1.3 V Inorganic Sequential Redox Chain with an All-Anionic Couple 1−/2− in a Single Framework

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ABSTRACT: The relatively low symmetry of [3,3′-Co(1,2-C2B9H11)2]− ([1]−), along with the high number of available substitution sites, 18 on the boron atoms and 4 on the carbon atoms, allows a fairly regioselective and stepwise chlorination of the platform and therefore a very controlled tuning of the electrochemical potential tuning. This is not so easily found in other systems, e.g., ferrocene. In this work, we show how a single platform with boron and carbon in the ligand, and only cobalt can produce a tuning of potentials in a stepwise manner in the 1.3 V range. The platform used is made of two icosahedra sharing one vertex. The tuning has been achieved from [1]− by sequential chlorination, which has given potentials whose values increase sequentially and linearly with the number of chloro groups in the platform. [Cl8-1]−, [Cl10-1]−, and [Cl12-1]− have been obtained, which are added to the existing [Cl-1]−, [Cl2-1]−, [Cl4-1]−, and [Cl6-1]− described earlier to give the 1.3 V range. It is envisaged to extend this range also sequentially by changing the metal from cobalt to iron. The last successful synthesis of the highest chlorinated derivatives of cobaltabis(dicarbollide) dates back to 1982, and since then, no more advances have occurred toward more substituted metallacarborane chlorinated compounds. [Cl8-1]−, [Cl10-1]−, and [Cl12-1]− are made with an easy and fast method. The key point of the reaction is the use of the protonated form of [Co(C2B9H11)2]−, as a starting material, and the use of sulfuryl chloride, a less hazardous and easier to use chlorinating agent. In addition, we present a complete, spectroscopic, crystallographic, and electrochemical characterization, together with a study of the influence of the chlorination position in the electrochemical properties.

INTRODUCTION

Redox reactions are key for life both in nature, principally in respiration and photosynthesis, and in any device where electrons are the means to store, release, or generate energy. In most of the redox reactions in industry to produce bulk materials or compounds, no fine-tuning of the reduction or oxidation power is sought. However, this is not so when it is necessary to ensure the synergy with surrounding materials or compounds that can be affected by an excess of oxidizing or reducing power. Tuning of man-made redox-reversible systems is largely based first on metals and second in ligands. Notice from this sentence that we emphasize metal-based redox-reversible systems. We will not deal with nonmetal-based systems because, for the case of boron clusters, these are derived from [CB11H12]− or [B12H12]−. It is important to point out that nature succeeds in getting a wide range of potentials with few metals, few coordinating elements, and few ligands for the primary coordination spheres but requires the involvement of one or two extra spheres of influence to modulate . Some robust metal-containing scaffolds have been developed on which to tune the redox potential by the sequential addition of electron-donor or -acceptor groups or acceptors. Some of the more studied scaffolds are due to ferrocene, or metal complexes, most commonly ruthenium, of polypyridyl ligands, e.g., bipyridine, 2,2′-bipyrimidine, 2,2′-bipyrazine, terpyridine, phenanthroline, and others. Their common factor is that they are usually outer-sphere electron-transfer octahedral complexes. A quite representative example of the type of tuning in these complexes is given by the ferrocene [FeCl10H10−Cl] chloro...
derivatives for which brusque, the opposite of stepwise, numbers of chloro units exist, e.g., 10, 5, 2 and 1, which result in brusque $E_{1/2}$ values, versus ferrocenium/ferrocene ($\text{Fc}^+$/Fc) of 1.24, 0.77, 0.31, and 0.17 V, respectively. Still, nearly 1 V has been tuned on the same platform. All of these complexes are positively charged, e.g., $[\text{Fe(C}_2\text{Cl}_3]_2]^+$ or $[\text{Ru(bpy)}_3]^2$. Indeed, despite the fact that ligands are either negative or neutral, very few chemically stable and robust anionic complexes are available ready for $E^0$ tuning. One could consider the couple $[\text{Fe(CN)}_6]^{3-}$/$[\text{Fe(CN)}_6]^{4-}$, or the polyoxometallates (POMs), e.g., Keggin [XW$_{12}$O$_{40}$]$^{3-}$, yet these are difficult to tune, although efforts are being made for POMs.

Thus, anionic metal-containing scaffolds that allow easy tuning with a wide span of voltages are not common. Also, what could be the advantage of using anionic scaffolds? In our opinion, if the reduced form of the redox couple is negative, it will have an increased tendency to release an electron, and if the oxidized form is negative, it will have less appetence for an electron. Plus, this can be easily spotted with the iodide/triiodide ($I^+$/I$^-$) redox couple in dye-sensitized solar cells (DSSCs) in which both the oxidized and reduced partners are negative. Cobalt- and copper-based electrolytes, thiolate/disulfide, $\text{Fc}/\text{Fc}^+$, hydroquinone/benzoquinone derivatives, and the redox couple TEMPO/TEMPO$^*$ all either have a partner whose charge is zero, have a partner with a positive charge, or have both partners with a positive charge. The success of a DSSC relies on the electrons preferring to recombining with the dye or oxidized electrolyte.

We have already indicated that it is not simple to have metal-based robust redox couples based on a single scaffold that allow for a wide range of potentials. In this work, we show that this is becoming possible with the anionic cobaltabis(dicarbollide) $[3,3'-\text{Co}(1,2-\text{C}_2\text{B}_{11}\text{H}_{13})_2]^-$ scaffold (abbreviated as [1]$^-$). This cluster displays interesting electrochemical and biological properties that have been thoroughly studied. Several [1]$^-$ derivatives have been published with the aim of tailoring its properties and finding applications in many different fields of science. Some examples are neutron capture therapies, sensors, anticancer therapies, electron acceptors, and electroactive electrolytes among others.

The relatively low symmetry of [1]$^-$, along with a high number of available substitution sites, allows a fairly regioselective and stepwise chlorination of the platform and therefore a very controlled tuning of the sought-after property, in this case potential tuning. Such characteristics are not easily found in other systems. On the other hand, a higher symmetry, as in many closo clusters, leads more easily to persubstitution but with more difficulty to a step-by-step process.

We present here the three highest chlorinated species of [1]$^-$, which will be named $[\text{Cl}_8-1]$-, $[\text{Cl}_{10}-1]$-, and $[\text{Cl}_{12}-1]$-, corresponding to the number of chloro substituents on the scaffold, which span the voltages from $-1.75$ V for [1]$^-$ to $-0.49$ V for $[\text{Cl}_{12}-1]$-, versus $\text{Fc}^+$/Fc in sequential chlorination steps, and very remarkably with very good electrochemical purity and high yield in simple one-pot reactions (Figure 1). This series is the widest range of sequentially tunable potentials on a single metal-containing anionic platform available today. Also, the range of potentials possible can be extended much further by keeping the same platform, changing the metal from cobalt to iron.

### RESULTS AND DISCUSSION

#### Synthesis.
Since the synthesis of the first halogenated derivative of COSAN, the hexabromocobaltabis(dicarbollide), many strategies have been devised to develop halo derivatives of [1]$^-$, yet the most advanced since that date is the development of iodo derivatives of [1]$^-$, whose methodology requires the buildup of molecules from the components, so the synthesis of $[1,5,6,10-I_4-7,8-\text{C}_2\text{B}_{10}\text{H}_{16}]^-$ followed by their complexation with $\text{CoCl}_2$, yields $[3,3'-\text{Co}(8,9,12,10-I_4-1,2-\text{C}_2\text{B}_{10}\text{H}_{16})_2]^-$, which is the halo derivative of cobaltabis(dicarbollide) with the highest number of halo substituents produced until now.

Chlorine gas was the most popular chlorinating agent for [1]$^-$, with $[3,3'-\text{Co}(8,9,12-\text{Cl}_1-1,2-\text{C}_2\text{B}_{10}\text{H}_{16})_2]$ being the highest chlorinated [1]$^-$ obtained as a pure compound since
This new method allowed the synthesis of pure \([\text{B}_{12}\text{Cl}_{12}]_2\) acetonitrile with sulfuryl chloride to increase the solubility. Chloride. In 2010, a step forward was achieved by mixing clusters was needed, but these are not fully soluble in sulfuryl isomeric mixture of \([3,3']\) and \([\text{Cl}_{10-1}]^-\) and \([\text{Cl}_{12-1}]^-\). B–H is represented by pink spheres, B–Cl by green spheres, and C–H by gray spheres.

Figure 2. Reaction conditions for the synthesis of compounds (a) \([\text{Cl}_{10-1}]^-\) and \([\text{Cl}_{12-1}]^-\) and (b) \([\text{Cl}_{10-1}]^-\) and \([\text{Cl}_{12-1}]^-\) requires a huge excess of SO\(_2\)Cl\(_2\) (650 equiv), the synthesis of \([\text{Cl}_{10-1}]^-\) needs less chlorinating agent (65 equiv). The methodology consists of a mixture of 0.1 and 65 equiv of AlCl\(_3\), and SO\(_2\)Cl\(_2\), respectively, are added to the solid reaction mixture, and the tube is closed again and is heated at 70 °C for 2 days more (Figure 2b).

Characterization. All new compounds were characterized by \(^1\)H, \(^1\)H\(^{11}\)B, \(^1\)C\(^{11}\)C, \(^1\)B, \(^1\)B\(^{11}\)H NMR, matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry (MALDI-TOF-MS) in the negative mode, elemental analysis, IR, and X-ray diffraction. The complete spectral information and crystallographic data can be found in the Supporting Information (SI). The IR spectra give us a qualitative analysis of the reaction by monitoring of the B–Cl bond, and this band appears in other boron clusters in the literature such as \([\text{B}_{12}\text{Cl}_{12}]^{2-}\), demonstrating the hypothesis.\(^{65}\) On the other hand, the MALDI-TOF-MS spectra in the negative mode provide faster and reliable information about the exact number of chloro substituents in the \([1^-]^-\) skeleton. MALDI-TOF-MS of the 8, 10, and 12 chlorinated derivatives of \([1^-]^-\) shows main peaks at \(m/z\) 598.7, 666.8, and 734.8 that correspond to \([\text{Cl}_8\text{Cl}_{10-1}^-]^-\), \([\text{Cl}_9\text{Cl}_{10-1}^-]^-\), and \([\text{Cl}_{10-1}]^-\) in \([\text{Cl}_{10-1}]^-\), \([\text{Cl}_{10-1}]^-\), and \([\text{Cl}_{12-1}]^-\) in Cs[Cl\(_{12-1}\)] and represent 82, 90, and 97% of the sample, respectively. However, the MALDI-TOF-MS unveils a
percentage of less than 10% of the side products corresponding to compounds with one chloro plus or less (see the SI).

The study of the NMR spectra, together with X-ray diffraction, led us to unveil the exact positions of the chloro substituents. Suitable single crystals of [NMe₄][Cl₈-1] and [NMe₄][Cl₁₀-1] were obtained by slow evaporation in acetone; for Cs[Cl₁₂-1], crystals were obtained in CH₂Cl₂, and as far as we are concerned, they are the highest halogenated derivatives of metallacarborane ever crystallized (Figure 3).

Structures and Intermolecular Nonbonding Interactions. The representation of a chloro and a hydrogen atom in the B(4,4′) positions of [NMe₄][Cl₋₁] indicates the isomers present in the crystal (B is in pink, C in gray, H in white, Cl in green, and Co⁺ in orange). X-ray analysis of [NMe₄][Cl₋₁] revealed the solid solution nature of the crystal due to the existence of two isomers in the same monocrystal. Specifically, the crystal demonstrated the existence of [NMe₄][Cl₁₀₋₁] in 80% and [NMe₄][Cl₁₀₋₁] in 20% (Figure 3).

The structures of [NMe₄][Cl₋₁] and [NMe₄][Cl₁₀₋₁] show different types of intermolecular interactions because of its cation (see the SI). The dihydrogen bond C₆₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_errno
explaining the extra peaks that appears in the $^{11}$B($^1$H) NMR spectra of both compounds (see the SI). The gauche conformation in the crystal structures of [NMe$_4$][Cl$_{10}$-1] and Cs[Cl$_{12}$-1] breaks all of the symmetry of the molecule and, consequently, the $^1$H NMR spectrum shows two C-C-H bonds are spectroscopically different (Figure 5c). Moreover, the signal downfield supports the fact that the intramolecular B−Cl⋯H−C$_{12}$ interactions are kept in solution.

The $^{11}$B NMR spectrum of Cs[Cl$_{10}$-1] displays three singlets at 12.4, 6.4, and 1.6 ppm with intensities 2:6:2, corresponding to 10 B−Cl units at B(8,8'), B(4,4', 9,9',12,12'), and B(7,7'). In addition, the four doublets that appear in the $^{11}$B NMR spectrum at 0.2, −14.3, −17.1, and −27.7 ppm, with intensities 2:2:2:2, correspond to the B−H units of the boron atoms B(10,10'), B(5,5',11,11'), and B(6,6'), respectively. In contrast, the $^{11}$B NMR spectrum of Cs[Cl$_{12}$-1] presents three singlets at 11.5, 5.6, and 0.7 ppm with intensities 2:8:2, corresponding to B(8,8'), B(4,4',9,9',10,10',12,12'), and B(10,10'), respectively, which confirms the 12-boron-cluster vertex substitution. Two further doublets with intensities 4:2, corresponding to the B(5,5',11,11') and B(6,6') B−H vertices, respectively, are also observed (see the SI).

Moreover, the $^{11}$B NMR spectra for Cs[Cl$_{10}$-1] and Cs[Cl$_{12}$-1] unveil a B(4)−Cl signal very different from its supposed equivalent B(7)−Cl (Δppm = 4.81), demonstrating again that the compounds retain the intramolecular B−Cl⋯H−C$_{12}$ interactions in solution, as shown above by $^1$H NMR.

Concerning the NMR characterization of [NMe$_4$][Cl$_{10}$-1], the situation is very different (Figure 6). Even though the elemental analysis and MALDI-TOF-MS at the negative mode confirm the purity of the product, the $^{11}$B NMR spectrum shows that many signals are difficult to characterize because of the presence of the different structural isomers [Cl$_{10}$-1]$^-$ and [Cl$_{12}$-1]$^-$.

Figure 5. B(7)−Cl⋯H−C(1') and C(2)−H⋯Cl−B(4') intramolecular interactions of the structures (a) [Cl$_{10}$-1]$^-$ and (b) [Cl$_{12}$-1]$^-$, responsible for their gauche conformation. (c) $^1$H NMR spectra in (CD$_3$)$_2$CO of Cs[Cl$_{10}$-1] (in orange) and Cs[Cl$_{12}$-1] (in purple).

The $^1$H NMR spectrum of [NMe$_4$][Cl$_{10}$-1] (Figure 6) presents three singlets at 4.92 and 4.87 ppm and one broad signal at 4.07 ppm, indicating the existence of an isomeric mixture, but integration of the proton peaks corresponding to the C−H signals of the $^1$H NMR spectrum provides a rough ratio of 55:45 α/β isomers (Figure 6). Fortunately, separation of the mixture was possible thanks to the different polarities of the isomers. In particular, the isomer [Cl$_{10}$-1]$^-$ was very insoluble in chloroform, leading to an isomeric pure product that could be analyzed by $^1$H, $^{13}$B, and $^{13}$C[$^1$H] NMR (see the SI).

Figure 6. $^1$H NMR spectra in (CD$_3$)$_2$CO of the mixture [NMe$_4$][Cl$_{10}$-1] (dark green), isolated [NMe$_4$][Cl$_{10}$-1] (light green), and isolated [NMe$_4$][Cl$_{12}$-1] (blue).

Electrochemical Redox Couples. The $E_{1/2}$(Co$^{III}$/Co$^{II}$) values for [Cl$_{10}$-1]$^-$, [Cl$_{12}$-1]$^-$, and [Cl$_{12}$-1]$^-$ were experimentally obtained by cyclic voltammetry (CV) and compared with the other chlorinated derivatives available in the literature (Figures 7 and Table 1). These results indicated not only the redox potential of Co$^{III}$/Co$^{II}$ but also the reversibility of the system. For [NMe$_4$][Cl$_{10}$-1] and [NMe$_4$][Cl$_{12}$-1], their ΔM values are less than 100, 99.8, and 62 mV. On the other hand, [NMe$_4$][Cl$_{14}$-1] shows a broader signal with a ΔM of 183 mV (Figure 7 and Table 1), most likely due to the mixture of isomers, which causes slightly different potentials, and because of the overlap of the two traces, a thicker signal is found.

As a rule of thumb, it was considered that each new chloro added to the structure contributes +0.12 V to the $E_{1/2}$(Co$^{III}$/Co$^{II}$) value. Figure 8 shows that indeed the increment of $E_{1/2}$(Co$^{III}$/Co$^{II}$) (Δ$E_{1/2}$) is quasilinear, except for the first ([Cl$_{12}$-1]$^-$) and last ([Cl$_{12}$-1]$^-$) points, showing a considerable deviation from the expected values. This accounts for the importance of the chlorinated position, a phenomenon previously observed in the iodinated derivatives. It has been demonstrated that the anionic [1]$^-$ cluster is a global 3D aromatic system with a negative charge delocalized all over the system.

Considering that the chloro substituent is an electron-withdrawing group, each additional chloride makes
the redox site more positive, and consequently the redox potential of the couple CoIII/CoII becomes more positive and then easier to reduce. In addition, the impact of this effect depends on the distance of the chlorinated position to the cobalt atom. The substituents that are in the plane nearest to cobalt (η5-C2B3) affect the redox potential of the CoIII/CoII couple more than those on a more distant plane (B5) or in the B(10) position (Figure 8a). Theoretical studies and the crystal structures of [NMe4][Cln−1], [NMe4][Cln−2]−, and Cs[Cln−2]− suggest that the chlorination order for [1]− is first B(8), followed by B(9,12) (equivalent positions), B(4,7), B(8), B(5,11), and finally B(6), where the last three are very difficult to chlorinate. Therefore, the largest potential gaps are found for [Cl2−]− and [Cl12−]−, which correspond to the chlorination of B(8) and B(10), respectively. To demonstrate our hypothesis, we synthesized [NMe4][3,3′-Co(4,7-Cl2-1,2-C2B9H9)2] and studied its electrochemistry. The synthesis was done following the methodology already described with some minor modifications (see the SI for the synthesis and characterization of [NMe4][3,3′-Co(4,7-Cl2-1,2-C2B9H9)2]); notice the distinct positions of chlorination of [NMe4][3,3′-Co(4,7-Cl2-1,2-C2B9H9)2] with regard to what we call [Cln−1]−, [NMe4][3,3′-Co(8,9-Cl1-1,2-C2B9H9)2]. In [Cln−1]−, one B−Cl is in the plane η5-C2B3 next to cobalt and the second B−Cl is in the more distant plane B5. In [NMe4][3,3′-Co(4,7-Cl1-1,2-C2B9H9)2], both B−Cl bonds are in the plane next to cobalt. Thus, E1/2(CoIII/CoII) should be more positive in [NMe4][3,3′-Co(4,7-Cl1-1,2-C2B9H9)2]. The CV experiment presents a redox potential of −1.13 V versus Fc+/Fc, a value of E1/2(CoIII/CoII) = 0.07 V more positive than the −1.20 V for [Cl2−]− (Table 1). In addition, this experiment demonstrates the hypothesis of a broad ΔmV.
value for \([\text{Cl}_1^{-1}]^−\) due to overlap of the two redox curves for the two isomers \([\text{Cl}_{1\alpha}^{-1}]^−\) and \([\text{Cl}_{1\beta}^{-1}]^−\), proving that both are reversible systems.

**CONCLUSIONS**

In this paper, we have demonstrated that, with a single platform, \([3,3′-\text{Co}-(1,2-\text{C}_2\text{B}_{9}\text{H}_{11})_2]^{-1}\), with a restricted number of equivalent sites, it has been possible by sequential halogenation to chlorinate up to 12 out of 18 possible positions. Earlier work indicated that each chloro substitution results in a potential modulation in the range 0.1−0.13 V. However, as is demonstrated here, it depends on the distance of the substitution site to the metal center. As a result of this, the number of chloro substituents × 0.1 is a quite predictive equation for the voltage modulation. We mentioned earlier that our system was quite simple. To do this, we synthesize the molecule with the desired potential in a single reaction in a single flask, and this was achieved. In this way, we have made derivatives with 8, 10, and 12 chloro substituents, \([\text{Cl}_1^{-1}]^−\), \([\text{Cl}_{1\alpha}^{-1}]^−\), and \([\text{Cl}_{1\beta}^{-1}]^−\), where \([\text{Cl}_1^{-1}]^−\) is \([\text{Co}_2(\text{C}_2\text{B}_{9}\text{H}_{11})_2]^{-}\). Then, add to the \([\text{Cl}_1^{-1}]^−\), \([\text{Cl}_{1\alpha}^{-1}]^−\), \([\text{Cl}_{1\beta}^{-1}]^−\), and \([\text{Cl}_{12}^{-1}]^−\) described earlier. A total of 1.3 V is modulated stepwise with the particularity that each molecule occupies the same or a very similar volume so that solid solutions have crystallographically been encountered. This is a major breakthrough, but we cannot go further with \([\text{Cl}_1^{-1}]^−\) because substitutions with more than 12 chloro substituents are very difficult, at least with the current procedure. Does this mean that we cannot go beyond these potential values with metallacarboranes? The answer is yes, it is possible, and this is what we are working on now. If instead of using only cobalt, we use the much more abundant iron, i.e., we move from \([\text{Fe}(\text{C}_2\text{B}_{9}H_{11})_2]^{-}\) to \([\text{Co}(\text{C}_2\text{B}_{9}H_{11})_2]^{-}\), we shift all at once 1 V to more positive values. It is only to be expected that the tuning achieved by halogenation is comparable to \([\text{Cl}_1^{-1}]^−\), and the first results support this. \([\text{Fe}(\text{C}_2\text{B}_{9}H_{11})_2]^{-}\) in terms of the potential is equivalent to \([\text{Cl}_1^{-1}]^−\). We hope that, with only two metals and the same platform, a potential range equivalent to 2 V can be achieved.

Up to now, \([\text{Cl}_1^{-1}]^−\) was the highest chloro derivative of COSAN synthetically quasi-pure. Now, after 39 years since the first synthesis of \([\text{Cl}_1^{-1}]^−\), three newly high chlorinated derivatives of \([\text{Cl}_1^{-1}]^−\) are introduced in good yield to the group of chloro derivatives of \([\text{Cl}_1^{-1}]^−, [\text{Cl}_{1\alpha}^{-1}]^−, [\text{Cl}_{1\beta}^{-1}]^−, \text{and} [\text{Cl}_{12}^{-1}]^−\).
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01822.

Instrumentation, materials and methods, syntheses and characterization of the compounds, 11B{[H]}, 1H, 1H-\{1B\}, 1B, and 13C{[H]} NMR, MALDI-TOF-MS, IR, and CV, crystal structures, crystal packaging across the a, b, and c axes, and crystallographic data (PDF)

Accession Codes
CCDC 2087208–2087210 contain the supplementary crystallographic data for this paper. These data can be obtained of free charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Pfannschmidt, T. Chloroplast redox signals: how photosynthesis controls its own genes. Trends Plant Sci. 2003, 8 (1), 33–41.
(2) Melin, F.; Hellwig, P. Redox Proteins of the Membrane Proteins from the Respiratory Chain. Chem. Rev. 2020, 120 (18), 10244–10297.
(3) Baier, M.; Dietz, K.-J. Chloroplasts as source and target of cellular redox regulation: a discussion on chloroplast redox signals in the context of plant physiology. J. Exp. Bot. 2005, 56 (416), 1449–1462.
(4) Beratan, D.; Onuchic, J.; Winkler, J.; Gray, H. Electron-tunneling pathways in proteins. Science 1992, 258 (5089), 1740–1741.
(5) Yang, Z.; Zhang, J.; Kintner-Meyer, M. C.; Lu, X.; Choi, D.; Lemmon, J. P.; Liu, J. Electrochemical energy storage for green grid. Chem. Rev. 2011, 111 (5), 3577–3613.
(6) Wang, Y.; Song, Y.; Xia, Y. Electrochemical capacitors: mechanism, materials, systems, characterization and applications. Chem. Soc. Rev. 2016, 45 (21), 5925–5950.
(7) Wang, Z.-L.; Xu, D.; Xu, J.-J.; Zhang, X.-B. Oxygen electrocatalysts in metal–air batteries: from aqueous to nonaqueous electrolytes. Chem. Soc. Rev. 2014, 43 (22), 7746–7786.
(8) Lim, H.-D.; Lee, B.; Bae, Y.; Park, H.; Ko, Y.; Kim, H.; Kim, J.; Kang, K. Reaction chemistry in rechargeable Li–O 2 batteries. Chem. Soc. Rev. 2017, 46 (10), 2873–2888.
(9) Hagfeldt, A.; Graetzel, M. Light-induced redox reactions in nanocrystalline systems. Chem. Rev. 1995, 95 (1), 49–68.
(10) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-sensitized solar cells. Chem. Rev. 2010, 110 (11), 6595–6663.
(11) Li, L.-L.; Diao, E.-W.-G. Porphyrin-sensitized solar cells. Chem. Soc. Rev. 2013, 42 (1), 291–304.
(12) Lu, Y.; Yeung, N.; Sieracki, N.; Marshall, N. M. Design of functional metalloproteins. Nature 2009, 460 (7257), 855–862.
(13) Solomon, E. I.; Szilagyi, R. K.; DeBeer George, S.; Basumallick, L. Electronic Structures of Metal Sites in Proteins and Models: Contributions to Function in Blue Copper Proteins. Chem. Rev. 2004, 104 (2), 419–458.
(14) Marshall, N. M.; Garner, D. K.; Wilson, T. D.; Gao, Y.-G.; Robinson, H.; Nilges, M. J.; Lu, Y. Rationally tuning the reduction potential of a single cupredoxin beyond the natural range. Nature 2009, 462 (7269), 113–116.
(15) Hosseinzadeh, P.; Lu, Y. Design and fine-tuning redox potentials of metalloproteins involved in electron transfer in bioenergetics. Biochim. Biophys. Acta, Bioenerg. 2016, 1857 (5), 557–581.
(16) Bains, R. K.; Warren, J. J. A single protein redox ruler. Proc. Natl. Acad. Sci. U. S. A. 2016, 113 (2), 248–250.
(17) Hosseinzadeh, P.; Marshall, N. M.; Chacón, K. N.; Yu, Y.; Nilges, M. J.; New, S. Y.; Takishima, S. A.; Blackburn, N. J.; Lu, Y. Design of a single protein that spans the entire 2-V range of physiological redox potentials. Proc. Natl. Acad. Sci. U. S. A. 2016, 113 (2), 262–267.
(18) Liu, J.; Chakraborty, S.; Hosseinzadeh, P.; Yu, Y.; Tian, S.; Petrik, I.; Bhagi, A.; Lu, Y. Metalloproteins Containing Cytochrome, Iron–Sulfur, or Copper Redox Centers. Chem. Rev. 2014, 114 (8), 4360–4499.
(19) Lever, A. Electrochemical parametrization of metal complex redox potentials, using the ruthenium (II)/ruthenium (II) couple to generate a ligand electrochemical series. Inorg. Chem. 1990, 29 (6), 1271–1285.
(20) Wahab, A.; Douvris, C.; Klima, J.; Šembera, F.; Ugolotti, J.; Kaleta, J.; Ludvik, J.; Michl, J. Anodic Oxidation of 18 Halogenated and/or Methylated Derivatives of CB11H12−. Inorg. Chem. 2017, 56 (1), 269–27621.
(21) Wixtrom, A. I.; Shao, Y.; Jung, D.; Machan, C. W.; Kever, S. N.; Qian, E. A.; Austell, 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, 711–71722.
(22) Marsh, B. J.; Hampton, L.; Goggin, S.; Frost, C. G. Fine-tuning of ferrocene redox potentials towards multiplex DNA detection. New J. Chem. 2014, 38 (11), 5260–5263.
(23) Simonova, A.; Magriá, I.; Šýkorová, V.; Pohl, R.; Ortiz, M.; Havran, L.; Fojta, M.; O’Sullivan, C. K.; Hocék, M. Tuning of oxidation potential of ferrocene for ratiometric redox labeling and coding of nucleotides and DNA. Chem. - Eur. J. 2020, 26 (6), 1286.
(24) Yang, W.-W.; Zhong, Y.-W.; Yoshikawa, S.; Shao, J.-Y.; Masaoka, S.; Sakai, K.; Yao, J.; Haga, M.-a. Tuning of redox potentials by introducing a cyclometallated bond to bis-tridentate ruthenium (II) complexes bearing bis (N-methylbenzimidazolyl) benzene or pyridine ligands. Inorg. Chem. 2012, 51 (2), 890–899.
(25) Brown, K. N.; Gulyas, P. T.; Lay, P. A.; McAlpine, N. S.; Masters, A. F.; Phillips, L. Electrochemistry of chlorinated ferrocenes: stability of chlorinated ferrocenium ions. J. Chem. Soc., Dalton Trans. 1993, No. 6, 835–840.
A simple membrane with the electroactive 
Water and N, N-dimethylformamide. 
Haloferrocenes revealed through a comprehensive study of the 
Organometallics 
Organometallics 
Fluoroferrocenes. 
J. Braz. Chem. Soc. 
Recombination study of dye sensitized solar cells with natural 
vehicles for neutron capture therapy. 
Crystallization and application to membrane translocation. 
Polyoxometalates for Efficient Electron-Coupled Proton-Buffered 
Sensitized Solar Cells Based on Hydroquinone/Benzoquinone as a 
Bioinspired Redox Couple. 
Acc. Chem. Res. 
50, 2019, 14340. 
Selective inhibitors of carbonic anhydrase IX. J. Med. Chem. 2019, 62, 9560−9575. 
Murphy, N.; McCarthy, E.; Dwyer, R.; Farrás, P. Boron clusters as breast cancer therapeutics. J. Inorg. Biochem. 2021, 218, 111412. 
Hosmane, N. S.; Yinghua, Z.; Maguire, J. A.; Kaim, W.; Takagaki, M. Nano and dendritic structured carbones and mettallcarboranes: From materials to cancer therapy. J. Organomet. Chem. 2009, 694 (11), 1690−1697. 
Couto, M.; Manfreda, I.; Cabrera, M.; Cabral, P.; Teixidor, F.; Cerecetto, H.; Viñas, C.; Metallcarborane sulfamides: Unconventional, specific, and highly selective inhibitors of carbomic anhydrase IX. J. Med. Chem. 2011, 54, 952−957. 
Mens, F.; Teixidor, F.; Sillanpää, R.; Lupu, M.; Vinás, C.; Sillanpää, R.; Haukka, M.; Frondotonda, X.; Paradinas, M.; Ocal, C.; Teixidor, F. Electron Accumulative Molecules. J. Am. Chem. Soc. 2018, 140 (8), 2957−2970. 
Axell, J. C.; Saleh, L. M.; Qian, E. A.; Wixtrom, A. I.; Spokony, A. M. Synthesis and applications of perfunctionalized boron clusters. Inorg. Chem. 2018, 57 (5), 2333−2350. 
Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reinjets, M.; Warren, L. F.; Jr; Weign, P. A.-P. Dicarbollid derivatives of the transition metals. Metalloocene analogs. J. Am. Chem. Soc. 1968, 90 (4), 879−896. 
Peipol, A.; Teixidor, F.; Sillanpää, R.; Lupu, M.; Viñas, C. Stepwise Sequential Redox Potential Modulation Possible on a Single Platform. Angew. Chem., Int. Ed. 2011, 50 (52), 12491−12495. 
Santos, E. C.; Pinkerton, A. B.; Kinkead, S. A.; Hurlburt, P. K.; Jasper, S. A.; Sellers, C. W.; Huffman, J. C.; Todd, J. L. Syntheses of nido-9,11-X2−7,8-C2B9H10− anions (X = Cl, Br or I) and the synthesis and structural characterization of N(C2H5)4[commodo-3,3′-Co(4,7-B2=3,1,2-CoC2B9H12)]. Polynorodon 2000, 19 (15), 1777−1781. 
Hurlburt, P. K.; Miller, R. L.; Abney, K. D.; Foreman, T. M.; Butcher, R. J.; Kinkead, S. A. New synthetic routes to B-halogenated derivatives of cobalt dicarbide. Inorg. Chem. 1995, 34 (21), 5215−5219. 
Máté, L.; Macácek, F.; Rajec, P.; Heimánhek, S.; Plešek, J. B-Halogen derivatives of the bis(1,2-dicarbollide)co(III) anion. Polyhedron 1982, 1 (6), 511−519. 
González-Cardoso, P.; Stoica, A.-I.; Farrás, P.; Peipol, A.; Viñas, C.; Teixidor, F. Additive Tuning of Redox Potential in Metalcarboranes by Sequential Halogen Substitution. Chem. - Eur. J. 2010, 16 (22), 6660−6665. 
Wong, E. H.; Kabbani, R. M. Boron halide clusters and radicals: synthesis and interconversions of the three oxidation states of a nine-boron polyhedral. Inorg. Chem. 1980, 19 (2), 451−455. 
Brown, H. C. J. I. Sulfurf chloride in organic chemistry. Ind. Eng. Chem. 1944, 36 (9), 785−791. 
Masilamani, D.; Rogie, M. M. Sulfur chloride as a reagent for selective chlorination of symmetrical ketones and phenols. J. Org. Chem. 1981, 46 (22), 4486−4489. 
Gu, W.; Ozerov, O. V. Exhaustive chlorination of [B12H12]+−without chlorine gas and the use of [B12C12]2− as a supporting anion in catalytic hydrodefluorination of aliphatic C−F bonds. Inorg. Chem. 2011, 50 (7), 2726−2728. 
García-Mendiola, T.; Bayon-Pizarro, V.; Zualet, A.; Fuentes, I.; Pariente, F.; Teixidor, F.; Viñas, C.; Lorenzo, E. Metallcarboranes as
tunable redox potential electrochemical indicators for screening of gene mutation. *Chem. Sci.* 2016, 7 (9), 5786–5797.

(62) Ruiz-Rosas, R.; Fuentes, I.; Viñas, C.; Teixidor, F.; Morallón, E.; Cazorla-Amorós, D. Tailored metallacarboranes as mediators for boosting the stability of carbon-based aqueous supercapacitors. *Sustainable Energy Fuels* 2018, 2 (2), 345–352.

(63) Fuentes, I.; Pujols, J.; Viñas, C.; Ventura, S.; Teixidor, F. Dual Binding Mode of Metallacarborane Produces a Robust Shield on Proteins. *Chem. - Eur. J.* 2019, 25 (55), 12820–12829.

(64) Zaulet, A.; Teixidor, F.; Bauduin, P.; Diat, O.; Hirva, P.; Ofori, A.; Viñas, C. Deciphering the role of the cation in anionic cobaltabis(dicarbollide) clusters. *J. Organomet. Chem.* 2018, 865, 214–225.

(65) Knoth, W. H.; Miller, H.; Sauer, J. C.; Balthis, J.; Chía, Y.; Muetterties, E. Chemistry of boranes. IX. Halogenation of B10H10−2 and B12H12−2. *Inorg. Chem.* 1964, 3 (2), 159–167.

(66) Juárez-Pérez, E. J.; Núñez, R.; Viñas, C.; Sillanpää, R.; Teixidor, F. The Role of C−H···H−B Interactions in Establishing Rotamer Configurations in Metallabis(dicarbollide) Systems. *Eur. J. Inorg. Chem.* 2010, 2010 (16), 2385–2392.

(67) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press, 1997.

(68) Lupu, M.; Zaulet, A.; Teixidor, F.; Ruiz, E.; Viñas, C. Negatively Charged Metallacarborane Redox Couples with Both Members Stable to Air. *Chem. - Eur. J.* 2015, 21 (18), 6888–6897.

(69) Poater, J.; Viñas, C.; Bennour, I.; Escayola, S.; Solà, M.; Teixidor, F. Too persistent to give up: Aromaticity in boron clusters survives radical structural changes. *J. Am. Chem. Soc.* 2020, 142 (20), 9396–940770.

(70) Masalles, C.; Borrós, S.; Viñas, C.; Teixidor, F. Are Low-Coordinating Anions of Interest as Doping Agents in Organic Conducting Polymers? *Adv. Mater.* 2000, 12 (16), 1199–1202.

(71) Farras, P.; Viñas, C.; Teixidor, F. Preferential chlorination vertices in cobaltabis(dicarbollide) anions. Substitution rate correlation with site charges computed by the two atoms natural population analysis method (2a-NPA). *J. Organomet. Chem.* 2013, 747, 119–125.

(72) Tarres, M.; Arderiu, V. S.; Zaulet, A.; Viñas, C.; Fabrizi de Biani, F.; Teixidor, F. How to get the desired reduction voltage in a single framework! Metallacarborane as an optimal probe for sequential voltage tuning. *Dalton Trans.* 2015, 44 (26), 11690–11695.

(73) Rudakov, D. A.; Shirokii, V. L.; Knizhnikov, V. A.; Bazhanov, A. V.; Vecher, E. I.; Maier, N. A.; Potkin, V. I.; Ryabtsev, A. N.; Petrovskii, P. V.; Sivaev, I. B.; Bregadze, V. I.; Eremenko, I. L. Electrochemical synthesis of halogen derivatives of bis(1,2-dicarbollyl)cobalt(III). *Russ. Chem. Bull.* 2004, 53 (11), 2554–2557.