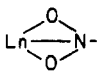
satisfactory correlation of $\delta(\Delta H)$ with $\sum pK_{a(N)}$, the sum of the pK_a values for the nitrogen donor sites of the ligand, for the series of Sm–amino polycarboxylate complexes provided support for such an analysis. A similar treatment has been used for interpretation of the thermodynamic data on 1:1 complexation of lanthanides with 1,4-dinitrilobutane-*N,N,N′,N′*-tetraacetate (TMEDTA).[7]

The plot of $-\delta(\Delta H_N)$ vs. $\sum pK_{a(N)}$ in Figure 3 shows that EDDA, MEDTA, and TMEDTA do not correlate with other complexes. In TMEDTA, the explanation offered[7] was that the 7-membered N–Ln–N chelate ring is much less stable than the 5-membered ring of LnEDTA. Consequently, the Ln–N interaction is weakened. Also, interaction with a nitrogen donor apparently is weakened when a single carboxylate group is associated with that nitrogen donor as there is only one O–Ln–N chelate ring compared to two such rings



in Ln–EDTA, etc. In Sm–MEDTA, only one of the nitrogen donor interactions is so "weakened", whereas in Sm–EDDA, both Sm–N interactions are affected, which is consistent with the data in Figure 3.

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Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto 860, Japan

Successful Photocatalytic Reduction of MV^{2+} with $[Cu(NN)(PPh_3)_2]^+$ (NN = 2,9-Dimethyl-1,10-phenanthroline or 4,4′,6,6′-Tetramethyl-2,2′-bipyridine) upon Near-UV-Light Irradiation and a Novel Solvent Effect on Its Catalytic Activity

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Methylviologen (MV^{2+}) is photocatalytically reduced by Cu(I) complexes $[Cu(NN)(PPh_3)_2]^+$ (NN = 2,9-dimethyl-1,10-phenanthroline or 4,4′,6,6′-tetramethyl-2,2′-bipyridine) in an alcohol–water mixed solvent. The quantum yields for the MV^{2+} reduction decrease in the order NN = 2,9-dimethyl-1,10-phenanthroline > 4,4′,6,6′-tetramethyl-2,2′-bipyridine >> 4,4′-dimethyl-2,2′-bipyridine > 1,10-phenanthroline, whereas the 2,2′-bipyridine and 4,7-diphenyl-1,10-phenanthroline analogues hardly reduce MV^{2+} at all. In this catalytic reaction, alcohol reduces the oxidized $[Cu^{II}(NN)(PPh_3)_2]^{2+}$ so as to complete the catalytic cycle. A reasonable reaction mechanism is deduced, which is supported by a kinetic study; the Cu(I) complex absorbs near-UV light to generate its photoexcited state, followed by the formation of the encounter complex with MV^{2+} and then an electron transfer from the Cu(I) complex to MV^{2+}. An interesting solvent effect is found in the present catalytic system, which is also examined by kinetic treatment; when the water content in the solvent is increased, the lifetime of the photoexcited Cu(I) complex becomes longer, and as a result, the catalytic activity of the Cu(I) complex becomes higher.

Introduction

In the last 10 years, many attempts have been made to find photocatalytic systems capable of reducing H^+ or MV^{2+} (methylviologen),[1] and several catalytic systems have hitherto been reported; for example, $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine),[2] Zn–porphyrin, and Ru–porphyrin complexes[3] catalytically reduce MV^{2+} upon visible-light irradiation, yielding H_2 gas in the presence of Pt–colloid. Also, $[CuCl_3]^{2-}$ can reduce H^+ stoichiometrically upon UV-light irradiation.[4] Nevertheless, there are only a few investigations on photoreduction catalysis of Cu(I) complexes, whereas Cu(I) complexes with bpy, 1,10-phenanthroline (phen), or their derivatives have the metal-to-ligand charge-transfer (MLCT) excited state as the lowest excited state,[5] similar to $[Ru(bpy)_3]^{2+}$. To our knowledge, two examples of photocatalytic reduction by Cu(I) complexes have been reported quite recently: the catalytic reduction of Co(III) complexes by $[Cu(dmp)(PPh_3)_2]^+$, (dmp = 2,9-dimethyl-1,10-phenanthroline)[6] and the catalytic reduction of H^+ (i.e., H_2 gas evolution) by $[Cu(dmp)_2]^+$ and $[Cu(2,9\text{-dpp})_2]^+$ (2,9-dpp = 2,9-diphenyl-1,10-phenanthroline) in the presence of MV^{2+} and its derivative.[7]

In this work, the effective photocatalytic reduction of MV^{2+} has been carried out with $[Cu(NN)(PPh_3)_2]^+$ (NN = bpy, phen, and their derivatives) in an alcohol–water mixed solvent upon

(1) For example, see: Cox, A. *Photochemistry* **1984**, *3*; **1985**, *4*.
(2) For example, see: Kirch, M.; Lehn, J.-M.; Sauvage, J.-P. *Helv. Chim. Acta* **1979**, *62*, 1345. Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298.
(3) Harriman, A.; Porter, G.; Richoux, M. C. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1939. Pileni, M.-P.; Braun, A. M.; Grätzel, M. *Photochem. Photobiol.* **1980**, *31*, 423. Kalyanasundaram, K.; Grätzel, M. *Helv. Chim. Acta* **1980**, *63*, 478. Okura, I.; Takeuchi, M.; Kim-Thuan, N. *Chem. Lett.* **1980**, 765. Okura, I.; Kim-Thuan, N. J. *J. Chem. Soc., Chem. Commun.* **1980**, 84.
(4) Ferraudi, G. *Inorg. Chem.* **1981**, *20*, 1370.
(5) (a) Bruckner, M. T.; Matthews, T. G.; Lytle, F. E.; McMillin, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 5846. (b) Balskie, M. W.; McMillin, D. R. *Inorg. Chem.* **1980**, *19*, 3519. (c) Ahn, B.-T.; McMillin, D. R. *Ibid.* **1978**, *17*, 2253; **1981**, *20*, 1427. (d) Rader, R. A.; McMillin, D. R.; Buckner, M. T.; Matthews, T. G.; Casadonte, D. J.; Lengel, R. K.; Whittaker, S. B.; Darmon, L. M.; Lytle, F. E. *J. Am. Chem. Soc.* **1981**, *103*, 5906. (e) Vante, N. A.; Ern, V.; Chartier, P.; Dietrich-Buchecker, C. O.; McMillin, D. R.; Marnot, P. A.; Sauvage, J. P. *Nouv. J. Chim.* **1983**, *7*, 3. (f) Del Paggio, A. A.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 691. (g) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P.; Kirchhoff, R.; McMillin, D. R. *J. Chem. Soc., Chem. Commun.* **1983**, 513. (h) Kirchhoff, J. R.; Gamache, R. E.; Blaskie, M. W.; Del Paggio, A. A.; Lengel, R. K.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 2380.
(6) Sakaki, S.; Koga, G.; Sato, F.; Ohkubo, K. *J. Chem. Soc., Dalton Trans.* **1985**, 1959.
(7) Edel, A.; Marnot, P. A.; Sauvage, J. P. *Nouv. J. Chim.* **1984**, *8*, 495.

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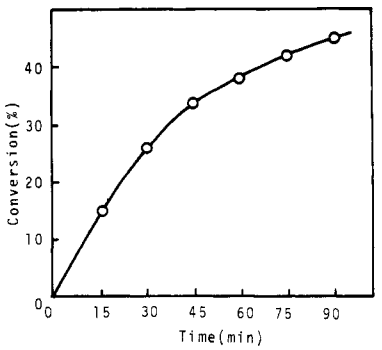


Figure 1. Time-conversion curve (based on the Cu(I) concentration) of MV^{2+} reduction photocatalyzed by $[Cu(dmp)(PPh_3)_2]^+$. Reaction conditions: $[Cu(dmp)(PPh_3)_2^+] = 1.0 \times 10^{-4}$ mol/dm^3; $[MV^{2+}] = 1.0 \times 10^{-3}$ mol/dm^3; $[PPh_3] = 5.0 \times 10^{-4}$ mol/dm^3; 60:40 v/v ethanol–H_2O.

near-UV-light irradiation (360–400 nm), and a novel solvent effect on the Cu(I) catalytic activity has been found; the quantum yield for MV^{2+} reduction, $\phi(MV^{2+})$, significantly depends on the vol % of alcohol. The reaction mechanism and the solvent effect are discussed, on the basis of the kinetic study.

Experiments

$[Cu(NN)(PPh_3)_2](NO_3)$ (NN = bpy, 4,4′-dimethyl-2,2′-bipyridine (dmbp), 4,4′,6,6′-tetramethyl-2,2′-bipyridine (tmbp), phen, dmp, or 4,7-diphenyl-1,10-phenanthroline (4,7-dpp)) was prepared from $[Cu(PPh_3)_2](NO_3)$, according to previous reports,[5d,8] and the purity was successfully ascertained by elemental analysis. MV^{2+} was purchased from Nakarai Chemical Co. (extrapure grade) and was used without further purification.

In typical runs, the Cu(I) complex (5.0×10^{-4} mol/dm^3)[9a] and MV^{2+} ($(0.5–2.0) \times 10^{-3}$ mol/dm^3) were dissolved in an ethanol–water (60:40 vol. ratio) mixed solvent and irradiated at 30 °C in a 1-cm Pyrex cell under N_2 atmosphere by using a 400-W high-pressure mercury-arc lamp (Toshiba H-400P), where PPh_3 (5 times excess relative to Cu(I) complex) was added to the solution in order to suppress the dissociation of PPh_3 from $[Cu(dmp)(PPh_3)_2]^+$.[9b] An incident light (360–400 nm) was isolated by using a combination of cutoff filters (Toshiba UV 35 and UV-D35). The light intensity absorbed by the reaction system was measured as the difference in the light intensity transmitted through the reaction and reference cells by using Reinecke's chemical actinometry.[10] The concentration of the reduction product, MV^+, was determined by spectrophotometrical measurement of MV^+ (λ_{max} = 605 nm).

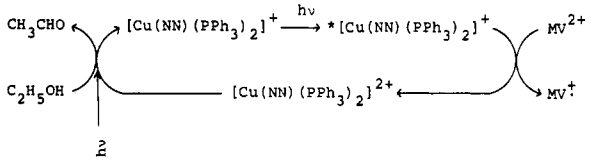
The emission spectra were measured at 30 °C by using a JASCO FP 550A spectrofluorometer, where the samples were deoxygenated by several freeze–pump–thaw cycles. The emission spectra of $[Cu(dmp)(PPh_3)_2]^+$ and its tmbp analogue were observed by exciting them at 395 and 350 nm, respectively, and their emission intensies were measured at 520 and 515 nm (uncorrected values), respectively.

Results and Discussion

A typical time-conversion curve given in Figure 1 indicates a successful reduction of MV^{2+} by a Cu(I) complex such as $[Cu(dmp)(PPh_3)_2]^+$. The quantum yields for the MV^{2+} reduction, $\phi(MV^{2+})$, decrease in the order NN = dmp (2.9×10^{-3}) > tmbp (7.8×10^{-4}) >> dmbp (3×10^{-5}) > phen (1×10^{-5}) >> bpy (~0) ~ 4,7-dpp (~0), where numbers in parentheses denote the $\phi(MV^{2+})$ value (reaction conditions: [Cu(I) complex] = 5.0×10^{-4} mol/dm^3; $[MV^{2+}] = 1.0 \times 10^{-3}$ mol/dm^3; an ethanol–water (60:40 vol ratio) solvent). The MV^{2+} reduction was not observed in the reaction systems with the bpy and 4,7-dpp complexes. In the case of the dmp complex, the turnover numbers of the MV^{2+} reduction are 1.8 and 2.2 for the 7- and 12-h reactions, respectively. This result means that the present reaction includes a catalytic process for the MV^{2+} reduction. In order to complete the catalytic cycle, it is necessary to reduce $[Cu(NN)(PPh_3)_2]^{2+}$ to $[Cu(NN)(PPh_3)_2]^+$. Triphenylphosphine and ethanol were considered as candidates for such reductant. Triphenylphosphine oxide, however, could not be found in the evaporated reaction solution by an infrared spectrum measurement.[11a] Further, addition of (2,4-dinitrophenyl)hydrazine to the reaction solution yields red precipitates of acetaldehyde hydrazone, which suggests that ethanol is the reductant. A similar reduction has been reported, in which $[Cu(dmp)_2]^{2+}$ is photoreduced by ethanol under near-UV-light (390-nm) irradiation.[12] Thus, a coherent picture of the catalytic cycle might emerge, as shown in Scheme I. It seems a merit of the present catalytic system that inexpensive ethanol is consumed as a reductant. Of course, the present Cu(I) catalyst must be investigated in the future regarding such important factors as the thermal stability of $[Cu(NN)(PPh_3)_2]^{2+}$,[11b] the concentration effect of sensitizer, and the back electron transfer from MV^+ to $[Cu(NN)(PPh_3)_2]^{2+}$, to compare the present catalyst with $[Ru(bpy)_3]^{2+}$ and $[Cu(NN)_2]^+$,[3,7,13] in detail.

A reaction mechanism shown in Scheme II, which has been proposed in the photoinduced electron-transfer reaction between Cu(I) complexes and several Co(III) complexes,[14] is considered to be operative in the present photoreduction of MV^{2+}.

Scheme I



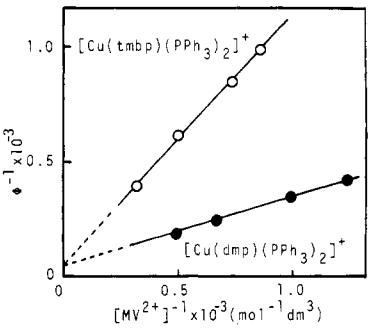


Figure 2. Stern–Volmer relation for the MV^{2+} photocatalytic reduction using $[Cu(dmp)(PPh_3)_2]^+$ and $[Cu(tmbp)(PPh_3)_2]^+$. Reaction conditions: $[Cu(dmp)(PPh_3)_2^+]$ and $[Cu(tmbp)(PPh_3)_2^+] = 0.5 \times 10^{-3}$ mol/dm^3; $[PPh_3] = 2.5 \times 10^{-3}$ mol/dm^3; 60:40 v/v ethanol–H_2O.

(8) Jardine, F. H.; Vohra, A. G.; Young, F. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2941.

(9) (a) A relationship between the concentration of $[Cu(dmp)(PPh_3)_2]^+$ and the MV^{2+} conversion was examined under the following reaction conditions: $[MV^{2+}] = 1.0 \times 10^{-3}$ mol/dm^3, $[PPh_3]$ = 5 times in excess of the Cu(I) complex, 50 vol % ethanol–water solvent, reaction time = 2 h, T = 30 °C. The MV^{2+} conversion linearly increases with increase of the $[Cu(dmp)(PPh_3)_2]^+$ concentration; the MV^{2+} conversion is 1.5% at [Cu(I)] = 2.5×10^{-5} mol/dm^3, 3.0% at [Cu(I)] = 5.0×10^{-5} mol/dm^3, 3.6% at [Cu(I)] = 1.0×10^{-4} mol/dm^3, 4.6% at [Cu(I)] = 1.43×10^{-4} mol/dm^3, and 6.7% at [Cu(I)] = 1.65×10^{-4} mol/dm^3. (b) The $[Cu(NN)(PPh_3)_2]^+$ solution has a large absorption at 360 nm and very small absorption near 440 nm. When excess PPh_3 is added to the solution, an absorption at 360 nm increases, but a small absorption at 440 nm decreases. It has been ascertained here that the small absorption at 440 nm is only barely observed by addition of a 5 times excess of PPh_3 relative to the Cu(I) complex and that further addition of PPh_3, more than 5 times excess, causes little change in the UV–vis spectrum of the $[Cu(dmp)(PPh_3)_2]^+$ solution.

(10) Wagner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.

(11) (a) Two characteristic peaks of $OPPh_3$ were not observed near 1190 and 1110 cm^{-1} by IR measurement of the evaporated reaction solution. When $OPPh_3$ (equimolar to Cu(I)) was added to the reaction solution, two such peaks were detected by IR measurement of the evaporated solution. (b) After the reaction (2h), the absorption spectrum of $[Cu(dmp)(PPh_3)_2]^+$ was almost the same as that before reaction, suggesting that $[Cu(dmp)(PPh_3)_2]^+$ is not unstable under the present reaction conditions (30 °C).

(12) Sundararajan, S.; Wehry, E. L. *J. Phys. Chem.* **1972**, *76*, 1528.

(13) There has been no report that MV^{2+} is photoreduced by $[Ru(bpy)_3]^{2+}$ in ethanol without any reductant such as triethylamine and triethanolamine, to our knowledge. Further, we tried to photochemically reduce MV^{2+} with $[Ru(bpy)_3]^{2+}$ in the ethanol–water solvent, but no MV^{2+} reduction was observed after 5-h irradiation (450 nm).

(14) Ahn, B.-T.; McMillin, D. R. *Inorg. Chem.* **1978**, *17*, 2253. *Ibid.* **1981**, *20*, 1427.

Scheme II

$$[Cu(NN)(PPh_3)_2]^+ \xrightarrow{\eta I_0/V} *[Cu(NN)(PPh_3)_2]^+$$

$$*[Cu(NN)(PPh_3)_2]^+ \xrightarrow{k_d} [Cu(NN)(PPh_3)_2]^+$$

$$*[Cu(NN)(PPh_3)_2]^+ + Sub \xrightarrow{k_r} \{[Cu(NN)(PPh_3)_2]^{2+}\cdots Sub^-\}$$

$$\{[Cu(NN)(PPh_3)_2]^{2+}\cdots Sub^-\} \xrightarrow{k_p} [Cu(NN)(PPh_3)_2]^{2+} + Sub^-$$

$$\{[Cu(NN)(PPh_3)_2]^{2+}\cdots Sub^-\} \xrightarrow{k_b} [Cu(NN)(PPh_3)_2]^+ + Sub$$

$$Sub = MV^{2+} \text{ or Co(III) complex}$$

From the steady-state approximation for the concentration of the excited state $*[Cu(NN)(PPh_3)_2]^+$ and the encounter complex $\{[Cu(NN)(PPh_3)_2]^{2+}\cdots MV^+\}$, the Stern–Volmer relation, eq 1, is obtained, where $[MV^{2+}]$ is the concentration of MV^{2+}, η means

$$\phi(MV^{2+})^{-1} = \eta^{-1}\{(k_p + k_b)/k_p\}\{(k_d/k_r)[MV^{2+}]^{-1} + 1\} \quad (1)$$

the probability to yield the photoreactive state, and k_p, k_b, k_d, and k_r are described in Scheme II. This equation requires a linear relation between $\phi(MV^{2+})^{-1}$ and $[MV^{2+}]^{-1}$. Of course, this relation cannot be meaningful for the whole reaction time but is valid only in the initial stage of the reaction, because the incident light would be consumed to reduce $[Cu(NN)(PPh_3)_2]^{2+}$ after the long reaction time. In the kinetic study, therefore, the reaction was stopped within 10% of conversion. As shown in Figure 2, good linear relations are obtained between $\phi(MV^{2+})^{-1}$ and $[MV^{2+}]^{-1}$, which supports the reaction mechanism proposed in Scheme II. In Figure 2, the tmbp and dmp complexes are compared with each other; both complexes have similar intercepts but different slopes. From eq 1, the intercept and the slope are given by $\eta^{-1}(k_p + k_b)/k_p$ and $\{\eta^{-1}(k_p + k_b)/k_p\}(k_d/k_r)$, respectively. Thus, the $\eta^{-1}(k_p + k_b)/k_p$ term is similar in the tmbp and dmp complexes, but the k_d/k_r term is much different in these two complexes. This result suggests that the higher $\phi(MV^{2+})$ value of the dmp complex would result from the slow k_d process and/or the fast k_r process. The emission intensity of the dmp complex is about 2.4 times as large as that of the tmbp complex (see Figure 3). The intensity of emission spectra is proportional to $\eta k_f/(k_f + k_{nd})$, where k_f and k_{nd} mean the rate constant of the emission and the rate constant of the nonradiative decay, respectively. Because the photoreactive state is the triplet spin state,[5] the η and k_f values mainly depend on the spin–orbit-coupling interaction. This interaction is mostly caused by heavy atoms such as Cu and P atoms. Because both dmp and tmbp complexes include a Cu atom and two P atoms, both complexes have a similar degree of spin–orbit-coupling interaction, and as a result, both the k_f and η values of the dmp complex would be similar to the corresponding k_f and η values of the tmbp complex. Thus, the relative intensity of emission spectra is considered to depend on $(k_f' + k_{nd}')/(k_f + k_{nd})$, i.e. τ/τ'. Through the above discussion, the lifetime of the excited $*[Cu(dmp)(PPh_3)_2]^+$ is estimated to be 2.4 times as long as that of the excited $*[Cu(tmbp)(PPh_3)_2]^+$; i.e., the k_d value of the tmbp complex would be 2.4 times as large as that of the dmp complex. Consequently, the dmp complex has a smaller k_d/k_r value and a higher $\phi(MV^{2+})$ value than the tmbp complex, as shown in Figure 2.

Solvent effects were then investigated in the dmp complex, because an interesting solvent effect has been reported in the emission study of $[Cu(NN)_2]^+$.[5b] As shown in Figure 4, the $\phi(MV^{2+})$ value decreases with decreasing vol % of alcohol from 100% to 80%, and the $\phi(MV^{2+})$ value arrives at a minimum value around 80 vol % of alcohol but then increases with decreasing vol % of alcohol from 80 to 60 vol %. The Stern–Volmer reaction was examined in various solvent systems, as shown in Figure 5. In all of the alcohol–water mixed-solvent systems, good linear relations were obtained and all of them have similar values of the intercepts. Thus, the solvent effect does not result from the $\eta^{-1}(k_p + k_b)/k_p$ term but from the k_d/k_r term. In other words, the composition of the alcohol–water mixed solvent influences the deactivation process, k_d, and/or the formation process of encounter

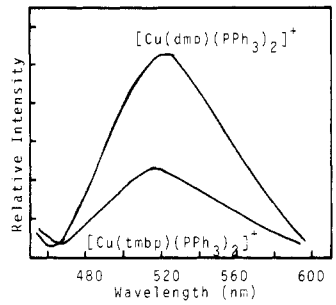


Figure 3. Emission spectra of $[Cu(dmp)(PPh_3)_2]^+$ and $[Cu(tmbp)(PPh_3)_2]^+$. Measurement conditions: $[Cu(dmp)(PPh_3)_2^+]$ and $[Cu(tmbp)(PPh_3)_2^+] = 2.0 \times 10^{-5}$ mol/dm^3; $[PPh_3] = 2.0 \times 10^{-4}$ mol/dm^3; 100% methanol.

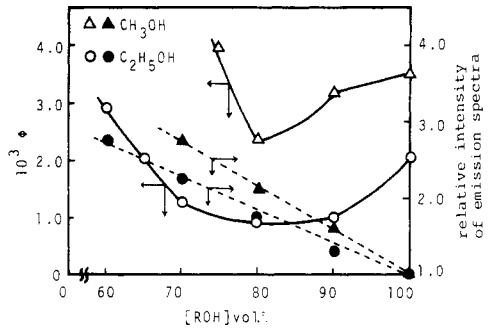


Figure 4. Solvent effect on the MV^{2+} photocatalytic reduction and the emission strength of $[Cu(dmp)(PPh_3)_2]^+$. Reaction conditions: $[Cu(dmp)(PPh_3)_2^+] = 0.5 \times 10^{-3}$ mol/dm^3; $[PPh_3] = 2.5 \times 10^{-3}$ mol/dm^3; $[MV^{2+}] = 1.0 \times 10^{-3}$ mol/dm^3.

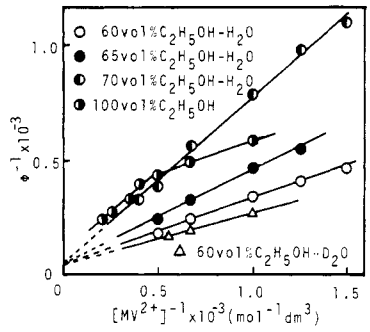


Figure 5. Stern–Volmer relation for the MV^{2+} photoreduction catalyzed by $[Cu(dmp)(PPh_3)_2]^+$ in various solvent systems. Reaction conditions are the same as given in Figure 2.

complex, k_r, in the mixed-solvent system. The intensity of the emission spectra of $[Cu(dmp)(PPh_3)_2]^+$ also increases linearly with decreasing vol % of alcohol, as shown in Figure 4. The relative intensity of emission spectra, I_0/I, is given in eq 2, where I and

$$I_0/I = 1 + k_r\tau[Q] \quad (2)$$

I_0 mean the emission intensity in the presence of quencher and the emission intensity in the absence of quencher, respectively, [Q] is the concentration of quencher, k_r is the second-order rate constant for quenching, and τ is the lifetime in the absence of the quencher. Because the intensities of emission spectra increases with decreasing vol % of alcohol (Figure 4), alcohol would play the role of quencher. Therefore, the decrease of alcohol vol % makes the quenching process slow, leading to a long lifetime of excited $*[Cu(NN)(PPh_3)_2]^+$. Consequently, the $\phi(MV^{2+})$ value increases with decreasing vol % of alcohol from 80 to 60 vol % (Figure 4). In the higher vol % of alcohol (80–100 vol %), the $\phi(MV^{2+})$ value increases with increasing vol % of alcohol, whereas the quenching of the excited $*[Cu(dmp)(PPh_3)_2]^+$ complex becomes easy with increasing vol % of alcohol (vide supra). Thus, the other factor would be important in this case. In this regard, it is worthwhile to examine the Stern–Volmer relation in the pure alcohol solvent. In the pure ethanol solvent, however, the relation

Table I. Quantum Yield and Emission Strength of $[Cu(dmp)(PPh_3)_2]^+$

solvent	$10^3\phi(MV^{2+})^a$	$\phi_{em,rel}{}^b$
60:40 v/v ethanol–H_2O	2.9	1.0
60:40 v/v ethanol–D_2O	3.8	1.2

[a] The quantum yield for the MV^{2+} reduction. [b] The relative value of emission strength (the 60:40 v/v ethanol–H_2O system is taken as the standard).

between $\phi(MV^{2+})^{-1}$ and $[MV^{2+}]^{-1}$ is not linear but curved at $[MV^{2+}]^{-1} = \sim 0.4 \times 10^3$ dm^3/mol, as shown in Figure 5. For a high concentration of MV^{2+}, the intercept of the Stern–Volmer relation is slightly higher than that in the alcohol–water mixed solvent, but for a low concentration of MV^{2+}, the intercept of the Stern–Volmer relation is much higher than that in the alcohol–water mixed solvent. One of the plausible reasons for such nonlinearity would be the aggregation of MV^{2+} in high concentration, because the critical aggregation concentration of MV^{2+} is 2.5×10^{-3} mol/dm^3 in methanol[15] and is expected to be lower in the less polar ethanol. In higher concentration of MV^{2+}, such aggregates would be the reactant, and in the lower concentration of MV^{2+}, molecular MV^{2+} would be the reactant. Since such aggregates would have a nature different from that of molecular MV^{2+}, the nonlinear Stern–Volmer relation was obtained in pure alcohol solvent, as shown in Figure 5. In the range of low MV^{2+} concentration of the pure ethanol solvent system, k_d/k_r is estimated to be 1.2×10^{-3}, which is much lower than the k_d/k_r value (1.9×10^{-2}) in the 70 vol % ethanol–water solvent. Because the k_d process in pure ethanol is considered to be faster than that in the 70 vol % ethanol–water system (vide supra), the smaller k_d/k_r value in the pure ethanol solvent would come from the larger k_r value. In other words, the higher $\phi(MV^{2+})$ value in the pure ethanol solvent would result from the easy formation of the encounter complex. Several reasons are conceivable for the large k_r value in the pure ethanol solvent; the first is the electrolytic dissociation of $MV^{2+}(Cl^-)_2$. In pure ethanol solvent, $MV^{2+}(Cl^-)_2$ and $[Cu(dmp)(PPh_3)_2](NO_3)$ hardly undergo electrolytic dissociation at all, and as a result, a neutral $MV^{2+}(Cl^-)_2$ would be able to approach a neutral $[Cu(dmp)(PPh_3)_2](NO_3)$. Since there is no Coulombic repulsion between them, such an approach is easy and the k_r process becomes fast, leading to a high $\phi(MV^{2+})$ value in pure ethanol solvent. In polar solvent, however, their electrolytic dissociation would occur, and a positive MV^{2+} approaching a positive $[Cu(dmp)(PPh_3)_2]^+$ would seem difficult from the viewpoint of Coulombic interaction. Also, the solvent effect on k_p and k_b processes should be taken into consideration. At low MV^{2+} concentration in pure ethanol solvent, a neutral $MV^{2+}(Cl^-)_2$ is reactant. $MV^{2+}(Cl^-)_2$ would receive an electron less easily than MV^{2+} does, because MV^{2+} has a +2 positive charge but $MV^{2+}(Cl^-)_2$ is neutral. In other words, the k_b process of $MV^{2+}(Cl^-)_2$ is probably faster and k_p is probably slower than the corresponding k_b and k_p processes of MV^{2+}. In reality the system with a low MV^{2+} concentration in pure alcohol solvent has an intercept of the Stern–Volmer relation higher than the system of alcohol–water mixed solvent, which suggests that the former system has the faster k_b process and/or the slower k_p process compared to the latter system. However, the slow k_p and fast k_b processes lead to the low $\phi(MV^{2+})$ value. Thus, the high $\phi(MV^{2+})$ value at low MV^{2+} concentration in pure alcohol solvent cannot be explained by the solvent effect on the k_p and k_b processes. Other factors are also considered: for example, the self-exchange-reaction rate constant of $MV^{2+}(Cl^-)_2$ would differ from that of MV^{2+}. However, further discussion is omitted here, because we have no experimental results regarding the self-exchange reaction.

At high MV^{2+} concentration in the pure alcohol solvent system, the aggregates of $\{MV^{2+}(Cl^-)_2\}_n$ are considered to be the reactant. Such an aggregation would suppress the k_r process because of its lower mobility, leading to a large value of k_d/k_r. The system with the high MV^{2+} concentration in the pure alcohol solvent has a slightly higher intercept for the Stern–Volmer relation than does the alcohol–water mixed-solvent system, suggesting a faster k_b process and/or a slower k_p process. In the former system, the k_b value is expected to be larger and the k_p value is expected to be smaller than the corresponding k_p and k_b values in the latter system, because the neutral aggregates of $\{MV^{2+}(Cl^-)_2\}_n$ are the reactants in the former system but the cationic MV^{2+} is the reactant in the latter system. Further, the k_d value in the pure alcohol solvent is higher than that in the alcohol–water mixed solvent, as described above. Consequently, the $\phi(MV^{2+})$ value becomes small at high MV^{2+} concentration in the pure alcohol solvent. However, further discussion is also omitted here, because no direct evidence has been obtained yet.

In conclusion, when the concentration of MV^{2+} is lower than about 2.0×10^{-3} mol/dm^3, the k_r value of the pure alcohol system is larger than that of the 80 vol % alcohol–water system, and as a result, the $\phi(MV^{2+})$ value increases with decreasing vol % of alcohol. When the concentration of MV^{2+} is higher than about 2.0×10^{-3} mol/dm^3, the $\phi(MV^{2+})$ value decreases with increasing vol % of alcohol (see Figure 5), perhaps due to the slow k_r, fast k_d, and fast k_b processes.

Finally, the D_2O effect on $\phi(MV^{2+})$ is examined. As given in Table I, $\phi(MV^{2+})$ in D_2O–ethanol solution is about 1.3–1.4 times as large as that in H_2O–ethanol solution. The Stern–Volmer relation in the D_2O–ethanol solvent is compared with that in the H_2O–ethanol solvent in Figure 5. The intercept is only slightly influenced by the deuteration of H_2O, but the slope in D_2O–ethanol is less than that in H_2O–ethanol. From the slope, $(k_d/k_r)_{H_2O}$ is estimated to be 1.3 times as large as $(k_d/k_r)_{D_2O}$. Because the k_r value does not depend so much on the deuteration of H_2O, $(k_d)_{D_2O}$ is considered to be less than $(k_d)_{H_2O}$. This result means the deactivation process in H_2O–ethanol is 1.3 times as fast as that in D_2O–ethanol. Also, the emission quantum yield, ϕ_{em}, in D_2O–ethanol is 1.2 times as large as that in H_2O–ethanol, as shown in Table I. ϕ_{em} is given as k_f/k_d, where $k_d = k_f + k_{nd}$, and k_f is considered not to depend on the deuteration of H_2O but to depend on the spin–orbit-coupling interaction. Thus, a larger ϕ_{em} value indicates a smaller k_{nd} value in the D_2O–ethanol system. This difference in k_{nd} between the H_2O and D_2O systems would result from the difference between the O–H and O–D vibration energies. Because D_2O has an O–D stretching vibration with an energy lower than that of the O–H stretching vibration, the energy transfer from the excited Cu(I) complex to D_2O is less easy than that to H_2O. Consequently, the deactivation process in the D_2O system becomes slow, leading to a $\phi(MV^{2+})$ value larger than that in the H_2O system.

Conclusion

A photocatalyst using a Cu(I) complex is newly presented here, and it can efficiently reduce MV^{2+}. Though the quantum yield for MV^{2+} reduction is less than that of $[Ru(bpy)_3]^{2+}$, the present catalytic system consumes inexpensive alcohol as the reductant. Thus, it is desired that the present catalytic system will be improved in the near future.

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Registry No. $[Cu(dmp)(PPh_3)_2]^+$, 78809-58-2; $[Cu(tmbp)(PPh_3)_2]^+$, 84130-47-2; $[Cu(dmbp)(PPh_3)_2]^+$, 47886-26-0; $[Cu(phen)(PPh_3)_2]^+$, 47886-23-7; $[Cu(bpy)(PPh_3)_2]^+$, 47879-64-1; $[Cu(4,7\text{-dpp})(PPh_3)_2]^+$, 102436-39-5; MV^{2+}, 4685-14-7; MV^+, 25239-55-8; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; H_2O, 7732-18-5; D_2O, 7789-20-0.

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