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Photocatalytic Oxygenation Reactions with a Cobalt Porphyrin Complex Using Water as an Oxygen Source and Dioxygen as an Oxidant

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Supporting Information Placeholder

ABSTRACT: Photocatalytic oxygenation of hexamethylbenzene occurs under visible light irradiation of an O_2-saturated acetonitrile solution containing a cobalt porphyrin complex, Co^{II}(TPP) (TPP^{2-} = tetraphenylporphyrin dianion), water (H_2O), and triflic acid (HOTf) via a one photon-two electron process, affording pentamethylbenzyl alcohol and hydrogen peroxide (H_2O_2) as products with a turnover number of >6000; in this reaction, H_2O and O_2 were used as an oxygen source and a two-electron oxidant, respectively. The photocatalytic mechanism has been clarified based on EPR, time-resolved fluorescence, and transient absorption measurements as well as by conducting ^{18}O-labeling experiments with $H_2{}^{18}O$ and ${}^{18}O_2$. To the best of our knowledge, we report the first example of achieving an efficient photocatalytic oxygenation of an organic substrate by a metal complex using H_2O as an oxygen source and O_2 as a two-electron oxidant.

In Photosystem II (PS II), water (H_2O) is used as an oxygen source to generate a postulated manganese(V)-oxo species in the oxygen-evolving complex (OEC).[1,2] In this context, a number of high-valent metal-oxo complexes, M$^{(n+2)+}$(O^{2-}), have been synthesized by the successive electron-transfer oxidation of metal complexes, M^{n+}, by two equiv of a one-electron oxidant (A) and using H_2O as the oxygen source of the oxo ligand (eq 1).[3,4] Then, high-valent metal-oxo complexes, M$^{(n+2)+}$(O^{2-}), oxidize substrates (S), accompanied by the regeneration of M^{n+} (eq 2).[4-8] Thus, M^{n+} can act as an effective catalyst for oxygenation of substrates (S) using two one-electron oxidants (A) and H_2O as an oxygen source, as shown in eq 3 that is the sum of eqs 1 and 2.[4-8]

$$\mathrm{M^{n+} + H_2O + 2A \longrightarrow M^{(n+2)+}(O^{2-}) + 2A^{\bullet-} + 2H^+} \qquad (1)$$

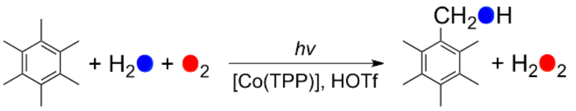
$$\mathrm{M^{(n+2)+}(O^{2-}) + S \longrightarrow M^{n+} + SO} \qquad (2)$$

$$\mathrm{S + H_2O + 2A \longrightarrow SO + 2A^{\bullet-} + 2H^+} \qquad (3)$$

$$\mathrm{S + H_2O + O_2 \longrightarrow SO + H_2O_2} \qquad (4)$$

Cerium ammonium nitrate (CAN) and [Ru(bpy)$_3$]$^{3+}$ have been used as a one-electron oxidant in the catalytic oxygenation of substrates using H_2O as an oxygen source.[4-8] [Ru(bpy)$_3$]$^{3+}$ can be replaced by a much weaker one-electron oxidant, such as [Co^{III}(NH$_3$)$_5$Cl]$^{2+}$, and [Ru(bpy)$_3$]$^{2+}$ as a photoredox catalyst.[9-11] If a one-electron oxidant (A) can be replaced by O_2, substrates (S) would be oxygenated by O_2 as a two-electron oxidant and H_2O as an oxygen source to produce the oxygenated product (SO) and hydrogen peroxide (H_2O_2), as shown in eq 4; both O_2 and H_2O are the greenest oxidant and oxygen source, respectively. However, such a catalytic oxygenation of substrates using O_2 as a two-electron oxidant and H_2O as an oxygen source has yet to be achieved. Herein, we report the photocatalytic oxygenation of hexamethylbenzene (HMB) using a cobalt porphyrin complex, Co^{II}(TPP) (TPP^{2-} = tetraphenylporphyrin dianion), as a catalyst in the presence of triflic acid (HOTf), H_2O as an oxygen source, and O_2 as a two-electron oxidant via a one photon-two electron process.[12] This is the first example of using O_2 and H_2O as the greenest oxidant and oxygen source, respectively, in the photocatalytic oxygenation of substrates by a metal complex.[13]

Photocatalytic oxygenation of HMB (40 mM) in O_2-saturated CD$_3$CN containing Co^{II}(TPP) (10 *μ*M), HOTf (0.20 mM), and H_2O (80 mM) under photoirradiation with a Xenon lamp at 298 K yielded pentamethylbenzyl alcohol (PMB-CH$_2$OH) and hydrogen peroxide as products (Figure 1) as monitored by ^{1}H NMR spectra (Supporting Information, Figure S1).[14] The rate of the photocatalytic reaction was increased with increasing concentrations of Co^{II}(TPP) and HMB (Figures S2 and S3), whereas the rate of the formation of PMB-CH$_2$OH was not affected by changing concenrations of O_2 and HOTf (Figure S4). Only a negligible amount of PMB-CH$_2$OH was produced without photoirradiation or in the absence of Co^{II}(TPP) and O_2, indicating that these are essential components for the photocatalytic oxygenation reaction (Figure S5). The stoichiometry of the photocatalytic oxygenation of HMB is given by eq 5, where PMB-CH$_2$OH and H_2O_2 are produced in a 1:1



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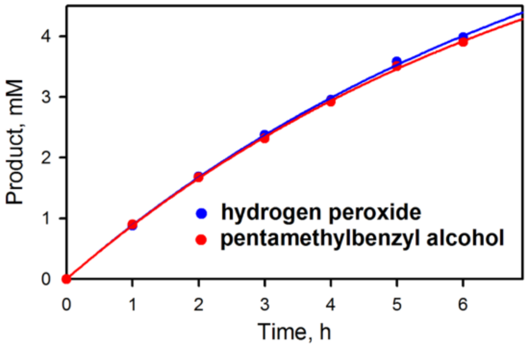


Figure 1. Time courses of photocatalytic oxygenation of HMB (40 mM) in an O_2-saturated MeCN containing $Co^{II}(TPP)$ (10 μM), H_2O (80 mM) and HOTf (0.20 mM) under photoirradiation with a Xenon lamp at 298 K.

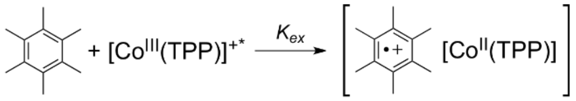
ratio (Figure 1). The quantum yield for the photocatalytic oxygenation of HMB (40 mM) in an O_2-saturated CD_3CN containing $Co^{II}(TPP)$ (10 μM), HOTf (0.20 mM), and H_2O (80 mM) was determined to be 5.2% by using a ferrioxalate actinometer (Figure S6).[15]

When the photocatalytic oxygenation of HMB was performed with ^{18}O-labeled water ($H_2{}^{18}O$) in $^{16}O_2$-saturated MeCN, ^{18}O-incorporation (~100%) was found in the PMB-CH_2OH product (Figure 2a). In contrast, when ^{18}O-labeled dioxygen ($^{18}O_2$) was used in the photocatalytic oxygenation of HMB in the presence of $H_2{}^{16}O$, no ^{18}O was found in the PMB-CH_2OH product (Figure 2b). These ^{18}O-labeling experiments indicate that oxygen atom in PMB-CH_2OH derived from H_2O, but not from O_2. These results are in sharp contrast to the photocatalytic oxygenation reactions of toluene derivatives using organic photocatalysts, in which the source of oxygen in the oxygenated products was O_2, not H_2O.[16,17] In the presence of HOTf, the oxygen atom in PMB-$CH_2{}^{16}OH$ was not exchanged with that in $H_2{}^{18}O$ (Figure S7).

$Co^{II}(TPP)$ was reported to be readily oxidized by O_2 in the presence of an acid to produce $[Co^{III}(TPP)]^+$ and H_2O_2 (eq 6).[17]

$$2[Co^{II}(TPP)] + O_2 + 2H^+ \longrightarrow 2[Co^{III}(TPP)]^+ + H_2O_2 \qquad (6)$$

$[Co^{III}(TPP)]^+$ exhibits fluorescence as shown in Figure 3, where the fluorescence (I) was quenched by addition of HMB. The Stern-Volmer plot of I_0/I vs concentration of HMB (Figure S8) afforded the quenching rate constant of 9.3×10^{10} M^{-1} s^{-1}, which is significantly larger than the diffusion rate constant in MeCN (2×10^{10} M^{-1} s^{-1}). This indicates that the quenching of the fluorescence of $[Co^{III}(TPP)]^+$ is static to produce the exciplex (eq 7), but not dynamic. Indeed, the fluorescence lifetime of $[Co^{III}(TPP)]^+$ remains the same with increasing concentration of HMB up to 50 mM (Figure S9). In the presence of an excess amount of HMB, the ratio of concentration of the exciplex to $[Co^{III}(TPP)]^{+*}$ is given by eq 8. Since $[Ex]/[[Co^{III}(TPP)]^{+*}]$ corresponds to $(I_0 - I)/(I_0 - I_\infty)$, eq 8 is rewritten by eq 9, which predicts a linear correlation between $(I_0 - I)^{-1}$ and $[HMB]^{-1}$. The K value was determined to be 65 ± 5 M^{-1} from the slope and the intercept of a plot of $(I_0 - I)^{-1}$ and $[HMB]^{-1}$ (Figure S10a).



(7)

$$[Ex]/[[Co^{III}(TPP)]^{+*}] = K[HMB]/(1 + K[HMB]) \qquad (8)$$

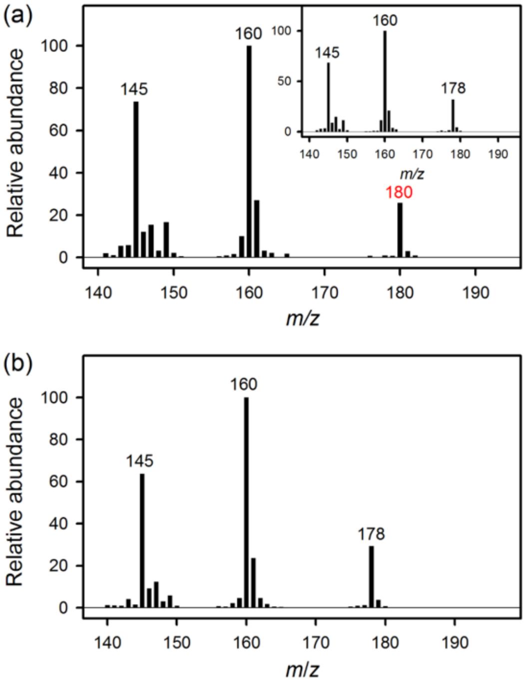


Figure 2. (a) GC-MS spectrum of pentamethylbenzyl alcohol (PMB-CH_2OH) produced by photoirradiation of an $^{16}O_2$-saturated MeCN (2.0 mL) containing $Co^{II}TPP$ (10 μM), $H_2{}^{18}O$ (550 mM), HOTf (0.20 mM) and HMB (40 mM) with a Xenon lamp for 20 h at 298 K. Inset shows fragmentation patterns of an authentic sample of PMB-CH_2OH. (b) GC-MS spectrum of PMB-CH_2OH produced by photoirradiation of an $^{18}O_2$-saturated MeCN (2.0 mL) containing $Co^{II}TPP$ (10 μM), $H_2{}^{16}O$ (550 mM), HOTf (0.20 mM) and HMB (40 mM) with a Xenon lamp for 20 h at 298 K. No ^{18}O-incorporation from $^{18}O_2$ into the PMB-CH_2OH product was obtained.

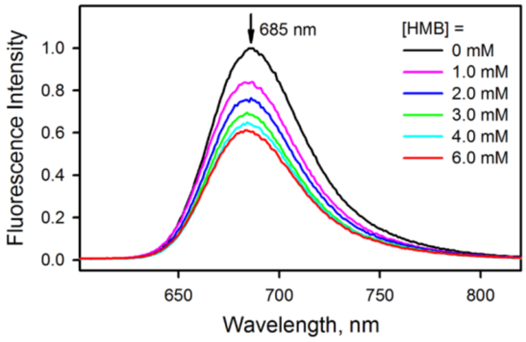
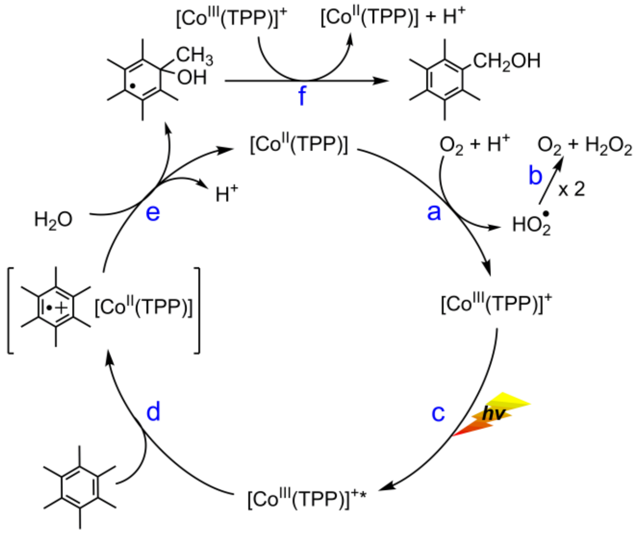


Figure 3. Emission spectra of $[Co^{III}(TPP)]^+$ (0.70 μM) in the presence of HMB (0 – 6.0 mM) upon visible light excitation (λ_{ex} = 430 nm) of an Ar-saturated MeCN solution at 298 K.

$$(I_0 - I_\infty)/(I_0 - I) = 1 + (K[HMB])^{-1} \qquad (9)$$

The exciplex formed between electron donor (i.e., HMB) and an electron acceptor (i.e., $[Co^{III}(TPP)]^+$) is generally composed of an electron donor radical cation (i.e., $HMB^{\bullet+}$) and an electron acceptor radical anion (i.e., $Co^{II}(TPP)$) (eq 7).[18] The formation of $HMB^{\bullet+}$ in the exciplex was confirmed by the transient absorption spectra at 5 ns taken after picosecond laser excitation using a RIPT method (Figure S11),[19] where the absorption band at ca. 500 – 510 nm is ascribed to that due to $HMB^{\bullet+}$.[20] The formation of $HMB^{\bullet+}$ was also confirmed by EPR measurements under photoirradiation of an MeCN solution of $[Co^{III}(TPP)]^+$ and HMB at 233 K (Figure S12), where an EPR signal due to $HMB^{\bullet+}$ (g_{eff} = 2.0031)[21] was overlapped

Scheme 1. Proposed Mechanism of Photocatalytic Oxygenation of Hexamethylbenzene Using O_2 as a Two-Electron Oxidant, Water as an Oxygen Source, and $Co^{II}(TPP)$ as a Redox Photocatalyst in the Presence of Acid (H^+)



with the broad signal due to $Co^{II}(TPP)$. The observed EPR signal in Figure S12 (black line) agrees with the sum (green line) of those of the authentic samples, $Co^{II}(TPP)$ (red line) and $HMB^{\bullet+}$ (blue line) produced by the electron-transfer oxidation of HMB by cerium ammonium nitrate (CAN). The yield of $HMB^{\bullet+}$ based on the initial concentration of $Co^{II}(TPP)$ was determined to be 20% by comparison of the doubly integrated value of the EPR signal due to $HMB^{\bullet+}$ with that of a reference radical, 2,2-diphenyl-1-picrylhydrazyl radical ($DPPH^{\bullet}$) (Figure S13).

Based on the experimental results described above, the mechanism of the photocatalytic oxygenation of HMB by $Co^{II}(TPP)$, O_2, and H_2O in the presence of HOTf is proposed as shown in Scheme 1. $Co^{II}(TPP)$ is oxidized by O_2 in the presence of H^+ to produce $[Co^{III}(TPP)]^+$ and $HO_2^{\bullet}$ (pathway *a*), followed by the disproportionation of $HO_2^{\bullet}$ to produce H_2O_2 and O_2 (pathway *b*).[16,17,22] Photoexcitation of $[Co^{III}(TPP)]^+$ results in the formation of the emissive excited state that forms the exciplex with HMB (pathways *c* and *d*); the exciplex is composed of $HMB^{\bullet+}$ and $Co^{II}(TPP)$. $HMB^{\bullet+}$ reacts with H_2O to produce the OH adduct radical and $Co^{II}(TPP)$ (pathway *e*), and the former species is oxidized by $[Co^{III}(TPP)]^+$ to produce PMB-CH_2OH (pathway *f*).[22] Thus, the one-photon process to produce $HMB^{\bullet+}$ resulted in the thermal oxidation of the OH adduct by $[Co^{III}(TPP)]^+$, making it possible to undergo a one photon-two electron process, yielding two-electron oxidized product (PMB-CH_2OH). When H_2O was replaced by other nucleophiles such as Cl^- and Br^-, PMBCl and PMBBr were produced as detected by GC-MS (Figures S14 and S15). According to Scheme 1, oxygen in PMB-CH_2OH derives from H_2O that reacts with $HMB^{\bullet+}$, whereas oxygen in H_2O_2 comes from O_2 via disproportionation of $HO_2^{\bullet}$ that is produced by proton-coupled electron transfer (PCET) from $Co^{II}(TPP)$ to O_2 with HOTf (Scheme 1). The oxygen source of H_2O_2 was confirmed to be O_2 by carrying out $^{18}O_2$ experiments, in which $^{18}O_2$ was reduced to produce $H_2{}^{18}O_2$. After the formation of $H_2{}^{18}O_2$, $^{18}O_2$ was removed and then MnO_2 was added to a solution of the $H_2{}^{18}O_2$ product. In the latter reaction, the formation of $^{18}O_2$ was detected by mass spectrometer for gas (Figure S16 in SI).

Since the rate of formation of PMB-CH_2OH increased with increasing concentration of HMB to reach a constant value but the rate was not dependent on the concenrations of O_2 and HOTf, the turnover-limiting step in the catalytic cycle is proposed to be the exciplex formation by the quenching of $[Co^{III}(TPP)]^{+*}$ with HMB (Scheme 1, pathway *d*). In such a case, the rate (R) is given by eq 10,

$$R = \Phi_0 IK[\mathrm{HMB}]/(1 + K[\mathrm{HMB}]) \tag{10}$$

where Φ_0 is the quantum yield of formation of $[Co^{III}(TPP)]^{+*}$ and I is the light intensity absorbed by $[Co^{III}(TPP)]^+$. Eq 10 is rewritten by eq 11, which predicts a linear correlation between R^{-1} and $[\mathrm{HMB}]^{-1}$.

$$R^{-1} = (\Phi_0 IK[\mathrm{HMB}])^{-1} + (\Phi_0 I)^{-1} \tag{11}$$

The K value was determined to be 65 ± 6 M^{-1} from the slope and intercept of a plot of $(I_0 - I)^{-1}$ and $[\mathrm{HMB}]^{-1}$ (Figure S10b), which agrees well with the value of 65 ± 5 M^{-1} obtained from the fluorescence quenching (Figure S10a). Such an agreement strongly supports the proposed mechanism depicted in Scheme 1.

The scope of substrates for the photocatalytic oxidation with $[Co^{III}(TPP)]^+$ has also been explored (vide infra). The photocatalytic oxygenation of thioanisole occurred under visible light irradiation of an O_2-saturated acetonitrile solution containing, $[Co^{II}(TPP)]$, H_2O, and HOTf, yielding methyl phenyl sulfoxide with a turnover number (TON) of >45000 based on $Co^{II}(TPP)$ (Figures S17 and 18). The formation constant of exciplex (K) of thioanisole was determined to be 83 ± 5 M^{-1} (Figures S17d and S19b), which is larger than that of HMB in agreement with the lower one-electron oxidation potential of thioanisole (E_{ox} = 1.34 V vs SCE) compared to that of HMB (E_{ox} = 1.49 V vs SCE).[23] The photocatalytic reactivity of HMB was also compared with toluene derivatives such as mesitylene and *p*-xylene (Figure S20), where HMB exhibited the highest reactivity and the fluorescence (I) of $[Co^{III}(TPP)]^+$ was not quenched by addition of mesitylene or *p*-xylene, although a small amount of aldehyde was produced in these reactions. These results are consistent with the higher E_{ox} values of mesitylene (1.98 V vs SCE) and *p*-xylene (1.93 V vs SCE) compared to that of HMB (1.49 V vs SCE).[23] Further, it was confirmed that $[Co^{III}(TPP)]^+$ remained the same after 18 h photoirradiation (Figure S21), demonstrating the high photorobustness of the photoredox catalyst.

Finally, the photocatalytic reactivity of $[Co^{III}(TPP)]^+$ was compared with other Co^{III} porphyrins with electron-donating and -withdrawing substituents, such as $[Co^{III}(TMP)]^+$ (cobalt(III) 5,10,15,20-tetrakis-(2,4,6-trimethylphenyl)porphyrin) and $[Co^{III}(TDFPP)]^+$ (cobalt(III) 5,10,15,20-tetrakis-(2,6-difluorophenyl)porphyrin). $[Co^{III}(TPP)]^+$ exhibited the highest reactivity among the tested Co^{III} porphyrins (Figure S22), because the electron-donating substituent in $[Co^{III}(TMP)]^+$ reduces the oxidizing capability of HMB, whereas the electron-withdrawing substituent in $[Co^{III}(TDFPP)]^+$ decreases the reducing capability of O_2 in Scheme 1.

In conclusion, $[Co^{III}(TPP)]^+$, which is produced by PCET oxidation of $Co^{II}(TPP)$ by O_2 in the presence of HOTf, acts as an efficient one-photon two-electron photoredox catalyst in the oxygenation of HMB using H_2O as an oxygen source and O_2 as a two-electron oxidant to produce PMB-CH_2OH and H_2O_2. The present study has paved a new way for the development of environmentally benign catalytic oxygenation reactions using the cleanest chemicals, such as H_2O as an oxygen source and O_2 as a two-electron oxidant.

ASSOCIATED CONTENT

Supporting Information.

Experimental details, Table S1 and Figures S1 – S22. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) It was confirmed that no decomposition of H_2O_2 occurred during the photocatalytic oxygenation of HMB with Co^{II}(TPP) in the presence of HOTf as shown in Figure 1, where the concentration of PMB-CH_2OH is always the same as that of H_2O_2.

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(22) If $HO_2^•$ abstracts a hydrogen atom from HMB, PMB-$CH_2^•$ would react with O_2 to produce PMB-$CH_2OO^•$ that disproportionates to produce PMB-CH_2OH and PMB-CHO in a 1:1 ratio. Since only a negligible amount of PMB-CHO (< 0.9%) was produced in the photocatalytic oxygenation of HMB with Co^{II}(TPP) in the presence of HOTf, $HO_2^•$ may disproportionate to produce H_2O_2 and O_2 rather than abstract a hydrogen atom from HMB. In addition, the pathway *b* is well known as reported in refs 16 and 17. Electron transfer from the OH adduct radical to $[Co^{III}(TPP)]^+$ (E_{red} = 0.35 V vs SCE) in pathway *f* in Scheme 1 may occur rapidly judging from the reported electron transfer from cyclohexadienyl radical, which is a weaker electron donor than the OH adduct radical, to $[Fe^{III}(C_2O_4)_3]^{3-}$ (E_{red} = 0.24 V vs SCE), which is a weaker electron acceptor than $[Co^{III}(TPP)]^+$; see: Anderson, R. T. Oxidation of the Cyclohexadienyl Radical by Metal Ions: A Pulse Radiolysis Study. *Radiat. Phys. Chem.* **1979**, *13*, 155-157.

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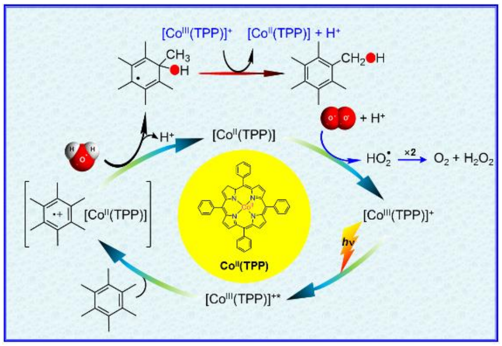
TOC Graph


$[Co^{III}(TPP)]^+$
$[Co^{II}(TPP)] + H^+$
CH_3
H
CH_2
H
$O^{\cdot}$ $O^{\cdot}$ + H^+
H H
$O^{\cdot}$
H^+
$[Co^{II}(TPP)]$
$HO_2^{\cdot}$
×2
$O_2 + H_2O_2$
•+
$[Co^{II}(TPP)]$
N
N
N
N
Co^{II}
$Co^{II}(TPP)$
$[Co^{III}(TPP)]^+$
hν
$[Co^{III}(TPP)]^{+*}$