Electrochromic materials

CHEMICAL SOCIETY REVIEWS

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Electrochromic materials are currently attracting much interest in academia and industry for both their fascinating fundamental spectroelectrochemical properties and their commercial applications. A large number of electrochromic materials are available from all branches of synthetic chemistry. In this review some of the most important examples from the major classes of electrochromic materials, namely the transition metal oxides, Prussian Blue systems, 1,1′-disubstituted-4,4′-bipyridylium salts (the viologens), conducting polymers, metallopolymers and metal phthalocyanines are described. Examples of their use in both prototype and commercial electrochromic devices are given.

1 Introduction

Chemical species that can be electrochemically switched between different colours are said to be electrochromic. Electrochromism results from the generation of different visible region electronic absorption bands on switching between redox states.[1] The colour change is commonly between a transparent ('bleached') state and a coloured state, or between two coloured states. In cases where more than two redox states are electrochemically available the electrochromic material may exhibit several colours and be termed polyelectrochromic. Likely applications of electrochromic materials include their use in controllable light-reflective or light-transmissive devices for optical information and storage, anti-glare car rear-view mirrors, sunglasses, protective eyewear for the military, controllable aircraft canopies, glare-reduction systems for offices, and 'smart windows' for use in cars and in buildings.[1–3] Of these, electrochromic car rear-view mirrors have already achieved considerable commercial success. These safety devices prevent mirror-reflected glare which causes an 'after image' to stay on the eye's retina.

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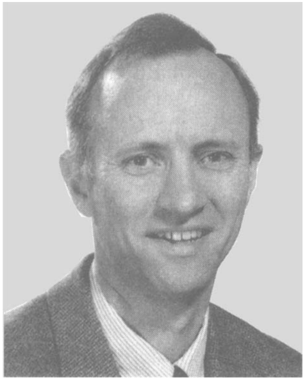


Whilst many types of chemical species exhibit electrochromism, only those with favourable electrochromic performance parameters[1] are potentially useful in commercial applications. Thus most applications require electrochromic materials with a high contrast ratio, colouration efficiency (absorbance change/charge injected per unit area), cycle life, and write-erase efficiency (% of originally formed colouration that may be subsequently electro-bleached). Whereas displays need fast response times, by contrast 'smart windows' can tolerate response times of up to several minutes.

Electrochromic materials are generally first studied at a single working electrode, under potentiostatic or galvanostatic control, using three-electrode circuitry. Traditional techniques such as cyclic voltammetry, coulometry, chronoamperometry, all with, as appropriate, *in situ* spectroscopic measurements are employed for characterisation. For electrochromic device (ECD) investigations a simple two-electrode system is constructed in a sandwich configuration (Fig. 1). Such an ECD can be thought of as a rechargeable electrochemical cell, in which the 'electrochromic electrode' (where the colour switching takes place) is separated from a charge-balancing counter electrode by a solid (often polymeric) or liquid electrolyte. Colour changes in the ECD occur by charging/discharging the electrochemical cell on application of an electrical potential. After the resulting pulse of current has decayed and the colour change has been effected, the new redox state persists, with little or no input of power, in the so-called 'memory effect'. The electrochromic electrode, which can work in the reflective or transmissive mode, is generally glass coated with an electrically conducting film such as tin-doped indium oxide (ITO), onto which is deposited the electrochromic material. Alternatively, if one or both redox states are soluble, the electrochromic material may be present dissolved in the electrolyte solution. In variable light transmissive devices the counter electrode substrate also has to be transparent ITO glass, with the counter electrode chemical species being either colourless in both its redox forms or electrochromic in a complementary mode to the primary electrochromic material. For applications that are designed to operate in the reflective mode, such as displays, the counter electrode can be of any material with a suitable reversible redox reaction.

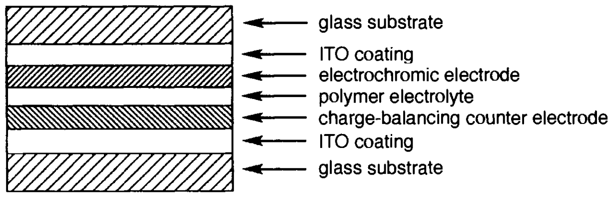


Fig. 1 Schematic diagram of a solid-state electrochromic device (ECD) suitable for a transmissive light-modulation application

The purpose of this review is to give a flavour of the diversity of this fascinating subject by the description of some of the most important examples from the major classes of electrochromic materials, and to give some examples of their use in both prototype and commercial ECDs.

2 Transition metal oxides

Many transition metal oxide films can be electrochemically switched to a non-stoichiometric redox state which has an intense electronic absorption band due to optical intervalence charge transfer.[1,4] A good example is the tungsten trioxide system, which, since its electrochromism was first reported in 1969, has been the most widely studied electrochromic material.[1,4] Tungsten trioxide, with all tungsten sites as oxidation state W^{VI}, is transparent as a thin film. On electrochemical reduction, W^{V} sites are generated to give the electrochromic effect. Although there is still controversy about the detailed colouration mechanism, it is generally accepted that the injection and extraction of electrons and metal cations (Li^+, H^+, . . .) play a key role. In the case of Li^+ cations the reaction can be written as eqn. (1).

$$\underset{\text{(transparent)}}{WO_3 + x(Li^+ + e^-)} \longrightarrow \underset{\text{(blue)}}{Li_xW^{VI}_{(1-x)}W^{V}_{x}O_3} \qquad (1)$$

At low x the films have an intense blue colour caused by photo-effected intervalence charge transfer (CT) between adjacent W^{V} and W^{VI} sites. At higher x, insertion irreversibly forms a metallic 'bronze' which is red or golden in colour.

Electrochromic tungsten trioxide coatings have been produced by a number of different deposition techniques including thermal evaporation *in vacuo*, electrochemical oxidation of tungsten metal, chemical vapour deposition (CVD), sol–gel methods and by RF-sputtering.[1] Tungsten trioxide research has always been driven by the many possible commercial applications and prototype alphanumeric displays and electrochromic mirrors were soon reported. A major present aim is the development of 'smart windows' for control of thermal conditions within a building, thereby reducing winter heating and summer cooling requirements. Glass manufacturers have recognised this opportunity, with the Pilkington Technology Centre having produced a prototype electrochromic window (dimensions 0.7 × 1 m) which when coloured is capable of reducing light transmission by a factor of four.[3] Such electrochromic systems are of a simple two-electrode sandwich-device construction, as described above. In the development of such variable transmission windows, glass companies favour the sputtering technique because it is already in place for the production of a range of coatings for architectural glazings.[5]

Many other thin-film transition metal oxides are electrochromic,[1,4] for example the oxides of molybdenum and vanadium, eqn. (2) and (3).

$$\underset{\text{(transparent)}}{MoO_3 + x(M^+ + e^-)} \longrightarrow \underset{\text{(blue)}}{M_xMo^{VI}_{(1-x)}Mo^{V}_{x}O_3} \qquad (2)$$

$$\underset{\text{(yellow)}}{V_2O_5 + x(M^+ + e^-)} \longrightarrow \underset{\text{(pale blue)}}{M_xV_2O_5} \qquad (3)$$

In these examples, the more intensely absorbing redox state is produced on reduction (cathodic ion-insertion). In contrast, Group VIII metal oxides become coloured on electrochemical oxidation (anodic ion-insertion); as in the case of hydrated iridium oxide (strictly iridium hydroxide). The mechanism of colouration is uncertain, with both proton extraction and anion insertion routes being proposed, eqn. (4) and (5).

$$\underset{\text{(transparent)}}{Ir(OH)_3} \longrightarrow \underset{\text{(blue–black)}}{IrO_2{\cdot}H_2O} + H^+ + e^- \qquad (4)$$

$$\underset{\text{(transparent)}}{Ir(OH)_3} + OH^- \longrightarrow \underset{\text{(blue–black)}}{IrO_2{\cdot}H_2O} + H_2O + e^- \qquad (5)$$

Another commonly studied anodic ion-insertion material is nickel oxide, a material more commonly known for its use in secondary batteries. Nickel oxide (strictly nickel hydroxide) in basic electrolytes switches from pale green to brown–black.

3 Prussian blue

Prussian blue [PB, iron(III) hexacyanoferrate(II)] is the prototype of a number of polynuclear transition metal hexacyanometallates which form an important class of insoluble mixed-valence compounds.[6] They have the general formula $M'_k[M''(CN)_6]_l$ (k, l integral) where M′ and M″ are transition metals with different formal oxidation numbers. The first report[7] concerning the electrochemistry and electrochromism of PB prompted numerous investigations into the properties of PB thin films.

PB thin films are generally formed by electrochemical reduction of solutions containing iron(III) and hexacyanoferrate(III) ions.[8] Reduction of the brown–yellow soluble complex Prussian brown [PX, iron(III) hexacyanoferrate(III), present in equilibrium with the iron(III) and hexacyanoferrate(III) ions], is the principal electron-transfer process in PB electrodeposition, eqn. (6).

$$\underset{\text{PX}}{[Fe^{III}Fe^{III}(CN)_6]} + e^- \longrightarrow \underset{\text{PB}}{[Fe^{III}Fe^{II}(CN)_6]^-} \qquad (6)$$

Charge-compensating cations (initially Fe^{3+}, then K^+ on potential cycling in K^+-containing supporting electrolyte) are present in the PB film for electroneutrality.[9] Partial electrochemical oxidation of PB in pure supporting electrolyte yields Prussian green (PG), a species historically known as Berlin green (BG), eqn. (7).

$$\underset{\text{PB}}{3[Fe^{III}Fe^{II}(CN)_6]^-} \longrightarrow \underset{\text{PG}}{[Fe^{III}_3\{Fe^{III}(CN)_6\}_2\{Fe^{II}(CN)_6\}]^-} + 2e^- \qquad (7)$$

Although in bulk form PG is believed to have a fixed composition with anion composition as above, for thin films there is a continuous composition range between PB and PX, which becomes a golden yellow in the fully oxidised form.[9] The latter may be obtained by electrochemical oxidation of a particularly pure form of PB,[8,9] eqn. (8).

$$\underset{\text{PB}}{[Fe^{III}Fe^{II}(CN)_6]^-} \longrightarrow \underset{\text{PX}}{[Fe^{III}Fe^{III}(CN)_6]} + e^- \qquad (8)$$

Reduction of PB yields Prussian white (PW), also known as Everitt's salt, which appears transparent as a thin film, eqn. (9).

$$\underset{\text{PB}}{[Fe^{III}Fe^{II}(CN)_6]^-} + e^- \longrightarrow \underset{\text{PW}}{[Fe^{II}Fe^{II}(CN)_6]^{2-}} \qquad (9)$$

For all the electrochromic redox reactions above, there is concomitant ion ingress/egress in the films for electroneutrality.

The spectra[9] of PX, PG, PB and PW are shown in Fig. 2, together with two intermediate states between blue and green. The intense blue colour in the $[Fe^{III}Fe^{II}(CN)_6]^-$ chromophore of PB is due to an intervalence charge-transfer (CT) absorption band centred at 690 nm. The yellow absorption band in PX corresponds with that of $[Fe^{III}Fe^{III}(CN)_6]$ in solution, both maxima (λ_{max} 425 nm) coinciding with the (weaker) $[Fe^{III}(CN)_6]^{3-}$ absorption maximum. On increase from +0.50 V to more oxidising potentials, the original PB peak continuously shifts to longer wavelengths with diminishing absorption, while the peak at 425 nm steadily increases, owing to the increasing $[Fe^{III}Fe^{III}(CN)_6]$ absorption. The reduction of PB to PW is in contrast abrupt, with transformation to all PW or all PB without pause, depending on the potential set. In the CV of a PB-modified electrode, the broad peak for PB↔PX in contrast with the sharp PB↔PW transition emphasises the range of compositions involved. This difference in behaviour, supported by ellipsometric measurements,[10] indicates continuous mixed-valence compositions over the blue to yellow range in contrast with the presumably immiscible PB and PW which clearly transform one into the other without intermediacy of composition.

Early PB ECDs employed PB as sole electrochromic material. Examples include a seven-segment display using PB-

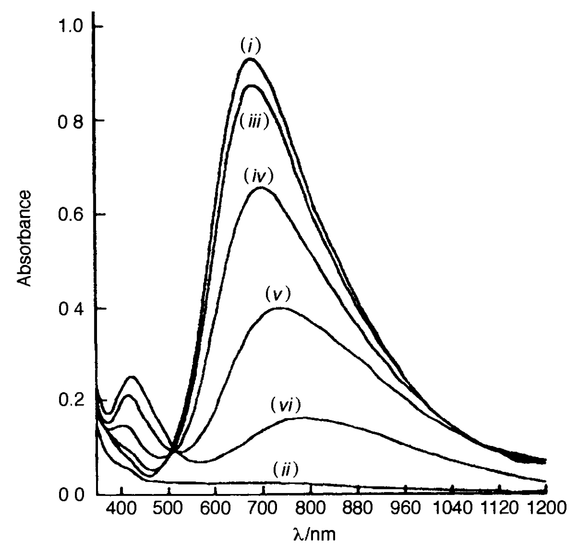


Fig. 2 Spectra of iron hexacyanoferrate films on ITO-coated glass at various potentials [(*i*) +0.50 (PB, blue), (*ii*) −0.20 (PW, transparent), (*iii*) +0.80 (PG, green), (*iv*) +0.85 (PG, green), (*v*) +0.90 (PG, green), and (*vi*) +1.20 V (PX, yellow) (*vs*. SCE)] with 0.2 mol dm^{-3} KCl +0.01 mol dm^{-3} HCl as supporting electrolyte (Reproduced with permission from *J. Chem. Soc., Dalton Trans.*, 1984, 2059)

modified SnO_2 working and counter electrodes at 1 mm separation[11] and an ITO | PB-Nafion | ITO solid-state device.[12] For the solid-state system, device fabrication involved chemical, rather than electrochemical formation of the PB on immersion of a membrane of the solid polymer electrolyte Nafion (a sulfonated polytetrafluoroethane polymer) in aqueous solutions of $FeCl_2$, then $K_3Fe(CN)_6$. The resulting PB-containing Nafion composite film was sandwiched between the two ITO plates. The construction and optical behaviour of an ECD utilising a single film of PB, without addition of a conventional electrolyte, has also been described.[13] In the design, a film of PB is sandwiched between two optically transparent electrodes (OTEs) [Fig. 3(a)]. Upon application of an appropriate potential across the film, oxidation occurs near the positive electrode and reduction near the negative electrode to yield PX and PW, respectively [Fig. 3(b)]. The conversion of the outer portions of the film results in a net bleaching of the device. The functioning of the device relies on the fact that PB can be bleached both anodically (to the yellow state) and cathodically (to a transparent state), and that it is a mixed conductor through which potassium ions can move to provide charge compensation required for the electrochromic redox reactions.

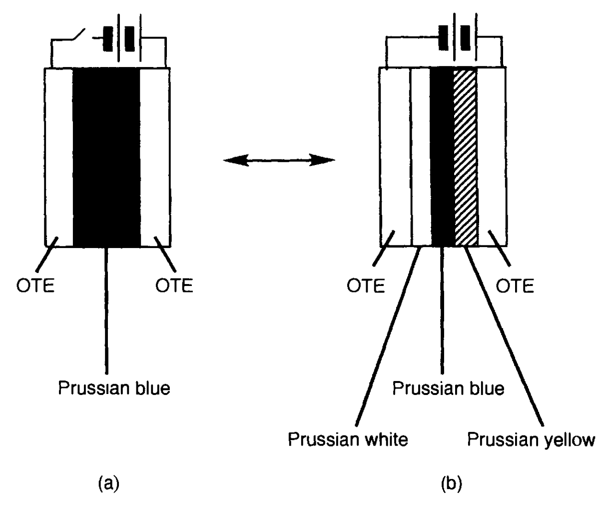


Fig. 3 Schematic cross section of a single film PB cell. The cell is shown (a) without and (b) with a voltage applied. (Reproduced by permission from *J. Electrochem. Soc.*, 1990, **137**, 2464.)

Since PB and tungsten trioxide are respectively anodically and cathodically colouring electrochromic materials, they can be used together in a single device so that their electrochromic reactions are complementary, eqn. (10) and (11).

$$\underset{\text{(blue)}}{[\mathrm{Fe^{III}Fe^{II}(CN)_6}]^-} + e^- \longrightarrow \underset{\text{(transparent)}}{[\mathrm{Fe^{II}Fe^{II}(CN)_6}]^{2-}} \qquad (10)$$

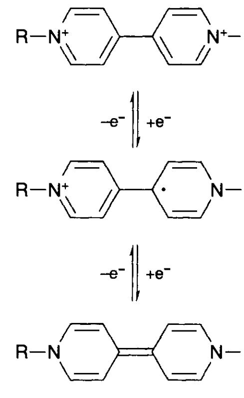
$$\underset{\text{(transparent)}}{\mathrm{WO_3}} + x(\mathrm{M^+} + e^-) \longrightarrow \underset{\text{(blue)}}{\mathrm{M}_x\mathrm{W}^{\mathrm{VI}}_{(1-x)}\mathrm{W}^{\mathrm{V}}_x\mathrm{O_3}} \qquad (11)$$

In the construction of such a device, thin films of these materials are deposited on OTEs that are separated by a layer of a transparent ionic conductor such as KCF_3SO_3 in poly(ethylene oxide).[14] The films can be coloured simultaneously (giving deep blue) when a sufficient voltage is applied between them such that the WO_3 electrode is the cathode and the PB electrode the anode. Conversely, the coloured films can be bleached to transparency when the polarity is reversed, returning the ECD to a transparent state.

Several PB analogues have been reported as thin films in modified-electrode studies.[15] Whilst the majority are expected to be electrochromic, absorption spectra as a function of redox state have rarely been reported, and only ruthenium purple [iron(III) hexacyanoruthenate(II)] and osmium purple [iron(III) hexacyanoosmate(II)] have been used in prototype seven-segment ECDs. The feld therefore appears to be open for further investigation and exploitation.

4 Viologens

Diquaternisation of 4,4′-bipyridyl produces 1,1′-disubstituted-4,4′-bipyridylium salts[16] (Scheme 1), commonly known as 'viologens'. The compounds are formally named as 1,1′-di-substituent-4,4′-bipyridylium if the two substituents at nitrogen are the same, and as 1-substituent-1′-substituent′-4,4′-bipyridylium should they differ. The prototype, 1,1′-dimethyl-4,4′-bipyridylium, is often known as methyl viologen (MV), with other simple symmetrical bipyridylium species being named substituent viologen.



Scheme 1

Of the three common viologen redox states (Scheme 1), the dication is the most stable and is colourless when pure unless optical charge transfer with the counter anion occurs. Reductive electron transfer to viologen dications forms coloured radical cations, the stability of which is attributable to the delocalisation of the radical electron throughout the π-framework of the bipyridyl nucleus, the 1 and 1′ substituents commonly bearing some of the charge. Electrochromism occurs in viologens because, in contrast to the viologen dications, the radical cations have a delocalised positive charge, colouration arising from an intramolecular electronic transition. Suitable choice of nitrogen substituents to attain the appropriate molecular orbital energy levels can, in principle, allow colour choice of the radical cation. Simple alkyl groups, for example, promote a blue–violet colour whereas aryl groups generally impart a green hue to the radical cation. The intensity of the colour exhibited by di-reduced viologens is low since no optical charge transfer or internal transition corresponding to visible wavelengths is accessible.

For display applications, the write–erase efficiency of ECDs using short alkyl chain viologens such MV in aqueous electrolytes would be low since both dicationic and radical-cation states are very soluble. Improvements may be made in MV-based ECDs by retarding the rate at which the radical-cation product of electron transfer diffuses away from the electrode and into the solution bulk either by tethering the dication to the surface of an electrode, or by immobilising the viologen species within a semi-solid electrolyte such as Nafion (Fig. 4).[17] The solubility–diffusion problem can be avoided by the use of viologens having long alkyl-chain substituents at nitrogen, for which the coloured radical-cation is insoluble. Of this type, 1,1′-diheptyl-4,4′-bipyridylium (heptyl viologen, HV) as the dibromide salt has been the most thoroughly studied.[18] HV^{2+} dication is soluble in water, but forms an insoluble film of crimson radical-cation salt adhering strongly to the electrode surface following a one-electron reduction. An ECD display (Fig. 5) using the HV system was reported to have a response time of 10–50 ms, with a cycle life of $> 10^5$ cycles between redox states.[18]

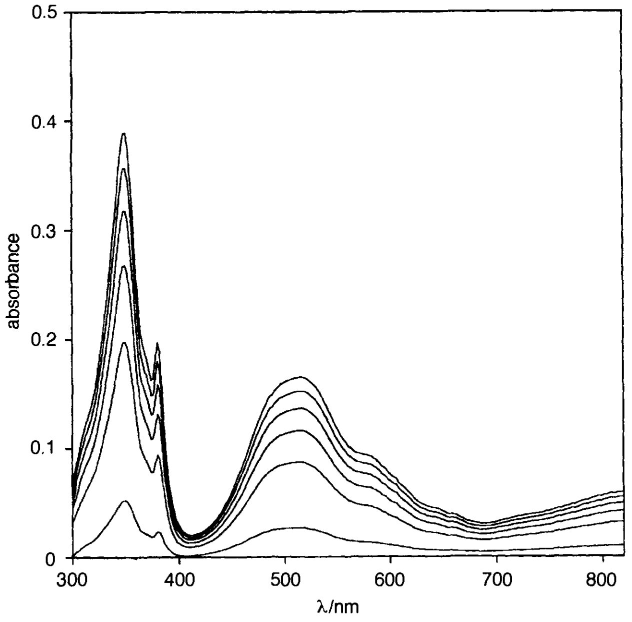


Fig. 4 Spectra recorded at t = 0, 10, 20, 30, 40 and 50 s in response to a potential step from +1.00 to −0.90 V for an ITO/Nafion/1,1′-dihexyl-4,4′-bipyridylium electrode in 0.1 mM 1,1′-dihexyl-4,4′-bipyridylium dibromide +0.2 mol dm^{-3} KCl (pH 5.5). The absorbance at all wavelengths increases with time. The colour appears pink, indicating a high proportion of radical cation dimers in the Nafion. (Reproduced by permission from *Electrochromic Materials III*, ed. K.-C. Ho, C. B. Greenberg and D. M. McArthur, PV 96-24, pp. 3–13, Electrochem. Soc. Proc. Ser., Pennington, New Jersey, 1997).

The high response times noted above are however not essential in other applications such as electrochromic car rear-view mirrors and 'smart windows'. In fact, Gentex's commercialised automatic-dimming interior 'Night Vision Safety' (NVS) mirror functions wholly by solution electrochromism.[2,3] In this system, an ITO-glass surface (conductive side inwards) and the reflective metallic surface, spaced a fraction of a millimetre apart, form the two electrodes of the cell, with a solvent containing two electroactive chemical species that function both as electrochromic materials and supporting electrolyte. The system may be inferred to operate as follows.[2,3]

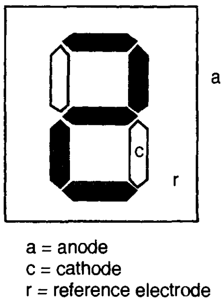


Fig. 5 Alphanumeric character, from a heptyl viologen display device. (Reproduced by permission from *Appl. Phys. Lett.*, 1973, **23**, 64).

A substituted (cationic) viologen serves as the cathodic-colouring electrochromic material, with a negatively charged (possibly) phenylene diamine as the anodically colouring electrochromic material. When the mirror is switched on, the species will move by electrical migration to their respective electrodes. After the dual electrochromic colouration process is initiated, the products will diffuse away from their respective electrodes and meet in the intervening solution where a mutual reaction regenerating the original uncoloured species takes place. Thus, in this type of ECD, maintenance of colouration requires application of a continuous small current for replenishment of the coloured electroactive species lost by their mutual redox reaction in solution. Bleaching occurs at short or open circuit by homogeneous electron transfer in the bulk of the solution. While not an electrochromic phenomenon, the ingenious control system is worth noting. A photosensitive detector is placed facing rearward to monitor any dazzling incident light but, in daylight, it would be triggered, resulting in an unwanted darkening of the mirror. This is avoided by the second forward-looking detector, which on seeing daylight, is programmed to cancel any operation of the controlling sensor, which thus responds only in the dark of night. Gentex Corporation sell their rearview mirrors to 16 major car manufacturers with (in 1996) NVS mirrors being available on 95 vehicle models. The company also manufacture exterior wing mirrors, and from 1987 to the end of 1996 have sold a total of 10 million electrochromic mirrors.

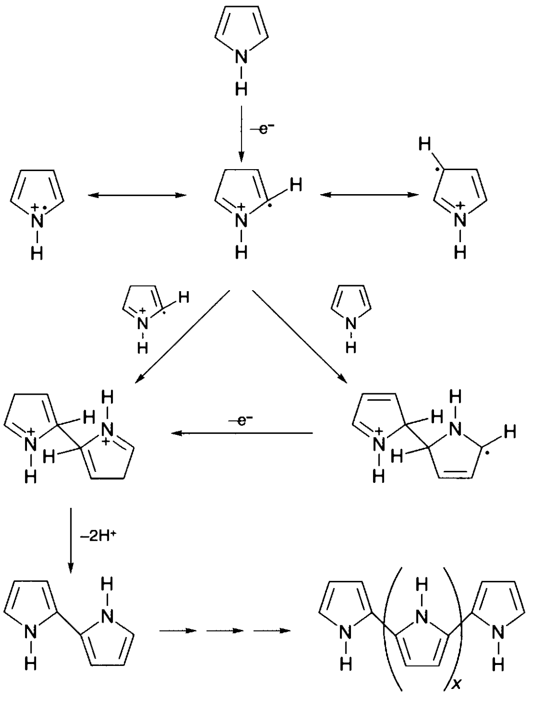
5 Conducting polymers

Chemical or electrochemical oxidation of numerous resonance-stabilised aromatic molecules including pyrrole, thiophene, aniline, furan, carbazole, azulene and indole produces novel electronically conducting polymers.[19] In their oxidised forms, such conducting polymers are 'doped' with counter anions (p-doping) and possess a delocalised π-electron band structure, the energy gap between the highest occupied π electron band (valence band) and the lowest unoccupied band (the conduction band) determining the intrinsic optical properties of these materials. The doping process (oxidation) introduces polarons (in polypyrrole for example, these are radical cations delocalised over *ca.* four monomer units) which are the major charge carriers. Reduction of conducting polymers with concurrent counter anion exit removes the electronic conjugation, to give the 'undoped' (neutral) electrically insulating form. Conducting polymers can also, in principle, undergo cathodic doping with cation insertion (n-doping) to balance the injected charge. However, n-doped forms are less stable than p-doped forms and few reports are available concerning the electrochromism of the n-doping process.

All conducting polymers are potentially electrochromic in thin-film form, redox switching giving rise to new optical absorption bands together with transfer of electrons/counter anions. In this review, some examples from the three main classes of conducting polymer that have been investigated for their electrochromic properties will be described. A major advantage of using conducting polymer for electrochromic applications lies in the fact that subtle modifications to the monomer can significantly alter the spectral properties of the electrochromic material. Examples will be noted where suitable monomer modification allows 'tuning' of colour states.

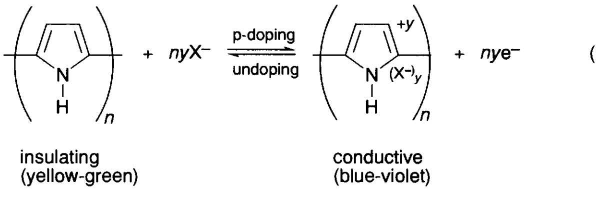
5.1 Polypyrrole(s)

The electrochromic properties of polypyrrole are generally investigated using thin-film polypyrrole prepared by electrochemical polymerisation of pyrrole from acetonitrile solution. The oxidative electropolymerisation process is initiated by monomer oxidation to yield a radical-cation species. Polypyrrole generation, in its oxidised conducting form, then follows *via* a mechanism[19] that is believed to involve either radical-cation/radical-cation coupling or attack of radical-cation on neutral monomer (Scheme 2). Polypyrrole thickness is controlled through the charge passed, further film growth occurring at the polypyrrole–solution interface.



Scheme 2

Doped (oxidised) polypyrrole is blue–violet (λ_{max} 670 nm),[20] electrochemical reduction yielding the yellow–green (λ_{max} 420 nm) 'undoped' form, eqn. (12).



$$[\text{C}_4\text{H}_2\text{NH}]_n + nyX^- \underset{\text{undoping}}{\overset{\text{p-doping}}{\rightleftharpoons}} [(\text{C}_4\text{H}_2\text{NH})^{+y}(X^-)_y]_n + nye^- \qquad (12)$$

Removal of all dopant anions from polypyrrole yields a pale-yellow film, however, complete de-doping is only achieved if films are extremely thin. This means that polypyrrole of thickness commensurate with device construction (> 1 μm) has a low contrast ratio.

The electrochromism of polypyrrole is unlikely to be exploited, mainly due to the degradation of the film on repetitive colour switching. Conducting polymers with improved electrochromic properties are however formed on electrochemical polymerisation of 3,4-disubstituted pyrroles.[1]

5.2 Polythiophene(s)

As for polypyrrole, polythiophene thin films may be prepared by the electrochemical oxidation of solution monomer *via* in this case the thiophene radical cation. The electrochromic properties of polythiophene and of the polymers of several substituted thiophenes are reproduced in Table 1.[20]

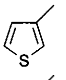
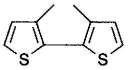
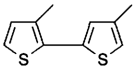
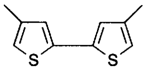
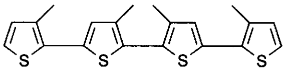
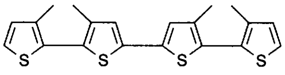
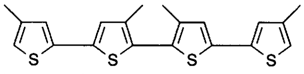
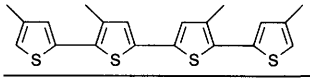
Table 1 Polythiophenes[a]

Monomer	Polymer λ_{max}/nm and colour: Oxidised	Reduced
Thiophene	730 Blue	470 Red
3-Methylthiophene	750 Deep blue	480 Red
3,4-Dimethylthiophene	750 Dark blue	620 Pale brown
2,2′-Bithiophene	680 Blue–grey	460 Red–orange

[a] Adapted with permission from F. Garnier, G. Tourillon, M. Gazard and J. C. Dubois, *J. Electroanal. Chem.*, 1983, **148**, 299.

Tuning of colour states is possible by suitable choice of thiophene monomer. For example, the electrochromic properties of polymer films prepared from 3-methylthiophene-based oligomers are strongly dependent on the relative positions of methyl groups on the polymer backbone (Table 2).

Table 2 Colours of polymers derived from oligomers based on 3-methylthiophene[a]

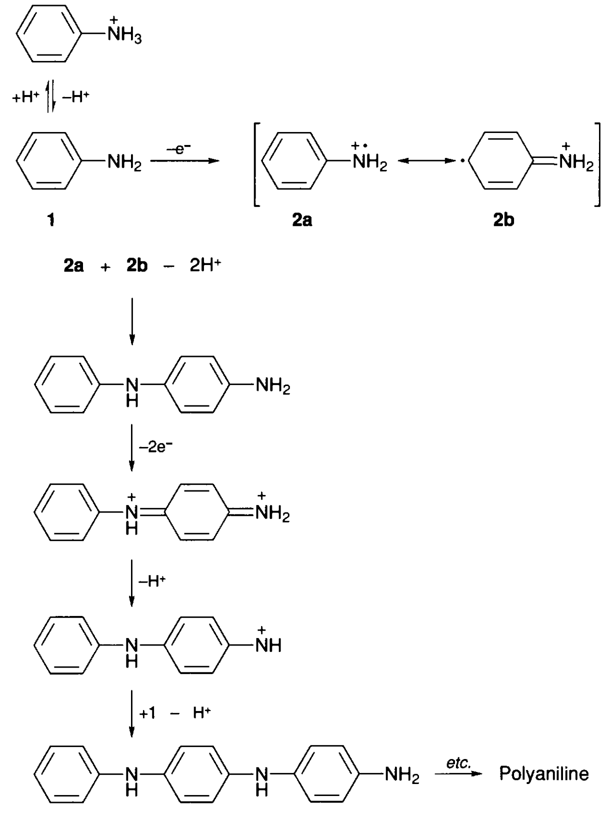
Monomer (figure does not represent the molecule's stereochemistry)	Polymer colour: Oxidised	Reduced
	Pale blue	Purple
	Violet	Yellow
	Blue	Red
	Blue	Orange
	Blue	Yellow
	Violet	Yellow
	Blue–violet	Yellow
	Blue	Yellow–orange

[a] Reproduced by permission from M. Mastragostino, in *Applications of Electroactive Polymers*, ed. B. Scrosati, Chapman and Hall, London, 1993, ch. 7, p. 244.

In research directed to using the same electrochromic material for both the working and counter electrodes, a series of conducting polymer films based on 3-(*p*-X-phenyl)thiophene monomers (X = –CMe$_3$, –Me, –OMe, –H, –F, –Cl, –Br, –CF$_3$, –SO$_2$Me) have been investigated.[21] The presence of electron-withdrawing groups on the phenyl ring serves to assist the stabilisation of the n-doped state and these materials can be both reversibly reduced and oxidized (n- and p-doped). A model ECD using poly(cyclopenta[2,1 -*b*; 4,3-*b*′]dithiophen-4-(cyano, nonafluorobutylsulfonyl)-methylidene), a low bandgap conducting polymer which is both p- and n-dopable, as both the anode and the cathode material has been reported.[22]

5.3 Polyaniline(s)

The electrical and electrochromic properties of polyaniline not only depend on its oxidation state, but also on its protonation state, and hence the pH of the electrolyte used. The electrochemistry of polyaniline thin films has been extensively investigated in aqueous acid solutions and in organic media, and several redox mechanisms involving protonation–deprotonation and/or anion ingress/egress have been proposed.[19] Scheme 3 depicts the mechanism of electropolymerisation of aniline,



Scheme 3

with Scheme 4 giving the composition and redox pathways of the various redox states in the product polyaniline.[23]

Polyaniline films are polyelectrochromic (transparent yellow to green to dark blue to black), the yellow–green transition being durable to repetitive colour switching. The wavelengths of the absorption maxima of polyaniline and the polymers of two substituted anilines are given in Table 3, with some of the spectra for poly(*m*-toluidine) illustrated in Fig. 6.[24] The two low-wavelength spectral bands observed in the polyanilines are assigned to an aromatic π–π* transition (≤330 nm) related to the extent of conjugation between the adjacent rings in the polymer chain, and to radical cations formed in the polymer matrix (≤440 nm). With increase in applied potential the ≤330 nm band absorbance decreases and the ≤440 nm increases (Fig. 6). Beyond +0.30 V the conducting region is entered; the ≤440 nm band decreases as a broad free carrier electron band *ca.* 800 nm is introduced.

Polyaniline has been combined with PB in complementary ECDs that exhibit deep blue ↔ green electrochromism.[1] Electrochromic compatibility is obtained by combining the coloured oxidised state of the polymer with the blue PB and the bleached reduced state of the polymer with PG:

Oxidised polyaniline + PB → emeraldine polyaniline + PG
(deep blue) (green)

Both liquid electrolyte and solid-state configurations have been described.

Table 3 Visible absorption spectra maxima, $\lambda_{max}(\pm 4)$/nm, with applied potentials (*E*/V) parenthesised for the polymer films on ITO glass[a]

Polyaniline	320, 440 (−0.20) 320, 440, > 820 (+0.20) 330, 430, 800 (+0.30) 340, 420, 800 (+0.40)
Poly(*o*-toluidine)	308, 420 (−0.20) 308, 420 (+0.20) 312, 410, > 820 (+0.30) 380, 800 (+0.40)
Poly(*m*-toluidine)	304, 420 (−0.20) 304, 420 (+0.20) 304, 410, > 820 (+0.30) 306, 390, > 820 (+0.40)

[a] Reproduced by permission from R. J. Mortimer, *J. Mater. Chem.*, 1995, **5**, 969.

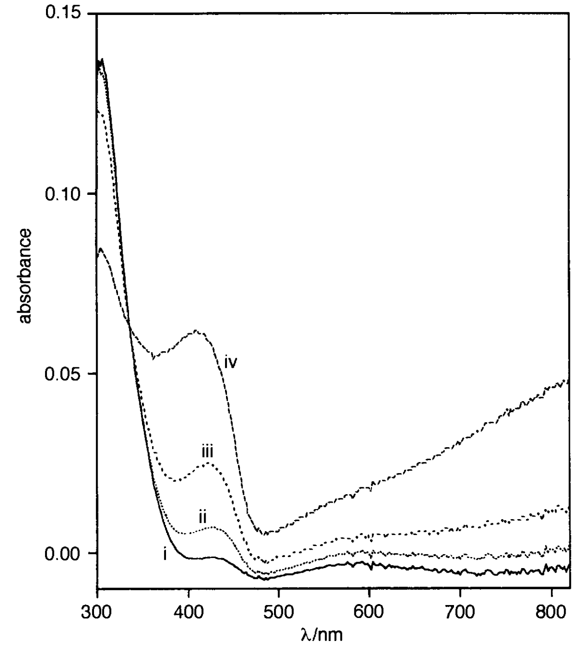
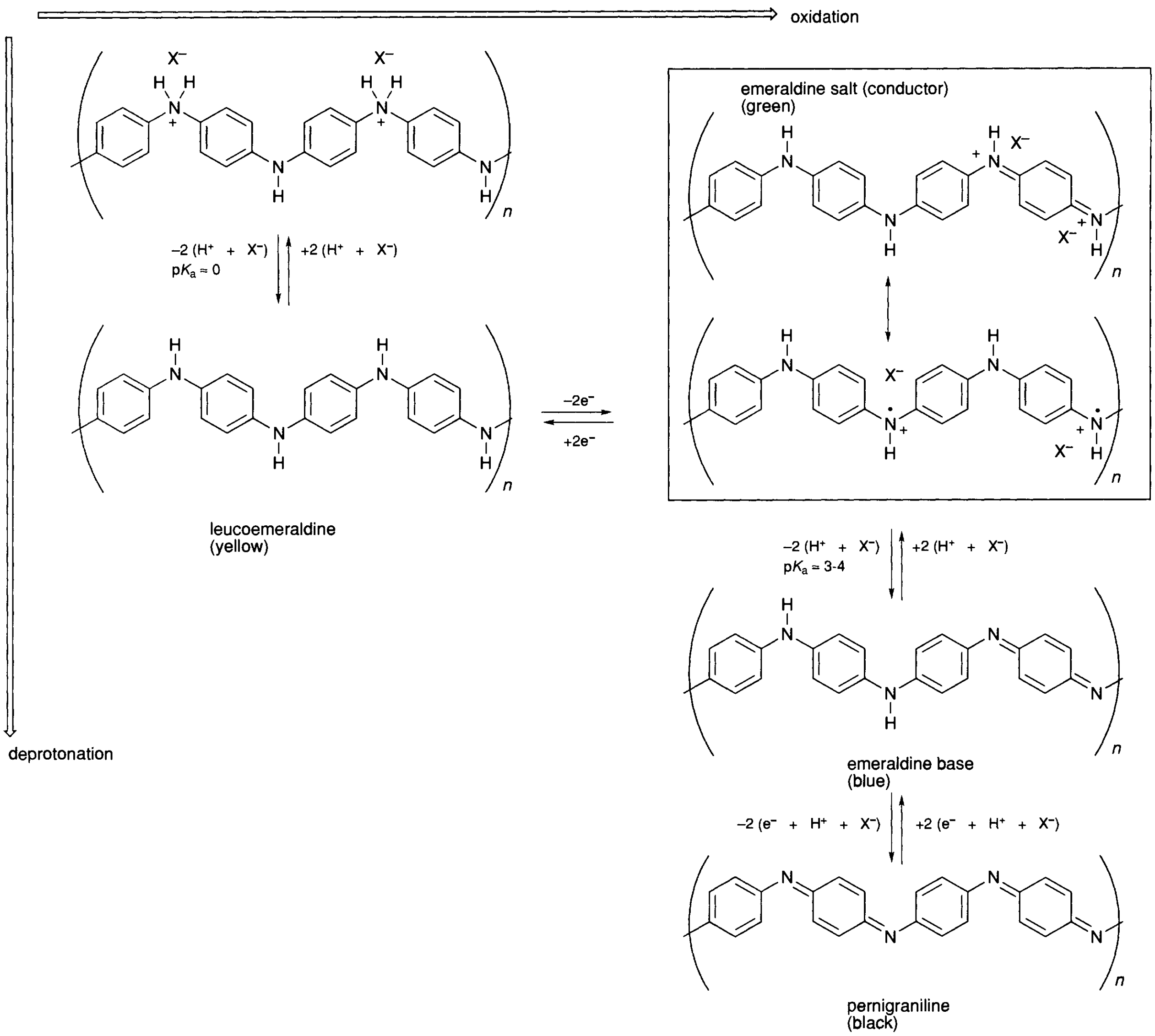


Fig. 6 Visible absorption spectra of poly(*m*-toluidine) films on ITO-coated glass in 1 mol dm^{-3} hydrochloric acid at the potentials: i, −0.20 V; ii, +0.10 V; iii, +0.20 V; iv, +0.30 V. (Reproduced by permission from *J. Mater. Chem.*, 1995, **5**, 969.)

Whilst electropolymerisation is a suitable method for the preparation of relatively low surface area electrochromic conducting polymer films, it may not be suitable for fabricating large-area coatings. Significant effort therefore goes into the synthesis of soluble conducting polymers such as poly(*o*-methoxyaniline) which can then be deposited as thin films by casting from solution. In a novel approach large-area electrochromic coatings have been prepared by incorporating polyaniline into polyacrylate–silica hybrid sol–gel networks using suspended particles or solutions and then spray or brush-coating onto ITO surfaces.[25] Silane functional groups on the polyacrylate chain act as coupling and cross-linking agents to improve surface adhesion and mechanical properties of the resulting composite coatings.

6 Metallopolymers

Transition metal coordination complexes are potentially useful electrochromic materials because of their intense colouration and redox reactivity. Chromophoric properties typically arise from low-energy metal-to-ligand charge transfer (MLCT), intervalence CT, intraligand excitation, and related visible-region electronic transitions. Because these transitions involve



Scheme 4

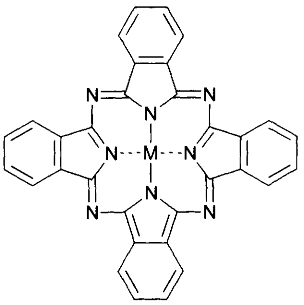
valence electrons, chromophoric characteristics are altered or eliminated upon oxidation or reduction of the complex.

While these spectroscopic and redox properties alone would be sufficient for direct use of transition metal complexes in solution-phase ECDs, polymeric systems have also been investigated. Many schemes have been described for the preparation of thin-film 'metallopolymers',[26] the reductive electropolymerisation of suitable polypyridyl complexes being a particularly versatile technique. This technique relies on the ligand-centred nature of the three sequential reductions of complexes such as $[Ru^{II}(vbpy)_3]^{2+}$ (vbpy = 4-vinyl-4′-methyl-2,2′-bipyridine), combined with the anionic polymerisability of suitable ligands. Vinyl-substituted pyridyl ligands (examples in Fig. 7) are generally employed, although metallopolymers have also been formed from chloro-substituted pyridyl ligands, *via* electrochemically initiated carbon–halide bond cleavage. In either case, electrochemical reduction of their metal complexes generated radicals leading to carbon–carbon bond formation and oligomerisation. Oligomers above a critical size are insoluble and thus thin films of the electroactive metallopolymer are produced on the electrode surface. Fig. 8(*a*) shows repetitive cyclic voltammograms (CVs) for a typical electropolymerisation process.[27] The film thickness increases with CV scan number owing to the electrocatalytic reduction of the fresh solution metal complex monomer by the growing electroactive polymer. The steady increase in current is attributable to the combined electroactivity of the orange polymeric film and the inward-diffusing metal complex monomer. The electroactivity of the resulting modified electrode [Fig. 8(*b*)] is stable on transfer to pure supporting electrolyte solution, orange ↔ transparent electrochromicity being observed. The colour of such metallopolymer films in the M^{II} redox state may be selected by suitable choice of the metal (*e.g.* M = Fe, red; M = Ru, orange; M = Os, green). Electrochromicity results from loss of the MLCT absorption band on switching between the M^{II} and the M^{III} redox states. Interestingly, the chromophoric properties of the coloured state of such supramolecular metallopolymers are modified on binding of Group I/II metal cations by the crown ether groups.[27]

In a recent development, spatial electrochromism has been demonstrated in metallopolymeric films.[28] Photolysis of poly-$[Ru^{II}(vbpy)_2(py)_2]Cl_2$ thin films on ITO glass in the presence of chloride ions leads to photochemical loss of the photolabile pyridine (py) ligands and sequential formation of poly$[Ru^{II}(vbpy)_2(py)Cl]Cl$ and poly$[Ru^{II}(vbpy)_2Cl_2]$ (Scheme 5). Contact lithography can be used to spatially control the photosubstitution process to form laterally resolved bicomponent films with image resolution below 10 μm. Dramatic changes occur in the colours and redox potentials of such ruthenium(II) complexes upon substitution of chloride for the pyridine ligands (Scheme 5). Striped patterns of variable colours are observed on addressing such films with a sequence of potentials.

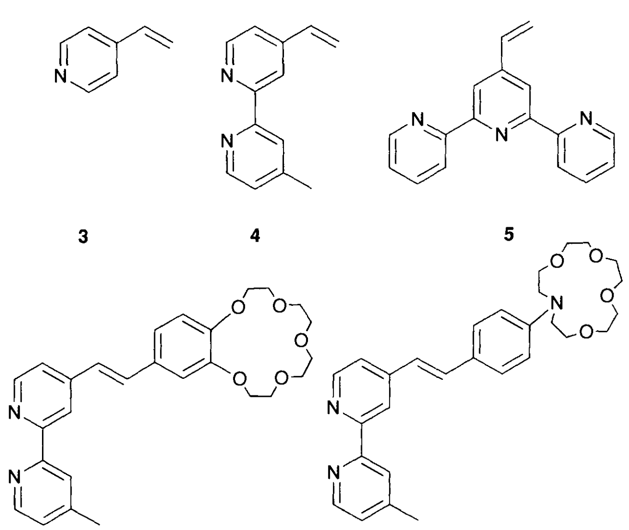
7 Metal phthalocyanines

Since the first report of the polyelectrochromism of thin films of lutetium bis(phthalocyanine) ($[Lu(Pc)_2]$) in 1970, numerous metal phthalocyanines have been investigated for their electrochromic properties.[1] Such compounds have a metal ion either at the centre of a single phthalocyanine (Pc) ring (**8**), or between two rings in a sandwich-type compound. $[Lu(Pc)_2]$, an example of the latter type, is generally formed as a vivid green film on vacuum sublimation. $[Lu(Pc)_2]$ films undergo a series of ring-based redox processes. On oxidation, films can be switched first to a yellow–tan form and then to a red form. On reduction the green state can be switched first to a blue redox form and then to a violet–blue form. Although, as described, $[Lu(Pc)_2]$ films can exhibit five colours, only the blue–green transition is utilised in most prototype ECDs. Mechanical problems, such as film fracture and/or loss of adhesion to the electrode substrate, arise from anion ingress/egress during colour switching. Despite such difficulties, $[Lu(Pc)_2]$-based electrochromic displays with good reversibility, fast response times, and little degradation over > 5 × 10^6 cycles have been described.[29]



8

Although as noted $[Lu(Pc)_2]$ films are usually prepared by vacuum sublimation, the practical problems encountered with extending this technology to the manufacture of practical devices have been recognised.[30] These include the slow rate of deposition, the partial decomposition of $[Lu(Pc)_2]$ under the sublimation conditions and the presence of electrochemically inaccessible sites in the resulting films. Electropolymerisation of $[Lu(T4APc)_2]$ (T4APc = 4,4′,4″,4‴-tetraaminophthalocyanine) has been reported as a possibly viable route to the fabrication of practical ECDs.[30] The oxidative film-formation mechanism is assumed to be analogous to that described for polyaniline, although the poly$[Lu(T4APc)_2]$ films are believed to be oligomeric in nature rather than truly polymeric. Although loss of electroactivity in such films was found on sweeping to positive potentials (likely to be the result of the loss of electronic and/or redox conductivity), the electrochemistry in DMSO at



3 **4** **5** **6** **7**

Fig. 7 Structures of various vinyl-substituted ligands. **3** = 4-vinyl-pyridine (vpy), **4** = 4-vinyl-4′-methyl-2,2′-bipyridine (vbpy), **5** = 4′-vinyl-2,2′:6′,2″-terpyridine (vtpy), **6** = 4-(benzo-15-crown-5)vinyl-4′-methyl-2,2′-bipyridine, **7** = 4-(aza-15-crown-5)styryl-4′-methyl-2,2′-bipyridine.

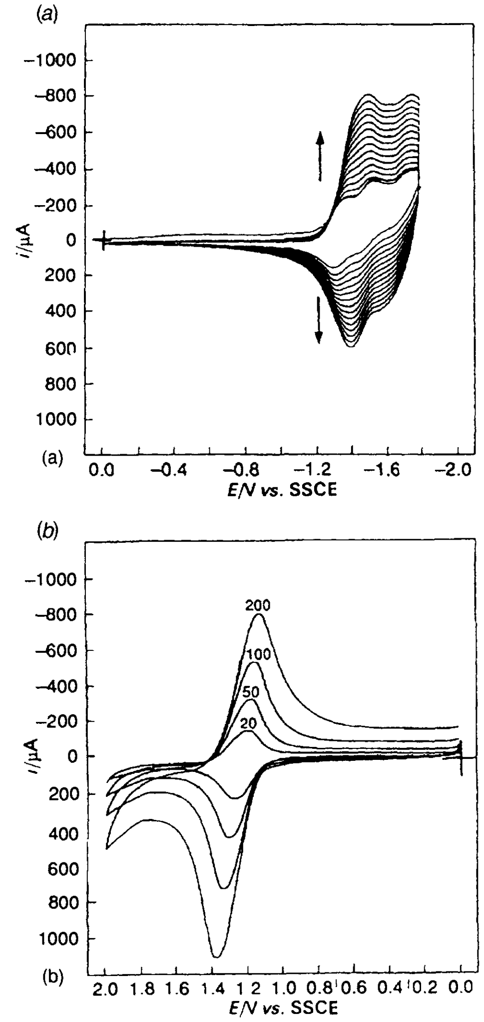


Fig. 8 (*a*) Fifteen sequential CVs at 100 mV s^{-1} in an acetonitrile solution containing 1.33 mmol dm^{-3} $[Ru^{II}L_3][PF_6]_2$ (L = 4-(benzo-15-crown-5)vinyl-4′-methyl-2,2′-bipyridine) and 0.1 mol dm^{-3} Bu_4NBF_4. Initial scan direction negative. (*b*) CVs as a function of scan rate (v/mV s^{-1} as labelled on each) for the poly$[RuL_3]^{2+}$ modified electrode from (*a*) in supporting electrolyte. (Reproduced by permission from *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 333.)

$$\text{poly}[Ru^{II}(vbpy)_2(py)_2]Cl_2 \quad \text{(orange)} \quad E_f(Ru^{III/II}) = +1.27 \text{ vs SCE}$$

$$\Big\downarrow h\nu \; -py$$

$$\text{poly}[Ru^{II}(vbpy)_2(py)Cl]Cl \quad \text{(red)} \quad E_f(Ru^{III/II}) = +0.77 \text{ vs SCE}$$

$$\Big\downarrow h\nu \; -py$$

$$\text{poly}[Ru^{II}(vbpy)_2Cl_2] \quad \text{(purple)} \quad E_f(Ru^{III/II}) = +0.35 \text{ vs SCE}$$

Scheme 5

negative potentials is well-behaved, with the observation of two broad quasi-reversible one-electron redox couples. Spectroelectrochemical measurements revealed switching times of < 2 s for the observed green–grey-blue colour transitions in this region. The electropolymerisation method is also applicable to single-ring transition metal phthalocyanine complexes,[31] the preparation of films with reasonable optical densities requiring minutes compared to the several hours potential cycling that is needed for $[Lu(T4APc)_2]$. The redox reactions and colour changes of two of the metal complexes studied are summarised in Scheme 6.

$\text{poly}[\text{Co}^{\text{II}}\text{T4APc}] + ne^- \longrightarrow \text{poly}[\text{Co}^{\text{I}}\text{T4APc}]^-$
(blue–green) (yellow–brown)

$\text{poly}[\text{Co}^{\text{I}}\text{T4APc}]^- + ne^- \longrightarrow \text{poly}[\text{Co}^{\text{I}}\text{T4APc}]^{2-}$
(yellow–brown) (red–brown as thick films or deep pink as thin films)

$\text{poly}[\text{Ni}^{\text{II}}\text{T4APc}] + ne^- \longrightarrow \text{poly}[\text{Ni}^{\text{II}}\text{T4APc}]^-$
(green) (blue)

$\text{poly}[\text{Ni}^{\text{II}}\text{T4APc}]^- + ne^- \longrightarrow \text{poly}[\text{Ni}^{\text{II}}\text{T4APc}]^{2-}$
(blue) (purple)

Scheme 6

The first reduction in the cobalt polymer is assigned to a metal-centred redox process, resulting in the appearance of a new MLCT transition, with the second reduction being ligand-centred. In the case of the nickel polymer, both redox processes are ligand-based.

A further alternative to the vacuum deposition method is the Langmuir–Blodgett (LB) technique, which is suitable for both monolayer and multilayer film formation.[32] The electrochemical properties of a variety of substituted and unsubstituted phthalocyanine metal complexes as multilayer LB films have been studied; the first paper on this subject reported the electrochemical study of alkoxy-substituted $[Lu(Pc)_2]$.[33] LB films exhibited a one-electron reversible reduction and a one-electron reversible oxidation corresponding to a transition from green to orange and blue forms, respectively, with the electron-transport through the multilayers being at least in part diffusion controlled. An explanation of the relatively facile redox reaction in such multilayers is that the Pc ring is large compared with the alkyl tail projected area, with enough space and channels present in the LB films to allow ion transport. Recently, high-quality LB films of M^{II} tetrakis[(3,3-dimethyl-1-butoxy)carbonyl]phthalocyanine (M = Cu, Ni) have been reported.[34] Ellipsometric and polarised optical absorption measurements suggest that the Pc molecules are orientated with their large faces perpendicular to the dipping direction and to the substrate plane. That the LB technique is amenable to the fabrication of ECDs is supported by the recent report of a new thin-film display based on LB films of the praseodymium bisphthalocyanine complex.[35] The electrochromic electrode in the display was fabricated by deposition of multilayers (10–20 layers, *ca.* 100–200 Å) of praseodymium bisphthalocyanine onto ITO-coated glass (7 × 4 cm^2) slides. The display exhibits blue–green–yellow–red polyelectrochromicity when a potential ranging from −2 to +2 V is applied. After 10^5 cycles no significant changes are observed in the spectra of these colour states. The high stability of the device was ascribed to the preparaton of well-ordered monolayers (by the LB technique) which seem to allow better diffusion of the counter ions into the film and improve the reversibility and stability of the system.

8 Concluding remarks

It has been shown in this article that a large number of electrochromic materials are available from all branches of synthetic chemistry. The ultimate usefulness of these fascinating materials hinges on a detailed understanding of their fundamental redox operation and the accompanying physico-chemical-structural changes. Indeed, even in the case of tungsten trioxide the colouration mechanism is still under debate with Deb and co-workers[36] recently proposing a new theory based on the intervalence transition between W^{V} and W^{IV} states instead of the W^{V} and W^{VI} states as suggested by previous theories.

The emphasis on applications of electrochromic materials has in recent years shifted from small-scale display devices to large-scale transmissive and reflective devices. Clearly, the commercial opportunities in the development of electrochromic systems are enormous, with electrochromic glazings for cars and buildings being forecast for the near future (three and five years, respectively).[3] Widespread application of ECDs, particularly for architectural applications, depends on reducing cost, increasing device lifetime and circumventing the problem of ECD degradation. Of further concern is that existing ‘smart window’ designs require an external power source, making the retro-fitting of existing buildings difficult and expensive. Photoelectrochromic systems, which change colour electrochemically but only on being illuminated, seem to be the way around this problem.[1] Thus, an important recent development in this area is a thin-layer cell where a light-absorbing layer of $Ru^{II}L_2L'$ (L = 2,2′-bipyridine-4,4′-dicarboxylate, L′ = 2,2′-bipyridine) adsorbed onto 4 μm thick nanocrystalline TiO_2 film on ITO glass is the working electrode in a thin-layer cell.[37] Absorption of solar radiation produces a photovoltage sufficient to colour a layer of tungsten trioxide deposited on the counter electrode. The successful fabrication of cells of dimensions 1–25 cm^2 suggests that this might be a suitable approach to the development of photoelectrochromic devices for large-area window applications. The acceptable lifetime of a retrofit, self-powered, photoelectrochromic window might be shorter compared to a conventional electrochromic window, because the former can easily be replaced.

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