

Cite this: *Dalton Trans.*, 2012, **41**, 3906

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## A manganese oxide with phenol groups as a promising structural model for water oxidizing complex in Photosystem II: a ‘golden fish’†

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Received 4th September 2011, Accepted 12th January 2012

DOI: 10.1039/c2dt11672c

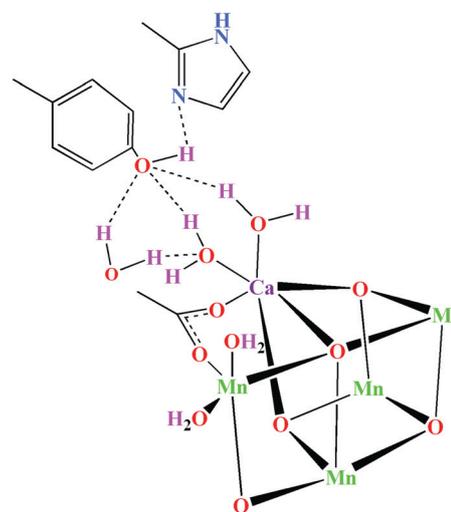
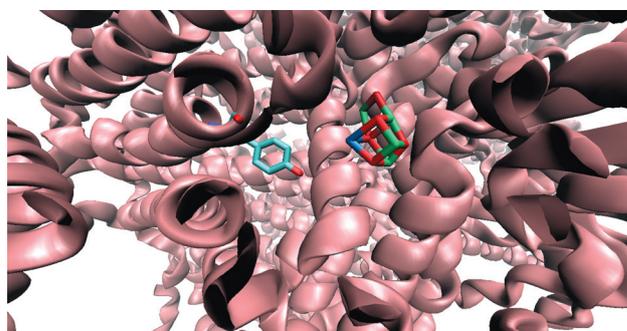
We describe here the ability of manganese oxide monosheets to aggregate to form layered structures with 4-aminophenol molecules. These aggregated monosheets could be considered as the first step to synthesize a self-assembled layered hybrid of phenol–manganese ions with phenol and manganese(III) and (IV) as exists in the water oxidizing complex of Photosystem II.

The splitting of water into gaseous H<sub>2</sub> and O<sub>2</sub> by using solar energy may be the best solution to solve not only the problem of depletion of fossil fuels but also to overcome the effects of global warming.<sup>1</sup> To evolve hydrogen efficiently, 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.<sup>2</sup>

We summarize below the steps that precede biological oxidation of water. After photons are absorbed by Photosystem II (PSII) antenna molecules, and the excitation energy is transferred to the reaction centers, primary charge separation occurs, where a special chlorophyll is oxidized (P<sub>680</sub><sup>+</sup>) and a pheophytin molecule is reduced (Pheo<sup>-</sup>).<sup>3</sup> This is followed by reduction of P<sub>680</sub><sup>+</sup> by electron transfer from a tyrosine (tyrosine 161) residue (Y<sub>Z</sub>), located on the D1 protein of PSII, and the formation of a tyrosine radical (Y<sub>Z</sub><sup>\*</sup>).<sup>3</sup> When Y<sub>Z</sub> is oxidized by P<sub>680</sub><sup>+</sup>, the phenolic group becomes very acidic and deprotonates to form a neutral radical phenolic group. The proton acceptor is a histidine residue, histidine 190, which is hydrogen bonded to the phenolic proton.<sup>3</sup>

Electrons for the reduction of Y<sub>Z</sub><sup>\*</sup> are extracted from the water oxidizing complex (WOC) leading, finally, to the oxidation of water to molecular oxygen. In PSII of plants, algae and cyanobacteria, the WOC is a manganese–calcium cluster that oxidizes water with turnovers up to 50 molecules of O<sub>2</sub> released per

second.<sup>3</sup> In addition to the earlier structure of PSII,<sup>4</sup> the most recent structure at 1.9 Å resolution reveals detailed atomic level information about the WOC (Fig. 1).<sup>5</sup> In this structure, there are four manganese ions and one calcium ion, and these are bridged by five oxygen atoms, with four water molecules in the complex (Mn<sub>4</sub>CaO<sub>5</sub>(H<sub>2</sub>O)<sub>4</sub>).<sup>5</sup> Among these water molecules, found at the active site, one of the pairs is suggested to be the precursor to oxygen.<sup>5</sup>



**Fig. 1** The water oxidizing complex, tyrosine 161 and the surrounding amino acids (Top).<sup>5</sup> The location of tyrosine 161, water molecules and CaMn<sub>4</sub>O<sub>5</sub> cluster in Photosystem II (Bottom).<sup>5</sup> The top image was made with VMD (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).

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†Electronic supplementary information (ESI) available. See DOI: 10.1039/c2dt11672c

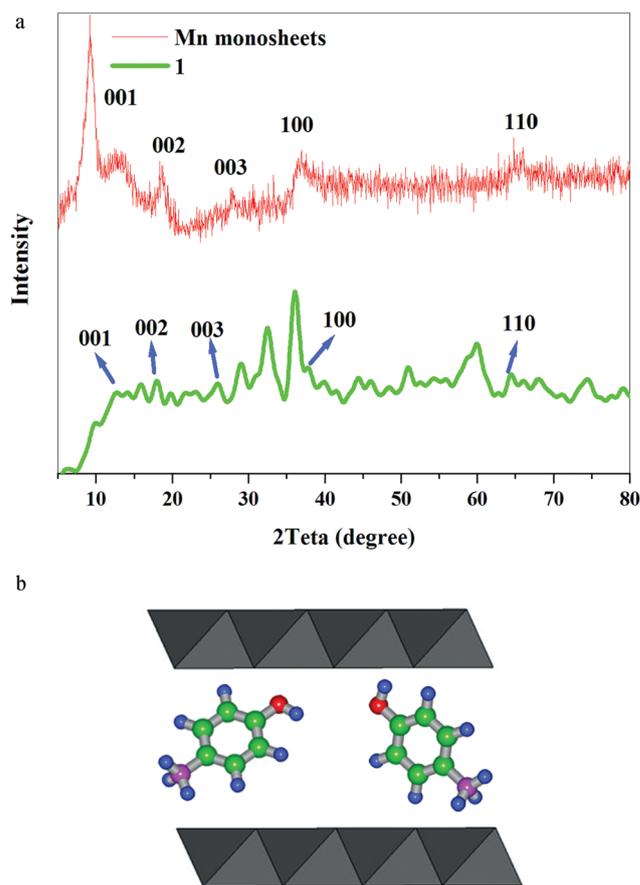
‡G. contributed in the interpretation, the discussion, and in the literature related to photosynthesis.

Details of the above-described results are expected to greatly improve our understanding of the water oxidation and help us in synthesizing a super catalyst for water oxidation that would efficiently split water using a totally artificial photosynthetic system.<sup>6</sup> In 2011, Umena *et al.*<sup>5</sup> showed that  $Y_z$  forms a strong hydrogen bond with one water molecule coordinated to calcium (Fig. 1).<sup>5</sup> Another hydrogen bond is shown to be between  $Y_z$  and the  $\epsilon$ -nitrogen of histidine 190 (Fig. 1).<sup>5</sup> This histidine is also further hydrogen-bonded to other amino acids or water molecules to form a hydrogen-bond network that has been suggested to act as the exit channel for protons.<sup>5</sup>  $Y_z$  is connected to a water molecule at 2.46 Å distance, which in turn is connected to another water molecule that is bound to the  $\text{Ca}^{2+}$  of the WOC. Hammarstrom and Styring reviewed and discussed the possible roles of  $Y_z$  in the WOC of PSII that are important for the understanding of PSII and have presented ways to design an artificial photosynthetic system.<sup>7</sup> Firstly,  $Y_z$  is a rapid electron donor to  $\text{P}_{680}^+$ ; reduction of  $\text{P}_{680}^+$  by  $Y_z$  is indeed very fast (ns to  $\mu\text{s}$ ) and competes favourably with the recombination reaction. Secondly, the presence of  $Y_z$  allows the WOC to be positioned at an appropriate distance from the  $\text{P}_{680}$ ; it is argued that a closer proximity of the WOC and  $\text{P}_{680}$  could lead to non-productive quenching of excited  $\text{P}_{680}$  by reverse electron transfer.<sup>7–9</sup> Thirdly,  $Y_z$  may possibly be directly involved in the water oxidation chemistry.<sup>7</sup> The phenolic proton transfers back and forth along the hydrogen bond between  $Y_z$  and the neighbouring histidine 190. Proton transfer to histidine 190 may possibly control electrostatics such that oxidation of  $Y_z$  triggers deprotonation of the WOC of PSII.<sup>7</sup>

Numerous manganese complexes have been synthesized<sup>10–13</sup> in the hope of oxidizing water, but few examples of a real water oxidizing catalyst have been reported.<sup>14</sup> Styring and coworkers<sup>7</sup> have designed Ru–Mn complexes aimed at mimicking the light-induced single-electron transfer and charge-separating functions found in PSII. They used a phenolic group in these structures aimed at mimicking  $Y_z$  in PSII. Manganese oxidation in the presence of light could be observed in this structure. Usually, in these models, the phenolic group is coordinated to manganese ions.<sup>7</sup>

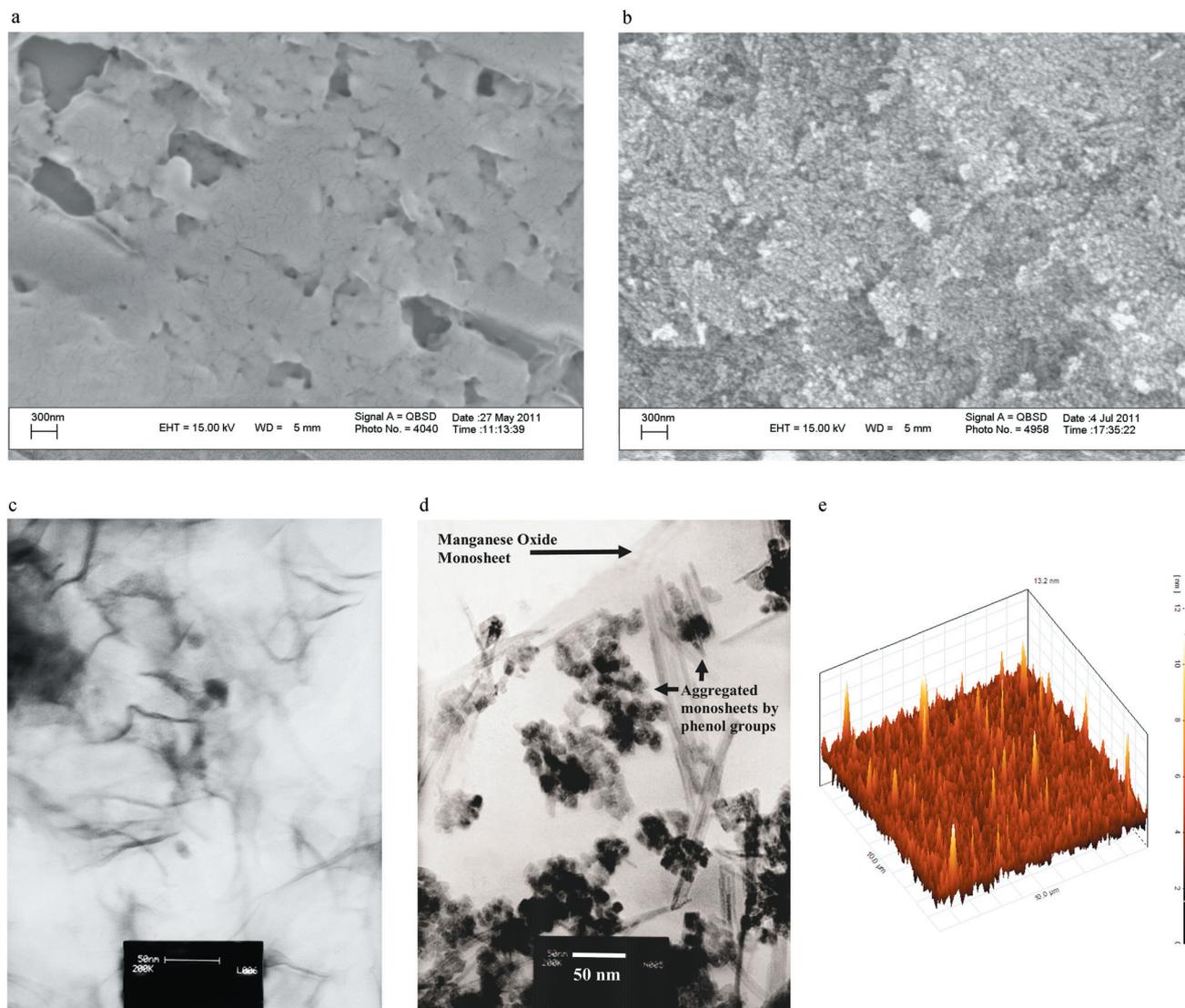
Various manganese oxides as heterogeneous catalysts for water oxidation have been reported by some groups.<sup>15</sup> Recently, layered manganese oxides<sup>16</sup> have been introduced as efficient catalysts and closest structural and functional analogs of the WOC in PSII but these model systems contain no groups analogous to  $Y_z$ , histidine and other features as exist in PSII. Aimed at simulating the  $\text{Mn}_4\text{CaO}_5(\text{H}_2\text{O})_4$  cluster and tyrosine 161 in PSII, we have selected manganese monosheets and present here data on a synthesized self-assembled layered hybrid phenol–manganese(III, IV) oxide. This compound could be the first step in the synthesis of a self-assembled layered hybrid of phenol–manganese compound, as exists in the WOC of PSII.

Monosheets are a class of two-dimensional nano-materials that are characterized by a thickness of the order of nanometres and lateral dimensions of submicrometres to micrometres.<sup>17</sup> These compounds have high specific surface areas, structural diversity and electronic properties that are important for a variety of applications.<sup>17</sup> The ability of the nanosheets to self-assemble allows formation of restacked lamellar aggregates.<sup>17</sup> To synthesize the water oxidizing catalyst (**1**; see Fig. 2) manganese oxide monosheets were first synthesized by a very simple



**Fig. 2** (a) Powder X-ray diffraction patterns of dried manganese(III, IV) oxide monosheets and **1** ( $\text{Mn}_3\text{O}_4$  was also detected in the XRD spectrum). (b) Schematic representation of the structure of **1**.

method by reacting an aqueous solution of  $\text{MnCl}_2$  with  $\text{H}_2\text{O}_2$  in the presence of tetramethylammonium hydroxide.<sup>18</sup> We characterized this sample by several methods: Fourier Transform Infrared Spectroscopy (FTIR), Scanning Tunneling Microscope (STM), Scanning Electron Microscope (SEM), Transmission Electron Microscopy (TEM) and powder X-ray diffraction (XRD). The manganese(III, IV) oxide monosheets, similar to other monosheets, could aggregate to form layered structures with organic and inorganic cations.<sup>19</sup> The 4-aminophenol molecule is protonated at  $\text{pH} \sim 6$ , and, thus it gets a positive charge. Thus, 4-aminophenol with positive charge could form self-assembled layered hybrid phenol–manganese(III, IV) oxide (**1**, Fig. 2) with the manganese(III, IV) oxide monosheets at  $\text{pH} \sim 6–7$ . Manganese oxides may oxidize phenol at higher or lower pHs than 6–7.<sup>19</sup> IR spectrum of **1** indicates the presence of both aminophenol and manganese oxide units in the structure. The location of phenol on the manganese ion is not exactly known but the manganese complexes with phenol groups exhibit a strong band between  $1290$  and  $1330\text{ cm}^{-1}$  attributable to  $\nu(\text{C–O})$ , which is shifted  $10$  to  $30\text{ cm}^{-1}$  higher than in the free ligand.<sup>20</sup> However, both the free phenol and **1** show a peak at  $1261\text{ cm}^{-1}$ , and no shift is observed in the IR spectrum (Fig. S5†). Thus, the oxygen of phenol in the artificial system similar to that in PSII, is not coordinated to the manganese ions.



**Fig. 3** SEM images of manganese(III, IV) oxide monosheets (a) and **1** (b). TEM images of manganese(III, IV) oxide monosheets (c) and **1** (d) and (e) STM image of **1**. Bar scales for a, b, c and d are 300, 300, 50 and 50 nm, respectively.

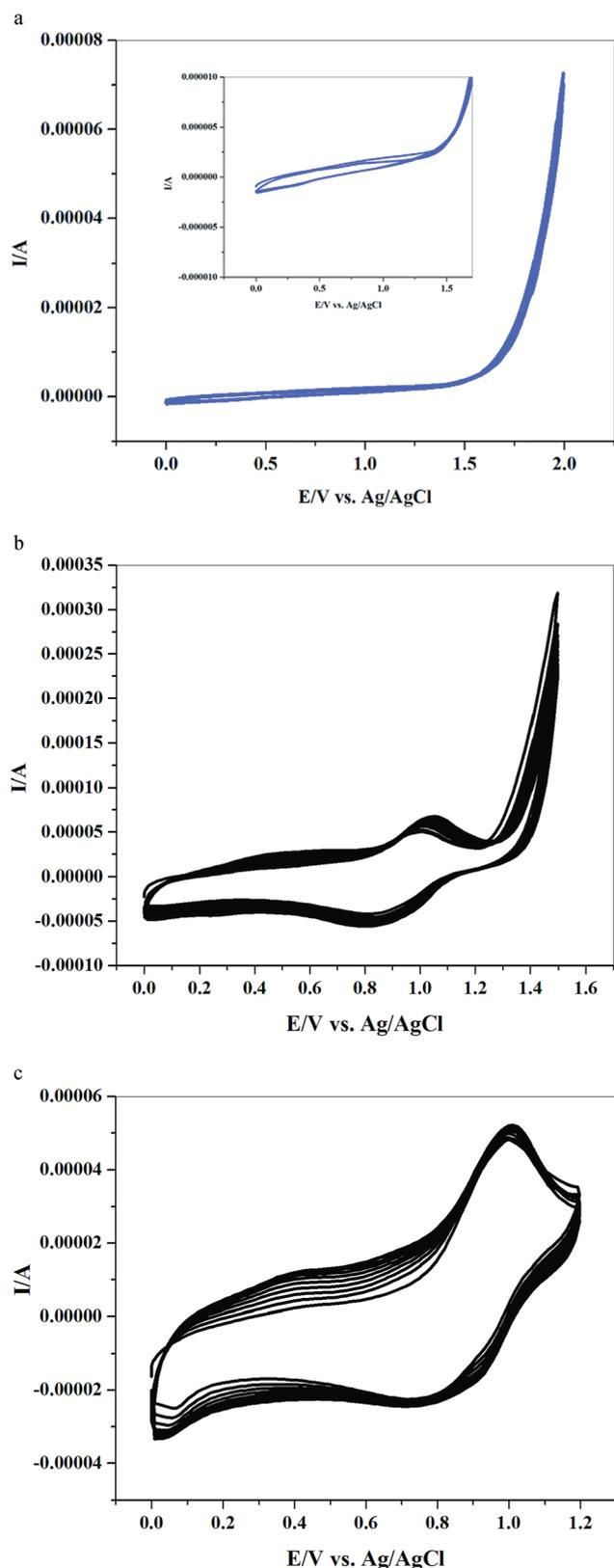
In order to obtain further evidence for the formation of manganese(III, IV) oxide monosheets and **1**, XRD of dried samples of the colloidal suspensions were measured. XRD patterns indicate a birnessite structure with an interlayer spacing of  $\sim 0.95$  nm for dried manganese(III, IV) oxide monosheets (Fig. 2).<sup>18</sup> These XRD patterns indicate the flocculation of the manganese(III, IV) oxide together with tetramethylammonium (TMA) and water molecules.<sup>21</sup> XRD patterns of a dried sample of **1** indicated that it has a birnessite structure as well, but the interlayer spacing is  $\sim 0.7$  nm related to the arrangement of 4-aminophenol between the layers (Fig. 2). A proposal for phenol analogues being oriented between the monolayers is shown in Fig. 2. The 4-aminophenol cations, similar to the TMA cations, is unique in that the structures formed in the thin films of **1** are poorly ordered as indicated by the broad peaks obtained in the XRD pattern.<sup>21</sup>

SEM and TEM images show manganese(III, IV) oxide monosheets or restacked lamellar aggregates in **1** (Fig. 3a–d).

Furthermore, the STM image displays a layered structure with a thickness of  $\sim 5$  nm, consistent with the thickness expected from the aggregated five or six manganese(III, IV) oxide monosheets (Fig. 3e).

In order to characterize **1**, electrochemical characterization was performed. Cyclic voltammetry and amperometric studies were performed using an Autolab potentiostat–galvanostat model PGSTAT30 (Utrecht, The Netherlands) with a conventional three electrode set-up, in which a Pt electrode (or Pt modified electrode with **1** or manganese(III, IV) oxide monosheets), an Ag–AgCl–KCl<sub>sat</sub> and a platinum rod served as the working, reference and auxiliary electrodes, respectively. The working potential was applied in the standard way using the potentiostat and the output signal was acquired by Autolab Nova software.

Cyclic voltammogram of aqueous phenols on the platinum electrodes shows the presence of an oxidation peak in the region of  $\sim 1$  V vs. Ag–AgCl under many conditions.<sup>22</sup> In many voltammetric experiments, the oxidation peak for a solution of



**Fig. 4** (a) Cyclic voltammograms of 4-aminophenol (0.1 mM) in lithium perchlorate solution (0.1 M in water, pH = 6.3) at a scan rate of  $50 \text{ mV s}^{-1}$  (b) Cyclic voltammograms peak current of modified electrode after continuous scanning for 30 cycles. (c) Voltammograms of modified electrode (1 on Pt electrode) in the potential range between 0.0–1.2 V at a scan rate of  $50 \text{ mV s}^{-1}$ .

phenol decreases with the number of cycles, and the oxidation peak is not observed after about four cycles. This behavior could be also observed for a solution of 4-aminophenol (Fig. 4a) suggesting that there is deactivation or blockage of the electrode surface by the adsorption of substances and/or phenoxy radical polymerization.<sup>22</sup> However, the cyclic voltammogram of 4-aminophenol in **1** is different from the cyclic voltammogram of a solution of 4-aminophenol. Repetitive cyclic voltammograms of modified electrode (**1** on Pt electrode) in the potential range between 0.0 and 1.2 V is shown in Fig. 4b. During the first cycle, as the potential is scanned forward, phenol begins to oxidize at  $\sim +0.68 \text{ V}$ , and then the oxidation current increases quickly to reach a maximum at  $+0.96 \text{ V}$ , a potential similar to the estimates for the  $Y_z/Y_z^*$  couple in PSII (0.8 to 1.0 V *versus* SCE).<sup>4</sup> In the reverse scan, there is a reduction wave with a main current peak at  $+0.77 \text{ V}$ . In the control experiments, the peaks are not observed for a Pt electrode, Pt electrode modified with dried manganese(III, IV) oxide monosheets and the Nafion immobilized 4-aminophenol compound at a Pt electrode (Fig. S6†). It is important to note that the separated phenol group near the manganese ions, as in PSII, could change the electrochemistry of phenol.

This was evaluated by examining the cyclic voltammetric peak current of a modified electrode after continuous scanning for 30 cycles. There was nearly no decrease of the voltammetric response, indicating that the modified electrode was stable in solution (Fig. 4c).

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–manganese ions that could, in the long-run, come close to what exists in the water oxidizing complex of Photosystem II.

## Acknowledgements

This work was supported by Institute for Advanced Studies in Basic Sciences (IASBS). We thank Professor Thomas Rauchfuss, of the Department of Chemistry of the University of Illinois at Urbana–Champaign, for critical comments that led to improvements in this paper.

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