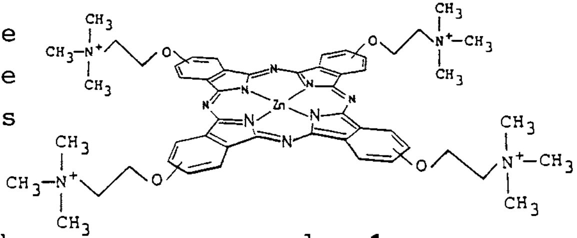
CHEMISTRY LETTERS, pp. 1877-1880, 1991.

Photoreduction of Methyl Viologen with a Water-soluble Phthalocyaninatozinc(II) Complex in an Aqueous Solution

Kuninobu KASUGA,* Hiroki HAYASHI, and Makoto HANDA
Department of Chemistry, Faculty of Science, Shimane University, Matsue 690

Tetrakis(2-trimethylaminoethoxy)phthalocyaninatozinc(II) iodide catalyzed photoreduction of methyl viologen with visible light in the presence of triethanolamine in an aqueous solution. The effects of an ionic strength, pH, and polarity of solvents on the photoreaction were also investigated.



complex **1**

Metallophthalocyanines, which show strong absorption bands in the wavelength region from 600 to 700 nm, are attractive candidates for a photosensitizer. While a few phthalocyanine derivatives acted as the photosensitizer in organic solvents or solvent mixtures with water,$^{1-6)}$ a water-soluble phthalocyanine complex such as tetraammonium tetrasulfophthalocyaninatozinc(II), $(NH_4)_4$ZnTSPc, has not carried out the photoreaction in an aqueous solution because it forms both a dimer of the complex and an adduct with an electron carrier such as 1,1'-dimethyl-4,4'-bipyridinium dication (MV^{2+}), suppressing the photoreaction.$^{7-10)}$

We describe here that a water-soluble phthalocyaninatozinc(II) iodide with peripheral substituents charged positively (complex **1**) first catalyzed the photoreduction of MV^{2+} in an aqueous solution.

The starting material of 4-(2'-dimethylaminoethoxy)phthalonitrile was prepared in a similar method described in the literature.$^{11)}$ The complex **1** was prepared as follows; the mixture of 1.1 g (8.0 mmol) of anhydrous zinc(II) chloride and 3.5 g (16 mmol) of 4-(2'-dimethylaminoethoxy)phthalonitrile was heated in the presence of 6 ml of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 90 °C for 4 h. The viscous solution was diluted with 50 ml of DMF, and then poured on an alumina column. Using DMF as an eluent, the green solution of tetrakis(2-dimethylaminoethoxy)phthalocyaninatozinc(II), $ZnPc(O(CH_2)_2N(CH_3)_2)_4$, was eluted out. By the addition of adequate amounts of water to the solution, lustrous powders were obtained and dried at room temperature (yield 10%). Anal Found: C, 61.85; H, 5.71; N, 17.64%. Calcd for $C_{48}H_{52}N_{12}O_4Zn$: C, 62.22; H, 6.10; N, 18.15%. Methylation of $ZnPc(O(CH_2)_2N(CH_3)_2)_4$ was carried out by standing the dichloromethane solution (10 ml) of the complex (1.5 g, 1.3 mmol) and methyl iodide (5.1 ml, 82 mmol) at room temperature for 14 h. The purple complex **1** precipitated was then washed with dichloromethane (yield 98%). Anal Found: C, 39.65; H, 4.82; N, 10.72%. Calcd for $C_{52}H_{64}N_{12}O_4ZnI_4\cdot 4H_2O$: C, 39.87; H, 4.64; N, 10.73%. ^1H NMR(DMSO-d_6, 270 MHz) 3.42(s, 36H, CH_3), 4.13(s, 8H, CH_2CH_2), 5.12(s, 8H, CH_2CH_2), 7.91(d, 4H, ring proton), 9.03(d, 4H, ring proton), 9.40(m, 4H, ring proton) ppm.

The complex **1** shows Q bands at 635 (log ε = 4.85) and 683^{sh} nm (4.61) in an aqueous solution (Fig. 1). An excited spectrum for fluorescence at 703 nm shows a band at 685 nm, exhibiting that the absorption band around 685 nm origins from a monomer species.12) In the solvent mixture of water - dimethylsulfoxide (DMSO) (1 : 1 v/v), the Q band is only shown at 686 nm; that is, the monomer species is predominant in the solvent mixture (Fig. 1). With increasing the polarity of the solvent, the more hydrophobic phthalocyanine moieties approach each other, thereby forming the dimer.13)

For steady-state irradiation, the sample solution in a glass cell with a 1-cm light path length was purged by argon gas and was irradiated with a 100-W Halogen lamp at 20 °C (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 characteristic absorption bands of a radical $MV^{\cdot +}$ species appeared upon irradiation with visible light of the purged aqueous solution (pH = 10) containing triethanolamine (1.00 x 10^{-1} M (= mol dm^{-3})), $MVCl_2$(5.00 x 10^{-3} M), and the complex **1** (1.60 x 10^{-6} M). The concentration of radicals generated upon irradiation for 1 h was estimated to be 11 times that of the complex. Without the complex, the radical was not generated upon irradiation. When air was introduced into the irradiated sample solution in order to oxidize the $MV^{\cdot +}$ radical, the visible spectrum of the system became identical with that before irradiation. Thus, in the course of the photoreduction, the complex **1** effectively

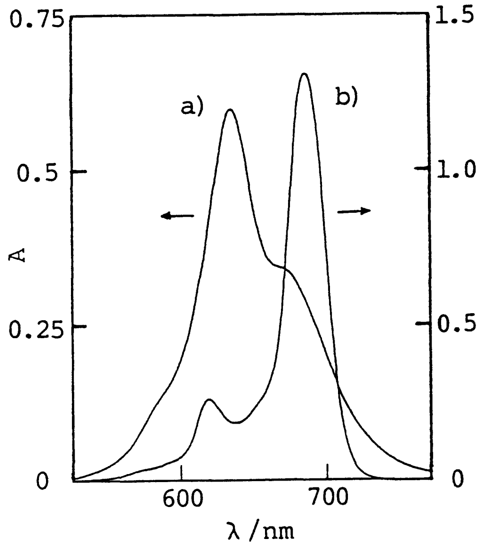


Fig. 1. Electronic spectra of the complex 1: a)in H_2O, b)in H_2O-DMSO (1 : 1), [complex] = 1.00 x 10^{-5} M.

catalyzed the reaction.

Both of $(NH_4)_4ZnTSPc$ and the complex **1** form large amounts of dimers in an aqueous solution. In addition, the former makes a ground-state complexation with MV^{2+} due to its negative charge, resulting in the static quenching of the photoreaction.[7,8] On the other hand, the complex **1** charged positively does not seem to form the adduct with the positive MV^{2+} ion in an aqueous solution, which might be a reason for the complex **1** to promote the photoreduction of MV^{2+}.

Furthermore, it has been reported that water-soluble tetramethyltetra-2,3-pyridinoporphyrazinatozinc(II) methylsulfate could not catalyze the photoreduction because its first reduction potential (-0.52 V *vs.* SCE) was more positive than that for MV^{2+} (-0.69 V *vs.* SCE).[14] The complex **1** shows the potential of the first reduction couple at -0.85 V (*vs.* SCE) (Fig. 2), which is almost the same with that for ZnPc (-0.86 V *vs.* SCE in DMSO). The more negative potential for the complex **1** compared with that for MV^{2+} results in the facile photoreduction.

Further studies on the photoreduction offer the following results; (i) the reaction was not accerelated by the addition of potassium iodide (10-fold molar quantity of the complex **1**) into the three component system, showing that the iodide ion did not affect the reaction. (ii) With increasing an ionic strength, the dimer formation increased, resulting in the suppression of the reaction. (iii) The reaction was also suppressed by lowering pH; relative quantum yield (RQY) = 1 for pH = 10, 0.2 for pH = 6.6.[15] (iv) With increasing the ratio of DMSO in the water - DMSO solvent mixture, the RQY increased (Fig. 3). The increase of the ratio of DMSO decreases the polarity of the solvent, which leads to the increase of the ratio of DMSO decreases the polarity of the solvent, which leads to the increase of the monomer concentration, thus increasing the RQY.

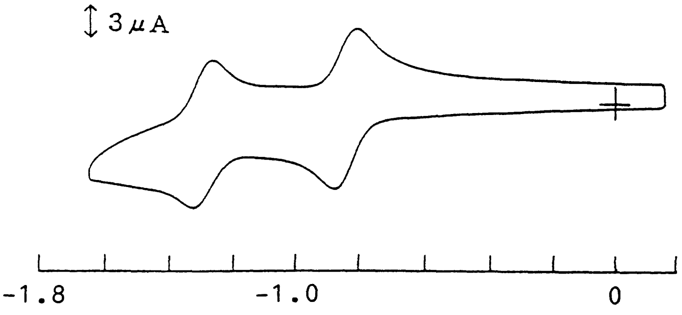


Fig. 2. The cyclic voltammogram of the complex **1** in DMSO: scan rate = 100 mV/s, [complex] = 1.0 x 10^{-3} M, [tetrabutylammonium perchlorate] = 0.1 M.

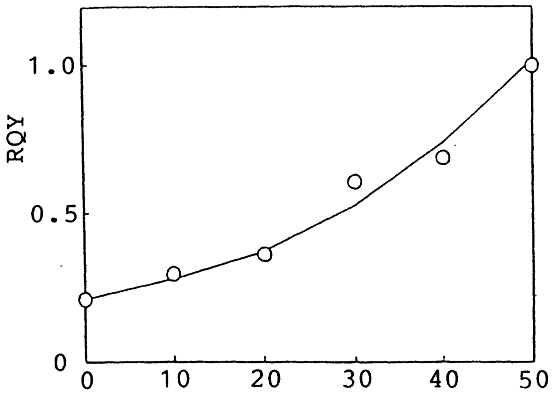


Fig. 3. The effect of DMSO on the relative quantum yield (RQY).

The quenching experiments were performed to elucidate the reaction mechanism and also compare the photo-activity of the complex **1** with that of the well-characterized ZnPc complex in the solvent mixture of water - DMSO (1 : 9 v/v) (Fig. 4). The fluorescence of the complex **1** was quenched by the addition of $MVCl_2$, but not by triethanolamine. That is, the photoreduction with the complex **1** may proceed *via* an oxidative quenching process as well as that with ZnPc.[5)] The quenching constant for the complex **1** is about half of that for ZnPc. The RQY of the complex **1** for ZnPc was also estimated to be 0.7 in the solvent mixture. Therefore, the substituents of the complex **1** have no significant effect on the quenching and the photoreaction at least in the solvent mixture.

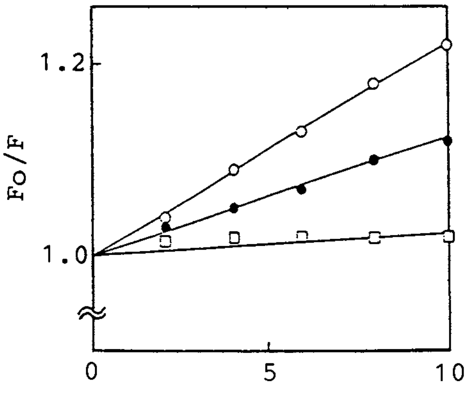


Fig. 4. Stern-Volmer Plots.[16)]
●) complex **1**, $MVCl_2$
□) complex **1**, triethanolamine
o) ZnPc, $MVCl_2$
[complex] = 1.0×10^{-5} M. Excitation was performed at the Q band peaks at room temperature.

References
1)T. Tanno, D. Wöhrle, M. Kaneko, and A. Yamada, Ber. Bunsenges. Phys. Chem., 84, 1032(1980).
2)T. Ohno, S. Kato, and N. N. Lichtin, Bull. Chem. Soc. Jpn., 55, 2753(1982).
3)T. Ohno, S. Kato, A. Yamada, and T. Tanno, J. Phys. Chem., 87, 775(1983).
4)T. Ohno and S. Kato, J. Phys. Chem., 88, 1670(1984).
5)H. Ohtani, T. Kobayashi, T. Ohno, S. Kato, T. Tanno, and A. Yamada, J. Phys. Chem., 88, 4431(1984).
6)K. Kasuga, S. Takahashi, K. Tsukahara, and T. Ohno, Inorg. Chem., 29, 354(1990).
7)A. Harriman and M.-C. Richoux, J. Photochem., 14, 253(1980).
8)A. Harriman and M.-C. Richoux, J. Chem. Soc., Faraday Trans. 2, 76, 1618(1980).
9)A. Harriman, G. Porter, and M.-C. Richoux, J. Chem. Soc., Faraday Trans. 2, 77, 1175(1981).
10)E. Adar, Y. Degani, Z. Goren, and I. Willner, J. Am. Chem. Soc., 108, 4696(1986).
11)W. O. Siegl, J. Heterocycl. Chem., 18, 1613(1981).
12)K. Kasuga and M. Tsutsui, Coord. Chem. Rev., 32, 67(1980).
13)N. Kobayashi, F. Ojima, T. Osa, S. Vigh, and C. C. Leznoff, Bull. Chem. Soc. Jpn., 62, 3469(1989).
14)D. Wöhrle, J. Gitzel, I. Okura, and S. Aono, J. Chem. Soc., Perkin Trans. 2, 1985, 1171.
15)In this study, RQY was estimated as a value to the largest one in the series.
16)F_0 and F are fluorescence intensities of the complexes in the absence of the additive and in the presence of the additive, respectively.

(Received July 10, 1991)