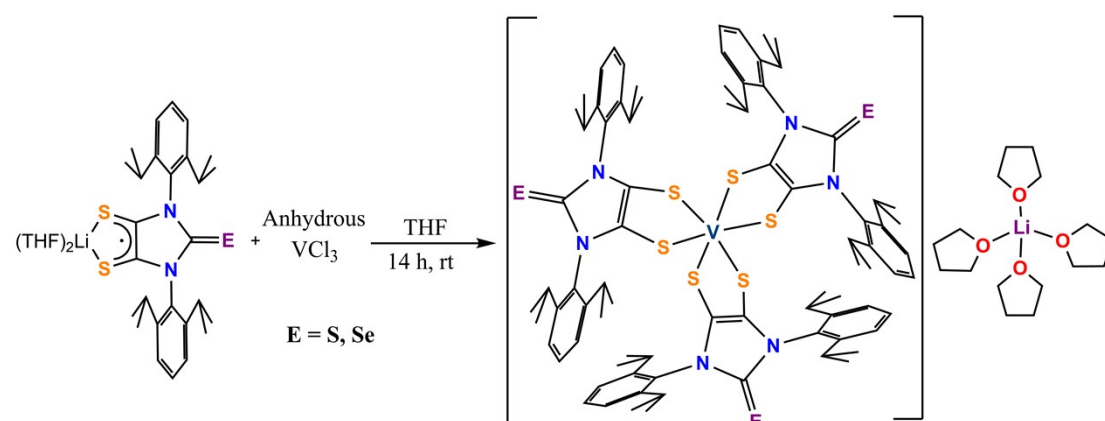




Scheme 1 Synthesis of complexes $[\text{Li}(\text{THF})_4][\text{V}(\text{SS-NHC}=\text{S})_3]$ ($\text{E} = \text{S}$; **1**) and $[\text{Li}(\text{THF})_4][\text{V}(\text{SS-NHC}=\text{Se})_3]$ ($\text{E} = \text{Se}$; **2**)

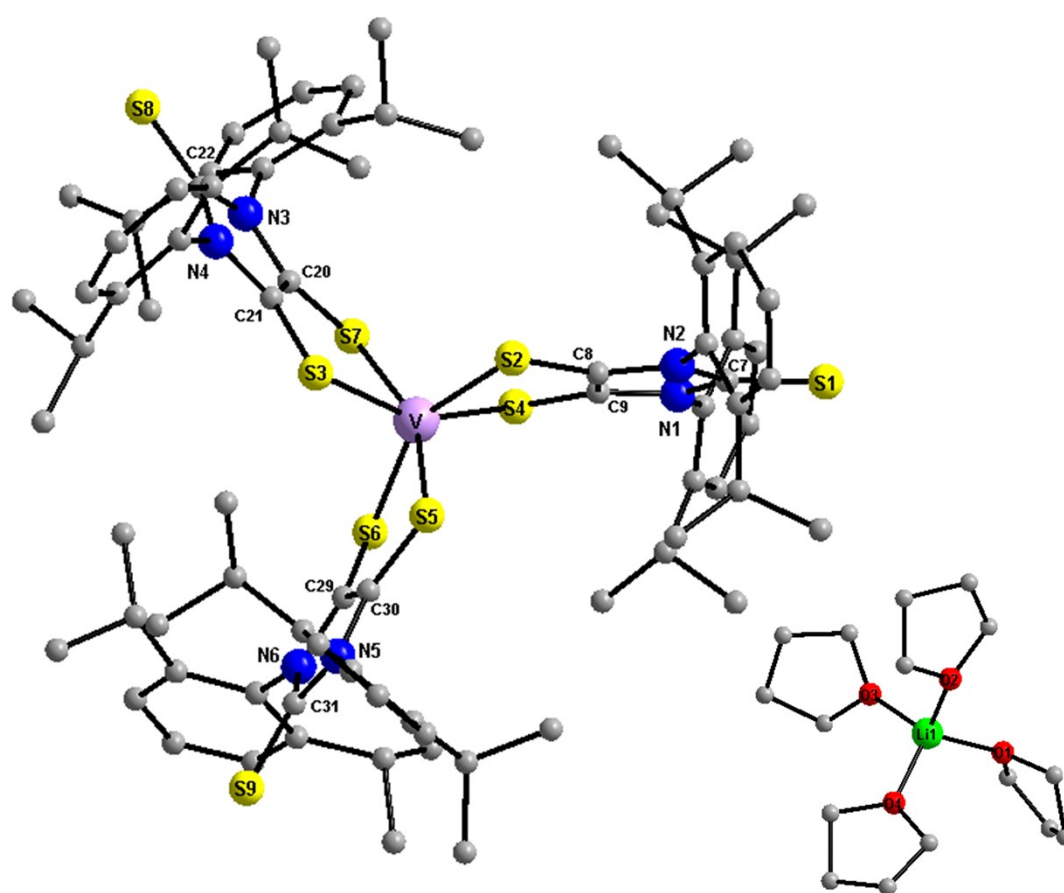


Fig. 1(a) Molecular structure of the complex **1**. All H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°) are 2.3826 (9) for V1—S2, 2.3634 (9) for V1—S3, 2.4075 (9) for V1—S4, 2.3682 (8) for V1—S5, 2.4244 (9) for V1—S6, 2.4383 (9) for V1—S7, 85.50 (3) for S2—V1—S4, 151.37 (3) for S2—V1—S6, 117.32 (3) for S2—V1—S7, 88.47 (3) for S3—V1—S2, 154.60 (3) for S3—

V1—S4, 80.08 (3) for S3—V1—S5, 111.49 (3) for S3—V1—S6, 84.79 (3) for S3—V1—S7, 84.11 (3) for S4—V1—S6, 76.22 (3) for S4—V1—S7, 78.58 (3) for S5—V1—S2, 122.55 (3) for S5—V1—S4, 84.73 (3) for S5—V1—S6, 157.82 (3) for S5—V1—S7, 85.85 (3) for S6—V1—S7.

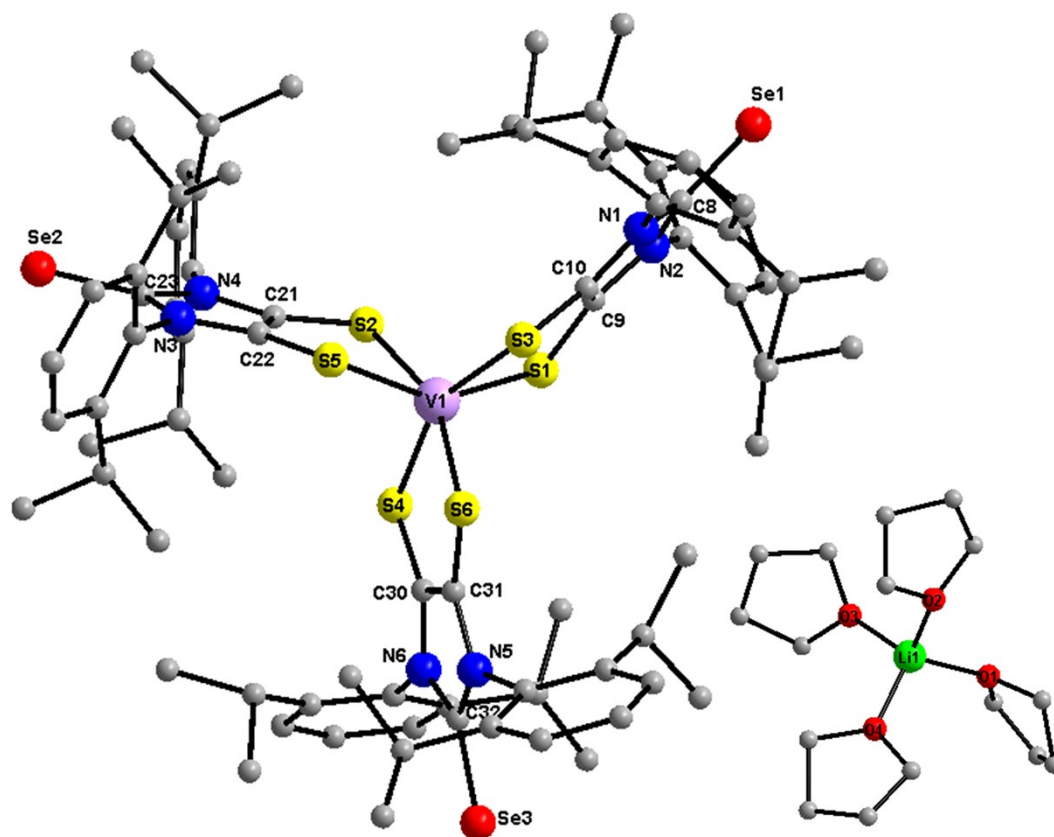


Fig. 1(b) Molecular structure of the complex **2**. All H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°) are 2.3832 (13) for V1—S1, 2.3700 (13) for V1—S2, 2.4139 (13) for V1—S3, 2.3694 (14) for V1—S4, 2.4257 (14) for V1—S5, 2.4369 (14) for V1—S6, 1.767 (5) for Se1—C8, 1.799 (5) for Se2—C23, 1.769 (5) for Se3—C32, 79.99 (5) for S4—V1—S2, 88.45 (5) for S4—V1—S1, 78.74 (5) for S2—V1—S1, 154.65 (5) for S4—V1—S3, 122.62 (5) for S2—V1—S3, 85.52 (5) for S1—V1—S3, 111.70 (5) for S4—V1—S5, 84.76 (5) for S2—V1—S5, 151.33 (5) for S1—V1—S5, 83.86 (5) for S3—V1—S5, 84.82 (5) for S4—V1—S6, 157.66 (5) for S2—V1—S6, 117.31 (5) for S1—V1—S6, 76.24 (5) for S3—V1—S6, 85.77 (5) for S5—V1—S6.

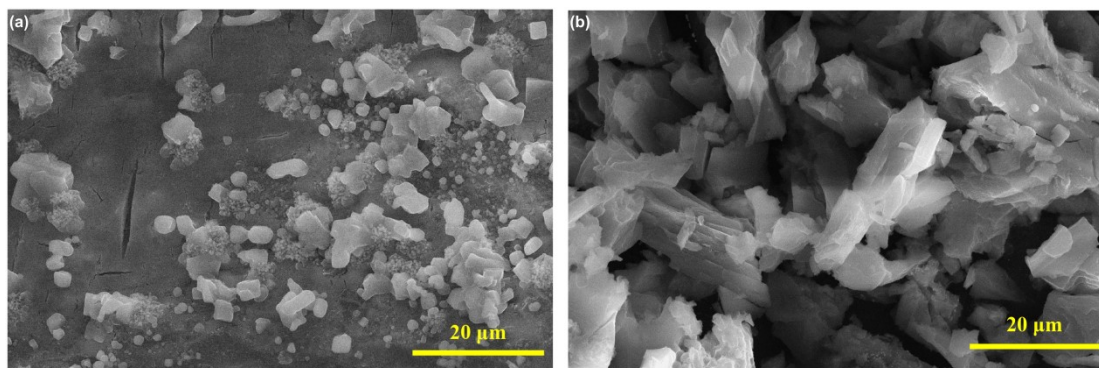


Fig 2. Field Emission Scanning Electron Microscopy (FE-SEM) images of (a) complex **1** and (b) complex **2** showing differences in surface morphology.

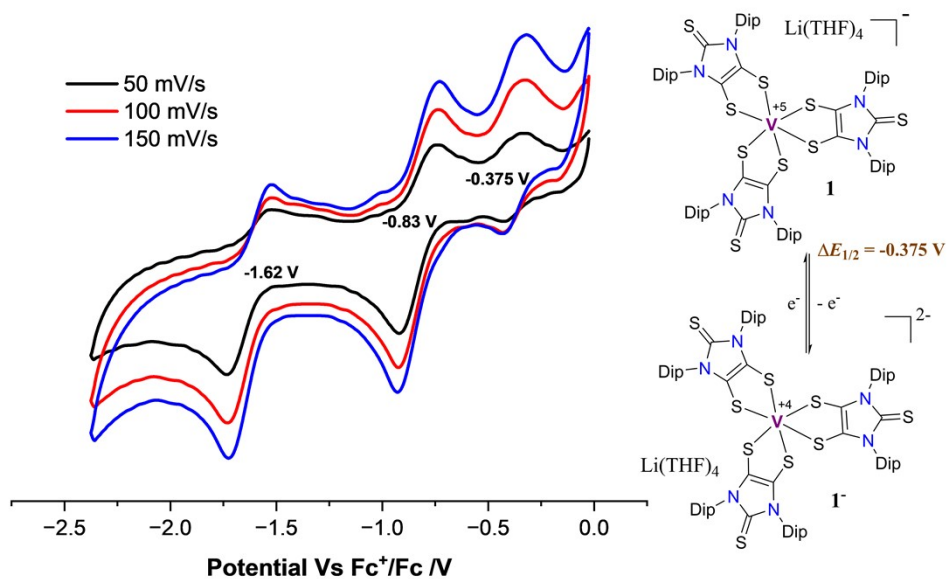


Fig 3. Cyclic voltammogram of complex **1** in THF solution of 0.1 M $[n\text{-Bu}_4\text{N}]\text{PF}_6$ with RE: Ag, WE: GC, and CE: Pt.

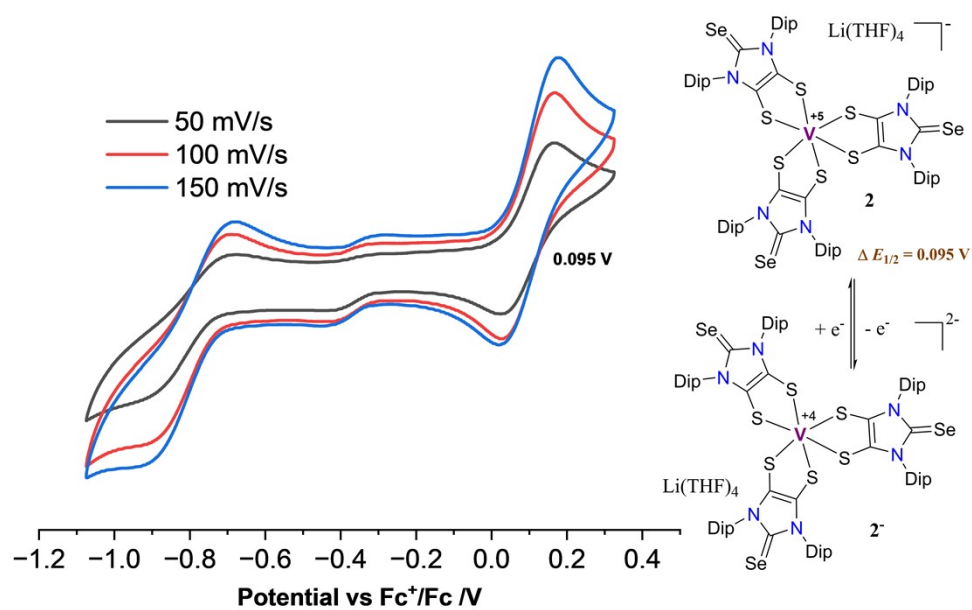


Fig 4. Cyclic voltammogram of complex **2** in THF solution of 0.1 M $[n\text{-Bu}_4\text{N}]\text{PF}_6$ with RE: Ag, WE: GC, and CE: Pt.

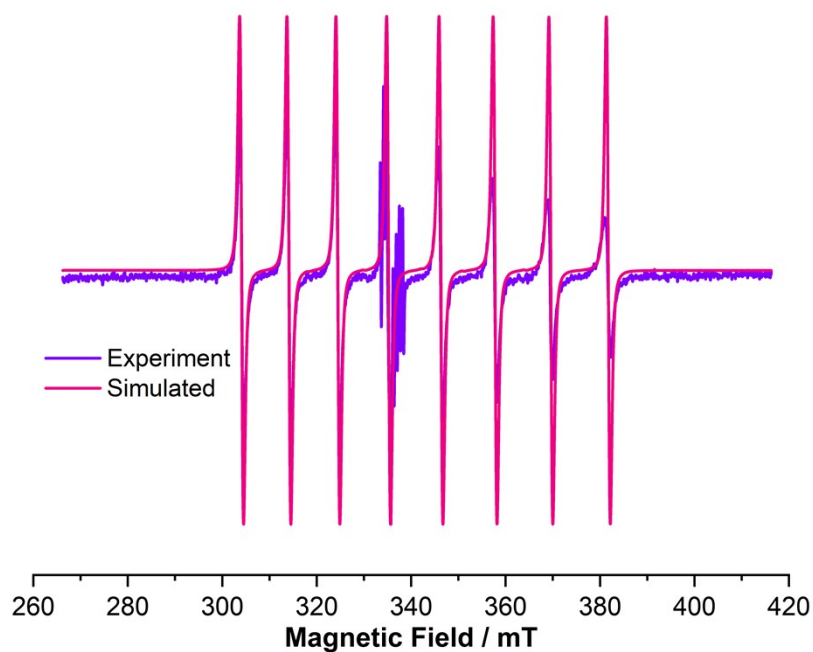


Fig. 5. X-band EPR spectra of complex **1** $^{\cdot-}$ at 298 K in THF. Blue and red lines represent the experimental and simulated spectra using the EasySpin program.

Simulation parameters: $g_{\text{iso}} = 1.96482$, $\text{LW1} = 0.509874$ mT, $\text{LW2} = 0.510566$ mT, $A(^{51}\text{V}) = 305.0132$ MHz. Centre of frequency 335.7 mT.

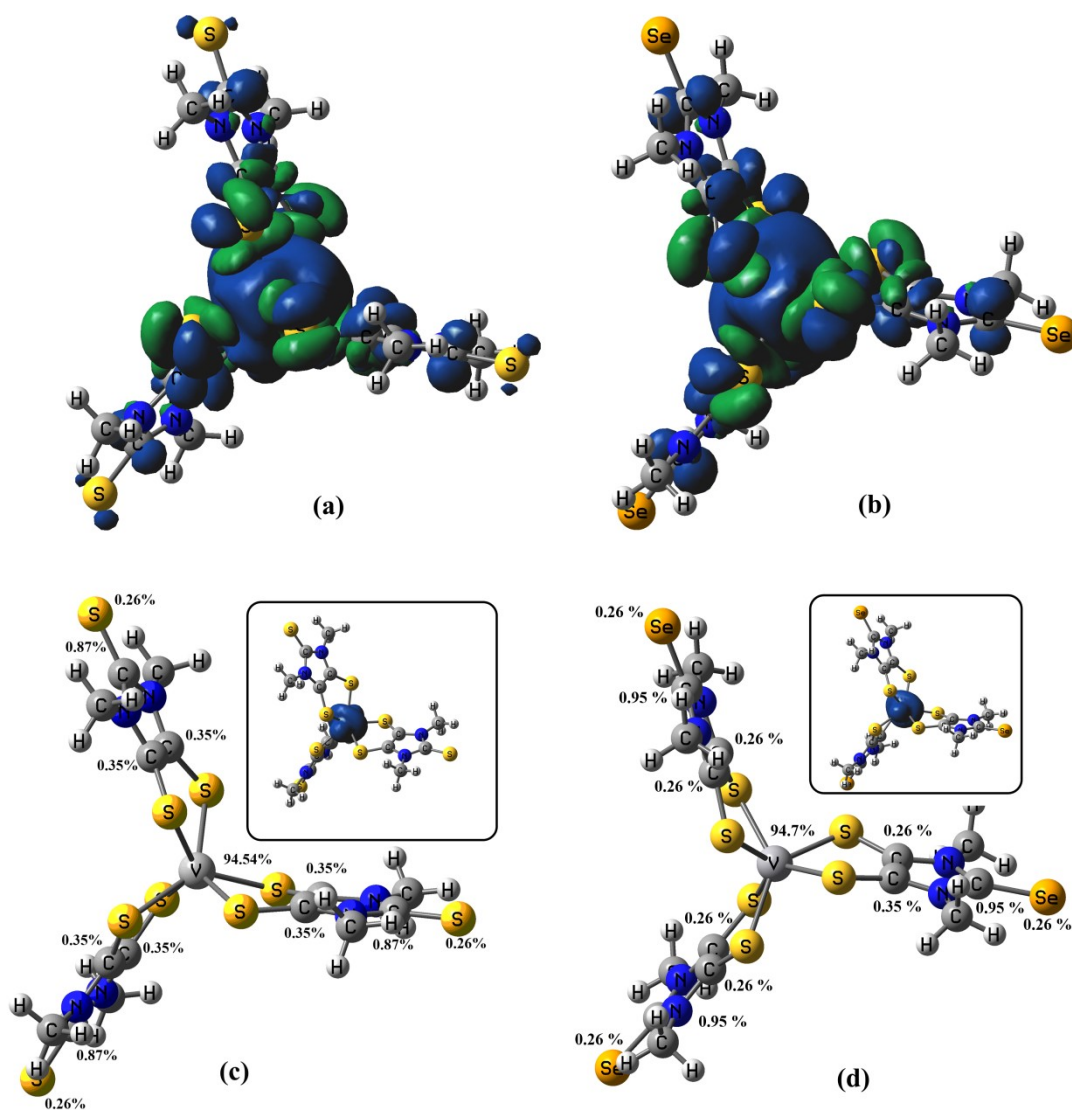


Fig. 6 (a) and (b) Mulliken α -spin densities of dianionic complex 1' and 2' in doublet states respectively. (c) and (d) percentage of α -spins on atoms of dianions 1' and 2'. The d_{z^2} orbital is shown *in set*.

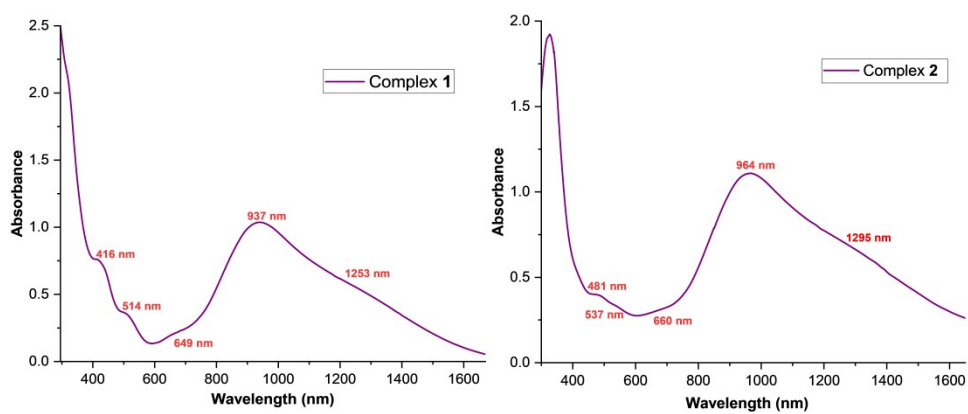


Fig. 7 UV-vis-NIR in THF (a) complex 1, (b) complex 2.

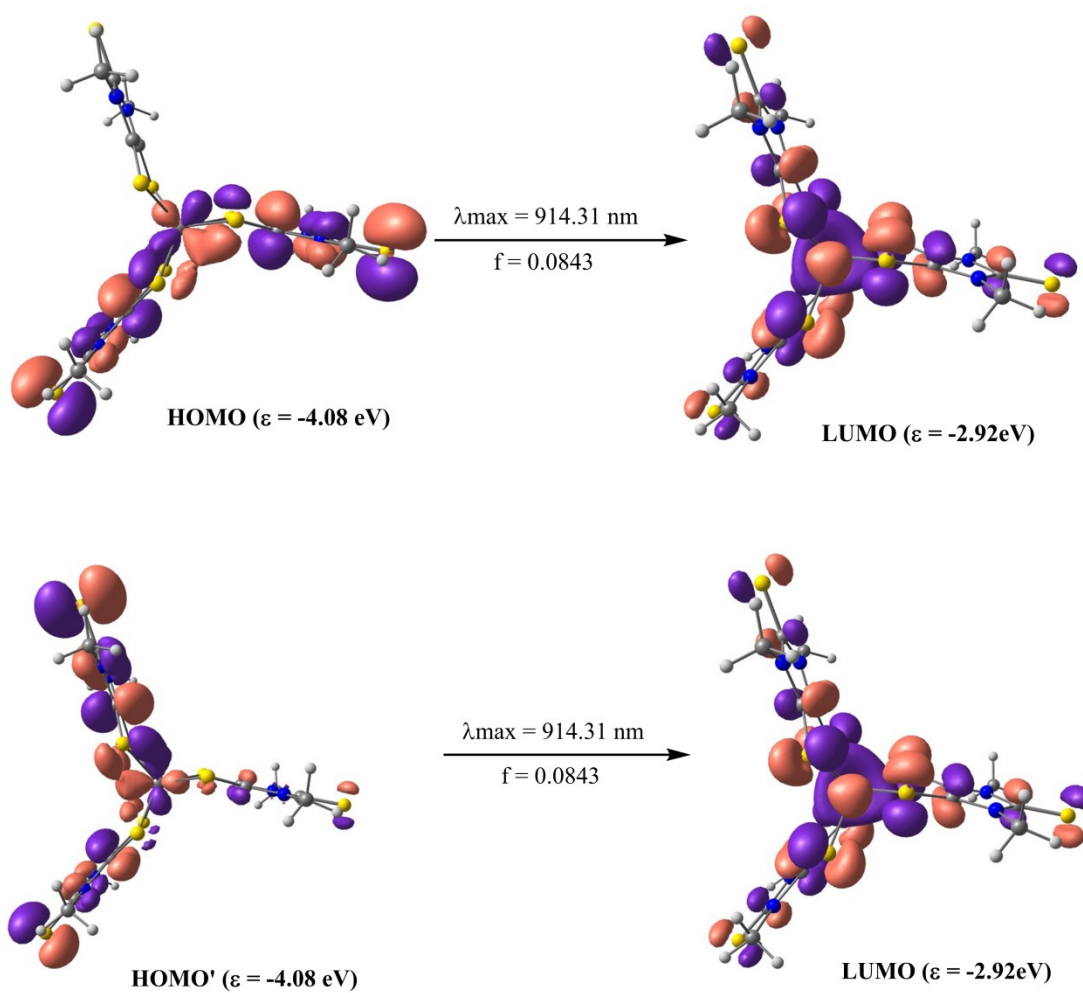


Fig. 8 TD-DFT results of complex 1 (ESI for details).

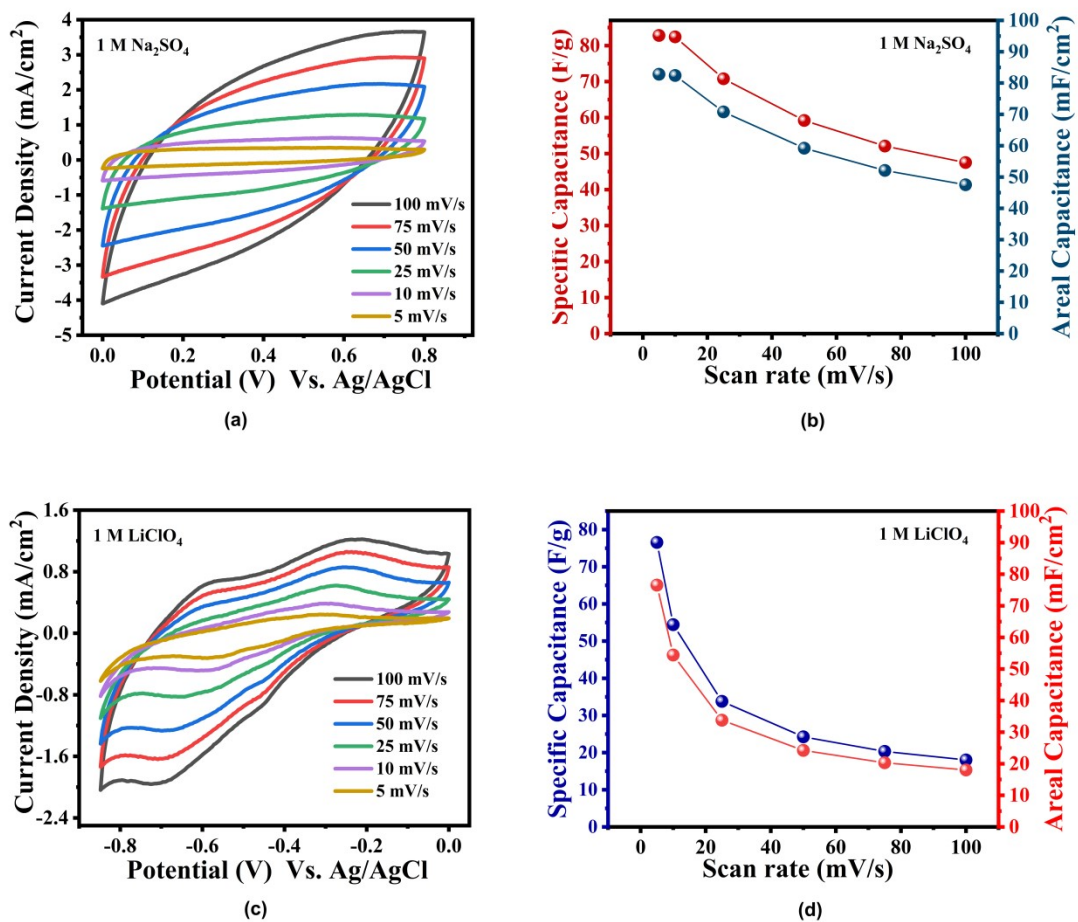
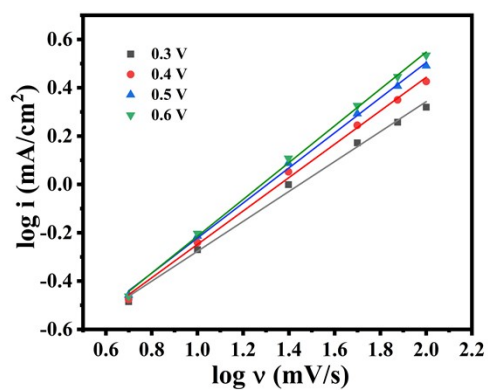
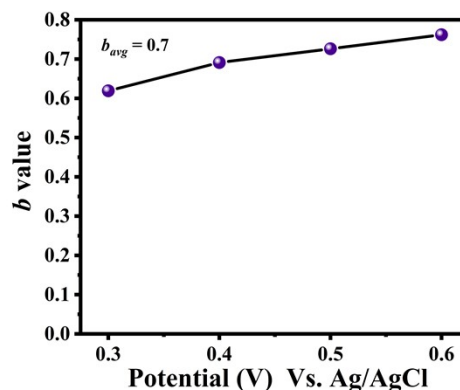


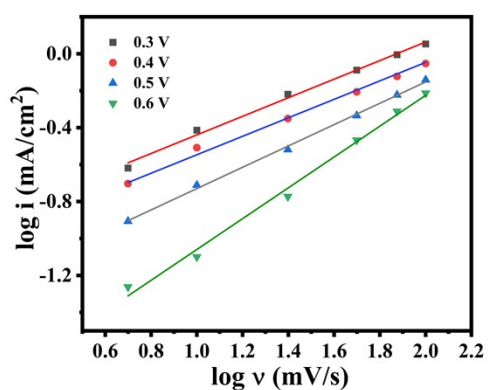
Fig. 9 CV plots of (a) complex 1, (c) complex 2 and specific capacitance of (b) complex 1, (d) complex 2 with varying scan rates of 5-100 mV s⁻¹.



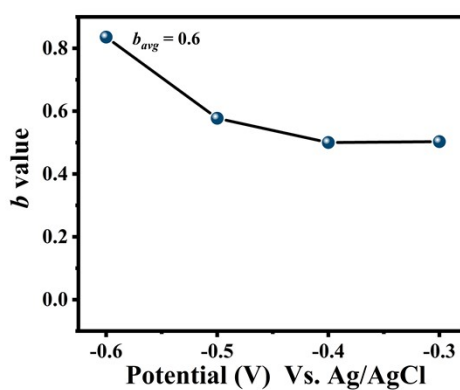
(a)



(b)



(c)



(d)

Fig. 10 Power law plots of (a) complex 1, (c) complex 2 and corresponding b values of (b) complex 1, (d) complex 2 obtained from the slopes of the power law plots.

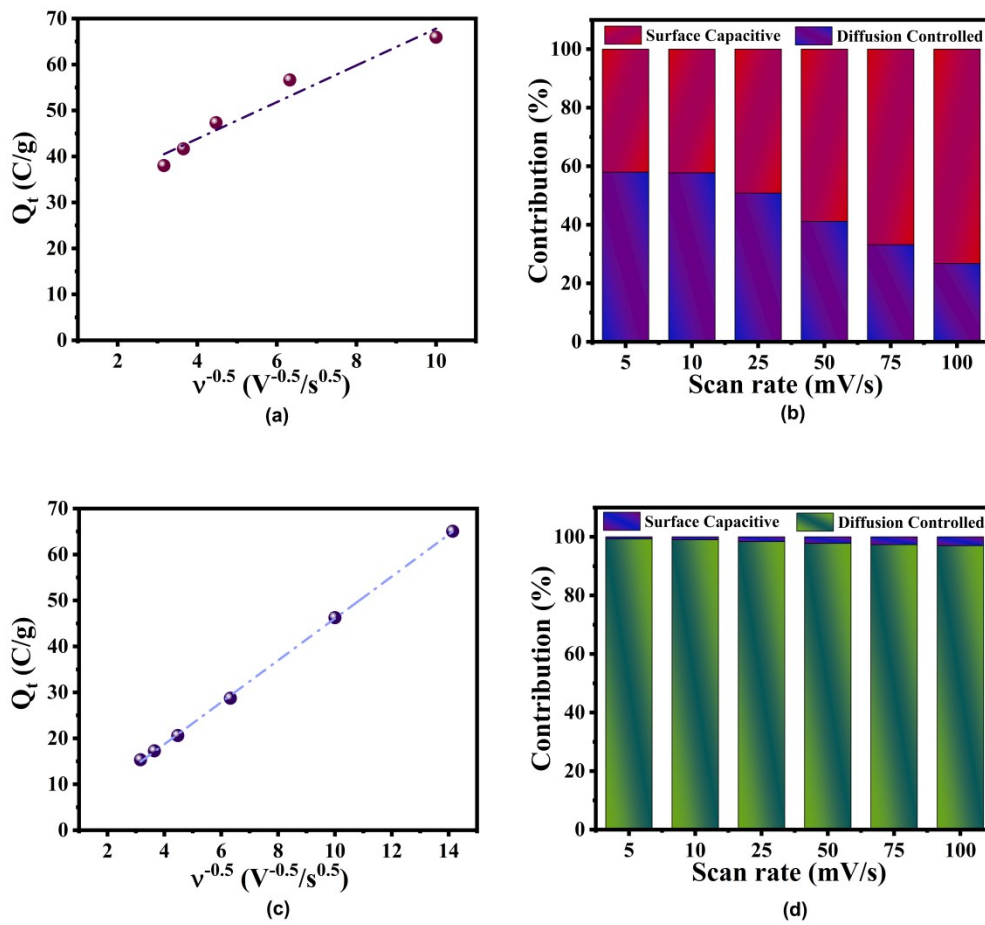


Fig. 11 Plots of total charge Q_t against the inverse square root of the scan rate of **(a)** complex 1, **(c)** complex 2 and corresponding plots showing the percentage contributions of each mechanism to the total charge of **(b)** complex 1, **(d)** complex 2 at different scan rates.

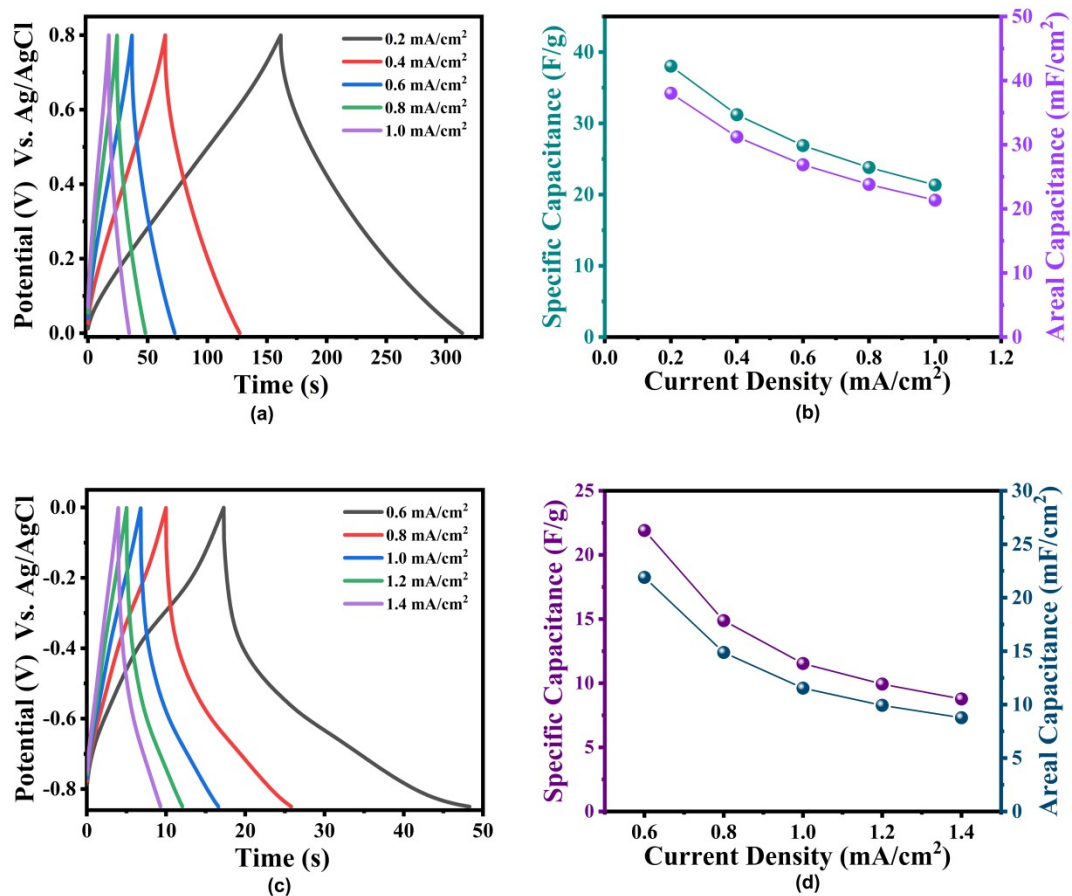


Fig. 12 Galvanostatic charge-discharge plots of **(a)** complex 1 and **(c)** complex 2 with different current densities. Specific capacitance of **(b)** complex 1 and **(d)** complex 2 vs current density.

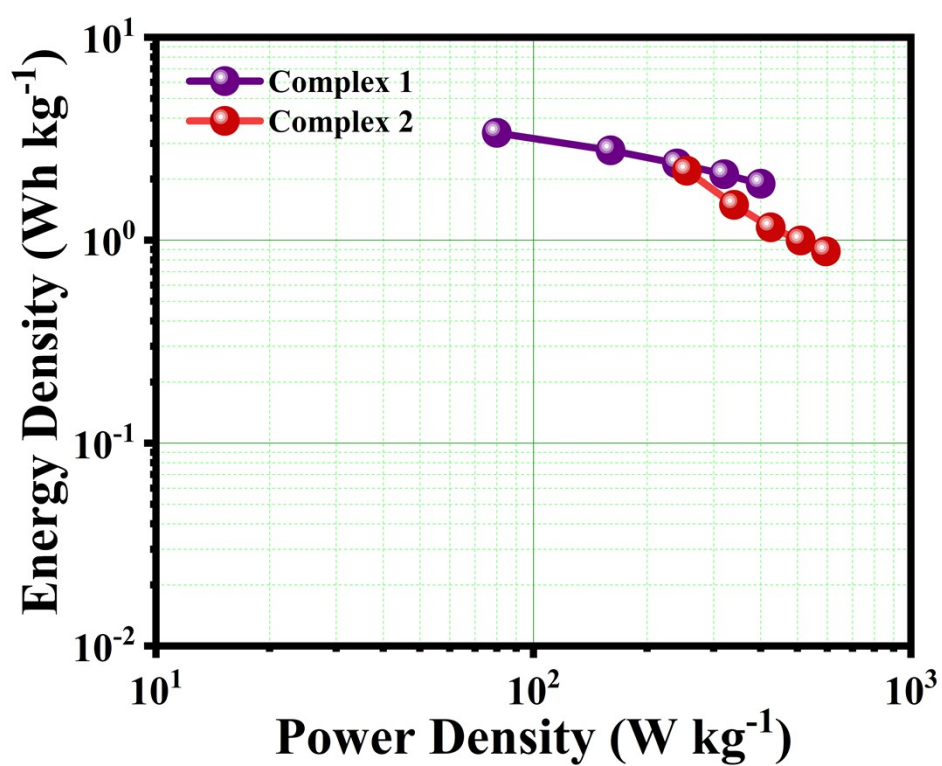


Fig. 13 Ragone plot showing energy and power densities of complexes **1** and **2** electrodes.

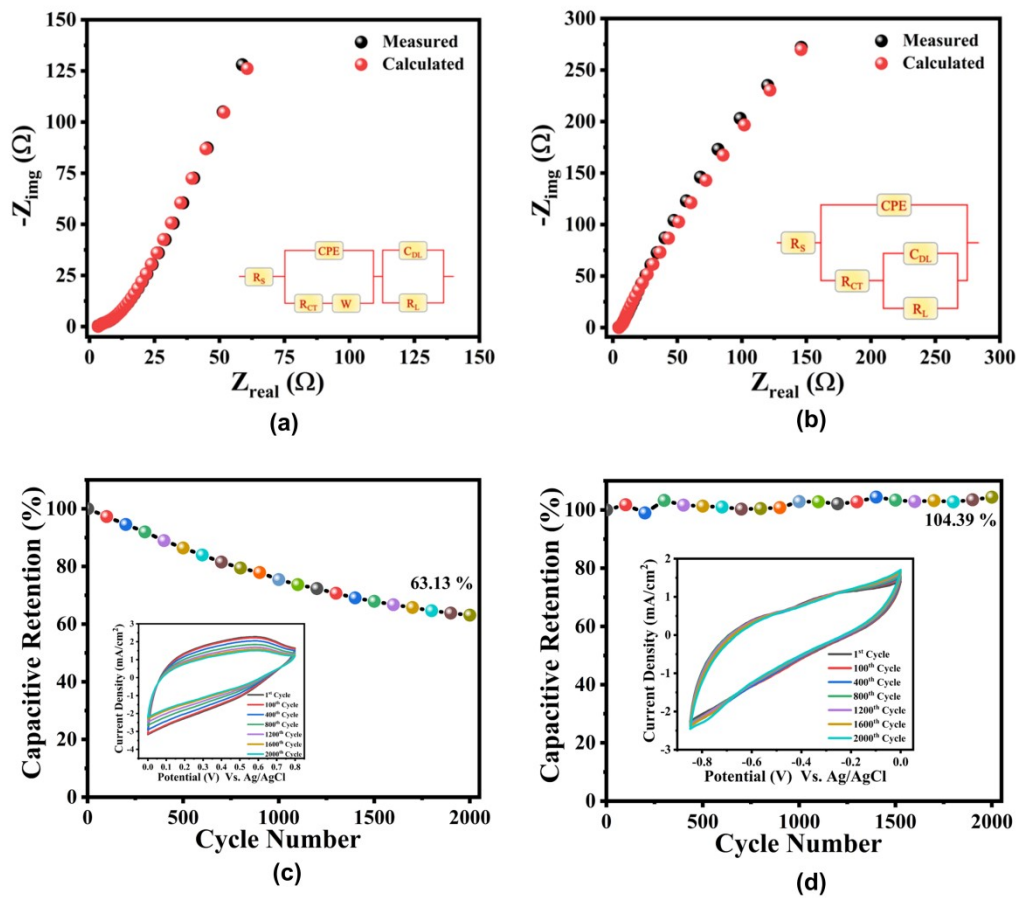


Fig. 14 Electrochemical impedance spectroscopy (EIS) analysis: Nyquist plots of (a) complex 1 and (b) complex 2. The fitting circuit is shown as an inset. Capacity retention and cyclic stability for the electrodes (c) complex 1 and (d) complex 2 for 2000 cycles.