Electronic Supplementary Information for Dalton Transactions

Electronic Coupling in 1,4-$(COS)_2$-C_6H_4 Linked MM Quadruple Bonds (M = Mo, W): The Influence of S for O Substitution

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Table S1. Atomic coordinates for the geometry optimized structure of

$[(HCO_2)_3Mo_2]_2(\mu\text{-}O_2C\text{-}C_6H_4\text{-}CO_2)$ (Mo4T') in D_{2h} symmetry.

Atom Number	Element	Coordinates / Å		
		x	y	z
1	C	-0.694498	0	1.214733
2	C	-0.694498	0	-1.214733
3	C	0.694498	0	1.214733
4	C	0.694498	0	-1.214733
5	C	1.400145	0	0
6	C	-1.400145	0	0
7	C	-2.87819	0	0
8	C	2.87819	0	0
9	O	-3.512544	0	1.116879
10	O	-3.512544	0	-1.116879
11	O	3.512544	0	1.116879
12	O	3.512544	0	-1.116879
13	Mo	5.611964	0	1.059302
14	Mo	5.611964	0	-1.059302
15	Mo	-5.611964	0	1.059302
16	Mo	-5.611964	0	-1.059302
17	O	-5.618818	2.120573	1.121521
18	O	-5.618818	2.120573	-1.121521
19	O	-5.618818	-2.120573	1.121521
20	O	-5.618818	-2.120573	-1.121521
21	O	5.618818	2.120573	1.121521
22	O	5.618818	2.120573	-1.121521
23	O	5.618818	-2.120573	1.121521
24	O	5.618818	-2.120573	-1.121521
25	O	-7.735463	0	-1.121738
26	O	-7.735463	0	1.121738
27	O	7.735463	0	-1.121738
28	O	7.735463	0	1.121738
29	H	1.246969	0	-2.147831
30	H	1.246969	0	2.147831
31	H	-1.246969	0	-2.147831
32	H	-1.246969	0	2.147831
33	C	-5.621398	2.721756	0
34	C	-5.621398	-2.721756	0
35	C	5.621398	2.721756	0
36	C	5.621398	-2.721756	0
37	C	-8.336254	0	0
38	C	8.336254	0	0
39	H	-5.626544	-3.816092	0
40	H	-5.626544	3.816092	0
41	H	5.626544	-3.816092	0
42	H	5.626544	3.816092	0
43	H	-9.430669	0	0
44	H	9.430669	0	0

Table S2. Atomic coordinates for the geometry optimized structure of

$[(HCO_2)_3W_2]_2(\mu\text{-}O_2C\text{-}C_6H_4\text{-}CO_2)$ (W4T') in D_{2h} symmetry.

Atom Number	Element	Coordinates / Å		
		x	y	z
1	C	0.693764	1.21483	0
2	C	0.693764	-1.21483	0
3	C	-0.693764	1.21483	0
4	C	-0.693764	-1.21483	0
5	C	-1.403336	0	0
6	C	1.403336	0	0
7	C	2.873576	0	0
8	C	-2.873576	0	0
9	O	3.514461	1.120899	0
10	O	3.514461	-1.120899	0
11	O	-3.514461	1.120899	0
12	O	-3.514461	-1.120899	0
13	W	-5.599555	1.101027	0
14	W	-5.599555	-1.101027	0
15	W	5.599555	1.101027	0
16	W	5.599555	-1.101027	0
17	O	5.609137	1.125147	2.111501
18	O	5.609137	-1.125147	2.111501
19	O	5.609137	1.125147	-2.111501
20	O	5.609137	-1.125147	-2.111501
21	O	-5.609137	1.125147	2.111501
22	O	-5.609137	-1.125147	2.111501
23	O	-5.609137	1.125147	-2.111501
24	O	-5.609137	-1.125147	-2.111501
25	O	7.715947	-1.125552	0
26	O	7.715947	1.125552	0
27	O	-7.715947	-1.125552	0
28	O	-7.715947	1.125552	0
29	H	-1.244588	-2.148921	0
30	H	-1.244588	2.148921	0
31	H	1.244588	-2.148921	0
32	H	1.244588	2.148921	0
33	C	5.612316	0	2.715473
34	C	5.612316	0	-2.715473
35	C	-5.612316	0	2.715473
36	C	-5.612316	0	-2.715473
37	C	8.319158	0	0
38	C	-8.319158	0	0
39	H	5.618671	0	-3.807856
40	H	5.618671	0	3.807856
41	H	-5.618671	0	-3.807856
42	H	-5.618671	0	3.807856
43	H	9.411737	0	0
44	H	-9.411737	0	0

Table S3. Atomic coordinates for the geometry optimized structure of

$[(HCO_2)_3Mo_2]_2(\mu\text{-SOC-}C_6H_4\text{-COS})$ [Mo_4ST'(A)] in C_2 symmetry.

Atom Number	Element	Coordinates / Å		
		x	y	z
1	C	0.589264	-0.30283	1.266501
2	C	-0.589264	-0.302865	-1.266498
3	C	0.792632	-0.299354	-1.147818
4	C	-0.792632	-0.29932	1.147821
5	C	-1.406629	-0.291793	-0.120566
6	C	1.406629	-0.291792	0.12057
7	C	2.87931	-0.239485	0.203146
8	C	-2.87931	-0.239485	-0.203144
9	S	3.713004	-0.324574	1.712371
10	S	-3.713004	-0.324596	-1.712367
11	O	3.542095	-0.112789	-0.88694
12	O	-3.542095	-0.112777	0.886941
13	Mo	-5.579579	0.105076	1.048925
14	Mo	5.57958	0.105063	-1.048926
15	Mo	-6.051296	-0.03094	-1.022262
16	Mo	6.051296	-0.030927	1.022262
17	O	6.384976	-2.119104	0.865702
18	O	-6.384976	-2.119115	-0.865674
19	O	5.910191	2.07774	1.252009
20	O	-5.910192	2.077724	-1.252036
21	O	5.856177	-1.979275	-1.310404
22	O	-5.856174	-1.979259	1.310429
23	O	5.38219	2.213997	-0.924471
24	O	-5.382192	2.214008	0.924443
25	O	7.621054	0.390691	-1.548505
26	O	-7.621054	0.390708	1.5485
27	O	8.140467	0.249368	0.628463
28	O	-8.140467	0.249361	-0.628466
29	H	-1.04345	-0.298708	-2.251758
30	H	1.04345	-0.298644	2.251762
31	H	-1.414946	-0.293969	2.035274
32	H	1.414947	-0.294031	-2.035271
33	C	6.219391	-2.638679	-0.283231
34	C	-6.219389	-2.638676	0.283265
35	C	5.611456	2.742985	0.210705
36	C	-5.611458	2.742982	-0.21074
37	C	8.460473	0.401732	-0.591277
38	C	-8.460473	0.401739	0.591272
39	H	5.548349	3.832503	0.293869
40	H	-5.548351	3.832499	-0.293918
41	H	6.399752	-3.712111	-0.396195
42	H	-6.399749	-3.712107	0.396242
43	H	9.51715	0.551371	-0.836308
44	H	-9.51715	0.551382	0.836302

Table S4. Atomic coordinates for the geometry optimized structure of

$[(HCO_2)_3Mo_2]_2(\mu\text{-SOC-}C_6H_4\text{-COS})$ [Mo_4ST'(B)] in C_2 symmetry.

Atom Number	Element	Coordinates / Å		
		x	y	z
1	C	0.278953	0.635365	-0.838978
2	C	-0.282424	-0.632954	1.583623
3	C	0.282424	0.632954	1.583623
4	C	-0.278953	-0.635365	-0.838978
5	C	-0.572232	-1.290891	0.372772
6	C	0.572232	1.290891	0.372772
7	C	1.175407	2.6376	0.339606
8	C	-1.175407	-2.6376	0.339606
9	S	1.697237	3.427377	1.783629
10	S	-1.697237	-3.427377	1.783629
11	O	1.319266	3.216482	-0.795281
12	O	-1.319266	-3.216482	-0.795281
13	Mo	-2.167578	-5.065985	-1.112702
14	Mo	2.167578	5.065985	-1.112702
15	Mo	-2.61085	-5.530643	0.916508
16	Mo	2.61085	5.530643	0.916508
17	O	4.555594	4.692384	0.736991
18	O	-4.555594	-4.692384	0.736991
19	O	0.757269	6.541339	1.148075
20	O	-0.757269	-6.541339	1.148075
21	O	4.071407	4.176822	-1.391483
22	O	-4.071407	-4.176822	-1.391483
23	O	0.282424	6.023747	-0.981773
24	O	-0.282424	-6.023747	-0.981773
25	O	2.998715	6.909755	-1.765835
26	O	-2.998715	-6.909755	-1.765835
27	O	3.467752	7.417472	0.367126
28	O	-3.467752	-7.417472	0.367126
29	H	-0.499565	-1.121376	2.527378
30	H	0.498658	1.134597	-1.775998
31	H	-0.498658	-1.134597	-1.775998
32	H	0.499565	1.121376	2.527378
33	C	4.86325	4.202667	-0.394807
34	C	-4.86325	-4.202667	-0.394807
35	C	-0.004156	6.572542	0.130759
36	C	0.004156	-6.572542	0.130759
37	C	3.469396	7.686468	-0.874214
38	C	-3.469396	-7.686468	-0.874214
39	H	-0.958994	7.1007	0.21475
40	H	0.958994	-7.1007	0.21475
41	H	5.864882	3.779959	-0.520693
42	H	-5.864882	-3.779959	-0.520693
43	H	3.899422	8.639902	-1.198505
44	H	-3.899422	-8.639902	-1.198505

Table S5. Atomic coordinates for the geometry optimized structure of $[(HCO_2)_3W_2]_2(\mu\text{-SOC-}C_6H_4\text{-COS})$ [W_4ST'(A)] in C_1 symmetry.

Atom Number	Element	Coordinates / Å		
		x	y	z
1	C	-0.594255	1.263405	-0.312214
2	C	0.594244	-1.263391	-0.312196
3	C	-0.786383	-1.15154	-0.309506
4	C	0.786375	1.151547	-0.309453
5	C	1.411855	-0.114225	-0.300403
6	C	-1.411865	0.114232	-0.300479
7	C	-2.874784	0.192255	-0.247262
8	C	2.874772	-0.192252	-0.247138
9	S	-3.722385	1.702444	-0.295529
10	S	3.722362	-1.702447	-0.295389
11	O	-3.547317	-0.907033	-0.142356
12	O	3.547317	0.907036	-0.142313
13	W	5.557597	1.101363	0.071533
14	W	-5.557597	-1.101366	0.071486
15	W	6.048558	-1.058395	-0.019881
16	W	-6.048554	1.058398	-0.019816
17	O	-6.398326	0.906718	-2.098117
18	O	6.398115	-0.906662	-2.098214
19	O	-5.91272	1.191001	2.091546
20	O	5.912935	-1.191057	2.091491
21	O	-5.871931	-1.280417	-2.006986
22	O	5.871901	1.28051	-2.006934
23	O	-5.383688	-0.995403	2.174251
24	O	5.383718	0.995297	2.1743
25	O	-7.603515	-1.563388	0.350849
26	O	7.603514	1.563376	0.350925
27	O	-8.125974	0.621895	0.260002
28	O	8.125997	-0.621888	0.259787
29	H	1.050973	-2.247577	-0.308717
30	H	-1.050978	2.247582	-0.308645
31	H	1.402248	2.043599	-0.30529
32	H	-1.402255	-2.043593	-0.305407
33	C	-6.245489	-0.236526	-2.642806
34	C	6.245335	0.236622	-2.642834
35	C	-5.619742	0.129212	2.732812
36	C	5.619891	-0.129317	2.732809
37	C	-8.445813	-0.604311	0.386301
38	C	8.445825	0.604306	0.386233
39	H	-5.567511	0.182132	3.822989
40	H	5.567722	-0.182279	3.822987
41	H	-6.444903	-0.329797	-3.712871
42	H	6.44468	0.329933	-3.712908

43	H	-9.500204	-0.853159	0.533871
44	H	9.500216	0.853146	0.533818

Table S6. Atomic coordinates for the geometry optimized structure of

$[(HCO_2)_3W_2]_2(\mu\text{-}SOC\text{-}C_6H_4\text{-}COS)$ [$W_4ST'(B)$] in C_2 symmetry.

Atom Number	Element	Coordinates / Å		
		x	y	z
1	C	0.261255	0.642348	-0.86895
2	C	-0.26218	-0.640018	1.553057
3	C	0.26218	0.640018	1.553057
4	C	-0.261255	-0.642348	-0.86895
5	C	-0.535758	-1.312054	0.342575
6	C	0.535758	1.312054	0.342575
7	C	1.098978	2.66512	0.320693
8	C	-1.098978	-2.66512	0.320693
9	S	1.502443	3.504671	1.782606
10	S	-1.502443	-3.504671	1.782606
11	O	1.307124	3.241177	-0.818445
12	O	-1.307124	-3.241177	-0.818445
13	W	-2.137187	-5.070903	-1.133854
14	W	2.137187	5.070903	-1.133854
15	W	-2.439862	-5.597635	0.998306
16	W	2.439862	5.597635	0.998306
17	O	4.396718	4.793393	0.933139
18	O	-4.396718	-4.793393	0.933139
19	O	0.57441	6.596879	1.029927
20	O	-0.57441	-6.596879	1.029927
21	O	4.076228	4.232941	-1.222255
22	O	-4.076228	-4.232941	-1.222255
23	O	0.26218	6.03844	-1.126977
24	O	-0.26218	-6.03844	-1.126977
25	O	3.003038	6.918674	-1.712722
26	O	-3.003038	-6.918674	-1.712722
27	O	3.31276	7.470041	0.44466
28	O	-3.31276	-7.470041	0.44466
29	H	-0.464484	-1.13171	2.498317
30	H	0.466607	1.144934	-1.807659
31	H	-0.466607	-1.144934	-1.807659
32	H	0.464484	1.13171	2.498317
33	C	4.796832	4.294953	-0.16951
34	C	-4.796832	-4.294953	-0.16951
35	C	-0.107255	6.612401	-0.046994
36	C	0.107255	-6.612401	-0.046994
37	C	3.403241	7.717455	-0.801385
38	C	-3.403241	-7.717455	-0.801385
39	H	-1.06054	7.146197	-0.048237
40	H	1.06054	-7.146197	-0.048237
41	H	5.813788	3.898316	-0.218209
42	H	-5.813788	-3.898316	-0.218209
43	H	3.848264	8.667061	-1.110834
44	H	-3.848264	-8.667061	-1.110834

Table S7. Atomic coordinates for the geometry optimized structure of $[(HCO_2)_3Mo_2]_2(\mu\text{-}S_2C\text{-}C_6H_4\text{-}CS_2)$ (Mo_4S_2T') in C_s symmetry. An imaginary frequency (34*i*) appeared in the frequency analysis despite repeated efforts at changing symmetry and basis set changes.

Atom Number	Element	Coordinates / Å		
		x	y	z
1	C	0.000195	0.692751	1.204035
2	C	0.000195	0.692751	-1.204035
3	C	0.000146	-0.692751	1.204035
4	C	0.000146	-0.692751	-1.204035
5	C	0.000056	-1.430487	0.000000
6	C	0.000161	1.430487	0.000000
7	C	0.000066	2.907310	0.000000
8	C	-0.000138	-2.907310	0.000000
9	S	-0.000013	3.755933	1.487450
10	S	-0.000013	3.755933	-1.487450
11	S	-0.000183	-3.755934	1.487450
12	S	-0.000183	-3.755934	-1.487450
13	Mo	-0.000069	-6.137829	1.065967
14	Mo	-0.000069	-6.137829	-1.065967
15	Mo	-0.000062	6.137829	1.065967
16	Mo	-0.000062	6.137829	-1.065967
17	O	2.122952	6.264114	1.121490
18	O	2.122952	6.264114	-1.121490
19	O	-2.123016	6.264068	1.121482
20	O	-2.123016	6.264068	-1.121482
21	O	2.122972	-6.263882	1.121491
22	O	2.122972	-6.263882	-1.121491
23	O	-2.122997	-6.264300	1.121481
24	O	-2.122997	-6.264300	-1.121481
25	O	0.000217	8.287396	-1.121861
26	O	0.000217	8.287396	1.121861
27	O	0.000473	-8.287396	-1.121861
28	O	0.000473	-8.287396	1.121861
29	H	0.000173	-1.214705	-2.154254
30	H	0.000173	-1.214705	2.154254
31	H	0.000255	1.214705	-2.154254
32	H	0.000255	1.214705	2.154254
33	C	2.718964	6.322823	0.000000
34	C	-2.719069	6.322644	0.000000
35	C	2.718983	-6.322540	0.000000
36	C	-2.719050	-6.322927	0.000000
37	C	0.000106	8.883647	0.000000
38	C	0.000373	-8.883648	0.000000
39	H	-3.808325	6.429308	0.000000
40	H	3.808199	6.429759	0.000000
41	H	-3.808296	-6.429680	0.000000
42	H	3.808229	-6.429387	0.000000
43	H	-0.000079	9.979303	0.000000
44	H	0.000218	-9.979302	0.000000

Table S8. Atomic coordinates for the geometry optimized structure of $[(HCO_2)_3W_2]_2(\mu\text{-}S_2C\text{-}C_6H_4\text{-}CS_2)$ (W_4S_2T') in C_1 symmetry. An imaginary frequency (29*i*) appeared in the frequency analysis despite repeated efforts at changing symmetry and basis set changes.

Atom Number	Element	Coordinates / Å		
		x	y	z
1	C	-0.692154	1.203515	-0.001519
2	C	-0.692169	-1.203479	-0.001367
3	C	0.692170	1.203506	-0.001488
4	C	0.692154	-1.203488	-0.001317
5	C	1.434811	0.000004	-0.001328
6	C	-1.434810	0.000022	-0.001413
7	C	-2.904499	0.000022	-0.001228
8	C	2.904499	-0.000001	-0.001069
9	S	-3.762348	1.490987	-0.001025
10	S	-3.762325	-1.490956	-0.001056
11	S	3.762341	1.490970	-0.000773
12	S	3.762341	-1.490969	-0.000924
13	W	6.126508	1.110707	0.000184
14	W	6.126510	-1.110711	0.000104
15	W	-6.126518	1.110707	0.000128
16	W	-6.126501	-1.110710	0.000140
17	O	-6.289966	1.124972	-2.113431
18	O	-6.289989	-1.124957	-2.113453
19	O	-6.287466	1.124951	2.113942
20	O	-6.287410	-1.124979	2.113920
21	O	6.289721	1.125011	-2.113432
22	O	6.289734	-1.124917	-2.113473
23	O	6.287693	1.124914	2.113945
24	O	6.287679	-1.125018	2.113903
25	O	-8.274823	-1.124479	0.001501
26	O	-8.274842	1.124440	0.001411
27	O	8.274834	-1.124457	0.001103
28	O	8.274832	1.124462	0.001209
29	H	1.212183	-2.154934	-0.001218
30	H	1.212213	2.154944	-0.001538
31	H	-1.212212	-2.154917	-0.001303
32	H	-1.212182	2.154960	-0.001593
33	C	-6.362564	0.000006	-2.709001
34	C	-6.359311	-0.000013	2.709571
35	C	6.362244	0.000066	-2.709020
36	C	6.359624	-0.000070	2.709554
37	C	-8.872169	-0.000024	0.001821
38	C	8.872170	0.000003	0.001464
39	H	-6.488822	-0.000043	3.794638
40	H	-6.493386	0.000034	-3.793910
41	H	6.489259	-0.000082	3.794607
42	H	6.492941	0.000077	-3.793944
43	H	-9.966390	-0.000034	0.002488
44	H	9.966391	0.000003	0.002008

Figure S1. Diagrams of the calculated structures for W4T', W_4ST'(A), W_4ST'(B) and W_4S_2T'. Structures for the molybdenum analogues are qualitatively similar.

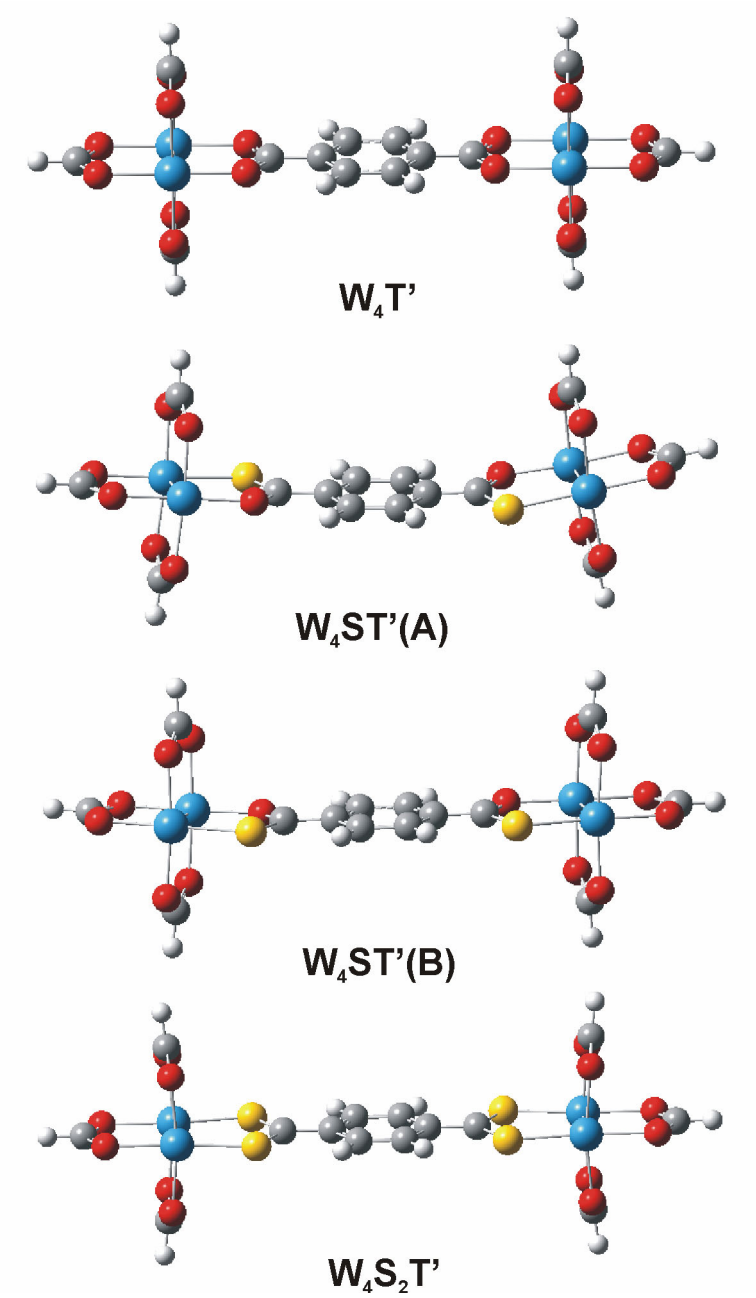

Figure S2. Cyclic voltammogram (bottom) and differential pulse voltammogram (top) for Mo4ST. Potentials are referenced to the $FeCp_2^{0/+}$ couple at 0 V.

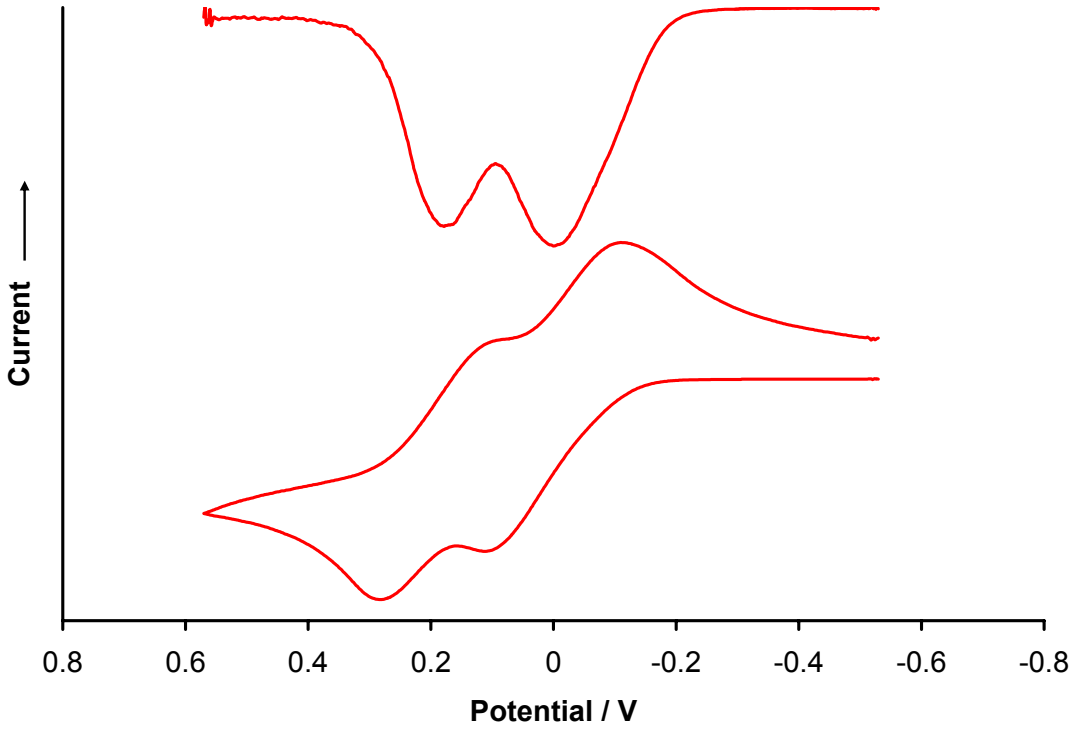

Figure S3. Cyclic voltammogram (bottom) and differential pulse voltammogram (top) for W4ST. Potentials are referenced to the $FeCp_2^{0/+}$ couple at 0 V.