INTRODUCTION

Cytochromes P450 can catalyze various oxidative metabolic reactions of endogenous and exogenous compounds in living organisms [1–8]. NAD(P)H provides electrons to the diflavins of the reductase, followed by the transfer of electrons to the catalytic P450 heme domain through an intermolecular electron transfer, resulting in the generation of a reactive iron(IV)-oxo porphyrin π-radical cation species (Compound I, Cpd I) via reductive activation of O$_2$ [1–8]. Efficient and continuous supplementation of electrons to P450s is required to produce iron-oxo species for the catalytic oxidation of substrates with O$_2$ [1–8]. Alternatively, iron-oxo species are produced by electron-transfer oxidation of the P450 heme via photoinduced electron transfer from the excited state of [Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2′-bipyridine) to sacrificial electron acceptors such as [Co(NH$_3$)$_5$Cl]$^{2+}$, which can oxidize the heme to produce iron-oxo species in which oxygen comes from water [9–11]. Thus, high-valent metal-oxo porphyrins (e.g. (P)M$_{V}$O) can be produced either by reductive activation of O$_2$ with one-electron reductants that can reduce (P)M$_{III}$ with O$_2$ or oxidative...

Thermal and photoinduced electron-transfer catalysis of high-valent metal-oxo porphyrins in oxidation of substrates

Shunichi Fukuzumi$^{a,b,*}$ and Wonwoo Nam$^{a*}$

$^a$Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea
$^b$Faculty of Science and Engineering, ALCA and SENTAN, Japan Science and Technology Agency (JST), Meijo University, Nagoya, Aichi 468-0073, Japan

Dedicated to Professor Kevin M. Smith on the occasion of his 70th birthday

Received 26 November 2015
Accepted 5 December 2015

ABSTRACT: In this manuscript, we haveoverviewed thermal and photoinduced electron transfer catalysis of high-valent metal-oxo porphyrins in oxidation of various substrates. The high-valent iron-oxo porphyrin in cytochrome P450 (P450) is produced by photoinduced electron transfer from electron donors, such as triethanolamine (TEOA), to the excited state of a photosensitizer such as eosin Y, followed by the reduction of the heme domain of P450 by the resulting radical anion of the photosensitizer and the subsequent reaction of the reduced heme with dioxygen (O$_2$). Various substrates were oxidized by O$_2$ in this visible light-driven electron-transfer catalytic reaction with several P450s from bacteria and humans. A manganese(V)-oxo corrorazine was produced by photoinduced electron transfer from the excited state of manganese(III) corrorazine to O$_2$, followed by hydrogen abstraction from toluene derivatives, catalyzing the oxidation of toluene derivatives with O$_2$ in the presence of an acid via photoinduced electron transfer catalysis. High-valent manganese-oxo porphyrins are also produced by photoinduced electron transfer from the excited state of [Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2′-bipyridine) to electron acceptors, followed by electron transfer oxidation of manganese(III) porphyrins with [Ru(bpy)$_3$]$^{3+}$, catalyzing oxidation of various substrates with O$_2$. Finally photoinduced electron-transfer catalysis of cobalt porphyrins is discussed for the photocatalytic water oxidation with persulfate.

KEYWORDS: electron-transfer catalysis, metal-oxo complexes, metalloporphyrins, photocatalytic oxidation.
activation of water with one-electron oxidants that can oxidize (P)M\textsuperscript{III} with H\textsubscript{2}O (Scheme 1) \[12, 13\]. In both cases, (P)M\textsuperscript{V}(O) can oxidize substrates to produce the oxidized products, accompanied by regeneration of (P)M\textsuperscript{III}, acting as catalysts for efficient oxidation of substrates [13].

This minireview focuses on thermal and photoinduced electron transfer catalysis of high-valent metal-oxo porphyrins which are produced either by reductive activation of O\textsubscript{2} with one-electron reductants or by oxidative activation of H\textsubscript{2}O with one-electron oxidants for the catalytic oxidation of various substrates.

PHOTOINDUCED ELECTRON-TRANSFER CATALYSIS OF P450 VIA REDUCTIVE ACTIVATION OF O\textsubscript{2}

Cofactor-free \textit{in vivo} photooxidation of P450s was achieved by using eosin Y [C\textsubscript{20}H\textsubscript{6}O\textsubscript{5}Br\textsubscript{4}Na\textsubscript{2}, 2,4,5,7-tetrabromofluorescein (EY)] as a photosensitizer that mediates direct electron transfer to the heme domain of P450 [14]. EY has frequently been used for various biomedical and diagnostic purposes [15–18]. EY can transfer photoexcited electrons directly to the heme domain of P450 for the photoactivation of P450 catalytic cycle in Scheme 2 [14]. The reduced heme reacts with O\textsubscript{2} to produce the iron-oxo species, while the oxidized EY was reduced by sacrificial electron donors such as triethanolamine (TEOA). The iron-oxo species can oxidize various substrates for catalytic conversions of marketed drugs including simvastatin, lovastatin, 17b-estradiol, and omeprazole by different human P450s [14]. This whole-cell P450 system, in which photoexcited EY can reduce P450 heme domain directly without the need for a redox partner and a cofactor, provides a powerful and cost-effective tool for visible light-driven P450-catalyzed reactions using an inexpensive photosensitizer and without the need for an expensive cofactor and a redox partner.
The light-driven cytochrome P450 catalyzed monoxygenation was also made possible by using a soluble deazaflavin mediator [19] in combination with an inexpensive sacrificial electron donor (EDTA) as shown in Scheme 3 [20]. By using deazaflavins as electron mediators, instead of normal flavins, a light-driven regeneration of flavin-dependent enzymes can also proceed efficiently under aerobic conditions [20]. Under aerobic conditions a pronounced reduction of the P450-BM3 heme domain is achieved only in the presence of deazaflavin [20]. In contrast to this, FAD as a mediator failed to yield notable reduction of the heme domain with additional NADP$^+$ or under positive control conditions (NADPH) [19]. This result suggests the superior electron mediator properties of deazaflavins compared to flavins of the isoalloxazine-type (FAD, FMN, riboflavin) under aerobic conditions [20]. The light-driven hydroxylation of lauric acid occurred by P450-BM3 with deazaflavin and NADP$^+$ with the same regioselectivity as the P450 catalyzed hydroxylation with NADPH [20].

Hybrid P450 BM3 enzymes consisting of a Ru(II)-diimine photosensitizer covalently attached to non-native single cysteine residues of P450 BM3 heme domain mutants [21]. The hybrid enzymes (Ru-K97C-BM3 and Ru-Q397C-BM3) were assembled by covalently attaching the photosensitizer Ru(II)-diimine to non-native single cysteine residues of P450 BM3 heme domain mutants [21]. These enzymes are capable, upon light activation, of selectively hydroxylating lauric acid using a sacrificial electron donor, sodium diethyldithiocarbamate (DTC), with a TON number that is 40 times higher than the value of the wild type heme domain (BM3-WT) using the peroxide shunt (Scheme 4) [21]. The hybrid enzymes most likely utilize reactive oxygen species generated.
in situ under the photoreductive conditions to perform the hydroxylation reaction for more than two hours [21]. The family of hybrid enzymes by site directed mutagenesis has been prepared by modifying the nature of the Ru(II)-diimine photosensitizer, resulting in diverse catalytic activities in the hydroxylation of lauric acid upon light activation [22–24]. When 10-undecenoic acid was employed as a substrate, the hydroxylation with the hybrid enzyme using DTC occurs exclusively at the 9 position to yield the R enantiomer with 85% ee [25]. Oxidation of 10-undecenoic acid by the light-activated hybrid WT/L407C-Ru1 enzyme leads directly to a highly enantioselectively enriched monohydroxylated product, highlighting the advantages of biophotocatalysis over traditional methods.

Reductive activation of O_2 in a nonenzymatic system was reported for a diiron(III) complex and a ruthenium(II)-polypyridine-type complex, which acts as a photosensitizer, and triethylamine (TEA), which functions as a sacrificial electron donor [26]. Exposure of the photogenerated diiron(II) complex to O_2 leads to the formation of the diiron(III)–peroxo intermediate responsible for oxygen-atom transfer to triphenylphosphine to produce triphenylphosphine oxide.

PHOTOINDUCED ELECTRON-TRANSFER CATALYSIS OF MANGANESE CORROLZAINES AND PORPHYRINS VIA REDUCTIVE ACTIVATION OF O_2

A well-characterized manganese(V)-oxo complex was produced by visible light irradiation of a manganese(III) corrolazine [Mn^{III}(TBP,Cz): TBP,Cz\(^{−}\) = octa(p-tert-butyphenyl)corrolizinato\(^{−}\)] in the presence of toluene derivatives with O_2 [27, 28]. Mn^{III}(TBP,Cz) is converted to the monoprotonated complex Mn^{IV}(OTf)(TBP,Cz(H)) in the presence of triflic acid (HOTf). The crystal structure of Mn^{III}(OTf)(TBP,Cz(H)) revealed that monoprotetration occurs at one of the meso-N-atoms (N5(H)) adjacent to the direct pyrrole–pyrrole bond of the corrolazine ligand, and that the manganese center is five-coordinate with an axially-ligated triflate (Mn^{III}−O = 2.115(3) Å) [28, 29]. The photodynamics of Mn^{III}(OTf)(TBP,Cz(H)) in the presence of hexamethylbenzene (HMB) and O_2 is shown in Scheme 5 [29]. Photoexcitation of Mn^{III}(OTf)(TBP,Cz(H)) resulted in formation of the triquintet state [Mn^{III}(OTf)(TBP,Cz(H))]\(^{•}\) (\(5\ T_1\)) upon photoirradiation as revealed by femtosecond laser transient absorption measurements [29]. The \(T_1\) of Mn^{III}(OTf)(TBP,Cz(H)) is converted rapidly by intersystem crossing (ISC) to the tripseptet excited state (\(5\ T_1\)), Electron transfer from \(5\ T_1\) to O_2 occurs to produce the superoxo complex Mn^{IV}(O−•) (OTf)(TBP,Cz(H)), which abstracts a hydrogen atom from HMB to produce the hydroperoxo complex, Mn^{IV}(OOH) (OTf)(TBP,Cz(H)), and pentamethylbenzyl radical, in competition with the back electron-transfer (\(k_{−et}\)) to regenerate the ground state Mn^{III}(OTf)(TBP,Cz(H)) and O_2. The subsequent homolytic O−O bond cleavage and combination with benzyl radical to yield PMB−OH is accompanied by generation of high-valent Mn(V)-oxo species [Mn^{V}(O)(OTf)(TBP,Cz(H))]. This species is proposed to react with another equivalent of substrate to produce PMB−OH, accompanied by regeneration of Mn^{III}(OTf)(TBP,Cz(H)) in the catalytic cycle (Scheme 5) [30]. The oxidation of HMB by [Mn^{IV}(O)(OTf)(TBP,Cz(H))] is accelerated by the further addition of

![Scheme 5. Photocatalytic cycle of oxygenation of hexamethylbenzene by O_2 with the monoprotonated complex [Mn^{III}(OTf)(TBP,Cz(H))] in the presence of HOTf.](image-url)
HOTf as reported for acid-promoted oxidation reactions of a variety of substrates with high-valent metal-oxo complexes [31–37]. When Mn^{III}(OTf)(TBP,Cz(H)) is further protonated to [Mn^{III}(OTf)(H,O)(TBP,Cz(H))][OTf] in the presence of a large excess of HOTf, however, no catalytic activity is observed, because the tripseptet excited state (\(^{7}T_{1}\)) of [Mn^{III}(OTf)(H,O)(TBP,Cz(H))] [OTf] cannot react with O\(_{2}\), possibly due to the higher oxidation potential for [Mn^{III}(OTf)(H,O)(TBP,Cz(H))] [OTf] as compared with that of Mn^{III}(OTf)(TBP,Cz(H)) [30]. When HMB was replaced with thioanisole in the photocatalytic reaction with Mn^{III}(OTf)(TBP,Cz(H)), a single S-oxygenated product, methylphenylsulfoxide (PhS(O)Me), was obtained with an excellent TON (902) and conversion (98%) of PhSMe to PhS(O)Me [30]. In this case as well, the triplet excited state of Mn^{III}(OTf)(TBP,Cz(H)) can react with O\(_{2}\) to produce the superoxo complex Mn^{IV}(O\(_{2}\)^{-})(OTf)(TBP,Cz(H)), which reacts with PhSMe to produce PhS(O)Me and high-valent Mn^{V}(O)(OTf)(TBP,Cz(H)) that can also oxygenate PhSMe to produce another PhS(O)Me, accompanied by regeneration of Mn^{III}(OTf)(TBP,Cz(H)) [30].

Manganese porphyrins [(P)Mn^{III}] 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphimatamanganese(III) hydroxide [(TMP)Mn^{III}(OH)] and 5,10,15,20-tetrakis pentfluorophenylporphyrinamanganese(III) acetate [(TFPFP)Mn^{III-}(CH\(_{3}\)COO)] also act as efficient photocatalysts for oxygenation of 10-methyl-9,10-dihydroacridine (AcRH) by O\(_{2}\) to yield 10-methyl-9,10-dihydroacridine (AcRHa) in an oxygen-saturated benzonitrile (PhCN) solution under visible light irradiation [38]. The mechanism of photocatalytic oxidation of AcRH by O\(_{2}\) with (P)Mn^{III} to give AcR=O as the product is shown in Scheme 6 [38]. The photoreduction of (P)Mn^{III} results in formation of the tripquintet excited state ([Mn^{III}]^* (\(^{7}T_{1}\)))

**Scheme 6.** Photocatalytic cycle of oxygenation of AcRH by O\(_{2}\) with (P)Mn^{III}

Electron-transfer catalysis of manganese(V) oxo porphyrins by oxidative activation of H\(_{2}\)O

Various high-valent metal-oxo species can also be produced by oxidative activation of H\(_{2}\)O in which the oxygen of the oxo group comes form H\(_{2}\)O accompanied by two-electron oxidation of the metal complexes [39–45]. Examples of formation of manganese(V)-oxo porphyrins ((P)Mn^{V-}(O)) via electron-transfer oxidation of manganese(III)
porphyrins ([P(Mn)]\textsuperscript{II}) are shown in Scheme 7, where ([P(Mn)]\textsuperscript{II}) is oxidized by electron transfer with two equivalents of [Ru(bpy)]\textsuperscript{3+} accompanied by deprotonation to produce ([P(Mn)]\textsuperscript{3+}(O)), which can oxygenate substrates (S) to SO, accompanied by regeneration of ([P(Mn)]\textsuperscript{II}) [45]. Manganese porphyrins employed as catalysts in this study are ([TMP]Mn\textsuperscript{III})\textsuperscript{+} (TMP\textsuperscript{2-} = 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin dianion), ([TDCPP]Mn\textsuperscript{III})\textsuperscript{+} (TDCPP\textsuperscript{2-} = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin dianion), ([TMOPP]Mn\textsuperscript{III})\textsuperscript{+} (TMOPP\textsuperscript{2-} = 5,10,15,20-tetrakis(2,4,6-trimethoxyphenyl)porphyrin dianion), and ([DTMPD]Mn\textsuperscript{III})\textsuperscript{+} (DTMPD\textsuperscript{2-} = di-trimesitylporphyrin dibenzofuran tetraanion). Addition of [Ru(bpy)]\textsuperscript{3+} to an MeCN solution of olefins (e.g., styrene and cyclohexene) containing water in the presence of a catalytic amount of (P)Mn\textsuperscript{II} afforded epoxides, diols and aldehydes. Epoxides were converted to the corresponding diols by hydrolysis, and the diols were further oxidized to the corresponding aldehydes which are four-electron oxidized products of olefins [45]. Hydroxylation of alkanes (ethylbenzene) also occurs by the manganese porphyrin-catalyzed electron-transfer oxidation with [Ru(bpy)]\textsuperscript{3+} to yield the corresponding alcohols [44]. The epoxidation of styrene and the hydroxylation of ethylbenzene with [Ru(bpy)]\textsuperscript{3+} in the presence of 95% \(^{18}\text{O}\)-water containing a catalytic amount of (P)Mn\textsuperscript{III} afforded the corresponding epoxide and alcohol with 90% incorporation of \(^{18}\text{O}\) in the oxygenated products [45]. Thus, the oxygen source in the oxygenated products in the manganese porphyrin-catalyzed electron-transfer oxygenation of substrates with [Ru(bpy)]\textsuperscript{3+} has been confirmed to be water in the mixed solvent (MeCN/H\textsubscript{2}O) [45]. When ([TMP]Mn\textsuperscript{III}(H\textsubscript{2}O))\textsuperscript{2+} was used as the catalyst, oxygenation of cyclohexene occurred more efficiently than that of styrene probably due to the stronger steric repulsion of styrene against the bulky TMP ligand of ([TMP]Mn\textsuperscript{3+}(O)) as compared with that of cyclohexene. In the case of TDCPP ligand, the oxygenation of cyclohexene and styrene is more reactive than TMP ligand because of the less steric effect of the TDCPP ligand as compared with the TMP ligand and high redox potentials [44]. In the case of ([DTMPD]Mn\textsuperscript{III})\textsuperscript{+} Cl\textsubscript{2}, the TON values are significantly smaller as compared with those with the corresponding monomer, ([TMP]Mn\textsuperscript{III})\textsuperscript{+} Cl, because the Mn\textsuperscript{3+} species derived from ([DTMPD]Mn\textsuperscript{III})\textsuperscript{+}Cl\textsubscript{2} may be produced inside the diporphyrin cavity to prevent the interaction with substrates [45].

The dependence of log \(k_\text{et}\) of electron-transfer oxidation of (P)Mn\textsuperscript{III} with one-electron oxidants on the free energy change of electron transfer (\(\Delta G^\text{et}\)) is shown in Fig. 1, where the log \(k_\text{et}\) value increases with increasing the driving force of electron transfer (–\(\Delta G^\text{et}\)) in accordance with the Marcus theory of adiabatic outer-sphere electron transfer (Equation 1), where Z is the collision frequency taken as \(1 \times 10^{11}\) s\textsuperscript{-1} and \(\lambda\) is the reorganization energy of electron transfer [46, 47].

\[
\log k_\text{et} = Z \exp\left[-\frac{(1/4)(\lambda + \Delta G^\text{et}/\lambda)^2}{RT}\right]
\]  

The best-fit value of \(\lambda\) in Fig. 1a, which includes both electron transfer from (TMP)Mn\textsuperscript{III}(OH) and (TMP) Mn\textsuperscript{III}(O) to one-electron oxidants, is determined to be 24 kcal mol\textsuperscript{-1}. The \(\lambda\) values for the first and second electron transfer from (TMP)Mn\textsuperscript{III}(Cl) (34 kcal mol\textsuperscript{-1}) and (DTMPD)Mn\textsuperscript{III}(Cl), (40 kcal mol\textsuperscript{-1}) to [Ru(bpy)]\textsuperscript{3+} (Fig. 1b) are larger than that for electron transfer from (TMP)Mn\textsuperscript{III}(OH) due to the large reorganization of the Cl ligand associated with the electron transfer [45].

The rate constant of the oxidation of cyclohexene by ([TMP]Mn\textsuperscript{3+}(O)) was determined by monitoring an increase in the absorption band at 470 nm due to ([TMP] Mn\textsuperscript{III}) to \(1.6 \times 10^4\) M\textsuperscript{-1}s\textsuperscript{-1} in MeCN/H\textsubscript{2}O (9:1 v/v) at 298 K. In such a case, the rate-determining step of the electron-transfer catalytic oxidation of cyclohexene...
with \([\text{[(TMP)Mn}^{II}(\text{H}_2\text{O})]^{+}}\) is electron transfer from \([\text{[(TMP)Mn}^{II}(\text{H}_2\text{O})]^{+}}\) to \([\text{[(Ru(bpy))}^{II}]^{1+}}\) to produce \([\text{[(TMP)Mn}^{V}(\text{O})]]^{+}\) rather than the oxidation of cyclohexene by \([\text{[(TMP)Mn}^{V}(\text{O})]]^{+}\) [45].

**PHOTOCATALYTIC OXIDATION OF SUBSTRATES WITH METALLOPORPHYRINS**

Photocatalytic oxygenation of olefins and an alkane by \([\text{[(Co}^{III}(\text{NH}_3)\text{Cl}])^{2+}}\), that is a weak one-electron oxidant, occurs using 5,10,15,20-tetrakis(2,4,6-trimethyl-3-sulfonato phenyl)porphinatromanganese(III) hydroxide ([(TMPS) Mn^{III}(OH)]) as an oxygenation catalyst and \([\text{[(Ru(bpy))}^{II}]^{1+}}\) as a photosensitizer in the presence of water which is shown to act as an oxygen source by labeling experiments using \(\text{H}_2\text{O}^2\text{O}\) (Scheme 8) [48].

The epoxides initially formed are converted to the corresponding diols by the hydrolysis because of the acid produced in the catalytic oxygenation of olefins. Photoirradiation (\(\lambda > 430\text{ nm}\)) of phosphate buffer (pH 7.4) containing sodium p-styrene sulfonate (NaSS), (TMPS)Mn^{III}(OH), \([\text{[(Ru(bpy))}^{II}]^{1+}}\), and \([\text{[(Co}^{III}(\text{NH}_3)\text{Cl}])^{2+}}\) led to formation of the epoxide, two-electron oxidation product in a good yield (90%) based on the amount of \([\text{[(Co}^{III}(\text{NH}_3)\text{Cl}])^{2+}}\) as a one-electron oxidant. The photocatalytic hydroxylation of sodium 4-ethylbenzene sulfonate also occurs efficiently to yield the secondary alcohol [48]. The oxygenation of these substrates has been achieved by the oxidation with a high-valent manganese-oxo species, \([\text{[(TMPS)Mn}^{III}(\text{O})]]^{+}\), produced by the two-electron oxidation of (TMPS)Mn^{III}(OH) with two equivalents of \([\text{[(Ru(bpy))}^{II}]^{1+}}\), which was obtained by the oxidative electron-transfer quenching of the excited state of \([\text{[(Ru(bpy))}^{II}]^{1+}}\) by \([\text{[(Co}^{III}(\text{NH}_3)\text{Cl}])^{2+}}\) as shown in Scheme 8 [48]. It was confirmed that no oxygenated product was obtained in the absence of (TMPS)Mn^{III}(OH) under otherwise the same experimental conditions [48]. The quantum yields (\(\Phi\)) of the photocatalytic epoxidation of NaSS with water increased with increasing concentration of \([\text{[(Co}^{III}(\text{NH}_3)\text{Cl}])^{2+}}\) to reach 50%, which is the maximum quantum efficiency expected from the stoichiometry of the photocatalytic oxygenation, because two photons are required for the two-electron oxidation of the substrate [48]. When DCIO\(_4\) (55 mM) was added to the (TMPS)Mn^{III}(OH)–[Ru(bpy)]^{1+} system, no catalytic oxygenation of cyclohexene was observed in D\(_2\)O/CD\(_3\)CN (1:9, v/v) [48]. This indicates that the formation of \([\text{[(TMPS)Mn}^{III}(\text{O})]]^{+}\) by the two-electron oxidation of (TMPS)Mn^{III}(OH) with two equivalents of \([\text{[(Ru(bpy))}^{II}]^{1+}}\), which requires the deprotonation process in Scheme 8, is retarded by a strong acid. The rate constant of the oxidation of NaSS with \([\text{[(TMPS)Mn}^{III}(\text{O})]]^{+}\) in H\(_2\)O/CH\(_3\)CN (1:3, v/v) at 298 K was determined to be \(4.0 \times 10^6\text{ M}^{-1}\text{s}^{-1}\), which is 67 times larger than the rate constant with \([\text{[(TMPS)Mn}^{III}(\text{O})]]^{+}\)

**Scheme 8.** Photocatalytic cycle of oxygenation of substrates (S) with H\(_2\)O and \([\text{[(Co}^{III}(\text{NH}_3)\text{Cl}])^{2+}}\), catalyzed by \([\text{[(Ru(bpy))}^{II}]^{1+}}\) and Mn\(^{III}\) porphyrins

---

**Fig. 1.** Dependence of log\((k_{\text{et}},\text{ M}^{-1}\text{s}^{-1})\) on \(\Delta G^0_{\text{et}},\text{ eV}\) for the electron-transfer oxidation of (TMPS)Mn^{III}(OH) with various oxidants ((\(\Delta\)) (Fe(5-NO\(_2\)-phen))\(_2\))(PF\(_6\))\(_2\), (\(\bullet\)) [Ru(bpy)](PF\(_6\))\(_2\), (\(\bigtriangledown\)) [Fe(5-CI-phen)](PF\(_6\))\(_2\), (\(\bigstar\)) [Fe(bpy)](PF\(_6\))\(_2\), and (\(\bigtriangleup\)) (TMPS)Mn^{III}(OH), (\(\bullet\)) [(TMP)Mn^{III}(H\(_2\)O)]\(^2+\), (\(\bigstar\)) (TMP)Mn^{III}(Cl)\(^+\), (\(\bigtriangleup\)) (TMPP)Mn^{III}(Cl)\(^+\)), [Ru(bpy)](PF\(_6\))\(_2\), and (\(\bigtriangleup\)) (TMPP)Mn^{III}(Cl)\(^+\)) in MeCN containing [H\(_2\)O] = 6.5 mM. The solid line represents the fits to Equation 1 with \(\lambda = 24\text{ kcal mol}^{-1}\) (b) \(\lambda = 34\text{ kcal mol}^{-1}\) and (c) \(\lambda = 40\text{ kcal mol}^{-1}\).
The reaction of (TMPS)MnIII(O) with NaSS occurs via the disproportionation of (TMPS)MnV(O) to give (TMPS)MnIV(OH) and (TMPS)MnIII(OH)2−, the latter of which is the actual oxidant for the oxidation reaction [48, 49].

The photosensitizer ([Ru(bpy)3]2+) was recently connected to an Fe(II) complex with a pentadentate amine/pyridine ligand and the RuII–FeII linked complex was used as a photocatalyst for oxygen generation from triphenylphosphine oxide via the formation of the FeIII(O) complex with [CoIII(NH3)6Cl]3− [50]. A mononuclear nonheme [MnIII(O) (BQCN)]2+ complex (BQCN = N,N′-dimethyl-N,N′-bis(2-quinolyl)cyclohexanediamine) was produced by the electron-transfer oxidation of [MnII(BQCN)]2+ by [Ru(bpy)3]3+ produced by photoinduced electron transfer from the excited state of [Ru(bpy)3]2+ to [CoIII(NH3)6Cl]3+, acting as a catalyst for the formation of benzyl alcohol and thiocyanate with [CoIII(NH3)6Cl]3+ [51]. A mononuclear nonheme [FeVI(O)(MePy2tacn)]2+ (MePy2tacn = N,N,N′,N′′-tetramethyl-1,4,7-triazacyclononane) was also produced by the electron-transfer oxidation of [FeIII(MePy2tacn)(solvent)]2+ by [Ru(bpy)3]3+ produced by photoinduced electron transfer from the excited state of [Ru(bpy)3]2+ to persulfate (Na2S2O8), acting as a catalyst for the oxidation of p-methoxythioanisole with persulfate [52].

PHOTOCATALYTIC OXIDATION OF WATER WITH METALLOPORPHYRINS

High-valent metal-oxo complexes are known to be active species for four-electron oxidation of water to evolve O2 including the oxygen evolving complex (OEC) in photosystem II (PSII) [53–58]. Sakai and coworkers reported that water-soluble cobalt porphyrins act as good catalysts for photocatalytic oxidation of water with Na2S2O8 using [Ru(bpy)3]3+ as a photocatalyst. The maximum TON (121) was obtained by photoinfrared CoTPPS (10 μM) in phosphate buffer (0.1 M, pH = 11) containing Na2S2O8 (5 mM) and [RuII(bpy)3(NO3)2] (1 mM) under Ar [59]. When CoTPPS was replaced by a fluorinated CoFPS, TON was increased to 570 [60]. Cobalt porphyrins are also reported to act as catalysts for electrochemical oxidation of water [61, 62]. On the other hand, the photocatalytic water oxidation to evolve O2 was also reported to occur by photoinfrared (λ > 420 nm) of an aqueous solution containing [Ru(bpy)3]2+, Na2S2O8 and water-soluble cobalt complexes with various organic ligands as precatalysts in the pH range of 6.0–10.0 [63]. The turnover numbers (TONs) based on the amount of Co for the photocatalytic O2 evolution with [CoIII(Me3tren)(OH)2]2+ and [CoIII(Cp*)(bpy) (OH)2]2+ [Me3tren = tris(N,N,N′-dimethylaminoethyl)amine,Cp* = η5-pentamethycyclopentadienyl] at pH9.0 reached 420 and 320, respectively [63]. Dynamic light scattering (DLS) experiments indicated the formation of particles with diameters of around 20 × 10 nm and 200 × 100 nm during the photocatalytic water oxidation with [CoIII(Me3tren)(OH)2]2+ and [CoIII(Cp*)(bpy)(OH)2]2+, respectively [63]. The particle sizes determined by DLS agreed with those of the secondary particles observed by TEM [63]. The XPS measurements of the formed particles suggest that the surface of the particles is covered with cobalt hydroxides, which could be converted to high-valent cobalt ions during the photocatalytic water oxidation [63]. There are many examples for metal complexes acting as only precatalysts, which are converted to actual catalysts that are metal nanoparticles during the water oxidation reaction [64–70]. In the case of CoFPS-catalyzed light-driven water oxidation by persulfate, no nanoparticulate materials were formed during the photocatalytic oxidation [60]. The kinetic study suggested that the rate-determining step of the photocatalytic water oxidation with CoIIIFPS is the nucelophilic attack of water to the two-electron oxidized CoIIIFPS (formally CoV(O)FPS), which is produced by the electron-transfer oxidation of CoIIIFPS by [Ru(bpy)3]3+ following electron transfer from the excited state of [Ru(bpy)3]2+ to persulfate [60]. However, the formation of CoV(O)FPS has yet to be clarified.

CONCLUSION

High-valent metal-oxo porphyrins are produced by the reductive activation of O2 with electron and proton source or by the oxidative activation of H2O with oxidants. The reductive activation of O2 results in the catalytic oxidation of substrates by O2 with reductants, via the formation of high-valent metal-oxo species as active oxidants. Relatively strong reductants required for the thermal reactions can be replaced by weak reductants for the photocatalytic reactions via photoinduced electron transfer from weak reductants to the photocatalyst. On the other hand, the oxidative activation of H2O results in the catalytic oxidation of substrates with oxidants and H2O as an oxygen source, also via the formation of high-valent metal-oxo species as active oxidants. In this case as well, relatively strong oxidants required for the thermal reactions can be replaced by weak oxidants for the photocatalytic reactions via photoinduced electron transfer from the photocatalyst to weak oxidants. Cofactor-free light-driven whole-cell cytochrome P450 catalysis has been achieved via reductive activation of O2. The alternative pathway of the oxidative activation of water for cofactor-free P450 photocatalysis has yet to be developed. It is hoped that the more efficient water oxidation catalysts will be developed by optimizing the oxidative activation of H2O.
Acknowledgements

The authors gratefully acknowledge the contributions of collaborators and co-workers mentioned in the references. The authors also appreciate financial support provided by Japan Science and Technology Agency (JST to S.F.) and the NRF of Korea through CRI (NRF-2012R1A3A2048842 to W.N.) and GRL (NRF-2010-00353 to W.N.).

REFERENCES