Supplementary information

Synthesis, Structure and Redox Properties of Bis(cyclopentadienyl)dithiolene Complexes of Molybdenum and Tungsten

Alexandra L. Whalley, Alexander J. Blake, David Collison, E. Stephen Davies, Helen J. Disley, Frank E. Mabbs, Madeleine Helliwell, Jonathan McMaster, Claire Wilson and C. David Garner

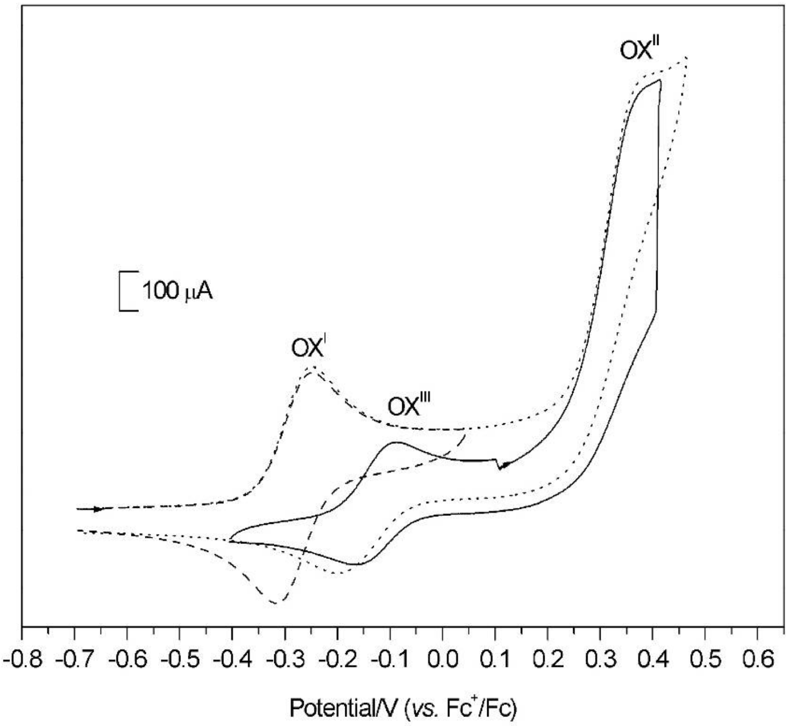

Fig. S1 Cyclic voltammograms recorded for [Cp_2Mo(2-pedt)] (**2**) (1 mmol) in dmf containing [^{n}Bu_4N][BF_4] (0.2 M) recorded at ambient temperature and a scan rate of 0.1 Vs^{-1}. The dashed line shows the current response for OX^I when the direct of sweep is reversed at +0.04 V; the dotted line shows the effect on current response for OX^I when the direction of sweep is reversed at +0.46 V; the solid line was generated by holding the potential at +0.41 V (ca. OX^{II}, see Table 1) for 10 seconds before reversing the potential sweep, this resulted in the depletion of OX^I and the generation of the new redox couple, OX^{III}.

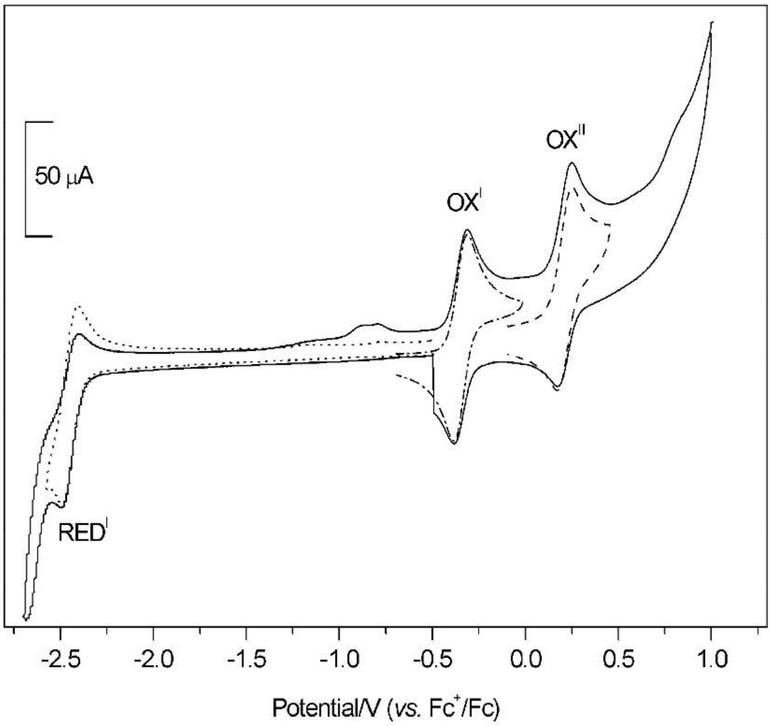

Fig. S2 Cyclic voltammograms recorded for [Cp_2W(sdt)] (**6**) (1 mmol) in dmf containing [^{n}Bu_4N][BF_4] (0.2 M) recorded at ambient temperature and a scan rate of 0.1 Vs^{-1}. Broken lines show the effect of switching potential on the current response for OX^I (E_λ; -0.02 V, dashed-dotted line), OX^{II} (E_λ; +0.45 V, dotted line) and RED^I (E_λ; -2.58 V, dashed line), all at 0.1 Vs^{-1}.

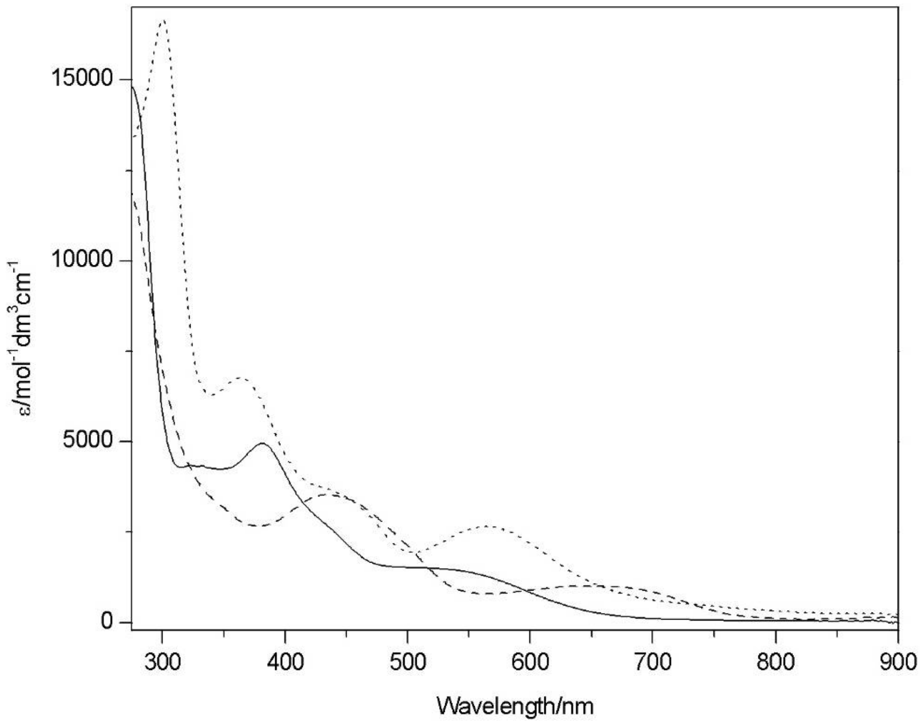

Fig. S3 UV/vis spectra of [Cp_2Mo(2-pedt)] (**2**) (solid line) and electrochemically generated [**2**]$^+$ (dashed line) and [**2**]$^-$ (dotted line) in dmf containing [^{n}Bu_4N][BF_4] (0.2 M) at 273 K.

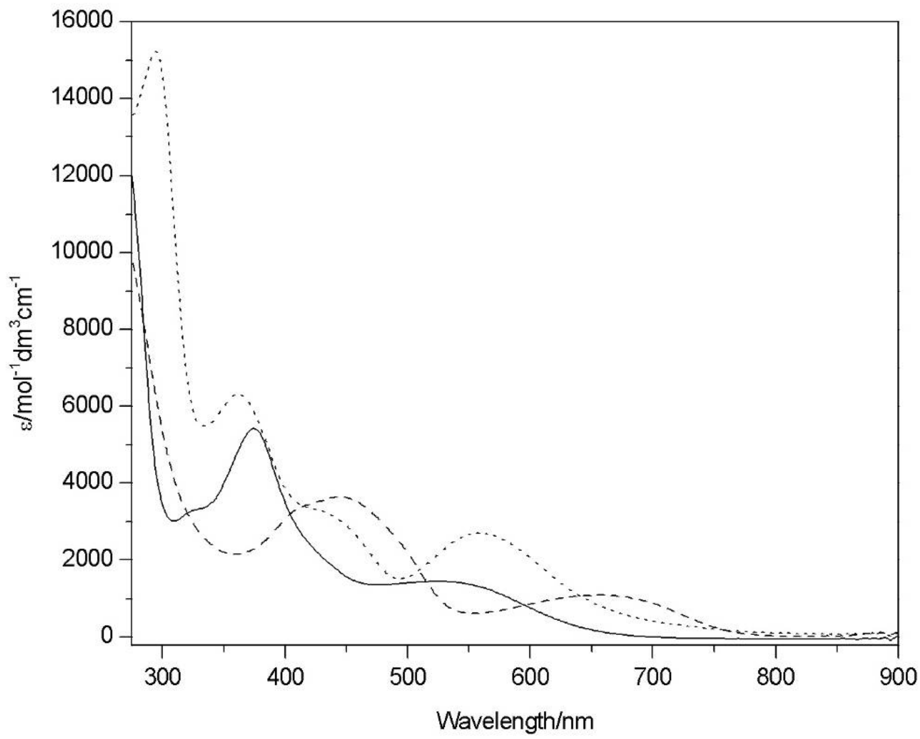

Fig. S4 UV/vis spectra of [Cp_2Mo(3-pedt)] (**3**) (solid line) and electrochemically generated [**3**]$^+$ (dashed line) and [**3**]$^-$ (dotted line) in dmf containing [^{n}Bu_4N][BF_4] (0.2 M) at 273 K. For [**3**]$^+$ an absorption at 1142 nm was observed analogous to that of [Cp_2Mo(sdt)]$^+$ (see Fig. 2).

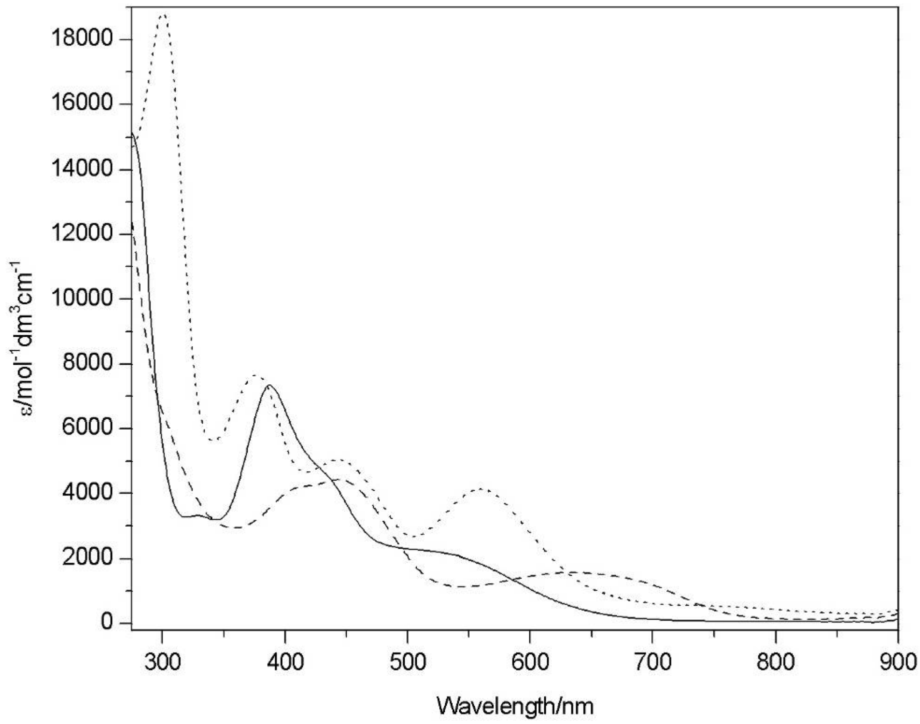

Fig. S5 UV/vis spectra of [Cp_2Mo(4-pedt)] (**4**) (solid line) and electrochemically generated [**4**]$^+$ (dashed line) and [**4**]$^-$ (dotted line) in dmf containing [^{n}Bu_4N][BF_4] (0.2 M) at 273 K.

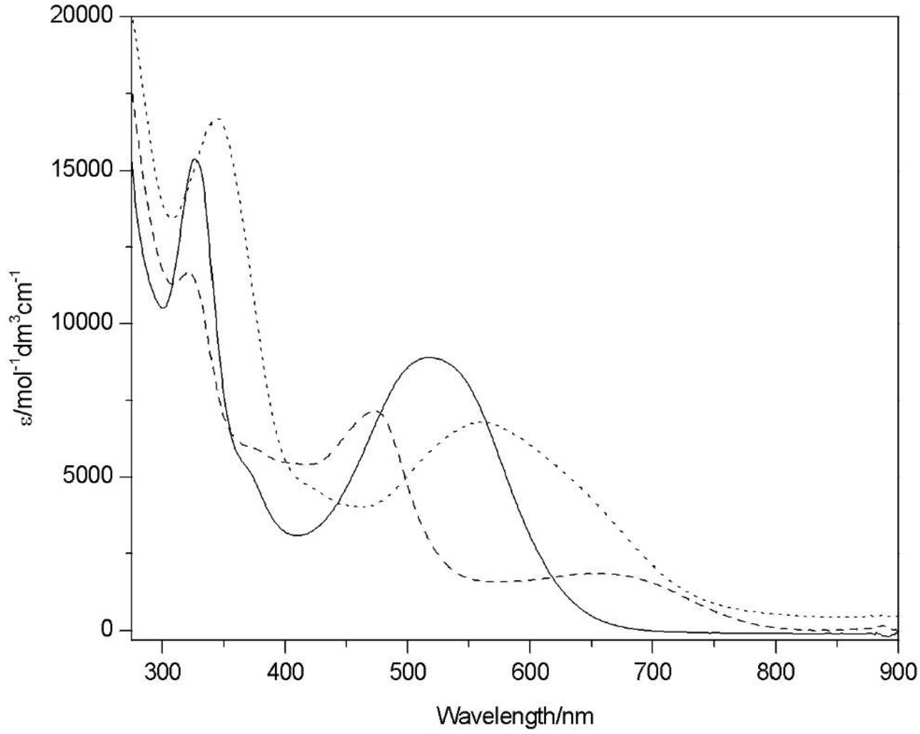

Fig. S6 UV/vis spectra of [Cp_2Mo(qedt)] (**5**) (solid line) and electrochemically generated [**5**]$^+$ (dashed line) and [**5**]$^-$ (dotted line) in dmf containing [^{n}Bu_4N][BF_4] (0.2 M) at 273 K. For [**5**]$^+$ an absorption at 1142 nm was observed analogous to that of [Cp_2Mo(sdt)]$^+$ (see Fig. 2).

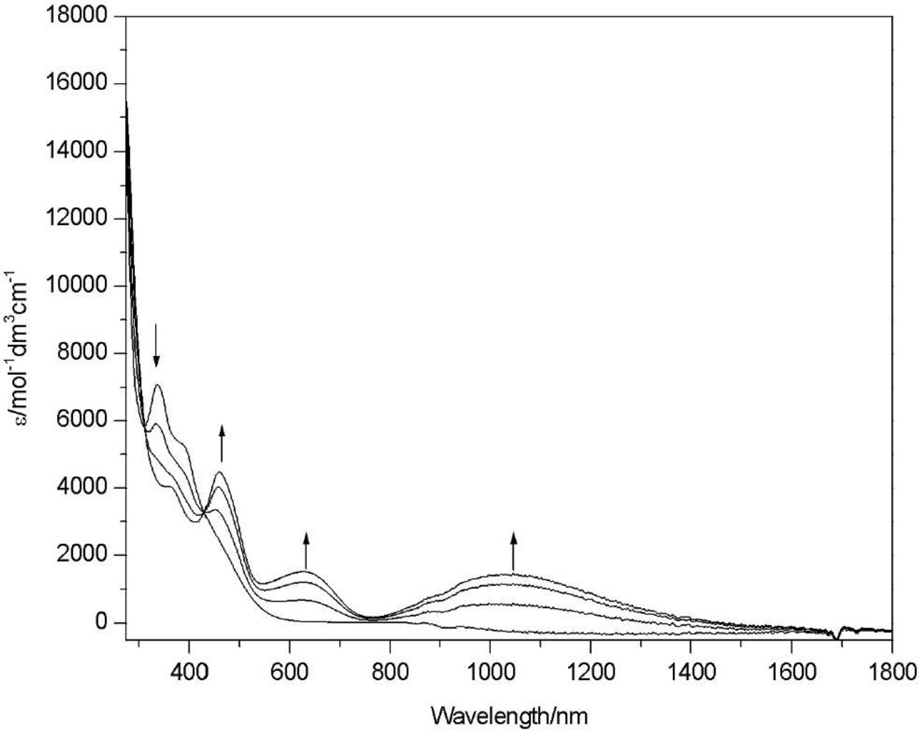

Fig. S7 Changes in the UV/vis/NIR spectra observed for the electrochemical conversion of [Cp_2W(sdt)] (**6**) to [**6**]$^+$ in dmf containing [$^nBu_4N$][BF_4] (0.2 M) at 273 K.

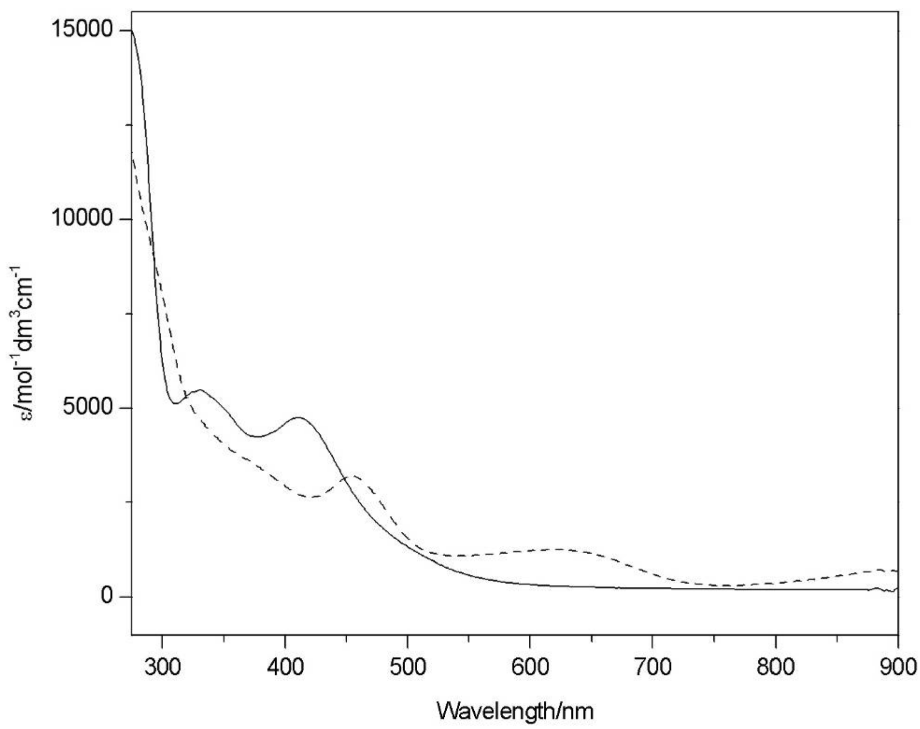

Fig. S8 UV/vis spectra of [Cp_2W(2-pedt)] (**7**) (solid line) and electrochemically generated [**7**]$^+$ (dashed line) in dmf containing [$^nBu_4N$][BF_4] (0.2 M) at 273 K.

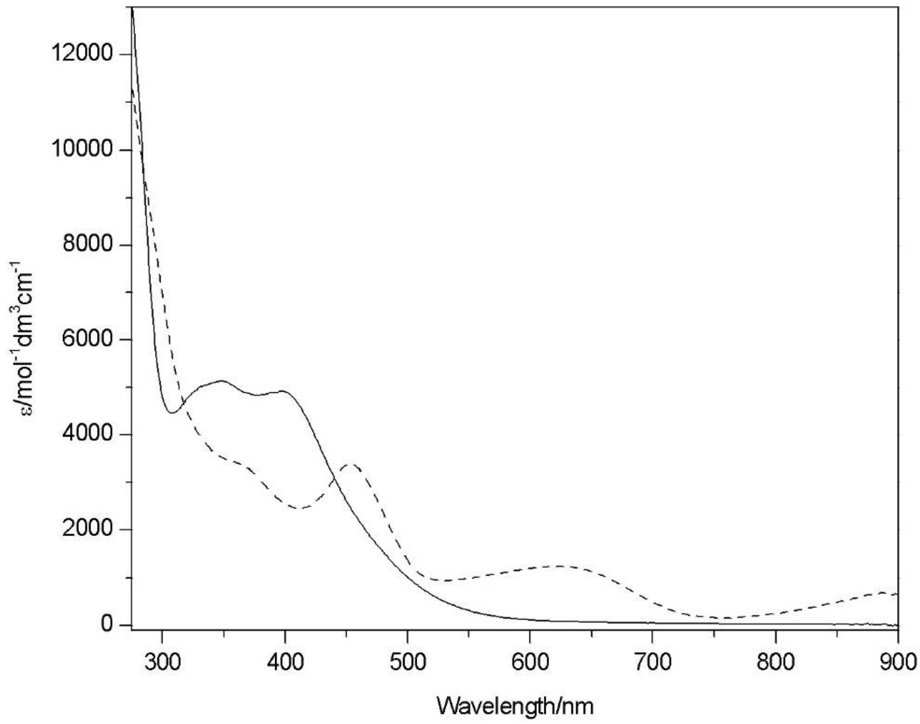

Fig. S9 UV/vis spectra of [Cp_2W(3-pedt)] (**8**) (solid line) and electrochemically generated [**8**]$^+$ (dashed line) in dmf containing [^{n}Bu_4N][BF_4] (0.2 M) at 273 K. For [**8**]$^+$ a NIR absorption at 1030 nm was observed analogous to that of [Cp_2W(sdt)]$^+$ ([**6**]$^+$) (see Fig. S7).

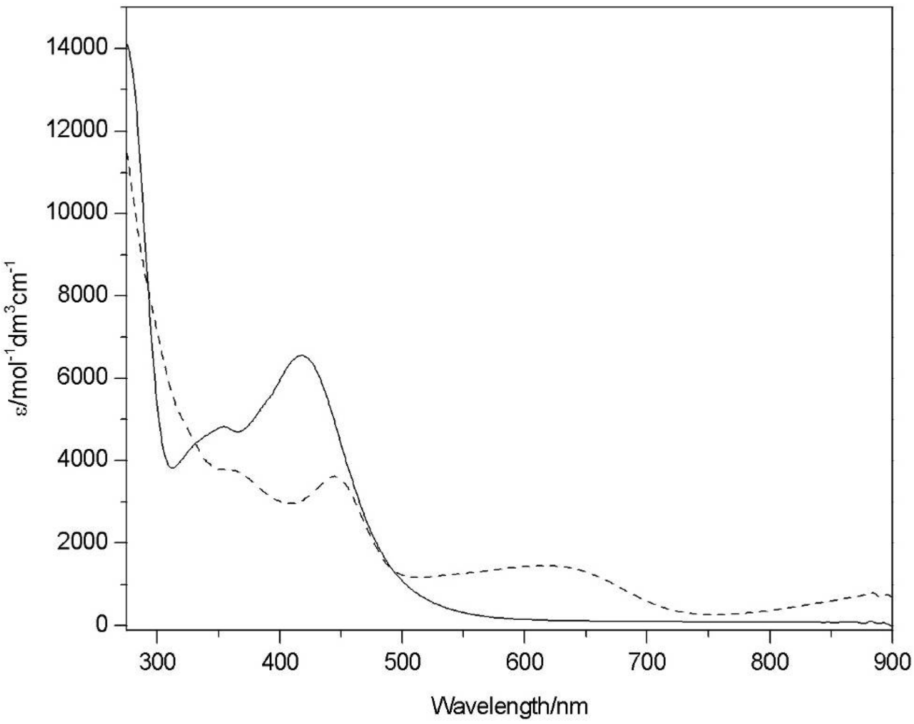

Fig. S10 UV/vis spectra of $[Cp_2W(4\text{-pedt})]$ (**9**) (solid line) and electrochemically generated $[\mathbf{9}]^+$ (dashed line) in dmf containing $[^nBu_4N][BF_4]$ (0.2 M) at 273 K.

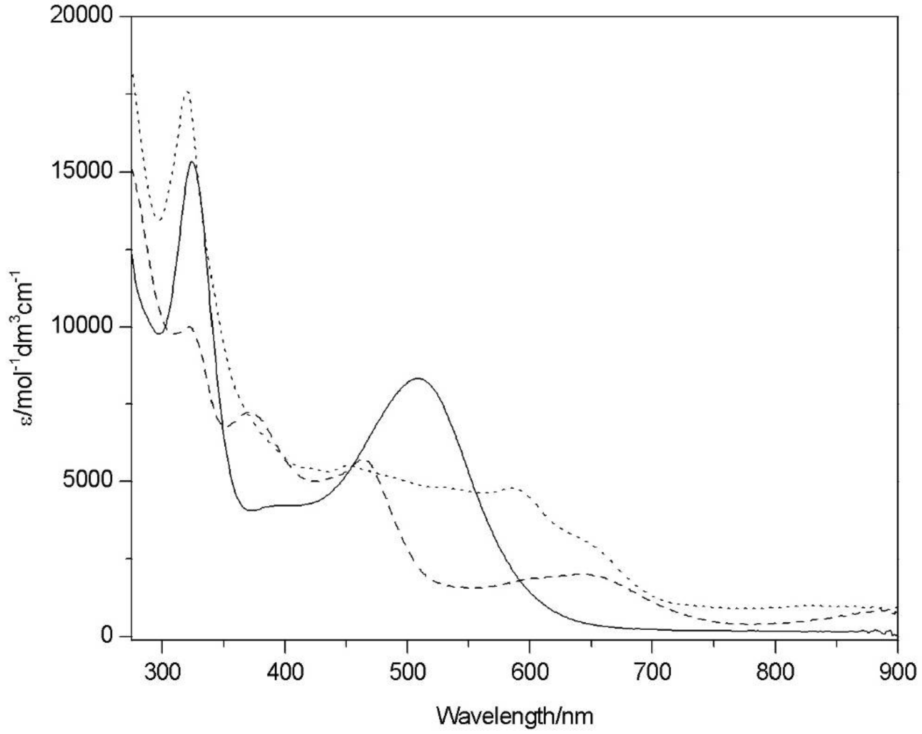

Fig. S11 UV/vis spectra of [Cp_2W(qedt)] (**10**) (solid line) and electrochemically generated [**10**]$^+$ (dashed line) and [**10**]$^-$ (dotted line) in dmf containing [^{n}Bu_4N][BF_4] (0.2 M) at 273 K. For [**2**]$^+$ an absorption at 1046 nm was observed analogous to that of [Cp_2W(sdt)]$^+$ (see Fig. S7).

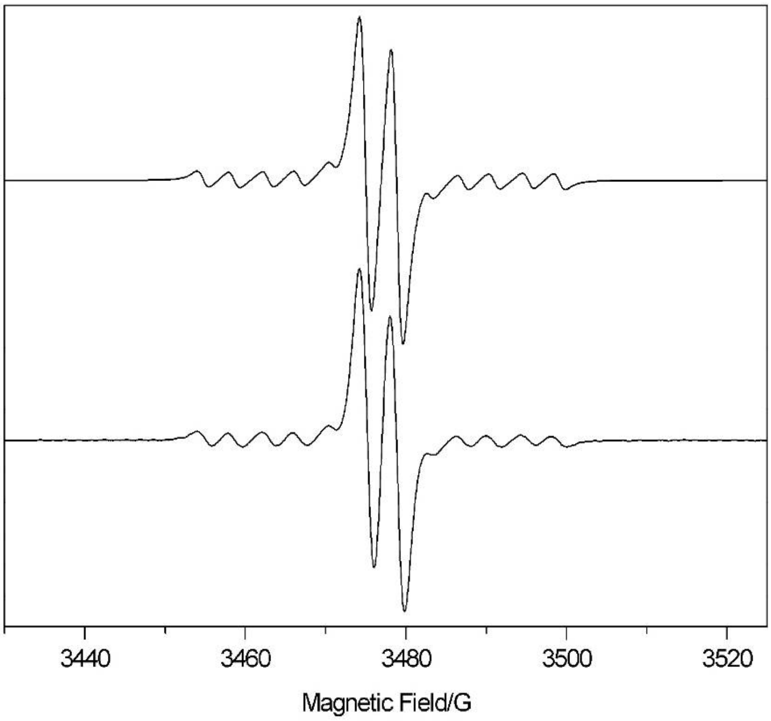

Fig. S12 X-band EPR spectra of $[Cp_2Mo(sdt)]^+$ ($[\mathbf{1}]^+$): lower trace, spectrum recorded for electrochemically generated $[\mathbf{1}]^+$ (1 mM) in dmf containing $[^n Bu_4N][BF_4]$ (0.2 M) at 273 K; upper trace, simulation of the experimental spectrum using the parameters given in Table 4 and a Lorentzian line shape.

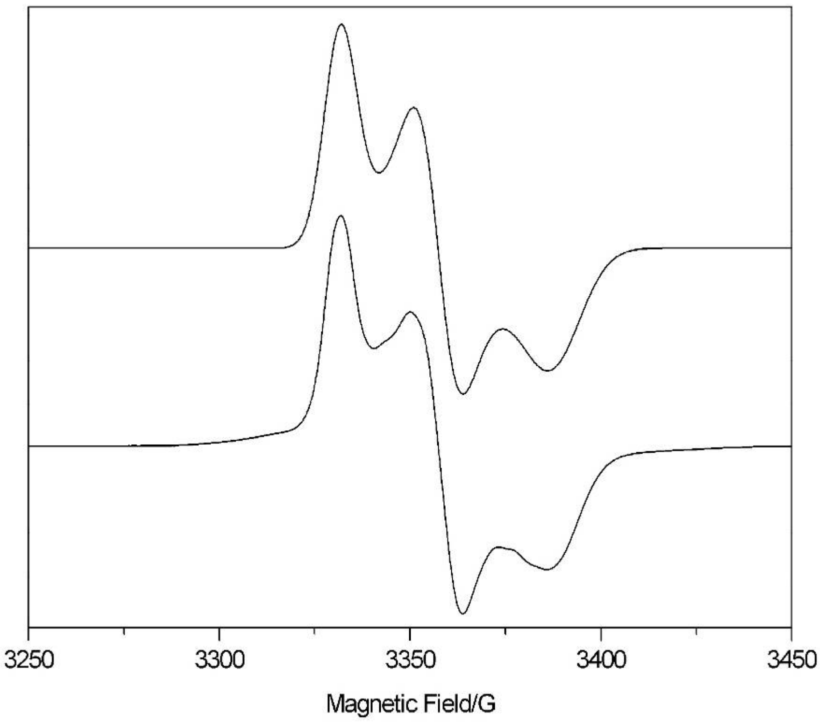

Fig. S13 X-band EPR spectra of [**1**]$^+$: lower trace, spectrum recorded for [**1**]$^+$ (1 mM) in CH_2Cl_2:dmf (4:1 v/v) at 77 K, [**1**]$^+$ was generated by the oxidation of **1** with *ca.* 1 equivalent of $[Cp_2Fe][BF_4]$; upper trace, simulation of the experimental spectrum using the parameters given in Table 4 and a Gaussian line shape.

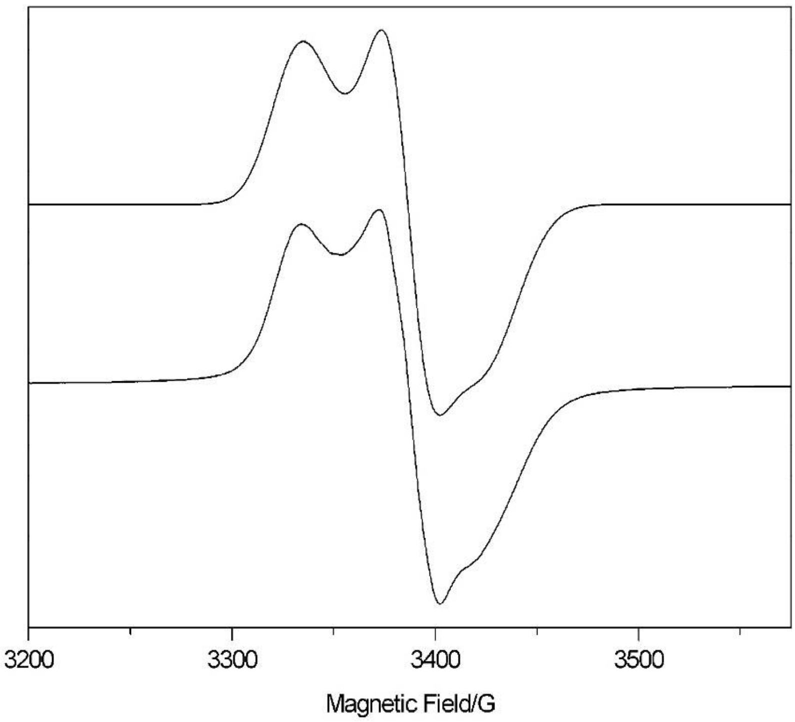

Fig. S14 X-band EPR spectra of [**6**]$^+$: lower trace, spectrum recorded for [**6**]$^+$ (1 mM) in CH_2Cl_2:dmf (4:1 v/v) at 77 K, [**6**]$^+$ was generated by the oxidation of **6** with *ca.* 1 equivalent of $[Cp_2Fe][BF_4]$; upper trace, simulation of the experimental spectrum using the parameters given in Table 4 and a Gaussian line shape.

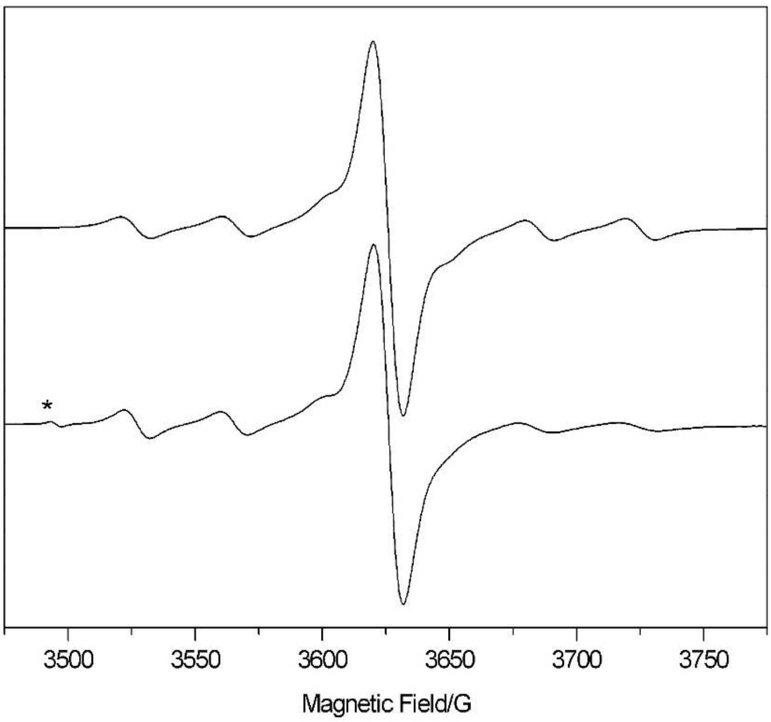

Fig. S15 X-band EPR spectra of [**3**]$^-$: lower trace, spectrum recorded for electrochemically generated [**3**]$^-$ (1 mM) in dmf containing [^{n}Bu$_4$N][BF$_4$] (0.2 M) at 273 K; upper trace, simulation of the experimental spectrum using the parameters given in Table 4 and a Lorentzian line shape. * indicates a small quantity of [**3**]$^+$ generated at the secondary electrode during the *in situ* generation of [**3**]$^-$

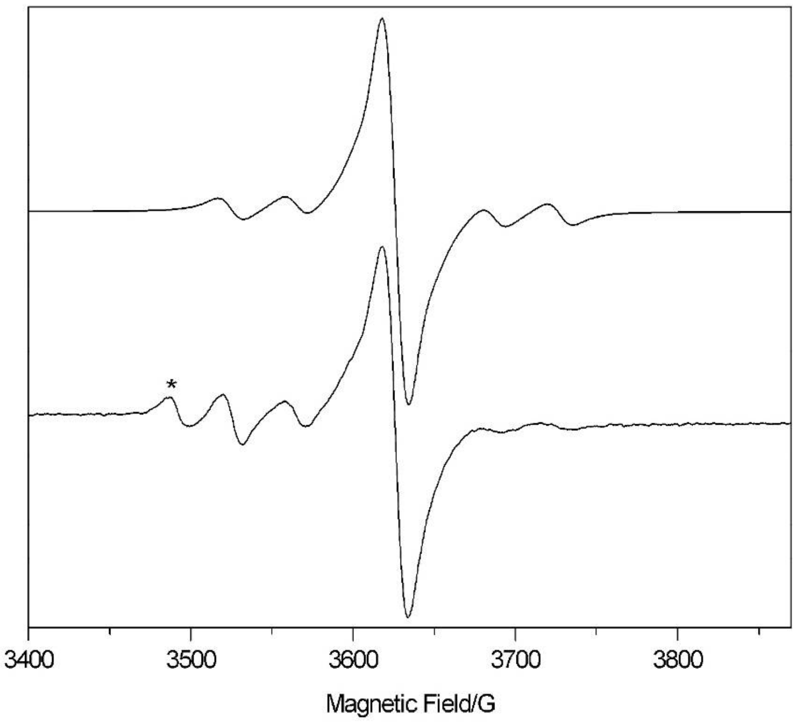

Fig. S16 X-band EPR spectra of [**5**]$^-$: lower trace, spectrum recorded for electrochemically generated [**5**]$^-$ (1 mM) in dmf containing [^{n}Bu$_4$N][BF$_4$] (0.2 M) at 273 K; upper trace, simulation of the experimental spectrum using the parameters given in Table 4 and a Lorentzian line shape. * indicates a small quantity of [**5**]$^+$ generated at the secondary electrode during the *in situ* generation of [**5**]$^-$.

Geometry optimised structure of **1**

H	-2.22119	2.10000	-0.35843
H	-1.23423	1.17933	-2.70128
H	-0.11667	2.72399	1.22646
H	1.45659	1.25847	-2.56942
H	2.15191	2.22303	-0.14822
H	-4.45187	1.09199	5.89830
H	-3.16193	1.05057	3.78226
H	-1.43522	-1.25928	-2.58109
H	-3.49846	0.08158	7.97333
H	1.25617	-1.18996	-2.69051
H	1.27920	0.04627	4.22154
H	-2.15527	-2.21258	-0.16091
H	-1.24367	-0.98908	7.88881
H	0.02238	-1.06406	5.76848
H	2.21976	-2.11046	-0.33799
H	0.09861	-2.72054	1.23178
C	-1.17274	1.98765	-0.61325
C	-0.64906	1.52629	-1.85575
C	-0.05982	2.34410	0.21392
C	0.77007	1.56770	-1.78743
C	1.14032	2.06365	-0.50685
C	-3.46552	0.62485	5.87663
C	-2.74252	0.59918	4.68249
C	-2.93254	0.06244	7.04051
C	-1.46365	0.01026	4.61773
C	-0.68461	-0.00018	3.36246
C	-0.75710	-1.56792	-1.79168
C	0.66266	-1.53317	-1.84906
C	0.67177	0.00123	3.31733
C	-1.66682	-0.53342	6.99211
C	-0.94689	-0.56601	5.79795
C	-1.14058	-2.05831	-0.51270
C	1.17383	-1.99459	-0.60205
C	0.05265	-2.34256	0.21798
Mo	-0.00000	0.00000	0.00000
S	-1.57269	-0.00000	1.81796
S	1.57269	-0.00000	1.82101

Energy: -233.49440977 eV

Geometry optimised structure of [**1**]$^{+}$

H	-2.23277	2.09928	-0.25100
H	-1.23741	1.21989	-2.59730
H	-0.12593	2.68168	1.36397
H	1.46150	1.29710	-2.45722
H	2.15353	2.22941	-0.02997
H	-4.41270	1.94662	5.65183
H	-3.17501	1.47685	3.55856
H	-1.42376	-1.31960	-2.45991
H	-3.38872	1.40660	7.85978
H	1.27372	-1.25647	-2.55894
H	1.27359	0.56410	4.16105
H	-2.16029	-2.21025	-0.02414
H	-1.12393	0.36951	7.95365
H	0.10605	-0.12344	5.87637
H	2.22948	-2.11791	-0.18723
H	0.09436	-2.67373	1.40003
C	-1.18307	1.97901	-0.49759
C	-0.65740	1.52563	-1.73161
C	-0.06600	2.28122	0.35841
C	0.77676	1.56756	-1.65894
C	1.14242	2.05430	-0.38327
C	-3.42213	1.49399	5.69891
C	-2.72912	1.22448	4.52090
C	-2.84610	1.19468	6.93826
C	-1.43844	0.65523	4.55774
C	-0.70006	0.37629	3.31584
C	-0.75283	-1.58336	-1.64814
C	0.67828	-1.55096	-1.70028
C	0.68763	0.35553	3.26500
C	-1.57079	0.61910	6.99144
C	-0.87180	0.35362	5.81717
C	-1.14378	-2.04479	-0.36734
C	1.18425	-1.98982	-0.45057
C	0.05314	-2.28825	0.38800
Mo	0.00000	0.00000	0.00000
S	-1.60465	0.00000	1.87258
S	1.60465	0.00000	1.86767

Energy: -227.66471372 eV

Geometry optimised structure of [**1**]$^-$

H	-2.18196	2.14022	-0.40150
H	-1.33774	1.36582	-2.85839
H	0.00697	2.66797	1.10334
H	1.33917	1.34719	-2.85761
H	2.19372	2.12180	-0.40515
H	-4.60915	0.57127	5.84061
H	-3.31191	0.52242	3.72496
H	-1.33626	-1.32749	-2.86130
H	-3.49113	0.05658	8.02119
H	1.34092	-1.31983	-2.85740
H	1.28520	0.01479	4.23561
H	-2.18638	-2.12982	-0.41470
H	-1.05430	-0.52477	8.02474
H	0.21722	-0.59349	5.92430
H	2.18970	-2.12721	-0.41431
H	-0.00172	-2.67948	1.08693
C	-1.14966	1.99639	-0.70771
C	-0.69774	1.65756	-2.02910
C	0.00576	2.29622	0.08547
C	0.70240	1.64729	-2.02840
C	1.15952	1.98281	-0.70780
C	-3.54474	0.32418	5.86632
C	-2.82082	0.29684	4.67242
C	-2.92461	0.03882	7.08816
C	-1.43855	-0.01009	4.64759
C	-0.68335	-0.01816	3.38536
C	-0.69873	-1.62973	-2.03400
C	0.70226	-1.62493	-2.03189
C	0.67787	-0.01394	3.32904
C	-1.55856	-0.28344	7.08597
C	-0.83619	-0.31277	5.89477
C	-1.15370	-1.98664	-0.71900
C	1.15624	-1.98171	-0.71659
C	0.00017	-2.29891	0.07221
Mo	0.00000	0.00000	0.00000
S	-1.59065	-0.00000	1.83107
S	1.59065	0.00000	1.83670

Energy: -234.82671100 eV

Geometry optimised structure of **6**

H	1.26630	-0.04089	4.22991
H	1.82791	-2.50438	0.44866
H	0.00902	1.06879	5.77834
H	1.32048	2.70045	0.94450
H	-1.25195	0.96001	7.89941
H	1.91523	-1.44848	-2.02090
H	2.20721	1.64629	-1.38279
H	-0.72591	-2.67720	1.21870
H	-3.49205	-0.14202	7.98085
H	-1.33729	2.68391	0.93782
H	-0.64864	-1.03189	-2.82409
H	-3.15475	-1.06421	3.77862
H	0.02077	1.00483	-2.85672
H	-4.43729	-1.14464	5.89754
H	-2.30168	-1.80021	-0.81825
H	-2.20169	1.62609	-1.39409
S	1.60353	-0.00000	1.83367
S	-1.60353	-0.00000	1.82297
C	0.66568	0.00588	3.32124
C	0.96900	-2.24272	-0.15878
C	-0.95350	0.55728	5.80512
C	-1.67063	0.50528	7.00006
C	0.69889	2.36284	0.12292
C	1.01653	-1.65420	-1.44711
C	-0.68679	0.00650	3.36458
C	1.17184	1.72554	-1.07002
C	-0.38379	-2.32218	0.25434
C	-1.46390	-0.01660	4.62030
C	-2.92819	-0.10871	7.04709
C	-0.70729	2.35447	0.11957
C	-0.33662	-1.40972	-1.85841
C	-2.73743	-0.61827	4.68257
C	-1.21864	-1.78718	-0.79329
C	0.00730	1.38793	-1.84471
C	-3.45699	-0.66566	5.87862
C	-1.16833	1.71474	-1.07675
W	0.00000	0.00000	0.00000

Energy: -233.58852039 eV

Geometry optimised structure of [**6**]$^+$

H	1.27689	0.11466	4.21117
H	1.36027	-2.66505	0.99359
H	0.14416	1.20909	5.69961
H	1.35329	2.67450	0.96967
H	-1.05397	1.24256	7.85123
H	2.21678	-1.63907	-1.35586
H	2.20557	1.63961	-1.37431
H	-1.31047	-2.68103	1.00269
H	-3.32210	0.22773	8.04487
H	-1.32084	2.67456	0.98993
H	0.00264	-1.07280	-2.83365
H	-3.18366	-0.88065	3.88635
H	-0.00971	1.06040	-2.84529
H	-4.38213	-0.82535	6.04780
H	-2.19549	-1.67375	-1.34482
H	-2.20567	1.65343	-1.35004
S	1.60979	-0.00000	1.85591
S	-1.60979	0.00000	1.86158
C	0.68984	0.10498	3.29237
C	0.72892	-2.30416	0.18763
C	-0.83658	0.73941	5.77047
C	-1.51681	0.77066	6.98473
C	0.71812	2.30825	0.16967
C	1.18474	-1.71236	-1.03018
C	-0.69951	0.10223	3.34970
C	1.17359	1.71271	-1.04769
C	-0.68976	-2.31473	0.19166
C	-1.42395	0.14576	4.62818
C	-2.79345	0.20677	7.09154
C	-0.69827	2.31144	0.17863
C	0.00789	-1.40174	-1.80255
C	-2.71708	-0.40746	4.75092
C	-1.16113	-1.73108	-1.02372
C	-0.00308	1.39758	-1.81659
C	-3.39000	-0.38117	5.96945
C	-1.17069	1.71843	-1.03324
W	0.00000	-0.00000	0.00000

Energy: -227.81724062 eV

Geometry optimised structure of [**6**]$^-$

H	1.26482	-0.37003	4.22241
H	1.25523	-2.87444	0.74200
H	0.17660	-1.41984	5.71299
H	1.70535	3.25513	0.94143
H	-1.08574	-1.70981	7.80226
H	2.16810	-1.58141	-1.45498
H	2.25555	1.72139	-1.23088
H	-1.40630	-2.80142	0.72827
H	-3.48776	-1.00765	7.94846
H	-0.92723	3.46313	1.17233
H	-0.00439	-0.76231	-2.88390
H	-3.29107	0.31465	3.83541
H	-0.08991	1.34338	-2.54745
H	-4.57608	0.00273	5.93197
H	-2.23683	-1.49716	-1.48875
H	-2.07952	2.09177	-0.86607
S	1.60532	-0.00000	1.85910
S	-1.60532	-0.00000	1.83698
C	0.67274	-0.27454	3.31001
C	0.64098	-2.44839	-0.04523
C	-0.85889	-1.08009	5.75693
C	-1.57671	-1.25334	6.93897
C	0.97161	2.84784	0.24906
C	1.12804	-1.67824	-1.15725
C	-0.69131	-0.29899	3.35710
C	1.26654	1.88420	-0.80653
C	-0.76244	-2.40935	-0.05330
C	-1.44445	-0.49653	4.60334
C	-2.92321	-0.86461	7.02447
C	-0.39639	2.95355	0.37039
C	-0.02319	-1.22845	-1.90319
C	-2.80854	-0.12622	4.70895
C	-1.20567	-1.62593	-1.17284
C	0.02326	1.60354	-1.49609
C	-3.52733	-0.30278	5.89294
C	-1.02062	2.08186	-0.61695
W	0.00000	-0.00000	0.00000

Energy: -234.36972160 eV

Geometry optimised structure of **5**

Mo	0.00000	0.00000	0.00000
S	-1.60140	0.00000	1.84146
S	1.60140	0.00000	1.82995
C	-0.67943	0.19128	3.30682
C	0.68062	0.22391	3.33990
C	1.45697	0.48181	4.55690
C	0.85376	1.14251	5.68398
N	1.51230	1.50244	6.76286
C	2.85198	1.19898	6.78598
C	3.63730	1.58374	7.89875
C	4.98393	1.27032	7.93795
C	5.58416	0.55951	6.86947
C	4.84238	0.18491	5.76475
C	3.46134	0.50624	5.68897
N	2.75233	0.16557	4.57280
C	1.20544	-1.83960	-0.79840
C	0.34893	-1.42014	-1.86709
C	-1.00895	-1.65142	-1.48384
C	-0.99285	-2.24935	-0.19674
C	0.35261	-2.36746	0.22850
C	0.86826	1.61720	-1.62615
C	-0.54417	1.50075	-1.81104
C	-1.19245	1.93135	-0.61843
C	-0.16212	2.31871	0.30364
C	1.10242	2.13093	-0.32986
H	-1.28239	0.26663	4.21163
H	-0.20680	1.40382	5.65391
H	3.14872	2.12778	8.70840
H	5.58883	1.56843	8.79462
H	6.64493	0.31044	6.92055
H	5.28667	-0.35590	4.92844
H	2.29020	-1.85355	-0.79991
H	0.67296	-1.00253	-2.81377
H	-1.86665	-2.52015	0.38675
H	0.67631	-2.74082	1.19145
H	1.63280	1.34678	-2.34865
H	-1.03682	1.12752	-2.70287
H	-2.26170	1.99264	-0.44868
H	-0.30887	2.67873	1.31423
H	2.06994	2.31175	0.12349
H	-1.89333	-1.43360	-2.07661

Energy: -266.93764740 eV

Geometry optimised structure of **10**

W	0.00000	0.00000	0.00000
S	1.60156	0.00000	1.83911
S	-1.60156	0.00000	1.82746
C	0.67943	-0.18866	3.30740
C	-0.68004	-0.22014	3.34036
C	-1.45724	-0.47633	4.55651
C	-0.85501	-1.13598	5.68470
C	-2.85349	-1.18929	6.78726
C	-3.63880	-1.57110	7.90095
C	-4.98554	-1.25713	7.94000
C	-5.58543	-0.54895	6.86983
C	-4.84338	-0.17754	5.76400
C	-3.46245	-0.49916	5.68867
C	-1.20644	1.83558	-0.79891
C	-0.34711	1.41624	-1.86743
C	1.01208	1.64769	-1.48237
C	0.99411	2.24752	-0.19617
C	-0.35248	2.36594	0.22850
C	-0.87037	-1.61356	-1.62670
C	0.54310	-1.49762	-1.81220
C	1.19342	-1.92734	-0.61910
C	0.16153	-2.31628	0.30399
C	-1.10426	-2.12757	-0.32987
N	-1.51383	-1.49333	6.76411
N	-2.75303	-0.16089	4.57200
H	1.28337	-0.26498	4.21135
H	0.20512	-1.39902	5.65436
H	-3.15030	-2.11337	8.71168
H	-5.59086	-1.55379	8.79738
H	-6.64622	-0.29984	6.92000
H	-5.28807	0.36024	4.92616
H	-2.29049	1.85002	-0.80232
H	-0.67103	0.99706	-2.81436
H	1.86766	2.51666	0.38802
H	-0.67844	2.73927	1.19184
H	-1.63638	-1.34081	-2.34735
H	1.03639	-1.12360	-2.70430
H	2.26262	-1.99003	-0.45059
H	0.31014	-2.67676	1.31535
H	-2.07186	-2.30639	0.12372
H	1.89779	1.42778	-2.07132

Energy: -267.03661898 eV