

Supporting information

for

**Electrochemical Generation of High-valent Oxo-manganese Complexes  
Featuring an Anionic N5 Ligand and their Role in O—O Bond Formation**

Sachidulal Biswas,<sup>1</sup> Srijan Narayan Chowdhury,<sup>1</sup> Panjo Lepcha,<sup>1</sup> Subhankar Sutradhar,<sup>2</sup> Abhishek Das,<sup>2</sup> Tapan Kanti Paine,<sup>\*2</sup> Satadal Paul,<sup>\*3</sup> and Achintesh N. Biswas<sup>\*1</sup>

<sup>1</sup>Department of Chemistry, National Institute of Technology Sikkim, Ravangla, South Sikkim 737139,  
India

<sup>2</sup>School of Chemical Sciences, Indian Association for the Cultivation of Science, 2A and 2B Raja S.C.  
Mullick Road, Jadavpur, Kolkata 700032, India

<sup>3</sup>Department of Chemistry, Bangabasi Morning College, 19, Rajkumar Chakraborty Sarani, Kolkata-  
700009, India

\*To whom correspondence should be addressed:

Achintesh N. Biswas ([achintesh@nitsikkim.ac.in](mailto:achintesh@nitsikkim.ac.in))

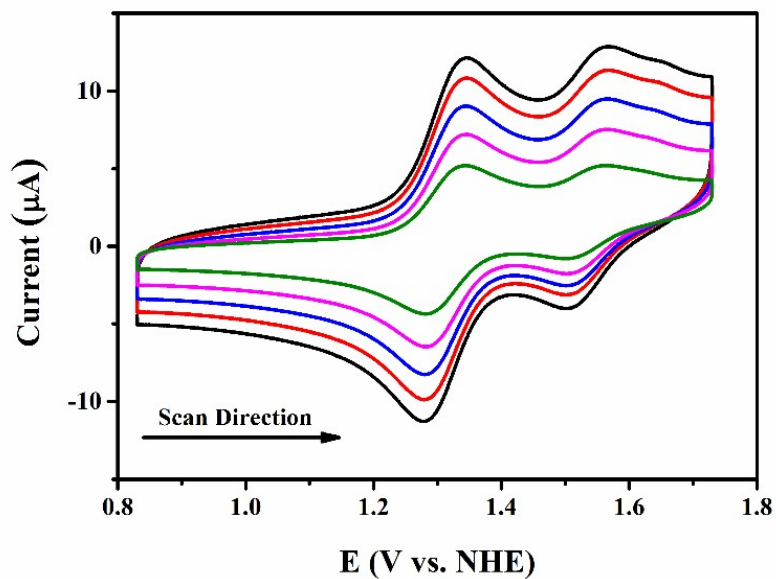


Figure S1: CVs of complex **1** (0.1 mM) in acetonitrile at different scan rates (green line = 100, magenta = 200, blue = 300, red = 400 and black = 500 mV/s) using a GC working electrode (WE) and Pt wire as both counter electrode (CE) and reference electrode (RE) at 293 K. Ferrocene was used as an internal standard.

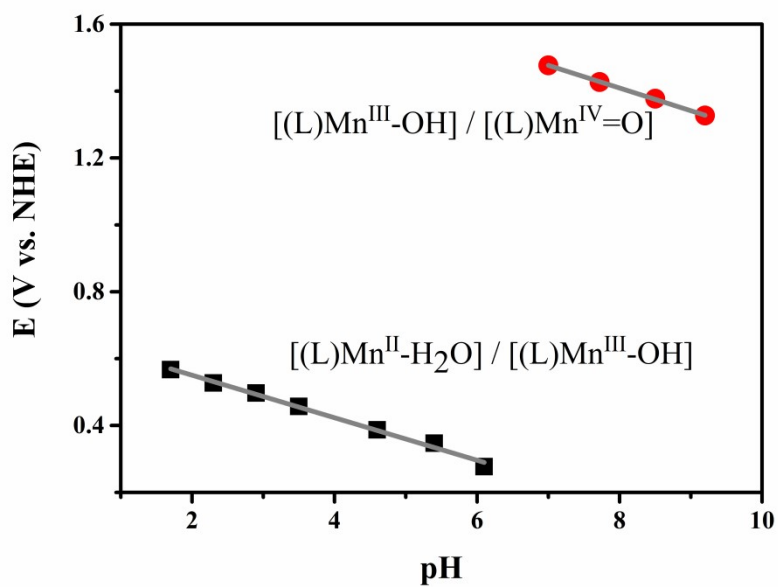


Figure S2: Pourbaix diagram for complex **1**.

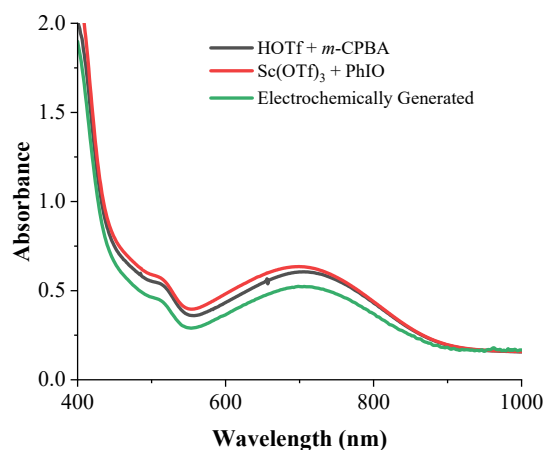


Figure S3: Top: Electronic spectra of oxomanganese(IV) transient (**2**) generated by the addition of HOTf and *m*-CPBA (black), Sc(OTf)<sub>3</sub> and PhIO (red) to a solution of **1** (0.5 mM) in acetonitrile at 293 K. The green line shows the UV-vis spectrum of the electrochemically generated **2** in wet acetonitrile. Bottom: Acetonitrile solution of 0.5 mM complex **1**, containing 0.1 M LiClO<sub>4</sub> as supporting electrolyte before (left, golden brown solution) and after controlled potential electrolysis (CPE) (right, green solution) at 1.45 V vs. NHE using a FTO plate as working electrode. The solution was stirred throughout the experiment. WE = FTO, CE = Pt, RE = Pt.

*Note: The Controlled potential electrolysis experiments were carried out using a large-surface-area porous carbon electrode (PCE) electrode as well.*

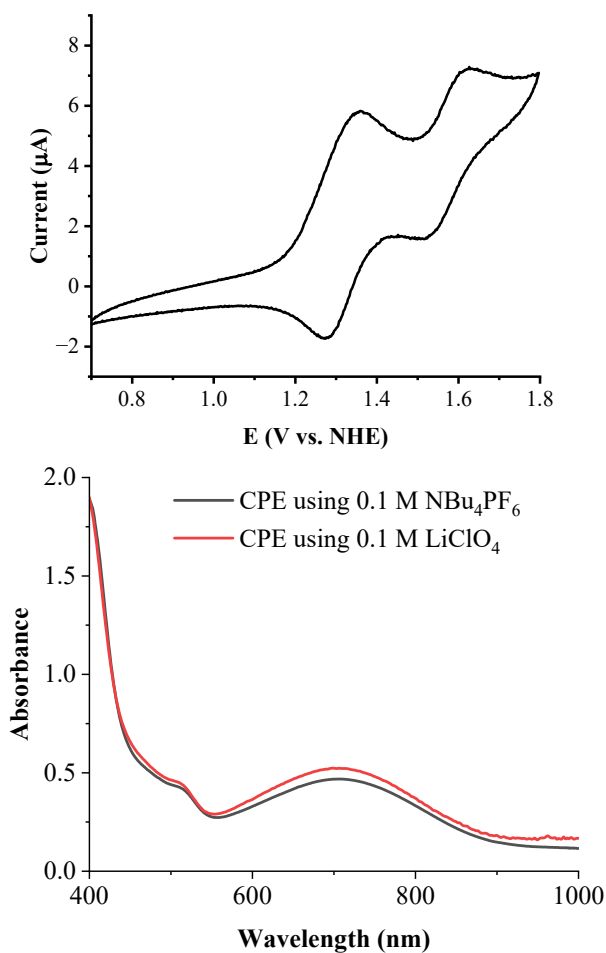


Figure S4: Top: CV of complex **1** (0.1 mM) in wet acetonitrile containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub> as the supporting electrolyte at a scan rate of 100 mV/s. A glassy carbon (GC) electrode was used as the working electrode (WE) and Pt wires were as both counter electrode (CE) and reference rectrode (RE) at 293 K. Ferrocene was used as an internal standard. Reference potentials were converted to NHE. Bottom: UV-Vis spectra showing the formation of [Mn<sup>IV</sup>(O)(dpaq)]<sup>+</sup> (**2**) during the electrolysis of an acetonitrile solution of complex **1** (0.5 mM) containing 0.1 M LiClO<sub>4</sub> (red) and NBu<sub>4</sub>PF<sub>6</sub> (black) as the supporting electrolyte at a potential 1.45 V vs. NHE in the presence of water.

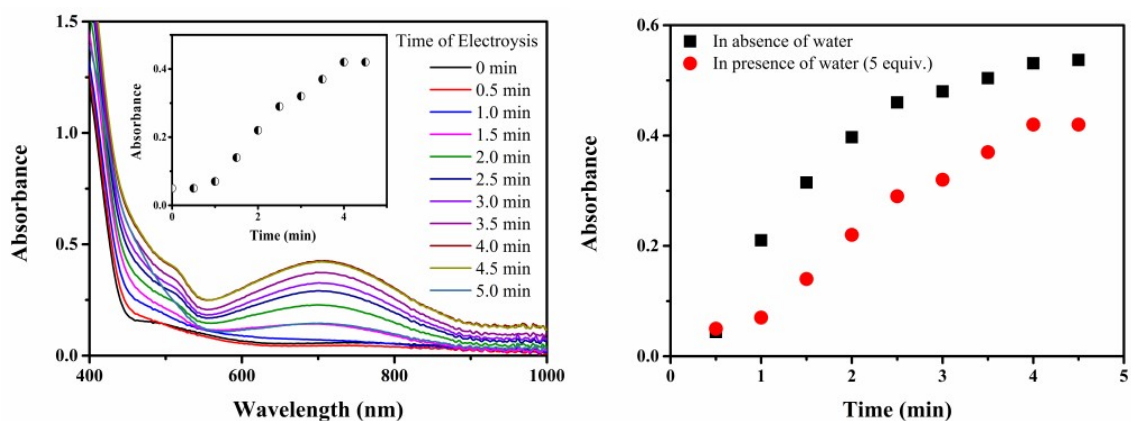


Figure S5: Left: UV-Vis spectra showing the formation of  $[\text{Mn}^{\text{IV}}(\text{O})(\text{dpaq})]^+(\mathbf{2})$  during the electrolysis of an acetonitrile solution of complex **1** (0.5 mM) at a potential 1.45 V vs. NHE in the presence of water. Inset shows the change in absorbance at 700 nm with time of electrolysis. Right: Plot of amount of **2** formed (in terms of absorbance of **2** at 700 nm) with respect to electrolysis time in the presence and absence of water.

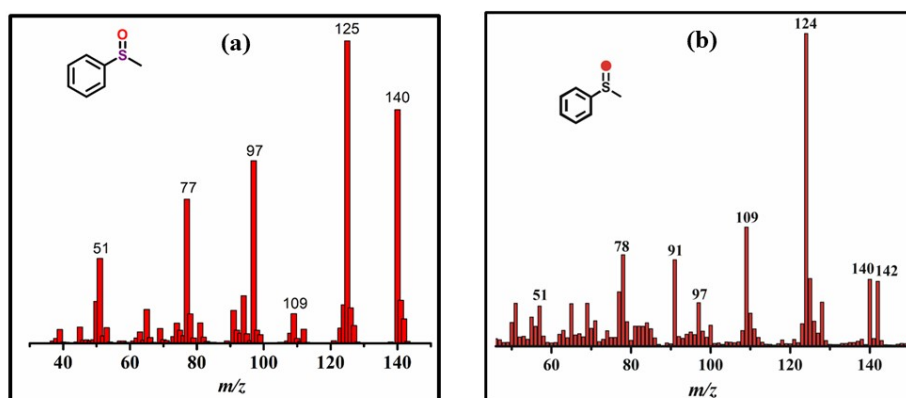


Figure S6: (a) GC-MS spectrum of thioanisole oxide formed in the reaction of **2** and thioanisole in presence of  $\text{H}_2^{18}\text{O}$ . (b) GC-MS spectrum of thioanisole oxide formed in the reaction of  $\mathbf{2}^{18}\text{O}$  and thioanisole.

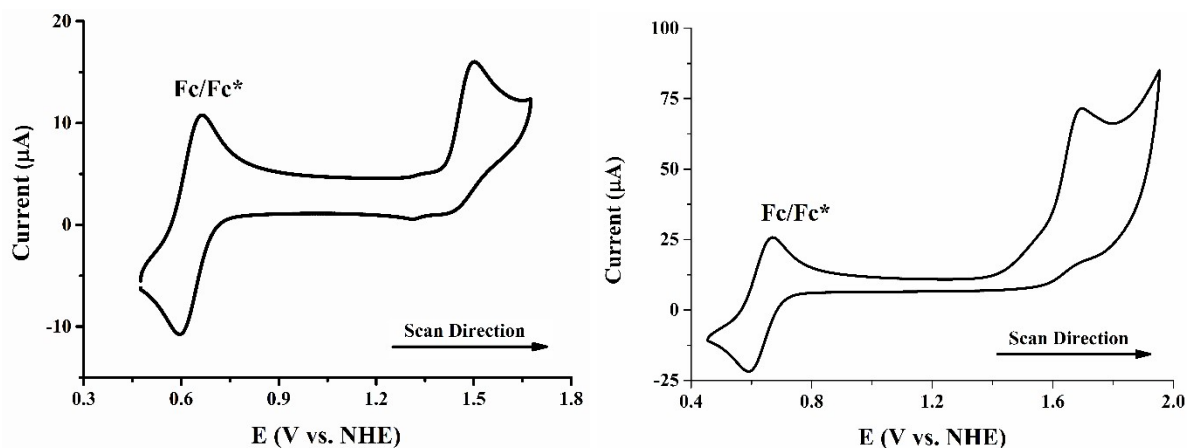


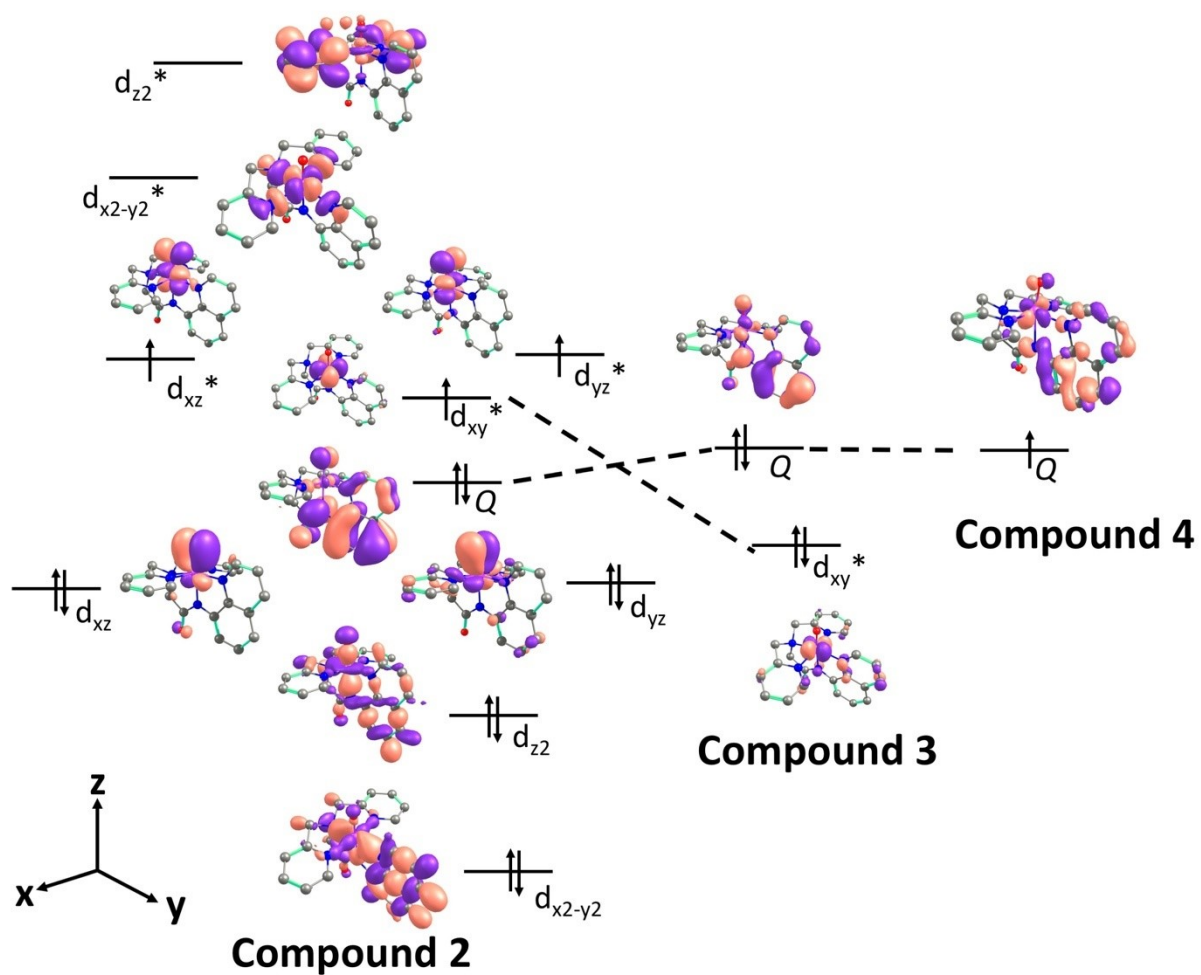
Figure S7: CVs of  $[\text{Zn}^{\text{II}}(\text{dpaq})]^+$  (left) and H-dpaq (right) in acetonitrile containing 0.1 M  $\text{LiClO}_4$  as the supporting electrolyte at a scan rate of 100 mV/s at 293 K. Ferrocene was used as an internal standard. (WE = GC, CE = Pt, RE = Pt.)

Table S1: Relative DFT-Energies ( $\text{kcal.mol}^{-1}$ ) of different spin states of **2** and **3**

Species	Complex 2	Complex 3
S = 3/2	0	----
S = 1/2	4	----
S = 1	----	3
S = 0	----	0

Table S2. Data related to the calculation of redox potential (RP) of reference  $\text{Fc}/\text{Fc}^+$ ,  $\text{Mn}(\text{IV})/\text{Mn}(\text{V})$  and  $\text{Mn}(\text{V})/\text{Mn}(\text{VI})$  couples in acetonitrile. Experimental values of absolute RP for  $\text{Fc}/\text{Fc}^+$  is taken from refs. <sup>1,2</sup> and those for  $\text{Mn}(\text{IV})/\text{Mn}(\text{V})$  and  $\text{Mn}(\text{V})/\text{Mn}(\text{VI})$  couples are from the present experiment.

Redox Couple	Calculated RP (V)	Experimental RP (V)	Error	Error-adjusted value (V) (Calculated + Error as obtained for reference $\text{Fc}/\text{Fc}^+$ )
$\Delta G_{\text{Fc}/\text{Fc}^+}$	4.48	4.98	0.50	-
$\Delta G_{\text{Mn}(\text{IV})/\text{Mn}(\text{V})}$	1.16	1.56	-----	1.66
$\Delta G_{\text{Mn}(\text{V})/\text{Mn}(\text{VI})}$	1.70	1.95	-----	2.20



**Figure S8.** Relative energy ordering (not up to any quantitative scale) of the DFT-derived MOs showing particularly the change in the relative energy ordering of Mn- $d_{xy}^*$  and Quinoline-based  $\pi$  orbital ( $Q$ ) with gradual one-electron oxidation of complex **2** having Mn(IV).

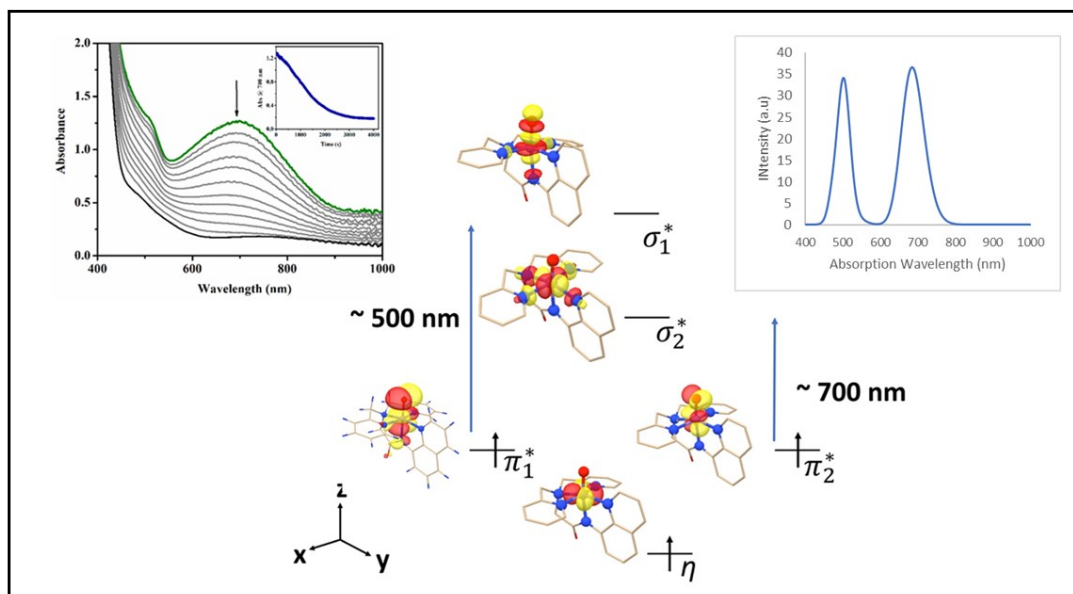
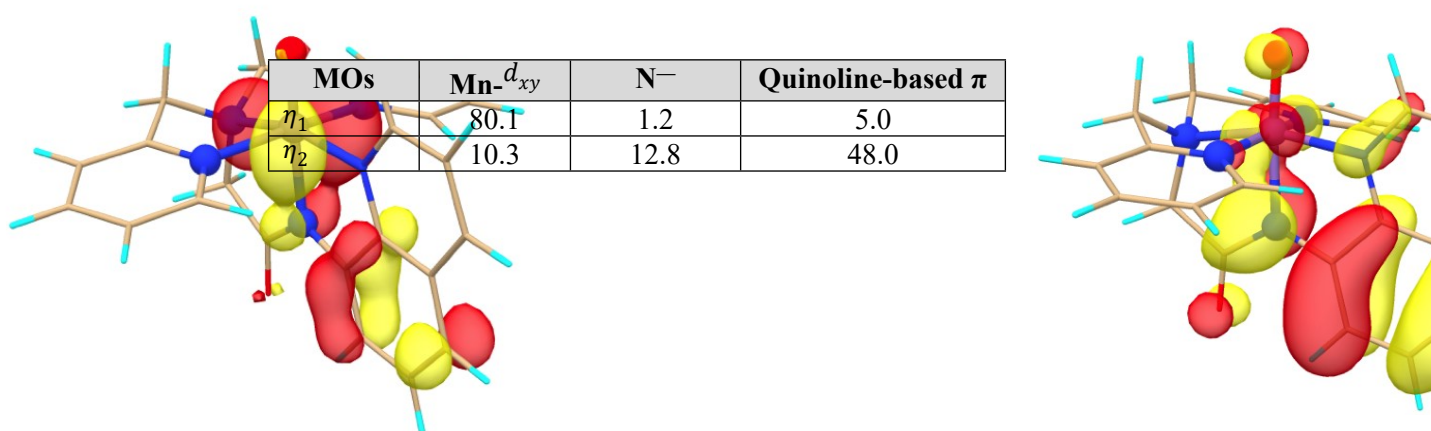


Figure S9: Molecular orbitals involved in the electronic transitions in **2**; inset shows the experimental (left) and simulated (right) optical absorption spectra of the complex **2**.



**Scheme S1.** Schematic of the MOs  $\eta_1$  (upper panel, left) and  $\eta_2$  (upper panel, right) in the complex **3** and the contribution of Mn- $d_{xy}$ , axial anionic nitrogen (N<sup>-</sup>) and quinoline based  $\pi$  orbital therein in the attached table (Lower panel).



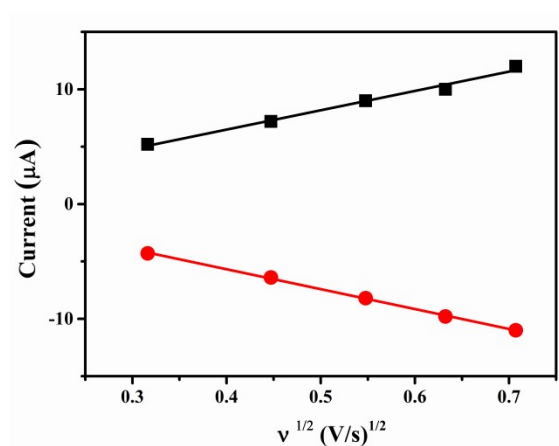


Figure S10: Plot of current for the Mn<sup>III/IV</sup> redox couple vs. square root of scan rate. (Anodic peak current = black cubes, Cathodic peak current = red dots).

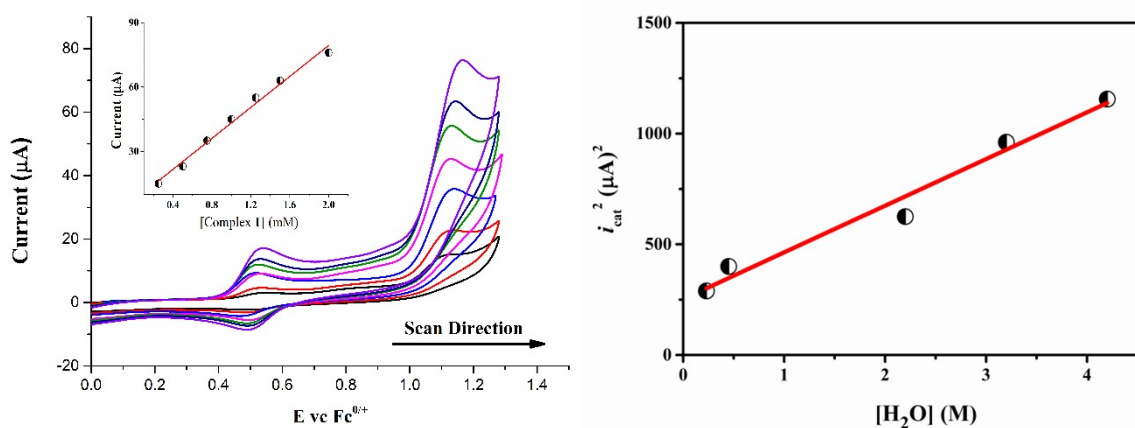


Figure S11: Left: CVs of complex **1** at different concentration in acetonitrile. (0.25 mM black line, 0.50 mM red line, 0.75 mM blue line, 1.00 mM pink line, 1.25 mM green line, 1.50 mM navy blue line and 2.00 mM purple line) at a scan rate of 100 mV/s at 293 K. Inset shows the change in anodic peak current at 1.9 V vs. NHE with respect to the concentration of complex **1**. Right: Plot of  $i_{cat}^2$  vs [H<sub>2</sub>O]. (WE = GC, CE = Pt, RE = Pt.)

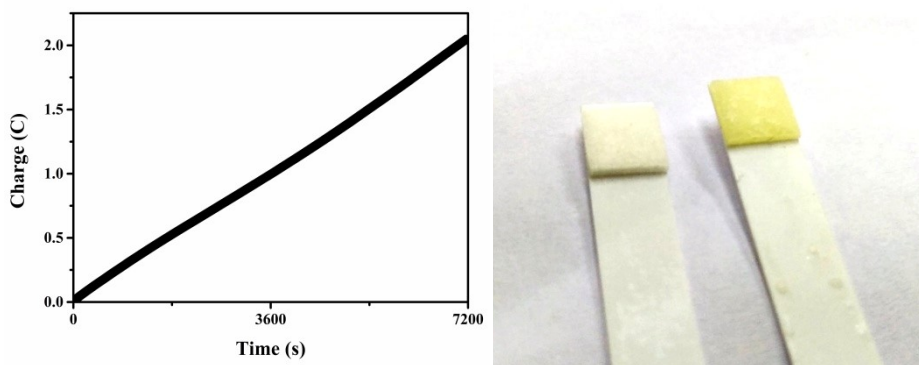


Figure S12: Left: Plot of charge passed with respect to the time of controlled potential electrolysis with 0.5 mM complex **1** at 1.95 V (vs. NHE) using a FTO plate as working electrode, Pt CE and Pt RE in 0.1M LiClO<sub>4</sub>. The solution was stirred throughout the experiment. Right: Hydrogen peroxide was detected using XploSens PS peroxide detection strip. Yellow colouration of the white strip confirms the presence of peroxide in solution.

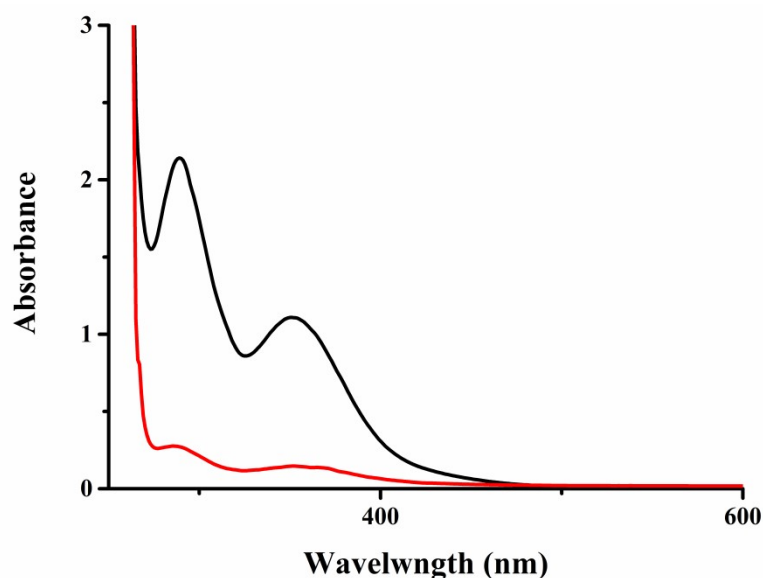


Figure S13: UV-Vis spectrum obtained from the reaction of a solution of 1 M KI in 0.05 M H<sub>2</sub>SO<sub>4</sub> with the electrolysed solution of complex **1** for 2 h (black line). Generation of I<sup>3-</sup> is confirmed from the appearance of absorption maxima at 288 and 353 nm. The red line indicates the blank reaction performed under identical conditions using the same solution of **1** which was not electrolysed.

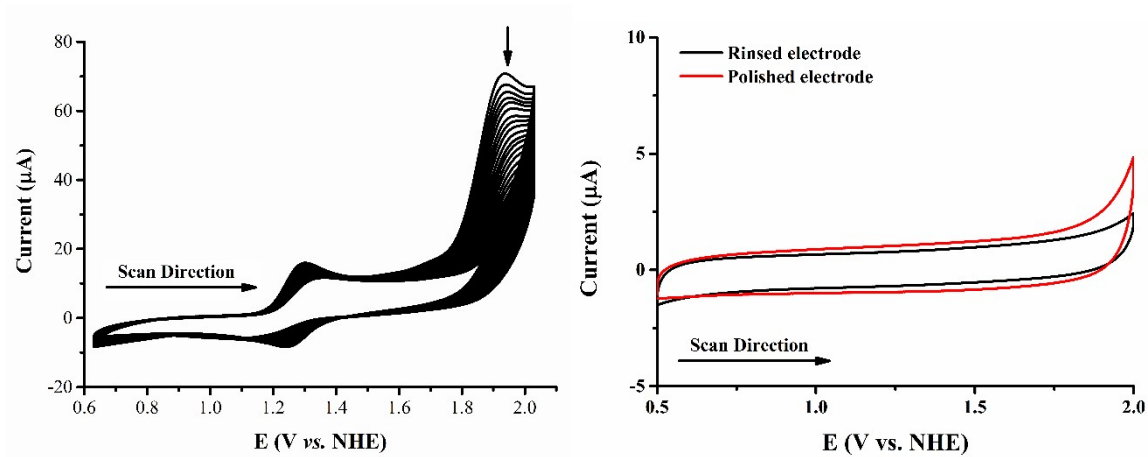


Figure S14: Left: CV of 1.0 mM complex 1 in acetonitrile/water showing 25 consecutive cycles. Right: CV of the GC working electrode after 25 cycles in acetonitrile containing 0.1 M LiClO<sub>4</sub>. (Scan rate 100 mV/s, WE = GC, CE = Pt, RE = Pt.)

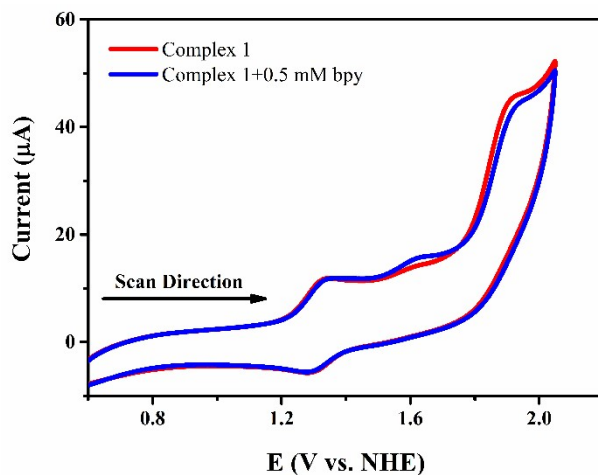


Figure S15: CVs of 0.5 mM complex 1 in the presence and absence of equimolar amounts of 2,2'-bipyridine at a scan rate of 100 mV/s at 293 K. (WE = GC, CE = Pt, RE = Pt.)

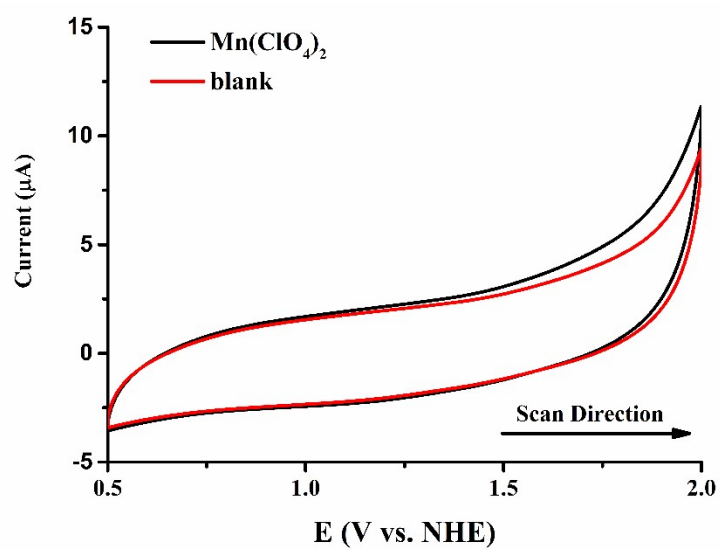


Figure S16: CV of 0.5 mM  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in acetonitrile/water (10%) containing 0.1 M  $\text{LiClO}_4$  at a scan rate of 100mV/s at 293 K. (WE = GC, CE = Pt, RE = Pt.)

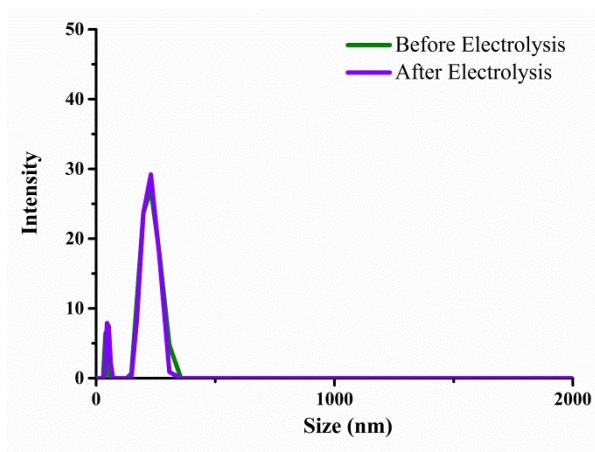


Figure S17: Dynamic light scattering (DLS) data of the solution before and after CPE.

## References

1. Namazian, M.; Lin, C. Y.; Coote, M. L. Benchmark Calculations of Absolute Reduction Potential of Ferricinium/Ferrocene Couple in Nonaqueous Solutions. *J. Chem. Theory Comput.* **2010**, *6*, 9, 2721-2725.
2. Konezny, S. J.; Doherty, M. D.; Luca, O. R.; Crabtree, R. H.; Soloveichik, G. L.; Batista, V. S. Reduction of System-atic Uncertainty in DFT Redox Potentials of Transition-Metal Complexes. *J. Phys. Chem. C* **2012**, *116*, 10, 6349-6356.

Table S3. Optimized coordinate of the compound **2** in its ground spin state.

Mn	0.000000000	0.000000000	0.000000000
O	0.586452041	1.181396084	3.895206424
O	-0.255520113	0.052474146	-1.665473331
N	0.045590580	-1.982894154	0.206037273
N	0.305202548	-0.116875008	1.984334431
N	0.035943967	2.003353453	0.326680741
N	-1.972169166	0.274843458	0.393882837
N	1.995171362	0.302526554	-0.217227260
C	-0.099161557	-2.863651306	-0.781449169
H	-0.254217204	-2.443549107	-1.771692040
C	-0.052346047	-4.251287558	-0.547608567
H	-0.175056523	-4.933775895	-1.384030788
C	0.149070531	-4.717177714	0.740733533
H	0.188983092	-5.785972828	0.942622721
C	0.306366727	-3.799235706	1.813775722
C	0.516973715	-4.174777237	3.168831884
H	0.565175869	-5.230078755	3.428330478
C	0.657135365	-3.191601892	4.134135349
H	0.818266001	-3.477654335	5.171941134
C	0.598063030	-1.811694528	3.817876345
H	0.711627890	-1.066521895	4.597799371
C	0.393199375	-1.401537769	2.499451840
C	0.247091011	-2.411974851	1.497491206
C	0.402373130	1.030486590	2.677701739
C	0.260143471	2.276870548	1.797559525
H	1.164741395	2.883338857	1.911632420
H	-0.575212226	2.873518347	2.178645572
C	-1.288242101	2.515664021	-0.137522699
H	-1.270259680	2.518221926	-1.233158517
H	-1.457379724	3.538933298	0.214720543
C	-2.358686498	1.568487189	0.321410335
C	-3.668889002	1.950147757	0.604548020
H	-3.947061833	2.999458298	0.550728138
C	-4.600450667	0.967809562	0.951840839
H	-5.629004893	1.241205568	1.175138771
C	-4.188781215	-0.366114673	1.014096272
H	-4.877373880	-1.162905771	1.281505015
C	-2.859524363	-0.673617862	0.734418258
H	-2.494417545	-1.694474280	0.781159561
C	1.152082068	2.532932665	-0.512924503

H	0.804979409	2.534384898	-1.552325850
H	1.406157687	3.558709514	-0.224643892
C	2.323817606	1.601104075	-0.401258245
C	3.652835769	2.001008142	-0.529172531
H	3.887429882	3.053806424	-0.663380055
C	4.659011868	1.032005447	-0.483645126
H	5.702943699	1.319805221	-0.583630814
C	4.303800122	-0.307235721	-0.301987806
H	5.051750791	-1.094166061	-0.259160052
C	2.956728510	-0.633239790	-0.164787082
H	2.636768921	-1.658828405	-0.012229911

Table S4. Optimized coordinate of the compound **3** in its ground spin state.

Mn	4.374246000	5.090567000	1.673684000
O	6.197056000	5.700237000	5.266627000
O	3.911144000	5.194444000	0.173189000
N	3.465619000	3.363385000	2.061631000
N	4.906608000	4.805558000	3.549534000
N	5.440241000	6.785002000	1.853014000
N	2.874946000	6.269121000	2.352040000
N	6.167787000	4.310338000	1.172272000
C	2.711489000	2.680493000	1.190504000
H	2.595007000	3.118384000	0.203141000
C	2.105934000	1.461366000	1.540091000
H	1.502255000	0.943059000	0.799711000
C	2.287117000	0.938807000	2.813760000
H	1.825324000	-0.005006000	3.097235000
C	3.083431000	1.647139000	3.748719000
C	3.351065000	1.226239000	5.085122000
H	2.924589000	0.292294000	5.444754000
C	4.148854000	2.003729000	5.919399000
H	4.343889000	1.668331000	6.935301000
C	4.715819000	3.219733000	5.490162000
H	5.334757000	3.806883000	6.159790000
C	4.472895000	3.669028000	4.179250000

C	3.656016000	2.870944000	3.318613000
C	5.735929000	5.752657000	4.148464000
C	6.016056000	6.937549000	3.233552000
H	7.099210000	7.082477000	3.172110000
H	5.594515000	7.830834000	3.706680000
C	4.463623000	7.880366000	1.539494000
H	4.294192000	7.865368000	0.456169000
H	4.874722000	8.858323000	1.814277000
C	3.168439000	7.586219000	2.246453000
C	2.296250000	8.563994000	2.716876000
H	2.556347000	9.616101000	2.628713000
C	1.084236000	8.167832000	3.293173000
H	0.384215000	8.912490000	3.665010000
C	0.789602000	6.805252000	3.386224000
H	-0.141689000	6.456468000	3.824309000
C	1.716305000	5.882173000	2.907656000
H	1.534934000	4.813818000	2.963916000
C	6.514772000	6.661313000	0.812669000
H	6.042591000	6.830496000	-0.162426000
H	7.288236000	7.423366000	0.961179000
C	7.072609000	5.265011000	0.853993000
C	8.389410000	4.939137000	0.541095000
H	9.102426000	5.722340000	0.295225000
C	8.770634000	3.592830000	0.540917000
H	9.792445000	3.312323000	0.295917000
C	7.822885000	2.617721000	0.861874000
H	8.078467000	1.561581000	0.870279000
C	6.527045000	3.017719000	1.179014000
H	5.757504000	2.298573000	1.440365000

Table S5. Optimized coordinate of the compound **4** in its ground spin state.

Mn	4.364519000	5.074050000	1.650825000
O	5.456633000	6.125229000	5.400948000
O	3.838497000	5.090924000	0.168671000
N	3.514314000	3.349648000	2.049626000
N	4.805190000	4.831676000	3.575337000
N	5.454489000	6.747599000	1.843426000
N	2.907633000	6.275214000	2.343031000
N	6.166682000	4.340002000	1.166875000
C	2.824611000	2.608917000	1.146426000
H	2.739108000	3.020399000	0.146042000
C	2.257954000	1.382113000	1.489597000
H	1.716061000	0.827312000	0.729591000
C	2.388967000	0.887650000	2.789162000
H	1.949241000	-0.065098000	3.073151000
C	3.104246000	1.654240000	3.735640000
C	3.313461000	1.285460000	5.092916000
H	2.908928000	0.341371000	5.450978000
C	4.037715000	2.115225000	5.973663000
H	4.183642000	1.792648000	7.000637000
C	4.576728000	3.325197000	5.558106000
H	5.145888000	3.946241000	6.240688000
C	4.384013000	3.736433000	4.200150000
C	3.649872000	2.882189000	3.308388000
C	5.446561000	5.939767000	4.211717000
C	6.121550000	6.817721000	3.186911000
H	7.147842000	6.441964000	3.088523000
H	6.168053000	7.852901000	3.531878000
C	4.512728000	7.897756000	1.631520000
H	4.336206000	7.979543000	0.553163000
H	4.972974000	8.825736000	1.981481000
C	3.221832000	7.589966000	2.320349000
C	2.362221000	8.545171000	2.851970000
H	2.644677000	9.593781000	2.833396000
C	1.147687000	8.124153000	3.401015000
H	0.459369000	8.850205000	3.825822000
C	0.832412000	6.762512000	3.403553000
H	-0.101915000	6.394252000	3.816825000
C	1.744445000	5.857832000	2.870824000
H	1.543354000	4.792401000	2.861630000
C	6.488109000	6.672615000	0.754088000
H	5.980653000	6.864853000	-0.197333000
H	7.250815000	7.440942000	0.911195000
C	7.048436000	5.285585000	0.769215000
C	8.344412000	4.951249000	0.394483000
H	9.036243000	5.732507000	0.093098000
C	8.725059000	3.606262000	0.419539000
H	9.732457000	3.318292000	0.130242000
C	7.801728000	2.641558000	0.830513000
H	8.057178000	1.586711000	0.868177000
C	6.525235000	3.045576000	1.206326000
H	5.783286000	2.327954000	1.5367260