Electronic Supplementary Information
prepared for Dalton Transactions

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A model for the water-oxidation and recovery systems of the oxygen-evolving complex

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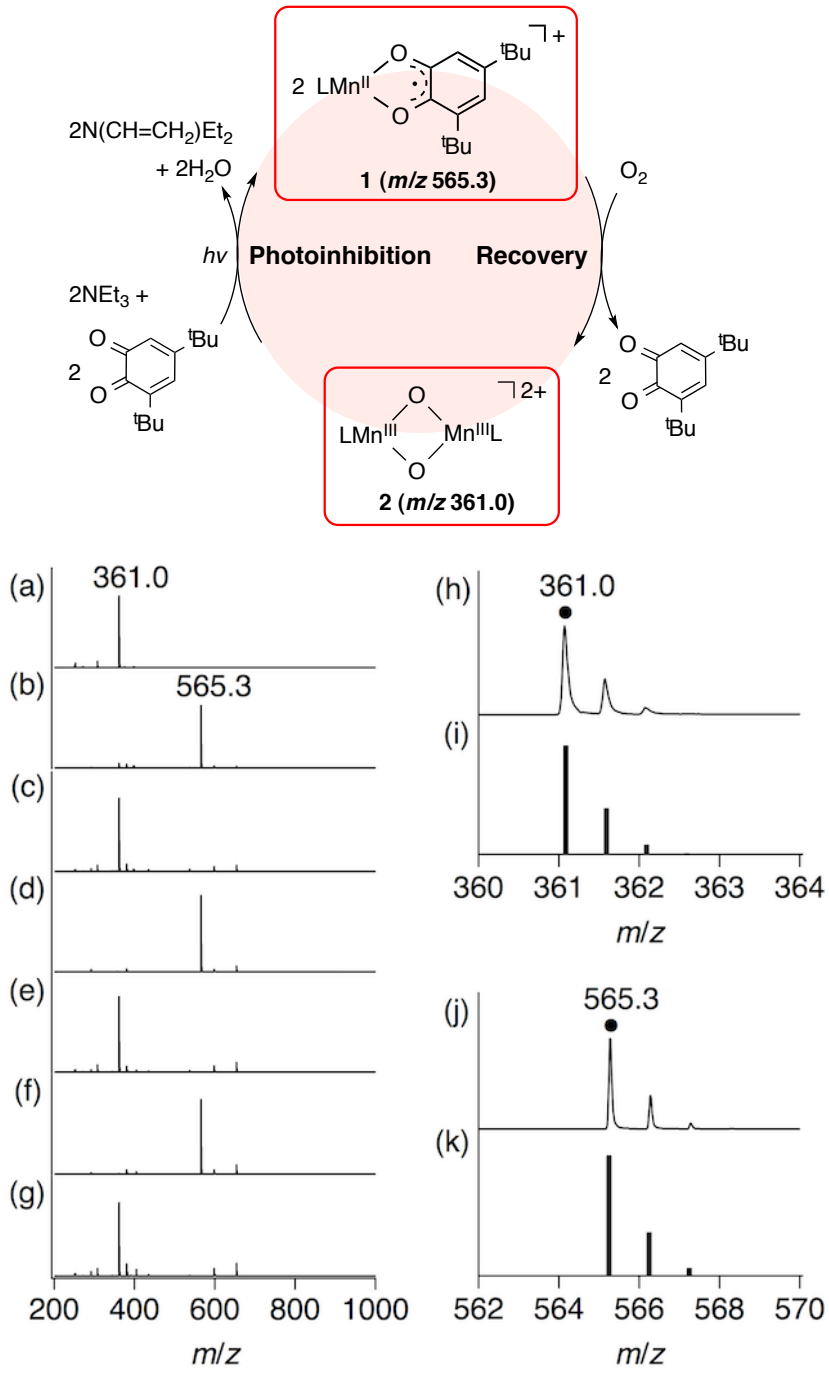

Fig. S1 Positive-ion ESI mass spectral change for the repeated cycle of photoreduction of **2** and oxygenation of **1**. The spectra of **1** shown in (b), (d) and (f) were obtained from photo-irradiation of **2** shown in (a), (c) and (e), respectively. The spectra of **2** shown in (c), (e) and (g) were obtained from oxygenation of **1** shown in (b), (d) and (f), respectively. (h) The signal at *m*/*z* 361.0 corresponds to $[\mathbf{2}]^{2+}$. (i) Calculated isotopic distribution for $[\mathbf{2}]^{2+}$. (j) The signal at *m*/*z* 565.3 corresponds to $[\mathbf{1}]^{+}$. (k) Calculated isotopic distribution for $[\mathbf{1}]^{+}$.

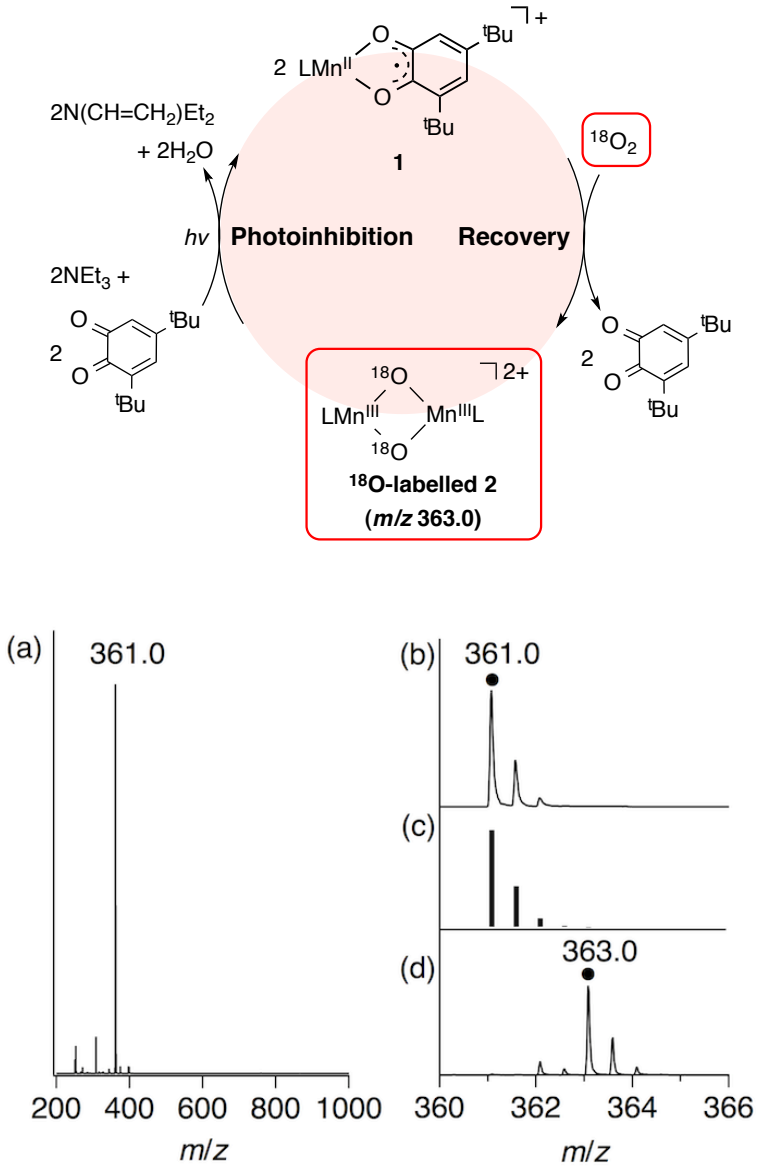

Fig. S2 (a) Positive-ion ESI mass spectrum of **2** in CH_3CN, which is obtained from the photo-irradiation of **2** and successive oxygenation of **1**. (b) The signal at *m*/*z* 361.0 corresponds to $[\mathbf{2}]^{2+}$. (c) Calculated isotopic distribution for $[\mathbf{2}]^{2+}$. (d) Positive-ion ESI mass spectrum of $[Mn^{III,III}_2(TPA)_2(\mu\text{-}^{18}O)_2]^{2+}$ (^{18}O-labelled **2**) in CH_3CN, which is obtained from the photo-irradiation of **2** and successive oxygenation of **1** using $^{18}O_2$. (b) The signal at *m*/*z* 363.0 corresponds to [^{18}O-labelled $\mathbf{2}]^{2+}$.

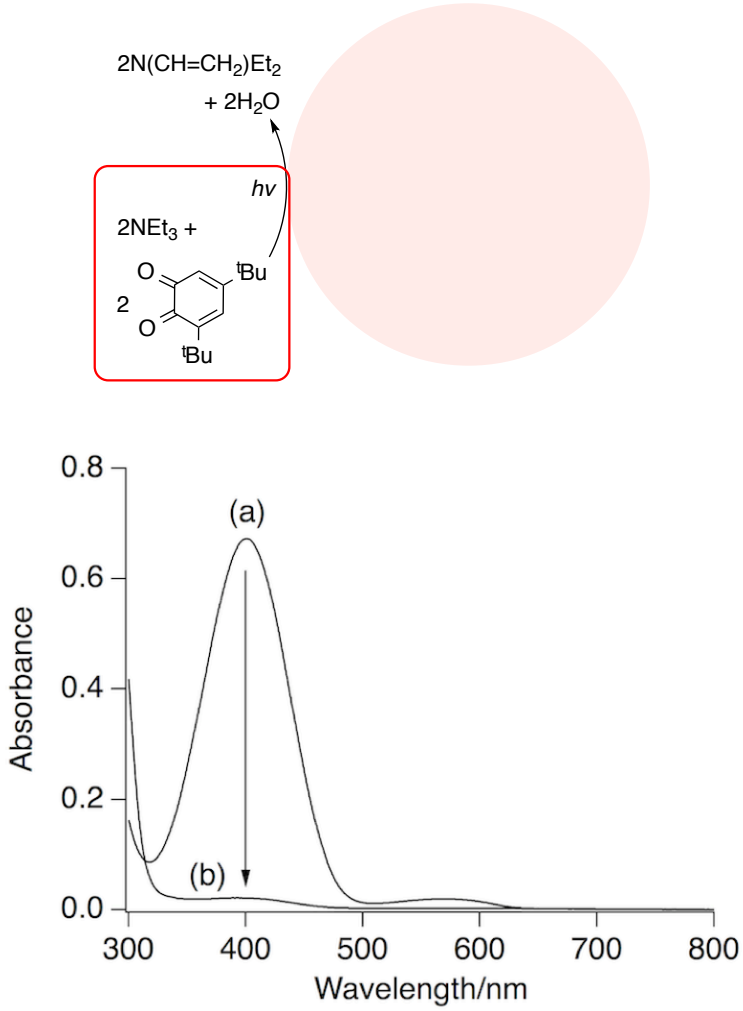

Fig. S3 UV-vis spectra of 3,5-di-*t*-butyl-1,2-benzoquinone (DTBBQ) (400 μM) and NEt_3 (4.0 mM) in CH_3CN (2.5 mL) (a) before and (b) after photo-irradiation (>550 nm).

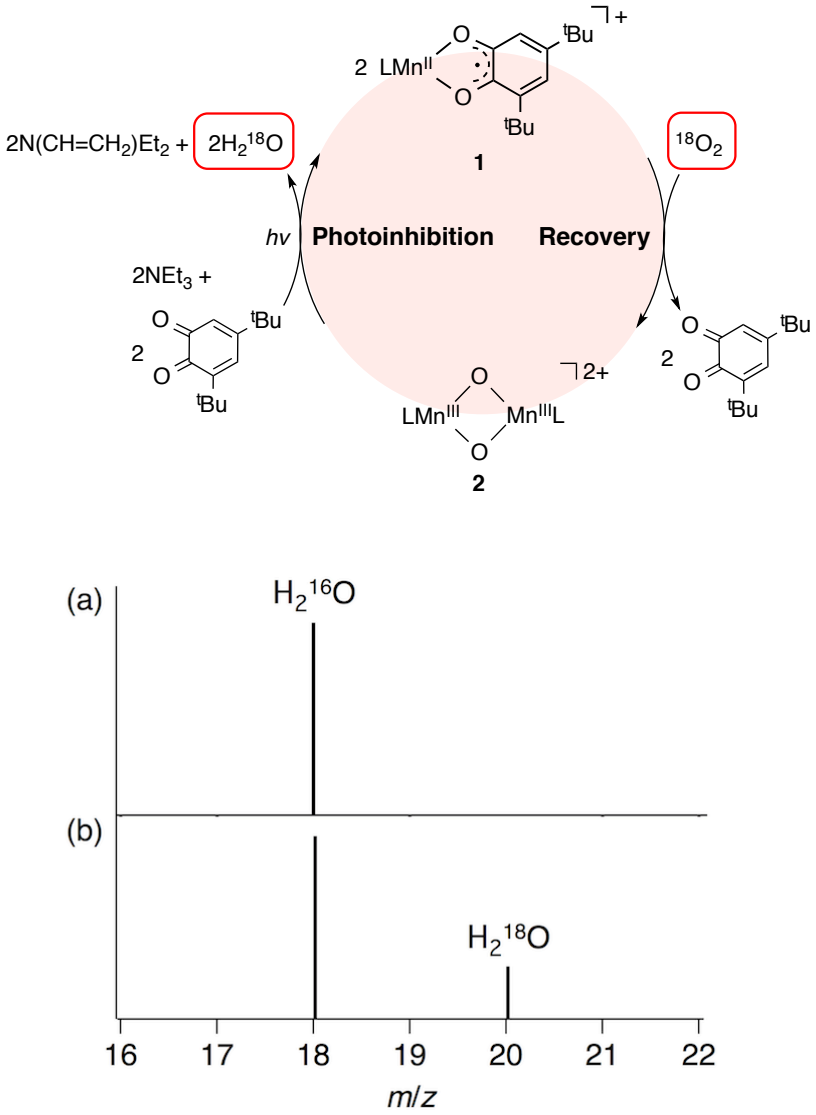

Fig. S4 Positive-ion GC-mass spectra of $H_2{}^{16}O$ and $H_2{}^{18}O$ obtained from the reaction of **2** (1.4 mg, 1.0 μmol) with (a) $^{16}O_2$ (5.0 mL) and (b) $^{18}O_2$ (5.0 mL) in the presence of 3,5-di-*t*-butyl-1,2-benzoquinone (DTBBQ) (22 mg, 100 μmol) and NEt_3 (140 μL, 1.0 mmol) in CH_3CN (200 μL) under photo-irradiation (>550 nm).

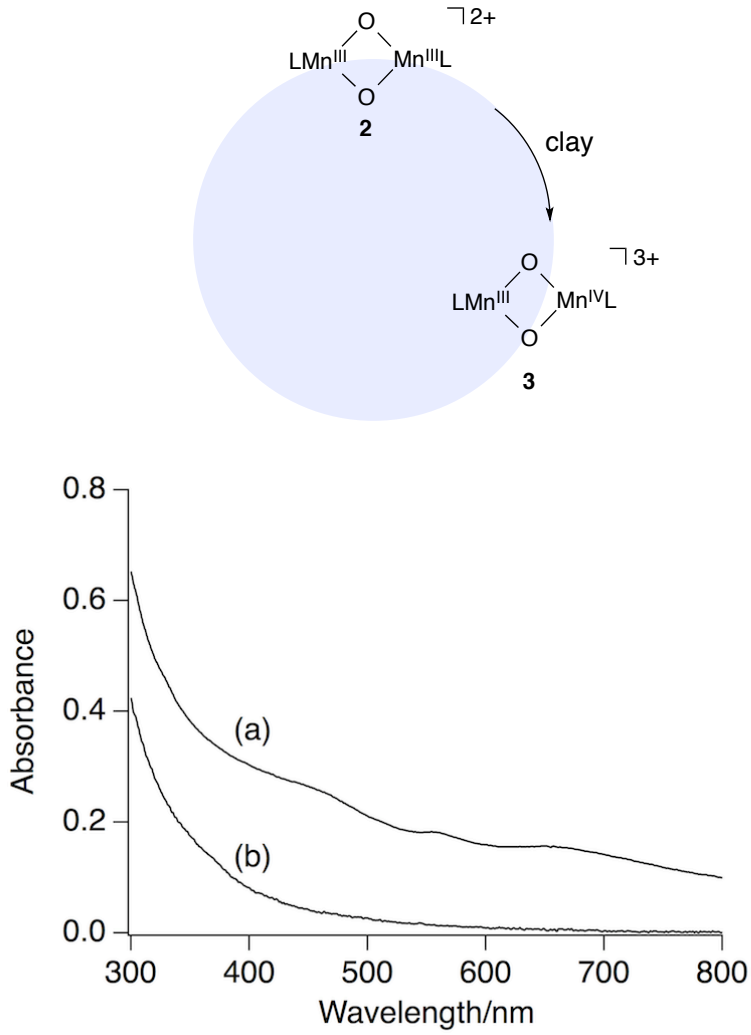

Fig. S5 Diffuse reflectance UV-vis spectra of (a) **2·3@Clay** and (b) clay.

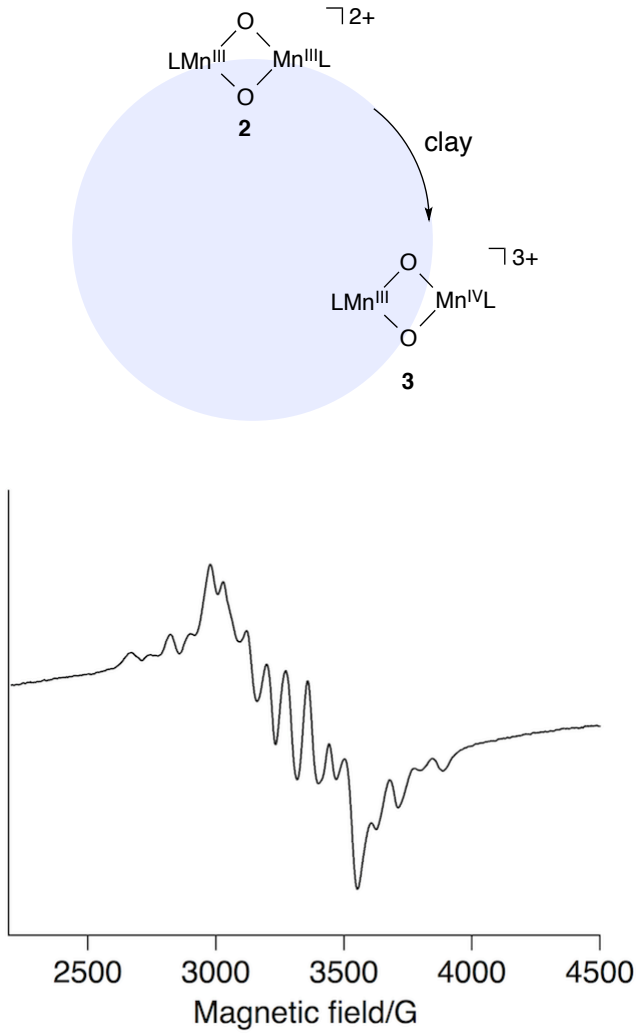

Fig. S6 ESR spectrum of **2·3@Clay** (5.0 mg, content of the mixture of **2** and **3**: 300 nmol) suspended in DMF (500 μL) at –150 ºC (microwave frequency: 9.16 GHz, microwave power: 1.0 mW).

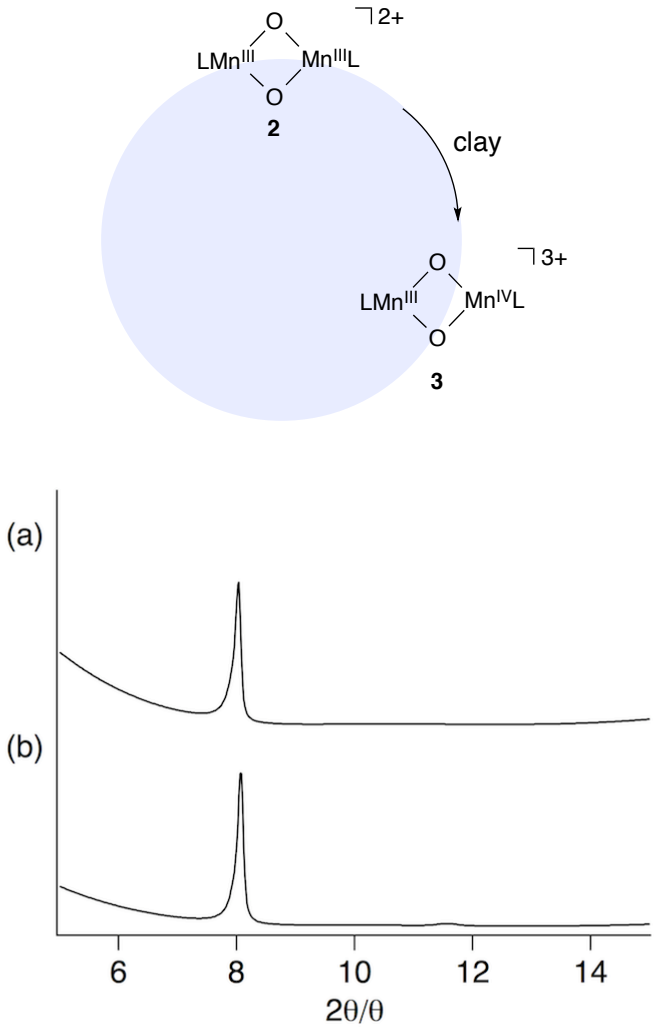

Fig. S7 XRD patterns of (a) **2·3@Clay** and (b) clay.

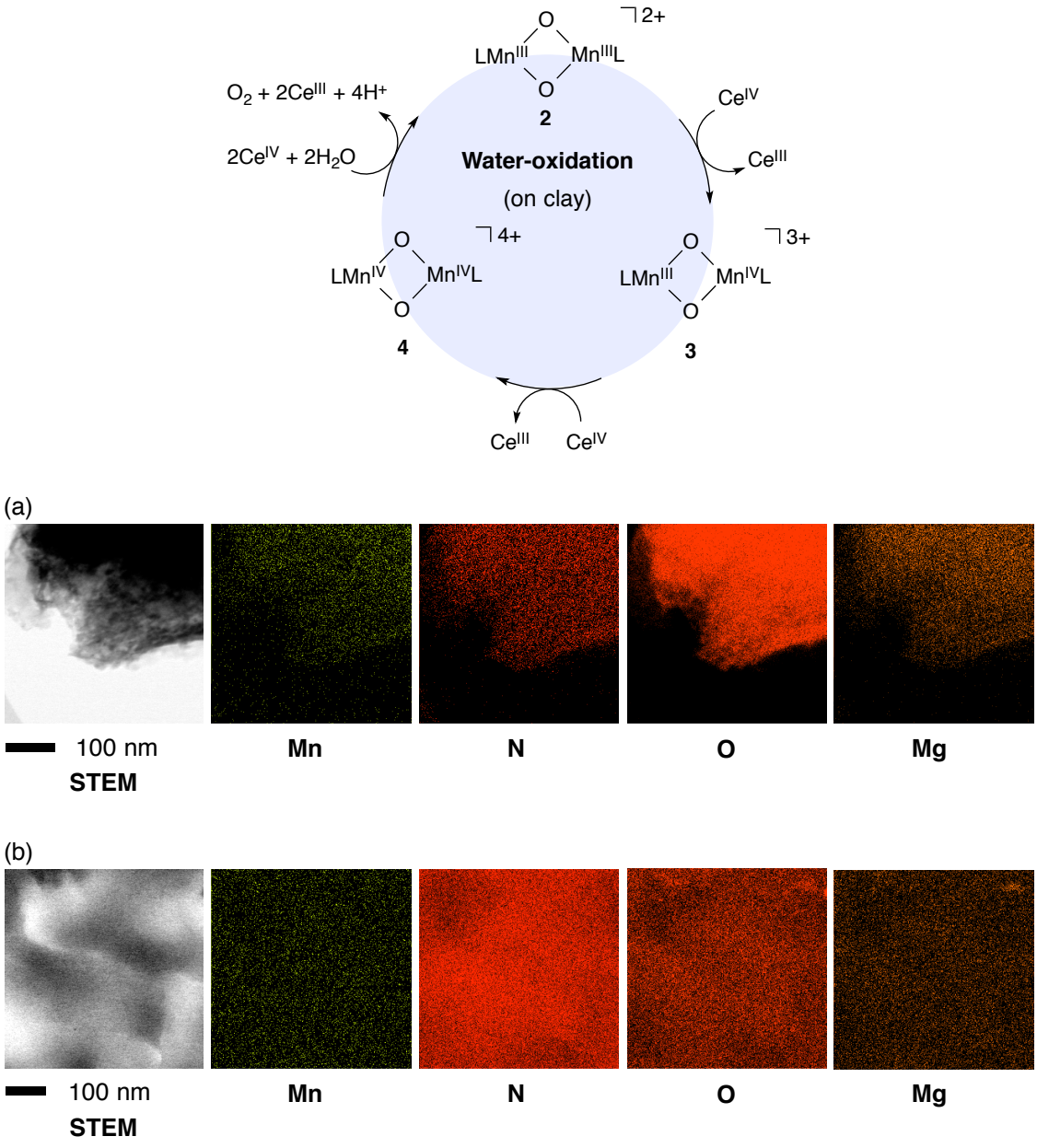

Fig. S8 STEM images and EDS elemental mappings of (a) **2·3@Clay** and (b) clay material isolated from the mixture of **2·3@Clay** and Ce^{IV}.

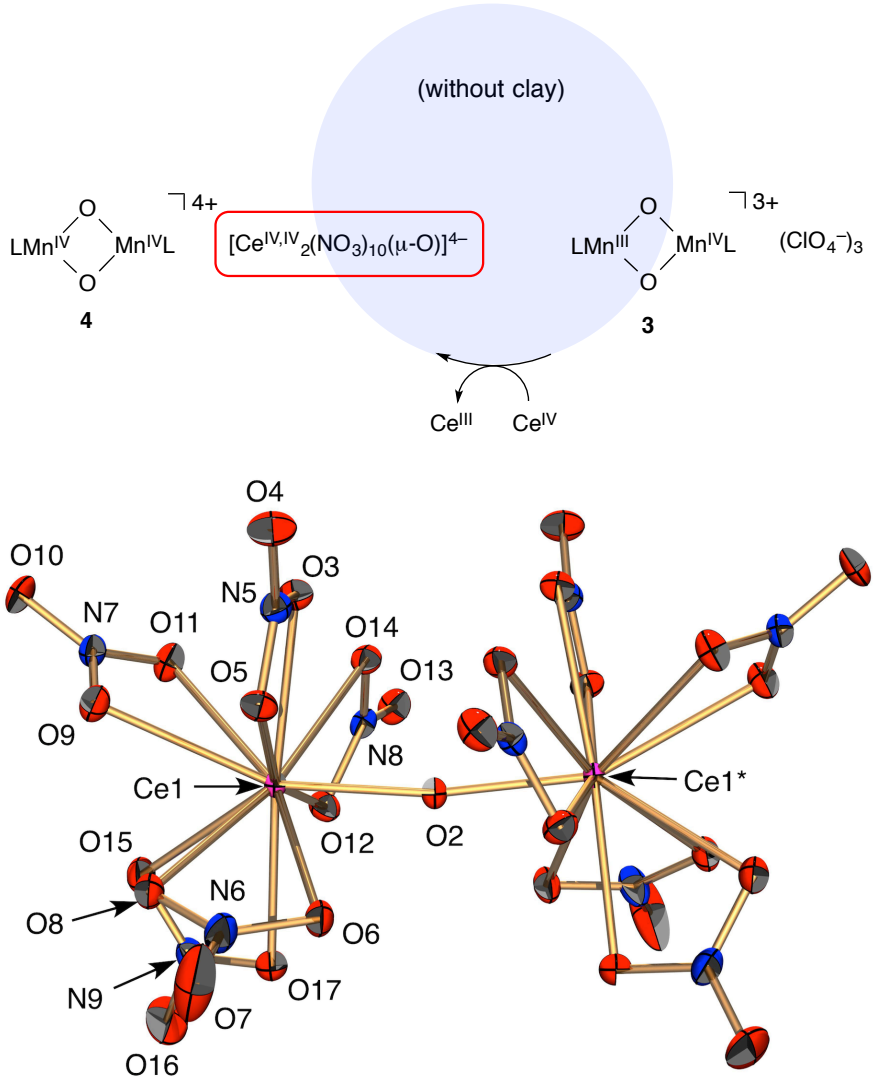

Fig. S9 ORTEP drawing of $[Ce^{IV,IV}_2(NO_3)_{10}(\mu\text{-}O)]^{4-}$ with ellipsoids at 50% probability. The counter cation $[Mn^{IV,IV}_2(TPA)_2(\mu\text{-}O)_2]^{4+}$ (**4**) is omitted for clarity. Selected interatomic distance (l/Å) and angle (ϕ/°): Ce1–O2 = 2.0480(2), Ce1–O2–Ce1* = 170.70(11).

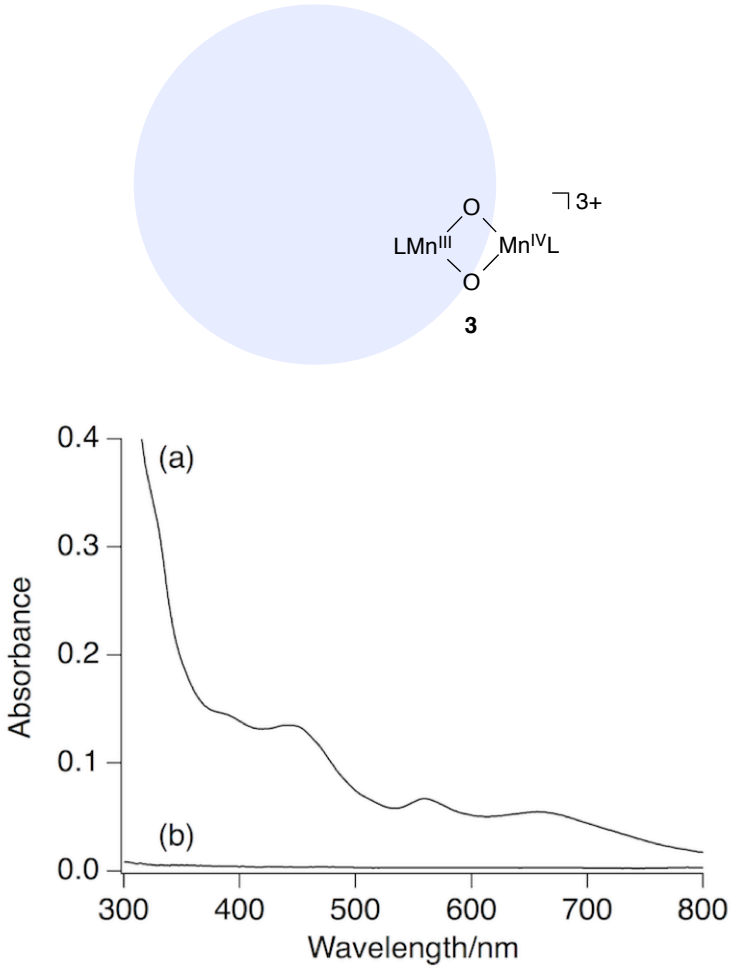

Fig. S10 UV-vis spectra of (a) the CH_3CN solution of **3** (100 μM) and (b) the supernatant CH_3CN/water solution after adsorption of **3** on clay.

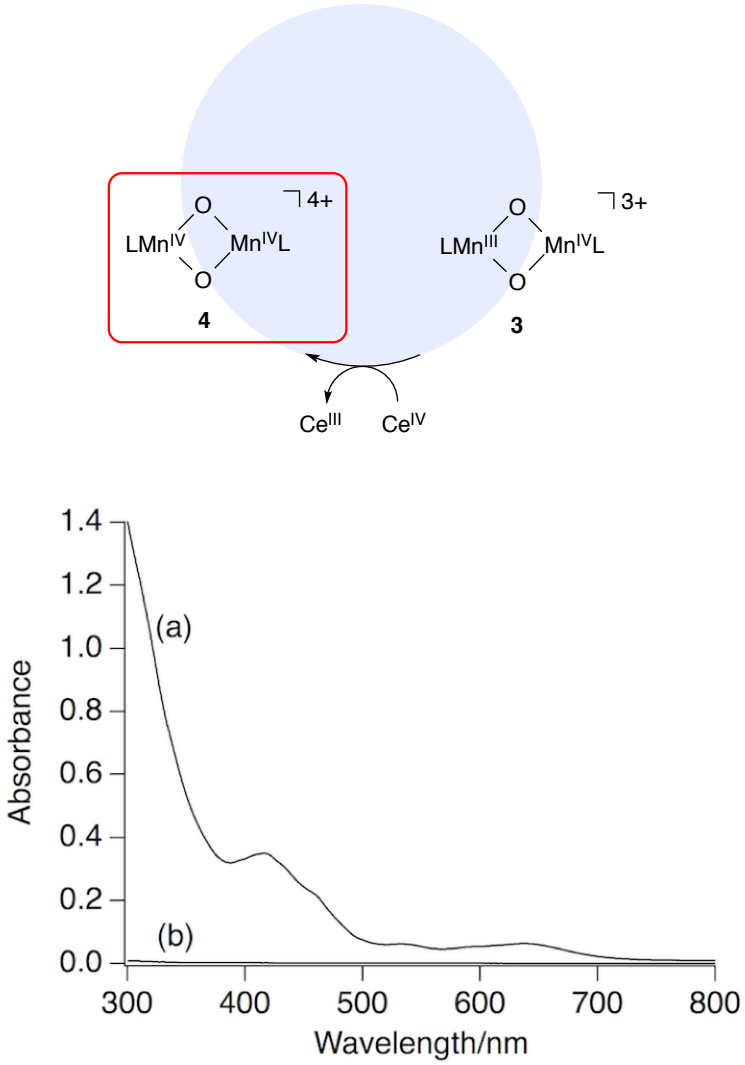

Fig. S11 UV-vis spectra of (a) the aqueous solution of **4** (1.0 mM) and (b) the supernatant aqueous solution after adsorption of **4** on clay.

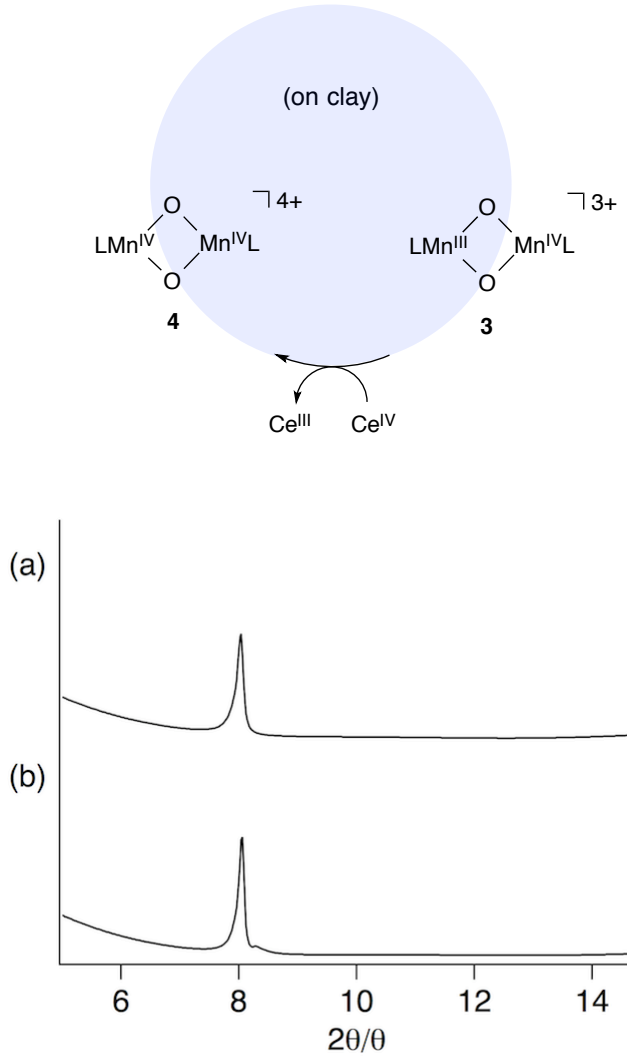

Fig. S12 XRD patterns of (a) **3@Clay** and (b) **4@Clay**.

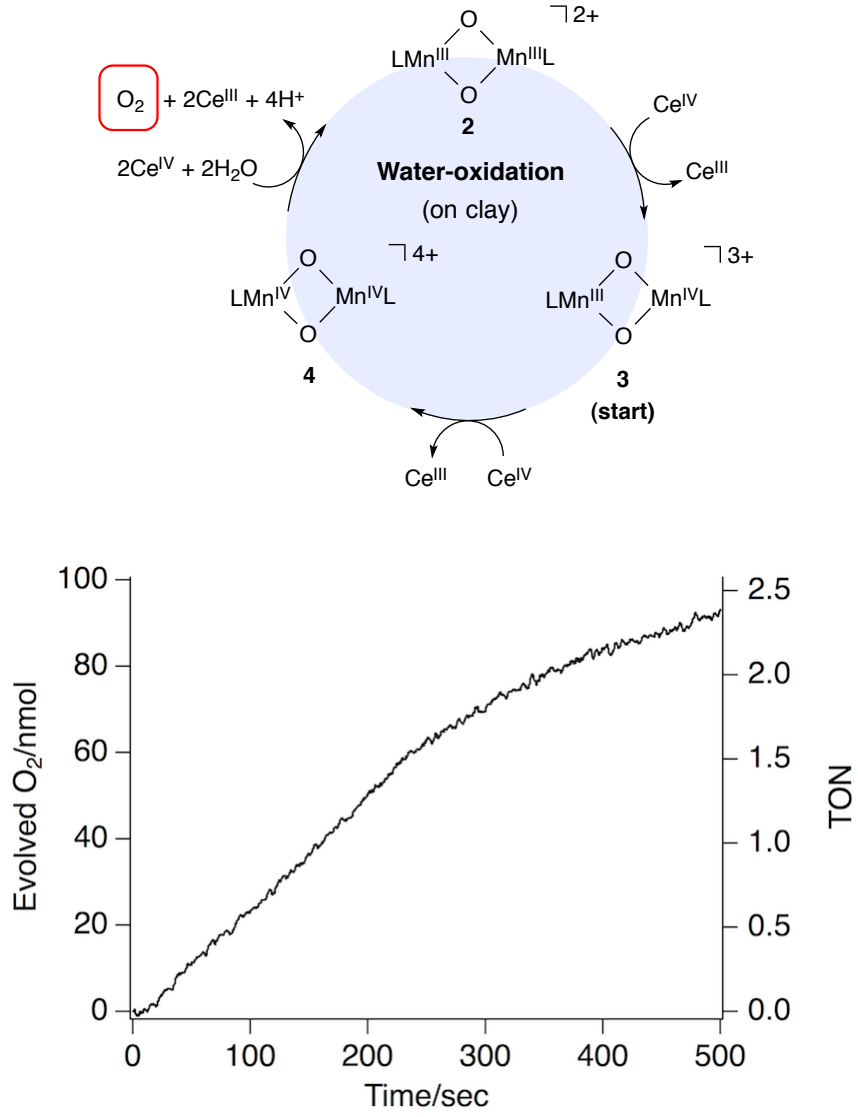

Fig. S13 Time course of the evolved O_2 from the aqueous suspension (2.0 mL) of **3@Clay** (600 μg, content of **3**: 39 nmol) with an excess amount of $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (137 mg, 250 μmol).

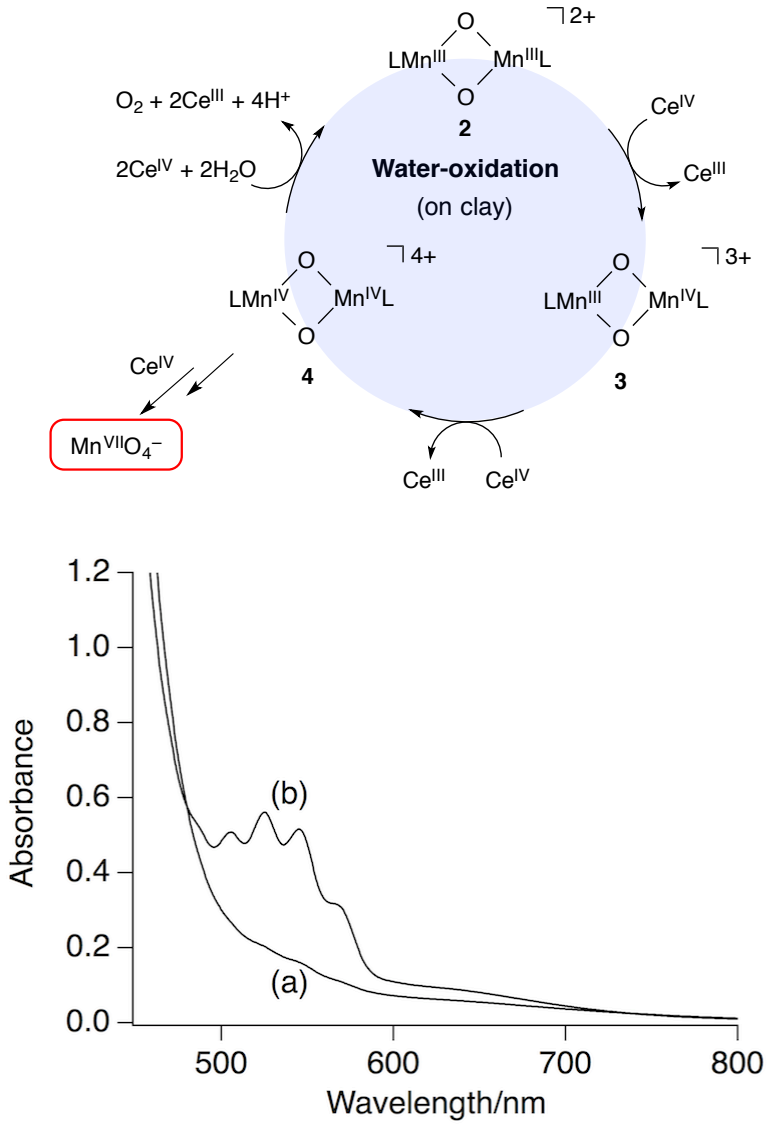

Fig. S14 UV-vis spectra of the supernatant solution (3.0 mL) of the reaction of **3@Clay** (30 mg, content of **3**: 2.0 μmol) with an excess amount of $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (274 mg, 0.50 mmol) after (a) 0.5 min and (b) 60 min.

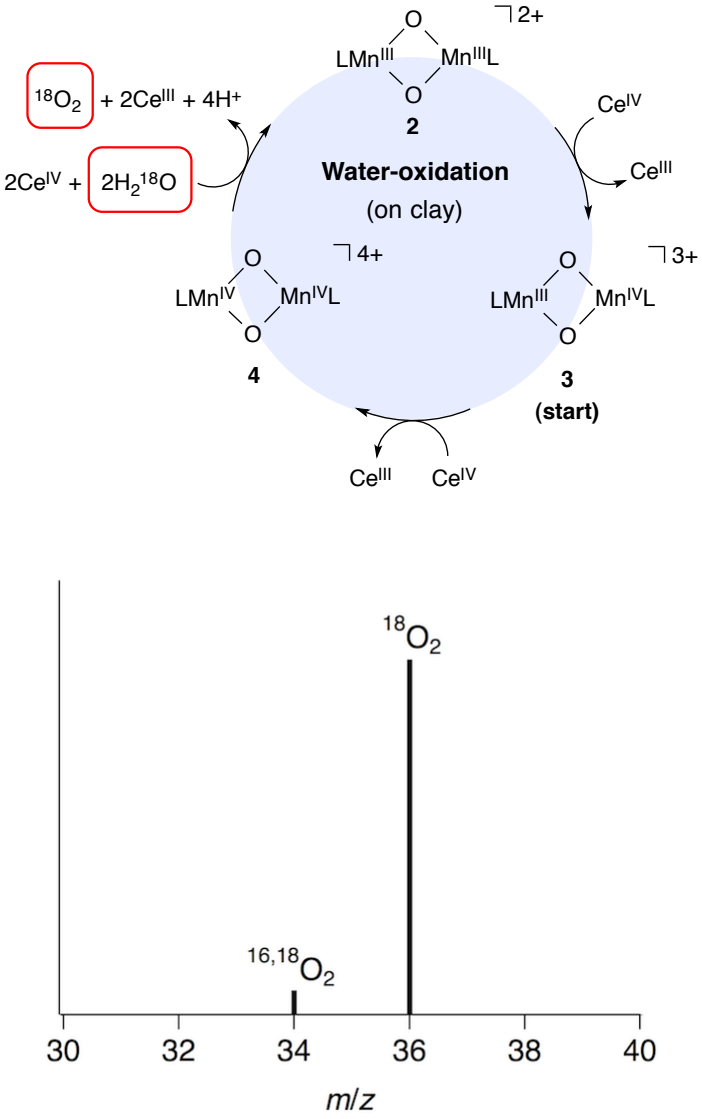

Fig. S15 Positive-ion GC mass spectrum of $^{16,18}O_2$ and $^{18}O_2$ obtained from the $H_2{}^{18}O$ suspension (100 µL) of **3@Clay** (15 mg, content of **3**: 980 nmol) and $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (27 mg, 49 µmol).

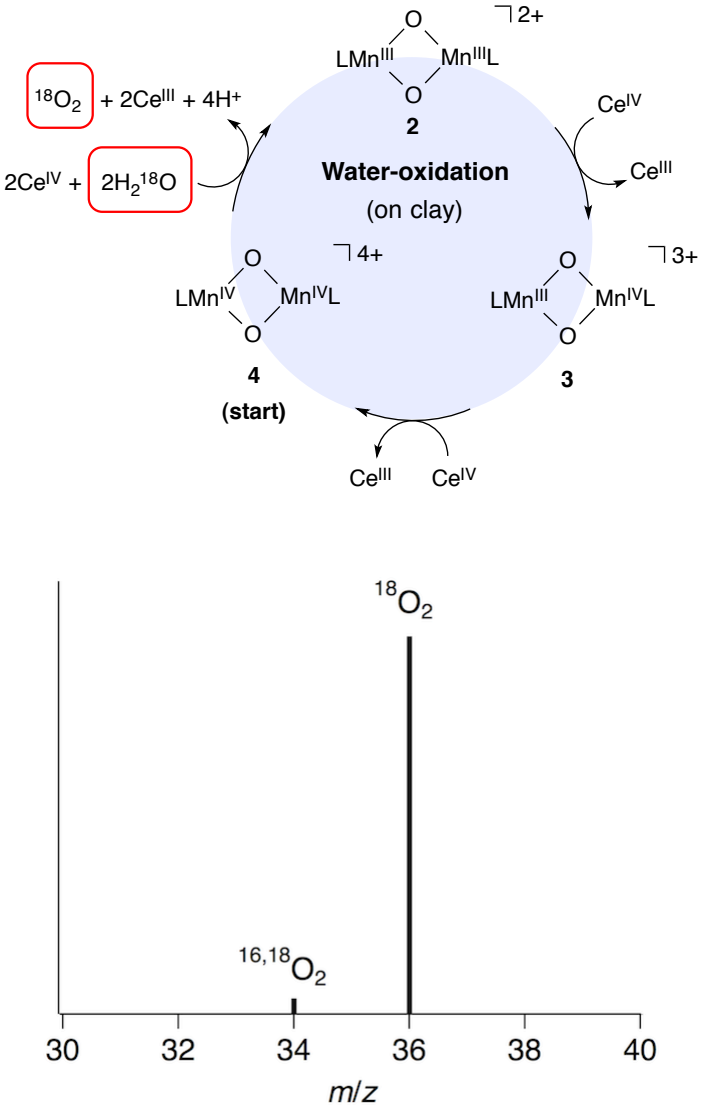

Fig. S16 Positive-ion GC mass spectrum of $^{16,18}O_2$ and $^{18}O_2$ obtained from the $H_2{}^{18}O$ suspension (100 µL) of **4@Clay** (50 mg, content of **4**: 1.0 µmol) and $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (27 mg, 49 µmol).