

# New organic electrochromic materials and their applications

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## Materials

### ABSTRACT

**Purpose:** The aim of this work is to perform the review of the recent most important results of experimental and theoretical investigations connected with the electrochromic materials and their selected applications.

**Design/methodology/approach:** The recent achievements in the field of designing and preparation methods of organic electrochromic materials and devices operating as optical data storage are presented.

**Findings:** We pointed out the physical phenomena that are important in the electrochromic effect occurring in organic materials and which can be used in numerous devices. Such phenomena as the change, evocation, or bleaching of color resulted either by an electron-transfer (redox) process or by a sufficient electrochemical potential have been evaluated as occurring in prosperous devices. Examples of the application of the organic electrochromic materials in electrochromic devices are shown.

**Research limitations/implications:** The main disadvantage of organic devices are reported to be connected with their short lives and weak resistivity to the moist but the improvements are advancing.

**Originality/value:** Our review concerns the most recent findings in this area. We also show some recent examples of electrochromic devices.

**Keywords:** Electrochromism; Organic materials; Optoelectronics

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## 1. Introduction

Generally the electrochromic effect relies on the change in the material coloring due to the current flowing through it. The change in the direction of the current through the colored material results in the reverse change (i.e. decoloring). The electrochromic effect has been discovered by Deb [1] (1973) in thin films of tungsten oxide.

An electrochromic material is one where a reversible color change takes place when electrical current flows through it resulting reduction (gain of electrons) or oxidation (loss of electrons) processes. In this review, the electrochromic phenomena

is introduced, with presentation of the types, applications, and chemical classes of electrochromic materials. The main classes of electrochromic organic materials are then surveyed, with descriptions of representative examples based on the transition metal coordination complexes, viologen systems, and conducting polymers. The electrochromic rearview mirrors are now widely available in cars. Extension of the controlled coloration to the windows and displays is under widespread studies, and several firms now show examples of the windows such as a switchable skylight.

The scheme of the coloring mechanism and decoloring in the system of the electrochromic layer is presented in Fig. 1.

The electrochromic effect can be obtained in the different materials in the solid or liquid states. In Fig. 2 is presented the cells with the solid and liquid materials. The electrodes are separated by electrolyte providing only ionic not electronic conduction, thus making up a typical electrochromic cell or device. The second electrode in some systems may also be electrochromic and in any case must undergo electron transfer in the reverse sense to that of the first electrode. The electrochemical reaction ensues from changing the potential applied between the electrodes, the system behaving as either an electrolytic or a current-producing cell, as determined by the intrinsic standard electrode potentials of the electrodes modified by the specific composition of the cell as used. On completion of the electrochemical coloration, the cell will usually retain its color the „memory effect”.

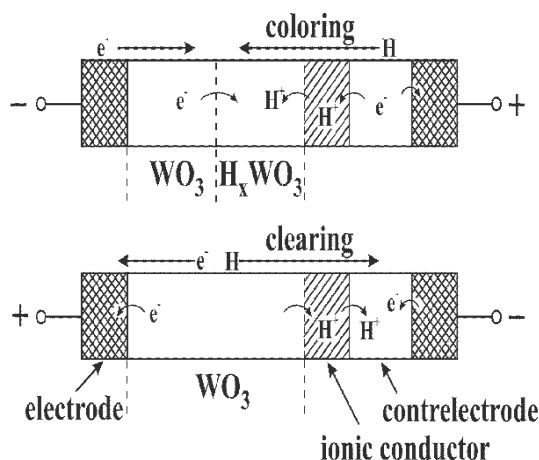


Fig. 1. Schematic of the coloring and clearing mechanism in the  $\text{WO}_3$  electrochromic film

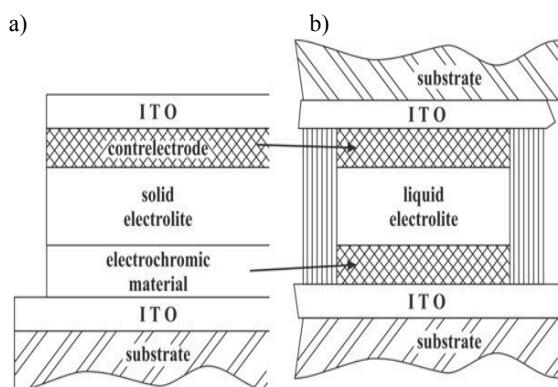


Fig. 2. Schematic cross-section of electrochromic cells; a) the solid electrolyte, b) the liquid electrolyte

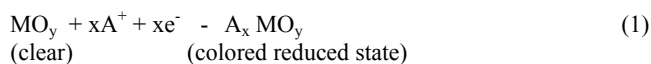
The review [2] focussed largely on solid-state devices. Two monographs [3, 4] cover the subject to about 1994, and more recent research results are presented in reviews [5-9]. Mortimer [5] reviewed some of the most important examples from the major classes of organic electrochromic materials. In this paper is given the short review of the electrochromic materials the

1,1'-disubstituted-4,4'-bipyridinium salts (the „viologens”), conducting polymers, metallopolymers and metallophthalocyanines. The examples of their use in both a commercial and several prototype electrochromic devices are given.

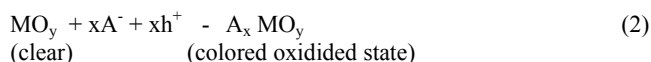
Our previous reviews appear to be the additional studies on the organic materials used in electronics concerning the application of organic materials in OLEDs, field-effect transistors and photochromism [10-14].

## 2. Inorganic electrochromic materials

Inorganic electrochromic materials may be divided on two categories: the cathode coloring materials i.e. with reduced state of coloring and the anode coloring materials i.e. the oxidized coloring state. For the oxide of the transition metals the processes of coloring and clearing are defined by the following reaction

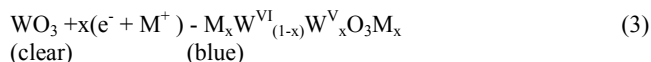


where  $\text{MO}_y$  is the metal oxide,  $\text{A}^+$  is the coloring ion,  $\text{A}_x\text{MO}_y$  is the complex metal oxide. While for the metal oxides anodic colored the coloring and decoloring processes are described by the following general chemical reaction:



where  $\text{A}^-$  is the coloring ion, i.e.  $\text{F}^-$ ,  $\text{CN}^-$ .

Following Deb's work, [1, 3] which revived modern electrochromism, the most widely studied system of this kind is [7]



where  $0 < x < 1$ , i.e., a fraction of the  $\text{W}^{\text{VI}}$  population is converted; the product may be viewed as a solid solution.  $x$  is the insertion coefficient.  $\text{M} = \text{H}, \text{Li}, \text{Na}$  or  $\text{K}$  and  $\text{e}^-$  is the electron. On coloration the counter-ion, for ingress or egress, must migrate through the lattice, a migration often greatly exceeding the purely electron-transfer factors in the energy requirements governing the rate, or indeed the possibility, of coloration. For a specific example, cation ingress from the electrolyte accompanies electron progress from the conductive electrode substrate, each charge species migrating at its own rate. Electrochromic coloration is sometimes considered as ion injection more-or-less accompanied by electron transfer, but all electrochromic coloration is fundamentally a consequence of the transfer of the electron (sometimes of two electrons). Many oxides [3, 4], e.g.,  $\text{Nb}_2\text{O}_5$ ,  $\text{NiO}$ ,  $\text{MoO}_3$ , and  $\text{Ir}_2\text{O}_3$ , mixed oxides, and polyoxometallates [15] can all be made electrochromic. Films of  $\text{WO}_3$  may be prepared by evaporation or sputtering of oxide, by sol-gel deposition, by spin-coating, dipping or spraying, by chemical vapor deposition (CVD), by the anodizing of metal, and other methods. The role of experimental parameters in determining the product properties in the sputtering of  $\text{W}$  in  $\text{Ar} + \text{O}_2 + \text{CF}_4$  was examined [5]. The variation in properties and structures depending on preparation was found to be significant.

Different roles of  $W^{IV}$ ,  $W^V$ , and  $W^{VI}$  in optical charge-transfer processes (the intrinsic color effects) may arise in O-deficient compared with the stoichiometric material. A theoretical model [15] employing density-functional calculations argues for  $W^V$ - $W^V$  dimers rather than  $W^{IV}$  in such situations. The electrochromic and photochromic properties of O-deficient  $WO_3$  have been found to depend on similar  $W^{IV}$  participation in both mechanisms [16]. Detailed density-of-state and associated structural calculations on initial and totally mono-reduced forms of  $MWO_3$  give some insight into the bonding and the disposition of the transferred electron. Incorporated  $Li^+$  (also  $Na^+$ ) turns out, realistically, to be nearly totally ionic, but  $H^+$  becomes attached to O; the transferred electron, acquired in the electrochemical coloration process, is in a conduction band largely comprising the  $Wd$  orbitals. Probably the most important barrier in oxide processes is ion-insertion and its reversal. An interesting study of this problem in  $TiO_2$  has been summarized [17].

### 3. Organic electrochromic materials

#### 3.1. 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 [3-5, 18]. 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. 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 chapter is to give a review of the recent research results concerning the organic electrochromic materials by surveying the major classes, namely the viologens, conducting polymers, metallopolymer and metallophthalocyanines. Whilst the latter two classes of metalcoordination 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.

#### 3.2. Viologens

Viologens have a long history as redox indicators in biological studies and some have important herbicidal properties [19]. Diquaternisation of 4,4'-bipyridyl produces 1,1'-disubstituted-4,4'-bipyridilium salts, commonly known as 'viologens' [4, 19, 20]. The prototype viologen, 1,1'-di-methyl-4,4'-bipyridilium, is known as methyl viologen (MV), with other simple symmetrical bipyridilium species being named substituent viologen. Of the three common viologen redox states (Fig. 3), 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 dication creates radical cations, the stability of which is attributable to the delocalisation of the radical electron

throughout the p-framework of the bipyridyl nucleus, the 1 and 1' substituents commonly being some of the charge. The viologen radical cations are intensely coloured, with high molar absorption coefficients, owing to optical charge transfer between +1 and 0 valent nitrogens. Nitrogen substituents in viologens can attain the appropriate molecular orbital energy levels and can allow a 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. 3) is low since no optical charge transfer or internal transition corresponding to visible wavelengths is accessible.

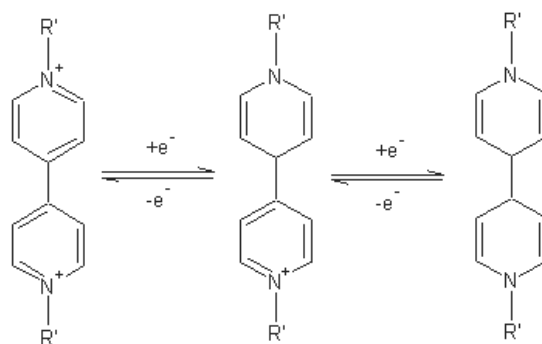


Fig. 3. The three common viologen redox states

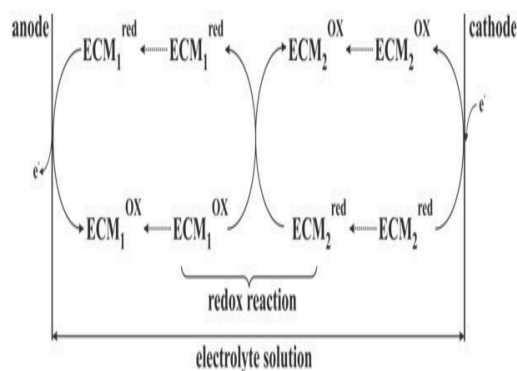


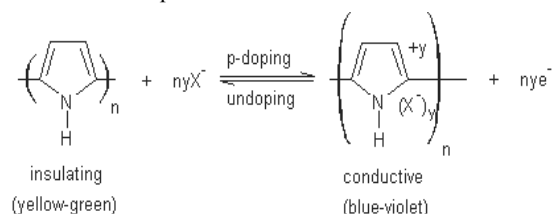
Fig. 4. Operating principles of an all-solution electrochromic device. The coloured redox states of the electrochromic materials are shown in bold type

Now we present the 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 [21, 22]. 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. In this system 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 [21, 22]. 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. 4). 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.

### 3.3. Conducting polymers

Chemical or electrochemical oxidation of numerous resonance-stabilised aromatic molecules produces electronically conducting polymers [22-24]. The oxidative polymerisation process is initiated by monomer oxidation to yield radical-cation species. Conducting polymer generation then follows via a mechanism [22] that is believed to involve either radical-cation/radical-cation coupling or attack of radical-cation on neutral monomer. In their oxidised states, conducting polymers are 'doped' with the counter anions (p-doping) and shows a delocalised p-electron band structure. The energy gap between the highest occupied p 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.



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.

**Polythiophene(s).** Polythiophene(s) [25-27] are of particular interest as electrochromic materials due to their chemical stability, ease of synthesis and processability. Polythiophene thin films are blue ( $\lambda_{\text{max}} = 730 \text{ nm}$ ) in their doped (oxidised) state and red ( $\lambda_{\text{max}} = 470 \text{ nm}$ ) 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 the 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 ascribed to the changes in the effective conjugation length of the polymer chain. Alkoxy-substituted polythiophenes are currently being intensively investigated for their electrochromic properties [28-33].

**Polyaniline(s).** Polyaniline films are polyelectrochromic (transparent yellow-green-dark blue-black) [34], the yellow-green transition being durable to repetitive colour switching [35]. Several redox mechanisms involving protonation-deprotonation and/or anion ingress/egress have been proposed [36, 37]. The two low-wavelength spectral bands observed in films of polyanilines are assigned to an aromatic  $\pi\pi^*$  transition ( $<330 \text{ nm}$ ) related to the extent of conjugation between the adjacent rings in the polymer chain, and to radical cations formed in the polymer matrix ( $<440 \text{ nm}$ ) [38, 39]. With increase in applied potential the  $<330 \text{ nm}$  band absorbance decreases and the  $<440 \text{ nm}$  increases. Beyond  $+0.30 \text{ V}$  the conducting region is entered; the  $<440 \text{ nm}$  band decreases as a broad free carrier electron band  $800 \text{ nm}$  is introduced. Numerous workers [40-42] 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 [43].

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 [44]. 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. Metallopolymers

Transition metal coordination complexes of organic ligands due to their intense colouration and redox reactivity are potentially useful electrochromic materials. Chromophoric properties typically arise from a low energy metal-to-ligand charge transfer (MLCT), the intervalence CT, the intraligand excitation and the related visible region electronic transitions. Because these transitions involve valence electrons, chromophoric characteristics are altered or eliminated upon oxidation or reduction of the complex. 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' [45], including both the reductive and oxidative electropolymerisation of suitable polypyridyl complexes.

**Reductive electropolymerisation.** The reductive electropolymerisation technique relies on the ligand-centred nature of the three sequential reductions of complexes such as  $[RuII(vbpy)3]^{2+}$  ( $vbpy=4\text{-vinyl-4'-methyl-2,2'-bipyridine}$ ), combined with the anionic polymerisability of suitable ligands. Vinyl-substituted pyridyl ligands (examples in Fig. 5) 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.

**Oxidative electropolymerisation.** Oxidative electropolymerisation has been described for  $Fe(II)$  and  $Ru(II)$  complexes containing amino- [46] and pendant aniline- [47] substituted 2,2'-bipyridyl ligands and amino- and hydroxy-substituted 2,2':6,2''-terpyridinyl ligands [48]. Analysis of IR spectra suggested that the electropolymerisation of bis[3-(aminophenyl)-2,2':6, 2''-terpyridinyl]- $Fe(II)$  proceeds via a reaction mechanism similar to that of aniline [48]. 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-(hydro-xyphenyl)-2,2':6, 2''-terpyridinyl] $Fe(II)$  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.

Such films are both oxidatively and reductively electrochromic; the electrochromic response was found in the film-based reduction leading reversibly to dark purple films (below - 1.0 V) [49], a colour and potential region indicative of the viologen dication/radical cation. The purple state towards negative limits has also been observed for polymeric films of tris[4-methyl-4'-(N-styryl-aza-15-crown-5)-2,2'-bipyridine] [50].

### 3.5. Metallophthalocyanines

Phthalocyanines (Fig. 6) are tetraazatetrabenzo derivatives of porphyrins with highly delocalised p electron systems. Metallophthalocyanines are important industrial pigments used primarily in inks and for colouring plastics and metal surfaces [51]. 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. 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 [50].

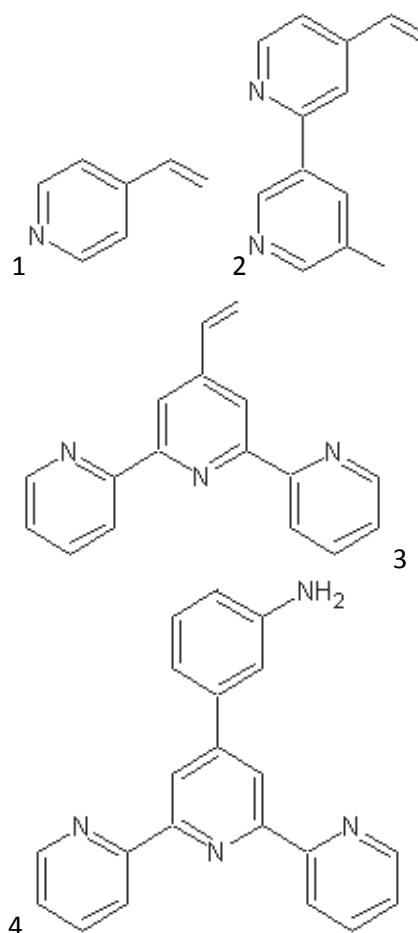


Fig. 5. Structures of various vinyl-substituted ligands. 1=4-vinylpyridine (vpy), 2=4-vinyl-4'-methyl-2,2'-bipyridine (vbpy), 3=4'-vinyl-2,2':6', 2''-terpyridine (vtpy), 4=4,4'-(3-aminophenyl)-2,2':6',2''-terpyridine

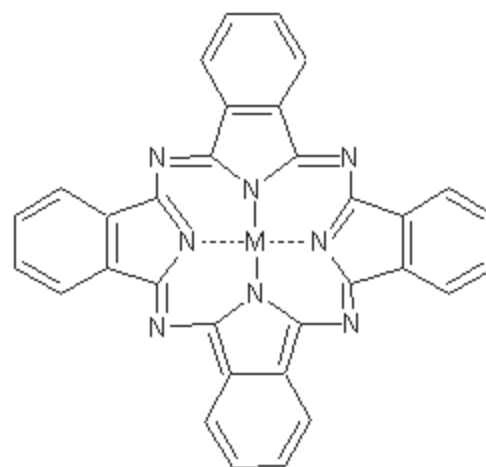


Fig. 6. Structure of a metallophthalocyanine with a single metal ion coordinated at the centre of the phthalocyanine (Pc) ring

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 [50]. 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 [4]. By sublimation of metallophthalocyanines can be achieved benefits of using heavy rare-earth element fraction bisphthalocyanine (HFBP) from partially refined ore [51]. Recent high-lights include report of the electrochromic properties of some silicon phthalocyanine thin films with the first study of a metallophthalocyanine that also contains a redox active ligand (ferrocenecarboxylato) in addition to the electrochromic centre [52]. The sandwich-type homoleptic complex, bis(phthalocyaninato) lutetium(III),  $[\text{Lu}(\text{Pc})_2]$ , is generally formed as a vivid green film on vacuum sublimation.  $[\text{Lu}(\text{Pc})_2]$  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,  $[\text{Lu}(\text{Pc})_2]$  films can exhibit five colours. Only the blue-green transition is utilised in most prototype ECDs [4]. Mechanical problems, such as film fracture and/or loss of adhesion to the electrode substrate, arise from anion ingress/egress during colour switching. Despite of such difficulties,  $[\text{Lu}(\text{Pc})_2]$ -based electrochromic displays with good reversibility, fast response times and little degradation over  $>5 \times 10^6$  cycles have been described [52]. Oxidative electropolymerisation, analogous to that described above for complexes with pendant aniline and hydroxy-substituted ligands, is an alternative route to metallophthalocyanine electrochromic films. Polymer films from  $[\text{Lu}(\text{T4APc})_2]$  (T4APc= 4,4',40,41-tetraaminophthalocyanine) monomer show loss of electroactivity on cycling to positive potentials, however, the electrochemical response in DMSO at negative potentials is well-behaved, with the observation of two broad quasi-reversible one-electron redox couples [53]. The spectroelectrochemical measurements revealed switching times of  $<2$  s for the observed green-grey-blue colour transitions in this region. The oxidative electropolymerisation technique using the pendant aniline substituents has also been applied to monophthalocyaninato transition metal complexes [54].

## 4. Applications and devices

### 4.1. Car rear-view mirrors

There are 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 [2, 3]. In the field of electrochromic data displays, the 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. The only widespread commercially available device at present is the car rear-view mirror (Nikon's costly electrochromically adjustable dark glasses on sale around 1990 were soon withdrawn). The all-solid mirror described in the literature [2] has not yet achieved distribution, but of liquid-state devices, more than 27 million Gentex mirrors [7] have been sold since inception, from work started in 1974. Their operation may be described as follows. The reflecting surface adjoins one of the two facing conductive-glass electrodes. These, spaced in parallel, make up the cell, which contains the all-liquid system; the two dissolved electrochromes colorize on oxidation and reduction respectively, one at each electrode, so that both electrodes are electrochromic. The cathodic coloring reaction is presented in Equation



where  $\text{Bipm}^{2+}$  represents a colorless bipyridilium ion. The solubility of the  $\text{Bipm}^+$  and the color evoked depend on attached substituents. Where the ionic species is ohmically driven to the cathode. The anodically coloring species, which may be of the Wurster's Blue type, are neutral in charge and thus diffuse to the electrode in a chemical-potential gradient created by the driven process at the cathode. The resulting intensely dark blue-green color permits only the outline of otherwise dazzling headlights to appear. Each colored species one now electron-deficient, the other electron-rich, compared to their initial states diffuses away from its colorconferring electrode, and some molecules collide in solution in mid-cell to undergo mutual electron transfer, both thereby losing color. Maintenance of color intensity hence requires a small current, negligible in a car, to continuously generate the colored species. This lack of memory effect the fading of color on disconnection of current-is an advantage. A minor chemical complication is that both electroactive species undergo some disproportionation, e.g., for bipyridiliums [55],



thus the particular bipyridilium or oxidizable species used requires a stable di-reduced (here  $\text{Bipm}^0$ ) or di-oxidized byproduct to avoid material loss. Reversible cyclic voltammetry are indicative of long-term device stability [7].

Here the anode connection is made to the top and the cathode to the bottom contact. The control system ensures that it is only at night that the darkening reaction is effected. For external mirrors a single glass plate is employed, the second electrode being an inert metal, acting also as reflector.

### 4.2. Windows

A compelling motivation for achieving the manufacture of electrochromic windows either for cars (including sunroofs), but more importantly for buildings, is the huge possible saving in air-conditioner fuel costs worth many billions of dollars per annum. It has been noted earlier [4] that only the totaly reflective state, as can be attained in  $\text{WO}_3$  (alas irreversibly) by heavy ( $>20\%$ ) reduction, completely prevents heat inflow. The merely

colored state of ordinary electrochromism, as with lightly reduced  $\text{WO}_3$ , acts by absorbing the radiation and hence itself becoming heated. Liquid systems present problems on the large scale and polymer gels are needed. Similar electrochromes to those in their mirrors we surmise are in use by Gentex [7]. For window purposes the systems are undergoing extensive sunlight-exposure tests in Arizona on larger expanses of the double-wall glass cells of size 11"x 14", i.e., 28 x 35  $\text{cm}^2$ ; these dim from 80% transmission to 4% transmission in a few minutes, and a sample tested for over a year in Florida.

Specimens twice this area are also under test, and a large 1 x 2  $\text{m}^2$  prototype window has been constructed (Fig. 9). The small sized samples shown in „on” and „off” states in Figure 10 illustrate the variety of colors accessible from chemical modifications of the molecules used by Gentex.

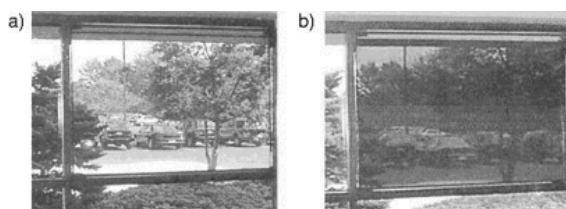


Fig. 9. Gentex window 1 x 2  $\text{m}^2$ : a) clear and b) darkened

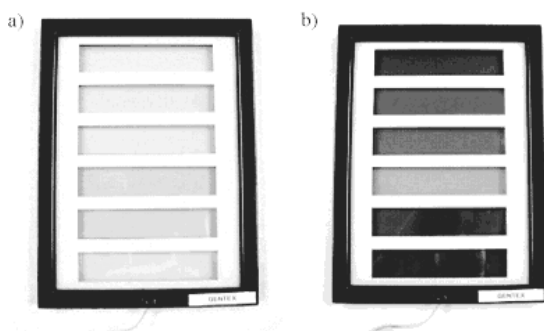


Fig. 10. Available Gentex colors, in off (a) and on (b) states

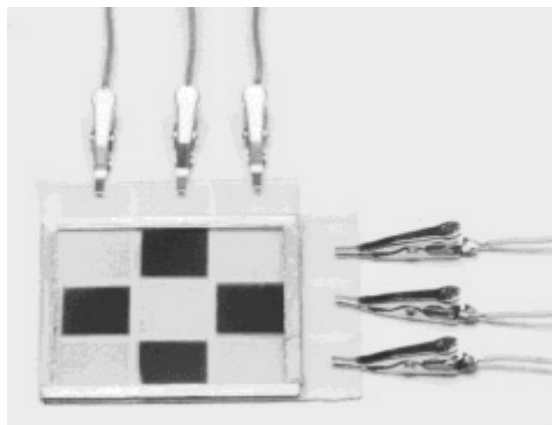


Fig. 11. Pixel array showing no cross-talk between close pixel elements, with solution-phase electrochromes

### 4.3. Displays

The requirement for addressable pixels, each comprising separate potentially electrochromic electrodes, is a complexity being tackled at present, e.g., Figure 11, where dissolved electrochromes at a 3 x 3 matrix of electrodes with six inputs operate without cross-talk, the unconnected pixels experiencing insufficient potential for coloration spread to ensue [56], even though the electrochromes (TMPD and heptylviologen) are always in solution. Large-scale traffic direction boards, rail and airport departure boards, and the myriad advertisements seen about sports-fields and elsewhere could ultimately be electrochromically operated.

### 4.4. Remarkable display and actuator

A remarkable display system of polypyrrole (PPy) on silicon has been shown [57] in which a pixel comprises a platelet of Si segregated by suitable etching processes from its surrounding parent wafer (Fig. 12). It is attached to the wafer by the gold layer of a PPy/gold bilayer abutting both pixel and its surround; the PPy (previously electrodeposited) is outermost. This bilayer prospectively forms a hinge between Si surround and Si platelet. In contact with electrolyte in a cell the PPy can be oxidized and reduced, allowing the change in volume of this side of the bilayer to cause the Si platelet to rotate from the plane of the wafer. The gold is etched so that connection to the hinge is separate from connection to the colorizing PPy+ deposited on the face of the platelet. The angle of rotation (up to at least  $170^\circ$ ) alters the depth of PPy+ viewed, which thereby changes its perceived color. The PPy had been deposited together with the large dodecylbenzenesulphonate (DBS) anion that remains lodged within the polymer, thus compelling the redox process to be

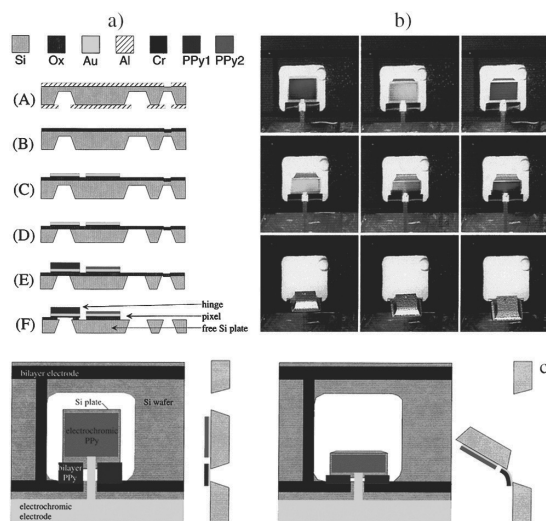


Fig. 12. The “hinged silicon flap” coated with PPy, constructed on a silicon chip. The hinge is a gold/PPy bilayer, operated by redox reaction of PPy, which has different molar volumes in the two redox states, hence effecting opening and closing of the hinge [57]. a) Schematic of the fabrication, b) snapshots taken during operation, and c) operating principle

A number of applications besides electrochromism is envisaged [57].

#### 4.5. A thermal-exposure indicator for frozen foodstuffs

A thin electrochromic cell can be attached as a part of the labeling of the frozen foodstuffs. The cell could have dual-layer conductive electrodes, one possibly a metal segment, the other transparent, either one bearing an electrochrome  $\text{WO}_3$ , with an intervening ion-bearing polymer electrolyte,  $\text{LiClO}_4$  or  $\text{ZnI}_2$ , in oxomethylene-linked polyethylene glycol. The composition of the cell is chosen so that it remains in the uncolored state when the foodstuff is frozen: the polymer electrolyte is such as to be virtually non-conductive at low temperature. The composition of the polymer electrolyte is chosen to have just the right temperature coefficient of conductivity so that, on warming, increased conductivity allows electrochromism to set in, thus warning of the thermal deterioration of the goods. The higher the temperature and/or the longer the exposure, the more intense could the color become and hence the greater the deterioration demonstrated. After accidental thermal exposure, re-freezing does not dispel the coloration. The conductivity temperature-coefficient of the electrolyte, expressible as an activation energy  $E_a$ , is adjusted by choice of polymer length and the kind and concentration of salt content to match the robustness or sensitivity of the sample goods to thermal deterioration. The degree of deterioration relates directly to the extent of coloration by integrating the rate expressed in Arrhenius form over time.

The prototype constructed [58] did not indicate exposure via color intensity; rather, the deterioration was shown by the length turned blue on a  $\text{WO}_3$  strip, thus avoiding the need of a calibration chart. Furthermore, in order to furnish the cell with its own driving potential, reactive metals Li or Zn were employed, to drive electrons to the  $\text{WO}_3$  when warming of the polymer electrolyte allowed sufficient ionic conduction. This device prototype seems to be a highly ingenious and exceedingly promising application of electrochromism.

## 5. Conclusions

Electrochromic materials have the property of a change, evocation, or bleaching of color as effected either by an electron-transfer (redox) process or by a sufficient electrochemical potential. Usually materials are considered as being electrochromic when they showed marked visible color changes. The field of electrochromism is rapidly expanding both in novel systems or applications. Recent interest in electrochromic devices for multispectral energy modulation by reflectance and absorbance has extended the working definition. Electrochromic devices are now being studied for modulation of radiation in the near infrared, thermal infrared and microwave regions and color can mean response of detectors of these wavelengths, not just the human eye. The representative examples of electrochromic materials may be useful from the metal oxides, viologens (in solution and as adsorbed or polymeric films), conjugated conducting polymers, metal coordination complexes (as polymeric, evaporated, or sublimed

films), and metal hexacyanometallates. It is shown the possibilities of using this effect in different applications. Examples of the applications of such electrochromic materials are described. Other materials aspects important for the construction of electrochromic devices include optically transparent electrodes, electrolyte layers, and device encapsulation. Commercial successes, current trends, and future challenges in electrochromic materials research and development are summarized.

In this article the main emphasis has been on the major classes of organic electrochromic materials, although it should be recognized that many other electrochromic compounds have been reported including carbazoles, methoxy-biphenyls, quinones, pyrazolines, tetracyano-quinodi-methane (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.

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