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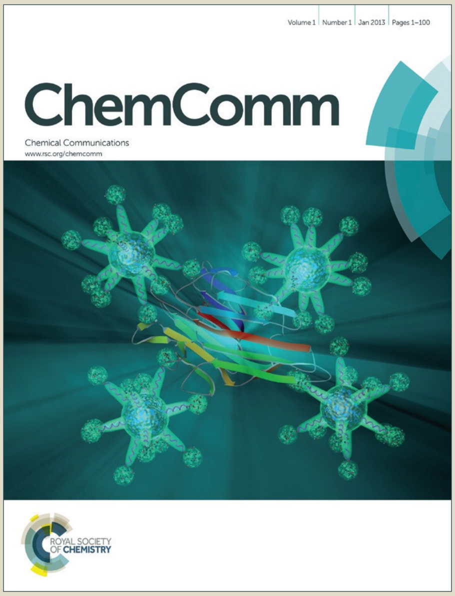

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Photocatalytic oxidation of iron(II) complexes by dioxygen with 9-mesityl-10-methylacridinium ion†

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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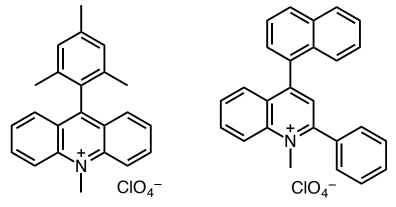
Photocatalytic oxidation of iron(II) complexes by dioxygen occurred using organic photocatalysts, 9-mesityl-10-methylacridinium ion (Acr^+–Mes) and 2-phenyl-4-(1-naphthyl) quinolinium ion ($QuPh^+$–NA), in the presence of triflic acid in acetonitrile under visible light irradiation. The electron-transfer state of Acr^+–Mes produced upon photoexcitation oxidized iron(II) complexes, whereas it reduced dioxygen with protons to produce iron(III) complexes and H_2O_2.

Metal complexes are usually oxidized by inorganic oxidants such as cerium ammonium nitrate and lead dioxide.[1-5] In such cases, the stoichiometric amounts of inorganic oxidants are required to obtain oxidized metal complexes, producing inorganic wastes which cause environmental problems. The ideal oxidant, which is environmentally benign, is dioxygen (O_2), producing only hydrogen peroxide or water as the reduced product. However, the oxidation of metal complexes by O_2 is often endergonic even in the presence of an acid. Thus, an appropriate photocatalyst is required for the oxidation of metal complexes by O_2 in the presence of an acid. Ruthenium(II) complexes, such as $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) are known to be oxidized by O_2 in the presence of an acid to yield the corresponding Ru(III) complexes.[6,7] On the other hand, organic photocatalysts have merited increasing attention for a variety of oxidation reactions.[8-14] However, there has been no report on photocatalytic oxidation of metal complexes by O_2 using organic photocatalysts.

We report herein photocatalytic oxidation of iron(II) complexes by O_2 using 9-mesityl-10-methylacridinium ion (Acr^+–Mes)[15] and 2-phenyl-4-(1-naphthyl)quinolinium ion ($QuPh^+$-NA)[16] as organic photocatalysts in the presence of triflic acid (HOTf) in acetonitrile (MeCN) under visible light irradiation [eqn (1)]. Visible light irradiation of an O_2-saturated acetonitrile was shown in Fig. 1, where the absorption band at 520 nm due to $[Fe^{II}(bpy)_3]^{2+}$ decreased, accompanied by increase in absorption at 650 nm due to $[Fe^{III}(bpy)_3]^{3+}$. $[Fe^{II}(bpy)_3]^{2+}$ was not oxidized without Acr^+–Mes under irradiation (Figs. S1 and S2 in ESI†). The reduced product of

$$2\,Fe^{II} + O_2 + 2\,H^+ \xrightarrow[\text{Photocatalyst}]{h\nu} 2\,Fe^{III} + H_2O_2 \qquad (1)$$



$[Acr^+–Mes](ClO_4^-)$ $[QuPh^+–NA](ClO_4^-)$

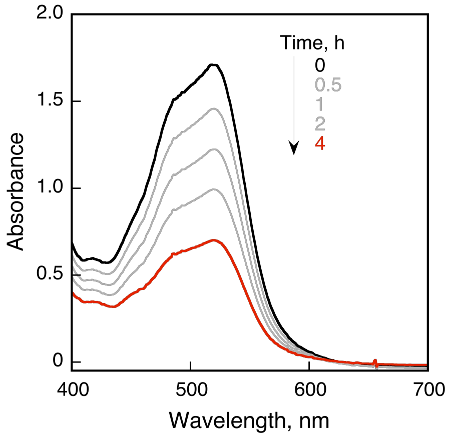


Fig. 1 Visible absorption change in photocatalytic oxidation of $[Fe^{II}(bpy)_3]^{2+}(PF_6^-)_2$ (2.0 mM) by O_2 in O_2-saturated MeCN in the presence of $[Acr^+–Mes](ClO_4^-)$ (0.20 mM) and HOTf (0.10 M) at 298 K under visible light irradiation with a xenon lamp with a cut filter (λ > 390 nm).

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† Electronic Supplementary Information (ESI) available: Experimental and kinetic details. See DOI:

Table 1 Product and quantum yields (Φ) of iron(III) complexes for photocatalytic oxidation of iron(II) complexes by O_2 in the presence of HOTf together with the one-electron oxidation potentials of iron(II) complexes (E_{ox}) and the free energy change of the oxidation (ΔG_{ox})

Entry	Fe^{II} complex	E_{ox} *vs.* SCE [a], V	ΔG_{ox}, eV	Acr^+–Mes Yield [d], %	TON	Φ [f], %	$QuPh^+$–NA Yield [e], %	TON	Φ [f], %
1 [b]	$[Fe^{II}(Clphen)_3]^{2+}$	1.20	0.90	5	0.25	0.11	30	1.5	0.34
2 [b]	$[Fe^{II}(bpy)_3]^{2+}$	1.06	0.62	42	4.2	0.32	32	3.5	0.73
3 [b]	$[Fe^{II}(Me_2bpy)_3]^{2+}$	0.88	0.26	22	2.1	1.6	30	3.0	5.2
4 [c]	$Fe^{II}(BrC_5H_4)_2$	0.72	–0.06	81	4.1	7.2	87	4.2	13
5 [c]	$Fe^{II}(BrC_5H_4)(C_5H_5)$	0.53	–0.44	81	4.1	19	60	3.0	26

Clphen = 5-chloro-1,10-phenanthroline, bpy = 2,2'-bipyridine, Me_2bpy = 4,4'-dimethyl-2,2'-bipyridine, BrC_5H_4 = bromocyclopentadienyl, C_5H_5 =cyclopentadienyl, Reaction conditions: [photocatalyst] = 0.20 mM; [HOTf] = 0.10 M; $[[Fe^{II}(Clphen)_3]^{2+}(PF_6^-)_2]$ = 1.0 mM, $[[Fe^{II}(bpy)_3]^{2+}(PF_6^-)_2]$ = 2.0 mM, $[[Fe^{II}(Me_2bpy)_3]^{2+}(PF_6^-)_2]$ = 2.0 mM, $[Fe^{II}(BrC_5H_4)_2]$ = 1.0 mM, $[Fe^{II}(BrC_5H_4)(C_5H_5)]$ = 2.0 mM; [a] Taken from ref. 19.; [b] MeCN (0.40 mL), Cell path length 0.1 cm; [c] MeCN (3.0 mL) , Cell path length 1 cm; [d] Photoirradiation (λ > 390 nm); [e] (λ > 300 nm); [f] see the experimental section in the ESI†

O_2 was H_2O_2, which was detected by spectral titration with use of the oxo[5,10,15,20-tetra(4-pyridyl)porphyrinato]titanium(IV) complex (see the experimental section in the ESI†).[17]

The photocatalytic oxidation of other iron(II) complexes by O_2 was examined in the presence of HOTf in O_2-saturated MeCN (Figs. S3-S6 in ESI†). The quantum yields of formation of iron(III) complexes were determined using a ferrioxalate actinometer (see Experimental Section in ESI†).[18] The quantum yields (Φ) of photocatalytic oxidation of iron(II) complexes by O_2 in the presence of HOTf in MeCN are listed in Table 1 together with the concentrations of iron(II) complexes, HOTf and O_2, the one-electron oxidation potentials of iron(II) complexes (E_{ox})[19] and the free energy change of the oxidation (ΔG_{ox}). The ΔG_{ox} values were evaluated from the E_{ox} values and the E_{red} value of O_2 in the presence of an acid in MeCN (0.75 V *vs.* SCE) [eqn (2)].[20]

$$\Delta G_{ox} = -2e(E_{red} - E_{ox}) \qquad (2)$$

Judging from the ΔG_{ox} values, the photocatalytic oxidation of $[Fe^{II}(Clphen)_3]^{2+}$, $[Fe^{II}(bpy)_3]^{2+}$ and $[Fe^{II}(Me_2bpy)_3]^{2+}$ is endergonic, whereas that of $Fe^{II}(BrC_5H_4)_2$ and $Fe^{II}(BrC_5H_4)(C_5H_5)$ is exergonic. The Φ values increased with decreasing the E_{ox} values of iron(II) complexes as the free energy change of the reaction in eqn (1) decreased to be thermodynamically more favourable. Dependence of Φ on concentrations of $[Fe^{II}(bpy)_3]^{2+}(PF_6^-)_2$, HOTf and O_2 is shown in Fig. 2 (part a, b and c, respectively). The Φ value became constant with increasing concentrations of $[Fe^{II}(bpy)_3]^{2+}(PF_6^-)_2$, HOTf and O_2, respectively. The photocatalytic oxidation of iron(II) complexes was enhanced by using $QuPh^+$–NA instead of Acr^+–Mes as shown in Table 1. (Figs. S7-S11 in ESI†)

Nanosecond laser flash photolysis measurements were performed in order to clarify the catalytic mechanism for photocatalytic oxidation of iron(II) complexes by O_2 with Acr^+–Mes in the presence of HOTf in MeCN. Transient absorption spectra were taken after the nanosecond laser excitation at 355 nm of a deaerated MeCN solution of Acr^+–Mes in the absence and presence of $[Fe^{II}(bpy)_3]^{2+}(PF_6^-)_2$ as shown in Fig. 3. The transient absorption band at 490 nm is due to the electron-transfer state of Acr^+–Mes. In the presence of $[Fe^{II}(bpy)_3]^{2+}$ the absorption at 490 nm decayed more rapidly and the decay rate increased with increasing concentration of $[Fe^{II}(bpy)_3]^{2+}$. The decay rate obeyed pseudo-first-order kinetics and the pseudo-first order rate constant increased linearly with increasing concentration of $[Fe^{II}(bpy)_3]^{2+}(PF_6^-)_2$. From the slope the rate constant (k_{ox}) of electron transfer from $[Fe^{II}(bpy)_3]^{2+}$ to the electron-transfer state of Acr^+–Mes was determined to be 3.7×10^8 M^{-1} s^{-1} as shown in the inset of Fig. 3. Similarly the k_{ox} values of other iron(II) complexes were determined (see Figs. S15-S23 in ESI†) as listed in Table 2

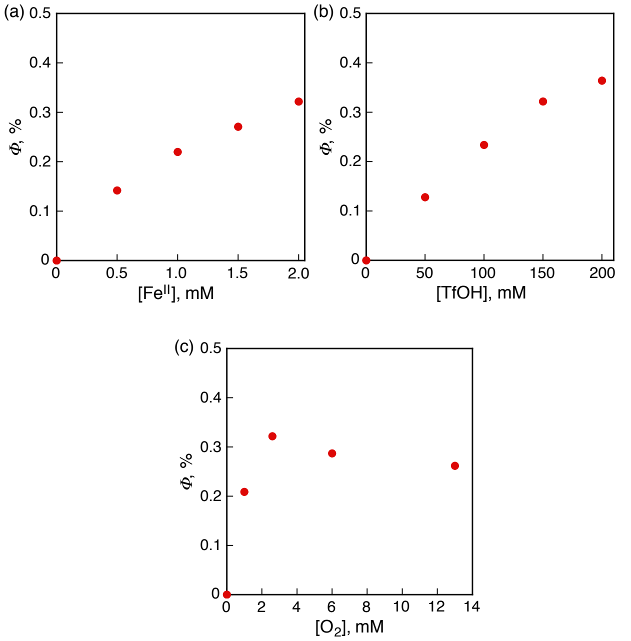


Fig. 2 Dependence of Φ on concentrations of (a) $[Fe^{II}(bpy)_3]^{2+}$, (b) HOTf and (c) O_2. Standard conditions: $[[Acr^+–Mes](ClO_4^-)]$ = 1.0 mM; $[[Fe^{II}(bpy)_3]^{2+}(PF_6^-)_2]$ = 2.0 mM; [HOTf] = 0.15 M; $[O_2]$ = 2.6 mM; dehydrated MeCN (0.40 mL); Cell path length 0.1 cm; Excitation wavelength: 420 nm.

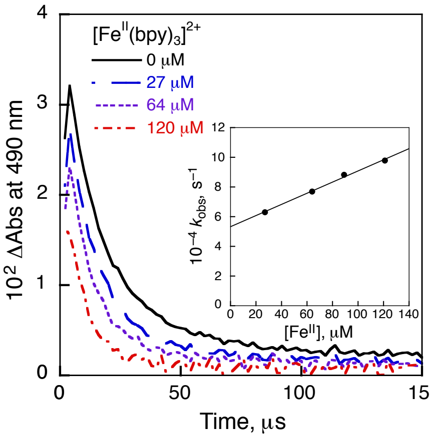
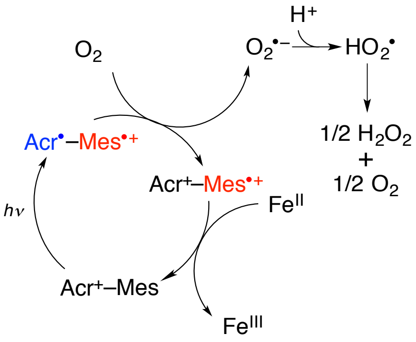


Fig. 3 Transient absorption decay at 490 nm due to the electron-transfer state of $[Acr^+–Mes](ClO_4^-)$ with various concentrations of $[Fe^{II}(bpy)_3]^{2+}(PF_6^-)_2$. Inset: decay rate constant versus concentrations of $[Fe^{II}(bpy)_3]^{2+}(PF_6^-)_2$.

Table 2 Rate constants of electron transfer from iron(II) complexes to the electron-transfer state of organic photocatalyst and the one-electron oxidation potentials of iron(II) complexes (E_{ox})

Entry	Fe^{II} complex	E_{ox} *vs.* SCE [a], V	Acr^+–Mes k_{et}, M^{-1} s^{-1}	$QuPh^+$–NA k_{et}, M^{-1} s^{-1}
1	$[Fe^{II}(Clphen)_3]^{2+}$	1.20	1.4×10^8	4.9×10^8
2	$[Fe^{II}(bpy)_3]^{2+}$	1.06	3.7×10^8	4.5×10^8
3	$[Fe^{II}(Me_2bpy)_3]^{2+}$	0.88	4.5×10^8	5.8×10^8
4	$Fe^{II}(BrC_5H_4)_2$	0.72	7.6×10^9	7.2×10^9
5	$Fe^{II}(BrC_5H_4)(C_5H_5)$	0.53	8.5×10^9	7.9×10^9



Scheme 1 Photocatalytic cycle for oxidation of iron(II) complexes to iron(III) complexes by O_2 with Acr^+–Mes.

together with E_{ox} values. The k_{ox} value increases with decreasing E_{ox} values. In the presence of O_2, electron transfer from the electron-transfer state of Acr^+–Mes to O_2 is known to occur with the rate constant of 6.8×10^8 M^{-1} s^{-1}.[21] The rate constant of electron transfer from the electron-transfer state of $QuPh^+$–NA to O_2 was determined to be 6.3×10^8 M^{-1} s^{-1} (see Figs. S24 in ESI†). Thus, the photocatalytic oxidation of iron(II) complexes (Fe^{II}) by O_2 in the presence of HOTf proceeds as shown in Scheme 1. Photoexcitation of Acr^+–Mes results in formation of the electron-transfer state of Acr^+–Mes, which oxidizes iron(II) complexes to iron(III) complexes and reduces O_2 with proton to produce $HO_2^•$, which disproportionates to yield H_2O_2.

In conclusion, iron(II) complexes are oxidized to iron(III) complexes by O_2 using Acr^+–Mes as an organic photocatalyst in the presence of HOTf in MeCN under visible light irradiation via electron-transfer oxidation of iron(II) complexes and reduction of O_2 by the electron-transfer state of Acr^+–Mes produced upon photoexcitation of Acr^+–Mes, respectively. The present study provides an environmentally benign way for oxidation of metal complexes by O_2 to obtain the oxidised metal complexes and hydrogen peroxide (H_2O_2). Because there are many synthetically useful oxidation reactions using H_2O_2,[22] this study has paved a new way for photocatalytic oxidation of substrates by O_2 with organic photocatalysts and iron(II) complexes.

This work was supported by Grants-in-Aid (nos. 26620154 and 26288037 to K.O.) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT); ALCA and SENTAN projects from JST, Japan (to S.F.).

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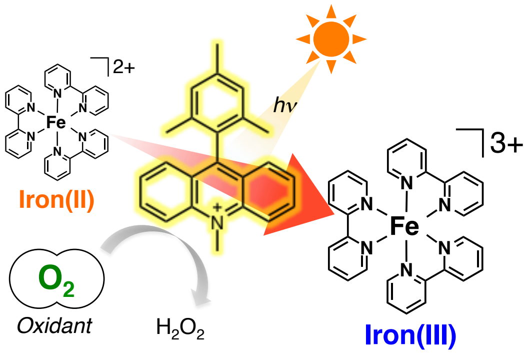

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