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

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Original:

Tarrés, M., Arderiu, V.S., Zaulet, A., Viñas, C., FABRIZI DE BIANI, F., Teixidor, F. (2015). How to get the desired reduction voltage in a single framework! Metallacarborane as an optimal probe for sequential voltage tuning. DALTON TRANSACTIONS, 44(26), 11690-11695 [10.1039/C5DT01464F].

Availability:

This version is availablehttp://hdl.handle.net/11365/983458 since 2015-12-21T13:21:26Z

Published:

DOI:10.1039/C5DT01464F

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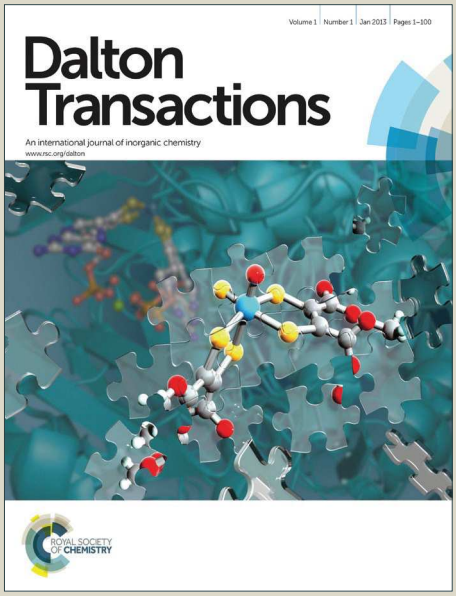

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COMMUNICATION

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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An appealingly wide set of redox couples ranging from -1.74 to -0.35 V based on a metallabisdicarbollide derivative, $[M(C_2B_9H_{11-y}I_y)_2]^-$ (M= Co, Fe), each being distinguished from the former by near 0.15V and all having the same structure has been demonstrated. The redox active methyl viologen moiety ($[MV]^{2+}$) has been used as a benchmark.

Redox couples with a sequential set of potentials are desirable for the many technical applications they may have, ranging from solar cells to multidetection electrochemical sensors. In this regard it is to be highlighted the seminal works of Pombeiro,[1] Pickett,[2] Lever[3] and Bursten[4] groups, that reviewed on the importance of establishing a relationship between the redox potential and the structure and ligand nature of complexes. Lever and coworkers reported[3] an electrochemical parameterization in sandwich complexes of the first row transition metals that can be established by assigning electrochemical parameters to the ligands.[5]

Ferrocene, with its high stability, is the archetype of a sandwich compound in which a metal is bound in a η^5 way to two arene ligands.[6] Cobaltocene could be also a model to compare, and indeed its redox potential for the couple $Co^{3+/2+}$ (-1.33 V *vs* $Fc^{+/0}$) is closer to the $Co^{3+/2+}$ in $[Co(C_2B_9H_{11})_2]^-$ (-1.74 V *vs* $Fc^{+/0}$), however cobaltocene does not have the air stability that is characteristic of ferrocene and cobaltabisdicarbollide, $[Co(C_2B_9H_{11})_2]^-$. Equally stable to ferrocene are the sandwich metallacarboranes.[7] These have a central metal sandwiched by two $[C_2B_9H_{11}]^{2-}$ icosahedron fragments, globally producing a $[M(C_2B_9H_{11})_2]^-$, (M= Co^{3+}, Fe^{3+}), clusters (Figure 1).[8]

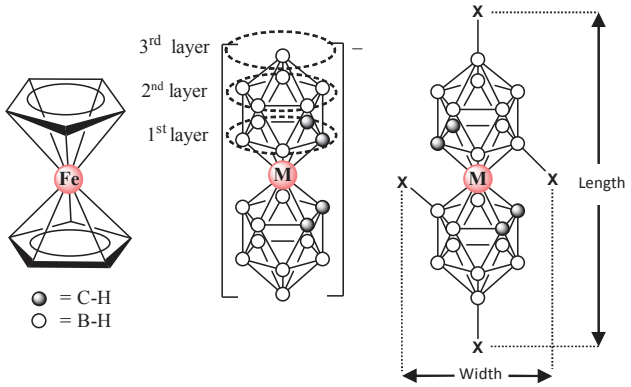

Fig. 1 Chemical structures of ferrocene and metallacarborane $[M(C_2B_9H_{11})_2]^-$ frameworks and the graphical definition of length and width concepts (X= H or I).

The substitution of hydrogen atoms for halogens leads to the halogenated $[M(C_2B_9H_{11-y}I_y)_2]^{z-}$ (M= Co^{3+}, Fe^{3+}) derivatives of the pristine $[M(C_2B_9H_{11})_2]^{z-}$.[9] Likewise to ferrocene, $[M(C_2B_9H_{11})_2]^{z-}$ species are reversibly electroactive,[10] but contrarily to ferrocene, they are anions.[11] Dehydrochlorination and dehydroiodination on $[Co(C_2B_9H_{11})_2]^-$ produces an anodic shifting of the $E_{1/2}$ of the associated redox couple.[9d,e] Actually, near 1 V modulation has been achieved from $[Co(C_2B_9H_{11})_2]^-$, $E_{1/2}$= -1.74 V ($Fc^{+/0}$), to $[Co(C_2B_9H_7I_4)_2]^-$, $E_{1/2}$= -0.71 V.[9d] Ferrocene has also been stated as a platform on which to modulate its $E_{1/2}$, but never overcoming a 1 V range and with much less intermediate redox potentials.[12] It is known that a high number of nine iodo groups in the *nido* $[7,8\text{-}C_2B_9H_{12}]^-$ stabilizes de dianionic nido $[7,8\text{-}C_2B_9H_2I_9]^{2-}$ and prevents open face protonation as well as metal capitation.[13] To overcome this situation keeping the same structural motif is offered by the equivalent $[Fe(C_2B_9H_{11})_2]^-$ platform, that has $E_{1/2}$= -0.78 V, very similar to this for the octaiodinated derivative $[Co(C_2B_9H_7I_4)_2]^-$.[14]

This possible extended $E_{1/2}$ modification with a sole framework seems to be unique,[15] and its applications can be very wide in molecular electronics,[16] as electrolytes in DSSC[17] or any case where electron transfer is paramount,[18] in particular when

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† This research has been financed by MEC (CTQ 2010-16237) and Generalitat de Catalunya (2009/SGR/00279). Dr. Màrius Tarrés was enrolled in the PhD program of the UAB. Víctor S. Arderiu and Adnana Zaulet are enrolled in the PhD program of the UAB. Dr. Màrius Tarrés and Víctor S. Arderiu thank MICINN for FPU and FPI predoctoral grants, respectively.

Electronic Supplementary Information (ESI) available: Materials, methods and experimental data of all the synthesized compounds. Sequential electrolyses of $[MV][\mathbf{11}]_2$. Graphical explanations of the redox processes involved in the sequential electrolyses of **10**. See DOI: 10.1039/x0xx00000x

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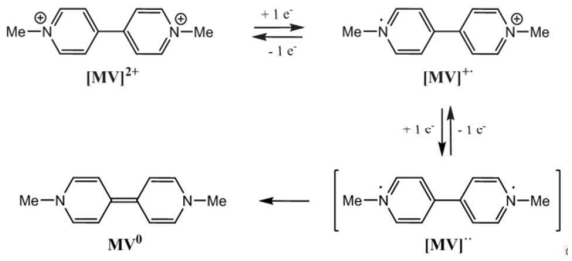
only one variable, the redox potential, is sought to be altered, as their structures can broadly be considered constant upon the addition of extra substituents. As an example, the dimensions of $[Co(C_2B_9H_{10}I)(C_2B_9H_{11})]^-$ (length (0.985 nm); width (0.656 nm))[19] do not differ much from $[Co(C_2B_9H_{10}I)_2]^-$ (length (1.018 nm); width (0.749 nm))[20] or $[Co(C_2B_9H_7I_4)_2]^-$ (length (1.235 nm); width (0.752 nm)),[9d] and their solubility properties differ minimally.

On the other hand, 1,1'-dimethyl-4,4'-bipyridylium, commonly known as methyl viologen ([MV]2+), is a well-known electrochromic material, which electrochemistry has also been well studied.[21] The addition of one electron forms the radical cation that is intensely coloured, with a high molar absorption coefficient. The addition of a second electron forms a diradical neutral species that for a short time reaction, like for Cyclic Voltammetry (CV) conditions, is reversible[22] (Scheme 1).

To give a clear picture of the sequential and regular modulation of the $E_{1/2}$ of metallacarboranes, we chose $[MV]^{2+}$ as a benchmark. Its choice was also related to the $E_{1/2}$ of its two redox transitions ($E_{1/2}([MV]^{2+/+\bullet})$= -0.82 V and $E_{1/2}([MV]^{+\bullet/\bullet\bullet})$= -1.23 V *vs* $Fc^{+/0}$), because these are situated in-between the $E_{1/2}$ for the concerned pristine platforms, $[Co(C_2B_9H_{11})_2]^-$ (-1.74 V *vs* $Fc^{+/0}$) and $[Fe(C_2B_9H_{11})_2]^-$ (-0.78 V *vs* $Fc^{+/0}$). Further, and very importantly, $[MV]^{2+}$ is a dication able to compensate the charge of the anionic metallacarborane derivatives. CV studies have been done on all compounds shown in Chart 1, in CH_3CN with 0.1 M of TBA[PF_6], as supporting electrolyte.

The salts were readily synthesized in water due to the solubility of $[MV]Cl_2$ and $H[Co(C_2B_9H_{11-y}I_y)_2]$ in this solvent, whereas the resulting $[MV][Co(C_2B_9H_{11-y}I_y)_2]_2$ salts are water-insoluble. Further experimental information and synthetic details of all compounds shown in Chart 1 as well as all the methods used and characterization data, may be found in the Supporting Information. The $E_{1/2}$ values of the covalently linked $[M(C_2B_9H_{11})_2]^-$ (M= Co, Fe) to central viologen cores were studied with the neutral species **2**, and **3**, for M= Co; and **10**, for M= Fe. Compounds **2** and **10** were prepared by reaction of the dioxanate derivative of the cobalt metallacarborane, [3,3'-Co(8-$C_4H_8O_2$-1,2-$C_2B_9H_{10}$)(1',2'-$C_2B_9H_{11}$)], with 4,4'-bipyridine in dry DME under reflux. **3** was prepared starting from **2**, and following the same procedure as for a normal monoiodination (i.e. [**6**]$^-$).[9a]

Scheme 1 Redox processes of $[MV]^{2+}$.



Mono and diiodination of $[Fe(C_2B_9H_{11})_2]^-$ ([**11**]$^-$, and [**12**]$^-$) is described first in this work, as salts of $[MV]^{2+}$. For the mono- and di-iodination, the addition of 1.05 (or 2.10) equivalents of *N*-iodosuccinimide to an EtOH solution containing the metallacarborane with overnight stirring at room temperature results in the formation of the desired compounds. After evaporation, the residue was dissolved in ether and extracted with 0.1M HCl followed by precipitation with $[MV]^{2+}$to produce the final compounds [**11**]$^-$ and [**12**]$^-$.

Figure 2 shows the CVs of the twelve compounds shown in Chart 1. The two vertical dashed lines correspond to the viologen $[MV]^{2+/+\bullet}$ and $[MV]^{+\bullet/\bullet\bullet}$ benchmarks redox couples. As the components of the salts are in a stoichiometric ratio and there are two metallacarborane units for each viologen, the intensities of the electrochemical waves are twice for the anionic metallacarborane. Therefore, in Figure 2 the $E_{1/2}$ of the metallacarborane is easily localized. Pristine cobaltabisdicarbollide or its oxygen substituted boron derivatives does not see their $E_{1/2}$ altered, see entries $[MV][\mathbf{1}]_2$ and **2**. Their $E_{1/2}$ is 0.51 V more cathodic than $[MV]^{+\bullet/\bullet\bullet}$ benchmark. Incorporation of one iodine in the η^5 C_2B_3 cluster open face produces an $E_{1/2}$ shift towards more positive voltage values, thus the former 0.51 V have been converted into only 0.23 V with regard to $[MV]^{+\bullet/\bullet\bullet}$ benchmark (entry $[MV][\mathbf{4}]_2$ on Table 1). The $E_{1/2}$ $[MV]^{+\bullet/\bullet\bullet}$ benchmark is exceeded by the metallacarborane in entries $[MV][\mathbf{5}]_2$ and $[MV][\mathbf{6}]_2$ with 4 iodo substituents on the 2nd layer and 2 iodo substituents on the 1st layer of the cobaltabisdicarbollide cluster. Its $E_{1/2}$ goes through the second $E_{1/2}$ benchmark $[MV]^{2+/+\bullet}$ if six iodo substituents are incorparated (see entry $[MV][\mathbf{7}]_2$). The observed CVs are very similar both with 6 iodo substituents on a cobalt platform or replacing the cobalt by Fe with and no iodo substituents in its platform (entries $[MV][\mathbf{6}]_2$ and $[MV][\mathbf{8}]_2$). The $E_{1/2}$ benchmark $[MV]^{2+/+\bullet}$ is exceeded in entry $[MV][\mathbf{9}]_2$ with eight iodo substituents on the cobaltabisdicarbollide cluster and definitely in entry **10**. The $E_{1/2}$ $[MV][\mathbf{11}]_2$ has already left the second benchmark ($[MV]^{2+/+\bullet}$) well behind and even more in $[MV][\mathbf{12}]_2$. The spanned voltage has been near 1.4 V, but it can well be close to 2 V if the $E_{1/2}$ behaviour of iodo substitutes of $[Fe(C_2B_9H_{11})_2]^-$ is similar to the case for $[Co(C_2B_9H_{11})_2]^-$, as it seems is the case. All $E_{1/2}$ are detailed in Table 1.

We have used also neutral species, compounds **2**, **3** and **10**. These show that minor differences in $E_{1/2}$ values are encountered among linked or free metallacarborane units. It is remarkable the similar $E_{1/2}$ values of $[Co(C_2B_9H_7I_4)_2]^-$ and $[Fe(C_2B_9H_{11})_2]^-$ observed between $[MV][\mathbf{9}]_2$ and $[MV][\mathbf{8}]_2$, and the stronger tuning effect when the substituent is located nearest to the metal observed between $[MV][\mathbf{5}]_2$ and $[MV][\mathbf{6}]_2$. If the layers shown in Figure 1 are considered, it is clear that the $E_{1/2}$ effect of substituents on the 1st layer is stronger to the effect of substituents at the 2nd layer. This distance dependence has recently been described.[23] As an example, the effect on $E_{1/2}$ of four iodo substituents in the 2nd layer ($[MV][\mathbf{5}]_2$)

Chart 1 Studied metallacarboranes.

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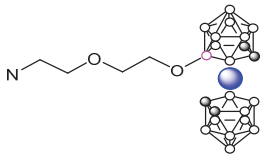

is almost the same as two iodo atoms in the 1st layer ([MV][**6**]$_2$), which could be clearly seen in Table 1.

The CV studies of [MV][**1**]$_2$, [MV][**4**]$_2$, [MV][**11**]$_2$, [MV][**12**]$_2$, and the zwitterions **2**, **3** and **10**, define three redox waves that might suggest a multicoloured electrochromic behaviour with four distinct reversible states. However, and despite that the $[MV]^{+\bullet/\bullet\bullet}$ redox couple appears reversible under the CV conditions utilized, it is not so under electrolysis conditions.

A setup consisting of two compartments separated by a frit was used to run the electrolysis and the posterior CV measurements. The working compartment contained the metallacarborane sample at a concentration of 1 mM in CH_3CN, 0.1 M of the inert electrolyte (TBA[PF_6]), one wound Pt

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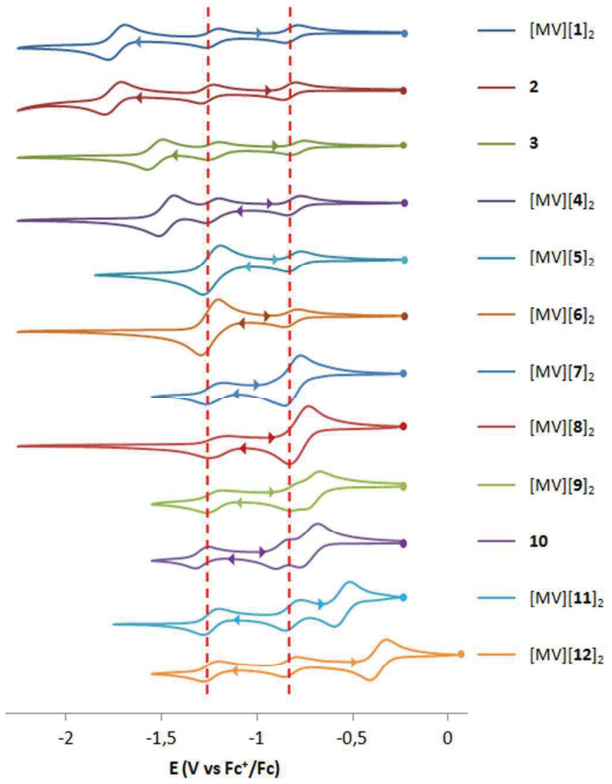

Fig. 2 Graphical view of the metallacarborane runner race passing through the $[MV]^{2+}$ benchmarks. CVs of all the synthesized compounds.

Table 1 $E_{1/2}$ (V) of $[MV]^{2+}$ and metallacarboranes of all compounds vs Fc^{+}/Fc. The number of iodo groups are referred to one metallacarborane unit.

Compound	Metal	Iodo groups	M^{3+}/M^{2+}	$[MV]^{+\bullet}/MV^{\bullet\bullet}$	$[MV]^{2+}/[MV]^{+\bullet}$
[MV][**1**]$_2$	Co	0	-1.74	-1.23	-0.82
2	Co	0	-1.75	-1.26	-0.84
3	Co	1	-1.53	-1.23	-0.79
[MV][**4**]$_2$	Co	1	-1.47	-1.24	-0.81
[MV][**5**]$_2$	Co	4	-1.24	-1.24	-0.80
[MV][**6**]$_2$	Co	2	-1.25	-1.25	-0.83
[MV][**7**]$_2$	Co	6	-0.82	-1.23	-0.82
[MV][**8**]$_2$	Fe	0	-0.78	-1.20	-0.78
[MV][**9**]$_2$	Co	8	-0.71	-1.22	-0.80
10	Fe	0	-0.72	-1.28	-0.86
[MV][**11**]$_2$	Fe	1	-0.56	-1.24	-0.81
[MV][**12**]$_2$	Fe	2	-0.35	-1.23	-0.81

string as working electrode, and a Ag/AgCl/TBACl (0.1 M) reference electrode. The CV was done in this compartment with a Glassy Carbon electrode, after disconnecting the electrolysis wound Pt string. The second compartment had the same inert electrolyte and a counter electrode (also a wound Pt string). Electrolyses have been conducted at the two edges of the metallacarborane voltage race; on **2** at the beginning of the race and on [MV][**11**]$_2$ and [MV][**12**]$_2$ at the end. Only **2** and [MV][**12**]$_2$ are described here (electrolysis for [MV][**11**]$_2$ is described in the Supporting Information). In Figure 3a it is reported the CV wave for **2** before performing electrolysis. This CV is replicated after electrolysis at -1.1 V but neither at -1.6 V nor at -2.1 V. The initial color of the 1 mM solution of **2** in 0.1 M of $TBAPF_6$ is pale yellow. Subsequent to electrolysis at -1.1 V, the colour becomes navy blue, and after -1.6 V, orange. This color remains after electrolysis at -2.1 V. The red dotted line in the CV corresponds to the CV of **2** after electrolysis at -2.1 V, which evidences that the MV^0 oxidation is no longer feasible, neither for the $[MV]^{+\bullet/\bullet\bullet}$ nor for $[MV]^{2+/+\bullet}$ redox processes, due to the internal electronic rearrangement after the final reduction (see Scheme 1).

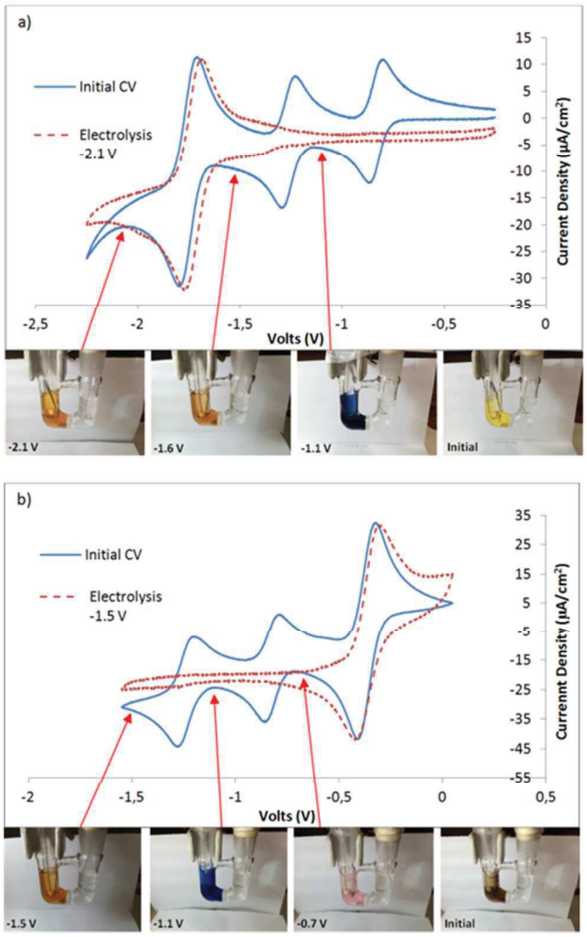

Fig. 3 a) Sequential electrolysis of **2**.Initial (blue solid line) and final (red dotted line) CVs (after electrolysis at -2.1 V).Obtained colors after each electrolysis. b) Sequential electrolysis of [MV][**12**]$_2$. Initial (blue solid line) and final CVs (red dotted line) (after electrolysis at -1.5 V).Obtained colors after each electrolysis.

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If the electrolysis is done at the other edge of the metallacarborane voltage race, for [MV][**12**]$_2$, it is found that initial color is brown, becoming pink after electrolysis at -0.7 V. This color change is due to the $Fe^{III/II}$ process from the metallacarborane, which is fully reversible. Further reduction the to -1.1 V alters the color to navy blue, which corresponds to the $[MV]^{2+/+\bullet}$ process. If a final controlled reduction is done at -1.5 V, the color of the compound is modified to orange. The CV after this process is shown as a red dotted line, showing only the reversibility of the metallacarborane (see Figure 3b). Again the MV^0 is no longer possible to oxidize. However, by having shifted the redox potential of the metallacarborane to more anodic potentials than $[MV]^{2+/+\bullet}$, it has been possible to produce a polyelectrochromic material with four distinct colors: brown, pink, navy blue and a final additional irreversible orange color. In addition, molecules [MV][**11**]$_2$ and [MV][**12**]$_2$ can accept up to 3 electrons reversibly, stating themselves as efficient "electron-buckets" or "electron-reservoirs" for further electronic applications. More graphical explanations of the redox processes involved in the sequential electrolyses are supplied in the Supporting Information, using **10** as an example.

A stepwise sequential voltage tuning has been achieved on a single metallacarborane platform. A perfect $E_{1/2}$ control all along 1.4 V has been demonstrated through successive halogenations of the initial platform. To visually evidence this fact, $[MV]^{2+}$ with two clearly distinguishable redox transitions in CV has been used. Ultimately, the electrochromic behaviour of the synthesized compounds has been studied through electrolysis experiments. Up to four different colors have been observed for the same compound (three of them perfectly reversible), corresponding to different electronic transitions taking place on different sites of the molecule.

Acknowledgment

This research has been financed by MEC (CTQ2013-44670-R) and Generalitat de Catalunya (2014/SGR/149). Dr. M. Tarrés, V. S. Arderiu and A. Zaulet were/are enrolled in the PhD program of the UAB. M.T. and V.S.A thank MICINN for FPU and FPI predoctoral grants, respectively.

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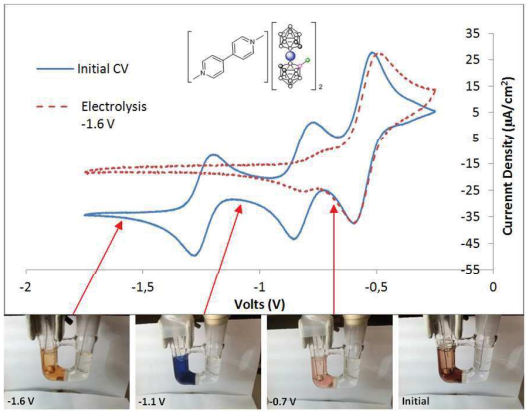
Graphical Abstract

A single platform, $[M(C_2B_9H_{11})_2]^-$ (M=Co, Fe) offers the possibility to choose the desired potential in a 1.4V range without noticeably changing the shape or modifying the volume of the platform. Methyl Viologen has been used as benchmark of the $E_{½}$ platform tuning.



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