SYNTHESIS AND PHOTO-INDUCED REDUCTION OF N,N'-DIALKYL-4,4'-BIPYRIDINIUM BIS-ALKANEPHOSPHONATES

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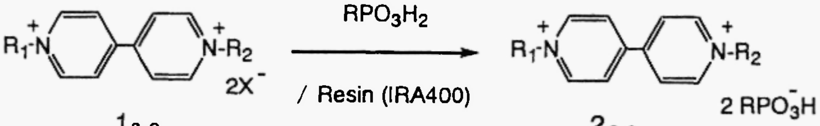
Abstract: Title compounds were synthesized by Menshutkin reaction with alkyl halides, followed by anion-exchange reaction with alkanephosphonates. The steady state UV-irradiation of their thin films induced the formation of viologen radical cations via intra-molecular ET-reaction.

The viologens, bis-quaternary salts of 4,4'-bipyridine turn to intensive blue radical cations by one-electron reduction with reducing agents,[1,2,3] or by electrochemical- and photochemical reaction.[4,5] With the intention to evaluate the reversible photo-reduction (photochromism), viologens with different structure and counter anions have been synthesized, and their spectral changes have been examined in polymer matrices.[6] Previously we had reported the photo-induced coloration of organized thin film solely made of viologen with alkylbenzenesulfonates and found the bleaching of the developed color at an elevated temperature.[7] The present paper describes the synthesis and photo-induced reduction of viologens with alkanephophonate anions which possess relatively good nucleophilicity[8] and anisotrophic character.[9]

Alkanephosphonic acids were prepared by Arbuzov reaction starting from alkyl bromides and tributyl phosphite.[10] N,N'-dialkyl-4,4'-bipyridinium dihalides (**1a-e**) were prepared by two steps of Menshutkin



1_{a-e} 2_{a-e}

	a	b	c	d	e
R_1	Et	Et	Et	Me	Me
R_2	Et	Et	Et	$C_{12}H_{25}$	$C_{12}H_{25}$
R	C_8H_{17}	$C_{12}H_{25}$	$C_{16}H_{33}$	CH_3	C_6H_5

X: halogen

reactions with different alkyl halides. Their counter ions were exchanged with alkanephosphonates using an anion-exchange resin (Amberlite IRA 400) in aqueous alcohol and the products (**2a-e**) were recrystallized from methanol-acetone.[11] ^{1}H-NMR and elemental analyses indicated that the viologens consist of two phosphonate anions, and α, β-protons at pyridinium rings are shifted to higher field compared with conventional bipyridinium halides (0.5 ppm for H_α; 0.45 ppm for H_β), presumably due to low electrostatic interaction with bulky bivalent phophonate anions. This causes that the phosphonate salts (**2a-e**) are thermally unstable compared with halides (**1a-e**) or alkylbenzenesulfonates and decompose at relative low temperature without melting.[7]

The steady state irradiation of the viologen was conducted in an N_2-saturated quartz cell for 1 sec through an UV-cut filter (Toshiba UV 290) from a 200 W high pressure Hg lamp equipped with a rotary shutter. A typical visible absorption spectrum immediately after UV-irradiation is given in Figure 1 for **2d** (solid line). The spectrum revealed characteristic absorption peaks of viologen radical cations for monomeric at 608 nm and dimeric ones around 530 nm, and the developed color persisted for hours at room temperature. Under these photo-reduction conditions, it is not clear whether viologen radical cations are produced by electron transfer from counter anions (RPO_3^-H) or surrounding solvent molecules.[12] Figure 2 shows the absorption at 606 nm in aqueous organic solvents for **2d**.[13] The extent of photo-reduction based on the absorbance decreased with increase in the water-content of the solution; in water alone, the color was no longer developed. The results suggest that water in organic solvent increases the dissociation of both bipyridinium dication and counter anion, thereby they rarely encounter in the high dilution conditions.[14]

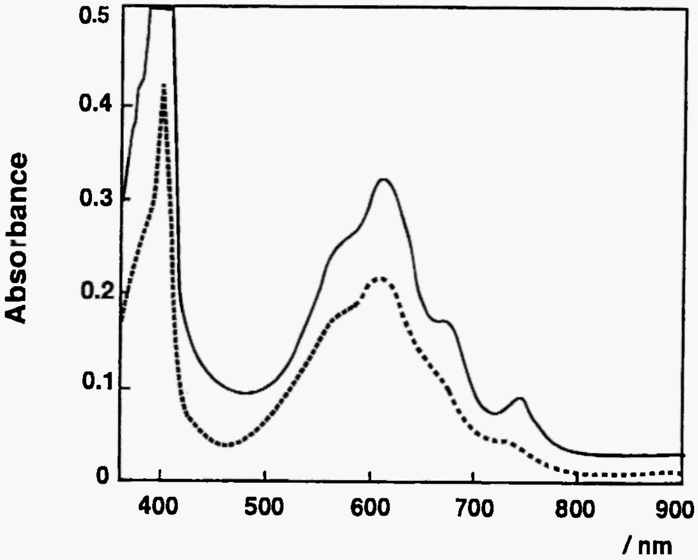


Figure 1. Absorption spectra of **2d** after near-UV irradiation at room temperature: solution of 90% 1-methyl-2-pyrrolidinone (NMP), 10^{-3} mol dm^{-3}, 1 mm-pathlength cell (solid); glass sandwiched film, thickness 30 μ mm (dotted).[15]

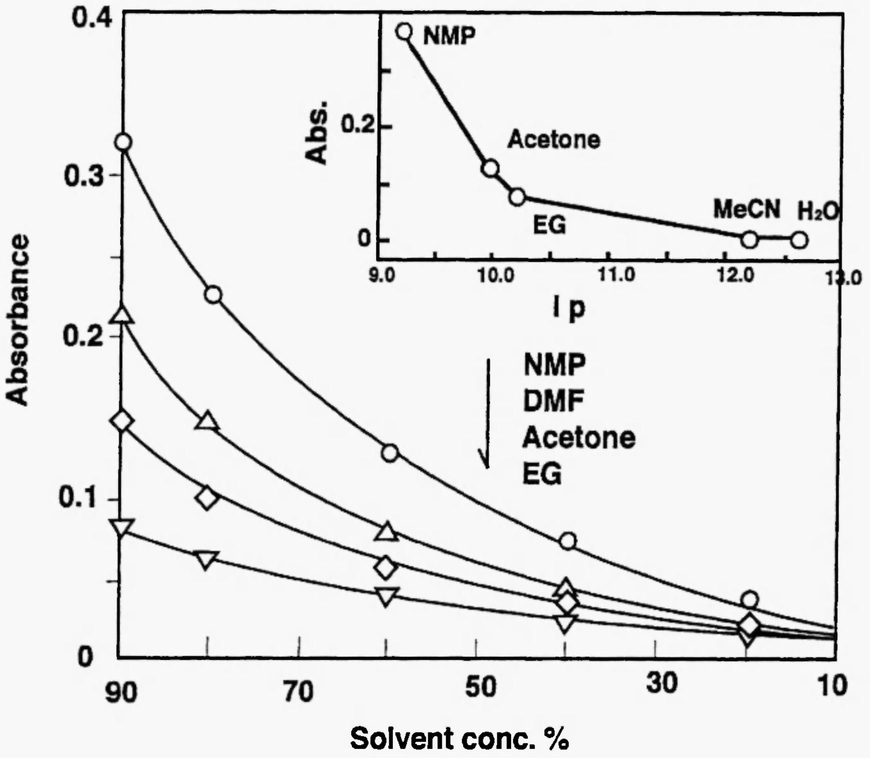
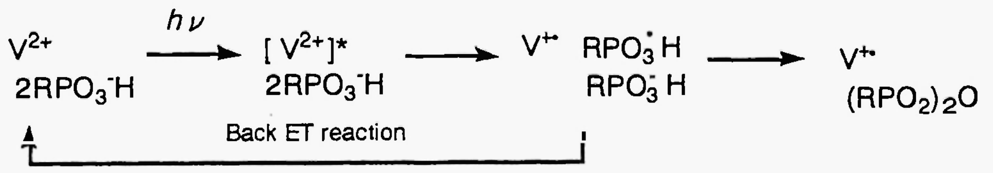


Figure 2. Effect of aqueous organic solvent on photo-reduction of **2d**. Absorbance indicates immediately after 1 sec-irradiation of 10^{-3} mol dm^{-3} solution, 1 mm-pathlength cell. 1-Methyl-2-pyrrolidinone (NMP), ethylene glycol (EG). The inset indicates the absorbance of 90 % solution against the ionization potential of solvents.[16]

Furthermore, back ET reaction in water is so rapid that the color change might not be perceived under the steady state irradiation conditions.[17] The inset in Figure 2 would serve to elucidate the ET-reaction of bipyridnium dications (V^{2+}) in organic solvents: the radical formation is small in the solvent possessing high ionization potential (IP). The photo-reduction of high-diluted **2a-e** in organic solvents possessing electron-donating property (low IP) mainly proceeds by the ET-reaction from surrounding solvent molecules.

The photo-reduction of viologens in solid state was not recognized in the layered form with metal phosphonate anions.[18] In contrast, the radical cations of **2a-d** were observed in glass sandwiched thin films by steady state UV-irradiation (dotted line in Fig.1), and the color of the radical cations persisted for several days. This indicates that the photo-induced reduction of solid phosphonate salts proceeds from phosphonate anion within a viologen molecule. The degree of photo-reduction of 2a-e was almost similar to that of viologens



(1)

with alkylbenzenesulfonate anions,[7] however the back ET-reaction of **2a-e** did not proceed by thermal reaction. The reason why the radical cation reduced by the phosphonate anion does not decrease by thermal back ET-reaction may be due to phosphonate radicals being subjected to self-dehydration giving the corresponding pyrophosphonates as sacrificial donors (see Eq. 1).[19] The residual radical cation of **2a-e** ($V^{+\cdot}$) exists for long time at an elevated temperature when air is absent in the system.

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11 Typical experimental data: **1d** (X= I, Br), Yield, 70 %; mp, 231 °C (dec.). **2d**, Yield, 46 %; mp, 84 °C, (dec.); ^{1}H-NMR (400 MHz, DMSO-d_6): δ , 0.75 (t, 3H, CH_3), 1.2 (m, 24H, -CH_2-, CH_3-P), 1.95 (t, β-CH_2), 4.4 (s, 3H, N-CH_3), 4.6 (t, 2H, N-CH_2), 8.45 (t, 4H, py-H_β), 8.95 (q, 4H, Py-H_α) ppm. Anal. Calcd for $C_{25}H_{44}N_2P_2O_6$: C, 56.59; H, 8.36; N, 5.28 %. Found: C, 56.45; H, 8.93; N, 4.80 %.

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13 Viologens **2a-e** are of low solubility in common organic solvents, so that the photo-reduction was carried out in aqueous solution (< 90 %).

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15 A glass sandwiched thin film of **2** was prepared as follows: viologens moistened with water were heated to a tacky appearance on a glass plate, covered tightly with another glass plate, and then dried for a week to afford an almost airtight film. The film was irradiated for 30 sec at a distance of 5 cm from the lamp.

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