

Supplementary Information

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1. Materials & methods

Chemicals required: Potassium hydroxide pellets (KOH), ethanol (EtOH), hydrochloric acid (HCl, 37%), trimethylamine hydrochloride (NMe₃.HCl, 98%), potassium *tert*-butoxide (^tBuOK, 1.7M), anhydrous iron (II) chloride (FeCl₂) and caesium chloride (CsCl) were all purchased from Sigma-Aldrich and used without any further purification. Caesium cobaltabisdicarbollide (Cs[*o*-COSAN])¹ and *o*-carborane were procured from Katchem Spol.sr.o.

Synthesis of Cs and Na [*o*-FESAN]: [*o*-FESAN]⁻ compounds were synthesized following a reported procedure.² Briefly, a ratio of 1:5 *o*-carborane (1 g, 144.43 g/mol) and KOH (1.96 g, 56g/mol), respectively, were dissolved in 25 mL EtOH and refluxed for 5 h. The mixture was then neutralized using 1 M HCl and the solvent was reduced by evaporating the EtOH. A saturated solution of NMe₃.HCl was added to the solution to obtain white precipitates of *nido-o*-carborane which were then filtered and vacuum dried.

1 g of *nido-o*-carborane (264.59 g/mol) was dissolved in 20 mL dry THF and cooled to 0°C. In a ratio of 1:2.5 *nido-o*-carborane to ^tBuOK, 5.88 mL of ^tBuOK (112.21 g/mol) was added to solution, drop by drop, and reacted for 1 h at 0°C followed by another 1 h at room temperature forming a white curdy solution. Subsequently, 0.937 g of anhyd. FeCl₂ (126.75 g/mol), following a ratio of 1:2 *nido-o*-carborane to FeCl₂, dissolved in 16 mL dry THF was added to the reaction mixture resulting in a brownish purple colour. The mixture was then refluxed for 3h and left exposed to oxygen, overnight, resulting in purple coloured solution. All these reactions were carried out in N₂ atmosphere with strict expulsion of oxygen in order to maximize the yield and avoid unsubstituted products. The reaction mixture was purified by evaporating the THF and dissolving the compound in minimum amount of

diethyl ether (30 mL) which was extracted using 0.1 M HCl. Then the solvent was reduced and the compound was further dissolved in distilled water. The solution was then added to a saturated solution of CsCl to obtain dark purple precipitates of Cs[*o*-FESAN] which were then filtered and vacuum dried.

The Na salts of [*o*-COSAN] and [*o*-FESAN] were obtained using a strong cationic exchange resin column.³ Briefly, a chromatographic column is loaded with strongly acidic cationic exchange resin and is pre-conditioned prior to use. Initially, 150 mL of 3M HCl is passed through the column slowly to load it with H⁺. Thereafter, distilled water is passed through it, quickly, until neutral pH is obtained to remove the excess HCl. A solution of 3M NaCl is flowed through the column to replace H⁺ with the cation Na⁺, until neutral pH is attained. After loading the column with Na⁺, to remove excess NaCl distilled water is passed through the column. Subsequently, the column is loaded with 30 mL of acetonitrile/water (50:50) mixture to adjust the column's liquid composition. Approximately, 200 mg of the Cs salts of the metallocarboranes were dissolved in minimum volume of acetonitrile/water (50:50) and repeatedly (3 times) flowed through the column. The solution is collected and the solvent is evaporated. The compound obtained is dried in vacuum and stored.

The compounds were characterized using MALDI-TOF: *m/z* calc. for [FESAN]: 320.64; found: 321.17 as well as IR.

General CV measurement protocol: Cyclic voltametric measurements were carried out in an AutoLab PGSTAT302N potentiostat/galvanostat from Metrohm using its in-built software as well as in an AutoLab PGSTAT30 from Eco-Chemie using the software package GPES 4.9. For a typical CV experiment, a three-electrode system consisting of Pt wire as the auxiliary electrode, glassy carbon (GC) as the working electrode and Ag/AgCl (1M KCl) or saturated calomel electrode (SCE) as the reference electrode in aqueous and non-aqueous systems, respectively, were used. The potential window for each of the compounds were: -0.7 - -1.7 V, 0.2 - -0.6 V, 0.8 - -0.2 V vs. Ag/AgCl (1M KCl) for Na[*o*-COSAN], Na[*o*-FESAN] and FcMe, respectively, for aqueous system and -0.9 - -1.9 V, 0 - -0.6 V, 0.8 - 0 V vs. SCE for Cs[*o*-COSAN], Cs[*o*-FESAN] and Fc, respectively, for non-aqueous systems. Each of the measurement involved 3 scans with a scan rate of 100mV/s in an inert atmosphere, unless stated otherwise.

The solutions were prepared by choosing a concentration suitable enough to produce a reasonable CV response. The final volume of all the solutions measured were 3 mL. 0.3 M KNO₃ (101.103 g/mol) solution was prepared by dissolving 90.99 mg of KNO₃ in 3 mL distilled water as the aqueous electrolyte. Similarly, 0.3 M tetrabutylammonium perchlorate (TBAP, 341.91 g/mol) solution was prepared by dissolving 307.7 mg TBAP in 3 mL dry acetonitrile (AcN) as the organic electrolyte. For Na[*o*-COSAN] (346.74 g/mol), a 30 mM solution was prepared by dissolving 31.2 mg of the metallocarborane in 0.3 M KNO₃ electrolytic solution. While, for Na[*o*-FESAN] (388.67 g/mol) 1mM solution was prepared by dissolving 1.16 mg in 0.3 M KNO₃. In case of FcMe (4.3 mg, 216.06 g/mol), as it was only partially soluble in water, a stock solution of 10 mM 2 mL solution in methanol was prepared, initially. For CV measurements, 0.3 mL of stock solution was taken to produce 1 mM FcMe in 0.3 M KNO₃. For Cs[*o*-COSAN] (456.65 g/mol), 5 mM solution was prepared for CV measurements by dissolving 6.8 mg in 0.3 M TBAP/dry AcN. While, for Cs[*o*-FESAN] (453.57 g/mol) and Fc (186.04 g/mol), 1 mM solutions were prepared by dissolving 1.3 mg and 0.5 mg, respectively, in 0.3 M TBAP/dry AcN.

The parameters analysed for each of the CV measurements to reach a conclusive understanding of the redox behaviour of the compounds were the redox peak potentials, namely cathodic (E_{pc}) and anodic (E_{pa}), the formal peak potential (E^0) calculated as $(E_{pc} + E_{pa})/2$ and the peak separation potential (ΔE) calculated as $E_{pa} - E_{pc}$.

Changing the electrolyte: To determine the effect of various electrolytes on the redox behaviour of Na[*o*-COSAN] and Na[*o*-FESAN] in comparison to FcMe, CV measurements were carried out in 0.3 M concentration of different electrolytes. CV measurements were performed in electrolytes such as KNO₃ and KCl, to understand the effect of varying the anion, while measurements in NaNO₃ were carried out to understand the influence of different cations on the peak potentials. Studies in

phosphate buffer (PB) and phosphate buffer saline (PBS) were done due their significance in biological experiments. Acetic acid was also used as an electrolyte of interest for measurement. In this experiment, most of the commonly used electrolytes were studied to ascertain the constant redox behaviour of the $[3,3'-M(1,2-C_2B_9H_{11})_2]^-$ (M= Co, Fe).

Varying the electrolyte concentration: In order to understand the reversible redox response of the compounds in varying concentration of the electrolyte, CV measurements were performed by changing the concentration of the electrolyte, KNO_3 , from 5 – 500 mM. The measurements were carried out by dissolving, sequentially, the required amount of KNO_3 to attain the desired concentration. Similar experiment was also performed using the organic electrolyte TBAP in dry AcN.

Scan rate experiment: The electrochemical response of the compounds in different scan rates were measured to understand their kinetic behaviour. CV measurements were carried out with scan rates varying from 10 – 1000 mV/s, for both aqueous and non-aqueous electrolytes. Following each measurement, the electrodes were cleaned to ensure to accuracy of the measurement.

Varying the concentration of $[3,3'-M(1,2-C_2B_9H_{11})_2]^-$ (M= Co, Fe): To understand the effect of self-assembly of the metallacarboranes to form micelles and vesicles⁴ in water on their redox behaviour, CV measurements were performed by sequentially varying the concentration of the metallacarboranes in aqueous solutions from 5 – 50 mM for Na[o-COSAN] and 1 – 65 mM for Na[o-FESAN] in 0.3 M KNO_3 electrolyte.

Changing the pH of the electrolytic solution: For a material to be employed as an internal reference, it is important that it has a constant redox potential in different pH as the CV measurements could involve solutions of any pH. Hence, in order to study the effect of varying pH, 0.1 M Britton-Robinson (BR) solution was prepared as the electrolyte by dissolving 6.74 mL H_3PO_4 (0.04 M), 5.76 mL acetic acid (0.04 M) and 6.19 g boric acid (0.04 M) in 1 L of distilled water. The initial pH of the electrolyte was 2, which was sequentially increased as 3, 4, 5 till 12 by the addition of 5 M NaOH. The pH of the solution was adjusted using a calibrated pH meter.

Changing the temperature of the solution: In general, most of the CV measurements are carried out in ambient temperature. Nevertheless, it is important to understand the effect of temperature on the redox behaviour of a compound having the potential application as an internal reference. Consequently, CV measurements were out by increasing the temperature from 25° – 50°C using a temperature controller in intervals of 2°C. The experiment was performed in 0.3 M KNO_3 with GC as the working electrode.

Different working electrode materials: To study the compatibility of $[3,3'-M(1,2-C_2B_9H_{11})_2]^-$ (M= Co, Fe) in different electrode materials such as Pt and Au, CV measurements were performed in both aqueous and non-aqueous electrolytes with the same parameters in comparison with GC. Before employing the electrodes for measurements, the electrodes were subjected to diamond polishing and their characteristic CV responses were recorded in 0.1 M and 0.5 M H_2SO_4 for Au and Pt, respectively, at 100 mV/s for 10 scans.

2. Effect of electrolyte and electrolyte concentration

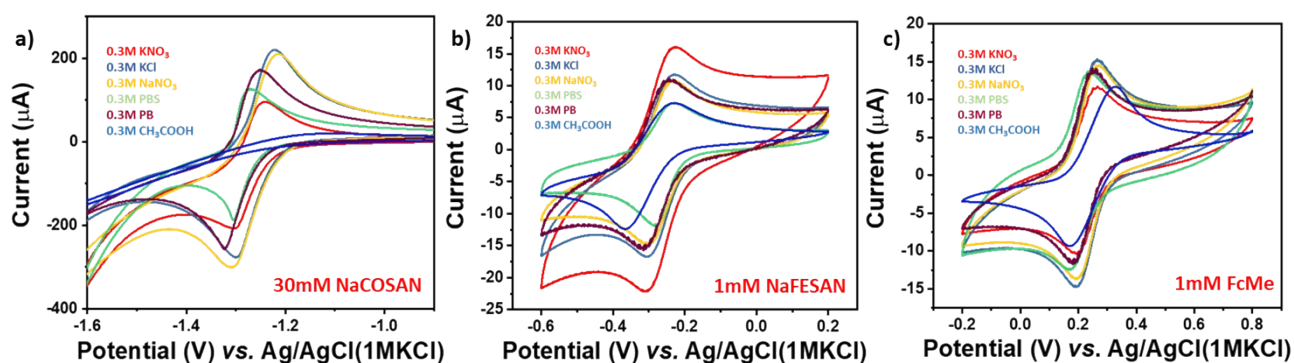
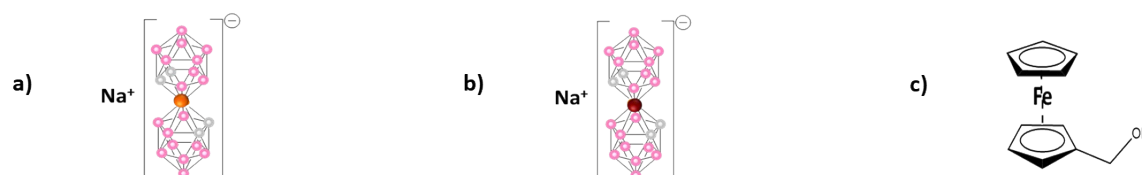


Fig. S1 CV response in different electrolytes of a) 30mM Na[o-COSAN]; b) 1mM Na[o-FESAN]; c) 1mM FcMe with GC as the working and Ag/AgCl (1MKCl) as the reference electrode.



Electrolyte (0.3M)	Epa (V)	Epc (V)	ΔE (V)	Electrolyte (0.3M)	Epa (V)	Epc (V)	ΔE (V)	Electrolyte (0.3M)	Epa (V)	Epc (V)	ΔE (V)
KNO ₃	-1.242	-1.304	0.062	KNO ₃	-0.227	-0.3	0.073	KNO ₃	0.262	0.193	0.069
KCl	-1.223	-1.299	0.076	KCl	-0.229	-0.3	0.071	KCl	0.265	0.19	0.075
NaNO ₃	-1.213	-1.307	0.094	NaNO ₃	-0.23	-0.3	0.07	NaNO ₃	0.268	0.192	0.076
PBS	-1.271	-1.305	0.034	PBS	-0.23	-0.28	0.05	PBS	0.238	0.169	0.069
PB	-1.251	-1.322	0.071	PB	-0.238	-0.3	0.069	PB	0.261	0.19	0.071
Acetic Acid	-	-	-	Acetic Acid	-0.228	-0.368	0.14	Acetic Acid	0.331	0.166	0.165

Table S1 The cathodic (Epc) and anodic (Epa) peak potentials and the peak separation (ΔE) potential vs. Ag/AgCl (1MKCl) for a) Na[o-COSAN]; b) Na[o-FESAN] and c) FcMe for different electrolytes.

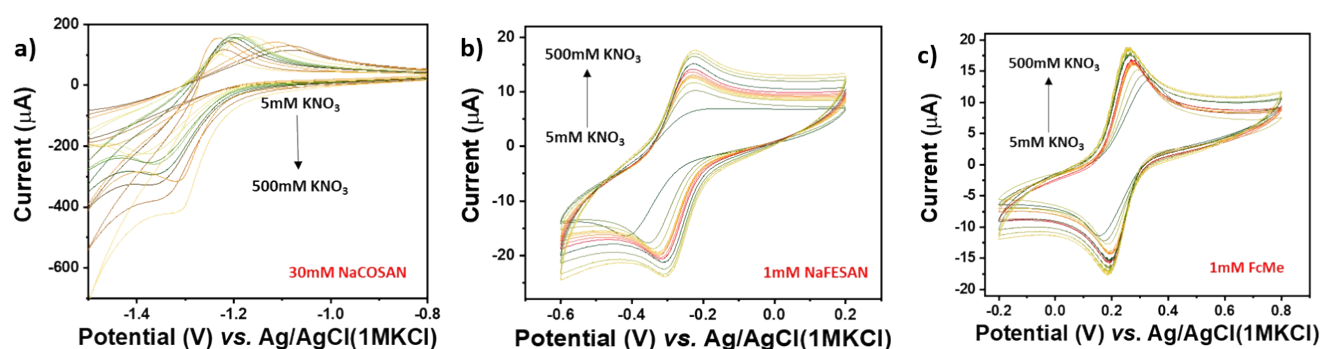


Fig. S2 Varying the concentration of the electrolyte, KNO₃, from 5 – 500 mM for a) Na[o-COSAN]; b) Na[o-FESAN] and c) FcMe with Ag/AgCl as reference and scan rate 100mV/s.

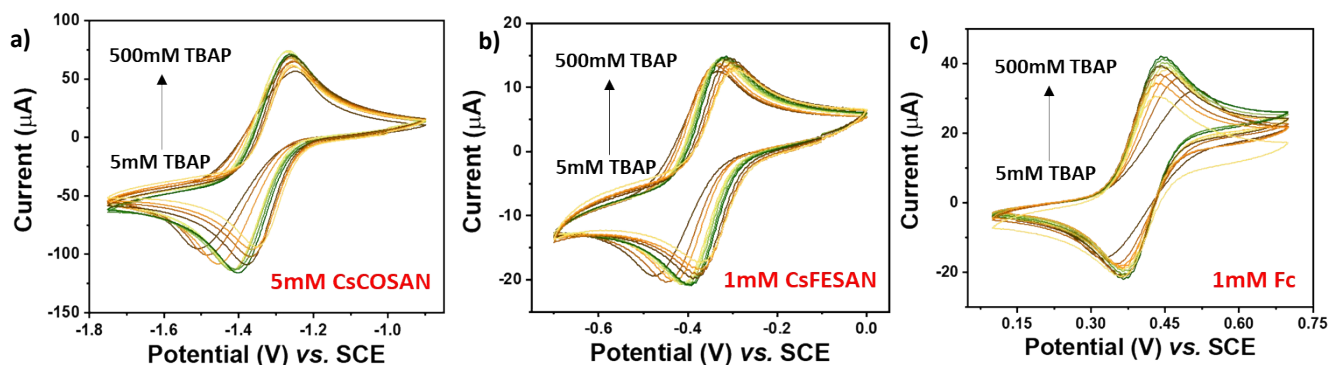


Fig. S3 Varying the concentration of electrolyte, TBAP in dry AcN, for **a)** Cs[σ -COSAN]; **b)** Cs[σ -FESAN] and **c)** Fc from 5 – 500 mM with SCE as reference and scan rate 100mV/s.

3. Varying the scan rates

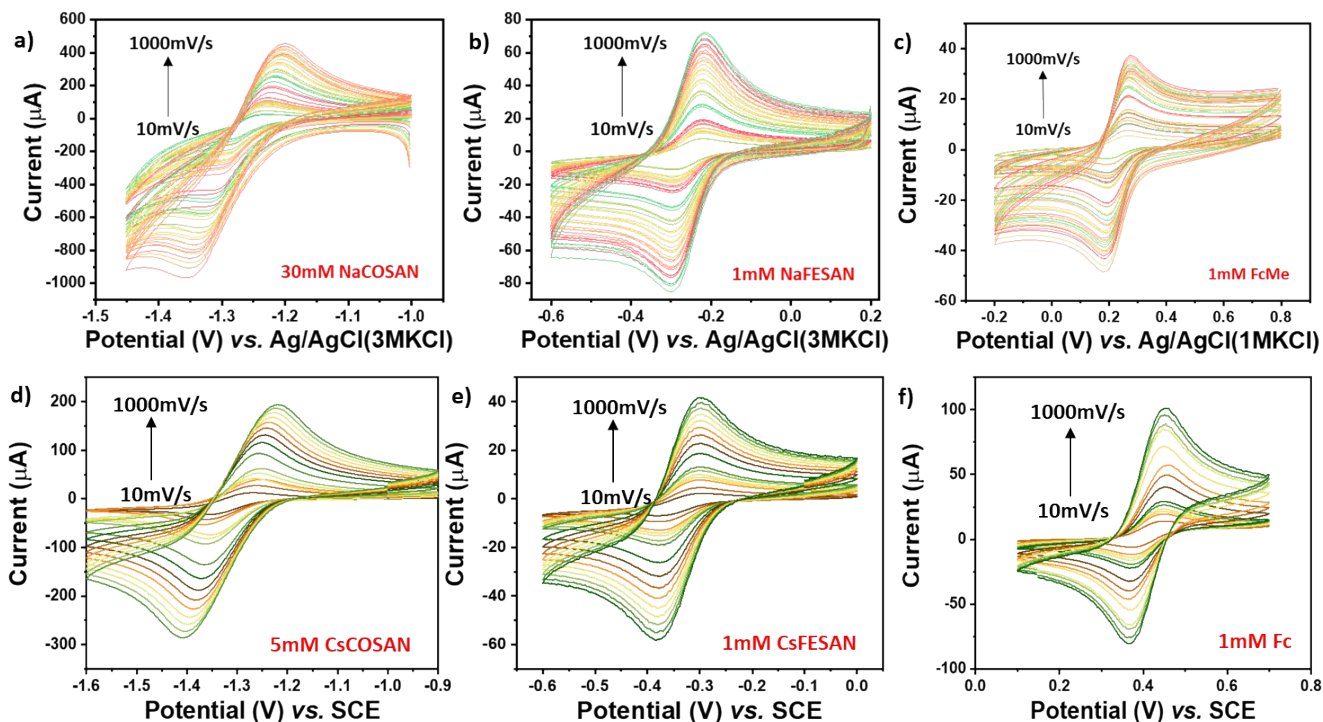


Fig. S4 CV response obtained for each of the compounds by varying the scan rate from 10 – 1000 mV/s in aqueous (0.3M KNO₃) and non-aqueous (0.3M TBAP in dry AcN) electrolytes. Changing the scan rates for: **a)** 30mM Na[σ -COSAN]; **b)** 1mM Na[σ -FESAN] and **c)** 1mM FcMe with Ag/AgCl as the reference (aqueous) and **d)** 5mM Cs[σ -COSAN]; **e)** 1mM Cs[σ -FESAN] and **f)** 1mM Fc with SCE as reference (non-aqueous).

4. Effect of self-assembling of [3,3'-M(1,2-C₂B₉H₁₁)₂] (M= Co, Fe) in aqueous solutions

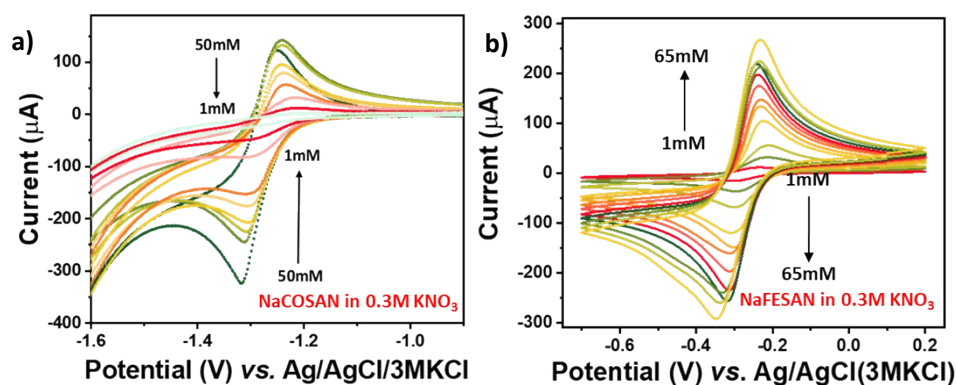


Fig. S5 Changing the concentration of the Na salts of [3,3'-M(1,2-C₂B₉H₁₁)₂] (M= Co, Fe) to study the effect of micellar and vesicle formation in aqueous solution on the electrochemical response. **a)** Na[σ-COSAN] and **b)** Na[σ-FESAN] with 0.3M KNO₃ as the electrolyte.

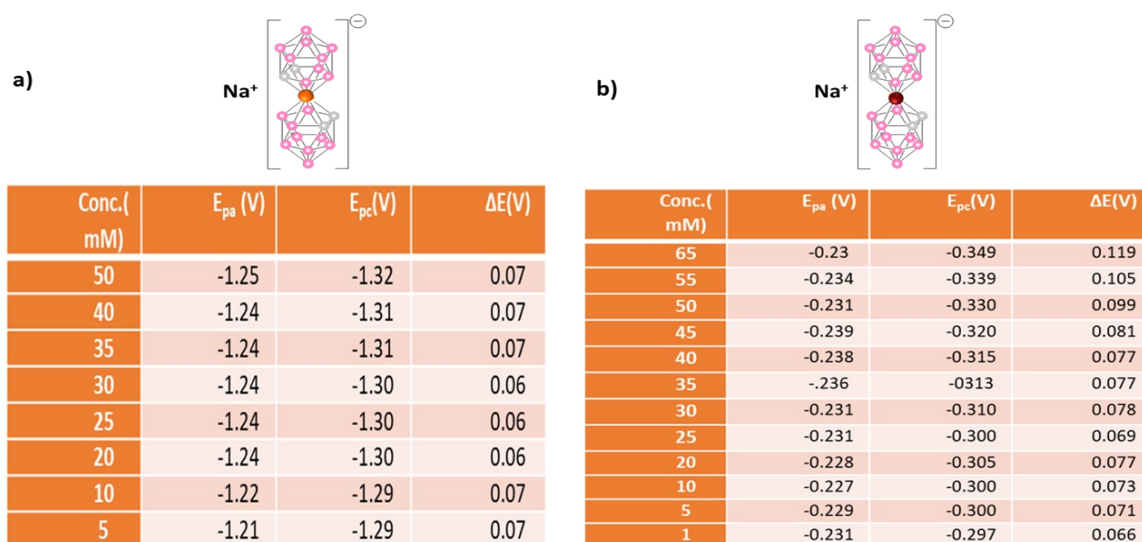


Table S2 The cathodic (E_{pc}) and anodic (E_{pa}) peak potentials and the peak separation (ΔE) potential vs. Ag/AgCl (3MKCl) at different concentrations of **a)** Na[σ-COSAN] and **b)** Na[σ-FESAN] in 0.3M KNO₃.

5. Effect of pH

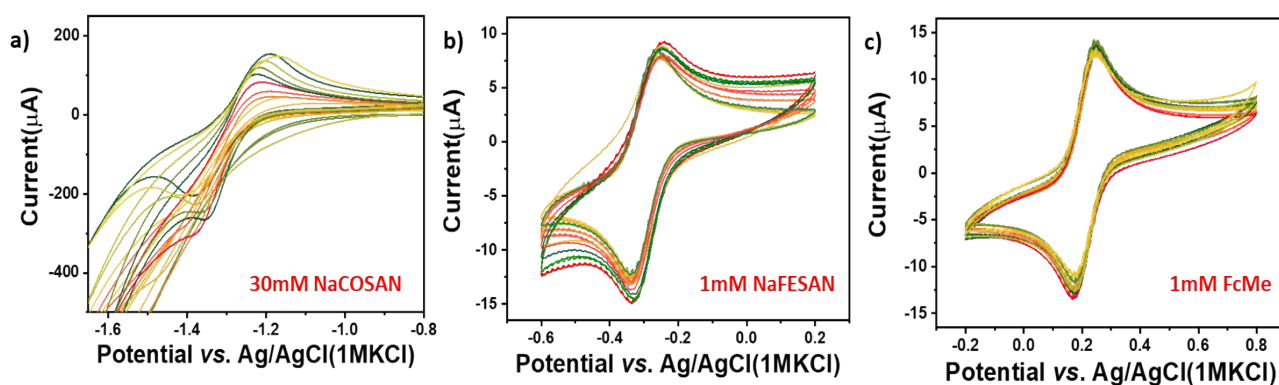


Fig. S6 Effect of changing the pH of the electrolytic solution, 0.1M Britton-Robinson, using 5M NaOH from 2 – 12 for **a)** Na[*o*-COSAN]; **b)** Na[*o*-FESAN] and **c)** FcMe with Ag/AgCl as reference and scan rate 100mV/s.

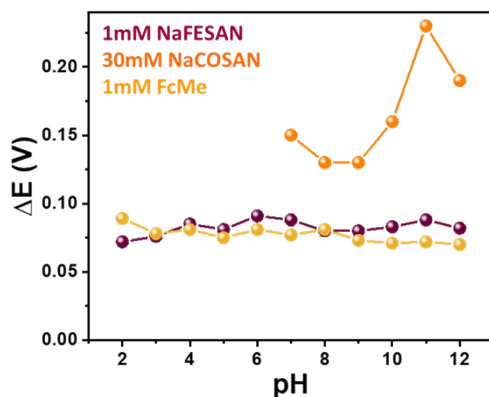


Fig. S7 Comparing the effect of changing the pH of the electrolyte from 2 - 12 on the peak separation potential (ΔE) for [3,3'-M(1,2-C₂B₉H₁₁)₂] (M= Co, Fe) to FcMe.

6. Effect of temperature

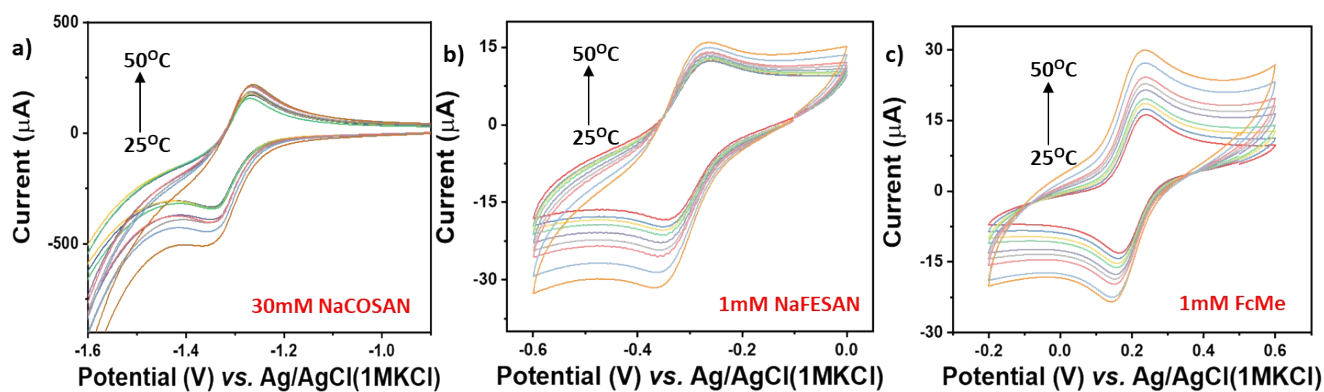


Fig. S8 Effect of changing the temperature from 25° – 50°C for **a)** 30mM Na[*o*-COSAN]; **b)** 1mM Na[*o*-FESAN] and **c)** 1mM FcMe with Ag/AgCl as reference and scan rate 100mV/s.

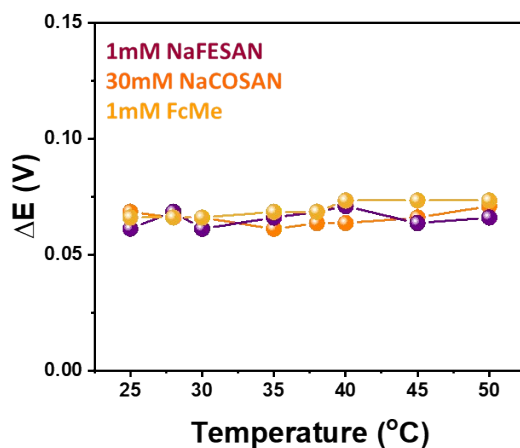


Fig. S9 Comparing the effect of changing the temperature on the peak separation potential (ΔE) for [3,3'-M(1,2-C₂B₉H₁₁)₂] (M= Co, Fe) to FcMe.

7. Different electrode materials

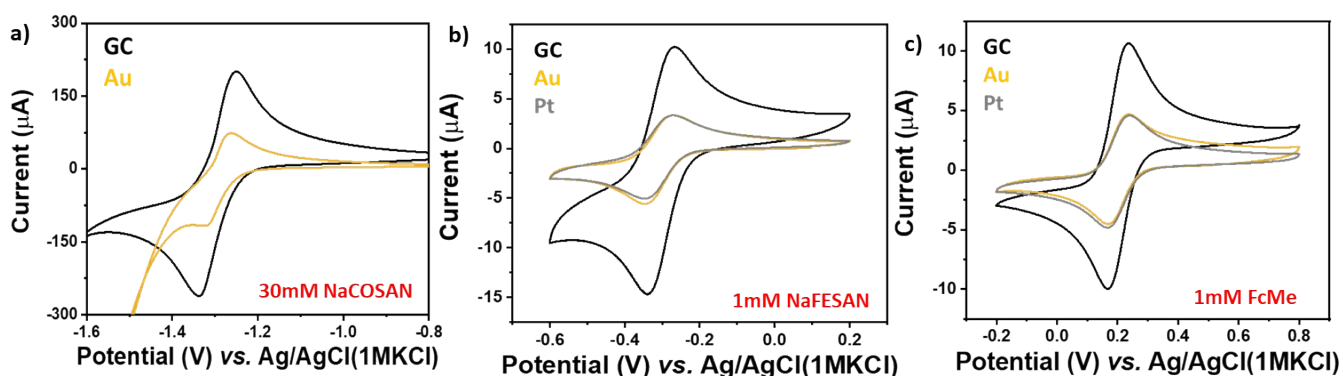


Fig. S10 Electrochemical response in different working electrode materials for **a)** 30mM Na[o-COSAN]; **b)** 1mM Na[o-FESAN] and **c)** 1mM FcMe with Ag/AgCl as the reference and 100 mV/s scan rate. In case of Na[o-COSAN], the Pt electrode could not be used due to the small potential window of it in aqueous solution.

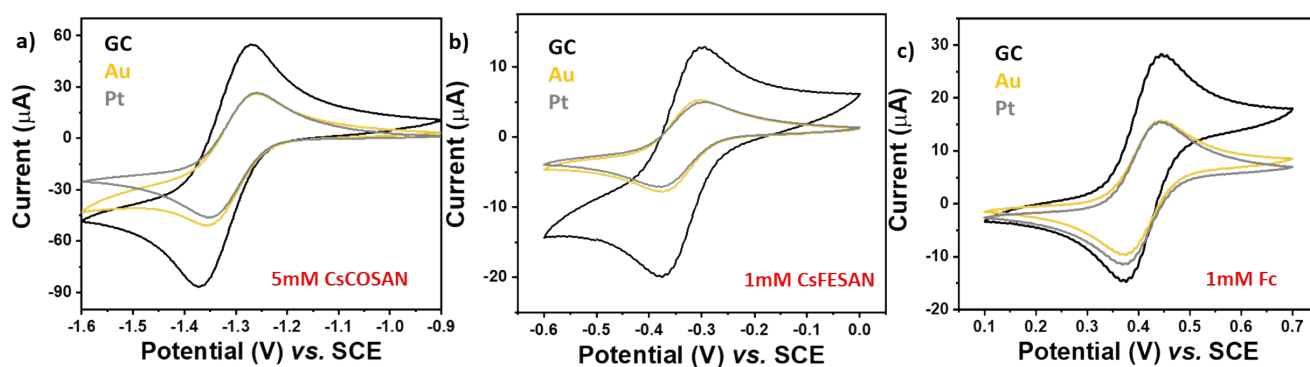


Fig. S11 Electrochemical response in different working electrode materials for **a)** 5mM Cs[o-COSAN]; **b)** 1mM Cs[o-FESAN] and **c)** 1mM Fc with SCE as the reference and 100 mV/s scan rate in 0.3M TBAP/dry AcN.

8. Comparison of Cs and Na [o-FESAN] in aqueous electrolyte

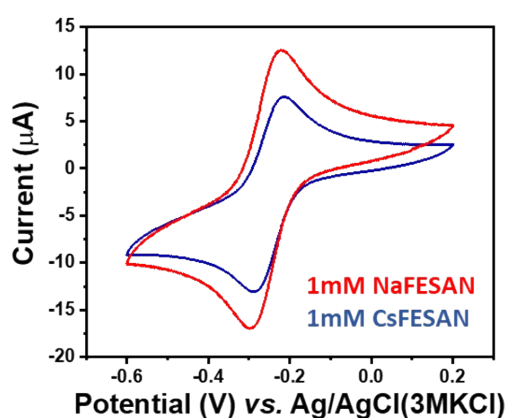


Fig. S12 CV of 1mM Cs and Na [o-FESAN] in 0.3M KNO₃ with Ag/AgCl as the reference and GC as the working electrodes at 100mV/s. The formal peak potentials (E^0) are -0.285 V and -0.282 V (vs. Ag/AgCl) for Na and Cs[o-FESAN], respectively, with ΔE as 70 mV.

9. Currently employed internal references (IR) and their redox parameters

Redox couple	Electrolyte	E_{pa} (V)	E_{pc} (V)	$E^{0'}$ (V)
Ferrocene (Fc^+/Fc) ⁵	0.1M TBAPF ₆ in ACN	+0.436	+0.370	+0.403 vs. NHE
Decamethylferrocene ($DmFc^+/DmFc$) ⁵	0.1M TBAPF ₆ in ACN	-0.093	-0.099	-0.096 vs. NHE
<i>Bis</i> (biphenyl)chromium (BCr^+/BCr) ⁶	0.1M TBAP in ACN	-0.674	-0.740	-0.707 vs. NHE
Cobaltacene (Cc^+/Cc)	0.1M TBAPF ₆ in ACN ⁷	-	-	-1.337 vs. Fc^+/Fc -0.226 vs. $Ag/AgCl(0.1M TBAC)$
	0.1M TBAPF ₆ in ACN ⁸	-0.187	-0.265	
Ferrocenemethanol ($FcMe$) ⁹	0.1M KCl	0.213	0.15	0.185 vs. SCE
Ferrocenecarboxylic acid (FCA) ¹⁰	0.1M TBAPF ₆ in ACN	0.218	0.138	0.178 vs. Fc^+/Fc
Ferroceneacetic acid (FAA) ¹⁰	0.1M TBAPF ₆ in ACN	-0.047	-0.129	-0.088 vs. Fc^+/Fc

Table S3. Redox parameters for various IR. TBAPF₆ – Tetrabutylammonium hexafluorophosphate; TBAP – Tetrabutylammonium perchlorate in acetonitrile (ACN).

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