Unusual Behavior of Zn-TPPS$_3$ in Photosensitization

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A study of photoreduction of MV^{2+} with Zn-TPPS$_3$ showed that the reduction rate strongly depended on Zn-TPPS$_3$ concentration; it first increased with Zn-TPPS$_3$ concentration and then decreased at the higher concentration. By using laser flash photolysis the lifetimes of the triplet state of Zn-TPPS$_3$ at various concentrations were measured, and a reaction mechanism is discussed.

Photoinduced hydrogen evolution systems containing an electron donor (D), a photosensitizer (S), an electron carrier (C), and a catalyst have been studied extensively [1–3]. Metalloporphyrins and ruthenium complexes have been used as photosensitizers in these studies. In the course of our investigations [4, 5], it was found that zinc *meso*-tetraphenylporphyrintrisulfonate (Zn-TPPS$_3$) exhibits a particularly high activity for the reaction of the above system. The activity, however, strongly depends on the Zn-TPPS$_3$ concentration and at higher concentrations in Zn-TPPS$_3$ a decrease in activity was found. In this letter we want to further describe this unusual phenomenon and to discuss the reaction mechanism.

Experimental

The sample solution containing Zn-TPPS$_3$, methylviologen (MV^{2+}) and 2-mercaptoethanol (RSH) as an electron donor was deaerated by freeze–pump–thaw cycles. For steady state irradiation, 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.

Conventional laser flash photolysis was carried out by using a Nd-YAG laser, following an experimental procedure described elsewhere [6].

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Results and Discussion

When the sample solution containing Zn-TPPS$_3$, MV^{2+} and RSH was irradiated, reduction of MV^{2+} occurred. The initial reduction rate (calculated from the concentration of reduced MV^{2+} obtained after 3 min irradiation) strongly depends on the concentration of Zn-TPPS$_3$ as shown in Fig. 1, curve a. Though the reduction rate of MV^{2+} increased with Zn-TPPS$_3$ concentration at lower concentrations, it decreased at higher concentrations. Zn-TPPS$_3$ (or Zn-TPPS$_4$) has often been used as a photosensitizer at the concentrations of 10^{-4} mol dm^{-3}. At these high concentrations, Zn-TPPS$_3$ does not work effectively and the efficiency of Zn-TPPS$_3$ as a photosensitizer has thus been underestimated.

The lifetimes of the triplet state of Zn-TPPS$_3$ were measured by using laser flash photolysis at various Zn-TPPS$_3$ concentrations: results are shown in Table I. Though the lifetimes are almost the same below 7.12×10^{-4} mol dm^{-3}, they decrease at higher concentrations of Zn-TPPS$_3$. As the probability of decay by collision of the triplet state species is low under the reaction conditions, the triplet state of Zn-TPPS$_3$ will be quenched by the ground state of that species.

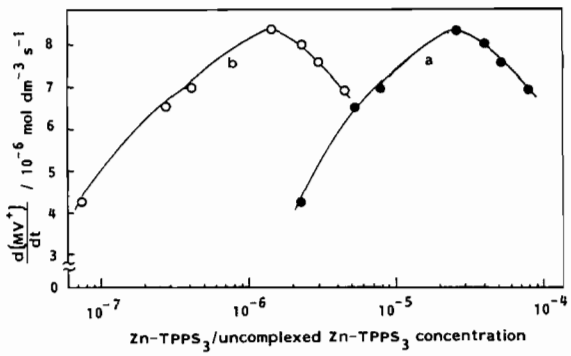

Fig. 1. Initial reduction rates of MV^{2+} *vs.* Zn-TPPS$_3$/uncomplexed Zn-TPPS$_3$ concentration. The sample solution contains Zn-TPPS$_3$, MV^{2+} (1.71×10^{-4} mol dm^{-3}) and RSH (2.19×10^{-1} mol dm^{-3}).

TABLE I. Triplet Lifetimes of Zn-TPPS$_3$ at Various Concentrations

[Zn-TPPS$_3$] (mol dm^{-3})	Lifetime (ms)
7.12×10^{-6}	1.49
1.19×10^{-5}	1.55
3.56×10^{-5}	1.74
7.12×10^{-5}	1.31
8.90×10^{-5}	0.77
1.19×10^{-4}	0.68

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When zinc 5, 10, 15, 20-tetra(4-pyridyl)porphyrin (Zn-TMPyP) was used instead of Zn-$TPPS_3$, no rate decrease at higher concentrations of Zn-TMPyP was observed. The unusual phenomenon of the concentration dependence may thus be specific for Zn-$TPPS_3$.

Another possibility might be a complex formation between Zn-$TPPS_3$ and MV^{2+}. As the complex does not work as a photosensitizer, it is the uncomplexed (free) Zn-$TPPS_3$ only which is effective in the system [7, 8]. This effective concentration of Zn-$TPPS_3$ is thus decreased by the complex formation, that when curve a in Fig. 1 is recalculated using the complex formation constant [7, 8], a relation between the reduction rate of MV^{2+} and the concentration of free Zn-$TPPS_3$ is obtained as shown in Fig. 1, curve b. As the reduction rate of MV^{2+} again decreases at higher concentrations of effective (free) Zn-$TPPS_3$, this unusual phenomenon is not explained either by complex formation.

At higher concentrations, the decrease of the effective concentration of active species is plausible by the formation of aggregated species such as dimers, trimers, and so on. If the triplet lifetimes of the aggregated species are very short like phthalocyanine dimers, these species are inert for laser flash photolysis measurement in this experimental time scale, and there may be no effect for the triplet lifetime of Zn-$TPPS_3$.

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