

A Bioinspired Construct That Mimics the Proton Coupled Electron Transfer between P680⁺ and the Tyr_Z-His190 Pair of Photosystem II

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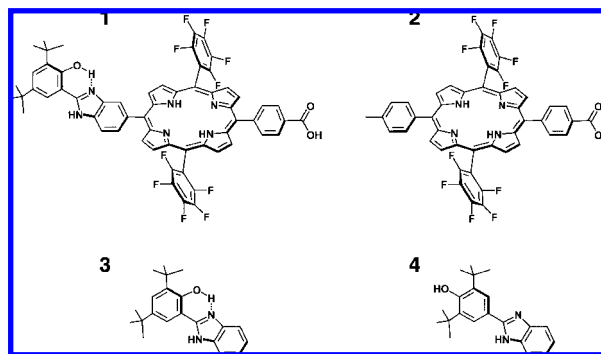
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Proton coupled electron transfer (PCET)¹ has been invoked in the description of a number of redox processes in biological systems.² In photosystem II (PSII), tyrosine Z (Tyr_Z) functions as a redox mediator between the photo-oxidized primary donor (P680⁺) and the Mn-containing oxygen evolving complex (OEC).³ The oxidation of Tyr_Z by P680⁺ likely occurs with transfer of the phenolic proton to a hydrogen-bonded histidine residue (His190).⁴ This change in the protonation state of Tyr_Z is thought to play an important role in the electron transfer by poising the potential of the mediator between that of P680⁺ and the Mn cluster of the OEC.^{5–7} In this Communication, we report the synthesis and functional studies of a bioinspired hybrid system composed of colloidal TiO₂ nanoparticles surface modified with **1** (BiP-P_{F10}), a photochemically active mimic of the photosynthetic chlorophyll-Tyr-His complex (Chart 1). This construct undergoes photoinduced stepwise electron transfer coupled to proton motion at the phenolic site. Electrochemical studies show that the phenoxyl/phenol couple of the model system is chemically reversible and thermodynamically capable of water oxidation.

The presence of an intramolecular hydrogen bond in compounds **1** and **3** (BiP)^{6b} is supported by the ¹H NMR spectra, which clearly show a downfield shift of the O–H resonance to >13 ppm in CDCl₃ and DMSO-*d*₆, as well as a dissymmetry in the resonance of the benzimidazole protons of **3** (see Supporting Information (SI)). In addition, the FTIR spectrum of **3** does not exhibit the free O–H vibration at 3600 cm^{–1} that is present in the para-substituted derivative **4**. Instead, a broadband centered at ~3200 cm^{–1} is observed in the FTIR spectrum of **3** (see SI).

Under most conditions the oxidation of phenols is coupled to deprotonation (i.e., the phenoxyl radical cation is a strong acid [pK_a ≈ –2]), and their electrochemistry is usually irreversible.⁸ For example, cyclic voltammetry of 2,4,6-tri-*tert*-butylphenol (see SI) shows an irreversible oxidation at ~1.4 V versus SCE. Because of the presence of the attached base, the phenoxyl/phenol couple of **3** shifts to 0.95 V versus SCE, a potential similar to estimates for the Tyr_Z/Tyr_Z couple in PSII (~0.8 to 1.0 V versus SCE).^{3d,5b} For **3**, the one-electron oxidation of the phenol is quasi-reversible, with the ratio of peak currents close to unity, but with a peak to peak separation larger than the theoretical 59 mV (see SI). In contrast, compound **4** exhibits irreversible electrochemistry. The chemical reversibility of the phenoxyl/phenol couple of **3** is attributed to the ability of the proton to shuttle between the oxygen of the phenol and the nitrogen lone pair electrons of the benzimidazole in the corresponding reduced and oxidized forms; effectively trapping the proton at the site of electrochemical activity.

Chart 1



Importantly, there is only a small change in the redox potential of **3** upon coupling to the porphyrin macrocycle. This is also the case in metalloporphyrin derivatives (see SI). Compound **1** is designed such that when adsorbed to nanostructured TiO₂, rapid primary electron transfer occurs from the photoexcited porphyrin moiety (¹P_{F10}) into the conduction band of the attached semiconductor. The covalently attached hydrogen-bonded phenol (BiP) is thermodynamically poised (1.00 V vs SCE) to quench the resulting high-potential porphyrin radical cation (P_{F10}^{•+}) (1.35 V vs SCE) via a secondary electron transfer, yielding the final charge separated state (BiP^{•+}-P_{F10}-TiO₂^{•–}). Thus, the potential of this model system decreases only ~350 mV in oxidizing the phenolic site, and thereby retains much of the relatively high potential of the initial photo-oxidized chromophore in the phenoxyl radical.

Electron paramagnetic resonance (EPR) provides a clear spectroscopic signature for phenoxyl radical formation.⁹ Following light excitation of an acetonitrile suspension of TiO₂ nanoparticles (0.2 mM) surface modified with **1** (0.6 mM), X-band EPR spectra confirm the generation of a charge separated state (**1**^{•+}-TiO₂^{•–}) (Figure 1a). Injected electrons are localized on the TiO₂ nanoparticles, in the interior (sharp signal *g* = 1.989 and *g* = 1.961) and on the surface (broad signal in the range 3395–3450 G). Corresponding holes are localized on **1**, either on the porphyrin (BiP-P_{F10}^{•+}-TiO₂^{•–}) or the phenol (BiP^{•+}-P_{F10}-TiO₂^{•–}). The superior spectral resolution of high-frequency EPR allows for detailed identification of the molecular structures involved in electron transfer. In photoinduced D-band EPR spectra (Figure 1b and SI), the anisotropic coupling tensors of the phenoxyl radical (*g*_x = 2.0064, *g*_y = 2.0042, *g*_z = 2.0022) are resolved, and in good agreement with previously reported *g*-tensors of tyrosine radicals in photosystem II.^{2b}

The EPR spectra reflect the steady-state distribution of trapped states formed following light excitation and show a clear temperature dependence (see SI). After illumination at 80 K, 95% of the

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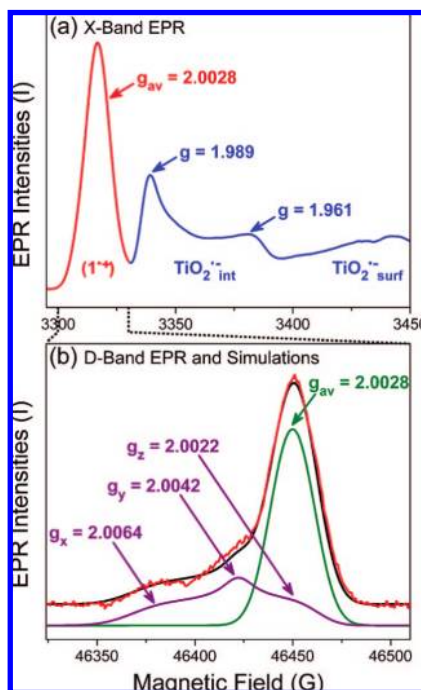


Figure 1. (a) Experimental photoinduced X-band (9.5 GHz) EPR spectrum, at 4.2 K, of an acetonitrile suspension of TiO_2 and **1**. (b) Experimental photoinduced D-band (130 GHz) EPR spectrum, at 13 K, of an acetonitrile suspension of TiO_2 and **1** (red line), simulated $2^{+\bullet}$ (green line), simulated $3^{+\bullet}$ (purple line), and the sum of simulations [$2^{+\bullet}$ + ($3^{+\bullet}$)] (black line). The experimental spectra were recorded as the magnetic field dependence of the two-pulsed electron spin echo intensity. The dotted lines connecting panels a and b indicate the region of the spectrum investigated by D-band EPR. In panel b, the $\text{TiO}_2^{\bullet-}$ signal is not shown.

resulting holes are localized on the phenol and 5% on the porphyrin. Following illumination at 4.2 K, only 48% of the holes are localized on the phenol and 52% on the porphyrin. Raising the temperature from 4.2 to 80 K results, once again, in localization of 95% of the holes on the phenol. The holes remain localized on the phenol moiety when the temperature is cycled back to 4.2 K.

The observed temperature dependence of the charge shift is attributed to restricted nuclear motion at low temperature. At 4.2 K approximately half of the molecules are trapped in a high-energy state, and only relax to a lower energy state upon warming to 80 K. This situation is reminiscent of the observation of a trapped high-energy state in natural photosynthetic systems.^{2b,10} The present data, complicated by heterogeneity¹¹ in the frozen sample, are insufficient to resolve a detailed relaxation mechanism. However, the model system reduces the variables present in the natural system that affect the redox behavior, and thereby sets the stage for a better understanding of the critical role of the phenol-imidazole H-bond in water oxidation.

In conclusion, a model for the donor side of PSII, which includes a chlorophyll-like photoactive species, has been prepared and characterized. The presence of a final charge separated state involving a phenoxyl radical is demonstrated using low temperature photoinduced D-band EPR spectroscopy. This construct models the Tyr_Z-His190 mediator coupling of $\text{P680}^{+\bullet}$ to the water-oxidizing unit (OEC) in the reaction center of PSII and provides a built in high-potential mediator thermodynamically capable of coupling the dye-sensitized anode of a photoelectrochemical cell¹² to an appropriate water-oxidation catalyst.¹³ The construct uses a bioinspired concept, a stepwise electron transfer process with tight control of

proton activity, to move the oxidizing equivalent from the sensitizer at the semiconductor surface to a mediator. Key features of the construct are that a considerable fraction of the high potential of the porphyrin radical cation is maintained in the phenoxyl radical and the notoriously irreversible phenoxyl/phenol redox couple is instead chemically reversible (an imperative for a mediator).

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Supporting Information Available: Synthesis and structural characterization, electrochemical data, TiO_2 preparation, EPR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) In the present work, no temperature dependent change in the g_x tensor of the phenoxyl radical was observed. For Tyr_D[•] in Mn-depleted PSII, a change in g_x upon warming from 1.8 to 77 K is mainly attributed to either deprotonation of a histidyl cation or movement of the uncharged histidine away from the tyrosyl radical.^{2b} In **1** the lack of a secondary proton acceptor and the covalent attachment of the benzimidazole base likely preclude such changes to the local electrostatic environment of the phenoxyl radical.
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