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Photo-induced Electron Transfer from Zn–TPPS$_3$ to Viologens

ICHIRO OKURA, SHIGETOSHI AONO

Department of Chemical Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo, 152, Japan

MIKIO HOSHINO and AKIRA YAMADA

The Institute of Physical and Chemical Research, Hirosawa, Wako-shi, Saitama, 351, Japan

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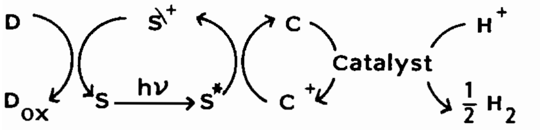
Photochemical redox systems have been proposed for the solar energy utilization [1]. The system as shown in the following scheme (1), including a photosensitizer (S), an electron donor (D), and an electron carrier (C) has been able to evolve hydrogen from water when a suitable catalyst is applied.



(1)

As photosensitizers, ruthenium complexes and metalloporphyrins have been employed extensively in these studies. In the course of our studies [2], zinc meso-tetraphenylporphyrintrisulfonate (Zn–TPPS$_3$) exhibits particularly high activity for the reaction of system (1). To clarify the reason why Zn–TPPS$_3$ is so active, kinetic studies on the triplet state of Zn–TPPS$_3$ were carried out by laser flash photolysis.

Experimental

Viologen propylsulfonate (PVS) was prepared according to the literature [3]. The solution which consisted of Zn–TPPS$_3$ and viologen (if included) was deaerated by repeated freeze–pump–thaw cycles. Conventional laser photolysis was carried out at room temperature by using a Nd-YAG laser, model HY-500 from JK Lasers Ltd., equipped with the second, third and fourth harmonic generators. The second harmonic (532 nm), *ca.* 100 mJ cm^{-2} and flash duration of 20 ns, was used for excitation of the sample solutions throughout this study. Light beams from a xenon lamp (Ushio UXL-150 D, 150 W) were intensified by a factor of *ca.* 20 during the detection of the transient spectra. Transient spectra having life-times longer than 200 μs were measured without intensification of the xenon lamp. The light beam, after passage through a sample cell, came into the entrance slit cell of a monochromator (Model NC-20 N from Ritsu Appl. Opt. Co.). The output from a Hamamatsu photomultiplier (R 758) attached to

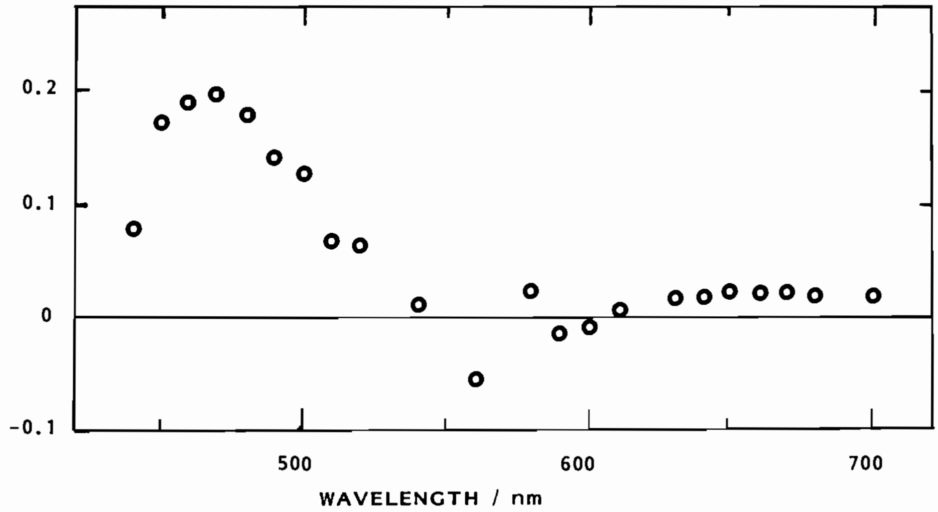


Fig. 1. Transient difference spectrum for Zn–TPPS$_3$ in deaerated aqueous solution observed at 1.5 μs after a laser flash.

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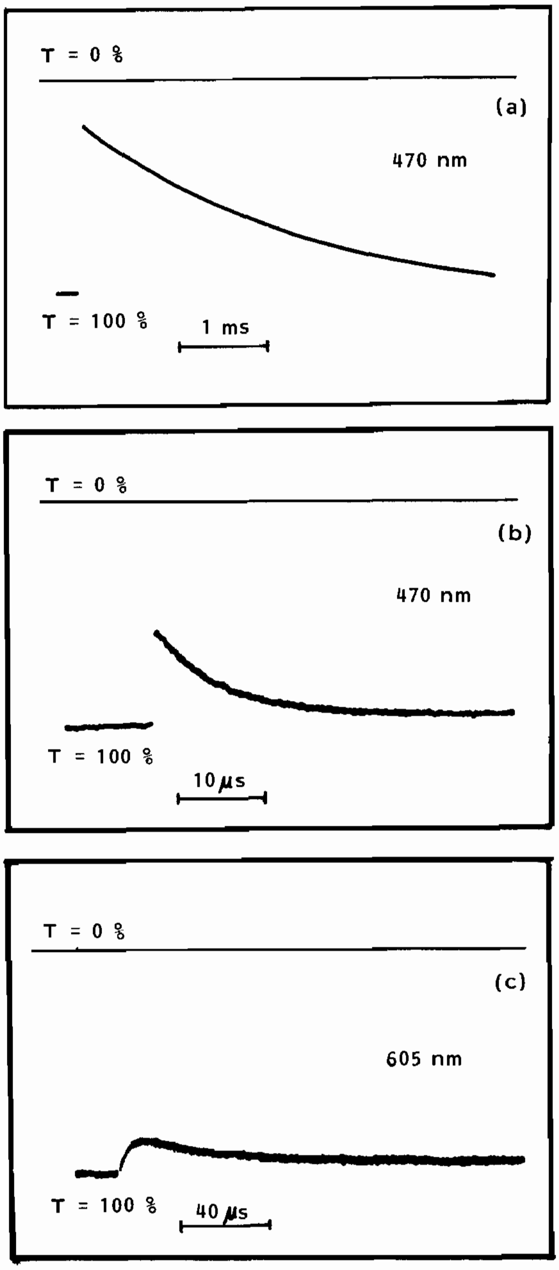

Fig. 2. Oscilloscope traces obtained from the laser flash photolysis of aqueous solution of (a) Zn–TPPS$_3$ (3.03 × 10^{-5} mol dm^{-3}), and (b, c) Zn–TPPS$_3$ (3.03 × 10^{-5} mol dm^{-3}) + methylviologen (1.21 × 10^{-5} mol dm^{-3}).

the exit of the monochromator was displayed on a Tektronix Model 7904 oscilloscope.

Results and Discussion

Figure 1 shows the transient spectrum of Zn-TPPS$_3$, which was identified as the spectrum of the photoexcited triplet state of Zn–TPPS$_3$ by

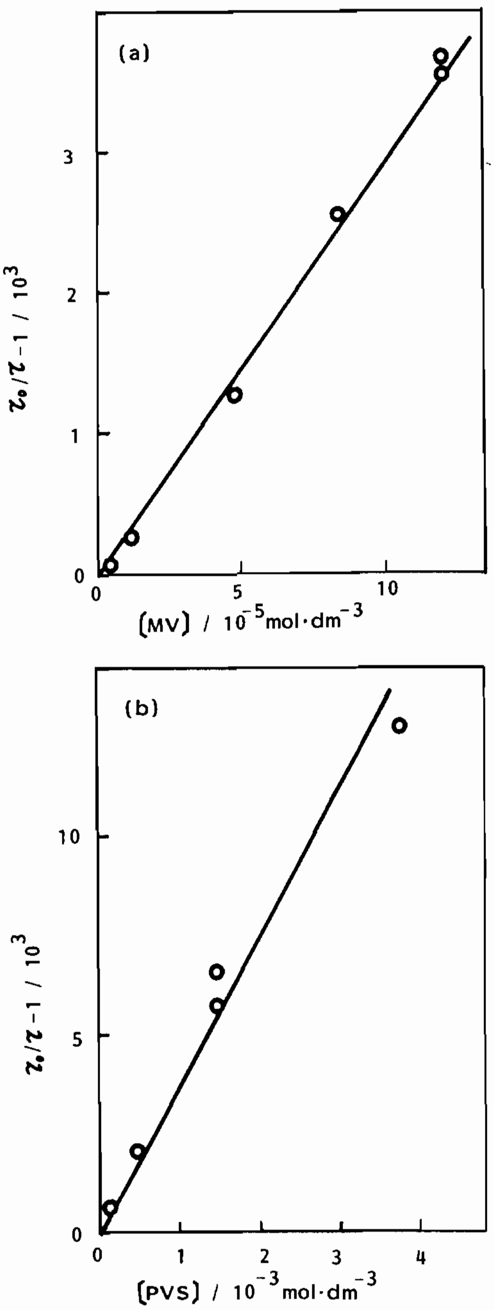

Fig. 3. Stern–Volmer plots of (a) Zn–TPPS$_3$–methylviologen system, and (b) Zn–TPPS$_3$–PVS system.

similarity with that of Zn–TMPyP reported previously [4]. Figure 2-a shows the oscilloscope trace monitored at 470 nm after a laser flash. From this figure the lifetime of the triplet state of Zn–TPPS$_3$ was obtained to be 1.6 ms which was markedly long compared with other photosensitizers, *e.g.*, 0.65 μs in the case of Ru(bpy)$_3^{2+}$ [5]. In the presence of methylviologen the decay rate of the transient spectrum with λ_{max} = 470 nm increased, as shown

TABLE I. Quenching Rate Constants and Relative Back Reaction Rate Constants.

Quencher	$k_q/dm^3\ mol^{-1}\ s^{-1}$	k_b
Methylviologen	$(1.5 \pm 0.3) \times 10^{10}$	100
PVS	$(2.3 \pm 0.3) \times 10^{9}$	14.2

in Fig. 2-b. From the Stern–Volmer plot (Fig. 3-a), the quenching rate constant, k_q, of the following reaction was determined as 1.5×10^{10} dm^3 mol^{-1} s^{-1}, which was close to that for the diffusion-controlled process:

$$\text{Zn–TPPS}_3^* + MV^{2+} \longrightarrow \text{Zn-TPPS}_3^+ + MV^{\dot{+}} \qquad (2)$$

From the above results the high activity of Zn–TPPS$_3$ as a photosensitizer is due to the long lifetime of the triplet state of Zn–TPPS$_3$ and also to the efficient electron-transfer from the triplet Zn–TPPS$_3$ to methylviologen.

At the same time, the transient spectrum at λ_{max} = 605 nm (which is assigned to methylviologen cation radical) initially increased and then decreased gradually with time, as shown in Fig. 2-c. From the decay of methylviologen cation radical and the molar absorption coefficient of $MV^{\dot{+}}$ (ϵ_{605} = 11000 mol^{-1} cm^{-1}) the relative back reaction rate constant, k_b, as shown in the following equation can be derived:

$$\text{Zn–TPPS}_3^+ + MV^{\dot{+}} \longrightarrow \text{Zn–TPPS}_3 + MV^{2+} \qquad (3)$$

When PVS was used instead of methylviologen, similar phenomena were observed, and k_q and k_b were obtained as listed in Table I. The difference of both constants for methylviologen and PVS could be explained by electrostatic effect between the triplet state of Zn–TPPS$_3$ and viologens. The larger k_q of methylviologen than that of PVS denotes that positively charged methylviologen is more favorable to attract negatively charged Zn–TPPS$_3^*$. Since the reduced form of PVS has negative charge, the back reaction of oxidized Zn–TPPS$_3$ with the reduced form of PVS would be suppressed by strong electrostatic repulsion.

References

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