Electronic Supplementary Information

Magnetic, electrochemical and spectroscopic properties of iron(III) amine-bis(phenolate) halide complexes†

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Additional electrochemical data

1a = FeCl[O$_2$NO]^{BuBuFurf} **4b = FeBr[O$_2$NO]^{BuMeMeth}**

Electrolytes: 0.2 M LiClO$_4$ or NaBF$_4$ or NaPF$_6$ in acetonitrile. The dissolution of NaBF$_4$ and NaPF$_6$ in acetonitrile requires the a mixture of 1:10 (water:acetonitrile, v/v). The compound **1a** had dark purple colour and **4b** had dark-brown colour in LiClO$_4$. However, both of the compounds were colourless in NaBF$_4$ and NaPF$_6$ electrolytes.

Three-electrode system included a working electrode (glassy carbon, platinum or gold) from Bioanalytical Systems (BAS) and a platinum wire as the counter electrode, and the Ag/AgCl reference electrode was connected to the system through a salt bridge. The measurements were taken using a CHinstruments 660A potentiostat and Ar gas was applied throughout the measurements.

Table S1: DPV; Pt electrode

Initial E: 0 V; Final E: 1.25 V; Amplitude: 50 mV, Pulse width; 50 ms; Sample width: 17 ms; Pulse period: 0.2 s, Quiet time: 5 s; Sensitivity: 10 μA.

	1a	**4b**
$LiClO_4$	Oxd. Peak 1 0.70 V; Peak 2 0.95 V	Peak 1 0.60 V; Peak 2 0.80 V
	Red. Peak 1 0.72 V	Peak 1 0.47 V; Peak 2 0. 87 V
$NaBF_4$	Oxd. Peak 1 0.75 V; Peak 2 0.95 V	Peak 1 0.55 V; Peak 2 0.75 V; Peak 3 0.95 V
	Red. Peak 1 0.65 V; Peak 2 0.75 V	Peak 1 0.65 V; Peak 2 0.75 V; Peak 3 0.95 V
$NaPF_6$	Oxd. Peak 1 0.35 V; Peak 2 0.70 V; Peak 3 0.95 V	Peak 1 0.30 V; Peak 2 0.55 V; Peak 3 0.90 V
	Red. Peak 1 0.25 V; Peak 2 0.65 V; Peak 3 0.90 V	Peak 1 0.25 V; Peak 2 0.50 V; Peak 3 0.85 V

Table S2: DPV; Glassy carbon electrode

	1a	**4b**
$LiClO_4$	Oxd. Peak 1 0.35 V; Peak 2 0.60 V; Peak 3 0.85 V	Peak 1 0.15 V; Peak 2 0.95 V
	Red. Peak 1 0.45 V; Peak 2 0.90 V	Peak 1 0.10 V; Peak 2 0. 82 V
$NaBF_4$	Oxd. Peak 1 0.65 V; Peak 2 0.95 V	Peak 1 0.60 V; Peak 2 0.785 V; Peak 3 1.15 V
	Red. Peak 1 0.60 V; Peak 2 0.90 V	Peak 1 0.55 V; Peak 2 0.80 V; Peak 3 1.10 V
$NaPF_6$	Oxd. Peak 1 0.35 V; Peak 2 0.65 V; Peak 3 0.90 V	Peak 1 0.40 V; Peak 2 0.65 V; Peak 3 1.15 V
	Red. Peak 1 0.30 V; Peak 2 0.60 V; Peak 3 0.85 V	Peak 1 0.30 V; Peak 2 0.55 V; Peak 3 1.0 V

Table S3: CV; Pt electrode

Initial E: open circuit potential; High E: 1.25 V, Low E: 0 V; Initial P/N: Positive; Scan rate: 100 mV; Sample interval: 1 mV; Quiet time: 5 s; Sensitivity: 10 µA.

E^0 $=(E_{ox}+E_{red})/2$; **$\Delta E=$** $E_{ox}-E_{red}$; **ΔE_{fwhm}**: Full-width at half-maximum, (Standard deviations in brackets, n=3).

		1a			**4b**		
		E^0	**ΔE**	**ΔE_{fwhm}**	**E^0**	**ΔE**	**ΔE_{fwhm}**
$LiClO_4$	Peak 1	1175 (7)	50(8)	120(9)	535(12)	130(13)	110(12)
	Peak 2	860(1)	8(4)	130(12)	835(23)	70(11)	120(10)
$NaBF_4$	Peak 1	625(14)	50(9)	120(14)	0.675(19)	0.150(13)	110(15)
	Peak 2	1050(18)	200(24)	80(13)	850(21)	200(12)	100(12)
$NaPF_6$	Peak 1	725(9)	50(12)	110(12)	625(13)	50(16)	110(12)
	Peak 2	900(14)	100(11)	90(8)	900(12)	100(8)	100(15)
	Peak 3	1100(17)	100(9)	80(7)	1150(15)	120(16)	90(11)

Table S4: CV; Glassy carbon electrode

		1a			**4b**		
		E^0	**ΔE**	**ΔE_{fwhm}**	**E^0**	**ΔE**	**ΔE_{fwhm}**
$LiClO_4$	Peak 1	375(10)	50(12)	90(7)	175(12)	50(13)	90(12)
	Peak 2	800(23)	100(19)	100(17)	775(28)	50(11)	90(15)
$NaBF_4$	Peak 1	625(26)	50(16)	110(15)	825(24)	50(16)	100(13)
	Peak 2	925(19)	50(15)	100(14)	-		
$NaPF_6$	Peak 1	375(24)	50(5)	100(10)	325(24)	50(7)	90(8)
	Peak 2	775(28)	150(18)	110(9)	875(25)	50(12)	100(7)
	Peak 3	1150(32)	100(21)	90(8)	1100(31)	125(12)	80(9)

NOTE: In general, CV measurements indicated a **pseudo-reversible redox process**, **which involved one-electron**. The appearance of multiple peaks might be attributed to the different configurations of the complex in solution, that would allow the oxidation of the Fe core at varying potentials.

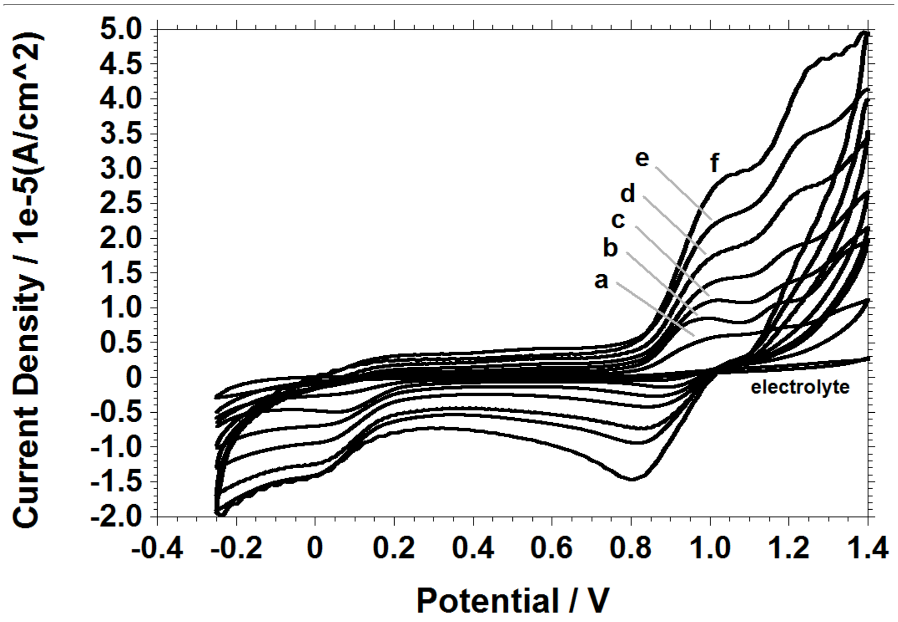

Figure S1. Scan rate dependence of 1 mM **1a** in 0.2 M $LiClO_4$ at (a) 0.05 V/s, (b) 0.1 V/s, (c) 0.25 V/s, (d) 0.5 V/s, (e) 1 V/s, (f) 2 V/s using a glassy carbon electrode.

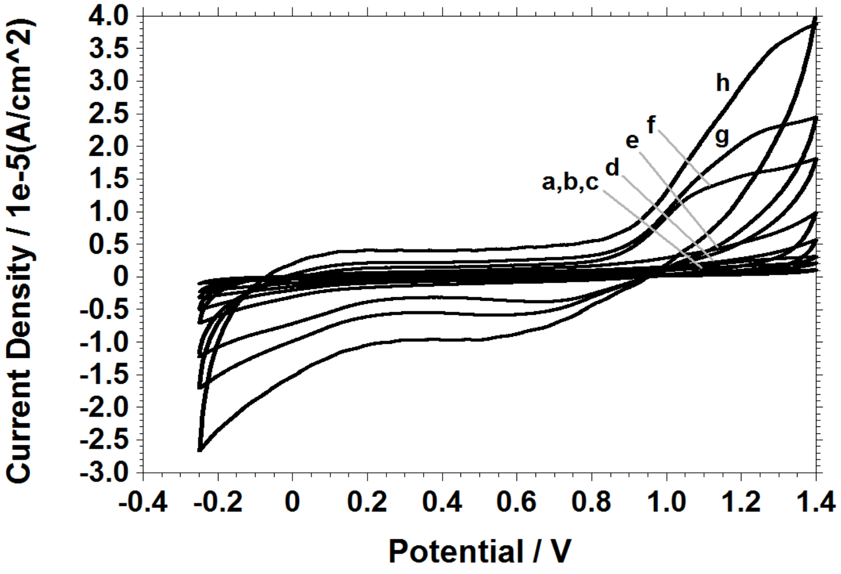

Figure S2. Scan rate dependence of 1 mM **1a** in 0.2 M $LiClO_4$ at (a) electrolyte, (b) 0.01 V/s, (c) 0.05 V/s, (d) 0.1 V/s, (e) 0.25 V/s, (f) 0.5 V/s, (g) 1 V/s, (h) 2 V/s using a platinum electrode.

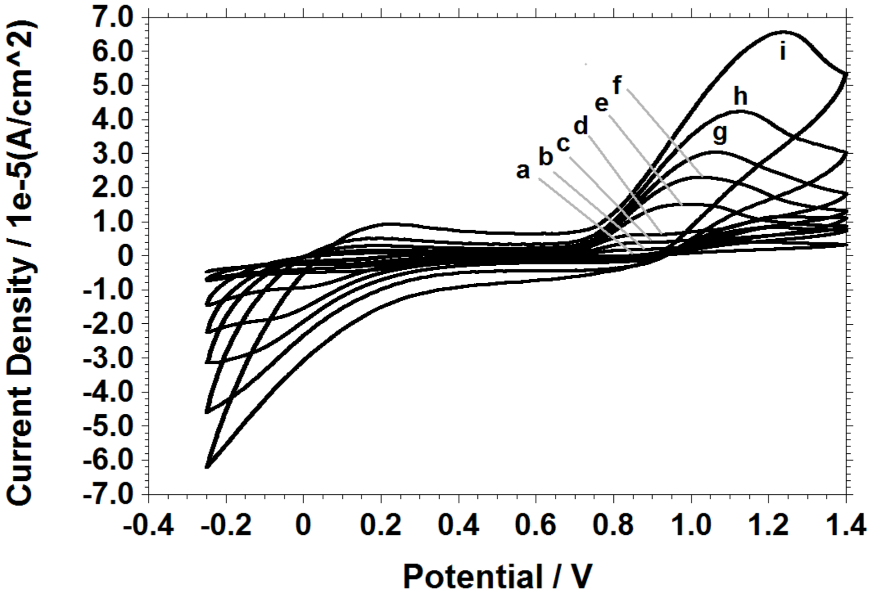

Figure S3. Scan rate dependence of 1 mM **4b** in 0.2 M $LiClO_4$ at (a) electrolyte, (b) 0.01 V/s, (c) 0.05 V/s, (d) 0.1 V/s, (e) 0.25 V/s, (f) 0.5 V/s, (g) 1 V/s, (h) 2 V/s (i) 5 V/s using a glassy carbon electrode.

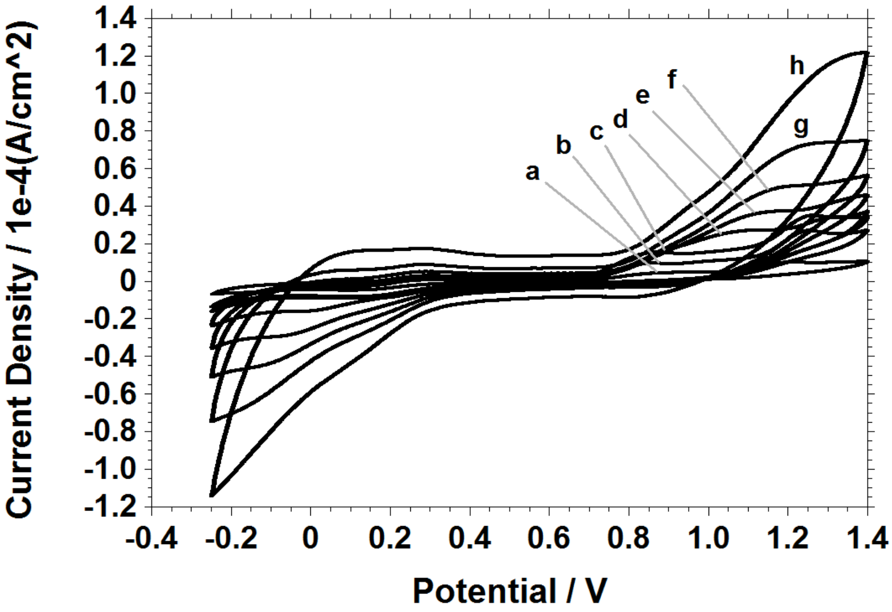

Figure S4. Scan rate dependence of 1 mM **4b** in 0.2 M $LiClO_4$ at (a) electrolyte, (b) 0.01 V/s, (c) 0.05 V/s, (d) 0.1 V/s, (e) 0.25 V/s, (f) 0.5 V/s, (g) 1 V/s, (h) 2 V/s using a platinum electrode.

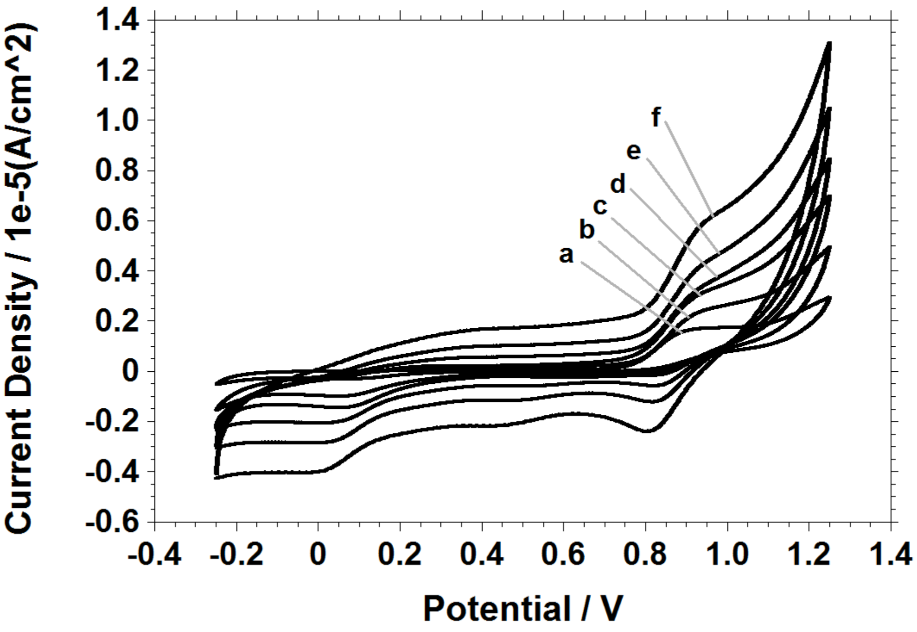

Figure S5. Scan rate dependence of 1 mM **1a** in 0.2 M $NaBF_4$ at (a) 0.05 V/s, (c) 0.1 V/s, (d) 0.25 V/s, (e) 0.5 V/s, (f) 1 V/s using a platinum electrode.

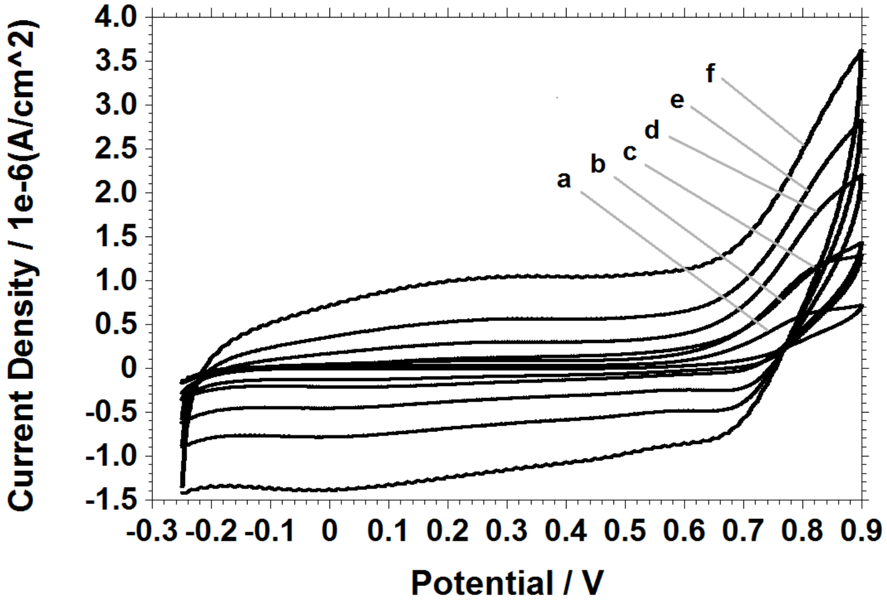

Figure S6. Scan rate dependence of 1 mM **1a** in 0.2 M $LiClO_4$ at (a) 0.05 V/s, (c) 0.1 V/s, (d) 0.25 V/s, (e) 0.5 V/s, (f) 1 V/s using a gold electrode.

NOTE: As expected from the solution-based studies, the dependence of the compounds between the anodic peak height and scan rate on all the electrode materials and electrolytes showed a linear relationship, which indicated a **diffusion-controlled process**.

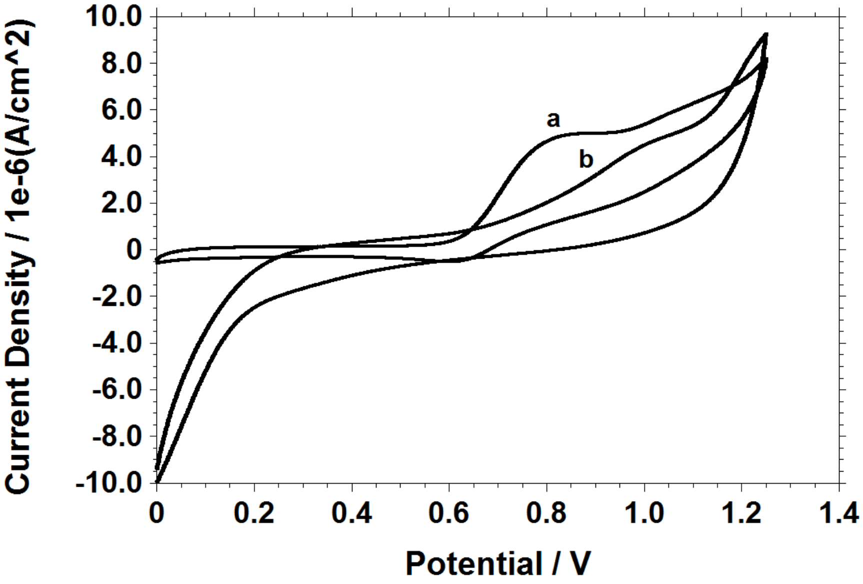

Figure S7. Cyclic voltammograms for 1 mM **1a** in (a) 0.2 M $LiClO_4$ and (b) 0.2 M $NaPF_6$ at 0.1 V/s using a platinum electrode.

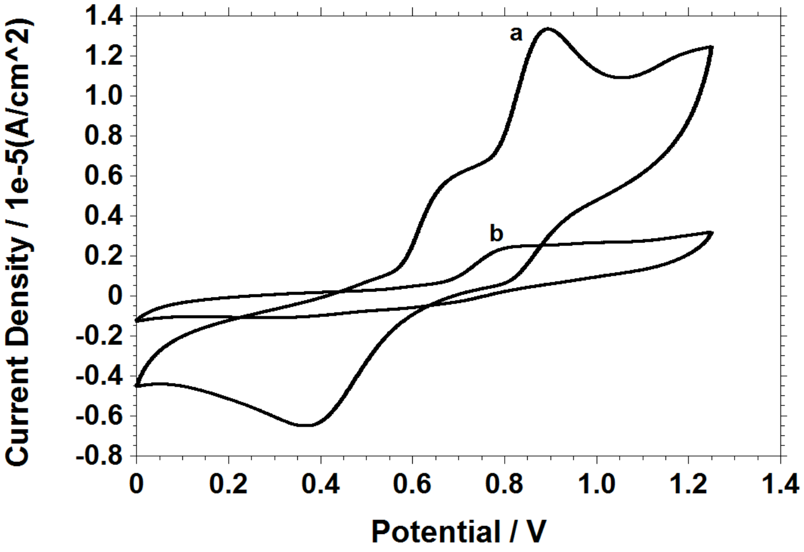

Figure S8. Cyclic voltammograms for 1 mM (a) **1a** and (b) **4b** in 0.2 M $NaBF_4$ at 0.1 V/s using a glassy carbon electrode.

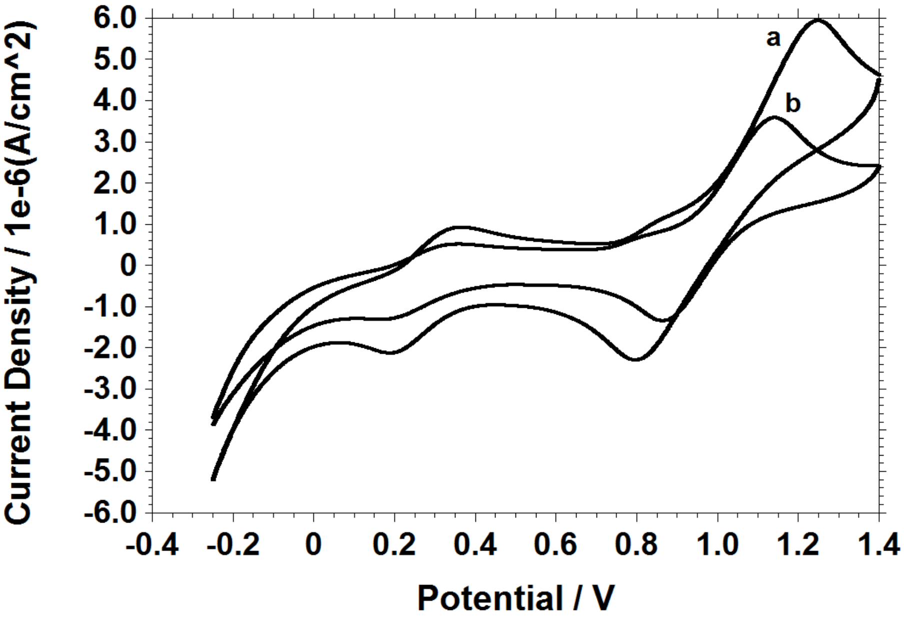

Figure S9. Cyclic voltammograms for 1 mM (a) **1a** and (b) **4b** in 0.2 M $NaPF_6$ at 0.1 V/s using a glassy carbon electrode.

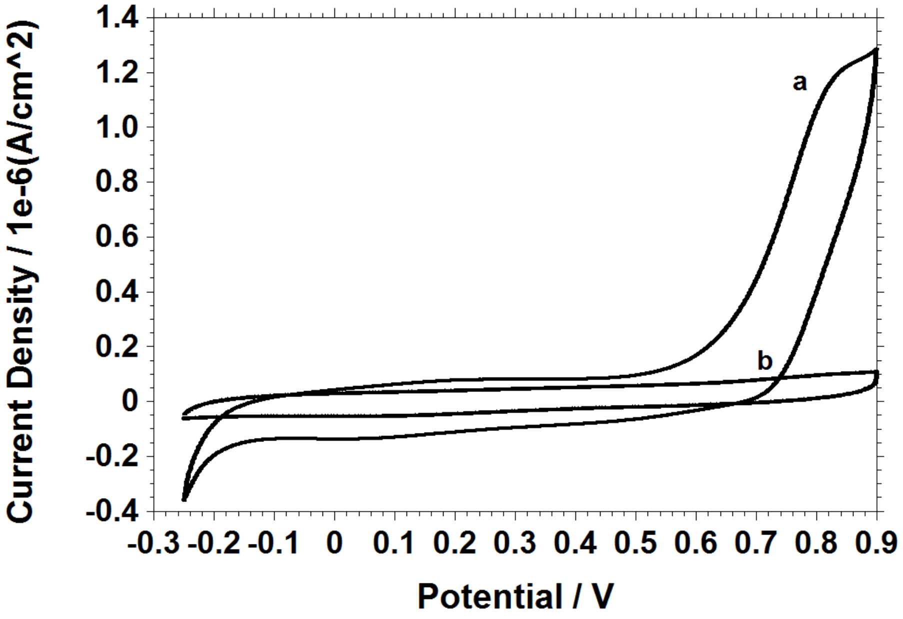

Figure S10. Cyclic voltammoaggrams for (a) 1 mM **1a** and (b) electrolyte in 0.2 M $LiClO_4$ at 0.1 V/s using a glassy carbon electrode.ag/

NOTE: As observed in Fig. 10, the redox signals were overlapping with the strong Au oxidation signal (0.9-1.1 V vs. Ag/AgCl), the further measurements were not taken using gold electrodes.

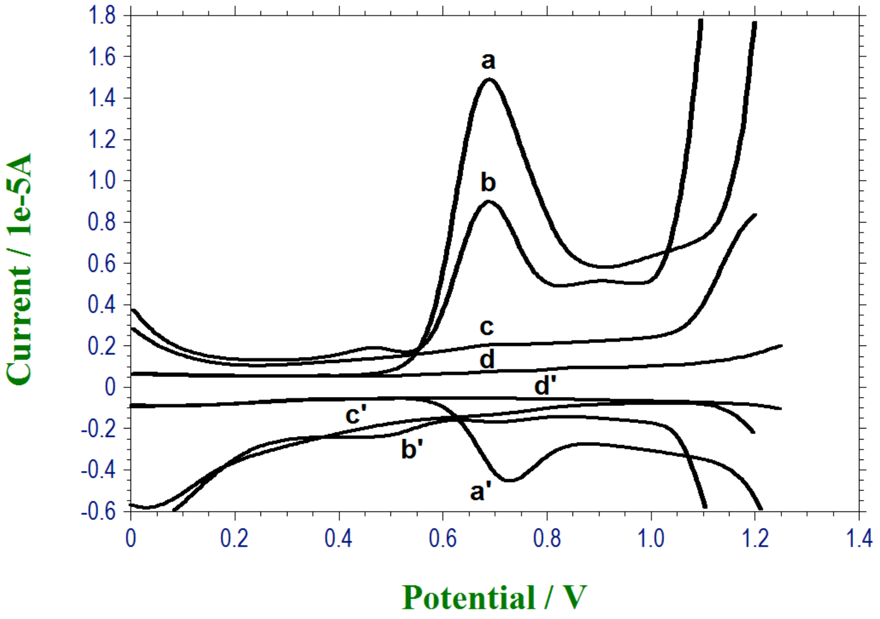

Figure S11. Differential pulse voltammograms for 1 mM **1a** in 0.2 M $LiClO_4$ at 0.1 V/s with the oxidation scans using (a) a glassy carbon electrode, (b) a platinum electrode, blank electrolyte at (c) glassy carbon electrode and (d) platinum electrode; the reduction scans using (a') a glassy carbon electrode and (b') a platinum electrode, blank electrolyte at (c') glassy carbon electrode and (d') platinum electrode.

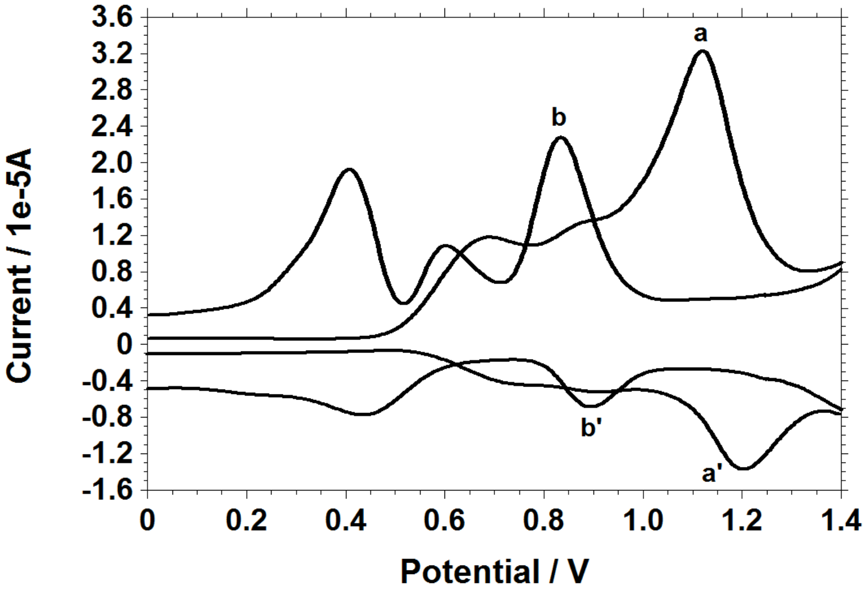

Figure S12. Differential pulse voltammograms for 1 mM **4b** in 0.2 M $NaPF_6$ with the oxidation scans using (a) a glassy carbon electrode and (b) a platinum electrode.