Oxygen isotopic exchange in a $Mn^{III}Mn_3^{IV}$-oxo cubane.

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Supporting information

Contents

S.0 ESI-MS spectrum of $[Mn^{III}Mn^{IV}_3O_4(PO_2\{C_6H_4OCH_3\}_2)_6]^+$

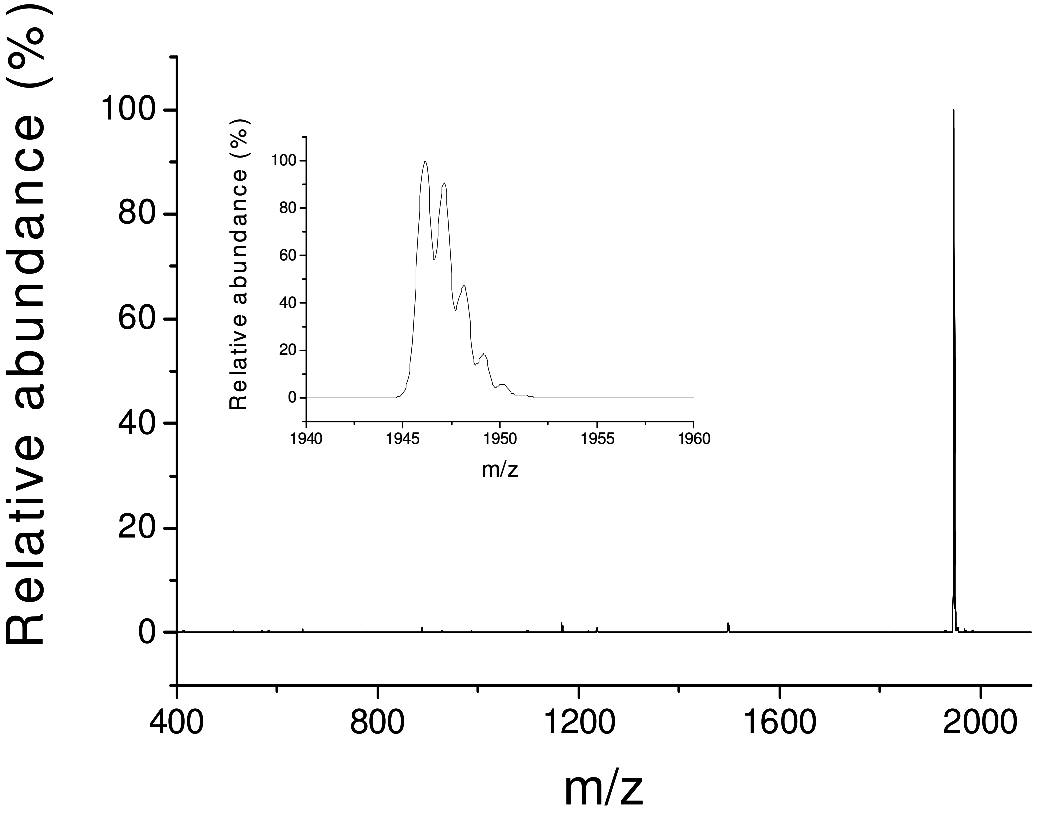

Fig. S.0.1 ESI-MS spectrum of $[Mn^{III}Mn^{IV}_4O_4(O_2P\{C_6H_4OCH_3\}_2)_6]^+$ in dry acetonitrile; +20 V cone-voltage.

S.1 Isotope deconvolution

Spectra were deconvoluted according to equation 1,

$$I_{Tot}(m/z) = \sum_{i=0}^{4} r_i I_i \qquad \text{(S.1.1)}$$

where I_{Tot} is the observed relative abundance at a given m/z, *i* is the number of ^{18}O in the molecule, r_i is proportional to the mol fraction of the molecule with *i* number of ^{18}O, and I_i is the theoretical relative abundance of the molecule with *i* number of ^{18}O at a given m/z. By fitting this equation for abundances at between 1946.0 m/z and 1959.0 m/z in parallel, the relevant r_i could be determined.

$$x_i = \frac{r_i}{\sum_{n=0}^{4} r_n} \qquad \text{(S.1.2)}$$

Normalisation (Eq. 2) gave the mol fraction, χ_i, from which the concentration of each species could be calculated.

Figure S.1.1 shows the isotopic pattern of unenriched $[Mn^{III}Mn^{IV}{}_4O_4(O_2P(C_6H_4OCH_3)_2)_6]^+$, whereas figure S.1.2 shows the isotopic pattern of a mixture of 10% $[Mn^{III}Mn^{IV}{}_4{}^{16}O_4(O_2P(C_6H_4OCH_3)_2)_6]^+$, 20% $[Mn^{III}Mn^{IV}{}_4{}^{16}O_3{}^{18}O(O_2P(C_6H_4OCH_3)_2)_6]^+$, 50% $[Mn^{III}Mn^{IV}{}_4{}^{16}O_2{}^{18}O_2(O_2P(C_6H_4OCH_3)_2)_6]^+$, 15% $[Mn^{III}Mn^{IV}{}_4{}^{16}O^{18}O_3(O_2P(C_6H_4OCH_3)_2)_6]^+$, and 5% $[Mn^{III}Mn^{IV}{}_4{}^{18}O_4(O_2P(C_6H_4OCH_3)_2)_6]^+$.

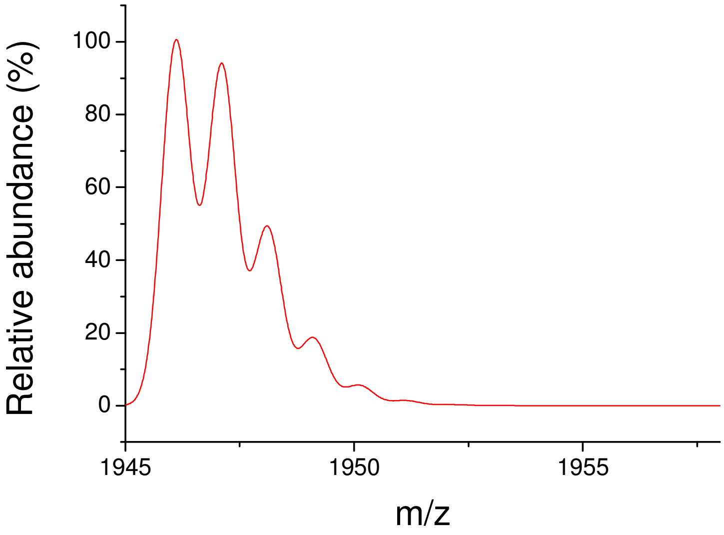

Fig. S.1.1 Isotopic pattern of unenriched $[Mn^{III}Mn^{IV}{}_4O_4(O_2P(C_6H_4OCH_3)_2)_6]^+$.

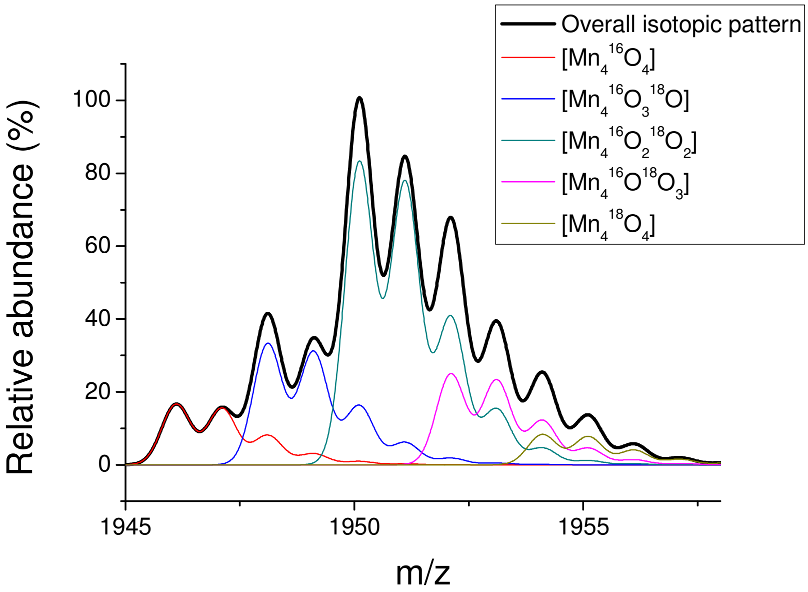

Fig. S.1.2 Isotopic pattern (black) of a system comprising 10% unenriched, 20% singly-, 50% doubly-, 15% triply- and 5% quadruply enriched $[Mn^{III}Mn^{IV}{}_4O_4(O_2P(C_6H_4OCH_3)_2)_6]^+$. The coloured traces show the contribution of each species.

S.2 Evaluation of kinetic data

Rate equations S.2.1-S.2.4 (see sections S.5 and S.6 for derivation) were used to estimate the rate constants k_A, $k_{A'}$,k_B, $k_{B'}$, k_C, $k_{C'}$ and k_D. Since water was present in large excess relative to the manganese cubane, the concentration of water was assumed to be constant and was ignored. While *e.g.* k_A and $k_{A'}$ would be expected to be identical (see equations S.6.13-S.6.17), they were fitted separately in order to avoid propagation of errors.

$$\frac{d[O_4]}{dt} = -4k_A[O_4] \qquad \text{S.2.1}$$

$$\frac{d[O_3O^*]}{dt} = 4k_{A'}[O_4] - 3k_B[O_3O^*] \qquad \text{S.2.2}$$

$$\frac{d[O_2O_2^*]}{dt} = 3k_{B'}[O_3O^*] - 2k_C[O_2O_2^*] \qquad \text{S.2.3}$$

$$\frac{d[O\ O_3^*]}{dt} = 2k_{C'}[O_2O_2^*] - k_D[O\ O_3^*] \qquad \text{S.2.4}$$

$$\frac{d[O_4^*]}{dt} = k_D[O\ O_3^*] \qquad \text{S.2.5}$$

Table S.2.1 Rate constants obtained using equation S.2.1

Entry	**T (°C)**	**C_M (10^{-3} M)**	**C_{H2O} (M)**	**k_A (s^{-1})**
1	30.0	0.250	0.250	$1.07\cdot10^{-5}\pm2.91\cdot10^{-7}$
2	40.0	0.250	0.250	$1.88\cdot10^{-5}\pm5.38\cdot10^{-7}$
3	50.1	0.250	0.250	$5.60\cdot10^{-5}\pm1.62\cdot10^{-6}$
4[a]	50.1	0.250	0.250	$6.35\cdot10^{-6}\pm1.25\cdot10^{-7}$
5[b]	50.1	0.250	0.250	$7.02\cdot10^{-6}\pm1.04\cdot10^{-7}$
6[c]	50.1	0.250	0.250	$5.38\cdot10^{-5}\pm9.60\cdot10^{-7}$
7	50.1	0.250	0.125	$2.23\cdot10^{-5}\pm2.65\cdot10^{-7}$
8	50.1	0.250	0.375	$3.92\cdot10^{-5}\pm1.06\cdot10^{-6}$
9	50.1	0.250	0.500	$3.68\cdot10^{-5}\pm7.95\cdot10^{-7}$
10	50.1	0.163	0.250	$3.10\cdot10^{-5}\pm7.97\cdot10^{-7}$
11	50.1	0.500	0.250	$7.44\cdot10^{-5}\pm2.79\cdot10^{-6}$
12	59.8	0.250	0.250	$9.65\cdot10^{-5}\pm3.61\cdot10^{-6}$

[a] $[HClO_4]=2.5\cdot10^{-3}$ M. [b] $[C_7H_7SO_3H]=2.5\cdot10^{-3}$ M. [c] $[HNO_3]=2.5\cdot10^{-3}$ M. M stands for mol·dm^{-3}.

Table S.2.2 Rate constants obtained using equation S.2.2

Entry	**T (°C)**	**C_M (10^{-3} M)**	**C_{H2O} (M)**	**$k_{A'}$ (s^{-1})**	**k_B (s^{-1})**
1	30.0	0.250	0.250	$5.95\cdot10^{-6}\pm6.16\cdot10^{-7}$	$1.33\cdot10^{-5}\pm2.36\cdot10^{-6}$
2	40.0	0.250	0.250	$1.33\cdot10^{-5}\pm9.03\cdot10^{-7}$	$2.15\cdot10^{-5}\pm2.23\cdot10^{-6}$
3	50.1	0.250	0.250	$3.88\cdot10^{-5}\pm3.17\cdot10^{-6}$	$6.30\cdot10^{-5}\pm7.25\cdot10^{-6}$

4[a]	50.1	0.250	0.250	$3.39\cdot10^{-6}\pm3.17\cdot10^{-7}$	$6.40\cdot10^{-6}\pm1.57\cdot10^{-6}$
5[b]	50.1	0.250	0.250	$3.49\cdot10^{-6}\pm2.15\cdot10^{-7}$	$2.88\cdot10^{-6}\pm1.01\cdot10^{-6}$
6[c]	50.1	0.250	0.250	$4.30\cdot10^{-5}\pm1.51\cdot10^{-6}$	$4.94\cdot10^{-5}\pm2.82\cdot10^{-6}$
7	50.1	0.250	0.125	$1.40\cdot10^{-5}\pm5.13\cdot10^{-7}$	$1.72\cdot10^{-5}\pm1.96\cdot10^{-6}$
8	50.1	0.250	0.375	$2.81\cdot10^{-5}\pm1.86\cdot10^{-6}$	$4.56\cdot10^{-5}\pm4.79\cdot10^{-6}$
9	50.1	0.250	0.500	$2.76\cdot10^{-5}\pm1.55\cdot10^{-6}$	$4.19\cdot10^{-5}\pm3.88\cdot10^{-6}$
10	50.1	0.163	0.250	$2.31\cdot10^{-5}\pm1.57\cdot10^{-6}$	$3.81\cdot10^{-5}\pm4.21\cdot10^{-6}$
11	50.1	0.500	0.250	$5.12\cdot10^{-5}\pm5.09\cdot10^{-6}$	$8.58\cdot10^{-5}\pm1.16\cdot10^{-5}$
12	59.8	0.250	0.250	$6.45\cdot10^{-5}\pm7.13\cdot10^{-6}$	$1.19\cdot10^{-4}\pm1.73\cdot10^{-5}$

[a][$HClO_4$]=$2.5\cdot10^{-3}$ M. [b][$C_7H_7SO_3H$]=$2.5\cdot10^{-3}$ M. [C][HNO_3]=$2.5\cdot10^{-3}$ M. M stands for mol·dm^{-3}.

Table S.2.3 Rate constants obtained using equation S.2.3

Entry	**T (˚C)**	**C_M (10^{-3} M)**	**C_{H2O} (M)**	**$k_{B'}$ (s^{-1})**	**k_C (s^{-1})**
1	30.0	0.250	0.250	$2.10\cdot10^{-5}\pm4.75\cdot10^{-6}$	$2.65\cdot10^{-5}\pm9.31\cdot10^{-6}$
2	40.0	0.250	0.250	$2.03\cdot10^{-5}\pm2.32\cdot10^{-6}$	$1.67\cdot10^{-5}\pm3.67\cdot10^{-6}$
3	50.1	0.250	0.250	$5.14\cdot10^{-5}\pm5.61\cdot10^{-6}$	$3.58\cdot10^{-5}\pm9.92\cdot10^{-6}$
4[a]	50.1	0.250	0.250	$2.83\cdot10^{-5}\pm6.70\cdot10^{-6}$	$3.47\cdot10^{-5}\pm1.16\cdot10^{-5}$
5[b]	50.1	0.250	0.250	$3.00\cdot10^{-5}\pm5.17\cdot10^{-6}$	$4.43\cdot10^{-5}\pm1.04\cdot10^{-5}$
6[c]	50.1	0.250	0.250	$6.11\cdot10^{-5}\pm3.53\cdot10^{-6}$	$5.63\cdot10^{-5}\pm5.78\cdot10^{-6}$
7	50.1	0.250	0.125	$5.70\cdot10^{-5}\pm5.96\cdot10^{-6}$	$8.11\cdot10^{-5}\pm1.40\cdot10^{-5}$
8	50.1	0.250	0.375	$5.45\cdot10^{-5}\pm7.07\cdot10^{-6}$	$6.39\cdot10^{-5}\pm1.26\cdot10^{-5}$
9	50.1	0.250	0.500	$4.71\cdot10^{-5}\pm5.\ 57\cdot10^{-6}$	$5.80\cdot10^{-5}\pm1.27\cdot10^{-5}$
10	50.1	0.163	0.250	$3.60\cdot10^{-5}\pm4.14\cdot10^{-6}$	$3.18\cdot10^{-5}\pm7.71\cdot10^{-6}$
11	50.1	0.500	0.250	$6.61\cdot10^{-5}\pm9.31\cdot10^{-6}$	$5.34\cdot10^{-5}\pm1.50\cdot10^{-5}$
12	59.8	0.250	0.250	$9.42\cdot10^{-5}\pm1.49\cdot10^{-5}$	$6.64\cdot10^{-5}\pm2.45\cdot10^{-5}$

[a][$HClO_4$]=$2.5\cdot10^{-3}$ M. [b][$C_7H_7SO_3H$]=$2.5\cdot10^{-3}$ M. [C][HNO_3]=$2.5\cdot10^{-3}$ M. M stands for mol·dm^{-3}.

Table S.2.4 Rate constants obtained using equation S.2.4

Entry	**T (˚C)**	**C_M (10^{-3} M)**	**C_{H2O} (M)**	**$k_{C'}$ (s^{-1})**	**k_D (s^{-1})**
1	30.0	0.250	0.250	$3.28\cdot10^{-3}\pm3.55\cdot10^{-2}$	$5.84\cdot10^{-3}\pm6.35\cdot10^{-2}$
2	40.0	0.250	0.250	$1.16\cdot10^{-4}\pm3.36\cdot10^{-5}$	$1.83\cdot10^{-4}\pm5.88\cdot10^{-5}$
3	50.1	0.250	0.250	$1.46\cdot10^{-2}\pm1.69\cdot10^{-1}$	$2.73\cdot10^{-2}\pm3.19\cdot10^{-1}$
4[a]	50.1	0.250	0.250	$1.00\cdot10^{-4}\pm8.81\cdot10^{-5}$	$2.71\cdot10^{-4}\pm2.61\cdot10^{-4}$
5[b]	50.1	0.250	0.250	$8.94\cdot10^{-3}\pm1.29\cdot10^{-1}$	$2.69\cdot10^{-2}\pm3.89\cdot10^{-1}$
6[c]	50.1	0.250	0.250	$1.24\cdot10^{-4}\pm1.37\cdot10^{-5}$	$2.28\cdot10^{-4}\pm3.48\cdot10^{-5}$
7	50.1	0.250	0.125	$4.56\cdot10^{-4}\pm3.51\cdot10^{-4}$	$1.40\cdot10^{-3}\pm1.14\cdot10^{-3}$
8	50.1	0.250	0.375	$1.43\cdot10^{-4}\pm2.95\cdot10^{-5}$	$2.07\cdot10^{-4}\pm5.57\cdot10^{-5}$
9	50.1	0.250	0.500	$2.04\cdot10^{-4}\pm6.33\cdot10^{-5}$	$4.24\cdot10^{-4}\pm1.16\cdot10^{-4}$
10	50.1	0.163	0.250	$1.84\cdot10^{-4}\pm5.21\cdot10^{-5}$	$3.14\cdot10^{-4}\pm1.05\cdot10^{-4}$
11	50.1	0.500	0.250	$1.14\cdot10^{-1}\pm2.80$	$1.93\cdot10^{-1}\pm4.74$
12	59.8	0.250	0.250	$2.26\cdot10^{-3}\pm2.79\cdot10^{-3}$	$3.70\cdot10^{-3}\pm4.68\cdot10^{-3}$

[a][$HClO_4$]=$2.5\cdot10^{-3}$ M. [b][$C_7H_7SO_3H$]=$2.5\cdot10^{-3}$ M. [C][HNO_3]=$2.5\cdot10^{-3}$ M. M stands for mol·dm^{-3}.

Table S.2.5 Rate constants obtained using equation S.2.5

Entry	**T (°C)**	**C_M (10^{-3} M)**	**C_{H2O} (M)**	**$k_{D'}$ (s^{-1})**
1	30.0	0.250	0.250	$4.51\cdot10^{-5}\pm3.51\cdot10^{-6}$
2	40.0	0.250	0.250	$2.90\cdot10^{-5}\pm1.91\cdot10^{-6}$
3	50.1	0.250	0.250	$1.10\cdot10^{-4}\pm7.37\cdot10^{-6}$
4[a]	50.1	0.250	0.250	$2.37\cdot10^{-5}\pm3.22\cdot10^{-6}$
5[b]	50.1	0.250	0.250	$1.80\cdot10^{-5}\pm2.31\cdot10^{-6}$
6[c]	50.1	0.250	0.250	$4.98\cdot10^{-5}\pm3.26\cdot10^{-6}$
7	50.1	0.250	0.125	$5.41\cdot10^{-5}\pm6.02\cdot10^{-6}$
8	50.1	0.250	0.375	$9.47\cdot10^{-5}\pm6.04\cdot10^{-6}$
9	50.1	0.250	0.500	$1.37\cdot10^{-4}\pm9.01\cdot10^{-6}$
10	50.1	0.163	0.250	$6.15\cdot10^{-5}\pm4.65\cdot10^{-6}$
11	50.1	0.500	0.250	$1.55\cdot10^{-4}\pm1.02\cdot10^{-5}$
12	59.8	0.250	0.250	$2.04\cdot10^{-4}\pm1.51\cdot10^{-5}$

[a] $[HClO_4]=2.5\cdot10^{-3}$ M. [b] $[C_7H_7SO_3H]=2.5\cdot10^{-3}$ M. [c] $[HNO_3]=2.5\cdot10^{-3}$ $mol\cdot dm^{-3}$. M stands for $mol\cdot dm^{-3}$.

S.3 Determination of activation enthalpy and entropy

Activation enthalpies and entropies were determined using the Eyring-Polanyi equation (Eq. 3).

$$k = (\frac{k_B T}{h}) e^{(\frac{\Delta S^\ddagger}{R})} e^{(-\frac{\Delta H^\ddagger}{RT})} \qquad \text{(S.3.1)}$$

where k is the rate constant at a given temperature, k_B is Boltzmann's constant, h is Planck's constant and R is the gas constant. T, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are the temperature, activation enthalpy and activation entropy, respectively.

Table S.3.2 Activation enthalpy and entropy calculated using equation S.3.1 with data from Entry 3 in tables S.2.1-S.2.5 and correcting the rate constants for $H_2{}^{18}O$ concentration.

	$\Delta S^\ddagger$ ($J\cdot K^{-1}\cdot mol^{-1}$)	**$\Delta H^\ddagger$ ($kJ\cdot mol^{-1}$)**
k_A	-135±22	59±7
$k_{A'}$	-141±25	58±8
k_B	-121±17	63±6
$k_{B'}$	-153±26	53±9
k_C	-197±46	39±15
k_D	-146±42	59±14

S.4 Kinetic traces as a function of different parameters

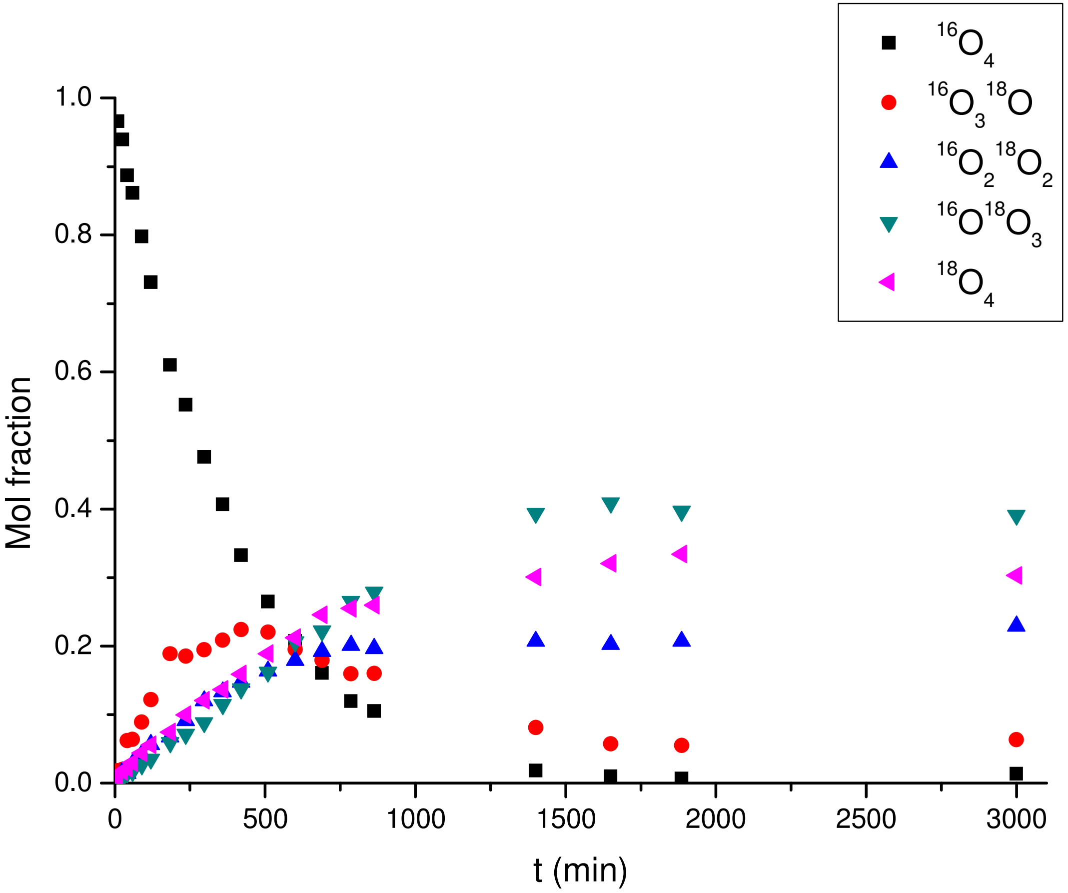

Fig. S. 4.1 $[Mn_4O_4(O_2P\{C_7H_7O\}_2)_6][ClO_4]$ (0.25 mM) and $H_2{}^{18}O$ (0.25 M) at 30.0 ˚C.

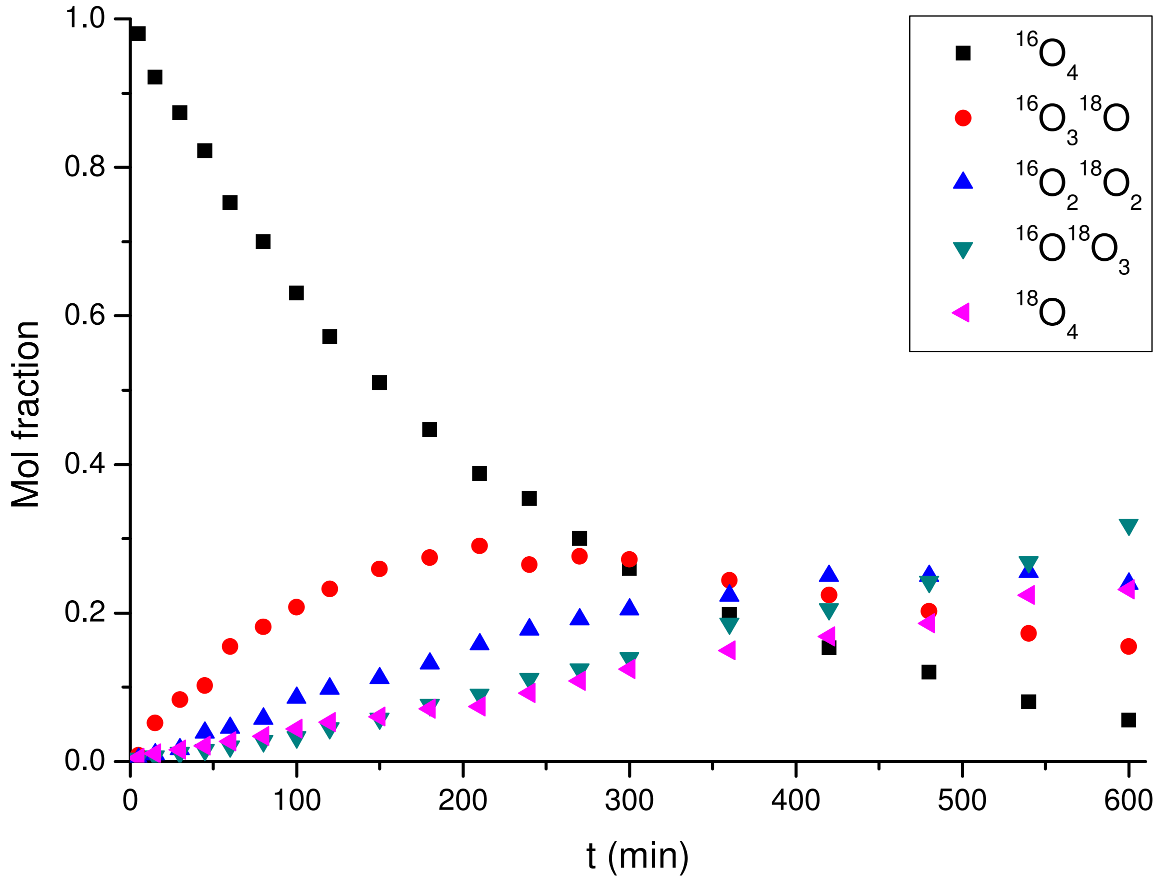

Fig. S. 4.2 $[Mn_4O_4(O_2P\{C_7H_7O\}_2)_6][ClO_4]$ (0.25 mM) and $H_2{}^{18}O$ (0.25 M) at 40.0 ˚C.

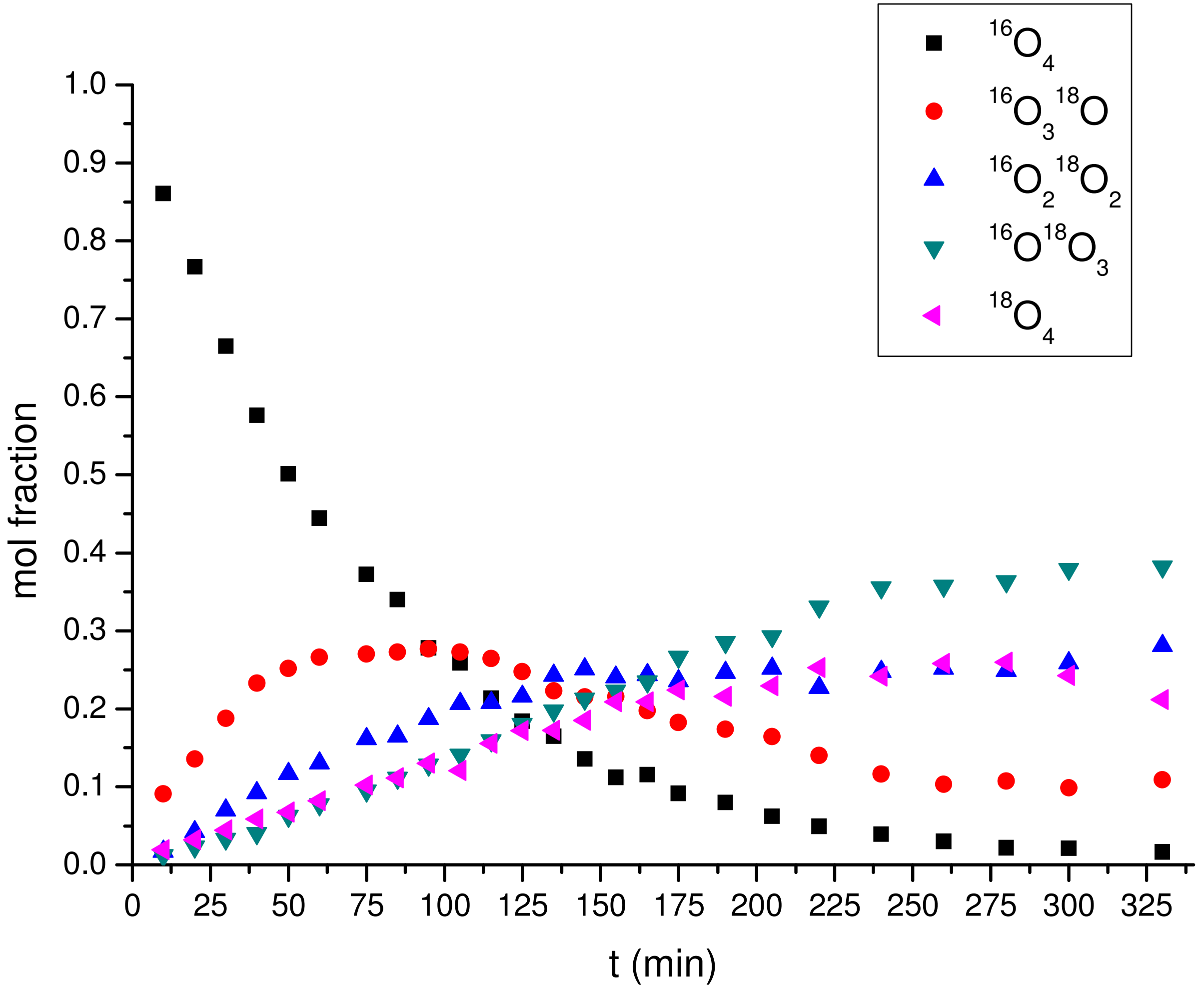

Fig. S. 4.3 $[Mn_4O_4(O_2P\{C_7H_7O\}_2)_6][ClO_4]$ (0.25 mM) and $H_2{}^{18}O$ (0.25 M) at 50.1 ˚C.

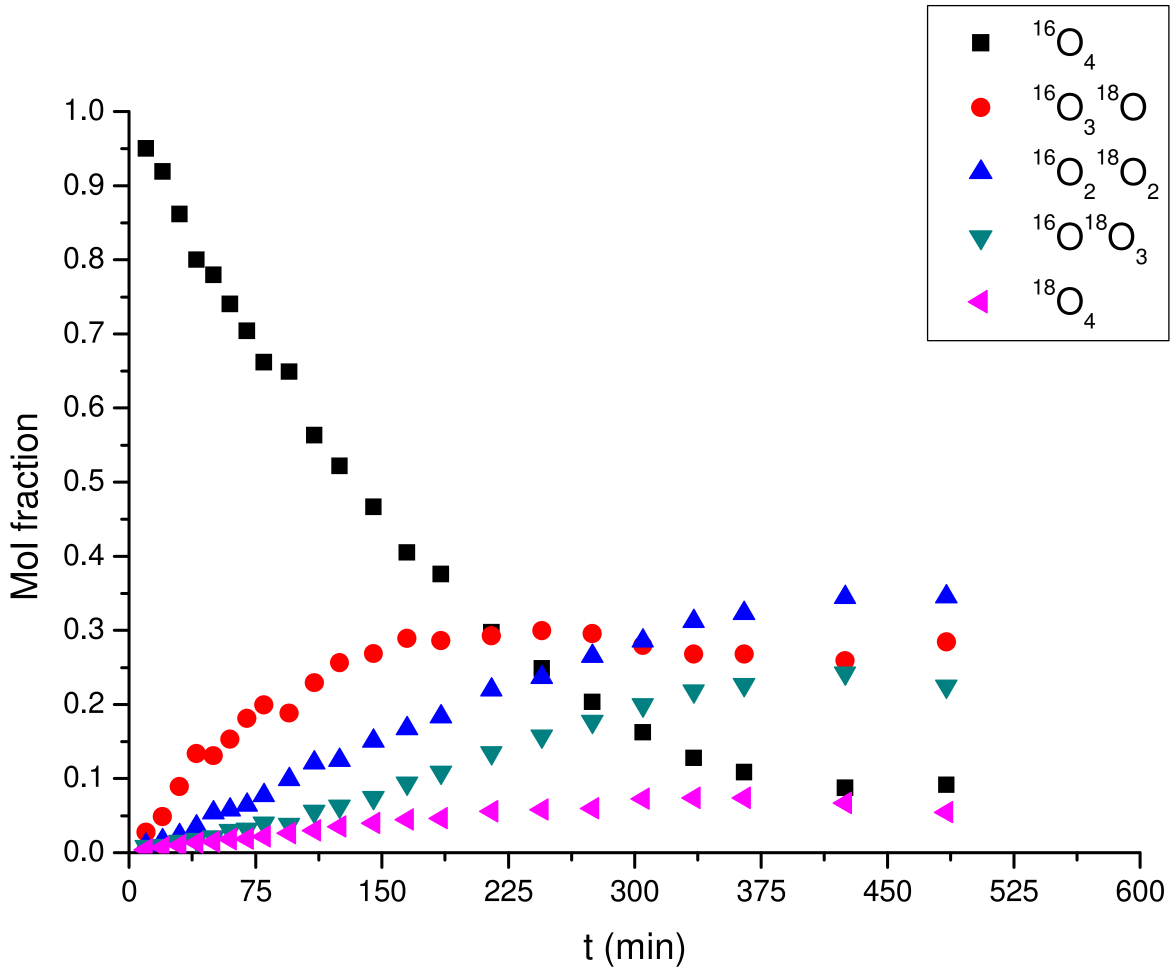

Fig. S. 4.4 $[Mn_4O_4(O_2P\{C_7H_7O\}_2)_6][ClO_4]$ (0.25 mM) and $H_2{}^{18}O$ (0.125 M) at 50.1 ˚C.

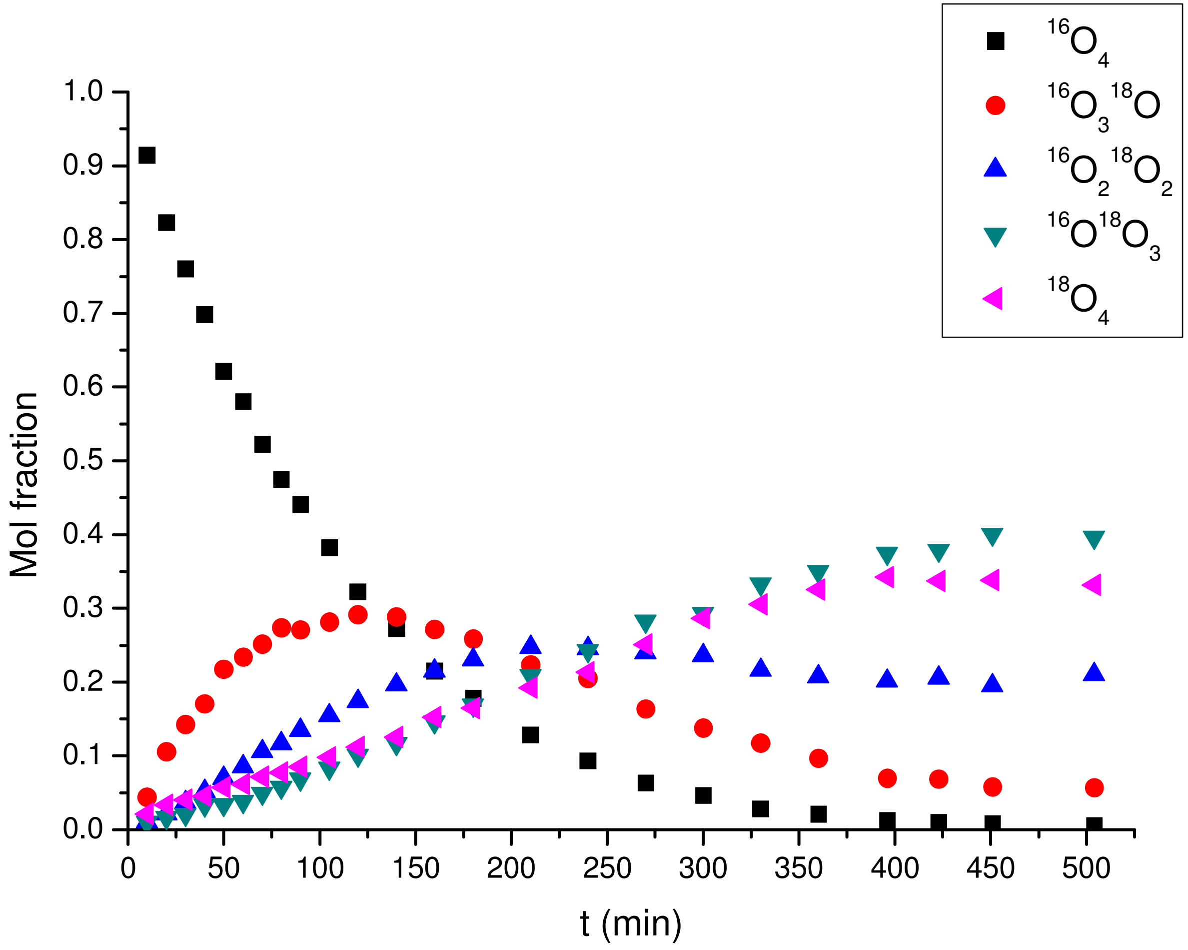

Fig. S. 4.5 $[Mn_4O_4(O_2P\{C_7H_7O\}_2)_6][ClO_4]$ (0.25 mM) and $H_2{}^{18}O$ (0.375 M) at 50.1 ˚C.

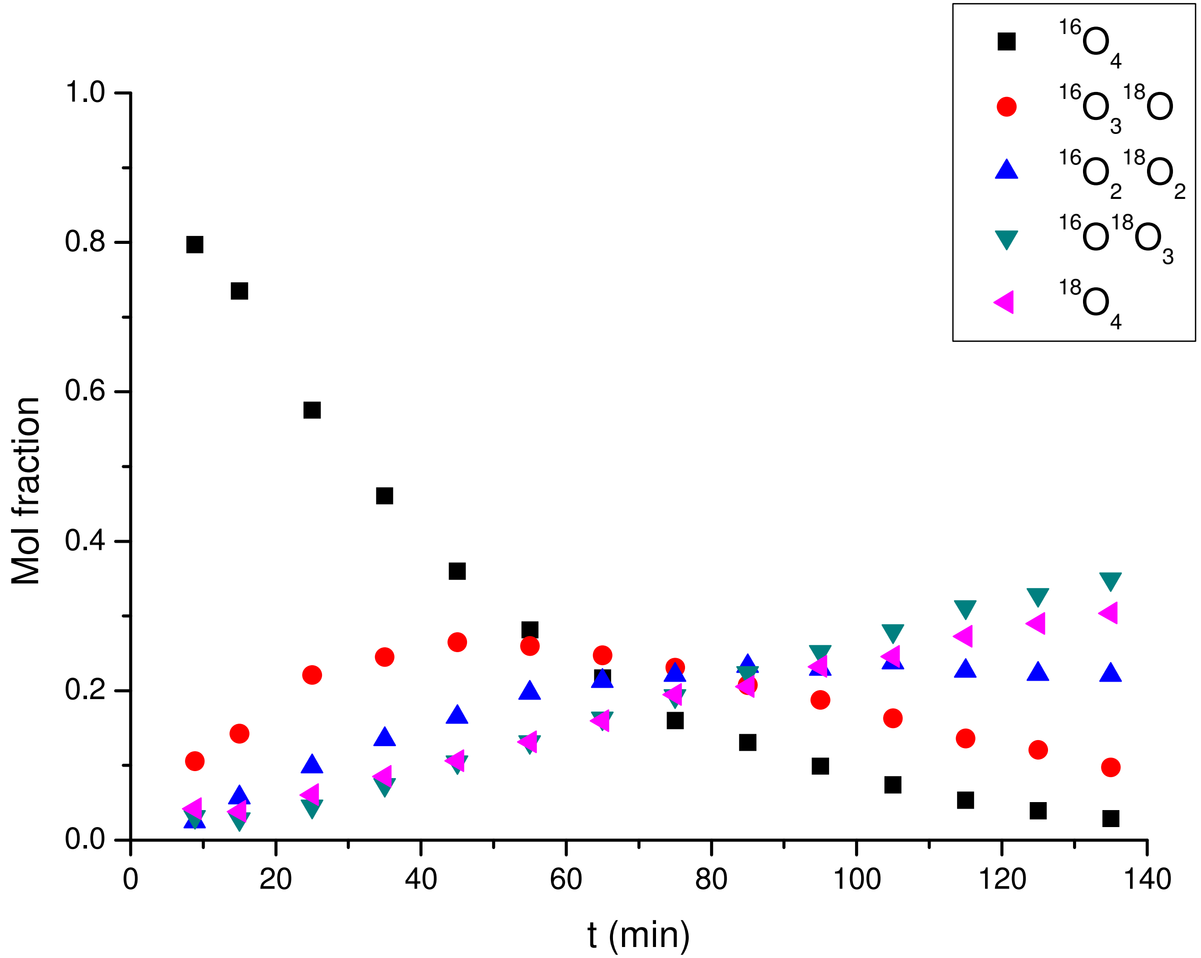

Fig. S. 4.6 $[Mn_4O_4(O_2P\{C_7H_7O\}_2)_6][ClO_4]$ (0.25 mM) and $H_2{}^{18}O$ (0.250 M) at 59.8 ˚C.

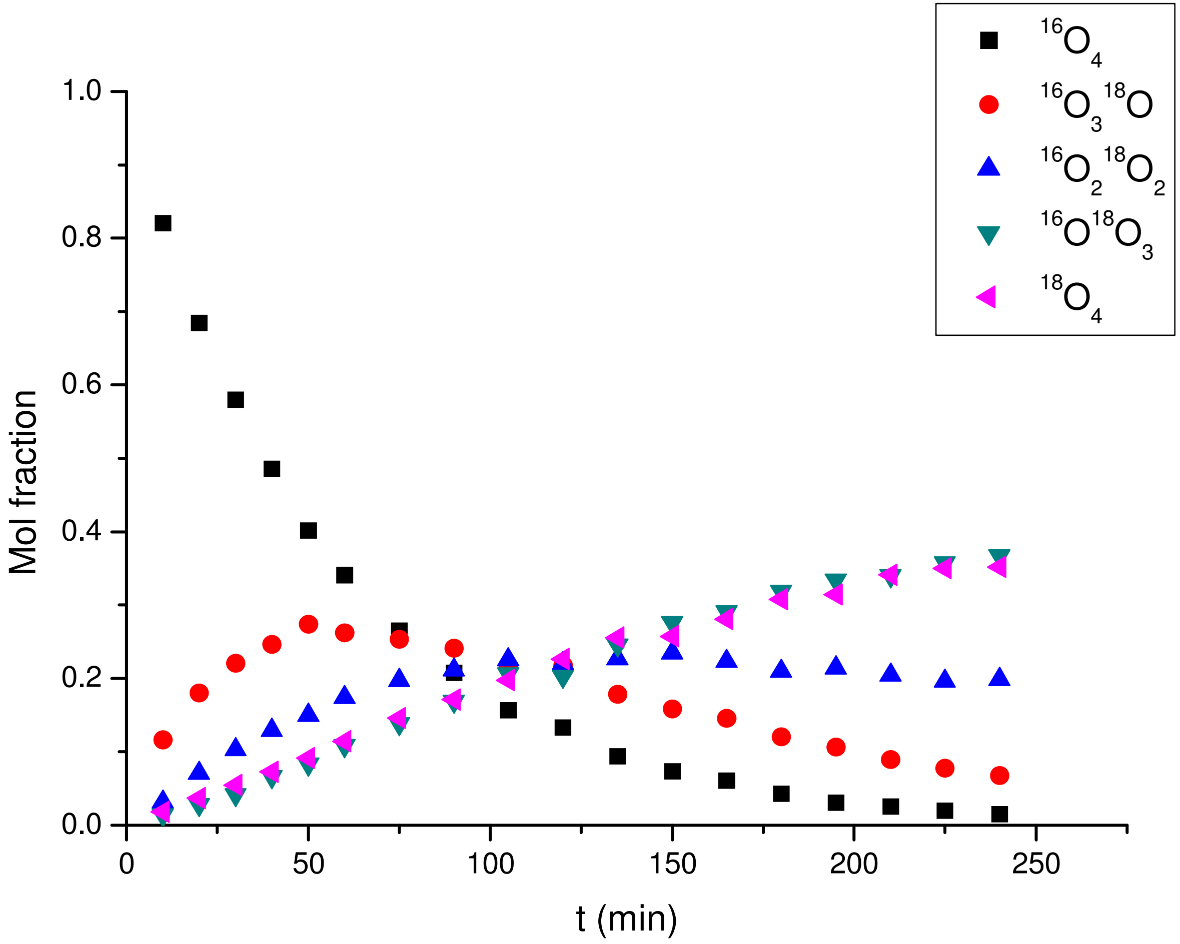

Fig. S. 4.7 $[Mn_4O_4(O_2P\{C_7H_7O\}_2)_6][ClO_4]$ (0.50 mM) and $H_2{}^{18}O$ (0.250 M) at 50.1 ˚C.

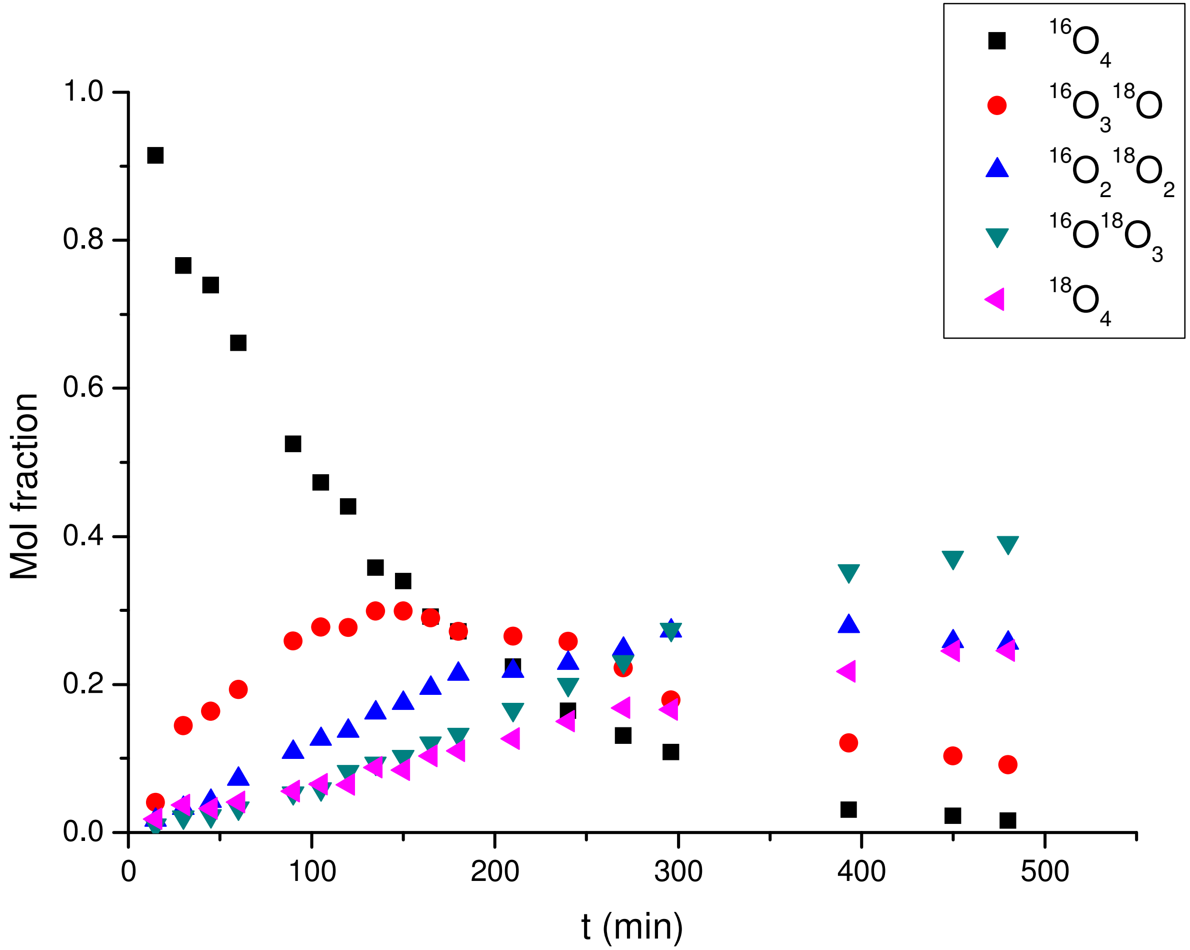

Fig. S. 4.8 $[Mn_4O_4(O_2P\{C_7H_7O\}_2)_6][ClO_4]$ (0.25 mM) and $H_2{}^{18}O$ (0.50 M) at 50.1 ˚C.

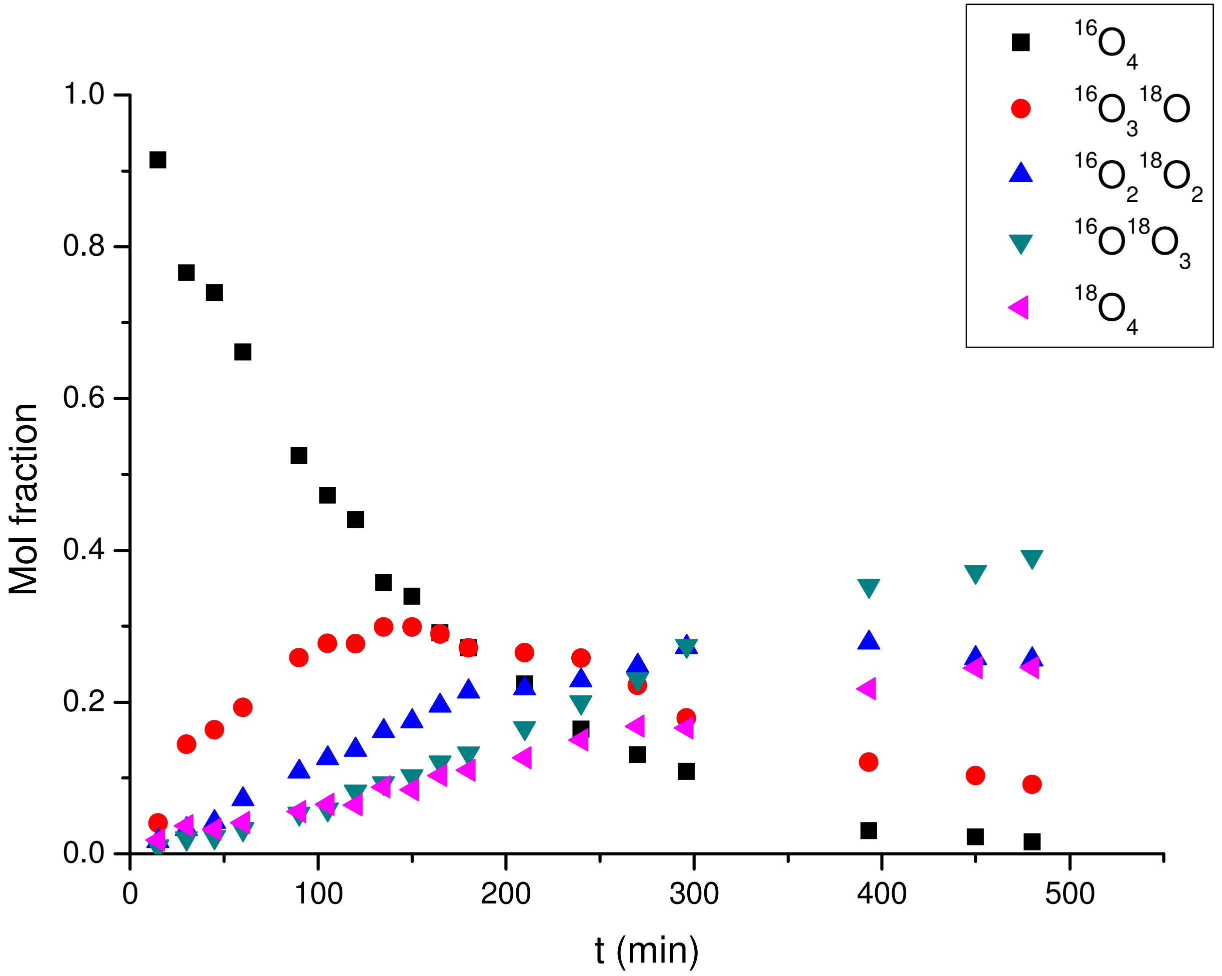

Fig. S. 4.9 $[Mn_4O_4(O_2P\{C_7H_7O\}_2)_6][ClO_4]$ (0.163 mM) and $H_2{}^{18}O$ (0.25 M) at 50.1 ˚C.

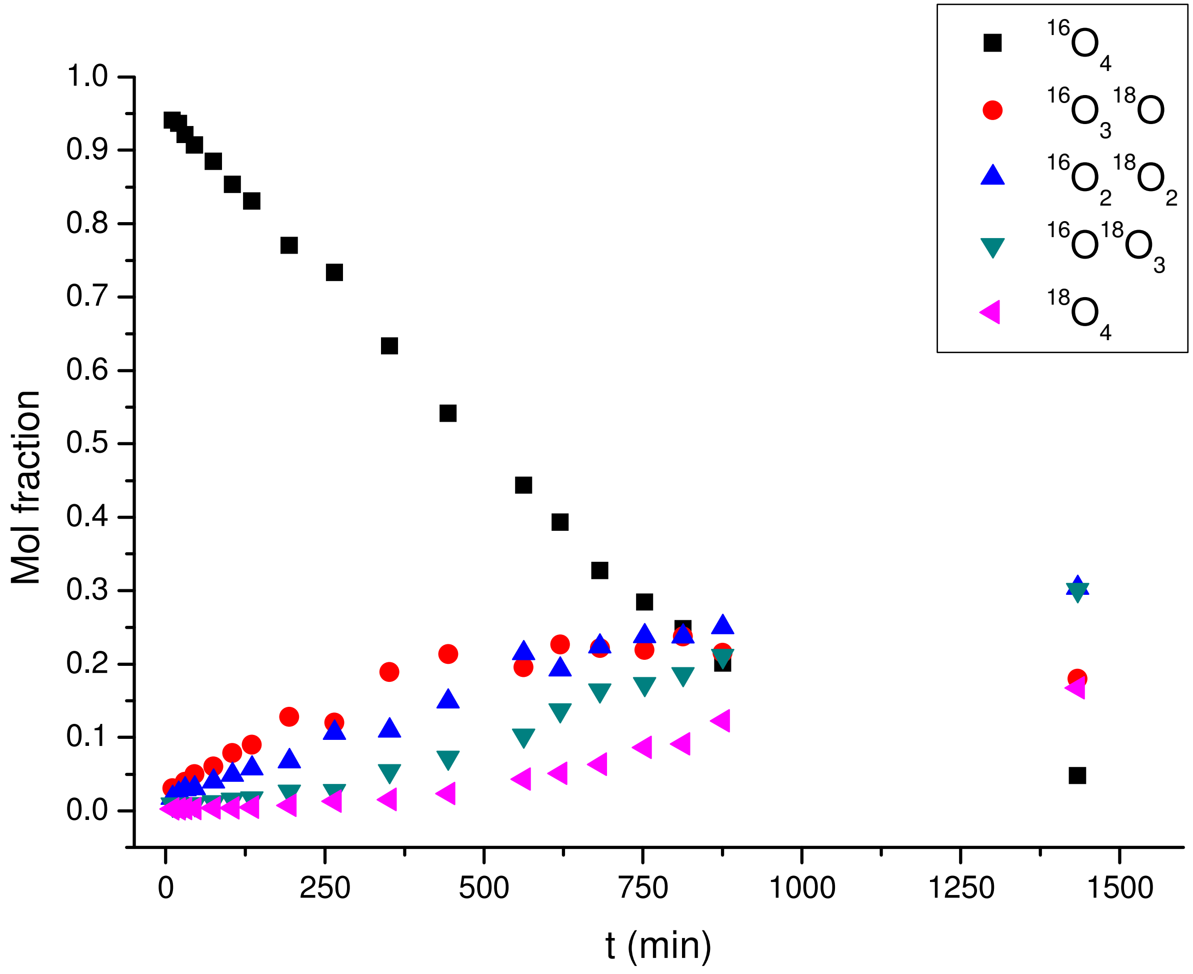

Fig. S. 4.10 $[Mn_4O_4(O_2P\{C_7H_7O\}_2)_6][ClO_4]$ (0.25 mM) and $H_2{}^{18}O$ (0.25 M) in the presence of $HClO_4$ (2.5 mM) at 50.1 ˚C.

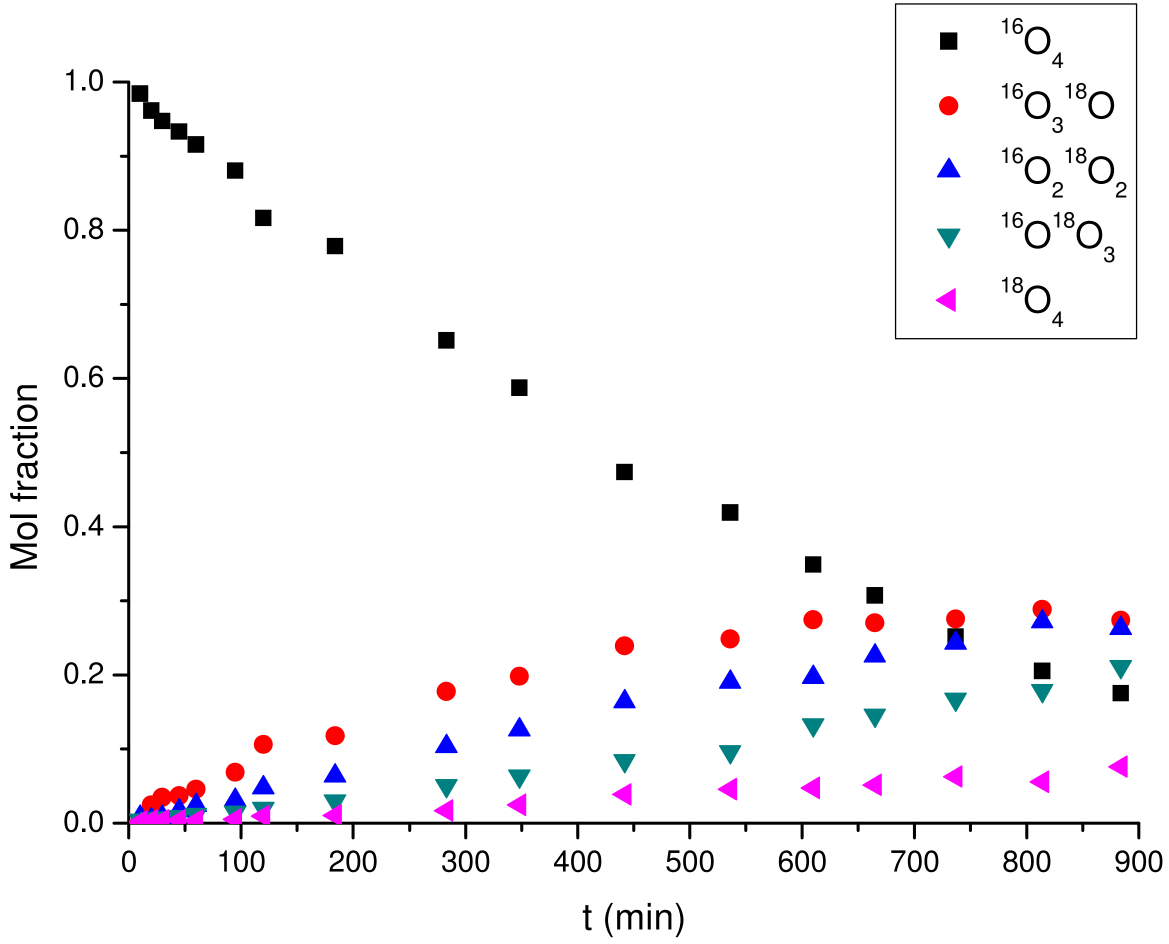

Fig. S. 4.11 $[Mn_4O_4(O_2P\{C_7H_7O\}_2)_6][ClO_4]$ (0.25 mM) and $H_2{}^{18}O$ (0.25 M) in the presence of toluenesulfonic acid (2.5 mM) at 50.1 ˚C.

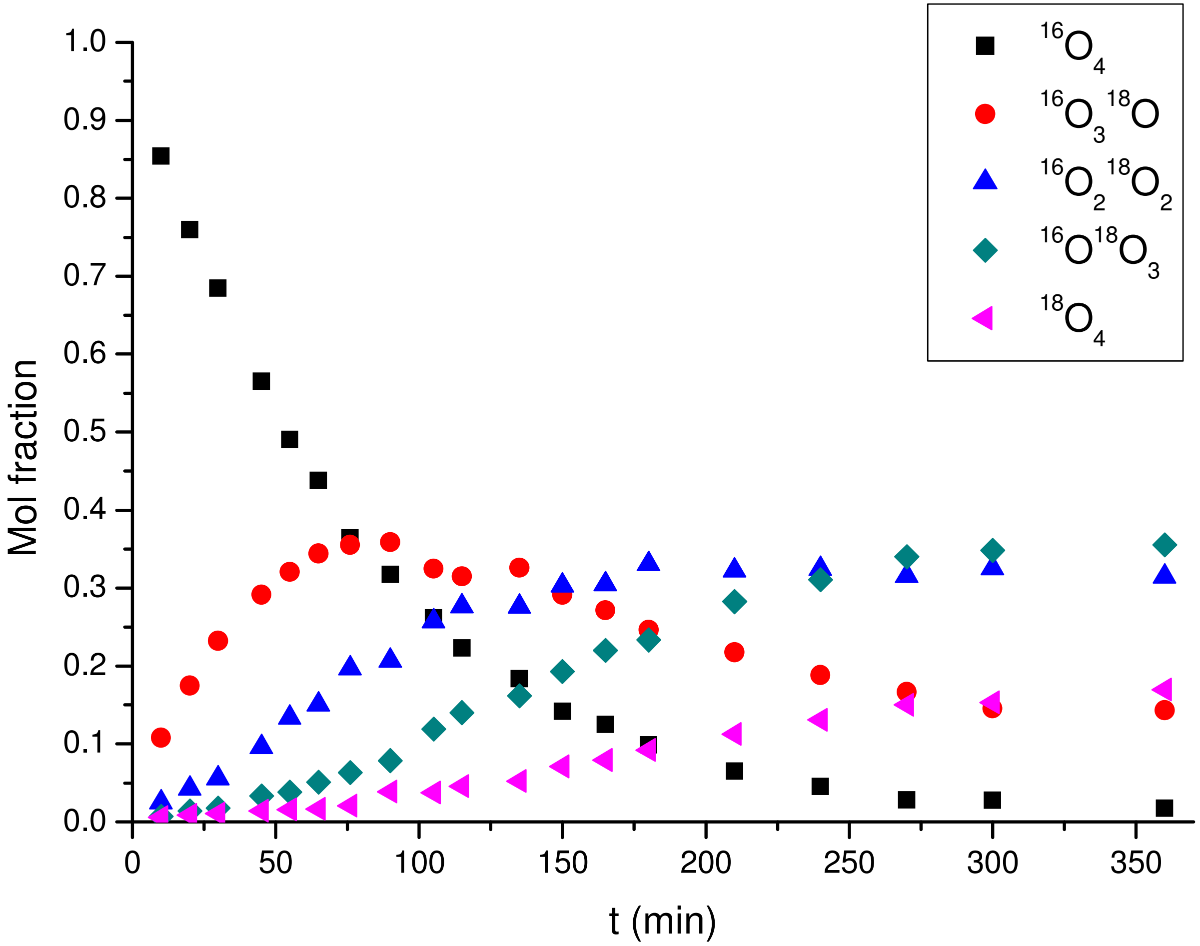

Fig. S. 4.12 $[Mn_4O_4(O_2P\{C_7H_7O\}_2)_6][ClO_4]$ (0.25 mM) and $H_2{}^{18}O$ (0.25 M) in the presence of HNO_3 (2.5 mM) at 50.1 ˚C.

S5. Kinetic model for isotopic exchange in a system with four distinct oxygen sites O_A, O_B, O_C and O_D.

A general system with four unique oxygen sites (O_A, O_B, O_C and O_D) in a compound $O_AO_BO_CO_D$, in which

- each oxygen is associated with a specific rate constant (k_A, k_B, k_C and k_D)
- O^* denotes an isoptopically labelled oxygen
- O_4, O_3O^*, $O_2O^*_2$, OO^*_3 and O^*_4 describes a system in which no oxygens have exchanged, one oxygen has exchanged, two oxygens have exchanged and four oxygens have exchanged, respectively

can be described by equations S.5.1-S.5.21

$$\frac{d[O_4]}{dt}=\frac{d[O_AO_BO_CO_D]}{dt} \qquad (S.5.1)$$

$$\begin{aligned}\frac{d[O_AO_BO_CO_D]}{dt}=&(k_A[O_A^*O_BO_CO_D]+k_B[O_AO_B^*O_CO_D]+k_C[O_AO_BO_C^*O_D]+k_D[O_AO_BO_CO_D^*])[H_2O]\\&-(k_A+k_B+k_C+k_D)[O_AO_BO_CO_D][H_2O^*]\end{aligned} \qquad (S.5.2)$$

$$\frac{d[O_3O^*]}{dt}=\frac{d[O_A^*O_BO_CO_D]}{dt}+\frac{d[O_AO_B^*O_CO_D]}{dt}+\frac{d[O_AO_BO_C^*O_D]}{dt}+\frac{d[O_AO_BO_CO_D^*]}{dt} \qquad (S.5.3)$$

$$\begin{aligned}\frac{d[O_A^*O_BO_CO_D]}{dt}=&(k_A[O_AO_BO_CO_D]-(k_B+k_C+k_D)[O_A^*O_BO_CO_D])[H_2O^*]\\&+(k_B[O_A^*O_B^*O_CO_D]+k_C[O_A^*O_BO_C^*O_D]+k_D[O_A^*O_BO_CO_D^*]-k_A[O_A^*O_BO_CO_D])[H_2O]\end{aligned} \qquad (S.5.4)$$

$$\begin{aligned}\frac{d[O_AO_B^*O_CO_D]}{dt}=&(k_B[O_AO_BO_CO_D]-(k_A+k_C+k_D)[O_AO_B^*O_CO_D])[H_2O^*]\\&+(k_A[O_A^*O_B^*O_CO_D]+k_C[O_AO_B^*O_C^*O_D]+k_D[O_AO_B^*O_CO_D^*]-k_B[O_AO_B^*O_CO_D])[H_2O]\end{aligned} \qquad (S.5.5)$$

$$\begin{aligned}\frac{d[O_AO_BO_C^*O_D]}{dt}=&(k_C[O_AO_BO_CO_D]-(k_A+k_B+k_D)[O_AO_BO_C^*O_D])[H_2O^*]\\&+(k_A[O_A^*O_BO_C^*O_D]+k_B[O_AO_B^*O_C^*O_D]+k_D[O_AO_BO_C^*O_D^*]-k_C[O_AO_BO_C^*O_D][H_2O]\end{aligned} \qquad (S.5.6)$$

$$\begin{aligned}\frac{d[O_AO_BO_CO_D^*]}{dt}=&(k_D[O_AO_BO_CO_D]-(k_A+k_B+k_C)[O_AO_BO_CO_D^*])[H_2O^*]\\&+(k_A[O_A^*O_BO_CO_D^*]+k_B[O_AO_B^*O_CO_D^*]+k_C[O_AO_BO_C^*O_D^*]-k_D[O_AO_BO_CO_D^*])[H_2O]\end{aligned} \qquad (S.5.7)$$

$$\begin{aligned}\frac{d[O_2O_2^*]}{dt} = {} & \frac{d[O_A^*O_B^*O_CO_D]}{dt}+\frac{d[O_A^*O_BO_C^*O_D]}{dt}+\frac{d[O_A^*O_BO_CO_D^*]}{dt}+\frac{d[O_AO_B^*O_C^*O_D]}{dt}\\ & +\frac{d[O_AO_B^*O_CO_D^*]}{dt}+\frac{d[O_AO_BO_C^*O_D^*]}{dt}\end{aligned} \tag{S.5.8}$$

$$\begin{aligned}\frac{d[O_A^*O_B^*O_CO_D]}{dt} = {} & ((k_A[O_AO_B^*O_CO_D]+k_B[O_A^*O_BO_CO_D])-(k_C+k_D)[O_A^*O_B^*O_CO_D])[H_2O^*]\\ & +(k_C[O_A^*O_B^*O_C^*O_D]+k_D[O_A^*O_B^*O_CO_D^*]-(k_A+k_B)[O_A^*O_B^*O_CO_D])[H_2O]\end{aligned} \tag{S.5.9}$$

$$\begin{aligned}\frac{d[O_A^*O_BO_C^*O_D]}{dt} = {} & ((k_A[O_AO_BO_C^*O_D]+k_C[O_A^*O_BO_CO_D])-(k_B+k_D)[O_A^*O_BO_C^*O_D])[H_2O^*]\\ & +(k_B[O_A^*O_B^*O_C^*O_D]+k_D[O_A^*O_BO_C^*O_D^*]-(k_A+k_C)[O_A^*O_BO_C^*O_D])[H_2O]\end{aligned} \tag{S.5.10}$$

$$\begin{aligned}\frac{d[O_A^*O_BO_CO_D^*]}{dt} = {} & ((k_A[O_AO_BO_CO_D^*]+k_D[O_A^*O_BO_CO_D])-(k_B+k_C)[O_A^*O_BO_CO_D^*])[H_2O^*]\\ & +(k_B[O_A^*O_B^*O_CO_D^*]+k_C[O_A^*O_BO_C^*O_D^*]-(k_A+k_D)[O_A^*O_BO_CO_D^*])[H_2O]\end{aligned} \tag{S.5.11}$$

$$\begin{aligned}\frac{d[O_AO_B^*O_C^*O_D]}{dt} = {} & ((k_B[O_AO_BO_C^*O_D]+k_C[O_AO_B^*O_CO_D])-(k_A+k_D)[O_AO_B^*O_C^*O_D])[H_2O^*]\\ & +(k_A[O_A^*O_B^*O_C^*O_D]+k_D[O_AO_B^*O_C^*O_D^*]-(k_B+k_C)[O_AO_B^*O_C^*O_D])[H_2O]\end{aligned} \tag{S.5.12}$$

$$\begin{aligned}\frac{d[O_AO_B^*O_CO_D^*]}{dt} = {} & ((k_B[O_AO_BO_CO_D^*]+k_D[O_AO_B^*O_CO_D])-(k_A+k_C)[O_AO_B^*O_CO_D^*])[H_2O^*]\\ & +(k_A[O_A^*O_B^*O_CO_D^*]+k_C[O_AO_B^*O_C^*O_D^*]-(k_B+k_D)[O_AO_B^*O_CO_D^*])[H_2O]\end{aligned} \tag{S.5.13}$$

$$\begin{aligned}\frac{d[O_AO_BO_C^*O_D^*]}{dt} = {} & ((k_C[O_AO_BO_CO_D^*]+k_D[O_AO_BO_C^*O_D])-(k_A+k_B)[O_AO_BO_C^*O_D^*])[H_2O^*]\\ & +(k_A[O_A^*O_BO_C^*O_D^*]+k_B[O_AO_B^*O_C^*O_D^*]-(k_C+k_D)[O_AO_BO_C^*O_D^*])[H_2O]\end{aligned} \tag{S.5.14}$$

$$\frac{d[O\ O_3^*]}{dt}=\frac{d[O_A^*O_B^*O_C^*O_D]}{dt}+\frac{d[O_A^*O_B^*O_CO_D^*]}{dt}+\frac{d[O_A^*O_BO_C^*O_D^*]}{dt}+\frac{d[O_AO_B^*O_C^*O_D^*]}{dt} \tag{S.5.15}$$

$$\frac{d[O_A^*O_B^*O_C^*O_D]}{dt} = (k_A[O_AO_B^*O_C^*O_D] + k_B[O_A^*O_BO_C^*O_D] + k_C[O_A^*O_B^*O_CO_D] - k_D[O_A^*O_B^*O_C^*O_D])[H_2O^*]$$
$$+(k_D[O_A^*O_B^*O_C^*O_D^*] - (k_A + k_B + k_C)[O_A^*O_B^*O_C^*O_D])[H_2O] \tag{S.5.16}$$

$$\frac{d[O_A^*O_B^*O_CO_D^*]}{dt} = (k_A[O_AO_B^*O_CO_D^*] + k_B[O_A^*O_BO_CO_D^*] + k_D[O_A^*O_B^*O_CO_D] - k_C[O_A^*O_B^*O_CO_D^*])[H_2O^*]$$
$$+(k_C[O_A^*O_B^*O_C^*O_D^*] - (k_A + k_B + k_D)[O_A^*O_B^*O_CO_D^*])[H_2O] \tag{S.5.17}$$

$$\frac{d[O_A^*O_BO_C^*O_D^*]}{dt} = (k_A[O_AO_BO_C^*O_D^*] + k_C[O_A^*O_BO_CO_D^*] + k_D[O_A^*O_BO_C^*O_D] - k_D[O_A^*O_BO_C^*O_D^*])[H_2O^*]$$
$$+(k_B[O_A^*O_B^*O_C^*O_D^*] - (k_A + k_C + k_D)[O_A^*O_BO_C^*O_D^*])[H_2O] \tag{S.5.18}$$

$$\frac{d[O_AO_B^*O_C^*O_D^*]}{dt} = (k_B[O_AO_BO_C^*O_D^*] + k_C[O_AO_B^*O_CO_D^*] + k_D[O_AO_B^*O_C^*O_D] - k_B[O_AO_B^*O_C^*O_D^*])[H_2O^*]$$
$$+(k_A[O_A^*O_B^*O_C^*O_D^*] - (k_B + k_C + k_D)[O_AO_B^*O_C^*O_D^*])[H_2O] \tag{S.5.19}$$

$$\frac{d[O_4^*]}{dt} = \frac{d[O_A^*O_B^*O_C^*O_D^*]}{dt} \tag{S.5.20}$$

$$\frac{d[O_A^*O_B^*O_C^*O_D^*]}{dt} = (k_A[O_AO_B^*O_C^*O_D^*] + k_B[O_A^*O_BO_C^*O_D^*] + k_C[O_A^*O_B^*O_CO_D^*] + k_D[O_A^*O_B^*O_C^*O_D])[H_2O^*]$$
$$-(k_A + k_B + k_C + k_D)[O_A^*O_B^*O_C^*O_D^*][H_2O] \tag{S.5.21}$$

S.6 Kinetic model for for isotopic exchange in a system with four oxygens occupying identical sites

We can adapt the model above (eqs S.5.1-S.5.21) to a system with four oxygens, but which all occupy identical sites, and in which k_A, k_B, k_C and k_D are identical.

We know that

$$\frac{d[O_4]}{dt}=\frac{d[O_AO_BO_CO_D]}{dt} \qquad \text{(S.5.1)}$$

where

$$\begin{aligned}\frac{d[O_AO_BO_CO_D]}{dt}&=(k_A[O_A^*O_BO_CO_D]+k_B[O_AO_B^*O_CO_D]+k_C[O_AO_BO_C^*O_D]\\&\quad+k_D[O_AO_BO_CO_D^*])[H_2O]-(k_A+k_B+k_C+k_D)[O_AO_BO_CO_D][H_2O^*]\end{aligned} \qquad \text{(S.5.2)}$$

Since all the sites are identical, and there are thus equal amounts of compound with sites A, B, C and D containing exchanged oxygens – the sum of concentrations of which equals $[O_3O^*]$ – we can rewrite equation S.6.2 as

$$\frac{d[O_AO_BO_CO_D]}{dt}=4k_A\frac{[O_3O^*]}{4}[H_2O]-4k_A[O_4][H_2O^*] \qquad \text{(S.6.1)}$$

Next, we know that

$$\frac{d[O_3O^*]}{dt}=\frac{d[O_A^*O_BO_CO_D]}{dt}+\frac{d[O_AO_B^*O_CO_D]}{dt}+\frac{d[O_AO_BO_C^*O_D]}{dt}+\frac{d[O_AO_BO_CO_D^*]}{dt} \qquad \text{(S.5.3)}$$

where

$$\begin{aligned}\frac{d[O_A^*O_BO_CO_D]}{dt}&=(k_A[O_AO_BO_CO_D]-(k_B+k_C+k_D)[O_A^*O_BO_CO_D])[H_2O^*]\\&\quad+(k_B[O_A^*O_B^*O_CO_D]+k_C[O_A^*O_BO_C^*O_D]+k_D[O_A^*O_BO_CO_D^*]-k_A[O_A^*O_BO_CO_D])[H_2O]\end{aligned}$$

(S.6.2)

This then becomes

$$\frac{d[O_A^*O_BO_CO_D]}{dt}=k_A[O_4][H_2O^*]-3k_A\frac{[O_3O^*]}{4}[H_2O^*]-(3k_A\frac{[O_2O_2^*]}{4}-k_A\frac{[O_3O^*]}{4})[H_2O]$$

(S.6.3)

Again, there is no preference towards any particular site, so

$$\frac{d[O_A^*O_BO_CO_D]}{dt}=\frac{d[O_AO_B^*O_CO_D]}{dt}=\frac{d[O_AO_BO_C^*O_D]}{dt}=\frac{d[O_AO_BO_CO_D^*]}{dt}=\frac{1}{4}\frac{d[O_3O^*]}{dt} \quad \text{(S.6.4)}$$

which in combination with equation S.6.5 allows us to rewrite equation S.6.4 as

$$\begin{aligned}\frac{d[O_3O^*]}{dt}&=4(k_A[O_4][H_2O^*]-3k_A\frac{[O_3O^*]}{4}[H_2O^*]+(3k_A\frac{[O_2O_2^*]}{6}-k_A\frac{[O_3O^*]}{4})[H_2O])\\&=4k_A[O_4][H_2O^*]-3k_A[O_3O^*][H_2O^*]+(2k_A[O_2O_2^*]-k_A[O_3O^*])[H_2O]\end{aligned} \quad \text{(S.6.5)}$$

Likewise,

$$\begin{aligned}\frac{d[O_2O_2^*]}{dt}&=\frac{d[O_A^*O_B^*O_CO_D]}{dt}+\frac{d[O_A^*O_BO_C^*O_D]}{dt}+\frac{d[O_A^*O_BO_CO_D^*]}{dt}+\frac{d[O_AO_B^*O_C^*O_D]}{dt}\\&+\frac{d[O_AO_B^*O_CO_D^*]}{dt}+\frac{d[O_AO_BO_C^*O_D^*]}{dt}\end{aligned} \quad \text{(S.5.2)}$$

Since we know that there is no particular, favoured, site,

$$\begin{aligned}\frac{d[O_A^*O_B^*O_CO_D]}{dt}&=\frac{d[O_A^*O_BO_C^*O_D]}{dt}=\frac{d[O_A^*O_BO_CO_D^*]}{dt}=\frac{d[O_AO_B^*O_C^*O_D]}{dt}\\&=\frac{d[O_AO_B^*O_CO_D^*]}{dt}=\frac{d[O_AO_BO_C^*O_D^*]}{dt}=\frac{1}{6}\frac{d[O_2O_2^*]}{dt}\end{aligned} \quad \text{(S.6.6)}$$

where, for example

$$\begin{aligned}\frac{d[O_A^*O_B^*O_CO_D]}{dt}&=((k_A[O_AO_B^*O_CO_D]+k_B[O_A^*O_BO_CO_D])-(k_C+k_D)[O_A^*O_B^*O_CO_D])[H_2O^*]\\&+(k_C[O_A^*O_B^*O_C^*O_D]+k_D[O_A^*O_B^*O_CO_D^*]-(k_A+k_B)[O_A^*O_B^*O_CO_D])[H_2O]\end{aligned} \quad \text{(S.6.7)}$$

This becomes

$$\frac{d[O_A^*O_B^*O_CO_D]}{dt}=2k_A\frac{[O_3O^*]}{4}[H_2O^*]-2k_A\frac{[O_2O_2^*]}{6}[H_2O^*]+(2k_A\frac{[O\ O_3^*]}{4}-2k_A\frac{[O_2O_2^*]}{6})[H_2O] \quad \text{(S.6.8)}$$

which yields

$$\begin{aligned}\frac{d[O_2O_2^*]}{dt} &= 6(2k_A\frac{[O_3O^*]}{4}[H_2O^*]-2k_A\frac{[O_2O_2^*]}{6}[H_2O^*]+(2k_A\frac{[O\ O_3^*]}{4}-2k_A\frac{[O_2O_2^*]}{6})[H_2O]) \\ &= 3k_A[O_3O^*][H_2O^*]-2k_A[O_2O_2^*][H_2O^*]+(3k_A[O\ O_3^*]-2k_A[O_2O_2^*])[H_2O]\end{aligned}$$

(S.6.9)

In the same way

$$\frac{d[O\ O_3^*]}{dt}=\frac{d[O_A^*O_B^*O_C^*O_D]}{dt}+\frac{d[O_A^*O_B^*O_CO_D^*]}{dt}+\frac{d[O_A^*O_BO_C^*O_D^*]}{dt}+\frac{d[O_AO_B^*O_C^*O_D^*]}{dt} \tag{S.5.15}$$

where *e.g.*

$$\frac{d[O_A^*O_B^*O_C^*O_D]}{dt}=3k_A\frac{[O_2O_2^*]}{6}[H_2O^*]-k_A\frac{[O\ O_3^*]}{4}[H_2O^*]+(k_A[O_4^*]-3k_A\frac{[O\ O_3^*]}{4})[H_2O] \tag{S.6.10}$$

So

$$\begin{aligned}\frac{d[O\ O_3^*]}{dt} = 4\frac{d[O_A^*O_B^*O_C^*O_D]}{dt} &= 2k_A[O\ O_3^*][H_2O^*]-k_A[O\ O_3^*][H_2O^*] \\ &+(4k_A[O_4^*]-3k_A[O\ O_3^*])[H_2O]\end{aligned} \tag{S.6.11}$$

Finally,

$$\begin{aligned}\frac{d[O_A^*O_B^*O_C^*O_D^*]}{dt} &= (k_A[O_AO_B^*O_C^*O_D^*]+k_B[O_A^*O_BO_C^*O_D^*]+k_C[O_A^*O_B^*O_CO_D^*]+k_D[O_A^*O_B^*O_C^*O_D])[H_2O^*] \\ &-(k_A+k_B+k_C+k_D)[O_A^*O_B^*O_C^*O_D^*][H_2O]\end{aligned} \tag{S.5.21}$$

which can be rewritten as

$$\begin{aligned}\frac{d[O_A^*O_B^*O_C^*O_D^*]}{dt} &= k_A[O_AO_B^*O_C^*O_D^*][H_2O^*]+k_B[O_A^*O_BO_C^*O_D^*][H_2O^*] \\ &+k_C[O_A^*O_B^*O_CO_D^*][H_2O^*]+k_D[O_A^*O_B^*O_C^*O_D][H_2O^*] \\ &-(k_A+k_B+k_C+k_D)[O_A^*O_B^*O_C^*O_D^*][H_2O] \\ &= 4k_A\frac{[O\ O_3^*]}{4}[H_2O^*]-4k_A[O_4^*][H_2O]=\frac{d[O_4^*]}{dt}\end{aligned} \tag{S.6.12}$$

The collected equations are thus

$$\begin{aligned}\frac{d[O_4]}{dt} &= -4k_A[O_4][H_2O^*] \\ &\quad +k_A[O_3O^*][H_2O]\end{aligned} \tag{S.6.1}$$

$$\begin{aligned}\frac{d[O_3O^*]}{dt} &= 4k_A[O_4][H_2O^*]-3k_A[O_3O^*][H_2O^*] \\ &\quad +2k_A[O_2O_2^*][H_2O]-k_A[O_3O^*][H_2O]\end{aligned} \tag{S.6.5}$$

$$\begin{aligned}\frac{d[O_2O_2^*]}{dt} &= 3k_A[O_3O^*][H_2O^*]-2k_A[O_2O_2^*][H_2O^*] \\ &\quad +3k_A[O\ O_3^*][H_2O]-2k_A[O_2O_2^*][H_2O]\end{aligned} \tag{S.6.9}$$

$$\begin{aligned}\frac{d[O\ O_3^*]}{dt} &= 2k_A[O_2O_2^*][H_2O^*]-k_A[O\ O_3^*][H_2O^*] \\ &\quad +4k_A[O_4^*][H_2O]-3k_A[O\ O_3^*][H_2O]\end{aligned} \tag{S.6.11}$$

$$\begin{aligned}\frac{d[O_4^*]}{dt} &= k_A[O\ O_3^*][H_2O^*] \\ &\quad -4k_A[O_4^*][H_2O]\end{aligned} \tag{S.6.12}$$

If we assume that the concentration of isotopically normal water is negligible, the full set of rate laws thus becomes

$$\frac{d[O_4]}{dt} = -4k_A[O_4][H_2O^*] \tag{S.6.13}$$

$$\frac{d[O_3O^*]}{dt} = 4k_A[O_4][H_2O^*]-3k_A[O_3O^*][H_2O^*] \tag{S.6.14}$$

$$\frac{d[O_2O_2^*]}{dt} = 3k_A[O_3O^*][H_2O^*]-2k_A[O_2O_2^*][H_2O^*] \tag{S.6.15}$$

$$\frac{d[O\ O_3^*]}{dt} = 2k_A[O_2O_2^*][H_2O^*]-k_A[O\ O_3^*][H_2O^*] \tag{S.6.16}$$

$$\frac{d[O_4^*]}{dt} = k_A[O\ O_3^*][H_2O^*] \tag{S.6.17}$$

S.7 Effect of water concentration, concentration of $[Mn_4O_4(O_2P\{C_7H_7O\}_2)_6][ClO_4]$ and temperature.

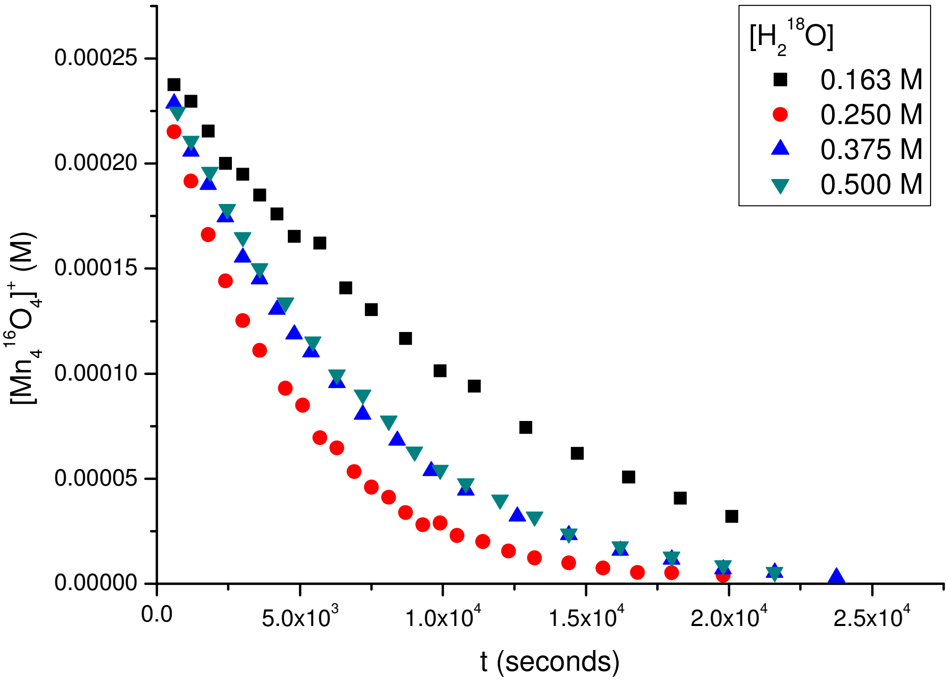

Fig. S.7.1 Kinetic traces for the disappearance of $[Mn_4{}^{16}O_4(O_2P\{C_7H_7O\}_2)_6]^+$ at different $H_2{}^{18}O$ concentrations.

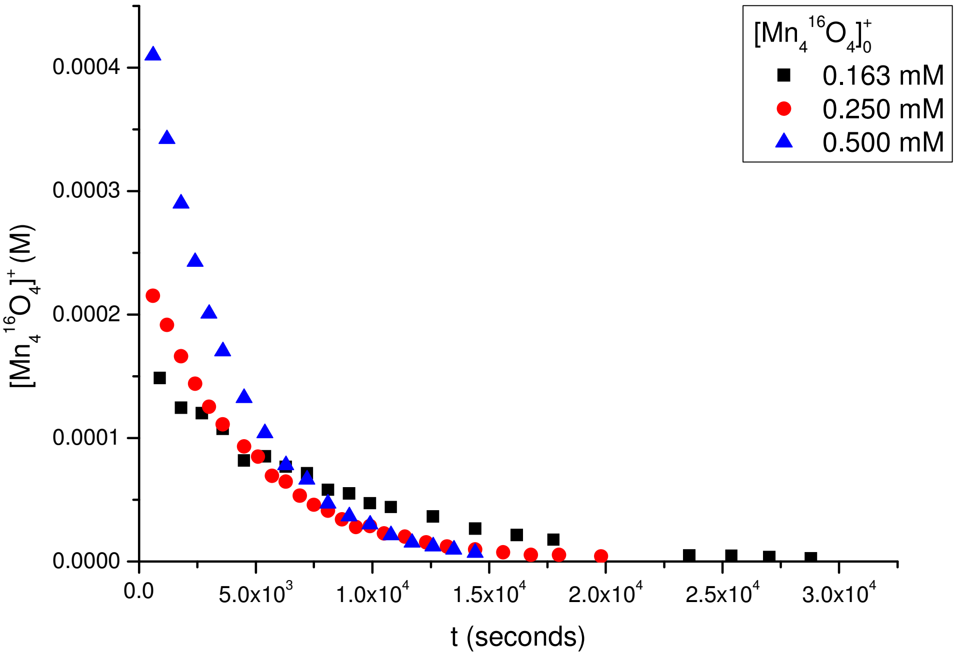

Fig. S.7.2 Kinetic traces for the disappearance of $[Mn_4{}^{16}O_4(O_2P\{C_7H_7O\}_2)_6]^+$ at different initial $[Mn_4{}^{16}O_4(O_2P\{C_7H_7O\}_2)_6]^+$ concentrations.

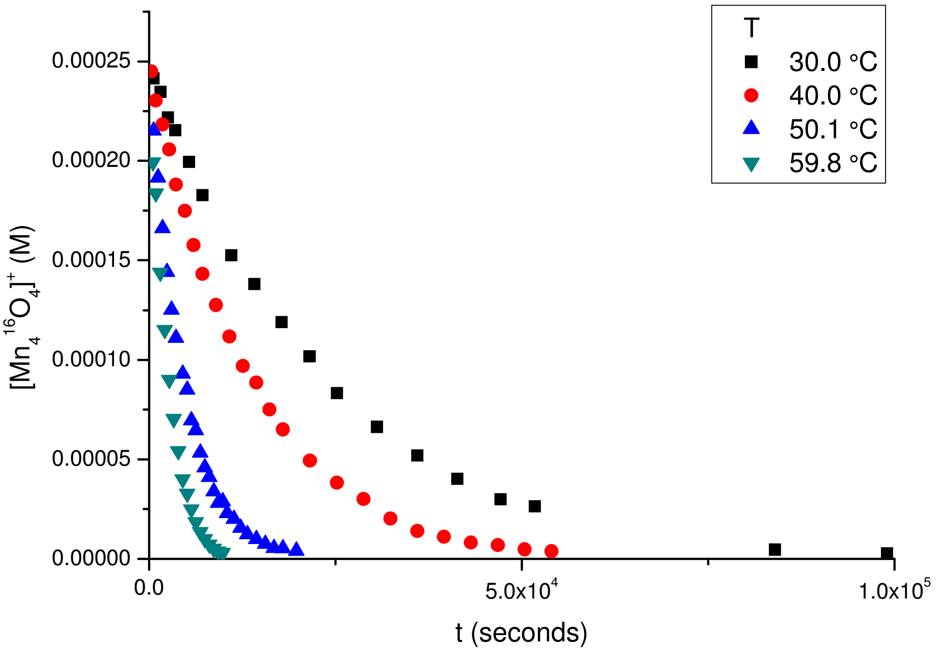

Fig. S.7.2 Kinetic traces for the disappearance of $[Mn_4{}^{16}O_4(O_2P\{C_7H_7O\}_2)_6]^+$ at different temperatures.

S8. Simulation of one- and two-oxygen-type systems

Kinetic traces were simulated in Micromath Scientist by using equations S.5.1-S.5.21. $[H_2O^*]$ was set to 1, $[H_2O^{16}]$ was set to 0, and the initial $[O_AO_BO_CO_D]$ was set to $25 \cdot 10^{-5}$ mol·dm^{-3}.

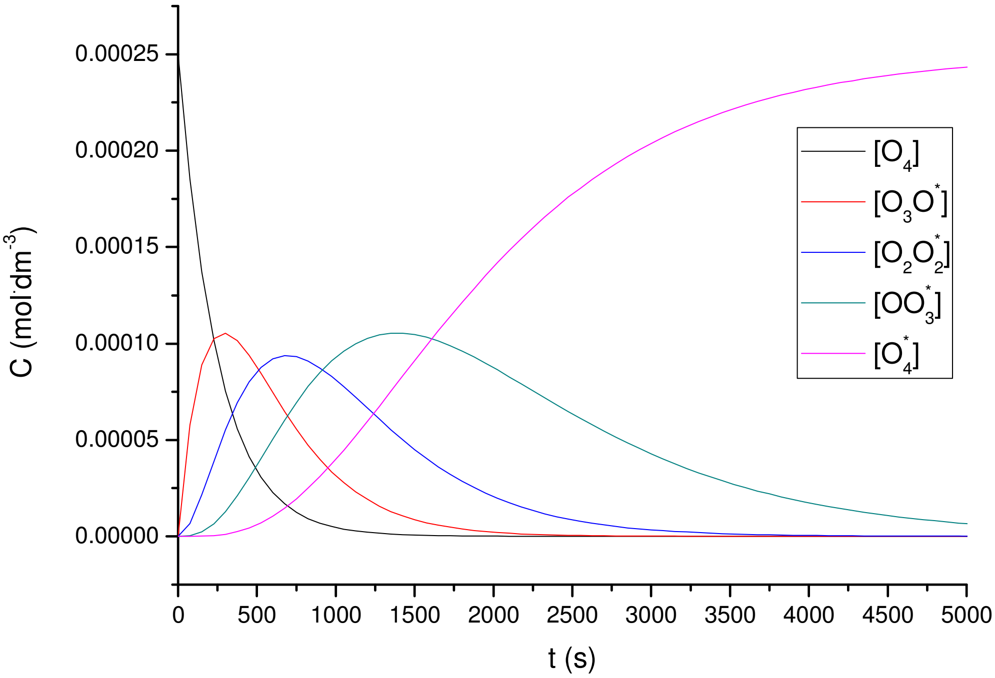

Fig. S.8.1 Simulated traces, setting $k_A=k_B=k_C=k_D=1 \cdot 10^{-3}$ s^{-1}.

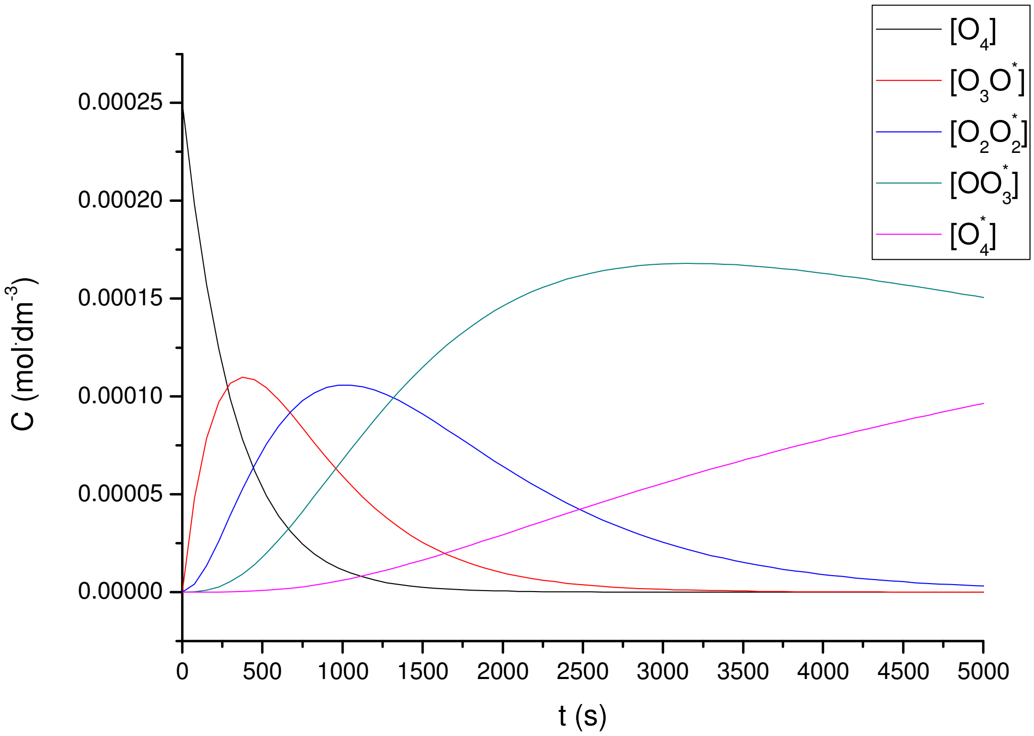

Fig. S.8.2 Simulated traces, setting $k_A=k_B=k_C=1\cdot10^{-3}$ and $k_D=1\cdot10^{-4}$ s^{-1}.

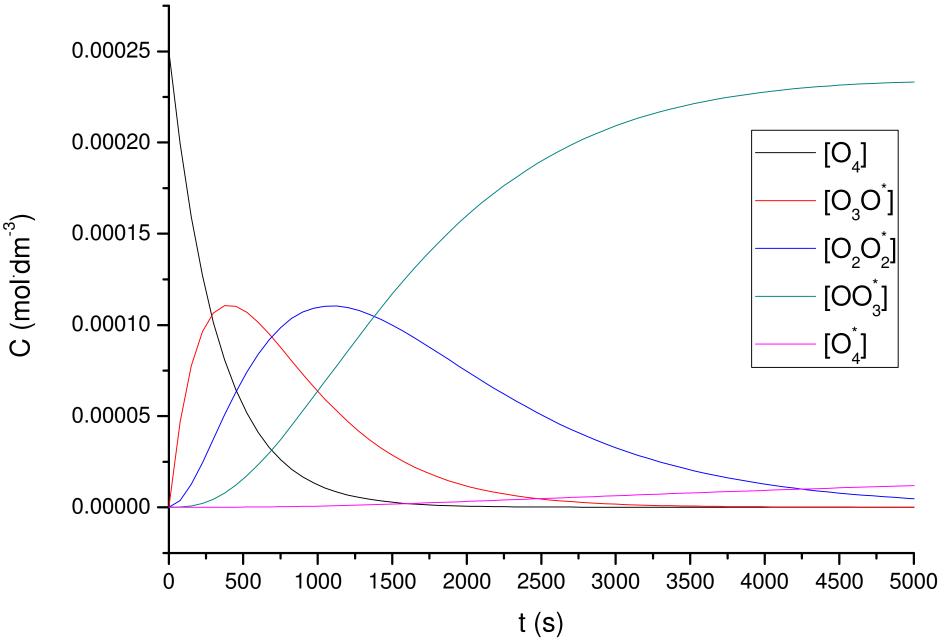

Fig. S.8.3 Simulated traces, setting $k_A=k_B=k_C=1\cdot10^{-3}$ and $k_D=1\cdot10^{-5}$ s^{-1}.

S.9 Structure of $[Mn^{III}Mn^{IV}{}_4O_4(O_2P\{C_6H_4OCH_3\}_2)_6]^+$

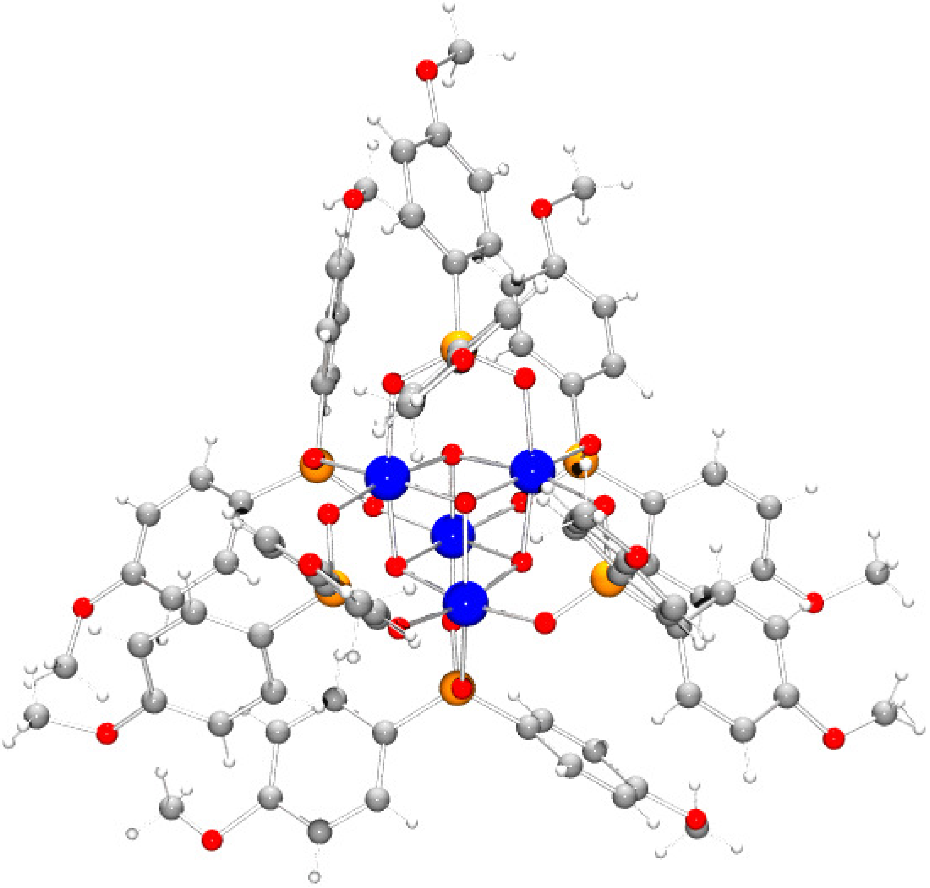

Fig. S.9.1 Structure of $[Mn^{III}{}_2Mn^{IV}{}_4O_4(O_2P\{C_6H_4OCH_3\}_2)_6]^+$. Mn in blue, P in orange, C in grey, H in wheat, O in red. Based on the structure of $[Mn^{III}{}_2Mn^{IV}{}_2O_4(O_2P\{C_6H_4OCH_3\}_2)_6]$ (CCDC 232599, Inorg. Chem. **2004**, *43(19)*, 5795-5797).

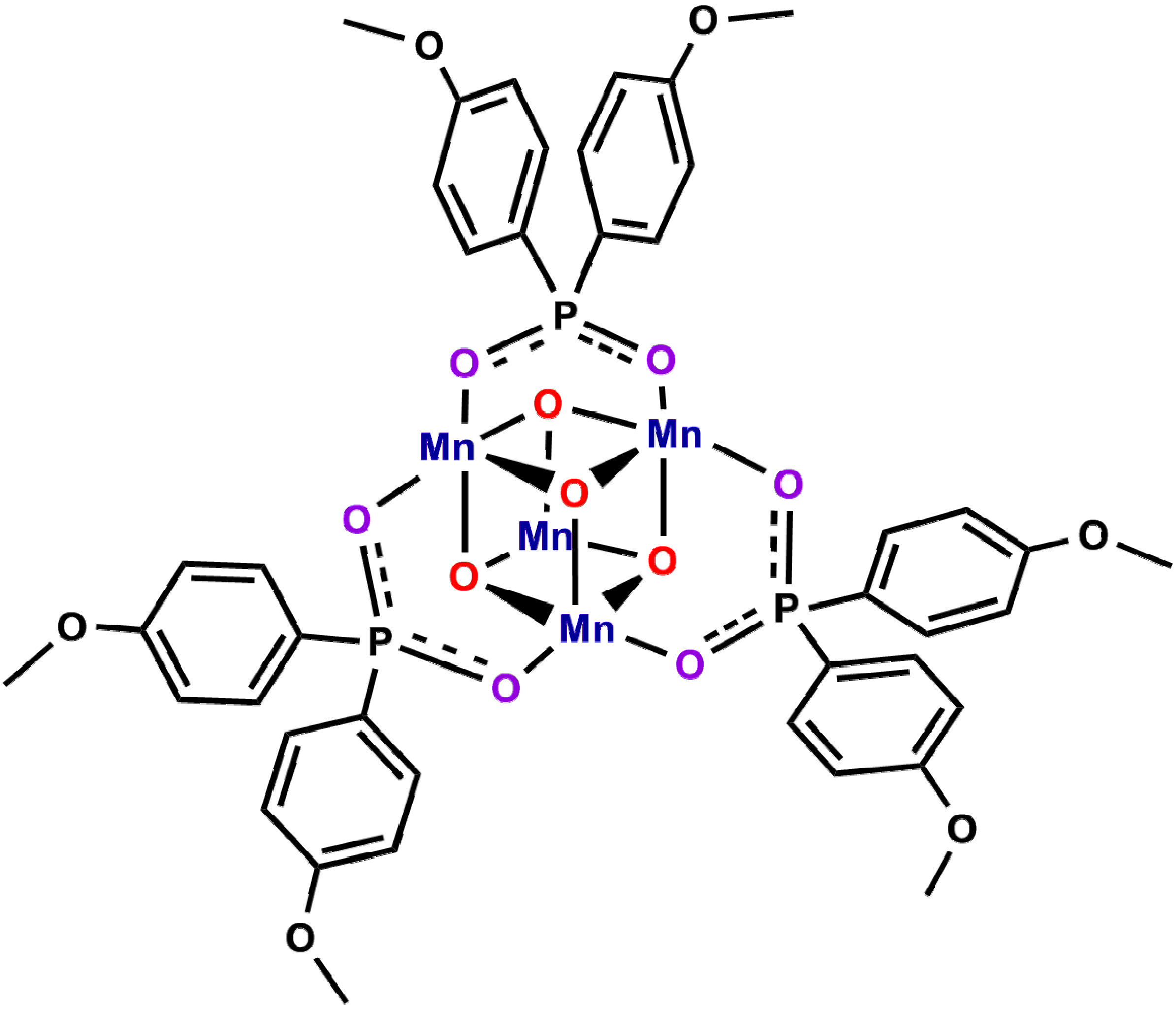

Fig. S.9.2 Structure of $[Mn^{III}{}_2Mn^{IV}{}_4O_4(O_2P\{C_6H_4OCH_3\}_2)_6]^+$. Only three of the six ligands are drawn.