

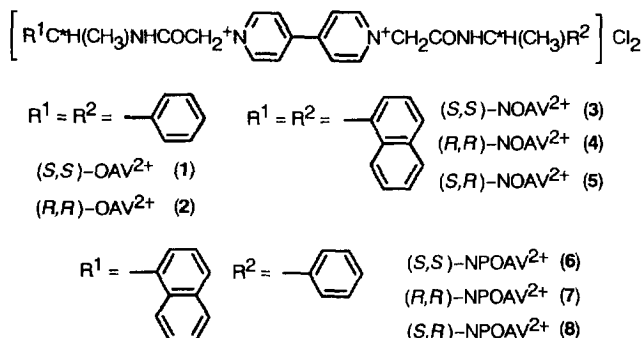
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## Charge-Transfer Interaction between Bipyridinium and Naphthyl Groups of Optically Active Viologens in an Aqueous Solution

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**Abstract:** Optically active viologens containing naphthyl group(s) show an intermolecular charge-transfer interaction between bipyridinium and naphthyl groups in an aqueous solution. Association constants are dependent on the chirality of the viologens. Copyright © 1996 Elsevier Science Ltd

Viologens are diquaternary salts of 4,4'-bipyridine and undergo one-electron reduction to give the strong colored radical cations.<sup>1,2</sup> Utilization of viologens has been reported in many electron-transfer processes, for example, as redox indicators in biochemical redox systems,<sup>3</sup> as mediators in catalytic photolysis of water under visible light<sup>4</sup> and as the main components of electrochromic display devices.<sup>5</sup> We have recently reported the stereoselectivity in the photoinduced electron-transfer quenching of zinc-substituted myoglobin by the optically active viologens (1 — 5):<sup>6</sup>



Chiral recognition in a charge-transfer complex has been reported for organic molecules,<sup>7</sup> such as naphthalene derivatives.<sup>8</sup> The bipyridinium ion is known to interact with a variety of organic molecules, where charge-transfer interactions have been observed.<sup>9-11</sup> However, the stereoselective association of viologens has not been reported previously. In this work we report the first example of the stereoselective association of the optically active viologens, containing both a donor and an acceptor in the molecule, through the intermolecular charge-transfer interaction between the naphthyl and bipyridinium groups in an aqueous solution.

Viologens containing both naphthyl and phenyl groups (6—8) were prepared by a previously reported method.<sup>6</sup> All of the bromide salts of 6, 7 and 8 gave satisfactory elemental analyses. UV (H<sub>2</sub>O), λ<sub>max</sub> 270 nm (log ε 4.46); <sup>1</sup>H NMR (270MHz, 5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup> in D<sub>2</sub>O, DSS) δ 1.49 (3H, d, J = 6.6 Hz, CH<sub>3</sub> (phenyl)), 1.65 (3H, d, J = 6.8 Hz, CH<sub>3</sub> (naphthyl)), 4.94 (1H, m, CH (phenyl)), 5.50 — 5.65 (4H, m, CH<sub>2</sub>), 5.78 (1H, m, CH (naphthyl)), 7.31 — 7.42 (5H, m, C<sub>6</sub>H<sub>5</sub>), 7.52 — 7.67 (3H, m, 3,6,7-naphthyl), 7.66 (1H, d, J = 6.8 Hz, 2-naphthyl), 7.88 (1H, d, J = 7.3 Hz, 4-naphthyl), 7.95 (1H, d, J = 7.3 Hz, 5-naphthyl), 8.12 (1H, d, J = 7.3 Hz, 8-naphthyl), 8.50 — 8.68 (4H, m, 3,5-bpy) and 8.94 — 9.00 (4H, m, 2,6-bpy); ORD (c 0.050, H<sub>2</sub>O, 20 °C) [Φ]<sub>589</sub> +126° for (R,R)-, [Φ]<sub>589</sub> -126° for (S,S)- and [Φ]<sub>589</sub> -97° for (S,R)-isomer. Bromide salts were converted to chloride salts by an anion-exchange column-chromatography

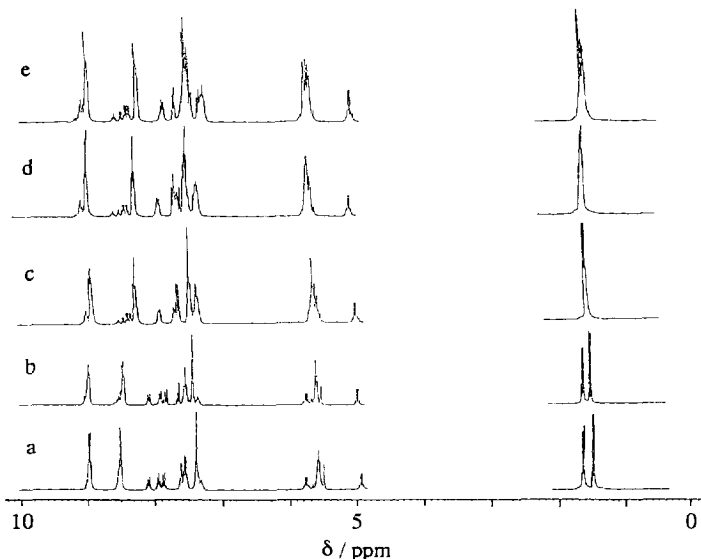


Fig. 1.  $^1\text{H}$  NMR spectra at various concentrations of  $(S,S)$ -[NPOAV] $\text{Cl}_2$  in  $\text{D}_2\text{O}$  at  $25\text{ }^\circ\text{C}$  and  $I = 0.20\text{ mol dm}^{-3}$ . (a)  $8.8 \times 10^{-3}\text{ mol dm}^{-3}$ , (b)  $1.8 \times 10^{-2}\text{ mol dm}^{-3}$ , (c)  $3.5 \times 10^{-2}\text{ mol dm}^{-3}$ , (d)  $5.3 \times 10^{-2}\text{ mol dm}^{-3}$  and (e)  $7.0 \times 10^{-2}\text{ mol dm}^{-3}$ .

for all of the measurements.  $^1\text{H}$  NMR spectra were measured with a JEOL JNM-GX270 FT NMR spectrometer. UV-vis spectra were recorded with a Shimadzu UV-240 spectrophotometer.

Figure 1 shows the  $^1\text{H}$  NMR spectra at various concentrations of  $(S,S)$ -[NPOAV] $\text{Cl}_2$  in  $\text{D}_2\text{O}$  at  $25\text{ }^\circ\text{C}$  and an ionic strength ( $I$ ) of  $0.20\text{ mol dm}^{-3}$  ( $\text{NaCl}$ ). At low concentrations of  $\text{NPOAV}^{2+}$ , distinct proton signals were observed for the naphthyl- and phenylethylcarbamoyl groups, although the bipyridinium ring protons were not clearly separated for the different substituents. With increased concentrations of  $\text{NPOAV}^{2+}$ , the proton signals for the naphthylethylcarbamoyl group and the bipyridinium rings shifted to higher fields. On the contrary, there was no appreciable shift in those for the phenylethylcarbamoyl group. These results strongly suggest that an intermolecular association occurs between the naphthyl group and the bipyridinium ring(s). The intramolecular interaction between the naphthyl and bipyridinium groups can be ruled out due to the steric restriction. The larger shift was observed for the bipyridinium protons which interact with the naphthyl group and equilibrated with the free viologen. The smaller signals that appeared at lower fields at higher concentrations in the region from  $8.5\text{--}9.0\text{ ppm}$  are those for the bipyridinium ring protons which do not interact with the naphthyl group and are also in equilibrium with the free viologen. The association constant ( $K_D$ ) of the equilibrium reaction 1 was evaluated from Eq. 2 for the concentration dependence of the observed chemical shift ( $\delta_{\text{obsd}}$ ) in the bipyridinium and methyl proton signals:



$$\delta_{\text{obsd}} = \delta_{\text{free}} + (\delta_{\text{comp}} - \delta_{\text{free}})\{(1 + 4K_D c) - (1 + 8K_D c)^{1/2}\}/4K_D c \quad (2)$$

where the symbols  $\delta_{\text{free}}$  and  $\delta_{\text{comp}}$  are the chemical shifts for the free viologen and the dimer, respectively. The symbol  $c$  is the total concentrations of viologen. One of the examples of the plot of  $\delta_{\text{obsd}}$  against the total concentrations of  $(S,S)$ - $\text{NPOAV}^{2+}$  is shown in Fig. 2. The solid curve is a calculated one with  $K_D = 19 \pm 1\text{ mol dm}^{-3}$  and  $\delta_{\text{comp}} = 8.45$  for the 2,6-bipyridinium protons. The results for the signals of 3,5-bipyridinium and methyl groups were similar to those for the 2,6-bipyridinium protons. The results are shown in Table 1.

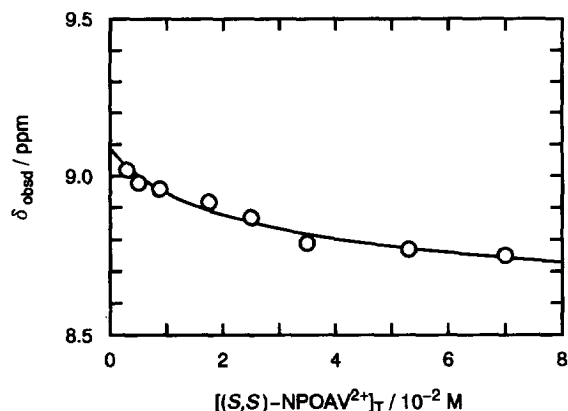


Fig. 2. Plots of  $\delta_{\text{obsd}}$  vs. the concentrations of  $(S,S)$ -NPOAV<sup>2+</sup> for the 2,6-bipyridinium protons.

Table 1. Association Constants of the Optically Active Viologens in an Aqueous Solution at 25 °C and  $I = 0.20 \text{ mol dm}^{-3}$

Viologen	$K_D^{\text{a)}}$ / $10 \text{ dm}^3 \text{ mol}^{-1}$	$K_D^{\text{b)}}$ / $10 \text{ dm}^3 \text{ mol}^{-1}$
$(S,S)$ -NOAV <sup>2+</sup>	$4.7 \pm 0.2$	$4.8 \pm 0.2$
$(R,R)$ -NOAV <sup>2+</sup>	$4.7 \pm 0.2$	$4.8 \pm 0.2$
$(S,R)$ -NOAV <sup>2+</sup>	$3.2 \pm 0.2$	$3.1 \pm 0.2$
$(S,S)$ -NPOAV <sup>2+</sup>	$1.9 \pm 0.1$	$1.8 \pm 0.1$
$(R,R)$ -NPOAV <sup>2+</sup>	$1.9 \pm 0.1$	$1.8 \pm 0.1$
$(S,R)$ -NPOAV <sup>2+</sup>	$0.76 \pm 0.19$	$0.73 \pm 0.20$

a) Determined from NMR measurements. b) Determined spectrophotometrically.

Methylviologen shows the charge-transfer band near 400 nm with the organic compounds such as naphthalene derivatives in solution.<sup>7-9</sup> We also observed that the charge-transfer band appears around 370 nm with increased concentrations of viologen in an aqueous solution under the same experimental conditions as for the <sup>1</sup>H-NMR measurements. Plots of the absorbance at 370 nm against the total concentrations of  $(R,R)$ -NOAV<sup>2+</sup> are shown in Fig. 3. The data were fitted to Eq. 3 derived from reaction 1:

$$A = \epsilon_{\text{free}} l \{-1 + (1 + 8K_{\text{DC}})^{1/2}\} / 4K_{\text{D}} + \epsilon_{\text{comp}} l \{1 + 4K_{\text{DC}} - (1 + 8K_{\text{DC}})^{1/2}\} / 8K_{\text{D}} \quad (3)$$

where the symbols  $A$ ,  $l$ ,  $\epsilon_{\text{free}}$  and  $\epsilon_{\text{comp}}$  are the absorbance at a given wavelength, the optical path length and the molar absorption coefficients of the free viologen and of the charge-transfer complex, respectively. The value of  $\epsilon_{\text{free}}$  ( $9.8 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) was determined from the data for the linear part at lower concentrations of viologen in Fig. 3. The values of  $K_{\text{D}}$  ( $48 \pm 0.2$ ) and  $\epsilon_{\text{comp}}$  ( $7.20 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) were evaluated from the fitting curve. The  $K_{\text{D}}$  values thus obtained are in good agreement with those from the <sup>1</sup>H-NMR measurements. Therefore, the association of optically active viologens containing naphthyl groups is based on the intermolecular charge-transfer interaction between the naphthyl group and the bipyridinium ring.

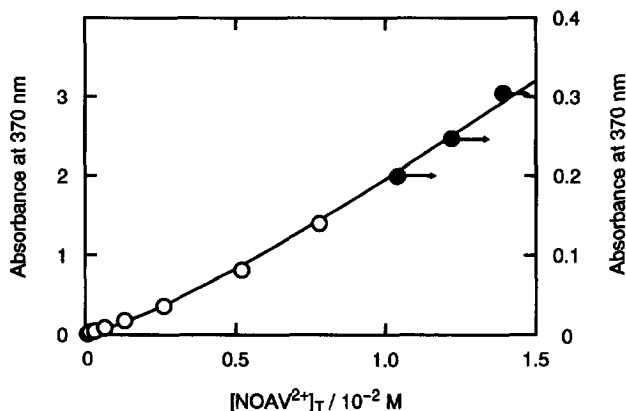


Fig. 3. Plots of the absorbance at 370 nm vs. the concentrations of (*R,R*)-NOAV<sup>2+</sup> at 25 °C and *I* = 0.20 mol dm<sup>-3</sup>. The data for the open and closed circles are measured by using 1.0 and 0.1 cm cells, respectively.

The tendency of the intermolecular charge-transfer interaction of optically active viologens is in the following order, (*S,S*)- or (*R,R*)-NOAV<sup>2+</sup> > (*S,R*)-NOAV<sup>2+</sup> > (*S,S*)- or (*R,R*)-NPOAV<sup>2+</sup> > (*S,R*)-NPOAV<sup>2+</sup> >> OAV<sup>2+</sup>. Weaker interaction for the (*S,R*)-isomers than that for the (*S,S*)- or (*R,R*)-isomers may arise from the steric repulsion between the methyl and the bipyridinium groups. The shift of the methyl proton signal is much smaller than that for the bipyridinium and naphthyl groups, suggesting that the association occurs at the opposite side of the methyl group and that the methyl group controls the association of the naphthyl group with the bipyridinium ring. This work is the first example of the stereoselective charge-transfer complexation of viologen and will provide useful information for molecular recognition in the charge-transfer complexes.

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