Photodriven Oxidation of Water by Plastoquinone Analogs with a Nonheme Iron Catalyst

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ABSTRACT: Photoirradiation of an acetonitrile solution containing p-benzoquinone derivatives (X-Q) as plastoquinone analogs, a nonheme iron(II) complex, [(N4Py)FeII]2+(N4Py = N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methyamine), and H2O afforded the evolution of O2 and the formation of the corresponding hydroquinone derivatives (X-QH2) quantitatively. During the photodriven oxidation of water by X-Q, [(N4Py)FeIV(O)]2+ was oxidized by the excited state of X-Q to produce the iron(IV)-oxo complex ([(N4Py)-FeIV(O)]3+) quantitatively. The concentration of [(N4Py)-FeIV(O)]2+ remained virtually the same during the repeated cycles of photodriven oxidation of water by X-Q. [(N4Py)FeIV(O)]2+ was further oxidized by the excited state of X-Q to [(N4Py)FeIV(O)]3+; this FeIV-oxo species is proposed as an active oxidant that affects the water oxidation. The photocatalytic mechanism of the water oxidation by X-Q with [(N4Py)FeIV(O)]2+ was clarified by detecting intermediates using various spectroscopic techniques, such as transient absorption and electron paramagnetic resonance measurements. To the best of our knowledge, the present study reports the first example of a functional model of Photosystem II (PSII) using X-Q as plastoquinone analogs in the photocatalytic oxidation of water.

INTRODUCTION

The oxidizing equivalents generated at the donor side of Photosystem II (PSII) are used to oxidize water, whereas the reducing equivalents accumulated at the acceptor side of PSII are used to reduce the two quinone molecules, Qa and Qb, which act as one-electron and two-electron gates, respectively.1−12 Finally, electrons with protons are transferred to plastoquinone (PQ) in quinone pool to produce plastoquinol (PQH2).1−12 The overall solar-driven reaction is given by eq 1, where PQ is reduced by H2O to produce O2 and PQH2:1−3

2H2O + 2PQ → O2 + 2PQH2

(1)

The photocatalytic oxidation of water by PQ as the oxidant in PSII makes it possible to connect PSII with PSI in the so-called Z-scheme, where PQH2 is used as the reductant to reduce NADP+ to NADPH and also to generate an electrochemical gradient for protons, across the thylakoid membrane, which can be used for the phosphorylation of ADP to ATP.1,2 Thus, the PQ/PQH2 redox couple plays an essential role in the Z-scheme for the overall photosynthesis.1,2

Tremendous efforts have so far been devoted to realizing artificial photosynthesis by mimicking charge-separation and redox processes in PSII as well as in PSI.3−5 However, neither the stoichiometry nor the intermediate of photodriven oxidation of water by PQ or PQ analogs has been established.10−12

We report herein the photodriven water oxidation reaction using p-benzoquinone derivatives (X-Q; Scheme 1 for the chemical structures) as plastoquinone analogs with a nonheme iron(II) catalyst, [(N4Py)FeII]2+, in acetonitrile (MeCN) containing H2O (eq 2). This is the first example of a functional mimic of PSII for the oxidation of water by PQ analogs in producing O2 and the corresponding PQH2 analogs. Moreover, an iron(IV)-oxo complex ([(N4Py)FeIV(O)]3+) has been identified as a catalytic intermediate during the photocatalytic water oxidation reaction.
photodriven oxidation of water when [(N4Py)FeII]2+ is fully converted to [(N4Py)FeIV(O)]2+. The photocatalytic mechanism is clarified by detecting intermediates using various spectroscopic techniques, such as transient absorption and electron paramagnetic resonance (EPR) measurements.

$$2\text{H}_2\text{O} + 2\text{DDQ} \xrightarrow{h\nu} \text{O}_2 + 2\text{DDQH}_2$$

**RESULTS AND DISCUSSION**

Photodriven Water Oxidation by \( \text{p}-\text{Benzoquinone Derivatives (X-Q)} \) with [(N4Py)FeII]2+. Photoirradiation of an MeCN solution of 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) (0.50 mM), [(N4Py)FeII]2+ (0.20 mM), and \( \text{H}_2\text{O} \) (0.50 M) with a xenon lamp (white light) resulted in \( \text{O}_2 \) evolution as shown in Figure 1, where the \( \text{O}_2 \) yield reaches nearly 100% based on the amount of DDQ added (eq 2). The oxygen yield was confirmed by gas chromatography (GC) as well as oxygen sensor (Foxy) measurements (Supporting Information (SI), Figure S1). The quantum yield for the photodriven water oxidation by DDQ reached up to 88% (SI, Figure S2) and the turnover number (TON) of 190 ± 10 was achieved based on [(N4Py)FeII]2+ (SI, Figure S3). Isotope-labeling experiments using \( ^{18}\text{O} \)-enriched water (97.4%) were performed to confirm the source of the evolved \( \text{O}_2 \) product; formation of \( ^{36}\text{O}_2 \) (99% based on the labeled \( ^{18}\text{O} \) percent) was observed as the sole product (Figure 2). The formation of DDQH\(_2\) in the photodriven oxidation of \( \text{H}_2\text{O} \) by DDQ (0.50 mM) with [(N4Py)FeII]2+ (0.20 mM) under photoirradiation (eq 2) was also observed by UV–vis spectral change at 350 nm due to DDQH\(_2\) (SI, Figure S4a) as well as appearance of a new \( ^1\text{H} \) NMR signal corresponding to DDQH\(_2\) (Figures 3 a,b).
Photodriven water oxidation was also achieved by other p-benzoquinone derivatives (X-Q) (0.50 mM), such as 1,4-benzoquinone (BQ), tetrachloro-1,4-benzoquinone (CA), tetramethyl-1,4-benzoquinone (DQ), and 2,5-dimethyl-1,4-benzoquinone (PXQ), with [(N4Py)Fe^III(OH)]^2+ (0.20 mM) and H_2O (0.50 M) as shown in Figure 1; the O_2 yields by BQ, CA, DQ, and PXQ were 91, 91, 49, and 90%, respectively (Figure 1). The formation of hydroquinone (QH_2),[14,15] 2,3,5,6-tetramethyl-1,4-hydroquinone (CAH_2), and durohydroquinone (DQH_2) as the products was confirmed by the UV-vis spectral changes (SI, Figure S4b), and the generation of QH_2 was also verified by taking 1H NMR spectra (Figure 3c,d).

Mechanistic Insights into the Photodriven Water Oxidation by DDQ with [(N4Py)Fe^II]^{2+}. During the photodriven H_2O oxidation by DDQ, the two-electron oxidation of [(N4Py)Fe^II]^{2+} occurs to produce [(N4Py)Fe^IV(O)]^{2+} (eq 3). Time course of the formation of [(N4Py)Fe^IV(O)]^{2+} in the photooxidation of [(N4Py)Fe^II]^{2+} by DDQ is shown in Figure 4, where the absorption band at 690 nm appeared due to [(N4Py)Fe^IV(O)]^{2+}. The formation of [(N4Py)Fe^IV(O)]^{2+} was also confirmed by CSI-MS (SI, Figure S7). Since the formation of DDQ^* is not observed in the photooxidation of [(N4Py)Fe^II]^{2+} by DDQ, [(N4Py)Fe^III]^3+ produced by electron transfer from [(N4Py)Fe^II]^{2+} to the triplet excited state of DDQ (3DDQ^*) may react with H_2O to produce [(N4Py)Fe^III(OH)]^{2+} and H^+ that reacts with DDQ^* to form DDQH^* (eq 4). The electron transfer from [(N4Py)Fe^II]^{2+} to 3DDQ^* is highly exergonic because of the much higher reduction potential of 3DDQ^* (3.1 V vs SCE) than the one-electron oxidation potential of [(N4Py)Fe^II]^{2+} (E_{ox} = 1.00 V vs SCE). The dispropor-

690 nm appeared due to [(N4Py)Fe^IV(O)]^{2+}.[13] The formation of [(N4Py)Fe^IV(O)]^{2+} was also confirmed by CSI-MS (SI, Figure S7). Since the formation of DDQ^* is not observed in the photooxidation of [(N4Py)Fe^II]^{2+} by DDQ, [(N4Py)Fe^III]^3+ produced by electron transfer from [(N4Py)Fe^II]^{2+} to the triplet excited state of DDQ (3DDQ^*) may react with H_2O to produce [(N4Py)Fe^III(OH)]^{2+} and H^+ that reacts with DDQ^* to form DDQH^* (eq 4). The electron transfer from [(N4Py)Fe^II]^{2+} to 3DDQ^* is highly exergonic because of the much higher reduction potential of 3DDQ^* (3.1 V vs SCE) than the one-electron oxidation potential of [(N4Py)Fe^II]^{2+} (E_{ox} = 1.00 V vs SCE). The dispropor-

nation of two DDQH^* species yields DDQ and DDQH_2 (eq 5):

\[
[(N4Py)Fe^{II}]^{2+} + 3DDQ^* + H_2O \xrightarrow{h\nu} [(N4Py)Fe^{III(OH)}]^2+ + DDQH_2
\]

The overall reaction of the one-electron photooxidation of [(N4Py)Fe^II]^{2+} by DDQ is given by eq 6. Then, [(N4Py)-Fe^III(OH)]^{2+} is further oxidized by 3DDQ^* to produce [(N4Py)Fe^IV(O)]^{2+} and DDQH^* (eq 7) that dispropor-

tionates to yield DDQ and DDQH_2 (eq 5), resulting in the overall reaction of two-electron photooxidation of [(N4Py)-Fe^II]^{2+} by DDQ with H_2O to produce [(N4Py)Fe^IV(O)]^{2+} (eq 3). It was reported previously that [(N4Py)Fe^IV(O)]^{2+} was produced by the two-electron oxidation of [(N4Py)Fe^II]^{2+} by two equivalents of [Ru(bpy)_3]^3+ with H_2O,[5,17,18] In addition, 18O-labeled water experiments demonstrated that the oxygen atom in [(N4Py)Fe^IV(O)]^{2+} derived from water.[13]

\[
2[(N4Py)Fe^{II}]^{2+} + 3DDQ^* + H_2O \xrightarrow{h\nu} 2[(N4Py)Fe^{III(OH)}]^2+ + DDQH_2
\]

\[
[(N4Py)Fe^{III(OH)}]^2+ + 3DDQ^* \xrightarrow{h\nu} [(N4Py)Fe^{IV(O)}]^2+ + DDQH^*
\]

Photoinduced electron transfer from [(N4Py)Fe^IV(O)]^{2+} to the triplet excited state of p-benzoquinone derivatives (X-Q) was examined by nanosecond laser transient absorption measurements (Figure 5; SI, Figures S8 and S9). Laser excitation of a deaerated MeCN solution of X-Q resulted in the formation of X-Q^* with \lambda_{max} (620 nm for 3DDQ^*, 420 nm for

![Figure 4](image-url) Absorption spectral changes showing the formation of [(N4Py)Fe^IV(O)]^{2+} in the photodriven oxidation of H_2O by DDQ (1.25 mM) with [(N4Py)Fe^II]^{2+} (0.50 mM) under photoirradiation (white light) in a MeCN solution containing H_2O (1.4 M) at 298 K. Inset shows time profile of absorbance change at 690 nm due to [(N4Py)Fe^IV(O)]^{2+}.

![Figure 5](image-url) (a) Transient absorption spectral changes after photoexcitation at 355 nm on a deaerated MeCN solution of DDQ (0.50 mM). (b) Decay time profiles at 620 nm due to the decay of 3DDQ^* at various concentrations of [(N4Py)Fe^II]^{2+} (0 black), 20 (blue), 40 (green), 80 (orange), and 200 (red) \mu M. (c) Plot of k_{obs} vs concentration of [(N4Py)Fe^II]^{2+}. (d) Plot of k_{obs} vs concentration of [(N4Py)Fe^IV(O)]^{2+}.

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The decay rate constants of 3-X-Q* also increased with increasing concentration of [(N4Py)FeIV(O)]2+ species, which was independently prepared by reacting [(N4Py)FeII]2+ complex with iodosylbenzene (PhI(O)). The rate constant of electron transfer from [(N4Py)FeIV(O)]2+ to 3DDQ* was determined from the slope of plot of kobs vs concentration of [(N4Py)FeIV(O)]2+ to be 9.4 ± 0.6 × 10^10 M^−1 s^−1, which is close to the diffusion rate constant in MeCN. The rate constants of electron transfer from [(N4Py)FeII]2+ to 3BQ*, 3CA*, 3DQ*, and 3PXQ* were also determined to be 1.2 ± 10^10, 1.7 ± 10^10, 1.1 ± 10^10, and 1.1 ± 10^10 M^−1 s^−1, respectively (Table 1). The decay rate constant of 3-X-Q* was determined from the slope of plot of kobs vs concentration of [(N4Py)FeIII(OOH)]2+ at 510 nm for 3CA*, 470 nm for 3DQ*, and 440 nm for 3PXQ*.

Table 1. Rate Constants of Electron Transfer from an Iron Complex to the Triplet Excited State of p-Benz HQ Derivatives (X-Q) in MeCN at 298 K

<table>
<thead>
<tr>
<th>X-Q</th>
<th>[(N4Py)FeII]2+</th>
<th>[(N4Py)FeIV(O)]2+</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDQ</td>
<td>(1.0 ± 0.1) × 10^10</td>
<td>(9.4 ± 0.6) × 10^10</td>
</tr>
<tr>
<td>BQ</td>
<td>(1.2 ± 0.1) × 10^10</td>
<td>(2.1 ± 0.2) × 10^10</td>
</tr>
<tr>
<td>CA</td>
<td>(1.7 ± 0.1) × 10^10</td>
<td>(9.7 ± 0.8) × 10^10</td>
</tr>
<tr>
<td>DQ</td>
<td>(1.1 ± 0.1) × 10^10</td>
<td>(3.2 ± 0.2) × 10^10</td>
</tr>
<tr>
<td>PXQ</td>
<td>(1.1 ± 0.1) × 10^10</td>
<td>(5.0 ± 0.4) × 10^10</td>
</tr>
</tbody>
</table>

Subsequently, the resulting [(N4Py)FeIV(O)]3+ species may react rapidly with H2O to produce an iron(III)-hydroperoxo complex [(N4Py)FeIII(OOH)]2+ and H2O2 (Scheme 2, reaction pathway d). The proton is used to protonate DDQ* to give DDQH*, followed by the disproportionation of DDQH* to yield DDQ and DDQH2, (eq 5), [(N4Py)FeIII(OOH)]2+ is further oxidized by DDQ via hydrogen atom transfer to afford [(N4Py)FeIII(O2•−)]2+ (Scheme 2, reaction pathway e), followed by a rapid release of O2 from [(N4Py)FeIII(O2•−)]2+ to regenerate [(N4Py)FeII]2+ (Scheme 2, reaction pathway f; see also SI, Figure S13). Indeed, when [(N4Py)FeIII(OOH)]2+ was independently prepared in the reaction of [(N4Py)FeII]2+ and H2O2 and oxidized by DDQ thermally, the yield of O2 derived from [(N4Py)FeIII(OOH)]2+ was determined to be ~100% based on DDQ concentration (SI, Figure S14).

In the photocatalytic cycle in Scheme 2, electron transfer from [(N4Py)FeIV(O)]2+ to 3DDQ* is the rate-determining step, when [(N4Py)FeIV(O)]2+ is produced at the initial photoirradiation as shown in Figure 4, and the concentration of [(N4Py)FeIV(O)]2+ decayed only little (Figure 6a), when DDQ was fully converted to DDQH2 (Figure 6b). The catalytic cycle was repeated three times by adding DDQ to the resulting solution to start the photodriven oxidation of water by DDQ to produce O2 and DDQH2, when the concentration of [(N4Py)FeIV(O)]2+ decayed only little again. Thus, [(N4Py)FeIV(O)]2+ acts as a robust homogeneous catalyst for the photodriven oxidation of water by DDQ under the neutral conditions. This shows sharp contrast to the reported nonheme iron complexes, such as FeII(BQEN)2+ (BQEN = N,N-dimethyl-N,N'-bis(8-quinolyl)ethane-1,2-diamine) and FeII(BQCN)2+ (BQCN = N,N'-dimethyl-N,N-bis(8-quinolyl)cyclohexane-diamine), which undergo demetalation under acidic conditions and decompose to produce iron hydroxide nanoparticles under basic conditions in catalytic oxidation of water. Low-temperature EPR measurements were also performed to detect paramagnetic intermediates in the photodriven oxidation of H2O by DDQ with [(N4Py)FeII]2+ in MeCN containing H2O. Before irradiation, no EPR signals were detected (SI, Figure S15, black spectrum). Photoirradiation of a deaerated MeCN solution of [(N4Py)FeII]2+ with DDQ and H2O resulted in the formation of [(N4Py)FeIII(OH)]2+ (Scheme 2, reaction pathway a), which exhibited a high-spin (S = 5/2) signal together with a sharp signal at g = 2.0050 due...
to DDQ•− (SI, Figure S15, red spectrum).28 Further photoirradiation of the reaction solution resulted in decrease in the EPR intensity due to [(N4Py)FeIV(O)]2+ and increase in the EPR intensity due to DDQ•− (SI, Figure S15, blue spectrum), indicating that [(N4Py)FeIII(OH)]2+ was oxidized by adding DDQ (second time; 0.50 mM) to the resulting solution; the absorbance at 690 nm due to [(N4Py)FeIV(O)]2+ (100% yield) was fully regenerated again by adding further DDQ (third time; 0.50 mM) to the resulting solution; the absorbance at 690 nm due to [(N4Py)FeIV(O)]2+ (0.10 mM, 100% yield) was fully converted to DDQH2 (inset of a, 3rd), when third added DDQ was fully converted to DDQH2 (0.10 mM, 100% yield) after photoirradiation from 3000 to 6600 s (inset of a, second), when second added DDQ was fully converted to DDQH2 (λmax = 350 nm; blue line in b), where the reaction solution was diluted by 1/20 after each irradiation.

**CONCLUSION**

We have shown the photodriven oxidation of H2O by plastoquinone analogs as an oxidant in the case of PSII in photosynthesis using an nonheme iron(III) complex as a water oxidation catalyst. This is the first time to establish the stoichiometry for the photodriven water oxidation by plastoquinone analogs with an iron(II) complex, thereby evolving O2 and yielding the corresponding hydroquinone derivatives, mimicking the function of PSI. The photocatalytic mechanism of H2O oxidation by DDQ with [(N4Py)FeII]2+ is clarified as shown in Scheme 2, where [(N4Py)FeII]2+ (SI, Figure S15, blue spectrum) was oxidized by adding DDQ (second time; 0.50 mM) to the resulting solution; the absorbance at 690 nm due to [(N4Py)FeIV(O)]2+ (100% yield) was fully converted to DDQH2 (λmax = 350 nm; green line in b). Then, [(N4Py)FeIV(O)]2+ (100% yield) was fully regenerated by adding DDQ (second time; 0.50 mM) to the resulting solution; the absorbance at 690 nm due to [(N4Py)FeIV(O)]2+ (100% yield) was fully regenerated again by adding further DDQ (third time; 0.50 mM) to the resulting solution; the absorbance at 690 nm due to [(N4Py)FeIV(O)]2+ (0.10 mM, 100% yield) was fully converted to DDQH2 (λmax = 350 nm, red line in b).

**EXPERIMENTAL SECTION**

**Materials.** All solvents and chemicals were of reagent-grade quality, obtained commercially, and used without further purification, unless otherwise noted. 2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ), 1,4-benzoquinone (BQ), tetrachloro-1,4-benzoquinone (CA), duroquinone (DQ), hydroquinone (QH2), and perchloric acid (70 wt % in H2O) were obtained commercially from Sigma-Aldrich Chemical Co., and p-xylenequinone (PXQ) was obtained from Tokyo Chemical Industry Co. Tetrabutylammonium hexafluorophosphate (TBAPF6) was obtained from Fluka Co. Deuterated acetonitrile (CD3CN) was obtained from Sigma-Aldrich Chemical Co. and used as received. Solvents, such as acetonitrile (CH3CN; MeCN) and methanol (CH3OH; MeOH), were dried according to the literature procedures and distilled under Ar prior to use.27 Nonheme iron(II) complex ([[(N4Py)FeII(MeCN)](ClO4)2] and its corresponding iron(IV)-oxo complex ([[(N4Py)FeIV(O)]2]) were prepared by the literature methods.28 1-Isodoxybenzene (PhIO) was prepared by the literature method.

**Instrumentation.** The amount of evolved oxygen was recorded by a commercial fast response fiber optic sensor (Foxy, Ocean Optics, Inc.) as well as gas chromatography (Acme 6000 GC, YOUNG LIN Ins.). Subnanosecond laser-induced transient absorption spectra were collected by a customized measuring system equipped with a picosecond-pulse laser for the photoexcitation and a photomultiplier detector developed by UNISOKU Co., Ltd.27 Nonheme iron(II) complex ([[(N4Py)FeII(MeCN)](ClO4)2] and its corresponding iron(IV)-oxo complex ([[(N4Py)FeIV(O)]2]) were prepared by the literature methods.28 1-Isodoxybenzene (PhIO) was prepared by the literature method.

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[\text{(N4Py)}Fe^{\text{II}}(O)]^{2-}\) to the excited X-Q derivatives in a deaerated MeCN solution at 298 K.

**Product Analysis.** The photodriven water oxidation by the excited state of \(p\)-benzoquinone with a nonheme iron complex was examined in a quartz cell (optical path length 1.0 cm) using a Xe lamp (white light; 300 W) on an ASAHI SPECTRA MAX-302 for irradiation at 298 K. Oxygen formed in the oxidation of water (500 mM) by the excited state of \(p\)-benzoquinone (0.50 mM) with a nonheme iron complex (0.20 mM) in \(\text{CH}_3\text{CN}\) after irradiation (white light) was identified by GC and Foxy.

**Quantum Yield Determination.** Quantum yield (QY) of photodriven water oxidation by \(p\)-benzoquinone with a nonheme iron complex has been determined under visible light irradiation of \(10\) mM \(p\)-benzoquinone with a nonheme iron complex \((\lambda = 420 \text{ nm})\) under photoirradiation \((\lambda = 420 \text{ nm})\) with irradiation time interval of 1 h (see Figure S2).

The initial slope of the graph is taken to determine the quantum yield. The quantum yield was estimated as \(\text{QY}(\%) = \frac{R/I \times 100}{R(I)}\), where \(R\) (mol s\(^{-1}\)) is \(O_2\) production rate and \(I\) (einstein s\(^{-1}\)) is coefficient based on the rate of the number of incident photons absorbed by \(p\)-benzoquinone. The total number of incident photons was measured by a standard method using an actinometer (potassium ferrioxalate, \(\text{K}_3[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]6\)) under photoirradiation \((\lambda = 420 \text{ nm})\) at 298 K where photon flux was determined to be \(2.03 \times 10^{-17}\) einstein s\(^{-1}\).

**REFERENCES**


(20) Electron transfer from [(N4Py)FeIV(O)]2+ to DDQ* to produce [(N4Py)FeIV(O)]2+ and DDQ* is highly exergonic to be located in the Marcus inverted region. In such a case, however, electron transfer from [(N4Py)FeIV(O)]2+ to DDQ* may produce an excited state of [(N4Py)FeIV(O)]2+ and DDQ* to keep the electron transfer in the diffusion-limited rate as reported for photoinduced electron transfer from electron donors to flavin derivatives. See: Murakami, M.; Ohkubo, K.; Fukuzumi, S. Inter- and Intramolecular Photoinduced Electron Transfer of Flavin Derivatives with Extremely Small Reorganization Energies. Chem. - Eur. J. 2010, 16, 7820–7832.


(22) It should be noted that no electron transfer occurs from [(N4Py)FeIII(O)]2+ to [(N4Py)FeIV(O)]2+ to produce the μ-oxo dimer, [(N4Py)FeIII···O·FeIII(N4Py)]4+, because the one-electron oxidation of [(N4Py)FeII(O)]2+ (Eox vs SCE = 1.00 V, ref 23) is higher than the one-electron reduction potential of [(N4Py)FeIV(O)]2+ (Ered vs SCE = 0.51 V, ref 16).


(25) Although the rate of electron transfer from FeIV=O is diffusion-limited, as soon as FeIII=O is produced, it reacts with H2O. In such a case, the electron transfer from FeIV=O to DDQ* is the rate-determining step for the catalytic water oxidation when FeIV=O is observed as an intermediate during the reaction.

(26) When DDQ was fully converted to DDQH2 (Figure 6b), only a trace amount of [(N4Py)FeIV(O)]2+ decayed (Figure 6a). Therefore, the reaction of [(N4Py)FeIV(O)]2+ with DDQH2 is negligible under the conditions.


