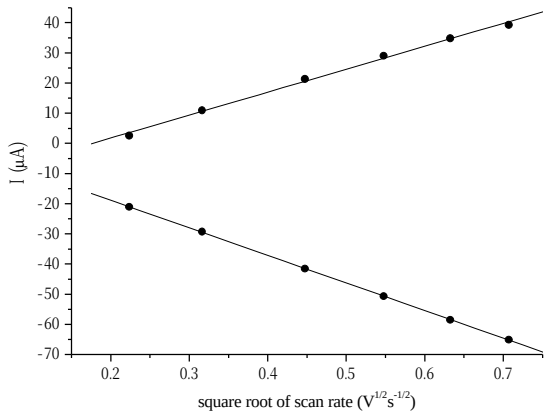


Figure S1 Square root of scan rate vs current peak of the redox wave (A, A') for $[V^{IV}OCl(tpa)]^{+}/[V^{III}OCl(tpa)]$ process.

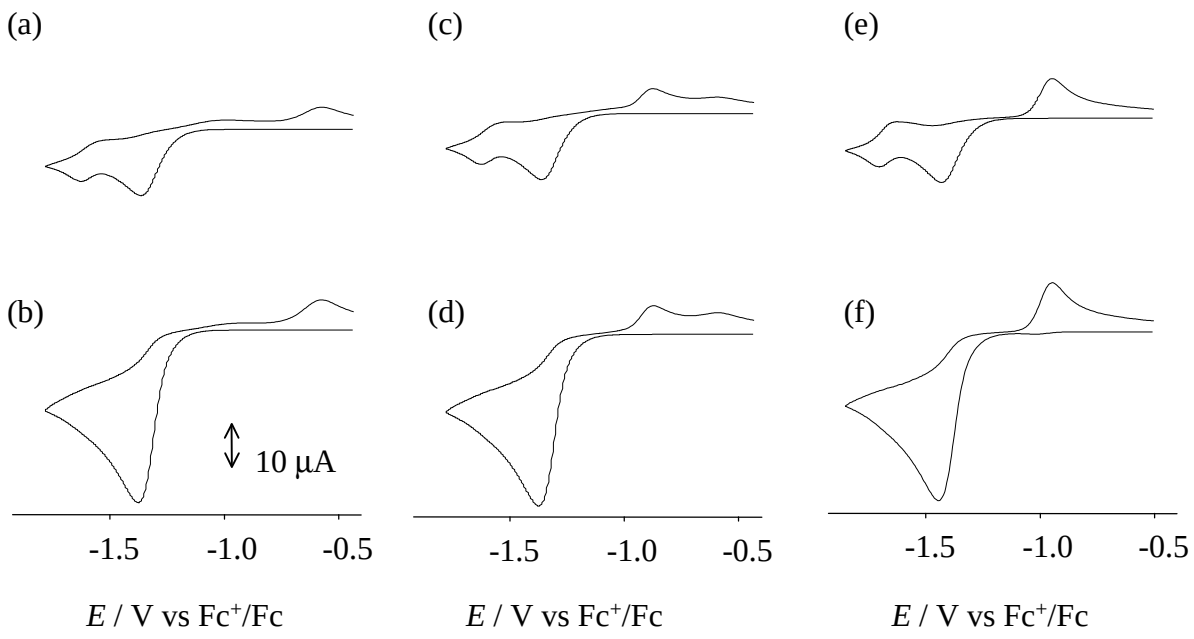


Figure S2 Simulated cyclic voltammograms using the parameters described in the text. Each CV corresponds to that in Figure 4.

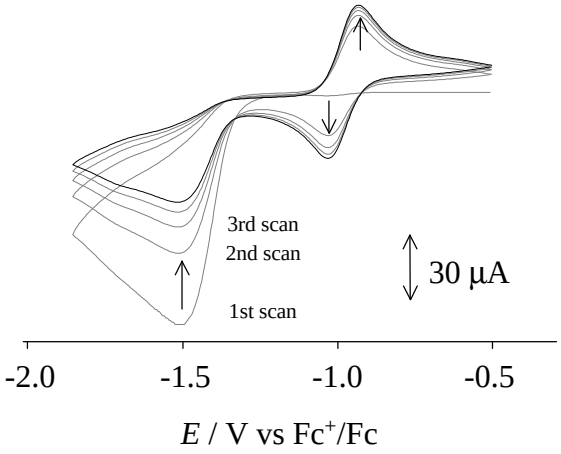
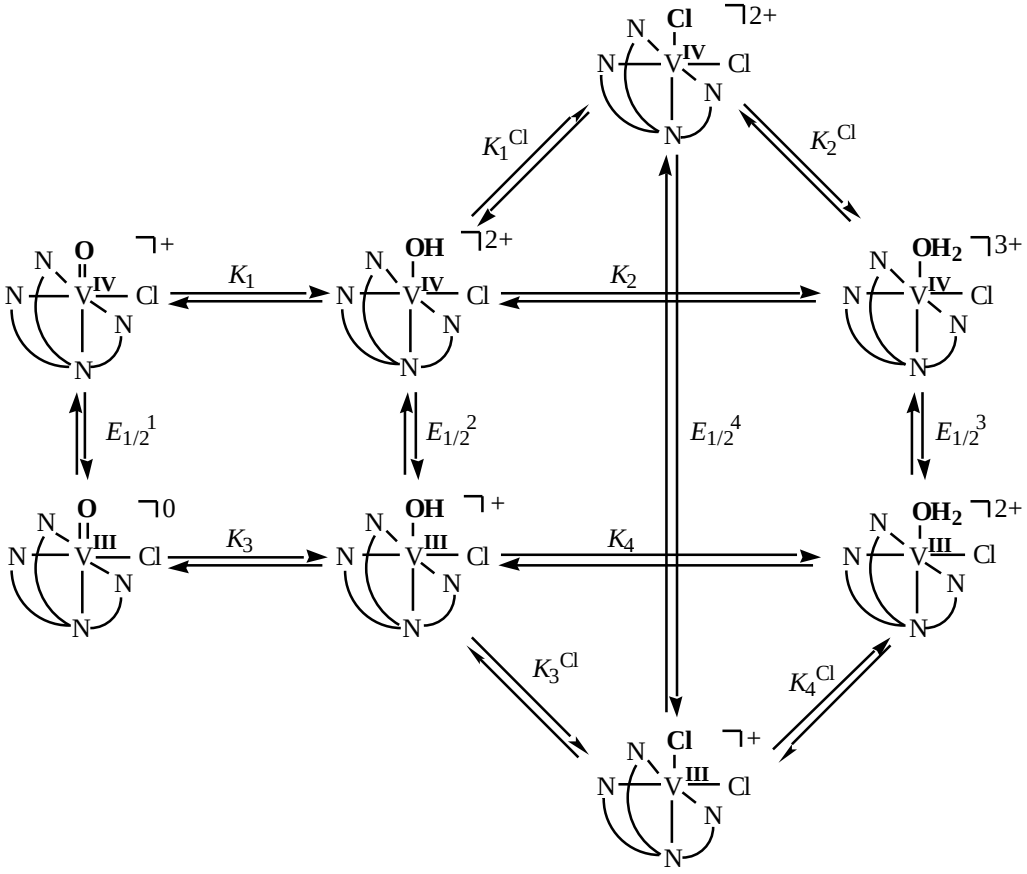


Figure S3 The simulated cyclic voltammogram corresponding to Fig. 5 (b). The black line corresponds the observed CV for 5th cycle.



Scheme S1 Redox scheme of $[VOCl(tpa)]^+$ for the simulation.

Parameters used in the simulation (redox potentials and formation constants (K_i and K_i^{Cl})) are defined as follows,

$K_1 = [\{V^{IV}(OH)Cl(tpa)\}^{2+}][TsO^-] / [\{V^{IV}OCl(tpa)\}^+][TsOH] = 5 \times 10^3$,

$K_2 = [\{V^{IV}(OH_2)Cl(tpa)\}^{3+}][TsO^-] / [\{V^{IV}(OH)Cl(tpa)\}^{2+}][TsOH] = 5 \times 10^{-6}$,

$K_3 = [\{V^{III}(OH)Cl(tpa)\}^+][TsO^-] / [\{V^{III}OCl(tpa)\}][TsOH] = 9 \times 10^9$,

$K_4 = [\{V^{III}(OH_2)Cl(tpa)\}^{2+}][TsO^-] / [\{V^{III}(OH)Cl(tpa)\}^+][TsOH] = 2.2 \times 10^5$,

$K_1^{Cl} = [\{V^{IV}Cl_2(tpa)\}^{2+}][OH^-] / [\{V^{IV}(OH)Cl(tpa)\}^{2+}][Cl^-] = 4.3 \times 10^{-22}$,

$K_2^{Cl} = [\{V^{IV}Cl_2(tpa)\}^{2+}][H_2O] / [\{V^{IV}(OH_2)Cl(tpa)\}^{3+}][Cl^-] = 9.1 \times 10^3$,

$K_3^{Cl} = [\{V^{III}Cl_2(tpa)\}^+][OH^-] / [\{V^{III}(OH)Cl(tpa)\}^+][Cl^-] = 1.1 \times 10^{16}$,

$K_4^{Cl} = [\{V^{III}Cl_2(tpa)\}^+][H_2O] / [\{V^{III}(OH_2)Cl(tpa)\}^{2+}][Cl^-] = 5 \times 10^{-2}$,

$E_{1/2}^1 = -1.59$ V, $E_{1/2}^2 = -1.23$ V, $E_{1/2}^3 = -0.59$ V, $E_{1/2}^4 = -0.90$ V.