[November, 1983] © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***56***, *3203—3207 (1983)* 3203

Light-induced Redox Characteristics of [Tetrakis(4-methylpyridyl)-porphyrinato]manganese(III)

Koushin TAKAHASHI,* Teruhisa KOMURA, and Hiroto IMANAGA
Faculty of Technology, Kanazawa University, Kanazawa 920

(Received March 10, 1983)

[Tetrakis(4-methylpyridyl)porphyrinato]manganese(III) (Mn^{III}(tmpp)) undergoes reversible one-electron transfer reactions in aqueous solutions. The half-wave potential of $Mn^{III/II}$(tmpp) redox couple is −0.21 V (*vs.* 3.33 M KCl, AgCl/Ag) between pH 4 and 12. On the other hand, the half-wave potential of $Mn^{IV/III}$-(tmpp) redox couple becomes less positive with increasing pH in alkaline solution. A small amount of methylviologen cation radical ($MV^{\cdot +}$) is built up by irradiating with visible light an alkaline solution containing Mn^{III}(tmpp), methylviologen (MV^{2+}), and sacrificial electron donors. The formation of $MV^{\cdot +}$ is attributed to either the reduction of photoexcited Mn^{III}(tmpp) (*Mn^{III}(tmpp)) with an electron donor or the oxidation of *Mn^{III}(tmpp) with MV^{2+}.

Much attention has been drawn to light-induced electron transfer reactions sensitized by tris(2,2′-bipyridyl)ruthenium(II) complex and metalloporphyrins from the standpoint of conversion of solar to chemical energy.[1–5] For example, MV^{2+} is reduced to $MV^{\cdot +}$ under irradiation with light in the presence of tris(2,2′-bipyridyl)ruthenium(II) complex and ethylenediaminetetraacetic acid (EDTA),[1] and colloidal platinum catalyzes the hydrogen generation from water in this system.[6,7] Ruthenium dioxide catalyzes the oxygen generation when it substitutes for EDTA. On the other hand, a Mn-protein possibly catalyzes the oxygen generation in the photosynthesis, but the mechanism has hardly been known. Calvin[8] has proposed a general scheme for the photochemical generation of oxygen sensitized by manganese porphyrin. Harriman *et al.*[9–11] reported on the photoredox characteristics of water-soluble Mn(III) porphyrin. The electron transfer reactions sensitized by these compounds are probably very complex since Mn can take several oxidation number.

We previously reported on the redox and photoreductive properties of Mn^{III}(tmpp).[13] This paper presents the light-induced redox characteristics of Mn^{III}(tmpp) in the presence of MV^{2+} and electron donors.

Experimental

The preparation of Mn^{III}(tmpp) was described in the previous paper.[13] [Tetrakis(4-methylpyridyl)porphyrinato]zinc(II) (Zn(tmpp))[14] and tris(2,2′-bipyridyl)ruthenium(II) chloride ([Ru(bpy)$_3$]Cl$_2$)[15] were prepared according to literature methods. Sodium acetate, sodium borate, and potassium phosphate (special grade) were recrystallized from water, and sodium sulfate (special grade) was recrystallized three times from water. Methylviologen dichloride (special grade) was recrystallized from ethanol and dried for 7 h at 60 °C *in vacuo*. Other chemicals (reagent grade) were used without further purification. All solutions were prepared with doubly distilled water.

Cyclic voltammetric experiments were performed in a purified nitrogen atmosphere by using a potentiostat (Nikko Keisoku NPGS-301), a potential sweeper (Nikko Keisoku NPG-2), and a three-electrode configuration. A Pt-wire was used as the warking electrode, a Pt-coil as the counter-electrode, and a commercially available 3.33 M KCl, AgCl/Ag electrode as the reference electrode (1 M = 1 mol dm^{-3}). An X-Y plotter (Riken Denshi Co., Ltd. Model F-3B) was used to record current-voltage curves. Half-wave potentials were measured as the average of cathodic and anodic peak potentials.

The pH of solutions was adjusted to a desired pH with 0.01 M acetate, phosphate, or borate buffer solution. The N_2-purged sample solution was transferred to an optical glass cell with a 1 cm-photopath length and a stopper in a nitrogen atmosphere. A 500 W Xenon arc lamp (Ushio Electric, Co., Ltd. UXL-500D-O) was used for steady-state irradiation experiments. The light was passed through a cut-off filter (Toshiba L-39) and water (1 cm), and focused onto a sample cell thermostated at 25 °C. The sample solution was continuously stirred with a magnetic stirrer throughout the irradiation period. Absorption spectra were measured with a Hitachi Model 124 spectrophotometer.

Results and Discussion

Cyclic Voltammetry of Mn^{III}(tmpp). [Tetrakis(4-methylpyridyl)porphyrinato]manganese(III) was reduced to Mn^{II}(tmpp) with sodium dithionite in a deoxygenated aqueous solution between pH 4 and 12, and was oxidized to Mn^{IV}(tmpp) with potassium peroxodisulfate, sodium hypochlorite, or pentaamminechlorocobalt(III) chloride between pH 9 and 12.[9,13] Table 1 shows the molar extinction coefficients for the absorption peaks of Mn^{II}(tmpp), Mn^{III}(tmpp), and Mn^{IV}(tmpp) in aqueous solution.[13]

Figure 1 shows a typical cyclic voltammogram of Mn^{III}(tmpp) in 0.2 M Na_2SO_4 aqueous solution at pH 12.0. The current-voltage curve shows two reversible waves. The following electrode reactions probably occur:

$$Mn^{III}(\text{tmpp}) + e^- \rightleftharpoons Mn^{II}(\text{tmpp}), \quad (1)$$

$$Mn^{IV}(\text{tmpp}) + e^- \rightleftharpoons Mn^{III}(\text{tmpp}). \quad (2)$$

TABLE 1. THE MOLAR EXTINCTION COEFFICIENTS AT ABSORPTION PEAK (λ_{max}/nm) OF Mn(tmpp) IN AQUEOUS SOLUTION[a)]

	pH	λ_{max}/nm	ε/M^{-1} cm^{-1}
Mn^{II}(tmpp)	6.0	449	1.92×10^5 [b)]
Mn^{III}(tmpp)	6.0	463	1.59×10^5
Mn^{IV}(tmpp)	10.0	429	9.80×10^4 [c)]

a) From Ref. 13. b) Mn^{II}(tmpp) was formed by the reduction of Mn^{III}(tmpp) with $Na_2S_2O_4$. c) Mn^{IV}-(tmpp) was formed by the oxidation of Mn^{III}(tmpp) with [CoCl(NH$_3$)$_5$]Cl$_2$.

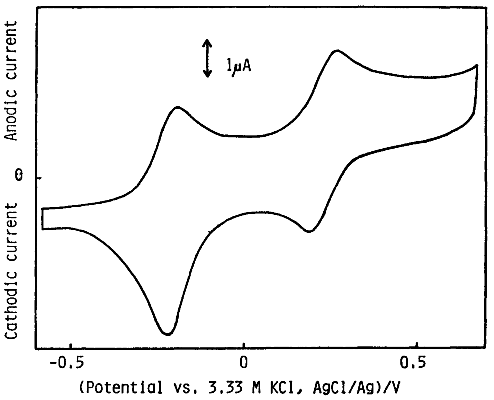

Fig. 1. A typical cyclic voltammogram of 1.0×10^{-3} M Mn^{III}(tmpp) in 0.2 M Na_2SO_4 aqueous solution at pH 12.0 (scan rate 20 mV/s).

TABLE 2. HALF-WAVE POTENTIALS/V (*vs.* 3.33 M KCl AgCl/Ag) OF $Mn^{III/II}$(tmpp) AND $Mn^{IV/III}$(tmpp) REDOX COUPLES IN 0.2 M Na_2SO_4 AQUEOUS SOLUTION AT ROOM TEMPERATURE

pH	$E_{1/2}$(III/III)	$E_{1/2}$(IV/III)
4.1	−0.20	—
5.6	−0.22	—
10.2	−0.21	0.45
10.7	−0.20	0.38
12.0	−0.22	0.23

The half-wave potentials of the two redox couples are given in Table 2. The half-wave potential of Reaction 1, $E_{1/2}$(III/II), is −0.21 V (*vs.* AgCl/Ag) between pH 4 and 12, but that of Reaction 2, $E_{1/2}$(IV/III), becomes less positive with increasing pH in alkaline solution. No anodic peak of Mn^{III}(tmpp) was observed below pH 8 because of the oxidation of water.

Photoreduction of Mn^{III}(tmpp). When a solution of Mn^{III}(tmpp) was irradiated with visible light in the presence of an electron donor (D) such as EDTA, triethanolamine (TEOA), triethylamine (TEA), or nicotine (NT), Mn^{III}(tmpp) was reduced to Mn^{II}(tmpp). Figure 2 shows the pH dependence of the concentration of Mn^{II}(tmpp) produced by irradiating an aqueous solution containing Mn^{III}(tmpp) (9.0×10^{-6} M) and EDTA (1×10^{-4} M) or TEOA (0.01 M).13) The concentration of Mn^{II}(tmpp) ($C_{Mn}{}^{II}$) was estimated from the following equation:

$$C_{Mn}{}^{II} = (A_{449}-A_{449}{}^{\circ})/(\varepsilon_{449}{}^{II}-\varepsilon_{449}{}^{III}), \qquad (3)$$

where $A_{449}{}^{\circ}$ and A_{449} are the absorbances at 449 nm before and after irradiation, and $\varepsilon_{449}{}^{II}$ and $\varepsilon_{449}{}^{III}$ are the molar extinction coefficients at 449 nm of Mn^{II}(tmpp) and Mn^{III}(tmpp), respectively. As shown in Fig. 2, Mn^{III}(tmpp) was almost completely reduced to Mn^{II}(tmpp) with EDTA between pH 6 and 10, but only at pH 10 with TEOA. Figure 3 shows the concentration of Mn^{II}(tmpp) produced by irradiation for 30 min at different concentrations of electron donor at pH 10.0. In a high concentration (0.01 M) of EDTA, the chromophore was partly bleached. The reducing power of electron donors can be regarded as being in the order EDTA>TEOA>TEA>NT.

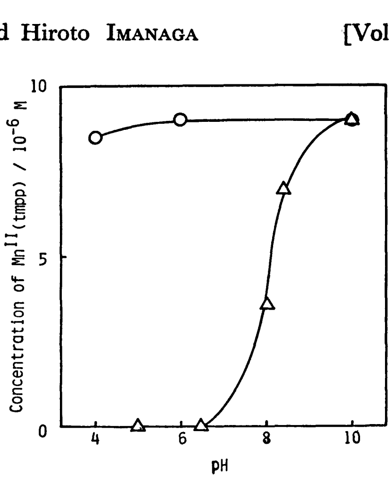

Fig. 2. The pH dependence of the concentration of Mn^{II}(tmpp) produced by irradiation for 30 min.
Total concentration of Mn(tmpp): 9.0×10^{-6} M.
○, 1×10^{-4} M EDTA; △, 0.01 M TEOA.

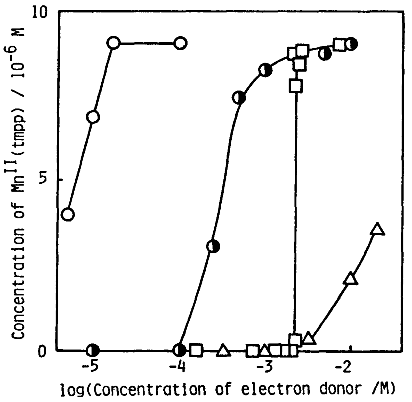

Fig. 3. The concentration of Mn^{II}(tmpp) produced by irradiation for 30 min at different concentrations of electron donors at pH 10.0.
Total concentration of Mn(tmpp): 9.0×10^{-6} M.
○, EDTA; ◑, TEOA; △, NT; □, TEA.

The following reactions can be proposed as the mechanism of the photoreduction of Mn^{III}(tmpp):

$$Mn^{III}(tmpp) \xrightarrow{h\nu} {}^{*}Mn^{III}(tmpp), \qquad (4)$$

$${}^{*}Mn^{II}(tmpp) + D \longrightarrow Mn^{II}(tmpp) + D_{ox}, \qquad (5)$$

or

$${}^{*}Mn^{III}(tmpp) + Mn^{III}(tmpp) \longrightarrow Mn^{II}(tmpp) + Mn^{IV}(tmpp), \qquad (6)$$

$$Mn^{IV}(tmpp) + D \longrightarrow Mn^{III}(tmpp) + D_{ox}, \qquad (7)$$

where D_{ox} is an oxidative decomposition product of D. Reaction 5 means that an excited Mn^{III}(tmpp) (${}^{*}Mn^{III}$(tmpp)) is reduced to Mn^{II}(tmpp) with D. Reaction 6 means that ${}^{*}Mn^{III}$(tmpp) is reduced or oxidized with a ground-state Mn^{III}(tmpp), and Reaction 7 means that Mn^{IV}(tmpp) is scavenged with D.

Porphyrinatomanganese(III)-sensitized Reduction of MV^{2+} with Strong Electron Donors. In an aqueous solution containing Mn^{III}(tmpp) (2.0×10^{-5} M), MV^{2+} (2.0×10^{-3} M), and EDTA (0.01 M) between pH 5 and 11, the color of the solution did not change in the dark, but under irradiation it rapidly changed from orange to yellow green and finally into green. Figure 4 shows the change in the absorption spectra of the solution as a function of irradiation time at pH 10.9. The absorption peaks at 463 and 570 nm of Mn^{III}(tmpp) rapidly disappeared under irradiation, and the new peaks at 395, 451, 579, and 606 nm appeared. The peaks at 395 and 606 nm originate from $\text{MV}^{\dot{+}}$,[16] and those at 451 and 579 nm from Mn^{II}(tmpp).[13] As shown in Fig. 4, Mn^{III}(tmpp) was almost completely reduced to Mn^{II}(tmpp) under irradiation. Because MV^{2+} was not photoreduced to $\text{MV}^{\dot{+}}$ in the absence of Mn^{III}(tmpp) or EDTA, Mn^{III}(tmpp) acts as a sensitizer and EDTA as an electron donor. Figure 5 shows the concentration of $\text{MV}^{\dot{+}}$ produced by irradiation for 30 min an aqueous solution containing Mn^{III}(tmpp) (2.0×10^{-5} M), MV^{2+} (2.0×10^{-3} M), and EDTA or TEOA (0.01 M). The concentration of $\text{MV}^{\dot{+}}$ ($C_{\text{MV}^{\dot{+}}}$) was estimated on the following equation from the measurements of absorbance at 606 nm (A_{606}):

$$C_{\text{MV}^{\dot{+}}} = (A_{606} - C_t\varepsilon_{606}{}^{\text{II}})/\varepsilon_{606}, \qquad (8)$$

where C_t is the total concentration of Mn(tmpp), $\varepsilon_{606}{}^{\text{II}}$ ($7.9\times10^{3}\ \text{M}^{-1}\,\text{cm}^{-1}$) and ε_{606} ($1.37\times10^{4}\ \text{M}^{-1}\,\text{cm}^{-1}$)[18] are the molar extinction coefficients at 606 nm of Mn^{II}(tmpp) and $\text{MV}^{\dot{+}}$, respectively. As shown in Fig. 5, a small amount of $\text{MV}^{\dot{+}}$ was built up between pH 5 and 8 in the presence of EDTA, but not in the presence of TEOA. On the other hand, above pH 9 $\text{MV}^{\dot{+}}$ was formed in considerable quantity in the presence of both the electron donors. This can be attributed to the pH dependence of the reducing powers of EDTA and TEOA. Their reducing powers increase with an increase in pH because the oxidative decompositions of EDTA and TEOA are attended by the formation of proton.[17,18] It is inferred from a comparison of Fig. 5 with Fig. 2 that a certain amount of $\text{MV}^{\dot{+}}$ is built up only when Mn^{III}(tmpp) is photoreduced to Mn^{II}(tmpp) with an electron donor. Figure 6 shows the concentration of $\text{MV}^{\dot{+}}$ produced by irradiation for 30 min and the turnover number of Mn^{III}(tmpp) at different concentrations of Mn^{III}(tmpp) at pH 10.1. The turnover number (N) was calculated by the following equation:

$$N = C_{\text{MV}^{\dot{+}}}/C_t. \qquad (9)$$

The concentration of $\text{MV}^{\dot{+}}$ rapidly increased with an increase in the concentration of Mn^{III}(tmpp) below 2×10^{-6} M, and the maximum turnover number of Mn^{III}(tmpp) was 37 at 5×10^{-7} M Mn^{III}(tmpp). Above 1×10^{-6} M Mn^{III}(tmpp), a photoexcited Mn(tmpp) is possibly self-quenched at high concentrations of Mn(tmpp).

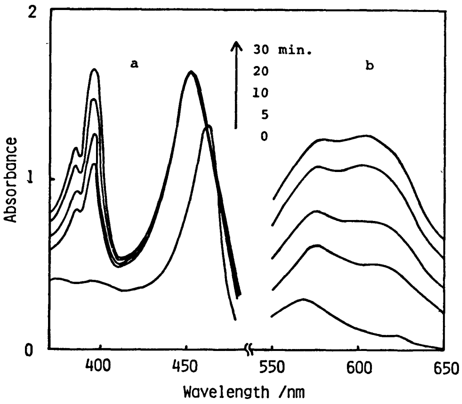

Fig. 4. Absorption spectral profiles showing the appearance of $\text{MV}^{\dot{+}}$ and Mn^{II}(tmpp) as a function of irradiation time at pH 10.9.
a, The concentrations of Mn^{III}(tmpp), MV^{2+}, and EDTA are 9.0×10^{-6}, 5.3×10^{-4}, and 0.01 M, respectively. b, The concentrations of Mn^{III}(tmpp), MV^{2+}, and EDTA are 2.0×10^{-5}, 2.1×10^{-3}, and 0.01 M, respectively.

The reaction scheme in Fig. 7 can be proposed as the mechanism for the Mn^{III}(tmpp)-sensitized reduction of MV^{2+} with strong electron donors. An excited Mn^{III}(tmpp) can first be reduced to Mn^{II}(tmpp) with an electron donor (Reaction 5). Furthermore, an excited Mn^{II}(tmpp) (*Mn^{II}(tmpp)) can be oxidized to

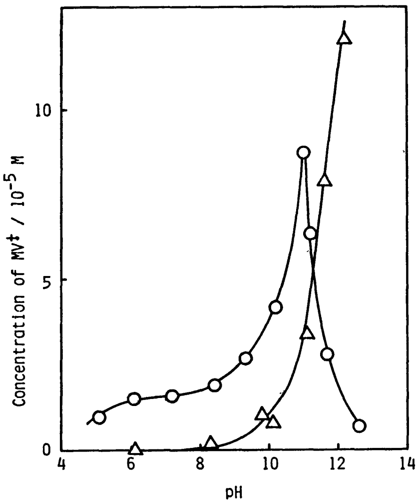

Fig. 5. The pH dependence of the concentration of $\text{MV}^{\dot{+}}$ produced by irradiation for 30 min.
Concentration of Mn^{III}(tmpp): 2.0×10^{-5} M. Concentration of MV^{2+}: 2.0×10^{-3} M. ○, 0.01 M EDTA; △, 0.01 M TEOA.

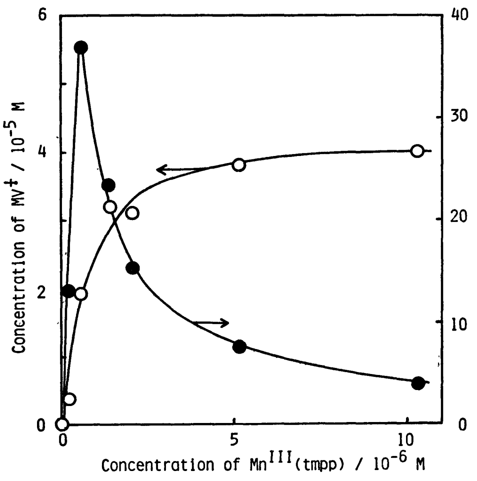

Fig. 6. The concentration of $\text{MV}^{\dot{+}}$ produced and the turnover number of Mn^{III}(tmpp) at different concentrations Mn^{III}(tmpp) at pH 10.1.
Concentration of MV^{2+}: 1.8×10^{-3} M. Concentration of EDTA: 0.01 M. Irradiation time: 30 min.

Mn^{III}(tmpp) with MV^{2+}, and MV$^{+\cdot}$ can be produced:

$$\mathrm{Mn^{II}(tmpp)} \xrightarrow{h\nu} \mathrm{{}^*Mn^{II}(tmpp)}, \tag{10}$$

$$\mathrm{{}^*Mn^{II}(tmpp)} + \mathrm{MV^{2+}} \longrightarrow \mathrm{Mn^{III}(tmpp)} + \mathrm{MV^{+\cdot}}. \tag{11}$$

MV^{2+} is not reduced with the ground-state Mn^{II}(tmpp) because the values of $E°(\mathrm{MV^{2+}/MV^{+\cdot}})$ and $E_{1/2}$(III/II) are −0.67 and −0.21 V (*vs.* AgCl/Ag), respectively. The energy level of *Mn^{II}(tmpp) is probably over 0.46 eV higher than that of Mn^{II}(tmpp). Mn^{III}(tmpp) is also reduced to Mn^{II}(tmpp) with MV$^{+\cdot}$ because of the back electron transfer:

$$\mathrm{Mn^{III}(tmpp)} + \mathrm{MV^{+\cdot}} \longrightarrow \mathrm{Mn^{II}(tmpp)} + \mathrm{MV^{2+}}. \tag{12}$$

The rate of Reaction 11 is probably higher than that of Reaction 12 because an appreciable amount of MV$^{+\cdot}$ is built up.

Porphyrinatomanganese(III)-sensitized Reduction of MV^{2+} with Weak Electron Donors. Figure 8 shows the concentration of MV$^{+\cdot}$ produced by irradiation for 30 min at different concentrations of electron donors in an aqueous solution containing Mn^{III}(tmpp) (2.1×10^{-5} M) and MV^{2+} (2.0×10^{-3} M) at pH 10.1. The concentration of MV$^{+\cdot}$ monotonously increased with an increase in the concentration of EDTA or TEA, but exhibited a maximum in the case of TEOA or NT. A comparison of Fig. 8 with Fig. 3 shows that a certain amount of MV$^{+\cdot}$ was built up even at the low concentration of NT, TEA, or TEOA, at which Mn^{III}(tmpp) was not photoreduced in the absence of MV^{2+}. The formation of Mn^{II}(tmpp) was also observed at such a low concentration (1×10^{-4} M) of NT, TEA, or TEOA.

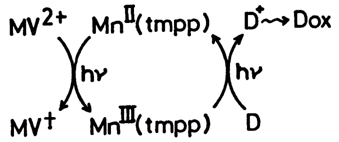

Fig. 7. A schematic representation of photosensitized reaction in the presence of EDTA.

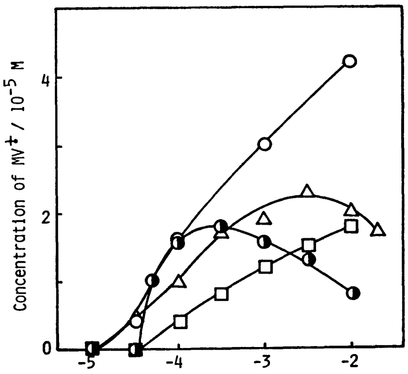

Fig. 8. The concentration of MV$^{+\cdot}$ produced by irradiation for 30 min at different concentrations of electron donors at pH 10.1.
Concentration of Mn^{III}(tmpp): 2.1×10^{-5} M. Concentration of MV^{2+}: 2.0×10^{-3} M. ○, EDTA; ◑, TEOA; △, NT; □, TEA.

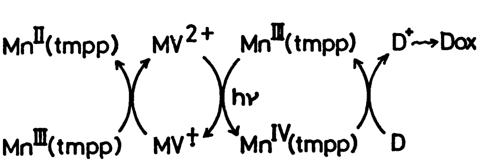

Fig. 9. A schematic representation of photosensitized reaction in the presence of weak electron donors (TEA, NT) below 2×10^{-3} M.

The reaction scheme in Fig. 9 can be proposed as the mechanism for the Mn^{III}(tmpp)-sensitized reduction of MV^{2+} with weak electron donors at low concentrations. An excited Mn^{III}(tmpp) can first be oxidized to Mn^{IV}(tmpp) with MV^{2+}, and MV$^{+\cdot}$ can be produced:

$$\mathrm{{}^*Mn^{III}(tmpp)} + \mathrm{MV^{2+}} \longrightarrow \mathrm{Mn^{IV}(tmpp)} + \mathrm{MV^{+\cdot}}. \tag{13}$$

The energy level of *Mn^{III}(tmpp) is probably over 1.12 eV higher than that of Mn^{III}(tmpp) at pH 10 because the values of $E°(\mathrm{MV^{2+}/MV^{+\cdot}})$ and $E_{1/2}$(IV/III) are −0.67 and 0.45 V (*vs.* AgCl/Ag), respectively. The back electron transfer reaction (14) can be suppressed if Mn^{IV}(tmpp) can rapidly be scavenged with an electron donor (Reaction 7):

$$\mathrm{Mn^{IV}(tmpp)} + \mathrm{MV^{+\cdot}} \longrightarrow \mathrm{Mn^{III}(tmpp)} + \mathrm{MV^{2+}}. \tag{14}$$

Furthermore, Reactions 12 and 11 can occur although Reaction 5 does not proceed with weak electron donors.

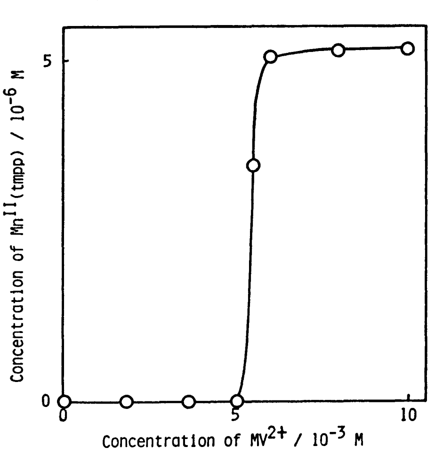

Fig. 10. The concentration of Mn^{II}(tmpp) photoproduced at pH 6.0 at different concentrations of MV^{2+}.
Total concentration of Mn(tmpp): 5.3×10^{-6} M. Concentration of TEOA: 0.01 M. Irradiation time: 30 min.

Figure 10 shows the dependence of the concentration of Mn^{II}(tmpp) photoproduced at pH 6.0 on the concentration of MV^{2+} in an aqueous solution containing Mn^{III}(tmpp) (5.3×10^{-6} M) and TEOA (0.01 M). Porphyrinatomanganese(III) was reduced to Mn^{II}(tmpp) above 5×10^{-3} M MV^{2+}, but the formation of MV$^{+\cdot}$ was not observed. At pH 6 the rate of Reaction 13 is slow since $E_{1/2}$(IV/III) becomes more positive with decreasing pH. When Ru(bpy)$_3^{2+}$ or Zn(tmpp) was used as a sensitizer, 6.1×10^{-5} or 1.6×10^{-4} M MV$^{+\cdot}$, respectively, was built up by irradiating for 10 min a solution (pH 6.0) containing the sensitizer (2.0×10^{-5} M), MV^{2+} (2.0×10^{-3} M), and TEOA (0.01 M). [Tetrakis(4-methylpyridyl)porphyrinato]manganese(III) emitted a very weak luminescence around 540 nm in aqueous solutions. The excited triplet state lifetime of [tetrakis(4-pyridyl)porphyrinato]manganese-(III) in ethanol glass at 77 K is below 0.1 ms,[10)] but that of [tetrakisphenylporphyrinato]zinc(II) in methylcyclohexane at 77 K is 26 ms.[19)] The oxidative electron transfer quenching of the excited Mn(III) porphyrin with MV^{2+} is less effective than that of the excited Zn(II) porphyrin.

References

1) K. Takuma, M. Kajiwara, and T. Matsuo, *Chem. Lett.*, **1977**, 1199.

2) N. Sutin, *J. Photochem.*, **10**, 19 (1979).

3) K. Kano, K. Takuma, T. Ikeda, D. Nakajima, Y. Tsutsui, and T. Matsuo, *Photochem. Photobiol.*, **27**, 695 (1978).

4) K. Kalyanasundaram and M. Grätzel, *Helv. Chem. Acta*, **63**, 478 (1980).

5) A. Harriman, G. Porter, and M. C. Richoux, *J. Chem. Soc., Faraday Trans. 2*, **77**, 833 (1981).

6) K. Kalyanasundaram and M. Grätzel, *Angew. Chem., Int. Ed. Engl.*, **18**, 701 (1979).

7) M. Grätzel, *Ber. Bunsenges. Phys. Chem.*, **84**, 981 (1980).

8) M. Calvin, *Faraday Discuss. Chem. Soc.*, **70**, 383 (1980).

9) A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **75**, 1532 (1979).

10) A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **75**, 1543 (1979).

11) I. A. Duncan, A. Harriman, and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **76**, 1415 (1980).

12) A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **76**, 1429 (1980).

13) K. Takahashi, T. Komura, and H. Imanaga, *Memoirs of the Faculty of Technology, Kanazwa University*, **16**, 103 (1983).

14) R. F. Pasternack, L. Francesconi, D. Raff, and E. Spiro, *Inorg. Chem.*, **12**, 2606 (1973).

15) "Shinjikken Kagaku Kohza 8, Mukikagohbutsu No Gohsei [III]," ed by the Chemical Society of Japan, Maruzen, Tokyo (1977), p. 1475.

16) T. Watanabe and K. Honda, *J. Phys. Chem.*, **86**, 2617 (1982).

17) W. E. Ford, J. W. Otvos, and M. Calvin, *Nature*, **274**, 507 (1978).

18) S. F. Chan, M. Chou, C. Creutz, T. Matsubara, and N. Sutin, *J. Am. Chem. Soc.*, **103**, 369 (1981).

19) A. Harriman, *J. Chem. Soc., Faraday Trans. 1*, **76**, 1978 (1980).