## Supporting Information

Formation of stoichiometrically <sup>18</sup>O-labelled oxygen from the oxidation of  $H_2$  <sup>18</sup>O mediated by a dinuclear manganese complex – a mass spectrometry and EPR study

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**Figure S1.** EPR spectrum of **1** (1 mM, in  $H_2O$  : MeCN = 3 : 1) 1 min after the addition of KHSO<sub>4</sub> (10 eq. per Mn centre ). EPR measurement conditions: temperature: 5 K; microwave frequency: 9.58 GHz; modulation amplitude: 10 G; microwave power: 200  $\mu$ W.



**Figure S2.** Oxygen evolution trace detected by MIMS for the reaction of  $Mn_2O_3$  (2 mM Mn suspended in  $H_2O$ ) with oxone. Injection of 10 eq.  $HSO_5^-$  per Mn centre at t = 0 min, water 8% enriched in  $H_2^{-18}O$ . Due to the suspended manganese oxide the traces show increased measurement noise.



**Figure S3.** Oxygen consumption detected by Clark electrode for the reaction of Hbpmp (2 mM in H<sub>2</sub>O: MeCN = 3 :1) with oxone. The solution was equilibrated with air at ambient pressure, before 10 eq.  $HSO_5^-$  per Hbpmp were injected at t = 0 min.

