

A 2-(2-hydroxyphenyl)-1H-benzimidazole–manganese oxide hybrid as a promising structural model for the tyrosine 161/histidine 190-manganese cluster in photosystem II†

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In this communication, we report the synthesis, characterization, and electrochemistry of a 2-(2-hydroxyphenyl)-1H-benzimidazole–manganese oxide hybrid. Our results suggest that this compound is a promising model for the manganese cluster together with tyrosine-161 and histidine-190 in photosystem II of plants, algae and cyanobacteria.

Catalysts for water oxidation are at the heart of key renewable-energy technologies. This could ultimately include water splitting and efficient evolution of hydrogen and, of course, oxygen, in an artificial system. In order to reach this goal, and in a sustainable manner, it is necessary first to develop a stable and efficient catalytic system for water oxidation, which is the more challenging part of the water splitting reaction.¹ One way to try to realize a new potential catalyst is by biomimetic means, *i.e.*, by using the understanding and the application of biological strategies found already in nature.²

In oxygenic photosynthesis, photons are absorbed by antenna molecules of both the photosystems (I and II), and then the excitation energy is transferred from them to their respective reaction centers. PSII oxidizes water, as mentioned above, and reduces plastoquinone.^{3,4}

Biological water oxidation occurs only at the water oxidizing complex (WOC) of photosystem II (PSII) in cyanobacteria, algae and plants.⁵ The most recent structure of PSII at 1.9 Å resolution reveals detailed atomic level information about the WOC (Fig. 1).^{6,7}

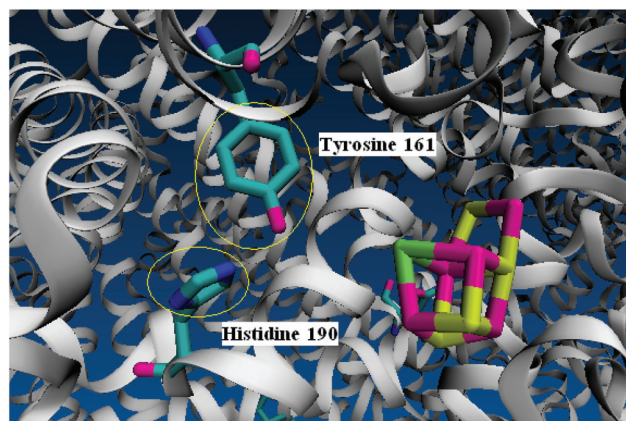


Fig. 1 Mn_4O_5Ca cluster in PSII is housed in a special protein environment (nitrogen: blue; oxygen: pink; manganese: yellow, calcium: green; protein environment: light grey). The locations of tyrosine 161 and histidine 190 are shown within yellow circles. The image was made with VMD and is owned by the Theoretical and Computational Biophysics Group, NIH Resource for Macromolecular Modeling and Bioinformatics, at the Beckman Institute, University of Illinois at Urbana-Champaign. The original data were from ref. 6 (PDB: 3ARC).

In the WOC cluster, there are four manganese ions and one calcium ion bridged by five oxygen atoms; there are also four water molecules, and one of the two pairs is suggested to be the precursor to oxygen in the structure.^{6,7}

At the reaction center II, primary charge separation occurs where a chlorophyll dimer (P_{D1} and P_{D2}), which is also referred to as P_{680} , is oxidized ($P_{680}^{\cdot+}$) and a pheophytin molecule is reduced (P_{heo}^-).⁸ This is followed by the reduction of $P_{680}^{\cdot+}$ by electron transfer from the tyrosine 161 residue (Y_z).⁸ Thus, the Y_z located on the D1 protein of PSII is oxidized by $P_{680}^{\cdot+}$ and forms a tyrosine radical (Y_z^{\cdot} : the dot on Y_z shows that there is an unpaired electron in the molecule).

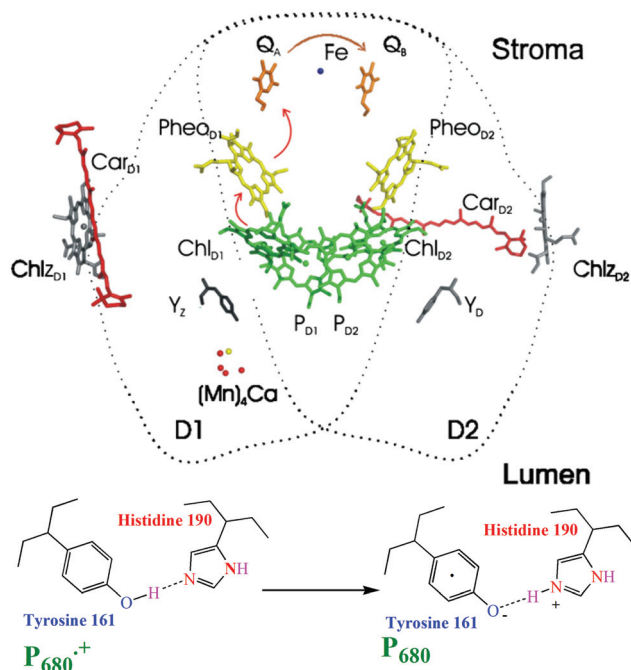
In other words, in PSII, Y_z^{8-10} functions as a redox mediator between the photo-oxidized primary electron donor ($P_{680}^{\cdot+}$) and the WOC and after four steps with five intermediates (S_n , $n = 0-4$), water is oxidized by the WOC.⁸ The oxidation

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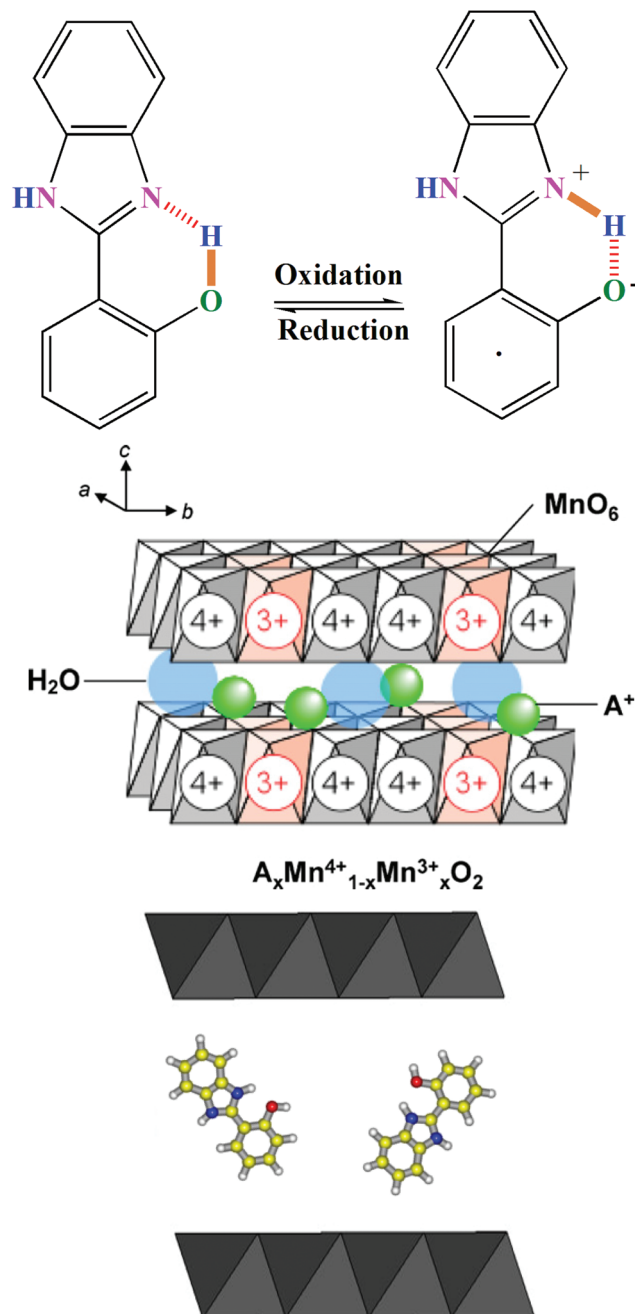


Scheme 1 Top: Redox cofactors in PSII. The arrows indicate different electron transfer reactions. All the protein subunits are not shown in detail (the image is from ref. 9).⁹ Bottom: Tyrosine 161 is oxidized by P_{680}^{++} . The dot within tyrosine shows that it is in its oxidized form. There is a hydrogen bond between Y_z (tyrosine 161) and the ϵ -nitrogen of a histidine (D1-His 190), which is important in proton coupled electron transfer.⁸

of Y_z by P_{680}^{++} likely occurs with the transfer of the phenolic proton to a hydrogen-bonded histidine residue and when Y_z is oxidized by P_{680}^{++} (Scheme 1), the phenolic group becomes very acidic and deprotonates to form a neutral radical phenolic group.⁸ As shown in Scheme 1, the proton acceptor is a histidine residue, histidine 190 (His 190), which is hydrogen bonded to the phenolic proton. The interaction could show the importance of the proton coupled electron transfer nature of the Y_z reactions.¹¹

The hydrogen bond is very important to the electron transfer from WOC to P_{680}^{++} that has been probed by site-directed mutagenesis of the hydrogen bonding pair and various spectroscopic measurements.⁸ When His-190 is deleted, the function of tyrosine is severely altered. However, the function of His-190 could be replaced by a buffer¹¹ or high pH¹² and thereby the Y_z could perform its function. After accumulating four oxidizing equivalents in WOC, two water molecules are oxidized, O_2 is released and the Mn_4Ca cluster returns to the reduced state.

Recently, 2-(2-hydroxyphenyl)-1H-benzimidazole phenol (IP) was used as a model for Y_z /His 190 in PSII by the research groups of Ally Aukauloo, and Thomas and Ana Moore.¹³ In our study, we have used monosheets,¹⁴ and we present a strategy to arrange IP between manganese layers in manganese(III, IV) oxide with birnessite structure to synthesize 2-(2-hydroxyphenyl)-1H-benzimidazole-manganese oxide (**1**),¹⁵ as a model for Y_z and His 190 near the manganese cluster in PSII (compare Scheme 1 bottom and Scheme 2). Birnessite-type manganese



Scheme 2 Top: 2-(2-Hydroxyphenyl)-1H-benzimidazole phenol (IP) used as a model for Y_z /His 190 in PSII. As shown in the scheme, oxidation of IP to oxidized IP (IP^\bullet) could change the hydrogen bond pattern as observed in PSII. The dot shows an unpaired electron in IP^\bullet . Middle: Schematic diagram of a birnessite-type layered manganese oxide incorporated with inorganic or organic cations (A^+) (the image is from ref. 15). Bottom: Schematic representation of the structure of model compound **1** (hydrogen: white; carbon: yellow; oxygen: red; nitrogen: blue and the blocks of MnO_6 are shown as triangles on the top and bottom of the IP molecules).

oxides have a two-dimensional layered structure with edge-sharing MnO_6 octahedra, with water molecules in the inter-layer space (Scheme 2 middle).¹⁵ The manganese oxide layers are negatively charged as a few Mn(III) ions are present in the layers.¹⁵ Thus, organic or inorganic cations are also

intercalated in the interlayer region depending on the precursors used.¹⁵

The ¹H NMR spectra of IP clearly show a downfield shift of the O–H resonance to >13 ppm in acetone-d₆ (Fig. S1†) that is characteristic of an intramolecular H-bond (Scheme 2).¹³

A nano-sized compound could be defined as a particle in the range of 1 to 100 nm (10² to 10⁷ atoms) from zero dimension (0 D) to three dimensions (3 D).¹⁴ Monosheets, 2 D nanosheets, which possess nanoscale dimensions only in thickness, are emerging as important materials due to their unique properties.¹⁴ Manganese oxide monosheets are exceptionally rich in both structural diversity and electronic properties, with potential applications in areas ranging from catalysis to electronics.¹⁴ These compounds have high specific surface area, structural diversity and electronic properties that are important for a variety of applications. The ability of the nanosheets to self-assemble allows formation of restacked lamellar aggregates and these compounds could be designed through the selection of nanosheets.¹⁴ To synthesize the model compound **1** (Scheme 2), manganese oxide monosheets were first synthesized with a very simple method by reacting MnCl₂ and H₂O₂ in the presence of tetramethylammonium hydroxide.¹⁴ In order to obtain evidence for the formation of manganese(III, IV) oxide monosheets and **1** (ESI†), powder X-ray diffraction (XRD) of dried samples of the colloidal suspensions was measured (Fig. 2).

XRD patterns indicate a layered structure with an interlayer spacing of ~0.95 nm for manganese(III, IV) oxide monosheets (Fig. 2).¹⁴ These XRD patterns indicate the flocculation of the manganese(III, IV) oxide together with tetramethylammonium (TMA) and water molecules. XRD patterns of a dried sample of **1** indicated a broad peak related to interlayer spacings of ~0.7–0.95 nm, most probably related to different arrangements of IP and TMA between layers (Fig. 2). Interestingly, in a previous model structure without an H acceptor (imidazole group),¹⁶ birnessite reduction transformation to Mn₃O₄ could

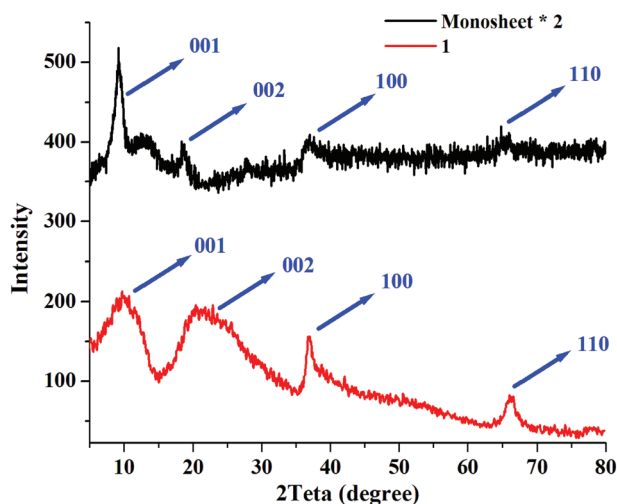
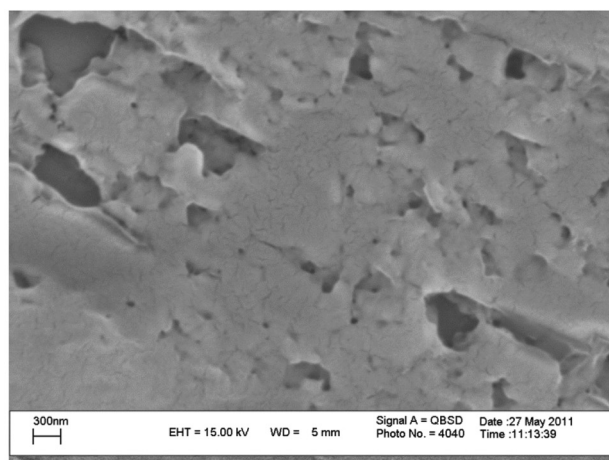
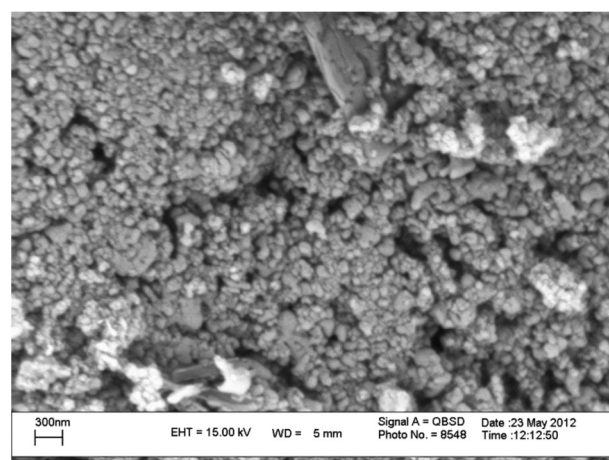


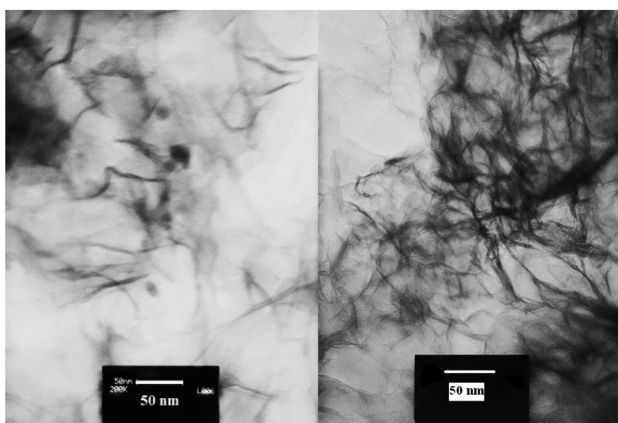
Fig. 2 Powder X-ray diffraction (XRD) patterns of dried manganese(III, IV) oxide monosheets and **1**.



(a)



(b)



(c)

(d)

Fig. 3 SEM (a,b) and TEM (c,d) images of manganese(III, IV) oxide monosheets (a,c) and **1** (b,d).

be detected¹⁶ in XRD, but in this study no such reduction was observed. This may suggest that the H-acceptor in IP (Scheme 1) could stabilize the phenol group toward decomposition by oxidation. Scanning electron microscopy and transmission electron microscopy show manganese(III, IV) oxide

monosheets or restacked lamellar aggregates in **1** (Fig. 3 and ESI, Fig. S2–S5†). In other words, the manganese(III, IV) oxide monosheets, similar to other monosheets, are known to aggregate to form layered structures with metal cationic organic and inorganic compounds.¹⁴

Thus, IP⁺ (IP is protonated at pH ~ 6, and thus it gets a positive charge) and the Mn oxide monolayer could form **1**. The IR spectrum of **1** indicates the presence of both IP and manganese oxide units in the structure. A proposal for IP analogues oriented between layers is shown in Scheme 2.

Cyclic voltammetry (CV) is one of the most versatile and popular electroanalytical techniques for the study of electroactive species from inorganic to biomolecules.¹⁷ Cyclic voltammetry of aqueous phenols shows the presence of an oxidation peak in the region of ~1 V *vs.* Ag|AgCl|KCl_{sat} under the many conditions evaluated.¹⁸ In many voltammetric experiments, the intensity of the oxidation peak for a phenol in solution decreases with the number of cycles, and the oxidation peak is not observed after about four cycles.¹⁸ The electrochemical reversibility of the phenoxyl/phenol couple in some compounds has been attributed¹³ to the ability of the proton to shuttle between the oxygen of phenol and the lone pair of other atoms (usually nitrogen) near the site (Scheme 1).¹³ In the control experiments, the peaks are not observed for a Pt electrode, and a Pt electrode modified with dried manganese(III, IV) oxide monosheets (Fig. 4). As seen in Fig. 4, one very small oxidation peak (green arrows) is observed in the anodic sweep of the Mn oxide monolayer between 0.8 and 1.0 V related to oxidation of Mn(III) to Mn(IV).¹⁹ It is important to note that the separated IP near the manganese ions, as in PSII, could change the electrochemistry of the phenol group. Interestingly, the cyclic voltammogram of IP in **1** is different from the cyclic voltammogram of a solution of IP. Repetitive cyclic voltammograms of a modified electrode (**1** on a Pt electrode) in the potential range between 0.0–1.6 V *versus* Ag|AgCl|KCl_{sat} are shown in Fig. 4. During the cycles, phenol oxidizes at ~+0.85 V *versus* Ag|AgCl|KCl_{sat} at a potential similar to the estimates for the Y_z/Y_z' couple in PSII (0.85 to 1.5 V *versus* Ag|AgCl|KCl_{sat}).²⁰

The oxidation peak for IP is not observed after about four cycles. However, by examining the peak current of the cyclic voltammogram of the modified electrode after continuous scanning for 30 cycles, we observed the voltammetric response, indicating that the IP in **1** is much more stable than IP in solution (Fig. 4). The peak may even be considered to be quasi-reversible. We relate the observation to the separated IP molecules between layered manganese oxide and the hydrophilic environment around IP that helps proton transfer between IP and protonic groups.

In conclusion, hundreds of amino acids are around the WOC and, thus, we have here a nano-sized manganese oxide in a protein environment.²¹ Only a small fraction of the residues come into direct contact with the manganese cluster, and few of them are directly involved in catalysis. Roles for the residues that come into direct contact with the manganese cluster may be involved in the regulation of charges, and in

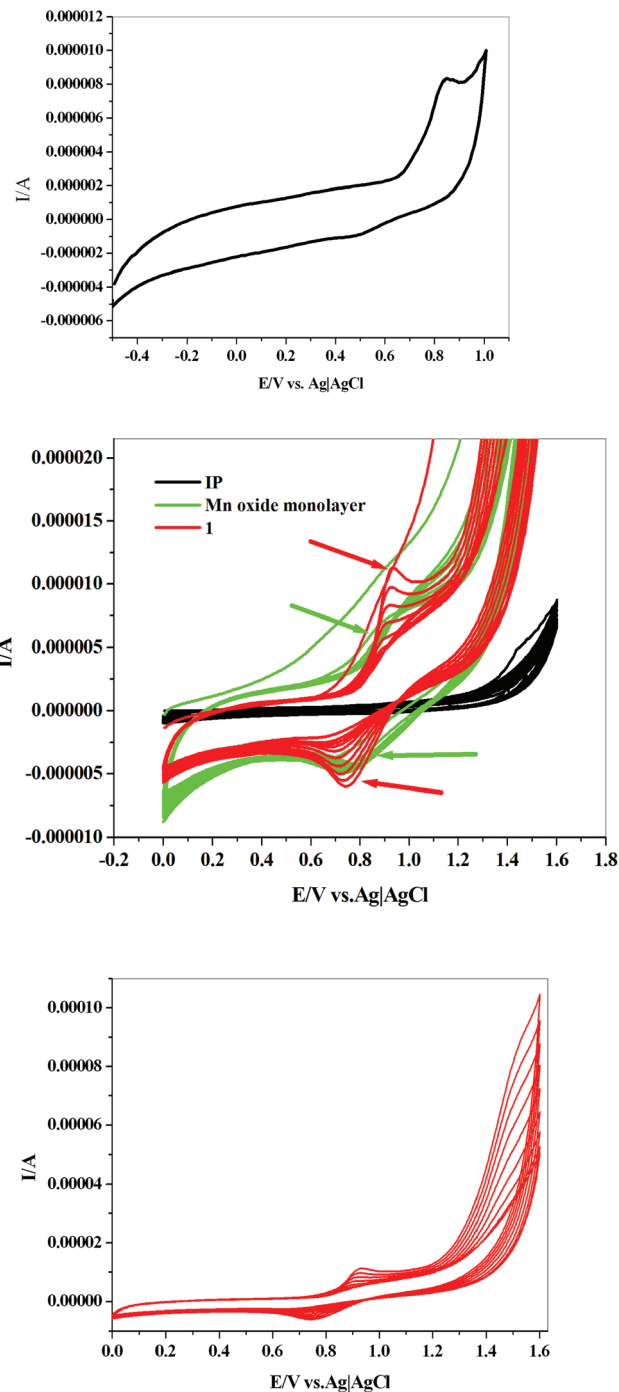


Fig. 4 Top: Cyclic voltammograms of IP (0.1 mM). Middle: Cyclic voltammograms of IP, Mn oxide monolayer and **1** (0.1 mM) in lithium perchlorate solution (0.1 M in water, pH = 6.3). Bottom: Voltammogram of a modified electrode (**1** on a Pt electrode) in the potential range between 0.0–1.6 V. Measurements performed in lithium perchlorate solution (0.1 M in water, pH = 6.3) at a scan rate of 50 mV s⁻¹. Green and red arrows show oxidation/reduction peaks for Mn(III) ↔ Mn(IV) and IP ↔ IP⁺, respectively.^{18,19}

electrochemistry of the manganese cluster; this could help in coordinating water molecules at appropriate metal sites, and in the stability of this cluster. Although the WOC of PSII is a discrete structure that interacts with a discrete tyrosine/

histidine redox pair, the model introduced here could be the first step in the synthesis of a self-assembled layered hybrid of phenol/imidazole–manganese oxide, and, thus, it could be a good model for the WOC in PSII. As manganese oxides are efficient catalysts toward water oxidation,²² this model could, in the long-run, come close to what exists in the water oxidizing complex of PSII.

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