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Response-Improved Electrochromic Two-Colour Display

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ABSTRACT

A two-colour electrochromic display (ECD) is studied by using a propylene carbonate/methanol solution incorporated with two viologens, 1,1′-Dibenzyl-4,4′-bipyridinium difluoroborate (DBV) and 1,1′-tetramethylene-bis-(1-benzyl-4,4′-bipyridinium)bromide (TBV), with Bu_4NBF_4 *as supporting electrolyte. This ECD changed in colour from blue at an applied voltage of 0.5–2.0 V to reddish-purple at 2.5 V, and the colour can be controlled by the applied voltage. Copyright © 1996 Elsevier Science Ltd*

INTRODUCTION

Electrochromism is the phenomenon of reversible change in colour produced electrochemically. Various types of electrochromic display (ECD) based on both organic and inorganic materials have been developed, with the objective of aiming at possible commercial application. Although inorganic systems can now be put to practical use,[1,2] organic systems have superior merits.[3–5]

Among organic ECD, one using viologen as chromophore is particularly attractive because of the possibility of selecting various colours by introducing different substituents into the molecule. Viologen, bis-quarternary salts of bipyridine, undergoes a one-electron reduction to give a coloured radical cation. The redox system of viologen is shown in Scheme 1.

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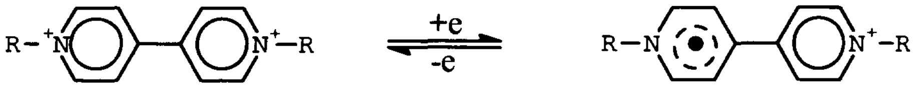


Scheme 1

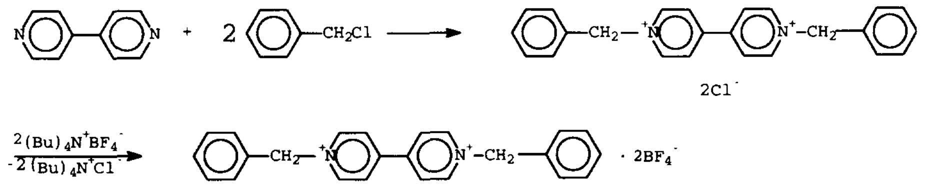
In this study, a two-colour display is obtained using propylene carbonate (PC)/methanol solution incorporated with two kinds of viologen derivatives. This type of display has the advantage that the colour of the solution, based on the redox reaction of each viologen derivative, can be controlled by an applied voltage across the display cell.

1,1′-Tetramethylene-bis-(1-benzyl-4,4′-bipyridinium)-bromide (TBV) and 1,1′-dibenzyl-4,4′-bipyridinium difluoroborate (DBV) were used in the experiments.

EXPERIMENTAL

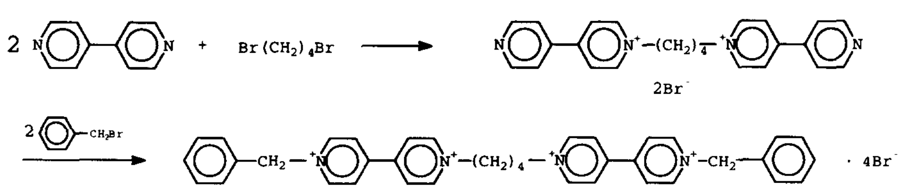
Materials

1,1′-Dibenzyl-4,4′-bipyridinium difluoroborate (DBV)
Bis-benzyl viologen dichloride was synthesized by refluxing a DMF solution of 4,4′-bipyridyl with benzyl chloride for 10 min. After refluxing, the white solid was collected, and reacted with tetrabutylammonium tetrafluoroborate (TATB) to give DBV (Scheme 2).



Scheme 2

1,1′-Tetramethylene-bis-(1-benzyl-4,4′-bipyridinium)bromide (TBV)
1,1′-Tetramethylene-bis-bipyridinium bromide was prepared by warming a solution of an excess of 4,4′-bipyridyl in DMF with 1,4-dibromobutane. A light yellow precipitate was separated and washed with chloroform. Treatment of 1,1′-tetramethylene-bis-bipyridinium bromide with an excess of benzyl bromide in DMF in a glass autoclave afforded TBV in quantitative yield (Scheme 3).



Scheme 3

Preparation of ECD cell

The ECD cell was comprised of two glass sheets (3 cm × 3 cm) separated by a 0.1 mm thickness spacer of PET film. The glass sheets had been coated on one side with transparent conductive electrodes of indium-doped tin oxide (ITO), and these sides were placed so as to face each other on the inside of the cell and the edges of the cell were sealed with insulating epoxide resin. Prior to final sealing, the space between the electrodes was filled with a PC/MeOH solution of 0.2 mmol DBV, 0.2 mmol TBV and 1.5 mmol TATB as electrolyte.

RESULTS AND DISCUSSION

The absorption spectra of the coloured ECD cell produced on the cathode after electrocolouration are shown in Fig. 1. The threshold voltages for the

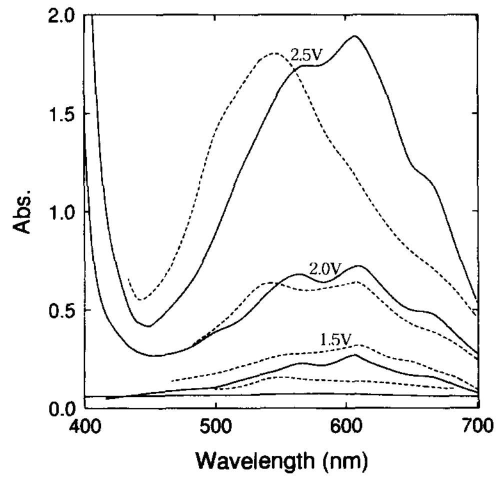


Fig. 1. Absorption spectra of the coloured DBV cell I (—) and TBV cell II (- - -) as a function of applied voltage.

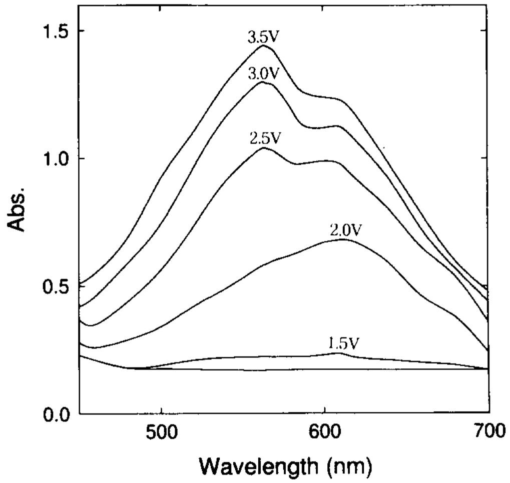


Fig. 2. Absorption spectra of the cell III depending on the applied voltage 1.5–2.0 V: blue 2.0–3.5 V: reddish purple.

colouration are about 1.5 V for DBV and TBV. In the DBV system (cell I), the prominent peak appears at 600 nm and is coloured blue. The absorbance increases significantly depending on increment of the applied voltage.

At an applied voltage of 0.5–2.0 V in the TBV (cell II), the absorption maximum was observed at around 600 nm, and the colour was blue, but in the range of 2.0–2.5 V, the absorption maximum appeared at 530 nm and the colour was reddish-purple. This is certainly caused by the second reduction of TBV.

An attempt was made to obtain a two-colour display by using PC/MeOH solution incorporated with the mixture of DBV and TBV with TATB-(Bu_4NBF_4) as supporting electrolyte. The ECD cell III coloured blue at 2.0 V, but changed to reddish-purple at 2.5 V (Fig. 2) These results were well in agreement with that of coloured TBV, as shown in Fig. 1, in the range higher than 2.0 V.

	DBV (cell I)	TBV (cell II)	DBV–TBV (cell III)
0.5–2.0 V	blue	blue	blue
2.0–3.5 V	blue	reddish-purple	reddish-purple

Figure 3 shows the optical density (OD) changes of the ECD cell at 560 and 620 nm as a function of applied voltage. Optical density increases with increasing applied voltage for both the 560 and 620 nm bands. The optical density at 620 nm is higher than that at 560 nm under 2.0 V, but on the other hand, the optical density at 560 nm is higher than that at 620 nm over 2.0 V.

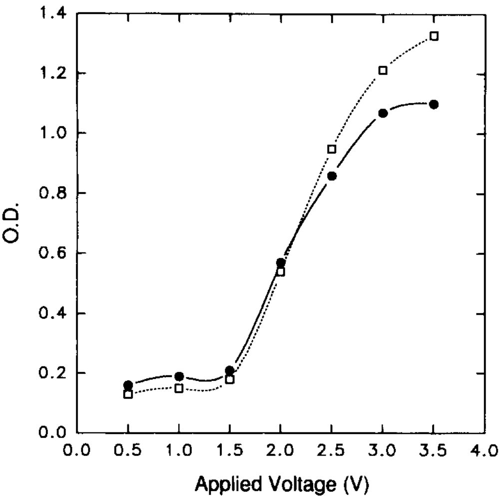


Fig. 3. Optical density changes as a function of applied voltage; ●: OD at 600 nm, □: OD at 550 nm.

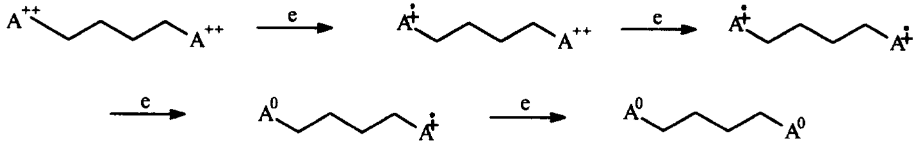
In the ECD cell, the colour produced on the cathode can be controlled by the applied voltage. The absorption spectrum of cell III is much broader than that of cells I and II, due to the overlap of both of the absorption spectra of the coloured DBV and TBV.

Figure 4(a) shows the cyclic voltammogram of DBV. The cathodic scan exhibits two successive reduction waves at −0.4 V and −0.8 V vs SCE, and two anodic peaks are shown in backward scan. It is known that the redox peak near −0.4 V corresponds to the first reduction of DBV (eqn (1)). The peak near −0.8 V is generally considered to involve the reduction of DBV$^{\cdot+}$, as shown in eqn (2).

$$DBV^{2+} + e^- \leftrightarrow DBV^{\cdot+} \tag{1}$$

$$DBV^{\cdot+} + e^- \leftrightarrow DBV^0 \tag{2}$$

The cyclic voltammogram of TBV was different to that of DBV, showing four consecutive reversible redox waves (Fig. 4(b)). From the redox wave patterns, it is proposed that TBV^{4+}, (A^{2+}  A^{2+}), is successively reduced step by step to TBV^0, (A^0  A^0)



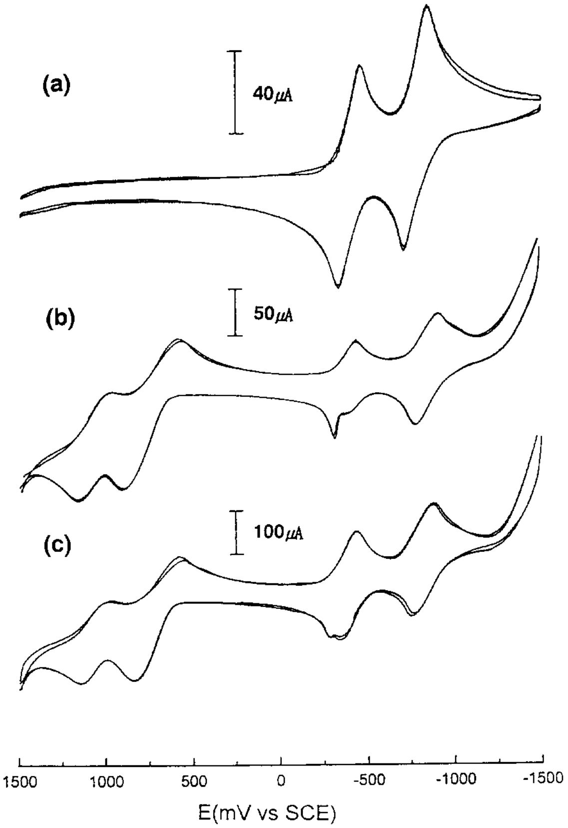


Fig. 4. Cyclic voltammogram of DBV (a), TBV (b) and DBV–TBV mixture (c) at a scan rate of 30 mV/s.

The cyclic voltammogram responses of the DBV–TBV mixture exhibit similar redox behaviour to TBV.

Advantages of the viologen ECD are that the quality of the display is excellent and a variety of colours can be obtained by changing the substituents. There can be a rather severe problem in this type of ECD, viz. erasing failure caused by the recrystallized molecule sticking to the display electrode. This crystallization gives rise to a residue on the electrode, which cannot be erased in open-circuit conditions. The residue formation, which appears after the separated redox cycle, can be decreased by using of two kinds of viologen derivatives such as DBV and TBV. Figure 5 shows the optical density changes at the λ_{max} of DBV (at 600 nm), TBV (at 530 nm), DBV-TBV (at 530 nm) as a function of decay time after open-circuit. As can be seen in Fig. 5, the DBV-TBV system shows more rapid bleaching compared to the DBV and TBV systems.

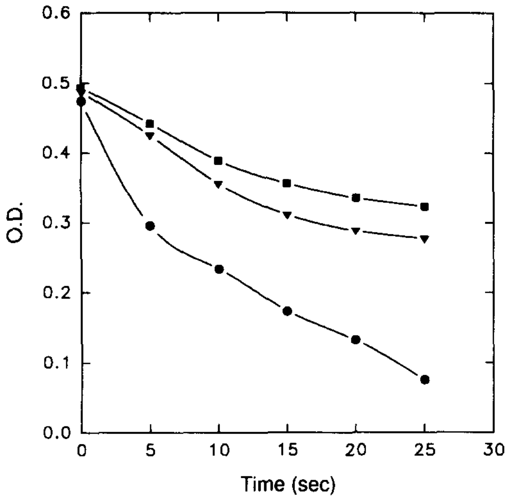


Fig. 5. Optical density changes at the λ_{max} of viologen derivatives as a function of decay time after open circuit; ■: DBV, ▼: TBV, ●: DBV–TBV mixture.

REFERENCES

1. Deb, S. K., *Applied Optics Supplement*, **3** (1969) 192.
2. Deb, S. K., *Philosophcal Magazine*, **27** (1973) 801.
3. Schoot, C.J., Ponjee, J.J., Van Dam, H.T., Van Doorn, R.A. & Bolwijn, P.T., *Appl. Phys. Lett.*, **23** (1973) 64.
4. Kawata, T., Yamamoto, M., Yamana, M., Tajima, M. & Nakano, T., *Jpn J. Appl. Phys.*, **14** (1975) 725.
5. Shelepin, I. V., Uskakov, O. A., Karpova, N. I. & Barachevskii, V. A., *Elektrokhim.*, **13** (1977) 32.