

Photo- and thermo-chromism of a ruthenium(II) complex and viologen-containing polymer film

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A ruthenium(II) complex and a viologen-containing partially quaternized poly(1-vinylimidazole) film demonstrates both photochromism and thermochromism as a result of photosensitized and thermosensitized charge separations.

1,1'-Dialkyl-4,4'-bipyridinium dications, so called viologens, are one of a group of electrochromic materials.^{1,2} Electrochromism takes place in bipyridinium segments because the positive charge in radical cations formed by one electroreduction is delocalized. Electrochromic devices (ECDs) have been fabricated by electrostatic incorporation of such viologens into anionic polyelectrolyte films.³⁻⁷ On the other hand, viologen radicals can be readily formed by photoinduced electron transfer from ruthenium(II) complexes to viologens in sacrificial systems.⁸⁻¹² The facts indicate that photochromism using photoinduced electron transfer is possible. Under an air atmosphere, however, the lifetime of viologen radicals is very short owing to reaction with O₂. Recently, we have reported that the viologen radical is efficiently formed by a photosensitized charge-separation reaction using a partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complex as a photosensitizer, alkylviologen and triethanolamine (TEOA) as a sacrificial donor.¹³ In this work a ruthenium(II) complex and a viologen containing partially quaternized poly(1-vinylimidazole) is synthesized and the photo- and thermo-chromic properties of this polymer film are investigated.

Poly(1-vinylimidazole) and ruthenium(II) complex-containing poly(1-vinylimidazole) (RuPIIm) were prepared as described elsewhere.^{13,14} 1-(6-Bromohexyl)-1'-hexadecyl-4,4'-bipyridinium dibromide was prepared by refluxing of an acetonitrile solution of 1,6-dibromohexane and 4-(4'-pyridyl)-1-hexadecylpyridinium bromide¹⁵ and identified by elemental analysis, ¹H NMR and FTIR spectroscopy. Ruthenium(II) complex and viologen-containing partially quaternized poly(1-vinylimidazole) (RuVQPIIm) was prepared by refluxing RUPIm and 1-(6-bromohexyl)-1'-hexadecyl-4,4'-bipyridinium dibromide in ethanol for 24 h under an argon atmosphere. After addition of *n*-hexadecyl bromide, the solution was further refluxed for 24 h. The RuVQPIIm was purified by reprecipitation from methanol into acetone and identified by its UV-VIS absorption spectrum and ¹H NMR spectroscopy (Fig. 1). The RuVQPIIm film casting on a glass plate was *via* a methanol solution of RuVQPIIm (5–10 mass%). The resulting film thickness was *ca.* 0.15 mm.

Upon light irradiation on an RuVQPIIm film in air, the film changed from orange to blue, and reverted to orange on standing in the dark. Similarly, changes in film colour to blue with heating and to orange upon standing (cooling) were also observed. These colour change reactions were reversible† with the responses being more rapid for the irradiated relative to the thermal system. In both systems, the blue to orange response was slower. These results indicate that the colour change to blue is caused by formation of viologen radicals which are formed by electron transfer from the photoexcited ruthenium(II) complex residue to the viologen. Absorbances at 611 and *ca.* 400 nm, corresponding to absorption maxima of the viologen radical,¹⁶ increased upon light irradiation or heating as shown in Fig. 2.

The absorption spectrum of RuVQPIIm showing an absorption maximum at 490 nm does not change even when viologen radicals are formed, indicating that the photo- and thermosensitized charge separation reactions take place in the film. In

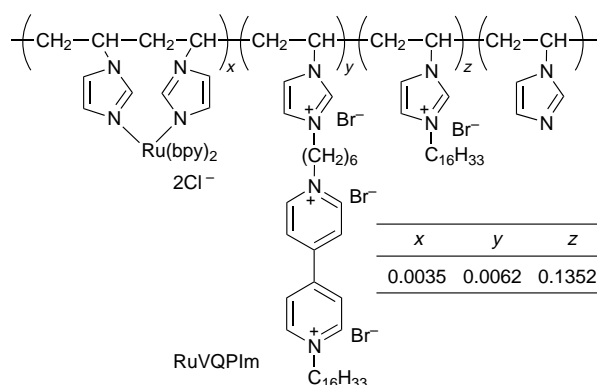


Fig. 1 Chemical structure of RuVQPIIm

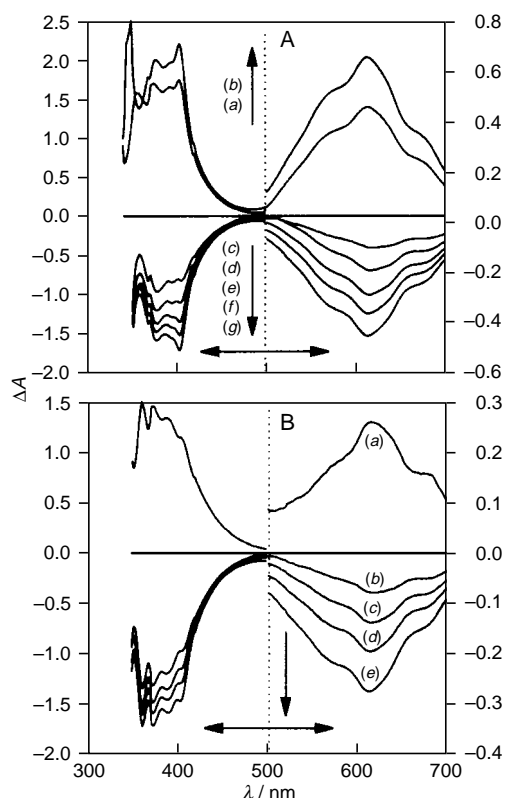


Fig. 2 UV-VIS absorption spectral changes for photochromism (A) and thermochromism (B) of RuVQPIIm film. (A): (a) light irradiation for 5 min, (b) 10 min, (c) standing in the dark for 5 min, (d) 10 min, (e) 20 min, (f) 30 min, (g) 50 min. (B): (a) heating at 120 °C for 2 min, (b) standing at room temp. for 10 min, (c) 20 min, (d) 30 min, (e) 50 min.

methanol solution, charge separation is observed in the presence of the sacrificial donor triethanolamine under an argon atmosphere, but not in the absence of triethanolamine in air.¹³ In Fig. 2, the absorbance at *ca.* 350 nm, which is independent of viologen radical and RuVQPIIm, increases with formation of viologen radicals. We have reported that the reaction product in intra-polymer electron-transfer between a cobalt(II) Schiff-base complex and quaternized imidazolium residue would be 3-ethylimidazoline(4⁻) having λ_{max} at *ca.* 340 nm.¹⁷ Considering this fact, 3-hexadecylimidazoline(4⁻) would also be formed in the charge separation reaction; the quaternized imidazolium residue acting as an electron donor.

On the other hand, the colour change to orange in air is caused by decrease in the viologen radical species concentration as shown in Fig. 2. It is likely that a reaction between 3-hexadecylimidazoline(4⁻) and viologen radical residues takes place. In addition, viologen radical reacts with dioxygen in air, although this is slow since the rate of colour change is little different from that in an argon atmosphere.[‡] This is supported by the fact that the absorbance at *ca.* 350 nm corresponding to the 3-hexadecylimidazoline(4⁻) roughly disappears and little colour change was observed after 24 h under dioxygen.

The thermal blue to orange colour change is slow in comparison to the system under irradiation. Since the glass transition temperature of the RuVQPIIm film is *ca.* 220 °C, a phase transition does not occur upon heating at 120 °C for 2 min. However, the DSC curve of the RuVQPIIm film shows endothermic behavior at 120–150 °C, suggesting that a conformational change takes place in the film. The heating treatment brings about charge separation in addition to conformational change. Therefore, the reverse colour change after heating is caused by decrease in viologen radical concentration through electron transfer and a concomitant conformational change.

The present results reveal orange to blue photo- and thermochromism using a new polymer film. The blue colour arises from viologen radicals formed by charge separation in which the quaternized imidazolium residue acts as an electron donor in the film. A detailed investigation on the photo- and thermochromism is now in progress in our laboratory.

Footnotes and References

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† The film is very stable for repeated experiments with light on and off as well as heating and cooling. Even after 30 repetitions, the spectroscopic properties of the film were unchanged.

‡ The decrease in viologen radical concentration after standing for 30 min in air was 1.2 times larger than that under Ar.

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