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Photoinduced electron transfer reaction between $[Cu(dmp)P_2]^{+ or -}$ ($P=PPh_3$ or $PPh_2(m\text{-}C_6H_4SO_3^-)$) and viologen derivatives

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Abstract

The copper(I) complex, $[Cu(dmp)P_2]^{+ or -}$ (dmp = 2,9-dimethyl-1,10-phenanthroline, P = triphenylphosphine PPh_3 or diphenylphosphinobenzene-*m*-sulfonate $PPh_2(m\text{-}C_6H_4SO_3^-)$), catalytically photoreduces viologen derivatives, dicationic methylviologen MV^{2+} and neutral propylviologen disulfonate PVS^0. The quantum yield Φ ($V^{\cdot}$) for the viologen photoreduction is discussed on the basis of the lifetime of the photosensitiser, formation of the encounter complex, dissociation of the encounter complex to products, and back electron transfer in the encounter complex. When $[Cu(dmp)\{PPh_2(m\text{-}C_6H_4SO_3)\}_2]^-$ is used for the photoreduction of MV^{2+}, the highest quantum yield ($\Phi(V^{\cdot})=0.03$) is obtained. Kinetic analysis and measurements of the excited state lifetime reveal that this best $\Phi(V^{\cdot})$ value arises from the rapid formation of the encounter complex, owing to the attractive electrostatic interaction between anionic $[Cu(dmp)\{PPh_2(m\text{-}C_6H_4SO_3)\}_2]^-$ and cationic MV^{2+}.

Keywords: Photoreduction; Photoinduced electron transfer; Copper complexes; Viologen derivatives

1. Introduction

Photoinduced electron transfer reactions of transition metal complexes have been extensively studied over the last two decades, in expectation of their application to solar energy conversion. For example, several catalytic systems using $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) [1], Zn–porphyrin [2] and Ru–porphyrin complexes [3] as a photocatalyst have hitherto been reported to yield H_2 gas under photoirradiation in the presence of Pt-colloid. In particular, $[Ru(bpy)_3]^{2+}$ has been widely investigated in the photoinduced electron transfer reaction [4], because of its excellent photochemical properties: (i) a metal to ligand charge transfer (MLCT) absorption band is observed in the visible region ($\lambda_{max}=451$ nm) with an extremely large molar extinction coefficient, (ii) the lowest energy excited state is the triplet MLCT state and it exhibits sufficient negative redox potential to reduce H^+ in water ($E^{III/II*}=-0.81$ V versus SCE) [5], and (iii) the triplet MLCT excited state has a long enough life to perform photoreactions ($\tau=790$ ns in H_2O at 25 °C) [6]. Copper(I) complexes possessing conjugated ligands such as dmp (2,9-dimethyl-1,10-phenanthroline) and dpp (2,9-diphenyl-1,10-phenanthroline) have similar properties to those of $[Ru(bpy)_3]^{2+}$; for instance, they exhibit a MLCT absorption band in the near-UV to visible region, and the triplet MLCT excited state is the lowest energy excited state [7]. Thus, these Cu(I) complexes are expected to be useful as photosensitisers, like $[Ru(bpy)_3]^{2+}$. Actually, photoreduction of several cobalt(III) complexes by $[Cu(dmp)_2]^+$ and $[Cu(dmp)(PR_3)_2]^+$ has been carried out by McMillin and co-workers [8] and by us [9]. However, application of the Cu(I) complex to the photoreduction of methylviologen (MV^{2+}) has so far been limited [10,11].

In our previous work [11], we succeeded in the photoreduction of methylviologen (MV^{2+}) using $[Cu(dmp)(PPh_3)_2]^+$ (PPh_3 = triphenylphosphine) as a photocatalyst. Unfortunately, the quantum yield for the photoreduction of MV^{2+} ($\Phi(MV^{\cdot +})$) was rather small. In this work, photoreduction of dicationic methylviologen (MV^{2+}) and neutral propylviologen disulfonate (PVS^0) is carried out by using cationic $[Cu(dmp)(PPh_3)_2]^+$ and anionic $[Cu(dmp)\{PPh_2(m\text{-}C_6H_4SO_3)\}_2]^-$. There are two motivations in this work. The first is to improve the quantum yield for viologen reduction $\Phi(V^{\cdot})$ by using anionic and cationic Cu(I)

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complexes for the photoreduction of cationic and neutral viologen derivatives, respectively, and the second is to clarify the charge effects of the photosensitiser and viologen derivative on the photoinduced electron transfer reactions.

2. Experimental

2.1. Materials

Commercially available methylviologen (MV^{2+}: 1,1′-dimethyl-4,4′-bipyridinium dichloride; Nakarai tesque, Inc., guaranteed grade) and 2,9-dimethyl-1,10-phenanthroline (dmp; Nakarai tesque, Inc., guaranteed grade) were used without further purification. All the solvents were purified by the correct methods before use.

2.2. Syntheses

Propylviologen disulfonate (PVS^0) was synthesised from 4,4′-bipyridine and 1,3-propane sultone, according to the literature [12], and washed with acetone. *Anal.* Calc. for $C_{16}H_{20}N_2O_6S_2$: C, 46.91; H, 5.17; N, 6.84. Found: C, 46.78; H, 5.08; N, 6.77%. Sodium diphenylphosphinobenzene-*m*-sulfonate $PPh_2(m\text{-}C_6H_4SO_3^-Na^+)$ was prepared from triphenylphosphine and fuming sulfuric acid, according to the previous report [13]. *Anal.* Calc. for $C_{18}H_{18}SO_5PNa$: C, 53.98; H, 4.53. Found: C, 54.17; H, 3.89%.

$[Cu(dmp)P_2]ClO_4$ (P = PPh_3 or $PPh_2(m\text{-}C_6H_4SO_3^-Na^+)$) was prepared from tetrakis(acetonitrile)-copper(I) perchlorate $[Cu(CH_3CN)_4]ClO_4$ [14] and two molar equivalents of PPh_3 or $PPh_2(m\text{-}C_6H_4SO_3^-Na^+)$, and was washed with ethyl ether, according to previous reports [11,15]. The purity was successfully ascertained by elemental analysis. *Anal.* Calc. for $[Cu(dmp)(PPh_3)_2]ClO_4$, $C_{50}H_{42}N_2O_4P_2ClCu$: C, 67.02; H, 4.73; N, 3.23. Found: C, 66.7; H, 4.80; N, 3.01%. Calc. for $[Cu(dmp)\{PPh_2(m\text{-}C_6H_4SO_3Na)\}_2]ClO_4 \cdot 4H_2O$, $C_{62}H_{56}N_2O_{16}P_2S_2Na_2ClCu$: C, 50.89; H, 4.17; N, 2.38. Found: C, 50.72; H, 3.71; N, 1.98%.

2.3. Photoreaction

In a typical run, a 60% vol./vol. $EtOH/H_2O$ solution of the copper(I) complex (0.20 mmol dm^{-3}), viologen derivative (1.0–2.5 mmol dm^{-3}) and phosphine (2.0–12 mmol dm^{-3}) [2] was placed in a flask equipped with a square quartz cuvette (10 mm i.d.). After degassing the solution by five successive cycles of freeze–pump–thaw, the reaction solution was transferred to the quartz cuvette. It was then irradiated by using a 400 W high-pressure mercury-arc lamp (Toshiba H-400P), where an incident light ($360 < \lambda < 400$ nm) was isolated with a combination of cutoff filters (Toshiba UV-35 and UV-D35 glass filters).

The reaction was monitored by determining spectroscopically the concentration of reduction product; methylviologen cation radical ($MV^{\cdot+}$: λ_{max} (ϵ) = 605 nm (1.71×10^4 mol^{-1} dm^3 cm^{-1})) and propylviologen disulfonate anion radical ($PVS^{\cdot-}$: λ_{max} (ϵ) = 602 nm (1.67×10^4 mol^{-1} dm^3 cm^{-1})). The light intensity absorbed by the reaction solution was measured with a Reineckate chemical actinometer, $K[Cr(NH_3)_2(NCS)_4]$ [16], as the difference in the light intensity transmitted through the reaction and reference cells. The quantum yield $\Phi(V^{\cdot})$ was defined as follows;

$$\Phi(MV^{\cdot+} \text{ or } PVS^{\cdot-}) = \frac{\text{amount of produced } MV^{\cdot+} \text{ or } PVS^{\cdot-}}{\text{amount of quanta absorbed by the copper complex}}$$

2.4. Emission spectra and lifetime of the excited state

The emission spectra of $[Cu(dmp)(PPh_3)_2]^+$ and $[Cu(dmp)\{PPh_2(m\text{-}C_6H_4SO_3)\}_2]^-$ were recorded at 30 °C with an Hitachi fluorescence spectrometer F3010, by irradiating them at 364 and 363 nm, respectively. Their emission intensities were measured at 520 and 518 nm (uncorrected values), respectively. The excited state lifetimes of $[Cu(dmp)(PPh_3)_2]^+$ and $[Cu(dmp)\{PPh_2(m\text{-}C_6H_4SO_3)\}_2]^-$ were recorded with an Horiba NAES-550 time-resolved fluorometer, in which the incident light was selected by a band-path filter (Toshiba U-360) and the change of emission intensity was measured at λ_{max} of the emission spectra. In the above measurements, the amount of sample solution was five times in excess of phosphine and was deaerated through five cycles of freeze–pump–thaw.

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[2] Phosphine (five times excess relative to Cu(I)) was added to the reaction solution in order to suppress the dissociation of phosphine from the Cu(I) complex. If excess PPh_3 is not added, the solution of $[Cu(dmp)(PPh_3)_2]^+$ exhibits a small absorption around 440 nm besides a large absorption at 360 nm. This small absorption appears when PPh_3 dissociates from $[Cu(dmp)(PPh_3)_2]^+$ [7d]. When excess PPh_3 is added to the solution, the absorption at 360 nm increases, but the small absorption at 440 nm decreases. It has been ascertained that the small absorption at 440 nm disappears upon addition of a five times excess of PPh_3 relative to the Cu(I) complex and that further addition of PPh_3 causes little change in the UV–Vis spectrum of the $[Cu(dmp)(PPh_3)_2]^+$ solution.

3. Results and discussion

3.1. Photochemical properties of newly synthesized $[Cu(dmp)\{PPh_2(m\text{-}C_6H_4SO_3)\}_2]^-$ *(2)*

$[Cu(dmp)(PPh_3)_2]^+$ (**1**) and $[Cu(dmp)\{PPh_2(m\text{-}C_6H_4SO_3)\}_2]^-$ (**2**) exhibit similar absorption and emission spectra, as follows. An MLCT absorption band of **2** is observed at 363 nm ($\epsilon = 2800$ mol^{-1} dm^3 cm^{-1}) and its emission spectrum is at 518 nm in 60% vol./vol. EtOH/H_2O (Table 1). Their absorption and emission maxima are slightly shifted to shorter wavelengths compared with those of **1** (absorption $\lambda_{max} = 364$ nm ($\epsilon = 2600$ mol^{-1} dm^3 cm^{-1}); emission $\lambda_{max} = 520$ nm), suggesting that introduction of the anionic SO_3^- group into the phenyl group of triphenylphosphine has little influence on the energy difference between the Cu d orbital and the dmp π^* orbital. The excited state oxidation potentials of the Cu(I) complexes ($E^{II/I*}$) were estimated from the relation between the reduction potential of the quencher and the oxidative quenching rate constant (Fig. 1), according to the method of Meyer and coworkers [5], where various nitrobenzene and *p*-quinone derivatives were used as quenchers[3]. The estimated excited state oxidation potential of **2** (-0.7 V versus SCE) is not much different from that of **1** (-0.8 V versus SCE). This is not surprising because the $E^{II/I*}$ value is mainly determined by the excited electron existing on the π^* orbital of dmp. The above consideration is consistent with the spectroscopic result that introduction of SO_3^- to PPh_3 has little effect on the absorption and emission spectra.

The excited state lifetime (τ) is almost the same in **1** and *2*; τ of **2** (650 ns in 60% vol./vol. EtOH/H_2O at 30 °C) is only slightly shorter than that of **1** (700 ns). The lifetime of the excited $[Cu(dmp)(PR_3)_2]^+$ has been considered to depend on the donating ability of phosphine [7m] and the solvent coordination to Cu(I) in the triplet MLCT excited state [7b,f,g,q,s,v]. Thus, the similar lifetimes of excited 1 and **2** suggest that introduction of SO_3^- to PPh_3 has little influence on the donating ability of PPh_3 and solvent coordination to Cu(I) in the excited state.

From the above results, we might expect that the charge effects of the photosensitiser on the photoinduced electron transfer reaction can be investigated independently of factors such as the lifetime and redox potential of the excited state.

3.2. Photoreduction of viologens

Reduction of MV^{2+} and PVS^0 by the Cu(I) complex **1** or **2** occurs smoothly under irradiation of near-UV light (360–400 nm), affording $MV^{\cdot+}$ and $PVS^{\cdot-}$ which are spectroscopically detected by observing their absorption bands at 605 and 602 nm, respectively. The time-courses of MV^{2+} reduction by **1** and **2** are given in Fig. 2, as an example. Apparently, the MV^{2+} reduction by **2** proceeds much more rapidly than that by **1**, which will be discussed in detail below. It has been ascertained that tertiary phosphine added in the solution does not participate in these photoreduction reactions, even under photoirradiation. Also, this photoreduction cannot occur without **1** and **2**.

As a result of the photoreduction of MV^{2+} and PVS^0, the Cu(I) complex is oxidised to the Cu(II) complex. In our previous work [11a], addition of 2,4-dinitrophenylhydrazine to the reaction solution after photoreaction yielded a red precipitate of 2,4-diphenylhydrazone, which suggests that acetaldehyde is formed from ethanol in the photoreaction. Furthermore, the similar complex, $[Cu^{II}(dmp)_2]^{2+}$, was reported to be photoreduced by ethanol under irradiation of near-UV light around 390 nm [17]. Considering these results, the resultant Cu(II) complex would be photoreduced by ethanol to the original Cu(I) complex, and the catalytic cycle of this photoreduction would be completed, as shown in Scheme 1.

Now, we will compare the photocatalytic activities of **1** and **2** and photoreactivities of MV^{2+} and PVS^0. As shown in Table 2, the quantum yield for the reduction of PVS^0 is much higher than that of MV^{2+} when **1** is used as a photosensitiser. Also, it is noted that photosensitiser **2** gives a much higher quantum yield than **1** for both MV^{2+} and PVS^0. The best value of the quantum yield ($\Phi(MV^{\cdot+}) \sim 0.03$) is obtained in the

Table 1
Photochemical and redox properties of $[Cu(dmp)(PPh_3)_2]^+$ (**1**) and $[Cu(dmp)\{PPh_2(m\text{-}C_6H_4SO_3)\}_2]^-$ (**2**)

Cu(I) complex	Absorption		Emission		τ^a (μs)	$E^{2+/+*}$ (V vs. SCE)
	λ_{max} (nm)	ϵ (mol^{-1} dm^3 cm^{-1})	λ_{max} (nm)	I_{rel}^b		
1	364	2600	520	1	0.70	-0.8
2	363	2800	518	0.7	0.65	-0.7

^{a}Lifetime measured at 298 K.
^{b}Relative intensity of emission spectra.

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[3] 2,6-Dichloro-*p*-benzoquinone, *p*-dinitrobenzene, *o*-dinitrobenzene, *m*-dinitrobenzene, methyl *p*-nitrobenzoate and methyl *m*-nitrobenzoate were used here.

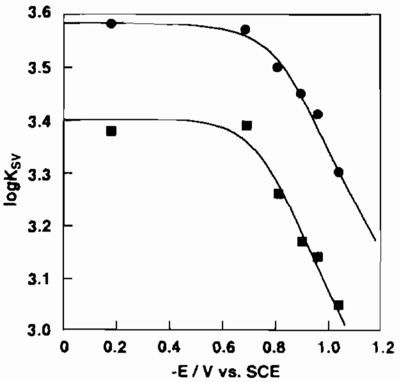


Fig. 1. Quenching rate constant (k_{sv}) of **1** (●) and **2** (■) vs. redox potential of quenchers.

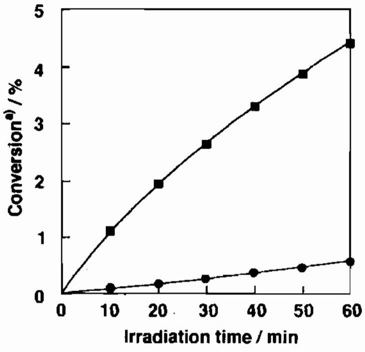
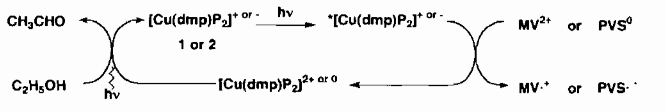


Fig. 2. Conversion of MV^{2+} photoreduction by **1** (●) and **2** (■). ^{a}Based on the Cu(I) complex.



Scheme 1.

photoreduction of MV^{2+} by **2**. The reason for this will be discussed below.

3.3. Reaction mechanism of the present photoreaction

The photoinduced electron transfer reaction is considered in general to proceed through either the dynamic quenching mechanism or the static quenching mechanism [7a,n,8b,c,9].

The dynamic quenching mechanism proceeds through the following elementary processes:

$$\mathrm{Cu(I)} \xrightarrow{\eta h\nu} {}^{*}\mathrm{Cu(I)} \qquad (1)$$

$$ {}^{*}\mathrm{Cu(I)} \xrightarrow{k_d} \mathrm{Cu(I)} \qquad (2)$$

$$ {}^{*}\mathrm{Cu(I)} + \mathrm{V}^{n+} \xrightarrow{k_r} [\mathrm{Cu(II)}\cdots\mathrm{V}^{\cdot(n-1)+}] \qquad (3)$$

$$[\mathrm{Cu(II)}\cdots\mathrm{V}^{\cdot(n-1)+}] \xrightarrow{k_p} \mathrm{Cu(II)} + \mathrm{V}^{\cdot(n-1)+} \qquad (4)$$

$$[\mathrm{Cu(II)}\cdots\mathrm{V}^{\cdot(n-1)+}] \xrightarrow{k_b} \mathrm{Cu(I)} + \mathrm{V}^{n+} \qquad (5)$$

First, the Cu(I) complex yields the triplet MLCT excited state by irradiating the MLCT absorption band (Eq. (1)), where η represents the possibility that the triplet MLCT excited state is yielded by photoirradiation. Some part of the excited Cu(I) complex is deactivated by radiation of either luminescence or heat (Eq. (2)). The remaining part of the excited Cu(I) complex collides (or contacts) with viologen to form an encounter complex in which one electron transfers from Cu(I) to viologen (Eq. (3)). This encounter complex then yields the Cu(II) complex and reduced viologen through the charge-separation process (Eq. (4)), or returns to the original Cu(I) complex and viologen through back electron transfer reaction (Eq. (5)). In this mechanism, a Stern–Volmer relationship (Eq. (6)) is obtained between the reciprocals of $\Phi(\mathrm{V}^{\cdot})$ and viologen concentration [V], by applying the approximation of steady-state concentration to the photoexcited Cu(I) complex and the encounter complex, $[\mathrm{Cu(II)}\cdots\mathrm{V}^{\cdot(n-1)+}]$.

$$\Phi(\mathrm{V}^{\cdot})^{-1} = \eta^{-1}\{(k_p + k_b)/k_p\}\{(k_d/k_r)[\mathrm{V}]^{-1} + 1\} \qquad (6)$$

In the static quenching mechanism, a photosensitiser forms an adduct with a substrate in their ground states and then the adduct absorbs the incident light to yield the excited state, as shown below.

$$\mathrm{Cu(I)} + \mathrm{V}^{n+} \overset{K}{\rightleftharpoons} [\mathrm{Cu(I)}\cdots\mathrm{V}^{n+}] \qquad (7)$$

$$[\mathrm{Cu(I)}\cdots\mathrm{V}^{n+}] \xrightarrow{\eta h\nu} [{}^{*}\mathrm{Cu(I)}\cdots\mathrm{V}^{n+}] \qquad (8)$$

$$[{}^{*}\mathrm{Cu(I)}\cdots\mathrm{V}^{n+}] \xrightarrow{k_d'} [\mathrm{Cu(I)}\cdots\mathrm{V}^{n+}] \qquad (9)$$

$$[{}^{*}\mathrm{Cu(I)}\cdots\mathrm{V}^{n+}] \xrightarrow{k_r'} [\mathrm{Cu(II)}\cdots\mathrm{V}^{\cdot(n-1)+}] \qquad (10)$$

$$[\mathrm{Cu(II)}\cdots\mathrm{V}^{\cdot(n-1)+}] \xrightarrow{k_b'} \mathrm{Cu(I)} + \mathrm{V}^{n+} \qquad (11)$$

$$[\mathrm{Cu(II)}\cdots\mathrm{V}^{\cdot(n-1)+}] \xrightarrow{k_p'} \mathrm{Cu(II)} + \mathrm{V}^{\cdot(n-1)+} \qquad (12)$$

Table 2

The quantum yield and the Stern–Volmer parameters for the MV^{2+} or PVS^0 photoreduction by $[Cu(dmp)(PPh_3)_2]^+$ (**1**) or $[Cu(dmp)\{PPh_2(m\text{-}C_6H_4SO_3)\}_2]^-$ (**2**) in 60% vol./vol. EtOH/H₂O

Cu(I) complex	Sub.	$10^2\ \Phi$	$\frac{10^3 k_d}{k_r}$	$\frac{\eta^{-1}(k_p+k_b)}{k_p}$	$\frac{10^8 k_r}{(s^{-1})}$
1	MV^{2+}	0.29	7.1	22	2.01
	PVS^0	0.63	2.11	47.3	6.77
2	MV^{2+}	2.67	1.10	17.0	14.0
	PVS^0	1.44	4.20	12.2	3.66

Also in this mechanism, a similar relation (Eq. (13)) is obtained between $\Phi(\mathrm{V}^{\cdot})^{-1}$ and $[\mathrm{V}]^{-1}$, by applying an approximation of the steady-state concentration to the adducts, $[{}^{*}\mathrm{Cu(I)}\cdots\mathrm{V}^{n+}]$ and $[\mathrm{Cu(II)}\cdots\mathrm{V}^{\cdot(n-1)+}]$.

$$\Phi(\mathrm{V}^{\cdot})^{-1}=\eta^{-1}\{(k_{\mathrm{p}}'+k_{\mathrm{b}}')/k_{\mathrm{p}}\} \times\{((k_{\mathrm{r}}'+k_{\mathrm{d}}')/k_{\mathrm{r}}')[\mathrm{V}]^{-1}+1\} \qquad (13)$$

Because $\Phi(\mathrm{V}^{\cdot})^{-1}$ is proportional to $[\mathrm{V}]^{-1}$ in both Eqs. (6) and (13), the reaction mechanism cannot be determined by kinetic analysis of the quantum yield $\Phi(\mathrm{V}^{\cdot})$. Although no direct evidence against the static quenching mechanism has been obtained at this moment, it is unlikely that a cationic Cu(I) complex forms an adduct with cationic MV^{2+} in the ground state. Furthermore, a highly polar solvent was used in this work[4]. Although the anionic Cu(I) complex **2** seems likely to form an ion-pair adduct with cationic MV^{2+}, no spectral change is observed on the Cu(I) complex upon mixing with MV^{2+}. From these results, it is reasonable to suggest that an ion-pair adduct does not seem to be formed in the ground state even between anionic **2** and cationic MV^{2+}, and that the present photoreduction proceeds through the dynamic quenching mechanism.

As expected in Eq. (6), a linear relationship between $\Phi(\mathrm{V}^{\cdot})^{-1}$ and $[\mathrm{V}]^{-1}$ is observed in all the reactions examined in this work, as clearly shown in Fig. 3. The slope and intercept of these relationships are related to the $k_{\mathrm{d}}/k_{\mathrm{r}}$ and $\eta^{-1}(k_{\mathrm{p}}+k_{\mathrm{b}})/k_{\mathrm{p}}$ values. The k_{d} value is the reciprocal of the lifetime (τ) which is measured independently (vide supra). Thus, the k_{r} value can be estimated, as listed in Table 2.

3.4. Determinating factors of the quantum yield

As shown by Eq. (6), the quantum yield of the viologen photoreduction is determined by the k_{r}, k_{d}, k_{p} and k_{b} values. The lifetime of the excited state (k_{d}^{-1}) is almost the same in **1** and **2**, as discussed above. Thus, we do not need to take into consideration the lifetime of the excited photosensitiser, and hereafter draw attention to k_{r}, k_{p} and k_{b} values.

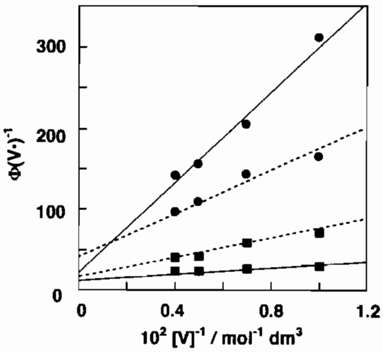


Fig. 3. Stern–Volmer relation in the photoreduction of MV^{2+} (——) and PVS^0 (– – –) by **1** (●) and **2** (■).

First, let us compare the photosensitisers **1** and **2** in the reduction of cationic MV^{2+}. As shown in Table 2, **2** yields a significantly higher $\Phi(\mathrm{MV}^{\cdot+})$ value than **1**. Apparently, the k_{r} value of **2** is much higher than that of **1**, whereas the $\eta^{-1}(k_{\mathrm{p}}+k_{\mathrm{b}})/k_{\mathrm{p}}$ value is similar in **1** and **2**. Thus, the higher $\Phi(\mathrm{MV}^{\cdot+})$ value of the MV^{2+} reduction by **2** arises from a much higher k_{r} value than that in the MV^{2+} reduction by **1**. In the photoreduction of PVS^0, $\Phi(\mathrm{PVS}^{\cdot-})$ by **2** is almost twice that by **1**. This difference in $\Phi(\mathrm{PVS}^{\cdot-})$ is much smaller than the difference in $\Phi(\mathrm{MV}^{\cdot+})$ between **1** and **2**, which is easily explained by considering the k_{r}, k_{p} and k_{b} values. The k_{r} value of **1** is about twice that of **2**, whereas the $\eta^{-1}(k_{\mathrm{p}}+k_{\mathrm{b}})/k_{\mathrm{p}}$ value of **1** is about four times greater than that of **2**. These two terms produce the reverse effects on the $\Phi(\mathrm{PVS}^{\cdot-})$ value (remember Eq. (6)). This would be the reason for the difference in $\Phi(\mathrm{PVS}^{\cdot-})$ between **1** and **2** being much smaller than the difference in $\Phi(\mathrm{MV}^{\cdot+})$ between **1** and **2**.

As expected, the $\Phi(\mathrm{V}^{\cdot})$ value in the present photoreaction is successfully discussed above, based on k_{r}, k_{p} and k_{b} values. The k_{r}, k_{p} and k_{d} values are, in general, considered to be influenced by the redox potentials of the photosensitisers **1** and **2**, and the viologen derivatives MV^{2+} and PVS^0. The redox potentials of MV^{2+} and PVS^0 are almost the same; $E=-0.57$ V (versus SCE) for MV^{2+} and -0.56 V (versus SCE) for PVS^0. Also, the redox potentials of **1** and **2** in the excited state are almost the same (vide supra). Although the redox potentials of **1** and **2** in the ground state could not be measured by cyclic voltammetry [5], their redox potentials would not differ very much, because **1** and **2** exhibit almost the same redox potentials at the excited state and almost the same absorption and emission maxima. Thus, the relative values of k_{r}, k_{p} and k_{b} are considered not to depend on the redox potentials of the photosensitiser and viologens but to depend on other factors such as the electrostatic interaction between the photosensitiser and viologen.

3.5. Charge effects of photosensitiser and viologen on k_r, k_p and k_b processes

Here we will discuss how the charges of the photosensitiser and viologen influence the k_{r}, k_{p} and k_{b} values. As schematically shown in Scheme 2, the k_{r} step is expected to occur most rapidly between **2** and MV^{2+} because the electrostatic interaction is attractive between anionic **2** and cationic MV^{2+}. Actually, the

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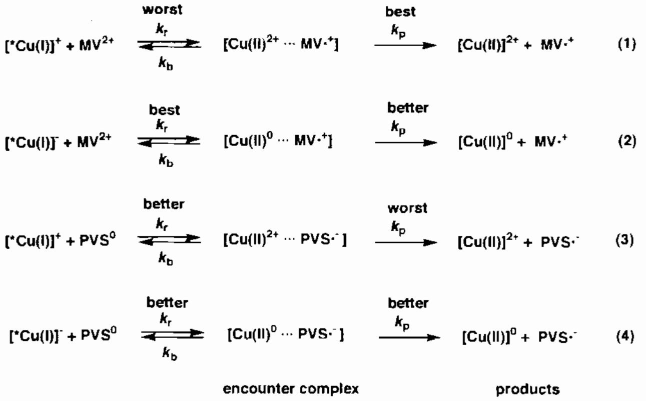
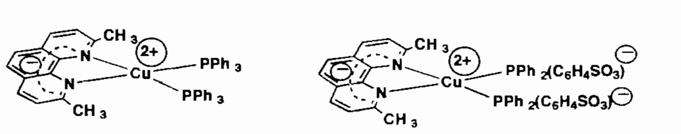
[4] The static quenching mechanism was adopted in the photoreaction that was carried out in a low polar solvent such as dichloromethane [7n].

[5] The reduction wave could not be obtained, which means that oxidation and reduction do not occur reversibly.



Scheme 2.



1 in the MLCT excited state **2** in the MLCT excited state

Scheme 3.

largest k_r value is observed for the reduction of MV^{2+} by **2** (see Table 2). The second highest k_r value is expected in the photoreduction of PVS^0 by **1** and **2**, because electrostatic attraction disappears but electrostatic repulsion does not appear in these reactions. In fact, the k_r values in these photoreduction reactions are smaller than in the MV^{2+} photoreduction by **2** (Table 2). The smallest k_r value is found in the MV^{2+} reduction by **1** (Table 2). This is not surprising because electrostatic repulsion exists between cationic **1** and cationic MV^{2+}.

A similar explanation based on the electrostatic interaction is possible for the k_p and k_b processes with only one exception described below. As shown in Scheme 2, the smallest k_p and the largest k_b values are expected for the reduction of PVS^0 by **1**, because anionic $PVS^{\cdot -}$ and cationic $[Cu^{II}(dmp)(PPh_3)_2]^{2+}$ interact in the encounter complex. This situation makes the escape of $PVS^{\cdot -}$ from the encounter complex difficult, which suppresses the k_p process but enhances the k_b process. Consequently, the $\eta^{-1}(k_p+k_b)/k_p$ value is the largest, as clearly shown in Table 2. In the photoreduction of PVS^0 and MV^{2+} by **2**, the encounter complex is composed of neutral $[Cu^{II}(dmp)\{PPh_2(m\text{-}C_6H_4SO_3)\}_2]^0$ and either $PVS^{\cdot -}$ or $MV^{\cdot +}$. This situation is much better than that observed in the encounter complex including $[Cu^{II}(dmp)(PPh_3)_2]^{2+}$ and $PVS^{\cdot -}$. As a result, the k_p process becomes faster but the k_b process becomes slower, which leads to the smaller $\eta^{-1}(k_p+k_b)/k_p$ value, as shown in Table 2.

A similar discussion, however, cannot be applied to the $\eta^{-1}(k_p+k_b)/k_p$ value for the reduction of MV^{2+} by **1**; this value is similar to those observed in the photoreduction of MV^{2+} and PVS^0 by **2** (Table 2), whereas this value should be the smallest due to the electrostatic repulsion between $MV^{\cdot +}$ and $[Cu^{II}(dmp)(PPh_3)_2]^{2+}$, because this interaction would accelerate the k_p process and suppress the k_b process. One possible explanation for this unexpected result is that η of **1** would be smaller than that of **2**. The η value represents the possibility that the triplet MLCT excited state is yielded from the singlet MLCT excited state. This process includes the change in spin state from the singlet to the triplet state and the change in geometry from the tetrahedral to the planar geometry[6]. The change in the spin state depends on the spin–orbit coupling constant. **1** includes three heavy atoms, i.e. one Cu and two P atoms. **2** includes five heavy atoms, i.e. one Cu atom, two P atoms and two S atoms. Because the heavy atom, in general, has a large spin–orbit coupling constant, the η value of **2** would be larger than that of **1**. The geometry change would accompany the change of solvent cage[7], which is closely related to the charge distribution. The charge distribution in the MLCT excited state is shown schematically in Scheme 3. Apparently, the solvent cage around **2** is weaker than that of **1**, because **2** includes one positive centre and three negative centres but **1** includes one positive centre and one negative centre. This means that **2** can cause the geometry change with a smaller solvent relaxation than **1**, which facilitates the geometry change of **2**. Thus, the η value of **2** would be larger than that of **1**, leading to the smaller $\eta^{-1}(k_p+k_b)/k_p$ value in the photoreduction by **2**. Of course, there is no direct evidence, and therefore, this explanation must be examined in more detail in the future.

4. Concluding remarks

Cationic $[Cu^I(dmp)(PPh_3)_2]^+$ (**1**) and anionic $[Cu^I(dmp)\{PPh_2(m\text{-}C_6H_4SO_3)\}_2]^-$ (**2**) were used as photosensitisers for the reduction of dicationic MV^{2+} and neutral PVS^0, in order to improve the quantum yield for viologen reduction and to clarify the charge effects of the photosensitiser and viologen on the photoinduced electron transfer reaction. **1** and **2** exhibit similar absorption and emission spectra, a similar lifetime of the excited state, and a similar redox potential at the excited state. The quantum yield for viologen photoreduction $\Phi(V^{\cdot})$ is determined by rate constants for the encounter

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[6] $[Cu^I(dmp)P_2]^{n+}$ takes a tetrahedral geometry in the singlet MLCT excited state, according to the Franck–Condon principle, because it is tetrahedral in the ground state [18,19]. However, $[Cu^I(dmp)P_2]^{n+}$ would take a planar geometry at the triplet MLCT excited state [19].

[7] It has been pointed out that the solvent medium has influence on the geometric relaxation in the ground state [7w].

complex formation (k_r), charge separation from the encounter complex (k_p), and back electron transfer in the encounter complex (k_b). The relative values of k_r, k_p and k_b are estimated from the lifetime of the excited state and the Stern–Volmer relation between $\Phi(V^{\cdot})^{-1}$ and $[V]^{-1}$. These k_r, k_p and k_b values primarily depend on the electrostatic interaction between the photosensitiser and viologen. For instance, the k_r value is the largest for the photoreduction of MV^{2+} by **2**, because the electrostatic interaction is attractive between cationic MV^{2+} and anionic **2**. As a result, the best quantum yield was obtained for the photoreduction of MV^{2+} by **2**. This quantum yield is about ten times greater than that of the MV^{2+} photoreduction by **1**.

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