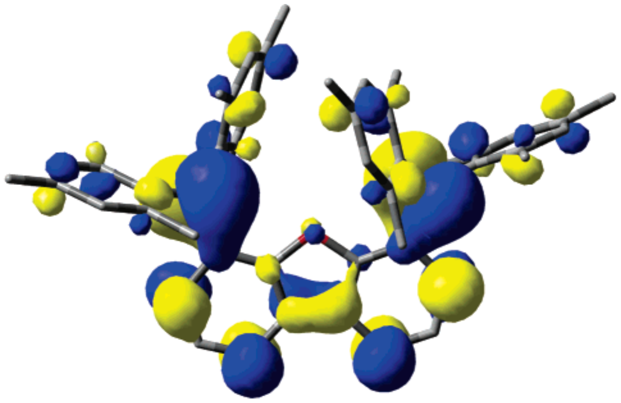

Figure 4. DFT orbital picture showing the LUMO of **3** (isovalue = 0.025). H atoms omitted for clarity.

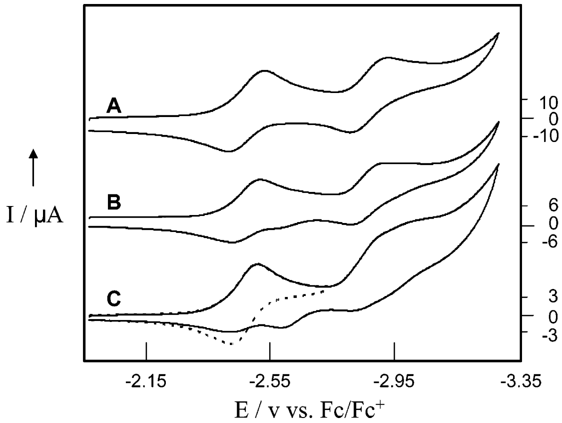

Figure 5. Cyclic voltammogram of **3** in THF with a glassy carbon working electrode (0.2 M n-Bu_4PF_6). Scan rates: $\nu = 500$ mV/s (A); 200 mV/s (B); 50 mV/s (C).

The cyclic voltammogram of **3** in THF shows a reversible wave at $E_{1/2(1)} = -2.45$ V (vs Fc/Fc$^+$) (Figure 5). The potential of this reduction is comparable to that observed for other triarylboranes[34–43] and corresponds to the formation of a radical anion. While the second reduction of triarylboranes is always irreversible, the cyclic voltammogram of **3** features a second reduction wave at $E_{1/2(2)} = -2.81$ V (vs Fc/Fc$^+$), which appears reversible at elevated scan rate ($\nu = 500$ mV/s) and irreversible at slower scan rates ($\nu < 400$ mV/s). The scan rate dependence of this second reduction wave suggests that the dianion generated at this potential undergoes rapid chemical reactions. The potential difference $\Delta E_{1/2}$ of 0.36 V ($\nu = 500$ mV/s) observed between the two reduction waves in the CV of **3** is larger than that observed for 4,4′-bis(dimesitylboryl)biphenyl ($\Delta E_{1/2} = 0.25$ V),[44] thus indicating substantial electronic coupling of the two boron centers.[45] As indicated by the aforementioned DFT calculation, both boron centers participate equally to the nondegenerate LUMO, thus providing grounds for this electronic coupling. Combination of diborane **3** with 18-C-6 and Na/Hg produced a dark green paramagnetic solution, which presumably contains the radical anion **3**$^{\bullet-}$. The EPR spectrum of this solution consists of a signal at $g = 2.00$; however, the ^{11}B hyperfine coupling could not be resolved.

Conclusion

The present investigations indicate that 4,6-dilithiodibenzofuran (**1**) and 4,5-dilithio-9,9-dimethylxanthene (**2**) can be isolated in the form of tmeda adducts. Isolation of these solid adducts, which can be kept under an inert atmosphere for extended periods of time, is a significant achievement that should provide new synthetic possibilities for the incorporation of the dibenzofuran-4,6-diyl and 9,9-dimethylxanthene-4,5-diyl backbone in organic and organometallic compounds. The preparation of diborane **3** by reaction of **1** with dimesitylboronfluoride illustrates this idea. Structural, computational, and electrochemical studies of diborane **3** indicate that the dibenzofuran-4,6-diyl backbone should, in principle, promote antiferromagnetic coupling of spin carriers directly attached to the 4- and 6-positions.

Experimental Section

General Procedures. Dibenzofuran was purchased from Aldrich and purified by recrystallization from ethanol. tmeda was purchased from Aldrich and dried over Na/K. 9,9-Dimethylxanthene, dimesitylboronfluoride, *n*-butyllithium (1.6 M in hexane), and *sec*-butyllithium (1.4 M in cyclohexane) were purchased from Aldrich and used without purification. Toluene, pentane, and hexane were dried by reflux under N_2 over CaH_2 and freshly distilled prior to use. Air-sensitive compounds were handled under N_2 atmosphere using standard Schlenk and glovebox techniques. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). Melting points were measured on samples in sealed capillaries and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Inova 300 and 500 spectrometers. Chemical shifts for ^{1}H and ^{13}C NMR spectra are reported with respect to Me_4Si standard ($\delta = 0$ ppm). ^{11}B NMR spectra were recorded on an Inova 400 spectrometer. Chemical shifts for ^{11}B NMR spectra are reported with respect to $Et_2O{\cdot}BF_3$ standard ($\delta = 0$ ppm). EPR spectra were recorded on a Bruker X-band EPR spectrometer (model ESP 300E).

Electrochemical experiments were performed with an electrochemical analyzer from CH Instruments (Model 610A) with a glassy-carbon working electrode and a platinum auxiliary electrode. The reference electrode was built from a silver wire inserted in a small glass tube fitted with a porous Vycor frit at the tip and filled with a CH_3CN solution containing $(^nBu)_4NPF_6$ (0.2 M) and $AgNO_3$ (0.005 M). All three electrodes were immersed in a THF solution (8 mL) containing $(^nBu)_4NPF_6$ (0.2 M) as a support electrolyte and the diborane **3** (0.003 M). The electrolyte was dried under vacuum prior to use. In all cases, ferrocene was used as an internal standard,

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and all reduction potentials are reported with respect to the $E_{1/2}$ of the Fc^+/Fc redox couple.

4,6-Dilithiodibenzofuran-1.5(tmeda) (1). *sec*-Butyllithium (1.4 M) in cyclohexane (6.4 mL, 9.0 mmol) was slowly added to a suspension of dibenzofuran (500 mg, 3.0 mmol) and tmeda (1.35 mL, 9.0 mmol) in hexane (2 mL) at room temperature. After standing at room temperature for 24 h, the solution was cooled to −20 °C. Compound **1** precipitated as a dark brown solid and was washed with hexane (10 mL). Yield: 71% (750 mg). ^{1}H NMR (pyridine-d_5, 500 MHz): δ 2.15 (s, 18 H, tmeda-CH_3), 2.38 (s, 6 H, tmeda −CH_2), 7.35 (pseudo t, $J_{apparent}$ = 7.0 Hz, 2 H, dibenzo-C*H*), 7.46 (d, J = 7.3 Hz, 2 H, dibenzo-C*H*), 8.03 (d, J = 7.6 Hz, 2 H, dibenzo-C*H*).

4,5-Dilithio-9,9-dimethylxanthene-1.5(tmeda) (2). *n*-Butyllithium (1.6 M) in hexane (4.6 mL, 7.4 mmol) was slowly added to a solution of 9,9-dimethylxanthene (524 mg, 2.5 mmol) and tmeda (0.9 mL, 6.0 mmol) in hexane (2 mL) at room temperature. After standing at room temperature for 24 h, the solution was cooled to −20 °C. Compound **2** precipitated as a pink solid and was washed with pentane (10 mL). Yield: 71% (701 mg). ^{1}H NMR (benzene-d_6, 300 MHz): δ 1.74 (s, 6 H, tmeda-CH_2), 1.80 (s, 24 H, tmeda-CH_3 and xanthene-CH_3), 7.28 (pseudo t, $J_{apparent}$ = 7.0 Hz, 2 H, xanthene-C*H*), 7.35 (d, J = 7.5 Hz, 2 H, xanthene −C*H*), 7.97 (d, J = 6 Hz, 2 H, xanthene −C*H*).

4,6-Bis(dimesitylboryl)dibezofuran (3). A solution of dimesitylboronfluoride (350 mg, 1.31 mmol) in toluene (5 mL) was added into a suspension of freshly isolated 4,6-dilithiodibenzofuran-1.5(tmeda) (264 mg, 0.75 mmol) in toluene (5 mL) at room temperature. The resulting mixture was stirred for 5 h and then filtered. The solvent was removed under vacuum, and the resulting solid was further purified by crystallization from toluene. Yield: 46% (198 mg). Melting point: 217−220 °C. ^{1}H NMR (benzene-d_6, 500 MHz): δ 2.16 (s, 24 H, Mes-*o*-CH_3), 2.17 (s, 12 H, Mes-*p*-CH_3), 6.70 (s, 8 H, Mes-C*H*), 7.10 (pseudo t, J = 7.4 Hz, 2 H, dibenzo-C*H*), 7.41 (d, J = 7.3 Hz, 2 H, dibenzo-C*H*), 7.75 (d, J = 7.5 Hz, 2 H, dibenzo-C*H*). ^{13}C NMR (benzene-d_6, 125.9 MHz): δ 21.4 (Mes-*p*-*C*H$_3$), 23.2 (Mes-*o*-*C*H$_3$), 122.9 (Mes-*o*-*C*), 123.1 (Mes-*p*−*C*), 123.7 (dibenzo-*C*1a/9a), 128.7 (Mes-*m*−*C*H), 132.4 (Mes-*C*B), 133.2 (dibenzo-*C*3/7 or 2/8 or 1/9), 138.8 (dibenzo-*C*3/7 or 2/8 or 1/9), 140.9 (dibenzo-*C*3/7 or 2/8 or 1/9), 142.3 (dibenzo-*C*B), 159.4 (dibenzo-*C*4a/6a). ^{11}B NMR (chloroform-*d*, 160.6 MHz): δ 74. Anal. Calcd for $C_{48}H_{50}OB_2$: C 86.76; H 7.58. Found: C 86.20; H 7.60.

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Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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