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Photocatalytic Hydrogen Evolution from Plastoquinol Analogues as a Potential Functional Model of Photosystem I

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ABSTRACT: The recent development of a functional model of photosystem II (PSII) has paved a new way to connect the PSII model with a functional model of photosystem I (PSI). However, PSI functional models have yet to be reported. We report herein the first potential functional model of PSI, in which plastoquinol (PQH₂) analogues were oxidized to plastoquinone (PQ) analogues, accompanied by hydrogen (H₂) evolution. Photo-irradiation of a deaerated acetonitrile (MeCN) solution containing hydroquinone derivatives (X-QH₂) as a hydrogen source, 9-mesityl-10-methylacridinium ion (Acr⁺-Mes) as a photoredox catalyst, and a cobalt(III) complex, Co^{III}(dmgH)₂pyCl (dmgH =



dimethylglyoximate monoanion; py = pyridine) as a redox catalyst resulted in the evolution of H₂ and formation of the corresponding *p*-benzoquinone derivatives (X-Q) quantitatively. The maximum quantum yield for photocatalytic H₂ evolution from tetrachlorohydroquinone (Cl_4QH_2) with Acr⁺-Mes and Co^{III}(dmgH)₂pyCl and H₂O in deaerated MeCN was determined to be 10%. Photocatalytic H₂ evolution is started by electron transfer (ET) from Cl_4QH_2 to the triplet ET state of Acr⁺-Mes to produce $Cl_4QH_2^{\bullet+}$ and Acr[•]-Mes with a rate constant of $7.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, followed by ET from Acr[•]-Mes to Co^{III}(dmgH)₂pyCl to produce $[Co^{II}(dmgH)_2pyCl]^-$, accompanied by the regeneration of Acr⁺-Mes. On the other hand, $Cl_4QH_2^{\bullet+}$ is deprotonated to produce Cl_4QH^{\bullet} , which transfers either a hydrogen-atom transfer or a proton-coupled electron transfer to $[Co^{II}(dmgH)_2pyCl]^-$ to produce a cobalt(III) hydride complex, $[Co^{III}(H)(dmgH)_2pyCl]^-$, which reacts with H⁺ to evolve H₂, accompanied by the regeneration of $Co^{III}(dmgH)_2pyCl]^-$ was detected by electron paramagnetic resonance measurements.

INTRODUCTION

There are two photosystems, photosystem I (PSI) and photosystem II (PSII), and both contain photosynthetic reaction centers where multistep charge-separation reactions proceed.^{1,2} The oxidizing equivalents generated at the donor side of PSII are used to oxidize water (H₂O), whereas the reducing equivalents accumulated at the acceptor side of PSII are used to reduce plastoquinone (PQ) in a quinone pool to produce plastoquinol (PQH₂).^{3–6} The overall solar-driven reaction is given by eq 1, where PQ is reduced by H₂O to produce O₂ and PQH₂.^{3–6}

$$2H_2O + 2PQ \xrightarrow{n_1} O_2 + 2PQH_2$$
 (1)

1...

Photocatalytic oxidation of H_2O 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.^{7–9} We reported recently a functional model of PSII in which H_2O is oxidized by PQ analogues to produce O_2 and PQH₂ analogues.¹⁰ The development of a PSII functional model provides an excellent opportunity to combine with a PSI

functional model to make it possible to mimic the overall photosynthetic process. However, there has been no report on the photodriven oxidation of PQH₂ or its analogues to reduce protons to achieve hydrogen (H₂) evolution, which is a PSI functional model (eq 2) despite extensive studies on photocatalytic H₂ evolution with various reductants except for PQH₂ or its analogues.¹¹⁻¹⁸ The development of the potential functional model of PSI and bioinspired catalysts is the key issue for achieving solar energy tranformations.¹⁹

$$PQH_2 \xrightarrow{n\nu} PQ + H_2 \tag{2}$$

We report herein photocatalytic H₂ evolution from hydroquinone derivatives (X-QH₂) as PQ analogues, a cobalt(III) complex, Co^{III}(dmgH)₂pyCl (dmgH = dimethylglyoximate monoanion; py = pyridine) as a H₂ evolution catalyst,²⁰ 9mesityl-10-methylacridinium ion $(Acr^+-Mes)^{21}$ as an organic

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photoredox catalyst, and H₂O using a light-emitting-diode (LED) lamp with a UV cut filter ($\lambda > 420$ nm; Scheme 1).

Scheme 1. (a) Schematic Illustration of PQH₂ and X-QH₂ and (b) Photocatalytic H₂ Evolution with Acr⁺-Mes and $Co^{III}(dmgH)_2pyCl$



Acr⁺-Mes is used as a simple and efficient photosynthetic reaction center model compound that undergoes fast electron transfer (ET) from the Mes moiety to the singlet excited state of the Acr⁺ moiety to produce a long-lived triplet ET state [³(Acr[•]-Mes^{•+})] via intersystem crossing from the singlet ET state, which shows the longest lifetime among photosynthetic reaction center model compounds.^{21–24} On the other hand, Co^{III}(dmgH)₂pyCl is used as an efficient H₂ evolution catalyst.^{25–28} Photocatalytic H₂ evolution is accompanied by oxidation of X-QH₂ to the corresponding *p*-benzoquinone derivatives (X-Q). This is the first example of a potential functional model of PSI, where PQH₂ analogues are oxidized to PQ analogues, accompanied by H₂ evolution. Once H₂ is produced, NAD⁺ is selectively reduced by H₂ to produce NADH in the presence of appropriate catalysts.^{29–31}

RESULTS AND DISCUSSION

Photodriven H₂ Evolution by Hydroquinone Derivatives (X-QH₂) with Acr⁺-Mes, Co^{III}(dmgH)₂pyCl, and H₂O. Photoirradiation of a deaerated MeCN solution containing hydroquinone derivatives (X-QH₂; 1.0 mM), Acr⁺-Mes (0.75 mM), $Co^{III}(dmgH)_2$ pyCl (0.60 mM), and H₂O (2.0 M) under Ar using a LED lamp with a UV cut filter ($\lambda > 420$ nm) resulted in H_2 evolution, as shown in Figure 1, where the H_2 yield determined by gas chromatography (GC; see the Experimental Section) reaches nearly 100% based on the amount of X-QH₂ added (Scheme 1b). In the absence of Acr⁺-Mes or Co^{III}(dmgH)₂pyCl or H₂O, no H₂ evolution was observed. Thus, both Acr⁺-Mes and Co^{III}(dmgH)₂pyCl are required for photocatalytic H₂ evolution from X-QH₂. The quantum yield (QY) for photocatalytic H₂ evolution from Cl_4QH_2 (10 mM) with Acr⁺-Mes (0.75 mM), Co^{III}(dmgH)₂pyCl (0.60 mM), and H₂O (2.0 M) in deaerated MeCN was determined to be 10% by using a ferrioxalate actinometer (see the Experimental Section and Figure S1).³



Figure 1. Time courses of H₂ evolution from X-QH₂ [1.0 mM; QH₂ (black circles), Cl₄QH₂ (red circles), and Me₄QH₂ (blue circles)] with Acr⁺-Mes (0.75 mM) and Co^{III}(dmgH)₂pyCl (0.60 mM) in the presence of H₂O (2.0 M) in deaerated MeCN under photoirradiation with a filter cutting UV light ($\lambda > 420$ nm) at 298 K.

The turnover number (TON) for photocatalytic H₂ evolution from Me₄QH₂ (10 mM) with Acr⁺-Mes (0.20 mM), Co^{III}(dmgH)₂pyCl (0.15 mM), and H₂O (11 M) in deaerated MeCN were 35 \pm 2 or 47 \pm 5 based on Acr⁺-Mes or Co^{III}(dmgH)₂pyCl, respectively (Figure S2). UV–vis absorption spectral change of the 40-times-diluted reaction solution obtained in photocatalytic H₂ evolution from Cl₄QH₂ (1.0 mM) with Acr⁺-Mes (0.75 mM), Co^{III}(dmgH)₂pyCl (0.60 mM), and H₂O (2.0 M) are shown in Figure 2, where the



Figure 2. UV–vis absorption spectral changes of a deaerated MeCN solution containing Cl₄QH₂ (1.0 mM), Acr⁺-Mes (0.75 mM), and Co^{III}(dmgH)₂pyCl (0.60 mM) in the presence of H₂O (2.0 M) in deaerated MeCN under photoirradiation with a filter cutting UV light ($\lambda > 420$ nm) at 298 K. The spectra were recorded after 40 times dilution of the reaction solution. The inset shows a plot of the yield of Cl₄Q versus irradiation time.

absorption band at 287 nm due to the formation of *p*-chloranil (Cl_4Q) increased during photoirradiation, accompanied by a decrease in absorption at 305 nm due to Cl_4QH_2 . The yield of Cl_4Q after 6 h of photoirradiation was determined to be 100% based on the initial amount of Cl_4QH_2 .

The absorption spectra of Acr⁺-Mes ($\lambda_{max} = 360$ and 423 nm) remained nearly the same during photocatalytic H₂ evolution from Cl₄QH₂ with Acr⁺-Mes, Co^{III}(dmgH)₂pyCl, and H₂O for 6 h (Figure 2), showing that Acr⁺-Mes is stable after long-time photoirradiation. In fact, photocatalytic H₂ evolution can be started again by the addition of Cl₄QH₂ was oxidized to Cl₄Q (Figure S3).

When hydroquinone (QH_2) was used instead of Cl_4QH_2 , photoirradiation of a deaerated MeCN solution containing

QH₂ (1.0 mM), Acr⁺-Mes (0.75 mM), Co^{III}(dmgH)₂pyCl (0.60 mM), and H₂O (2.0 M) using a LED lamp with a UV cut filter ($\lambda > 420$ nm) for 6 h also afforded *p*-benzoquinone (BQ) evolution with 100%, which was the monitored absorbance at 280 nm due to BQ (Figure S4). Oxidation of QH₂ to BQ in photocatalytic H₂ evolution with Acr⁺-Mes and Co^{III}(dmgH)₂pyCl was confirmed clearly by ¹H NMR spectral changes in deaerated CD₃CN, as shown in Figures 3 and 4.



Figure 3. ¹H NMR spectra of the reaction solution containing BQ produced by photoirradiation with a UV cut filter ($\lambda > 420$ nm) of a deaerated CD₃CN solution containing QH₂ (1.0 mM), Acr⁺-Mes (0.75 mM), Co^{III}(dmgH)₂pyCl (0.60 mM), and H₂O (2.0 M) for (a) 0 h, (b) 1 h, (c) 4 h, (d) 7 h, (e) 10 h, (f) 15 h at 298 K. The peak at 6.80 ppm originated from BQ (H_a), and the peak at 6.64 ppm was due to QH₂ (H_b). H_c is exchangeable in the presence of H₂O. In all cases, 1,4-dioxane (1.0 mM; the peak at 3.60 ppm) was added as a reference after the photoreaction.

When QH₂ was replaced by durohydroquinone (Me₄QH₂) under the same experimental conditions, Me₄QH₂ ($\lambda_{max} = 285$ nm) was oxidized to Me₄Q₄ as shown in Figure S5. In the cases of DDQH₂ and Me₂QH₂, they were oxidized to DDQ and Me₂Q to evolve H₂ under the same conditions.

Mechanistic Insights into the Photodriven H₂ Evolution by Hydroquinone Derivatives with Acr⁺-



Figure 4. Plot of the concentration of BQ or QH₂ versus time for photocatalytic H₂ evolution by QH₂ (1.0 mM) with Acr⁺-Mes (0.75 mM), Co^{III}(dmgH)₂pyCl (0.60 mM), and H₂O (2.0 M) under photoirradiation with a UV cut filter (λ > 420 nm) of a deaerated CD₃CN solution at 298 K.

Mes, Co^{III}(dmgH)₂pyCl, and H₂O. In order to obtain the mechanistic insight into photocatalytic H₂ evolution in Scheme 1b, nanosecond laser transient absorption measurements were performed. Laser excitation of a deaerated MeCN solution of Acr⁺-Mes resulted in formation of the triplet ET state [³(Acr[•]-Mes^{•+})] as reported previously (Figure S6a).^{21,22} In the presence of Cl₄QH₂, the decay rate of the absorption band at 500 nm due to the Mes^{•+} moiety of ³(Acr[•]-Mes^{•+}) increased with increasing concentration of Cl₄QH₂ (Figure 5a). The



Figure 5. (a) Decay time profiles at 500 nm due to the Mes⁺⁺ moiety of ³(Acr[•]-Mes⁺⁺) at various concentrations of Cl_4QH_2 [0 (black), 1.0 (blue), 2.0 (green), 3.0 (orange), and 4.0 (red) mM] after photoexcitation (λ_{ex} = 355 nm) of a deaerated MeCN solution of Acr⁺-Mes (0.10 mM). (b) Plot of k_{obs} versus concentration of Cl_4QH_2 . (c) Decay time profiles at 520 nm due to decay of the Acr⁺ moiety of Acr⁺-Mes at various concentrations of $Co^{III}(dmgH)_2pyCl$ [0 (black), 0.10 (blue), 0.20 (green), 0.40 (orange), and 0.60 (red) mM] after photoexcitation at 355 nm in a deaerated MeCN solution of Acr⁺-Mes (0.10 mM) and Cl_4QH_2 (1.0 mM). (d) Plot of k_{obs} versus concentration of $Co^{III}(dmgH)_2pyCl$.

second-order rate constant of ET from Cl₄QH₂ to the Mes^{•+} moiety of ³(Acr[•]-Mes^{•+}) was determined from the slope of the first-order decay rate constant versus concentration of Cl₄QH₂ to be 7.2 × 10⁷ M⁻¹ s⁻¹ at 298 K (Figure 5b). ET from Cl₄QH₂ to the Mes^{•+} moiety of ³(Acr[•]-Mes^{•+}) is exergonic, judging from the one-electron oxidation peak potential of Cl₄QH₂ (E_{pa} vs SCE = 1.05 V; Figure S7a) and the one-

electron reduction peak potential of the Mes⁺⁺ moiety of ³(Acr[•]-Mes^{•+}) (E_{red} vs SCE = 2.06 V)²² in CH₃CN. When the concentration of Cl₄QH₂ (200 mM) was increased, the formation of Cl₄QH[•] was detected at 430 nm (Figure S8a). ET from the Acr[•] moiety of Acr[•]-Mes (E_{ox} vs SCE = -0.57 V) to $Co^{III}(dmgH)_2$ pyCl (E_{red} vs SCE = -0.16 V) (Figure S7b) is exergonic. In fact, ET from the Acr[•] moiety of Acr[•]-Mes to Co^{III}(dmgH)₂pyCl observed; the decay rate of absorbance at 520 nm due to Acr[•] increased with increasing concentration of Co^{III}(dmgH)₂pyCl (Figure 5c). The second-order rate constant of ET from the Acr[•] moiety of Acr[•]-Mes to Co^{III}(dmgH)₂pyCl was determined from the slope of the first-order decay rate constant versus concentration of $Co^{III}(dmgH)_2$ pyCl to be $4.2 \times 10^7 M^{-1} s^{-1}$ at 298 K (Figure 5d). It was reported previously that the triplet excited state of Acr⁺-Mes showed phosphorescence with 1.96 eV.³³ However, it was later assigned to phosphorescence from the acridine impurity.³⁴ It should be noted that ET from the triplet excited state of Acr⁺-Mes (E_{ox} vs SCE = 2.06-1.96 = 0.10 V) to $Co^{III}(dmgH)_2$ pyCl (E_{red} vs SCE = -0.16 V) is by 0.26 eV endergonic, and thereby no ET would occur from the triplet excited state of Acr⁺-Mes to Co^{III}(dmgH)₂pyCl. It should also be noted that no singlet state of the ET of Acr⁺-Mes, which has a lifetime of 7 ns,²² is involved in the ET to $Co^{III}(dmgH)_2$ pyCl, as indicated in the 0–60 μ s time range. The strong oxidizing ability of the Mes^{•+} moiety (E_{red} vs SCE = 2.06 V) and the reducing ability of the Acr[•] moiety (E_{ox} vs SCE = -0.57 V) have been well utilized as efficient photoredox catalysts in various photocatalytic reactions.^{21,22,35-42}

When Cl₄QH₂ was replaced by QH₂ and Me₄QH₂, laser transient absorption resulted. The second-order rate constants of ET from QH_2 and Me_4QH_2 to the Mes⁺ moiety of ³(Acr⁺-Mes^{•+}) were determined from the slopes of the first-order decay rate constants versus concentration of QH₂ and Me_4QH_2 to be 1.6 \times 10⁶ and 5.8 \times 10⁶ M⁻¹ s⁻¹ at 298 K, respectively (Figure S9a,c). ET from QH₂ and Me₄QH₂ to the $Mes^{\bullet+}$ moiety of ³(Acr[•]-Mes^{•+}) are highly exergonic, judging from the one-electron oxidation peak potential of QH_2 (E_{pa} vs SCE = 0.98 V) and Me₄QH₂ (E_{pa} vs SCE = 0.85 V) (Figure S7a) and the one-electron reduction peak potential of the Mes^{•+} moiety of ³(Acr[•]-Mes^{•+}) (E_{red} vs SCE = 2.06 V).^{21,22} The second-order rate constants of ET from the Acr[•] moiety of Acr[•]-Mes to Co^{III}(dmgH)₂pyCl in the presence of QH₂ and Me₄QH₂ were determined from the slopes of the first-order decay rate constant versus concentration of Co^{III}(dmgH)₂pyCl to be 4.3×10^7 and 4.1×10^7 M⁻¹ s⁻¹ at 298 K, respectively (Figure S9b,d). In the presence of a large concentration of QH_2 (400 mM) and Me_4QH_2 (5.0 mM), semiquinone radicals, QH[•] and Me₄QH[•], were detected at $\lambda_{max} = 400$ and 410 nm, respectively (Figures S10 and S11),⁴³ which were blue-shifted compared to that of Cl₄QH[•] ($\lambda_{max} = 430$ nm).⁴⁴ Thus, a hydroquinone radical cation $(QH_2^{\bullet+})$ produced by ET from QH₂ to the Mes^{$\bullet+$} moiety of ³(Acr^{$\bullet-$}Mes^{$\bullet+$}) deprotonates rapidly to produce a semiquinone radical (QH[•]).

Catalytic Mechanism of the Photodriven H₂ Evolution by Hydroquinone Derivatives with Acr⁺-Mes, Co^{III}(dmgH)₂pyCl, and H₂O. Scheme 2 shows the proposed mechanism of photocatalytic H₂ evolution from X-QH₂ with Acr⁺-Mes and Co^{III}(dmgH)₂pyCl. As shown in Figure 5a, ET from X-QH₂ to the Mes^{•+} moiety of the ET state of Acr⁺-Mes [³(Acr[•]-Mes^{•+})] produced upon photoexcitation of Acr⁺-Mes occurs with the diffusion-limited rate to produce X-QH₂^{•+} and Acr[•]-Mes. ET from Acr[•]-Mes to Co^{III}(dmgH)₂pyCl occurs to

Scheme 2. Proposed Mechanism of Photocatalytic H_2 Evolution from QH_2 with Acr^+ -Mes and $Co^{III}(dmgH)_2pyCl$



produce $[Co^{II}(dmgH)_2pyCl]^-$, accompanied by the regeneration of Acr⁺-Mes. X-QH₂^{•+} is known to be deprotonated rapidly to produce a semiquinone radical, X-QH[•] (Figures S8, S10, and S11).⁴³ ET from Acr[•]-Mes to $[Co^{II}(dmgH)_2pyCl]^$ to produce the cobalt(I) complex is energetically infeasible because of the lower one-electron reduction peak potential of $[Co^{II}(dmgH)_2pyCl]^-$ (E_{red} vs SCE = -1.06 V)⁴⁵ than the oneelectron oxidation peak potential of Acr[•]-Mes (E_{ox} vs SCE = -0.57 V).^{21,22} Then either hydrogen-atom transfer or protoncoupled electron transfer (PCET) from X-QH[•] to $[Co^{II}(dmgH)_2pyCl]^-$ may occur to produce X-Q and the cobalt(III) hydride complex, which reacts with H⁺ to release H₂, accompanied by regeneration of Co^{III}(dmgH)₂pyCl.

In order to detect reactive intermediates in Scheme 2, electron paramagnetic resonance (EPR) measurements were performed for a deaerated MeCN solution containing Cl₄QH₂, Acr⁺-Mes, Co^{III}(dmgH)₂pyCl, and H₂O under photoirradiation with a UV cut filter ($\lambda > 420$ nm) at 233 K (Figure 6a). The observed EPR spectrum was identical with that of $[Co^{II}(dmgH)_2pyCl]^{-}$ produced in the reaction of $Co^{III}(dmgH)_2pyCl$ with Acr[•]-Mes, which was formed in the photochemical reduction of Acr⁺-Mes by the 1-benzyl-1,4dihydronicotinamide dimer (BNA)₂ under photoirradiation with a UV cut filter ($\lambda > 420$ nm) for 10 min (Figure 6b). The yield of [Co^{II}(dmgH)₂pyCl]⁻ shown in Figure 6a was determined to be 20% based on the initial amount of Co^{III}(dmgH)₂pyCl by comparison of the double integration with that of the reference EPR signal of the DPPH radical (Figure S12). The simulated EPR spectrum using g = [2.2500,]2.2500, 1.9950] with hyperfine coupling tensor $A_{\text{Co}} = [28, 28, 28]$ 302] MHz is also shown in Figure 6a (black dashed line). When Cl₄QH₂ was replaced by QH₂ or Me₄QH₂, the EPR signal of [Co^{II}(dmgH)₂pyCl]⁻ was also detected (Figure S13). The above results obtained by analysis of the EPR data indicate that the rate-determining step in the catalytic cycle in Scheme 2 is either hydrogen-atom transfer or PCET from Cl_4QH^{\bullet} to $[Co^{II}(dmgH)_2pyCl]^-$, in competition with the disproportionation of Cl_4QH^{\bullet} to Cl_4Q and Cl_4QH_2 . When H₂O was replaced by D₂O, the H₂ evolution rate became slower, as shown in Figures 7 and S14, to afford the kinetic



Figure 6. (a) EPR spectra of a deaerated MeCN solution containing Cl_4QH_2 (1.0 mM), Acr⁺-Mes (0.75 mM), $Co^{III}(dmgH)_2pyCI$ (0.60 mM), and H_2O (3.0 M) observed after photoirradiation with a UV cut filter ($\lambda > 420$ nm) for 0 min (black), 10 min (blue), 15 min (green), 20 min (orange), and 30 min (red) at 233 K. Spectra were recorded at 77 K. The dashed black line shows the simulated EPR spectrum of $[Co^{II}(dmgH)_2pyCI]^-$ using $g_{\perp} = 2.2500$ and $g_{\parallel} = 1.9950$ with $A_{\perp} = 28$ MHz and $A_{\parallel} = 302$ MHz. (b) EPR spectra of Acr⁺-Mes (black line), which was produced in the photochemical reduction of Acr⁺-Mes by (BNA)₂ in deaerated MeCN under photoirradiation with a UV cut filter ($\lambda > 420$ nm) at 233 K for 10 min, and of $[Co^{II}(dmgH)_2pyCI]^-$ (red line), which was produced in the ET reduction of $Co^{III}(dmgH)_2pyCI$ by Acr⁺-Mes in deaerated MeCN at 233 K. Spectra were recorded at 77 K.

deuterium isotope effect (KIE = 2.0). In the presence of D₂O, the protons of Cl₄QH₂ are exchanged rapidly with D₂O to produce Cl₄QD₂ and H₂O.⁴⁶ In such a case, the KIE may result from the dissociation of a proton from Cl₄QH₂^{•+} or from hydrogen atom transfer (or PCET) from Cl₄QH[•] to $[Co^{II}(dmgH)_2pyCl]^-$.

CONCLUSION

Photocatalytic H₂ evolution was achieved using hydroquinone derivatives as PQH₂ analogues, which are electron and proton sources, Acr^+ -Mes as an organic photocatalyst, and $Co^{III}(dmgH)_2pyCl$ as a H₂ evolution catalyst under visible-light irradiation, mimicking the function of PSI. Acr^+ -Mes acts as a photosynthetic reaction center model, undergoing photoinduced ET to produce the charge-separated (ET) state, which oxidizes hydroquinone derivatives and reduces $Co^{III}(dmgH)_2pyCl$ at the same time to produce semiquinone radical derivatives and $[Co^{II}(dmgH)_2pyCl]^-$, respectively. Semiquinone radical derivatives after deprotonation undergo either hydrogen-atom transfer or PCET to $[Co^{II}(dmgH)_2pyCl]^-$ to produce the cobalt(III) hydride complex $[Co^{III}(H)-(dmgH)_2pyCl]^-$, which reacts with a proton to evolve H₂.



Figure 7. (a) Time profiles of mass spectra monitoring H₂ isotopes [two (¹H–¹H ; black circles), three (²D–¹H ; blue circles), and four (²D–²D ; red circles)] produced in the photodriven D₂ evolution observed by photoirradiation of a deaerated MeCN solution of Cl₄QH₂ (1.0 mM), Acr⁺-Mes (0.75 mM), Co^{III}(dmgH)₂pyCl (0.60 mM), and D₂O (3.0 M) with a UV cut filter ($\lambda > 420$ nm) at 298 K. The amounts of ¹H–¹H (black circles) and ²D–¹H (blue circles) produced were negligible. (b) Time profiles of H₂ or D₂ evolution observed by photoirradiation of a deaerated MeCN solution of Cl₄QH₂ (1.0 mM), Acr⁺-Mes (0.75 mM), Co^{III}(dmgH)₂pyCl (0.60 mM), and H₂O [5.6 M (black), 3.0 M (gray), and 2.0 M (blue)] or D₂O [5.6 M (green), 3.0 M (orange), and 2.0 M (red)] at 298 K. (c) Plots of k_{obs} versus concentration of H₂O and D₂O. The KIE value was 2.0.

This study provides the first example of a potential functional model of PSI, where protons are reduced by PQH₂ analogues to H_2 because once H_2 is produced, NAD(P)⁺ is known to be reduced thermally by H_2 to produce NAD(P)H regioselectively with an appropriate catalyst.³¹ This study has also paved a way to combine PSI and PSII models, which is now in progress.

EXPERIMENTAL SECTION

Materials. All solvents and chemicals were of reagent-grade quality, were obtained commercially, and were used without further purification, unless otherwise noted. Hydroquinone (QH_2) , chloro-(pyridine)bis(dimethylglyoximato)cobalt(III) [Co^{III}(dmgH)₂pyCl],

1,4-benzoquinone (BQ), tetrachloro-1,4-benzoquinone (Cl_4Q), and duroquinone (Me₄Q) were obtained commercially from Sigma-Aldrich Chemical Co., and tetrachlorohydroquinone (Cl₄OH₂) and durohydroquinone (Me₄QH₂) were obtained from Tokyo Chemical Industry Co. 9-Mesityl-10-methylacridinium ion (Acr⁺-Mes) was prepared by the reaction of 10-methylacridone in dichloromethane with mesitylmagnesium bromide, followed by the addition of perchloric acid for hydrolysis and sodium hydroxide for neutralization, and then purified by recrystallization from methanol/diethyl ether.³ 9-Mesityl-10-methylacridinium (Acr⁺-Mes) perchlorate. Anal. Calcd for C₂₃H₂₂ClNO₄·0.15H₂O: C, 66.63; H, 5.42; N, 3.38. Found; C, 66.44; H, 5.22; N, 3.49. ¹H NMR (300 MHz, CD₃CN): δ 8.16 (d, J = 9.0 Hz, 2H), 7.93 (t, J = 9.0 Hz, 2H), 7.40 (s, 4H), 6.79 (s, 2H), 4.37 (s, 3H), 2.02 (s, 3H), 1.25 (s, 6H). Tetrabutylammonium hexafluorophosphate (TBAPF₆) was obtained from Fluka Co. Deuterated acetonitrile (CD₃CN or MeCN) was obtained from Sigma-Aldrich Chemical Co. and used as received. Solvents, such as acetonitrile (CH₃CN or MeCN) and water (H₂O), were dried according to literature procedures and distilled under Ar prior to use.4

Instrumentation. The amount of evolved H₂ was recorded by a commercial gas chromatograph (Acme 6000 GC, Young Lin Ins.; GC-2030, Shimadzu Ins.). Nanosecond time-resolved transient absorption measurements were carried out using an Nd:YAG laser. Measurements of nanosecond transient absorption spectra were performed according to the following procedure: A mixture solution in a quartz cell (1.0 cm \times 1.0 cm) was excited by a Nd:YAG laser (Continuum SLII-10, 4–6 ns fwhm, $\lambda_{ex} = 355$ nm, 80 mJ pulse⁻¹, 10 Hz). The photodynamics were monitored by continuous exposure to a Xe lamp for the visible region and a halogen lamp for the near-IR region as a probe light and a photomultiplier tube (Hamamatsu 2949) as a detector. The kinetic traces at the appropriate wavelengths were assembled from the time-resolved spectral data. UV-vis spectra were recorded on a Hewlett-Packard 8453 diode-array spectrophotometer equipped with a UNISOKU Scientific Instruments USP-203A cryostat. X-band EPR spectra were recorded at 77 K using a JEOL X-band spectrometer (JES-FA100). The experimental parameters for EPR measurements by JES-FA100 were as follows: microwave frequency = 9.028 GHz, microwave power = 1.0 mW, modulation amplitude = 1.0 mT, modulation frequency = 100 kHz, and time constant = 0.03 s. ¹H NMR spectra were measured with Bruker model AVANCE III 400 FT-NMR digital spectrometer. Electrochemical measurements were performed on a CHI630B electrochemical analyzer in a deaerated MeCN solution containing 0.10 M nBu₄NPF₆ $(TBAPF_6)$ as a supporting electrolyte at 298 K. A conventional threeelectrode cell was used with a Pt working electrode (surface area of 0.3 mm²), a Pt wire counter electrode, and an Ag/Ag(NO₃) (0.010 M) reference electrode. The Pt working electrode (BAS) was routinely polished with a BAS polishing alumina suspension and rinsed with MeCN before use. The measured potentials were recorded with respect to an Ag/Ag⁺ reference electrode. All potentials (vs Ag/Ag⁺) were converted to values versus saturated calomel electrode by adding 0.29 V.47

Kinetic Studies. Typically, photoinduced ET from X-QH2 to the Mes^{•+} moiety of the ET state of Acr⁺-Mes [³(Acr[•]-Mes^{•+})] and ET from Acr $\mbox{-Mes}$ to $Co^{III}(dmgH)_2 pyCl$ were examined by monitoring nanosecond time-resolved transient spectral changes. The kinetic traces were assembled, monitoring the decay at 500 nm due to the Mes^{•+} moiety of ${}^{3}(Acr^{\bullet}-Mes^{\bullet+})$ (0.10 mM) with various concentrations of X-QH₂ (0–8.0 mM) in deaerated MeCN. First-order rate constants were determined under pseudo-first-order conditions by fitting the changes in transient absorbance for the decay of the peak at 500 nm due to the excited Acr[•]-Mes^{•+} in ET from X-QH₂ to 3 (Acr[•]-Mes^{•+}) in deaerated MeCN at 298 K. Monitoring the decay at 520 nm due to the Acr[•] moiety of ${}^{3}(Acr^{\bullet}-Mes^{\bullet+})$ (0.10 mM) with various concentrations of Co^{III}(dmgH)₂pyCl (0-0.60 mM) in deaerated MeCN. First-order rate constants were determined under pseudofirst-order conditions by fitting the changes in transient absorbance for the decay of the peak at 520 nm due to Acr[•]-Mes in ET from Acr[•]-Mes to $Co^{III}(dmgH)_2$ pyCl in deaerated MeCN at 298 K.

Product Analysis. Photodriven H₂ evolution by hydroquinone derivatives (X-QH₂) with Acr⁺-Mes, Co^{III}(dmgH)₂pyCl, and H₂O was examined in a quartz cell (optical path length = 1.0 cm) using a LED lamp (white light; 150 W) on a Hayashi WATCH-WORKS Co. LA-HDF158AS for irradiation at 298 K. H₂ formed in the oxidation of X-QH₂ (1.0 mM) by an excited state of Acr⁺-Mes (0.75 mM) with Co^{III}(dmgH)₂pyCl (0.60 mM) and H₂O (2.0 M) in deaerated CH₃CN after irradiation (white light) with a UV cut filter ($\lambda > 420$ nm) from Sigma Koki Co. was identified by GC.

QY Determination. The QY of photodriven H_2 evolution from hydroquinone with Acr⁺-Mes, Co^{III}(dmgH)₂pyCl, and H₂O was determined under visible-light irradiation of monochromatized light using a Xe lamp (300 W) on an ASAHI SPECTRA MAX-302 through a band-pass filter transmitting ($\lambda = 470$ nm) at 298 K. Typically, the amount of H₂ produced during the photochemical reaction has been determined under photoirradiation ($\lambda = 470$ nm) with an irradiation time interval of 1 h (Figure S1c). The initial slope of the graph is taken to determine the QY. The QY was estimated as QY (%) = R/I \times 100, where *R* (mol s⁻¹) is the initial rate of the H₂ production rate and I (einstein s^{-1}) is a coefficient based on the rate of the number of incident photons absorbed by Acr⁺-Mes per second. The total number of incident photons was determined using a standard actinometer as follows. A quartz cell containing an aqueous solution (1.0 mL) of potassium ferrioxalate (K3[Fe^{III}(C2O4)3], 0.15 M) was irradiated using monochromatized light (λ = 470 nm) for 1, 2, and 3 min at 298 K, separately. At the end of the irradiation, a sodium acetate buffer solution (2.0 mL) of phenanthroline was added to 1.0 mL of the actinometer solution, and the solution was kept in the dark for 1 h. Then, the solution was diluted by half using H₂O (i.e., 1.0 mL of the solution and 1.0 mL of H₂O). The absorbance at 510 nm due to $[Fe(phen)_3]^{2+}$ ($\varepsilon = 11050 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda_{max} = 510 \text{ nm}$) was measured to determine the total number of incident photons using the QY for photodecomposition of ferrioxalate ($\Phi = 0.92$ at 468 nm)³² to be 1.43 \times 10⁻⁹ einstein s⁻¹ [rate of formation of [Fe(phen)₃]²⁺ after dilution = 1.22×10^{-3} (slope of an inset)/11050 (ϵ) = 1.10×10^{-7} M s⁻¹ and rate of formation of $[Fe(phen)_3]^{2+}$ before dilution = 1.10×10^{-7} M $s^{-1} \times (2 \times 10^{-3} \text{ L}) \times 6$ (dilution factor) = $1.32 \times 10^{-9} \text{ mol s}^{-1}$; I = 1.32×10^{-9} mol s⁻¹/0.92 = 1.43×10^{-9} einstein s⁻¹]. The QY was determined to be 10% from the amount of H₂ produced during the photocatalytic reaction under photoirradiation ($\hat{\lambda} = 470$ nm) for 5 h (Figure S1c) measured by a standard method using an actinometer $(K_3[Fe^{III}(C_2O_4)_3])^{32}$ under photoirradiation ($\lambda = 470$ nm) at 298 K (see Figure S1b), where the photon flux was determined to be $1.43 \times$ 10^{-9} einstein s⁻¹.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02254.

Figures S1–S14 for the QY, TON, and stability of the catalysts, UV–vis absorption, transient absorption, and EPR spectral changes for photocatalytic H_2 evolution, and cyclic voltammograms of the reactants (PDF)

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Notes

The authors declare no competing financial interest.

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