Table III. Derived Solvent Parameters[a]

solvent	E^*_{MLCT}	solvent	E^*_{MLCT}
isooctane	0.00	3-phenyl-1-propanol	0.53
carbon tetrachloride	0.12	1-butanol	0.55
tetrachloroethylene	0.13	tetrahydrofuran	0.59
triethylamine	0.23	1,2-dichloroethane	0.64
trichloroethylene	0.23	2-picoline	0.65
mesitylene	0.25	methylene chloride	0.67
toluene	0.30	benzyl alcohol	0.67
diethyl ether	0.32	cyclohexanone	0.69
benzene	0.34	ethanol	0.69
piperidine	0.41	3-pentanone	0.71
chloroform	0.42	methanol	0.73
1-pentanol	0.45	pyridine	0.77
chlorobenzene	0.46	acetone	0.82
2-propanol	0.46	dimethylacetamide	0.93
o-dichlorobenzene	0.48	dimethylformamide	0.95
cyclohexanol	0.49	acetonitrile	0.98
2-methyl-2-propanol	0.51	dimethyl sulfoxide	1.00

[a] From the data of $W(CO)_4bpy$.

(E^1_{MLCT}). The derived solvent parameter (E^*_{MLCT}) takes on values in an increasing polarity scale from 0 to 1. Values of E^*_{MLCT} for $W(CO)_4bpy$ are shown in Table III. The value of E^*_{MLCT} for acetonitrile has been added (E_{MLCT} = 264.7 kJ mol^{-1} for $W(CO)_4bpy$). The applicability of this solvent scale to other solvent-sensitive metal complexes was demonstrated by plotting E^*_{MLCT} vs. previously reported MLCT absorption maxima of $(\eta^5\text{-}C_5H_5)M(CO)_2py$ complexes (M = Mn and Re).[21] The least-squares regressions for the Mn (slope 34.52 kJ mol^{-1}, correlation coefficient 0.962) and Re (slope 42.13 kJ mol^{-1}, correlation coefficient 0.991) complexes indicate excellent fits; the E^*_{MLCT} solvent scale appears to be a good one for the low-lying MLCT states of transition-metal complexes. The E^*_{MLCT} scale could be used to estimate the position of a MLCT transition hidden by overlapping absorption bands, a situation often encountered in interpreting UV-visible spectra.

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Registry No. $Cr(CO)_4bpy$, 15668-63-0; $Mo(CO)_4bpy$, 15668-64-1; $W(CO)_4bpy$, 15668-66-3; $W(CO)_4$(4-Me-phen), 87655-71-8; $W(CO)_4phen$, 14729-20-5; $W(CO)_4$(5-Me-phen), 59136-52-6; $W(CO)_4$(5-Ph-phen), 87655-72-9; $W(CO)_4$(5-Cl-phen), 59136-53-7; $W(CO)_4(5\text{-}NO_2\text{-}phen)$, 87655-73-0.

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Complexation of $Zn(TPPS_3)$ by Methylviologen and Its Role in the Photoinduced Hydrogen Evolution with Hydrogenase

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As reported previously, water-soluble [*meso*-phenyltris(4-sulfonatophenyl)porphyrinato]zinc ($Zn(TPPS_3)$) has been found to be a suitable photosensitizer[1,2] for the photoinduced hydrogen evolution system containing a photosensitizer, an electron donor, an electron acceptor, and a suitable catalyst. Recently the complex formations between methylviologen and metalloporphyrins have been reported,[3-5] but the role of the complex formation in photoredox reactions has not been clarified yet. In this paper, we hope to describe the complex formation between $Zn(TPPS_3)$ and methylviologen and to discuss its role in photoredox processes.

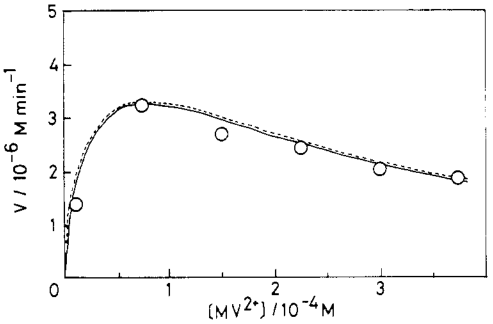

Figure 1. Relation between initial reduction rate of methylviologen and methylviologen concentration ($[Zn(TPPS_3)] = 8.33 \times 10^{-8}$ mol·dm^{-3}; [RSH] = 0.21 mol·dm^{-3}; reaction temperature 30 °C). The dotted line indicates a theoretical result.

As the reduced form of methylviologen (MV^+) has been known to produce hydrogen in the presence of a suitable catalyst, an attempt was also made to produce hydrogen by the use of an electron-transfer method that combines the $Zn(TPPS_3)$ and methylviologen photoirradiation system and hydrogenase, for hydrogenase is known as a specific enzyme for methylviologen.

Experimental Section

Methylviologen was purchased from Tokyo Kasei Kogyo Co., and the other chemicals, obtained from Wako Pure Chemical Co., were of the highest available purity. $Zn(TPPS_3)$ was synthesized by refluxing $TPPS_3$ and zinc acetate (molar ratio 1:10) in methanol for 2 h. Hydrogenase from Desulfovibrio vulgaris (Miyazaki type) was purified according to Yagi's method.[6]

The sample solution, which consisted of photosensitizer, methylviologen, 2-mercaptoethanol (RSH), and hydrogenase (if included), was deaerated by repeated freeze-pump-thaw cycles. A typical experiment was performed as follows under anaerobic conditions. To 5.00×10^{-10} mol of $Zn(TPPS_3)$, 7.56×10^{-7} mol of methylviologen, and 1.26×10^{-3} mol of RSH was added 1 mL of hydrogenase (if included). The volume of the mixture was adjusted to 6.0 mL with 0.02 mol·dm^{-3} of Tris-HCl buffer (pH 7.0). In the photolysis with continuous irradiation, the sample in a Pyrex cell with a magnetic stirrer was irradiated with light from a 200-W tungsten lamp (from a slide projector). The sample solution settled at distance 7 cm from the light source. Light of wavelength less than 390 nm was cut off by a Toshiba L-39 filter.

Results and Discussion

When an aqueous solution containing $Zn(TPPS_3)$, methylviologen, and RSH was irradiated, the growth of the cation radical of methylviologen, which has characteristic absorption bands at 395 and 605 nm, was observed. The formation rate of reduced methylviologen (MV^+) increased with methylviologen concentration and then decreased through a maximum point as shown in Figure 1. This abnormal phenomenon may imply the complexation of $Zn(TPPS_3)$ by methylviologen. When $Zn(TPPS_3)$ was mixed with methylviologen, the characteristic Soret absorption band (418 nm) decreased with the

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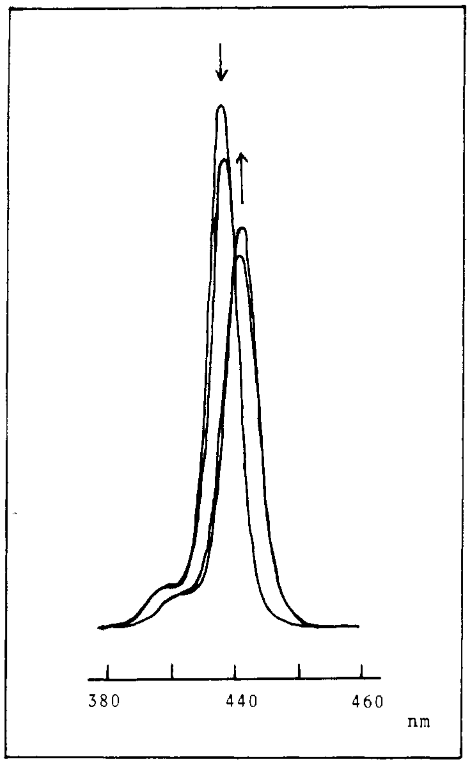

Figure 2. Spectrum change of $Zn(TPPS_3)$ by the addition of methylviologen.

increase of methylviologen concentration and a new spectrum appeared, which has a characteristic absorption band at 425 nm through an isosbestic point at 422 nm (Figure 2). If the complex is formed by the reaction

$$Zn(TPPS_3) + MV^{2+} \rightleftarrows \text{complex}$$

the equilibrium constant, K, is detected as (2.1 ± 0.1) × 10^{-4} $mol^{-1} \cdot dm^3$ by spectrophotometric titration. From comparison of the reaction mechanisms reported on similar systems[7-9] and the above results, the following scheme containing the complex-formation process is proposed:

$$Zn(TPPS_3) + MV^{2+} \xrightleftharpoons{K} \text{complex}$$

$$Zn(TPPS_3) \xrightleftharpoons[k_{-1}]{h\nu,\ k_1} Zn(TPPS_3)^*$$

$$Zn(TPPS_3)^* + MV^{2+} \xrightarrow{k_2} Zn(TPPS_3)^+ + MV^+$$

$$Zn(TPPS_3)^+ + MV^+ \xrightarrow{k_3} Zn(TPPS_3) + MV^{2+}$$

$$Zn(TPPS_3)^+ + RSH \xrightarrow{k_4} Zn(TPPS_3) + {}^1/_2RSSR$$

MV^{2+} and MV^+ are the oxidized and reduced forms of methylviologen, respectively. k_{-1}, k_2, k_3, and k_4 are rate constants, but k_1 is not, for it is a function of light flux. As the fraction of light absorption is small in this experimental condition, i.e. the value of ϵCl is small enough, ΦI_0 can be replaced by $k_3[Zn(TPPS_3)]_0$.

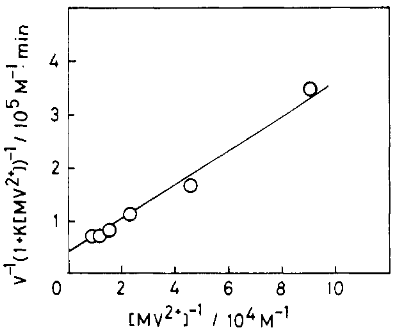

Figure 3. Relation between $V^{-1}(1 + K[MV^{2+}])^{-1}$ and $[MV^{2+}]^{-1}$.

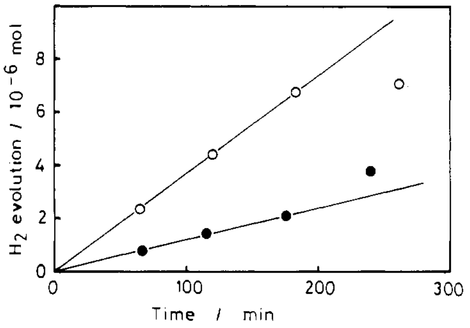

Figure 4. Time dependence of hydrogen evolution in the presence of excess hydrogenase ($[Zn(TPPS_3)] = 1.31 \times 10^{-7}$ $mol \cdot dm^{-3}$; $[RSH] = 0.21$ $mol \cdot dm^{-3}$; [methylviologen] = 3.46×10^{-4} $mol \cdot dm^{-3}$ (○), 7.40×10^{-4} $mol \cdot dm^{-3}$ (●); reaction temperature 30 °C).

If the complex is not effective for viologen photoreduction and only free $Zn(TPPS_3)$ is effective for this reaction as Rougee et al. has reported already for a similar system,[5] the following rate expression is derived by the use of the steady-state approximation for $[Zn(TPPS_3)^*]$ and $[Zn(TPPS_3)^+]$ on the basis of the above reaction mechanism:

$$V = \frac{d[MV^+]}{dt} = \left(\frac{k_1[Zn(TPPS_3)]_0}{1 + K[MV^{2+}]}\right) \times \left(\frac{k_2[MV^{2+}]}{k_{-1} + k_2[MV^{2+}]}\right)\left(\frac{k_4[RSH]}{k_3[MV^+] + k_4[RSH]}\right) \quad (1)$$

At the initial stage of the reaction MV^+ grows linearly with reaction time, for the rate of the back-reaction ($Zn(TPPS_3)^+$ reduction by MV^+) is negligibly small at this stage. Equation 1 is rewritten

$$\frac{1}{V(1 + K[MV^{2+}])} = \left(\frac{1}{k_1[Zn(TPPS_3)]_0}\right)\left(1 + \frac{k_{-1}}{k_2[MV^{2+}]}\right) \quad (2)$$

According to eq 2, $1/V(1 + K[MV^{2+}])$ should be linearly related to $1/[MV^{2+}]$. The good linear relation as shown in Figure 3 indicates that eq 1 is adequate. From the slope and the intercept of the straight line k_1 and a ratio of rate constants such as k_2/k_{-1} were obtained. With these values the relation between V and $[MV^{2+}]$ is obtained from eq 1 as shown by the dotted line in Figure 1. The good fitting of the theoretical results to the experimental values shows that the above mentioned scheme explains the experimental results satisfactorily.

By the addition of hydrogenase to the system, photoinduced hydrogen evolution was carried out. Experiments were performed by using higher initial concentrations of methylviologen in order to minimize the free $Zn(TPPS_3)$ where more than 70% of the porphyrin was complexed and also by using the optimum concentration where the maximum reduction rate of methylviologen was given. In these experiments, excess hyd-

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rogenase was used to make the photoreduction of methylviologen the rate-determining step of the hydrogen evolution reaction. As shown in Figure 4, continuous hydrogen evolution was observed in both cases. The higher hydrogen evolution rate was obtained by using the optimum concentration of methylviologen.

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Registry No. Zn(TPPS$_3$), 78521-08-1; MV^{2+}, 1910-42-5; MV^{+}, 25239-55-8; RSH, 60-24-2; hydrogen, 1333-74-0; water, 7732-18-5; hydrogenase, 9027-05-8.