# **SUPPORTING INFORMATION**

How to get the desired reduction voltage in a single framework! Metallacarborane as an optimal probe for sequential voltage tuning

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### MATERIALS

Cesium salt of cobaltabisdicarbollide was purchased from Katchem. Protonated salt of ferrabisdicarbollide was synthesized following a reported method<sup>1</sup> starting from o-carborane, purchased also from KatChem. Anhydrous dioxane was purchased from Panreac. The dioxanate forms of the metallacarborane derivatives shown in this paper were synthesized according to well-established procedures.<sup>2</sup>Boron trifluoride etherate and DME were purchased from Sigma-Aldrich, as was the origin of NaCl and CsCl(grade>99%). Hydrochloric acid (37%), acetone, diethyl ether, acetonitrile, dichloromethane, ethanol, petroleum ether and hexane were purchased from Carlo Erba Reagents. DME and ethanol were purified via distillationunder nitrogen atmosphere from sodium and benzophenone as indicator.MVCl<sub>2</sub>, 4,4'-bipyridine and Na<sub>2</sub>SO<sub>3</sub> were also purchased from Sigma-Aldrich. Silica gel for preparative layer chromatography (containing a 13% of calcium sulphate) was purchased from Fluka Analytical. I<sub>2</sub> and N-Iodosuccinimide used to synthesize themetallacarborane derivatives were purchased from Sigma-Aldrich and ABCR-labs respectively. Compounds H[**4**],<sup>3</sup> H[**5**],<sup>4</sup> H[**6**],<sup>5</sup> H[**7**]<sup>6</sup> and H[**9**]<sup>7</sup> were synthesized following previously reported methods.

## METHODS

Elemental analyses were performed using a Carlo Erba EA1108 micro analyzer.

*IR spectra* (v, cm<sup>-1</sup>;ATR) were obtained on a Shimadzu FTIR-8300 spectrophotometer.

*NMR measurements:* The <sup>1</sup>H{<sup>11</sup>B}NMR (300.13 MHz), <sup>13</sup>C{<sup>1</sup>H}NMR (75.47MHz) and <sup>11</sup>BNMR (96.29 MHz) spectra were recorded on a BrukerARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were performed in deuterated acetone (purchased from Sigma-Aldrich) at 22°C. <sup>11</sup>BNMRshifts were referenced to external BF<sub>3</sub>·OEt<sub>2</sub>, while <sup>1</sup>H{<sup>11</sup>B} and <sup>13</sup>C{<sup>1</sup>H} NMR shifts were referenced to SiMe<sub>4</sub>. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz.

*MALDI-TOF Mass Spectra* were collected in the negative mode using a Brucker Biflex instrument ( $N_2$  laser;  $\lambda_{exc}$  337 nm, pulses of 0.5 ns), with an ion source of 20000 kV (Uis1) and 17500 kV (Uis2). This technique is ideal to detect mono-anions.

*Cyclic Voltammetries* were obtained with a Radiometer Analytical VoltaLab PGZ402, Universal Pulse Dynamics – EIS Voltammetry, at a scan rate of 100 mV/s. A three-electrode set up was used, being a glassy carbon the working electrode; a Ag/AgCl/TBACl (0.1M) as the reference electrode and a Pt wire as counter electrode. All measurements were done in dry and pure acetonitrile\* with TBAPF<sub>6</sub>\*\* 0.1 M as the inert electrolyte. The concentrations of all the measured samples were always 1 mM. All solvents and electrolytes used for the electrochemical measurements were purchased from Sigma-Aldrich.

*Electrolysis experiments* were carried out using the same equipment as for the cyclic voltammetries. The same three-electrodes set up was used, but changing the working electrode (in this case a wound Pt string was used instead of the prior mentioned glassy carbon).

\* Reagent grade acetonitrile was pre-dried over  $CaCO_3$ , and then distilled over  $P_2O_5$ . Prior to use, acetonitrile was degassed by the standard freeze-pump-thaw technique in order to remove the dissolved oxygen, and stored over 0.4 nm molecular sieves.

\*\* TBAPF<sub>6</sub> was dried overnight at 50<sup>o</sup> under vacuum to remove possible traces of water.

### SYNTHESES AND CHARACTERIZATION

**Synthesis of [MV][1]**<sub>2</sub>:100 mg of H[1](0.31 mmol) were dissolved in the minimum quantity of distilled water. A saturated solution of methyl viologen chloride,  $[MV]Cl_2$ , in distilled water,was added drop wise until the  $[MV][1]_2$  salt fully precipitates. The suspension was filtrated under vacuum and washed 3 times with distilled water and hexane. The solid was dried under vacuum. The precipitation process is quantitative.'H{"B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : 9.45 (4H, d, <sup>3</sup>J<sub>H-H</sub> 5.0, CH<sub>3</sub>-N<sup>+</sup>-CH<sub>pyr</sub>), 8.89 (4H, d, <sup>3</sup>J<sub>H-H</sub> 4.2, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 4.77 (6H, s, CH<sub>3</sub>-N<sup>+</sup>-), 3.94 (8H, s, C<sub>C</sub>-H), 3.31 (4H, s, B-H), 2.96 (4H, s, B-H), 2.66 (8H, s, B-H), 1.90 (8H, s, B-H), 1.55 (12H, s, B-H). "B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : 7.08 (4B, d, 'J<sub>B-H</sub> 145, **B**-H), 1.85 (4B, d, 'J<sub>B-H</sub> 141, **B**-H), -5.55 (16B, m, **B**-H), -16.83 (8B, d, 'J<sub>B-H</sub> 154, **B**-H), -22.34 (4B, d, 'J<sub>B-H</sub> 166, **B**-H). FTIR-ATR (v in cm<sup>-1</sup>): 3041.24 (w, v(C<sub>c</sub>-H)), 2565.70 (s, v(B-H)), 2527.88 (s, v(B-H)), 1640.57 (m, v(N<sup>+</sup>-C)). MALDI-TOF (m/z): Calculated, 323.75; Found,323.27 ([1]<sup>-</sup>).Elem. Anal. (Co<sub>2</sub>C<sub>20</sub>H<sub>58</sub>N<sub>2</sub>B<sub>36</sub>) (%): Calculated, C 28.81, H7.01, N3.36; Found, C 29.85, H 6.78, N 3.17. Mw: 833.75 g/mol.

# Synthesis of 2:

215 mg of cobaltabisdicarbollide dioxanate (0.52mmol), [3,3]-Co $(8-C_4H_8O-1,2-C_2B_9H_{10})(1,2]$ - $C_2B_9H_1$ ], were added to a stirring solution of 4,4'-bipyridine (27.3 mg, 0.17mmol) in 10 mL of dry DME under nitrogen atmosphere. The mixture was heated up to 60 °C overnight. Then, the solution was cooled down at room temperature and the solvent was removed under vacuum. The resulting solid was extracted for 3 times with Et<sub>2</sub>O/H<sub>2</sub>O/NaCl (0.1 M). The organic fraction was again evaporated, and the obtained solid was passed through a preparative layer chromatography, using a mixture of acetonitrile and dichloromethane (50:50) as eluent ( $R_f = 0.63$ ). The desired fraction was extracted from the silica with acetone and again evaporated under vacuum conditions. An orange solid was obtained. Weight: 146 mg. Yield: 85%.'H {"B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 9.56 (4H, d, <sup>3</sup>J<sub>H-H</sub>6.0, CH<sub>3</sub>-N<sup>+</sup>-CH<sub>pyr</sub>), 8.81 (4H, d, <sup>3</sup>J<sub>H-H</sub>6.0, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 5.13 (4H, t, <sup>3</sup>J<sub>H-H</sub>4.5, N<sup>+</sup>-CH<sub>2</sub>-CH<sub>2</sub>), 4.18 (4H, t, <sup>3</sup>J<sub>H-H</sub>4.5, N<sup>+</sup>-CH<sub>2</sub>-CH<sub>2</sub>-O), 4.07 (4H, s, C<sub>C</sub>-H), 3.96 (4H, s, C<sub>C</sub>-H), 3.67 (8H, bs, O-CH<sub>2</sub>-CH<sub>2</sub>-O), 3.04 (2H, s, B-H), 2.66 (5H, s, B-H), 2.06 (7H, s, B-H), 1.83 (5H, s, B-H), 1.63 (3H, s, B-H), 1.56 (3H, s, B-H), 1.53 (3H, s, B-H), 1.42 (3H, s, B-H), 1.30 (2H, s, B-H), 0.90 (1H, s, B-H). <sup>11</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>), δ: 26.38 (2B, s, B-O), 8.16 (2B, d, <sup>1</sup>J<sub>B-H</sub>126, B-H), 1.97 (4B, d, <sup>1</sup>J<sub>B-H</sub>132, B-H), -1.08 (4B, d, <sup>1</sup>J<sub>B-H</sub>153, B-H), -3.44 (2B, d, <sup>1</sup>J<sub>B-H</sub>180, B-H), -5.28 (8B, d, <sup>1</sup>J<sub>B-H</sub>142, B-H), -7.25 (2B, d, B-H), -15.67 (4B, d, <sup>1</sup>J<sub>B-H</sub>157, B-H), -18.52 (4B, d, <sup>1</sup>J<sub>B-H</sub>157, B-H), -20.52 (2B, d, B-H), -27.13 (2B, d, <sup>1</sup>J<sub>B-H</sub>142, B-H). <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 150.37 (CH<sub>pyr</sub>-C<sub>pyr</sub>), 146.86 (N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 126.86 (CH<sub>pyr</sub>-CH<sub>pyr</sub>-C<sub>pyr</sub>), 72.61 (B- O-CH<sub>2</sub>-CH<sub>2</sub>-O), 69.12 (B-O-CH<sub>2</sub>), 68.89 (N<sup>+</sup>-CH2-CH2), 61.95 (N+-CH2-CH2), 52.06 (Cc-H), 46.56 (Cc-H).FTIR-ATR (v in cm-1): 3052.04 (w, v(Cc-H)), 2920.26 (w, v(C-H)), 2851.30 (w, v(C-H)), 2528.13 (s, v(B-H)), 1635.92 (m, v(N<sup>+</sup>-C)), 1200-900 (w, v(C-O)).MALDI-TOF (m/z): Calculated, 977.88; Found, 978.81 (2). Elem. Anal.  $(Co_2C_{26}H_{66}N_2B_{36}O_4 \cdot C_3H_6O)$  (%): Calculated, C 33.62, H 7.01, N2.70; Found, C 33.60, H 7.04, N 3.08. Mw: 977.88 g/mol.

#### Synthesis of 3:

52 mg of I<sub>2</sub> (0.20 mmol) were added to a stirring solution containing50 mg of 2 (0.05mmol)in3 mL of dry ethanol under nitrogen atmosphere and left for stirring overnight. Then, the solution was refluxed for 2.5 hours and cooled down at room temperature. A solution of 10 mg of  $Na_2SO_3$  (0.08) mmol) in 2.5 mL of water was added to the ethanol solution. The mixture was then refluxed for 10 more minutes and again cooled down. The resulting solution was evaporated until precipitation of an orange solid occurs. The solid was then filtrated and washed 3 times with water and 3 more times with petroleum ether. The obtained solid was finally dried under vacuum conditions. An orange solid was obtained. Weight: 38 mg. Yield: 60%.<sup>1</sup>H {<sup>11</sup>B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>),δ: 9.55 (4H, d, <sup>3</sup>J<sub>H-H</sub> 6.0, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 8.95 (4H, d, <sup>3</sup>J<sub>H-H</sub> 6.0, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 5.19 (4H, t, <sup>3</sup>J<sub>H-H</sub> 4.5, N<sup>+</sup>-CH2-CH2), 4.33 (4H, s, CC-H), 4.21 (4H, s, CC-H), 4.17 (4H, t, <sup>3</sup>J<sub>H-H</sub> 4.5, N<sup>+</sup>-CH2-CH2-O), 3.62 (4H, t, <sup>3</sup>J<sub>H-H</sub> 4.5, O-CH<sub>2</sub>-CH<sub>2</sub>-O-B), 3.52 (4H, t, <sup>3</sup>J<sub>H-H</sub> 4.5, CH<sub>2</sub>-CH<sub>2</sub>-O-B), 3.05 (4H, s, B-H), 2.82 (4H, s, B-H), 2.37 (3H, s, B-H), 2.08 (7H, s, B-H), 1.99 (3H, s, B-H), 1.84 (1H, s, B-H), 1.65 (7H, s, B-H), 1.32 (2H, s, B-H), 0.93 (1H, s, B-H). <sup>11</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>), δ: 23.53 (2B, s, B-O), 1.42 (8B, s, <sup>1</sup>J<sub>B</sub>-H 134, B-H), -3.74 (12B, d, <sup>1</sup>J<sub>B-H</sub> 144, B-H), -5.43 (2B, s, B-I), -16.09 (4B, s, <sup>1</sup>J<sub>B-H</sub> 167, B-H), -17.97 (4B, s, <sup>1</sup>J<sub>B-H</sub> 163, **B**-H), -21.79 (2B, s, <sup>1</sup>J<sub>B-H</sub> 176, **B**-H), 25.22 (2B, s, <sup>1</sup>J<sub>B-H</sub> 166, **B**-H). <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 150.02 (CH<sub>pyr</sub>-C<sub>pyr</sub>-C<sub>pyr</sub>), 146.65 (N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 126.96 (CH<sub>pyr</sub>-CH<sub>pyr</sub>-C<sub>pyr</sub>), 72.10 (B-O-CH<sub>2</sub>-CH<sub>2</sub>-O), 68.84 (B-O-CH<sub>2</sub>), 68.18 (N<sup>+</sup>-CH<sub>2</sub>-CH<sub>2</sub>), 62.15 (N<sup>+</sup>-CH<sub>2</sub>-CH<sub>2</sub>), 56.48 (C<sub>c</sub>-H), 54.11 (C<sub>c</sub>-H). FTIR-ATR (v in cm<sup>-1</sup>): 3056.22 (w,  $v(C_c-H)$ ), 2914.49 (w, v(C-H)), 2859.10 (w, v(C-H)), 2544.83 (s, v(B-H)), 1637.00 (m, v(N+-C)), 1200-900 (w, v(C-O)). MALDI-TOF (m/z): Calculated, 1229.66; Found, 1229.65 (3). Elem. Anal. (Co<sub>2</sub>C<sub>26</sub>H<sub>66</sub>N<sub>2</sub>B<sub>36</sub>O<sub>4</sub>I<sub>2</sub> · I<sub>2</sub>) (%): Calculated, C 21.05, H 4.35, N1.89; Found, C 20.83, H 4.05, N 1.84. Mw: 1229.66 g/mol.

#### Synthesis of [MV][4]<sub>2</sub>:

The same procedure as for  $[MV][1]_2$  was done, but using H[4] (100 mg, 0.22 mmol) instead of H[1].<sup>1</sup>H {<sup>11</sup>B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : 9.49 (4H, d, <sup>3</sup>J<sub>H-H</sub> 6.7, CH<sub>3</sub>-N<sup>+</sup>-CH<sub>pyr</sub>), 8.94 (4H, d, <sup>3</sup>J<sub>H-H</sub> 6.1, N<sup>+</sup>-CH<sub>pyr</sub>), 4.79 (6H, s, CH<sub>3</sub>-N<sup>+</sup>-), 4.52 (4H, s, C<sub>C</sub>-H), 4.29 (4H, s, C<sub>C</sub>-H), 2.62 (4H, s, B-H), 2.46 (6H, s, B-H), 1.93-1.71 (24H, m, B-H). <sup>11</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$ : 7.81 (2B, d, <sup>1</sup>J<sub>B-H</sub> 135, **B**-H), 4.48 (2B, d, <sup>1</sup>J<sub>B-H</sub> 150, **B**-H), 2.36 (2B, d, <sup>1</sup>J<sub>B-H</sub> 155, **B**-H),-0.83 (4B, d, <sup>1</sup>J<sub>B-H</sub> 159, **B**-H), -4.3 (14B, m, **B**-H), -14.97 (4B, d, <sup>1</sup>J<sub>B-H</sub> 144, **B**-H), -16.50 (4B, d, <sup>1</sup>J<sub>B-H</sub> 148, **B**-H),-20.05 (2B, d, <sup>1</sup>J<sub>B-H</sub> 189, **B**-H) -22.02 (2B, d, <sup>1</sup>J<sub>B-H</sub> 189, **B**-H). FTIR-ATR (v in cm<sup>-1</sup>): 3049.22 (w, v(C<sub>c</sub>-H)), 2544.76 (s, v(B-H)), 1639.32 (m, v(N<sup>+</sup>-C)). MALDI-TOF (m/z): Calculated, 449.65; Found, 449.15 ([4]<sup>-</sup>).Elem. Anal.

 $(Co_2C_{20}H_{56}N_2B_{36}I_2)$  (%): Calculated, C 22.13, H 5.20, N 2.58; Found, C 21.74, H 5.16, N 2.41. Mw: 1085.54 g/mol.

#### Synthesis of MV[5]<sub>2</sub>:

The same procedure as for  $[MV][1]_2$  was performed, but starting from H[5] (100 mg, 0.12 mmol) instead of H[1]. <sup>1</sup>H {<sup>u</sup>B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$ : 9.49 (4H, d, <sup>3</sup>J<sub>H-H</sub> 6.6, CH<sub>3</sub>-N<sup>+</sup>-CH<sub>pyr</sub>), 8.94 (4H, d, <sup>3</sup>J<sub>H-H</sub> 6.5, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 4.80 (6H, s, CH<sub>3</sub>-N<sup>+</sup>-), 4.46 (8H, s, C<sub>C</sub>-H), 4.20 (4H, s, B-H), 3.63 (8H, s, B-H), 3.36 (8H, s, B-H), 1.63 (8H, s, B-H). <sup>u</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$ : 8.13 (4B, d, <sup>1</sup>J<sub>B-H</sub> 109, **B**-H), 6.12 (4B, d, <sup>1</sup>J<sub>B-H</sub> 166, **B**-H), -4.26 (8B, d, <sup>1</sup>J<sub>B-H</sub> 148, **B**-H), -13.97 (8B, bs, **B**-H), -13.97 (8B, bs, **B**-I), -20.84 (4B, d, <sup>1</sup>J<sub>B-H</sub> 158, **B**-H). FTIR-ATR (v in cm<sup>-1</sup>): 3024.63 (w, v(C<sub>c</sub>-H)), 2576.69 (m, v(B-H)), 1638.12 (m, v(N<sup>+</sup>-C)).MALDI-TOF (m/z): Calculated, 827.33; Found, 827.78 ([5]<sup>-</sup>). Elem. Anal. (Co<sub>2</sub>C<sub>20</sub>H<sub>50</sub>N<sub>2</sub>B<sub>36</sub>I<sub>8</sub>) (%): Calculated, C 13.05, H 2.74, N 1.52; Found, C 12.92, H 2.76, N 1.42. Mw: 1840.92 g/mol.

### Synthesis of MV[6]<sub>2</sub>:

The same procedure as for  $[MV][1]_2$  was followed, but using H[6] (100 mg, 0.17 mmol) instead of H[1].<sup>1</sup>H {<sup>11</sup>B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : 9.50 (4H, d, <sup>3</sup>J<sub>H-H</sub> 6.4, CH<sub>3</sub>-N<sup>+</sup>-CH<sub>pyr</sub>), 8.95 (4H, d, <sup>3</sup>J<sub>H-H</sub> 5.9, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 4.80 (6H, s, CH<sub>3</sub>-N<sup>+</sup>-), 4.41 (8H, s, C<sub>C</sub>-H), 3.22 (8H, s, B-H), 3.07 (4H, s, B-H), 2.59 (8H, s, B-H), 2.12 (4H, s, B-H), 1.83 (8H, s, B-H). <sup>11</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$ : 4.24 (4B, d, <sup>1</sup>J<sub>B-H</sub> 141, **B**-H), -1.92 (16B, d, <sup>1</sup>J<sub>B-H</sub> 144, **B**-H), -3.67 (4B, s, **B**-I), -15.65 (8B, d, <sup>1</sup>J<sub>B-H</sub> 154, **B**-H), -21.23 (4B, d, <sup>1</sup>J<sub>B-H</sub> 166, **B**-H). FTIR-ATR (v in cm<sup>-1</sup>): 3035.51 (w, v(C<sub>c</sub>-H)), 2557.54 (s, v(B-H)), 1638.38 (m, v(N<sup>+</sup>-C)). MALDI-TOF (m/z): Calculated, 575.54; Found, 575.03 ([6]<sup>-</sup>).Elem. Anal. (Co<sub>2</sub>C<sub>20</sub>H<sub>54</sub>N<sub>2</sub>B<sub>36</sub>I<sub>4</sub>) (%): Calculated, C 17.96, H 4.07, N 2.09; Found, C 18.19, H 4.00, N 2.20. Mw: 1337.34 g/mol.

### Synthesis of MV[7]<sub>2</sub>:

The same procedure as for  $[MV][1]_2$  was done, but starting from H[7] (100 mg, 0.09 mmol) instead of H[1].<sup>1</sup>H {<sup>11</sup>B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : 9.51 (4H, d, <sup>3</sup>J<sub>H-H</sub> 6.8, CH<sub>3</sub>-N<sup>+</sup>-CH<sub>pyr</sub>), 8.96 (4H, d, <sup>3</sup>J<sub>H-H</sub> 6.4, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 5.02 (8H, s, C<sub>C</sub>-H), 4.80 (6H, s, CH<sub>3</sub>-N<sup>+</sup>-), 3.97 (4H, s, B-H), 3.55 (6H, s, B-H), 2.48 (8H, s, B-H), 2.25 (6H, s, B-H). <sup>11</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$ : 7.28 (4B, d, <sup>1</sup>J<sub>B-H</sub> 145, B-H), -2.00 (8B, d, <sup>1</sup>J<sub>B-H</sub> 163, B-H), -2.85 (4B, s, B-I), -12.15 (8B, s, B-I), -13.40 (8B, d, <sup>1</sup>J<sub>B-H</sub> 240, B-H) - 20.37 (4B, d, <sup>1</sup>J<sub>B-H</sub> 166, B-H). FTIR-ATR (v in cm<sup>-1</sup>): 3034.04 (w, v(C<sub>c</sub>-H)), 2582.67 (m, v(B-H)), 1638.38 (m, v(N<sup>+</sup>-C)).MALDI-TOF (m/z): Calculated, 1079.13; Found, 1078.60 ([7]<sup>-</sup>). Elem. Anal.

 $(Co_2C_{20}H_{46}N_2B_{36}I_{12})$  (%): Calculated, C 10.25, H 1.98, N 1.19; Found, C 10.46, H 1.94, N 1.23. Mw: 2344.51g/mol.

#### Synthesis of MV[8]<sub>2</sub>:

The same procedure as for  $[MV][1]_2$  was done, but using H[**8**] (50 mg, 0.15 mmol), instead of H[1]. <sup>1</sup>H {<sup>1</sup>B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : 70.45 (s), 45.10 (s, C<sub>c</sub>-H), 41.49 (s), 7.83 (s, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 6.78 (s, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 3.63 (s, N<sup>+</sup>-CH<sub>3</sub>), 3.14 (s), 1.33 (s), 1.10 (s), -8.12 (s), <sup>11</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$ : 102.06 (4B, s, **B**-H), 19.86 (8B, s, **B**-H), -0.08 (8B, s, **B**-H), -31.51 (4B, s, **B**-H), -400.66 (8B, s, **B**-H), -453.30 (4B, s, **B**-H). FTIR-ATR (v in cm<sup>-1</sup>): 3038.91 (w, v(C<sub>c</sub>-H)), 2521.63 (s, v(B-H)), 1639.72 (m, v(N<sup>+</sup>-C)). MALDI-TOF (m/z): Calculated, 321.28; Found, 321.33 ([**8**]<sup>-</sup>). Elem. Anal. (Fe<sub>2</sub>C<sub>20</sub>H<sub>58</sub>N<sub>2</sub>B<sub>36</sub>) (%): Calculated, C 29.03, H 7.05, N 3.39; Found, C 29.89, H 7.25, N 3.36. Mw: 827.57 g/mol.

# Synthesis of MV[9]<sub>2</sub>:

The same procedure as for  $[MV][1]_2$  was performed, but starting from H[9] (100 mg, 0.08mmol) instead of H[1].<sup>1</sup>H {<sup>u</sup>B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : 9.51 (4H, d, <sup>3</sup>J<sub>H-H</sub> 6.3, CH<sub>3</sub>-N<sup>+</sup>-CH<sub>pyr</sub>), 8.97 (4H, d, <sup>3</sup>J<sub>H-H</sub> 5.7, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 5.14 (8H, s, C<sub>C</sub>-H), 4.80 (6H, s, CH<sub>3</sub>-N<sup>+</sup>-), 3.62 (8H, s, B-H), 2.75 (8H, s, B-H), 2.65 (4H, s, B-H). <sup>u</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$ : -2.86 (8B, d, <sup>1</sup>J<sub>B-H</sub> 169, **B**-H), -4.85 (4B, s,B-I), -7.70 (4B, s,B-I), -10.69 (8B, s, **B**-I), -14.28 (8B, d, <sup>1</sup>J<sub>B-H</sub> 157, **B**-H), -21.12 (4B, d, <sup>1</sup>J<sub>B-H</sub> 174, **B**-H). FTIR-ATR (v in cm<sup>-1</sup>): 3024.83 (w, v(C<sub>c</sub>-H)), 2581.75 (m, v(B-H)), 1636.77 (m, v(N<sup>+</sup>-C)).MALDI-TOF (m/z): Calculated, 1330.92; Found, 1331.37 ([9]<sup>-</sup>).Elem. Anal. (Co<sub>2</sub>C<sub>20</sub>H<sub>42</sub>N<sub>2</sub>B<sub>36</sub>I<sub>16</sub>) (%): Calculated, C 8.43, H 1.49, N 0.98; Found, C 9.17, H 1.56, N 1.06. Mw: 2848.10g/mol.

#### Synthesis of 10:

The same procedure as for **2** was followed, but using ferrabisdicarbollide dioxanate (200 mg, 0.49mmol),  $[3,3'-Fe(8-C_4H_8O-1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})]$ , instead of cobaltabisdicarbollide dioxanate. A brown solid was obtained. Weight: 128 mg. Yield: 81%.<sup>1</sup>H {<sup>11</sup>B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : 72.10 (s), 43.42 (s, C<sub>c</sub>-H), 42.75 (s, C<sub>c</sub>-H), 39.06 (s), 26.23 (s), 7.78 (s, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 7.68 (s, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 4.40-3.50 (m, N<sup>+</sup>-CH<sub>2</sub>-CH<sub>2</sub>, O-CH<sub>2</sub>-CH<sub>2</sub>-O), 3.26 (s), 1.24 (s), -0.97 (s), -4.20 (s), -9.84 (s), -13.19 (s). <sup>11</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$ : 115.59 (2B, s, B-H), 100.18 (2B, s, B-H), 24.79 (4B, s, B-H), 22.96 (4B, s, B-H), -0.80 (4B, s, B-H), -4.67 (4B, s, B-H), -33.33 (2B, s, B-H), -37.33 (2B, s, B-H), -374.75 (4B, s, B-H), -397.95 (2B, s, B-O), -439.61 (4B, s, B-H), -487.94 (2B, s, B-H). <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$ : 144.60 (CH<sub>pyr</sub>-C<sub>pyr</sub>), 140.30 (N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>),

121.48 ( $CH_{pyr}$ - $CH_{pyr}$ - $C_{pyr}$ ), 60.47 (B- O- $CH_2$ - $CH_2$ -O), 58.74 (B-O- $CH_2$ ), 58.66 (N<sup>+</sup>- $CH_2$ - $CH_2$ ), 55.76 (N<sup>+</sup>- $CH_2$ - $CH_2$ ). FTIR-ATR (v in cm<sup>-1</sup>): 3044.60 (w, v(C<sub>c</sub>-H)), 2922.42 (w, v(C-H)), 2858.73 (w, v(C-H)), 2519.87 (s, v(B-H)), 1635.99 (m, v(N<sup>+</sup>-C)), 1200-900 (w, v(C-O)). MALDI-TOF (m/z): Calculated, 971.70; Found, 972.82 (10). Elem. Anal. ( $Fe_2C_{26}H_{66}N_2B_{36}O_4 \ge C_3H_6O$ ) (%): Calculated, C 35.33, H 7.23, N 2.58; Found, C 35.56, H 7.20, N 2.81. Mw: 971.70 g/mol.

#### Synthesis of Cs[11]:

25 mg of N-iodosuccinimide (0.11 mmol), were added to a stirring solution of Cs[**8**](50 mg, 0.11 mmol) in 15 ml absolute ethanol. The mixture was left overnight at room temperature. After evaporation of the solvent under vacuum, the resulting solid was extracted 3 times with Et<sub>2</sub>O/HCl (0.1 M). The mixed organic fractions were washed with water and dried over anhydrous MgSO<sub>4</sub>. After evaporation and re-crystallization from CH<sub>2</sub>Cl<sub>2</sub>, a brownish powder was obtained. Weight: 58.5 mg. Yield: 92%. <sup>1</sup>H {<sup>n</sup>B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : 62.32 (s), 46.00 (s, C<sub>c</sub>-H), 44.81 (s, C<sub>c</sub>-H), 6.64 (s), 3.15 (s), 1.28 (s), 0.84 (s), 0.41 (s), 0.12 (s), -2.17 (s), -3.76 (s), -5.06 (s), -16.20 (s), <sup>n</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$ : 114.39 (2B, s, B-H), 11.08 (2B, s, B-H), 34.52 (4B, s, B-H), 30.50 (4B, s, B-H), 12.05 (4B, s, B-H), -0.44 (4B, s, B-H), -34.12 (2B, s, B-H), -40.90 (2B, s, B-H), -331.88 (4B, s, B-H), -370.39 (4B, s, B-H), -368.42 (2B, s, B-H), -518.81 (2B, s, B-H). <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : -490.69 (C<sub>c</sub>-H), -564.16 (C<sub>c</sub>-H). FTIR-ATR (v in cm<sup>-1</sup>): 3030.08 (w, v(C<sub>c</sub>-H)), 2523.15 (s, v(B-H)). MALDI-TOF (m/z): Calculated, 447.18; Found, 447.22 ([11]<sup>-</sup>). Elem. Anal. (CsFeC<sub>4</sub>H<sub>21</sub>B<sub>18</sub>I · 2CH<sub>2</sub>Cl<sub>2</sub>) (%): Calculated, C 9.62, H 3.36; Found, C 9.56, H 3.39. Mw: 579.46 g/mol.

# Synthesis of MV[11]<sub>2</sub>:

The same procedure as for  $[MV][\mathbf{1}]_2$  was done, but starting from H[ $\mathbf{n}$ ] (50 mg, 0.11 mmol) instead of H[ $\mathbf{1}$ ]. <sup>1</sup>H {<sup>u</sup>B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : 62.32 (s), 46.00 (s, C<sub>c</sub>-H), 44.81 (s, C<sub>c</sub>-H), 8.95 (s, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 8.26 (s, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 6.64 (s), 4.39 (s, N<sup>+</sup>-CH<sub>3</sub>), 3.15 (s), 1.28 (s), 0.84 (s), 0.41 (s), 0.12 (s), -2.17 (s), -3.76 (s), -5.06 (s), -16.20 (s), <sup>u</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$ : 114.39 (2B, s, **B**-H), 111.08 (2B, s, **B**-H), 34.52 (4B, s, **B**-H), 30.50 (4B, s, **B**-H), 12.05 (4B, s, **B**-H), -0.44 (4B, s, **B**-H), -34.12 (2B, s, **B**-H), -40.90 (2B, s, **B**-H), -331.88 (4B, s, **B**-H), -370.39 (4B, s, **B**-H), -388.42 (2B, s, **B**-H), -518.81 (2B, s, **B**-H). FTIR-ATR (v in cm<sup>-1</sup>): 3048.32 (w, v(C<sub>c</sub>-H)), 2527.88 (s, v(B-H)), 1637.89 (m, v(N<sup>+</sup>-C)). MALDI-TOF (m/z): Calculated, 447.18; Found, 447.22 ([**1**]<sup>-</sup>). Elem. Anal. (Fe<sub>2</sub>C<sub>20</sub>H<sub>56</sub>N<sub>2</sub>B<sub>36</sub>I<sub>2</sub>) (%): Calculated, C 22.26, H 5.23, N 2.60; Found, C 22.87, H 5.43, N 2.33. Mw: 1079.37 g/mol.**Synthesis of Cs[12]:** 

52 mg of N-iodosuccinimide (0.23 mmol), were added to a stirring solution of Cs[**8**](50 mg, 0.11 mmol) in 15 ml absolute ethanol. The mixture was left overnight at room temperature and then refluxed for 2 hours. After evaporation of the solvent under vacuum, the resulting solid was extracted 3 times with  $Et_2O/HCl$  (0.1 M). The mixed organic fractions were washed with water and dried over anhydrous MgSO<sub>4</sub>. Further purification was made, after evaporation, by washing the solid several times with toluene followed by a filtration. A dark-greenish powder was obtained. Weight: 49.1 mg. Yield: 63%. <sup>1</sup>H {<sup>u</sup>B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : 62.32 (s), 46.00 (s, C<sub>c</sub>-H), 44.81 (s, C<sub>c</sub>-H), 7.20 (s), 1.87 (s), -0.95 (s), -6.41 (s), -21.33 (s), <sup>u</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : 19.95 (2B, s, B-H), 25.50 (4B, s, B-H, <sup>1</sup>J<sub>B-H</sub> 99.8), 7.57 (4B, s, B-H, <sup>1</sup>J<sub>B-H</sub> 99.8), -46.53 (2B, s, B-H, <sup>1</sup>J<sub>B-H</sub> 103.7), -330.51 (4B, s, B-H), -563.03 (2B, s, B-I). <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : -489.09 (C<sub>c</sub>-H). FTIR-ATR (v in cm<sup>-1</sup>): 3026.02 (w, v(C<sub>c</sub>-H)), 2535.31 (s, v(B-H)). MALDI-TOF (m/z): Calculated, 572.45; Found, 572.13 ([12]<sup>-</sup>). Elem. Anal. (CsFeC<sub>4</sub>H<sub>20</sub>B<sub>18</sub>I<sub>2</sub> ·0.1C<sub>7</sub>H<sub>8</sub>) (%): Calculated, C 7.89, H 2.93; Found, C 7.83, H 3.11. Mw: 705.36 g/mol.

# Synthesis of MV[12]<sub>2</sub>:

The same procedure as for  $[MV][1]_2$  was performed, but using H[12] (50 mg, 0.087 mmol) instead of H[1]. <sup>1</sup>H {<sup>u</sup>B} NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>), $\delta$ : 62.32 (s), 46.00 (s, C<sub>c</sub>-H), 44.81 (s, C<sub>c</sub>-H), 9.30 (s, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 8.70 (s, N<sup>+</sup>-CH<sub>pyr</sub>-CH<sub>pyr</sub>), 6.64 (s), 4.63 (s, N<sup>+</sup>-CH<sub>3</sub>), 3.15 (s), 1.28 (s), 0.84 (s), 0.41 (s), 0.12 (s), -2.17 (s), -3.76 (s), -5.06 (s), -16.20 (s), <sup>u</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$ : 114.39 (2B, s, **B**-H), 111.08 (2B, s, **B**-H), 34.52 (4B, s, **B**-H), 30.50 (4B, s, **B**-H), 12.05 (4B, s, **B**-H), -0.44 (4B, s, **B**-H), -34.12 (2B, s, **B**-H), -40.90 (2B, s, **B**-H), -331.88 (4B, s, **B**-H), -370.39 (4B, s, **B**-H), -388.42 (2B, s, **B**-H), -518.81 (2B, s, **B**-H). FTIR-ATR (v in cm<sup>-1</sup>): 3026.02 (w, v(C<sub>c</sub>-H)), 2535.31 (s, v(B-H)), 1636.03 (m, v(N<sup>+</sup>-C)). MALDI-TOF (m/z): Calculated, 573.16; Found, 572.13 ([12]<sup>-</sup>). Elem. Anal. (Fe<sub>2</sub>C<sub>20</sub>H<sub>56</sub>N<sub>2</sub>B<sub>36</sub>I<sub>4</sub> · 0.5C<sub>7</sub>H<sub>8</sub>) (%): Calculated, C 20.49, H 4.24, N 2.09; Found, C 20.11, H 4.27, N 2.09. Mw: 1331.16 g/mol.

# SEQUENTIAL ELECTROLYSIS OF [MV][11]2

Sequential electrolysis of  $[MV][\mathbf{n}]_2$ . Initial CV (blue solid line) and final CV (red dotted line) after electrolysis at -2.1 V and the obtained colour after each electrolysis are shown.



# Scheme of the synthesis of neutral species 2 and 3



The first step was the same used for the preparation of compound 10.

# Scheme of the synthesis of compound [MV][11]<sub>2</sub>



The same procedure was used for the synthesis of the compound  $[MV]_{12}_{2}$ , but using 2.1 eq of NIS instead of 1.05.

# **Redox processes for 10**

Graphical representation of the sequential redox processes occurring for molecule 10.



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