

Sustained Water Oxidation Photocatalysis by a Bioinspired Manganese Cluster**

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The creation of efficient catalysts for splitting water into H_2 and O_2 is one of the greatest challenges for chemists working on the production of renewable fuel.^[1,2] The water oxidizing center (WOC) within photosynthetic organisms is the only natural system able to efficiently photooxidize water using visible light, and is thus a blueprint for catalyst design.

One of the atomic structural models of the WOC derived from X-ray diffraction involves a “cubelike” core comprised of a $\{CaMn_3O_4\}$ unit tethered to a fourth manganese atom through one or two bridging oxo units.^[3] A few nonbiological tetramanganese complex mimics of this site have been prepared that contain an incomplete or distorted cubic $\{Mn_4O_x\}$ core^[4–7] or are part of a larger Mn_x -oxo lattice.^[4] However, none of these have shown activity towards water oxidation.

We have previously synthesized a prototypical molecular manganese-oxo cube $[Mn_4O_4]^{n+}$ in a family of “cubane” complexes $[Mn_4O_4L_6]$, where L^- is a diarylphosphinate ligand ($p\text{-}R\text{-}C_6H_4)_2PO_2^-$ ($R = H, \text{alkyl}, \text{OMe}$).^[6,8] The diphenylphosphinate complex (**1**, $R = H$, Figure 1) assembles spontaneously from manganese(II) and permanganate salts in high yield in non-aqueous solvents.^[9] The release of O_2 by the $\{Mn_4O_4\}^{6+}$ core in **1** was shown to be possible on thermodynamic grounds, but cannot take place because of the rigidity of the core arising from the six diarylphosphinate ligands, which bridge pairs of manganese atoms on the six cube faces. The assembly of **1** is also driven by intramolecular van der

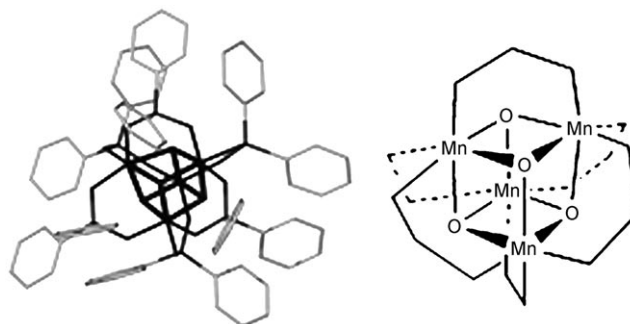


Figure 1. X-ray crystal structure of **1**.^[6]

Waals forces that attract three aryl rings from adjacent phosphinate ligands.

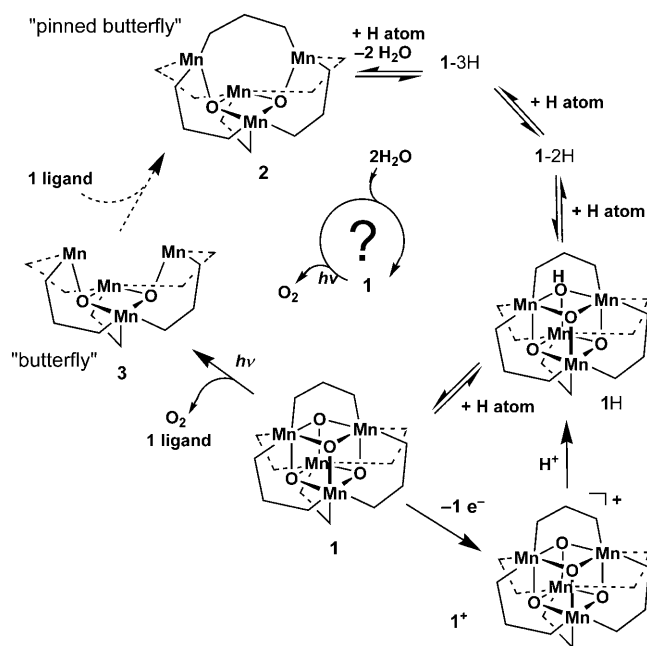
The cubic core in **1** is a much stronger oxidant than any known dimanganese complex with $\{Mn_2O_2\}^{3+}$ cores. Cubane **1** abstracts hydrogen atoms from various organic substrates by breaking O–H and N–H bonds with dissociation energies greater than 390 kJ mol^{-1} .^[10] Titrations of **1** against compounds containing either amine or phenol groups reach an end point after the abstraction of four successive hydrogen atoms, yielding two water molecules (from corner oxo groups) plus $[L_6Mn_4O_2]$, the so-called “pinned butterfly” complex **2** (Scheme 1).^[11] $\{Mn_4O_4\}$ cubane complexes are unique in releasing an O_2 molecule upon photoexcitation of the $Mn-O$ charge transfer band, which reaches a maximum at 350 nm .^[12,13] This process, which occurs with high quantum efficiency only in the gas phase, involves the core oxygen atoms and is triggered by ejection of one phosphinate ligand, thereby generating the $[L_5Mn_4O_2]^+$ “butterfly” complex **3** (Scheme 1). In contrast, noncuboidal manganese molecular complexes possessing $\{Mn_2O\}$, $\{Mn_2O_2\}$, and $\{Mn_3O_6\}$ cores in the Mn^{3+} or Mn^{4+} oxidation states fail to release O_2 , but instead photodecompose into multiple fragments.^[13] Thus, O_2 release is favored by complexes with a $\{Mn_4O_4\}$ cubane core.

The composition of the butterfly complexes **2** and **3** differs only by one phosphinate ligand (Scheme 1). This finding suggests the possibility of creating a catalytic cycle that could oxidize two water molecules bound to **2** along the reverse pathway in Scheme 1 ($1\text{-}3H \rightarrow 1\text{-}2H \rightarrow 1\text{-}H \rightarrow 1$), eventually forming **3** by photochemical release of O_2 and a phosphinate ligand. Thus far it has proved impossible to realize a catalytic cycle, as in Scheme 1, because O_2 is not photodissociated from **1** or **1**⁺ (the one-electron oxidized cubane) in condensed phases.^[12–14] This was attributed to a large activation barrier for O_2 release when all the phosphinate ligands remain ligated or re-ligate by fast geminate recombination.

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Scheme 1. Reaction pathways and a possible photocatalytic cycle for **1**. Observed reduction reactions of **1** and **1**⁺ in solution and the gas-phase photodissociation to yield O₂. Reverse arrows show the proposed reoxidation steps that regenerate the cubanes.

The highest oxidation state observed in the cubane family contains the {Mn₄O₄}⁷⁺ core, ([L₆Mn₄O₄]⁺ (**1**⁺) or “cubium”), which has been structurally characterized.^[14,15] **1**⁺ is capable of abstracting hydride anions by cleaving bonds with enthalpies greater than 527 kJ mol⁻¹.^[10] Cubiums are ferocious oxidants with thermodynamic overpotential to drive water oxidation, but are kinetically prevented from doing so.

The insolubility of **1** in water and most organic solvents makes the investigation of these transformations in the presence of water virtually impossible. We have overcome these limitations by the use of a two-phase water/Nafion system. This allows the photooxidation system to function in the presence of water, as well as providing possible alternative binding sites on the polymer-bound sulfonate anions within Nafion. We report that ion exchange of cubium **4**⁺ (L⁻ = bis(4-methoxyphenyl)phosphinate)^[14] into a thin Nafion membrane deposited on a conducting electrode yields a robust catalyst that sustains the photo-electrooxidation of water to O₂.

The perfluorinated polymer Nafion can be cast as a membrane that comprises hydrophobic domains separated by ionizable, hydrated head groups (sulfonic acids) that line the aqueous channels (reported diameter ca. 20 nm) traversing the polymer domains.^[16] These channels are good proton conductors that are permeable to cations but not to anions.^[17] These properties make Nafion an excellent medium within which to immobilize hydrophobic cations, whilst maintaining direct contact with an aqueous electrolyte. Several hydrophobic Ru-oxo complexes have been found to function as water oxidation catalysts when immobilized within a Nafion membrane.^[18,19]

Colorimetric, NMR, EPR, and electrochemical studies (see Figures S1 and S2 in the Supporting Information) show that **4**⁺ in CH₃CN solution readily exchanges with protons in Nafion membranes (3–8 μm thick) deposited onto quartz or conducting electrodes. Subsequent immersion in water prevents **4**⁺ from leaching from the Nafion. The UV/Vis spectrum of this material (**4**⁺/Nafion/quartz) in water reveals the presence of bands that are characteristic of an intact {Mn₄O₄}ⁿ⁺ core with a red-shift of 30 nm relative to **4**⁺ in CH₂Cl₂ (see Figure S1 in the Supporting Information). Cyclic voltammetry on the **4**⁺/Nafion/glassy carbon system immersed in aqueous electrolyte displays a broad oxidation peak (see Figure S2 in the Supporting Information) at E_f⁰ = 0.84 V (all potentials referenced to Ag/AgCl). The **4** ↔ **4**⁺ transition is sharper than that in CH₂Cl₂ but at similar potential (E_f⁰ = 0.74 V).

When the **4**⁺/Nafion/glassy carbon electrode is polarized at 1.00 V it generates a transient dark current that decays nearly to zero (solid line in Figure 2a). Illumination with white light (filtered Xe source) results in a substantial increase in this current. The photocurrent decays to the baseline when the light is switched off. Extended illumination experiments reveal that the photocurrent slowly degrades to approximately 75% of the initial current, where it remains

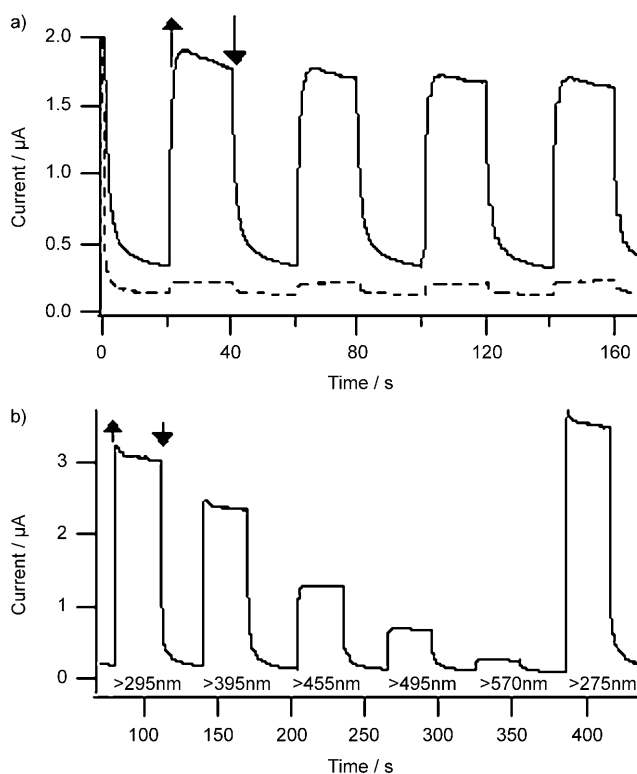


Figure 2. Photocurrent of **4**⁺/Nafion/glassy carbon: a) Amperogram at 1.00 V (vs Ag/AgCl) of doped Nafion (—) and undoped Nafion (---) in Na₂SO₄ (aq, 0.1 M) at 22 °C. The samples were exposed to a filtered Xe light source (275–750 nm, 150 mW cm⁻²), the “up” arrow indicates light on, the “down” arrow light off. b) Photocurrents generated by using long wavelength pass filtered light in alternating periods of 30 s of light followed by 30 s of dark (labels under peaks specify filter cutoff wavelength, 275 nm is the cutoff of the pyrex glass electrochemical cell).

stable for up to 65 h (see Figure S3 in the Supporting Information). The undoped Nafion/glassy carbon electrode generates a small background current under these conditions (as shown) which is comparable to the current of the unmodified electrode.

The photocurrent increases from zero at potentials less than 0.80 V, to reach a maximum at 1.00 V, which coincides with the completion of the $4^+/4$ oxidation process observable in the dark. Thereafter, the photocurrent remains constant at least up to 1.2 V. It also increases linearly with an increase in the pH value from 2 to 12 when an unbuffered solution is used (Figure 3a). This result is consistent with the oxidation of water, for which the electrochemical potential decreases by 59 mV per pH unit.^[20]

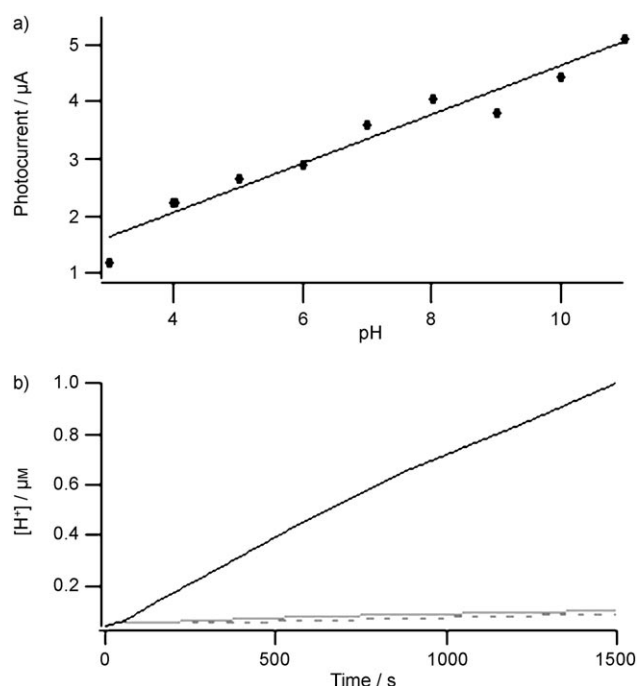


Figure 3. a) Dependence of the photocurrent from 4^+ /Nafion/glassy carbon electrode at 1 V (vs Ag/AgCl) in Na_2SO_4 (aq, 0.1 M) on the pH value. This dependence was fully reversible. b) Proton production by illuminated cubane-doped Nafion (black) and undoped Nafion (gray, 365 nm light emitting diode (LED) output 5 mWcm^{-2}) and Nafion dark current (dashed) on 10 mm^2 indium-tin oxide (ITO) electrode in Na_2SO_4 (aq, 0.1 M).

Further tests confirmed that the photocurrent is observed only when water is present in the electrolyte solution. No photocurrent is produced in pure acetonitrile (0.1 M Bu_4NPF_6 electrolyte). The products of the sustained photocurrent reaction were identified by pH determination, oximetry (O_2 Clarke electrode), and mass spectrometry. For the 4^+ /Nafion/glassy carbon photoanode the observed accumulation of protons in solution was over 18 times that observed for the system that contained only Nafion (Figure 3b; see the Supporting Information for all experimental details). Detection of dissolved O_2 in the electrochemical cell by using a Clarke electrode confirmed photoproduction of O_2 . Electrical interference between the electrodes meant that this config-

uration could not be used for continuous O_2 measurements; therefore, gas-phase detection of O_2 was examined.

Mass spectrometry of the gas evolved during a 1 h illumination period of the 4^+ /Nafion/glassy carbon photoanode immersed in ^{18}O -labeled water (50% H_2^{18}O , 0.1 M Na_2SO_4), revealed a significant increase in $^{36}\text{O}_2$ concentration ($m/z = 36$, see Figure S4 in the Supporting Information). Control experiments using an undoped Nafion/glassy carbon electrode yielded no significant increase in $^{36}\text{O}_2$. Thus, bulk water is unequivocally the source of O_2 .

The volume of the evolved gas was compared to the integrated photocurrent passed during water photoelectrolysis using a custom-built gas collection vessel. A total of $32 \mu\text{L}$ of gas was collected from the surface of a 4^+ /Nafion/Pt working electrode ($10 \times 15 \text{ mm}$) held at 1.00 V during illumination with filtered Xe light (7.5 h, 100 mWcm^{-2}). This volume corresponds to $1.31 \mu\text{mol}$ of O_2 at standard temperature and pressure. The total charge collected was 0.49 C, which corresponds to $5.1 \mu\text{mol}$ of electrons. This amount of charge would be expected to produce $1.27 \mu\text{mol}$ of O_2 , based on a 4:1 stoichiometry of electrons per O_2 molecule, and is in agreement with the volumetric result. No gas bubbles or significant photocurrent were detected from an equivalent unmodified electrode under the same illumination and biasing conditions.

Electrolysis of a typical 4^+ /Nafion/glassy carbon electrode in the dark using the observed one-electron couple for $4^+/4$ at 0.84 V was used to estimate that 0.27 nmol of electroactive species are present in a typical membrane. During photoelectrolysis for 65 h (see Figure S3 in the Supporting Information), the membrane passed a net charge of 0.163 C under illumination in aqueous Na_2SO_4 (0.1 M) at 1.00 V. This charge equates to approximately 1000 turnovers per putative Mn_4 unit.

Long wavelength pass filters were used to measure the spectral range of the photocurrent. As depicted in Figure 2b, the 4^+ /Nafion electrode generates a photocurrent when irradiated with visible light (wavelength $> 395 \text{ nm}$). The photocurrents (illuminated current minus dark current) were typically 15–20 times larger than those observed for unmodified Nafion-coated electrodes. To the best of our knowledge, sustained water photooxidation catalysis in the visible region is quite rare, having been reported only for complex multielemental semiconductors.^[21]

Electrodes in which Nafion is doped with manganese(II) salts $[(\text{bipy})_2\text{Mn}(\mu\text{-O})_2\text{Mn}(\text{bipy})_2]^{3+}$ ($\text{bipy} = 2,2'$ -bipyridine)^[22] from aqueous or acetonitrile solutions, and either colloidal MnO_2 or MnO_2 synthesised in situ from manganese(II) within Nafion by electrolysis were prepared in a similar fashion. They produced no significant photoeffect at comparable loadings and biasing conditions of 1.00 V. Additionally, the photocurrent produced by 4^+ /Nafion/glassy carbon electrodes declined to that of undoped Nafion/glassy carbon electrodes when the catalytically active ingredient was leached out by extended immersion/ion exchange with other cations, including $[(\text{bipy})_2\text{Mn}(\mu\text{-O})_2\text{Mn}(\text{bipy})_2]^{3+}$ or copper(II) in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ solutions. The photocurrent is, moreover, observed with a wide range of electrolytes (Na_2SO_4 , NaF , Bu_4NPF_6 , Bu_4NClO_4) and for 4^+ -doped

Nafion membranes deposited on a range of conductive surfaces (glassy carbon, platinum, fluorine-doped SnO_2 -coated glass). No photocurrent is observed for undoped Nafion-coated electrodes or for Nafion doped with salts such as NaClO_4 or sodium diphenylphosphinate. Thus, photocurrent generation requires the presence of 4^+ , Nafion, water, and electrical bias, and the final products of the photoanode reaction are O_2 and protons.

In summary, we have shown that a Nafion membrane doped with cubium 4^+ electrooxidizes water at potentials between 0.8–1.2 V (vs Ag/AgCl) upon activation with light. The active species and mechanism of the catalysis remain to be fully elucidated. The requirement for light implies that there is an additional limiting reaction required for catalyst activation, which effectively contributes to a larger overpotential.

The accumulated evidence points to a catalytically active species originating from the photolysis of 4^+ which is bound to or activated by the sulfonate groups of the aqueous Nafion membrane. We postulate that the aqueous 4^+ /Nafion/electrode system exhibits the same photoreaction as seen for 4 and 4^+ in the gas phase,^[14] with O_2 being released only upon photodissociation of a phosphinate anion to yield the “reduced butterfly” species $[\text{L}_5\text{Mn}_4\text{O}_2]^{2+}$ (Scheme 1). This species is known to slowly polymerize if formed in organic solvents,^[11] but appears to be more stable in the restricted hydrophobic pockets of Nafion. The charge-transfer absorption band of the $[\text{Mn}_4\text{O}_4]$ core of 4^+ is red-shifted by 30 nm in Nafion (see Figure S1 in the Supporting Information), which contributes to the extension of photoactivity into the visible spectrum in Nafion. Water is known to bind to manganese ions in a reduced butterfly complex that forms reductively in solution.^[11] Thus, the most plausible, albeit postulated, mechanism for the oxidative branch of the catalytic cycle in Nafion is the light-independent electrooxidation of $[\text{L}_5\text{Mn}_4\text{O}_2]^{2+} + \text{L}^- + 2\text{H}_2\text{O}$ to reform the cubium 4^+ and four hydrogen ions that are released into solution.

If the requirement for light proves to be associated only with the one-ligand release step and not oxidation (Scheme 1), then a plan of attack to lower the barrier can be readily envisioned for future work.

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