

Photocatalytic Water Oxidation by a Mixed-Valent $\text{Mn}^{\text{III}}_3\text{Mn}^{\text{IV}}\text{O}_3$ Manganese Oxo Core that Mimics the Natural Oxygen-Evolving Center**

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Abstract: The functional core of oxygenic photosynthesis is in charge of catalytic water oxidation by a multi-redox $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ manifold that evolves through five electronic states (S_i , where $i = 0-4$). The synthetic model system of this catalytic cycle and of its $S_0 \rightarrow S_4$ intermediates is the expected turning point for artificial photosynthesis. The tetramanganese-substituted tungstosilicate $[\text{Mn}^{\text{III}}_3\text{Mn}^{\text{IV}}\text{O}_3(\text{CH}_3\text{COO})_3(\text{A}-\alpha\text{-SiW}_6\text{O}_{34})]^{6-}$ (Mn_4POM) offers an unprecedented mimicry of the natural system in its reduced S_0 state; it features a hybrid organic-inorganic coordination sphere and is anchored on a polyoxotungstate. Evidence for its photosynthetic properties when combined with $[\text{Ru}(\text{bpy})_3]^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ is obtained by nano-second laser flash photolysis; its $S_0 \rightarrow S_1$ transition within milliseconds and multiple-hole-accumulating properties were studied. Photocatalytic oxygen evolution is achieved in a buffered medium (pH 5) with a quantum efficiency of 1.7 %.

The oxygen-evolving complex of photosystem II (PSII-OEC) in green plants, algae, and cyanobacteria is the unique catalytic site where, upon illumination, H_2O is oxidized to form O_2 .^[1] The natural OEC is a tetramanganese

calcium oxo cluster ($\text{Mn}_4\text{O}_5\text{Ca}$) that is harbored within the PSII complex, with a flexible and adaptive coordination environment provided by the protein residues.^[2] In particular, carboxylate ligands play a major role in the assembly of the OEC cluster by bridging Mn ions and the Ca^{2+} site. Dynamic binding throughout a sequence of five one-electron-step redox states (S_i , where $i = 0-4$) underpins the efficient photo-induced water oxidation that is catalyzed by the PSII-OEC and occurs under visible-light irradiation and with an exceptional turnover frequency (TOF) of $100-400 \text{ s}^{-1}$.^[3] The Achilles' heel of the PSII-OEC lies in its conceivable fragility and its mutable asset, which hampers a precise mapping of the geometry and electronic configuration for all $S_0 \rightarrow S_4$ intermediates (Figure 1). Indeed, the available X-ray data refer to an ill-defined average of highly reduced cluster states (S_{-}), which are likely formed under beam irradiation, but not directly involved in the photosynthetic cycle. A structural

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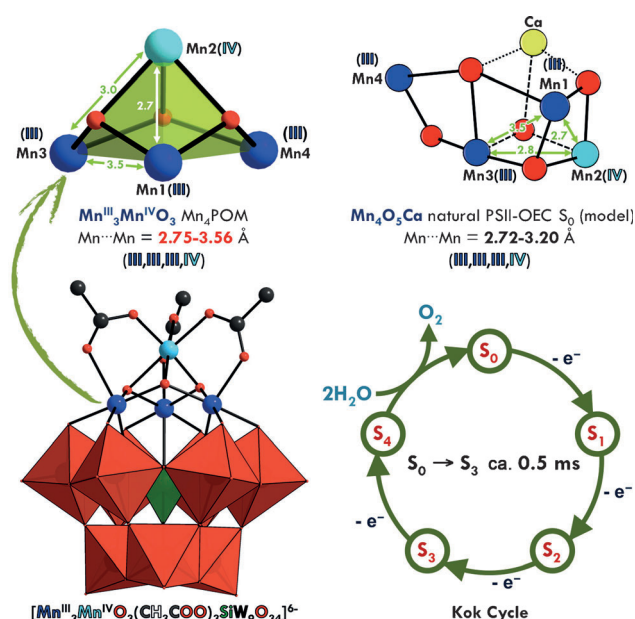


Figure 1. Combined polyhedral/ball-and-stick representation of Mn_4POM (bottom left, counter cations and water molecules in the crystal are not shown for clarity). Comparison of the Mn_4POM core (top left) with the S_0 state of the natural OEC as described by a quantum mechanics/molecular mechanics (QM/MM) model (top right).^[4] Photo-induced electron flow within the $S_0 \rightarrow S_4$ Kok cycle of the natural PSII-OEC (bottom right). Balls: calcium yellow, carbon dark grey, manganese(III) blue, manganese(IV) light blue, oxygen red; polyhedra: SiO_4 green, WO_6 red.

model for the S_0 initial state is only available in silico, addressing the starting point of the OEC four-electron oxidative staircase.^[4] In agreement with EXAFS and EPR results, the computational model for the OEC S_0 state shows a mixed-valent $Mn_4(III,III,III,IV)$ core with two short $Mn\cdots Mn$ distances (ca. 2.7 Å) and two longer ones (up to 3.2 Å).^[4]

To mimic structure and activity of the PSII-OEC, special attention has been dedicated to tetranuclear metal catalysts, including Mn-based complexes.^[5] However, only few ruthenium or cobalt tetrametallic cores have been recognized as feasible oxygen-evolving catalysts under photocatalytic conditions.^[5] We focus herein on a unique tetramanganese core that is stabilized by a hybrid set of ligands, including an all-inorganic tungstosilicate platform and three acetate bridges. The resulting polyanion, $[Mn^{III}_3Mn^{IV}O_3(CH_3COO)_3(A-\alpha-SiW_9O_{34})]^{6-}$ (Mn_4POM), displays striking similarities with the natural OEC in its S_0 state compared to the Mn_4 oxo structure and its Mn^{III}/Mn^{IV} mixed valency (Figure 1). Our results confirm that Mn_4POM undergoes fast and multiple electron transfers under visible-light irradiation, leading to water photooxidation and oxygen evolution. The structural analogy with the natural photosynthetic catalyst is thus nicely complemented by a unique functional behavior, which follows a bio-inspired mechanism (Figure 1).

Mn_4POM is readily synthesized in aqueous solution (sodium acetate buffer, pH 6) and on a gram scale by reaction of the mixed-valence compound $[Mn^{III}_8Mn^{IV}_4O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$ (Mn_{12}) with $Na_{10}[A-\alpha-SiW_9O_{34}]$ in a 1:1 molar ratio at room temperature.^[6] The key motif is a $Mn^{III}_3Mn^{IV}O_3$ core with a defective cubane arrangement, which differs from that of literature analogues (Figure 1).^[7,8] Three μ -acetate bridges define the geometry of the $Mn^{III}_3Mn^{IV}O_3$ core, with $Mn^{III}\cdots Mn^{IV}$ distances in the range of 2.749(6)–2.955(6) Å.^[6] These structural features show a direct correspondence with the calculated geometry of the natural PSII-OEC S_0 state, where $Mn^{III}\cdots Mn^{IV}$ distances fall in the range of 2.7–3.2 Å (Figure 1; see also the Supporting Information, Table S1).^[4]

According to the bio-inspired Kok cycle and the envisaged $S_0\rightarrow S_4$ four-electron transfer mechanism (Figure 1), one key requirement for efficient electrocatalytic water oxidation is a sequential multi-electron oxidation in a narrow potential window. Therefore, we have addressed the oxidation manifold of the synthetic Mn_4POM to go beyond the S_0 state analogy.

In the oxidative scan, cyclic voltammetry (CV) of Mn_4POM [0.5 mM in $Na_2SiF_6/NaHCO_3$ buffer (50 mM), Na_2SO_4 (0.5M), pH 5.2] shows one broad anodic wave at a peak potential of $E_a = 0.87$ V versus Ag/AgCl, which stems from a multi-electron oxidation of the Mn core (three electrons according to Cottrell equation analysis, in agreement with literature evidence; Figure S1).^[6] This process is then followed by the onset of a strong catalytic wave that is due to water oxidation, ($E = 1.25$ V vs. Ag/AgCl, overpotential = 0.53 V; Figure S1).^[9]

For applications within artificial photosynthesis, the final aim is to power the Mn_4POM $S_0\rightarrow S_4$ manifold by light irradiation. This is expected to occur through multiple photo-induced electron transfers, with concomitant generation of

high-valent Mn-based reactive states, enabling the water oxidation cycle and oxygen evolution. Therefore, we have explored the photocatalytic potential of Mn_4POM in a so-called sacrificial system with $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) as the visible-light photosensitizer and sodium persulfate ($Na_2S_2O_8$) as a terminal electron acceptor.^[5] In such a system, the $[Ru(bpy)_3]^{3+}$ oxidant is photo-generated by oxidative quenching of the $[Ru(bpy)_3]^{2+}$ excited state with persulfate and by a second dark reaction that involves the sulfate radical $SO_4^{\cdot-}$ [Eq. (1)–(3) in Figure 2].^[10,11] Under the

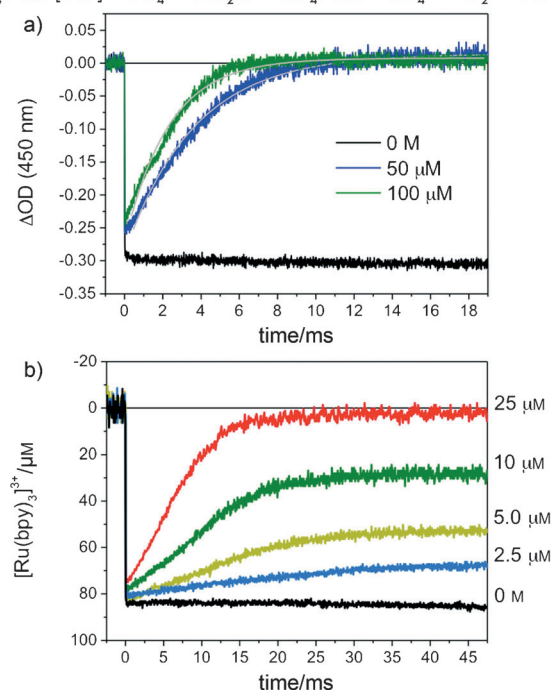
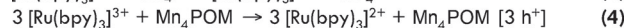
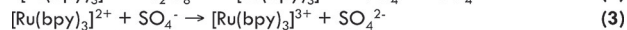
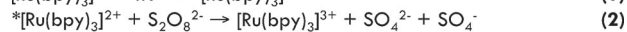


Figure 2. Laser flash photolysis experiments ($\lambda_{exc} = 355$ nm) in $NaHCO_3/Na_2SiF_6$ buffer (50 mM, pH 5.2) containing a) $[Ru(bpy)_3]^{2+}$ (50 μM), Mn_4POM (0–100 μM), and $S_2O_8^{2-}$ (5 mM; with related mono-exponential fitting), or b) $[Ru(bpy)_3]^{2+}$ (100 μM), Mn_4POM (0–25 μM), and $S_2O_8^{2-}$ (5 mM).

conditions explored, photo-generated $[Ru(bpy)_3]^{3+}$ ($E = 1.06$ V vs. Ag/AgCl) is expected to leverage the three-electron ($S_0\rightarrow S_3$) oxidation of Mn_4POM [Eq. (4) in Figure 2], whereas the $SO_4^{\cdot-}$ radical ($E = 2.40$ V vs. Ag/AgCl) is likely to be responsible for the generation of higher-valent states and oxygen evolution [Eq. (5) in Figure 2].^[12]

In this study, the photocatalytic cycle involving Mn_4POM was dissected and analyzed within two different time frames to address: 1) electron transfer (ET) kinetics spanning a millisecond time domain by laser flash photolysis and 2) oxygen-evolution kinetics, which were monitored over several tens of minutes. Fast ET between the photo-activated reaction center (RC) and the OEC is one prerogative of the natural PSII system, where the $S_0\rightarrow S_4$ Kok cycle takes place in a few

milliseconds. In this artificial cycle, ET from the Mn_4POM S_0 state to $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ proceeds through a bimolecular process [Eq. (4) in Figure 2], and its rate is expected to have a major impact on the sensitizer stability and on the overall photocatalytic performance.^[13] In the present system, the ET kinetics are conveniently probed by nanosecond laser flash photolysis upon the photo-generation of a suitable amount of $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ [Eq. (1)–(3) in Figure 2], which is detected as an instantaneous bleach of the $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ absorption ($\lambda = 450$ nm; negative ΔOD in Figure 2; ΔOD = differential optical density). ET from Mn_4POM is then expected to yield a “bleach recovery” (decay to the baseline in Figure 2), that is, the recovery of the $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ metal-to-ligand charge transfer band ($\lambda = 450$ nm).^[5] The latter observation is indicative of a parallel oxidation of the Mn_4POM S_0 state to a high-valent state.

Through proper experimental design, two pieces of information can thus be obtained from laser flash photolysis studies: 1) the second-order kinetic constant of the primary ET event from the catalyst to the photo-generated oxidant (Figure 2a), and 2) the number of electrons that can be extracted from Mn_4POM with excess $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ within milliseconds (Figure 2b). In particular, laser flash photolysis performed under pseudo-first-order conditions ($[\text{Mn}_4\text{POM}] \gg [\text{Ru}(\text{bpy})_3]^{3+}$) yielded quantitative recovery kinetics that obey a mono-exponential law (Figure 2a) with rates that are linearly dependent on the Mn_4POM concentration (Figure S4). A second-order rate constant, $k = (4.6 \pm 0.6) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, can thus be obtained for the primary ET event in the cycle, which corresponds to the Mn_4POM $\text{S}_0 \rightarrow \text{S}_1$ transition by photo-generated $[\text{Ru}(\text{bpy})_3]^{3+}$. This value is significantly lower than literature benchmarks for Mn^{II} coordination complexes^[14a] or other tetramanganese POM-based systems^[14b] and may be ascribed to the $\text{Mn}^{\text{III}} \rightarrow \text{Mn}^{\text{IV}}$ transition.^[14] Significantly, no variations of the ET kinetics were observed by laser flash photolysis upon aging of the catalyst stock solution.^[15,16]

The potential of Mn_4POM as a light-driven “hole accumulator” was assessed with laser flash photolysis using sub-stoichiometric amounts of Mn_4POM (0–25 μM) with respect to photo-generated $[\text{Ru}(\text{bpy})_3]^{3+}$ (ca. 80 μM ; Figure 2b), while extending the bleaching recovery analysis to a time scale of 50 ms (Figure 2b). On this time scale, the kinetic data confirm a well-behaved first-order dependence of the ET rate on the Mn_4POM concentration (Figure S6). Moreover, the absorption recovery reaches a plateau value that is consistent with a multi-electron oxidation of the catalyst core, and amounts to an average of three ET events, with concomitant reduction of three equivalents of $[\text{Ru}(\text{bpy})_3]^{3+}$ per catalyst. These results highlight the evolution of the Mn core within a $\text{S}_0 \rightarrow \text{S}_3$ manifold by sequential electron extraction and preceding water oxidation, which supports the mechanistic scenario in Figure 2 [Eq. (4)].^[17]

Oxygen evolution was observed in the presence of Mn_4POM (6.3–50 μM), $[\text{Ru}(\text{bpy})_3]^{2+}$ (1 mM), and $\text{S}_2\text{O}_8^{2-}$ (5 mM) in $\text{NaHCO}_3/\text{Na}_2\text{SiF}_6$ buffer (50 mM, pH 5.2) under illumination with a 150 W tungsten lamp with a 375 nm cut-off filter (illumination spot of 1 cm diameter, with a power density of 90 mW cm^{-2}). Oxygen formation was immediately

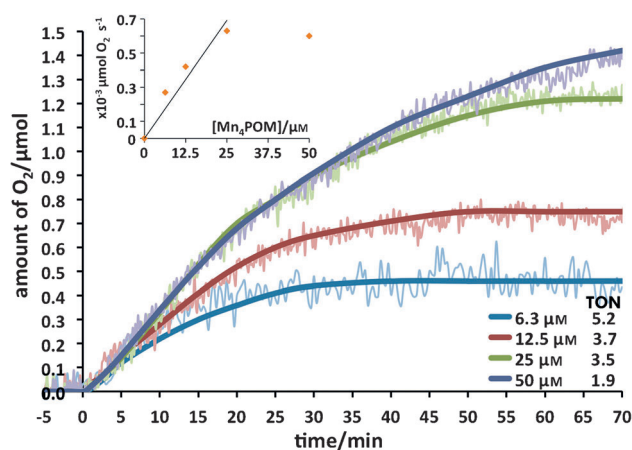


Figure 3. Oxygen production upon illumination of a solution containing Mn_4POM (6.3–50 μM), $[\text{Ru}(\text{bpy})_3]^{2+}$ (1 mM), and $\text{Na}_2\text{S}_2\text{O}_8$ (5 mM) in $\text{NaHCO}_3/\text{Na}_2\text{SiF}_6$ buffer (50 mM; pH 5.2). Raw data are presented as light traces; smooth, dark lines were added for reasons of clarity. Inset: plot of the initial rate of O_2 production versus the Mn_4POM concentration.

observed, leveling off to a plateau yield after 30–70 minutes of irradiation (Figure 3). Both the initial reaction rate and overall O_2 production depend on the catalyst concentration, with chemical yields in the range of 1.2–3.7% depending on the persulfate conversion, and a total turnover number for Mn_4POM of up to 5.2 (Table S2). The low chemical yield can be ascribed to the irreversible bleaching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ sensitizer, which occurs upon continuous irradiation and was confirmed by UV/Vis analysis of the used reaction mixture (Figure S8).^[5] The competitive degradation of $[\text{Ru}(\text{bpy})_3]^{2+}$ appears to be dominant especially at low catalyst loading (Figure S8), where the bimolecular scavenging of the reactive Ru^{III} state is slowed down. Indeed, the O_2 plateau yield increased when the Mn_4POM concentration was increased to up to 50 μM (Figure 3).

Linear fitting of the reaction kinetics that were obtained 5–20 minutes after irradiation provided the initial rate of O_2 evolution (R_0 , $[\mu\text{mol O}_2 \text{ s}^{-1}]$), which also showed a well behaved first-order dependence on the Mn_4POM concentration below 25 μM and then levels off at higher catalyst concentrations (Figure 3; see also Figure S9 and Table S2). Turnover frequency (TOF) values per manganese center of up to $0.71 \times 10^{-3} \text{ s}^{-1}$ were calculated: these values are significantly higher than those generally observed for bulk Mn oxides, which are on the order of 10^{-5} s^{-1} (Tables S2 and S3).^[18,19]

Control experiments using an equimolar amount of Mn^{2+} ions, which were introduced as $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, led to negligible O_2 production (Table S2). Moreover, the FT-IR features of the solid material that was recovered after the reaction are reminiscent of the fingerprint of pristine Mn_4POM (Figure S10). Altogether, these results are indicative of a mechanism for oxygen evolution that involves the four Mn centers of the catalyst core. A quantum efficiency^[5] of 1.7% was calculated for a kinetic trace at a Mn_4POM concentration of 25 μM , when the reaction mixture was irradiated with

a monochromatic light-emitting diode (LED) emitting at 450 nm (power: 7 mW, photon flux: 2.63×10^{-8} einstein s⁻¹).

In conclusion, a novel strategy to access a synthetic Mn₄ oxygen-evolving center is based on the combined presence of an inorganic POM platform and carboxylate bridges. This hybrid set of ligands is used to shape a defective Mn₄ core with mixed valence, multi-redox properties, and photocatalytic behavior. The interplay of organic and inorganic residues provides a coordination environment with both stability and flexibility to assist stepwise one-electron oxidation of the catalytic core and to access high-valent Mn states that are responsible for water oxidation. Mn₄POM is the first manganese-containing POM that is catalytically active towards photo-induced water oxidation.^[19] XAS spectroscopy will be used in the future to study the Mn-based manifold. Further work will be dedicated to tune the composite ligand set to lower the overpotential and increase quantum efficiency with the perspective of developing a regenerative photoelectrochemical cell.

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