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Novel Color-Reinforcing Electrochromic Device Based on Surface-Confined Ruthenium Purple and Solution-Phase Methyl Viologen

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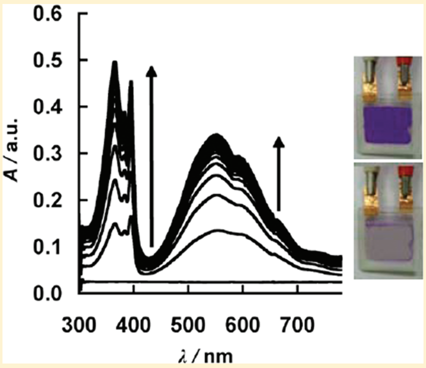
ABSTRACT: A novel color-reinforcing electrochromic device (ECD) is described in which the anode and cathode reactions simultaneously exhibit reversible colorless to intense purple changes. Under coloration, the mixed-valence iron(III) hexacyanoruthenate(II) chromophore is formed on oxidation of iron(II) hexacyanoruthenate(II), with simultaneous reduction of the methyl viologen dication to form a mixture of the radical cation monomer/dimer. Using the CIE (Commission Internationale de l'Eclairage) system of colorimetry, the color stimulus of such ECDs and the changes that take place on reversibly switching between the colored and colorless states have been calculated from in situ visible spectra recorded under electrochemical control. On ECD color switching, with the excellent color-matching between the two purple states, sharp and reversible changes in the hue and saturation occur, as shown by the minimal hysteresis of the track of the CIE 1931 *xy* chromaticity coordinates. Extrapolation of the *xy* track to the color locus gave a complementary wavelength (λ_c) of 565 (±5) nm in close agreement with values obtained for the individual electrochromic materials. The concentration of the solution-phase methyl viologen and its diffusion to the cathode controlled both the proportion of surface-confined Ruthenium purple (RP) that is switched to the intense purple form and the overall ECD changes. For the ECDs' "on" states, the CIELAB 1976 color space coordinates were $L^* = 86$, $a^* = 9$, and $b^* = -15$, and $L^* = 79$, $a^* = 15$, and $b^* = -22$, respectively, for 5 and 10 mmol dm^{-3} methyl viologen solution concentrations. CIELAB 1976 color space coordinates showed that the ECDs were fully transparent and colorless in the "off" states, with $L^* = 100$, $a^* = 0$, and $b^* = 0$. Switching times, as estimated for 95% of the total absorbance change, were 4 and 10 s respectively, for coloration and bleaching for the 5 mmol dm^{-3} methyl viologen ECD, and 8 and 16 s for the 10 mmol dm^{-3} methyl viologen ECD.



KEYWORDS: electrochromic, electrochromism, ruthenium purple, methyl viologen, CIE chromaticity coordinates, colorimetry

INTRODUCTION

Electrochromic devices (ECDs)[1,2] operate as rechargeable electrochemical cells, with each containing a minimum of two electrodes separated by a layer of electrolyte. The liquid, gel, or solid electrolyte is sandwiched between the primary electrochromic electrode and a charge-balancing secondary electrode. Color switching takes place on charge/discharge by application of an appropriate electrical potential. ECDs are designed to operate in either absorptive/transmissive or reflective modes. For absorptive/transmissive devices, the secondary electrode redox reaction is chosen to be a system where there is imperceptible visible color change or as an electrochromic system where the change in color is complementary to that at the primary electrochromic electrode, thus providing enhancement of the colored/bleached contrast. Redox-complementary ECDs that have been investigated include, for example, those with Prussian blue (PB, containing the iron(III) hexacyanoferrate(II) chromophore) as the anodically coloring (colorless to blue on oxidation) electrochromic material and tungsten trioxide (WO_3)[3−5] (colorless to blue on reduction), poly[3,4-(ethylenedioxy)thiophene] (PEDOT)[6] (light blue transmissive to deep blue on reduction), poly[3,3-diethyl-3,4-dihydro-2*H*-thieno-[3,4-b][1,4]dioxepine] (PProDOT-Et_2)[7] (light blue transmissive to deep blue-violet on reduction) and poly(butyl viologen)[8] (colorless to purple on reduction) as cathodically coloring electrochromic materials. Absorptive/transmissive devices based on pairs of complementary-coloring conjugated polymers have been summarized in reviews that concern electrochromism of conjugated conducting polymers,[9,10] color control in π-conjugated organic polymers for use in ECDs,[11] and solution-processable electrochromic polymers.[12] Examples include prototypes made with PEDOT and the anodically coloring PBisEDOT-Cz (poly[3,6-bis(2-(3,4-ethylenedioxy)thienyl)-*N*-methylcarbazole], with a dark opaque violet to pale transparent green switch,[13,14] and the cathodically coloring PProDOT-Me_2 (dimethyl substituted poly(3,4-propylenedioxythiophene) paired with the anodically coloring *N*-propylsulfonated PProDOP (poly(3,4-propylene-dioxypyrrole), with a purple to pale transparent gray-green switch.[15,16]

We have observed that the Prussian blue analogue, Ruthenium purple (RP) in its colored state[17] and reduced methyl viologen (*N*,*N*′-dimethyl-4,4′-bipyridylium) in water[18] have closely matching visible-region absorption spectra, and their colors

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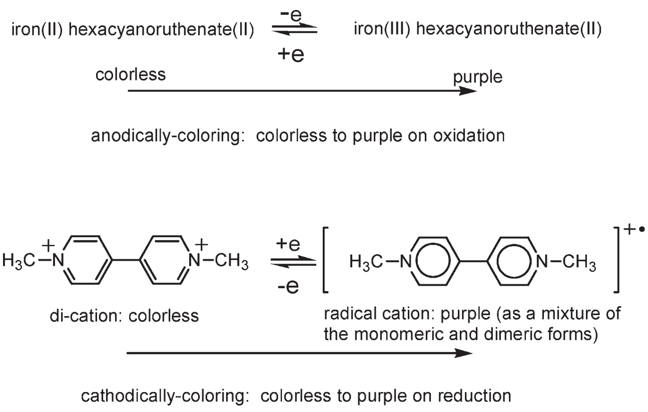
Scheme 1



appear identical to the eye. This provided motivation to explore their use as color-reinforcing electrochromic materials in an ECD; the color-forming reactions being shown in the Scheme 1 above.

The intense color of the iron(III) hexacyanoruthenate(II) chromophore in RP arises from intervalence charge-transfer (IVCT) between the mixed-valence iron and ruthenium oxidation states,[19] with an absorption maximum (λ_{max}) at about 550 nm, the average human eye perceiving the color as bright purple. Bipyridylium dications are colorless, but absorb strongly in the UV region.[20] Reductive electron transfer forms the radical cation, the stability of which is attributable to the delocalization of the radical electron throughout the π-framework of the bipyridyl moiety. Viologen radical cations are intensely colored, with high molar absorption coefficients, owing to optical charge transfer between the (formally) +1-valent and zerovalent nitrogens.[20] In aqueous electrolyte solution, the blue methyl viologen radical cation is in equilibrium with the red methyl viologen radical cation dimer,[21] the resulting observable color being an intense purple.

In the results presented here, ECD color changes were quantified using CIE (Commission Internationale de l'Eclairage) principles. Color[22,23] is a subjective phenomenon; however, much effort has been given to the development of *colorimetric analysis*, which allows a quantitative description of color and relative transmissivity as sensed by the human eye. Colorimetry provides a more precise way to define color than qualitatively interpreting spectral absorption bands. In colorimetry, the human eye's sensitivity to light across the visible region is measured, and a numerical description of the color stimulus is given. The first attribute for the description of color identifies its location in the spectral sequence, that is, what wavelength is associated with the color. This is known as the hue, dominant wavelength, or chromatic color, and is the wavelength where maximum contrast occurs. The second attribute, relating to the level of white and/or black, is known as saturation, chroma, tone, intensity, or purity. The third attribute is the luminance of the color, also referred to as value, lightness, or brightness. Luminance is very informative in considering the properties of electrochromic materials, because, with only one value, it provides information about the perceived transparency of a sample over the entire visible range. For application in the field of electrochromism, in 2000 Reynolds and co-workers introduced an in situ colorimetry method for the precise control and measurement of color in electrochromic materials and display devices.[24] This methodology, with use of a simple portable colorimeter, has since been extensively applied to color measurement of numerous electrochromic conjugated polymer films and devices,[15,16,25−45] thin films of Prussian blue,[46] and the *n*-heptyl viologen system.[47] In the results presented here, chromaticity coordinates and luminance data were calculated from in situ visible region absorption spectra recorded in transmission mode under electrochemical control. The methodology of the colorimetric transformations using a computer spreadsheet, with absorbance-wavelength data being taken as input, and chromaticity coordinates/luminance data being generated as output, has been described earlier.[18]

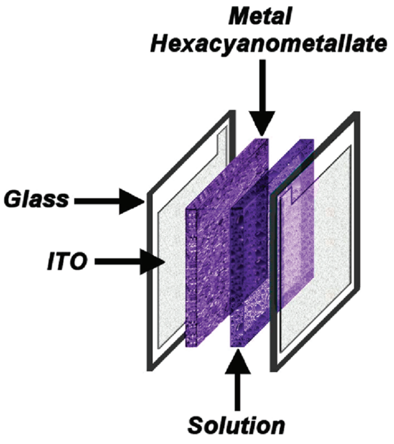


Figure 1. ECD design, with the spacers used omitted for clarity. For the devices described here, the metal hexacyanometallate was Ruthenium purple, and the electrolyte solution consisted of aqueous 5 or 10 mmol dm^{-3} methyl viologen dichloride/0.5 mol dm^{-3} potassium chloride.

EXPERIMENTAL SECTION

ECD Fabrication. Tin-doped indium oxide (ITO)-coated optically transparent substrates (Corning 1737 aluminosilicate glass, 25 × 25 × 1.1 mm, R_s 4−8 $\Omega\ \square^{-1}$ (CB-50IN-0111)) were from Delta Technologies. Figure 1 shows an exploded schematic of the ECD design, which allowed spectral measurements to be made in transmission mode, and also functioned as a mini prototype electrochromic window.

The ITO-glass substrates were patterned by wet chemical etching at 50 °C for 90 s in an aqueous solution containing 6.0 mol dm^{-3} hydrochloric acid and 0.2 mol dm^{-3} iron(III) chloride. The exposed area was defined by masking with Scotch Magic Tape (3M), ITO removal at the edges being confirmed by scanning electron microscopy and four-point probe conductance measurements. Although a rectangular shape was chosen here, in principle, using an appropriate stencil, any desired shape could be created onto the substrates' surfaces.

Ruthenium purple (RP) film on one of the ITO-glass substrates was synthesized by an electrochemical coagulation technique using an aqueous RP colloidal suspension prepared from separate very dilute aqueous solutions of iron(III) chloride and potassium hexacyanoruthenate(II), with dilute aqueous potassium chloride as supporting electrolyte solution. Precise details of the formulation of the RP colloidal suspension have been described earlier.[17] The ITO-glass substrate potential was held at +0.60 V for 5 s and then cycled, +0.60 V → −0.20 V → +0.60 V (vs. Ag/AgCl in 3.0 mol dm^{-3} NaCl), 50 times at 50 mV s^{-1}.

Polyamide−Nylon 6 film (0.25 mm thick, from Goodfellows) was used as spacer and secured to three sides of the RP-coated ITO-glass substrate using epoxy resin and positioned where ITO had been etched away. At the point where the ITO film extends to the edge of the slide, copper tape, as current collector, was then attached to the top edge of both slides, and coated with a thin layer of epoxy resin to prevent any copper coming into contact with the electrolyte solution. Epoxy resin was also used to secure the second slide onto the first, creating a small volume between the slides. Rinsing with 10 mmol dm^{-3} ascorbic acid reduced the iron(III) hexacyanoruthenate(II) chromophore in RP to the colorless/transparent iron(II) hexacyanoruthenate(II) oxidation state. Finally, the methyl viologen salt in the electrolyte solution layer was injected with a microbore 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.

Electrochemical and Spectroelectrochemical Measurements. An ECO Chemie Autolab PGSTAT 20 potentiostat was used for electrode potential control of each ECD, with in situ visible region spectra being recorded in transmission mode using a Hewlett-Packard 8452A diode array spectrophotometer. For each ECD, the potentiostat working electrode lead was connected to the RP-coated ITO-glass electrode, with the counter and reference electrodes' leads shorted together and connected to the second ITO-glass electrode. CIE 1931 *xy* chromaticity coordinates and luminance data were calculated from the spectra using a computer spreadsheet, as described earlier,[18] with the use of the spectral power distribution of a D_{55} light source (a constant temperature (5500 K) light source, for the simulation of midmorning to midafternoon natural light). Chromaticity coordinates were also transformed to $L^*a^*b^*$ coordinates, a uniform color space (CIELAB) defined by the CIE in 1976.[48]

RESULTS AND DISCUSSION

The electrochemical coagulation technique, with use of the colloidal RP suspension and potential cycling conditions as described above, provided RP films with a uniform distribution of submicrometer sized particles with an average film thickness of 100 nm, as calculated from the 1.85 mC cm^{-2} charge passed on electrochemically switching color states. For the ~4 cm^2 active ECD area, this corresponds to ~8 × 10^{-8} moles of surface-confined RP.

ECDs were investigated, with both 5 and 10 mmol dm^{-3} methyl viologen dichloride/0.5 mol dm^{-3} potassium chloride as the electrolyte solutions. The optimum switching potentials of the ECDs were established as −0.5 V for the "off" state and +1.5 V for the "on" state, representing a compromise between enhancing the switching kinetics and avoidance of over oxidation/reduction of the electrochromic materials and/or decomposition of the solvent. For each ECD, measurement of spectral data was repeated six times and found to be coincident. When the measurements were repeated after 7 days, using no specific storage conditions and exposed to both light and air, the ECDs exhibited no degradation in appearance and performance. Continuous switching over several hours, holding each potential for 30 s, led to no change in performance of the ECDs. Figure 2 shows spectral changes on reversibly switching RP/methyl viologen ECDs at the two concentrations between the colorless ("off") and purple ("on") states.

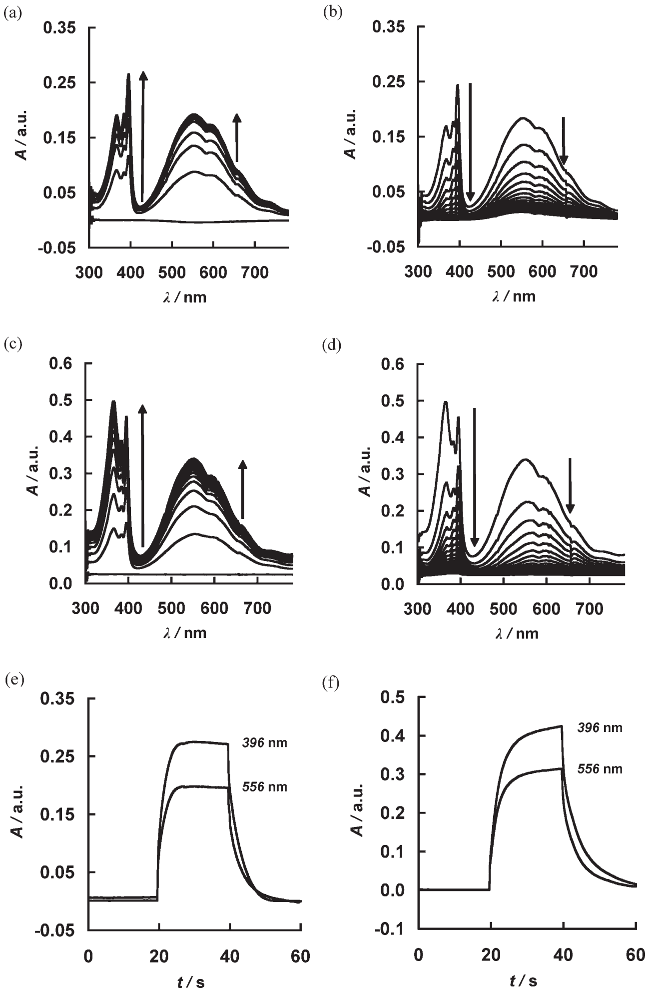


Figure 2. UV−visible absorbance responses of ECDs subjected to potential steps from −0.5 V (held 0 to 20 s) to +1.5 V (at 20 s) to −0.5 V (at 40 s). The ECDs consisted of Ruthenium purple/methyl viologen (at 5 mmol dm^{-3} ((a), (b), (e)) and 10 mmol dm^{-3} ((c), (d), (f))) with potassium chloride (0.5 mol dm^{-3}) as the supporting electrolyte. The UV−visible absorbance spectra at multiple wavelengths were recorded every 1 s and for single wavelength measurements ((e) and (f)) every 0.1 s. The working electrode lead was connected to the RP coated electrode, and the counter/reference wires were shorted together and connected to the *other* ITO electrode. Plots (a) and (c) are the UV−visible absorbance spectra between 20 and 40 s, and plots (b) and (d) are the UV−visible absorbance spectra between 40 and 60 s. The arrows indicate the direction of change in absorbance. Plots (e) and (f) show the absorbance changes at the two $\lambda_{\max}$ values in the UV and visible regions.

The total absorbance change for the 5 mmol dm^{-3} methyl viologen ECD (Figure 2a,b,e), is less than would be obtained (A = 0.30 at 556 nm) at a single electrode with surface-confined RP prepared under the same conditions.[17] Although the quantity of methyl viologen in this solution-phase ECD exceeds the number of moles of surface-confined RP, with the chosen solution thickness defined by the spacer (0.25 mm), the ECD does not act as a thin-layer cell, and not all the methyl viologen in the bulk solution is electrolyzed. The concentration of methyl viologen and its diffusion to the cathode will control the proportion of surface-confined RP that is switched to the intense purple form. A greater depth of color is accessible, with use of higher methyl viologen concentrations, for example, the 10 mmol dm^{-3} viologen ECD provides a higher total absorbance change of just under twice (Figure 2c,d,f) that for a 5 mmol dm^{-3} viologen ECD. Compared to measurements for single surface-confined RP electrodes, where switching times were <1 s, ECD switching times, are longer owing to the diffusional limitations of the solution-based viologen system. Switching times, as estimated for 95% of the total absorbance change, were 4 and 10 s respectively, for coloration and bleaching for the 5 mmol dm^{-3} viologen ECD, and 8 and 16 s for the 10 mmol dm^{-3} viologen

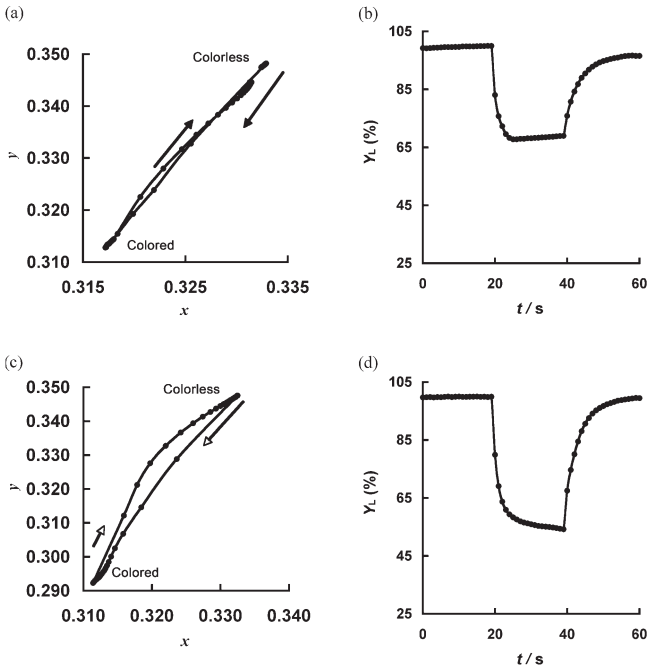


Figure 3. Calculated color trajectory in the CIE 1931 color space ((a) and (c)) and relative luminance vs time ((b) and (d)), for the electrochemical switching of an ECD consisting of Ruthenium purple/methyl viologen (5 ((a) and (b)) and 10 ((c) and (d)) mmol dm^{-3}). The arrows show the colorimetric path taken during the potential steps (−0.5 to +1.5 V to −0.5 V).

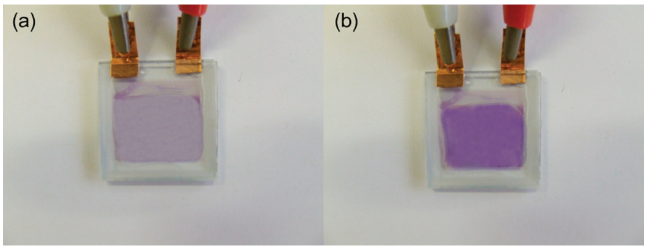


Figure 4. Photographs of the electrochromic switching of a Ruthenium purple/methyl viologen (5 mmol dm^{-3}) ECD, in (a) its colorless and (b) its colored state.

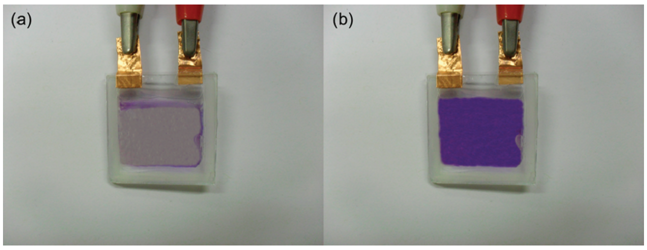


Figure 5. Photographs of the electrochromic switching of a Ruthenium purple/methyl viologen (10 mmol dm^{-3}) ECD, in (a) its colorless and (b) its colored state.

ECD. On switching the ECDs, the coloration/bleaching process was observed by eye to initiate from the center and propagate outward, implying that the potential distribution was not wholly uniform in these prototype devices. As the ECDs were positioned with the light beam of the spectrophotometer directed through the center of each, then the switching times will be low estimates. The longer switching times for the bleaching process are a result of the slower diffusion of the methyl viologen radical cation dimers, compared to the methyl viologen dications in the coloration process.

The broad absorption (400−780 nm) (Figure 2a−d) in the visible region is a composite of the superimposed RP and methyl viologen radical cation charge-transfer bands, and this emphasizes the benefit of this color-reinforcing ECD design. Using a thin-layer spectroelectrochemical technique, the molar extinction coefficient of the metal viologen radical cation has been reported[49] to be 13700 dm^{3} mol^{-1} cm^{-1}. Spectral measurements with an aqueous dispersion[19] and thin-layer[50] RP give molar extinction coefficients of 10000 and 11400 dm^{3} mol^{-1} cm^{-1}, respectively. The comparability of the molar extinction coefficients in the ECD therefore provide similar absorbance changes for the same charge input at the respective electrodes.

It is to be noted that in the aqueous electrolyte solution, the perceived purple color of the reduced methyl viologen is actually the result of color mixing of the blue methyl viologen radical cation, which is in equilibrium with the red methyl viologen radical cation dimer. The spectral peaks below 400 nm are also due to the methyl viologen radical cation monomer/dimer, but do not contribute to the perceived color. That the RP contributes to the visible region absorption is proved by the higher ratio of absorbance in this region compared to the spectral peaks below 400 nm, in comparison to the spectral data of the methyl viologen radical cation system[18] in the absence of RP. For the ECDs, Figures 2e and f demonstrate that the rate of absorbance change in the two main absorption regions is the same.

Figure 3 shows the CIE 1931 *xy* chromaticity coordinates and relative luminance changes for the two viologen concentration ECDs as calculated from the in situ spectra of Figure 2.

For these color-reinforcing ECDs, with excellent color-matching between the two purple states, there is minimal hysteresis in the track of the CIE 1931 *xy* coordinates on reversibly switching between the “off” and “on” states (Figure 3a and c). Overlaying the *xy* data onto the CIE 1931 color space template, and extrapolation, provides 565 (±5) nm as the complementary wavelength (λ_c) of the ECD color state, in good agreement with the wavelength of maximum absorbance (556 nm) in the visible region spectra (Figure 2), and values calculated for the individual electrochromic materials.

In CIE theory, colors cannot be specifically associated with a given pair of *xy* coordinates, because the third dimension of color, lightness, is not included in the diagram. The relative lightness or darkness of a color is very important in how it is perceived, and is presented as the relative or percentage luminance, Y_L, of the sample, to that of the background, Y_0. Luminance is very informative in considering the properties of electrochromic materials, because, with only one value, it provides information about the perceived transparency of a sample over the entire visible range. Relative luminance values can range from 100% for white samples (no light absorbed) to zero for samples that absorb all the light. Figure 3b and d show in graphical form the changes in the % colorimetric luminance (%Y_L) on switching between the “off” and “on” ECD states. When the ECD is switched on, the luminance decreases, as the purple color becomes more saturated.

Figures 4 and 5 show photographs of the colorless and purple states, with the CIE 1931 (%Y_L, *x*, and *y*) and CIELAB ($L^*a^*b^*$) numerical data given in Table 1.

Table 1. Numerical Chromaticity Coordinates (CIE 1931 %$Y_L xy$ and CIELAB $L^*a^*b^*$) for Ruthenium purple/methyl viologen (5[a] and 10[b] mmol dm^{-3}) ECDs[a]

ECD state	x	y	%Y_L	L^*	a^*	b^*
"off" (colorless)	0.333	0.348	100%	100	0	0
"on" (colored)[a]	0.317	0.313	68%	86	9	−15
"on" (colored)[b]	0.311	0.292	54%	79	15	−22

[a] The ECDs were switched between "off" and "on" states *via* a square wave potential step from −0.5 V to +1.5 V, and vice versa.

When the ECDs are in the "off" state (−0.5 V), the redox states are the colorless methyl viologen dication and the colorless iron(II) hexacyanoruthenate(II) oxidation state of RP. The chromaticity coordinates of the ECDs in the "off" state (x = 0.333, y = 0.348, and %Y_L = 100) are coincident to that of the white point (x = 0.332, y = 0.348, and %Y_L = 100) for a D_{55} illuminant source, demonstrating full transparency of the ECD. When the ECD is switched on (+1.5 V), in an oxidative direction with respect to the RP electrode and a reductive direction with respect the methyl viologen, the ECD changes from colorless to purple because of the formation of the purple methyl viologen radical cation/dimer and the purple iron(III) hexacyanoruthenate(II) chromophore. In terms of CIELAB ($L^*a^*b^*$) chromaticity coordinates (Table 1), with a decrease in L^*, a positive change (toward red) in a^*, and a negative change (toward blue) in b^* takes place, quantifying the perceived purple color state as a combination of red and blue.

CONCLUSION

A novel color-reinforcing ECD, in which the anode and cathode reactions simultaneously exhibit comparable color responses, has been described. On coloration, the iron(II) hexacyanoruthenate(II) chromophore is oxidized to the purple iron(III) hexacyanoruthenate(II) chromophore of RP, and the methyl viologen dication is reduced to the methyl viologen cation radical/dimer which as a mixture also appears purple. The concentration of methyl viologen and its diffusion to the cathode controlled the proportion of surface-confined RP that is switched to the intense purple form and hence the overall absorbance/color change of the ECD. The current, UV−visible absorbance and colormetric responses of the ECD with two concentrations of methyl viologen were recorded. Using a calculation method based on the integration of experimental spectral power distributions derived from in situ visible region spectra over the CIE 1931 color-matching functions, the ECD color stimulus, and the changes that take place on reversibly switching to the colorless form have been calculated.

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