

Supporting Information for:

The experimental determination of Th(IV)/Th(III) redox potentials in organometallic thorium complexes

Christopher J. Inman and F. Geoffrey N. Cloke

University of Sussex, Brighton, BN1 9QJ, UK

Email: f.g.cloke@sussex.ac.uk

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Synthesis of Compounds

All manipulations involving air- or moisture-sensitive materials were performed under an inert atmosphere of argon using standard Schlenk techniques or in an MBraun N₂ or Ar-filled glovebox. Solvents were dried over appropriate drying agents (NaK_{2.8} for pentane and Et₂O; K for THF and toluene) before distilling under N₂ and stored under Ar. Solvents were stored over K mirrors, except for THF and Et₂O, which were stored over activated 4 Å molecular sieves. ThCp^{TMS}₂,¹ ThCp^{TMS}₂Cl,¹ and ThCOT^{TBDMS}₂,² were prepared using standard literature procedures. ThCOT^{TIPS}₂Cp*Cl³ was previously synthesised in our laboratory. The purity of all compounds was checked using NMR spectroscopy prior to CV studies.

Cyclic Voltammetry

Cyclic voltammetry studies were performed in an Ar glovebox using a BASi-Epsilon potentiostat under computer control. iR drop was compensated using the positive-feedback method. CV experiments were performed using a three-electrode configuration with a glassy carbon disk (7.0 mm²) as the working electrode, Pt wire as the counter electrode and Ag wire (directly in solution) as the pseudoreference electrode. Sample solutions were prepared by dissolving the appropriate supporting electrolyte in 2 mL of solvent followed by addition of the analyte to give a concentration of *ca* 5 mM unless otherwise stated. The reported half potentials are referenced to FeCp₂⁺⁰ redox couple, which was measured by adding ferrocene (*ca.* 1 mg) to the sample solution. Prior to addition of the analyte in CV experiments, the electrolyte and solvent mixture were scanned as part of a blank experiment (**Fig. S1** and **Fig. S2**).

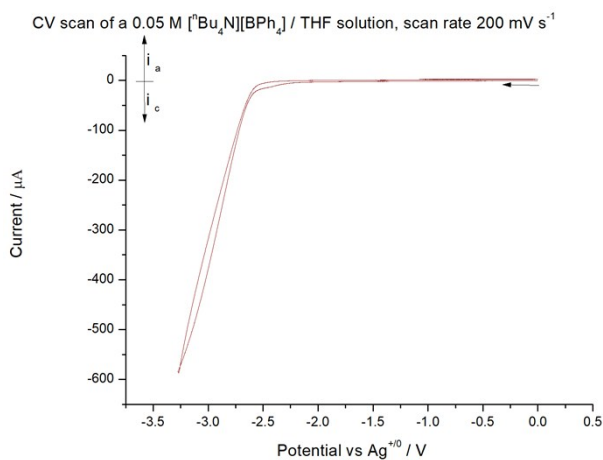


Fig. S1 CV scan of a 0.05 M [ⁿBu₄N][BPh₄] / THF mixture, scan rate 200 mV s⁻¹.

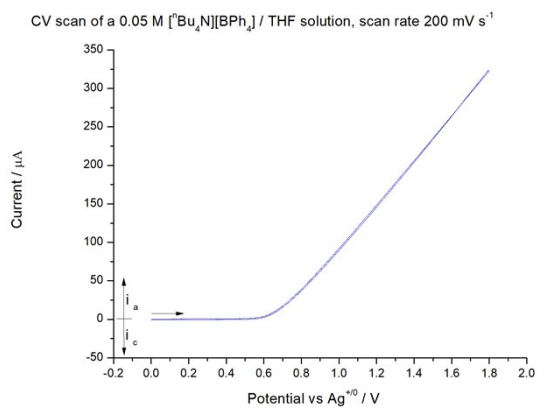


Fig. S2 CV scan of a 0.05 M $[n\text{Bu}_4\text{N}][\text{BPh}_4]$ / THF mixture, scan rate 200 mV s⁻¹.

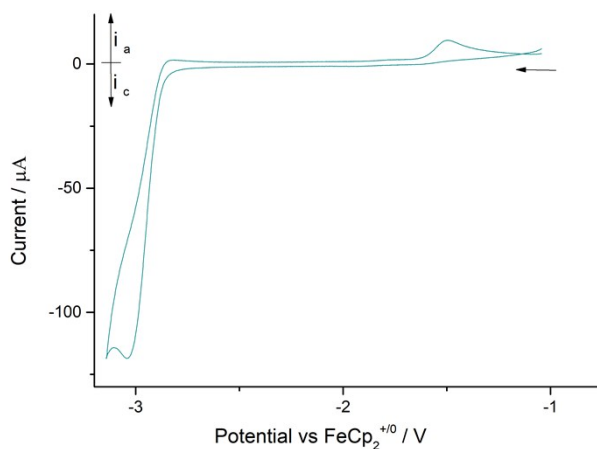


Fig. S3 CV scan for 7.81 mM ThCp^{TM523}Cl in 0.0542 M $[n\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ / THF, scan rate 200 mV s⁻¹.

Table S1 Electrochemical parameters for 8.72 mM ThCp^{TM523} in THF / 0.0525 M $[n\text{Bu}_4][\text{BPh}_4]$. 200 mV s⁻¹ scan rate.

	Process I	Process II	Process III
E_{pa} / V vs $\text{FeCp}_2^{+/0}$	-2.85	-	-
E_{pc} / V vs $\text{FeCp}_2^{+/0}$	-3.06	-2.29	-1.50
$E_{1/2}$ / V vs $\text{FeCp}_2^{+/0}$	-2.96	-	-
ΔE_{pp} / mV	210	-	-
i_{pa} / μA	53	52	52
i_{pc} / μA	45	-	-
$ i_{pa}/i_{pc} $	1.17	-	-
$\Delta E_{pp} = E_{pc} - E_{pa} $			

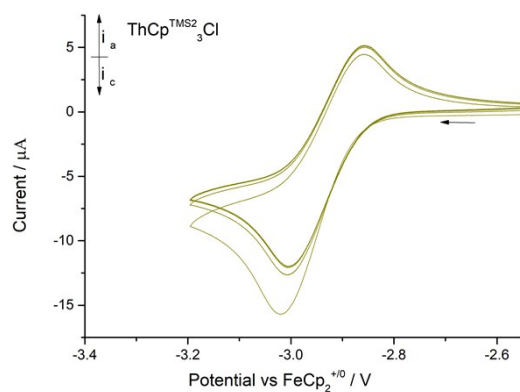
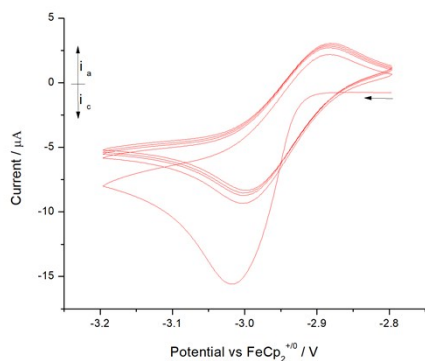


Fig. S4 Overlaid CV scans for $\text{ThCp}^{\text{TMS}_2}_3\text{Cl}$ (5 cycles, 3 mM) (bottom) in 0.05 M $[\text{nBu}_4\text{N}][\text{BPh}_4]$ / THF, scan rate 100 mV s^{-1} .

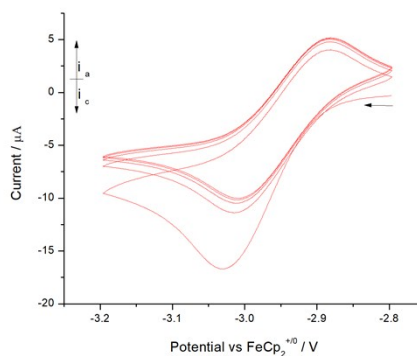
Table S2 Electrochemical parameters for 3.19 mM $\text{ThCp}^{\text{TMS}_2}_3\text{Cl}$ in THF / 0.0525 M $[\text{nBu}_4][\text{BPh}_4]$. 200 mV s^{-1} scan rate.

	Process I	Process II
$E_{pa} / \text{V vs FeCp}_2^{+/0}$	-2.85	-1.47
$E_{pc} / \text{V vs FeCp}_2^{+/0}$	-3.06	-
$E_{1/2} / \text{V vs FeCp}_2^{+/0}$	-2.96	-
$\Delta E_{pp} / \text{mV}$	210	-
$i_{pa} / \mu\text{A}$	20	5
$i_{pc} / \mu\text{A}$	21	-
$ i_{pa}/i_{pc} $	0.95	-
$\Delta E_{pp} = E_{pc} - E_{pa} $		

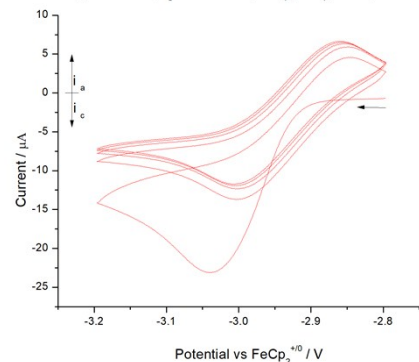
Voltammogram of ThCp^*_3Cl in 0.05 M $[\text{NBu}_4][\text{BPh}_4]$ / THF, 50 mVs⁻¹



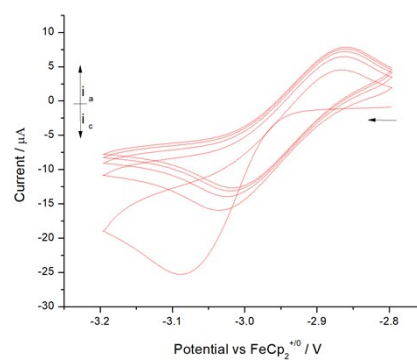
Voltammogram of ThCp^*_3Cl in 0.05 M $[\text{NBu}_4][\text{BPh}_4]$ / THF, 100 mVs⁻¹



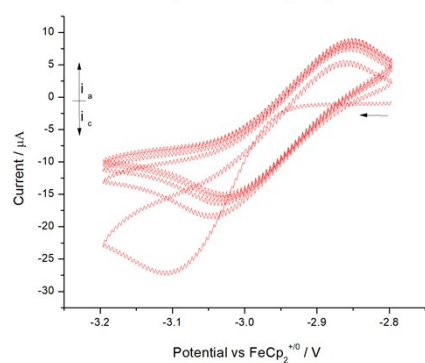
Voltammogram of ThCp^*_3Cl in 0.05 M $[\text{NBu}_4][\text{BPh}_4]$ / THF, 150 mVs⁻¹



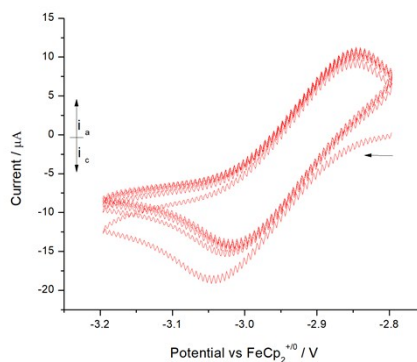
Voltammogram of ThCp^*_3Cl in 0.05 M $[\text{NBu}_4][\text{BPh}_4]$ / THF, 200 mVs⁻¹



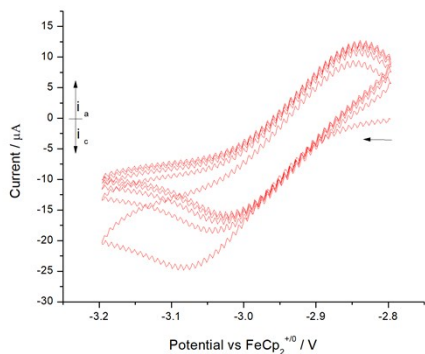
Voltammogram of ThCp^*_3Cl in 0.05 M $[\text{NBu}_4][\text{BPh}_4]$ / THF, 250 mVs⁻¹



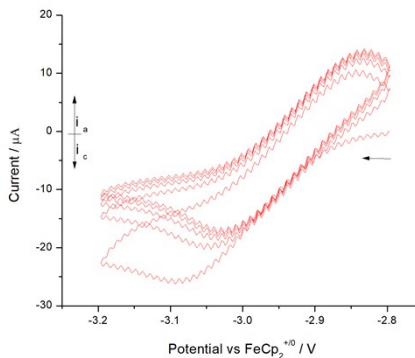
Voltammogram of ThCp^*_3Cl in 0.05 M $[\text{NBu}_4][\text{BPh}_4]$ / THF, 300 mVs⁻¹



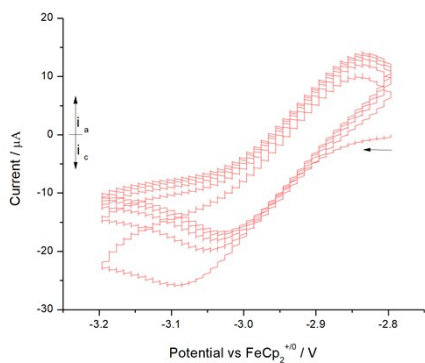
Voltammogram of $\text{ThCp}^{\text{TM}}_3\text{Cl}$ in 0.05 M $[\text{NBu}_4][\text{BPh}_4]$ / THF, 400 mVs^{-1}



Voltammogram of $\text{ThCp}^{\text{TM}}_3\text{Cl}$ in 0.05 M $[\text{NBu}_4][\text{BPh}_4]$ / THF, 500 mVs^{-1}



Voltammogram of $\text{ThCp}^{\text{TM}}_3\text{Cl}$ in 0.05 M $[\text{NBu}_4][\text{BPh}_4]$ / THF, 750 mVs^{-1}



Voltammogram of $\text{ThCp}^{\text{TM}}_3\text{Cl}$ in 0.05 M $[\text{NBu}_4][\text{BPh}_4]$ / THF, 1000 mVs^{-1}

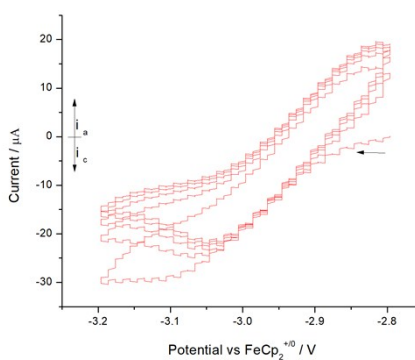


Fig. S5 CV scans (5 cycles) of 3.19 mM $\text{ThCp}^{\text{TM}}_3\text{Cl}$ in THF / 0.0525 M $[\text{nBu}_4][\text{BPh}_4]$. Scan rate is shown above each plot.

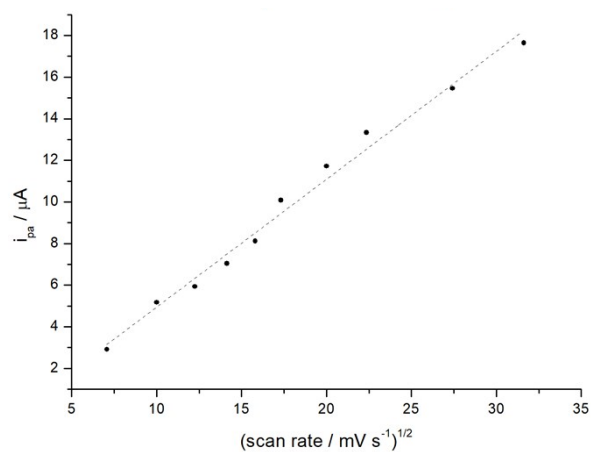


Fig. S6 Plot of i_{pa} versus $v^{1/2}$ for process I in the CV of 3.19 mM $\text{ThCp}^{\text{TM}}_3\text{Cl}$ in THF / 0.0525 M $[\text{nBu}_4][\text{BPh}_4]$. $R^2 = 0.988$.

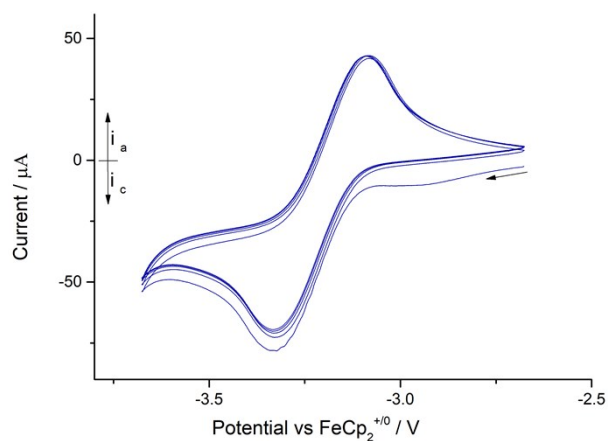


Fig. S7 Overlaid CV scans (5 cycles) for 7.25 mM ThCOT^{TBDMs}₂ in 0.05 M [ⁿBu₄N][BPh₄] / THF, scan rate 100 mV s⁻¹.

Table S3 Electrochemical parameters for 7.25 mM ThCOT^{TBDMs}₂ in THF / 0.0533 M [ⁿBu₄N][BPh₄]. 200 mV s⁻¹ scan rate.

	Process I	Process II	Process III
$E_{pa} / \text{V vs FeCp}_2^{+/0}$	-3.02	-2.20	-0.89
$E_{pc} / \text{V vs FeCp}_2^{+/0}$	-3.44	-	-
$E_{1/2} / \text{V vs FeCp}_2^{+/0}$	-3.23	-	-
$\Delta E_{pp} / \text{mV}$	420	-	-
$i_{pa} / \mu\text{A}$	95	17	5
$i_{pc} / \mu\text{A}$	84	-	-
$ i_{pa}/i_{pc} $	1.13	-	-
$\Delta E_{pp} = E_{pc} - E_{pa} $			

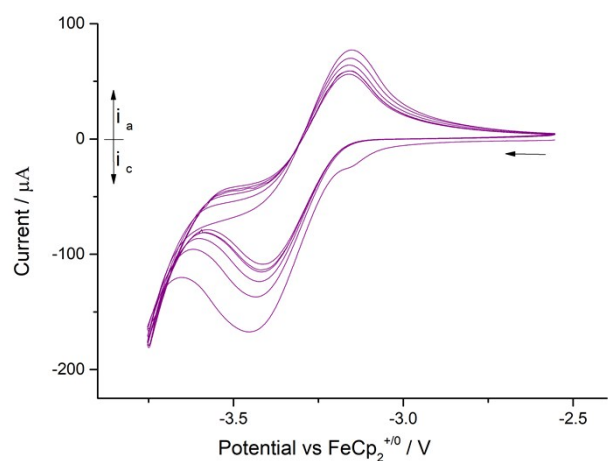


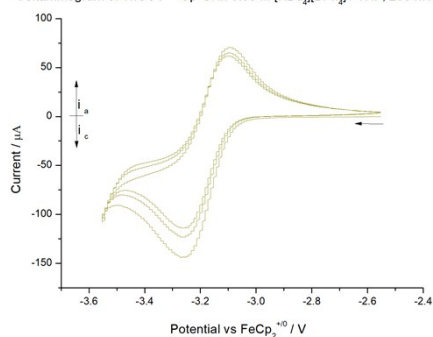
Fig. S8 Overlaid CV scans (6 cycles) for 11.0 mM ThCOT^{TIPS2}Cp*Cl in 0.05 M [ⁿBu₄N][BPh₄] / THF, scan rate 200 mV s⁻¹.

Table S4 Electrochemical parameters for 11.0 mM ThCOT^{TIPS2}Cp*Cl in THF / 0.0534 M [ⁿBu₄N][BPh₄]. 200 mV s⁻¹ scan rate.

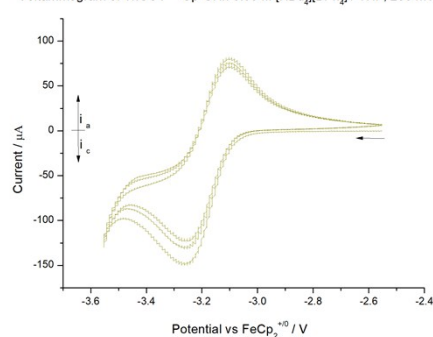
	Process I	Process II
$E_{pa} / \text{V vs FeCp}_2^{+/0}$	-3.18	-1.50
$E_{pc} / \text{V vs FeCp}_2^{+/0}$	-3.46	-
$E_{1/2} / \text{V vs FeCp}_2^{+/0}$	-3.32	-
$\Delta E_{pp} / \text{mV}$	280	-
$i_{pa} / \mu\text{A}$	138	13
$i_{pc} / \mu\text{A}$	168	-
$ i_{pa}/i_{pc} $	0.82	-

$\Delta E_{pp} = |E_{pc} - E_{pa}|$

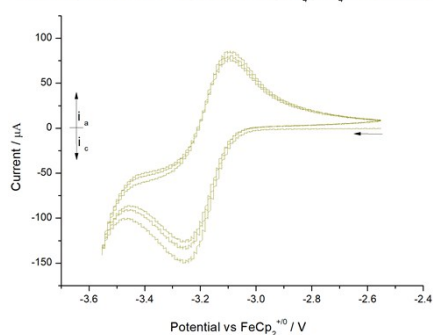
Voltammogram of ThCOT^{TIPS2}Cp*Cl in 0.05 M [NBu₄][BPh₄] / THF, 200 mVs⁻¹



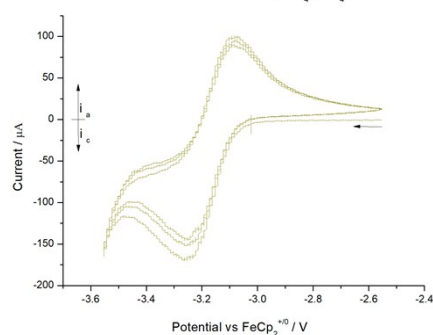
Voltammogram of ThCOT^{TIPS2}Cp*Cl in 0.05 M [NBu₄][BPh₄] / THF, 250 mVs⁻¹



Voltammogram of ThCOT^{TIPS2}Cp*Cl in 0.05 M [NBu₄][BPh₄] / THF, 300 mVs⁻¹



Voltammogram of ThCOT^{TIPS2}Cp*Cl in 0.05 M [NBu₄][BPh₄] / THF, 400 mVs⁻¹



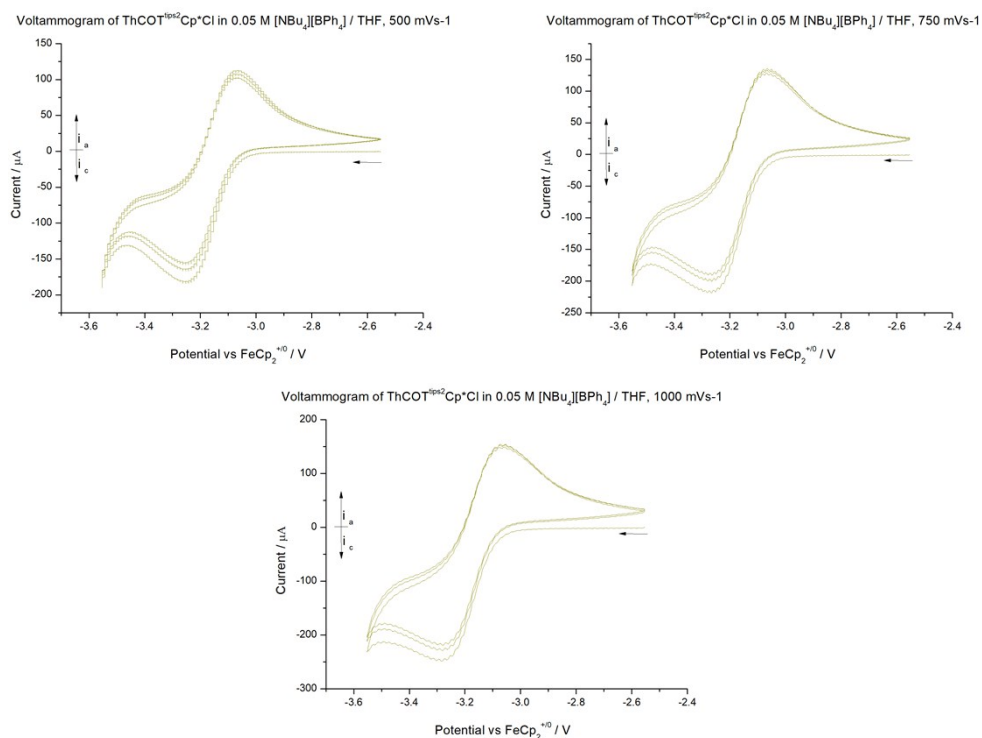


Fig. S9 CV scans (3 cycles) of 11.0 mM ThCOT^{TIPS2}Cp*Cl in THF / 0.0534 M [ⁿBu₄N][BPh₄]. Scan rate is shown above each plot.

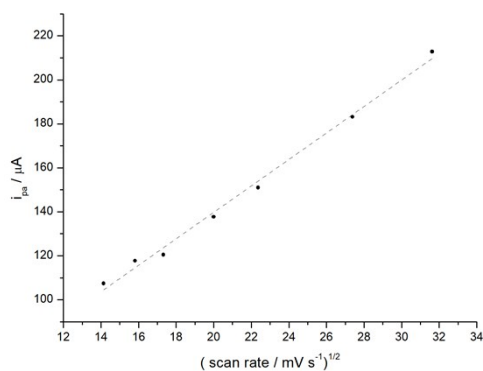


Fig. S10 Plot of i_{pa} versus $(\text{scan rate})^{1/2}$ for process I in the CV of 11.0 mM ThCOT^{TIPS2}Cp*Cl in THF / 0.0534 M [ⁿBu₄N][BPh₄]. $R^2 = 0.997$.

References

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- ² J. S. Parry, Cloke, S. J. Coles and M. B. Hursthouse, *J. Am. Chem. Soc.*, 1999, **121**, 6867–6871.
- ³ Z. E. Button, J. A. Higgins, M. Suvova, F. G. N. Cloke and S. M. Roe, *Dalton Trans.*, 2015, **44**, 2588–2596.