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Syntheses, Characterizations, and Redox Behavior of Optically Active Viologens and Bisviologens

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Optically active viologens, containing [1-(1-naphthyl)-, 1-phenyl-, and 1-cyclohexylethyl]carbamoylmethyl groups, have been synthesized and characterized. The redox behavior of the chiral viologens was studied compared with achiral viologens. The monoviologens containing naphthyl groups show an *inter*molecular charge-transfer interaction between the bipyridinium and naphthyl groups in aqueous solution. The association constants are dependent on the chirality of the viologens and larger in the (*S*,*S*)- and (*R*,*R*)-isomers than in the (*R*,*S*)-one. Chiral bisviologens, in which two viologen units are linked with a trimethylene chain, have also been synthesized and characterized. Although the intermolecular charge-transfer interaction between the bipyridinium and viologen units of bisviologens was very weak in solution, such an interaction was appreciably observed in a solid state, which was confirmed by X-ray crystallography. Monoradical trications produced by a one-electron reduction of bisviologens disproportionate more easily in the (*R*,*S*)-isomers than in the (*S*,*S*)- and (*R*,*R*)-ones. The disproportionation is controlled by the steric bulk of the chiral substituents in *intra*molecular association between two viologen radical units of diradical dications.

Viologens, such as 1,1′-dimethyl-4,4′-bipyridinium dichloride ([MV]Cl_2, also known as methylviologen), have been used as electron acceptors in a great variety of studies in such areas as biochemical redox systems, herbicidal activity, electrochemistry, photochemistry, and solar-energy conversion.[1] Rau and Ratz[2] first synthesized optically active viologen, 1-methyl-1′-[(3*S*)-(−)-3-pinanylmethyl]-4,4′-bipyridinium dichloride, and found the stereoselectivity in the luminescence quenching of the excited triplet state of chiral tris(2,2′-bipyridine)ruthenium(II) by the chiral viologen. Chiral recognition in a charge-transfer complex has been reported for organic molecules,[3] such as naphthalene derivatives.[4] The bipyridinium ion is known to interact with a variety of organic molecules, where charge-transfer interactions have been observed.[1a,5,6] In this work we have reported on details concerning the syntheses of a new type of optically active viologens containing [1-(1-naphthyl)-, 1-phenyl-, and 1-cyclohexylethyl]carbamoylmethyl groups (**1**, **2**, **3**, and **4**), and found the stereoselective association of the chiral viologens, containing both a donor and an acceptor in the molecule, through an *inter*molecular charge-transfer interaction between the naphthyl and bipyridinium groups in an aqueous solution (Chart 1). Bisviologens, 1,1″-polymethylenebis(1′-methyl-4,4′-bipyridinium) ions, are tetraquaternary salts that contain two viologen units, joined by a varying number of methylene groups.[7—9] A one-electron reduced monoradical trication bridged with a trimethylene chain ($PTQ^{\bullet 3+}$) disproportionates easily to the diradical dication ($PTQ^{2\bullet 2+}$) and the parent bisviologen (PTQ^{4+}, **20**) in solution.[8,9] It has been suggested that the doubly reduced $PTQ^{2\bullet 2+}$ adopts an *intra*molecular associated form (a "closed" conformation) and that the disproportionation is

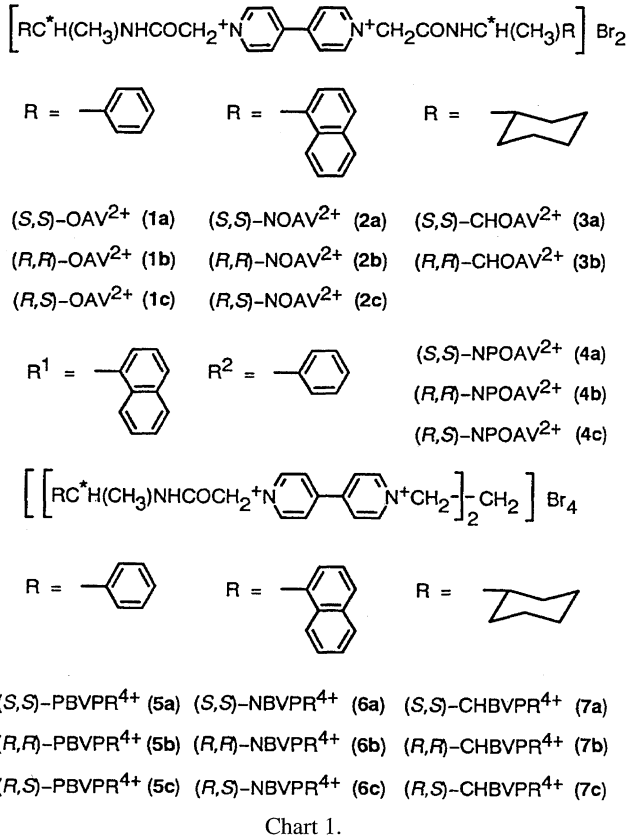


Chart 1.

mainly controlled by the comproportionation rate constant.[9] We have also synthesized optically active bisviologens (**5**, **6**, and **7**), and found chiral recognition in disproportionation of the monoradical trication of these bisviologens. The preliminary communications have been published elsewhere.[10]

Results and Discussion

Synthesis. The (*S*,*S*)- and (*R*,*R*)-isomers of monoviologens (**1**, **2**, and **3**) were prepared by the reaction of 4,4′-bipyridine with chiral bromocarbamoylmethane (**8**, **9**, and **10**) in 12—20% yield, the latter of which was obtained from the condensation of bromoacetic acid with a chiral amine by using dicyclohexylcarbodiimide (DCC). The purity of compounds **8**, **9**, and **10** is important to obtain pure samples of chiral viologens (**1**, **2**, and **3**), because a small amount of carbodiimide derivative, being a by-product in the synthesis of compounds **8**, **9**, and **10**, was always contained in the samples of chiral viologens, even after repeated recrystallization. (*R*,*S*)-Isomers of monoviologens (**1c** and **2c**) and viologens containing both phenyl and naphthyl groups (**4**) were prepared by a stepwise method, where the first 4-(4-pyridyl)pyridinium derivatives (**11** and **12**) were isolated and then reacted with bromocarbamoylmethane (**8** and **10**) in excess (yield 10—13%) (Chart 2).

To prepare the (*S*,*S*)- and (*R*,*R*)-isomers of bisviologens (**5**, **6**, and **7**) we employed the reaction of 1,1″-trimethylenebis[4-(4-pyridyl)pyridinium] dibromide[7] with chiral bromocarbamoylmethane in excess in *N*,*N*-dimethylformamide (DMF): yield, 12—44%. Crude products were recrystallized repeatedly from warm water. An attempt to obtain pure samples of bisviologens by an alternative method, reacting 1,3-dibromopropane with excess of 4-(4-pyridyl)-pyridinium derivatives (**11**, **12**, and **13**), was unsuccessful, because a small amount of 3-bromopropyl derivatives (**14**, **15**, and **16**) and the starting materials were always contained in recrystallized samples. The (*R*,*S*)-isomers of bisviologens (**5c**, **6c**, and **7c**) were prepared by the stepwise method shown in Scheme 1. 1-[(*S*)-(1-Phenylethyl)carbamoylmethyl]-4-(4-pyridyl)pyridinium bromide (**11a**) was treated with 1,3-dibromopropane in excess in DMF. The resulting 1-(3-bromopropyl)-1′-[(*S*)-(1-phenylethyl)carbamoylmethyl]-4,4′-bipyridinium dibromide (**14a**, yield 85%) was reacted with excess 4,4′-bipyridine to give 1-[(*S*)-(1-phenylethyl)-carbamoylmethyl]-1′-{3-[4-(4-pyridyl)pyridinio]propyl}-4,4′-bipyridinium tribromide (**17a**, yield 48%). Compound **17a** was further reacted with **8b** in excess to give the desired compound (**5c**, yield 68%). An alternative method to obtain compounds, **17**, **18**, and **19** by the reaction of **8a**, **9a**, or **10a** with excess of 1,1″-trimethylenebis[4-(4-pyridyl)-pyridinium] dibromide gave unsuccessful results, because the starting material of 1,1″-trimethylenebis[4-(4-pyridyl)-pyridinium] dibromide could not be removed completely from the product.

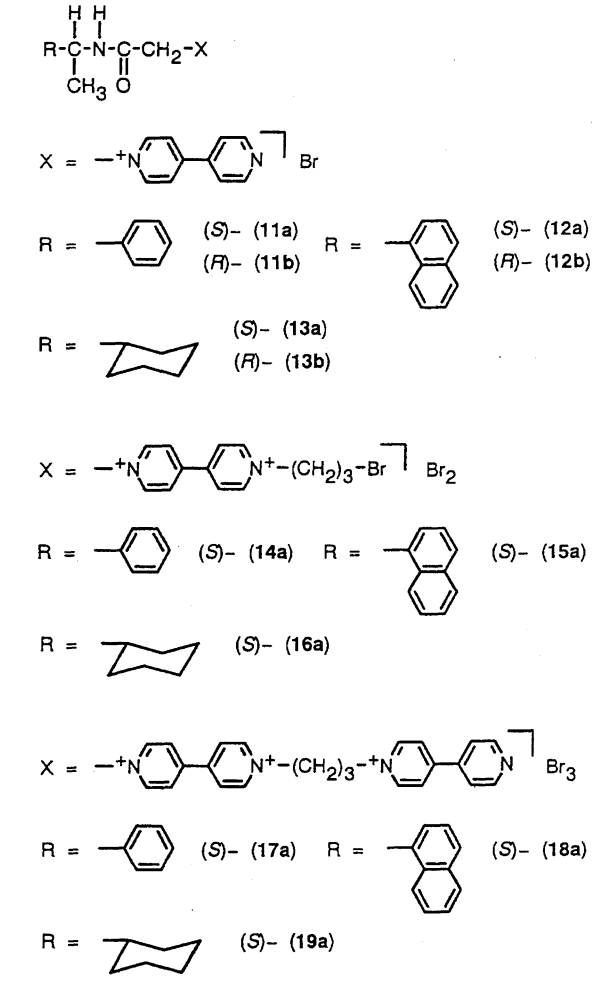
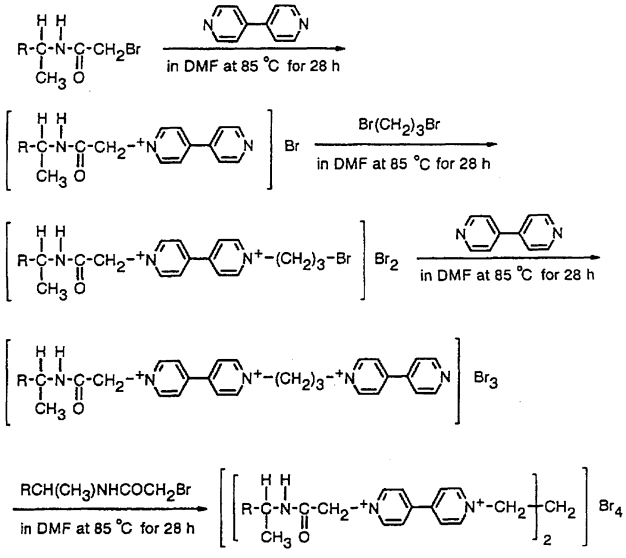


Chart 2.



Scheme 1.

^{1}H NMR Spectroscopy. The structures of chiral viologen and bisviologens were confirmed by ^{1}H–^{1}H DQF COSY and phase-sensitive NOESY NMR spectra in D_2O. ^{1}H NMR spectra of viologens containing naphthyl group(s) were dependent on the concentrations of the viologens (vide infra); therefore, the assignment of signals was performed for low concentrations of viologens (ca. 10^{-3} mol dm^{-3}). The proton signals of the bridged methylene between the pyridinium and the carbamoyl groups showed a singlet, and then gradu-

ally disappeared with a multiplet in D_2O at room temperature ($t_{1/2} \approx 20$ h), suggesting that a keto–enol equilibrium on the carbonyl group in the chiral viologens induces a H–D exchange reaction of the CH_2 group.

Chiral Recognition in Charge-Transfer Interactions of Naphthyl Viologens. Figure 1 shows the ^{1}H NMR spectra at various concentrations of the chloride salts of (*R,R*)-NOAV^{2+} (**2b**) in D_2O at 25 °C and an ionic strength (*I*) of 0.20 mol dm^{-3} (NaCl). With increased concentrations of NOAV^{2+}, the proton signals for the 1-(1-naphthyl)ethylcarbamoyl group and the bipyridinium rings shifted to higher fields. In the case of NPOAV^{2+} (**4a**), distinct proton signals were observed for the 1-(1-naphthyl)- and 1-phenylethylcarbamoyl groups, although the bipyridinium ring protons were not clearly separated for the different substituents:[10a] δ = 1.49 (CH_3 for phenyl), 1.65 (CH_3 for naphthyl), 4.94 (CH for phenyl), 5.50—5.65 (CH_2 for both phenyl and naphthyl), 5.78 (CH for naphthyl), 7.31—7.42 (C_6H_5), 7.52—7.67 (3,6,7-naphthyl), 7.66 (2-naphthyl), 7.88 (4-naphthyl), 7.95 (5-naphthyl), 8.12 (8-naphthyl), 8.50—8.68 (3,5-bpy), and 8.94—9.00 (2,6-bpy). With increased concentrations of NPOAV^{2+}, the proton signals for the 1-(1-naphthyl)ethylcarbamoyl group and the bipyridinium rings shifted to higher fields as well as those for NOAV^{2+}. On the contrary, there was no appreciable shift in those for the 1-phenylethylcarbamoyl group. These results suggest that an *inter*molecular association occurs between the naphthyl group and the bipyridinium ring(s). The *intra*molecular 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 that 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—9.0 ppm are those for the bipyridinium ring protons that do not interact with the naphthyl group, and are also in equilibrium with the free viologen. The shift in the proton signals with increasing concentrations of viologens was larger for NOAV^{2+} than for NPOAV^{2+}. The association constant (K_c) of the equilibrium (1) was evaluated from Eq. 2 for the concentration dependence of the observed chemical shift (δ_{obsd}) in the bipyridinium and methyl proton signals:

$$2\text{NPOAV}^{2+} \rightleftarrows \{\text{NPOAV}^{2+}\}_2 \qquad K_c \qquad (1)$$

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

where the symbols δ_{free} and δ_{comp} are the chemical shifts for the free viologen and the dimer, respectively. The symbol *c* is the total concentrations of viologen. One example of the plots of δ_{obsd} against the total concentrations of (*R,R*)-NOAV^{2+} is shown in Fig. 2. The solid curve is a calculated one with $K_c = 47 \pm 2$ dm^3 mol^{-1} and $\delta_{comp} = 8.45$ 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 given in Table 1.

Methylviologen shows a charge-transfer band near 400 nm with such organic compounds as naphthalene derivatives in solution.[1a,3,4] We also observed that the charge-transfer band

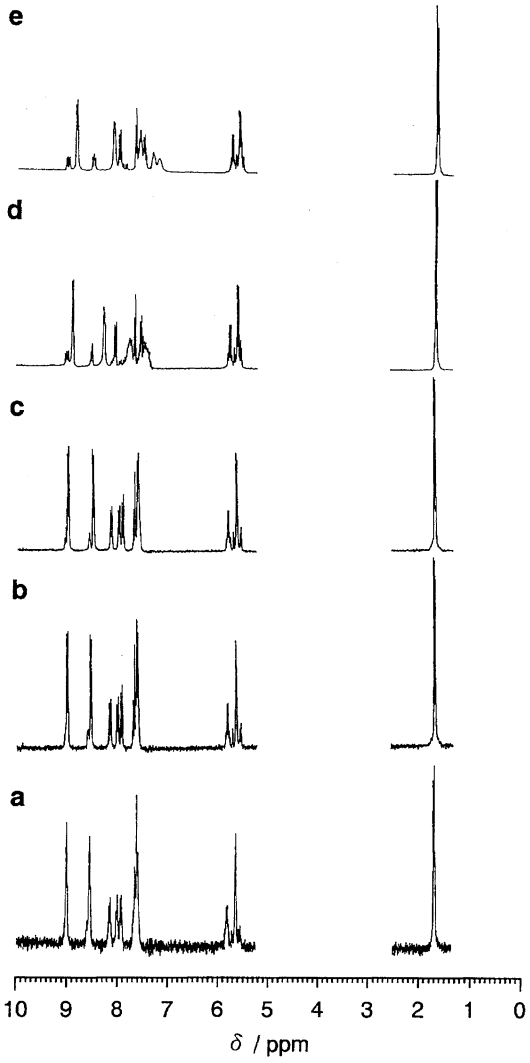


Fig. 1. ^{1}H NMR spectra at various concentrations of the chloride salt of (*R,R*)-NOAV^{2+} (**2b**) in D_2O at 25 °C and *I* = 0.20 mol dm^{-3}. (a) 1.8×10^{-3} mol dm^{-3}, (b) 3.5×10^{-3} mol dm^{-3}, (c) 7.0×10^{-3} mol dm^{-3}, (d) 1.4×10^{-2} mol dm^{-3}, and (e) 1.7×10^{-2} mol dm^{-3}.

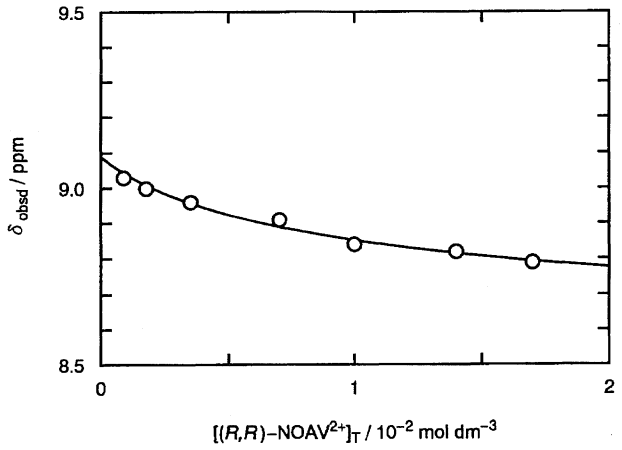


Fig. 2. Plots of δ_{obsd} vs. the concentrations of the chloride salt of (*R,R*)-NOAV^{2+} (**2b**) for the 2,6-bipyridinium protons.

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

Viologen	K_c[a]/10 dm^3 mol^{-1}	K_c[b]/10 dm^3 mol^{-1}
(*S*,*S*)-NOAV^{2+} (**2a**)	4.7±0.2	4.8±0.2
(*R*,*R*)-NOAV^{2+} (**2b**)	4.7±0.2	4.8±0.2
(*R*,*S*)-NOAV^{2+} (**2c**)	3.2±0.2	3.1±0.2
(*S*,*S*)-NPOAV^{2+} (**4a**)	1.9±0.1	1.8±0.1
(*R*,*R*)-NPOAV^{2+} (**4b**)	1.9±0.1	1.8±0.1
(*R*,*S*)-NPOAV^{2+} (**4c**)	0.76±0.19	0.73±0.20

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

appears at around 370 nm with increased concentrations of viologens in an aqueous solution under the same experimental conditions as for the ^{1}H NMR measurements. Plots of the absorbance at 370 nm against the total concentrations of (*R*,*R*)-NOAV^{2+} are shown in Fig. 3. The data were fitted to Eq. 3 derived from reaction (1):

$$A = \varepsilon_{free} l\{-1+(1+8K_c c)^{1/2}\}/4K_c + \varepsilon_{comp} l\{1+4K_c c-(1+8K_c c)^{1/2}\}/8K_c, \quad (3)$$

where the symbols A, l, ε_{free}, and ε_{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 ε_{free} (9.8×10^2 dm^3 mol^{-1} cm^{-1}) was determined from the data for the linear part at lower concentrations of viologen in Fig. 3. The values of K_c (48±2) and ε_{comp} (7.20×10^2 dm^3 mol^{-1} cm^{-1}) were evaluated from the fitting curve. The thus-obtained K_c values are in good agreement with those from the ^{1}H NMR measurements. Therefore, the association of optically active viologens containing naphthyl groups is based on the *inter*molecular charge-transfer interaction between the naphthyl group and the bipyridinium ring. The tendency of the *inter*molecular charge-transfer interaction of optically active viologens is in the following order: (*S*,*S*)- or (*R*,*R*)-NOAV^{2+} > (*R*,*S*)-NOAV^{2+} > (*S*,*S*)- or (*R*,*R*)-NPOAV^{2+} ≫ OAV^{2+}. The weaker interaction for the (*R*,*S*)-isomers than that for the (*S*,*S*)- or (*R*,*R*)-isomers may arise due to the steric repulsion between the methyl and the bipyridinium groups. The shift of the methyl proton signals is much smaller than that for the bipyridinium and naphthyl groups, suggesting that association occurs at the opposite side of the methyl group, and that the methyl group controls the association on the naphthyl group with the bipyridinium ring.

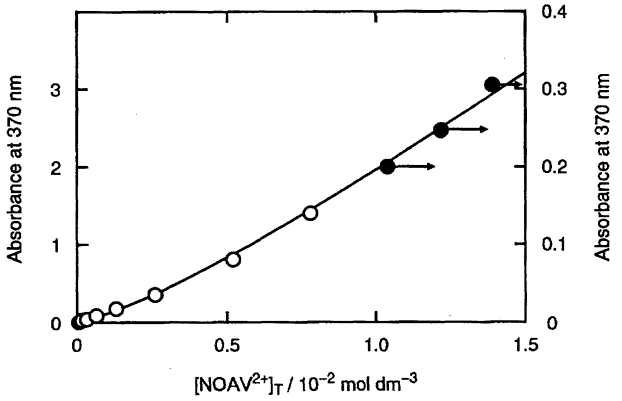


Fig. 3. Plots of the absorbance at 370 nm vs. the concentrations of the chloride salt of (*R*,*R*)-NOAV^{2+} (**2b**) in an aqueous NaCl solution at 25 °C and $I = 0.20$ mol dm^{-3}. The data for the open and closed circles are measured by using 1.0 and 0.1 cm cells, respectively.

In the case of bisviologens containing naphthyl groups, no intermolecular charge-transfer interaction was observed appreciably in solutions. The difference from the monoviologens (**2**) may arise from the charge repulsion and/or steric repulsion due to the flexible trimethylene chain. In a solid state of bisviologen (a chloride salt of **6b**) the charge-transfer interaction between the naphthyl group and the bipyridinium ring was observed (vide infra).

X-Ray Crystal Structure. A yellow crystal of (*R*,*R*)-[NBVPR]$Cl_4\cdot11H_2O$ consisted of stacking the bipyridinium rings with the naphthyl group of the other molecule, as shown in Figs. 4 and 5. A mean separation of 3.40 Å (1 Å = 1×10^{-10} m) in the face-to-face orientation between the two is characteristic of the van der Waals contact between aromatic rings. The closed approach between the naphthyl group and the bipyridinium rings is 3.28 Å from C(124) to C(237). The dihedral angles between two pyridinium rings for the two viologen units are 7.8° and 10.0°, being smaller than those for [MV]Cl_2 (38°), [MV]Br_2 (35°), and [MV]I_2 (34°)[11] and similar to or slightly larger than those for the charge-transfer complexes of MV^{2+} with anionic or neutral donors.[6,12] Yoon and Kochi have demonstrated the X-ray crystal structure of

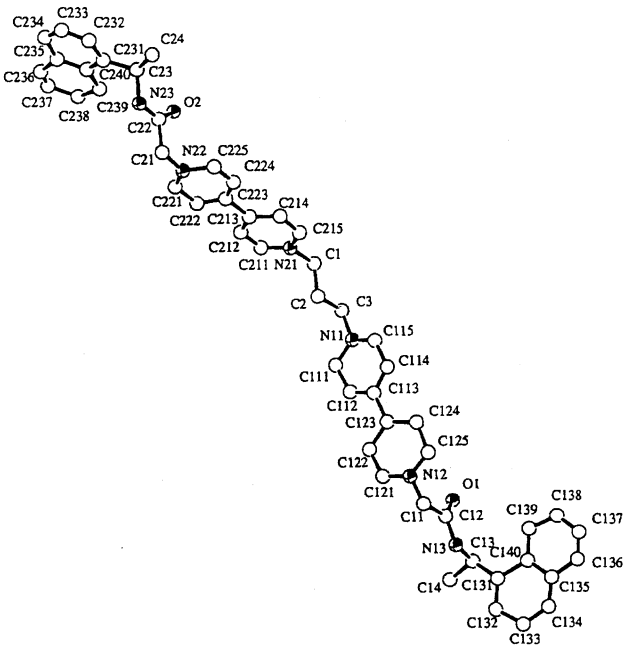


Fig. 4. ORTEP drawing of the cation of (*R*,*R*)-[NBVPR]-$Cl_4\cdot11H_2O$ (chloride salts of **6b**) with the atomic numbering scheme.

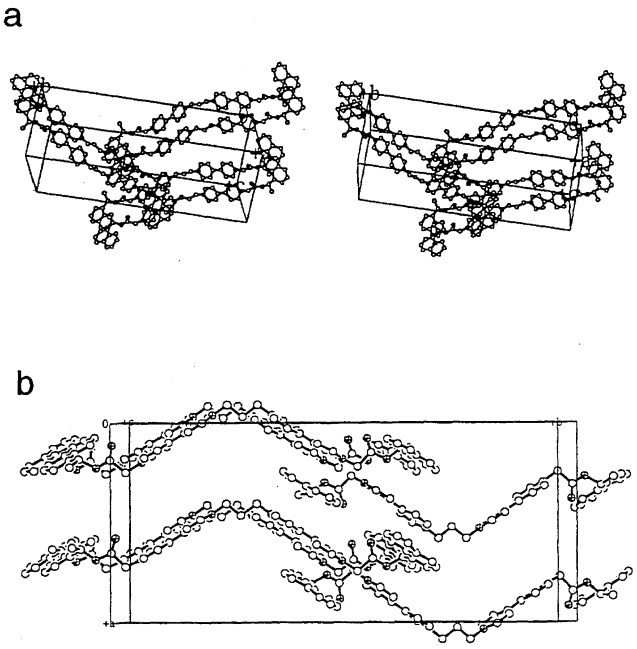


Fig. 5. (a) Stereoview for the crystal packing of (*R*,*R*)-NBVPR^{4+} ions. (b) Packing diagram viewed nearly down the c-axis and the a axis is vertically down the page.

the charge-transfer complex of [MV](PF$_6$)$_2$ with 2,6-methoxynaphthalene.[6] A similar stack of a pyridinium ring with a phenyl group has been reported for 1,1′-dibenzyl-4,4′-bipyridinium diiodide ([BV]I$_2$).[13] Therefore, the *inter*molecular interaction between the naphthyl group and the bipyridinium rings in a yellow crystal of (*R*,*R*)-[NBVPR]Cl$_4$·11H$_2$O must be in charge-transfer nature.

Cyclic Voltammetry. Cyclic voltammograms of optically active viologens were recorded in an aqueous 0.050 mol dm^{-3} KCl solution at 25 °C under a N$_2$ atmosphere with a Pt or glassy carbon electrode used as a working electrode. Although MV^{2+} shows stepwise reversible one-electron redox waves at −0.45 and −0.88 V vs. NHE (normal hydrogen electrode) in an aqueous solution,[1] the optically active monoviologens prepared in this work showed less reversible waves due to adsorption of the reduced species on the electrodes. Therefore, the redox potentials were determined from cathodic waves. On the other hand, chiral bisviologens showed reversible waves, except for NBVPR^{4+}. In the case of NBVPR^{4+}, adsorption of the reduced species was observed on the electrode. The redox potentials are given in Table 2 along with those for achiral viologens. Achiral bisviologen, PTQ^{4+}, having a trimethylene bridge, has a higher one-electron redox potential (−0.33 V)[9] compared to that of MV^{2+} (−0.45 V).[1] This may arise from a charge effect on the viologens, because the redox potential of viologen is insensitive to alkyl groups.[1] The redox potentials of chiral viologens and bisviologens are higher than those of PTQ^{4+} and MV^{2+}, arising from the electron-withdrawing nature of the carbamoyl groups of the optically active viologens.

Spectral Properties of Radical Cations of Chiral Viologens. Viologens are easily reduced by dithionite ions

Table 2. Redox Potentials and Disproportionation Constants of Viologens at 25 °C, pH 7.0, and I = 0.040 mol dm^{-3}

Viologen	K_{disp}	E_{12}^{0} [a]/V	E_{1}^{0} [b,c]/V	E_{2}^{0} [b,d]/V
OAV^{2+} (**1**)			−0.20	
NOAV^{2+} (**2**)			−0.17	
CHOAV^{2+} (**3**)			−0.20	
PBVPR^{4+} (**5**)				
(*S*,*S*)- & (*R*,*R*)-	4.6±1.3	-0.21_0	-0.23_0	-0.19_0
(*R*,*S*)-	7.4±2.0	-0.21_0	-0.23_6	-0.18_4
NBVPR^{4+} (**6**)				
(*S*,*S*)- & (*R*,*R*)-	2.5±0.4	-0.17_0	-0.18_2	-0.15_8
(*R*,*S*)-	10.0±3.0	-0.17_0	-0.20_0	-0.14_0
CHBVPR^{4+} (**7**)				
(*S*,*S*)- & (*R*,*R*)-	9.9±3.4	-0.21_0	-0.23_9	-0.18_4
(*R*,*S*)-	18.0±4.0	-0.21_0	-0.24_7	-0.17_3
PTQ^{4+} (**20**)[e]	260±60	−0.26	−0.33	−0.19

a) For two-electron redox process (vs. NHE). b) Determined from the E_{12}^{0} values by a cyclic voltammetry and the K_{disp} values. Errors are ±0.005 V. c) For the couple of the parent bisviologen/monoradical trication. d) For the couple of monoradical trication/diradical dication. e) Ref. 9.

in an aqueous solution under an Ar atmosphere to give radical cations.[1] Figure 6 shows the absorption spectra of the radical cations of chiral viologens in the presence of a slight excess of dithionite ion, indicating that the radical cations of monoviologens are in equilibrium between a monomer (λ_{max} near 600 nm and 400 nm) and a dimer (λ_{max} near 520 nm and 360 nm), the latter of which is an associated species between the viologen radical cation units (λ_{max} ca. 520 nm), and that the bisviologen gave a diradical dication (λ_{max} 532 and 363 nm), where the viologen radical units are in an *intra*molecular face-to-face orientation.

The association constant (K_d) of Eq. 4 was evaluated using Eq. 5, where the concentrations of the monomer and the

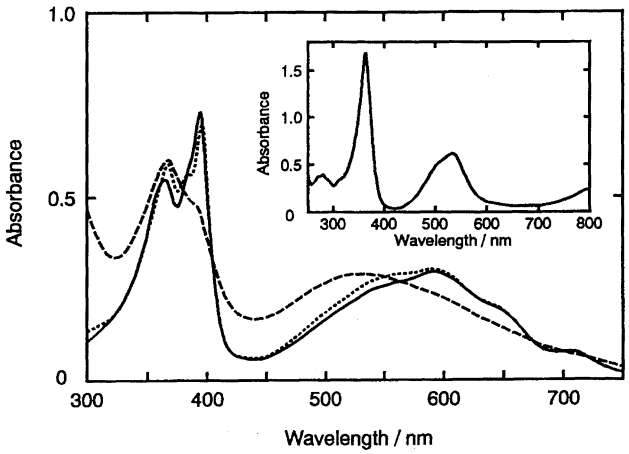


Fig. 6. Absorption spectra of the radical cations of **1a** (a solid line), **4a** (a dotted line), and **2a** (a broken line) of 3.0×10^{-5} mol dm^{-3} in the presence of excess dithionite ions at 25 °C and pH 7.0 (a 0.010 mol dm^{-3} sodium phosphate buffer) under Ar atmosphere. Inset shows the absorption spectrum of the diradical dication of **6a** (2.2×10^{-5} mol dm^{-3}) in the presence of excess dithionite ions.

dimer were estimated from the molar absorption coefficients at 604 nm of 1.40×10^4 $dm^3\,mol^{-1}\,cm^{-1}$ for the monomer and 1.40×10^4 $dm^3\,mol^{-1}\,cm^{-1}$ for the dimer, being estimated for methylviologen:[14]

$$2NOAV^{\bullet+} \rightleftarrows \{NOAV^{\bullet+}\}_2 \quad (4)$$

$$K_d = [\{NOAV^{\bullet+}\}_2]/[NOAV^{\bullet+}]^2. \quad (5)$$

The values of K_d at 25 °C, pH 7.0 (a 0.010 mol dm^{-3} sodium phosphate buffer), and $I = 0.020$ mol dm^{-3} are $(9.0\pm1.0)\times10^5$ $dm^3\,mol^{-1}$, $(4.0\pm1.0)\times10^4$ $dm^3\,mol^{-1}$, and $(2.0\pm1.0)\times10^4$ $dm^3\,mol^{-1}$ for $NOAV^{\bullet+}$, $NPOAV^{\bullet+}$, and $OAV^{\bullet+}$, respectively. No appreciable chiral recognition was observed between the (*S*,*S*)- or (*R*,*R*)- and (*R*,*S*)-isomers. This may arise from the interaction between only viologen units. The values of K_d for $MV^{\bullet+}$ and $BV^{\bullet+}$ have been reported: $(6\pm1)\times10^2$ $dm^3\,mol^{-1}$ at $I = 0.020$ mol dm^{-3} for $MV^{\bullet+}$ [14] and 5.0×10^4 $dm^3\,mol^{-1}$ at $I = 0.20$ mol dm^{-3} [15] and $(3.5\pm1.4)\times10^4$ $dm^3\,mol^{-1}$ ($k_f = (1.8\pm0.3)\times10^9$ $dm^3\,mol^{-1}\,s^{-1}$ and $k_b = (5.2\pm1.4)\times10^4$ s^{-1}) at $I = 0.10$ mol dm^{-3} [16] for $BV^{\bullet+}$. Therefore, the tendency for dimerization of viologen radical cations is in the order $NOAV^{\bullet+} \gg NPOAV^{\bullet+} \approx BV^{\bullet+} > OAV^{\bullet+} \gg MV^{\bullet+}$. A facile dimerization of $NOAV^{\bullet+}$ may arise from the electron-withdrawing nature of the 1-(1-naphthyl)ethylcarbamoylmethyl groups, whose redox potential (−0.17 V) is higher than that for MV^{2+} (−0.45 V).

Chiral Recognition in Disproportionation of Monoradical Cation of Bisviologens. The absorption spectrum of the radical cation of bisviologens was dependent on the concentrations of the parent bisviologens. This behavior has been interpreted by a disproportionation of the monoradical cation.[8,9] Figure 7 shows spectral changes for the equilibrium between $CHBVPR^{\bullet3+}$and $CHBVPR^{2\bullet2+}$ (Eq. 6) in the presence of large excess of $CHBVPR^{4+}$ at a constant total concentrations of the radicals.

$$2CHBVPR^{\bullet3+} \rightleftarrows CHBVPR^{2\bullet2+} + CHBVPR^{4+} \quad (6)$$

When the concentrations of $CHBVPR^{4+}$ increased, the absorption at 615 nm (λ_{max} for $CHBVPR^{\bullet3+}$) increased along with a concurrent decrease in the absorption at 532 nm (λ_{max} for $CHBVPR^{2\bullet2+}$) with isosbestic points at 560 and 740 nm. The spectral change for the (*R*,*R*)-isomer is larger than that for the (*R*,*S*)-one, indicating that the disproportionation of $CHBVPR^{\bullet3+}$ occurs more easily in the latter than in the former. The disproportionation constants (K_{disp}) were determined at both 532 and 615 nm at a variety of total concentrations of radicals ($(0.53—1.70)\times10^{-4}$ mol dm^{-3}). The values of K_{disp} are listed in Table 2. The K_{disp} values of (*S*,*S*)- and (*R*,*R*)-isomers are identical and smaller than those of (*R*,*S*)-isomers for all of the chiral bisviologens. The ratios of K_{disp} for the (*R*,*S*)-isomer to that for the (*S*,*S*)- or (*R*,*R*)-one are 4.0 (naphthyl) > 1.8 (cyclohexyl) ≥ 1.6 (phenyl), whose tendency is responsible for the steric bulk of the chiral substituents. It has been suggested that the diradical dication adopts a "closed" conformation, where each viologen radical-cation unit interacts *intra*molecularly.[9] Since the value

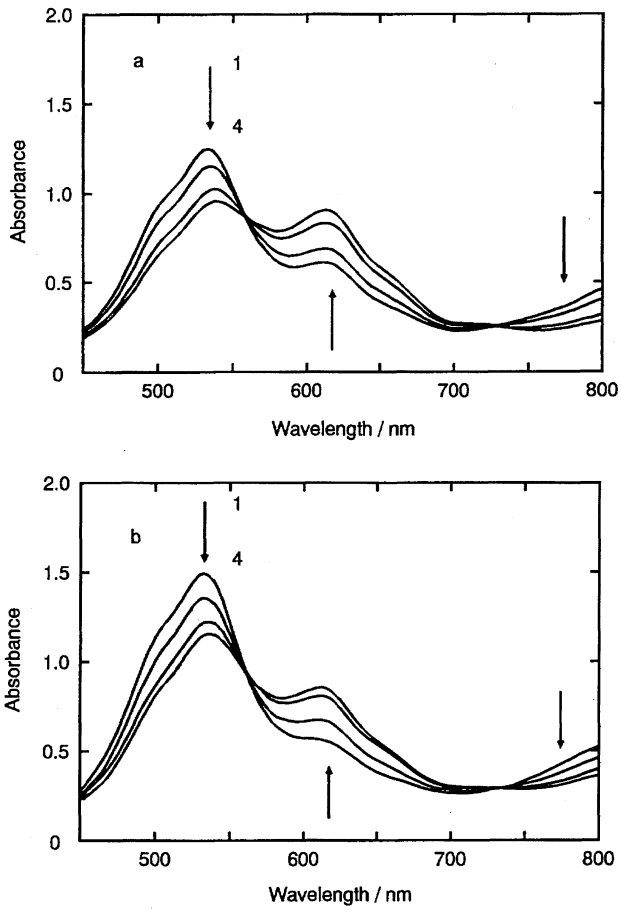


Fig. 7. Absorption spectral changes for the equilibrium between $CHBVPR^{\bullet3+}$ and $CHBVPR^{2\bullet2+}$ of the chloride salt of **7** in the presence of the parent $CHBVPR^{4+}$ ion in excess at 25 °C, pH 7.0 (a 0.010 mol dm^{-3} sodium phosphate buffer), and $I = 0.040$ mol dm^{-3} (NaCl) under Ar atmosphere. Total concentrations of radicals are 1.30×10^{-4} mol dm^{-3}. (a) Total concentrations of (*R*,*R*)-isomer (**7b**) = 5.00×10^{-4} mol dm^{-3} (1), 1.00×10^{-3} mol dm^{-3} (2), 2.00×10^{-3} mol dm^{-3} (3), and 3.00×10^{-3} mol dm^{-3} (4). (b) Total concentrations of (*R*,*S*)-isomer (**7c**) = 5.00×10^{-4} mol dm^{-3} (1), 1.00×10^{-3} mol dm^{-3} (2), 2.00×10^{-3} mol dm^{-3} (3), and 3.00×10^{-3} mol dm^{-3} (4).

of K_{disp} for a 1 : 1 mixture of (*S*,*S*)- and (*R*,*R*)-isomers was in agreement with that for the (*S*,*S*)- or (*R*,*R*)-isomer, an *inter*molecular interaction between viologen radical units in the diradical dication might be negligible. Kinetic studies have demonstrated that the disproportionation is mainly controlled by the comproportionation rate constant, which is smaller for stronger interactions in the closed conformation.[9] Chiral recognition in disproportionation may arise from the difference in the steric repulsion between the chiral substituents in the closed form of the diradical dication. The (*R*,*S*)-isomer can adopt a mirror-image conformation in such an *intra*molecular association, and the steric repulsion decreases in contrast to (*S*,*S*)- and (*R*,*R*)-isomers; therefore, disproportionation occurs easily in the former. In contrast, a relatively small methyl substituent of $PTQ^{\bullet3+}$ facilitates disproportionation ($K_{disp} = 260\pm60$).[9]

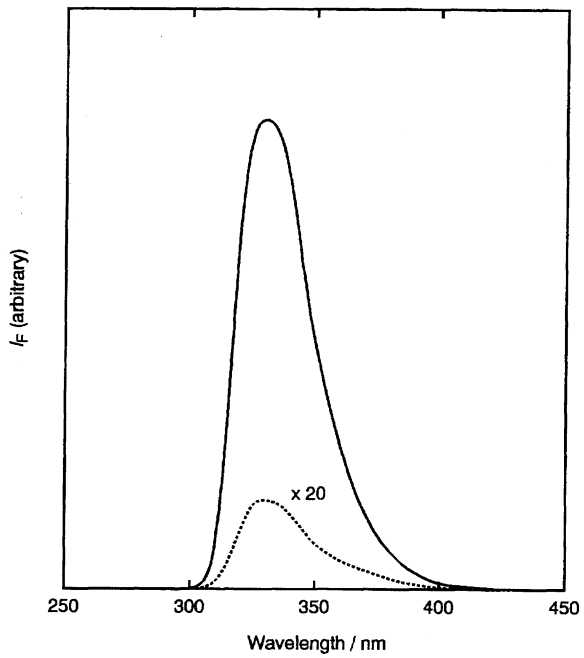


Fig. 8. Fluorescence spectra of 1.00×10^{-5} mol dm^{-3} sodium naphthalene-1-sulfonate (a solid line) and the chloride salt of (*S*,*S*)-NOAV^{2+} (a dotted line) in a degassed aqueous solution at 25 °C. An excitation wavelength is 221 nm.

Fluorescence Properties of NOAV^{2+} (2). Figure 8 shows the fluorescence spectra of a chloride salt of chiral viologen (*S*,*S*)-NOAV^{2+} (**2a**) and sodium naphthalene-1-sulfonate in an Ar-saturated aqueous solution with an excitation wavelength of 221 nm (an emission maximum at 335 nm). A relative fluorescence intensity of (*S*,*S*)-NOAV^{2+}, compared with a naphthalene-1-sulfonate ion, was 1/100 and independent of the chirality. The fluorescence lifetimes were 0.2 ns for NOAV^{2+} and 16 ns for naphthalene-1-sulfonate at 25 °C. It is, therefore, suggested that the decrease in the fluorescence intensities arises from *intra*molecular electron-transfer quenching of the excited singlet state of the naphthyl group by the bound viologen moiety. The rate constant of the *intra*molecular electron-transfer quenching is estimated to be 5×10^9 s^{-1}. The free-energy change of the reaction can be estimated to be -1.99 eV from the redox potentials and the singlet energy of the naphthyl group: E^0(naphthyl$^{\bullet+}$/^{1}(naphthyl)*) = E^0(naphthyl$^{\bullet+}$/naphthyl) $-E_{00}$(^{1}(naphthyl)*) = 1.54 − 3.70 = −2.16 V vs. NHE and E^0(NOAV^{2+}/NOAV$^{\bullet+}$) = −0.17 V.

Experimental

General Methods. The starting materials were purchased from commercial sources and used without further purification. The solvents were dried by standard methods. ^{1}H NMR spectra were recorded on a JEOL JNM-GX270 FT NMR spectrometer (270 MHz). UV-vis spectra were measured at 25 °C in an aqueous solution with a Shimadzu UV-240 spectrophotometer. Cyclic voltammetry was performed in an N_2-saturated aqueous KCl solution (0.050 mol dm^{-3}) at 25 °C with a Yanako Model P-900 instrument. A three-electrode system (BAS Ind.) was used with a Pt auxiliary electrode and a glassy carbon or a Pt working electrode against an Ag/AgCl (3.33 mol dm^{-3} KCl) reference electrode. Fluorescence spectra and lifetimes were measured in an Ar-saturated aqueous solution at 25 °C using a Hitachi 850 spectrofluorimeter and a Horiba NAES-500 ns-fluorimeter, respectively. All of the samples for the measurements were converted to chloride salts by ion-exchange chromatography.

General Procedure for the Synthesis of Chiral Bromo-[1-phenyl-, 1-(1-naphthyl)-, and 1-cyclohexylethylcarbamoyl]-methane (8, 9, and 10). To a stirred solution of bromoacetic acid (4.0 g, 0.029 mol) in dichloromethane (DCM, 20 cm^3) was slowly added DCC (6.0 g, 0.029 mol) in DCM (20 cm^3) at −5 °C. After the mixture was stirred at −5 °C for 30 min, substituted chiral ethylamine, such as 1-(1-naphthyl)ethylamine (5.0 g, 0.029 mol), in DCM (70 cm^3) was added dropwise at −5 °C. Stirring was continued for a further 90 min, after which the mixture was warmed to room temperature. After the mixture was filtered, 35 cm^3 of ice-water was added into the DCM solution. The organic layer was washed successively with 2 mol dm^{-3} HCl, saturated $NaHCO_3$, and saturated NaCl aqueous solutions (50 cm^3 each). After the DCM solution was dried over anhydrous Na_2SO_4 overnight, removal of solvent gave a white powder. Recrystallization from EtOH yielded white crystals.

Bromo[(*S*)-(1-phenylethyl)carbamoyl]methane (8a) and Bromo[(*R*)-(1-phenylethyl)carbamoyl]methane (8b). Yield, 1.1 g (16%) for **8a**, 1.05 g (15%) for **8b**. ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ = 1.53 (3H, d, J = 6.8 Hz, C*H*$_3$), 3.88 (2H, s, C*H*$_2$), 5.10 (1H, m, C*H*), 6.68 (1H, br, N*H*), 7.23—7.39 (5H, m, C$_6$*H*$_5$). Found: C, 49.49; H, 4.90; N, 5.48% (**8a**), C, 49.75; H, 4.98; N, 5.88% (**8b**). Calcd for $C_{10}H_{12}BrNO$: C, 49.61; H, 5.00; N, 5.79%.

Bromo{(*S*)-[1-(1-naphthyl)ethyl]carbamoyl}methane (9a) and Bromo{(*R*)-[1-(1-naphthyl)ethyl]carbamoyl}methane (9b). Yield, 2.0 g (24%) for **9a**, 2.2 g (26%) for **9b**. ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ = 1.73 (3H, d, J = 6.8 Hz, C*H*$_3$), 3.90 (2H, s, C*H*$_2$), 5.92 (1H, m, C*H*), 6.70 (1H, br, N*H*), 7.43—7.60 (4H, m, 2,3,6,7-naphthyl), 7.82 (1H, d, J = 7.3 Hz, 4-naphthyl), 7.90 (1H, d, J = 7.3 Hz, 5-naphthyl), 8.08 (1H, d, J = 7.3 Hz, 8-naphthyl). Found: C, 57.91; H, 4.88; N, 4.51% (**9a**), C, 57.81; H, 4.91; N, 4.56% (**9b**). Calcd for $C_{14}H_{14}BrNO$: C, 57.55; H, 4.83; N, 4.79%.

Bromo[(*S*)-(1-cyclohexylethyl)carbamoyl]methane (10a) and Bromo[(*R*)-(1-cyclohexylethyl)carbamoyl]methane (10b). Yield, 1.5 g (21%) for **10a**, 1.2 g (17%) for **10b**. ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ = 0.90—1.05 (2H, m, cyclohexyl), 1.08—1.27 (2H, m, cyclohexyl), 1.13 (3H, d, J = 6.8 Hz, C*H*$_3$), 1.30—1.43 (1H, m, cyclohexyl), 1.60—1.80 (6H, m, cyclohexyl), 3.78—3.88 (1H, m, C*H*), 3.87 (2H, s, C*H*$_2$), 6.32 (br, 1H, N*H*). Found: C, 48.34; H, 7.02; N, 5.40% (**10a**), C, 48.25; H, 7.05; N, 5.70% (**10b**). Calcd for $C_{10}H_{18}BrNO$: C, 48.40; H, 7.31; N, 5.64%.

General Procedure for the Synthesis of (*S*,*S*)- and (*R*,*R*)-Isomers of Monoviologens (1, 2, and 3). A bromo derivative, such as **8a** (1.6 g, 6.8 mmol), in DMF (40 cm^3) was heated at 85 °C under N_2, to which 4,4′-bipyridine (0.27 g, 1.7 mmol) in DMF (10 cm^3) was slowly added over a period of 2 h. The solution was further heated for 22 h. After removal of the solvent, 50 cm^3 of water was added and washed with DCM several times (50 cm^3 each). The aqueous phase was evaporated to dryness and yellow solids were washed with DCM–Me_2CO (2 : 1). Recrystallization from MeOH gave yellow crystals.

1,1′-Bis[(*S*)-(1-phenylethyl)carbamoylmethyl]-4,4′-bipyridinium Dibromide (1a·1.5H$_2$O) and 1,1′-Bis[(*R*)-(1-phenylethyl)carbamoylmethyl]-4,4′-bipyridinium Dibromide (1b·1.5H$_2$O). Yield, 0.23 g (20%) for **1a**·1.5H_2O, 0.22 g (19%) for

1b·1.5H_2O. ^{1}H NMR (270 MHz, 1.0×10^{-3} mol dm^{-3} in D_2O, DSS) δ = 1.50 (6H, d, J = 6.6 Hz, CH_3), 4.94 (2H, m, CH), 5.59 (4H, d, J = 4.9 Hz, CH_2), 7.32—7.40 (10H, m, C_6H_5), 8.54 (4H, d, J = 6.4 Hz, 3,5-bpy), 8.98 (4H, d, J = 6.4 Hz, 2,6-bpy). UV-vis (H_2O, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})) 264 (2.14×10^4). ORD (c 0.025 in H_2O, 20 °C) $[\Phi]_{589}$ −175° for **1a**·1.5H_2O, 176° for **1b**·1.5H_2O. Found: C, 53.60; H, 4.92; N, 8.37% (**1a**·1.5H_2O), C, 53.83; H, 4.95; N, 8.38% (**1b**·1.5H_2O). Calcd for $C_{30}H_{32}Br_2N_4O_2$·1.5H_2O: C, 53.99; H, 5.29; N, 8.39%.

1,1′-Bis{(*S*)-[1-(1-naphthyl)ethyl]carbamoylmethyl}-4,4′-bipyridinium Dibromide (2a·2H_2O) and 1,1′-Bis{(*R*)-[1-(1-naphthyl)ethyl]carbamoylmethyl}-4,4′-bipyridinium Dibromide (2b·2H_2O). Yield, 0.18 g (13%) for **2a**·2H_2O, 0.16 g (12%) for **2b**·2H_2O. ^{1}H NMR (270 MHz, 1.0×10^{-3} mol dm^{-3} in D_2O, DSS) δ = 1.64 (6H, d, J = 6.8 Hz, CH_3), 5.58 (4H, d, J = 7.3 Hz, CH_2), 5.77 (2H, m, CH), 7.50—7.60 (6H, m, 3,6,7-naphthyl), 7.66 (2H, d, J = 6.8 Hz, 2-naphthyl), 7.88 (2H, d, J = 7.3 Hz, 4-naphthyl), 7.95 (2H, d, J = 7.3 Hz, 5-naphthyl), 8.11 (2H, d, J = 7.3 Hz, 8-naphthyl), 8.51 (4H, d, J = 7.3 Hz, 3,5-bpy), 8.97 (4H, d, J = 6.8 Hz, 2,6-bpy). UV-vis (H_2O, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})) 260sh (2.69×10^4), 271 (3.09×10^4), 278 (2.95×10^4), 290sh (1.91×10^4). ORD (c 0.050 in H_2O, 20 °C) $[\Phi]_{589}$ −78° for **2a**·2H_2O, +78° for **2b**·2H_2O. Found: C, 58.68; H, 4.97; N, 7.30% (**2a**·2H_2O), C, 58.37; H, 5.13; N, 7.23% (**2b**·2H_2O). Calcd for $C_{38}H_{36}Br_2N_4O_2$·2H_2O: C, 58.77; H, 5.19; N, 7.21%.

1,1′-Bis[(*S*)-(1-cyclohexylethyl)carbamoylmethyl]-4,4′-bipyridinium Dibromide (3a·H_2O) and 1,1′-Bis[(*R*)-(1-cyclohexylethyl)carbamoylmethyl]-4,4′-bipyridinium Dibromide (3·H_2O). Yield, 0.14 g (12%) for **3a**·H_2O, 0.15 g (13%) for **3b**·H_2O. Found: C, 53.69; H, 6.63; N, 8.14% (**3a**·H_2O), C, 53.49; H, 6.55; N, 8.36% (**3b**·H_2O). Calcd for $C_{30}H_{44}Br_2N_4O_2$·H_2O: C, 53.74; H, 6.91; N, 8.36%. ^{1}H NMR (270 MHz, 1.0×10^{-3} mol dm^{-3} in D_2O, DSS) δ = 0.90—1.03 (4H, m, cyclohexyl), 1.08—1.27 (4H, m, cyclohexyl), 1.13 (6H, d, J = 6.8 Hz, CH_3), 1.32—1.43 (2H, m, cyclohexyl), 1.60—1.76 (12H, m, cyclohexyl), 3.68—3.77 (2H, m, CH), 5.53—5.58 (4H, m, CH_2), 8.59 (4H, d, J = 5.5 Hz, 3,5-bpy), 9.04 (4H, d, J = 5.5 Hz, 2,6-bpy). UV-vis (H_2O, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})) 267 (2.19×10^4). ORD (c 0.050 in H_2O, 20 °C) $[\Phi]_{589}$ −68° for **3a**·H_2O, 68° for **3b**·H_2O.

General Procedure for the Synthesis of (*R,S*)-Isomers of Monoviologens (1c and 2c). 4,4′-Bipyridine (1.9 g, 0.012 mol) in DMF (50 cm^3) was heated at 85 °C under N_2, to which solution was added dropwise the bromo derivative, such as **8b** (0.99 g, 4.1 mmol), in DMF (50 cm^3) over 2 h. The mixture was further heated for 22 h and evaporated to a small volume. Yellow solids (**11b**, yield 40%; **12b**, yield 70%) were collected and washed with cold Me_2CO and then with ether. To a DMF solution (50 cm^3) of **8a** (1.2 g, 5.0 mmol) was added dropwise compound **11b** (0.67 g, 1.6 mmol) in DMF (20 cm^3) at 85 °C under N_2 over 2 h, followed by further reacting for 22 h. After removal of the solvent, 50 cm^3 of water was added and the mixture was washed with DCM several times (50 cm^3 each). The aqueous phase was evaporated to dryness and yellow solids were washed with DCM–Me_2CO (2 : 1). Recrystallization from MeOH gave yellow crystals.

1-[(*R*)-(1-Phenylethyl)carbamoylmethyl]-1′-[(*S*)-(1-phenylethyl)carbamoylmethyl]-4,4′-bipyridinium Dibromide (1c·1.5H_2O). Yield, 0.13 g (12%). ^{1}H NMR (270 MHz, 1.0×10^{-3} mol dm^{-3} in D_2O, DSS) δ = 1.50 (6H, d, J = 6.6 Hz, CH_3), 4.94 (2H, m, CH), 5.59 (4H, d, J = 4.9 Hz, CH_2), 7.32—7.40 (10H, m, C_6H_5), 8.54 (4H, d, J = 6.4 Hz, 3,5-bpy), 8.98 (4H, d, J = 6.4 Hz, 2,6-bpy). UV-vis (H_2O, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})) 264 (2.14×10^4). ORD (c 0.025 in H_2O, 20 °C) $[\Phi]_{589}$ 0°. Found: C, 54.22; H, 5.15; N, 8.16%. Calcd for $C_{30}H_{32}Br_2N_4O_2$·1.5H_2O: C, 53.99; H, 5.29; N, 8.39%.

1-{(*R*)-[1-(1-Naphthyl)ethyl]carbamoylmethyl}-1′-{(*S*)-[1-(1-naphthyl)ethyl]carbamoylmethyl}-4,4′-bipyridinium Dibromide (2c·2H_2O). Yield, 0.16 g (13%). ^{1}H NMR (270 MHz, 1.0×10^{-3} mol dm^{-3} in D_2O, DSS) δ = 1.64 (6H, d, J = 6.8 Hz, CH_3), 5.58 (4H, d, J = 7.3 Hz, CH_2), 5.77 (2H, m, CH), 7.50—7.60 (6H, m, 3,6,7-naphthyl), 7.66 (2H, d, J = 6.8 Hz, 2-naphthyl), 7.88 (2H, d, J = 7.3 Hz, 4-naphthyl), 7.95 (2H, d, J = 7.3 Hz, 5-naphthyl), 8.11 (2H, d, J = 7.3 Hz, 8-naphthyl), 8.51 (4H, d, J = 7.3 Hz, 3,5-bpy), 8.97 (4H, d, J = 6.8 Hz, 2,6-bpy). UV-vis (H_2O, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})) 260sh (2.69×10^4), 271 (3.09×10^4), 278 (2.95×10^4), 290sh (1.91×10^4). ORD (c 0.050 in H_2O, 20 °C) $[\Phi]_{589}$ 0 °. Found: C, 58.66; H, 4.99; N, 7.33%. Calcd for $C_{38}H_{36}Br_2N_4O_2$·2H_2O: C, 58.77; H, 5.19; N, 7.21%.

General Procedure for the Synthesis of Monoviologens Containing Both Naphthyl and Phenyl Groups (4a, 4b, and 4c). The same method as that for compounds **1c** and **2c** was employed. The bromo derivative of **9a** or **9b** was used for a starting material and the resulted **12a** or **12b** was further reacted with **8a** or **8b**.

1-{(*S*)-[1-(1-Naphthyl)ethyl]carbamoylmethyl}-1′-[(*S*)-(1-phenylethyl)carbamoylmethyl]-4,4′-bipyridinium Dibromide (4a·3.5H_2O), 1-{(*R*)-[1-(1-Naphthyl)ethyl]carbamoylmethyl}-1′-[(*R*)-(1-phenylethyl)carbamoylmethyl]-4,4′-bipyridinium Dibromide (4b·3.5H_2O), and 1-{(*R*)-[1-(1-Naphthyl)ethyl]carbamoylmethyl}-1′-[(*S*)-(1-phenylethyl)carbamoylmethyl]-4,4′-bipyridinium Dibromide (4c·3.5H_2O). Yield, 0.14 g (12%) for **4a**·3.5H_2O, 0.16 g (13%) for **4b**·3.5H_2O, 0.12 g (10%) for **4c**·3.5H_2O. ^{1}H NMR (270 MHz, 5.0×10^{-3} mol dm^{-3} in D_2O, DSS) δ = 1.49 (3H, d, J = 6.6 Hz, CH_3 (phenyl)), 1.65 (3H, d, J = 6.8 Hz, CH_3 (naphthyl)), 4.94 (1H, m, CH (phenyl)), 5.50—5.65 (4H, m, CH_2), 5.78 (1H, m, CH (naphthyl)), 7.31—7.42 (5H, m, C_6H_5), 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), 8.94—9.00 (4H, m, 2,6-bpy). UV-vis (H_2O, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 270 (2.88×10^4). ORD (c 0.050 in H_2O, 20 °C) $[\Phi]_{589}$ −126° for **4a**·3.5H_2O, 126° for **4b**·3.5H_2O, 48° for **4c**·3.5H_2O. Found: C, 53.84; H, 5.38; N, 7.80% (**4a**·3.5H_2O), C, 54.32; H, 5.09; N, 7.71% (**4b**·3.5H_2O), C, 53.99; H, 5.10; N, 7.75% (**4c**·3.5H_2O). Calcd for $C_{34}H_{34}Br_2N_4O_2$·3.5H_2O: C, 54.19; H, 5.48; N, 7.44%.

General Procedure for the Synthesis of (*S,S*)- and (*R,R*)-Isomers of Bisviologens (5, 6, and 7). To a DMF solution (50 cm^3) of the bromo derivative, such as **8a** (0.99 g, 4.1 mmol), was slowly added 1,1″-trimethylenebis[4-(4-pyridyl)pyridinium] dibromide[7] (0.72 g, 1.4 mmol) in DMF (200 cm^3) over a period of 3 h at 85 °C under N_2, followed by further reacting for 24 h. After the solution was evaporated to a small volume, yellow solids were collected and washed with cold Me_2CO and then with ether. Recrystallization from warm water gave yellow crystals.

1,1″-Trimethylenebis{1′-[(*S*)-(1-phenylethyl)carbamoylmethyl]-4,4′-bipyridinium} Tetrabromide (5a·2H_2O) and 1,1″-Trimethylenebis{1′-[(*R*)-(1-phenylethyl)carbamoylmethyl]-4,4′-bipyridinium} Tetrabromide (5b·2H_2O). Yield, 0.39 g (27%) for **5a**·2H_2O, 0.17 g (12%) for **5b**·2H_2O. Found: C, 49.63; H, 4.68; N, 8.02% (**5a**·2H_2O), C, 50.02; H, 4.57; N, 8.15% (**5b**·2H_2O). Calcd for $C_{43}H_{46}Br_4N_6O_2$·2H_2O: C, 49.92; H, 4.87; N, 8.12%. ^{1}H NMR (270 MHz, D_2O, DSS) δ = 1.50 (6H, d, J = 6.8 Hz, CH_3), 2.86—2.97 (2H, m, β-CH_2), 4.95 (4H, t, J = 7.5 Hz, α-CH_2), 4.96 (2H, q, J = 7.4 Hz, CH), 5.53—5.67 (4H, m, $COCH_2$–$^+$N), 7.30—7.45 (10H, m, C_6H_5), 8.55 (4H, d, J = 7.3 Hz, 3,5-bpy),

8.59 (4H, d, J = 7.3 Hz, 3′,5′-bpy), 9.00 (4H, d, J = 6.8 Hz, 2,6-bpy), 9.19 (4H, d, J = 6.8 Hz, 2′,6′-bpy). UV-vis (H_2O, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})) 265 (6.76×10^4). ORD (c 0.050 in H_2O, 20 °C) $[\Phi]_{589}$ −144° for **5a**·2H_2O, 145° for **5b**·2H_2O.

1,1″-Trimethylenebis(1′-{(*S*)-[1-(1-naphthyl)ethyl]carbamoylmethyl}-4,4′-bipyridinium) Tetrabromide (6a·4.5H_2O) and 1,1″-Trimethylenebis(1′-{(*R*)-[1-(1-naphthyl)ethyl]carbamoylmethyl}-4,4′-bipyridinium) Tetrabromide (6b·4.5H_2O). Yield, 0.73 g (44%) for **6a**·4.5H_2O, 0.61 g (37%) for **6b**·4.5H_2O. ^{1}H NMR (270 MHz, D_2O, DSS) δ = 1.66 (6H, d, J = 6.8 Hz, CH_3), 2.84—2.96 (2H, m, β-CH_2), 4.94 (4H, t, J = 7.6 Hz, α-CH_2), 5.58—5.62 (4H, m, COCH_2–$^+$N), 5.78 (2H, q, J = 7.5 Hz, CH), 7.53—7.62 (6H, m, 3,6,7-naphthyl), 7.64 (2H, d, J = 5.9 Hz, 2-naphthyl), 7.90 (2H, d, J = 7.8 Hz, 4-naphthyl), 7.98 (2H, d, J = 8.3 Hz, 5-naphthyl), 8.12 (2H, d, J = 8.1 Hz, 8-naphthyl), 8.54 (4H, d, J = 6.8 Hz, 3,5-bpy), 8.57 (4H, d, J = 7.3 Hz, 3′,5′-bpy), 8.99 (4H, d, J = 6.8 Hz, 2,6-bpy), 9.18 (4H, d, J = 6.8 Hz, 2′,6′-bpy). UV-vis (H_2O, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})) 260sh (5.75×10^4), 270 (6.03×10^4), 280sh (5.37×10^4). ORD (c 0.050 in H_2O, 20 °C) $[\Phi]_{589}$ −60° for **6a**·4.5H_2O, 61° for **6b**·4.5H_2O. Found: C, 52.04; H, 4.64; N, 7.23% (**6a**·4.5H_2O), C, 51.70; H, 4.86; N, 7.16% (**6b**·4.5H_2O). Calcd for $C_{51}H_{50}Br_4N_6O_2$·4.5H_2O: C, 51.93; H, 5.04; N, 7.12%. Single crystals, suitable for X-ray crystallography, were grown in an aqueous solution of chloride salts of **6b** converted by an ion-exchange chromatography ((*R*,*R*)-[NBVPR]Cl_4·11H_2O).[17]

1,1″-Trimethylenebis{1′-[(*S*)-(1-cyclohexylethyl)carbamoylmethyl]-4,4′-bipyridinium} Tetrabromide (7a·4H_2O) and 1,1″-Trimethylenebis{1′-[(*R*)-(1-phenylethyl)carbamoylmethyl]-4,4′-bipyridinium} Tetrabromide (7b·3H_2O). Yield, 0.38 g (25%) for **7a**·4H_2O, 0.19 g (13%) for **7b**·3H_2O. ^{1}H NMR (270 MHz, D_2O, DSS) δ = 0.90—1.03 (4H, m, cyclohexyl), 1.13 (6H, d, J = 6.8 Hz, CH_3), 1.08—1.27 (4H, m, cyclohexyl), 1.32—1.43 (2H, m, cyclohexyl), 1.60—1.76 (12H, m, cyclohexyl), 2.88—2.98 (2H, m, β-CH_2), 3.68—3.77 (2H, m, CH), 4.97 (4H, t, J = 7.3 Hz, α-CH_2), 5.53—5.58 (4H, m, COCH_2–$^+$N), 8.59 (4H, d, J = 5.6 Hz, 3,5-bpy) 8.61 (4H, d, J = 5.6 Hz, 3′,5′-bpy), 9.04 (4H, d, J = 5.4 Hz, 2,6-bpy), 9.21 (4H, d, J = 5.4 Hz, 2′,6′-bpy). UV-vis (H_2O, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})) 265 (5.01×10^4). ORD (c 0.050 in H_2O, 20 °C) $[\Phi]_{589}$ −43° for **7a**·4H_2O, 43° for **7b**·3H_2O. Found: C, 48.39; H, 5.91; N, 7.74% for **7a**·4H_2O. Calcd for $C_{43}H_{58}Br_4N_6O_2$: C, 47.70; H, 6.14; N, 7.76%. Found: C, 47.78; H, 6.08; N, 7.80% for **7b**·3H_2O. Calcd for $C_{43}H_{58}N_6O_2Br_4$: C, 48.51; H, 6.06; N, 7.89%.

General Procedure for the Synthesis of (*R*,*S*)-Isomers of Bisviologens (5c, 6c, and 7c). The (*R*,*S*)-isomer (**5c**) was prepared by the following way under the reaction conditions at 85 °C for 28 h in DMF under nitrogen. 1-(*S*)-[(1-Phenylethyl)carbamoylmethyl]-4-(4-pyridyl)pyridinium bromide (**11a**), which was obtained by the reaction of **8a** with 3-fold excess of 4,4′-bipyridine by the same method as for **11b**, was treated with a 40-fold excess of 1,3-dibromopropane. The resulted 1-(3-bromopropyl)-1′-[(*S*)-1-(1-phenylethyl)carbamoylmethyl]-4,4′-bipyridinium dibromide (**14a**) was reacted with a 4-fold excess of 4,4′-bipyridine to give 1-[(*S*)-(1-phenylethyl)carbamoylmethyl]-1′-{3-[4-(4-pyridyl)-pyridinio]propyl}-4,4′-bipyridinium tribromide (**17a**). Compound **17a** was further reacted with a 2.5-fold excess of **8b** to give the desired compound **5c**. Crude intermediate compounds were used for the naphthyl derivatives. Compounds **6c** and **7c** were also prepared by the same method as described above. Crude products were recrystallized from warm water.

1-(*S*)-[(1-Phenylethyl)carbamoylmethyl]-4-(4-pyridyl)pyridinium Bromide (11a·0.5H_2O). Yield, 40%. ^{1}H NMR (270 MHz, D_2O, DSS) δ = 1.50 (3H, d, J = 6.6 Hz, CH_3), 4.94 (1H, m, CH), 5.50 (2H, m, CH_2), 7.30—7.45 (5H, m, C_6H_5), 7.88 (2H, d, J = 6.8 Hz, 2′,6′-bpy), 8.38 (2H, d, J = 6.8 Hz, 3,5-bpy), 8.73 (2H, d, J = 6.8 Hz, 3′,5′-bpy), 8.82 (2H, d, J = 6.8 Hz, 2,6-bpy). Found: C, 58.78; H, 5.15; N, 10.03%. Calcd for $C_{20}H_{20}BrN_3O$·0.5H_2O: C, 58.98; H, 5.20; N, 10.32%.

1-(*S*)-[(1-Cyclohexylethyl)carbamoylmethyl]-4-(4-pyridyl)-pyridinium Bromide (13a·1.5H_2O). Yield, 82%. ^{1}H NMR (270 MHz, D_2O, DSS) δ = 0.85—1.03 (2H, m, cyclohexyl), 1.08—1.25 (2H, m, cyclohexyl), 1.13 (3H, d, J = 6.8 Hz, CH_3), 1.30—1.43 (1H, m, cyclohexyl), 1.55—1.76 (6H, m, cyclohexyl), 3.68—3.77 (1H, m, CH), 5.46 (2H, s, CH_2), 7.92 (2H, d, J = 6.8 Hz, 2′,6′-bpy), 8.43 (2H, d, J = 6.8 Hz, 3,5-bpy), 8.77 (2H, d, J = 6.8 Hz, 3′,5′-bpy), 8.85 (2H, d, J = 6.8 Hz, 2,6-bpy). Found: C, 55.82; H, 6.40; N, 9.85%. $C_{20}H_{26}BrN_3O$·1.5H_2O : C, 55.69; H, 6.78; N, 9.74%.

1-(3-Bromopropyl)-1′-[(*S*)-(1-phenylethyl)carbamoylmethyl]-4,4′-bipyridinium Dibromide (14a·2H_2O). Yield, 85%. ^{1}H NMR (270 MHz, D_2O, DSS) δ = 1.51 (3H, d, J = 7.3 Hz, CH_3), 2.59—2.68 (2H, m, $CH_2CH_2CH_2$), 3.52 (2H, t, J = 6.2 Hz, CH_2–Br), 4.90 (2H, t, J = 7.0 Hz, N^+–CH_2), 4.92—5.00 (1H, m, CH), 5.53—5.67 (2H, m, NHCO–CH_2–N^+), 7.30—7.43 (5H, m, C_6H_5), 8.55 (4H, d, J = 6.8 Hz, 3,3′,5,5′-bpy), 8.99 (2H, d, J = 6.8 Hz, 2,6-bpy), 9.15 (2H, d, J = 6.8 Hz, 2′,6′-bpy). Found: C, 43.19; H, 4.79; N, 6.72%. Calcd for $C_{23}H_{26}Br_3N_3O$·2H_2O: C, 43.42; H, 4.75; N, 6.60%.

1-(3-Bromopropyl)-1′-[(*S*)-(1-cyclohexylethyl)carbamoylmethyl]-4,4′-bipyridinium Dibromide (16a·H_2O). Yield, 85%. ^{1}H NMR (270 MHz, D_2O, DSS) δ = 0.85—1.05 (2H, m, cyclohexyl), 1.08—1.25 (2H, m, cyclohexyl), 1.13 (3H, d, J = 6.8 Hz, CH_3), 1.30—1.43 (1H, m, cyclohexyl), 1.55—1.76 (6H, m, cyclohexyl), 2.60—2.70 (2H, m, $CH_2CH_2CH_2$), 3.52 (2H, t, J = 6.1 Hz, CH_2–Br), 3.67—3.75 (1H, m, CH), 4.90 (2H, t, J = 7.0 Hz, N^+–CH_2), 5.55 (2H, s, NHCO–CH_2-N^+), 8.57 (2H, d, J = 6.8 Hz, 3,5-bpy), 8.58 (2H, d, J = 6.8 Hz, 3′,5′-bpy), 9.03 (2H, d, J = 6.8 Hz, 2,6-bpy), 9.16 (2H, d, J = 6.8 Hz, 2′,6′-bpy). Found: C, 44.49; H, 5.09; N, 6.78%. Calcd for $C_{23}H_{32}Br_3N_3O$·H_2O: C, 44.25; H, 5.49; N, 6.73%.

1-[(*S*)-(1-Phenylethyl)carbamoylmethyl]-1′-{3-[4-(4-pyridyl)-pyridinio]propyl}-4,4′-bipyridinium Tribromide (17a·5H_2O). Yield, 48%. ^{1}H NMR (270 MHz; D_2O; DSS) δ = 1.50 (3H, d, J = 6.8 Hz, CH_3), 2.86—2.94 (2H, m, $CH_2CH_2CH_2$), 4.85—4.95 (1H, m, CH), 4.93 (2H, t, J = 7.8 Hz, N^+–CH_2), 4.94 (2H, t, J = 7.8 Hz, N^+–CH_2), 5.53—5.66 (2H, m, NHCO–CH_2–N^+), 7.32—7.44 (5H, m, C_6H_5), 7.90 (2H, d, J = 6.4 Hz, bpy), 8.44 (2H, d, J = 6.8 Hz, bpy), 8.54 (2H, d, J = 7.3 Hz, bpy), 8.58 (2H, d, J = 6.8 Hz, bpy), 8.76 (2H, d, J = 6.4 Hz, bpy), 8.99 (2H, d, J = 7.3 Hz, bpy), 9.02 (2H, d, J = 6.8 Hz, bpy), 9.17 (2H, d, J = 6.8 Hz, bpy). Found: C, 46.80; H, 5.01; N, 8.27%. Calcd for $C_{33}H_{34}Br_3N_5O$·5H_2O: C, 46.83; H, 5.24; N, 8.27%.

1-(*S*)-[(1-Cyclohexylethyl)carbamoylmethyl]-1′-{3-[4-(4-pyridyl)pyridinio]propyl}-4,4′-bipyridinium Tribromide (19a·2H_2O). Yield, 31%. ^{1}H NMR (270 MHz, D_2O, DSS) δ = 0.87—1.03 (2H, m, cyclohexyl), 1.08—1.25 (2H, m, cyclohexyl), 1.13 (3H, d, J = 6.8 Hz, CH_3), 1.30—1.43 (1H, m, cyclohexyl), 1.55—1.76 (6H, m, cyclohexyl), 2.85—2.97 (2H, m, $CH_2CH_2CH_2$), 3.68—3.78 (1H, m, CH), 4.89 (2H, t, J = 7.3 Hz, N^+–CH_2), 4.95 (2H, t, J = 7.3 Hz, N^+–CH_2), 5.56 (2H, s, CO–CH_2–N^+), 7.89 (2H, d, J = 6.4 Hz, bpy), 8.45 (2H, d, J = 6.8 Hz, bpy), 8.59 (2H, d, J = 6.8 Hz, bpy), 8.61 (2H, d, J = 6.8 Hz, bpy), 8.76 (2H, d, J = 6.4 Hz, bpy), 9.03 (4H, d, J = 6.8 Hz, bpy), 9.19 (2H, d, J = 6.8 Hz, bpy). Found: C, 49.43; H, 5.24; N, 8.88%. Calcd for $C_{33}H_{40}Br_3N_5O$·2H_2O: C, 49.64; H, 5.55; N, 8.77%.

(*R*,*S*)-[PBVPR]$Br_4 \cdot 3H_2O$ (5c·$3H_2O$). Yield, 68%. ^{1}H NMR (270 MHz, D_2O, DSS) δ = 1.50 (6H, d, J = 6.8 Hz, CH_3), 2.86—2.97 (2H, m, β-CH_2), 4.95 (4H, t, J = 7.5 Hz, α-CH_2), 4.96 (2H, q, J = 7.4 Hz, CH), 5.53—5.67 (4H, m, CO–CH_2–N$^+$), 7.30—7.45 (10H, m, C$_6H_5$), 8.55 (4H, d, J = 7.3 Hz, 3,5-bpy), 8.59 (4H, d, J = 7.3 Hz, 3′,5′-bpy), 9.00 (4H, d, J = 6.8 Hz, 2,6-bpy), 9.19 (4H, d, J = 6.8 Hz, 2′,6′-bpy). UV-vis (H_2O, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})) 265 (6.76×10^4). ORD (c 0.050 in H_2O, 20 °C) [Φ]$_{589}$ 0°. Found: C, 48.79; H, 4.68; N, 7.90%. Calcd for $C_{43}H_{46}Br_4N_6O_2 \cdot 3H_2O$: C, 49.07; H, 4.98; N, 7.98%.

(*R*,*S*)-[NBVPR]$Br_4 \cdot 5H_2O$ (6c·$5H_2O$). Yield, 21%. ^{1}H NMR (270 MHz, D_2O, DSS) δ = 1.66 (6H, d, J = 6.8 Hz, CH_3), 2.84—2.96 (2H, m, β-CH_2), 4.94 (4H, t, J = 7.6 Hz, α-CH_2), 5.58—5.62 (4H, m, COCH_2–$^+$N), 5.78 (2H, q, J = 7.5 Hz, CH), 7.53—7.62 (6H, m, 3,6,7-naphthyl), 7.64 (2H, d, J = 5.9 Hz, 2-naphthyl), 7.90 (2H, d, J = 7.8 Hz, 4-naphthyl), 7.98 (2H, d, J = 8.3 Hz, 5-naphthyl), 8.12 (2H, d, J = 8.1 Hz, 8-naphthyl), 8.54 (4H, d, J = 6.8 Hz, 3,5-bpy), 8.57 (4H, d, J = 7.3 Hz, 3′,5′-bpy), 8.99 (4H, d, J = 6.8 Hz, 2,6-bpy), 9.18 (4H, d, J = 6.8 Hz, 2′,6′-bpy). UV-vis (H_2O, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})) 260sh (5.75×10^4), 270 (6.03×10^4), 280sh (5.37×10^4). ORD (c 0.050 in H_2O, 20 °C) [Φ]$_{589}$ 0°. Found: C, 51.01; H, 4.54; N, 7.25%. Calcd for $C_{51}H_{50}Br_4N_6O_2 \cdot 5H_2O$: C, 51.53; H, 5.09; N, 7.07%.

(*R*,*S*)-[CHBVPR]$Br_4 \cdot 3H_2O$ (7c·$3H_2O$). Yield, 39%. ^{1}H NMR (270 MHz, D_2O, DSS) δ = 0.90—1.03 (4H, m, cyclohexyl), 1.13 (6H, d, J = 6.8 Hz, CH_3), 1.08—1.27 (4H, m, cyclohexyl), 1.32—1.43 (2H, m, cyclohexyl), 1.60—1.76 (12H, m, cyclohexyl), 2.88—2.98 (2H, m, β-CH_2), 3.68—3.77 (2H, m, CH), 4.97 (4H, t, J = 7.3 Hz, α-CH_2), 5.53—5.58 (4H, m, COCH_2–$^+$N), 8.59 (4H, d, J = 5.6 Hz, 3,5-bpy) 8.61 (4H, d, J = 5.6 Hz, 3′,5′-bpy), 9.04 (4H, d, J = 5.4 Hz, 2,6-bpy), 9.21 (4H, d, J = 5.4 Hz, 2′,6′-bpy). UV-vis (H_2O, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})) 265 (5.01×10^4). ORD (c 0.050 in H_2O, 20 °C) [Φ]$_{589}$ 0°. Found: C, 48.79; H, 5.69; N, 7.65%. Calcd for $C_{43}H_{58}Br_4N_6O_2 \cdot 3H_2O$: C, 48.51; H, 6.06; N, 7.89%.

Determination of the Association Constants by UV-vis and ^{1}H NMR Spectroscopy. The association constants for the intermolecular charge-transfer complexes of monoviologens, **2** and **4**, were determined in aqueous solutions by both UV-vis and ^{1}H NMR spectroscopies at 25 °C and an ionic strength of 0.20 mol dm^{-3} (NaCl). The former method was employed to an increase in absorbance over 350—400 nm of the solutions of 0—0.02 mol dm^{-3} viologens. The chemical shift of both bipyridinium- and naphthyl-ring protons with increasing concentrations of viologens (0—0.07 mol dm^{-3}) was measured in D_2O for the latter method.

Determination of the Disproportionation Constants and the Dimerization Constants by UV-vis Spectroscopy. The disproportionation constants of the monoradical trications were determined spectrophotometrically by the same method as that described in the literature,[9] where sodium dithionite (Fluka) was used as a reducing agent at 25 °C, pH 7.0 (a 0.010 mol dm^{-3} sodium phosphate buffer), and I = 0.040 mol dm^{-3} (NaCl) under argon atmosphere. The molar absorption coefficients used to calculate the disproportionation constant (K_{disp}) at 532 and 615 nm for each bisviologen species are as follows: ε_{532}/dm^3 mol^{-1} cm^{-1} 2.81×10^4 (NBVPR$^{2\bullet2+}$), 4.96×10^3 (NBVPR$^{\bullet3+}$), 3.36×10^4 (PBVPR$^{2\bullet2+}$), 5.60×10^3 (PBVPR$^{\bullet3+}$), 2.74×10^4 (CHBVPR$^{2\bullet2+}$), 4.34×10^3 (CHBVPR$^{\bullet3+}$); ε_{615}/dm^3 mol^{-1} cm^{-1} 4.59×10^3 (NBVPR$^{2\bullet2+}$), 1.30×10^4 (NBVPR$^{\bullet3+}$), 4.40×10^3 (PBVPR$^{2\bullet2+}$), 1.47×10^4 (PBVPR$^{\bullet3+}$), 3.44×10^3 (CHBVPR$^{2\bullet2+}$), 1.14×10^4 (CHBVPR$^{\bullet3+}$).

X-Ray Crystallography. A crystal of (*R*,*R*)-[NBVPR]-$Cl_4 \cdot 11H_2O$ used in the data collection was mounted on the end of a glass fiber with Paraton N oil; data collection was carried out at −99 °C on a Rigaku RASA-7A automatic four-circle diffractometer equipped with graphite monochromated Mo $K\alpha$ (λ = 0.71069 Å) radiation. The crystal was very delicate in air at room temperature, which might have led a somewhat low-grade reflection data set. Crystal data and experimental conditions are as follows: $C_{51}H_{72}Cl_4N_6O_{13}$, M_w 1118.97, orthorhombic, $P2_12_12_1$ (No. 19), a = 15.913(4), b = 35.479(14), c = 12.914(4) Å, V = 7290(3) Å^3, Z = 4, D_{calcd} = 1.019 g cm^{-3}, μ (Mo $K\alpha$) 2.13 cm^{-1}, 4° < 2θ < 50°, scan method ω, scan speed 8° min^{-1}. Three standard reflections were monitored every 150 reflections and showed no systematic decrease in intensity. Of 6415 reflections measured, 2415 independent reflections with $I > 3\sigma(I)$ were used in solution and refinement of the structure. Reflection data were corrected for Lorentz-polarization effects, and absorption corrections were applied by the ψ-scan method. The known absolute configuration (*R*) of the methine carbon center was used as an internal reference asymmetric center.

The structure was solved by direct methods with SIR92.[17] The most non-hydrogen atoms were located initially and subsequent difference Fourier syntheses gave remaining atoms. The C–H hydrogen atoms were located at ideal positions with a distance of 0.95 Å and were not refined. The structure was refined with full-matrix least square techniques minimizing $\sum w(|F_o|-|F_c|)^2$. The Cl(4) and Cl(5) atoms were refined with a disordered model with 0.5 multiplicity. Final refinement with anisotropic thermal parameters for the Cl and O atoms and isotropic ones for other non-hydrogen atoms converged at R = 0.119 and R_w = 0.120, where $R = \sum||F_o|-|F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$). The small calculated density indicated that some other solvent molecules still remained unidentified, owing to their disorder. The final refinement still showed the maximum (0.67 e Å^{-3}) and minimum (−0.38 e Å^{-3}) residual electron densities.

The atomic scattering factors and values of f' and f'' for Cl, O, N, and C were taken from the literature.[18,19] All of the calculations were carried out on a Silicon Graphics Indigo with the teXsan program package.[20] Lists of the structure factors, positional and thermal parameters for all atoms, anisotropic thermal parameters for Cl and O atoms, and bond lengths and angles for the non-hydrogen atoms have been deposited as Document No. 72001 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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