

Supplementary Information

***o*-Carborane as Electron-Transfer Mediator in Electrocatalytic Reduction**

Kohei Hosoi, Shinsuke Inagi,* Tatsuya Kubo and Toshio Fuchigami*

Department of Electronic Chemistry, Tokyo Institute of Technology,

4259 Nagatsuta, Midori-ku, Yokohama 226-8502 Japan

E-mail: fuchi@echem.titech.ac.jp (T. Fuchigami); inagi@echem.titech.ac.jp (S. Inagi);

Phone: +81-45-924-5406, Fax: +81-45-924-5406

Experimental Section

Measurements

Cyclic voltammetry measurements of all samples were recorded on an ALS 600A Electrochemical Analyzer in 0.1 M Bu₄NClO₄/DMF using GC working electrode, Pt counter electrode, and saturated calomel reference electrode (SCE) in an undivided cell under nitrogen atmosphere. Controlled potential electrolysis was carried out with HOKUTO DENKO HABF-501A potentiationstat. ¹H, ¹³C, ¹¹B and ¹⁹F NMR spectra were recorded on a JEOL EX-270 spectrometer (¹H: 270 MHz, ¹³C: 67.8 MHz, ¹¹B: 86.6 MHz ¹⁹F: 254 MHz). The chemical shifts for ¹H, ¹³C, ¹⁹F and ¹¹B NMR spectra were given in δ (ppm) from internal TMS (0.0 ppm), CDCl₃ (77.0 ppm),

monofluorobenzene (-36.5 ppm), and external boron trifluoride-diethyl ether complex (0.0 ppm) standards, respectively. High resolution mass spectrum (HRMS) was recorded on JEOL The MStation JMS-700. Molecular orbital were obtained using Gaussian 03W calculated by DFT B3LYP/6-31G+(2d,p)//B3LYP/6-31G(d).

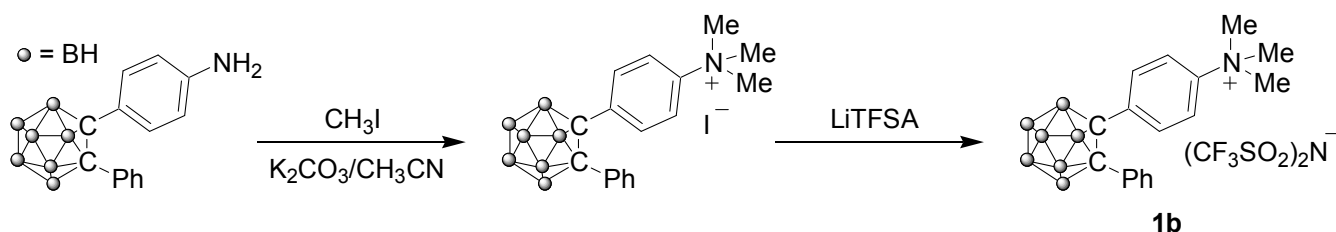
Materials

All reagents and solvent were purchased commercial sources and used without further purification.

Preparation of carborane derivative 1b

1-(*N*-Trimethyl-4-ammoniumphenyl)-2-phenyl-*o*-carborane bis(trifluoromethanesulfonyl)-amide (1b) (Scheme S1): To a stirred solution of 1-(4-aminophenyl)-2-phenyl-*o*-carborane¹ (0.30 g, 1.0 mmol) and potassium carbonate (0.35 g, 2.5 mmol) in CH₃CN (30 ml) was added an excess amount of methyl iodide (4.0 ml) under Ar atmosphere and the reaction mixture was stirred for 6 h at room temperature. Then the organic solvent was removed under reduced pressure, and the residue was dissolved in CHCl₃. After filtration, the filtrate was washed with water and the organic phase was condensed. The crude oil was purified by washing with hexane to give 1-(*N*-trimethyl-4-ammoniumphenyl)-2-phenyl-*o*-carborane iodide as a yellow solid (0.39 g, 0.82 mmol, yield: 82%). This compound (0.30 g, 0.62 mmol) was then dissolved in CH₂Cl₂ (10 ml) and

mixed with water (10 ml) containing lithium bis(trifluoromethanesulfonyl)amide (0.54 g, 1.87 mmol) and the reaction mixture was stirred vigorously for 2 h at room temperature. The organic phase was separated and washed with water. The removal of the solvent under reduced pressure afforded the titled compound in 61% yield (0.24 g, 0.39 mmol) as a yellow oil. ^1H NMR (270 MHz, CDCl_3) δ 7.66 (d, $J = 9.4$ Hz, 2H), 7.55 (d, $J = 9.4$ Hz, 2H), 7.44 (d, $J = 7.8$ Hz, 2H), 7.24 (m, 3H), 3.54 (s, 9H), 3.7-1.3 (br, 10H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 147.2, 133.9, 133.1, 130.8, 130.5, 129.8, 128.7, 119.7 (q, $J = 320$ Hz) 119.5, 85.4, 81.7, 57.4; ^{11}B NMR (86.6 MHz, CDCl_3) δ -2.26, -10.8; ^{19}F NMR(254 MHz, CDCl_3) δ -2.21; HRMS Calcd for $\text{C}_{17}\text{H}_{28}\text{B}_{10}\text{N}^+$: 356.3152, found: 356.3159. Calcd for $\text{C}_2\text{F}_6\text{NO}_4\text{S}_2^-$: 279.9173, found: 279.9174.



Scheme S1

A typical procedure for macroelectrolysis

A divided cell equipped with electrodes and a salt bridge was sealed by rubber closure under a nitrogen atmosphere. Bu_4NClO_4 (510 mg, 1.5mmol), $(\text{PhBrCH})_2$ (51.0 mg, 0.15 mmol) and $o\text{-Ph}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ were dissolved in DMF (15 ml) and the mixture was stirred for 10 min with N_2 bubbling. Then, controlled potential electrolysis was carried out at -1.30 V under N_2 . After the

theoretical electricity was passed, water was added to quench the reaction. The product was extracted with hexane and the organic phase was dried over anhydrous MgSO_4 . Then, the solvent was evaporated under reduced pressure to give a product. ^1H -NMR yields were estimated by comparing the intensities of peaks with that of CH_3NO_2 as an internal standard material.

Reference

1. Y. Endo, C. Songkram, R. Yamasaki, A. Tanatani, H. Kagechika, K. Takaishi, K. Yamaguchi, *J. Organomet. Chem.*, 2002, **657**, 48-58.

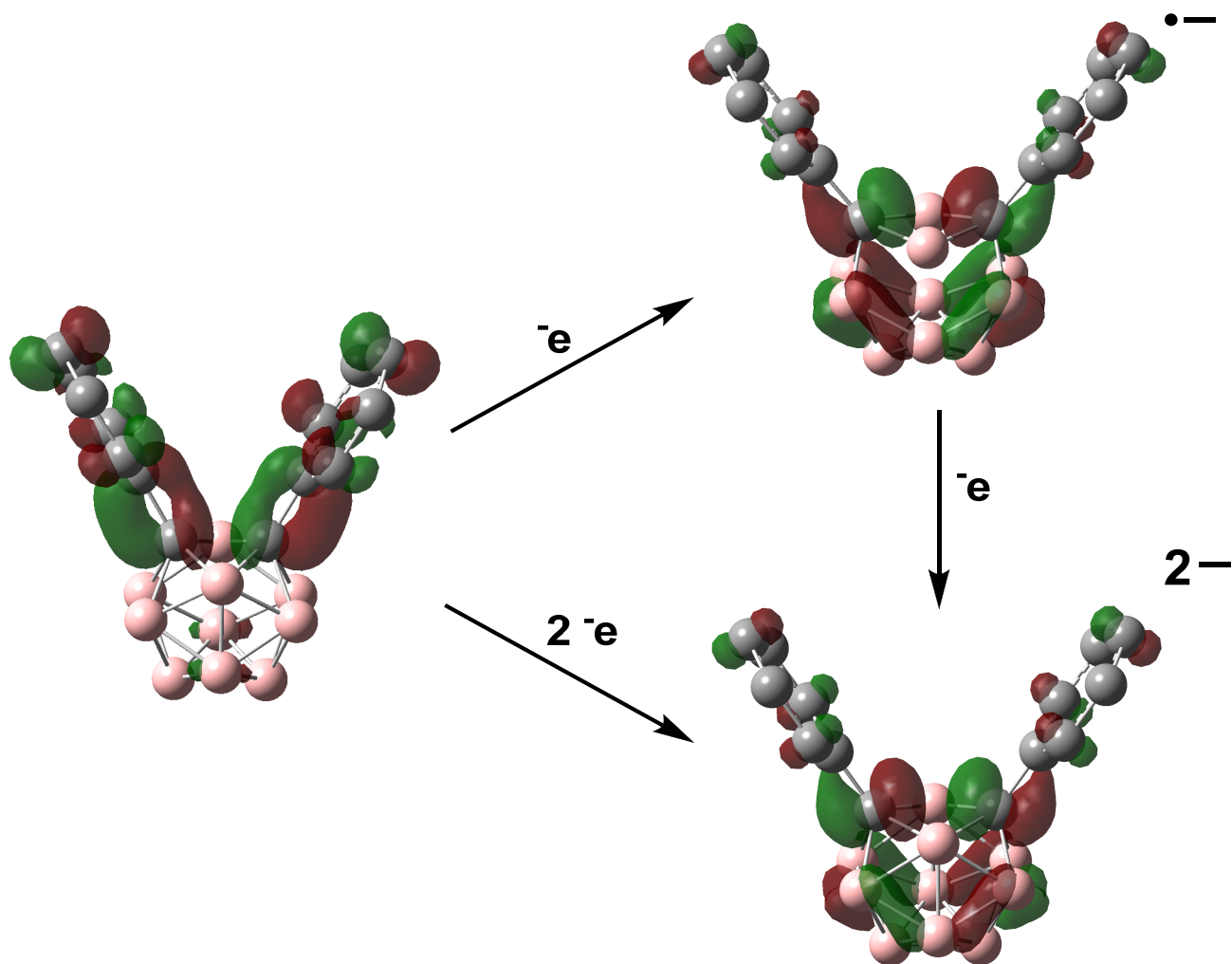


Fig. S1. Graphical diagrams of LUMO of neutral state, SOMO of anion radical state and HOMO of dianion state of *o*-carborane **1a** displayed with hydrogen omitted.

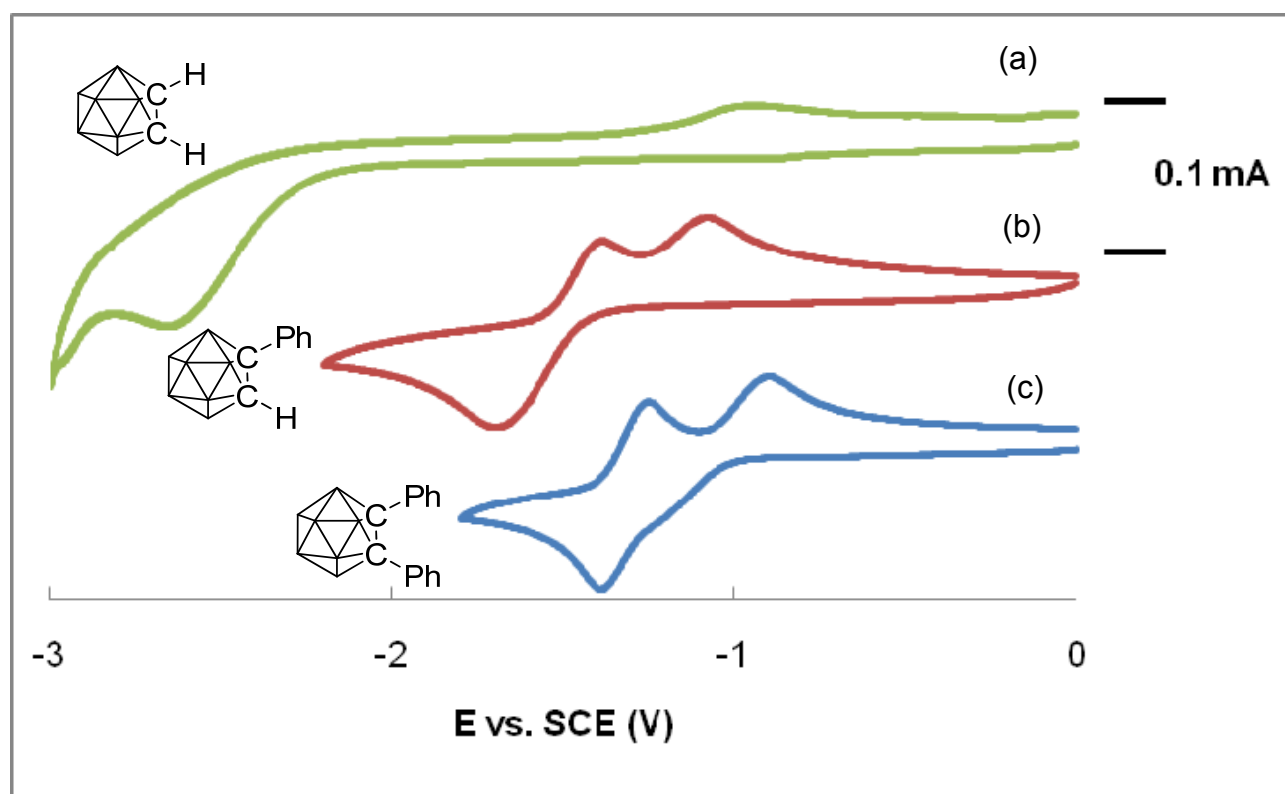


Fig. S2. Cyclic voltammograms of 4 mM *o*-carborane (a), 1-phenyl-*o*-carborane (b), **1a** (c), measured in 0.1 M TBAP/DMF using GC working electrode at a scan rate of 100 mV/s.

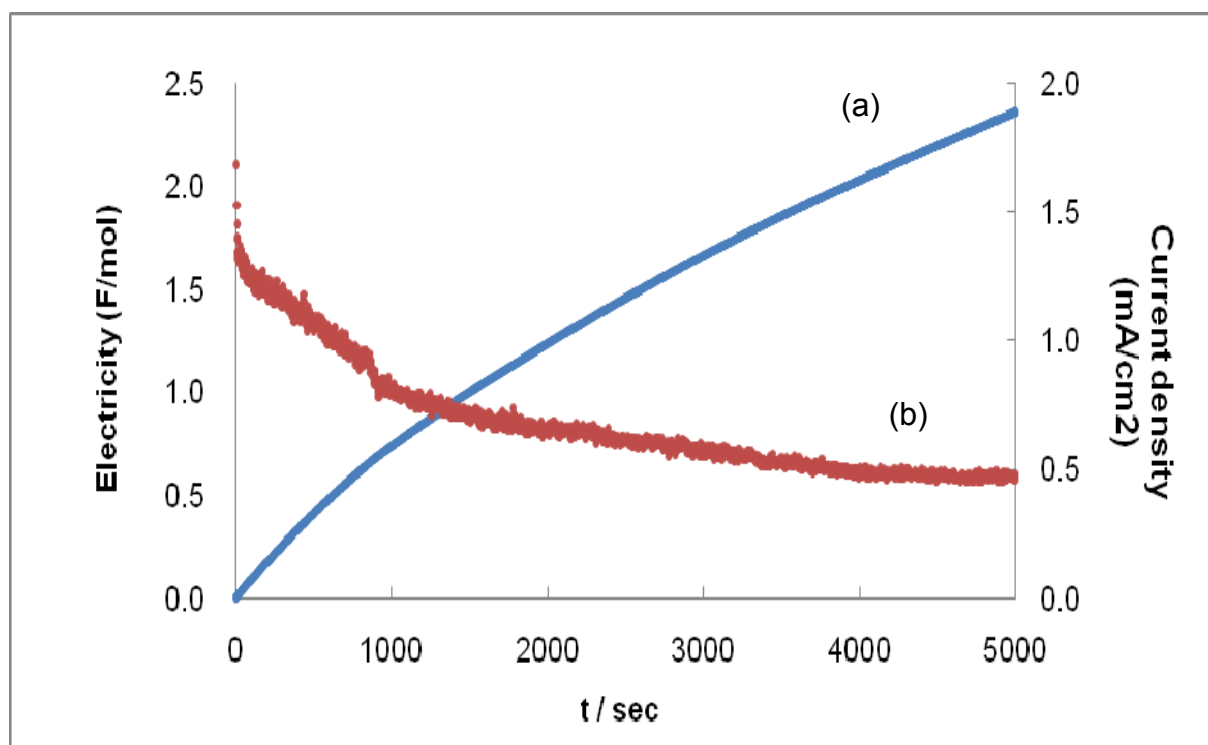


Fig. S3. Coulometry measured at -1.30 V under N_2 in the presence of *o*-carborane **1a** plotted with (a) electricity and (b) current density using GC working and Pt counter plate electrode (2×2 cm²).

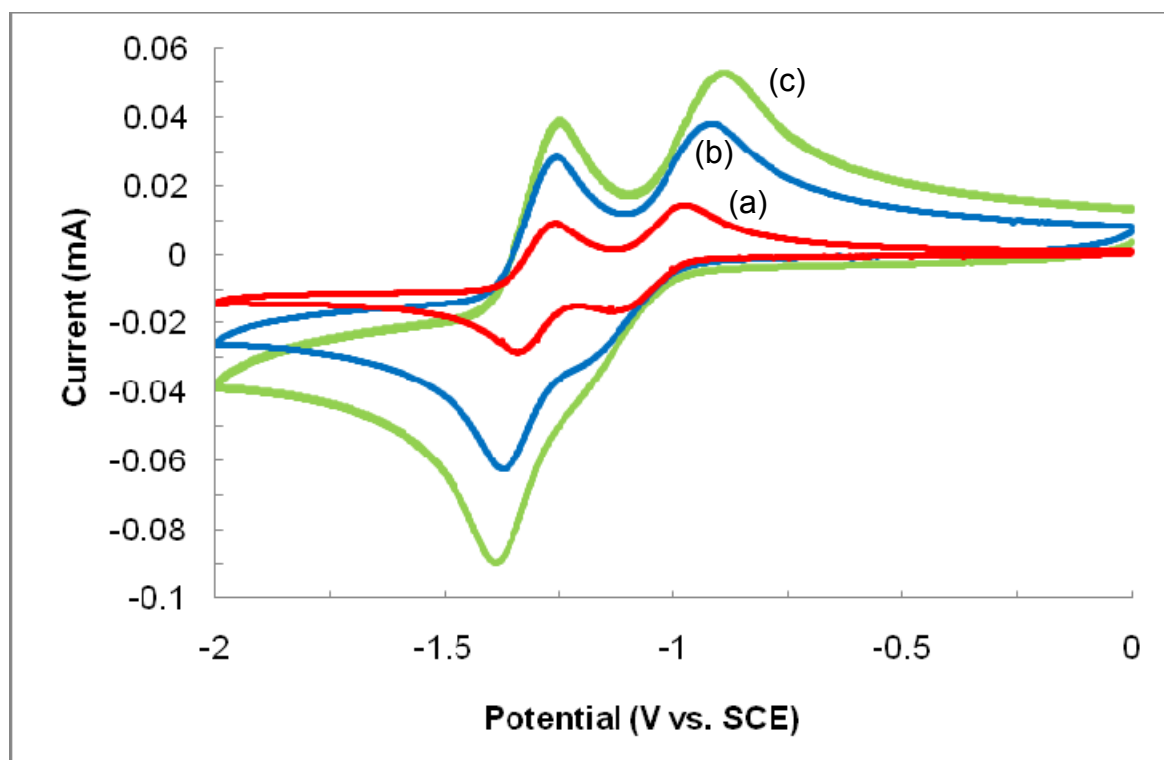


Fig. S4. Cyclic voltammograms of *o*-carborane **1a** measured in 0.1 M TBAP/DMF using GC working electrode at (a) 10 mV/s, (b) 50 mV/s and (c) 100 mV/s.

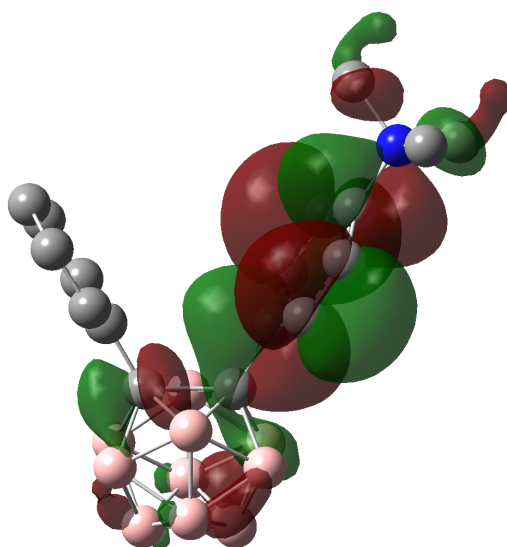


Fig. S5. Graphical diagrams of LUMO of neutral state of *o*-carborane **1b** displayed with hydrogen omitted.

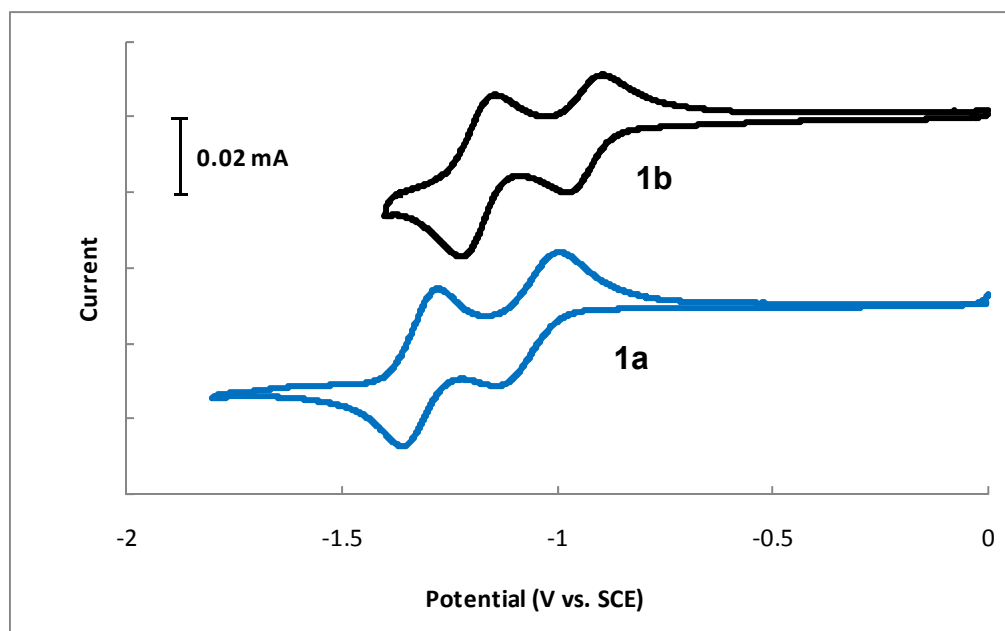


Fig. S6. Cyclic voltammograms of **1a** and **1b** (5 mM) in 0.1 M TBAP/DMF using GC working electrode at a scan rate of 10 mV/s.

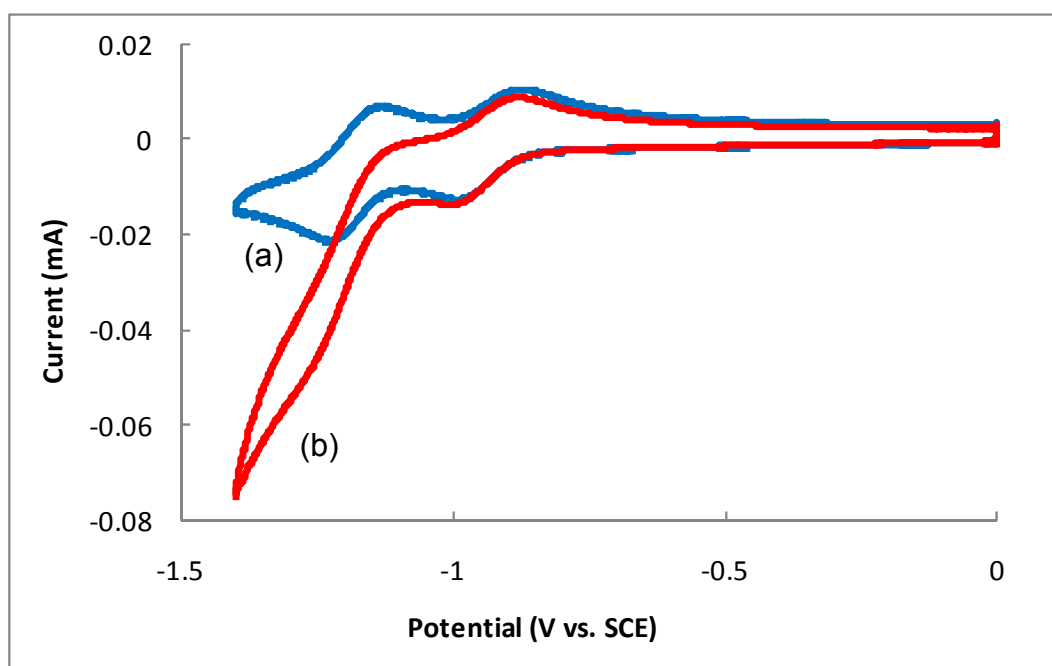


Fig. S7. Cyclic voltammograms of 1 mM *o*-carborane **1b** (a) in the absence of $(\text{PhBrCH})_2$ **2**, (b) in the presence of **2** (5 eq.), measured in 0.1 M TBAP/DMF using GC working electrode at a scan rate of 100 mV/s.