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Organic electrochromic materials

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Abstract

In this article some of the most important examples from the major classes of organic electrochromic materials, namely the 1,1'-disubstituted-4,4'-bipyridilium salts (the 'viologens'), conducting polymers, metallopolymers and metallophthalocyanines are reviewed. Examples of their use in both a commercial and several prototype electrochromic devices are given. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Many organic materials exhibit redox states with distinct electronic (UV/visible) absorption spectra. Where the switching of redox states generates new or different visible region bands, the material is said to be *electrochromic* [1–4]. Colour changes are commonly between a transparent ('bleached') state, where the chromophore only absorbs in the UV region, and a coloured state or between two coloured states. Where more than two redox states are electrochemically accessible in a given electrolyte solution, the electrochromic material may exhibit several colours and be termed *polyelectrochromic*. Electrochromic anti-glare car rear-view mirrors have already been commercialised, with other proposed applications of electrochromic materials including their use in controllable light-reflective or light-transmissive devices for optical information and storage, 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]. In the field of electrochromic

data displays, present devices have insufficiently fast response times to be considered for such applications and cycle lives are probably also too low. Accordingly, the most exciting and attractive roles presently envisaged involve long-term display of information, such as at transport termini, re-usable price labels and advertising boards.

As might be expected from the enormity of the field of organic chemistry, there are a vast number of organic compounds that exhibit electrochromism. The purpose of this review is to give a flavour of the diverse range of organic electrochromic materials by surveying the major classes, namely the viologens, conducting polymers, metallopolymers and metallophthalocyanines. Whilst the latter two classes of metal coordination complexes might be considered as inorganic, they are included here because, in the main, the exhibited colours are a result of transitions that involve organic ligands.

2. Viologens

2.1. Preparation and redox states

Diquaternisation of 4,4'-bipyridyl produces 1,1'-disubstituted-4,4'-bipyridilium salts, commonly known

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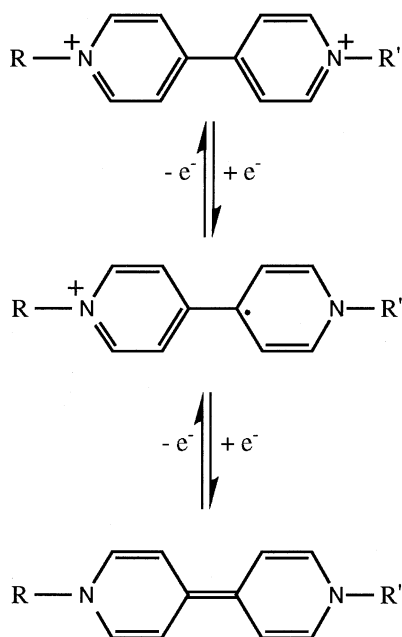


Fig. 1. The three common viologen redox states.

as ‘viologens’ [1,5,6]. Viologens have a long history as redox indicators in biological studies and some have important herbicidal properties [6]. The prototype viologen, 1,1'-di-methyl-4,4'-bipyridilium, is often known as methyl viologen (MV), with other simple symmetrical bipyridilium species being named *substituent* viologen.

Of the three common viologen redox states (Fig. 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 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.

The viologen radical cations are intensely coloured, with high molar absorption coefficients, owing to optical charge transfer between the (formally) +1 and zero valent nitrogens. A suitable choice of nitrogen substituents in viologens 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 such as 4-cyanophenyl in 1,1'-bis(4-cyanophenyl)-4,4'-bipyridilium generally impart a green hue to the radical cation. The intensity of the colour exhibited by di-reduced viologens Fig. 1 is low since no optical charge transfer or internal transition corresponding to visible wavelengths is accessible.

2.2. Viologen radical-cation dimerisation

Most viologen radical cations will spin pair to form the diamagnetic dimer with different spectral properties to the monomer. For example, the MV radical-cation monomer in water is blue ($\lambda_{\text{max}} \sim 600$ nm) while the dimer is red ($\lambda_{\text{max}} \sim 550, 900$ nm) [7]. Often the spectrum will show the presence of both the monomeric and dimeric radical cation forms. Electro-oxidation of radical-cation dimer is not very fast (so oxidation is said to be ‘quasi reversible’), implying that electrobleaching of viologen colour will be slower than predicted by the Cottrell equation for semi-infinite linear diffusion. Dimerisation is particularly prevalent for viologens in aqueous solution and at low temperatures in non-aqueous solutions.

2.3. Heptyl viologen in displays

Early studies directed towards the exploitation of viologen electrochromicity were concerned with their use in display systems [8]. It was recognised that the write-erase efficiency of displays with short alkyl chain viologens in aqueous electrolytes would be low since both dicationic and radical-cation states are very soluble and the electrogenerated coloured form would diffuse away from the electrode surface. This problem was 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'-di-*n*-heptyl-4,4'-bipyridilium (heptyl viologen, HV) as the dibromide salt has been the most thoroughly studied [8]. HV^{2+} dication has a rich yellow colour when solid, owing to charge transfer (CT) with the bromide anion. In solution, the HV^{2+} is pale yellow, or colourless if quite dilute. It may be that the radical-cation product of electro-reduction is also soluble, but, as soon as it is generated, it forms ion pairs with anions in solution to form an insoluble layer of solid maroon-coloured radical-cation salt on the electrode surface. Since alkyl-substituted viologens generally evince a blue radical cation, the maroon colour here implies incorporation of red radical-cation dimer in the solid-state deposit.

The maroon HV radical-cation salt is amorphous as deposited, but soon after electrodeposition slight crystallisation occurs and films appear patchy as this ‘ageing’ process takes place. This problem can be overcome by addition of a redox mediator such as hexacyanoferrate(II) to aqueous solutions of viologen dication [9,10]. In operation, the electrogenerated hexacyanoferrate(III) chemically oxidises the solid deposits of the radical-cation salt. An alternative approach to the ageing problem is the use of asymmetric viologens [11]. Since crystallisation of viologen radical-cation salts is an ordering phenomenon, it was

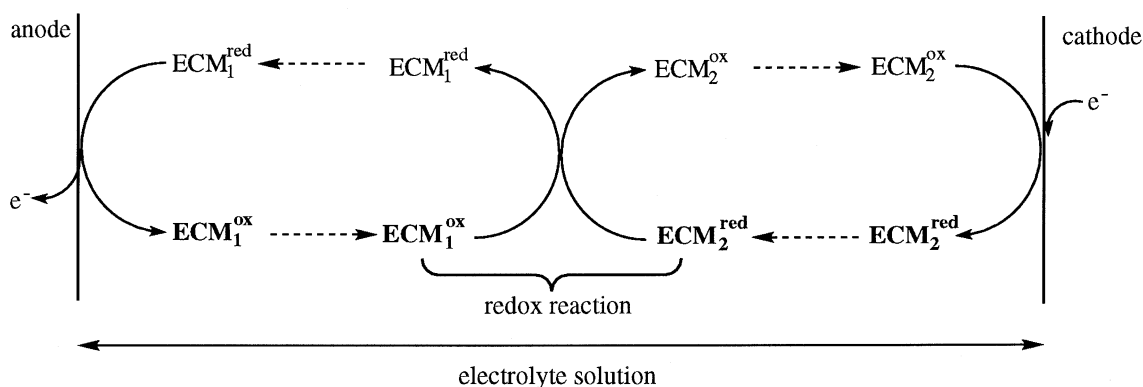


Fig. 2. Operating principles of an all-solution electrochromic device. The coloured redox states of the electrochromic materials are shown in bold type.

rationalised that crystallisation could be inhibited by decreasing the extent of molecular symmetry.

Despite the drawbacks, many prototype electrochromic devices have been made, including an alphanumeric display (response time, τ , 10–50 ms, with a cycle life of $> 10^5$) [8] and a 64×64 pixel integrated device with 8 levels of grey tone on a 1 inch square silicon chip, capable of giving quite detailed images [12]. These have not been exploited further owing to competition with liquid-crystal displays, though they may still have a size advantage in large devices.

2.4. Viologens in polyelectrolytes and polymeric viologens

As noted above, the write-erase efficiency of an electrochromic device (ECD) using for example aqueous MV would be low since both the dicationic and radical-cation states are very soluble. Improved MV-based systems may be made by retarding the rate at which the radical-cation product of electron transfer diffuses away from the electrode by use of an anionic polyelectrolyte such as polyAMPs (poly(2-acrylamido-2-methylpropane-sulphonic acid) [13,14] or Nafion[®] [15]. An alternative approach is the modification of an electrode surface using silanisation methodology [16], a preformed polymer [17] or electropolymerisation [18].

2.5. Viologen solution electrochromic systems

Whilst the benefit to displays of an insoluble viologen radical-cation phase has been noted, a different type of device, the commercialised electrochromic rear-view mirror, functions wholly by solution electrochromism [2,19]. In this device, an indium tin oxide (ITO)-coated glass surface (conductive side inwards) and a 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 [2,19]. A substituted (cationic) viologen serves as the cathodic-colouring electrochromic material, with a negatively-charged (possibly) molecular thiazine or perhaps 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 to generate an intense composite green-blue colour. 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 (Fig. 2).

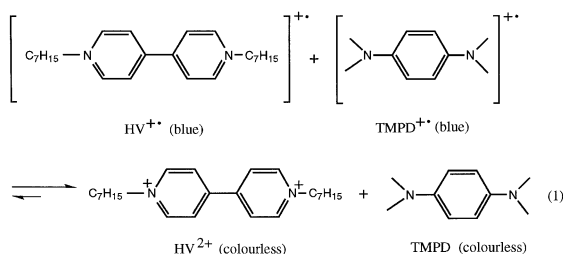
Thus in this type of device, maintenance of colouration requires application of a continuous small current for replenishment of the coloured electroactive species lost by their mutual redox reaction in solution. Bleaching occurs at short or open circuit by homogeneous electron transfer in the bulk of the solution.

2.6. Progress in viologen electrochromism studies

Recent developments have been directed towards improving the performance characteristics of viologen ECDs. Monk et al. [20] have shown that application of a square-wave pulsed potential to an ECD enhances the rate at which electrochromic colour is formed, relative to dc potentiostatic colouration. In this technique a sufficiently high potential is employed in order to electrogenerate the di-reduced viologen redox state, which as a powerful reducing agent will disproportionate with the dication to produce radical-cation dimer in a follow-up chemical reaction to the initial electroreduction. With this pulse technique the rate of

development of colour is enhanced, with a greater extent of colouration.

Leventis et al. [21] have investigated a solution electrochromic system in acetonitrile comprising nine solution-phase electrochromic thin-layer cells based on 1,1'-di-*n*-heptyl-4,4'-bipyridilium perchlorate, and *N,N',N,N'*-tetramethyl-*p*-phenylenediamine (TMPD). Eq. (1) shows the spontaneous reaction between HV^{+} and $TMPD^{+}$ associated with bleaching, while the electrolytic reverse reaction generates an intense blue colouration.



The cells were arranged in three rows and three columns, and were matrix-addressed without crosstalk with six inputs. The absence of crosstalk is attributed to the fact that the voltage communicated to the pixels peripheral to the one intended for colouration never exceeds the threshold voltage for colouration.

Stapp and Schlenoff [22] have constructed polyelectrolyte multilayers of poly(butanyl viologen) dibromide (PBV) and poly(styrene sulphonate) sodium salt (PSS) using an alternating polyion solution deposition technique. In their technique the ITO substrate is alternatively exposed to positive and negative polyelectrolytes, with spontaneous polymer deposition via coulombic interactions between surface and polyion of opposite charge. In this 'layer-by-layer' deposition technique all redox material is electrochemically addressable, with good electrochromic performance characteristics.

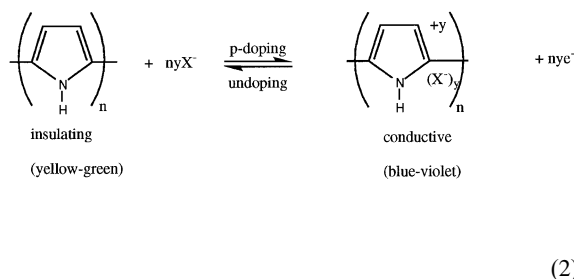
3. Conducting polymers

3.1. Preparation and conductivity

Chemical or electrochemical oxidation of numerous resonance-stabilised aromatic molecules produces electronically conducting polymers [23–25]. The oxidative polymerisation process is initiated by monomer oxidation to yield radical-cation species. Conducting polymer generation then follows via a mechanism [23] that is believed to involve either radical-cation/radical-cation coupling or attack of radical-cation on neutral monomer. In their oxidised states, conducting poly-

mers 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. 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 undergo cathodic doping with cation insertion (n-doping) to balance the injected charge.

All conducting polymers are potentially electrochromic in thin-film form, redox switching giving rise to new optical absorption bands in accompaniment with transfer of electrons/counter anions. A good example is polypyrrole which in its 'doped' (oxidised) state is blue/violet ($\lambda_{\text{max}} = 670$ nm) [26], electrochemical reduction yielding the yellow/green ($\lambda_{\text{max}} = 420$ nm) 'undoped' form (2).



The electrochromism of polypyrrole is unlikely to be exploited, mainly due to the degradation of the film on repetitive colour switching. Electrochromic conducting polymers based on thiophene and aniline have received greater attention.

3.2. Polythiophene(s)

Polythiophene(s) [27] are of particular interest as electrochromic materials due to their chemical stability, ease of synthesis and processability. Polythiophene thin films are blue ($\lambda_{\text{max}} = 730$ nm) in their doped (oxidised) state and red ($\lambda_{\text{max}} = 470$ nm) in their 'undoped' form. Tuning of colour states is possible by suitable choice of thiophene monomer, and this represents a major advantage of using conducting polymers for electrochromic applications. Subtle modifications to the monomer can significantly alter spectral properties. For example, the colours available with polymer films prepared from 3-methylthiophene-based oligomers are strongly dependent on the relative positions of methyl groups on the polymer backbone [28]. Colours available include pale blue, blue and violet in the oxidised form, and purple, yellow, red and orange in the reduced form. The colour variations have been

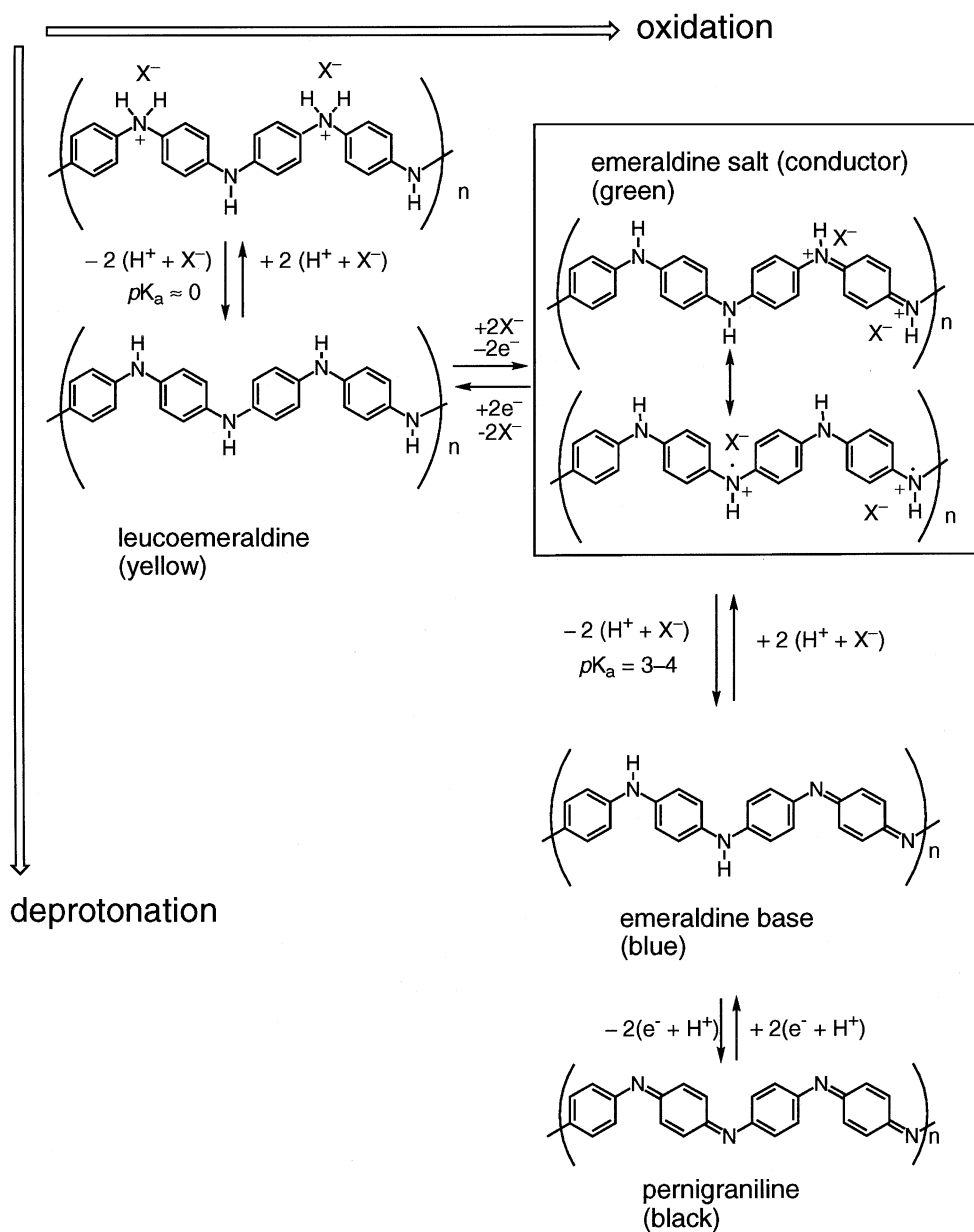


Fig. 3. Proposed composition and redox pathways of the various redox states of polyaniline.

ascribed to changes in the effective conjugation length of the polymer chain.

Alkoxy-substituted polythiophenes are currently being intensively investigated for their electrochromic properties [29–36]. Materials based on poly(3, 4-(ethylenedioxy)thiophene) (PEDOT) have a band gap lower than polythiophene and alkyl-substituted polythiophenes, owing to the presence of the two electron-donating oxygen atoms adjacent to the thiophene unit. For example, the band gap of PEDOT ($E_g = 1.6$ eV) is

0.5 eV lower than polythiophene which results in an absorbance maximum in the near infra-red region. Relative to other substituted polythiophenes these materials exhibit an exceptional stability in the doped state associated with high conductivity. Doped PEDOT is almost transparent in the visible region (with a sky-blue tint) and the neutral polymer is blue-black. As PEDOT and its alkyl derivatives are cathodically colouring electrochromic materials they are suitable for use with anodically-colouring conducting

polymers in the construction of dual polymer ECDs [36].

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 = -CMe₃, -Me, -OMe, -H, -F, -Cl, -Br, -CF₃, -SO₂Me) have been investigated [37]. The presence of electron-withdrawing groups on the phenyl ring serve to assist the stabilisation of the n-doped state and these materials can be both reversibly reduced and oxidised (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 [38].

3.3. Polyaniline(s)

Polyaniline films are polyelectrochromic (transparent yellow–green–dark blue–black) [39], the yellow–green transition being durable to repetitive colour switching [40]. Several redox mechanisms involving protonation–deprotonation and/or anion ingress/egress have been proposed [41–43], with Fig. 3 giving the composition and redox pathways of the various redox states.

The two low-wavelength spectral bands observed in films of 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) [44,45]. With increase in applied potential the ≤ 330 nm band absorbance decreases and the ≤ 440 nm increases. Beyond +0.30 V the conducting region is entered; the ≤ 440 nm band decreases as a broad free carrier electron band ~ 800 nm is introduced. Numerous workers [46–50] have combined polyaniline with the inorganic mixed valence complex Prussian blue in complementary ECDs that exhibit deep blue–green electrochromism. Other polyaniline-based ECDs include a device that exhibits yellow-transparent electrochromicity using electropolymerised 1,1'-bis[*p*-phenylamino(phenyl)]amido-]ferrocene [51].

Of the numerous conducting polymers based on substituted anilines that have been investigated, those with alkyl substituents have received much attention. Poly(*o*-toluidine) and poly(*m*-toluidine) films have been found to offer enhanced stability of polyelectrochromic response in comparison with polyaniline [52]. Absorption maxima and redox potentials shift from values found for polyaniline due to the lower conjugation length in poly(toluidines). Response times, τ , for the yellow–green electrochromic transition in the films correlate with the likely differences in the conjugation length implied from the spectroelectrochemical data. τ values for polyaniline are found to be lower

than for poly(*o*-toluidine), which in turn has lower values than poly(*m*-toluidine). As for polyaniline, response times indicate that the reduction process is faster than the oxidation. Recent electrochemical quartz crystal microbalance studies have demonstrated the complexity of redox switching in poly(*o*-toluidine) films in aqueous perchloric acid solutions which occurs in two stages and is accompanied by nonmonotonic mass changes that are the result of perchlorate counterion, proton co-ion and solvent transfers [53]. The extent and rate of each of these transfers are dependent upon electrolyte concentration, experimental time scale and the switching potential, so that observations in a single electrolyte on a fixed time scale cannot be unambiguously interpreted.

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 [54]. 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.

3.4. Composite conducting polymer materials

The electropolymerisation of monomers in the presence of additives which may have electrochromic or other properties has been a popular approach to the preparation of materials with tailored properties [1].

Shannon and Fernandez prepared a water-soluble poly(styrenesulphonic acid)-doped polyaniline both by persulphate oxidative coupling an anodic oxidation of aniline in aqueous dialysed poly(styrenesulphonic acid) solution [55]. De Paoli et al. [56] prepared composites of polyaniline and cellulose acetate both by casting of films from a suspension of polyaniline in a cellulose acetate solution and deposition of cellulose acetate films onto electrochemically prepared polyaniline films. The electrochromic properties of the latter films were studied by spectroelectrochemistry and the presence of the cellulose acetate was found not to impede the redox processes of the polyaniline. Tassi et al. [57] studied the electroactivity and electrochromism of the graft copolymer of polyaniline and nitrilic rubber using stress-strain measurements, cyclic voltammetry, frequency response analysis and visible range spectroelectrochemistry. Results indicated that the graft copo-

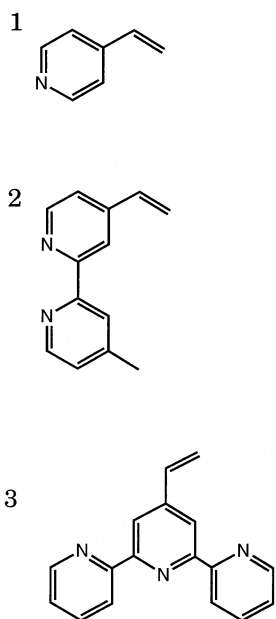


Fig. 4. Structures of various vinyl-substituted ligands. 1 = 4-vinylpyridine (vpy), 2 = 4-vinyl-4'-methyl-2,2'-bipyridine (vbpy), 3 = 4'-vinyl-2,2':6',2''-terpyridine (vtpy).

lymer exhibits mechanical properties similar to a cross-linked elastomer with the electrochromic and electrochemical properties typical of polyaniline.

An example of a case where the additive itself is electrochromic is the encapsulation of the redox indicator dye indigo carmine within a polypyrrole matrix [58,59]. More recently Giroto and De Paoli [60] have reported 3D graphs constructed from absorbance data acquisition during cyclic voltammetry that showed the enhancement and modulation of the colour change by indigo carmine insertion into polypyrrole or polypyrrole/dodecylsulphonate films. As expected, the use of indigo carmine as dopant improves the films' electrochromic contrast ratio.

4. Metallopolymers

Transition metal coordination complexes of organic ligands 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 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 which have potential use in all-solid-state systems. Many schemes have been described for the preparation of thin-film 'metallopolymers' [61], including both the reductive and oxidative electropolymerisation of suitable polypyridyl complexes.

4.1. Reductive electropolymerisation

The reductive electropolymerisation technique relies on the ligand-centred nature of the three sequential reductions of complexes such as $[\text{Ru}^{\text{II}}(\text{vbpy})_3]^{2+}$ (vbpy = 4-vinyl-4'-methyl-2,2'-bipyridine), combined with the anionic polymerisability of suitable ligands. Vinyl-substituted pyridyl ligands (examples in Fig. 4) are generally employed, although metallopolymers have also been formed from chloro-substituted pyridyl ligands, via electrochemically initiated carbon-halide bond cleavage.

For either case, electrochemical reduction of their metal complexes generates 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. 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.

4.2. Oxidative electropolymerisation

Oxidative electropolymerisation has been described for iron(II) and ruthenium(II) complexes containing amino- [62] and pendant aniline- [63] substituted 2,2'-bipyridyl ligands and amino- and hydroxy- substituted 2,2':6',2''-terpyridinyl ligands [64]. Analysis of IR spectra suggested that the electropolymerisation of bis[3-(aminophenyl)-2,2':6,2''-terpyridinyl]iron(II) proceeds via a reaction mechanism similar to that of aniline [64]. The resulting modified electrode reversibly switched from purple to pale pink on oxidation of Fe(II) to Fe(III). For polymeric films of bis[2-(hydroxyphenyl)-2,2':6,2''-terpyridinyl]iron(II) the colour switch was from brown to dark yellow. The dark yellow was attributed to an absorption band at 455 nm, probably due to quinone moieties in the polymer formed during electropolymerisation. IR spectra confirmed the absence of hydroxyl groups in the initially deposited brown films.

Metallopolymer films have also been prepared by oxidative polymerisation of complexes of the type $[\text{M}(\text{phen})_2(4,4'\text{-bipy})_2]^{2+}$ (M = Fe, Ru, or Os;

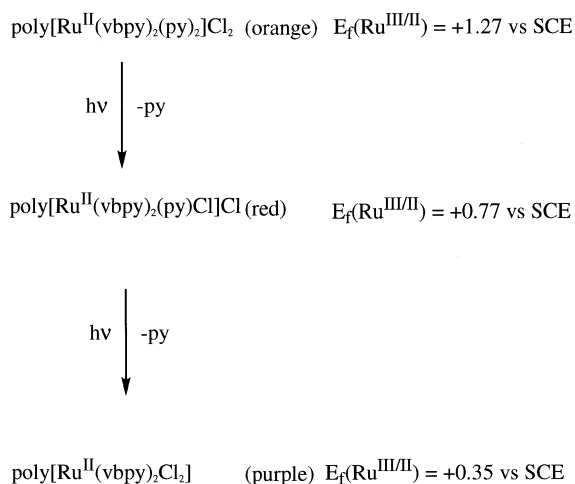


Fig. 5. Spatial electrochromism in metallopolymeric films using photolabile pyridine ligands.

phen = 1,10-phenanthroline, 4,4'-bipy = 4,4'-bipyridine) [65]. Such films are both oxidatively and reductively electrochromic; film-based reduction leading reversibly to dark purple films (below -1.0 V) [65], a colour and potential region indicative of the viologen dication/radical cation electrochromic response. The purple state towards negative limits has also been observed for polymeric films of tris[4-methyl-4'-(*N*-styril-aza-15-crown-5)-2,2'-bipyridine] [66].

4.3. Spatial electrochromism

Spatial electrochromism has been demonstrated in metallopolymeric films [67]. Photolysis of $\text{poly}[\text{Ru}^{\text{II}}(\text{vbpy})_2(\text{py})_2]\text{Cl}_2$ thin films on ITO glass in

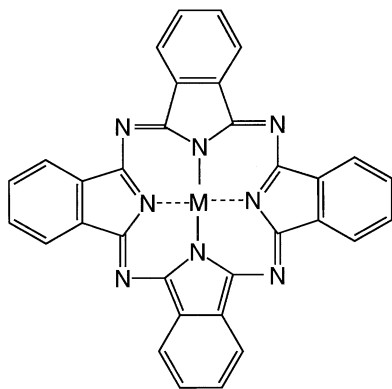


Fig. 6. Structure of a metallophthalocyanine with a single metal ion coordinated at the centre of the phthalocyanine (Pc) ring.

the presence of chloride ions leads to photochemical loss of the photolabile pyridine ligands and sequential formation of $\text{poly}[\text{Ru}^{\text{II}}(\text{vbpy})_2(\text{py})\text{Cl}]\text{Cl}$ and $\text{poly}[\text{Ru}^{\text{II}}(\text{vbpy})_2\text{Cl}_2]$ (Fig. 5).

Contact lithography can be used to spatially control the photosubstitution process to form laterally resolved bicomponent films with image resolution below $10 \mu\text{m}$. Dramatic changes occur in the colours and redox potentials of such ruthenium(II) complexes upon substitution of chloride for the pyridine ligands Fig. 5. Striped patterns of variable colours are observed on addressing such films with a sequence of potentials.

5. Metallophthalocyanines

5.1. Properties

Phthalocyanines (e.g. Fig. 6) are tetraazatetrabenzod derivatives of porphyrins with highly delocalised π electron systems.

Metallophthalocyanines are important industrial pigments used primarily in inks and for colouring plastics and metal surfaces [68]. The water soluble sulphonate derivatives are used as dyestuffs for clothing. The purity and depth of the colour of metallophthalocyanines arise from the unique property of having an isolated, single band located in the far red end of the visible spectrum near 670 nm , with ϵ often exceeding $10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The next most energetic set of transitions is generally much less intense, lying just to the blue of the visible region near 340 nm . Introduction of additional bands around 500 nm , for example, from charge transfer transitions between the metal and the phthalocyanine ring, allows tuning of the hue [68].

In addition to the familiar applications above, the metallophthalocyanines have been intensely investigated in many fields including catalysis, liquid crystals, gas sensors, electronic conductivity, photosensitisers, non-linear optics and electrochromism [68]. The metal ion in metallophthalocyanines lies either at the centre of a single phthalocyanine, or between two rings in a sandwich-type complex. Polyelectrochromism of bis(phthalocyaninato) lutetium(III) ($[\text{Lu}(\text{Pc})_2]$) thin films was first reported in 1970, and since that time this complex has received most attention, although numerous other (mainly rare earth) metallophthalocyanines have been investigated for their electrochromic properties [1]. Silver and co-workers have been particularly active in the field of sublimed metallophthalocyanines. Amongst their many advances they have emphasised the cost and performance benefits of using heavy rare-earth element fraction bisphthalocyanine (HFBP) from partially refined ore [69]. Recent highlights include their report of the electrochromic proper-

ductive step is seen for both cases but the green/blue reductive step is absent in the butoxy-substituted material.

High-quality LB films of tetrakis((3,3-dimethyl-1-butoxy)carbonyl)phthalocyaninato) M(II) (M = Cu, Ni) have been reported [77]. Ellipsometric and polarised optical absorption measurements suggest that the Pc rings are oriented with their large faces perpendicular to the dipping direction and to the substrate plane.

The LB technique is amenable to the fabrication of ECDs as demonstrated by the report of a thin-film display based on bis(phthalocyaninato)praseodymium(III) [78]. The electrochromic electrode in the display was fabricated by deposition of multilayers (10–20 layers, ≈ 100 – 200 Å) of the complex onto ITO-coated glass (7×4 cm²) slides. The display exhibited 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 preparation 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.

6. Conclusion

It has been shown that a large number of electrochromic materials are available from many branches of organic chemistry. In this article the main emphasis has been on the major classes of organic electrochromic materials, although it should be recognised that many other electrochromic compounds have been reported [1] including carbazoles, methoxybiphenyls, quinones, pyrazolines, tetracyanoquinodimethane (TCNQ) and tetrathiafulvalene (TTF). Further developments in the field seem only limited by the skills, resources and imagination of synthetic organic chemists and material scientists. However, the ultimate usefulness of such fascinating materials hinges on a detailed understanding of their fundamental redox operation and the accompanying physicochemical–structural changes, and therefore the field is truly interdisciplinary.

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