Supplementary Material (ESI) for PCCP

Electrochemical Investigation of Mn4O4-Cubane Water Oxidizing Clusters

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Electronic Supplementary Information

Table S1. Summary of cyclic voltammetric data obtained for the oxidation of 0.4 mM **1** at a glassy carbon disc electrode in CH_2Cl_2 (0.1 M Bu_4NPF_6) at 22 °C.

Scan rate (mVs^{-1})	E_p^{ox} (mV*)	i_p^{ox} (μA)	E_p^{red} (mV*)	i_p^{red} (μA)	ΔE_p (mV*)	E_f^o (mV*)	$[i^{red}/i^{ox}]$
10	729	1.6	645	1.4	84	687	0.9
50	733	3.3	647	2.8	86	690	0.8
100	740	4.9	645	4.1	95	692	0.8
200	747	6.5	634	5.5	113	690	0.8
500	750	9.8	636	8.3	129	693	0.9

*mV vs Fc/Fc^+.

Table S2. Summary of cyclic voltammetric data obtained for the oxidation of 0.4 mM **2** at a glassy carbon disc electrode in CH_2Cl_2 (0.1 M Bu_4NPF_6) at 22°C.

Scan rate (mVs^{-1})	E_p^{ox} (mV*)	i_p^{ox} (μA)	E_p^{red} (mV*)	i_p^{red} (μA)	ΔE_p (mV*)	E_f^o (mV*)	$[i^{red}/i^{ox}]$
10	578	1.6	492	1.3	86	535	0.8
50	592	3.3	482	2.6	110	537	0.8
100	606	4.2	471	3.3	135	538	0.8
200	633	5.6	458	4.0	175	545	0.7
500	656	9.8	444	9.0	212	550	0.9

*mV vs Fc/Fc^+.

Table S3. Summary of cyclic voltammetric data obtained for the reduction of 0.4 mM CH_2Cl_2 solutions of **1** and **2** at a glassy carbon disc electrode at 22 °C (0.1 M Bu_4NPF_6).

Compound 1					**Compound 2**				
Scan rate (mVs^{-1})	E_p^{red} (mV^*)	i_p^{red} (μA)	E_p^{ox} (mV^*)	ΔE_p (mV)	Scan rate (mVs^{-1})	E_p^{red} (mV^*)	i_p^{red} (μA)	E_p^{ox} (mV^*)	ΔE_p (mV)
10	-591	1.4	Undetected	-	10	-582	1.6	Undetected	-
50	-591	2.4	Undetected	-	50	-617	3.1	Undetected	-
100	-608	3.3	Undetected	-	100	-654	4.2	Undetected	-
200	-646	5.0	-346	-302	200	-657	5.9	-371	286
500	-662	7.3	-365	-299	500	-716	8.0	-387	329

*mV vs Fc/Fc^+

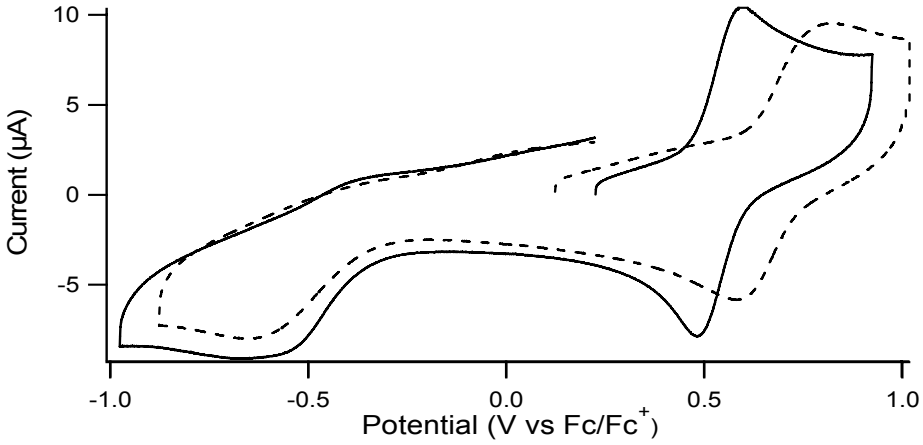

Figure S1. Cyclic voltammograms obtained at 22 °C at a glassy carbon electrode for oxidation and reduction of: A) 0.4 mM CH_2Cl_2 (0.1 M Bu_4NPF_6) solutions of **1** (- - - -) and **2** (——), scan rate 250 mVs^{-1}.

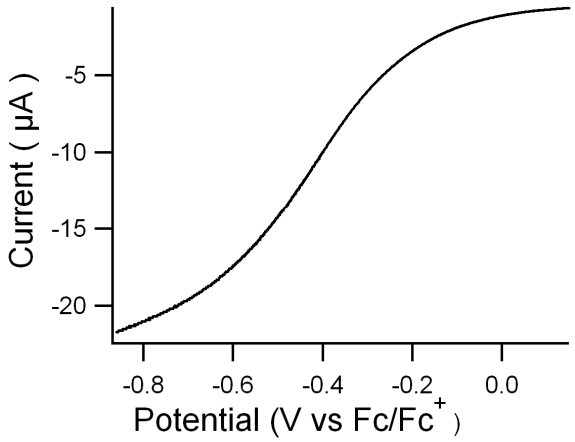

Figure S2. Glassy carbon rotated disc voltammogram obtained at 22°C for reduction of a 0.4 mM CH_2Cl_2 (0.1 M Bu_4NPF_6) solution of **1**, rotation rate = 1000 rpm, scan rate = 5 mV/s