Photoinduced electron transfer between $[Cu(dmphen)L_2]^+$ [dmphen = 2,9-dimethyl-1,10-phenanthroline, L = $PPh_n(C_6H_4OMe\text{-}p)_{3-n}$ (n = 0–3)] and methyl viologen

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Photocatalytic reduction of methyl viologen (1,1′-dimethyl-4,4′-bipyridinium mv^{2+}) was efficiently carried out with copper(I) complexes $[Cu(dmphen)L_2]^+$ [dmphen = 2,9-dimethyl-1,10-phenanthroline, L = $PPh_n(C_6H_4OMe\text{-}p)_{3-n}$, n = 0–3] upon irradiation of the metal-o-ligand charge-transfer band at around 360 nm. The quantum yield for reduction, $\varphi(mv^{\bullet +})$, increases considerably in the order L = $PPh_3 \ll PPh_2(C_6H_4OMe\text{-}p) < PPh(C_6H_4OMe\text{-}p)_2 < P(C_6H_4OMe\text{-}p)_3$, *i.e.* in increasing order of the phosphine donation ability. The best quantum yield (0.1) was recorded when $[Cu(dmphen)\{P(C_6H_4OMe\text{-}p)_3\}_2]^+$ was used. Kinetic analysis and measurement of the lifetime of the excited copper(I) complex revealed the reason why $\varphi(mv^{\bullet +})$ increases as the phosphine donation ability increases: first, the excited state becomes longer-lived and secondly, the charge-separation step becomes easier with increasing donation ability. The significant phosphine effects on the excited-state lifetime are discussed in terms of the solvent interaction with the copper(I) centre.

The photochemical properties of tris(2,2′-bipyridine)ruthenium(II), $[Ru(bipy)_3]^{2+}$, have been extensively investigated in the last two decades.[1] One of the reasons is that this complex can be applied to photoreduction of H^+ to hydrogen gas.[2] Copper(I) complexes of 2,2′-bipyridine, 1,10-phenanthroline and their derivatives exhibit interesting photochemical properties,[3–7] some of which are similar to those of $[Ru(bipy)_3]^{2+}$: (1) the metal-to-ligand charge-transfer (m.l.c.t.) state is the long-lived lowest excited state,[3c,d,f,g,i,n,q,s,t,5–7] (2) they have a large m.l.c.t. absorption band in visible–near UV region,[3c,f,n,t] and (3) $[Cu(dmphen)_2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline),[3d,e] $[Cu(dmphen)(PPh_3)_2]^+$[3f] and $[Cu(dpphen)_2]^+$[3j,l] (dpphen = 2,9-diphenyl-1,10-phenanthroline) have a considerably negative redox potential at the m.l.c.t. excited state. These copper(I) complexes have been applied to photoreduction of cobalt(III) complexes[3a,b,d,8] and methyl viologen (mv^{2+} 1,1′-dimethyl-4,4′-bipyridinium).[4c,9] However, the quantum yield for methyl viologen reduction, $\varphi(mv^{\bullet +})$, was very low, for instance 0.003 when $[Cu(dmphen)(PPh_3)_2]^+$ was used as a photosensitizer.[9a] It was improved later by using $[Cu(dmphen)\{P(C_6H_{11})Ph_2\}]^+$, $[Cu(dmphen)\{P(C_6H_4OMe\text{-}p)_3\}_2]^+$ and $[Cu(dmphen)\{PPh_2(C_6H_4SO_3\text{-}m)\}_2]^-$.[9b,c] The improvement achieved by using $[Cu(dmphen)\{PPh_2(C_6H_4SO_3\text{-}m)\}_2]^-$ was interpreted in terms of the acceleration of the encounter-complex formation, due to the electrostatic attraction between positively charged methyl viologen and the negatively charged copper(I) complex.[9c] Although $[Cu(dmphen)\{P(C_6H_4OMe\text{-}p)_3\}_2]^+$ leads to much greater improvement than does $[Cu(dmphen)\{PPh_2(C_6H_4SO_3\text{-}m)\}_2]^-$,[9b] very little is known of the photochemical properties of the former complex.

In the present work, a series of copper(I) complexes, $[Cu(dmphen)\{PPh_n(C_6H_4OMe\text{-}p)_{3-n}\}_2]^+$ (n = 0–3), were synthesised and their photochemical properties investigated in detail. Our purposes here are (1) to investigate in detail phosphine effects on m.l.c.t. absorption and emission spectra, and the lifetime and the oxidation potential of the m.l.c.t. excited state, (2) to apply these copper(I) complexes to the photoreduction of mv^{2+}, and (3) to clarify the reason why the photochemical reactivity of these copper(I) complexes is improved by substituting $PPh_n(C_6H_4OMe\text{-}p)_{3-n}$ for triphenylphosphine.

Experimental

Materials

Commercially available methyl viologen (1,1′-dimethyl-4,4′-bipyridinium dichloride) and 2,9-dimethyl-1,10-phenanthroline (both Nakarai tesque, Inc., guaranteed grade) were used without further purification. All the solvents were purified by appropriate methods before use.

Synthesis

Tri(p-methoxyphenyl)phosphine was prepared from trichlorophosphine and p-bromoanisole, according to a previous report.[10] Similarly, di(p-methoxyphenyl)phenylphosphine and (p-methoxyphenyl)diphenylphosphine were synthesised from dichlorophenyl- and chlorodiphenyl-phosphine respectively (Found: C, 71.55; H, 6.00. Calc. for $C_{21}H_{21}O_3P$: C, 71.00; H, 6.00. Found: C, 74.25; H, 5.95. Calc. for $C_{20}H_{19}O_2P$: C, 74.50; H, 5.95. Found: C, 78.55; H, 5.90. Calc. for $C_{19}H_{17}OP$: C, 78.05; H, 5.85%).

The complexes $[Cu(dmphen)L_2]ClO_4$ [L = PPh_3, $PPh_2(C_6H_4OMe\text{-}p)$, $PPh(C_6H_4OMe\text{-}p)_2$ or $P(C_6H_4OMe\text{-}p)_3$] were prepared as follows, according to previous reports:[9b,11] tetrakis(acetonitrile)copper(I) perchlorate[12] (125 mg; 0.38 mmol) and 2 molar equivalents of the phosphine were mixed in ethanol (50 cm^3) for 1 h at room temperature under a nitrogen atmosphere. The solvent was slowly evaporated at low temperature (in an ice-bath), and the yellow precipitate obtained was washed with cool diethyl ether. The purity was ascertained by elemental analysis (Found: C, 66.75, H, 4.80; N, 3.00. Calc. for $C_{50}H_{42}ClCuN_2O_4P_2$: C, 67.00; H, 4.75; N, 3.25. Found: C, 64.55; H, 4.85; N, 2.65. Calc. for $C_{52}H_{46}ClCuN_2O_6P_2$: C, 65.05; H, 4.85; N, 2.90. Found: C, 63.30; H, 4.85; N, 2.40. Calc. for $C_{54}H_{50}ClCuN_2O_8P_2$: C, 63.10; H, 4.70; N, 2.85. Found: C, 62.05; H, 5.10; N, 2.25. Calc. for $C_{56}H_{54}ClCuN_2O_6P_2$: C, 62.50; H, 5.15; N, 2.60%).

Photoreaction

In a typical run, an EtOH–water (60:40 v/v) solution of a copper(I) complex (0.20 mmol dm^{-3}), methyl viologen (1.0–2.5 mmol dm^{-3}) and phosphine (1.0–2.0 mmol dm^{-3})* was placed in a flask equipped with a Pyrex square cuvette (inside diameter 10 mm) under a nitrogen atmosphere. After deaerating the solution by five freeze–pump–thaw cycles, it was transferred to the Pyrex cuvette and irradiated by using a 400 W high-pressure mercury-arc lamp (Toshiba H-400P). The incident light ($360 < \lambda < 400$ nm) was selected with a combination of glass cut-off filters (Toshiba UV-35 and UV-D35).

The reaction was monitored by determining spectrophotometrically the concentration of the one-electron reduced methyl viologen radical [$mv^{\bullet +}$: λ_{max}/nm (EtOH) 605 (ε/dm^3 mol^{-1} cm^{-1} 17 100)]. The light intensity absorbed by the reaction solution was measured with a Reineckate chemical actinometer, $K[Cr(NH_3)_2(NCS)_4]$,[13] as the difference in light intensity transmitted through the reaction and reference cells. The quantum yield for methyl viologen reduction, $\varphi(mv^{\bullet +})$, was defined as the amount of $mv^{\bullet +}$ produced divided by the number of quanta absorbed by the copper(I) complex.

Emission spectra and excited-state lifetime

The emission spectra of the copper(I) complexes were recorded at 30 °C with a Hitachi fluorescence spectrometer (model F3010) by irradiating at their m.l.c.t. absorption maxima. The lifetimes of the excited copper(I) complexes were recorded with a Horiba NAES-550 time-resolved fluorometer, where the incident light was selected with a band-path filter (Toshiba U-360) and the decrease in emission intensity was monitored at λ_{max} of the emission spectra. The sample solution was deaerated by five freeze–pump–thaw cycles, and excess of phosphine was added to suppress phosphine dissociation from the copper(I) complexes.

Oxidation potentials of the copper(I) complexes

Cyclic voltammograms of the copper(I) complexes were measured at room temperature under a nitrogen atmosphere with a combined potentiostat-function generator system (Toho technical research; model PS-06), and a glassy carbon working electrode. The sample solution was prepared by dissolving the copper(I) complex (1.0×10^{-3} mol dm^{-3}) and a five-fold excess of phosphine (5.0×10^{-3} mol dm^{-3}) in EtOH containing $NBu^n{}_4ClO_4$ (0.1 mol dm^{-3}).

Results and Discussion

Photochemical properties of $[Cu(dmphen)L_2]^+$ [L = PPh_3 **1**, $PPh_2(C_6H_4OMe\text{-}p)$ **2**, $PPh(C_6H_4OMe\text{-}p)_2$ **3** or $P(C_6H_4OMe\text{-}p)_3$ **4**

In general, two factors should be taken into consideration when discussing the co-ordinate bond of phosphine: one is the bulkiness which is represented by the cone angle, and the other is the donation and back-donation ability. The donation abilities of *p*-methoxyphenylphosphines has been experimentally estimated to become greater in the order $PPh_3 < PPh_2(C_6H_4OMe\text{-}p) < PPh(C_6H_4OMe\text{-}p)_2 < P(C_6H_4OMe\text{-}p)_3$.[14] On the other hand, the cone angle is considered to be almost the same in all the phosphines used here, since a methoxy group is introduced at the *para* position of the phenyl group in each case and a substituent at this position has little influence on the cone angle. Thus, not the cone angle but the donation ability of the phosphine is considered below.

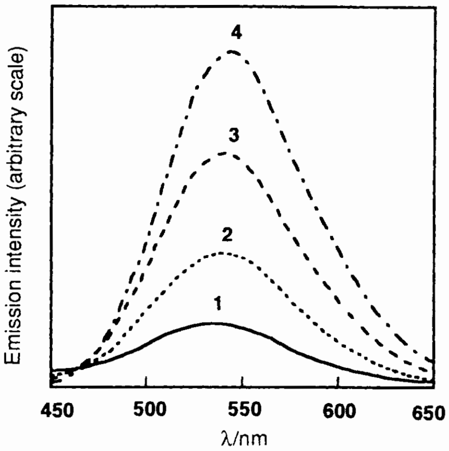

Fig. 1 Emission spectra of $[Cu(dmphen)(PPh_3)_2]^+$ **1** (——), $[Cu(dmphen)\{PPh_2(C_6H_4OMe\text{-}p)\}_2]^+$ **2** (- - -), $[Cu(dmphen)\{PPh(C_6H_4OMe\text{-}p)_2\}_2]^+$ **3** (– – –) and $[Cu(dmphen)\{P(C_6H_4OMe\text{-}p)_3\}_2]^+$ **4** (– · –), in EtOH–water (60:40 v/v) at 30 °C, 2.0×10^{-4} mol dm^{-3} complex and a five-fold excess of phosphine. The excitation was carried out at the λ_{max} in the absorption spectrum; *i.e.* 364 for **1**, 366 for **2**, 368 for **3** and 373 nm for **4**

All the copper(I) complexes examined exhibit a similar m.l.c.t. absorption band around 360 nm and an emission band around 540 nm, as shown in Table 1 and Fig. 1. Both absorption and emission bands shift somewhat to longer wavelengths in the order **1** < **2** < **3** < **4**, *i.e.*, in increasing order of the donation ability of the phosphine. These changes indicate that the energy difference between the copper d orbital and the dmphen π^* orbital decreases as the phosphine donation ability increases. Consistent with this, the oxidation potentials of the copper(I) complexes examined become less positive upon going to **4** from **1** (see Table 1),† suggesting that the copper(I) d-orbital energy increases in the order **1** $\leqslant$ **2** < **3** < **4**. Interestingly, the intensity and the quantum yield of the emission spectrum increase in the order **1** < **2** < **3** < **4**, as shown in Fig. 1 and Table 1. This result would be related to the lifetime of the excited state.

The oxidation potential of the excited copper(I) complex (E^{II/I^*}) was estimated from the relation between the reduction potential of the quencher and the oxidative quenching rate constant, according to the method of Meyer and co-workers.[15] As is clearly shown in Fig. 2, the oxidation potential at the excited state is almost the same (−0.8 V *vs.* saturated calomel electrode, SCE) in all the copper(I) complexes examined. It seems strange that although the absorption and emission spectra shift somewhat to longer wavelengths upon going from **1** to **4**, all the complexes examined exhibit a similar excited-state oxidation potential. Considering that the oxidation potential of the m.l.c.t. excited state would be mainly determined by the energy level of the dmphen π^* orbital, however, a coherent picture might emerge as follows: the donating phosphine increases the energy of the copper d orbital in the order **1** < **2** < **3** < **4**, leading to the above-mentioned spectral changes. On the other hand, the energy of the dmphen π^*

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* A five-fold excess of PPh_3 relative to $[Cu(dmphen)(PPh_3)_2]^+$ was added to the reaction solution to suppress the dissociation of phosphine from the complex. If not, the solution exhibited a small absorption around 440 nm besides a large absorption at 360 nm. The former band appears when PPh_3 dissociates from $[Cu(dmphen)(PPh_3)_2]^+$.[3f,m] When the excess is added the band at 360 nm increases and that at 440 nm decreases. It was ascertained that the band at 440 nm disappeared upon addition of the five-fold excess and that further addition of PPh_3 resulted in little change in the UV/VIS spectrum. For the other copper(I) complexes the appropriate excess of phosphine was added.

† Only the oxidation wave was observed. The reduction wave could not be seen, probably because the oxidation of $[Cu(dmphen)L_2]^+$ is accompanied by some additional reaction, and the reduction does not occur reversibly.

Table 1 Photochemical properties of complexes **1**–**4**

	Absorption[a]		Emission[a]					
Complex	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}	λ_{max}/nm	I_{rel}	$10^2\ \varphi_{em}$[e]	τ^b/µs	$E^{II/I*c}$/ V *vs.* SCE	$E_p^{ox\ d}$/ V *vs.* SCE
1	364	2600	532	1.0	0.36	0.70	−0.8	+1.23
2	366	2600	538	2.1	0.73	1.40	−0.8	+1.23
3	368	2900	543	3.7	1.62	2.70	−0.8	+1.16
4	373	2700	546	5.3	3.09	5.5	−0.8	+1.10

[a] In EtOH (100%). [b] Excited-state lifetime in EtOH–water (60:40 v/v) at 30 °C. [c] In EtOH–water (60:40 v/v). [d] In EtOH at room temperature under a nitrogen atmosphere. [e] Anthracene was used as a standard.

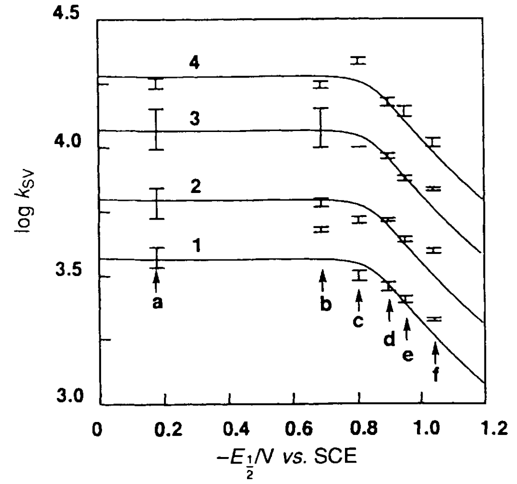
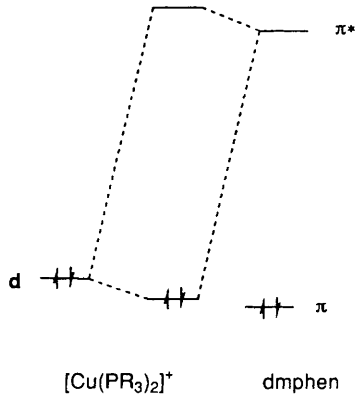


Fig. 2 Plots of the Redox potential of quenchers *vs.* the quenching rate constant (K_{sv}) for complexes **1**–**4**. The quenching experiments were performed at 30 °C in EtOH–water (60:40 v/v), using *p*-dinitrobenzene (*a*), 2,6-dichloro-*p*-benzoquinone (*b*), *o*-dinitrobenzene (*c*), *m*-dinitrobenzene (*d*), methyl *p*-nitrobenzoate (*e*) and methyl *m*-nitrobenzoate (*f*), 2.0 × 10^{-5} mol dm^{-3} complex and a five-fold excess of phosphine



Scheme 1

orbital is little influenced by the copper d_π orbital, because the π-back donation between the two orbitals (Scheme 1) is not strong. Actually, *ab initio* molecular orbital calculations of a model copper(I) complex, [Cu(HN=CHCH=NH)(PH$_3$)$_2$]$^+$,[16] indicated that the π-back bonding is weak.* As a result, the redox potential of the m.l.c.t. excited state is almost the same in **1**–**4**, whereas the absorption and emission maxima shift to longer wavelength in the order **1** < **2** < **3** < **4**.

The lifetime (τ) of the excited state increases in the order **1** < **2** < **3** < **4**. It is believed that the solvent molecule plays the role of quencher for these copper(I) complexes, and that the m.l.c.t. excited state of [Cu(dmphen)L$_2$]$^+$ would become longer-lived when the solvent interaction with the Cu^I is suppressed.[3c,h,o,p,r,x,4a] Water and ethanol in the solvent are Lewis bases, and can therefore interact with the Lewis acid. Thus, the solvent interaction with the Cu^I weakens as the positive charge on the complex decreases. Since the donating phosphine increases the electron density on Cu^I and decreases its positive charge, the solvent interaction with Cu^I weakens as the phosphine donation ability increases. As a result, the excited state becomes longer-lived in the order **1** < **2** < **3** < **4**.

Photoreduction of methyl viologen (mv^{2+})

Methyl viologen is smoothly reduced by the copper(I) complexes **1**–**4** under irradiation by near-UV light (360–400 nm), affording the one-electron reduced methyl viologen radical, mv$^{\bullet+}$. This is because the redox potential (−0.8 V *vs.* SCE) of the excited copper(I) complex is more negative than that of mv^{2+} [−0.60 V in EtOH–water (60:40 v/v)]. The time courses of the mv^{2+} reduction are given in Fig. 3. Apparently, the reduction by **2**–**4** proceeds much more rapidly than that by **1**. The quantum yield for mv^{2+} reduction, φ(mv$^{\bullet+}$), considerably increases in the order **1** < **2** < **3** < **4**, as shown in Table 2. The best value of 0.12 was observed when **4** was used as the photosensitizer.† It has been ascertained that the excess of phosphine does not participate in the reduction even under photoirradiation. Of course, this photoreduction cannot occur without **1**–**4**.

The copper(I) complex is oxidised to the copper(II) complex, accompanied by one-electron reduction of mv^{2+}. In our previous work,[9a] addition of 2,4-dinitrophenylhydrazine to the reaction solution yielded a red precipitate of the corresponding hydrazone. This result suggests that acetaldehyde is formed from ethanol in the photoreaction. Furthermore, the complex [Cu^{II}(dmphen)$_2$]$^{2+}$ was reported to be photoreduced by ethanol upon irradiation by near-UV light at around 390 nm.[17] From these results, it was reasonably proposed that the copper(II) complex would be photoreduced by ethanol to the

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[*] The geometry of HN=CHCH=NH was calculated to cause little changes upon co-ordination to Cu^I.[16] If the back bonding is strong, the N=C bond would be considerably lengthened upon co-ordination. Thus, the back bonding in [Cu(HN=CHCH=NH)(PH$_3$)$_2$]$^+$ is considered to be weak. Actually, the Mulliken population of HN=CHCH=NH decreases upon co-ordination to Cu^I. See ref. 16 for details.

[†] This value is greater than that reported previously,[9b] probably because the deaeration was thoroughly carried out in this work by five freeze–pump–thaw cycles. In the previous work the deaeration was carried out by passing pure nitrogen gas through the solution. The φ(mv$^{\bullet+}$) value obtained with complex **1** was also re-examined in this work but found not to be changed.

Table 2 Quantum yields and Stern–Volmer parameters for the methyl viologen photoreduction by complexes **1**–**4** in EtOH–water (60:40 v/v) at 30 °C

Complex	$10^2\ \varphi$*	$10^3\ k_d k_r^{-1}$/mol dm^{-3}	$\eta^{-1}(k_p + k_b)/k_p$	$10^{-8}\ k_r$/s^{-1}
1	0.26 ± 0.02	13.7 ± 1.8	25.8 ± 4.0	1.04 ± 0.14
2	4.2 ± 0.2	2.1 ± 0.01	7.8 ± 0.6	3.46 ± 0.02
3	7.2 ± 0.5	0.87 ± 0.07	7.5 ± 0.4	4.28 ± 0.33
4	12.2 ± 0.2	0.68 ± 0.01	4.8 ± 0.1	2.67 ± 0.05

* $[\mathrm{Cu^I}]$ = 0.20 mmol dm^{-3}, [phosphine] = 1.0 mmol dm^{-3}, $[\mathrm{mv^{2+}}]$ = 1.0 mmol dm^{-3}.

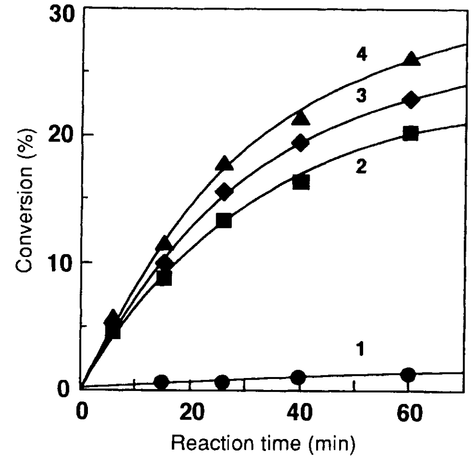
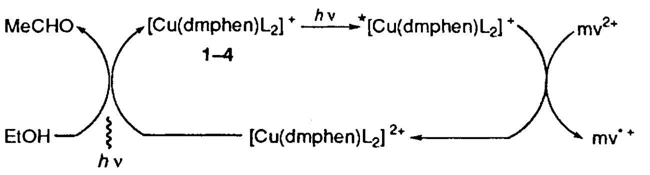


Fig. 3 Time-conversion curves of the photoreduction of methyl viologen by complexes **1**–**4**. Reaction conditions: 2.0×10^{-4} mol dm^{-3} complex and 1.0×10^{-3} mol dm^{-3} $\mathrm{mv^{2+}}$ at 30 °C in EtOH–water (60:40 v/v) solution, excess of phosphine (1.0×10^{-3} mol dm^{-3}). The percentage conversion is based on the amount of copper(I) complex



Scheme 2

original copper(I) complex, and that the catalytic cycle of this photoreduction would be completed, as shown in Scheme 2.[9a] The results presented here are not affected by the photoreduction of the copper(II) complex by ethanol shown in Scheme 2. In the quenching experiments the copper(I) complex is little oxidised to the copper(II) complex because the irradiation light is of very low intensity. Furthermore, even if the copper(II) complex is formed, the reduction by ethanol cannot occur because of the lack of light irradiation at 390 nm which is necessary for the photoreduction.[17] The quantum yield for the $\mathrm{mv^{2+}}$ reduction was measured in the early stage of the reaction (1–2% conversion of $\mathrm{mv^{2+}}$), to avoid the effect of the photoreduction of the copper(II) complex [at this, only a little copper(II) complex is formed and the photoreduction of such a small amount does not seem important].

Reaction mechanism

The photoinduced electron-transfer reaction is considered in general to proceed through either a dynamic or a static quenching mechanism.[3b,c,e,o,p,8,9] The minimum kinetic scheme for dynamic quenching is represented in equations (1)–(5).[3b]

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

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

$$\mathrm{{}^*Cu^I} + \mathrm{mv^{2+}} \xrightarrow{k_r} [\mathrm{Cu^{II}} \cdots \mathrm{mv^{\bullet+}}] \qquad (3)$$

$$[\mathrm{Cu^{II}} \cdots \mathrm{mv^{\bullet+}}] \xrightarrow{k_p} \mathrm{Cu^{II}} + \mathrm{mv^{\bullet+}} \qquad (4)$$

$$[\mathrm{Cu^{II}} \cdots \mathrm{mv^{\bullet+}}] \xrightarrow{k_b} \mathrm{Cu^{I}} + \mathrm{mv^{2+}} \qquad (5)$$

This mechanism consists of the excitation (1), the deactivation (2), the encounter-complex formation (3), the charge separation (4), and the back electron transfer (5), where η represents the possibility that the photoirradiation yields the triplet m.l.c.t. excited state. In this mechanism, τ_0/τ and I_0/I linearly increase with the concentration of $\mathrm{mv^{2+}}$ [see equation (6)], where τ and

$$\tau_0/\tau = I_0/I = 1 + (k_r/k_d)[\mathrm{mv^{2+}}] \qquad (6)$$

I are the excited-state lifetime and the intensity of the emission spectrum respectively and the subscript 0 represents the absence of $\mathrm{mv^{2+}}$.

The static quenching mechanism consists of the formation of an adduct of the copper(I) complex with $\mathrm{mv^{2+}}$ in their ground states [equation (7)], excitation of the adduct (8), deactivation

$$\mathrm{Cu^I} + \mathrm{mv^{2+}} \xrightleftharpoons{K} [\mathrm{Cu^I} \cdots \mathrm{mv^{2+}}] \qquad (7)$$

$$[\mathrm{Cu^I} \cdots \mathrm{mv^{2+}}] \xrightarrow{\eta h\nu} [\mathrm{Cu^I} \cdots \mathrm{mv^{2+}}] \qquad (8)$$

$$[\mathrm{{}^*Cu^I} \cdots \mathrm{mv^{2+}}] \xrightarrow{k_d'} [\mathrm{Cu^I} \cdots \mathrm{mv^{2+}}] \qquad (9)$$

$$[\mathrm{{}^*Cu^I} \cdots \mathrm{mv^{2+}}] \xrightarrow{k_r'} [\mathrm{Cu^{II}} \cdots \mathrm{mv^{\bullet+}}] \qquad (10)$$

$$[\mathrm{Cu^{II}} \cdots \mathrm{mv^{\bullet+}}] \xrightarrow{k_b'} \mathrm{Cu^{I}} + \mathrm{mv^{2+}} \qquad (11)$$

$$[\mathrm{Cu^{II}} \cdots \mathrm{mv^{\bullet+}}] \xrightarrow{k_p'} \mathrm{Cu^{II}} + \mathrm{mv^{\bullet+}} \qquad (12)$$

(9), one-electron transfer (10), back electron transfer (11), and charge separation (12). In this mechanism I_0/I is defined as in equation (13).

$$I_0/I = 1 + K[\mathrm{mv^{2+}}] \qquad (13)$$

In general, the reaction mechanism is considered to depend on the $\mathrm{mv^{2+}}$ concentration: the static quenching mechanism becomes predominant at high concentration, the dynamic quenching mechanism at low concentration. Thus, we must consider the reaction including both dynamic and static quenching mechanisms. In this case, equations (14) and (15) are

$$I_0/I = 1 + \frac{k_r + K}{k_d}[\mathrm{mv^{2+}}] \qquad (14)$$

$$\tau_0/\tau = 1 + \frac{k_r}{k_d}[\mathrm{mv^{2+}}] \qquad (15)$$

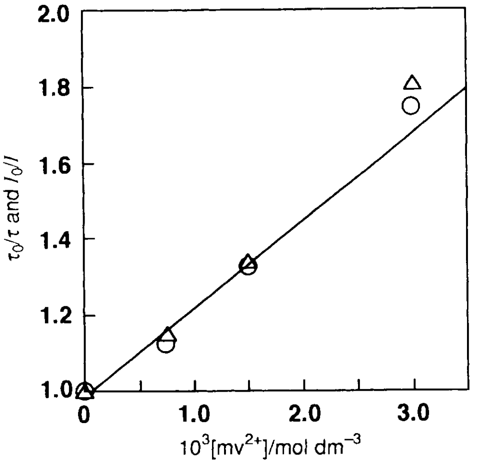


Fig. 4 Plots of τ_o/τ (○) and I_o/I (△) *vs.* methyl viologen concentration in the quenching reaction of $[Cu(dmphen)(PPh_3)_2]^+$ with mv^{2+}. Reaction conditions: 2.0×10^{-5} mol dm^{-3} and complex 1.0×10^{-4} mol dm^{-3} PPh_3 in EtOH–water (60:40 v/v) solution at 30 °C

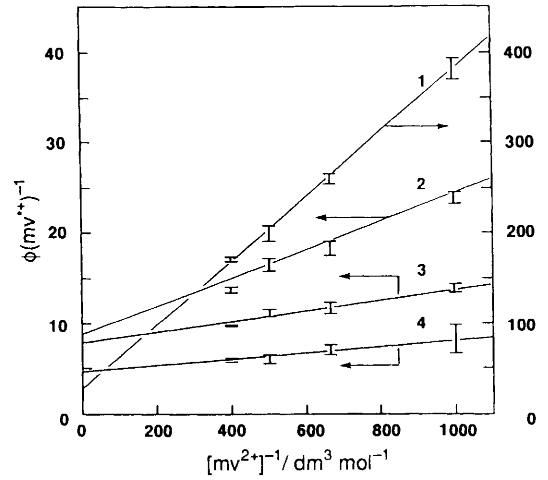


Fig. 5 Stern–Volmer relations in the methyl viologen photoreduction by complexes **1**–**4**. Reaction conditions: 2.0×10^{-4} mol dm^{-3} complex in EtOH–water (60:40 v/v) solution at 30 °C, with excess of phosphine (1.0×10^{-3} mol dm^{-3})

derived under the assumption that $[{}^*Cu^I \cdots mv^{2+}]$ was rapidly deactivated without luminescence. This assumption is reasonable because the excited copper(I) complex is in contact with the quencher (mv^{2+}) in $[{}^*Cu^I \cdots mv^{2+}]$. Equations (14) and (15) are useful to determine whether or not the static quenching mechanism is involved. As shown in Fig. 4, the τ_o/τ value is almost the same as the I_o/I value. This result clearly indicates that K is negligible in equation (14) and that the mv^{2+} photoreduction by the copper(I) complex proceeds through the dynamic quenching mechanism.

In the case of the dynamic quenching mechanism, the reciprocal of the quantum yield, $\varphi(mv^{\bullet+})^{-1}$, increases linearly with the reciprocal of the methyl viologen concentration, $[mv^{2+}]^{-1}$ [equation (16)]. In fact, such a linear relationship is

$$\varphi(mv^{\bullet+})^{-1} = \eta^{-1}[(k_p + k_b)/k_p]\{(k_d/k_r)[mv^{2+}]^{-1} + 1\} \quad (16)$$

observed for all the reactions examined in this work, as shown in Fig. 5. The slope and the intercept of these relationships yield the values of k_d/k_r and $\eta^{-1}[(k_p + k_b)/k_p]$ respectively; k_d is the reciprocal of the lifetime (τ_o) which was measured independently (see above). Thus, k_r can be estimated, see Table 2.

Factors determining the quantum yield

As seen in Table 2, k_d/k_r considerably decreases in the order **1** > **2** > **3** > **4**, indicating that this term is responsible for the increase in $\varphi(mv^{\bullet+})$ in the order **1** < **2** < **3** < **4**. However, the rate constant for the encounter complex formation, k_r, is not very sensitive to the kinds of phosphine ligand (Table 2). This is not surprising because all the complexes examined are positively charged and have a similar structure and a similar oxidation potential at the m.l.c.t. excited state. On the other hand, k_d ($= \tau_o^{-1}$) is very sensitive to the nature of the phosphine ligand and decreases considerably in the order **1** > **2** > **3** > **4** (Table 2). As a result, k_d/k_r considerably decreases upon going from **1** to **4**. Thus, the excited-state lifetime is one of the important factors in determining $\varphi(mv^{\bullet+})$.

The $\eta^{-1}[(k_p + k_b)/k_p]$ value also decreases somewhat in the order **1** > **2** > **3** > **4**. This means that the charge-separation step becomes easier (or the back electron-transfer step more difficult) upon going from **1** to **4** and therefore, the $\eta^{-1}[(k_p + k_b)/k_b]$ term contributes to the increase in $\varphi(mv^{\bullet+})$ in the order **1** < **2** < **3** < **4**. The charge-separation step is considered to depend on the ground-state redox potential.[3e] As shown in Table 1, the oxidation potential becomes less positive upon going from **1** to **4**, *i.e.* in the increasing order of the phosphine donation ability. Thus, the charge separation becomes easier (or the back electron transfer more difficult) as the phosphine donation ability increases.

In summary, the donating *p*-methoxyphenylphosphine leads not only to a longer-lived m.l.c.t. excited state but also to an acceleration of the charge-separation step, and thus stimulates the photoreduction of mv^{2+}.

Conclusion

A series of copper(I) complexes $[Cu(dmphen)L_2]^+$ [L = $PPh_n(C_6H_4OMe\text{-}p)_{3-n}$, n = 0–3] were synthesised. Their absorption and emission maxima shift somewhat to longer wavelengths, their emission intensity increases and their excited states become longer-lived in the order **1** < **2** < **3** < **4**, *i.e.* in the increasing order of phosphine donation ability. On the other hand, all these complexes exhibit similar oxidation potentials at the m.l.c.t. excited state. Their photoreduction of mv^{2+} proceeds through a dynamic quenching mechanism. Although the encounter-complex formation (k_r) is not sensitive to the nature of the phosphine ligand, the deactivation rate constant (k_d) decreases considerably in the order **1** > **2** > **3** > **4**. This is the main reason that the quantum yield for methyl viologen reduction, $\varphi(mv^{\bullet+})$, increases in the order **1** < **2** < **3** < **4**. The best $\varphi(mv^{\bullet+})$ value was 0.12 when $[Cu(dmphen)\{P(C_6H_4OMe\text{-}p)_3\}_2]^+$ was used.

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