Supporting Information

General Methods

Reagents were purchased from commercial suppliers and used without further purification. Solvents were used as received, except diethyl ether (Et₂O), which was dried over activated alumina in an mBraun solvent purification system.

NMR spectra were obtained on JEOL ECX-400 and ECA-500 spectrometers, with working frequencies (for ¹H nuclei) of 400 and 500 MHz, respectively. ¹H NMR chemical shifts are reported in ppm units relative to the residual signals of the solvents (CDCl₃, 7.26 ppm and DMSO-d₆, 2.50 ppm). ¹¹B NMR shifts are given relative to external BF₃·Et₂O standard. All NMR spectra were recorded at 25 °C. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer using Pike MIRacle Micrometer pressure clamp. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 25 UV-Vis spectrophotometer. Microanalyses were conducted by Intertek USA, Inc. Thermal gravimetric analysis (TGA) was carried out on a TA Instruments Hi-Res TGA 2950 thermogravimetric analyzer.

Experiments are presented in the order following the discussion in the manuscript. Compound numbers are identical to those in the main text of the manuscript.
Preparation of 1,1'-Ferrocenediboronic Acid (I)

A mixture of butyllithium (1.6 M in hexane, 37.5 mL, 60.0 mmol) and \(N,N,N',N'-\text{tetramethyl-ethane-1,2-diamine} \) (9.0 mL, 60.0 mmol) in Et\(_2\)O (50 mL) was added, under nitrogen, to a stirred solution of ferrocene (5.00 g, 26.9 mmol) in Et\(_2\)O (100 mL) in a 250 mL Schlenk flask. After overnight stirring at 20 °C, the suspension was added slowly via cannula to a 500 mL Schlenk flask which contained a stirred and cooled (−78 °C) solution of triisopropylborate (14.7 mL, 65.0 mmol) in Et\(_2\)O. The mixture was allowed to warm up to 20 °C over 1 h, and stirring was continued overnight. After hydrolysis with 10% aqueous KOH solution, the organic layer was extracted with \(\text{H}_2\text{O} \). The combined aqueous layers were acidified with 10% \(\text{H}_2\text{SO}_4 \) in an ice bath and kept at 20 °C for 24 h. The precipitate was filtered and washed with water and Et\(_2\)O and air dried to yield pure 1 (2.50 g, 34%).

IR: 3315 (s, \(\tilde{\nu}_{\text{BO-H}} \)), 1469 (s, \(\tilde{\nu}_{\text{C=C}} \)), 1393 (s, \(\tilde{\nu}_{\text{O-B}} \)), 1334 (s, \(\tilde{\nu}_{\text{O-B}} \)), 1322 (s, \(\tilde{\nu}_{\text{C-C}} \)) cm\(^{-1}\). \(^1\)H NMR (DMSO-\(d_6\)): \(\delta \) 4.17 (t, \(J_{\text{H-H}} = 2.0 \text{ Hz}, 4\text{H}\)), 4.34 (t, \(J_{\text{H-H}} = 2.0 \text{ Hz}, 4\text{H}\)), 7.48 (s, 4H, O–H) ppm. \(^{13}\)C\(^{\text{1H}}\) NMR (DMSO-\(d_6\)): \(\delta \) 64.81, 71.65, 73.66 ppm. \(^{11}\)B NMR (DMSO-\(d_6\)): \(\delta \) 29.07 ppm. Spectral data are identical to those previously reported in the literature.\(^1\)

Preparation of Compound 2

A 20 mL vial was charged with 1,1'-ferrocenediboronic acid (1, 30.0 mg, 0.11 mmol), mesitylene (5 mL), and 1,4-dioxane (5 mL). The resulting suspension was sonicated for 1 h at 20 °C, and was then placed into an oven at 80 °C for 1 d. Orange crystals were formed after this treatment. The supernatant was decanted and the crystals were soaked in EtOH to dissolve unreacted starting material and impurities. The resulting crystals were then filtered and washed with \(\text{N,N-dimethylformamide} \) (DMF) and hot EtOH. After drying for 1 d in an 150 °C vacuum oven, 14.2 mg (54%) of single crystals of 2 was isolated. UV-Vis (CHCl\(_3\)): \(\lambda_{\text{max}} \) (log\(\varepsilon \)) = 448 (4.51) nm (lower limit of the extinction coefficient, on account of low solubility). IR: 1474 (s, \(\tilde{\nu}_{\text{C=C}} \)), 1386 (s, \(\tilde{\nu}_{\text{O-B}} \)), 1353 (s, \(\tilde{\nu}_{\text{O-B}} \)), 1322 (s, \(\tilde{\nu}_{\text{C-C}} \)) cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)): \(\delta \) 4.66 (t, \(J_{\text{H-H}} = 1.7 \text{ Hz}, 12\text{H}\)), 4.52 (t, \(J_{\text{H-H}} = 1.7 \text{ Hz}, 12\text{H}\)). \(^{11}\)B NMR (CDCl\(_3\)): \(\delta \) 28.81. Anal. calcd for C\(_{30}\)H\(_{32}\)Fe\(_3\)B\(_6\)O\(_6\): C 50.50, H 3.37; Found: C 50.56, H 3.16.
Figure S1. Thermogravimetric analysis (TGA) profile of compound 2 under N₂ flow.
**Figure S2.** Fourier transform infrared (FT-IR) spectrum of 1,1'-ferrocenediboronic acid (1).
Figure S3. Fourier transform infrared (FT-IR) spectrum of compound 2.
Figure S4. $^1$H NMR spectrum of 1,1'-ferrocenediboronic acid (1).
Figure S5. $^{13}\text{C}^{1\text{H}}$ NMR spectrum of 1,1'-ferrocenediboronic acid (I).
Figure S6. $^1$H NMR spectrum of compound 2.
### Crystal Data of Compound 2

- **Empirical formula**: $C_{30}H_{24}B_6O_6Fe_3$
- **Formula weight**: 712.90
- **Temperature**: 223(2) K
- **Wavelength**: 0.71073 Å
- **Crystal system**: Monoclinic
- **Space group**: $C2$
- **Unit cell dimensions**:
  - $a = 21.8605(9) \text{ Å}$, $\alpha = 90^\circ$
  - $b = 19.4421(8) \text{ Å}$, $\beta = 96.620(1)^\circ$
  - $c = 25.7885(10) \text{ Å}$, $\gamma = 90^\circ$
- **Volume**: 10887.4(8) Å$^3$
- **Z**: 16
- **Density (calculated)**: 1.740 Mg/m$^3$
- **Absorption coefficient**: 1.626 mm$^{-1}$
- **$F(000)$**: 5760
- **Crystal size**: 0.30 × 0.15 × 0.05 mm$^3$
- **Theta range for data collection**: 1.41° to 25.04°
- **Index ranges**: $-26 \leq h \leq 25$, $-23 \leq k \leq 17$, $0 \leq l \leq 30$
- **Reflections collected**: 28076
- **Independent reflections**: 17093 [$R_{int} = 0.0671$]
- **Completeness to theta = 25.04°**: 99.9%
- **Absorption correction**: Empirical
- **Max. and min. transmission**: 0.9959 and 0.5538
- **Refinement method**: Full-matrix least-squares on $F^2$
- **Data / restraints / parameters**: 9438 / 145 / 1621
- **Goodness-of-fit on $F^2$**: 0.955
- **Final $R$ indices [$I > 4\sigma(I)$]**: $R_1 = 0.0398$, $wR_2 = 0.0915$
- **$R$ indices (all data)**: $R_1 = 0.0777$, $wR_2 = 0.1128$
- **Absolute structure parameter**: 0.037(17)
- **Largest diff. peak and hole**: 0.514 and $-0.344$ e$^-$/Å$^3$
Solid-State Cyclic Voltammetry of Compound 2

Cyclic voltammetry of compound 2 was performed using a Macpile potentiostat in the potential range of 2.80 to 3.55 V (vs. Li/Li⁺) with a scan rate of 1 mV/s. The experiments were carried out using two-electrode Swagelok™-type cells. The working electrodes were prepared by mixing 10 wt% of polyvinylidene fluoride (PVDF) binder, 10 wt% of the active material, and 80 wt% of carbon black (a conducting additive) in an agate mortar. Celgard 2400 was used as the separator and pure lithium foil (Aldrich) was used as the counter electrode. The electrolyte consisted of a solution of 1.0 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) mixture (1:1 w/w). The cells were assembled inside an argon-filled glove box.

The CV curves of compound 2 (Figure. S8a) show three anodic peaks at approx. 3.05, 3.30, and 3.50 V during the first cycle; these peaks drastically decrease upon cycling, indicating irreversible oxidation of the ferrocene cores. Theoretically, the three ferrocenyl groups in compound 2 are equivalent; therefore, oxidation of any of them in the neutral structure would occur at the same redox potential to produce a monocationic species. However, the removal of a second electron from another ferrocenyl group requires more energy than the first because of electrostatic repulsion (the relatively short distance between these groups of about 7 Å allows significant through-space electrostatic interaction). As a result, the potential of oxidation of the second ferrocenyl group is more positive than the first, resulting in the splitting of the CV waves into three distinct oxidation peaks from three corresponding ferrocenyl groups.

Figure S7. Photographs of crystals of compound 2.
Figure S8. Solid-state cyclic voltammograms of (a) compound 2 (with polymer binder and carbon), and (b) a blank electrode (polymer binder and carbon only).

Oxidation of a ferrocenyl species requires an additional counteranion (PF$_6^-$) from the electrolyte to maintain the electroneutrality of the structure. The appearance of the CV waves therefore also depends on the strength of ion pairing between the ferrocenium cation and the electrolyte anion. The insertion of the bulky PF$_6^-$ into the rigid structure of the ferrocene boroxine cyclophane might be responsible for the irreversible electrochemical behavior of compound 2.

References