Inorganica Chimica Acta, *201* (1992) 11–13

Inorganica Chimica Acta

LETTER

Photoinduced intramolecular electron transfer in viologen-linked zinc porphyrins in acetonitrile

Ichiro Okura* and Hideyuki Hosono

Department of Bioengineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227 (Japan)

(Received March 17, 1992)

Viologen-linked porphyrins have been synthesized to develop suitable redox systems for the photochemical utilization of solar energy [1–8]. As reported previously we prepared a series of two compounds, viologen-linked porphyrins connected with viologen at the 3 (*meta*) and 4 (*para*) positions of the pyridine ring (the structures are shown in Fig. 1) [7–9]. A comparison of these compounds in the intramolecular electron transfer process was made in this paper and the solvent effect was also discussed.

The preparation and the characterization of these compounds have been reported previously [7–9]. The luminescence intensity was measured using a Hitachi-850 spectrometer. The excitation wavelength was 500 nm. The lifetime of the luminescence was measured using a Horiba NAES-500 spectrometer. The lifetimes of the photoexcited triplet states of the viologen-linked zinc porphyrins were measured by laser flash photolysis. Laser flash photolysis was carried out by the method described elsewhere [3].

The transient difference spectrum of p-ZnPC$_5$V in deaerated acetonitrile (MeCN) solution, which is attributed to the T–T absorption of the excited triplet state of the compound, was observed as shown in Fig. 2. As indicated by closed circles, the T–T absorption spectrum of p-ZnPC$_5$V at 0.3 μs after the excitation changed from the initial T–T absorption spectrum (open circles) and the absorption at around 600 nm increased. The results show that the photoexcited triplet state of zinc porphyrin of p-ZnPC$_5$V is quenched by the bonded viologen and the electron transfers from the porphyrin to the bonded viologen and the reduced form of viologen is formed. In the case of viologen free zinc porphyrin, p-ZnPC$_5$, the T–T absorption at 0.3 μs after the excitation was the same as the initial T–T absorption spectrum. The transient spectrum as indicated by closed circles in Fig. 2 should be attributed to the one-electron oxidation product of zinc porphyrin and reduced viologen, which may be produced through reaction (1).

$$^3(p\text{-ZnPC}_5)^* - \text{V} \longrightarrow (p\text{-ZnPC}_5)^+ - \text{V}^- \qquad (1)$$

The decay of the T–T absorption of p-ZnPC$_5$, as shown in Fig. 3(a), obeyed first-order kinetics and the lifetime of the photoexcited triplet state was estimated to be about 100 μs by the first-order plot. In the case of p-ZnPC$_5$V, the decay of the T–T absorption is shown in Fig. 3(b). Compared with the T–T absorption of p-ZnPC$_5$, the triplet lifetime of p-ZnPC$_5$V became shorter, indicating that the triplet state is quenched by the bonded viologen. As shown in Fig. 3(c), the decay of the transient absorption observed at 590 nm, at which the reduced viologen has the characteristic absorption band, increased rapidly and then decreased gradually. This result is consistent with eqn. (2).

$$(p\text{-ZnPC}_5)^+ - \text{V}^- \longrightarrow p\text{-ZnPC}_5 - \text{V} \qquad (2)$$

The lifetime of the charge separated species was obtained from the decay of the transient absorption at 590 nm as 1.17 μs. The decay profile of the T–T absorption of the *meta* compounds was almost the same as those of the *para* compounds. The intramolecular electron transfer rate constants (k_{et}), the back electron transfer rate constants (k_{b}), and the lifetimes of the charge separated species (τ) are calculated as shown in Table 1. A comparison of the kinetic parameters between p-ZnPC$_5$V and m-ZnPC$_5$V, shows that the k_{et} and k_{b} values of the *meta* compounds are a little bit larger than those of the *para* compounds in both solvents DMSO and MeCN. In the *meta* compound the bonded viologen can come close to the porphyrin ring by conformational change compared with the *para* compound and the electron may transfer more easily. k_{et} and k_{b} values also strongly depend on the solvent used. When a solvent with a lower dielectric constant, which can solvate easily, was used, larger k_{et} and k_{b} values were obtained, indicating that the coordinated solvent disturbs the electron transfer.

The fluorescence spectra of p-ZnPC$_5$ and p-ZnPC$_5$V were recorded. Although the shapes of the fluorescence spectra of these compounds are almost the same, the fluorescence intensities are strongly affected by the bonded viologen. In these experiments the concentration of the sample solution was adjusted in order to keep the absorbance at the excited wavelength (500 nm) constant for all sample solutions. The relative fluorescence intensity of p-ZnPC$_5$ was much smaller compared with that of p-ZnPC$_5$V (the relative ratio was 0.243 in DMSO, 0.139 in MeCN), indicating that the

---

*Author to whom correspondence should be addressed.

0020-1693/92/$5.00

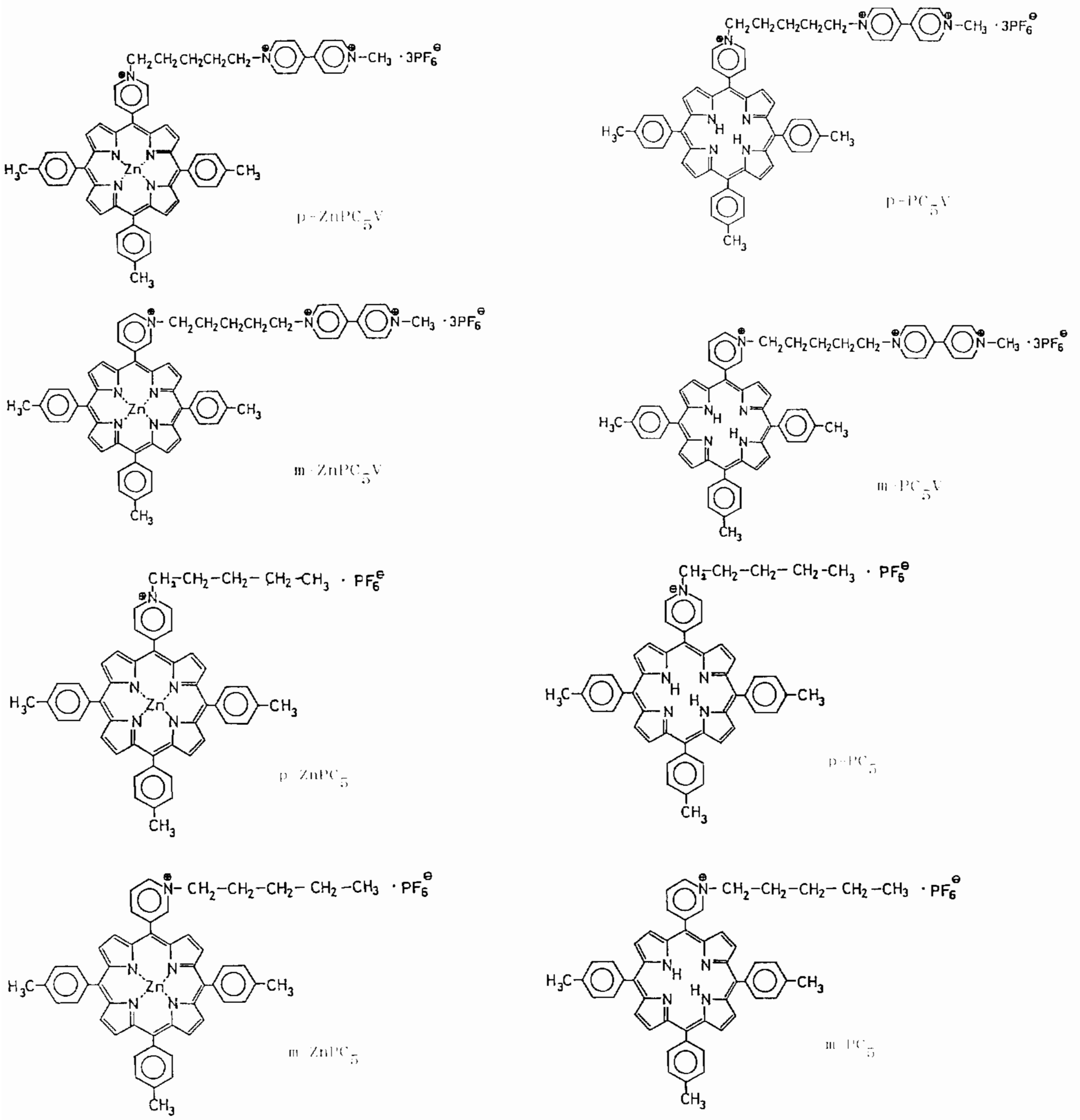

Fig. 1. Structures of viologen-linked porphyrins.

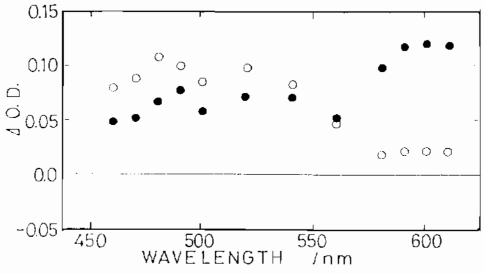

Fig. 2. Difference transient absorption spectra for p-ZnPC$_5$V obtained immediately (○) and 0.3 μs (●) after excitation.

photoexcited singlet state is quenched by the bonded viologen in p-ZnPC$_5$V.

In the case of the *meta* compound, the relative fluorescence intensity of m-ZnPC$_5$V was 0.248 in DMSO and 0.152 in MeCN. Though there is not much difference between the relative fluorescence intensities of p-ZnPC$_5$V and m-ZnPC$_5$V, these values are much smaller than those of metal free compounds such as 0.820 for p-PC$_5$V and 0.716 for m-PC$_5$V in DMSO. These results show that the photoexcited singlet state of viologen-linked zinc porphyrins is more efficiently quenched by the bonded viologen compared with viologen-linked metal free porphyrins.

In the case of p-ZnPC$_5$, the fluorescence decay obeyed first-order kinetics. Its fluorescence decay profile was found to be described by a single exponential decay function and a lifetime of 1.08 ± 0.02 ns in DMSO and

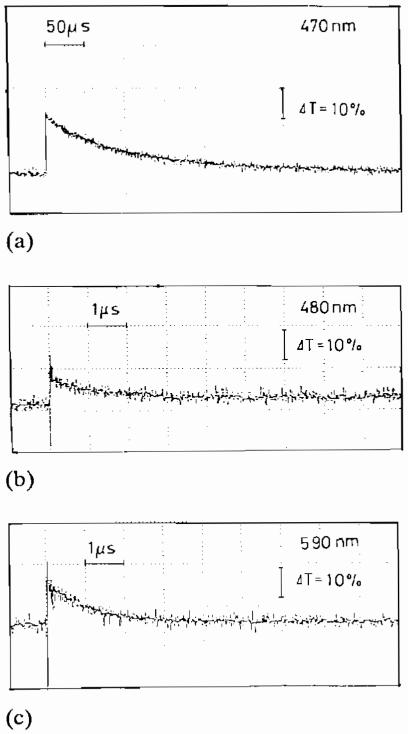

Fig. 3. Typical oscillograms obtained from laser flash photolysis observed at 470 (a, b) and 605 (c) nm. (a) p-ZnPC$_5$, (b, c) p-ZnPC$_5$V.

TABLE 1. Intramolecular electron transfer rate constant (k_{et}), back electron transfer rate constant (k_b) and lifetime of charge separated species

	k_{et} (s^{-1})	k_b (s^{-1})	τ (μs)	Solvent
p-ZnPC$_5$V	5.52×10^6	8.05×10^5	1.25	DMSO
m-ZnPC$_5$V	9.58×10^6	1.00×10^6	1.00	DMSO
p-ZnPC$_5$V	3×10^7	8.62×10^5	1.17	MeCN
m-ZnPC$_5$V	1×10^8	1.06×10^6	0.95	MeCN

TABLE 2. Fluorescence lifetime of viologen-linked zinc porphyrins

	τ (ns)	Solvent
p-ZnPC$_5$	1.08 ± 0.02	DMSO
p-ZnPC$_5$V	0.55 ± 0.11	DMSO
m-ZnPC$_5$	1.47 ± 0.02	DMSO
m-ZnPC$_5$V	0.53 ± 0.13	DMSO
p-ZnPC$_5$	1.07 ± 0.01	MeCN
p-ZnPC$_5$V	0.33 ± 0.02	MeCN
m-ZnPC$_5$	1.46 ± 0.02	MeCN
m-ZnPC$_5$V	0.14 ± 0.02	MeCN

TABLE 3. Intramolecular electron transfer rate constant in viologen-linked zinc porphyrins

	k_e (s^{-1})	Solvent
p-ZnPC$_5$V	9.02×10^8	DMSO
m-ZnPC$_5$V	1.06×10^9	DMSO
p-ZnPC$_5$V	2.10×10^9	MeCN
m-ZnPC$_5$V	6.51×10^9	MeCN

1.07 ± 0.01 ns in MeCN was obtained. Though the fluorescence decay profile also obeyed single exponential decay in the case of viologen-linked porphyrins, there are some deviations (about 25%). As summarized in Table 2, the lifetimes become larger for porphyrins with viologen. Therefore, the fluorescence decay may arise from the direct quenching of the photoexcited singlet state of the porphyrin by the linked viologen.

From the lifetimes shown in Table 2, intramolecular electron transfer rate constants (k_e) were calculated by the following equation.

$$k_e = 1/\tau - 1/\tau_0$$

where τ_0 is the fluorescence lifetime of the viologen free porphyrin. The results are shown in Table 3. A comparison of k_e values between p-ZnPC$_5$V and m-ZnPC$_5$V, shows that the k_e value of the *meta* compound is a little bit larger than that of the *para* compound in both solvents. In the *meta* compound the bonded viologen can come more closely to the porphyrin ring by steric effect compared with the *para* compound and the electron may transfer more easily.

Acknowledgement

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas 'Bioinorganic Chemistry' (No. 03241208) from the Ministry of Education, Science and Culture, Japan.

References

1 A. Harriman, G. Porter and A. Wilowska, *J. Chem. Soc., Faraday Trans. 2, 80* (1984) 191.
2 S. Aono, N. Kaji and I. Okura, *J. Chem. Soc., Chem. Commun.*, (1986) 170.
3 I. Okura, N. Kaji, S. Aono and T. Nishisaka, *Bull. Chem. Soc. Jpn., 60* (1987) 1243.
4 R. J. McMahon, R. K. Force, H. H. Patterson and M. S. Wrighton, *J. Am. Chem. Soc., 110* (1988) 2670.
5 S. Aono, N. Kaji and I. Okura, *J. Mol. Catal., 45* (1988) 175.
6 P. K. Force, R. J. McMahon, J. Yu and M. S. Wrighton, *Spectrochim. Acta, Part A, 45* (1989) 23.
7 S. Noda, H. Hosono, I. Okura, Y. Yamamoto and Y. Inoue, *J. Chem. Soc., Faraday Trans., 86* (1990) 811.
8 S. Noda, H. Hosono, I. Okura, Y. Yamamoto and Y. Inoue, *J. Photochem. Photobiol. A, 53* (1990) 423.
9 I. Okura and H. Hosono, *Inorg. Chim. Acta, 189* (1991) 145.