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Water Splitting

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A Porphyrin-Doped Polymer Catalyzes Selective, Light-Assisted Water Oxidation in Seawater

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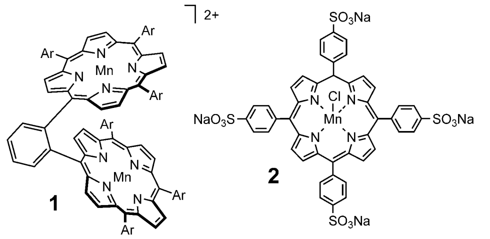
In a classic experiment, Naruta and co-workers demonstrated in 1994 that the dimanganese complexes **1** (Scheme 1) facilitate water oxidation catalysis yielding dioxygen (O_2) at potentials above 1.2 V vs. Ag/AgCl.[1] The corresponding, unconnected Mn-porphyrin monomers were, however, catalytically inactive.[1] Subsequent work suggested that O–O bond formation leading to O_2 generation by **1** involved a concerted interaction between two short-lived, high-valent Mn^{V}=O intermediates at each of the porphyrins, presumably during conformational flexing of the dimer.[2] The transience and brief lifetime of these intermediates likely rendered the free monomers inactive. Catalytic actions like those of **1**, which encompass a synchronized, cooperative interplay between two or more catalytic groups, are of significant fundamental and practical interest.[3] For example, enzymes are believed to employ synchronous protein motions to cooperatively harness reactive intermediates that are often too short-lived to be utilized in other classes of catalyst.[3–5] This may explain how they can catalyze some reactions that cannot be catalyzed outside of biology. The question that arises is: how can one design simple, practical abiological molecular catalysts to synchronously harness very short-lived reactive intermediates? In a previous report[6] we described an approach to this problem that involved drastically concentrating the corresponding monomeric catalytic groups within a limited volume. This may conceivably cause some small but statistically significant proportion of the monomers to be adventitiously ideally placed to facilitate cooperative catalysis. If the monomer-bound reactive intermediates are too short-lived to be sequestered and exploited in any other way, then only the product deriving from cooperative catalysis should be obtained.[6] Here we report the application of this “statistical proximity” approach[6] to water oxidation catalyzed by Mn-porphyrins. We show that concentration of the sulfonated, monomeric Mn-porphyrin **2** (Scheme 1), which is normally catalytically inactive,[7] within a thin layer of poly(terthiophene) (PTTh) yields a remarkable light-assisted catalyst with a low overpotential for water oxidation at pH 7. The catalyst selectively oxidizes water before chloride in seawater.



Scheme 1. Diporphyrin **1** and monomer porphyrin **2**. Ar = 4-tBuC_6H_4, 2,4,6-$Me_3C_6H_2$, or C_6F_5.

Mn-porphyrin monomer **2** was uniformly incorporated as an anionic counter-ion into a thin PTTh film during the electrochemical polymerization of TTh monomer in ethanol/dichloromethane (1:1 by volume) containing **2** (see Supporting Information). PTTh-**2** was deposited as a composite film onto indium tin oxide (ITO) glass or flexible ITO-coated poly(ethylene terephthalate) (PET) sheet. Figure S1 (Supporting Information) shows the flexible electrode obtained when PTTh-**2** was coated on ITO-PET. UV/vis measurements confirmed the incorporation of **2** in the coating. Energy-dispersive X-ray mapping indicated that **2** was uniformly dispersed in the coating (Figure S3). Elemental analysis indicated a high density of **2** within the PTTh-**2**, with the mole ratio of **2** (identified by Mn + S):terthiophene (identified by S) being ca. 1:3.

The PTTh-**2** films were then studied as putative working electrodes in photocatalytic oxygen generation from water. Cyclic voltammograms (CVs) of the PTTh-**2**/ITO glass electrode were taken with and without illumination using SoLux daylight MR16 halogen light bulbs (12 V, 50 W, 24°) in an aqueous 0.1 M Na_2SO_4 electrolyte. Figure 1 depicts the data that was obtained. As can be seen, the CVs with and without light are significantly different. Substantially larger currents were observed positive of 0.68 V with illumination than without illumination. This is a region in which we have previously observed water oxidation in comparable systems.[8] Moreover, the reduction peak A in Figure 1 was also observed only under illumination. In our experience, peaks of this type are often characteristic of adsorbed dioxygen.[6]

To study the peak at A, we conditioned the PTTh-**2** coating in aqueous 0.1 M Na_2SO_4, by maintaining it at 0.8 V (**I**), 0.9 V (**II**), or 1.0 V (**III**) for 1 h, and then immediately thereafter, performing a linear sweep voltammogram (LSV). The resulting LSV data are shown as the inset in Figure 1. As can be seen, under these conditions the broad peak at A resolves into two separate peaks: a large peak A′ and a small

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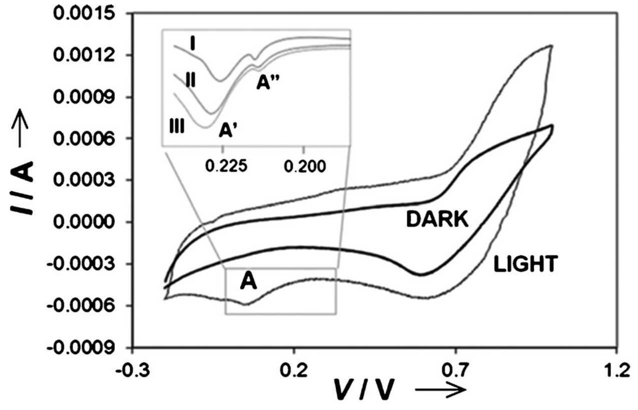

Figure 1. Cyclic voltammograms (vs. Ag/AgCl) of PTTh-**2** on ITO glass in aqueous 0.1 M Na_2SO_4 (pH 7) with ("light") and without ("dark") illumination using SoLux daylight MR16 halogen light bulbs (12 V, 50 W, 24°). The inset displays linear sweep voltammograms of the peak A taken immediately after the electrode was pre-conditioned for 1 h by maintaining it at potentials of 0.8 V (**I**), 0.9 V (**II**), and 1.0 V (**III**). Scan rate: 50 mV s^{-1}.

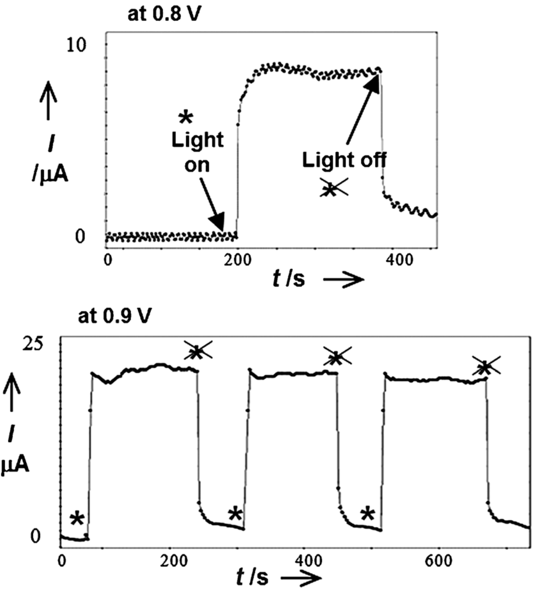

Figure 2. Currents with and without illumination, by PTTh-**2**/ITO glass in 0.1 M Na_2SO_4 (aq) at 0.8 V (top) and 0.9 V (bottom) vs. Ag/AgCl. Stars signify "light on". Stars with crosses through them indicate "light off".

peak A″. In previous studies of oxygen reduction catalysts we demonstrated that the large peak at A′ was indicative of adsorbed dioxygen, while the small peak at A″ was characteristic of adsorbed peroxide.[6] Thus, it appeared that dioxygen was formed in large proportions on the PTTh-**2** coating when it was poised at one of the above voltages. Moreover, the peak height of A′ increased from **I** to **II** to **III**, suggesting that the quantity and proportion of O_2 increased with the applied voltage from 0.8 to 1.0 V. The ratio of the peak areas of A″ (H_2O_2):A′ (O_2) in **III** was ca. 7:93.

To examine this effect, we studied the PTTh-**2**/ITO glass electrode in aqueous 0.1M Na_2SO_4 (pH 7) at constant potentials of 0.8 V and 0.9 V vs. Ag/AgCl, with and without illumination. Figure 2 depicts representative data. As can be seen, in the dark, PTTh-**2**/ITO glass yielded essentially no current when poised at both 0.8 V and 0.9 V. However, under illumination, an immediate photocurrent of ca. 9 µA at 0.8 V and 23 µA at 0.9 V was observed. The photocurrent disappeared when the light was turned off and re-appeared when the light was turned on (Figure 2, bottom). The photocurrent persisted in overnight runs. Under comparable conditions, PTTh doped with *p*-toluene sulfonate (PTTh-pTS), coated onto ITO glass, yielded much smaller photocurrents (ca. 0.5 µA at 0.8 V and 1.6 µA at 0.9 V) and did not display peaks A, A′ or A″ in LSV's like Figure 1. The use of 0.1M Na_2SO_4 electrolytes containing **2** in up to 0.1M also yielded no current when poised at 0.8 V or 0.9 V, with or without illumination. By contrast, under constant illumination over 24 h at 0.9 V, the PTTh-**2**/ITO glass electrode yielded a steady photocurrent with associated gas bubble formation. GC-MS confirmed the bubbles were pure O_2.

The standard potential for water oxidation at pH 0 is 1.23 V vs. standard hydrogen electrode (SHE). However, at pH 7 the minimum theoretical potential to drive water oxidation falls to 0.82 V vs. SHE.[8] Figure 1 indicates that the earliest onset of water oxidation using illuminated PTTh-**2**/ITO glass is 0.68 V vs. Ag/AgCl, which equates to 0.91 V vs. SHE. The overpotential for water oxidation catalysis by PTTh-**2** at pH 7 is therefore suggested to be 0.09 V.

This compares favorably with other efficient water oxidation catalysts, like IrO_2 and Co-pi, which facilitate catalysis from 1.23 V vs. SHE at pH 7 without light-assistance.[9] The photosystem II water oxidizing complex of photosynthesis operates from 1.25 V vs. SHE.[8] Of course, deposition of catalysts like Co-pi on light-activated semiconductors like Si or WO_3, yields water oxidation at much lower applied potentials under illumination.[10] But these potentials need not reflect the true overpotential of the catalyst. They may arise because, under illumination, the semiconductor facilitates catalysis at an anomalously low applied potential.

One way to test whether PTTh-**2** genuinely diminishes the overpotential is to examine its catalytic selectivity for O_2 generation over Cl_2 generation in near-neutral solutions containing chloride ions, like seawater. While water oxidation is thermodynamically favored over chloride oxidation (E° 1.36 V vs. SHE), its overpotential is higher for virtually all catalysts.[11,12] When near-neutral solutions containing chloride ions are electrolyzed, Cl_2 is therefore preferentially formed.[11,12] In previous work, we demonstrated that such Cl_2 formation in seawater typically commences at 1.15 V vs. Ag/AgCl.[11] However, Figure 1 and Figure 2 show that illuminated PTTh-**2** catalyzes O_2 formation at applied potentials above 0.68 V vs. Ag/AgCl, which is well below 1.15 V. If this reflects a genuinely low overpotential, then PTTh-**2** should selectively oxidize water before chloride in seawater.

To perform this test, we repeated the studies using seawater electrolyte (pH 8.57, conductivity 16.02 mS, after filtration). Comparable data were obtained to the earlier experiments. Figure 3 depicts experimental data which illustrate the key effects observed. Figure 3a shows LSVs of a

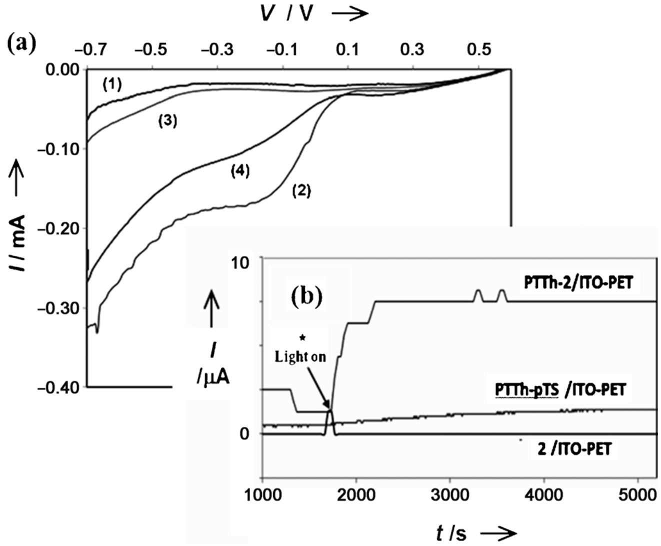

Figure 3. a) Linear sweep voltammograms using seawater as electrolyte, showing the region of peak A in Figure 1 for: (1) Pt electrode under an atmosphere of N_2, (2) Pt electrode under an atmosphere of O_2, (3) PTTh-pTS deposited on Pt, after potentiostatic conditioning under illumination at 0.9 V (vs. Ag/AgCl) for 60 min, and (4) PTTh-**2** deposited on Pt, after potentiostatic conditioning under illumination at 0.9 V (vs. Ag/AgCl) for 60 min. Scan rate: 50 mVs^{-1}. b) Chronoamperogram under illumination, using seawater as electrolyte at a fixed potential of 0.9 V for PTTh-**2** on ITO-PET, PTTh-pTS on ITO-PET, and ITO-PET in a solution containing 0.1 M **2**.

bare Pt wire electrode positioned in the middle of the seawater after degassing and re-gassing under a strict: (1) N_2-atmosphere and (2) O_2-atmosphere. As can be seen, the presence of O_2 created the expected, distinctive voltammetric wave at potentials negative of 0.1 V, which is typical for oxygen reduction reactions. As shown in curve (3) in Figure 3a, when the electrode was coated with PTTh-pTS, which was then conditioned by being poised at 0.9 V (vs. Ag/AgCl) for 60 min, the LSV of the Pt wire was found to be not dissimilar to that of the Pt wire under N_2. However, as depicted in curve (4), when the electrode was coated with PTTh-**2** and conditioned under the same circumstances, the LSV of the Pt wire was found to be distinctly similar to that of the Pt wire under O_2. The only reasonable explanation is that O_2 was evolved from the PTTh-**2**, but not from the PTTh-pTS coating.

The graph in Figure 3b shows photocurrents over time under illumination with light, at a static potential of 0.9 V vs. Ag/AgCl, for a flexible ITO-PET electrode in seawater. When the seawater contained 0.1 M **2**, no catalytic photocurrent was observed. When the electrode was coated with PTTh-pTS, only a small photocurrent (0.5–1.25 μA) was seen. However, when the electrode was coated with PTTh-**2**, a large and sustained photocurrent was observed, with accompanying formation of bubbles. GC-MS confirmed the evolution of pure O_2, with no Cl_2 detected. Independent measurements using Merckoquant analytical test strips indicated an absence of chlorine down to the limit of detection for this technique, which equated to 0.8% of the photocurrent going into Cl_2 production (see section S5 in the Supporting Information). Thus, more than 99.2% of the photocurrent was consumed by water oxidation.

In summary: under illumination, the composite PTTh-**2** selectively catalyzed water oxidation before chloride oxidation in seawater at 0.9 V vs. Ag/AgCl. PTTh-pTS does not display a comparable effect, nor does **2** when it is dissolved in the electrolyte. It therefore appears to be a combination of a high loading of **2** and the PTTh that creates the catalytic effect.

This conclusion is supported by the action spectrum of PTTh-**2** relative to PTTh-pTS (Figure S7), which indicates that the photocatalytic effect derives from light absorption by **2** in a band having $\lambda_{max} = 375$ nm and which tails out to 525 nm. Electrochemical impedance spectroscopy indicates that the charge transfer resistance of PTTh-**2** was drastically decreased under light illumination (Figure S8).

This data suggests that **2** injects electrons into PTTh upon absorption of light at applied potentials above 0.68 V vs. Ag/AgCl. The resulting reduced form of PTTh must necessarily be immediately re-oxidized by the electrode back to its conducting form. The high-valent, oxidized form of **2** that remains then presumably facilitates water oxidation by extracting electrons from water. The resulting catalytic reaction clearly has a lower overpotential than that of chloride oxidation.

An electron shuttle effect therefore appears to be created in which the illuminating light induces an overall flow of electrons from water to **2** to PTTh to the electrode. PTTh doped with anionic light-harvesting dyes have previously been shown in our laboratory to display photovoltaic properties.[13] The sulphonic acid groups on **2** could form a conduction pathway for transfer of the H^+ ions generated during water oxidation to the electrolyte solution.

Water oxidation catalysts are known to generally operate by either a bimolecular (e.g. **1**) or monomolecular (nucleophilic attack) mechanism.[14] Some species, like Mn corroles, simultaneously facilitate both bimolecular and monomolecular mechanisms.[14] In the case of PTTh-**2**, however, nucleophilic attack in the presence of Cl^- should also generate HClO which spontaneously equilibrates to form Cl_2 in water. As no Cl_2 was observed, the monomolecular mechanism presumably has a negligible role. Water oxidation catalysis in PTTh-**2** is therefore implied to occur by a bimolecular mechanism not dissimilar to that employed by **1**. A synchronous action of this type would be available to only a statistically small proportion of the monomers **2** that happened to be adventitiously disposed for cooperative interactions within the PTTh.

Further work is underway to unambiguously ascertain the mechanism and the roles of the different components in PTTh-**2**. As yet, no physical evidence is available to demonstrate catalytic interactions between monomeric porphyrins, nor the intermediacy of dinuclear peroxides which release O_2 upon illumination.

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