Electronic Supplementary Material (ESI) for Dalton Transactions
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Investigating the Coordination, Electrochemistry, and Kinetics of Cu^{2+} Reduction by Biologically Relevant Selone and Thione Compounds

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SUPPLEMENTARY INFORMATION

X-ray structural data. Crystal packing diagrams of **1** and **2** along the *a*-axis and **4b** along the *b*-axis showing short contact interactions between S-O, Se-O, O-H, H-F and Se-Se (Figs. S1-S3).

Electrochemical studies. Cyclic voltammograms of MISeox and $Cu^{2+/+}$ reduction couples of $[Cu(dmit)_3][OTf]$ (**3**) and $[Cu(dmise)_4][OTf]$ (**4**) (Fig. S4).

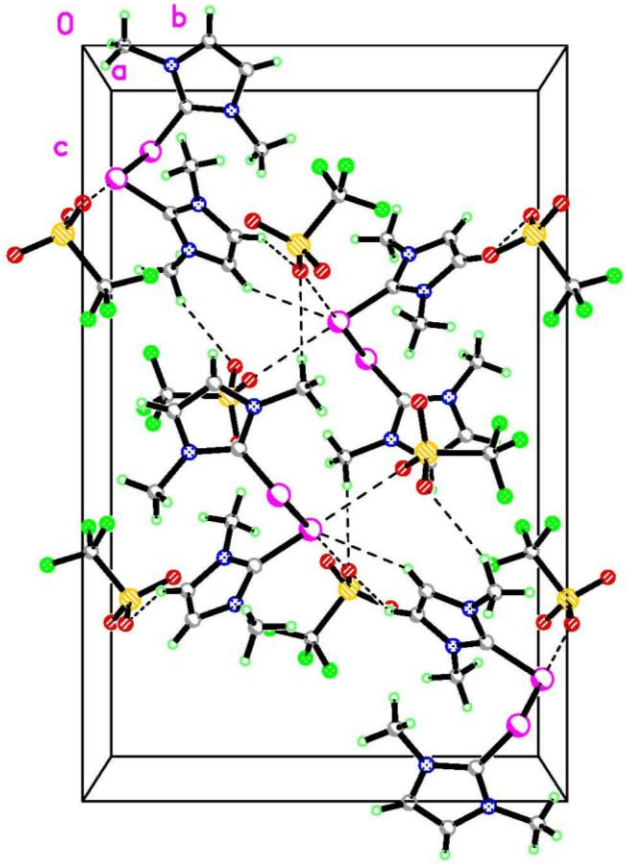

Fig. S1. Crystal packing diagram of $[(dmise)_2][(OTf)_2]$ (**1**) along the *a*-axis showing short contact interactions and hydrogen bonds between Se-O, H-O, and F-H atoms.

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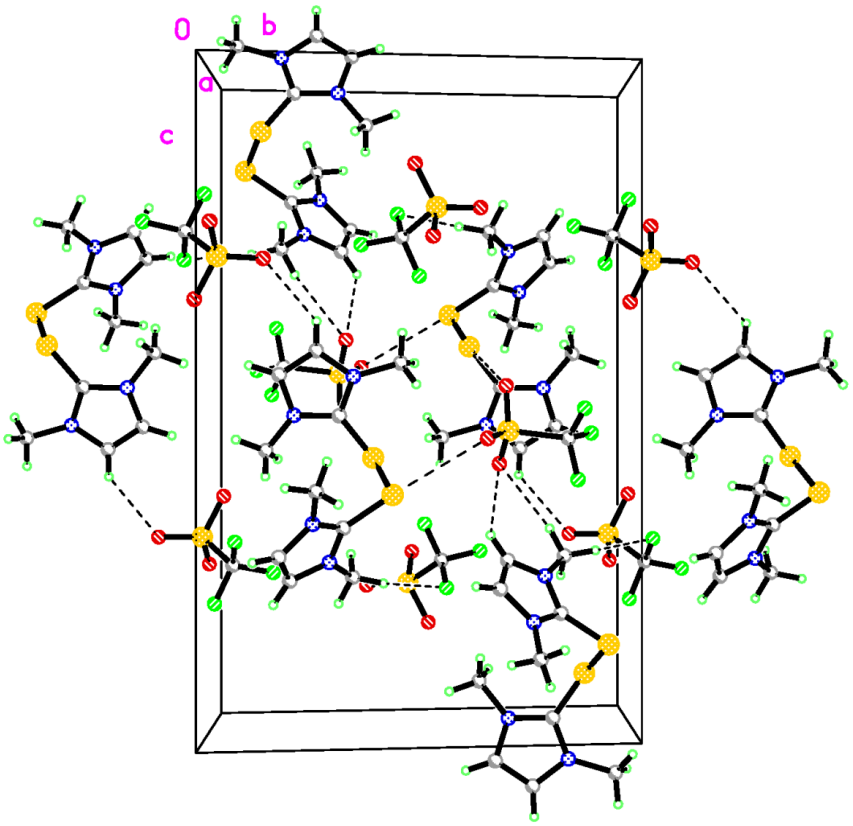

Fig. S2. Crystal packing diagram of $[(dmit)_2][(OTf)_2]$ (**2**) along the *a*-axis showing short contact interactions and hydrogen bonds between S-O, H-O, and F-H atoms.

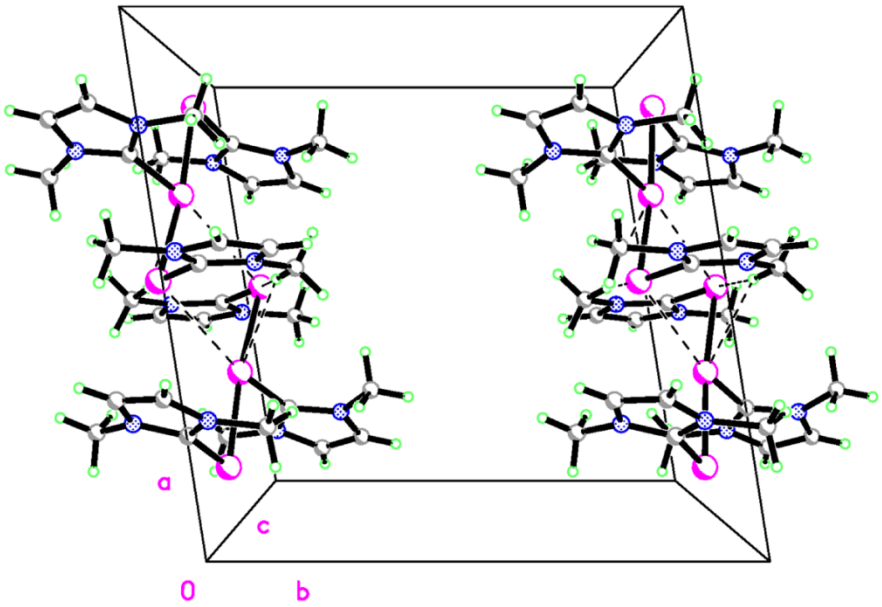

Fig. S3. Crystal packing diagram of $[(dmise)_3][(OTf)_2]$ (**4b**) along the *b*-axis showing short contact interactions between Se-Se atoms.

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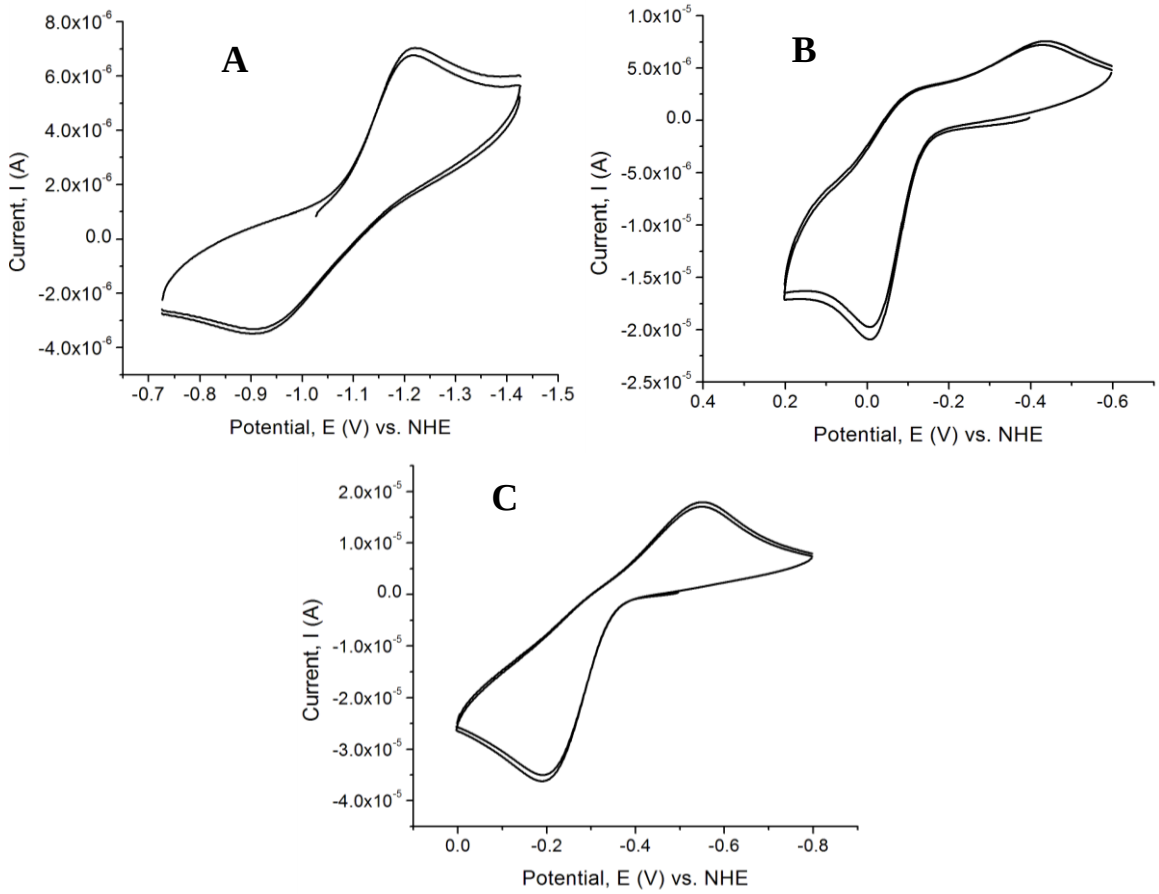

Fig. S4. Cyclic voltammetry scans for A) MISeox, B) $[Cu(dmit)_3][OTf]$ (**3**), and C) $[Cu(dmise)_4][OTf]$ (**4a**). All data were collected with 1 mM complex in acetonitrile. Potentials are reported versus normal hydrogen electrode (NHE).

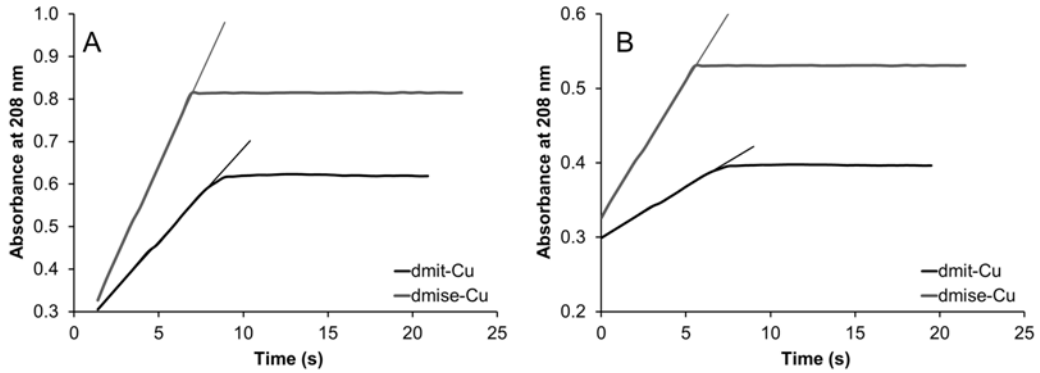

Fig. S5. Kinetics plots of $Cu(OTf)_2$ reduction by dmit and dmise in acetonitrile with different molar ratios of Cu^{2+} to ligand showing the initial rate fitting: A) 1 to 0.5 and B) 1 to 0.1. For these experiments, $Cu(OTf)_2$ concentration was 25 µM and dmise or dmit concentrations were 2.5 and 12.5 µM, respectively.

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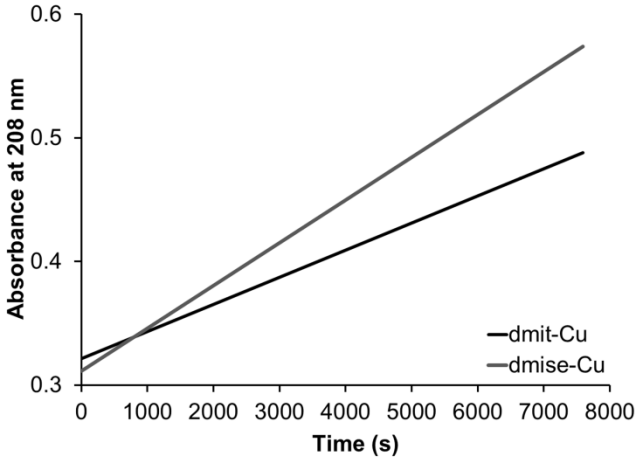

Fig. S6. Kinetics plots of $Cu(OTf)_2$ (25 μM) reduction by dmit and dmise (25 μM) in acetonitrile under anaerobic conditions.

Table S1. Initial rates of $Cu(OTf)_2$ reduction by dmise and dmit in acetonitrile with different molar ratios of ligand to Cu^{2+}.

Ligand to Cu^{2+} ratio	**Rate with dmit (s^{-1})**	**Rate with dmise (s^{-1})**
1 : 1	0.18 ± 0.01	0.50 ± 0.03
0.5 : 1	0.044 ± 0.001	0.087 ± 0.001
0.1 : 1	0.0135 ± 0.0006	0.0363 ± 0.0005
1 : 1 (anaerobic)	$2.000 \pm 0.001 \times 10^{-5}$	$3.015 \pm 0.001 \times 10^{-5}$