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
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# ISE 2010 Symposium 5: Electroactive Polymers, Inorganic Electroactive Solids, Nanocomposite Materials

Synthesis, electrochromism and display-device applications  
of electroactive Ruthenium Purple films prepared by 'directed  
assembly' and electrochemical precipitation techniques

Roger J Mortimer, Thomas S Varley

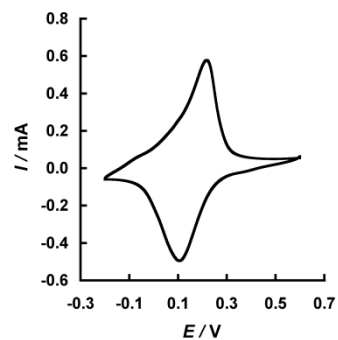
*Department of Chemistry, Loughborough University,  
Loughborough, Leicestershire, LE11 3TU, UK*

# Aim and objectives

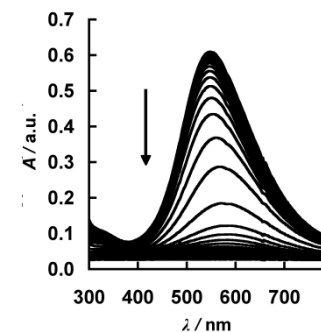
- **Aim:** to fabricate thin-layer electrochromic devices and to quantify colour changes
- **Objectives:**
  - to prepare stable films of the inorganic electroactive solid Ruthenium Purple (RP)
  - to pair with viologens in the fabrication of colour-reinforcing electrochromic devices
  - to quantify the colour stimulus of the individual electrochromic materials and the electrochromic devices

# Structure of presentation

1. Background to Ruthenium Purple (RP)
2. Directed assembly of RP
3. Electrochemical precipitation of RP and spectroelectrochemistry
4. Quantification of colour stimuli – colorimetry of RP and viologen systems
5. Thin-layer electrochromic devices



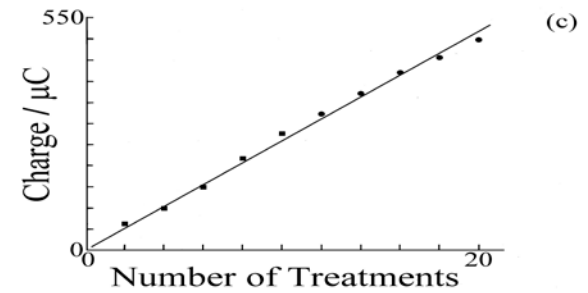
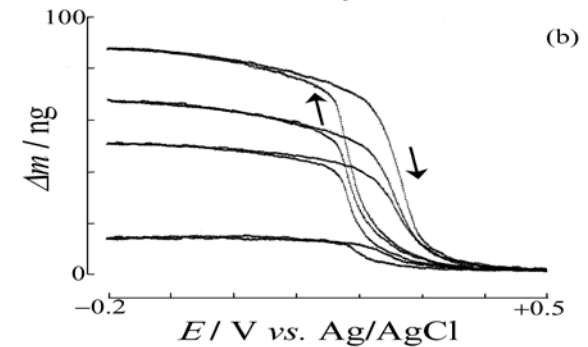
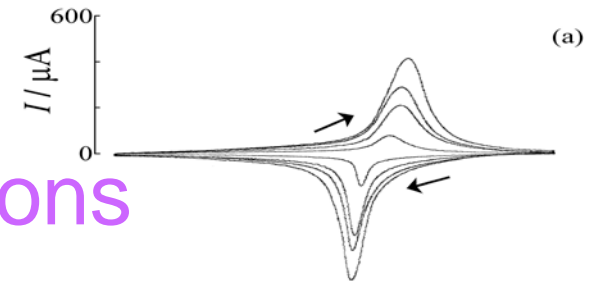
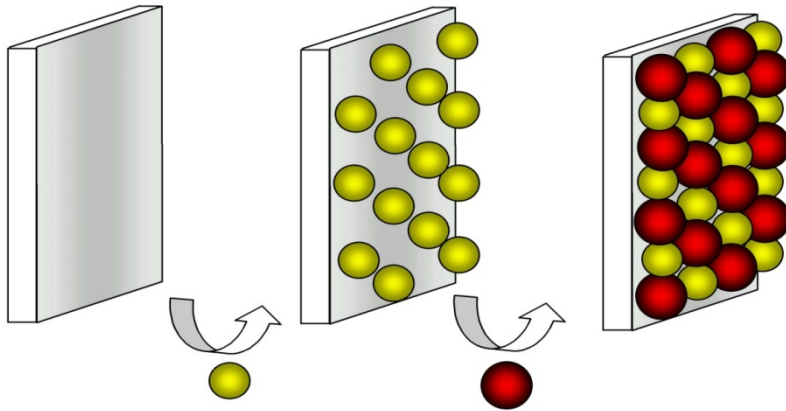
# Ruthenium Purple (RP)



- general formula of metal hexacyanomellates:
  - $M^A_x[M^B(CN)_6]_y$  (x, y integral)
- the  $M^B$  metal ions are coordinated in a strong cyanide ligand field and are low spin
- the  $M^A$  metal ions are coordinated in a weak nitrile ligand field and are high spin
- in RP the two transition metals in the formula are  $Ru^{II}$  (bonded to C) and  $Fe^{III}$  (bonded to N)
- exhibits a broad  $Ru^{II} - Fe^{III}$  IVCT band

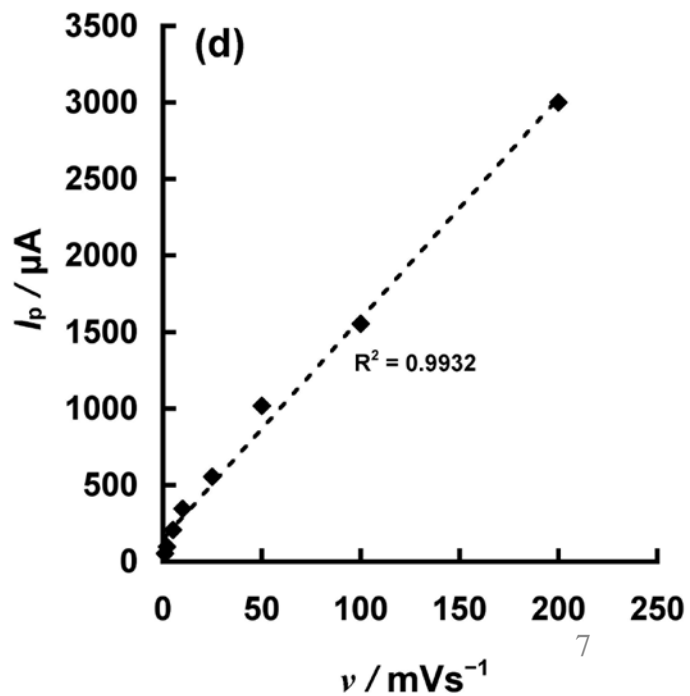
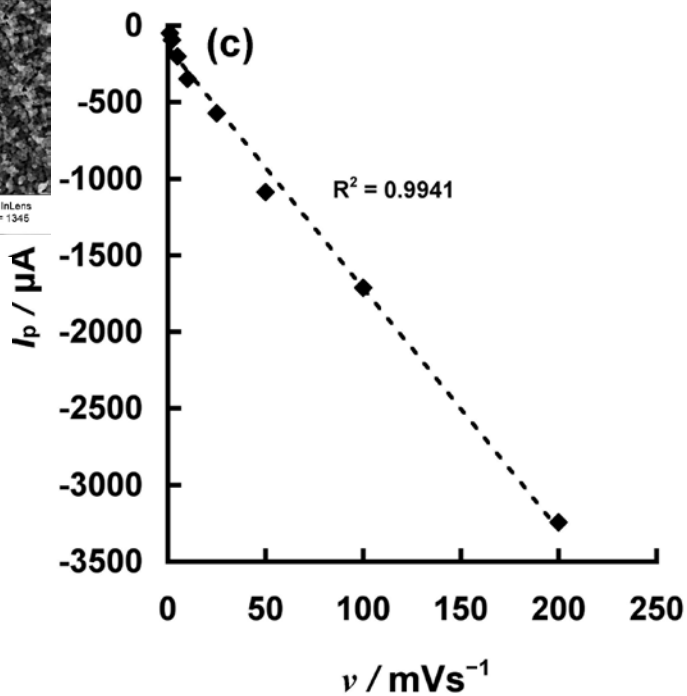
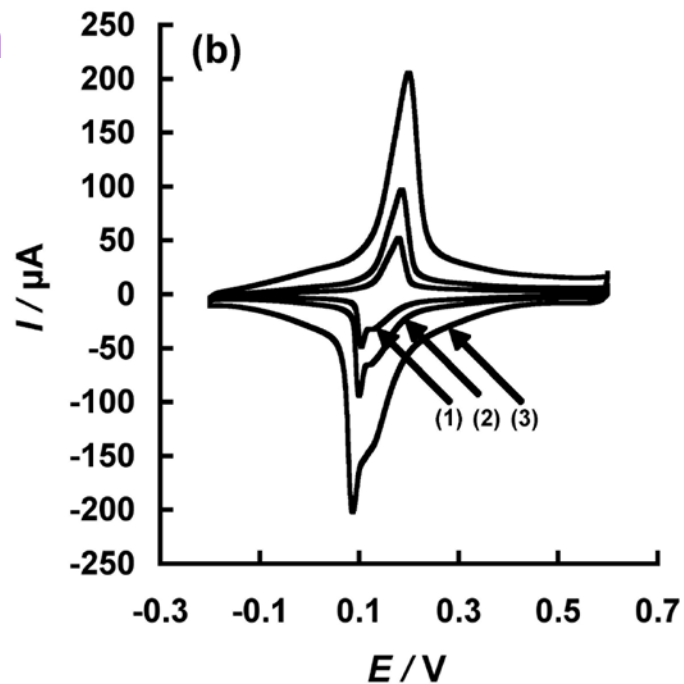
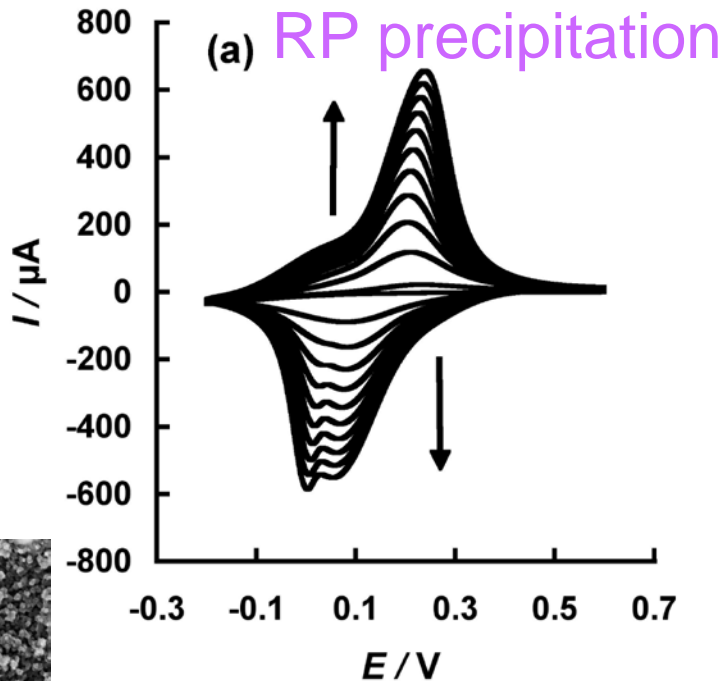
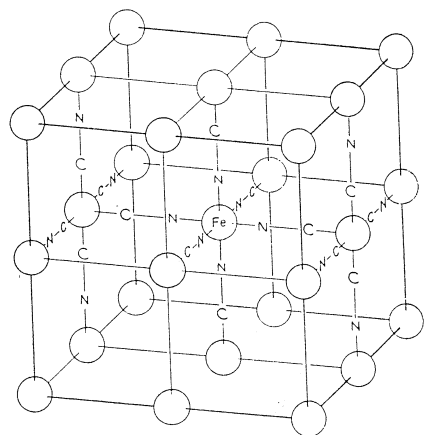
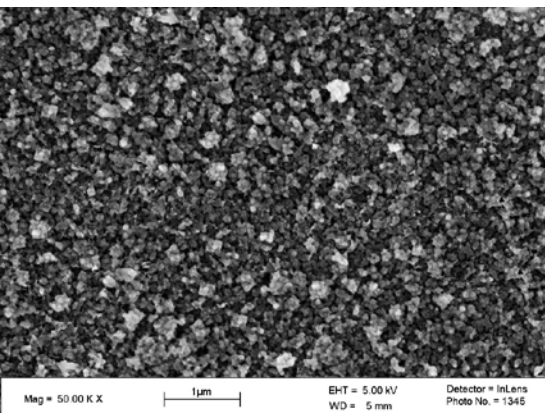
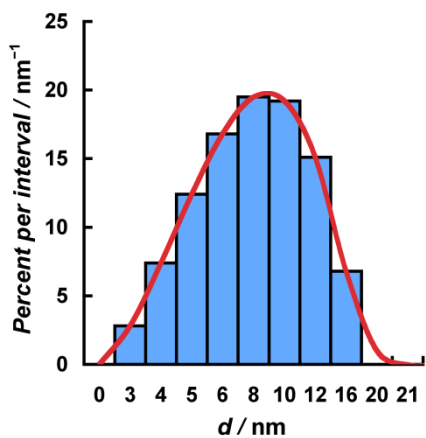
# Directed assembly of RP

- adsorb iron(III) cations then hexacyanoruthenate(II) anions



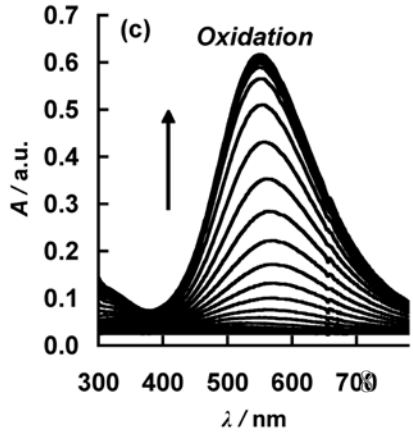
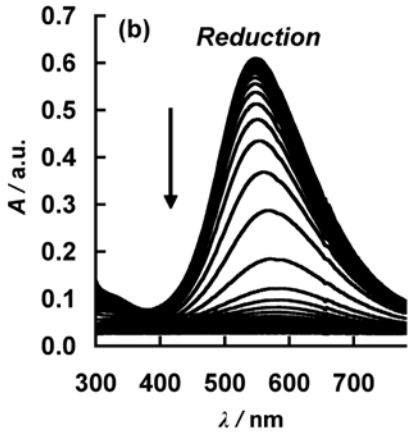
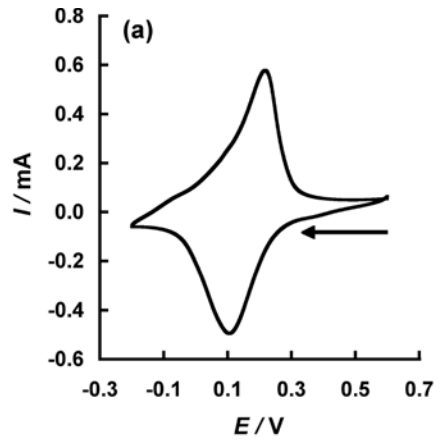
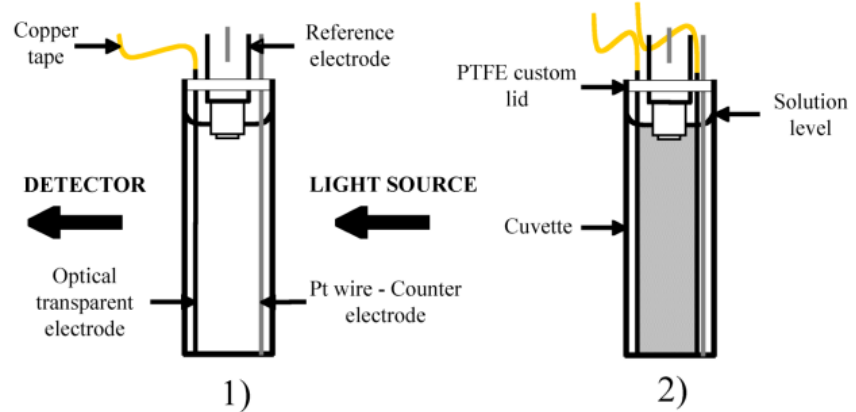
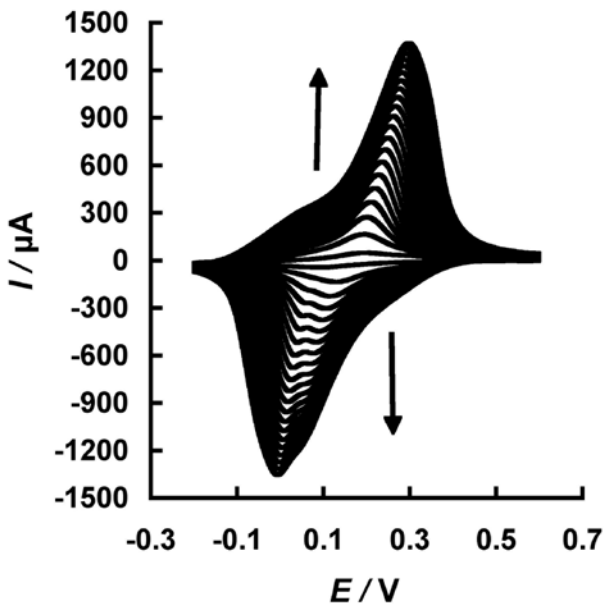
# Electrochemical precipitation of RP

- synthesised by an electrochemical coagulation technique using an aqueous nanoparticulate RP colloidal suspension prepared from separate very dilute aqueous solutions of iron(III) chloride and potassium hexacyanoruthenate(II), with dilute potassium chloride as supporting electrolyte solution. To aid stability of the RP films, ruthenium(III) chloride was added to the RP colloidal suspension.





# RP precipitation and spectroelectrochemistry

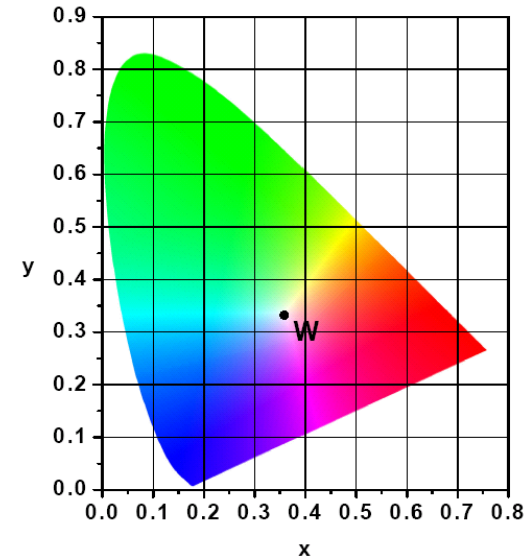
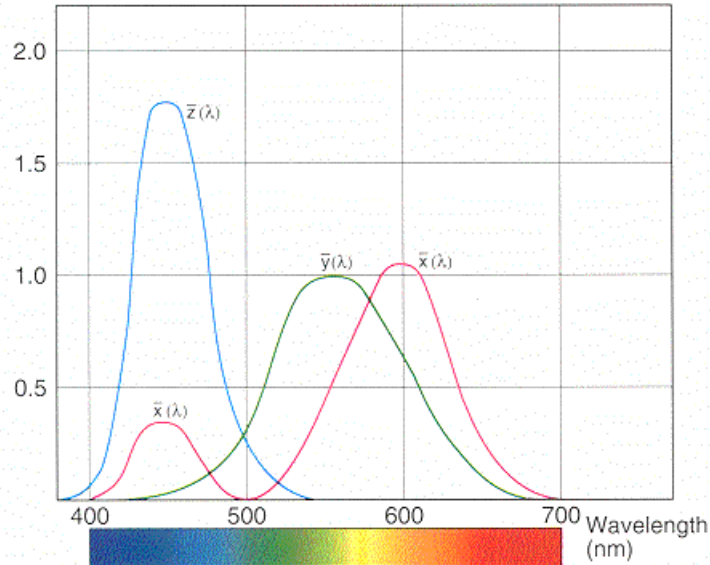


# Colorimetry

- **Luminance** – the brightness of the colour ... with one value, luminance provides information about the perceived transparency of a sample over the entire visible range
- **Hue** – identifies a colour by its location in the spectral sequence ... **red**, **yellow**, **green**, **blue** .... dominant wavelength associated with the colour, where maximum contrast occurs
- **Saturation** – the level of white and/or black ... vivid colours, dull colours .... (*chroma, tone, intensity, or purity*)

# CIE 1931 colour space

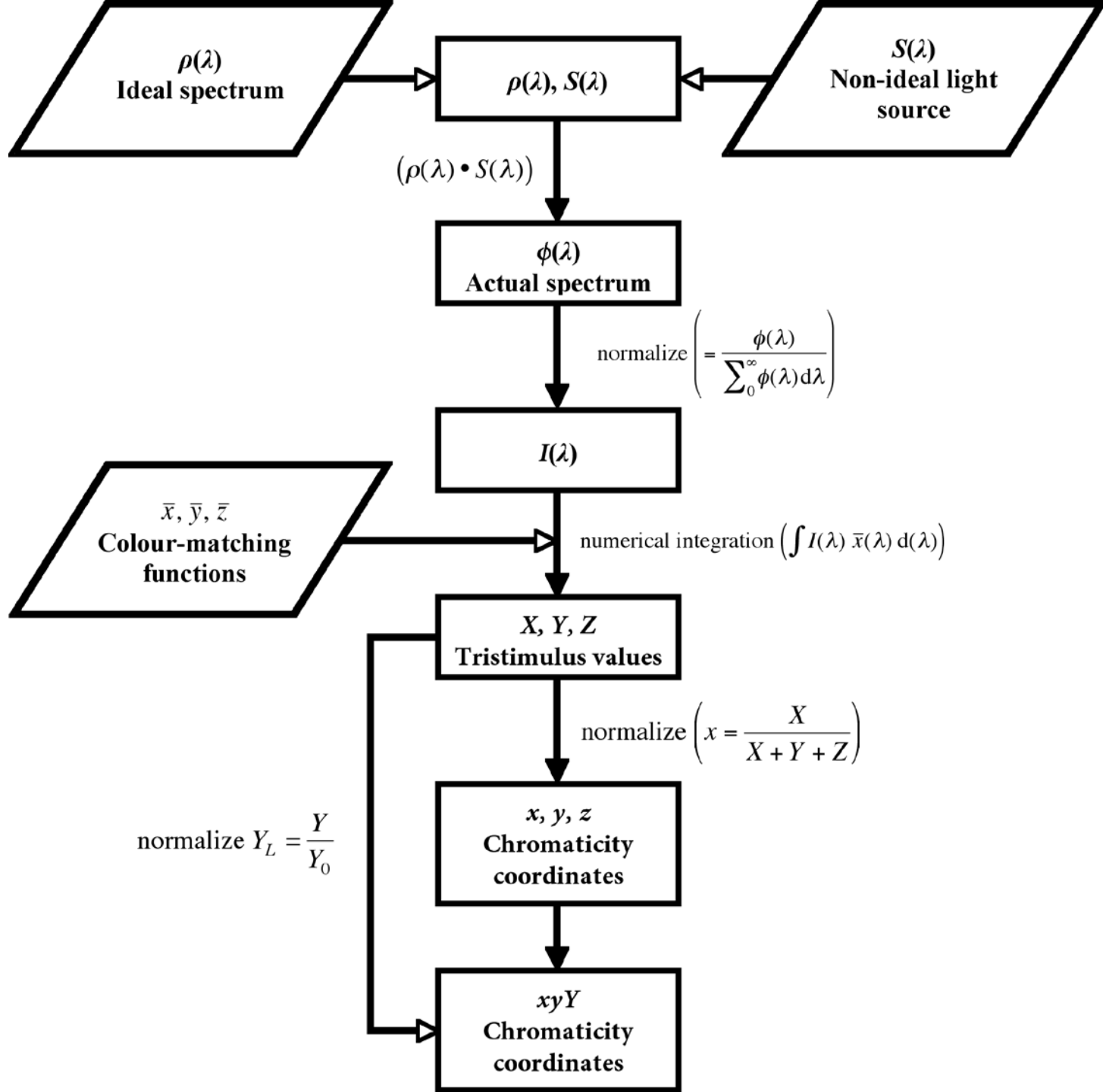
(Color-matching functions of the 1931 Standard Observer)



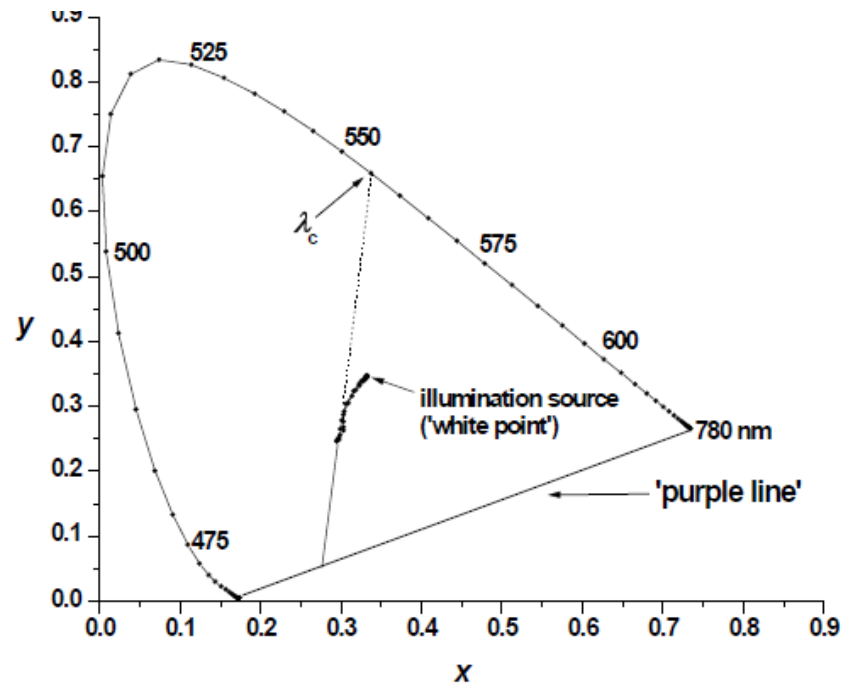
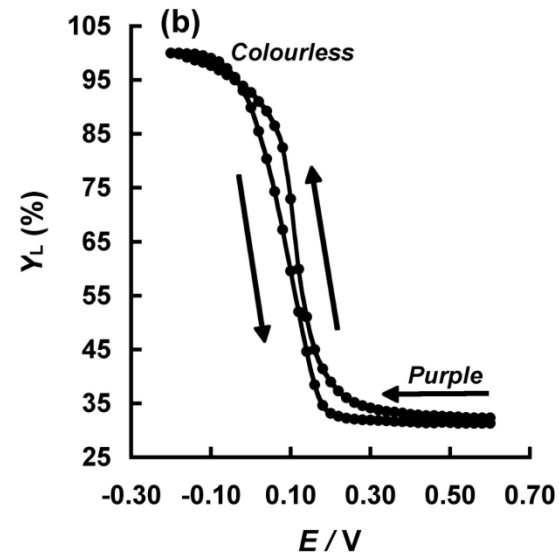
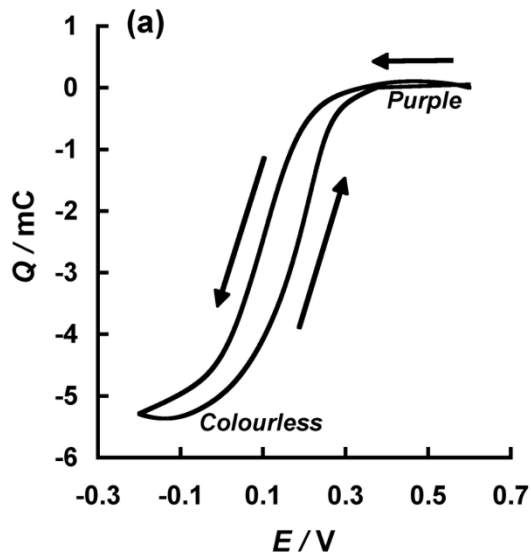
CIE 1931 colour matching functions

CIE 1931 xy diagram

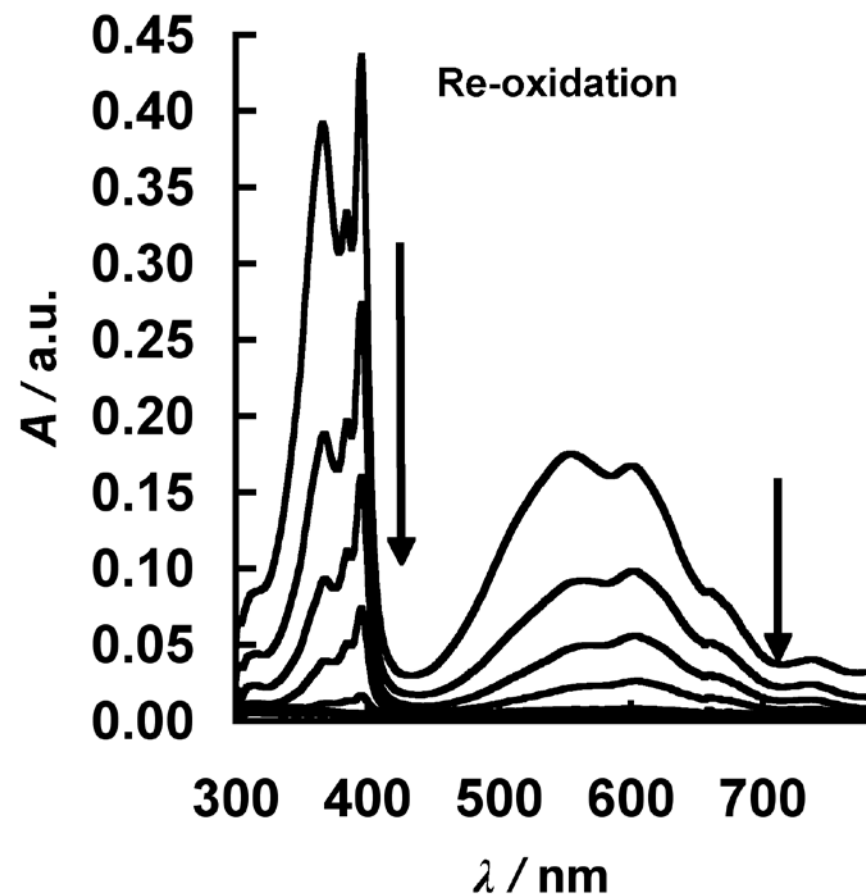
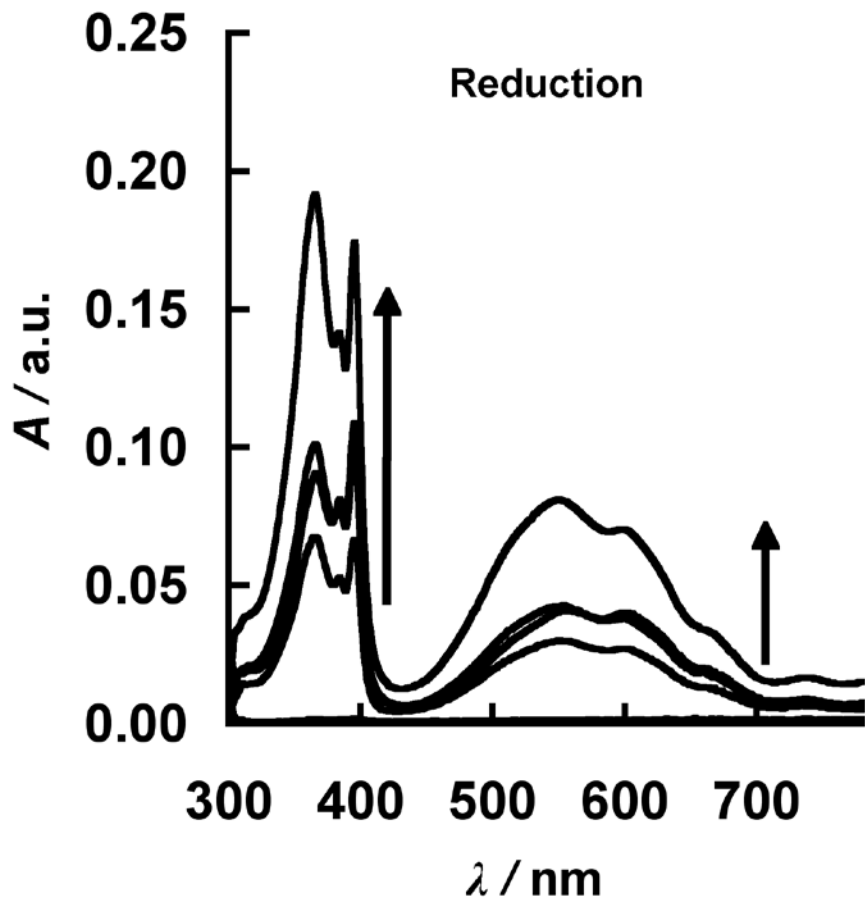
- CIE System of Colorimetry  
(Commission Internationale de l'Eclairage)
- 3 attributes of colour: Luminance, Hue, Saturation
- Colour matching functions  $\Rightarrow$  tristimulus values (XYZ)



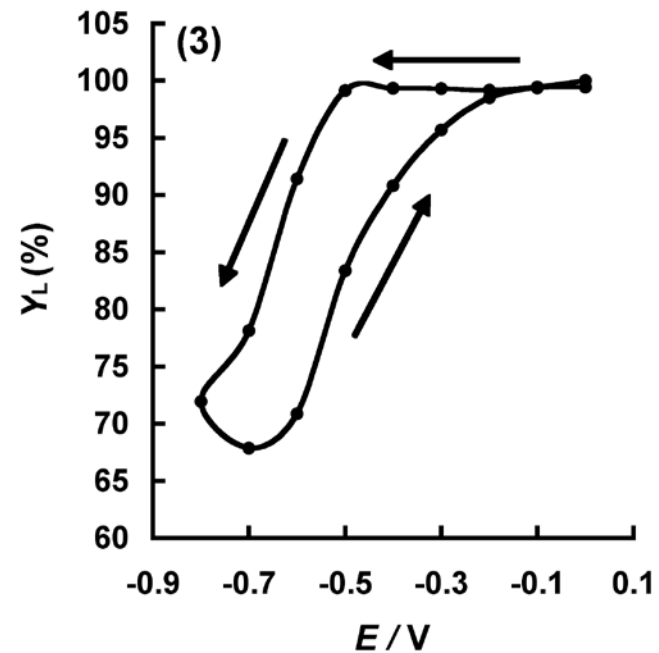
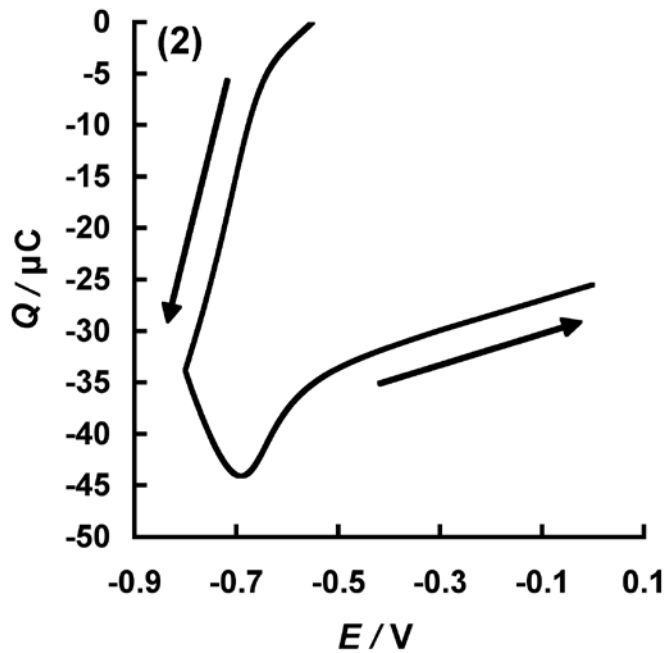
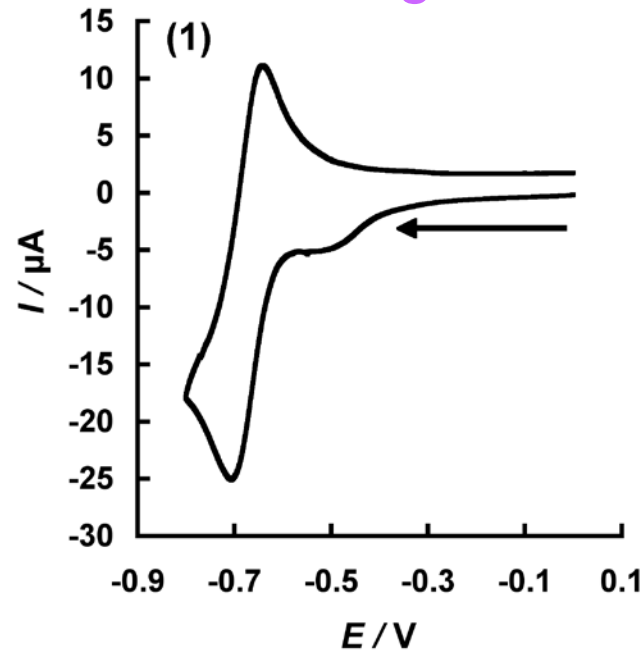
# RP colour switching and colorimetry



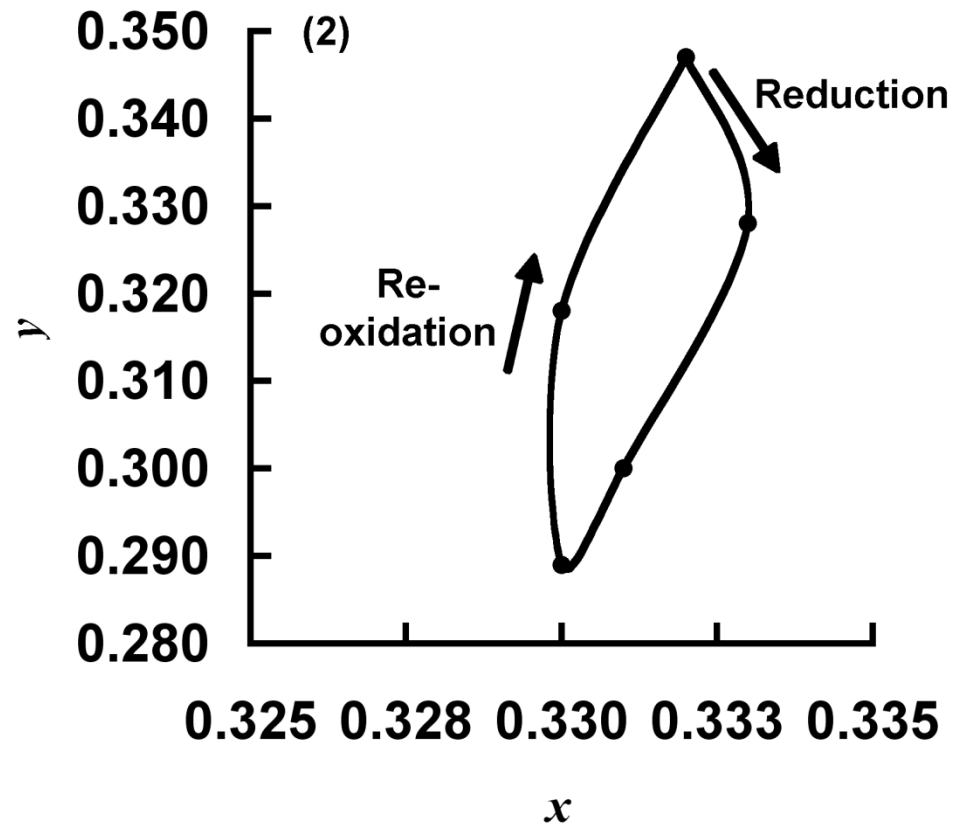
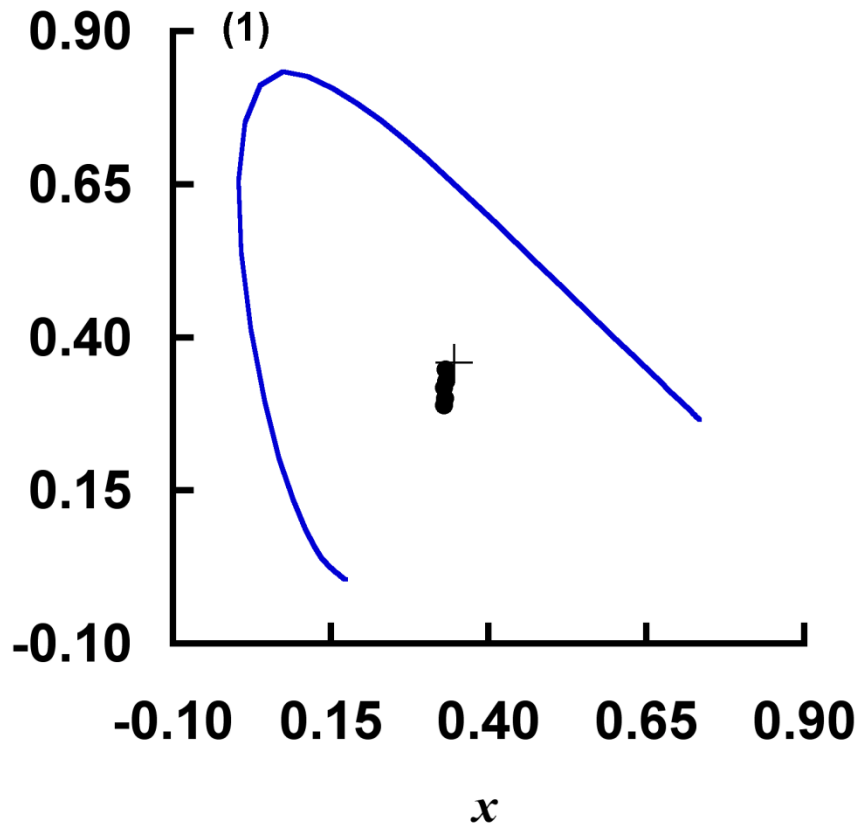
# Methyl viologen spectroelectrochemistry



# Methyl viologen colour switching and colorimetry (I)

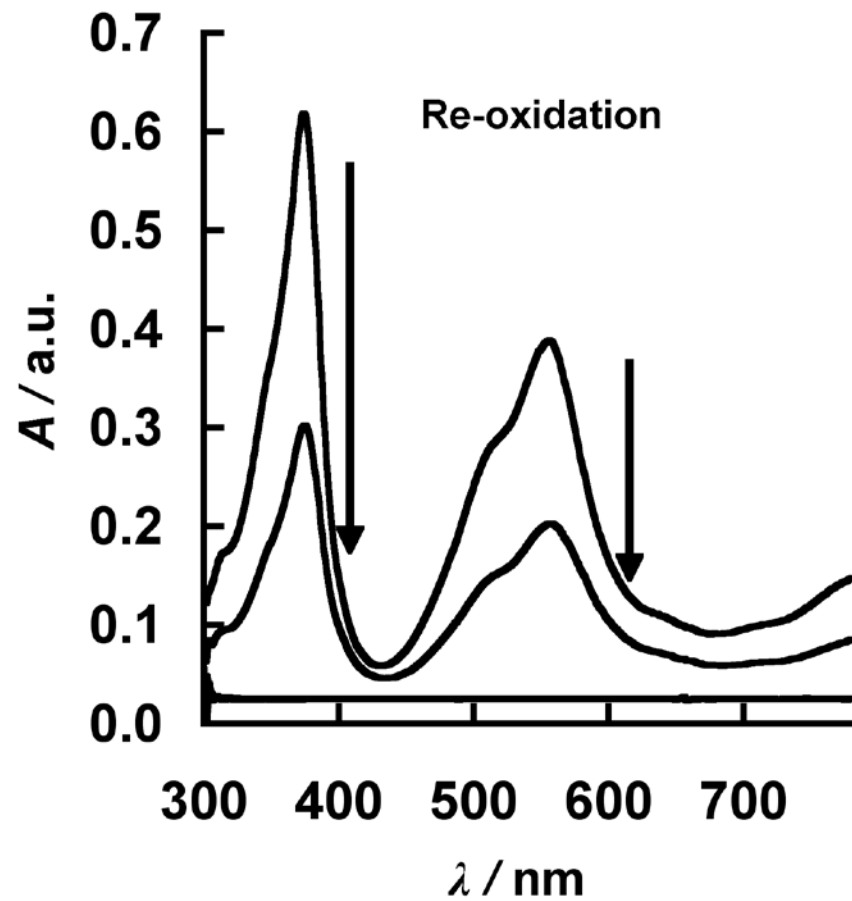
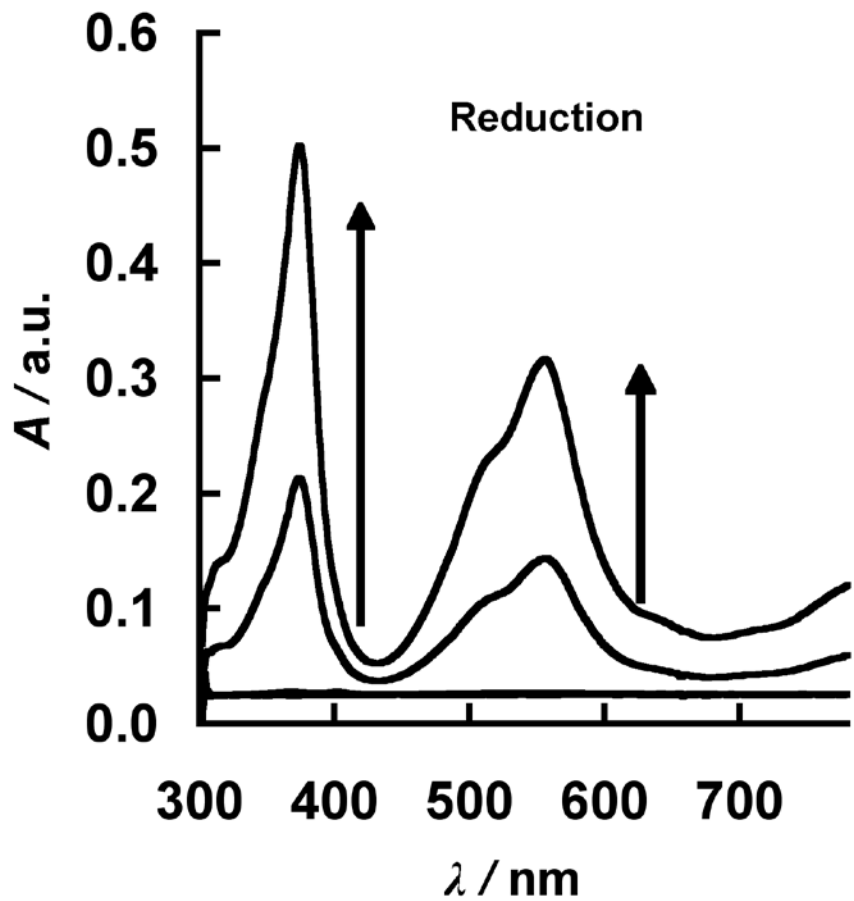


# Methyl viologen colour switching and colorimetry (II)

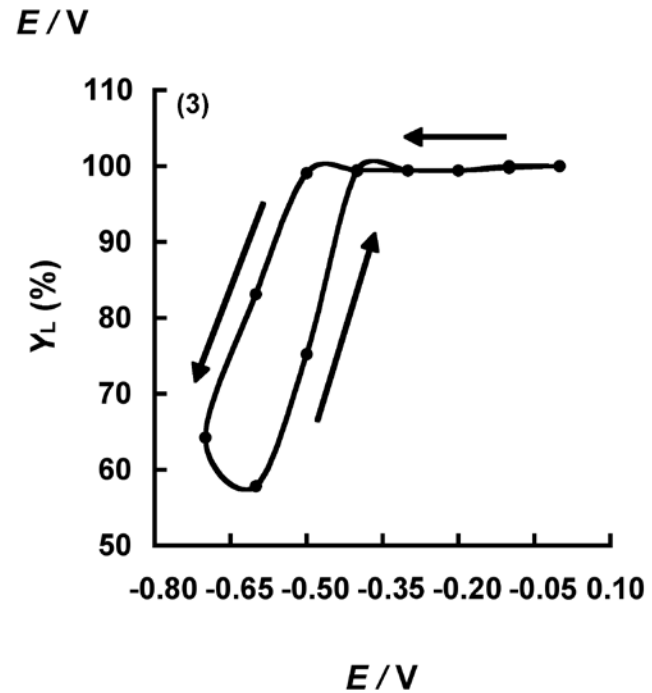
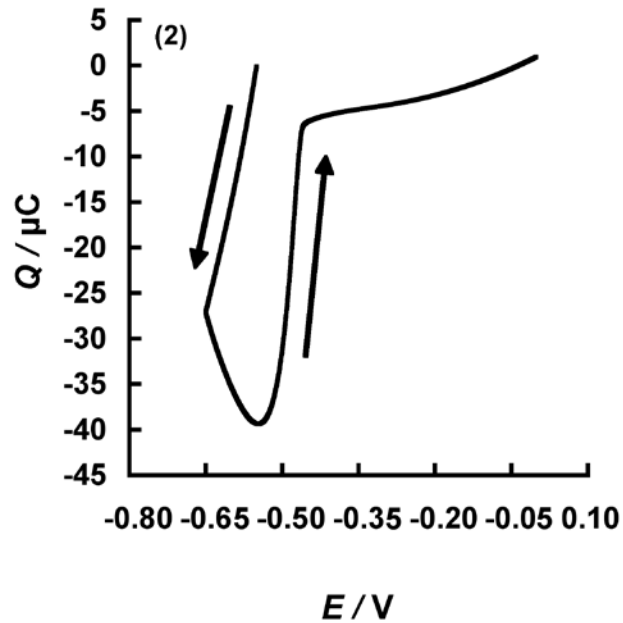
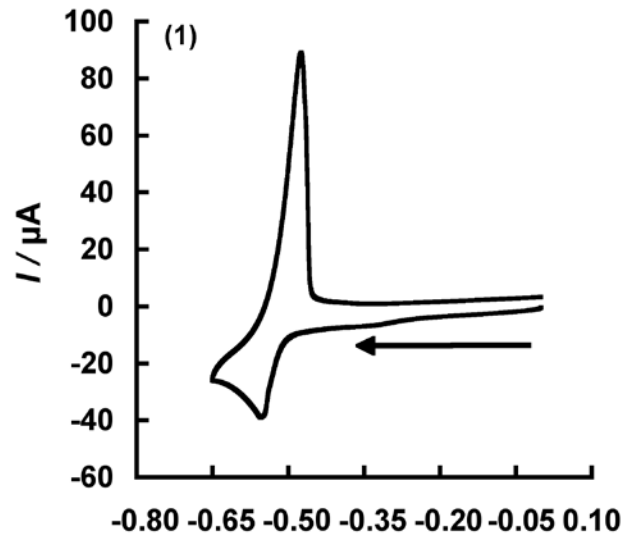




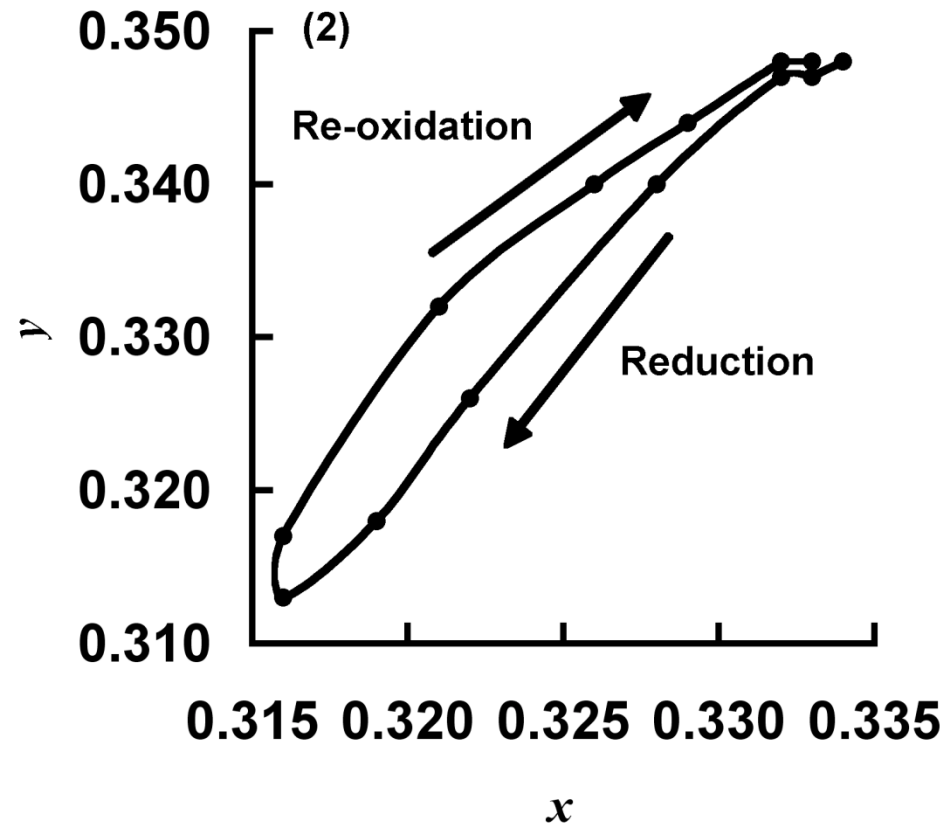
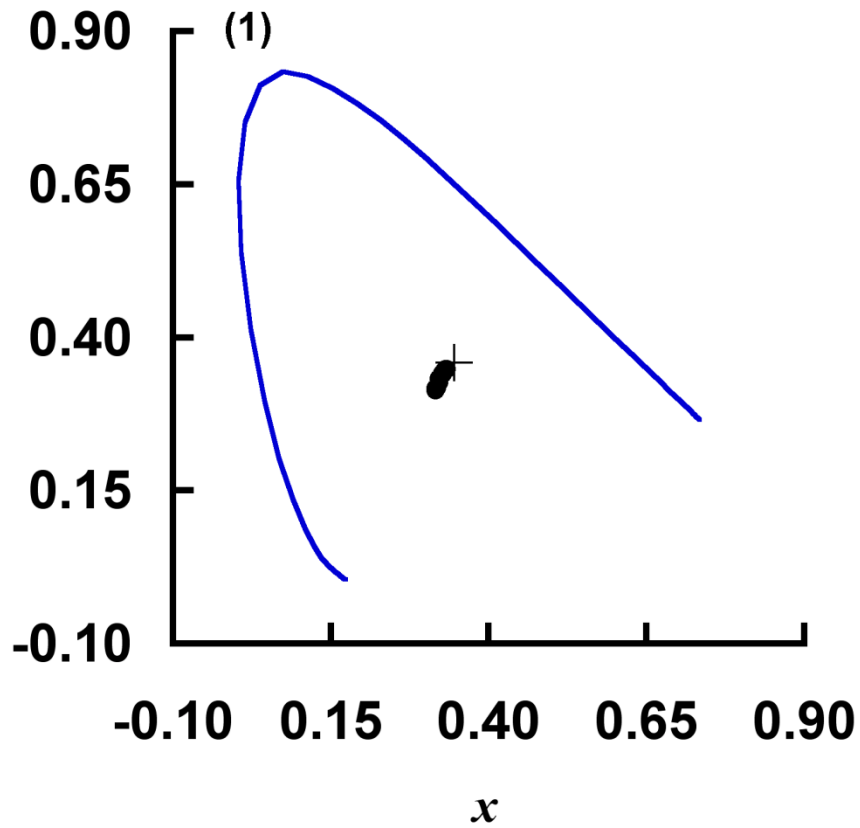
# Heptyl viologen spectroelectrochemistry



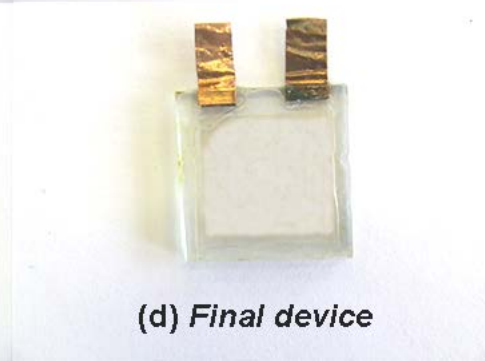
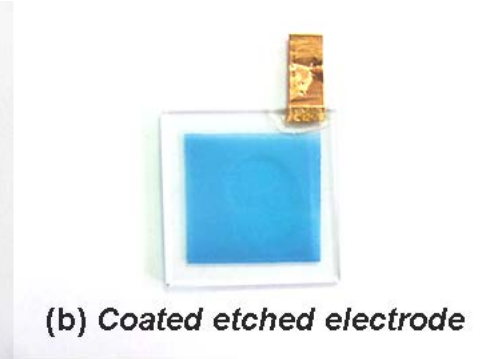
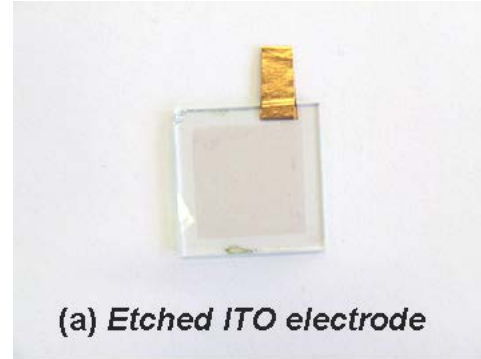
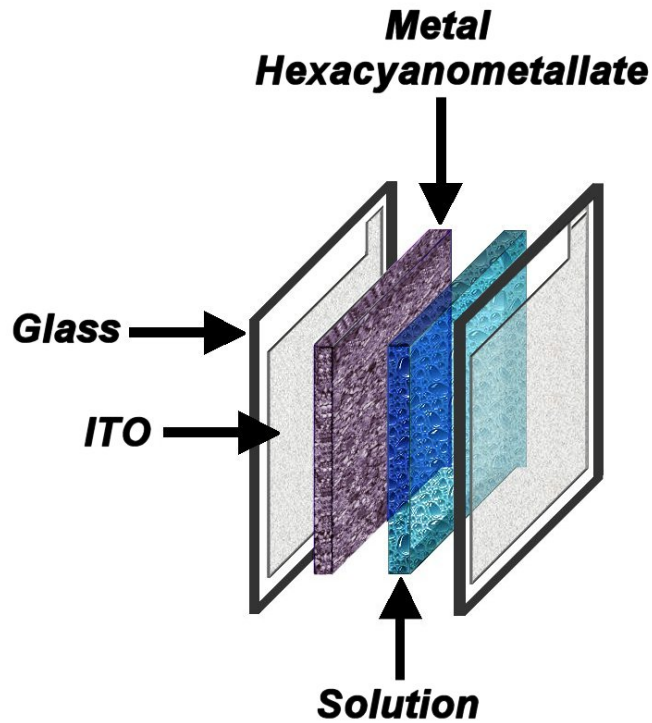
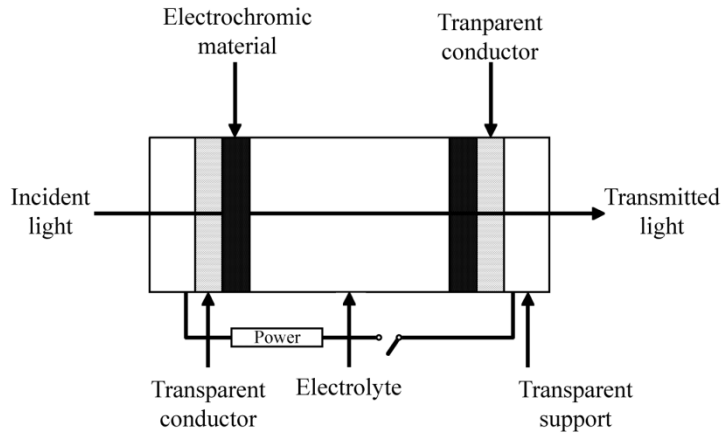
# Heptyl viologen colour switching and colorimetry (I)



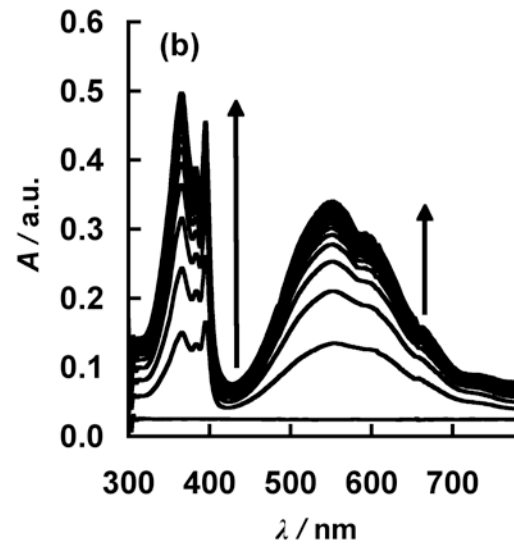
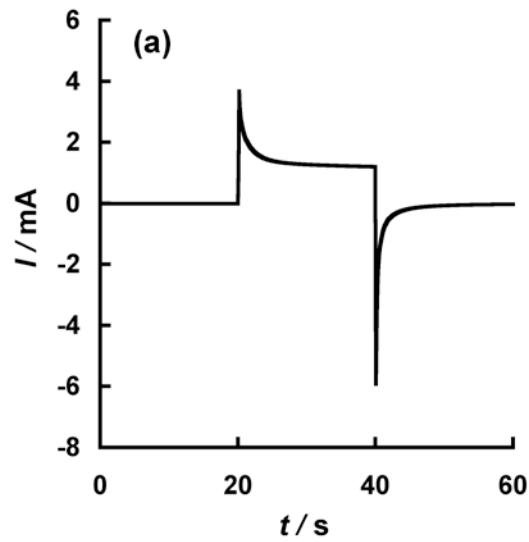
# Heptyl viologen colour switching and colorimetry (II)



# Thin-layer electrochromic device fabrication



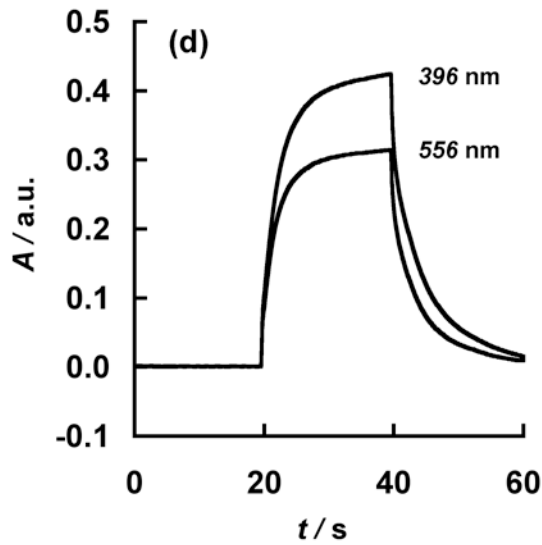
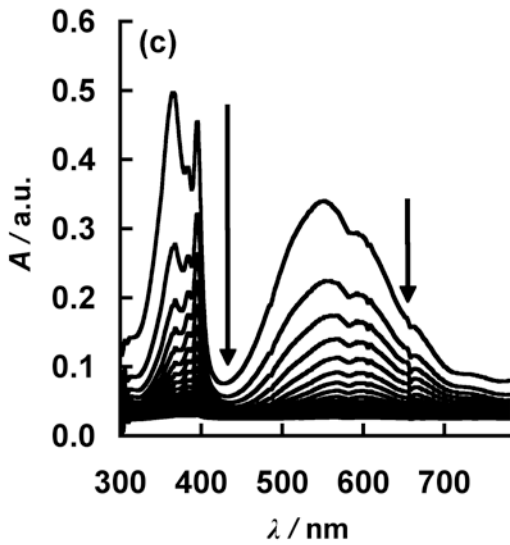
# RP/10 mM methyl viologen device (I)



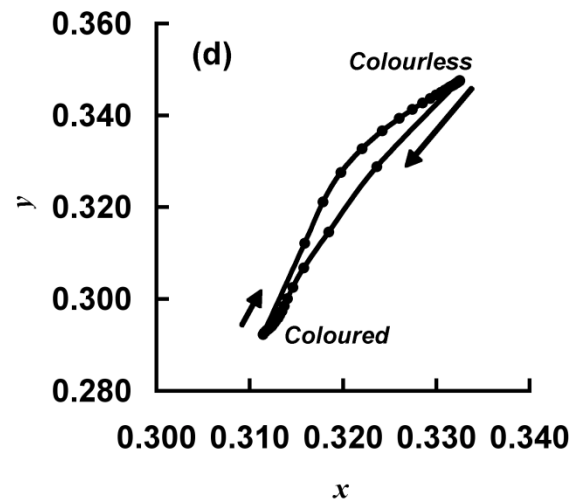
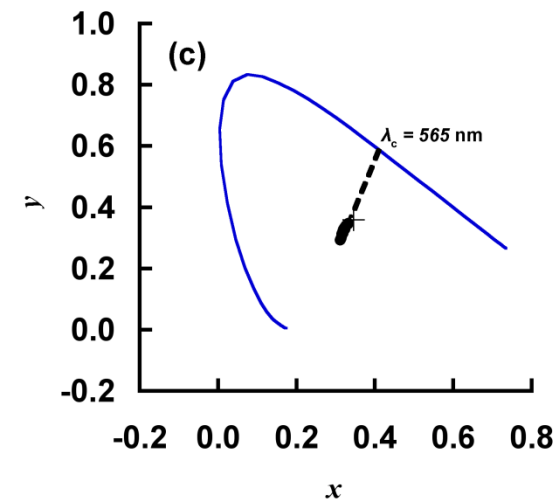
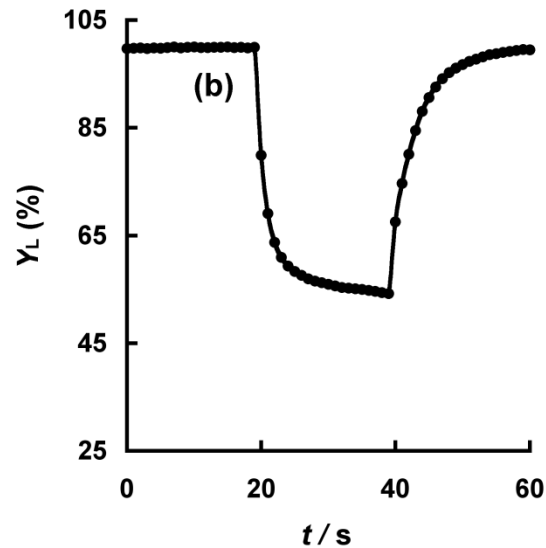
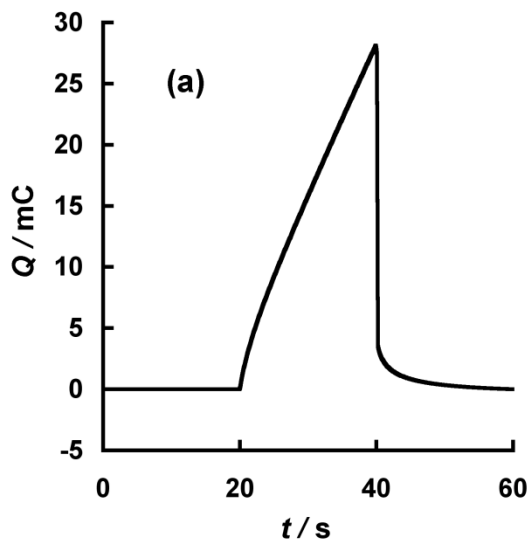
(a) Colourless



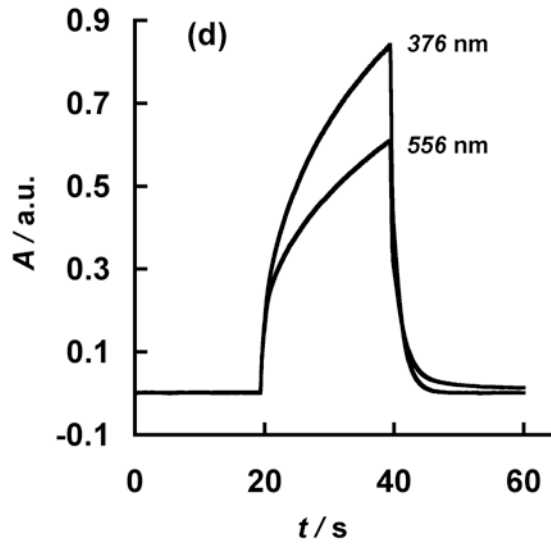
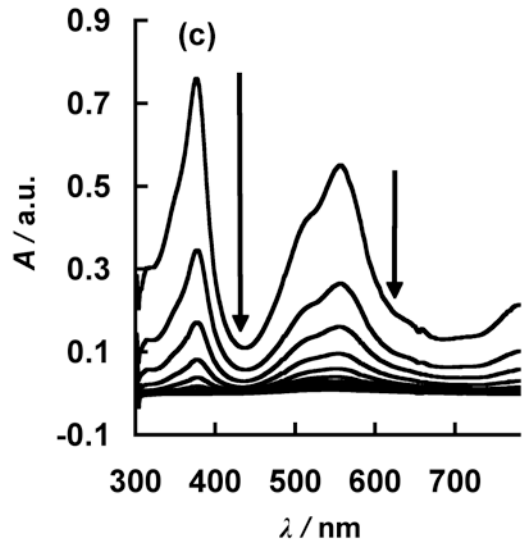
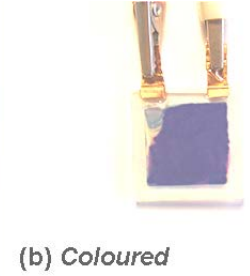
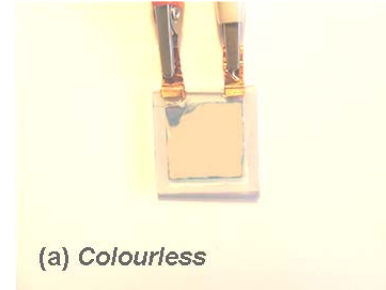
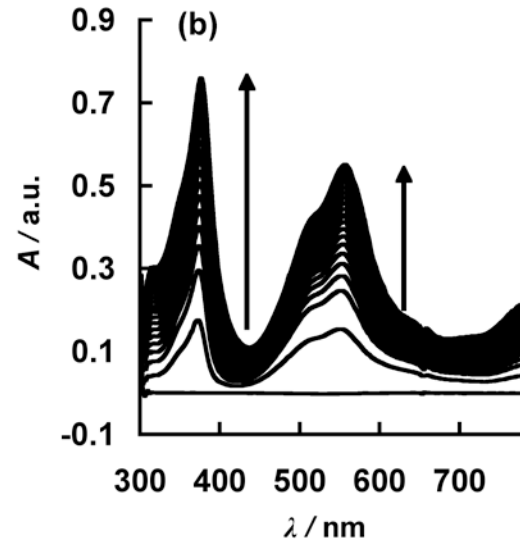
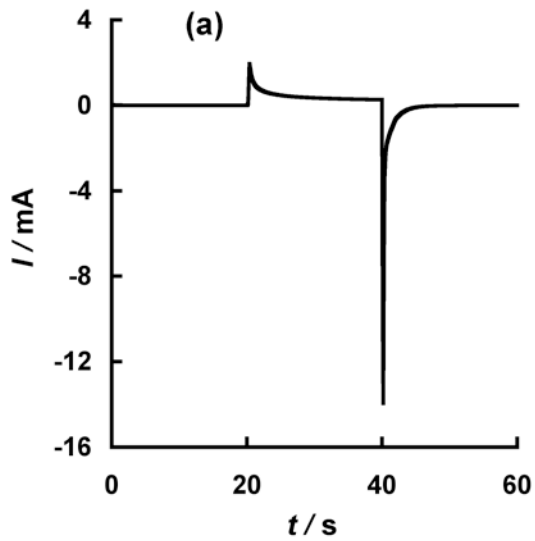
(b) Coloured



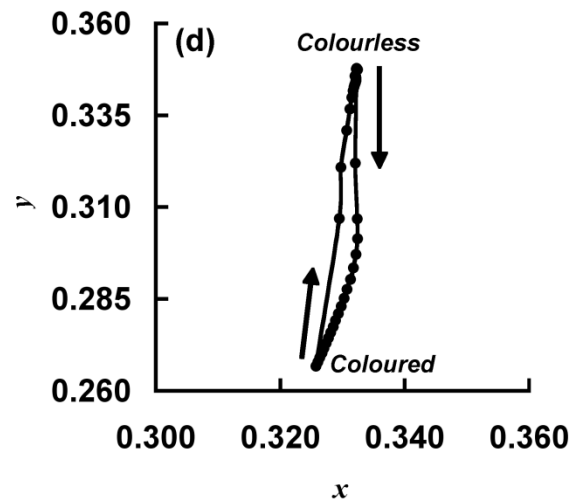
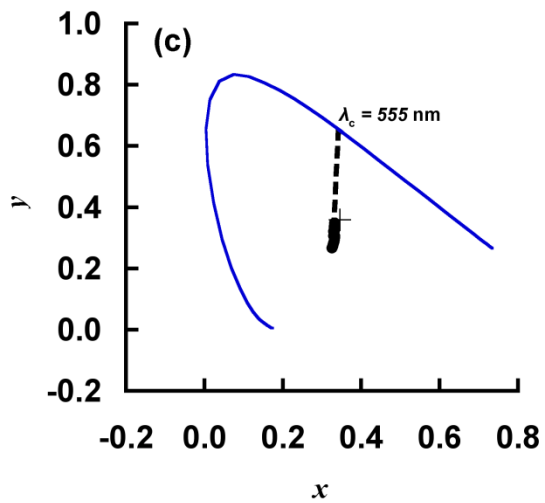
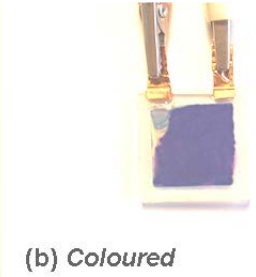
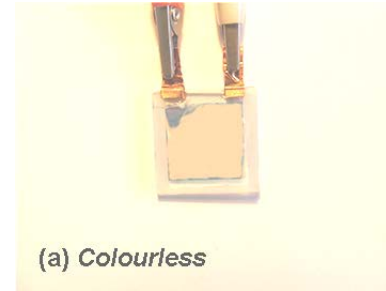
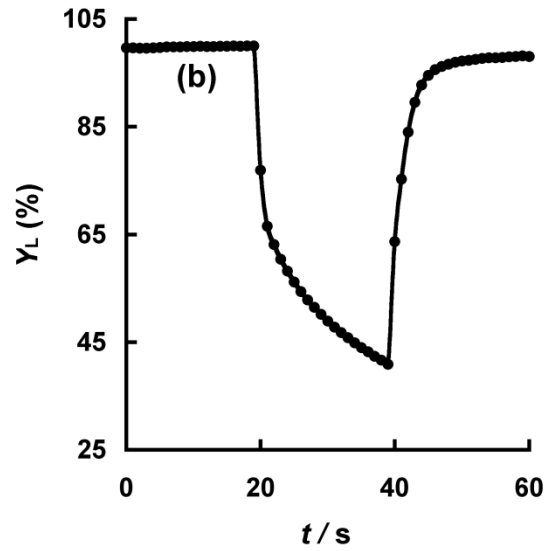
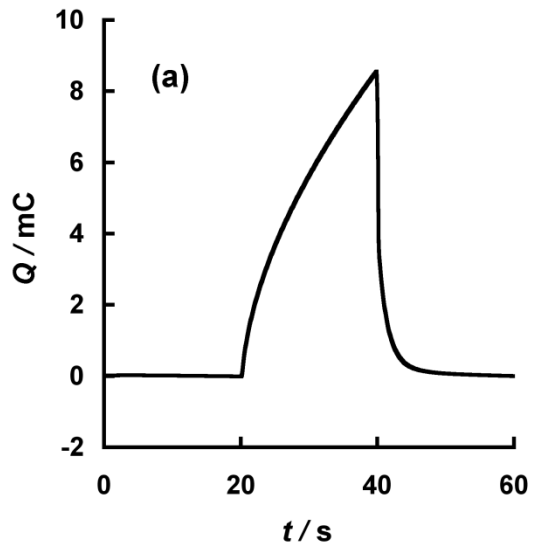
# RP/10 mM methyl viologen device (II)



# RP/10 mM heptyl viologen device (I)



# RP/10 mM heptyl viologen device (II)





# Summary

- The electroactive inorganic solid Ruthenium Purple has been paired with methyl and heptyl viologens in colour-reinforcing thin-layer electrochromic devices
- The colour stimuli of the individual electrochromic materials and the devices have been quantified by transformation of absorption spectra recorded during colour switching
- The colour measurement and device fabrication methods will be applicable to other electrochromic materials