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COMMUNICATION

PREPARATION AND PHOTOCATALYTIC PROPERTIES OF AN AMPHIPHILIC PHTHALOCYANINATOSILICON(IV) COMPLEX HAVING METHOXO LIGANDS AT ITS AXIAL POSITIONS

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Abstract—Photo-sensitized reduction of methyl viologen in the presence of triethanolamine was studied with the use of the phthalocyaninatosilicon(IV) complex which exists as a monomer due to the axial hindrance by two methoxo groups. The yield for the radical formation of methyl viologen was low in water and extremely increased with the increase of dimethylsulfoxide in aqueous solution. This shows that the dimer formation is not a main factor for depression of the photocatalytic reaction.

Metallophthalocyanines are attractive candidates for a photosensitizer due to their intense absorption in the visible region from 600 to 700 nm which can collect energy in the solar spectrum.[1] It has been reported that a few phthalocyanine derivatives acted as the photosensitizer in organic solvents,[2,3] but a water-soluble tetrasulfophthalocyanine complex of zinc(II) hardly undergoes the photoreduction of methyl viologen (MV^{2+}) which is widely used as an electron carrier for the evolution of hydrogen gas from water[4–6] or photoreduction of carbon dioxide.[7,8] This has been hitherto explained by the reason that the complex forms its photoinactive aggregate and/or an adduct with the electron carrier in water.[4,6]

We previously reported that an amphiphilic phthalocyanine complex of zinc(II) having positively charged peripheral substituents for depression of the adduct formation with MV^{2+} (complex **1** in Fig. 1) could first catalyze the photoreduction of MV^{2+} in water but its photocatalytic activity was low.[9] This low activity was attributable to the dimer formation of complex **1**.

To confirm this we prepared a new amphiphilic phthalocyanine complex of silicon(IV) where methoxo groups were introduced at both axial positions to prevent the dimer formation (complex **2** in Fig. 1), and investigated the solvent effect of the photoreduction of $MVCl_2$ in the presence of triethanolamine (TEOA).

Complex **2** was prepared by a modified method for the preparation of complex **1**;[9] 1,3-diimino-6-(2′-dimethylaminoethoxy)isoindoline was quan-

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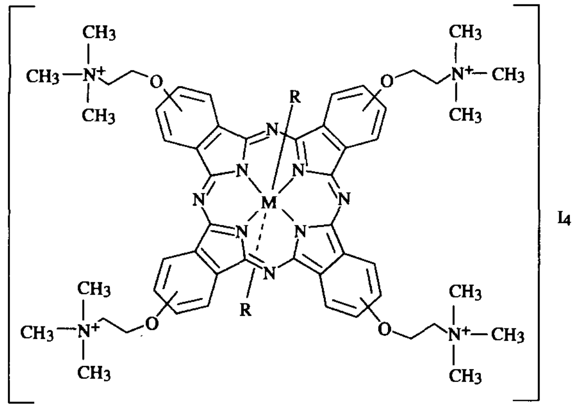

Fig. 1. Complex **1**: M = Zn; complex **2**: M = Si, R = OCH_3.

titatively prepared by bubbling ammonia gas through the methanol solution of 4-(dimethylaminoethoxy)phthalonitrile in the presence of sodium methoxide for 30 min. Then, isoindoline (2 g, 8.9 mmol) and silicon(IV) chloride (6 cm^3, 24 mmol) were stirred in 30 cm^3 quinoline at 160°C under argon for 6 h. The crude complex and sodium methoxide (3 g, 56 mmol) were subsequently stirred in 50 cm^3 methanol at room temperature for 4 h. The methoxo derivative obtained was purified by means of alumina column chromatography. By adding methyl iodide (0.3 g, 2.1 mmol) to 5 cm^3 dichloromethane solution of the methoxo derivative, complex **2** was obtained as hygroscopic dark blue powder (yield 0.2 g). Found: C, 41.4; H, 4.7; N, 10.6. Calc. for $C_{54}H_{70}N_{12}O_6I_4Si \cdot 2H_2O$: C, 41.7; H, 4.8; N, 10.8%; ^{1}H-NMR ($(CD_3)_2SO$): -1.9 (s, 6H, OCH_3), 3.4 (s, 36H, CH_3), 4.2 (s, 8H, CH_2), 5.2 (s, 8H, CH_2), 8.1 (d, 4H, ring proton), 9.2 (d, 4H, ring proton), 9.6 (m, 4H, ring proton) ppm.

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 25°C for 30 min (the cell was situated 3 cm away form the light). The light with wavelength shorter than 420 nm was cut off by the use of a Toshiba L-42 glass filter.

Complex **1** shows an absorption band at 635 nm and the shoulder at 683 nm in water, while complex **2** has a band at 687 nm (Fig. 2). The fluorescence excitation spectra of complexes **1** and **2** both show bands at 690 nm in water. It has been reported that the dimer of metallophthalocyanine shifts its absorption band to the shorter wavelength region compared with that of a monomer, and the dimer also shows emission quenching.[3,4,10] That is, complex **2** exists as the monomer in water, while complex **1** almost exists as the dimer. However, as shown in Fig. 3, the relative quantum yield (RQY)[11] for MV^+ cation radical formed by complex **2** as the photosensitizer is very small in water and increases with increase in the dimethylsulfoxide (DMSO) ratio in aqueous solution in a similar manner with complex **1**. The increase of RQY with increase in the DMSO ratio cannot be interpreted by the dimer formation of the complexes because complex **2** does not form the dimer even in water. This fact shows that dimer formation is not the main factor for decreasing the photoactivity in water.

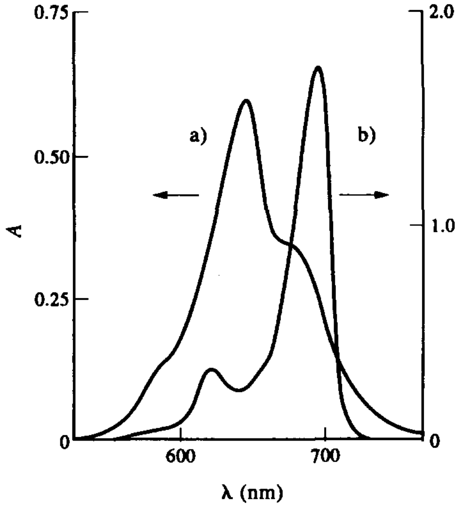

Fig. 2. Electronic spectra of complexes **1** and **2** in water: (a) complex **1**, (b) complex **2**, [complex] = 1.0×10^{-5} M.

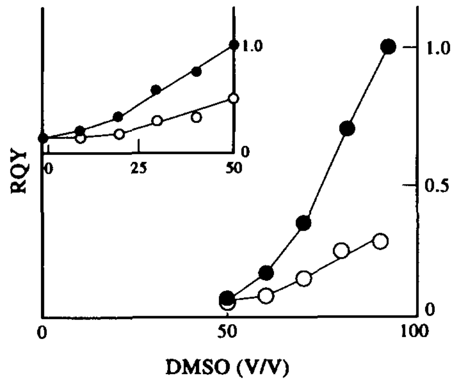

Fig. 3. Effect of the DMSO concentration on RQY: ●, complex **1**: ○, complex **2**, [complex] = 1.0×10^{-6} M, [TEOA] = 1.0×10^{-2} M, [MV^{2+}] = 5.0×10^{-4} M.

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11. RQY was estimated as a value to the largest one in the series.