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Photochromism of Viologen Hexacyanoferrate(II) Complexes via Intramolecular Electron Transfer

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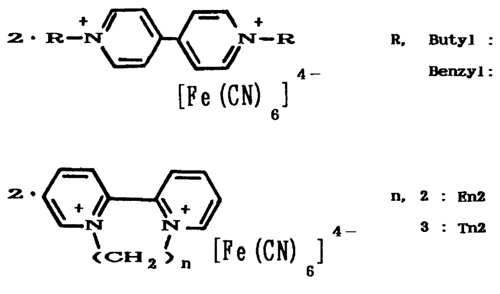
Viologen metal complexes comprising 2,2′- and 4,4′-bipyridinium hexacyanoferrate(II) were synthesized starting from the corresponding halides by an anion-exchange reaction. The charge-transfer bands appeared in aqueous solutions, whereas radical cation peaks in visible region appeared in solid polymer matrices via a photoinduced electron transfer within the viologen molecule; their absorptions were dependent upon both the kind of bipyridinium dication and the media, such as the solvents and polymer matrices. The reversible redox reaction by photon mode (color development) and by heat mode (bleaching) can be repeated in the absence of atmospheric oxygen.

The viologens, bis-quartanary salts of bipyridine undergo a one-electron transfer to give highly colored radical cations.[1)] This property has stimulated much interest in utilizing in the mediation of the electron-transfer process, for example, in biological redox systems, and in solar energy collection and storage systems. Radical formation has been found by radiation of the solar-level light in solutions in the presence of reductants.[2)] A photoinduced intramolecular reduction also takes place in a polar aprotic media, in spite of the large differences in the redox potential between the bipyridinium and counter anions;[3)] oxidation of the produced radical cations proceeds by air oxygen, while a reverse electron transfer proceeds when air is absent in the system.[4)]

In order to evaluate the reversible redox reaction (photochromism) of viologens, this paper describes a peculiar behavior concerning a photoinduced intramolecular electron transfer within a viologen molecule bearing a metal-complexed counter anion, which posseses a relatively low redox potential.[5)] Although the rate constant of an internal electron transfer of a mixture of 4,4′-bipyridinium salts with externally added potassium hexacyanoferrate(II)[6,7)] and covalently linked tris(2,2′-bipyridine)ruthenium[8)] had been measured by laser-flash photolysis, we synthesized the complexes of 2,2′- and 4,4′-bipyridinium hexacyanoferrate(II) by an anion-exchange reaction, and investigated their charge-transfer(CT)-complex-forming properties in aqueous solutions as well as their photochromic behaviors via a photoinduced electron transfer when enbedded in polymer matrices (Scheme 1).



Scheme 1.

Experimental

Materials. ***N, N′*-Ethylene-2, 2′-bipyridinium hexacyanoferrate(II) (En2):** To the solution of *N, N′*-ethylene-2,2′-bi-pyrininium dibromide (2 g, 5.8 mmol) in water (50 ml) was added an anion exchange resin (16 g, Amberlite IRA-400), loaded with hexacyanoferrate(II) anion by exchanging the OH type with potassium hexacyanoferrate(II). The reaction atmosphere was replaced with nitrogen gas, and the mixture was gently stirred for two days in a dark place. The resin was filtered off, and the filtrate was lyophilized to leave a pale-brown powder (1.7 g). Found: C, 64.98; H, 4.87; N, 24.07%; corresponding to the formula $C_{12}H_{12}N_2[Fe\ (CN)_6]_{0.44}Br_{0.24}\cdot 3H_2O$.

***N, N′*-Trimethylene-2, 2′-bipyridinium hexacyanoferrate(II) (Tn2):** Yield, 1.8 g (orange). Found: C, 64.02; H, 4.98: N, 21.96%; $C_{13}H_{14}N_2[Fe(CN)_6]_{0.43}Br_{0.28}\cdot 3H_2O$.

***N,N′*-Dibutyl-4,4′-bipyridinium hexacyanoferrate (II) (Bu4):** Similar conditions to that for En2 with *N,N′*-dibutyl-4,4′-bipyridinium diiodide. Yield, 1.9 g (pale indigo-blue). Found: C, 68.17; H, 7.37; N, 18.23%; $C_{18}H_{26}N_2[Fe(CN)_6]_{0.46}I_{0.16}\cdot 3H_2O$.

***N, N′*-Dibenzyl-4, 4′-bipyridinium hexacyanoferrate(II) (Bz4):** Yield, 1.7 g (pale green). Found: C, 70.36; H, 5.42; N, 14.37%; $C_{24}H_{22}N_2[Fe(CN)_6]_{0.45}I_{0.2}\cdot 3H_2O$.

Preparation of Sandwiched Films A solution of the complex (1.5 mg) and a matrix polymer (30 mg) in water (0.3 ml) was spread over a glass plate, followed by standing overnight in a dark-brown disiccator filled with nitrogen gas. A moistened film was then covered tightly with a white polypropylene sheet to exclude the effect of atmospheric oxygen, followed by drying for one week to afford air-tight sandwiched films of ca. 0.1 mm in thickness

Photochromic Measurements. Irradiation of the solution or sandwiched films were carried out at 25 °C using a 75 W high-pressure Hg lamp with a visible cut filter (Toshiba UV-D35). The resulting spectral changes were determined by means of a Shimadzu UV-160 spectrometer and a Hitachi 200-10 reflection spectrophotometer.

The matric polymers employed were poly(vinyl alcohol) (Average M_w, 20000. Tokyo Kasei Co.) and poly(*N*-vinyl-2-pyrrolidone) (M_w, 10000, Iwai Chem. Co.). The other chemicals used were of the highest grade and were employed as supplied.

Result and Discussion

Viologen-Hexacyanoferrate(II). Bipyridinium hexacyanoferrate(II) derivatives (En2, Tn2, Bu4, and Bz4) were synthesized starting from the corresponding halides by an anion-exchange reaction using an anion exchange resin.[9] Based on the result of the elemental analyses, the exchange reaction took place in approximately 90% yield. The complexes thus synthesized were colored, varing from orange to pale green, which gradually became deeper when exposed to air oxygen. The operation was thereby conducted without exposure to light or air; the freshly prepared solutions and films which were sandwiched tightly between two plates in order to exclude any effect of atmospheric oxygen were used for spectral measurements.

Absorption Change in Solution A pale indigo-blue solid-Bu4 turned to violet immediately upon dissolving in an aqueous solution. The CT-absorption peaks of the complexes shifted by approximately 5 nm to longer wavelengths, compared with those of the equimolar mixture of bipyridinium halides with the externally added tetrakis(hydroxyethyl)ammonium hexacyanoferrate(II); their absorbances are almost consistent with those of the equimolar mixture.[5] This suggests that since the complexes are hightly hydrated, they are mainly present as an unpaired mixture in water; some of them exist in a mixture of 1 : 1- and 2 : 1 CT-complexes of bipyridinium dications and hexacyanoferrate(II) ions.[9] The CT-bands largely shifted to longer wavelengths with a highter EtOH content in solution. The linear relationship between the Kosower *Z*-values of aqueous EtOH[10] and the band transition energies ($h\nu$) indicates that the complex exists in the π-δ structure (Fig. 1).[11]

Benesi–Hidldebrandi plots[12] were linear at concentrations of 2.5×10^{-3}—4×10^{-2} mol dm^{-3}, while a linear relation was not recognized between the transition energies and the difference in the half redox potential of both ions ($\Delta E_{1/2}$).[13] Plots for 2,2′-bipyridinium complexes slightly deviate above a straight line between two plots of 4,4′-bipyridinium complexes. This might be caused by an electrostatic interaction:[14] The solvation of 2,2′-bipyridinium dications are relatively small compared with 4,4′-bipyridines possessing a symmetrical molecular structure, thus causing a low transition energy.

Cyclic voltamograms of the complexes in an aqueous tetraethylammonium chloride solution also indicate the relation among the absorption maxima, solvent polarities, and $E_{1/2}$ values of the parent viologen dications.[15] The $E_{1/2}$ values for the [Fe^{II}(CN)$_6$]–[Fe^{III}(CN)$_6$] transformation did not vary upon changing the EtOH contents in an aqueous solution, whereas the values for the V^{2+}–$V^{+\bullet}$ (viologen dication–viologen radical cation) in the presence of Bu4 was 0.16 V higher than that in water. The complexes in EtOH might be liable to be transformed to the CT-complex, rather than those strongly solvated with water (Table 1).[16]

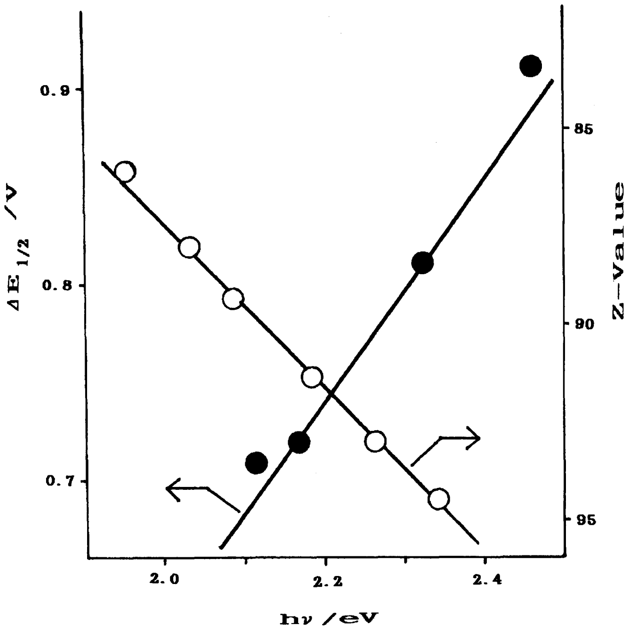


Fig. 1. Relation of the transition energy against the half redox potential and *Z*-value. 0.5% solution at 25 °C.

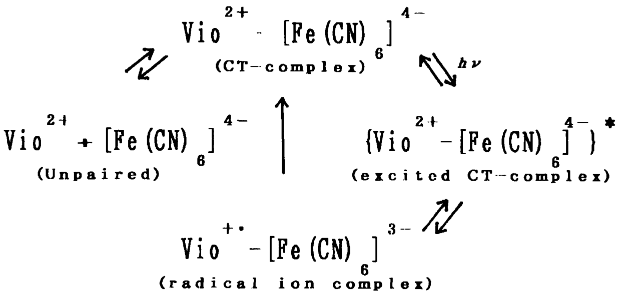
The CT-bands for Bu4 and Bz4 almost linearly increased in absorbance upon UV-irradiation;[17] the absorbance increment progressively decreased in the dark, and even more rapidly upon heating.[18] UV-irradiation of the complexes may cause an activation (excitation) of either hexacyanoferrate(II)[19] or bipyridinium dication.[3] The 2,2′-bipyridinium ions, which yield a low amount of radical cations,[20] induce the low extent of CT-formation. The following is thus proposed to account for reversible CT-formation (Scheme 2).

Exited CT-complex might therefore be generated from the ground-state CT-complex by application of UV-light, leading to the formation of a radical ion complex by intramolecular electron transfer. Since there is no absorption peak at around 398 nm, a characteristic of the viologen radical cation,even in the absence of oxygen (Fig. 2),[21] and the absorption was not affected by

Table 1. Absorption Maxima of Viologen–[Fe(CN)$_6$]$^{a)}$

	$E_{1/2}{}^{b)}$/V	$\lambda_{max}{}^{c)}$/nm	
		H_2O	50% aq EtOH
En2	−0.35	580 (0.126)	591 (0.161) $^{d)}$
Tn2	−0.55	500 (0.152)	531 (0.208)
Bu4	−0.45	533 (0.270)	586 (0.335)
			620 (0.318) $^{e)}$
Bz4	−0.36	569 (0.128)	613 (0.207)

a) 1% solution in 1 mm-pathlength cell at 25 °C. b) half redox potential of parent viologen (Ref. 13). c) Figures in parentheses indicate absorbance. d) In 12% aq EtOH. e) In 50% aq *N*-methyl-2-pyrrolidone.



Scheme 2.

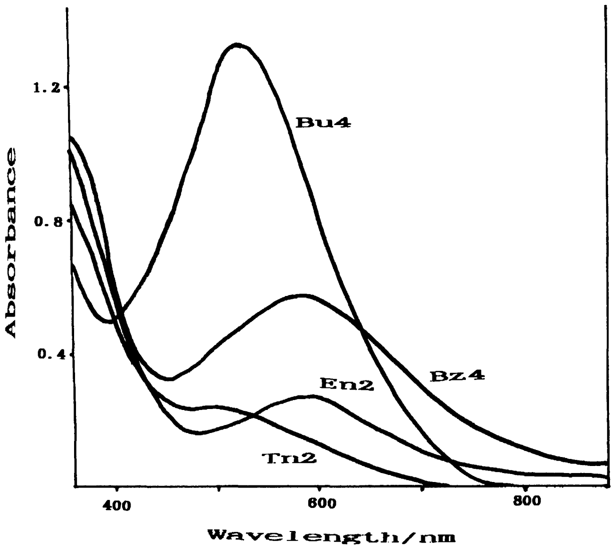


Fig. 2. Absorption spectra of a viologen–[Fe(CN)$_6$] solution after UV-irradiation. 1 min-irradiation of 1%-solution of complexes in water (1 mm pathlength cell).

introducing air oxygen, the radical ion complex bearing [Fe^{III}(CN)$_6$] in solution may be unstable[6,7] that it causes a spontaneous reverse electrion transfer to generate a ground-state CT-complex, which, upon standing in the dark, reaches equibrium with the unpaired mixtures.

Absorption Changes in Solid State. The films became opaque with evaporating water in a polymer solution due to the low compatibility of the metal complexes with poly(vinyl alcohol) (PVA) and poly(*N*-vinyl-2-pyrrolidone) (PVP); the absorbances at the CT-bands decreased with decreasing water content in polymer solutions, and radical cation peaks appeared at longer wavelenghts after evaporation of the water. Figure 3 indicates the typical visible reflection spectra when the irradiation was stopped after 1 min; the resulting spectral changes are given in Table 2. The complexes existing in CT-complexes and the unpaired mixture strongly hydrated in aqueous solutions might become colorless ion pairs in solid polymer matrices. In the solid state the intramolecular electron transfer to naked bipyridinium dication may partly take place from hexacyanoferrate(II) and generate colored radical cation. The extent of electron transfer at the ground state is large for complexes with bipyridinium ions possessing a higher half redox potential (Table 2, No. 1, 5, and 6).

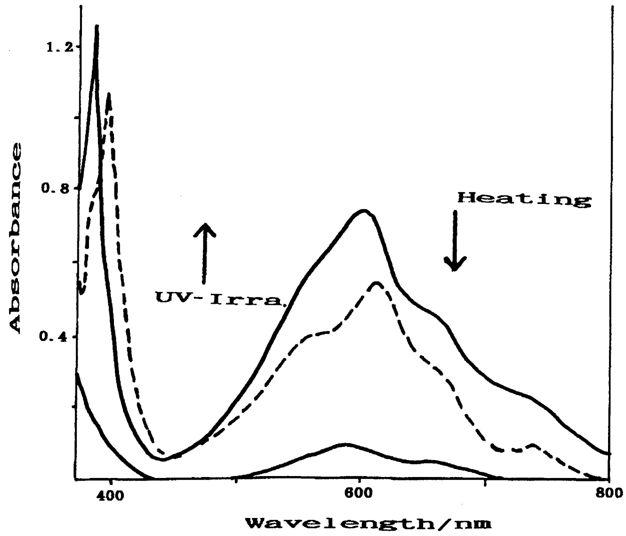


Fig. 3. Visible reflection spectra of Bu4-film embedded in a PVA matrix. The dashed spectrum represents the visible absorption spectra of *N,N′*-dibutyl-4,4′-bipyridinium dibromide under the same irradiation conditions.

Upon near-UV irradiation the absorption for the radical cation was enhanced, and the absorbance increment gradually decreased in the dark. The absorbance in the near-infrared region attributable to the radical cation for En2 did not change to any appreciable extent, and the extent of photoreduction for Bz4 is small compared with that for Bu4. This did not agree with the photoreduction behaviours of bipyridinium halides embedded in the same polymer matrices.[3,20] In the case of 2, 2′-bipyridinium cations, the resonance stabilization of radical cations might be restricted by two bonds at the 1,1′- and 2,2′- positions. The low sensitivity for Bz4 in the solid state appears to be caused by the fact that the electron transfer to dications from the counter anion already took place at the ground state and/or bulky hexacyanoferrate(II) ions may be hardly brought close to positive pyridinium nitrogens attached to the benzyl group possessing a relatively bulky molecular size.

The absorption of viologen halides induced by near-UV irradiation is stable for more than one year in the absence of air oxygen,[22] whereas the developed color of Bu4 recovered to the original state upon standing at room temperature for 4 d, or heating at 60 °C for 5 min under the same film forming conditions. The reverse election transfer to hexacyanoferrate(III) possessing a low redox potential from colored bipyridinium radical cation takes place, resulting in the formation of colorless ion pairs. The reversible redox reaction by the photon mode (color development) and by the heat

Table 2. Visible Reflection Spectra of Viologen–[Fe(CN)$_6$] Films Embedded in Polymer Matrices

Exp.		Appearance	$\lambda_{\max}$	Absorbance[a]		$t_{1/2}$[b]	
No.			nm	A_0	A_t	25 °C	60 °C
						h	min
1	En2/PVA	Pale green	680	0.12	0.12		
2	Tn2/PVA	Pale orange	500	0.15	0.16		
3	Bu4/PVP	Pale blue	610	0.09	0.80	6	<1
4	Bu4/PVA	Pale indigo-blue	600	0.08	0.73	50	2
5	Bz4/PVP	Pale green	610	0.21	0.26	2	
6	Bz4/PVA	Pale green	610	0.17	0.20	3	

a) Absorbance befor (A_0) and after (A_t) UV-irradiation (1 min). b) Half recovery time.

mode (bleaching) can repeated; bleaching is also possible by an electrochemical oxidation–reduction of both ions. This is promising for use as photothermo- or photoelectrochromic devices.

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