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Photocatalytic Generation of a Non-Heme Oxoiron(IV) Complex with Water as an Oxygen Source

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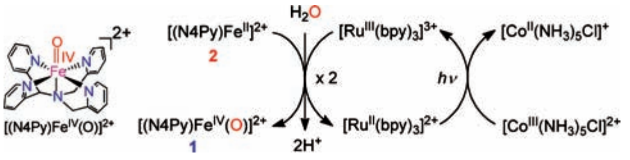
S *Supporting Information*

ABSTRACT: The photocatalytic formation of a non-heme oxoiron(IV) complex, $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ [N4Py = *N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine], efficiently proceeds via electron transfer from the excited state of a ruthenium complex, $[\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})_3]^{2+*}$ (bpy = 2,2′-bipyridine) to $[\mathrm{Co}^{\mathrm{III}}(\mathrm{NH}_3)_5\mathrm{Cl}]^{2+}$ and stepwise electron-transfer oxidation of $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{II}}]^{2+}$ with 2 equiv of $[\mathrm{Ru}^{\mathrm{III}}(\mathrm{bpy})_3]^{3+}$ and H_2O as an oxygen source. The oxoiron(IV) complex was independently generated by both chemical oxidation of $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{II}}]^{2+}$ with $[\mathrm{Ru}^{\mathrm{III}}(\mathrm{bpy})_3]^{3+}$ and electrochemical oxidation of $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{II}}]^{2+}$.

Heme-containing enzymes, such as cytochromes P450, peroxidases, and catalases, catalyze a number of important metabolic oxidation reactions by reductive activation of O_2 using two electrons and two protons and by production of oxoiron(IV) porphyrin π-cation radicals as the ultimate oxidant in these enzymatic systems.[1,2] Non-heme oxoiron(IV) intermediates have also been identified as active oxidizing species in the catalytic cycles of *Escherichia coli* taurine:α-ketoglutarate dioxygenase (TauD), prolyl-4-hydroxylase, and halogenase CytC3.[3] Synthetic model compounds of such high-valent oxoiron(IV) intermediates have been produced in the reactions of heme and non-heme iron complexes with artificial oxidants such as iodosylbenzene (PhIO), *m*-chloroperoxybenzoic acid (*m*-CPBA), and hydroperoxides (H_2O_2 and ROOH) or with O_2 in the presence of electron and proton donors.[4−6] Alternatively, high-valent oxometal intermediates have been produced by two-electron oxidation of the metal complexes with water as an oxygen source.[7,8] In the latter case, a strong one-electron oxidant [e.g., cerium(IV) ammonium nitrate] was required for the generation of high-valent oxoiron(IV) intermediates.[8] In addition, the light-driven reaction has enabled the use of much weaker oxidants to produce high-valent oxometal porphyrins;[9,10] however, to date there has been no report on the photocatalytic generation of non-heme oxoiron(IV) complexes with water as an oxygen source.

We report herein the efficient photocatalytic generation of a non-heme oxoiron(IV) complex, $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ (**1**) [N4Py = *N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine],[11] from the corresponding iron(II) complex, $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{II}}]^{2+}$ (**2**), using $[\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})_3]^{2+}$ (bpy = 2,2′-bipyridine) as a photosensitizer, $[\mathrm{Co}^{\mathrm{III}}(\mathrm{NH}_3)_5\mathrm{Cl}]^{2+}$ as a relatively cheap and weak one-electron oxidant, and water as an oxygen source (Scheme 1).

Scheme 1



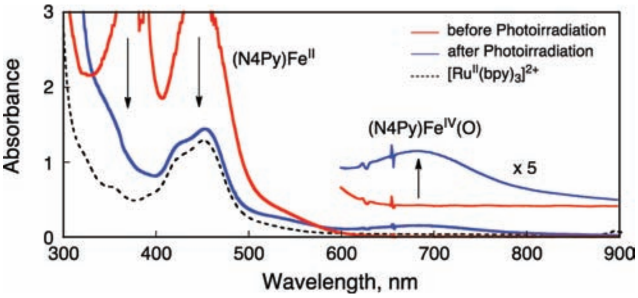


Figure 1. Spectral changes observed upon photoirradiation (λ = 450 nm) of a deaerated acetate buffer (pH 5.0, 50 mM) and MeCN [3:1 (v/v)] mixed solution (2.0 mL) containing $[\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})_3]^{2+}$ (2.0×10^{-4} M), $[\mathrm{Co}^{\mathrm{III}}(\mathrm{NH}_3)_5\mathrm{Cl}]^{2+}$ (2.0×10^{-3} M), and **2** (5.0×10^{-4} M) at 298 K.

Visible-light irradiation (λ = 450 nm) of the absorption band of $[\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})_3]^{2+}$ (2.0×10^{-4} M) in a deaerated acetate buffer (pH 5.0, 50 mM) and acetonitrile (MeCN) [3:1 (v/v)] mixed solution (2.0 mL) containing **2** (5.0×10^{-4} M) and $[\mathrm{Co}^{\mathrm{III}}(\mathrm{NH}_3)_5\mathrm{Cl}]^{2+}$ (2.0×10^{-3} M) resulted in the formation of **1**, as shown in Figure 1. No photocatalytic generation of **1** occurred in the absence of $[\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})_3]^{2+}$. The yield of **1** was determined to be ∼80% from the absorption at λ = 690 nm due to **1** (ε = 400 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$).[11] Further addition of **2** to the resulting solution followed by visible-light irradiation resulted in the additional formation of **1**, which was confirmed to take place repeatedly. No degradation of $[\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})_3]^{2+}$ or $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{II}}]^{2+}$ was observed after irradiation with visible light at λ = 450 nm. The spectral changes shown in Figure 1 were mainly due to the conversion of **2** to **1**, whereas the absorption band due to $[\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})_3]^{2+}$ remained virtually the same after photoirradiation.

It is worth noting that in the absence of **2**, $[\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})_3]^{2+}$ was oxidized by $[\mathrm{Co}^{\mathrm{III}}(\mathrm{NH}_3)_5\mathrm{Cl}]^{2+}$ to $[\mathrm{Ru}^{\mathrm{III}}(\mathrm{bpy})_3]^{3+}$ through electron transfer from the excited state of $[\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})_3]^{2+}$ (i.e., $[\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})_3]^{2+*}$, where * denotes the excited state) to $[\mathrm{Co}^{\mathrm{III}}(\mathrm{NH}_3)_5\mathrm{Cl}]^{2+}$

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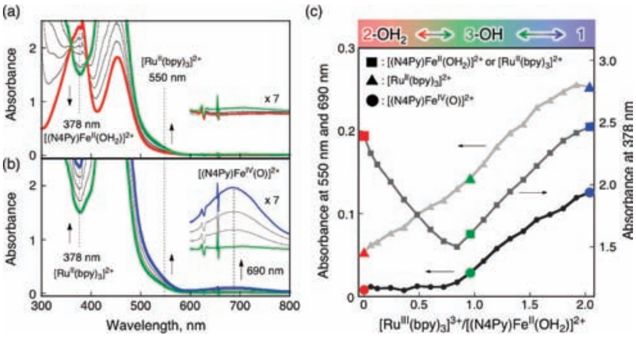


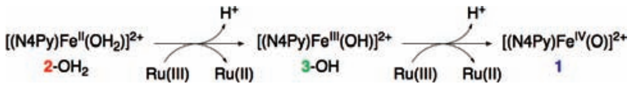
Figure 2. (a, b) UV−vis spectral changes observed upon addition of $[Ru^{III}(bpy)_3]^{3+}$ in the range from (a) 0 M (red line) to 5.0×10^{-4} M (green line) and (b) 5.0×10^{-4} M (green line) to 1.0×10^{-3} M (blue line) to a solution of **2**−OH_2 (5.0×10^{-4} M) in a 3:1 (v/v) solvent mixture of deaerated acetate buffer (pH 2.6, 50 mM) and MeCN. (c) Plots of absorbance at λ = 378 (■), 550 (▲), and 690 nm (●) vs the $[Ru^{III}(bpy)_3]^{3+}$/**2**−OH_2 ratio. Red, green, and blue points denote data at the ratios 0, 1, and 2, respectively.

under 450 nm photoirradiation of the absorption band of $[Ru^{II}(bpy)_3]^{2+}$ in a 3:1 (v/v) solvent mixture of acetate buffer (pH 3.7, 50 mM) and MeCN under an Ar atmosphere [see Figure S1 in the Supporting Information (SI)]. The quenching constant of $[Ru^{II}(bpy)_3]^{2+*}$ by $[Co^{III}(NH_3)_5Cl]^{2+}$ was determined to be 140 M^{-1} (Figure S2).[10,12] In addition, the quantum yields (Φ) of the photocatalytic generation of $[Ru^{III}(bpy)_3]^{3+}$ with $[Co^{III}(NH_3)_5Cl]^{2+}$ were determined using a ferrioxalate actinometer under irradiation with monochromatic light at λ = 450 nm (see the experimental section in the SI). The Φ value increased with increasing $[Co^{III}(NH_3)_5Cl]^{2+}$ concentration to reach a constant value close to 80% (Figure S3).

1 was independently generated by the electrochemical oxidation of $[(N4Py)Fe^{II}]^{2+}$ in a 3:1 (v/v) solvent mixture of deaerated acetate buffer (pH 4.7, 50 mM) and MeCN. The cyclic voltammograms of **2** in a mixed solution exhibited two reversible redox waves at 0.4 and 0.8 V (vs SCE) that are assignable to the redox couples of $[(N4Py)Fe^{II}(OH_2)]^{2+}$ (**2**−OH_2) and $[(N4Py)Fe^{III}(OH)]^{2+}$ (**3**−OH), respectively (Figure S4). During the first oxidation, the absorption band at λ = 450 nm due to **2** decreased as the applied potential was increased (Figure S5). **1** was then gradually formed under the applied potential at 1.2 V.[13] These results on the electrochemical oxidation indicate that the oxidation potential of $[Ru^{III}(bpy)_3]^{3+}$ (E_{ox} = 1.18 V vs SCE)[14] is high enough to oxidize **2**−OH_2 to **1**.

Therefore, we carried out the chemical oxidation of **2**−OH_2 by $[Ru^{III}(bpy)_3]^{3+}$ in a 3:1 (v/v) solvent mixture of deaerated acetate buffer (pH 2.6, 50 mM) and MeCN to confirm the formation of **1** via the reaction of iron(II) complexes with $[Ru^{III}(bpy)_3]^{3+}$. First, the formation of **1** was found to depend on the amount of $[Ru^{III}(bpy)_3]^{3+}$ added to the solution of **2**−OH_2; we observed a stepwise UV−vis spectral change in response to the concentration ratio $[Ru^{III}(bpy)_3]^{3+}$/**2**−OH_2 = 0−1 (red and green lines) and 1−2 (green and blue lines), as shown in Figure 2. For example, when the changes in the absorbance at λ = 378 nm due to **2**−OH_2, at λ = 550 nm due to $[Ru^{II}(bpy)_3]^{2+}$, and at λ = 690 nm due to **1** were plotted against $[Ru^{III}(bpy)_3]^{3+}$/**2**−OH_2, the formation of **1** (λ = 690 nm) was observed at $[Ru^{III}(bpy)_3]^{3+}$ concentrations above the 1:1 ratio of $[Ru^{III}(bpy)_3]^{3+}$ to **2**−OH_2 (i.e., for $[Ru^{III}(bpy)_3]^{3+}$/**2**−OH_2 > 1 in Figure 2c). Such stepwise spectral changes are ascribed to the stepwise oxidation of **2**−OH_2 to **1** via **3**−OH with 1 and 2 equiv of $[Ru^{III}(bpy)_3]^{3+}$ (Scheme 2). Finally, we confirmed that the source of oxygen in **1** is H_2O by performing experiments using isotopically labeled water ($H_2{}^{18}O$) (Figure 3).[8,15,16]

Scheme 2



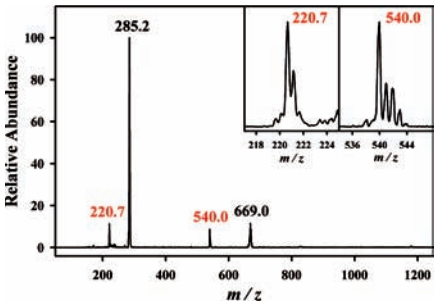


Figure 3. ESI-MS spectrum of $[(N4Py)Fe^{IV}({}^{18}O)]^{2+}$ formed in the reaction of $[(N4Py)Fe^{II}(CH_3CN)](ClO_4)_2$ (1.0×10^{-3} M) and $[Ru^{III}(bpy)_3](ClO_4)_3$ (3.0×10^{-3} M) in a 3:1 (v/v) solvent mixture of $H_2{}^{18}O$ (pH 2.6, 50 mM) and MeCN at 298 K. Peaks at m/z 220.7, 540.0, 285.2, and 669.0 correspond to $[(N4Py)Fe^{IV}({}^{18}O)]^{2+}$ (calcd m/z 220.6), $[(N4Py)Fe^{IV}({}^{18}O)(ClO_4)]^{+}$ (calcd m/z 540.1), $[Ru^{II}(bpy)_3]^{2+}$ (calcd m/z 285.1), and $[Ru^{II}(bpy)_3(ClO_4)]^{+}$ (calcd m/z 669.1), respectively. The insets show the observed isotope distribution patterns for (left) $[(N4Py)Fe^{IV}({}^{18}O)]^{2+}$ and (right) $[(N4Py)Fe^{IV}({}^{18}O)(ClO_4)]^{+}$.

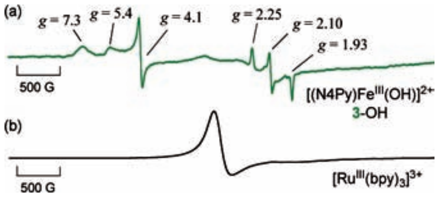


Figure 4. (a) EPR spectrum of **3**−OH produced by the addition of 1 equiv of $[Ru^{III}(bpy)_3]^{3+}$ (2.0 mM) to **2**−OH_2 (2.0 mM) in a 1:1 (v/v) solvent mixture of deaerated acetate buffer (pH 2.6, 50 mM) and MeCN at 77 K. (b) EPR spectrum of $[Ru^{III}(bpy)_3]^{3+}$ (2.0 mM) in MeCN at 77 K.

The stepwise electron-transfer oxidation of **2**−OH_2 to **1** was further confirmed by EPR measurements of reaction solutions. Upon addition of 1 equiv of $[Ru^{III}(bpy)_3]^{3+}$, **2**−OH_2 was oxidized to **3**−OH, which exhibited EPR signals at g = 7.3, 5.4, and 4.1 due to high-spin Fe^{III} species ($S = {}^5/_2$) together with those at 2.25, 2.10, and 1.93 due to low-spin Fe^{III} species ($S = {}^1/_2$) (Figure 4a).[17] Further addition of 1 equiv of $[Ru^{III}(bpy)_3]^{3+}$ resulted in a decrease in the **3**−OH signals because of conversion of **3**−OH to **1**, which is EPR-silent (S = 1). The EPR signal due to $[Ru^{III}(bpy)_3]^{3+}$ at g = 2.64 also disappeared (Figure 4b).[18]

In conclusion, we have demonstrated that the photocatalytic generation of a non-heme oxoiron(IV) complex, $[(N4Py)Fe^{IV}(O)]^{2+}$ (**1**), proceeds efficiently via electron transfer from $[Ru^{II}(bpy)_3]^{2+*}$ to $[Co^{III}(NH_3)_5Cl]^{2+}$ to produce $[Ru^{III}(bpy)_3]^{3+}$, followed by the electron-transfer oxidation of $[(N4Py)Fe^{II}]^{2+}$ using 2 equiv of $[Ru^{III}(bpy)_3]^{3+}$ and H_2O as an oxygen source. The expansion of the photocatalytic generation of non-heme oxoiron(IV) complexes to photocatalytic oxygenation of substrates by non-heme iron catalysts is underway in our laboratories.[19]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental section and Figures S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.

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