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^{1}H NMR Conformational Study of Viologen-Linked Porphyrins

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Novel porphyrins to which the viologen is linked (*m*-PC*n*V) were synthesized. The linkage methylene chain between the porphyrin and the bipyridine moieties was systematically changed from $(CH_2)_3$ to $(CH_2)_6$. The molecular structure of *m*-PC*n*V was characterized by ^{1}H NMR in some detail. The orientation of the viologen with respect to the porphyrin plane in *m*-PC*n*V was semiquantitatively estimated from the porphyrin ring current induced chemical shift changes on the resonances from the viologen moiety. The NMR conformational analyses on *m*-PC*n*V in dimethyl sulfoxide and acetonitrile clearly revealed the effect of the solvent on its molecular structure.

Porphyrins to which a variety of electron acceptor units are covalently bonded have been investigated intensively to gain insight into the intramolecular electron transfer between the porphyrin and the viologen which results in the generation of a high-energy charge-separated state that has a potential of various applications.[1—7] The intramolecular electron transfer process has been clearly detected in various covalently linked porphyrin–viologen molecules by fluorescence quenching techniques or lifetime measurements[1,5,6] and more directly by resonance Raman spectroscopy.[3] Electron-transfer quenching of the photoexcited porphyrin by the linked viologen was found to depend on solvent and the length of linkage between the porphyrin and viologen.[1] Although the photoinduced electron-transfer process occurs during the lifetime of the excited state of porphyrin which is on nanosecond time scale, it would be of interest to characterize the ground state molecular structure of those porphyrin derivatives and to relate those structures to the rate of the intramolecular electron transfer.

We have synthesized novel porphyrins covalently linked to viologen (*m*-PC*n*V, Fig. 1). The length of the methylene chain ($\left(\!-CH_2\!-\right)_n$) between the porphyrin and bipyridine was systematically changed from n=3 to n=6 to investigate the effect of the methylene chain length on the molecular structure which in turn determines the spatial relationship between the porphyrin ring and the bipyridine moiety of the viologen. The solution structure of *m*-PC*n*V was investigated using ^{1}H NMR. The individual resonances have been completely and unambiguously assigned by the combined use of ^{1}H–^{1}H two-dimensional chemical shift correlated spectroscopy (COSY) and two-dimensional nuclear Overhauser effect spectroscopy (NOESY). Based on the porphyrin ring current induced chemical shift,[2,8—11] a spatial relationship between the porphyrin ring and the bipyridine moiety of the viologen in *m*-PC*n*V was semiquantitatively determined. Analyses on the porphyrin ring current induced shifts in terms of the position of a nucleus with respect to the porphyrin plane require appropriate model compound which, ideally, possesses all structure features present in *m*-PC*n*V but the porphyrin ring current, because the induced chemical shift change originates solely from the magnetic anisotropy due to the magnetic dipole arising from the porphyrin ring current. We therefore synthesized the compounds,

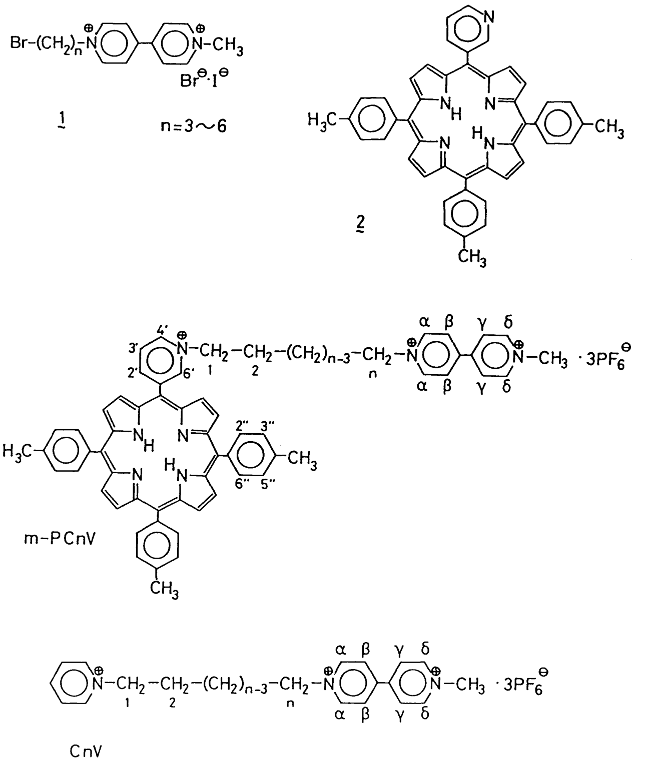

Fig. 1. Molecular structures of 1-methyl-1′-(ω-bromoalkyl)-4,4′-bipyridinium salt (**1**), 5-(3-pyridyl)-10,15,20-tritolylporphyrin (**2**), viologen-linked porphyrin synthesized (*m*-PC*n*V), and model compounds (C*n*V). The numbering systems for *m*-PC*n*V and C*n*V are shown with the structures.

C*n*V, shown in Fig. 1 as models for *m*-PC*n*V. Their NMR spectra were characterized and the difference in the observed chemical shifts between *m*-PC*n*V and C*n*V for the corresponding viologen proton resonances is discussed in terms of the spatial orientation of the viologen moiety with respect to the porphyrin plane in *m*-PC*n*V molecule. Conformational analyses were carried out in two different solvents, i.e., dimethyl sulfoxide and acetonitrile, to investigate the effect of solvent on the molecular structure of *m*-PC*n*V. The difference in conformation of *m*-PC*n*V in different solvents which in turn results in placing the bipyridine moiety of the viologen at spatially different position with respect to the porphyrin plane was clearly reflected in the porphyrin ring current induced shift changes for the viologen proton resonances. Although the linkage methylene chain is flexible, the bipyridine moiety of the viologen does not appear to fold back above the porphyrin plane in *m*-PC*n*V studied here.

Experimental

Materials; All chemicals and solvents were of reagent grade and were obtained from commercial sources.

Syntheses; The viologen-linked porphyrins with a series of methylene chain length (*m*-PC*n*V) were synthesized from the coupling reaction of **1** and **2** (Fig. 1) which were prepared using the literature procedures.[12,13] **1** (0.3 mM; 1 M=1 mol dm^{-3}) and **2** (0.6 mM) were reacted in *N*,*N*-dimethylformamide at 80 °C for 48 hours and then toluene (300 ml) was added to precipitate the product and unreacted **2**. The solids were filtered and then washed with toluene and distilled water. The products were dissolved in MeOH and NH$_4$PF$_6$ (0.2 g) was added to replace the counter anion to PF$_6^-$. The desired products should be insoluble in MeOH with PF$_6^-$. The precipitate is collected, washed with MeOH, and then dried under vacuum at room temperature for 1 hour. The yield was about 30%. The purity of the products was established from their ^{1}H NMR spectra.

Model compounds, C*n*V, were synthesized using the reaction of **1** with pyridine in MeOH for 8 hours followed by the replacement of the counter anion to PF$_6^-$ using NH$_4$PF$_6$. C*n*V was filtered and then washed by MeOH. Solids were dried under vacuum at room temperature.

NMR Measurements; The compounds were dissolved in either dimethyl-*d*$_6$ sulfoxide (DMSO-*d*$_6$) or acetonitrile-*d*$_3$ (MeCN-*d*$_3$) for the NMR samples and the concentrations of the samples were 10 and 30 mM for *m*-PC*n*V and C*n*V, respectively. 500 MHz ^{1}H NMR spectra were recorded on a JEOL GSX-500 FT-NMR spectrometer. Typical spectra were recorded with 16 transients, 32 k data points over a 5000 Hz spectral width, and 5.3 μs 90° pulse. Chemical shifts were referenced to the residual solvent peak, which in turn was calibrated against tetramethylsilane, TMS, and are reported in parts per million, ppm, referenced to TMS.

COSY and NOESY spectra were obtained using the standard pulse sequences[14] and data processing procedures. The mixing time of 700 ms was used for NOESY.

Results and Discussion

^{1}H NMR Signal Assignment. 500 MHz ^{1}H NMR spectrum of *m*-PC4V in MeCN-*d*$_3$ at 27 °C is illustrated in Fig. 2. The spectrum indicates the purity of the sample prepared. The unambiguous ^{1}H signal assignments are obtained from ^{1}H–^{1}H COSY and NOESY spectra shown in Figs. 3 and 4, respectively. The scalar coupling connectivities in the COSY

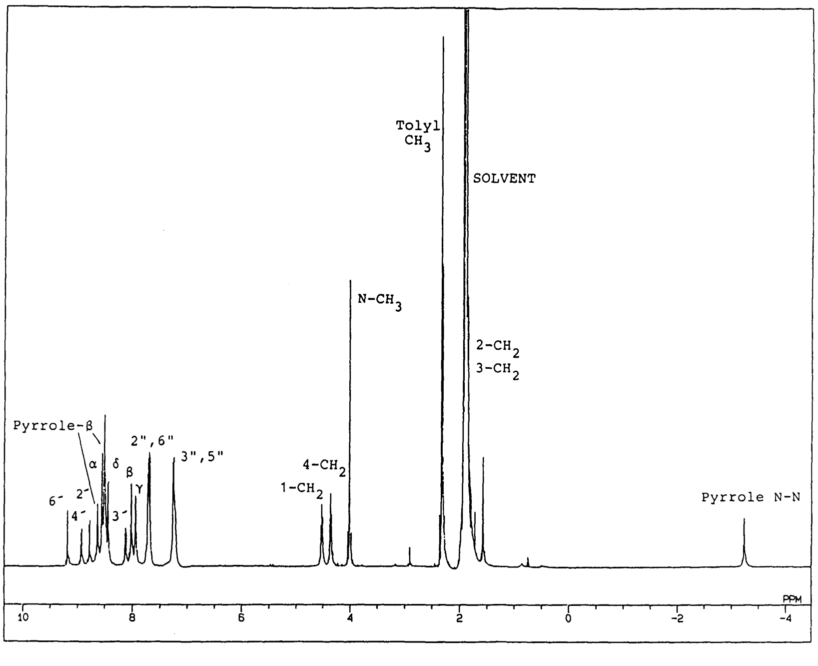

Fig. 2. 500 MHz ^{1}H NMR spectrum of *m*-PC4V in MeCN-*d*$_3$ at 27 °C. The signal assignment is attached with the spectrum.

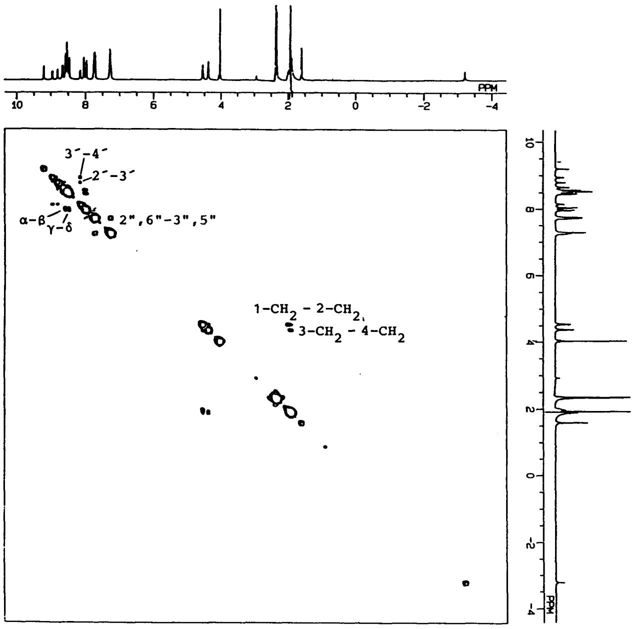

Fig. 3. COSY spectrum of *m*-PC4V in MeCN-d_3 at 27 °C.

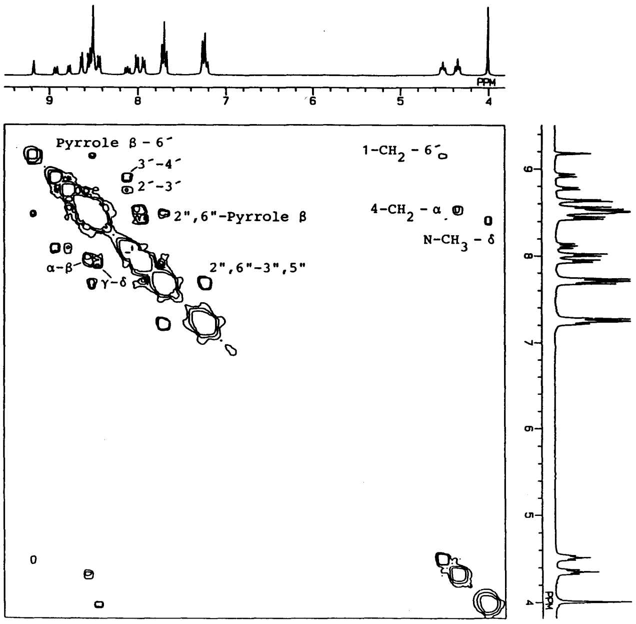

Fig. 4. A portion of NOESY spectrum of *m*-PC4V in MeCN-d_3 at 27 °C.

spectrum establish most of the assignment but the differentiation of the bipyridine, terminal methylene, or tolyl proton resonances was hampered by the discontinuity of spin–spin coupling network. The dipolar coupling connectivities in NOESY spectrum allow the specific assignment of those resonances. The singlet N–CH$_3$ resonance at δ 4.14 exhibits a cross-peak with a doublet resonance at δ 8.57 in the NOESY spectrum, indicating the assignment of this resonance to the bipyridine δ proton. The terminal methylene proton resonances can be differentiated using the connectivities with the pyridine 4′ or/and 6′ and bipyridine α proton resonances and the tolyl proton can be specifically assigned from the NOESY cross-peak with the singlet tolyl CH$_3$ resonance. The unambiguous assignments of all the resonances for the other *m*-PC*n*V prepared were similarly obtained and the chemical shift values are summarized in Tables 1 and 2. The solvent dependence of the chemical shifts of *m*-PC*n*V ^{1}H resonance is apparent. But, in a given solvent, the shifts of the pyridine resonances as well as the pyrrole N–H proton resonances were found to be essentially independent of the length of the methylene chain of *m*-PC*n*V. The fine structure of the line shape of the resonances arising from the tolyl 2″, 6″ and 3″, 5″ protons was altered by the length of the methylene chain, indicating small deviation in the chemical shift among the resonances from the three tolyl groups on the molecule. The shift values of the tolyl resonances are interpreted in terms of both the orientation of the aromatic ring with respect to the porphyrin plane and the asymmetric nature in electronic structure of the porphyrin ring. Considering that the electronic structure of the porphyrin ring in *m*-PC*n*V is essentially C_2 symmetric, the asymmetry of the porphyrin ring electronic structure does not account for the deviation of the chemical shifts of the resonances from the three tolyl ring protons of *m*-PC*n*V. But no evidence was detected for a direct interaction of those aromatic rings with the bipyridine moiety of the viologen which can be thought to perturb the chemical shifts of the tolyl ring protons.

Table 1. Chemical Shifts[a)] of Porphyrin and Tolyl ^{1}H Resonances of *m*-PC*n*V(*n*=3—6) in DMSO-d_6 and MeCN-d_3

Resonance[b)]	DMSO-d_6	MeCN-d_3
Pyridyl		
2′	9.51	8.90
3′	8.65	8.25
4′	9.58	9.05
6′	10.09	9.31
Tolyl		
2″,6″[c)]	8.10	7.84
3″,5″[c)]	7.66	7.38
CH$_3$	2.69	2.44
Pyrrole-β	8.88, 9.02	8.63, 8.76
Pyrrole N–H	−2.92	−3.10

a) Chemical shifts are given in ppm and referenced to TMS through the residual solvent signal. Deviation of less than ±0.03 ppm among *m*-PC*n*V(*n*=3—6) prepared. b) Numbering system is shown in Fig. 1. c) Resonances exhibit multiplet structures in their line shape.

Analyses of the Porphyrin Ring Current Induced Shift. Spatial relationship between the porphyrin and the viologen can be deduced from the analyses on the porphyrin ring current induced chemical shift changes on the resonances from the viologen.[2,11] The

Table 2. Chemical Shifts$^{a)}$ of Viologen ^{1}H Resonances of *m*-PC*n*V(n=3—6) in DMSO-d_6 and MeCN-d_3

Resonance$^{b)}$	DMSO-d_6				MeCN-d_3			
	m-PC3V	*m*-PC4V	*m*-PC5V	*m*-PC6V	*m*-PC3V	*m*-PC4V	*m*-PC5V	*m*-PC6V
Methylene chain								
1-CH$_2$	5.04	4.96	4.91	4.89	4.74	4.65	4.57	4.58
2-CH$_2$	2.95	2.2$^{c)}$	2.28$^{c)}$	2.2$^{c)}$	2.74	1.96$^{c)}$	2.05$^{c)}$	2.00$^{c)}$
3-CH$_2$	4.93	2.2$^{c)}$	1.57$^{c)}$	1.5$^{c)}$	4.63	1.88$^{c)}$	1.38	1.35
4-CH$_2$		4.79	2.11$^{c)}$	1.5$^{c)}$		4.49	1.88$^{c)}$	1.28
5-CH$_2$			4.72	2.01			4.38	1.80$^{c)}$
6-CH$_2$				4.66				4.36
Bipyridyl								
α	9.41	9.38	9.37	9.34	8.72	8.68	8.63	8.59
β	8.81	8.77	8.77	8.74	8.19	8.14	8.09	8.09
γ	8.71	8.69	8.71	8.69	8.10	8.07	8.03	8.05
δ	9.25	9.25	9.25	9.25	8.59	8.57	8.52	8.55
N-CH$_3$	4.41	4.42	4.42	4.42	4.15	4.14	4.10	4.13

a) Chemical shifts are given in ppm and referenced to TMS through the residual solvent signal. b) Numbering system is shown in Fig. 1. c) Resonating under the residual solvent signal and shifts were obtained from the COSY cross-peaks.

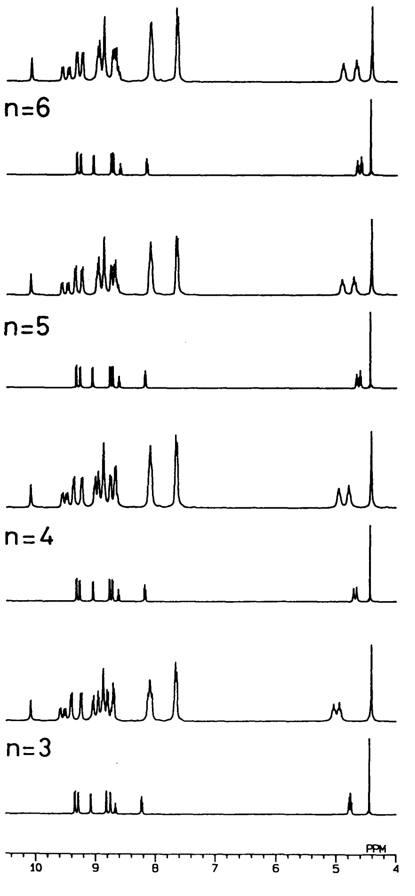

Fig. 5. 500 MHz ^{1}H NMR spectra of *m*-PC*n*V and C*n*V (n=3—6) in DMSO-d_6 at 27 °C. Chemical shift region of δ 4—10.5 is presented. For each set of the spectra, the lower trace is the spectrum of C*n*V.

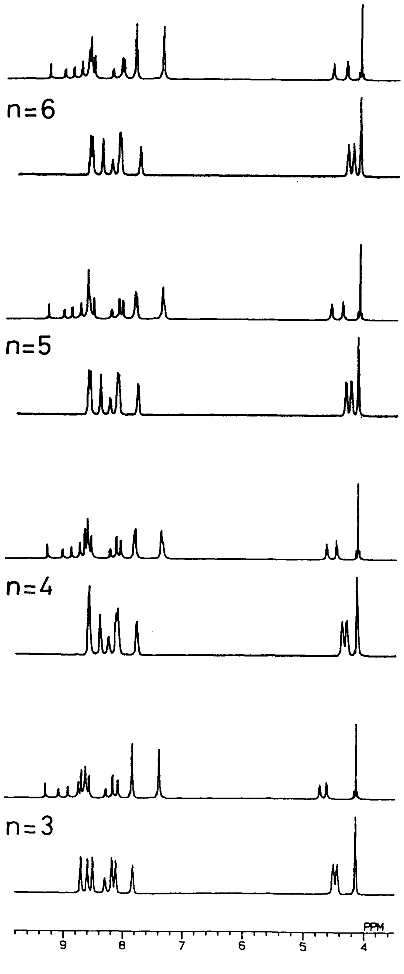

Fig. 6. 500 MHz ^{1}H NMR spectra of *m*-PC*n*V and C*n*V in MeCN-d_3 at 27 °C. Chemical shift region of δ 3.5—9.8 is presented. For each set of the spectra, the lower trace is the spectrum of C*n*V.

dipolar field arising from the ring current of the porphyrin ring π-electrons strongly influences the resonance frequencies of the nuclei which are located in the close proximity to the porphyrin and the induced chemical shift change spans up to several ppm depending on the position of the nucleus with respect to the porphyrin ring. The porphyrin ring current induced chemical shift change ($\Delta\delta$) is calculated as the difference in the observed shift between *m*-PC*n*V and appropriate model which, ideally, possesses

Table 3. Porphyrin Ring Current Induced Chemical Shift Changes[a] on Viologen ^{1}H Resonances of *m*-PC*n*V(n=3—6) in DMSO-d_6 and MeCN-d_3

Resonances[b]	DMSO-d_6				MeCN-d_3			
	m-PC3V	*m*-PC4V	*m*-PC5V	*m*-PC6V	*m*-PC3V	*m*-PC4V	*m*-PC5V	*m*-PC6V
Methylene Chain								
1-CH_2	+0.29	+0.30	+0.30	+0.30	+0.30	+0.33	+0.30	+0.31
2-CH_2	+0.24	+0.19[c]	+0.26[c]	+0.27[c]	+0.28	+0.15[c]	+0.21[c]	+0.29[c]
3-CH_2	+0.15	+0.19[c]	+0.21[c]	+0.16[c]	+0.14	+0.07[c]	+0.19	+0.18
4-CH_2		+0.18	+0.13[c]	+0.13[c]		+0.10	+0.08[c]	+0.11
5-CH_2			+0.05	+0.08			+0.02	+0.09[c]
6-CH_2				0.00				0.00
Bipyridyl								
α	+0.07	+0.05	+0.02	0.00	+0.01	+0.06	−0.01	−0.05
β	−0.02	−0.01	−0.01	−0.03	0.00	−0.01	−0.04	−0.06
γ	−0.05	−0.04	−0.03	−0.04	−0.03	−0.05	−0.08	−0.07
δ	−0.04	−0.03	−0.03	−0.03	−0.01	−0.04	−0.09	−0.05
N-CH_3	−0.04	−0.02	−0.02	−0.02	+0.01	−0.01	−0.05	−0.02

a) Chemical shift changes ($\Delta\delta=\delta_{m\text{-PC}n\text{V}}-\delta_{\text{C}n\text{V}}$) are given in ppm and uncertainty is ±0.01 ppm unless specified. Positive $\Delta\delta$ value indicates the downfield shift of *m*-PC*n*V proton with respect to the corresponding C*n*V proton. b) Numbering system is shown in Fig. 1. c) Uncertainty is ±0.03 ppm.

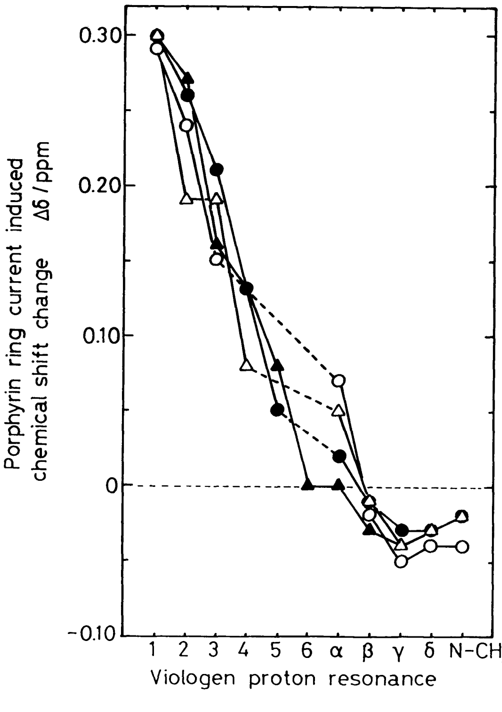

Fig. 7. Plots of the porphyrin ring current induced chemical shift change (Δδ) vs. viologen proton resonance of *m*-PC*n*V in DMSO-d_6. The viologen protons are arranged in the order of he distance away from the porphyrin ring along the covalent bond on the horizontal axis. *m*-PC3V (○), *m*-PC4V (△), *m*-PC5V (●), *m*-PC6V (▲).

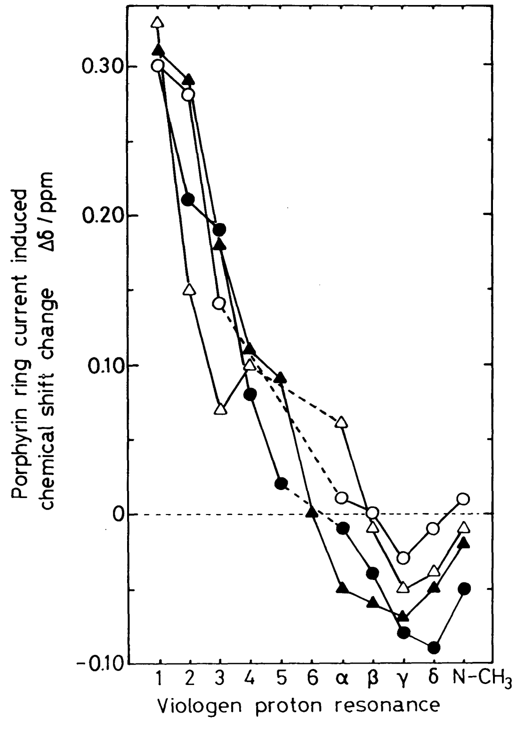

Fig. 8. Plots of the porphyrin ring current induced chemical shift change (Δδ) vs. viologen proton resonance of *m*-PC*n*V in MeCN-d_3. The viologen protons are arranged in the order of he distance away from the porphyrin along the covalent bond on the horizontal axis. *m*-PC3V (○), *m*-PC4V (△), *m*-PC5V (●), *m*-PC6V (▲).

all structure features present in *m*-PC*n*V but the porphyrin ring current. Therefore the model compounds, C*n*V, have been synthesized. Their ^{1}H NMR spectra were recorded and the signals were assigned using COSY and NOESY (results not shown). The spectra of *m*-PC*n*V in DMSO-d_6 and MeCN-d_3 are compared with those of the corresponding model C*n*V in Figs. 5 and 6, respectively. The obtained Δδ values, $\Delta\delta=\delta_{m\text{-PC}n\text{V}}-\delta_{\text{C}n\text{V}}$, for corresponding viologen proton resonances are summarized in Table 3. The Δδ values of *m*-PC*n*V in DMSO-d_6 and MeCN-d_3 are compared in Figs. 7 and 8, respectively. Although the patterns of the Δδ plots for both solvents look similar, they are slightly and subtly different with each other (see below).

Conformational Analyses of *m*-PC*n*V. The $\Delta\delta$ value for 1-CH_2 of *m*-PC*n*V in DMSO-d_6 is about +0.3 ppm, reflecting the strong deshielding effect due to the porphyrin ring current. The $\Delta\delta$ value of methylene proton decreases as ^1H nucleus is oriented away from the porphyrin ring along the methylene chain of the viologen and eventually becomes nagative for the resonances from the bipyridine moiety, indicating that the viologen is oriented across the boundary expressed by the equation, $(3\cos^2\theta-1)/r^3=0$, where r is the magnitude of the vector connecting the center of the porphyrin ring and the nucleus and θ is the angle between $\vec{r}$ and the z-axis which is defined normal to the porphyrin plane; in particular, the θ is called the magic angle when θ satisfies the equation $3\cos^2\theta-1=0$, i.e., $\theta=54.7°$. The sign of the $\Delta\delta$ value changes between bipyridyl α and β protons of the viologen, dictating that the part around these nuclei of the viologen moiety is located close to the boundary expressed by $3\cos^2\theta-1=0$. Because of the difficulties arising from nonlinear averaging of the porphyrin ring current induced chemical shift changes in terms of the relative orientation of the nucleus with respect to the porphyrin plane, the flexibility in conformation of the methylene chain, and the uncertainty in the orientation of the pyridine ring with respect to the porphyrin ring, we have not attempted to determine the time averaged conformation of *m*-PC*n*V molecule. The insensitivity of the $\Delta\delta$ values for the length of the methylene chain, however, is consistent with the extended all-anti conformation and the bipyridine moiety being just across the boundary of the magic angle. Since the pyridine ring is neither coplanar nor orthogonal to the porphyrin plane but slightly tilted,[15] the length of the methylene chain linkage does not have a significant effect on the position of the bipyridine moiety of the viologen with repect to the dipolar field arising from the porphyrin ring π-electrons. With the energetically stable all-anti methylene chain conformation,[16] the closest edge-to-edge distance of the π-systems of the porphyrin and bipyridine of *m*-PC*n*V are ca. 6 to ca. 12 Å for $n=3$ to 6. If there is a direct relationship between that distance and the rate of the intramolecular electron transfer as Gust et al.[2] have suggested, the larger distance for the greater n value is completely consistent with the linkage length dependency of the electron-transfer rate found in viologen-linked zinc porphyrin.[1]

The patterns of the $\Delta\delta$ plots for *m*-PC*n*V in MeCN-d_3 are similar to those in DMSO-d_6, but slightly different features are observed. In the plot illustrated in Fig. 9, the sign of the value changes at bipyridine β proton for *m*-PC3V and *m*-PC4V and between α and 5- or 6-CH_2 resonances for *m*-PC5V and *m*-PC6V, respectively, suggesting either that the dihedral angle between the pyridine and porphyrin planes is closer to orthogonal in MeCN-d_3 than that in DMSO-d_6 or that the direction of the vector connecting pyridyl N and N-CH_3 is directed more toward z axis of the porphyrin ring in MeCN-d_3. These results strongly suggest that the orientations of the viologen with respect to the porphyrin ring of *m*-PC*n*V in DMSO-d_6 and MeCN-d_3 are different and the difference in the spatial relationship between the porphyrin and the viologen in different solvents could explain the solvent dependency of the rate of the intramolecular electron transfer.[1] Similar porphyrin ring current induced shift for 1-CH_2 resonance of *m*-PC*n*V in both solvents indicates that the magnetic anisotropy of the porphyrin ring current is not significantly altered by solvent. As can be seen in the $\Delta\delta$ plots, the difference in conformation between the two solvents is clearly manifested in the difference in the patterns of the $\Delta\delta$ plots. Such difference in conformation between the two solvents appears to be enhanced with the n value. But it is not easy at present to interpret the solvent

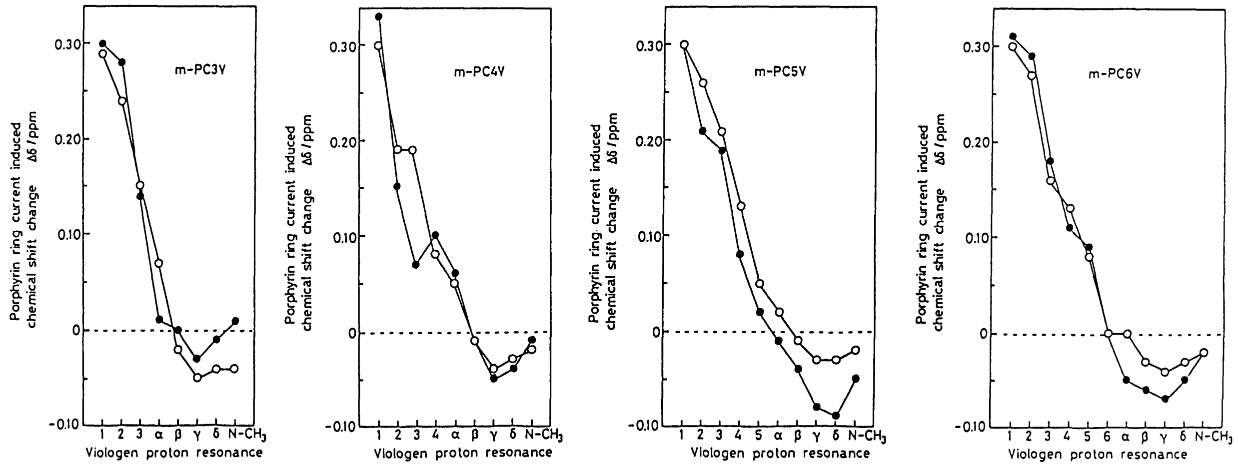

Fig. 9. Plots of the porphyrin ring current induced chemical shift change ($\Delta\delta$) vs. viologen proton resonance of *m*-PC*n*V in DMSO-d_6 (○) and MeCN-d_3 (●).

dependency of *m*-PC*n*V conformation because of the absence of the knowledge of the interaction of *m*-PC*n*V with the surrounding solvent molecules.

Conclusion

Novel porphyrins linked to viologen (*m*-PC*n*V) which are expected to serve as both a photosensitizer and an electron carrier in the same molecule have been synthesized. The flexible methylene chain was used to link the porphyrin ring and the bipyridine and the constituent methylene unit was systematically changed from 3 to 6 to observe the effect of the methylene chain length on the spatial relationship of the bipyridine moiety with respect to the porphyrin. Using the porphyrin ring current induced chemical shift change, the orientation of the viologen with respect to the porphyrin ring in *m*-PC*n*V was semiquantitatively determined and the results suggested that the viologen does not fold back in a way that the bipyridine moiety of the viologen is oriented above the porphyrin plane and that the bipyridine moiety is oriented around the boundary defined by the magic angle where the porphyrin ring current induced shift change vanishes. The conformational analyses of *m*-PC*n*V in DMSO-d_6 and MeCN-d_3 indicated that the spatial orientation of the bipyridine with respect to porphyrin ring is slightly different between the two solvents and such difference in the conformation of *m*-PC*n*V appears to be enhanced with the length of the methylene chain.

With the extended methylene chain conformation, the closest edge-to-edge distance between the π-systems of the porphyrin and the bipyridine increases with the methylene chain length. Therefore the rate of the intramolecular electron transfer of *m*-PC*n*V would be smaller with the longer methylene chain linkage, if there is a direct relationship between the electron transfer rate and the distance of two π-systems.[2] Fluorescence lifetime measurements are currently under way on these *m*-PC*n*V in DMSO and MeCN.

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