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LETTER

Preparation and characterization of viologen-linked zinc porphyrins

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Various viologen-linked porphyrins have been synthesized to develop suitable redox systems for the photochemical utilization of solar energy [1–8]. As the compound serves as a photosensitizer and an electron carrier in the same molecule, simpler redox systems for solar energy conversion can be established. To improve the quantum yield, viologen-linked porphyrins with longer lifetimes of the charge separated species are desired. In this paper we describe the preparation and characterization of viologen-linked zinc porphyrins with longer charge separated lifetimes.

All the materials were of analytical grade or the highest grade available.

The structures of viologen-linked zinc porphyrins are shown in Fig. 1. For the preparation of p-ZnPC$_n$V the starting material 5-(4-pyridyl)-10,15,20-tritolylporphyrin (PyTP) was synthesized and the by-products were removed as described in the literature [9, 10]. PyPT was then quaternized with an excess of α,ω-dibromoalkane at 130 °C. The quaternized porphyrin and a 100-fold molar excess of 1-methyl-1'-bromoalkylbipyridinium were stirred at 80 °C in DMF for 48 h to obtain viologen-linked metal free (protonic) porphyrins (p-PC$_n$V). The protons of the porphyrin ring were replaced by metal cations as follows. To the solution of p-PC$_n$V (3.98×10^{-5} mol) dissolved in 100 ml of MeCN, zinc chloride (1.84×10^{-4} mol) was added and stirred at 30 °C for 48 h without light. After the removal of MeCN by evaporation, the solid was washed with water to remove excess zinc chloride. The solid was dissolved in acetone and $(C_2H_5)_4NCl$ was added to replace the counter anion by Cl^-. The desired product should be insoluble in acetone with Cl^-. The precipitate was collected and dissolved in MeOH and was developed in a Sephadex LH-20 column (1.8×10 cm, developer: $(C_2H_5)_4NCl$–MeOH solution) without light. After the development the solution corresponding to the second band was collected and the MeOH removed by evaporation. The solid was washed with water to remove $(C_2H_5)_4NCl$, and the solid was dissolved in MeOH again and NH_4PF_6 (0.2 g) was added to replace the counter anion with PF_6^-. The precipitate was collected, washed with MeOH, and then dried under vacuum at room temperature. The purity of the products was established by ^{1}H NMR.

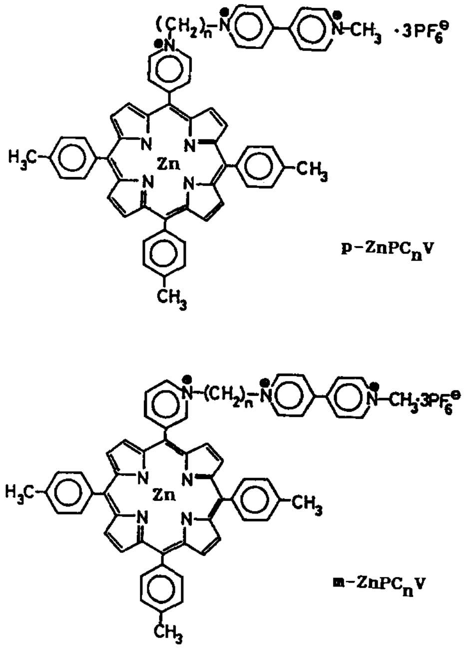

Fig. 1. Structures of viologen-linked zinc porphyrins.

In the case of the preparation of m-ZnPC$_n$V, 5-(3-pyridyl)-10,15,20-tritolylporphyrin was used instead of 5-(4-pyridyl)-10,15,20-tritolylporphyrin as the starting material.

The molecular structure of the synthesized viologen-linked porphyrins was characterized by ^{1}H NMR. The compounds were dissolved in dimethyl-d$_6$ sulfoxide (DMSO-d$_6$) for the NMR samples and the concentrations of the samples were 10 mM for p-ZnPC$_n$V and m-ZnPC$_n$V. Chemical shifts were referenced to the residual solvent peak, which in turn was calibrated against tetramethylsilane. As an example the 200 MHz ^{1}H NMR spectrum of m-ZnPC$_n$V in DMSO-d$_6$ at 27 °C is given in Fig. 2. Each absorption peak was identified as indicated in Fig. 2. The spectrum indicates the purity of the sample prepared.

The absorption spectra of p-ZnPC$_n$V and m-ZnPC$_n$V were similar to those of viologen-free zinc

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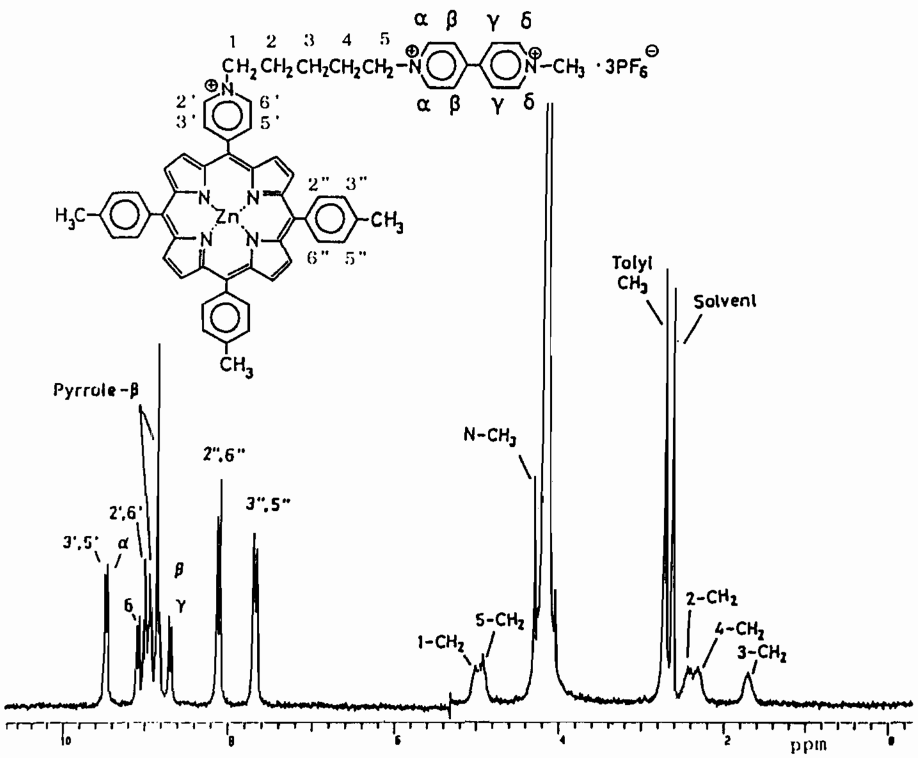

Fig. 2. 200 MHz ^1H NMR spectrum of p-ZnPC$_5$V in DMSO-d$_6$ at 27 °C. The signal assignment is given with the spectrum.

TABLE 1

Peak wavelength of various viologen-linked and viologen-free porphyrins in DMSO

	Soret band (nm)		Q band (nm)	
p-ZnPC$_5$	432 (244000)[a]	525 (4200)	563 (18100)	611 (10300)
p-ZnPC$_5$V	431 (276000)	526 (4100)	563 (18200)	612 (10900)
m-ZnPC$_5$	432 (371000)	523 (3800)	562 (21200)	603 (8900)
m-ZnPC$_5$V	432 (358000)	523 (3900)	562 (20800)	603 (9100)

[a] Absorption coefficient (M^{-1} cm^{-1}) given in parentheses.

porphyrins (Table 1), indicating the absence of any ground state electronic interaction between the porphyrin ring and the bonded viologen.

The lifetimes of the photoexcited triplet states of p-ZnPC$_n$V and m-ZnPC$_n$V were measured by laser flash photolysis. Laser flash photolysis was carried out by the method described elsewhere [3]. The T–T absorption decay obeyed first-order kinetics. From the slopes of their first-order plots, the lifetimes of the triplet state of these compounds were obtained, e.g. *c*. 100 μs for viologen-free zinc porphyrins and *c*. 0.1 μs for p-ZnPC$_n$V and m-ZnPC$_n$V, indicating that the triplet state of the viologen-linked porphyrins was quenched by the linked viologen. The lifetimes of the charge separated species (porphyrin cation and reduced viologen) were *c*. 1 μs. By using viologen-linked zinc porphyrins the formation of relatively long charge separated species was accomplished.

The study of the photochemical properties of the newly synthesized viologen-linked zinc porphyrins is now being investigated.

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