**SUPPORTING INFORMATION**

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

*Màrius Tarrès, Victor S. Arderiu, Adnana Zaulet, Clara Viñas, Fabrizia Fabrizi de Biani, Francesc Teixidor*

Corresponding Author:

Prof. Francesc Teixidor

Email: teixidor@icmab.es

Phone: (+34) 93 5805729
MATERIALS

Cesium salt of cobaltabisdicarbollide was purchased from Katchem. Protonated salt of ferrabisdicarbollide was synthesized following a reported method 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. 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 distillation under nitrogen atmosphere from sodium and benzophenone as indicator. MVCl2, 4,4'-bipyridine and Na2SO3 were also purchased from Sigma-Aldrich. Silica gel for preparative layer chromatography (containing a 13% of calcium sulphate) was purchased from Fluka Analytical. I2 and N-Iodosuccinimide used to synthesize the metallacarborane derivatives were purchased from Sigma-Aldrich and ABCR-labs respectively. Compounds H[4], H[5], H[6], H[7] and H[9] were synthesized following previously reported methods.

METHODS

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

IR spectra (ν, cm⁻¹; ATR) were obtained on a Shimadzu FTIR-8300 spectrophotometer.

NMR measurements: The ¹H[¹B]NMR (300.13 MHz), ¹3C[¹H]NMR (75.47 MHz) and ¹¹BNMR (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. ¹BNMR shifts were referenced to external BF3·OEt2, while ¹H[¹B] and ¹³C[¹H] NMR shifts were referenced to SiMe4. 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 (N2 laser; λexc 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 TBAPF6** 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$_2$O$_5$. 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$_6$ was dried overnight at 50º under vacuum to remove possible traces of water.
SYNTHESES AND CHARACTERIZATION

Synthesis of [MV][I]$_2$: 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, in distilled water, was added drop wise until the [MV][I]$_2$ salt fully precipitates. The suspension was filtered under vacuum and washed 3 times with distilled water and hexane. The solid was dried under vacuum. The precipitation process is quantitative.

Synthesis of 2: 215 mg of cobaltabisdicarbollide dioxanate (0.52 mmol), $[3,3'-\text{Co}(8-\text{C}_4\text{H}_4\text{O}-1,2-C_2\text{H}_5\text{H}_4)](1',2'-C_2B_{9}H_{11})$, were added to a stirring solution of 4,4'-bipyridine (27.3 mg, 0.17 mmol) 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 EtOH/H$_2$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%. 1H NMR (300 MHz, CD$_3$COCD$_3$) $\delta$: 9.45 (4H, d, $J_{36} = 6.0$, CH$_2$N'-CH$_2$), 8.89 (4H, d, $J_{36} = 4.2$, N'-CH$_2$pyr'-CH$_2$pyr'), 4.77 (6H, s, CH$_2$N'-), 3.94 (8H, s, C-C-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). 13C NMR (96 MHz, CD$_3$COCD$_3$) $\delta$: 7.08 (4B, d, $J_{36} = 4.2$, C-C), 69.12 (B-O-CH$_2$pyr), 72.61 (B-O-CH$_2$pyr), 4.54 (3B, m, B-H), -16.83 (8B, d, $J_{36} = 14.5$, B-H), -18.52 (4B, d, $J_{36} = 14.5$, B-H), -3.44 (2B, d, $J_{36} = 14.5$, B-H), -5.55 (16B, m, B-H), -16.83 (8B, d, $J_{36} = 15.4$, B-H), -22.34 (4B, d, $J_{36} = 15.4$, B-H). FTIR-ATR (v in cm$^{-1}$): 3041.24 (w, v(C-C)), 2965.70 (s, v(B-H)), 2527.88 (s, v(B-H)), 1640.57 (m, v(N'-C)). MALDI-TOF (m/z): Calculated, 323.75; Found, 323.27 ([MV]).

Elemental Analysis. (Co$_3$C$_4$H$_{11}$N$_8$B$_{30}$) (%): Calculated, C 28.81, H 7.01, N 3.63; Found, C 29.85, H 6.78, N 3.17. Mw: 833.75 g/mol.

Synthesis of 2:
215 mg of cobaltabisdicarbollide dioxanate (0.52 mmol), $[3,3'-\text{Co}(8-\text{C}_4\text{H}_4\text{O}-1,2-C_2\text{H}_5\text{H}_4)](1',2'-C_2B_{9}H_{11})$, were added to a stirring solution of 4,4'-bipyridine (27.3 mg, 0.17 mmol) 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 EtOH/H$_2$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%. 1H NMR (300 MHz, CD$_3$COCD$_3$) $\delta$: 9.45 (4H, d, $J_{36} = 6.0$, CH$_2$N'-CH$_2$), 8.89 (4H, d, $J_{36} = 4.2$, N'-CH$_2$pyr'-CH$_2$pyr'), 4.77 (6H, s, CH$_2$N'-), 3.94 (8H, s, C-C-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). 13C NMR (96 MHz, CD$_3$COCD$_3$) $\delta$: 7.08 (4B, d, $J_{36} = 4.2$, C-C), 69.12 (B-O-CH$_2$pyr), 72.61 (B-O-CH$_2$pyr), 4.54 (3B, m, B-H), -16.83 (8B, d, $J_{36} = 14.5$, B-H), -22.34 (4B, d, $J_{36} = 14.5$, B-H), -5.55 (16B, m, B-H), -16.83 (8B, d, $J_{36} = 15.4$, B-H), -22.34 (4B, d, $J_{36} = 15.4$, B-H). FTIR-ATR (v in cm$^{-1}$): 3041.24 (w, v(C-C)), 2965.70 (s, v(B-H)), 2527.88 (s, v(B-H)), 1640.57 (m, v(N'-C)). MALDI-TOF (m/z): Calculated, 323.75; Found, 323.27 ([MV]).

Elemental Analysis. (Co$_3$C$_4$H$_{11}$N$_8$B$_{30}$) (%): Calculated, C 28.81, H 7.01, N 3.63; Found, C 29.85, H 6.78, N 3.17. Mw: 833.75 g/mol.
(Co,C₉H₆N₅B₆O₄ : C₃H₆O) (%): 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 I₂ (0.20 mmol) were added to a stirring solution containing 50 mg of 2 (0.05 mmol) in 3 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 Na₂SO₃ (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%.

Synthesis of [MV][4]:

The same procedure as for [MV][1] was done, but using H[4] (100 mg, 0.22 mmol) instead of H[1]. H NMR (300 MHz, CD₂COCD₂), δ: 9.55 (4H, d, JHH 6.0, N'-CH₂pyr-CH₄pyr), 8.95 (4H, d, JHH 6.0, N'-CH₂pyr-CH₄pyr), 5.19 (4H, t, JHH 4.5, N'-CH₂pyr), 4.33 (4H, s, C₃-H), 4.25 (4H, s, C₃-H), 4.17 (4H, t, JHH 4.5, N'-CH₂pyr-CH₂O), 3.62 (4H, t, JHH 4.5, O-CH₂pyr-CH₄pyr), 3.52 (4H, t, JHH 4.5, CH₂-CH₂O-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), 1.93 (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). ¹³B NMR (96 MHz, CD₂COCD₂), δ: 23.53 (2B, s, B-O), 1.42 (8B, s, JBB 134, B-H), -3.74 (12B, d, JBB 144, B-H), -5.43 (2B, s, B-I), -16.09 (4B, s, JBB 167, B-H), -17.97 (4B, s, JBB 163, B-H), -21.79 (2B, s, JBB 176, B-H), 25.22 (2B, s, JBB 166, B-H). ¹³C [H] NMR (75 MHz, CD₂COCD₂) δ: 150.02 (CH₂pyr-Cpyr-Cpyr), 146.65 (N'-CH₂pyr-CH₄pyr), 126.96 (CH₄pyr-CH₄pyr-Cpyr), 72.10 (B-O-CH₂-CH₂O), 68.84 (B-O-CH₂), 68.18 (N'-CH₂-CH₂), 62.15 (N'-CH₂-CH₂), 56.48 (C₃-H). FTIR-ATR (ν in cm⁻¹): 3056.22 (w, ν(C-H)), 2914.49 (w, ν(C-H)), 2859.10 (w, ν(C-H)), 2544.83 (s, ν(B-H)), 1637.00 (m, ν(N=C)), 1200-900 (w, ν(C-O)). MALDI-TOF (m/z): Calculated, 1229.66; Found, 1229.65 (3). Elem. Anal. (Co,C₉H₆N₅B₆O₄·I₂) (%): 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]:

The same procedure as for [MV][1] was done, but using H[4] (100 mg, 0.22 mmol) instead of H[1]. H NMR (300 MHz, CD₂COCD₂), δ: 9.49 (4H, d, JHH 6.7, CH₂-N'-CH₄pyr), 8.94 (4H, d, JHH 6.1, N'-CH₂pyr-CH₄pyr), 4.79 (6H, s, CH₄-N'-), 4.52 (4H, s, C₃-H), 4.29 (4H, s, C₃-H), 2.62 (4H, s, B-H), 2.46 (6H, s, B-H), 1.93-1.71 (24H, m, B-H). ¹³B NMR (96 MHz, CD₂COCD₂), δ: 7.81 (2B, d, JBH 135, B-H), 4.48 (2B, d, JBH 150, B-H), 2.36 (2B, d, JBH 155, B-I), -0.83 (4B, d, JBH 159, B-H), -3.43 (14B, m, B-H), -14.97 (4B, d, JBH 144, B-H), -16.50 (4B, d, JBH 148, B-I), -20.05 (2B, d, JBH 189, B-H), -22.02 (2B, d, JBH 189, B-H). FTIR-ATR (ν in cm⁻¹): 3049.22 (w, ν(C-H)), 2544.76 (s, ν(B-H)), 1639.32 (m, ν(N=C)). MALDI-TOF (m/z): Calculated, 449.65; Found, 449.15 ([4]). Elem. Anal.
(Co$_2$C$_5$H$_9$N$_2$B$_9$H$_4$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]:

The same procedure as for [MV][1], was performed, but starting from H[5] (100 mg, 0.12 mmol) instead of H[1]. $^1$H [$^13$B] NMR (300 MHz, CD$_3$COCD$_3$), $\delta$: 9.49 (4H, d, $\delta_{H}$H 6.6, CH$_3$N$^-$-CH$_{pyr}$), 8.94 (4H, d, $\delta_{H}$H 6.5, N$^+$-CH$_{pyr}$-CH$_{pyr}$), 4.80 (6H, s, CH$_3$N$^-$-), 4.46 (8H, s, C$_2$-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). $^13$B NMR (96 MHz, CD$_3$COCD$_3$), $\delta$: 8.13 (4B, d, $\delta_{B}$H 109, B-H), 6.12 (4B, d, $\delta_{B}$H 144, B-H). FTIR-ATR (v in cm$^{-1}$): 3024.63 (w, v(C=N)), 2576.69 (m, v(B-H)), 1638.12 (m, v(N=C)). MALDI-TOF (m/z): Calculated, 1079.13; Found, 1078.60 ([5]). Elem. Anal. (Co$_2$C$_5$H$_9$N$_2$B$_9$H$_4$I$_2$) (%): 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[6]:

The same procedure as for [MV][1], was followed, but using H[6] (100 mg, 0.17 mmol) instead of H[1]. $^1$H [$^13$B] NMR (300 MHz, CD$_3$COCD$_3$), $\delta$: 9.50 (4H, d, $\delta_{H}$H 6.4, CH$_3$N$^-$-CH$_{pyr}$), 8.95 (4H, d, $\delta_{H}$H 5.9, N$^+$-CH$_{pyr}$-CH$_{pyr}$), 4.80 (6H, s, CH$_3$N$^-$-), 4.41 (8H, s, C$_2$-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). $^13$B NMR (96 MHz, CD$_3$COCD$_3$), $\delta$: 4.24 (4B, d, $\delta_{B}$H 104, B-H), -0.92 (16B, d, $\delta_{B}$H 114, B-H), -3.67 (4B, s, B-I), 3.65 (8B, d, $\delta_{B}$H 154, B-H), -0.23 (4B, d, $\delta_{B}$H 146, B-H). FTIR-ATR (v in cm$^{-1}$): 3035.51 (w, v(C=N)), 2557.54 (s, v(B-H)), 1638.38 (m, v(N=C)). MALDI-TOF (m/z): Calculated, 575.54; Found, 575.03 ([6]). Elem. Anal. (Co$_2$C$_5$H$_9$N$_2$B$_9$H$_4$I$_2$) (%): 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]:

The same procedure as for [MV][1], was done, but starting from H[7] (100 mg, 0.09 mmol) instead of H[1]. $^1$H [$^13$B] NMR (300 MHz, CD$_3$COCD$_3$), $\delta$: 9.51 (4H, d, $\delta_{H}$H 6.8, CH$_3$N$^-$-CH$_{pyr}$), 8.96 (4H, d, $\delta_{H}$H 6.4, N$^+$-CH$_{pyr}$-CH$_{pyr}$), 5.02 (8H, s, C$_2$-H), 4.80 (6H, s, CH$_3$N$^-$-), 3.97 (4H, s, B-H), 3.55 (6H, s, B-H), 2.48 (8H, s, B-H), 2.25 (6H, s, B-H). $^13$B NMR (96 MHz, CD$_3$COCD$_3$), $\delta$: 7.28 (4B, d, $\delta_{B}$H 145, B-H), -2.00 (8B, d, $\delta_{B}$H 163, B-H), -2.85 (4B, s, B-I), -12.15 (8B, s, B-I), -13.40 (8B, d, $\delta_{B}$H 145, B-H), -20.37 (4B, d, $\delta_{B}$H 166, B-H). FTIR-ATR (v in cm$^{-1}$): 3034.04 (w, v(C=N)), 2582.67 (m, v(B-H)), 1638.38 (m, v(N=C)). MALDI-TOF (m/z): Calculated, 1079.13; Found, 1078.60 ([7]). Elem. Anal.
(Co$_2$C$_2$H$_y$N$_x$B$_y$I$_{10}$) (%): Calculated, C 10.25, H 1.98, N 1.19; Found, C 10.46, H 1.94, N 1.23. Mw: 2344.51 g/mol.

Synthesis of MV[8]:

The same procedure as for [MV][1]$_2$ was done, but using H[8] (50 mg, 0.15 mmol), instead of H[1].

$^1$H $^{11}$B NMR (300 MHz, CD$_3$COCD$_3$), $\delta$ : 70.45 (s), 45.10 (s, C$_3$-H), 41.49 (s), 7.83 (s, N=CH$_{pyr}$-CH$_{pyr}$), 6.78 (s, N=CH$_{pyr}$-CH$_{pyr}$), 3.63 (s, N=CH$_y$), 3.14 (s), 1.33 (s), -8.12 (s), $^1$B NMR (96 MHz, CD$_3$COCD$_3$), $\delta$ : 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 ($\nu$ in cm$^{-1}$): 3038.91 (w, v(C=C-H)), 2521.63 (s, v(B-H)), 1639.72 (m, v(N=C)). MALDI-TOF (m/z): Calculated, 321.28; Found, 321.33 ([M+H]). Elem. Anal. (Fe$_x$C$_y$H$_y$N$_y$B$_y$I$_{10}$) (%): Calculated, C 10.25, H 1.98, N 1.19; Found, C 10.46, H 1.94, N 1.23. Mw: 827.57 g/mol.

Synthesis of MV[9]:

The same procedure as for [MV][1]$_2$ was performed, but starting from H[9] (100 mg, 0.08 mmol) instead of H[1]: $^1$H $^{11}$B NMR (300 MHz, CD$_3$COCD$_3$), $\delta$ : 9.51 (4H, d, $^3$J$_{HH}$ 6.3, CH$_y$N=CH$_{pyr}$), 8.97 (4H, d, $^3$J$_{HH}$ 5.7, N=CH$_{pyr}$-CH$_{pyr}$), 5.14 (8H, s, C$_3$-H), 4.80 (6H, s, CH$_y$N=-), 3.62 (8H, s, B-H), 2.75 (8H, s, B-H), 2.65 (4H, s, B-H). $^1$B NMR (96 MHz, CD$_3$COCD$_3$), $\delta$ : -2.86 (8B, d, $^3$J$_{BB}$ 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, $^3$J$_{BB}$ 157, B-H), -21.12 (4B, d, $^3$J$_{BB}$ 174, B-H). FTIR-ATR ($\nu$ in cm$^{-1}$): 3024.83 (w, v(C=C-H)), 2581.75 (m, v(B-H)), 1636.77 (m, v(N=C)). MALDI-TOF (m/z): Calculated, 1330.92; Found, 1331.37 ([M$^+$]). Elem. Anal. (Co$_2$C$_{20}$H$_{28}$N$_{10}$B$_{10}$I$_{10}$) (%): Calculated, C 8.43, H 1.49, N 0.98; Found, C 9.17, H 1.56, N 1.06. Mw: 2848.10 g/mol.

Synthesis of 10:

The same procedure as for 2 was followed, but using ferrabisdicarbollide dioxanate (200 mg, 0.49 mmol), [3,3'-Fe(8-C$_4$H$_4$O-1,2-C$_8$B$_2$I$_{10}$)($^{'}$3,3'-C$_8$B$_2$I$_{10}$)], instead of cobaltabisdicarbollide dioxanate. A brown solid was obtained. Weight: 128 mg. Yield: 81%. $^1$H $^{11}$B NMR (300 MHz, CD$_3$COCD$_3$), $\delta$ : 72.10 (s), 43.42 (s, C$_3$-H), 42.75 (s, C$_3$-H), 39.06 (s), 26.23 (s), 7.78 (s, N=CH$_{pyr}$-CH$_{pyr}$), 7.68 (s, N=CH$_{pyr}$-CH$_{pyr}$), 4.40-3.50 (m, N=CH$_y$-CH$_y$, O-CH$_y$-CH$_y$), 3.26 (s), 1.24 (s), -0.97 (s), -4.20 (s), -9.84 (s), -13.19 (s). $^1$B NMR (96 MHz, CD$_3$COCD$_3$), $\delta$ : 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), -37.47 (4B, s, B-H), -39.75 (2B, s, B-O), -439.61 (4B, s, B-H), -487.94 (2B, s, B-H). $^{13}$C $^{11}$B NMR (75 MHz, CD$_3$COCD$_3$), $\delta$ : 144.60 (CH$_{pyr}$-C$_{pyr}$-C$_{pyr}$), 140.30 (N=CH$_{pyr}$-CH$_{pyr}$),
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 Et2O/HCl (0.1 M). The mixed organic fractions were washed with water and dried over anhydrous MgSO4. After evaporation and re-crystallization from CH2Cl2, a brownish powder was obtained. Weight: 58.5 mg. Yield: 92%.

1H {11B} NMR (300 MHz, CD3COCD3), δ: 62.32 (s), 46.00 (s, Cc-H), 44.81 (s, Cc-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), 11B NMR (96 MHz, CD3COCD3), δ: 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 (ν in cm⁻¹): 3030.08 (w, ν(Cc-H)), 2523.15 (s, ν(B-H)). MALDI-TOF (m/z): Calculated, 447.18; Found, 447.22 ([11]⁻). Elem. Anal. (CsFeC4H21B18I · 2CH2Cl2) (%): Calculated, C 9.62, H 3.36; Found, C 9.56, H 3.39. Mw: 579.46 g/mol.

Synthesis of MV[11]2:

The same procedure as for [MV][1]2 was done, but starting from H[11] (50 mg, 0.11 mmol) instead of H[1]. 1H {11B} NMR (300 MHz, CD3COCD3), δ: 62.32 (s), 46.00 (s, Cc-H), 44.81 (s, Cc-H), 8.95 (s, N⁺-CHpyr-CHpyr), 8.26 (s, N⁺-CHpyr-CHpyr), 6.64 (s), 4.39 (s, N⁺-CHpyr), 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), 11B NMR (96 MHz, CD3COCD3), δ: 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 (ν in cm⁻¹): 3048.32 (w, ν(Cc-H)), 2527.88 (s, ν(B-H)), 1637.89 (m, ν(N⁺-C)). MALDI-TOF (m/z): Calculated, 447.18; Found, 447.22 ([11]⁻). Elem. Anal. (Fe2C20H56N2B36I2) (%): 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]:

121.48 (CHpyr-CHpyr-Cpyr), 60.47 (B-O-CH2-CH2-O), 58.74 (B-O-CH2), 58.66 (N⁺-CH2-CH2), 55.76 (N⁺-CH2-CH2). FTIR-ATR (ν in cm⁻¹): 3044.60 (w, ν(Cc-H)), 2922.42 (w, ν(C-H)), 2858.73 (w, ν(C-H)), 2519.87 (s, ν(B-H)), 1635.99 (m, ν(N⁺-C)), 1200-900 (w, ν(C-O)). MALDI-TOF (m/z): Calculated, 971.70; Found, 972.82 ([10]). Elem. Anal. (Fe2C20H56N2B36O4 2 C3H8O) (%): 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.
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 Et₂O/HCl (0.1 M). The mixed organic fractions were washed with water and dried over anhydrous MgSO₄. 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%.

1H {11B} NMR (300 MHz, CD₃COCD₃), δ: 62.32 (s), 46.00 (s, C₆-H), 44.81 (s, C₆-H), 7.20 (s), 1.87 (s), -0.95 (s), -6.41 (s), -21.33 (s), 11B NMR (96 MHz, CD₃COCD₃), δ: 119.95 (2B, s, N-H), 25.50 (4B, s, N-H), 7.57 (4B, s, N-H), -46.53 (2B, s, N-H), -21.33 (s, N-H). FTIR-ATR (ν in cm⁻¹): 3026.02 (w, ν(C=H)), 2535.31 (s, ν(B-H)). MALDI-TOF (m/z): Calculated, 572.45; Found, 572.13 (12). Elem. Anal. (CsFeCcH₂₀B₁₈I₂·0.1C₇H₈) (%): Calculated, C 7.89, H 2.93; Found, C 7.83, H 3.11. Mw: 705.36 g/mol.

Synthesis of MV[12]₂:

The same procedure as for [MV][1], was performed, but using H[12] (50 mg, 0.087 mmol) instead of H[1]. 1H {11B} NMR (300 MHz, CD₃COCD₃), δ: 62.32 (s), 46.00 (s, C₆-H), 44.81 (s, C₆-H), 9.30 (s, N=CH pyr-CH pyr), 8.70 (s, N=CH pyr-CH pyr), 6.64 (s, 4.63 (s, N=CH pyr), 3.15 (s), 1.28 (s), 0.84 (s), 0.4 (s), 0.12 (s), -2.17 (s), -3.76 (s), -5.06 (s), -16.20 (s), 11B NMR (96 MHz, CD₃COCD₃), δ: 114.39 (2B, s, N-H), 111.08 (2B, s, N-H), 34.52 (4B, s, N-H), 30.50 (4B, s, N-H), 12.05 (4B, s, N-H), -0.44 (4B, s, N-H), -34.12 (2B, s, N-H), -40.90 (2B, s, N-H), -331.88 (4B, s, N-H), -370.39 (4B, s, N-H), -388.42 (2B, s, N-H), -518.81 (2B, s, N-H). FTIR-ATR (ν in cm⁻¹): 3026.02 (w, ν(C=H)), 2535.31 (s, ν(B-H)), 1636.03 (m, ν(N=)). MALDI-TOF (m/z): Calculated, 573.16; Found, 572.13 ([12]). Elem. Anal. (FeCcH₂₀N₂B₁₈I₄·0.5C₇H₈) (%): 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][11]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

1) DME, 1 eq \( \text{N}_{2} \), 2) \( 60 \, ^\circ \text{C} \) overnight

1) \( 2 \, \text{eq I}_2 \) in \( \text{EtOH} \), 2) Stirring overnight at r.t., 3) Reflux 2.5 h, 4) 1.6 eq \( \text{N}_2\text{SO}_3 \) in \( \text{H}_2\text{O} \), 5) Reflux 10 min

The first step was the same used for the preparation of compound 10.
Scheme of the synthesis of compound $[\text{MV}[11]]_2$

1) 1.05 eq. NIS in EtOH, stirring overnight, r.t.
2) Cation exchange
3) $[\text{MV}][\text{Cl}]_2$ in water

$[\text{MV}[11]]_2$ (92%)

The same procedure was used for the synthesis of the compound $[\text{MV}[12]]_2$, 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.
BIBLIOGRAPHY


