Perfunctionalized Dodecaborate Clusters as Stable Metal-Free Active Materials for Charge Storage

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Supporting Information (SI)

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Experimental Section

General Considerations

Microwave synthesis reactions and all post-microwave work-up and characterization was performed under ambient conditions. The "ambient conditions" for this manuscript refer to room temperature (20 - 25 °C) and uncontrolled laboratory air.

Materials

Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. MilliQ water described in this manuscript refers to purified potable water with a resistivity at 25 °C of ≤ 18.2 MΩ·cm. $[NEt_3H]_2[B_{12}H_{12}]$ was purchased from Boron Specialties (USA). Ethanol (200 proof) was purchased from Decon Labs and used as received. Dowex 50W X8 (100-200 mesh, hydrogen form), $FeCl_3 \cdot 6H_2O$ (≥ 97%), $CsOH \cdot 1H_2O$ (≥ 99.5%), $[N^nBu_4]OH$ (40% in H_2O), acetonitrile (≥ 99.99%), dichloromethane (≥ 99.5%), ethyl acetate (≥ 99.5%), hexanes (≥ 98.5%), triethylamine (≥ 99%), and *N,N*-diisopropylethylamine (≥ 99%) were purchased from Sigma-Aldrich. 3,5-Bis(trifluoromethyl)benzyl bromide (97%) and 1-bromo-3-methoxypropane (98%) were purchased from Oakwood. NaOH (Certified ACS, 99.2%) and hydrogen peroxide (30% in H_2O) were purchased from Fisher. For electrolyte preparation, acetonitrile (MeCN, 99.9%, Extra Dry AcroSeal®) was purchased from Acros Organics, and tetraethylammonium tetrafluoroborate (TEABF4, 99.9%) was purchased from BASF. All electrolyte solutions were prepared in an Ar-filled (Airgas, 99.999%) glovebox at room temperature in volumetric flasks. All reagents were used as received unless otherwise indicated.

Instrumentation

A Bruker AV400 spectrometer was used to obtain ^{11}B, ^{1}H, and ^{19}F NMR spectra and Bruker Topspin software was used to process the NMR data. ^{1}H NMR spectra were referenced to residual solvent resonances in deuterated solvents (δ 7.26 for $CDCl_3$). ^{11}B and ^{19}F NMR spectra were referenced to $BF_3{\cdot}Et_2O$ (δ 0.00 and δ -153.38 for ^{11}B and ^{19}F, respectively). Mass spectrometry data was acquired using a Thermo Scientific™ Q-Exactive™ Plus instrument with a quadrupole mass filter and Orbitrap mass analyzer. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA). X-ray photoelectron spectroscopy (XPS) was performed using a monochromatic Al Kα X-ray source (12 mA for both survey and high resolution scans, 15 kV) with a 300 × 700 nm oval spot size. The pressure of the analyzer chamber was maintained below 1×10^{-9} Torr during the measurement. Data were collected with 160 eV and 20 eV pass energy for the survey spectra and high-resolution spectra of B 1*s,* respectively, using a 200 ms dwell time. All peaks were charge referenced to the adventitious carbon 1 *s* signal at 284.6 eV. Mass spectrometry data were acquired using a Waters LCT Premier TOF system with ACQUITY LC and autosampler.

Microwave Synthesis

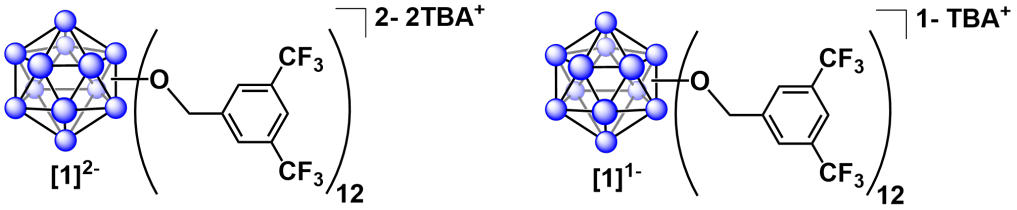
Microwave reactions were performed using a CEM Discover SP microwave synthesis reactor. Except where noted otherwise, all reactions were performed in glass microwave reactor vials purchased from the vendor. Reaction vials were sealed with silicone/PTFE caps, or using the 80 mL vessel pressure regulator accessory cap. Small (1 cm long) egg-shaped PTFE-coated stir bars were used in the vials with magnetic stirring set to high and 15 seconds of premixing prior to the temperature ramping. All microwave reactions were carried out at 140 °C with the pressure release limit set to 250 psi (no reactions exceeded this limit to trigger venting) and the maximum

wattage set to 250 W (the power applied was dynamically controlled by the microwave instrument and did not exceed this limit for any reactions). Column chromatography was performed using 4 cm inner diameter glass fritted chromatography columns with 20-30 cm of slurry-packed silica gel to ensure full separation of reagents and products. Unfiltered pressurized air was used to assist column chromatography.

Synthesis of $[N^nBu_4]_2B_{12}(OH)_{12}$

Synthesis of $[N^nBu_4]_2B_{12}(OH)_{12}$ was performed starting with $Cs_2[B_{12}H_{12}]$ (ion exchanged from $[NEt_3H]_2[B_{12}H_{12}]$ using $CsOH{\cdot}1H_2O$) according to a reported procedure.[1] *Note: the hydroxylation procedure should always be undertaken with caution and careful planning to ensure the $Cs_2[B_{12}H_{12}]$ reagent is pure and contains no organic contaminants. Blast shielding to contain any possible explosions should be utilized. Under no circumstances should the hydrogen peroxide used in the reaction come into contact with any organic material or solvents due to possibility of an explosion.*

Synthesis of $[1]^{2-}$ & $[1]^{1-}$



Clusters $[\mathbf{1}]^{2-}$ and $[\mathbf{1}]^{1-}$ were synthesized using an adapted method from a previous report.[2]

$[1]^{2-}$: $[N^nBu_4]_2B_{12}(OH)_{12}$ (2.0 g, 2.4 mmol) was added to an 80 mL glass microwave vial and dissolved in 15 mL of acetonitrile. *N,N*-diisopropylethylamine (8.0 mL, 45.9 mmol) and 3,5-bis(trifluoromethyl)benzyl bromide (8.0 mL, 43.6 mmol) were added along with a stir bar, the

vial was sealed with an 80 mL vessel pressure regulator accessory cap, and the mixture was heated at 140 °C with stirring in the microwave for 1.5 hours. The excess acetonitrile was evaporated by rotary evaporation in a round bottom flask, and the residue was loaded onto a slurry-packed silica gel column (pre-flushed with 30 mL triethylamine dissolved in 140 mL 35/65 [v/v] ethyl acetate/hexane) using 35/65 [v/v] ethyl acetate/hexane and ~3-4 mL acetone (to rinse the sides of the round bottom flask). The remaining 3,5-bis(trifluoromethyl)benzyl bromide reagent was eluted through the silica column using 35/65 [v/v] ethyl acetate/hexane, followed by acetone to elute the light-yellow product band (near solvent front). The acetone was removed by rotary evaporation and transferred to a 20 mL glass vial, and the oily substance was dried under high vacuum at 60 °C for 2 hours to obtain 8.04 g (93.6%) of pure, isolated product. Compound $[\mathbf{1}]^{2-}$ is a very light yellow solid ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (br s, 24H, *ortho*-$C_6\underline{H}_3$), 7.50 (br s, 12H, *para*-C_6H_3), 5.55 (br s, O-$C\underline{H}_2$), 3.06 – 2.96 (m, 16H, N-$C\underline{H}_2$), 1.60 – 1.47 (m, 16H, N-$CH_2C\underline{H}_2$), 1.41 – 1.27 (m, 16H, N-$(CH_2)_2C\underline{H}_2$), 0.94 (t, 24H, N-$(CH_2)_3C\underline{H}_3$). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -15.43 (br s, 12B). ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.50 (s, 72F). HRMS (Orbitrap): *m/z* calculated for $C_{108}H_{60}B_{12}F_{72}O_{12}$ (M^{2-}), 1523.7079 Da; found, 1523.7042 (z=2) Da. Calc. for $C_{140}H_{132}B_{12}F_{72}N_2O_{12}$: C, 47.61; H, 3.77. Found: C, 47.17; H, 3.76.

[1]$^-$: $[N^nBu_4]_2B_{12}(OH)_{12}$ (2.0 g, 2.4 mmol) was added to an 80 mL glass microwave vial and dissolved in 15 mL of acetonitrile. *N,N*-diisopropylethylamine (8.0 mL, 45.9 mmol) and 3,5-bis(trifluoromethyl)benzyl bromide (8.0 mL, 43.6 mmol) were added along with a stir bar, the vial was sealed with an 80 mL vessel pressure regulator accessory cap, and the mixture was heated at 140 °C with stirring in the microwave for 1.5 hours. The excess acetonitrile was evaporated by rotary evaporation in a round bottom flask, and the residue was loaded onto a slurry-packed silica gel column using 35/65 [v/v] ethyl acetate/hexane and ~1-2 mL acetonitrile

(to rinse the sides of the round bottom flask). The remaining 3,5-bis(trifluoromethyl)benzyl bromide reagent was eluted through the silica column using 35/65 [v/v] ethyl acetate/hexane, followed by acetone to elute the slightly pink/light-yellow product band (near solvent front). The acetone was removed by rotary evaporation and the residue was dissolved in 21 mL 9:1 [v/v] ethanol/acetonitrile, 1.67 g $FeCl_3 \cdot 6H_2O$ was added, and the mixture was left to stir at room temperature overnight. The volatiles were removed *via* rotary evaporation, and the residue was dissolved in dichloromethane and filtered through a 1 cm thick silica plug in a wide glass fritted funnel (8.5 cm inner diameter) to remove most of the iron. The filtrate was concentrated *via* rotary evaporation, then eluted through a silica gel column with dichloromethane, collecting the purple band containing the product. The dichloromethane was removed *via* rotary evaporation, and the solids were transferred to a 20 mL glass vial and dried under high vacuum overnight to obtain 5.80 g (72.5%) of pure, isolated product. Compound $[\mathbf{1}]^{1-}$ is a red-purple solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 – 7.41 (br m, 36H, $C_6\underline{H}_3$), 3.19 – 3.07 (m, 8H, N-$C\underline{H}_2$), 1.72 – 1.63 (m, 8H, N-$CH_2C\underline{H}_2$), 1.53 – 1.42 (m, 8H, N-$(CH_2)_2C\underline{H}_2$), 1.05 (t, 12H, N-$(CH_2)_3C\underline{H}_3$). *Note: The CH_2 signal for the cluster is masked and all other peaks are quite broad due to the paramagnetic radical state of the molecule.* No resonances are visible by ^{11}B NMR, due to paramagnetic broadening. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.45 (s, 72F). HRMS (Orbitrap): *m/z* calculated for $C_{108}H_{60}B_{12}F_{72}O_{12}$ (M^{2-}), 1523.7079 Da; found, 1523.7059 (z = 2) Da. Calc. for $C_{124}H_{96}B_{12}F_{72}NO_{12}$: C, 45.27; H, 2.94. Found: C, 45.26; H, 3.06.

Synthesis of $[\mathbf{2}]^0$

$[N^nBu_4]_2B_{12}(OH)_{12}$ (0.5 g, 0.61 mmol) was added to an 35 mL glass microwave vial and dissolved in 10 mL of acetonitrile. *N,N*-diisopropylethylamine (2.0 mL, 11.5 mmol) and 1-bromo-3-methoxypropane (8.2 mL, 73.4 mmol) were added along with a stir bar, the vial was

sealed with a silicone/PTFE cap, and the mixture was heated at 140 °C with stirring in the microwave for 2 hours. The excess acetonitrile was evaporated by rotary evaporation in a round bottom flask, and the residue was loaded onto a slurry-packed silica gel column using 35/65 [v/v] ethyl acetate/hexane. The remaining 1-bromo-3-methoxypropane reagent was eluted through the silica column using 35/65 [v/v] ethyl acetate/hexane, followed by 3:1 [v/v] hexane/acetone to elute the product, initially a pink band which turns orange as it oxidizes along the length of the column. After elution of the orange neutral product band, the remaining pink 1-/2- cluster was eluted with acetone. For the pink fraction, the acetone was removed by rotary evaporation and eluted through a second slurry-packed silica gel column using the same 3:1 [v/v] hexane/acetone solution. The orange product was collected and combined with the first orange fraction, the acetone was removed by rotary evaporation, the product was transferred to a 20 mL glass vial, and the oily substance was dried under high vacuum overnight to obtain 231 mg (31.5%) of pure, isolated product. Compound $[\mathbf{2}]^0$ is a dark brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.10 (t, 24H, B-O-C$\underline{H}_2$), 3.44 (t, 24H, C$\underline{H}_2$-OCH$_3$), 3.31 (s, 36H, CH$_2$-OC$\underline{H}_3$), 1.83 (quin, 24H, O-CH$_2$-C$\underline{H}_2$-CH$_2$-O). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 41.60 (br s, 12B). HRMS (Orbitrap): *m/z* calculated for $C_{48}H_{108}B_{12}O_{24}$ (M^-), 1198.8420 Da; found, 1198.8425 Da. Calc. for $C_{48}H_{108}B_{12}O_{24}$: C, 48.08; H, 9.08. Found: C, 48.65; H, 9.19.

Solubility Test Procedure

In three 4-mL screw-top glass vials, $\mathbf{1}^{2-}$ (1.766 g, 0.5 mmol), $\mathbf{1}^{1-}$ (1.645 g, 0.5 mmol), and $\mathbf{2}^0$ (0.121 g, 0.1 mmol) were added along with flea micro stir bars. HPLC-grade acetonitrile was then added to each vial to make 0.5 M solutions, and the vials were sealed with PTFE/silicone caps. The solutions were stirred at 400 rpm at room temperature for 16 hours, after which they

were sonicated at room temperature for 30 minutes. They were then subjected to centrifugation at 2,000 x g for 5 minutes and the presence of any pellets was checked by visual inspection.

Solubility Test Result: No pellets were observed in any of the solutions after centrifugation (photos below), indicating $\mathbf{1}^{2-}$, $\mathbf{1}^{1-}$, and $\mathbf{2}^{0}$ have solubility ≥ 0.5 M in acetonitrile under the conditions tested.

$\mathbf{1}^{2-}$ $\mathbf{1}^{1-}$ $\mathbf{2}^{0}$

Cyclic Voltammetry and Randles-Sevcik Analysis

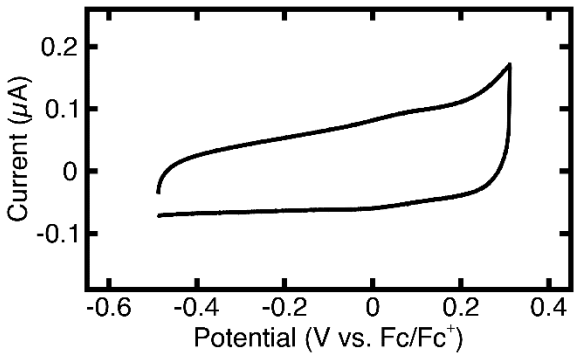


Figure S1. Background cyclic voltammograms of 0.5 M $TBAPF_6$ in MeCN taken at a scan rate of 10 mV s^{-1}.

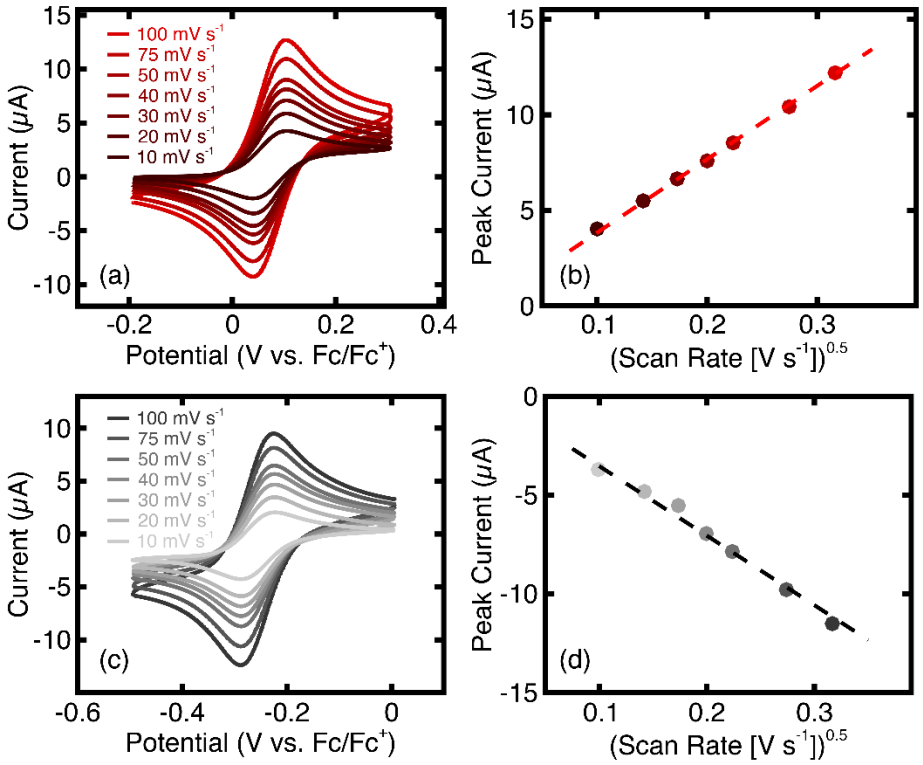


Figure S2. Cyclic voltammograms as a function of scan rate for **1** (a) and **2** (c), and the corresponding Randles-Sevcik peak-current analysis for **1** (b) and **2** (d). All of the experiments were conducted with 1 mM active material in 0.5 M $TBAPF_6$ in MeCN.

Flow Cell Supplementary Data

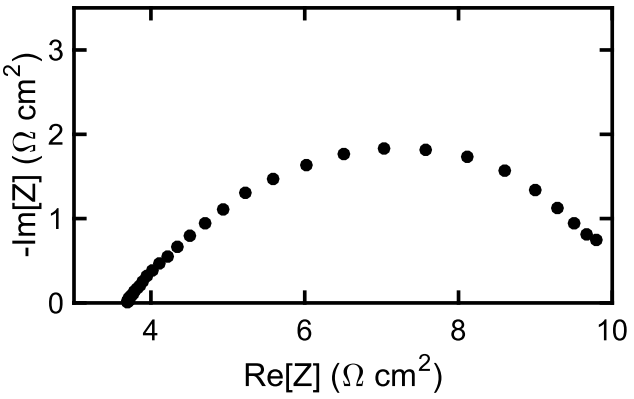


Figure S3. Symmetric cell EIS at 50% state-of-charge.

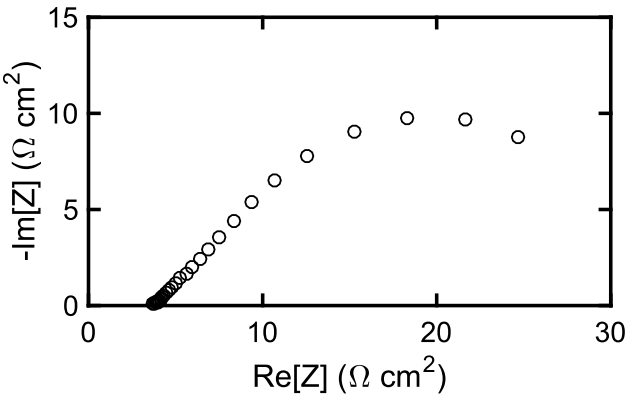


Figure S4. Full cell EIS at 0% state-of-charge.

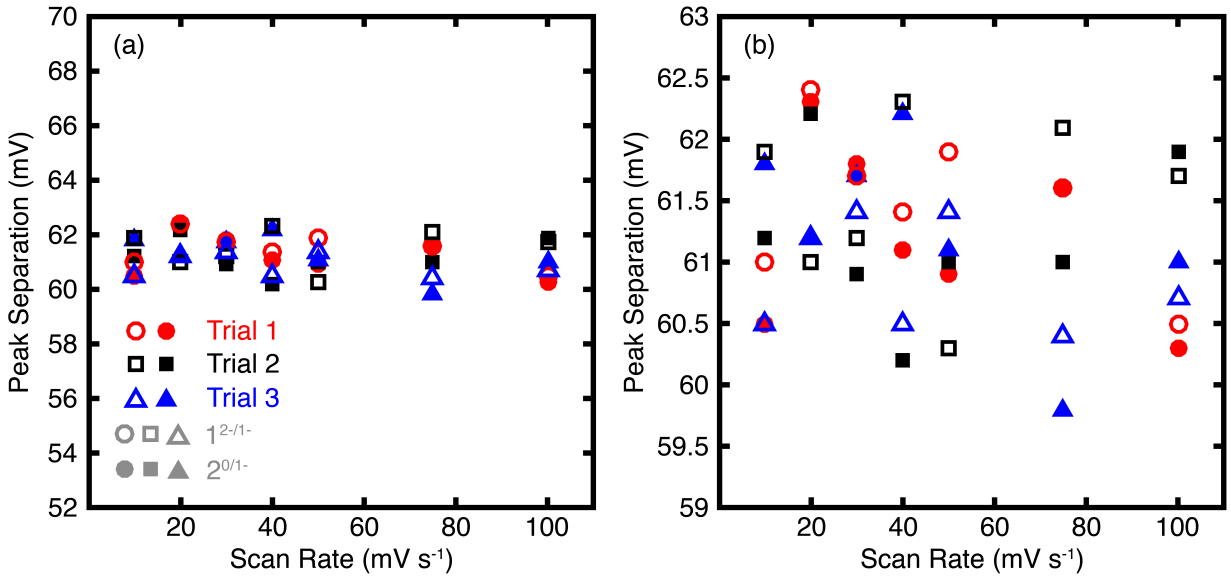


Figure S5. Peak separation as a function of scan rate for both borate clusters tested for all trials shown as an overview (a) and as a detailed view (b). The open and closed shapes correspond to $1^{2-/1-}$ and $2^{0/1-}$, respectively. Analysis shows that there is not an increase in peak separation as a function of scan rate and instead that all of the peak separations measured are close to the range of 61 +/- 1.

Post-Flow Cell Analysis of $[1]^{2-}$ & $[1]^{1-}$

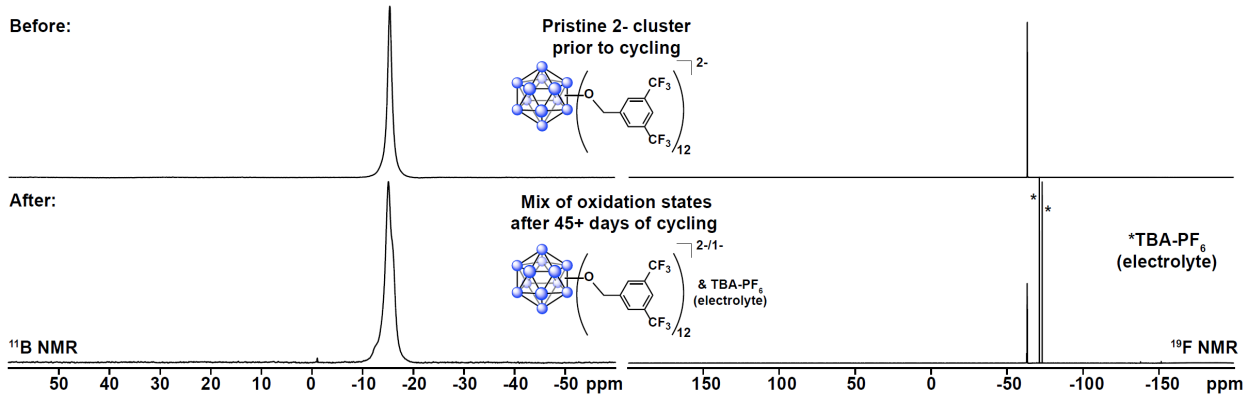


Figure S6. Post-flow cell NMR analysis of cluster materials indicating no observable degradation of the boron clusters.

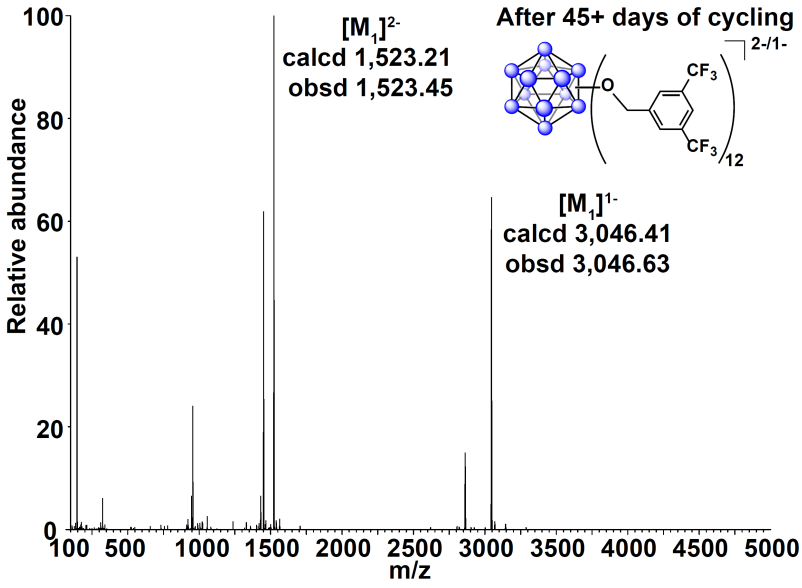


Figure S7. Post-flow cell negative ion mode mass spectrometry analysis of **1** indicating no observable degradation of the boron clusters

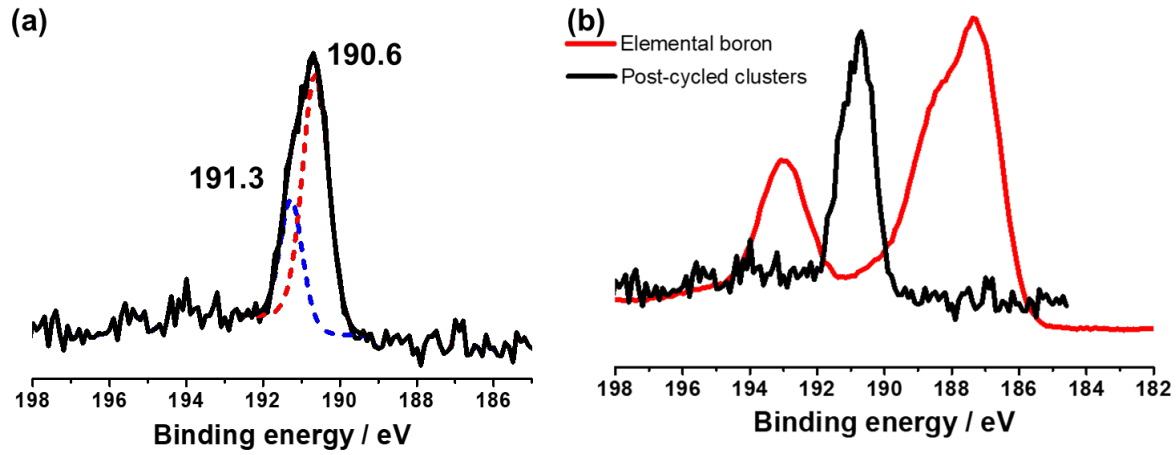


Figure S8. (a) B 1*s* XPS spectra for post-cycled $\mathbf{1}^{2-/1-}$, showing two oxidation states. (b) B 1*s* XPS spectra for post-cycled $\mathbf{1}^{2-/1-}$ and elemental boron, confirming no borates are present after cycling.

References

(1) Bondarev, O., Khan, A. A., Tu, X., Sevryugina, Y. V, Jalisatgi, S. S., Hawthorne, M. F., "Synthesis of [closo-$B_{12}(OH)_{11}NH_3$]$^-$: A New Heterobifunctional Dodecaborane Scaffold for Drug Delivery Applications". *J. Am. Chem. Soc.* **2013**, *135*, 13204–13211. doi:10.1021/ja4069613.

(2) Wixtrom, A. I., Shao, Y., Jung, D., Machan, C. W., Kevork, S. N., Qian, E. A., Axtell, J. C., Khan, S.I., Kubiak, C. P., Spokoyny, A. M., "Rapid Synthesis of Redox-Active Dodecaborane $B_{12}(OR)_{12}$ Clusters Under Ambient Conditions". *Inorg. Chem. Front.* **2016**, *3*, 711–717.