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# Electrochromic devices based on surface-confined Prussian blue or Ruthenium purple and aqueous solution-phase di-*n*-heptyl viologen

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## Abstract

Prototype electrochromic devices (ECDs) based on *anodically-colouring* thin-film Prussian blue (PB) or Ruthenium purple (RP) and *cathodically-colouring* aqueous solution-phase di-*n*-heptyl viologen are described. The initial ('off') state of each ECD is set with the PB (or RP) in the colourless reduced form and the di-*n*-heptyl viologen as the colourless di-cation. Switching the ECDs to the coloured state ('on'), forms on oxidation the coloured mixed-valence PB (or RP), with simultaneous reduction of the di-*n*-heptyl viologen di-cation to form the purplish-red di-*n*-heptyl viologen radical cation dimer salt as a thin film. The overall perceived reversible colour changes were colourless to deep blue/purple for the PB/di-*n*-heptyl viologen ECDs and colourless to pinkish-purple for the RP/di-*n*-heptyl viologen ECDs. Using the Commission Internationale de l'Eclairage (CIE) system of colorimetry, the colour stimuli of the ECDs were calculated from *in situ* visible region spectra recorded under electrochemical control, the depth of colour being controlled by the di-*n*-heptyl viologen concentration. For the coloured states of the PB/di-*n*-heptyl viologen ECDs, the CIELAB 1976 colour space coordinates for a D55 illuminant were  $L^* = 60$ ,  $a^* = 22$  and  $b^* = -47$ , and  $L^* = 39$ ,  $a^* = 47$  and  $b^* = -55$ , respectively for 5 and 10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen solution concentrations. For the RP/di-*n*-heptyl viologen ECDs, the coordinates were  $L^* = 70$ ,  $a^* = 31$  and  $b^* = -27$ , and  $L^* = 63$ ,  $a^* = 44$  and  $b^* = -34$ , respectively for 5 and 10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen solution concentrations.  $L^*$  quantifies the lightness, with  $+a^*$ ,  $-a^*$ ,  $+b^*$  and  $-b^*$  respectively giving the red, green, yellow and blue directions away from the achromatic point (0, 0).

## Keywords

Electrochromic; Electrochromism; Prussian blue; Ruthenium purple; di-*n*-Heptyl viologen; CIE chromaticity coordinates

## 1. Introduction

Prototype electrochromic devices (ECDs) [1,2] may be fabricated using optically-transparent electrodes in a ‘sandwich’ configuration, the primary electrochromic electrode and charge-balancing secondary electrode being separated by a layer of liquid, gel or solid electrolyte. On application of appropriate electrode potentials, the ECD charge/discharge process provides switching between two coloured states or between a ‘bleached’ and a coloured state. For absorptive/transmissive ECDs, the secondary electrode system is chosen to be a redox reaction where there is imperceptible visible colour change or as an electrochromic material where the change in colour is complementary [3] or reinforcing [4] to that at the primary electrode.

We have recently described [3,4] the fabrication and colour-switching properties of ECDs, with surface-confined metal hexacyanometallates as the *anodically-colouring*, and aqueous solution-phase methyl viologen (*N,N'*-dimethyl-4,4'-bipyridylum) as the *cathodically-colouring* electrochromic materials. Both Prussian blue (PB, containing the iron(III) hexacyanoferrate(II) chromophore) [3] and Ruthenium purple (RP, containing the iron(III) hexacyanoruthenate(II) chromophore) [4] have been used as the metal hexacyanometallate film in separate ECDs. The initial (‘off’) state of each ECD is set with the PB (or RP) as the colourless (reduced) form and the methyl viologen as the colourless di-cation. At the ‘primary’ electrode, electrochemical *oxidation* of the metal hexacyanometallate film generates the iron(III) hexacyanoferrate(II) and iron(III) hexacyanoruthenate(II) chromophores in PB ( $\lambda_{\max} = 690$  nm) and RP ( $\lambda_{\max} = 550$  nm), which are intensely coloured due to intervalence charge-transfer (IVCT) between the mixed-valence metal oxidation states [5]. At the ‘secondary’ electrode, electrochemical *reduction* of methyl viologen generates the methyl viologen radical cation, which is intensely coloured (purple as a mixture of blue monomeric and red dimeric methyl viologen radical cations) due to optical charge transfer between the (formally) +1 and zero valent nitrogens [6]. The perceived colour of each ECD is the summation of the colours formed at both electrodes.

Suitable choice of the *N* and *N'* (or nuclear) viologen substituents, to attain the appropriate molecular orbital energy levels, allows tuning of the viologen radical cation colour and other physical properties such as diffusion coefficient and solubility [6]. We report here the fabrication, *in situ* spectroelectrochemistry and colour measurement of ECDs, where aqueous solution-phase di-*n*-heptyl viologen (*N,N'*-di-*n*-heptyl-4,4'-bipyridylum) [7-11] is now used as the cathodically-

colouring electrochromic material, again with PB and RP as the anodically-colouring materials. In contrast to the soluble methyl viologen radical cation, on electrochemical reduction of di-*n*-heptyl viologen from aqueous solution, the di-*n*-heptyl viologen radical cation forms on the working electrode as a film of insoluble salt with the supporting electrolyte anion. In water, viologen radical cations dimerise, the colour being concentration dependent on the equilibrium between the dimeric and monomeric forms [6]. The observed colour of *N,N'*-di-*n*-alkyl viologen radical cations is most typically purple, resulting from contribution from both the blue monomeric and red dimeric forms. The extent of dimerisation is enhanced if the radical cation is adsorbed on a solid surface, as in the case of the di-*n*-heptyl viologen system [12]. A film of di-*n*-heptyl viologen radical cation salt, as the dimer, appears purplish-red. Scheme 1 summarises the colouring-forming reactions at each electrode in the ECDs we report here, the observed overall colour state being a combination of the two coloured forms.

Scheme 1 here

## 2. Experimental procedure

### 2.1. ECD fabrication

ECDs in a sandwich configuration were fabricated as described earlier [3,4] for similar systems, using tin-doped indium oxide (ITO)-coated optically transparent substrates (Corning 1737 aluminosilicate glass, 25 x 25 x 1.1 mm,  $R_s$  4-8  $\Omega \square^{-1}$  (CB-50IN-0111)) from Delta Technologies. Following electrochemical deposition of PB [3] or RP [4] thin films onto one ITO-coated substrate, a Nylon 6 film (0.25 mm thick, from Goodfellows), was applied as a spacer to three sides using epoxy resin. A second ITO-coated substrate was then secured to the first, creating a small volume between the substrates. Rinsing with 10 mmol dm<sup>-3</sup> ascorbic acid reduced the iron(III) hexacyanometallate(II) chromophore in PB or RP to the colourless/transparent iron(II) hexacyanometallate(II) oxidation state. Finally, a 5 or 10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen dibromide/0.5 mol dm<sup>-3</sup> aqueous KBr solution was injected with a micro-bore needle, through the top, unsealed side, or by capillary action on gently squeezing together the device and placing the unsealed edge into the solution and releasing. The upper opening was then sealed with epoxy resin.

### 2.2. Instrumentation and colour measurement

An ECO Chemie Autolab PGSTAT 20 potentiostat was used for electrode potential control. For the ECD measurements, the potentiostat working electrode lead was connected to the PB- or RP-coated ITO/glass electrode, with the counter and reference electrodes' leads shorted together

and connected to the second ITO/glass electrode, all contacts being with adhesive copper tape. *In situ* visible region spectra were recorded in transmission mode using a Hewlett Packard 8452A diode array spectrophotometer. CIE 1931  $xy$  chromaticity coordinates and luminance data were calculated from the spectral absorbance-wavelength data as described earlier [13]. For the simulation of mid-morning to mid-afternoon natural light, the relative spectral power distribution of a D55 constant temperature (5500 K black body radiation) standard illuminant was used in the calculations. Chromaticity coordinates were also transformed to CIELAB  $L^*a^*b^*$  coordinates, a uniform colour space defined by the CIE in 1976 [14].

### 3. Results and discussion

#### 3.1. PB/di-*n*-heptyl viologen ECDs

PB/di-*n*-heptyl viologen ECDs were investigated, with separately 5 and 10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen/0.5 mol dm<sup>-3</sup> KBr as the layer of liquid aqueous electrolyte containing the dissolved secondary electrochromic material. Fig. 1 shows spectral changes on reversibly switching the ECDs at the two concentrations between the colourless ‘off’ state and the ‘on’ state, which was perceived as deep blue/purple. The absorbance spectra comprise the overlap of visible-region bands in PB ( $\lambda_{\text{max}} = 690$  nm) and the di-*n*-heptyl viologen radical cation in the dimeric form ( $\lambda_{\text{max}} = 545$  nm [15]), the latter being somewhat more dominant in the 10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen ECD than the absorbance of the PB. The spectral peaks below 400 nm, also due to the di-*n*-heptyl viologen radical cation dimer, do not contribute to the perceived colour.

Figure 1 here

With use of a higher di-*n*-heptyl viologen concentration, a greater depth of colour is accessible (contrast the absorbance changes in fig. 1 (a, b) with fig. 1 (c, d)). Changes in the transmittance (at  $\lambda_{\text{max}}$ ) were 78% (5 mmol dm<sup>-3</sup> di-*n*-heptyl viologen) and 89% (10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen) between the ‘off’ (bleached) and ‘on’ (coloured) states of the ECDs. Contrast ratios (at  $\lambda_{\text{max}}$ ), expressed as the ratio of the percentage transmitted light in the ‘off’ (bleached) to the percentage transmitted light in the ‘on’ (coloured) states were 5 (5 mmol dm<sup>-3</sup> di-*n*-heptyl viologen) and 10 (10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen), demonstrating that the contrast ratio can be controlled by altering the amount of viologen in the ECD. Power consumption, expressed as the coloration efficiency (at  $\lambda_{\text{max}}$ ), was 146 and 132 cm<sup>2</sup> C<sup>-1</sup> for the 5 mmol dm<sup>-3</sup> and 10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen ECDs, respectively. ECD switching times for colouration, as estimated for 95% of the total absorbance change at the PB  $\lambda_{\text{max}}$ , were ~10 s (5 mmol dm<sup>-3</sup> di-*n*-heptyl viologen) and ~4 s (10 mmol dm<sup>-3</sup> di-*n*-

heptyl viologen). ECD switching times for bleaching were shorter ( $\sim 2$  s for  $5 \text{ mmol dm}^{-3}$  di-*n*-heptyl viologen, and  $\sim 3$  s for  $10 \text{ mmol dm}^{-3}$  di-*n*-heptyl viologen), owing to the formation from aqueous solution of thin-film di-*n*-heptyl viologen radical cation salt. For the bleaching process, both electrochromic materials therefore start off as surface confined, providing faster switching, as no solution diffusion of electrochromic material is required.

### 3.2. Colour measurement of the PB/di-*n*-heptyl viologen ECDs

Table 1 shows calculated CIE 1931 ( $\% Y_L$ ,  $x$ , and  $y$ ) and CIELAB ( $L^*a^*b^*$ ) chromaticity coordinates of the ‘off’ and ‘on’ states for both the PB/5  $\text{mmol dm}^{-3}$  di-*n*-heptyl viologen and PB/10  $\text{mmol dm}^{-3}$  di-*n*-heptyl viologen ECDs. In the CIE 1931 representation,  $Y_L$  is the luminance factor and the parameters  $x$  and  $y$  represent the red-to-blue and the green-to-blue ratios, respectively [16]. In CIELAB,  $L^*$  is the lightness, with  $+a^*$ ,  $-a^*$ ,  $+b^*$  and  $-b^*$  respectively giving the red, green, yellow and blue directions away from the achromatic point (0, 0) [16].

Table 1 here

When the ECDs are in the ‘off’ state ( $-1.00$  V), the redox states are the colourless (reduced PB) iron(II) hexacyanoferrate(II) and the colourless di-*n*-heptyl viologen di-cation. The chromaticity coordinates of the ECDs in the ‘off’ state ( $x = 0.337$ ,  $y = 0.349$ , and  $\% Y_L = 100$ ) are close to that of the white point ( $x = 0.332$ ,  $y = 0.348$ , and  $\% Y_L = 100$ ) for a D55 illuminant, demonstrating close to full transparency of the ECD. When the ECD is switched on ( $+1.00$  V), in an oxidative direction with respect to the PB electrode and a reductive direction with respect the di-*n*-heptyl viologen, the ECD changes from near colourless to deep blue/purple due to the formation of the blue iron(III) hexacyanoferrate(II) chromophore and the purplish-red di-*n*-heptyl viologen radical cation dimer. The deep blue/purple ‘on’ state is different in hue to the overall blue state reported by Lin *et al.* [17] for similar PB/di-*n*-heptyl viologen ECDs. In this recent work [17], the electrolyte solvent was an equi-volume mixture of water and isopropanol, rather than pure water. As confirmed by spectra (with  $\lambda_{\text{max}} = 605$  nm) [17] of the reduced di-*n*-heptyl viologen, the monomeric radical cation form is dominant in the mixed solvent, thus providing colourless to blue as the cathodically-colouring electrochromic reaction. In the present work, the CIELAB ( $L^*a^*b^*$ ) chromaticity coordinates (Table 1), show that with a decrease in  $L^*$ , a positive change (towards red) in  $a^*$  occurs, coupled with a negative change (towards blue) in  $b^*$ , quantifying the perceived coloured state as a combination of blue and purplish-red. In such PB/di-*n*-heptyl viologen ECDs, the red component is more dominant than for the earlier studied PB/methyl viologen ECDs, which appeared as deep blue

in the 'on' state [3]. Furthermore, the red component in the overall deep blue/purple colour may be enhanced by an increase in the di-*n*-heptyl viologen concentration (compare the larger change in  $a^*$  (22 to 47), than that in  $b^*$  (-47 to -55) on doubling the di-*n*-heptyl viologen concentration). By overlaying  $xy$  data onto the CIE 1931 colour space template, and extrapolation from the white point to the spectral locus, the dominant wavelength ( $\lambda_d$ ) at both di-*n*-heptyl viologen concentrations was found to be 450 nm, compared to the 475 nm found for PB/methyl viologen ECDs [3].

### 3.3. RP/di-*n*-heptyl viologen ECDs

As for the PB/di-*n*-heptyl viologen ECDs, RP/di-*n*-heptyl viologen ECDs were next investigated, with separately 5 and 10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen/0.5 mol dm<sup>-3</sup> KBr as the layer of liquid aqueous electrolyte containing the dissolved secondary electrochromic material. Fig. 2 shows spectral changes on reversibly switching the ECDs at the two concentrations between the 'off' state (colourless) and the 'on' state (pinkish-purple). The absorbance spectra comprise the overlap of visible-region bands in RP ( $\lambda_{\max} = 550$  nm) and the di-*n*-heptyl viologen radical cation dimer ( $\lambda_{\max} = 545$  nm).

Figure 2 here

As for the PB/di-*n*-heptyl viologen ECDs, with use of a higher di-*n*-heptyl viologen concentration, a greater depth of colour is accessible (contrast the absorbance in fig. 2 (a, b) with fig. 2 (c, d)). Changes in the transmittance (at  $\lambda_{\max}$ ) were 75% (5 mmol dm<sup>-3</sup> di-*n*-heptyl viologen) and 81% (10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen) between the 'off' (bleached) and 'on' (coloured) states of the ECDs. Contrast ratios (at  $\lambda_{\max}$ ) were 4 (5 mmol dm<sup>-3</sup> di-*n*-heptyl viologen) and 5 (10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen). Coloration efficiencies (at  $\lambda_{\max}$ ) were 281 and 179 cm<sup>2</sup> C<sup>-1</sup> for 5 mmol dm<sup>-3</sup> and 10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen, respectively. Switching times for coloration were ~33 s (5 mmol dm<sup>-3</sup> di-*n*-heptyl viologen) and ~40 s (10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen). Switching times for bleaching were again shorter (~4 s for 5 mmol dm<sup>-3</sup> di-*n*-heptyl viologen, and ~3 s for 10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen). The longer switching times for coloration for the RP ECDs compared to the PB ECDs are likely to be due to the slight differences in formal potential of the redox couples, structural differences resulting from different RP/PB deposition techniques, and the lower applied potential to cause the ECD to switch (+0.75 V compared to +1.00 V for the PB ECDs).

### 3.4. Colour measurement of the RP/di-*n*-heptyl viologen ECDs

Table 2 shows calculated CIE 1931 (% $Y_L$ ,  $x$ , and  $y$ ) and CIELAB ( $L^*a^*b^*$ ) numerical data of the ‘off’ and ‘on’ states for both the RP/5 mmol dm<sup>-3</sup> di-*n*-heptyl viologen and RP/10 mmol dm<sup>-3</sup> di-*n*-heptyl viologen ECDs.

Table 2 here

When the ECDs are in the ‘off’ state (-1.00 V), the redox states are the colourless (reduced RP) iron(II) hexacyanoruthenate(II) and the colourless di-*n*-heptyl viologen di-cation. When the ECD is switched on (+0.75 V), in an oxidative direction with respect to the RP electrode and a reductive direction with respect the di-*n*-heptyl viologen, the ECD changes from near colourless to pinkish-purple due to the formation of the purple iron(III) hexacyanoruthenate(II) chromophore and the purplish-red di-*n*-heptyl viologen radical cation dimer salt. In terms of CIELAB ( $L^*a^*b^*$ ) chromaticity coordinates (Table 2), with a decrease in  $L^*$ , significant positive changes (towards red) in  $a^*$  and negative changes (towards blue) in  $b^*$  occur, quantifying the perceived coloured state as pinkish-purple. For purple hues, establishment from the CIE 1931 colour space template of complementary, rather than dominant, wavelengths is appropriate and in this case, the complementary wavelength at both di-*n*-heptyl viologen concentrations was found to be 555 nm compared to the 556 nm for RP/methyl viologen ECDs [4].

## 4. Conclusion

ECDs based on thin-film Prussian blue (PB) or Ruthenium purple (RP) and solution phase di-*n*-heptyl viologen (*N,N'*-di-*n*-heptyl-4,4'-bipyridylum) have been described. The concentration of di-*n*-heptyl viologen and its diffusion to the cathode controlled the proportion of surface-confined PB or RP that is switched to the coloured form and hence the overall absorbance/colour change of each ECD. Choice of the *n*-heptyl substituent in the viologen provides ECDs with colour states showing a higher dominance of red, when compared to those fabricated with methyl viologen as the cathodically-colouring electrochromic material. The red component in the overall perceived colour of the ECD may be enhanced by an increase in the di-*n*-heptyl viologen concentration. In contrast to our self-bleaching PB- or RP-methyl viologen ECDs [3.4], the ECDs described here have electrochromic memory. At open-circuit potential, the colour of the ‘on’ state remains indefinitely because under this condition both electrochromic materials are present as thin films. The colour may then be rapidly erased by switching to the bleached state.



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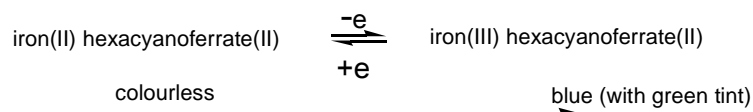
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## Scheme 1

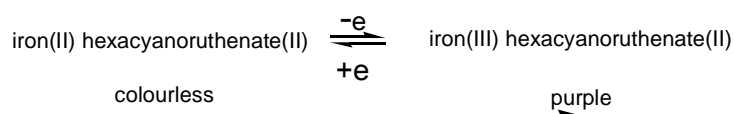
### Prussian blue



*anodically-colouring: colourless to blue (with green tint) on oxidation*

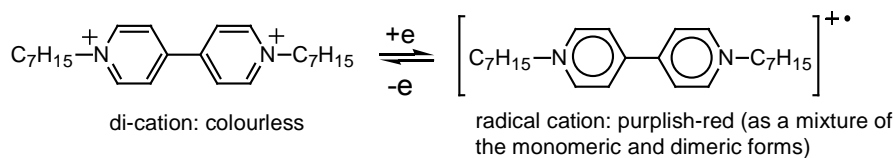
OR

### Ruthenium purple



*anodically-colouring: colourless to purple on oxidation*

### di-*n*-heptyl viologen



*cathodically-colouring: colourless to purplish-red on reduction*

## Fig. captions

**Fig. 1.** UV-visible spectra (recorded every 1 s) for ECDs subjected to potential steps from -1.00 V to +1.00 V (held 20 s) ((a) and (c)) and +1.00 V to -1.00 V (held 20 s) ((b) and (d)). The ECDs consisted of thin-film PB with a layer of aqueous 5 ((a) and (b)) or 10 ((c) and (d)) mmol dm<sup>-3</sup> di-*n*-heptyl viologen in 0.5 mol dm<sup>-3</sup> KBr. The arrows indicate the direction of change in absorbance.

**Fig. 2.** UV-visible spectra (recorded every 1 s) for ECDs subjected to potential steps from -1.00 V to +0.75 V (held 20 s) ((a) and (c)) and +0.75 V to -1.00 V (held 20 s) ((b) and (d)). The ECDs consisted of thin-film RP with a layer of aqueous 5 ((a) and (b)) or 10 ((c) and (d)) mmol dm<sup>-3</sup> di-*n*-heptyl viologen in 0.5 mol dm<sup>-3</sup> KBr. The arrows indicate the direction of change in absorbance.

Fig.1 (a)

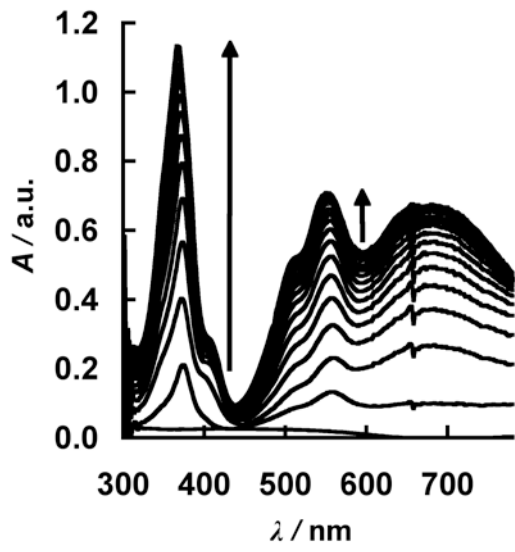


Fig. 1 (b)

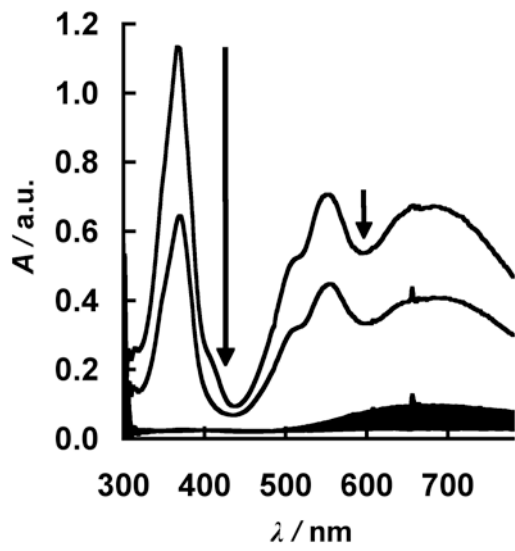


Fig. 1 (c)

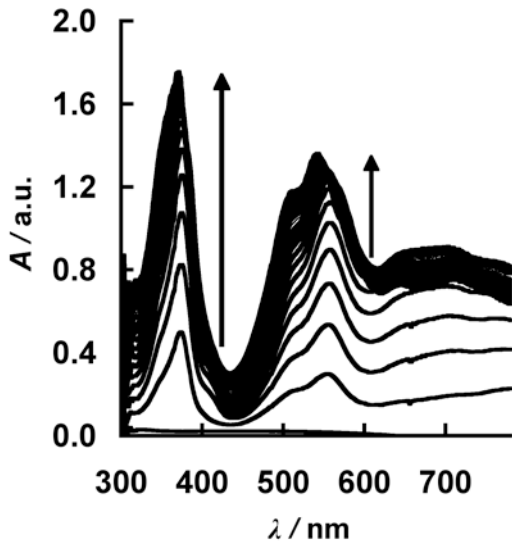


Fig. 1 (d)

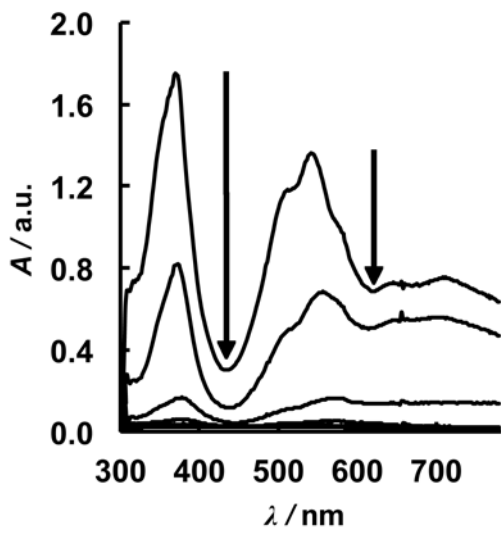


Fig. 2 (a)

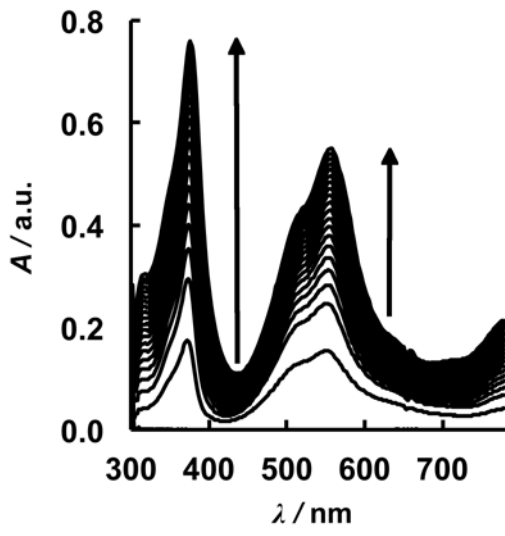


Fig. 2 (b)

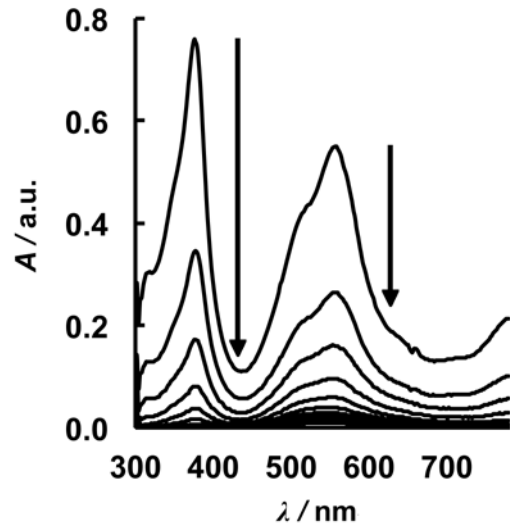


Fig. 2 (c)

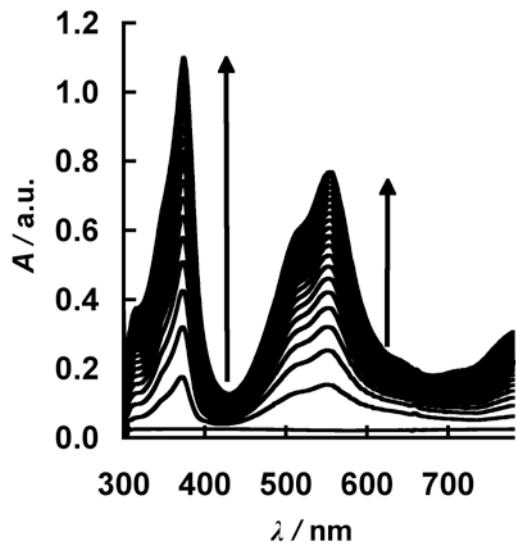
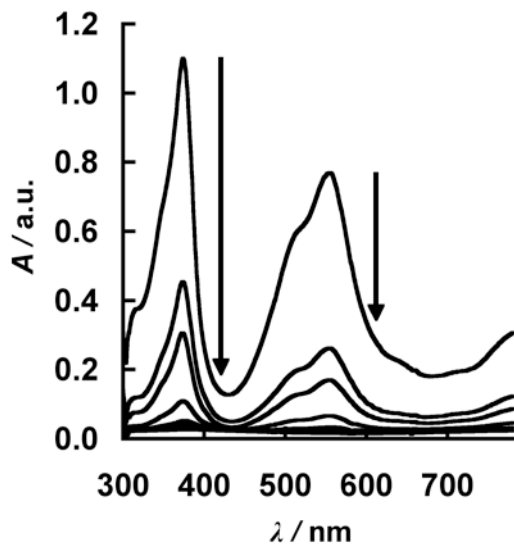


Fig. 2 (d)





**Table 1**

Chromaticity coordinates (CIE 1931 % $Y_{Lxy}$  and CIELAB  $L^*a^*b^*$ ) for PB/ di-*n*-heptyl viologen ( $5^a$  and  $10^b$  mmol dm $^{-3}$ ) ECDs. The ECDs were switched between ‘off’ and ‘on’ states via square wave potential steps from -1.00 V  $\rightarrow$  +1.00 V and +1.00 V  $\rightarrow$  -1.00 V.

ECD state	$x$	$y$	% $Y_L$	$L^*$	$a^*$	$b^*$
‘off’ (colourless)	0.337	0.349	100	100	1	2
‘on’ (coloured) <sup>a</sup>	0.260	0.223	28	60	22	-47
‘on’ (coloured) <sup>b</sup>	0.261	0.157	10	39	47	-55

**Table 2**

Chromaticity coordinates (CIE 1931 % $Y_{Lxy}$  and CIELAB  $L^*a^*b^*$ ) for RP/ di-*n*-heptyl viologen ( $5^a$  and  $10^b$  mmol dm $^{-3}$ ) ECDs. The ECDs were switched between ‘off’ and ‘on’ states via square wave potential steps from -1.00 V  $\rightarrow$  +0.75 V and +0.75 V  $\rightarrow$  -1.00 V.

ECD state	$x$	$y$	% $Y_L$	$L^*$	$a^*$	$b^*$
‘off’ (colourless)	0.332	0.348	100	100	0	0
‘on’ (coloured) <sup>a</sup>	0.326	0.267	41	70	31	-27
‘on’ (coloured) <sup>b</sup>	0.329	0.240	32	63	44	-34