Supporting Information for:

Evaluating Electrochemical Accessibility of $4f^n5d^1$ and $4f^{n+1}$ Ln(II) Ions in $(C_5H_4SiMe_3)_3Ln$ and $(C_5Me_4H)_3Ln$ Complexes

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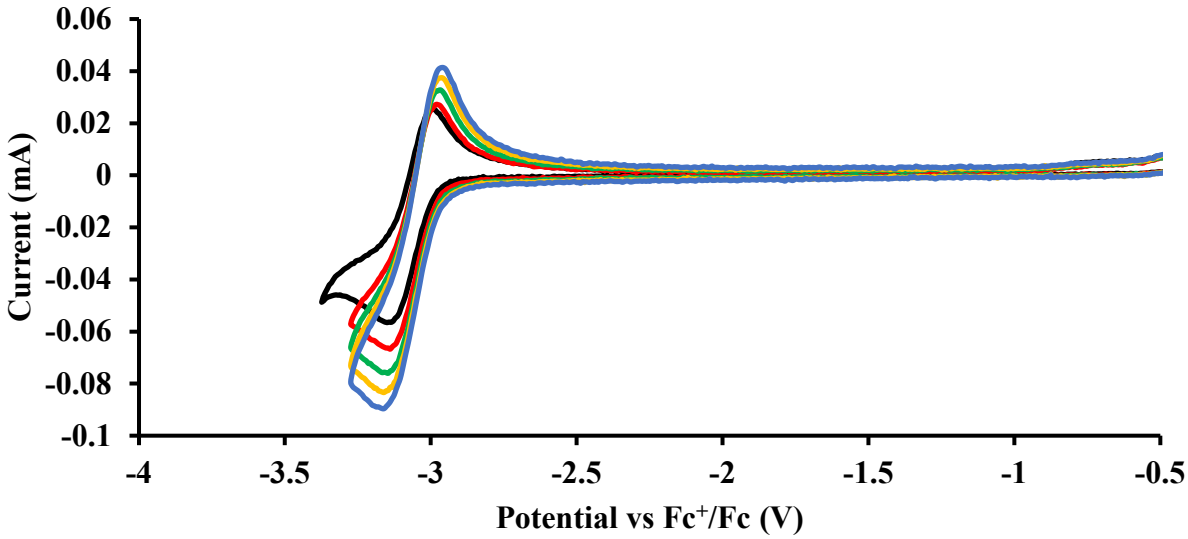

Figure S1: Cyclic voltammogram of Cp'_3Y at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

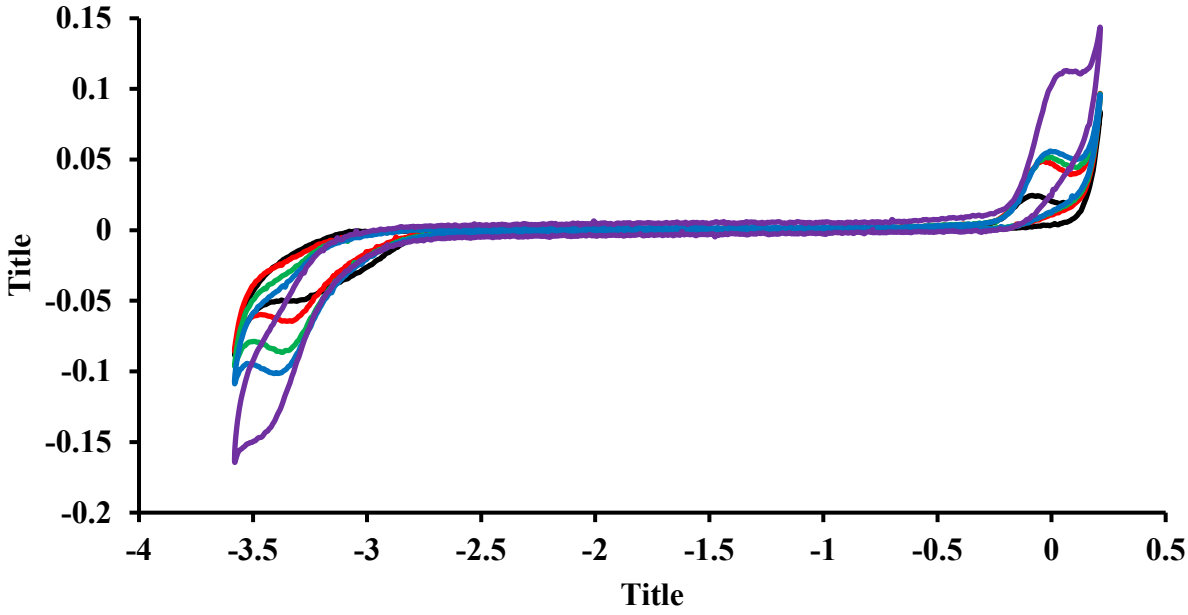

Figure S2: Cyclic voltammogram of Cp'_3La at v = 200 (black), 400 (red), 600 (green), 1000 (blue) and 2000 (purple) mV/s.

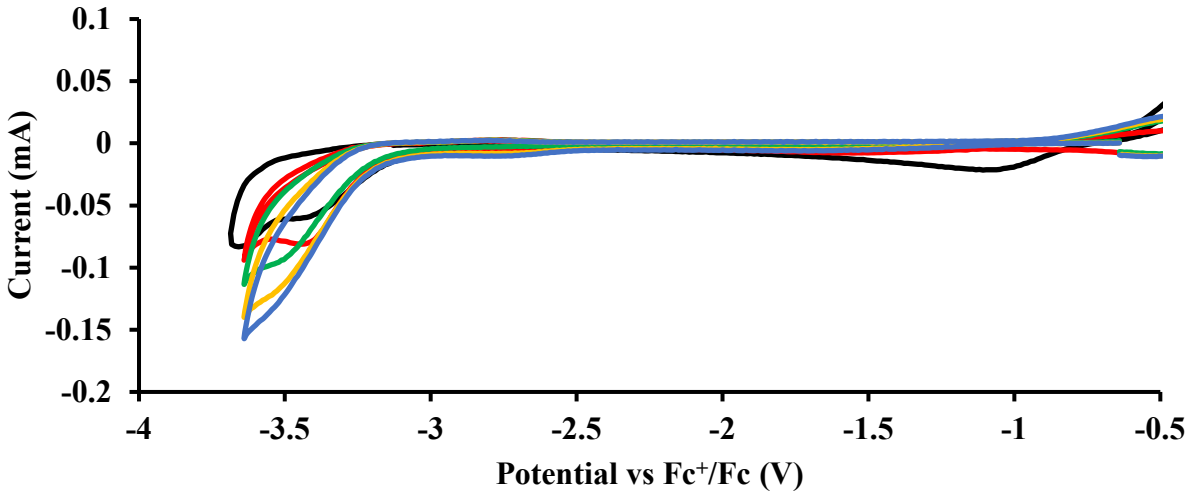

Figure S3: Cyclic voltammogram of Cp'_3Ce at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

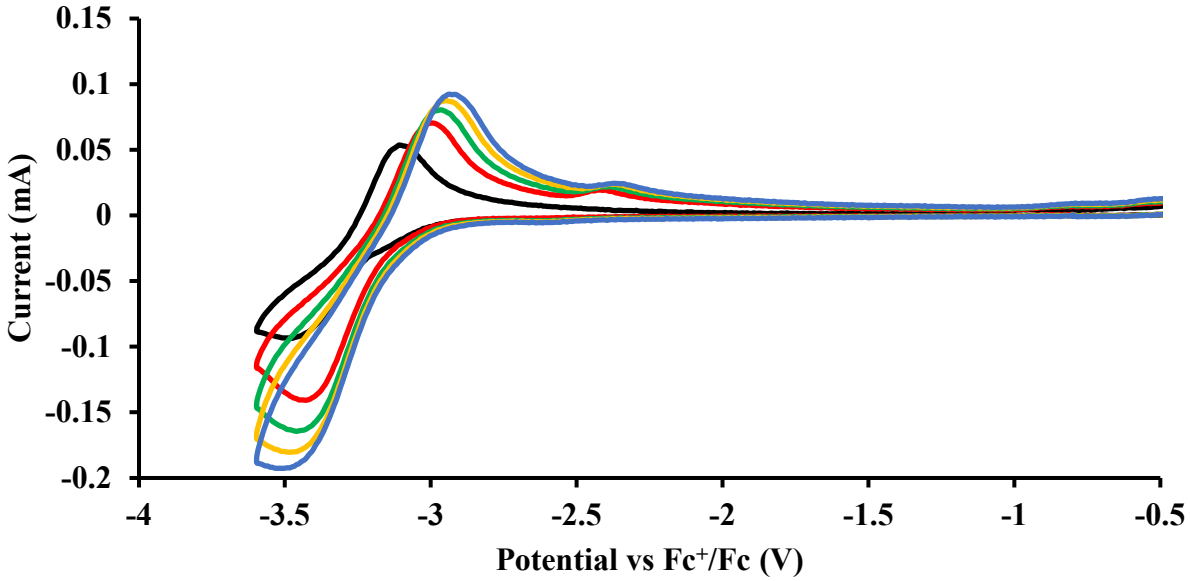

Figure S4: Cyclic voltammogram of Cp'_3Pr at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

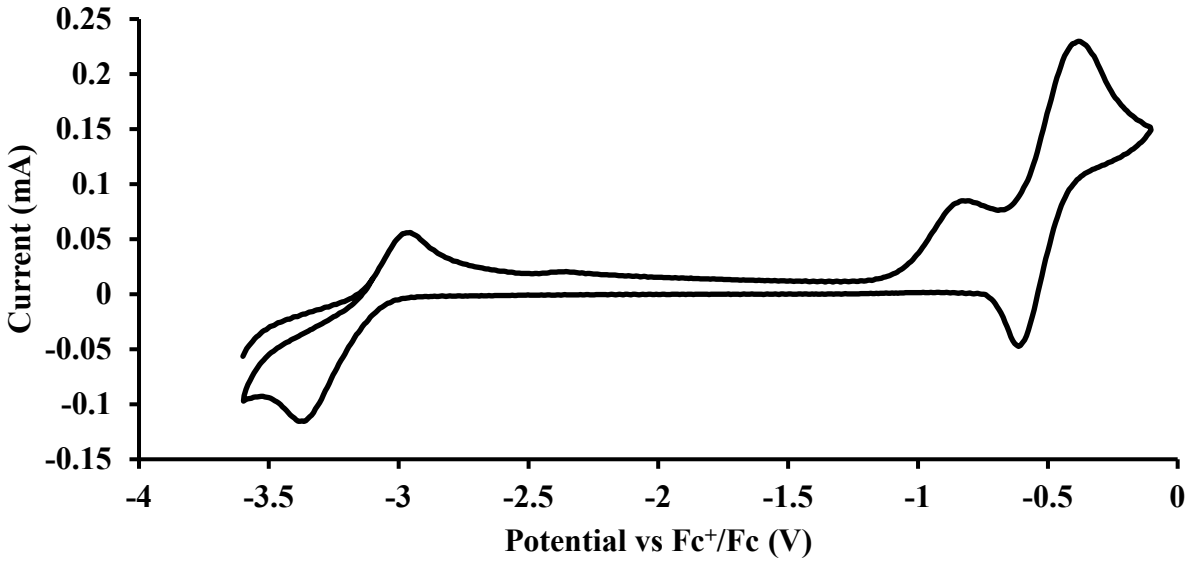

Figure S5: Cyclic voltammogram of [K(crypt)][Cp′$_3$Pr] at v = 200 mV/s with internal standard $(C_5Me_5)_2Fe$.

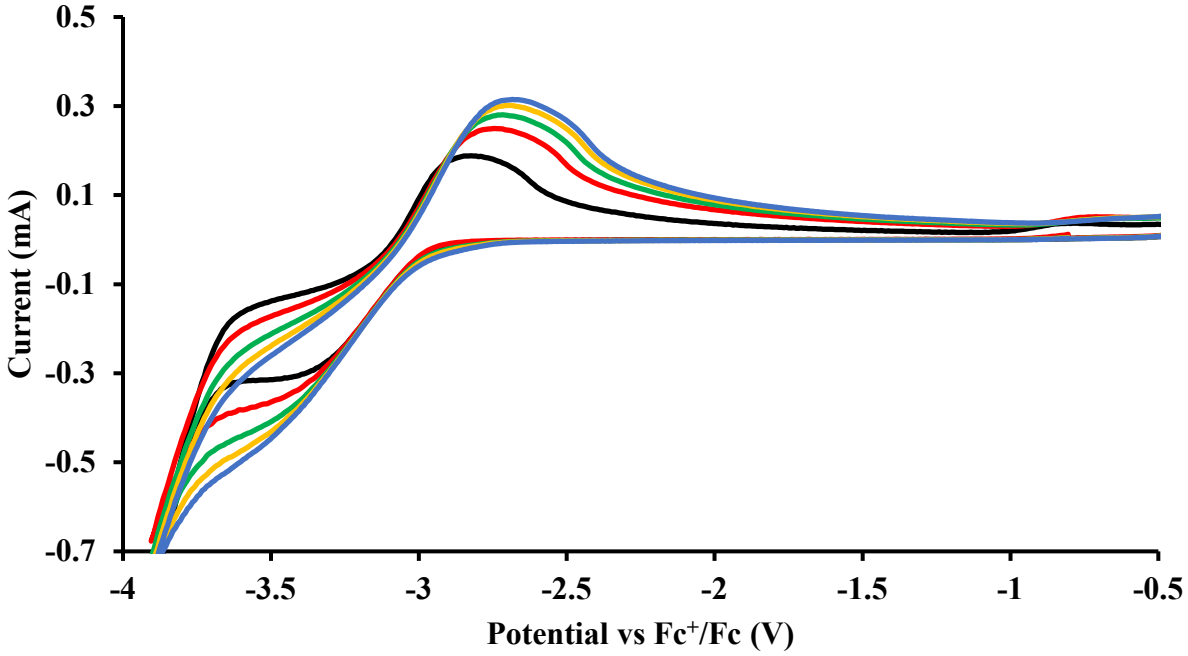

Figure S6: Cyclic voltammogram of Cp′$_3$Nd at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

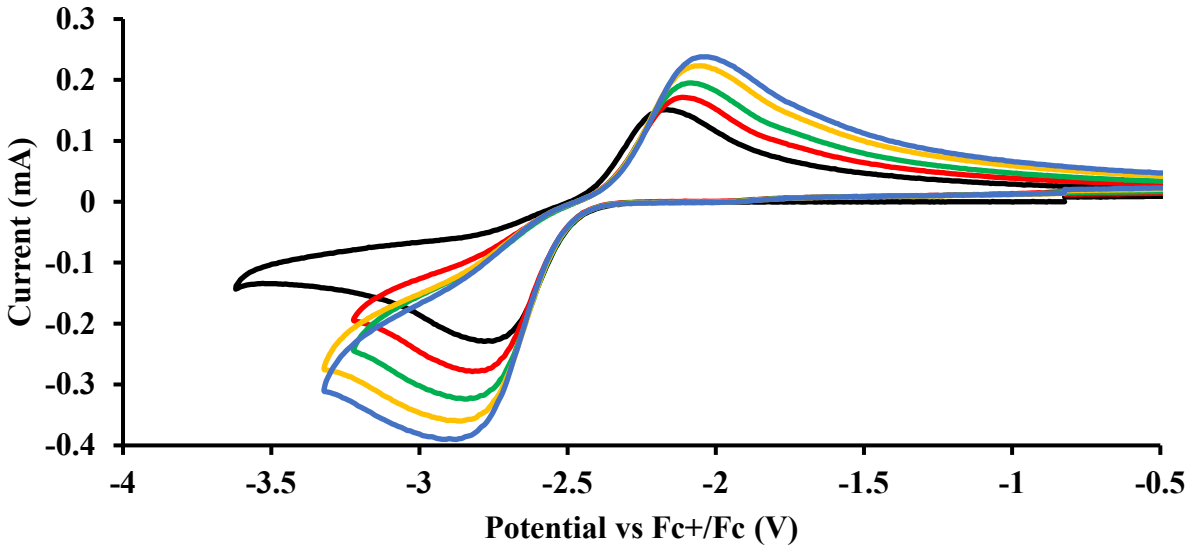

Figure S7: Cyclic voltammogram of Cp'_3Sm at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

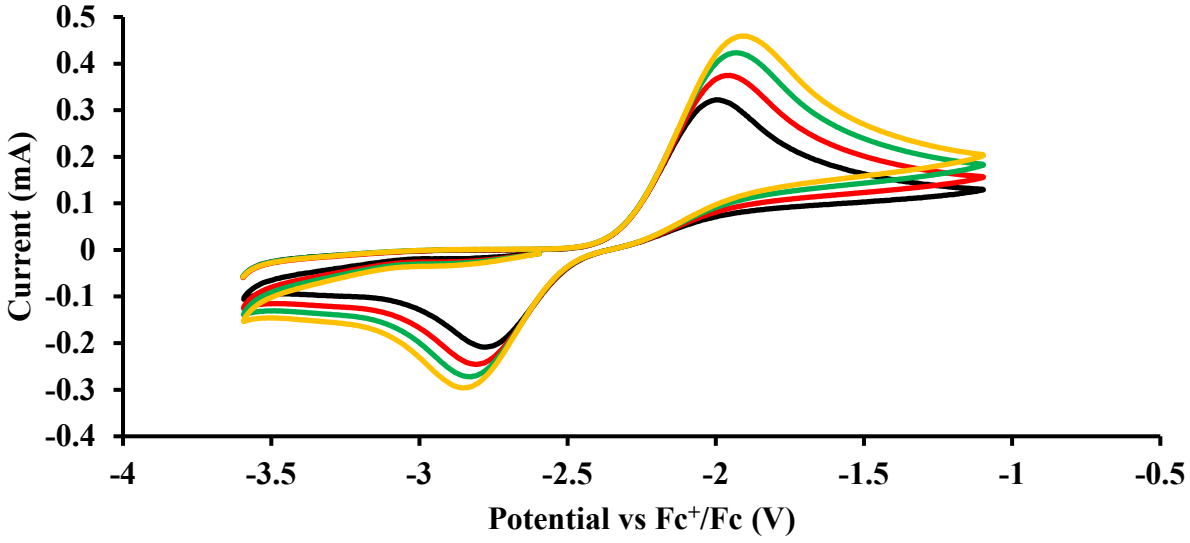

Figure S8: Cyclic voltammogram of [K(crypt)][Cp'_3Sm] at v = 200 (black), 400 (red), 600 (green) and 800 (yellow) mV/s.

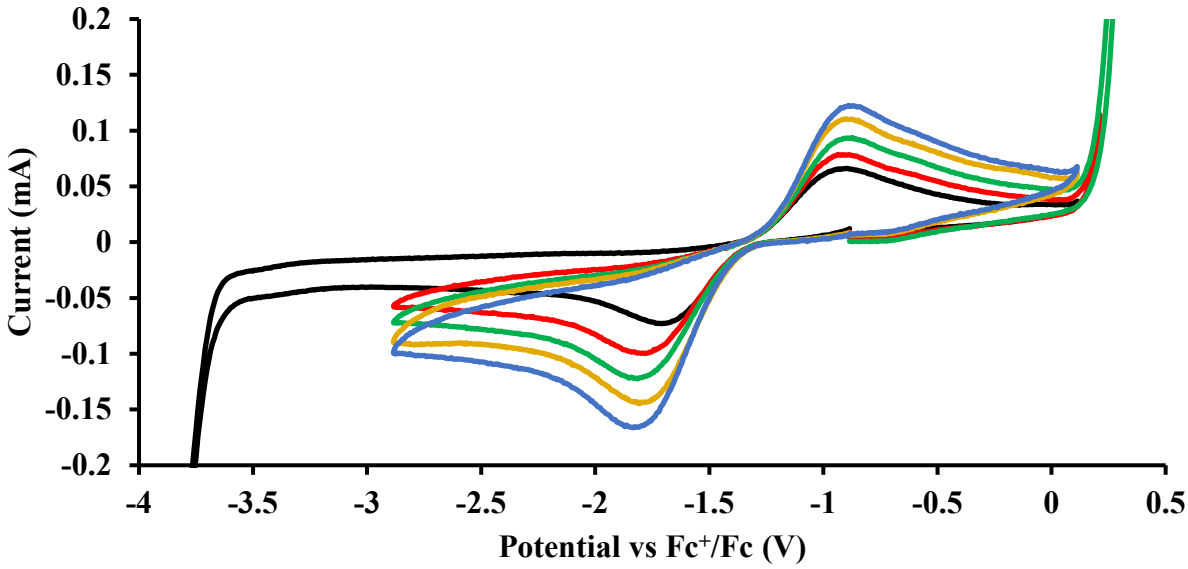

Figure 9S: Cyclic voltammogram of Cp'_3Eu at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

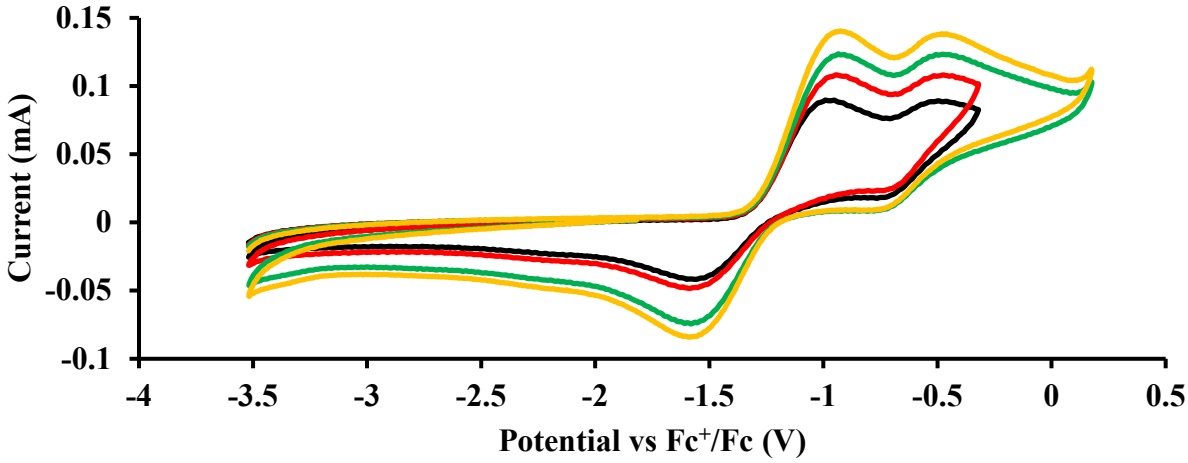

Figure S10: Cyclic voltammogram of [K(crypt)][Cp'_3Eu] at v = 200 (black), 400 (red), 600 (green), and 800 (yellow) mV/s.

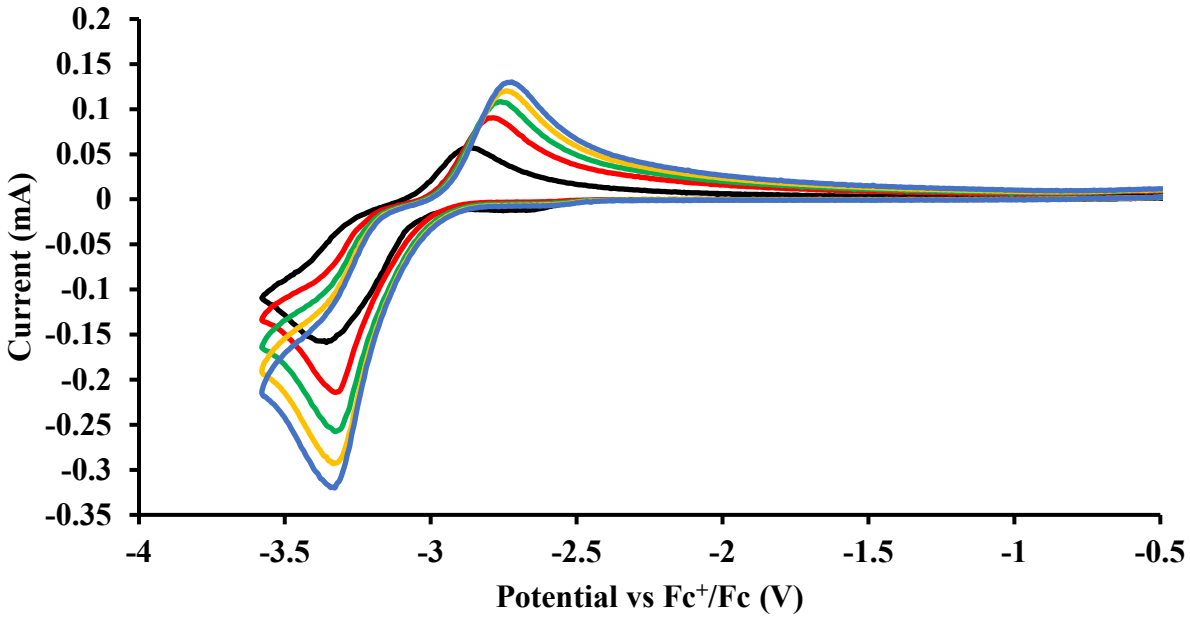

Figure S11: Cyclic voltammogram of Cp'_3Gd at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

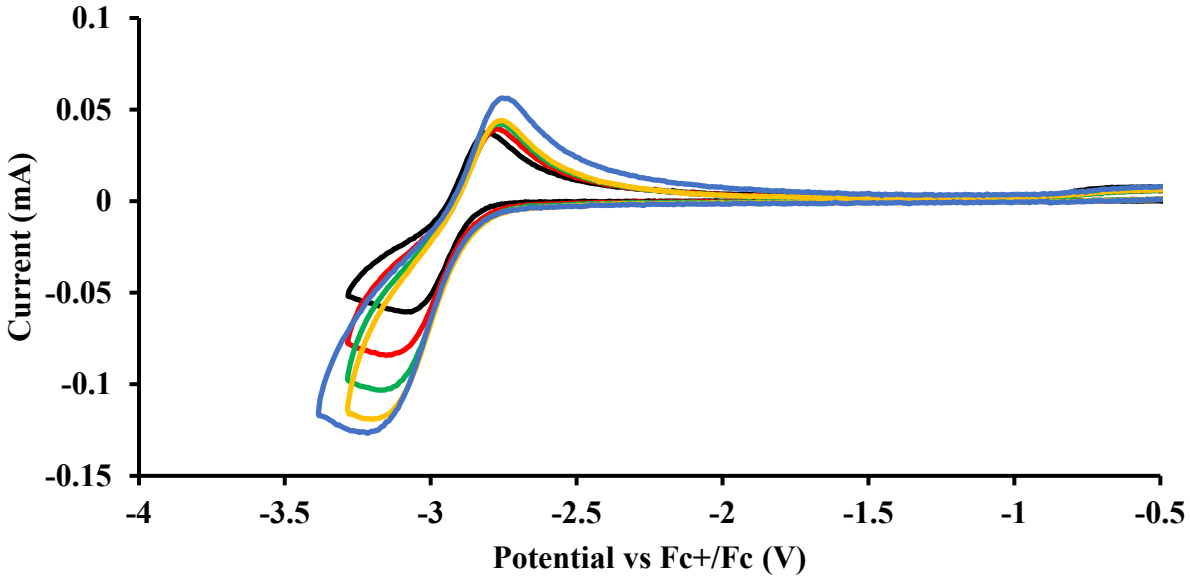

Figure S12: Cyclic voltammogram of Cp'_3Tb at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

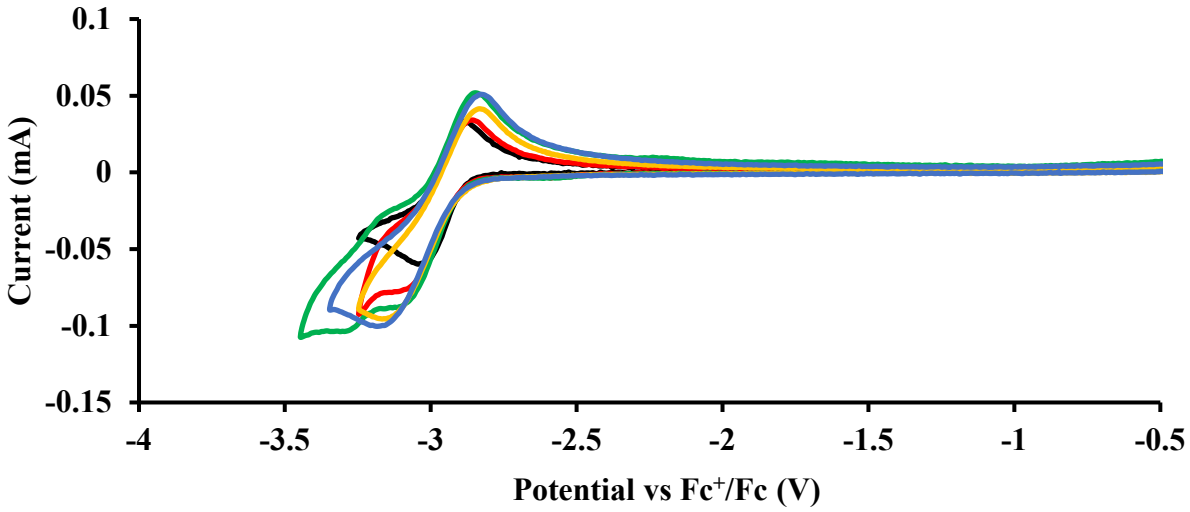

Figure S13: Cyclic voltammogram of Cp'_3Dy at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

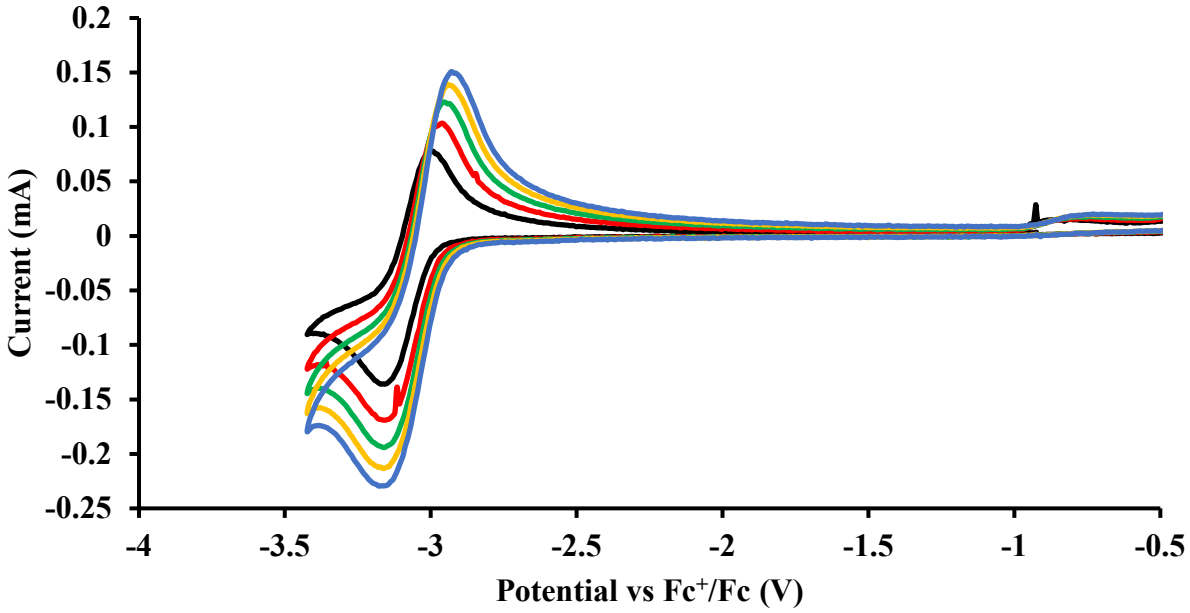

Figure S14: Cyclic voltammogram of Cp'_3Ho at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

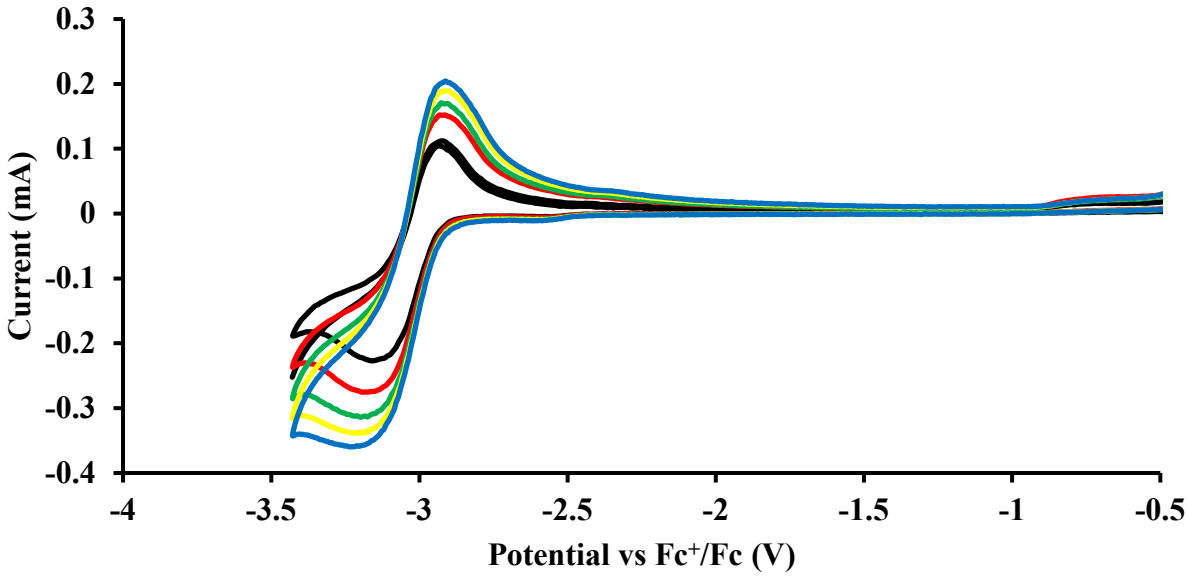

Figure S15: Cyclic voltammogram of Cp'_3Er at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

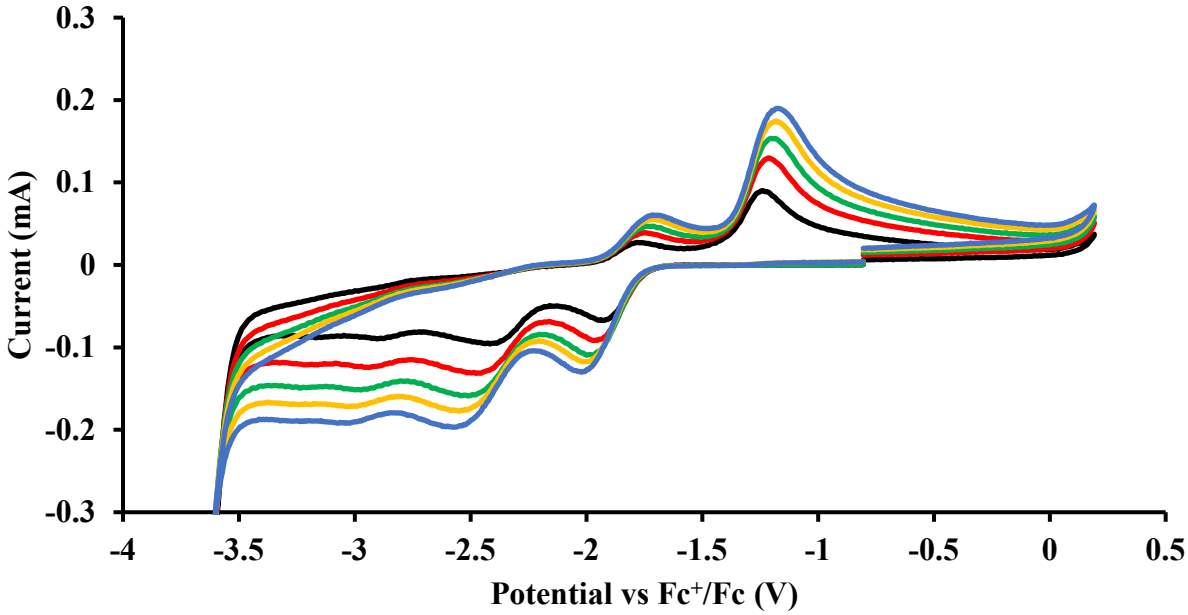

Figure S16: Cyclic voltammogram of Cp'_3Yb at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s. The cathodic event at −2.5 V and anodic event at −1.7 V are likely due to electrolyte degradation or decomposition of Cp'_3Yb.

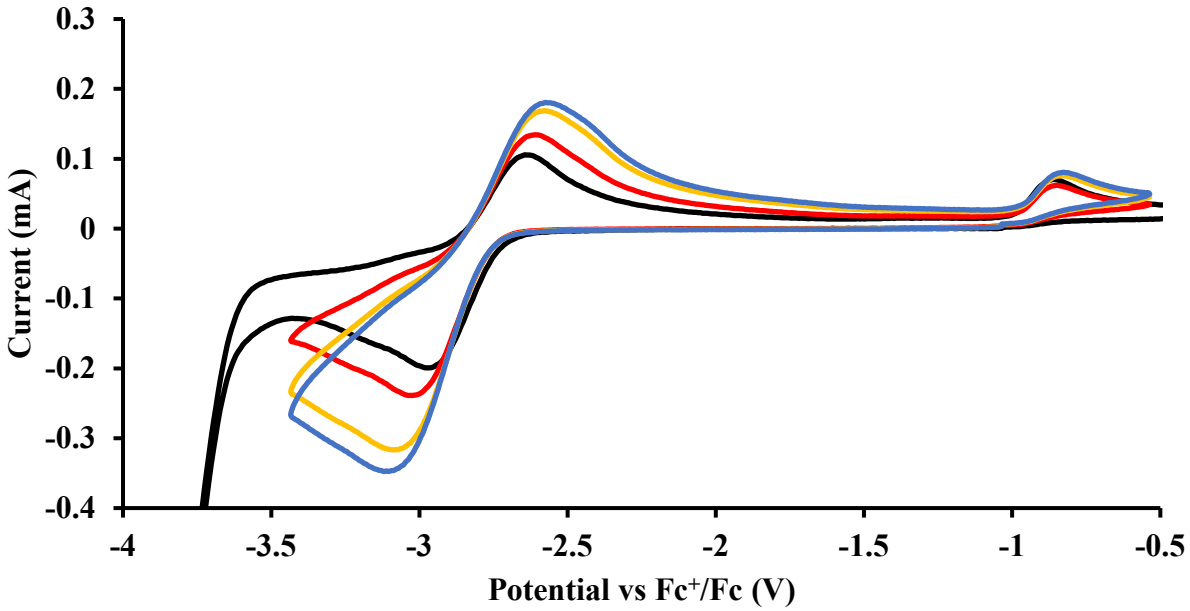

Figure S17: Cyclic voltammogram of Cp'_3Tm at v = 200 (black), 400 (red), 800 (yellow) and 1000 (blue) mV/s.

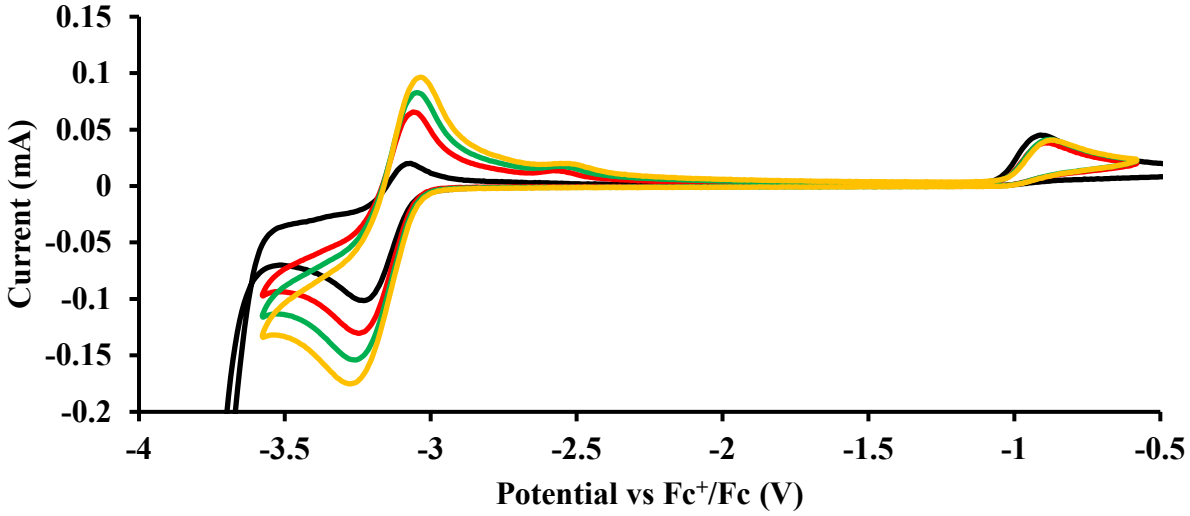

Figure S18: Cyclic voltammogram of Cp'_3Lu at v = 200 (black), 400 (red), 600 (green), and 800 (yellow) mV/s.

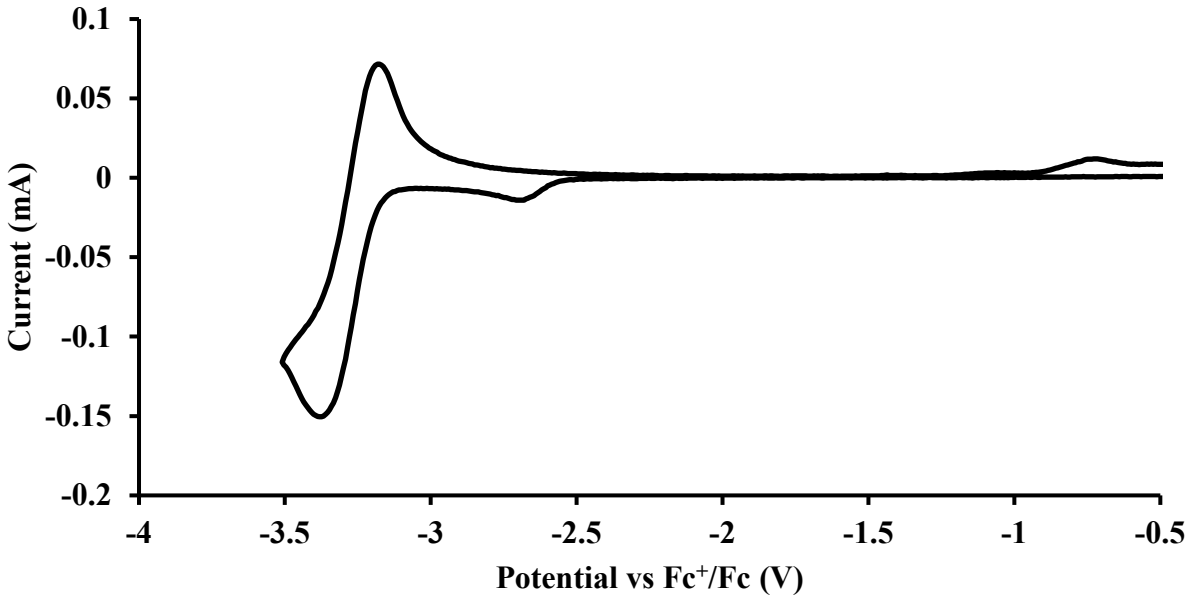

Figure S19: Cyclic voltammogram of Cp^{tet}_3La at v = 200 mV/s.

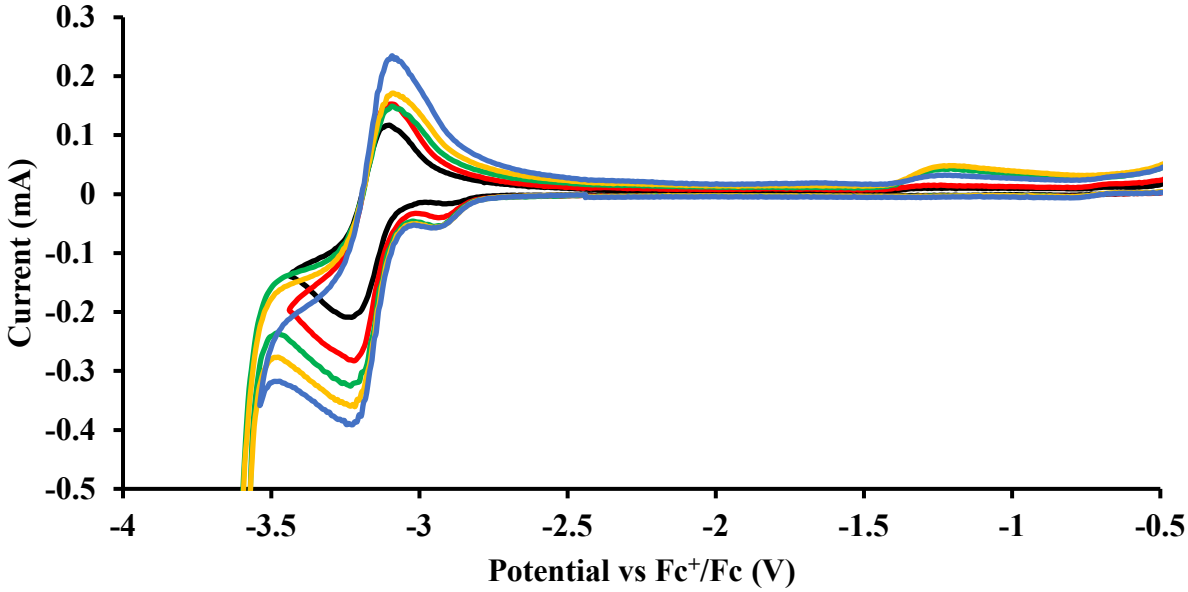

Figure S20: Cyclic voltammogram of Cp^{tet}_3Ce at v = 200 (black), 400 (red), 600 (green), 800 (yellow), and 1000 (blue) mV/s.

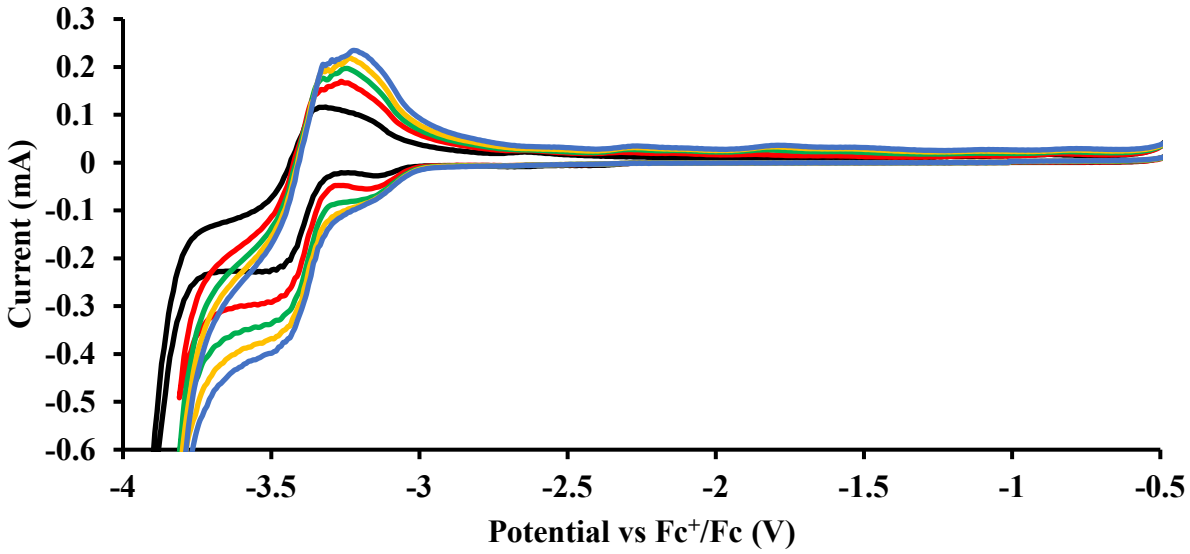

Figure S21: Cyclic voltammogram of Cp^{tet}_3Pr at ν = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

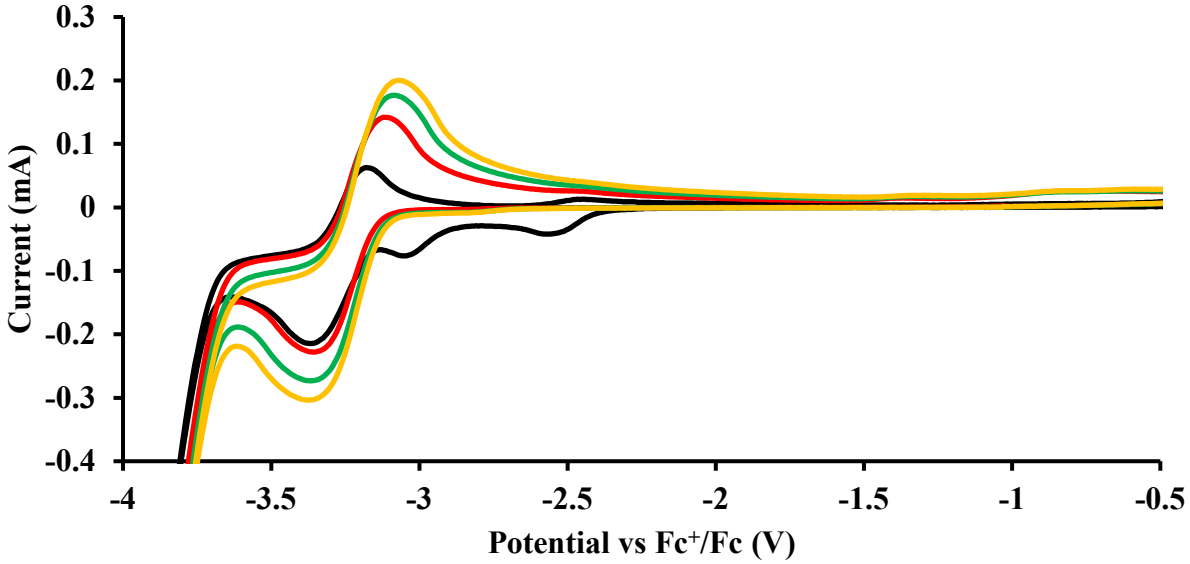

Figure S22: Cyclic voltammogram of Cp^{tet}_3Nd at ν = 200 (black), 400 (red), 600 (green), and 800 (yellow) mV/s.

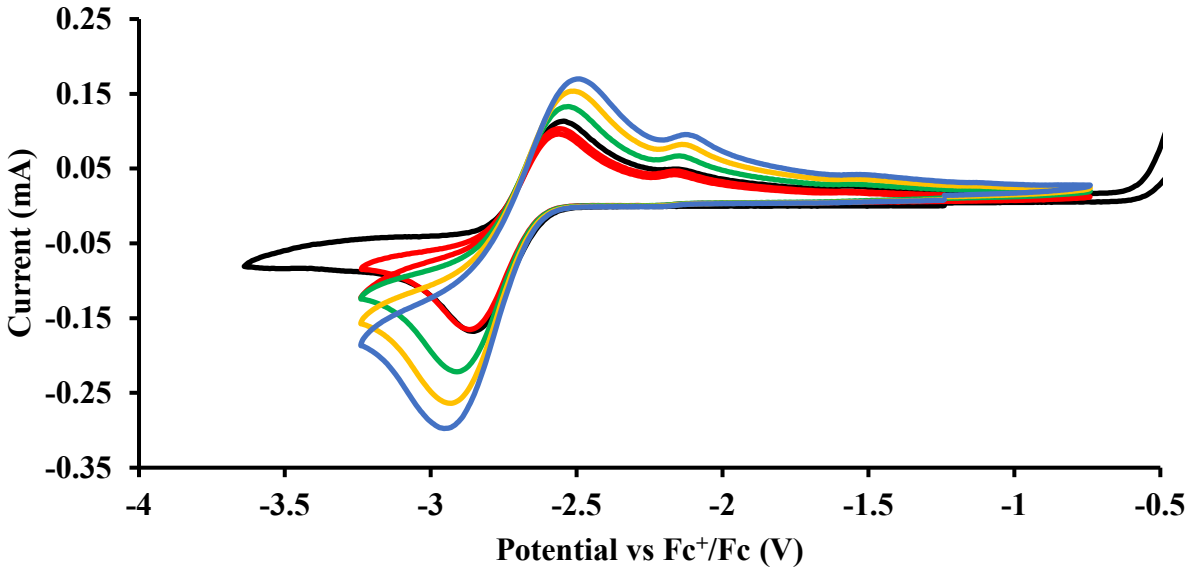

Figure S23: Cyclic voltammogram of Cp^{tet}_3Sm at ν = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

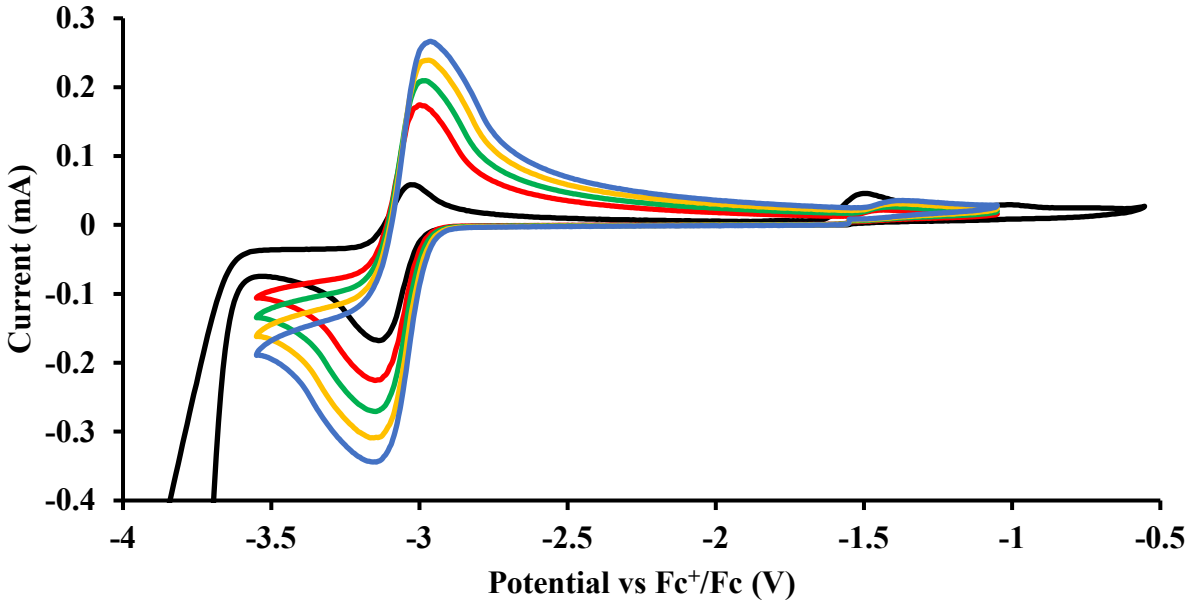

Figure S24: Cyclic voltammogram of Cp^{tet}_3Gd at ν = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

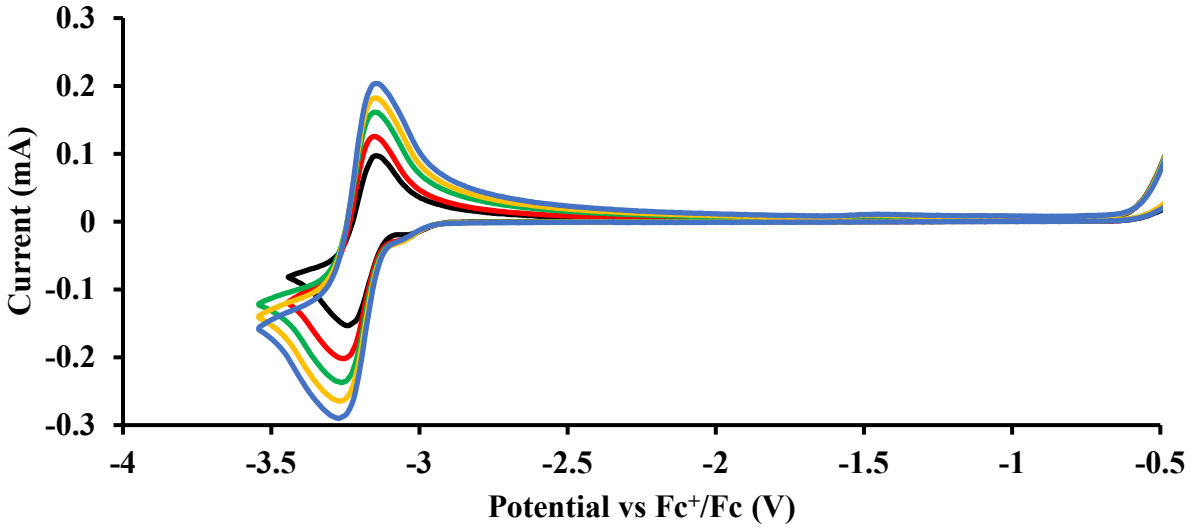

Figure S25: Cyclic voltammogram of Cp^{tet}_3Tb at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

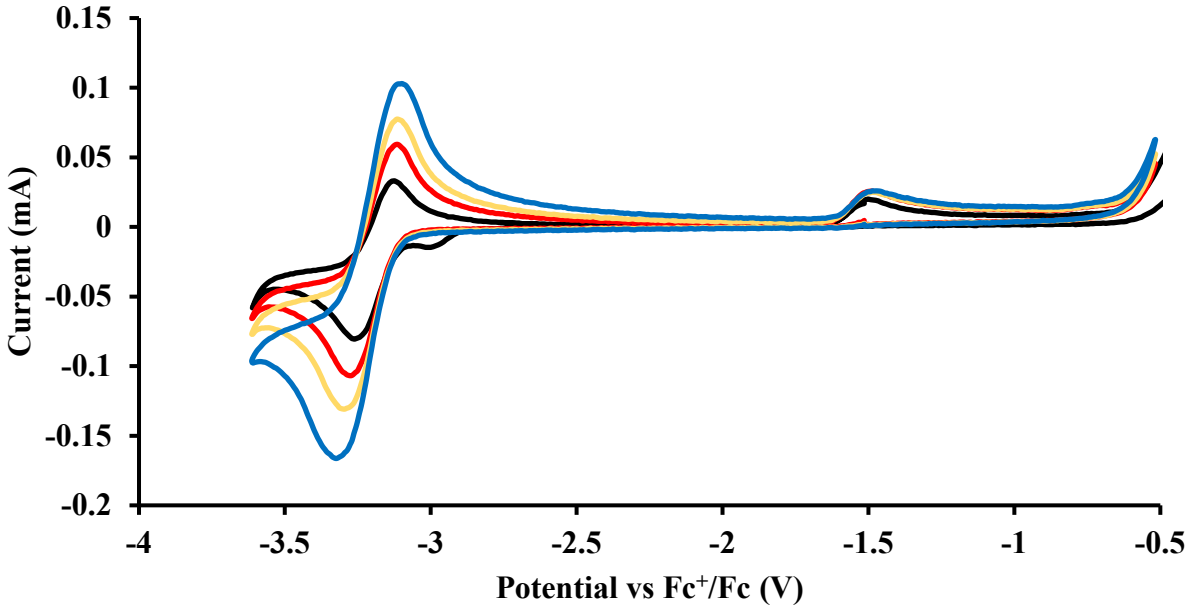

Figure S26: Cyclic voltammogram of Cp^{tet}_3Dy at v = 200 (black), 400 (red), 800 (yellow) and 1000 (blue) mV/s.

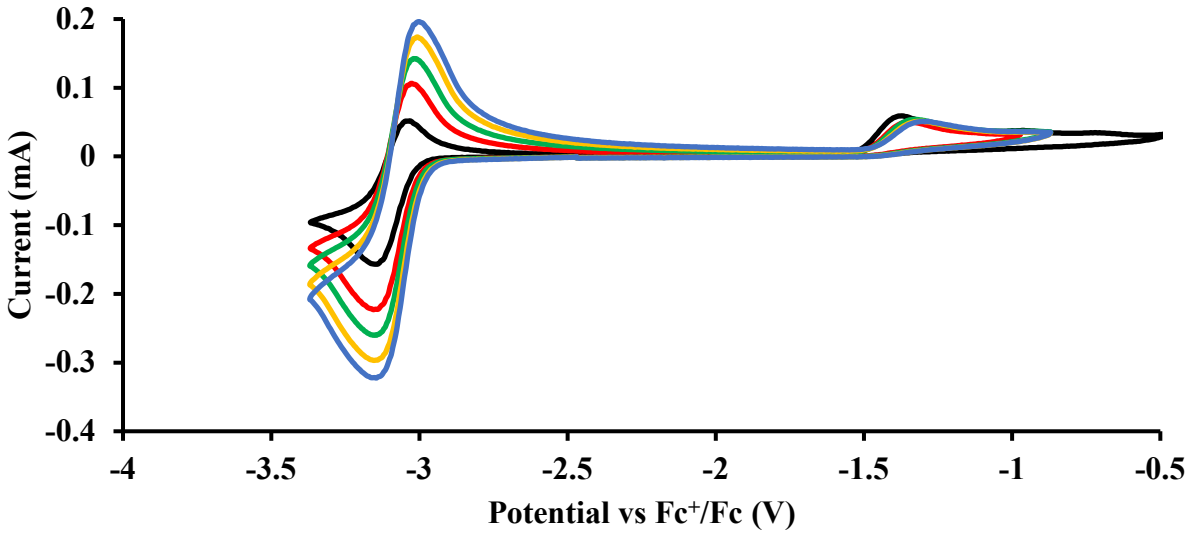

Figure S27: Cyclic voltammogram of Cp^{tet}_3Ho at v = 200 (black), 400 (red), 600 (green), 800 (yellow) and 1000 (blue) mV/s.

Table S1: Experimental and theoretical calculated Ln(III)/Ln(II) reduction potentials for the lanthanide ions. Values are reported vs Fc^+/Fc (reported as −0.40 V vs NHE).[1]

	Experimental $E_{1/2}$ in Cp'_3Ln	Thermochemical estimates[2,a]	Thermodynamic estimates[3,a]	Atomic spectroscopy estimates[4]
La	N/A	−3.34	−3.4[b]	−2.7
Ce	N/A	−3.36	−3.3[b]	−2.8
Pr	−3.14	−2.63	−2.7	−2.3
Nd	−3.14	−2.22	−2.4	−2.2
Sm	−2.41	−1.17	−1.2	−1.2
Eu	−1.07	0.15	0.1	0.1
Gd	−2.98	−3.42	−3.1[b]	−3.5
Tb	−2.95	−3.07	−3.1[b]	−3.3
Dy	−2.96	−2.02	−2.3	−2.2
Ho	−3.02	−2.40	−2.5	−2.5
Er	−3.02	−2.56	−2.7	−2.7
Tm	−2.83	−1.87	−1.9	−1.9
Yb	−1.64	−0.64	−0.7	−0.7
Lu	−3.12		−4.2[b]	

a: Values are for aqueous ions

b: Ln^{2+} (aq) is predicted to be $4f^n5d^1$

References

1. N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.
2. L. R. Morss, *Chem. Rev.*, 1976, **76**, 827–841.
3. S. G. Bratsch and J. J. Lagowski, *J. Phys. Chem.*, 1985, **89**, 3317–3319.
4. L. J. Nugent, R. D. Baybarz, J. L. Burnett and J. L. Ryan, *J. Phys. Chem.*, 1973, **77**, 1528–1539.