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Highly Active Water-soluble Zinc Porphyrins for Photoredox Reactions

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Various attempts have been made to develop suitable redox systems for the photochemical utilization of solar energy. Recent works have shown that three-component systems containing a photosensitizer, an electron donor and an electron acceptor can be used to evolve hydrogen from water when a suitable catalyst is present [1–3]. The photosensitizers employed almost exclusively in these studies are ruthenium complexes and porphyrins. In the course of our studies, zinc tetraphenylporphyrin trisulfonate (Zn–TPPS$_3$) has been found to be a highly active photosensitizer [4, 5]. Zn–TPPS$_3$, however, was easily complexed with electron carriers like methyl viologen at high concentrations, and the complex was inactive as a sensitizer [6, 7]. Thus, Zn–TPPS$_3$ is unsuitable for use at high concentrations. It is desirable to explore other suitable photosensitizers. In this study, water-soluble zinc porphyrins with a methylene chain were found to be effective for the photoreduction of methyl viologen; the reasons for the ligand effects are also discussed.

Experimental

All materials were of analytical grade or the highest grade available. The starting material, 4-pyridyl-4′,4″,4‴-tetra(ethylcarboxyphenyl)porphyrin (H_2PyTECPP), was synthesized according to the methods described in the literature [8]. By-products were removed by the method of Dolphin and Rousseau [9]. H_2PyTECPP was then quaternized with an excess amount of α,ω-dibromoalkane at 130 °C to get 4-methylpyridyl-4′,4″,4‴-tri(ethylcarboxyphenyl)porphyrin bromide (H_2MPyTECPP). After hydroxylation of H_2MPyTECPP by excess NaOH in ethanol, zinc porphyrins with a methylene chain (Zn–PC$_3$(C$_n$Br), $n = 2$–6, Fig. 1) were synthesized by the addition of zinc acetate (*ca.* 10-fold excess).

For steady-state irradiation, a sample solution containing Zn–PC$_3$(C$_n$Br), an electron donor and methyl viologen was deaerated by repeated freeze–thaw cycles. A 200 W tungsten lamp was used as the light source. Light of wavelengths less than 390 nm was removed by a Toshiba L-39 filter.

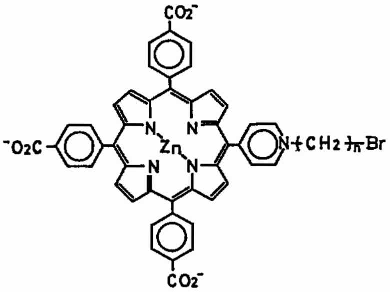

Fig. 1. Structure of Zn–PC$_3$(C$_n$Br) ($n = 2$–6).

Conventional laser flash photolysis was carried out by using an Nd-YAG laser, model DCR-2A-10 from Quanta-Ray Inc. This generated second-harmonic (532 nm) pulses of 10-ns duration with an energy of 200 mJ per pulse; a repetition rate of 10 Hz was used for the excitation of sample solutions throughout this study. The light beam, after passing through a sample cell, was collimated into the entrance slit of a monochromator (model BM 50/50 from B & M Spectronik Co.). The output signal from a photomultiplier (Hamamatsu Photonics 446) attached to the slit of the monochromator was displayed on a Hitachi oscilloscope, model V-1050F.

Results and Discussion

The electronic spectra of the compounds Zn–PC$_3$(C$_n$Br) were measured. Peak wavelengths of the spectra are summarized in Table I. When the methylene chain length becomes longer ($n = 5$ and 6), the Q-band peak wavelength shifts to longer wavelengths. When the methylene chain length is long enough, the electrons in the porphyrin ring may be significantly influenced by an interaction between the central metal ion and bromide ions connected at the end of the methylene chain.

When a sample solution containing mercaptoethanol (electron donor), Zn–PC$_3$(C$_n$Br) and methyl viologen was irradiated, formation of the reduced

TABLE I. Peak Wavelengths of Various Porphyrins

	Soret band (nm)	Q band (nm)			
H_2PyTECPP	419.8	514.8	549.6	589.2	644.6
H_2MPyTECPP	423.0	520.6	563.6	589.8	651.0
Zn–PC$_3$(C$_2$Br)	422.0	557.4	597.6		
Zn–PC$_3$(C$_3$Br)	422.8	521.0	558.4	599.4	
Zn–PC$_3$(C$_4$Br)	422.0	557.0	598.0		
Zn–PC$_3$(C$_5$Br)	423.2	558.8	600.6		
Zn–PC$_3$(C$_6$Br)	423.2	521.0	559.4	604.2	

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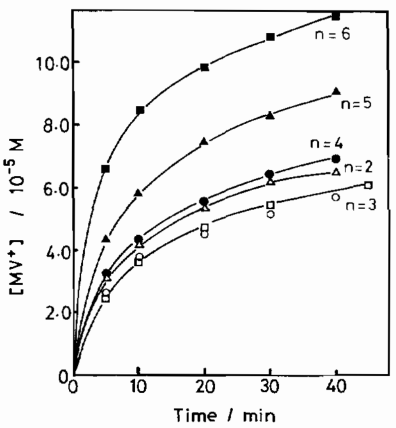

Fig. 2. Time dependence of the formation of the reduced form of methyl viologen. A sample solution containing mercaptoethanol (1.3×10^{-1} mol dm^{-3}), Zn–PC$_3$(C$_n$Br) (2.0×10^{-6} mol dm^{-3}), and methyl viologen (2.0×10^{-4} mol dm^{-3}) was irradiated at 30 °C. ○: Zn–TPPS$_3$; △: $n = 2$; □: $n = 3$; ●: $n = 4$; ▲: $n = 5$; ■: $n = 6$.

form of methyl viologen was observed (Fig. 2). The concentration of the reduced form of methyl viologen increased with the irradiation time and tended to reach a constant value. The reduction rate strongly depended on the methylene chain length. Zn–PC$_3$(C$_6$Br) and Zn–PC$_3$(C$_5$Br) were particularly highly active; the activities of compounds with n = 2–4 were almost the same as that of Zn–TPPS$_3$. In the cases of Zn–PC$_3$(C$_n$Br) with longer methylene chains, complex formation with methyl viologen may be disturbed by the steric hindrance of the methylene group.

By using laser flash photolysis, the lifetimes of the triplet states of these compounds were obtained (Table II). The fact that there was no remarkable difference in the lifetimes of the compounds strongly supports the hypotheses that the activity difference depends on the ease of complex formation between Zn–PC$_3$(C$_n$Br) and methyl viologen.

TABLE II. Lifetimes of Excited Triplet States of Zn–PC$_3$(C$_n$Br)

	τ (μs)
Zn–PC$_3$(C$_2$Br)	237
Zn–PC$_3$(C$_3$Br)	295
Zn–PC$_3$(C$_4$Br)	290
Zn–PC$_3$(C$_5$Br)	205
Zn–PC$_3$(C$_6$Br)	240

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