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PHOTOREDUCTION OF METHYLVIOLOGEN CATALYSED BY TRI- OR TETRA-SULPHOPHTHALOCYANINATOZINC(II) IN AQUEOUS SOLUTIONS

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Abstract—Photocatalytic activity of tetra- and tri-sulphophthalocyaninatozinc(II) was studied in aqueous solution of triethanolamine, complexes and electron acceptors such as methylviologen and *N,N′*-bis(3-sulphonatopropyl)-4,4′-bipyridinium. Adduct formation of the complexes with the electron acceptors affected their activity, but dimerization scarcely affected the activity. The activity was also investigated by measurements of redox potentials of the species used for the photoreduction of the electron acceptors.

Metallophthalocyanines have intense absorption bands in the wavelength region from 600 to 700 nm and can collect energy in the solar spectrum, so they are attractive candidates for photosensitizers.[1]

In organic solvents, a few phthalocyanine derivatives have been reported to act as photosensitizers,[2,3] but a water-soluble tetrasulphophthalocyanine complex of zinc(II) has not carried out the photoreduction of methylviologen (MV^{2+}), which is widely used as an electron carrier for the evolution of hydrogen gas from water,[4,5] and photoreduction of carbon dioxide.[6–8] This was hitherto explained by the fact that the complexes form photo-inactive aggregates and/or adducts with the electron carrier in water.[4,5]

We have previously reported that a zinc(II) phthalocyanine derivative having positively charged peripheral substituents to depress the adduct formation with MV^{2+} could first catalyse the photoreduction of MV^{2+} in water, but its photocatalytic activity was low.[9]

Recently, it was reported that trisulphophthalocyanine derivatives of zinc(II) (Fig. 1) and aluminium(III) do not form dimers in water.[10] Thus, it was of interest to study the photoreduction of MV^{2+} with the trisulpho derivative of zinc(II). In this paper, we report the photoreduction of MV^{2+} cation or neutral *N,N′*-bis(3-sulphonatopropyl)-4,4′-bipyridinium (PVS) catalysed by tetrasulphophthalocyaninatozinc(II) (**1**) or trisulphophthalocyaninatozinc(II) (**2**) in the presence of triethanolamine (TEOA) as an electron donor.

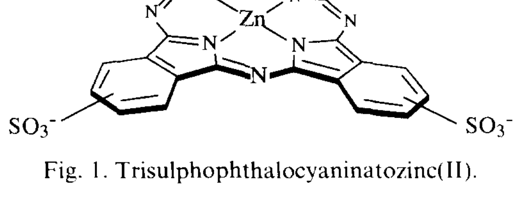

Fig. 1. Trisulphophthalocyaninatozinc(II).

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EXPERIMENTAL

Synthesis

Sodium tetrasulphophthalocyaninatozinc(II) and sodium trisulphophthalocyaninatozinc(II) were prepared according to the procedures of Weber and Bush[11] and Gouterman *et al.*[10] respectively. Methylviologen chloride was commercially available, and PVS was prepared according to the procedure of Degani and Willner.[12]

Measurements

Continuous irradiation. The sample solution in a glass cell with a 1-cm light path length was purged by argon and was irradiated with a 100-W halogen lamp at 25°C for 1 h (the cell was situated 3 cm away from the light). The light with wavelength shorter than 420 nm was cut off by the use of a Toshiba L-42 glass filter. The relative quantum yield (RQY)* was estimated from the absorbance arising from the radical species of MV^+ ($\varepsilon = 12{,}800$ M^{-1} cm^{-1}) or PVS^- (13,800 M^{-1} cm^{-1}) at 602 nm.[13] The pH adjustments were carried out by 0.1 M (M = mol dm^{-3}) hydrochloric acid or 0.1 M sodium hydroxide solution.

Cyclic voltammetry. Cyclic voltammetry measurements were performed in aqueous solution containing 0.1 M potassium chloride as an electrolyte under argon on a Hokuto Denko HA-501 potentiostat with a Hokuto Denko HF-201 function generator. A glassy carbon disc, a platinum coil and a saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively.

Other measurements. The visible and fluorescence spectra were recorded on a Shimadzu UV-3100 spectrophotometer and a Hitachi 850 fluorescence spectrophotometer, respectively. Adduct formations of complex **2** with $MVCl_2$ and PVS were measured by following the absorbance change at 668 nm of complex **2** at room temperature. The pH adjustments were carried out with buffer solutions. The concentration of complex **2** was 1.0×10^{-6} M, and those of the electron acceptors were varied in the range from 0 to 1.0×10^{-2} M.

RESULTS AND DISCUSSION

Complex **1** shows an absorption band at 634 nm and a shoulder at 670 nm at pH 10, while complex **2** has a band at 668 nm (Fig. 2). The fluorescence excitation spectrum of complex **1** shows a band at 675 nm. It has been reported that the dimer of metallophthalocyanine shifts its absorption band to shorter wavelength compared with that of the monomer, and the dimer also shows emission quenching.[9,14,15] That is, the shoulder at 670 nm of the absorption spectrum arises from the monomer, and the absorption band at 634 nm is assigned to the dimer. On the other hand, complex **2** has only a band at 668 nm with the excitation band at 670 nm, showing that it exists as a monomer at pH 10.

The fluorescence intensities of complexes **1** and **2** decreased with decrease in pH (Fig. 3); the intensity of complex **2** at pH 7 is about 90% of that at pH 10. Furthermore, at pH 10, the monomer concentration of complex **1** is about 20% of that of complex **2**.

The pH dependence of the radicals formed under irradiation shows three significant features (Fig. 4); (i) the RQY value for complex **2** is larger than that for complex **1**; (ii) the values for the PVS system are larger than those for the MV^{2+} system; (iii) according to the pH increase, the values increase. Furthermore, the turnover number with respect to complex **2** using PVS as the electron acceptor is 144 at pH 10, showing that the reaction proceeds catalytically. To elucidate the above three features, some factors such as dimerization, adduct formation and redox potential were investigated.

Dimerization

While the monomer concentration of complex **2** at pH 7 is about 90% of that at pH 10, the RQY values at pH 7 are only 20–40% of those at pH 10 (Fig. 4). That is, the significant decreases of RQY are not explained by dimerization alone. Furthermore, the RQY value for complex **2** is almost the same as that for complex **1** which exists as the dimer in the pH region from 7 to 10. These results show that dimerization slightly affects the photoactivity of the complexes.

Adduct formation

By the addition of MV^{2+} and PVS into aqueous solution of complex **2**, the Q bands shifted to longer wavelengths with accompanying isosbestic points at 676 nm for MV^{2+} and 673 nm for PVS.

The formation constant (K) for the following equation was estimated from the absorption spectral change by the addition of the electron acceptors:

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* RQY was estimated in comparison with the largest one in the series.

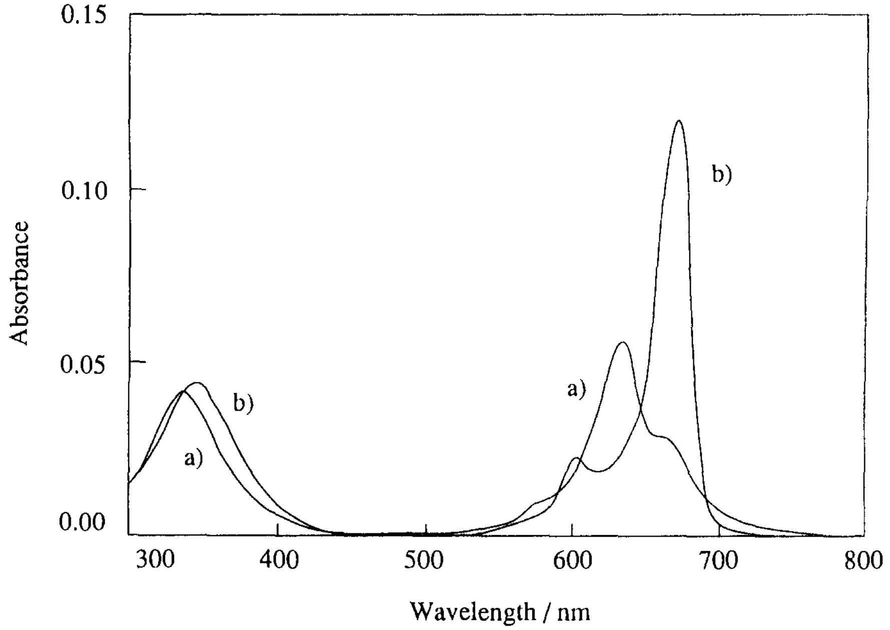

Fig. 2. Absorption spectra of complexes **1** and **2**: (a) complex **1**; (b) complex **2**. [complex] = 1.0×10^{-6} M, pH 10.

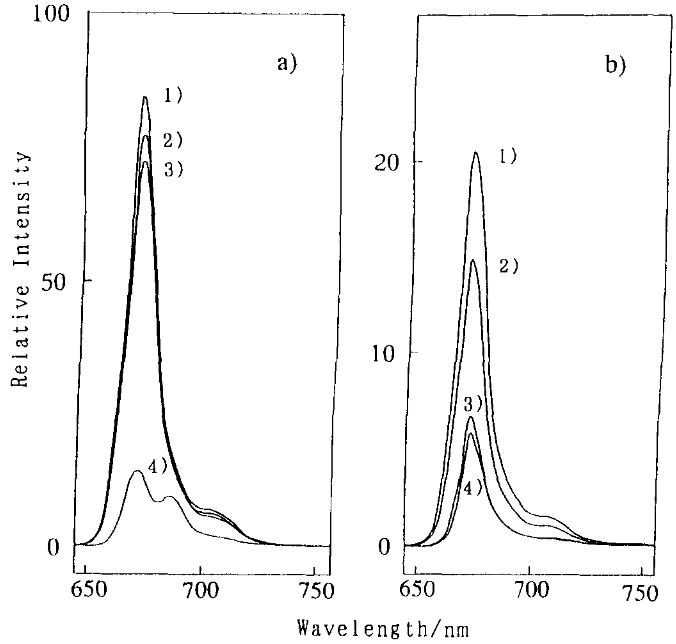

Fig. 3. The pH dependence of fluorescence intensities of complexes **1** and **2**: (a) complex **1**; (b) complex **2**; (1) pH 10; (2) pH 8; (3) pH 7; (4) pH 4. [complex] = 1.0×10^{-6} M.

$$C + EA \overset{K}{\rightleftharpoons} C\text{—}EA, \qquad (1)$$

where C and EA denote the complex and the electron acceptors, respectively.

The formation constant for complex **1** was not estimated due to the complex absorption spectrum caused by the large amounts of its dimeric species. The adduct formation hardly depends on pH (Table 1). The *K* value for MV^{2+} is *ca* six times that for PVS, probably because negative charges on the complex prefer MV^{2+} rather than the neutral PVS species. The RQY value for MV^{2+} is *ca* 20% of the

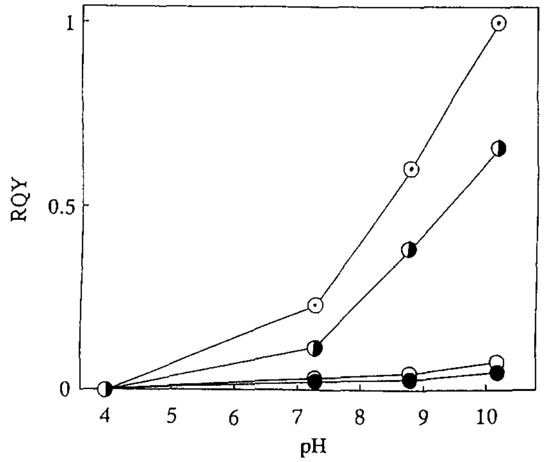

Fig. 4. Effect of pH on the RQY : (⊙) complex **2**, PVS ; (◑) complex **1**, PVS ; (○) complex **2**, MV^{2+} ; (●) complex **1**, MV^{2+}. [complex] = 1.0×10^{-6} M, [EA] = 5.0×10^{-3} M, [TEOA] = 1.0×10^{-1} M.

Table 1. The adduct formation constants of complex **2**

Electron acceptor	*K* pH 7	*K* pH 10
MV^{2+}	1.2×10^4	1.6×10^4
PVS	2.2×10^3	2.6×10^3

value for PVS, consistent with the result of adduct formation.

Reaction scheme

It is reported that an electron is transferred from the excited triplet state of phthalocyanine derivatives of zinc(II) via an oxidative quenching process,[2,9,16] then the reaction scheme might be proposed as follows :

$$C + EA \overset{K}{\rightleftharpoons} C\text{—}EA \qquad (1)$$

$$2C \longrightarrow C_2 \qquad (2)$$

$$C \xrightarrow{h\nu} C^* \qquad (3)$$

$$C^* + EA \longrightarrow C^+ + EA^- \qquad (4)$$

$$C^+ + EA^- \longrightarrow C + EA \qquad (5)$$

$$C^+ + TEOA \longrightarrow C + TEOA^+ \qquad (6)$$

$$TEOA^+ \longrightarrow \text{Decomposed products,} \qquad (7)$$

where C^+, C_2 and C^* denote the oxidized complex, the dimer and the excited triplet state complex, respectively.

The reactants which form the adduct in the ground state might also form a rigid exciplex, promoting back-electron transfer within the solvent cage, as was discussed previously for $ZnTmPyP^{4+}$ and $ZnTsP^{4-}$ species.[14,17] The positive MV^+ radical further promotes the back reaction [eq. (5)] more easily than the negative PVS^- radical. For these reasons, adduct formation must decrease the photocatalytic activity of the complexes.

Redox potentials

For facile photoreduction of MV^{2+} or PVS, thermodynamic driving forces for eqs (4) and (6) are required with the depression of that for the back reaction (5). The thermodynamic energies, E_4, E_5 and E_6 for eqs (4), (5) and (6) were obtained from the redox potentials for MV^{2+} (MV^{2+}/MV^+), TEOA ($TEOA^+/TEOA$) and the complexes (C^+/C), as well as the redox potentials for the excited triplet states of the complexes (C^+/C^*), which were estimated from electrochemical and spectroscopic data according to the method described by Lever *et al.*[18] Then, the value of E_4, E_5 and E_6 were calculated by means of the following equations: $E_4 = (EA/EA^-) - (C^+/C^*)$, $E_5 = (C^+/C) - (EA/EA^-)$, $E_6 = (C^+/C) + (TEOA^+/TEOA)$.

The redox potentials also show pH dependence (Table 2) ; with the increase of pH, the redox potentials (MV^{2+}/MV^+, PVS/PVS^-) scarcely change, while that of $TEOA^+/TEOA$ shifts slightly to the negative side. Furthermore, the redox potentials for complex **2** (C^+/C, C^+/C^*) shift to the negative side, but those for complex **1** scarcely shift.

That is, in the case of complex **1**, the value of E_6 is suitable for the photoreduction of the electron acceptors, and those for E_4 and E_5 are slightly advantageous and disadvantageous, respectively. In the case of complex **2**, E_4 and E_5 are both suitable for the photoreduction, and the value of E_6 is slightly advantageous. These results show that complex **2** is a better photosensitizer than complex **1** with regard to the thermodynamic energies.

Consequently, the photocatalytic activity of the phthalocyaninatozinc(II) complexes are affected by their adduct formation with the electron acceptors, but scarcely affected by their dimerization. Furthermore, complex **2** is more suitable for the photoreduction than complex **1** from the viewpoint of their redox potentials.

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Table 2. Redox potentials and thermodynamic energies

pH	TEOA/TEOA$^-$		MV^{2+}/MV$^+$		PVS/PVS$^-$
7	0.75		−0.68		−0.64
8	0.73		−0.68		−0.64
10	0.71		−0.68		−0.63
Complex **1**	C$^+$/C	C$^+$/C*	E_4	E_5	E_6
7	0.55	−0.55	−0.13	1.23	−0.20
8	0.56	−0.54	−0.14	1.24	−0.17
10	0.57	−0.53	−0.15	1.25	−0.14
Complex **2**	C$^+$/C	C$^+$/C*	E_4	E_5	E_6
7	0.65	−0.45	−0.23	1.33	−0.10
8	0.60	−0.50	−0.18	1.28	−0.13
10	0.59	−0.51	−0.17	1.27	−0.12

The redox potentials were estimated by $E_{1/2} = (E_{pa} + E_{pc})/2$ (V *vs* SCE).

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