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# *Solar Control*
# *Solid Organic Electrochromic Films*

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# INDEX

## INTRODUCTION

## CHAPTER 1

**Electrochromism**

## CHAPTER 2

**Solid Thermoplastic Laminable Electrochromic Film**

**CHAPTER 3**

**Electrochromic Properties of a New Bipyridinylium Derivative**

## CHAPTER 4

## Photoelectrochromic Behaviour of a Spirooxazine Based Organic Film

# INTRODUCTION

Until recently, clear glass was the primary glazing material used to commercially produce windows. Although glass is durable and allows a high percentage of sunlight to enter in buildings, it has very little resistance to heat flow. During the past two decades, glazing technology has greatly changed. Research and development into types of glazing have created a new generation of materials that offer improved window efficiency and performance for consumers. While this new generation of glazing materials has quickly gained acceptance in the marketplace, the research of even more efficient technologies is continuously developing . Today, several types of advanced glazing systems are available to help control heat loss or gain. The advanced glazings include double- and triple-pane windows with coatings such as low emissivity (low-e), spectrally selective, heat-absorbing (tinted), or reflective gas-filled windows~~,~~ and windows incorporating combinations of these options. Low-e glazings have special coatings that reduce heat transfer through windows. The coatings are thin, almost invisible metal oxide or semiconductor films that are placed directly on one or more surfaces of the glass or on plastic films between two or more panes. When applied inside a double-pane window, the low-e coating is placed on the outer surface of the inner pane of glass to reflect heat back into the living space during the cooling season. This same coating slightly reduces heat gain during the heating season. Windows manufactured with low-e films typically reduce energy loss by as much as 30% to 50%. Selective (optical) coatings are considered to be the last generation of low-e technologies. These coatings filter out from 40% to 70% of the heat normally transmitted through clear glass, while allowing the full amount of light to be transmitted. Spectrally selective coatings can be applied on various types of tinted glass to produce "customized" glazing systems capable of either increasing or decreasing solar gains according to the aesthetic and climatic effects desired. Another technology uses heat-absorbing glazings with tinted coatings to absorb solar heat gain. Some heat, however, continues to pass through tinted windows by conduction and reradiation, but inner layers of clear glass or spectrally selective coatings can be applied with tinted glass to further reduce this heat transfer. Heat-absorbing glass reflects only a small percentage of light and therefore does not have the mirror-like appearance of reflective glass. Gray- and bronze-tinted windows reduce the penetration of both light and heat into buildings in equal amounts and are the most common tint colours used. In hot climates black-tinted glass should be avoided because it absorbs more light than heat. Like black-tinted coatings, reflective coatings greatly reduce the transmission of daylight through clear glass. Although they typically block more light than heat, reflective coatings, when applied to tinted or clear glass, can also slow the transmission of heat. Reflective glazings are commonly applied in hot climates in which solar control is critical; however, the reduced cooling energy demands they achieve can be offset by the resulting need for additional electrical lighting. Chromogenic (optical switching) glazings is still under development to meet frequent changes in lighting and heating or cooling requirements of buildings. These "smart windows" can be separated into either passive or active glazing categories. Passive glazings are capable of varying their light transmission characteristics according to changes in sunlight (photochromic) and their heat transmittance characteristics according to ambient temperature swings (thermochromic). Active (electrochromic) windows will use a small electric current to alter the transmission properties.

The main purpose of this thesis has been to explore these smart materials (electrochromic and photochromic glazings) which are able to perform solar control both in active and passive mode. New kind of devices operating in the latter mode have been realized performing the optimization of the optical parameters. In particular a new solid organic electrochromic film was obtained by simply doping preformed thermoplastic polymers with electrochromic molecules and plasticizers.

In the first part of this research the characterization of the electrooptical properties of this new ECD was performed, in order to explore operational mechanisms and to optimize electrochromic parameters such as contrast ratio, response times and thickness. In particular, the effect of charge-transfer (CT) complex formation between electrochromic molecules on the rates of bleaching of the ECD was studied. Adjusting the percentage of electron-donor molecules in the chemical formulation, it was possible to modulate the spontaneous bleaching times of the electrochromic film. This behaviour can be ascribed to the formation of a very stable complex between the electrochromophore viologen (electron-poor) and anodic molecules (electron-rich). The effect on the response times of various charge-donor molecules with different rate constants of dissociation of the charge-transfer complex, was explored.

Some applications for electrochromic devices need particular anti-glare properties, as car rear-view mirrors. In these systems the adjustment of the optical absorption spectrum of the electrochromophore is very important. Under normal lighting conditions, the human eye is most sensitive to a greenish yellow colour, or more exactly, the human eye sensitivity curve is peaked at 550 nanometers. For this reason, to have an electrochromic substance in which the coloured form is characterized by a $\lambda_{max}$ at approximately 550 nm in the absorption spectrum, is the optimum for devices requiring anti-glare properties. In the second part of this research, the electrochromic behaviour of 1-(11-heptanoyloxyundecyl)-[4,4']bipyridinyl-1-ium dibromide (HBB) was explored. The absorption of the green-yellow part of visible spectrum, which is more desirable for anti-glare applications, was obtained in the case of a cell based on this new electrochromic bipyridinium salt synthesized in the laboratory of “New organic syntheses via organometallic catalysis” of University of Calabria. Some problems concerning the stability of HBB was also studied, in order to optimize ECD based on this molecule. In fact, this chromophore is almost reactive and this causes problems on the performance of the electrochromic anti glare device.

In the final part of this research, the possibility to obtain a bifunctional photoelectrochromic device was explored and characterization of its electrooptical properties was performed. Photoelectrochromic materials change colour both on absorption of light and on application of an external electric field, so these materials are interesting for solar control, in fact they can be used both in passive way (switched by sunlight), or by an active way (switched by a voltage). A bifunctional device using a spirobenzopyran derivative dissolved in a thermoplastic polymer was obtained and the spectroelectrochemical characterization of this solid film was performed, as discussed in chapter 4. This system is very innovative because no photoelectrochromic device made by a single active molecule was obtained before. In particular, in chapter 4 the optimization of response times and contrast ratio are described. These parameters are closely related to the presence of the appropriate electrochemical counterpart for spirobenzopyran.

# CHAPTER 1

# ELECTROCHROMISM

## 1.1 Introduction

An electroactive species often exhibits new optical absorption bands in accompaniment with an electron-transfer or redox reaction in which it either gains or loses an electron. Such colouration was first termed “electrochromism” in 1961 by Platt[1] whose discussions were amongst the first published. Byker has discussed the historical development of electrochromism[2].

Many simple species exhibit electrochromism. To take a laboratory example, the ferrocyanide ion in aqueous solution is pale yellow in colour, but on electrochemical oxidation:

$$\underset{\text{(pale)}}{\left[\mathrm{Fe^{II}(CN)_6}\right]^{4-}} \rightarrow \underset{\text{(yellow)}}{\left[\mathrm{Fe^{III}(CN)_6}\right]^{3-}} + \mathrm{e^-}_{\text{electrode}} \qquad (1.1)$$

a pool brilliant yellow forms around the electrode, and thence diffuses into the bulk. The change in colour is directly attributable to the oxidation of iron(II) to iron(III) in the complex. A somewhat different case is ferrous ion in aqueous solution , in the presence of thiocyanate with which $Fe^{2+}$ is only weakly complexed. Initially the solution is colourless, but a brilliant blood-red colour appears after oxidation on the formation of electro-generated iron (III). In this case, the colour may not be directly electro-generated, but is possibly due to interaction between electro-generated $Fe^{3+}$ and the electro-inactive $CNS^-$ion in solution: it is the iron(III) thiocyanate charge-transfer complex that ultimately provides the colour. In this context, a "charge-transfer" species is one in which a photo-effected transfer of charge within the species, sometimes between species, evokes colour, by "optical charge-transfer".

The simplest electrochromic light modulators have two electrodes directely in the path of the light beam. If both electrodes bear an electrochromic layer, then the colour formation within the two must operate in a complementary sense, which can be illustrated here with the example of $WO_3$ and vanadium pentoxide: $WO_3$ becomes strongly coloured (blue) when oxidised. By contrast, $V_2O_5$ is a rich brown/yellow colour when oxidised, yet faintly coloured (blue) when reduced. In an electrochromic device (ECD) constructed with these materials, one oxide layer is present in its reduced form while the other is oxidised; thus the operation of the device is:

$$\overbrace{WO_3 + M_X V_2 O_5}^{\text{bleached}} \rightarrow \overbrace{M_X WO_3 + V_2 0_5}^{\text{coloured}} \qquad (1.2)$$

(pale yellow) (pale blue) (blue) (brown)

The tungsten-oxide is termed the *primary* electrochrome since it is the more strongly coloured species and, in this example, $V_2O_5$ acts as the *secondary*[3].

## 1.2 Electrochromic parameters

Visible light can be viewed as electromagnetic waves of wavelength 420 nm (violet) to 700 nm (red) or equivalently[4] as particulate photons of energy $4.7 \times 10^{-19}$ J (violet) to $2.8 \times 10^{-19}$ J (red). The colours cited refer to light directly entering the eye. However, colour is a subjective visual impression involving retinal responses of the eye to particular wavelengths of the impinging light (table 1.1). Light comprising all visible wavelengths appears white. Reflected colours result from absorption by the reflecting material of some of these wavelengths, that is, from subtraction from the full wavelength range comprising incident white light. In with light, the perceived colour of a material is the complementary colour of the light it absorbs (figure 1.1)[5,6].

A single wavelength of absorption is encountered only with single-atom or single-ion photon absorption, the photon energy being transformed into internal electronic energy by the excitation of an electron between precise energy levels associated with the two orbitals accommodating the electron before and after the photon absorption, or "transition" as it is termed. In molecules the energy levels involved are somewhat broadened by contributory vibrational (and to a lesser extent, rotational) energies. Thus, on light absorption, transitions occur between two "spreads" of energy levels, (of, however, narrow spread) allowing the absorption of photons with a restricted range of energies, that is, of light a restricted range of wavelengths, giving an absorption *band*. The maximum absorption, roughly in the centre of such a band, corresponds to the "average" transition.

The target molecule here is called a *chromophore,* and when the colour resulting from absorption is evoked electrochemically, an *electrochromophore* or more briefly, an *electrochrome.*

The absorption spectrum of a substance represents the relative intensity (relative number of photons) absorbed at each wavelength.

| | **$\lambda$/nm** | **$\lambda^{-1}$/cm$^{-1}$** | **$10^{-14}\nu$/s$^{-1}$** | **h$\nu$/eV** | **$10^{19}$h$\nu$/J** | **Lh$\nu$/kJ mol$^{-1}$** |
|---|---|---|---|---|---|---|
| | 750 | 13,300 | 4.00 | 1.65 | 2.65 | 159 |
| Red | | | | | | |
| | 635 | 15,800 | 4.72 | 1.95 | 3.13 | 1.88 |
| Orange | | | | | | |
| | 596 | 16,800 | 5.03 | 2.08 | 3.33 | 200 |
| Yellow | | | | | | |
| | 580 | 17,200 | 5.17 | 2.14 | 3.42 | 206 |
| Green | | | | | | |
| | 520 | 19,200 | 5.77 | 2.38 | 3.82 | 230 |
| Blue | | | | | | |
| | 470 | 21,300 | 6.38 | 2.64 | 4.23 | 255 |
| Indigo | | | | | | |
| | 440 | 22,700 | 6.81 | 2.82 | 4.51 | 272 |
| Violet | | | | | | |
| | 390 | 25,600 | 7.69 | 3.18 | 5.09 | 307 |
| UV | | | | | | |

**Table 1.1** *Wavelength and energy ranges for perceived colours of emitted light. The numbers above and below each colour represent its range.*

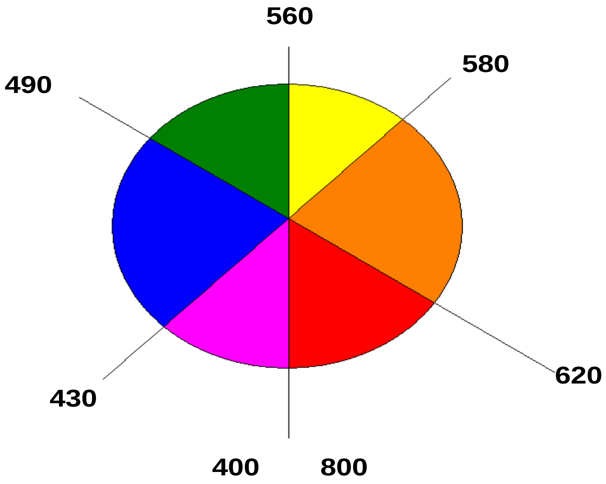

**Fig. 1.1** *Approximate wavelength (in nm) of reflected colours. Colours in directly opposite segments are called complementary.*

The Beer-Lambert law[7] for optical absorption relates the absorbance, expressed as log of the ratio of the intensities, to the concentration *c* of chromophore and optical pathlength *l* through the sample:

$$A = \log\left(\frac{I_0}{I}\right) = \varepsilon c l \tag{1.3}$$

The proportionality factor ε is the molar extinction coefficient or molar absorptivity of the absorbing species. From the preceding account, it should be clear that ε will vary with wavelength λ since A does, and it is the parameter quantifying the strength of the optical absorption at each wavelength. ε(λ) (the value at wavelength λ) and $\varepsilon_{max}$ (the value at the maximum, often written without subscript) will depend on solvent, or solid matrix, to a greater or lesser extent. When the absorption results from optical CT, Kosower's parameter Z[8], which is the energy (inverse wavelength) for the maximum absorption of a particular chromophore in a given solvent, varies with solvent in a manner followed proportionately by other similar chromophores, Z is a useful indicator of solvation in the chromophore-solvent system involved, which will clearly determine the transition energy, that is, where the absorption maximum occurs.

The absorption can thus arise from photo-excitation of an electron from a lower (or ground-state) energy level to a higher one either in the same molecule, which is an *intramolecular excitation*, or within a neighbouring moiety, which involves an intermolecular interaction termed *optical charge-transfer.* The redistribution on photon absorption of electron density in the absorbing species is more or less exactly depends on the *transition moment* M. M is measured from the area of the absorption band; the molar absorptivity at the maximum is commonly taken as being proportional to M.

The most intense optical absorptions are often a consequence of optical CT, since like intramolecular electronic transitions these are processes "allowed" by wave mechanical selection rules for spectral transitions.

In any electrochromic system, a quantitative measure of the intensity of the colour change is required. That commonly used is the contrast ratio CR:

$$\mathrm{CR} = \frac{\mathrm{R}_0}{\mathrm{R}_x} \tag{1.4}$$

where $R_x$ is the intensity of light diffusely reflected through the coloured state of the display, and $R_0$ is the intensity of light diffusely reflected from the bleached (uncoloured) state from a (diffuse) white black plate[9].

In transmission mode, the optical absorption of an electrochromic film is related to the injected per unit area Q (assuming no side reactions) by an expression akin to the Berr-Lambert law, since Q is proportional to the number of colour centres:

$$A = \log\left(\frac{I_0}{I}\right) = \eta Q \qquad (1.5)$$

where $\eta$ is the "colouration efficiency" of the film. A CR of less than 2 or 3 is not easily perceived by eye, and as high a value as possible is desirable. Commonly CR is expressed as ratio, and is best measured at the wavelength of maximum absorption by the coloured state.

Where there is a great difference in colour between the two redox states, but both are highly coloured, then the contrast is not perceived to be great. In this case, the CR is highly wavelength dependent.

The colouration efficiency $\eta$ is related to an optical absorbance change $\Delta A$ via equation (1.5), and to the linear absorption coefficient $\alpha$, film thickness $d$ and charge injected $Q$ per unit area, by the relationship[10]:

$$\eta = \left(\frac{\alpha d}{Q}\right) = \frac{\Delta A}{Q} \qquad (1.6)$$

In the use of these equations, it is assumed that all optical effects are absorptive, that only a single absorbing species is effective at the wavelength chosen for monitoring, and that the Lambert-Beer law is obeyed. $\eta$ may be regarded as that electrode area which may be coloured to unit absorbance by unit change. $\eta$ is designated as positive for cathodically induced colouration (by electron gain, or reduction) and negative for anodic colour formation (by electron loss, i.e. oxidation).

If $\eta_p$ is the colouration efficiency of the primary electrochromophore, and $\eta_s$ that of the secondary, then the colouration efficiency $\eta_o$ of the complete ECD device is obtained as $\eta_0=(\eta_p-\eta_s)$. For the most intense electrochromism, the parenthesized entity should be maximised, that is, a large change in A is required for injection of a small charge. This may be achieved in two ways, either by using a large $\eta_p$ together with an $\eta_s$ of the opposite sign (i.e. complementary electrochromism), or by using a combination of large $\eta_p$ and small $\eta_s$ both of the same sign. In other words, both electrodes colourise simultaneously or unwanted colour in one electrode is feeble.

In general, organic electrochromes exhibit a greater $\eta$ than do inorganic species because the molar absorbivities of the former are usually higher.

The write-erase efficiency is the percentage of the originally formed colouration that may be subsequently electro-bleached; it can be conveniently be expressed as a ratio of absorbance changes. For a successful display, the efficiency should closely approach 100%. Species remaining in solution in both coloured and uncoloured states, such as methyl viologen, diffuse from the electrode surface after electro-colouration. Since bleaching of such an ECD requires all the coloured materials to diffuse back to the electrode for electrooxidation, which relatively slow process, the write-erase efficiency on a pratical time-scale is poor for all-solution systems.

The time required for an ECD to colour from its bleached state to (or vice versa) is termed its response time $\tau$. For most devices, $\tau$ values are of the order of few seconds. For ECDs in general, $\tau$ is slower than for either LCDs or CRTs, usually because of the necessity for diffusion, either of charged species through the electrode film or, for all-solution systems, of the electrochrome to the electrode. In applications such as electrochromic windows or mirrors, response times of seconds can be tolerated, but if devices such as optical switches or television screen are envisaged, then very fast response times will be necessary.

Unfortunately, there is no consistency in the criteria employed for determining $\tau$: it may be the time necessary for some fraction (arbitrary or defined) of the colour to form, such as indicated by a particular increment of optical density, or the time for all or part of the charge to be injected.

An other important electrochromic parameter of ECD is its stability. When an ECD is continually cycled between its coloured and bleached states, device failure will eventually occur resulting from physical changes in solid phases or from chemical side reactions. The *cycle life* is a measure of its stability, being the number of cycles possible before such failure. The cycle life is a complicated function of the colouration required in the cycle: the cycle life generally decreases if wide changes in composition are required, that is if the quantity of charge injected or removed is large.

## 1.3 Electrochemistry and mechanism of electrochromic sistems

The electron-transfer process during colouration is denoted by *anodic* or *cathodic:* cathodically colouring materials form colour when reduced at an electrode made negative, a *cathode*, and anodically colouring electrochromes are colored at an *anode,* or positive electrode.

The electrode potential for the electrochromic redox couple is related to the ratio of their respective concentrations by a form of Nerst equation:

$$E_{Ox,Red} = E^{0}_{Ox,Red} + \frac{RT}{nF}\ln\left(\frac{[Ox]}{[Red]}\right) \tag{1.7}$$

where concentrations are denoted by square brackets, $R$ is the gas constant, $F$ the Faraday constant, $T$ the thermodynamic temperature and $n$ is the number of electrons involved in the electron transfer reaction. $E^0$ is the *standard electrode potential,* and is defined as the electrode potential measured at standard pressure and temperature, with both Ox and Red present at unit concentration (or formally and more accurately, at unit activity[11]).

In an electrochromic cell current flows when appropriate ranges of potentials are applied. Such current will comprise two components, faradaic and non-faradaic. The former current is directly linked with the sum of the electron-transfer reactions effected, and the charge (current-time integrated) indicates directly the extent of the cell reaction, since faradaic current involves that charge which yields product.

Electrochromic operation involves the quantity of electrochrome that changes redox state on passage of current, as governed by Faraday’s laws, which are as follows.

1. The number of moles of species formed at an electrode during electrode reaction is proportional to the charge passed;
2. A given charge liberates (or deposits) masses of different species in the ratio of their “equivalent weights” (relative molar masses divided by the number of electrons involved in the electrode reaction).

Non-faradaic current is caused by processes such as charging of the electric double layer at the electrode-solution interface (a local separation of unreactive-solute ions into layers of anion and cation partly governed by application of potential, which results in excess accumulation of ions of one particular charge sign at interfaces). In precise mechanistic descriptions of electrode processes, double layer effects need to be taken into account; this may be complicated.

The rate of electron-transfer at an electrode is a function of the gradient of electric potential applied to the electrode, and follows the Butler-Volmer equation[11,12] which, for a reduction reaction Ox + ne$^-$ $=$ Red is

$$i = nFAk_f c_R (\exp(-\alpha_f n\Theta\eta)) - nFAk_b c_O (\exp(\alpha_b n\Theta\eta)) \qquad (1.8)$$

where, for brevity, $\Theta$ = F/RT; $c_O$ is the concentration of the oxidised form of the electroactive species (starting material) and $c_R$ that of the reduced form; $\alpha$ is a fraction termed the transfer coefficient (subscripted f and b for forward and back reaction respectively), itself a measure of the symmetry of the energy barrier to the electron transfer[1]; $\eta$ is the overpotential, ($E - E_{OC}$), where $E$ is the potential applied to the electrode and $E_{OC}$ is the zero-current electrode potential. $k_f$ and $k_b$ are the rate constants of electron transfer for the forward and back processes.

### 1.3.1 Semiconducting electrodes

In the construction of electrochromic display devices, the substrate most commonly used as the optically transparent electrode (OTE) is indium thin oxide (ITO) as a thin film on glass. The thickness of the ITO layer is typically 0.3 μm. Indium(III) oxide, when doped whit *ca.* 8% tin(IV) oxide, is a semiconductor[13] of conductivity *ca.* 8 x $10^{-4}$ Scm$^{-1}$, so the thickness and exact conductivity of the ITO layer will affect the ECD response time. The rate of supply (flux *j*) of electrons through the conductor and corresponding current *i* are obtained from the general applicable equations:

$$\mathrm{i = nAve} \qquad \text{and} \qquad \mathrm{j = n\nu} \qquad (1.9)$$

where *n* is the number density of charge carriers, *A* the cross-sectional area of the conductor, *v* the electronic velocity and *e* the electronic charge. In thin-film indium thin oxide (ITO), the number of charge carriers is relatively small, restricting the rate of charge uptake or loss of the ITO/electrochrome interface. However, some authors believe that the response time of an ECD device with very thin films of ITO depends rather on the rate of electron transport, that is, *v*, through the ITO[14,15].

### 1.3.2 Mass transport

Before the electron-transfer reaction can occur, of necessity material must move from the solution bulk and approach close to an electrode. This movement is "mass transport", and proceeds via three separate mechanisms: migration, convenction and diffusion. Mass transport is formally defined as the flux $j_i$ of electroactive species *i* to an electrode, as defined in the Nerst-planck equation:

$$j_i = \underbrace{\mu_i c_i \left( \frac{\partial \phi}{\partial x} \right)}_{\text{migration}} + \underbrace{c_i \overline{v_i}}_{\text{convenction}} - \underbrace{D_i \left( \frac{\partial c_i}{\partial x} \right)}_{\text{diffusion}} \tag{1.10}$$

where $\mu_i$ is the ionic mobility of the species $i$; $\Phi$ is the strength of the electric field, $\overline{v_i}$ is the velocity of solution, and $D_i$ and $c_i$ are respectively the diffusion coefficient and concentration of species $i$. Convenction will not concern us further since it is irrelevant for solid electrolytes and otherwise uncontrolled in other ECDs.

Migration is the movement of ions through solution or solid in response to an electric field, an anode attracting any negatively charged anions, the cathode attracting the cations. For liquid electrolytes containing an excess of unreactive ionic salt, migration may be neglected since the transport number of the electroactive material becomes negligibly small. Migration is an important form of mass transport for ionic movement within solid polymer electrolytes or solid-solution electrochromic layers since transport numbers of the electroactive species become appreciable[15]. The phenomenon of electrode "polarisation" by excess unreactive electrolyte (the build up of concentration of oppositely-charged electrolyte ions at an electrode) brings about diminution then suppression of migration; diffusion is the only remaining means of approach to the electrode available to a possibly electroactive species, as follows.

Of particular interest to any kinetic study is the diffusion coefficient $D$ of the diffusing species, being representative of its spontaneous motion. Diffusive behaviour obeys Fick's laws[11,12], the first being for the flux $j_i$,

$$j_i = -D_i\left(\frac{\partial c_i}{\partial x}\right) \tag{1.11}$$

where $(\partial c_i/\partial x)$ is the concentration gradient, the change in concentration of species *i* per unit distance. In electrochemical processes, $(\partial c_i/\partial x)$ arises (i.e. is non-zero) because some of the electroactive species is consumed around the electrode; diffusion is evoked by subsequent concentration gradient.

Fick's second law describes the time dependence of diffusion:

$$\left(\frac{\partial c_i}{\partial t}\right) = D_i\left(\frac{\partial^2 c_i}{\partial x^2}\right) \tag{1.12}$$

The required integration of the second order differential equations often leads to difficulty in the accurate modelling of diffusive systems. However, a useful approximate solution to Fick's second law gives

$$l = \sqrt{D_i t} \tag{1.13}$$

where $D_i$ is the diffusion coefficient of species *i*, and *t* is the time required for species *i* to move a distance *l*.

Another indicator of the rate of ionic movement is the ionic mobility $\mu$ (velocity $v$ divided by driving field), which is related to the diffusion coefficient D by the Nernst-Einstein equation

$$\frac{D}{\mu} = \frac{k_B T}{ze} \tag{1.14}$$

where symbols have their usual electrochemical meanings and $k_B$ is the Boltzmann constant.

When the impressed potential of an electrode is stepped from a value giving zero current to one at which the current can reach a maximum, then all the electroactive material at the electrode-solution interface will undergo electrochemical change "instantly". Electroactive material from the solution bulk then diffuses toward the electrode, coming (diffusing) from successively further distances from the electrode. The flux at the electrode therefore decreases with time. The Cottrell equation[16] describes this current/time response as

$$i = nFA\sqrt{\frac{D}{\pi t}} \tag{1.15}$$

The Cottrell equation is a convenient means of determining diffusion coefficients of solution-phase species[11].

### 1.3.3 Voltammetry

In electrochemistry of equilibrium (zero-current) the prospect of transfer of electron remains latent and the amounts of electrochrome present do not change, and thus study of the actual electrochromic colouration reaction is precluded. To allow these studies, *dynamic* electrochemistry is used, in which current is passed in a controlled way, by applying a potential $E$ to a particular electrode that is different from the steady value, which we know re-label $E_{OC}$. The subscript OC means "open circuit" (implying conjunction only to a voltmeter); $E_{\text{cell}}$ is equivalently an open-circuit or zero-current value.

Voltammetry is the most common of these dynamic techniques and is useful for discerning rates and mechanism, in addition to the thermodynamic data related to $E_{\text{cell}}$ and $E^{o}$ usually obtained at zero current or open circuit. Processes occurring at one electrode are monitored by observing the current change when the potential applied to that electrode (actually between the electrode and the counter-electrode) is varied steadily trough a range which evokes an electron-transfer process. The current is recorded as a function of the potential impressed on the electrode. The potential is varied steadily, the rate *dE/dt* being kept constant know a either the *scan rate* or the *sweep rate, v.*

The electrode at which the electrochemical changes of interest occur is called the *working electrode,* WE. In order that the potential at the WE be known, the potential difference $E$ between the WE and a third *reference* electrode, RE, is taken. The saturated calomel electrode (SCE) is usually employed as reference. The scan rate is of course referred to the RE.

In equilibrium (zero-current) electrochemical experiments, voltages between the WE and RE are measured via a voltmeter, and the potential recorded as a function of the externally varied concentration of the electroactive species present, according to the Nernst equation (1.7). by contrast, during voltammetry, compositions at electrodes are perturbed by the passage of charge at electrolyte/working electrode interface when electrode reactions occur; while minimum perturbation occurs in electro-analytical experiments, quite substantial changes generally occur in electrochromic processes. If current were to pass trough the RE, then the electrode composition would alter and the electrode potential of the RE would change to give inaccurate potential measurement; in addition, the simple passage of current itself shifts the potential of the electrode. For these reasons, no charge can be allowed to flow trough the RE. A third electrode, the *counter electrode,* CE, is therefore used to complete the current-flow circuit, to obviate the apparent paradox of requiring current passage at the WE while using a zero-current RE. As the third electrode is needed only because current must flow at the WE, the nature and composition of the counter electrode are largely irrelevant to the operation of a voltammetric cell. The potential of the CE is not monitored although electrode reactions must clearly take place at the CE if current is to flow; if oxidation occurs at the WE then reduction occurs at the CE, and vice vers, hence current. Figure 1.2 illustrate the connections.

The control of voltage across the working-electrode/counter-electrode pair is achieved using a *potentiostat.* This device adjusts the voltage in order to mantain the potential difference across the working and reference electrodes (sensed using a high impedance feedback loop). The potential is varied in a pre-programmed manner via a function generator. The potentiostat forces current trough the working electrode to achieve the potential desired.

In voltammetric experiment, an electro-inactive electrolyte is required in excess of the reactant species, in order to carry current trough the cell. Its role at the WE is to affect a kind of charge saturation which forces electroactive species to approach this electrode by diffusion rather than any field-effected conduction process (migration).

In voltammetric experiments, electroactive species depleted by electrode prior to the electron-transfer reaction. Product if soluble diffuses back to the bulk after the electron-transfer reaction is complete.

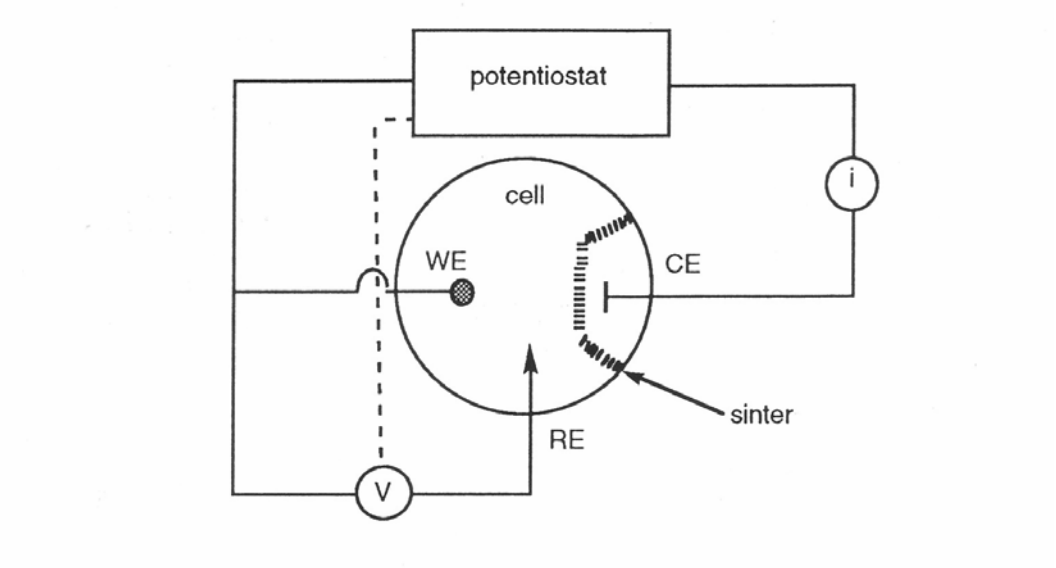

**Fig. 1.2** *Schematic representation of a three-electrode cell for voltammetric use. Here the voltmeter V is in practice part of the control circuitry of the potentiostat, as is implied by the dotted line.*

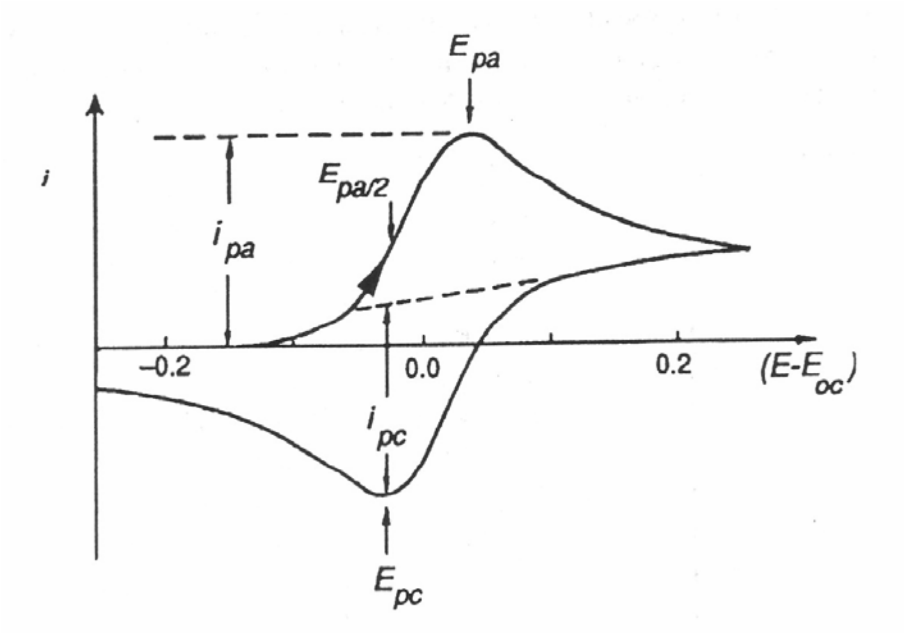

**Fig. 1.3** *Typical cyclic voltammogram (CV) obtained for a simple, reversible redox couple in solution, illustrating the key quantities.*

The flux of material at the electrode dictates the shape of the current-voltage curve (voltammogram) obtained.

We shall be concerned only with the equation for the peak current $i_p$ as derived by Randles and Sevcik[16]:

$$i_p = 0.4463 AnF\left(\frac{nF}{RT}\right)^{1/2} D_i^{1/2} \nu^{1/2} c_i \qquad (1.16)$$

where $A$ is the area of the electrode and $c_i$ is the bulk concentration of the electroactive species. $D_i$ is its diffusion coefficient. This equation is applicable to "reversible" all-solution systems (those undergoing rapid electron-transfer at the electrode). Commonly $i_{pc}$ refears to the peak for a cathodic process, while $i_{pa}$ refers to an anodic process.

The peak in the voltammetrically monitored current $i_p$ here is thus proportional to the concentration of the electroactive species, and to the square root of the scan rate. In *cyclic* voltammetry, the potential is ramped twice: the potential of the WE starts at an initial value $E_{in}$ and is ramped to a limit, $E_\lambda$ known as the *switch potential*, and is then swept back to $E_{in}$. A plot of current against this potential $E$ is then recorded as a *cyclic voltammogram* or CV. A typical CV for a one electron process is shown in Fig. 1.4. The peak potentials for the anodic and cathodic electron-transfer processes are labelled $E_{pa}$ and $E_{pc}$ respectively. The peak separation is 58/n mV for reversible (i.e. rapid) n-electron reactions[11]. The same general shape but with peak separation greater than 58/n mV indicates “quasi-reversibility” resulting from somewhat slow electron-transfer at the electrode, or from intrusive resistance of electrolyte in a cell comprising less than ideal compositions for voltammetry. Conventionally the sign of $v$ is cited as a positive number and the range of scan rates commonly employed in cyclic voltammetry is $1< v<500$ mVs$^{-1}$.

## 1.4 Classification of Electrochrome Type

The type of electrochrome used in ECD governs the kinetic behaviour evinced. A classification is presented here, borrowed largely from an earlier treatment by Chang *et al.*[17]

For “Always is solution” electrochromes, the electrochemical electron-transfer reaction occurs at the solid-liquid interface. The electroactive species in solution encounters the solid electrode, undergoes an electron-transfer reaction, be it reduction at a cathode or anodic oxidation, and then in its new form moves away from the electrode, returning to the solution bulk. The electrochrome changes colour on undergoing the electron-transfer reaction. A simple example of this kind of electrochrome is methyl viologen dication in water. $MV^{2+}$ in the initial solution is colourless (or faint yellow in the presence of some anions), a bright blue radical cation $MV^{+*}$ when the electrode is made cathodic (negative). The rate-limiting process during the (reductive) electron-transfer reaction is the rate at which $MV^{2+}$ dication reaches (diffuse toward) the electrode from the solution bulk, the rate of electron acquisition when $MV^{2+}$ reaches the electrode interface being much faster.

In electrochromic devices on methyl viologen, if a fixed potential, substantially more negative than the (zero-current) electrode potential for $MV^{2+}$ reduction, is applied to the working electrode, then the observed current follows the Cottrell[18] time dependence, $i \propto t^{-1/2}$. This dependence follows from the laws diffusion. Hence the absorbance $A \propto t^{+1/2}$ if the current flow is wholly faradaic, that is, if each electron-transferred generates a colour centre. The *t* exponent follows because the amount of $MV^{+\bullet}$ generated depends on the integral of *I* with time.

In "Solution-to-solid" systems the electrochromes are initially soluble and colourless but, following electron-transfer, they form a coloured solid film on the surface of the electrode. An example of this kind of electrochrome is heptyl viologen (HV). $HV^{2+}$ dication dibromide is pale yellow is pale yellow in aqueous solution but form a layer of deeply coloured radical cation salt on reduction. The reduction is, in fact, a two-step process (possibly concerted[19]) involving first an electron-transfer reaction

$$HV^{2+} + e^{-} \rightarrow HV^{+\bullet} \qquad (1.17)$$

and subsequent precipitation

$$HV^{+\bullet} + X^{-} \rightarrow HV^{+\bullet}X^{-}{}_{(s)} \qquad (1.18)$$

The deposit is initially amorphous but becomes more crystalline soon after formation[20]. The morphology, solubility and colour of such radical-cation salts depend on the accompanying counter anion[20].

The Cottrell current-time relationship of $i \propto t^{-1/2}$ together with $A \propto t^{+1/2}$ is followed fairly closely during short times as soluble $HV^{2+}$ diffuses toward the electrode[21]. At longer times, however, the kinetic response becomes more complicated: $HV^{+\bullet}X^{-}$ is a solid dielectric of relatively poor conductivity, and further colouration involving generation of additional coloured product must proceed via slow electron transport trough the solid deposit at the solution/electrode interface. Again, during electro-oxidative colour erasure of the radical cation salt achieved by the reversal of reactions (1.17) + (1.18), complications, in this system become apparent, which necessitate the presence in the electrochemical deposition solution of electron mediators such ferrocyanide ion which acts catalitically to facilitate electron transfer[22,23].

The most commonly used electrochromes for “All-Solid” systems are Rare-earth phthalocyanines, Prussian blue, and metal oxides, for example, of tungsten, molybdenum, nickel or vanadium. For metal oxides and Prussian blue, the electrogenerated colour appears as a conseguence of an optical charge-transfer transition between metal centres in the solid-state lattice.

The rate-limiting process usually encountered with this type of electrochromes is the ionic charge transport the solid electrochrome. The diffusing species, enters the electrochrome via the electrolyte-film interface and then moves through the film although it does not reach the metal-conductor substrate at the other side of the electrochrome.

Two separate diffusion processes will occur within the solid: both the ion diffusion from the electrolyte/solid interface, and electron from the electrode-electrochrome interface. *Only the slowest, rate limiting, of these diffusion processes will be measurable* in systems in fast electron-transfer in the redox processes.

## 1.5 Electrochromic devices

Many ECDs comprise a sandwich structure of thin layers, the number and nature of which depend on the intended use. The construction of ECDs will be the same whether a large area cell or one small element (pixel) of a multi-electrode array is required[24].

Electrochromism is used in one of two modes: in adjustment of either reflected or transmitted intensity, Fig. 1.4.

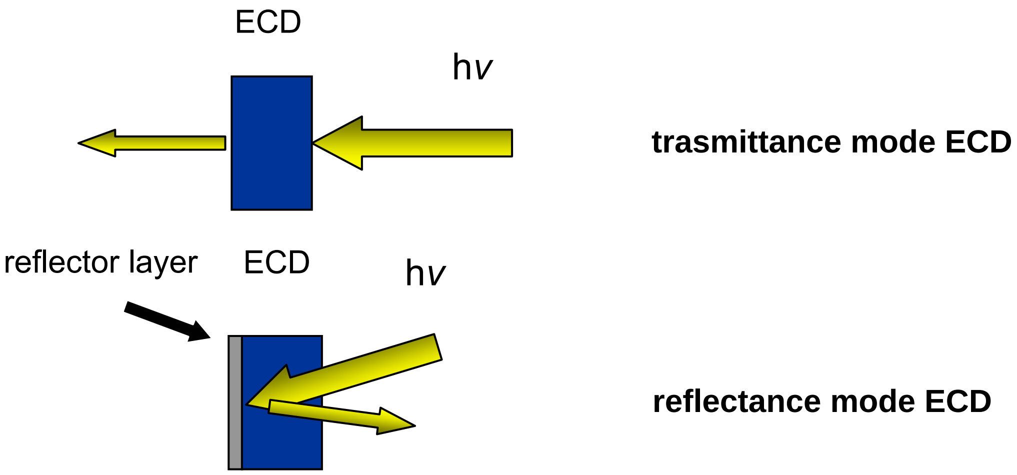

**Fig 1.4** *Schematic diagram showing the different modes of ECD operation.*

### 1.1.1 All-solid cells with reflective operation

For all-solid systems, reflective cells may be assembled according to the schematic diagram in Fig. 1.5. The front panel is an optically transparent electrode (OTE), that is, a solid support, for example glass bearing a thin transparent but conductive film on its solution-facing side. Tin-doped indium oxide (ITO) is commonly employed[25]. Typically about 0.3 μm thick. The glass of chosen thickness may be reinforced to give structural strength. The OTE acts as the conductor of the electrons necessary for the required electron-transfer to take place in the electrochromic material. If the latter is the primary electrochrome, a secondary electrochrome may be deposited on the counter electrode. The layers are deposited by electrodeposition,

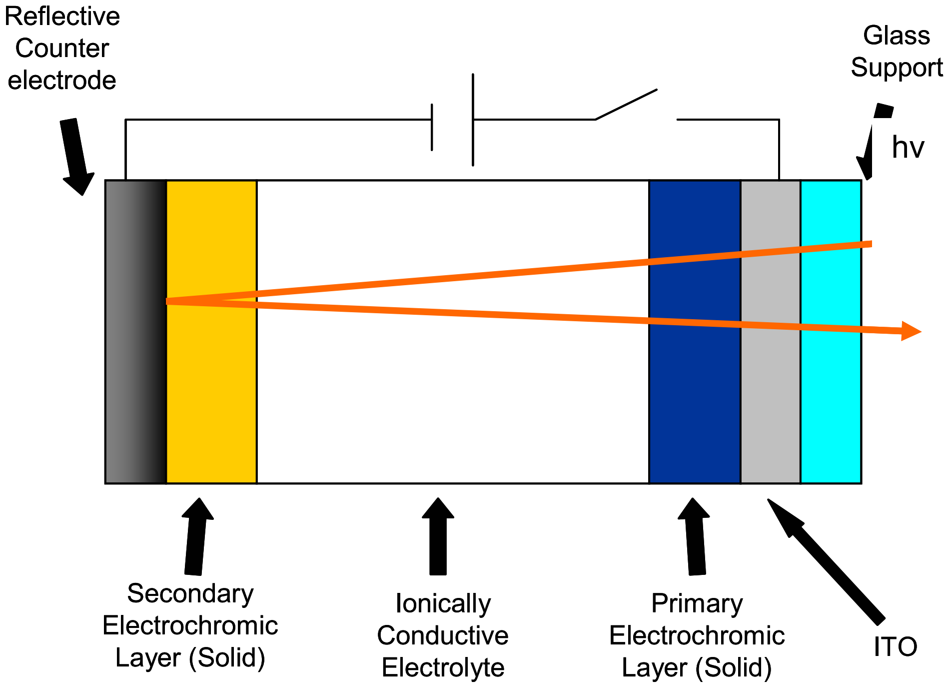

**Fig. 1.5** *Schematic diagram of an EC mirror operating in reflectance mode (with the reflector as counter electrode).*

evaporation or some other method directly on to the OTE surface to minimise contact resistances. The use of OTEs for electrochromic applications has been reviewed by Lyman[26] and Granquist[27]. ECDs operating in a reflective mode (Fig. 1.5) employ a reflective material in the path of the light-beam, both the primary and secondary electrochromes being positioned before it. Examplex of reflector include polished platinum[28] and rhodium alloy[29]. The potential is applied between the front OTE and rear electrode/reflector. Displays may have a metallic (e.g. gold) working electrode on which the electrochrome acts, with transparent ITO as counter electrode and window.

Diffusion is usually the predominant mode of mass transport of counter ions in the electrochromic layer while migration is the transport mechanism in the electrolyte.

ECDs in which a separate reflector is placed before the secondary layer have been described at legth by Baucke[28, 30-32]. Although this arrangement this has practical advantages, the counter electrode need not to be electrochromic since it is never in the path of the ligth beam, the reflector must be ion permeable if charge is to pass across the cell, requiring a porosity which diminuishes its reflectivity.

### 1.1.2 All-solid cell with transmissive operation

Transmissive cells are assembled according to the schematic diagram in Fig. 1.6. Such ECDs are very similar to reflective devices except that the rear electrode obviously cannot be opaque: all layers must fully transparent in the visible spectral range. The apparent intensity change in a transmissive device is only half that of an otherwise identical ECD acting in a reflective mode. This follows since light passes trough the primary electrochrome twice in a reflective device, before and after reflection, but only once in a transmissive cell in which the optical path length is thus, in effect, halved.

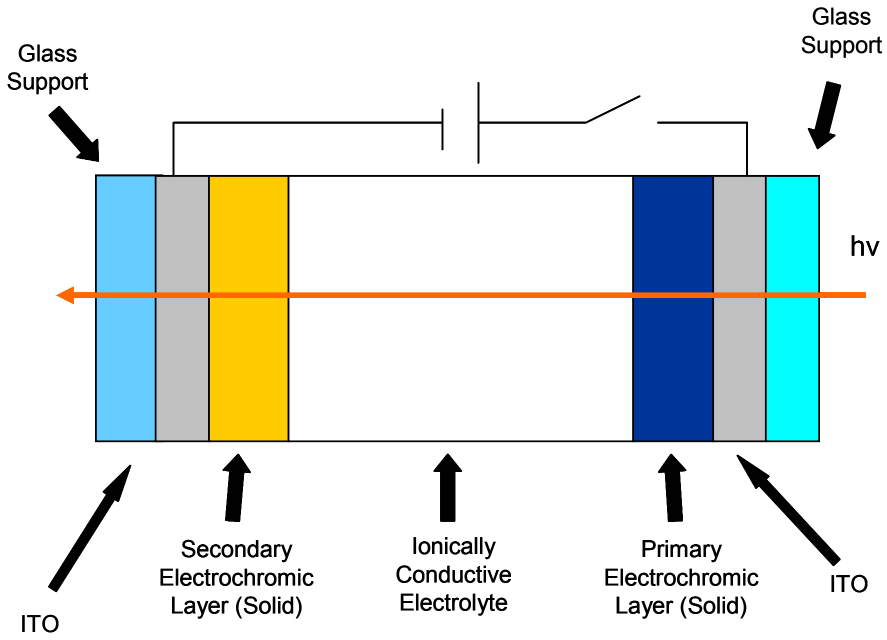

**Fig. 1.6** *Schematic diagram of an all-solid ECD operating in transmittance mode.*

## 1.6 Bipyridilium systems

One of the major group of electrochromes are the bipyridilium species formed by the diquaternising of 4,4'-bipyridil to form 1,1'-disubstituted-4,4'-bipyridilium salts (Fig. 1.7). The positive charge shown localised on N is in general delocalised over the rings. The compounds are formally named as 1,1'-di-substituent-4,4'-bipyridilium if the two substituents at nitrogen are the same, and as 1-substituent-1'-substituent'-4,4'-bipyridilium should they differ. The anion $X^-$ in Fig. 1.7 need not be monovalent and can be part of a polymer. A convenient abbreviation for any bipyridyl unit regardless of its redox state is "bipm" with its charge indicated. The most common name for these salts is viologen which is the colour formed when 1,1'-dimethyl-4,4'-bipyridilium undergoes a one-electron reduction to form a radical cation[33,34].

There are three common bipyridilium redox states: a dication ($bipm^{2+}$), a radical cation ($bipm^{\bullet+}$) and a di-reduced neutral compound ($bipm^0$). The dication is the most stable of the three and is the species purchased or first prepared in the laboratory. It is colourless when pure unless optical charge-transfer with the counter anion occurs. Such absorbances are feeble for anions like chloride but are stronger for CT-interactive anions like iodide[35].

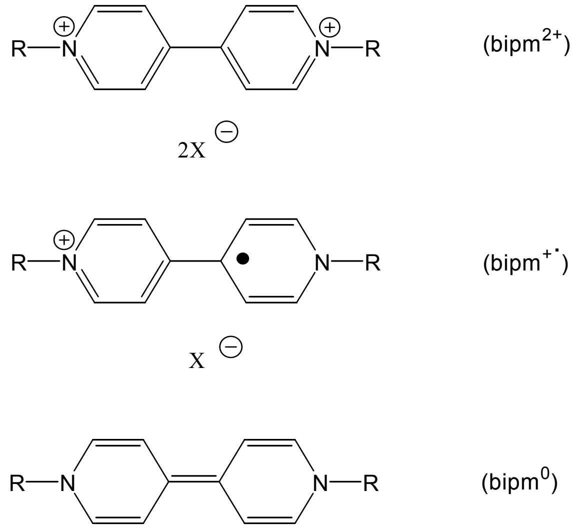

**Fig. 1.7** *Bipyridilium salt redox states.*

Reductive electron-transfer to the dication forms a radical cation (equation 1.19). Bipyridilium radical cations are amongst the most stable organic radicals, and may be prepared as air-stable solids[36,37]. The stability of the radical cation is attributable to the delocalization of the radical electron throughout the π-framework of the bipyridyl nucleus, the 1 e 1’ substituents commonly bearing some of the charge.

$$\mathrm{bipm}^{2+} + \mathrm{e}^{-} \rightarrow \mathrm{bipm}^{+\bullet} \tag{1.19}$$

(colourless) (intense colour)

Electrochromism occurs in bipyridilium species because, in contrast to the bipyridilium dications, radical cations are intensely coloured owing to optical charge-transfer between the (formally) +1 and zero valent nitrogens, in a simplified view of the phenomenom (in fact, because of the delocalisation referred to, the source of the colour is probably better viewed as an internal photo-effected electronic excitation). The colours of radical cations depend on the substituents on the nitrogen. Simple alkyl groups, for example, promote a blue/violet colour whereas aryl groups generally impart a green hue to the radical cation. Manipulation of the substituents at N to attain the appropriate molecular orbital energy levels can, in principle, tailor the colour as desired.

Comparatively little is known about the third redox form of the bipyridilium series, the di-reduced or so called "di-hydro"[38] compounds formed by one-electron reduction of the respective radical cation (reaction 1.20)

$$\mathrm{bipm}^{+\bullet} + \mathrm{e}^{-} \rightarrow \mathrm{bipm}^{0} \qquad (1.20)$$

(intense colour) (colourless)

The same species is formed by a two-electron reduction of the dication. The intensity of the colour exhibited by bipm$^0$ species is low since no optical charge-transfer or internal transition corresponding to visible wavelengths is accessible.

Bipyridilium salts are some of the few organic species that undergo the comproportionation reaction in solution, in which two redox states of the same compound react to form an intermediate redox state, equation 1.21:

$$\mathrm{bipm}^{2+} + \mathrm{bipm}^{0} \rightarrow 2\mathrm{bipm}^{+\bullet} \qquad (1.21)$$

the first product of the comproportionation reaction is in fact spin-paired radical-cation dimer[39]. The transition state of reaction 1.21 is thus assumed to have the two redox states lying face to face in a “sandwich”–type configuration.

## 1.7 The charge transfer equilibria of bipyridilium species

The bipyridilium dication is a relatively weak electrolyte and almost always evinces some forms of ion association. The association takes the form of ion pairing if the interaction is predominantly ionic, or as charge-transfer complexation if a significant extent of orbital overlap can occur.

The term charge-transfer is used in some of the literature to imply that a discrete electronic charge has transferred from donor to acceptor, i.e. that the wavefunction for the excited system describes the quantity of charge which transfers as being that of an integral electron. The fraction of electronic charge actually transferred in a ground-state configuration can be small for viologen-donor complexes.

Typically, a charge-transfer complex is detected in UV-visible spectrophotometry. When two compounds in solution are brought together and a new optical absorption band is formed that was not present in the spectrum of either component, then it is likely that a CT complex has been formed:

$$A + D \leftrightarrow AD \tag{1.22}$$

colourless coloured

The viologens are all excellent electron acceptors (that is, have a high electron affinity *E*): for example, White[40] cites an electron affinity of 120 kj mol$^{-1}$ for methyl viologen.

During complex formation, the orbitals of the approaching molecules overlap, and the resultant distortion causes a movement of charge from the donor to the unoccupied orbitals of the acceptor molecule, this attractive charge-transfer interaction occurs in tandem with the other low-energy interactions always present; a stable complex forms if the attractive interactions outweigh the repulsive energetic forces[40].

CT bands tend to be rather intense owing to the electronic transition being wholly allowed quantum mechanically[41]. The CT band is also quite wide because both acceptor and donor species can have a range of energies and bond separations following a Boltzmann-type distribution. For this reason, the spectroscopic CT band is essentially gaussian[41] when drawn with an energy-related abscissa.

The energy for the electron-transfer reaction is supplied by a photon:

$$\mathrm{AD} + \mathrm{h\nu} \rightarrow \mathrm{A^{-}D^{+}} \tag{1.23}$$

The CT complex is coloured because of the uptake of this photon; and the colour seen in the laboratory is the complementary colour to that absorbed.

In addition to collision between acceptor and donor followed by photon absorption, equation 1.23, there is also an extensive literature on the formation of CT complexes via redox reactions, as represented here by electron-transfer within an ion pair

$$\left[\mathrm{bipm}^{+\bullet}\mathrm{D}^{n-}\right] \rightarrow \left[\mathrm{bipm}^{2+}\mathrm{D}^{(n+1)-}\right] \qquad (1.24)$$

Photon absorption by the product of equation 1.24 yields the familiar colour of a CT complex.

Since the viologen dication is almost always involved in some form of CT equilibria, electro-reduction will involve electron transfer to a bipm$^{2+}$ moiety that is complexed. In fact, complexes of methyl viologen can be relatively electro-inert at solid electrodes and the rate determining step during electro-reduction is the prior dissociation of the complex before electron-transfer: it is thus a CE reaction. This CE reaction (that is, a chemical reaction followed by an electrochemical reaction) is demonstrated in figure 1.8, where the rates of electron-transfer $k_{et}$ and of complex dissociation are plotted together: the correlation is seen to be more than coincidental, which would surely have been the case in the absence of a CE-type process.

The inorganic ion to have received most attention as a CT donor to methyl viologen is hexacyanoferrate(II)[42-46]. The CT of aqueous methyl viologen with ferrocyanide depends[47] on pressure, ε increasing by 35% and $\lambda_{max}$ shifting by ~ 1700 $cm^{-1}$ when the pressure was increased from 0.001 kBar 10 kBar. The spectral peak width did not alter, although the peak is slightly non-gaussian (too wide) on the low-energy side on the band.

Nitrogen-containing species are represented by amines such as aniline[42, 48, 49], *p*-toluidine[42], *p*-phenylenediamine[50], N,N-dimethyl-aniline[42], benzidine[42]. In passing, it should be noted pyridine or 4,4'-bipyridine also acts as a donor (particularly in organic solution) owing to the lone pairs at nitrogen: when conditions are opposite, the quaternization of 4,4'-bipyridine will proceed with a faintly coloured solution since the unreacted bipyridine forms a weak complex with the newly formed viologen product. No quantitative measurements of association between pyridine or 4,4'-bipyridine and viologens are extant.

The best oxygen-containing donors are the phenols such as *p*-cresol[42], *p*-methoxyphenol[42], and pyrogallol[42]. There is some evidence that a few aliphatic alcohols[51] (such as propan-1-ol and propan-2-ol) can also effect CT with viologens.

Another type of CT is seen when the donor is an aromatic species. Here, it is the π-orbitals of the arene which donates charge to viologens. In this case, it is the (charge) centroid of the arene which is directed toward the nitrogens of the bipyridilium salt acceptor, rather from a specific donor atom[52-57].

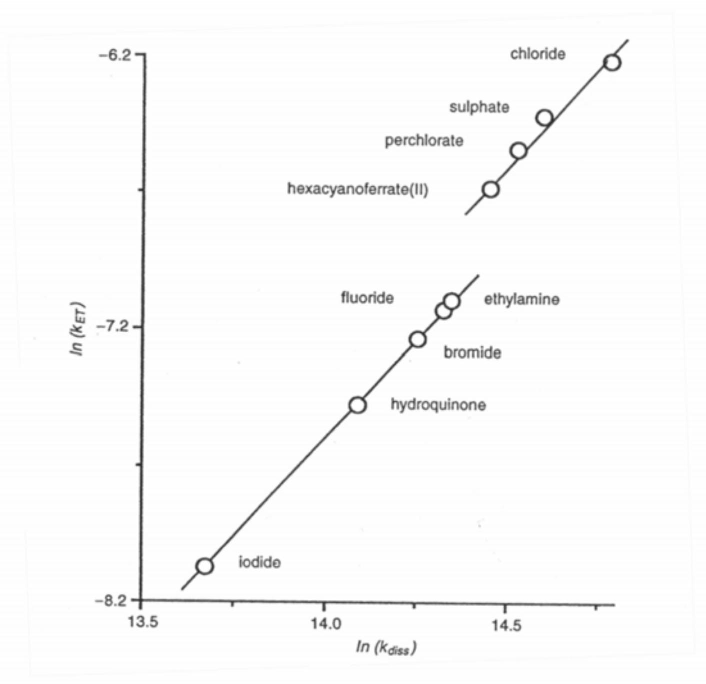

**Fig. 1.8** *Plot of ln$k_{ET}$ ($k_{ET}$=rate constant of electron-transfer to the methyl viologen dication$_t$) against ln$k_{diss}$ ($k_{diss}$=rate constant of the dissociation of methyl viologen charge-transfer complex). Both rates relate to solution-phase complexes in water at 298 K. The lower line relates to a straightforward correlation between $k_{et}$ and $k_{diss}$; the upper line represents anomalous kinetiks, with adsorption-catalysed electron-transfer ($Cl^-$), slow $k_{diss}$($[Fe(CN)_6]^{4-}$) and ion pairs without CT ($ClO_4^-$ and $SO_4^-$). (Electrochim. Acta 1998, vol.* ***43****, P.M.S. Monk and Hodgkinson, page 245).*

The energy of the charge-transfer band in the solid state usually relates to the energy necessary for photo-excitation across the band gap between the valence and conduction bands, although it could still refer to the energy required for electron hopping between acceptor and donor.

The viologen radical cation is comparatively electron rich and can, in the solid state, act as a modest donor. When acting as donor to a viologen dication, the formal oxidation state per viologen moiety is non-integral and the solid is thus deemed to be “mixed valent”[58]. These mixed-valence species are well-conducting semiconductors or even have metallic electrical properties. It should be recognized that anions are also present in a non-interactive capacity. (The magnitude of anion interactions, hitherto the sole interactions of interest, are probably much smaller here than the other forces in the solid state, so anions can be ignored except insofar as they may influence the resultant crystal structure).

Samples of solid solid-state viologen are held together in a highly stereospecific conformation by charge-transfer-type associatives forces.

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# CHAPTER 2

# SOLID THERMOPLASTIC LAMINABLE ELECTROCHROMIC FILM

## 2.1 Introduction

The vast majority of EC devices manufactured today are based on solutions containing at least one, and in most cases more than one, EC redox materials. These materials are free to diffuse and/or migrate to the surface of the electrodes and undergo oxidation or reduction. During EC device operation solution-based EC redox materials are subjected to natural convection or to processes known as aggregation[1] or segregation[2]. In this processes the oxidation of the anodic materials causes the density of the solution near the anode to increase with respect to the bulk of the solution and the density gradient causes this more dense solution to sink in the gravitational field of the Earth. The increase in density can be explained in terms of the tendency of polar organic solvents used in EC devices to solvate cations and neutral materials better than anions. Thus as anodic material is oxidized it becomes better solvated or the solvation sphere tends to move in toward the newly formed oxidized materials and hence the solution becomes more dense. The reverse happens at cathode for the same reason and the solution becomes less dense and it rises in the gravitational field of the Earth; this behaviour is outlined in figure 2.1.

During electrolysis of solutions containing these types of anodic and cathodic materials the coloured solutions can be readily observed to “stream” up at the cathode and down at the anode, for this reason when the ECD left in coloured state for 20 min or more, will exhibit coloured bands of the cathodic material near the top and the anodic material near the bottom when an attempt is made to clear the device.

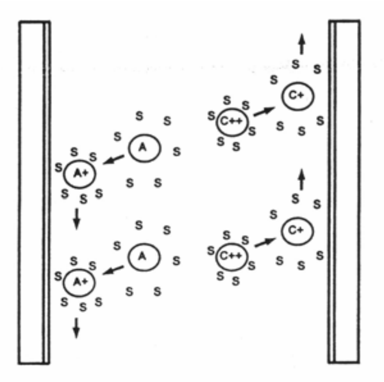


**Fig. 2.1** *Illustration of segregation phenomenon in solution-phase EC devices. In the absence of polymers, the solution of oxidized material sinks while the solution of reduced cathodic material rises during electrolysis.*

The segregation phenomena is significantly reduced by adding polymers to the solution, moreover this provides some benefit when a device leaks or cracks, it is often desirable to completely retain the liquid portion of the device. An even greater motivation for the development of EC devices with self-supporting or free-standing EC systems comes from the need to eliminate hydrostatic pressure in windows that are reasonably large. A simple liquid sealed between two pieces of glass over a surface area of say 1 $m^2$ will exert forces large enough to bow out the glass on the bottom half of the window, collapse the glass pieces together in the top half of the window, and in some cases rupture the seals holding the assembly together. All these drawbacks related to the solution type EC devices induced us to explore the possibility to obtain an electrochromic film in which redox molecules are contained in a solid self-supported polymeric matrix which have also a good adhesion ability to glassy support.

Moreover, the production of electrochromic devices (ECDs) is often very expensive. In fact, generally, ECDs comprise of a sandwich structure of many alternating thin layers: electrochromics cathodic and anodic, electrolyte and conductive indium tin oxide coated glasses. In our laboratory a new kind of solid electrochromic film was studied. This film is obtainable by simply doping preformed solid thermoplastic polymers with electrochromic molecules and plasticizers. The film preparation does not require solvent evaporation or UV curing, and allows to get a self-consistent monolayer suitable for application in a wide range of devices. Moreover, when thermoplastic poly vinyl butanal (PVB) is used as supporting polymer, the electrochromic film could be used as interlayer in laminate safety glass.

## 2.2 Experimental section

### 2.2.1 Chemicals

All chemical reagents were commercially available and were used as purchased without further purification. Poly(vinyl formal) (PVF), propylene carbonate (PC), hydroquinone, ethyl viologen diperchlorate (EV), ferrocene, tetrabutylammonium hexafluorophosphate (TBAEFP) and tetrabutylammonium perchlorate (TBAP) were purchased from Aldrich Chemical.

### 2.2.2 Samples Preparation

Different electrochromic samples with different compositions and thickness were prepared in order to study their electrooptical parameters and properties; there we describe the general preparation procedure of an electrochromic solid film first; in the following paragraphs the details of the amount of each component will be supplied.

Ethyl viologen diperchlorate, hydroquinone (or ferrocene, or a different anodic molecule) and propylene carbonate were mixed in appropriate amounts, the so obtained electrochromic solution was stirred at 100° C. for approximately 10 minutes for good homogenization. All-liquid systems were obtained introducing this mixture by capillarity into homemade cells, whose thickness was assured by mylar spacers. The cell walls had an indium tin oxide (ITO) conductive substrate, which was 120 nm thick. All-solid electrochromic films were obtained mixing at 150° C. PVF and the electrochromic solution, until an homogeneous perfectly transparent film was obtained (thermal blending process). After cooling the mixture at room temperature, an homogenous solid film, with EC properties and great adhesion ability to a glassy support was obtained. The all-solid ECD is then very easily obtained, by simply heating the electrochromic film to the temperature of softening of the plasticized thermoplastic polymer (100 – 150 °C), this molted mixture is laminated between two pieces of ITO coated conductive glasses. No spacer need to be added to control thickness of the cell, in fact, the control of parameters of the lamination process, as temperature and pressure applied to the pieces of conductive glass, are enough to obtain the electrochromic cell of the appropriate and homogeneous thickness.

### 2.2.3 Experimental setup

The oxidation/reduction behavior of electroactive species was investigated by CV, for solutions of $1,5 \bullet 10^{-3}$ M of anodic and/or cathodic electrochromic substances and $1,5 \bullet 10^{-2}$ M of inert electrolyte in the presence of propylene carbonate as solvent. Experiments were carried out in a three electrode system with Pt as the counter electrode, Ag/AgCl as the reference electrode, and a glassy carbon electrode was the working electrode. The potential control was achieved by means of an Amel 2049 model potentiostat/galvanostat, an Amel 568 programmable function generator with scan rate of 30 mV/sec. Measurements were carried out at room temperature.

Response time is one of the most important characteristics of ECD’s, which is defined as time required for switching between two coloured states. The variation in % transmittance (% *T*) at the wavelength of maximum contrast was monitored using a YASCO V550 UV-VIS spectrophotometer, while applying a square wave potential by means of a Amel 2049 model potentiostat/galvanostat and an Amel 568 progammable function generator. The switching time was calculated at 95% of the full switch because it is difficult to perceive any further colour change with the naked eye.

Morphology analysis was performed on cross section of the electrochromic film with a Leica LEO 420 scanning electron microscope after evacuating the solvent under vacuum ($10^{-3}$ torr) for twelve hours.

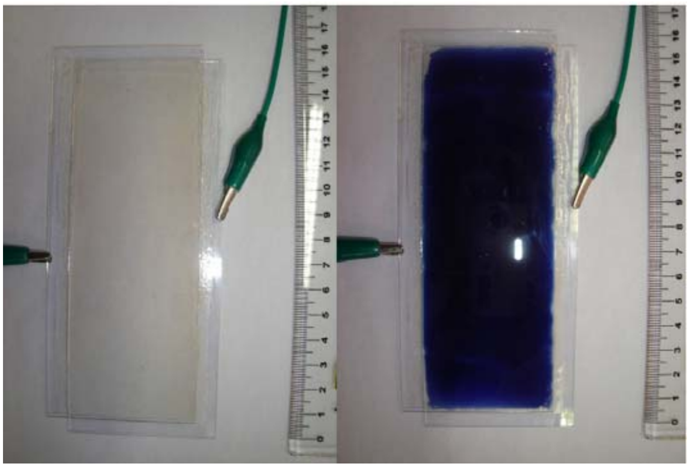
## 2.3 Results and discussion

### 2.3.1 Morphological and electrooptical characterization

In figure 2.2 the non operated and operated (by 2.0 volts DC current) device are reported for comparison. The lamination has been performed by pressing the plastic film between the conductive glasses supports by means of a vacuum press at the temperature of 150 °C. The two glass supports remained strongly glued together. Any efforts to delaminate the glass supports at room temperature without breaking the cell was unsuccessful. The system could be delaminated only at 80°C. The thickness of the plastic electrochromic film after lamination was 100 microns.

In order to perform a morphological characterization of our plastic electrochromic film, to exclude the existence of cavities inside the solid electroactive layer able to contain solvent in which molecules are free to migrate and to diffuse, a SEM analysis of ECD device cross section was carried out. This information is important to understand the charge propagation mechanism of the redox materials.

An electrochromic all-solid cell was frozen by immersion in liquid nitrogen and after it was cut. Cross section of the film was left under vacuum at $10^{-3}$ torr, for twelve hours in order to extract solvent.



**(a)** **(b)**

**Fig. 2.2** *Visual response of an all-solid electrochromic device made of 40 wt.%, poly(vinyl formal), 4 wt.% ethyl viologen diperchlorate, 1 wt. % hydroquinone and 55 wt. % propylene carbonate, in the OFF state (a) and after application of 2.0 V DC (b).*

In figure 2.3 the SEM image of the electrochromic film cross section is reported. The film reveals an homogeneous and continuous structure without visible phase separation. A complete absence of porosity and channels greatly restricts the migration of the electrochromic molecules inside the film. In literature ECDs in which redox materials are mixed with a solid polymeric matrix are known[1], but in such systems ionic chromophores anodic and cathodic are able to migrate in solution phase towards the electrodes when a voltage is applied, because morphological analysis show presence of high porosity which contains solvent. EC system with similar

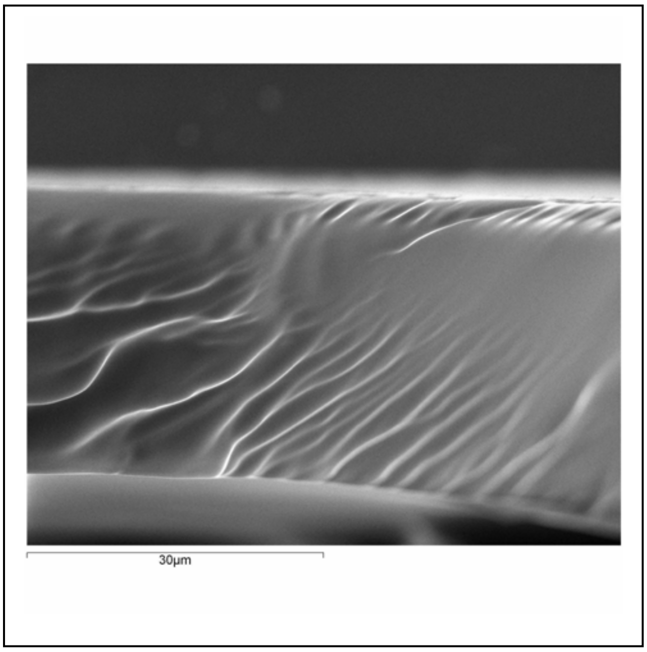


**Fig. 2.3** *Cross section scanning electron microscopy image of the electrochromic film containing 40 wt.% poly vinyl formal, 4 wt. %f ethyl viologen diperchlorate, 1 wt. %f hydroquinone, 55 wt. % propylene carbonate.*

compositions are described as “free-standing gels” [3-8]. A “free-standing gel” is described as a “system of polymer matrix with interspersed EC solution...”. Once again the EC layers are formed by filling devices with a relatively low viscosity solution of monomers, followed by in situ reaction to give a crosslinked polymer matrix. Preferred polymer or crosslink forming reactions are addition reaction of isocyanates with alcohols since no by product are formed, or radicalic polymerization of acrylate promoted by presence of UV light and suitable initiators. These gels can be thought as a two phase system in which a continuous solution phase is interspersed in a three-dimensional matrix formed by a polymer phase. The solution portion of the gel is open enough to allow relatively large molecules and ions to diffuse and/or migrate through out the phase, to and from the electrodes. The morphology of a gelled solution phase EC system is very different from that of our electrochromic solid film which has a continuous structure without visible phase separation, and redox materials are not free to migrate. Moreover EC materials are present at high concentration, for this reason they are close enough to allow electrons to hop from one electrochromic molecule to another.

In figure 2.4 the cyclic voltammetry experiment for the ethyl viologen in propylene carbonate is showed. The following electrochemical parameters were obtained form above mentioned CV experiment: $E''_{ap}$= -0.7593 V, $E'_{ap}$= -0.3491 V, $E'_{cp}$= -0.5566 V, $E''_{cp}$= -0.9692 V, which are respectively the second and the first anodic peaks and the first and the second cathodic peaks. $E'_{ap}$ and $E'_{cp}$ are related to the first reduction of viologen (equation 1.19); $E''_{ap}$ and

E''$_{cp}$ arise from the second reduction (equation 1.20). The formal redox potentials for the two redox steps of ethyl viologen in propylene carbonate were calculated by the following two equations:

$$E_1^0 = \frac{E'_{pa} + E'_{pc}}{2} = -0.45V \tag{2.1}$$

$$E_2^0 = \frac{E''_{pa} + E''_{pc}}{2} = -0.86V \tag{2.2}$$

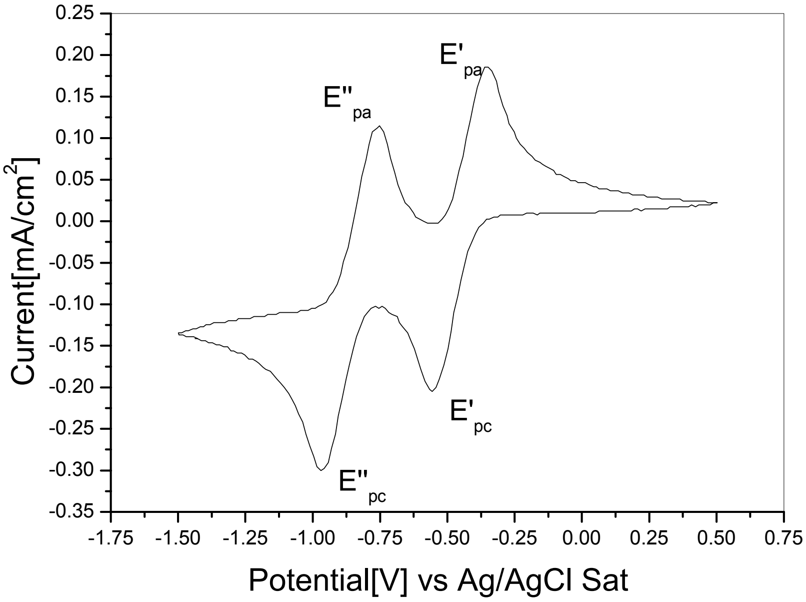


**Fig. 2.4** *Cyclic voltammetry experiment of ethyl viologen diperchlorate (EV) 1,5•10$^{-3}$ M in propylene carbonate (PC) and tetrabutylammonium perchlorate (TBAP) 1,5•10$^{-2}$ M as inert electrolyte, scan rate=10 mV/s, working electrode: glassy carbon.*

In figure 2.5 the cyclic voltammogram for hydroquinone in propylene carbonate as solvent is reported. The experiment was carried out under nitrogen inert atmosphere, because the presence of oxygen causes some extra peaks due to redox reaction of $O_2$ in protic environment to appear in the voltammogram, being $H^+$ ions produced during the oxidation of hydroquinone to quinone Moreover presence of oxygen in the electrochemical mixture causes a shift in formal potentials of hydroquinone making easier the oxidation to quinone. From the voltammogram in figure 2.5 is further possible to understand that the redox reactions of hydroquinone in propylene carbonate is not a perfectly reversible process, in fact the condition $\left|i_{pa}/i_{pc}\right| = 1$ is not obeyed as we can see from the graph.

The absorption spectrum of the coloured and uncoloured electrochromic cell are shown in figure 2.6. 606 nm and 413 nm are the maximum wavelengths of absorption related to the radical cation of ethyl viologen ($bipm^{+\bullet}$), the resulting colour of the film is blue. This radicalic viologen specie is intensely coloured owing to the presence of the single electron acquired on reduction, which is delocalized extensively over the bipyridilium core.

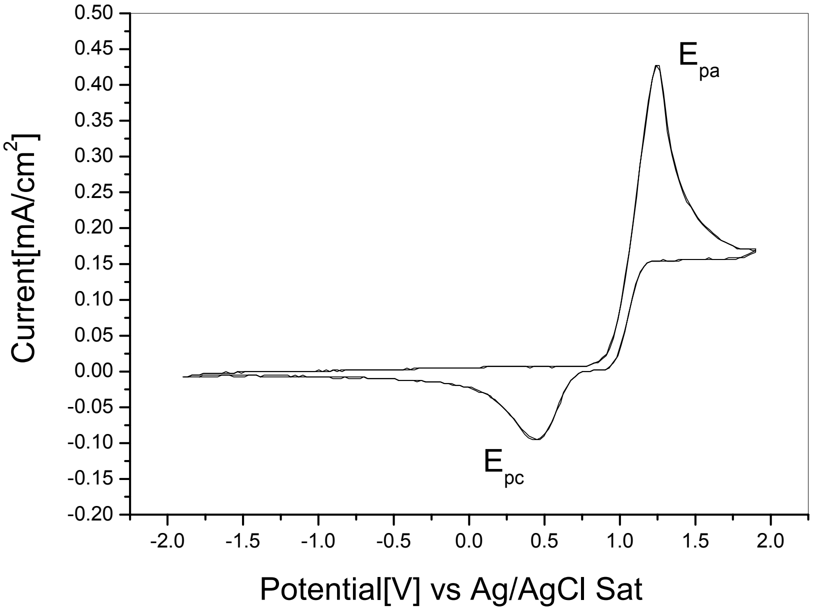


**Fig. 2.5** *Cyclic voltammetry experiment of hydroquinone 1,5•10$^{-3}$ M in propylene carbonate (PC) and tetrabutylammonium perchlorate (TBAP) 1,5•10$^{-2}$ M as inert electrolyte,under inert atmosphere ($N_2$), scan rate=10 mV/s, working electrode: glassy carbon.*

From the spectrum there is no evidence for dimer formation. When viologen is reduced, the colour of radical cation can change from blue though to purple, this change in colour of the absorbing molecules being due to formation of a viologenic dimeric species. Monomer-dimer equilibration was proposed by Schwarz in 1962[9], and it is outlined in equation 2.3:

$$2\text{bipm}^{+\bullet} = (\text{bipm})_2^{2+} \qquad (2.3)$$

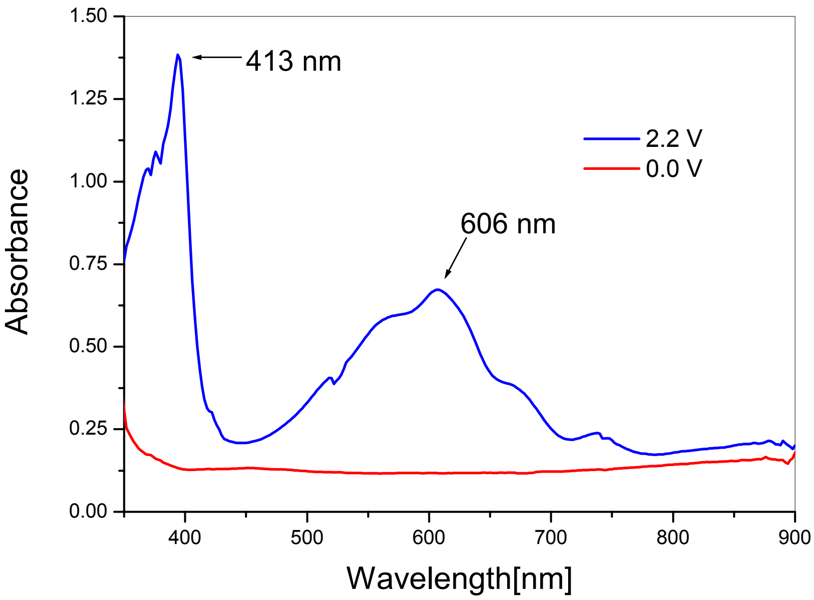


**Fig. 2.6** *UV-vis spectrum of an electrochromic film made of 40 wt% poly(vinyl formal), 2 wt% ethyl viologen diperchlorate, 0.9 wt% ferrocene, 57.1 wt% propylene carbonate, in the ON state (blue line), and in the OFF state (red line).*

The associated changes in UV-visible spectra are quite marked with absorption bands shifting to lower wavelengths and new bands appearing at high wavelengths for the dimer form how we can see in figure 2.7. The shape of the spectrum in the range 400-600 nm (the band for both the monomer and the dimer of the radical cation) does not change, suggesting that the bands arising from the monomer and dimer transitions fall in the same spectral region and exhibit only minimal structural differences. Then we can argue that the dimer is not a complex of dication and di-reduced bipyridilium redox states[9].

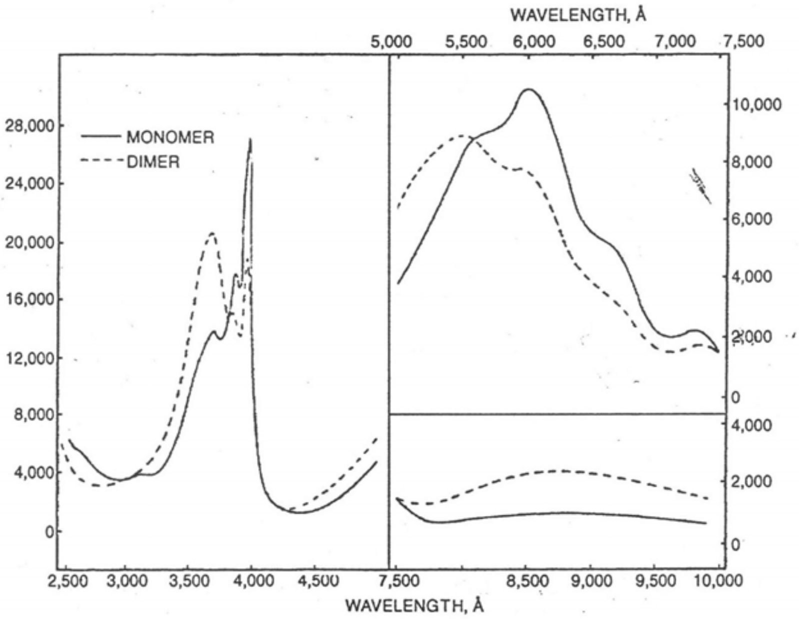


**Fig. 2.7** *A comparison of the UV-visible spectra for methyl viologen radical cation as monomer and as dimer*[9].

The new spectral band at high wavelengths (at c. 900 nm) is best regarded as an allowed transition within the dimer according to energy scheme of Kosower[9]. The new band is not a charge-transfer transition, which would be forbidden. Since both and monomer absorb in approximately the same region, and both have similar extinction coefficients, the colour of the radical cation is not directly attributable to the unpaired radical electron.

Comparing the UV-visible spectrum obtained for the ethyl viologen in the solid electrochromic film (figure 2.6), with UV-visible spectra of radical cationic methyl viologen and dimer in water reported in work of Kosower and Cotter (figure 2.7), as said before there is no evidence for dimeric specie existence, in fact ispectral profiles of ethyl viologen in our solid polymeric matrix, in range 400-

600 nm, 350-450 nm and 900 nm are very different from that of the dimeric form in the same range of wavelengths. In particular the absorption maximum of the dimer was observed at around 530 nm and the colour was violet, while, for the monomeric radical cation the absorption maximum appeared at 606 nm and the colour was blue. Then all alkyl-substituted viologen radical cations in solution have the similar spectra, because the electron resides within the bipyridine *core* and electronic interactions beyond the first carbon of the alkyl chain are minimal, for these reasons comparison between the spectrum of methyl viologen (figure 2.7) and that of ethyl viologen (figure 2.6) is possible.

The spatial orientation postulated for the dimer[10] is one in which the two radical cations lie face to face in a sandwich-type structure, linked by the two $\pi$-clouds overlapping to form a $\pi$- $\pi'$ bond

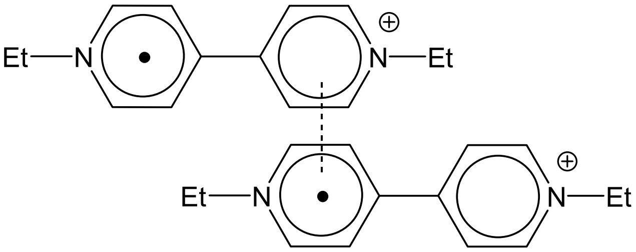


**Fig. 2.8** *Head to head structure of the ethyl viologen dimer with two monomeric molecules having a π-interaction*

Such a dimer would be expected to be unstable with respect to coulumbic repulsion as caused by the close proximity of the two positive charges, implying that the spin-pairing energy of dimer formation is greater than the instability engendered by coulombic repulsion.

For our solid film the energy of solvation, in the non-aqueous polymeric plasticized system, is probably not great enough to be equal to Coulomb repulsion, and so the monomeric species is stabilized, or in other terms the ethyl viologen prefers to interact with some species present in the mixture giving a stable interaction which prevents formation of dimer. Successively, in this chapter, we will see that a strong interaction exists between dicationic ethyl viologen and charge donor molecules as hydroquinone and others. This interaction affecting the kinetic of electrochromic device could also involve radical cationic ethyl viologen and these charge-transfer complex forming species, in this case the steric hindrance all around the ethyl viologen aromatic rings makes very difficult the approach of two monomeric viologens to pair their unpaired electrons forming a dimer.

Alternatively another reason which prevents dimerisation could be the strongly limited freedom of motion of bipyridilium molecules inside the polymer matrix of the electrochromic film.

Viologen molecules are dissolved in the polymer when they are in the dicationic form, no tendency to dimer formation exists because there is no unpaired electron and molecules are arranged apart because of the coulombic repulsion When the coloured radical cation is generated by a suitable voltage, molecules motion is prevented by the hindrance of polymeric chains, thus monomers cannot approach in order to overlap the two $\pi$-clouds and to form a $\pi$- $\pi'$ bond making a dimer, this behaviour is outlined in figure 2.8.

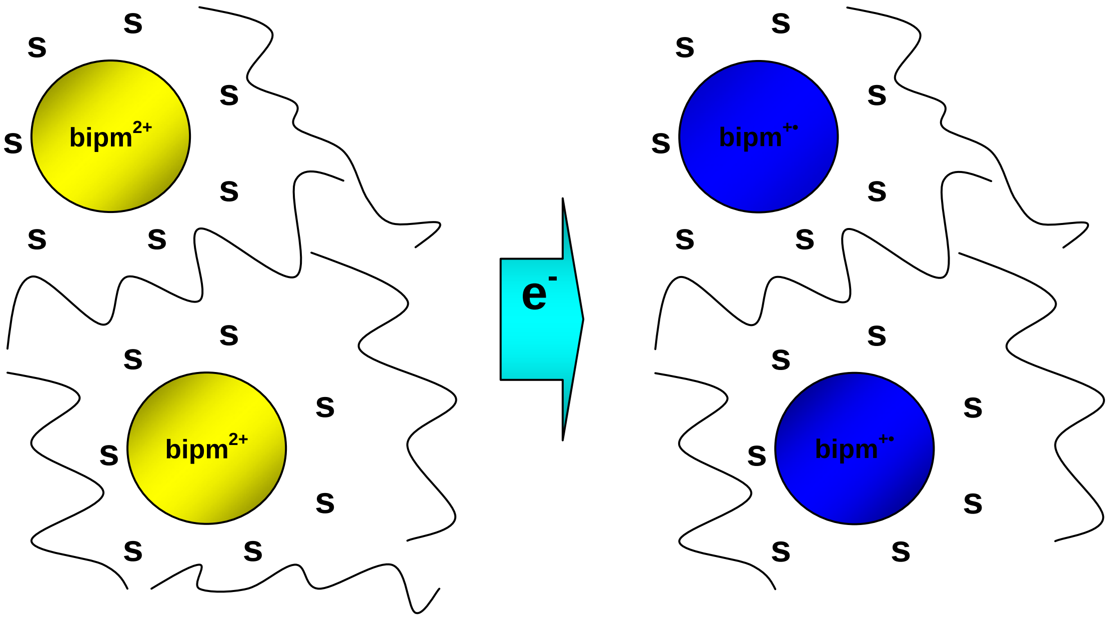


**Fig. 2.9** *Dicationic bipyridilium molecules (yellow spheres) and radicalic bipyridilium (blue spheres) inside the plasticized solid matrix, the polymeric chains prevent motion of bipm*$^{+\bullet}$ *to form a dimer.*

We have chosen to follow the absorption band centred at 606 nanometers as a function of applied voltages and as function of time to characterize the response of the ECD. A DC square pulse has been applied to the cell. Some results are reported in fig 2.10 where the transmittance of the film is graphed as a function of the applied voltage.

An EC response is obtained for voltages around 1.4 volts, which is the minimum voltage required to make change colour to the electrochromic device and can be defined as the threshold voltage ($V_{TH}$), although the contrast ratio for this applied pulse is not very high. This is better observable in figure 2.11 where CR at 606 nm is reported as function of the applied voltage for the electrochromic film.

CR is defined as the ratio between the maximum value of transmittance (in the OFF state) at 606 nm of the electrochromic cell and the minimum value of transmittance.

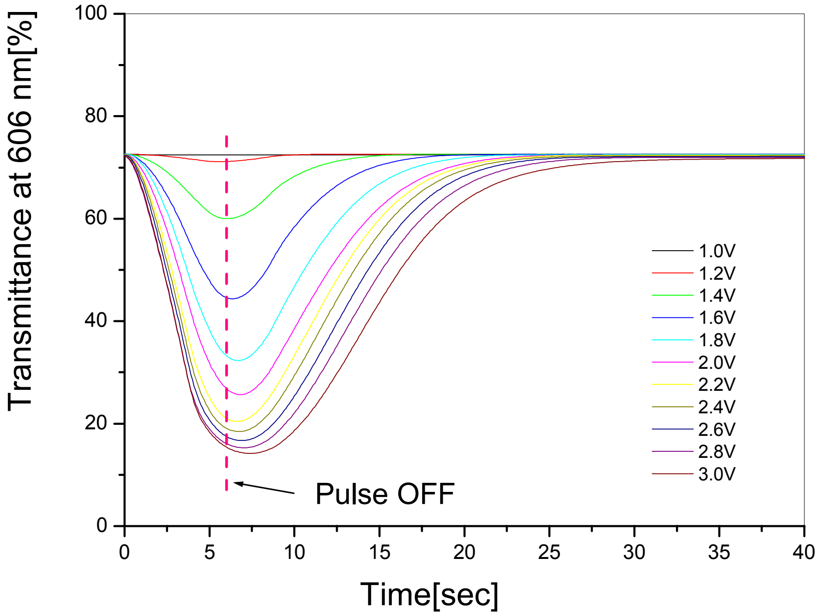


**Fig.2.10** *Transmittance of the EC cell at 606 nanometers, as a function of the time and of the applied voltage. DC Pulses of 5 seconds have been applied to the cell having the following composition: 40 wt% poly(vinyl formal), 2 wt% ethyl viologen diperchlorate, 0.9 wt% ferrocene, 57.1 wt% propylene carbonate, with a cell thickness of 60 μm; pulse length was 5 seconds for all the experiments.*

As we can see in this graph the contrast ratio does not increase so much up to 1.4 volts, while from 1.4 volts to 3.0 volts a small variation in amplitude of the pulse causes a significant increase in the contrast ratio. In practice, the overcoming of 3 volts can cause some inconveniences to the electrochromic device due to further reduction of the radical viologenic cation, however contrast ratio can be increased also lengthening the colouration times rather than increasing voltages as we will see later when some experiments in which pulse length was varied and pulse amplitude was kept constant will be discussed.

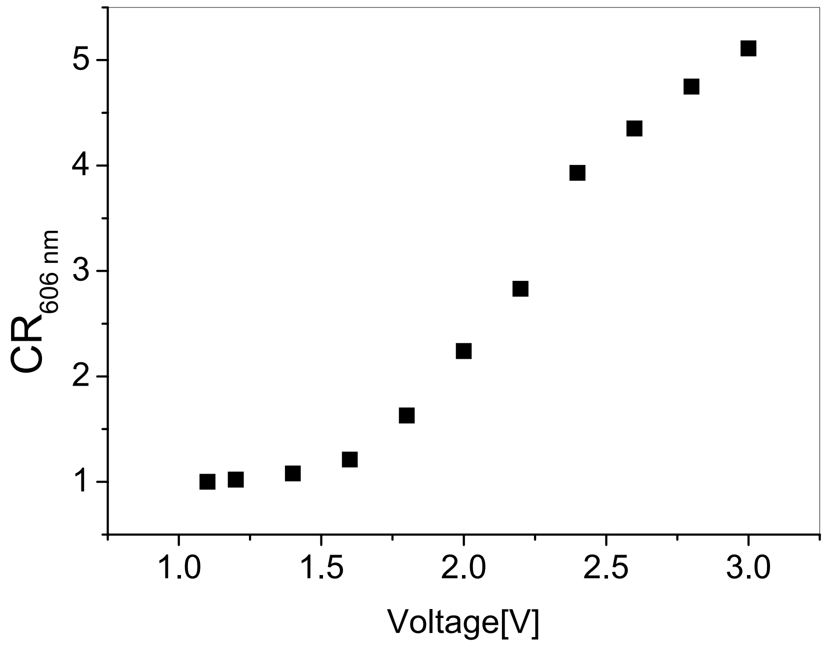


**Fig. 2.11** *Contrast ratio at 606 nm as function of the applied voltage for an EC device with the following composition: 40 wt% poly(vinyl formal), 2 wt% ethyl viologen diperchlorate, 0.9 wt% ferrocene and 57.1 wt% propylene carbonate, with a cell thickness of 60 µm; pulse length was 5 seconds for all the experiments.*

The maximum value in $CR_{606\ nm}$ that can be obtained with this set of voltages is 5.1, which corresponds to a $\Delta T\%$ of 58.42%. This is a very high value compared with other electrochromic devices which are characterized by not very high CR, being based on polymeric electrochromics as PEDOT or polyaniline intensely coloured also in the OFF state. In our ECD, on the contrary, in the OFF state only a very weak pale yellow colour is present due to presence of charge-transfer equilibrium of ethyl viologen with other molecules, while the colour in the ON state is deep blue. Moreover, the rigidity of the polymeric film allows colouration of many electrochromic layer near the electrode, whereas in liquid ECDs only the molecules at the electrode-solution interface are coloured by the application of a voltage. For all these reasons high value of optical contrast are obtained.

From figure 2.10 we can also observe the transmittance decreases during the DC pulse application, due to the population of the radical cation ($\mathrm{bipm}^{+\bullet}$) that gradually increases, as response to the electrode charge injection. The absorption does not decrease immediately after the pulse removing, but keeps increasing for a little while; this behaviour is better observed at voltages greater than 1.6 volts. The explanation of this behaviour is straightforward. At the applied voltages, both the process shown in equations 2.1 and 2.2 occur, so the $\mathrm{bipm}^0$ not coloured species also starts to form. This clearly reduces the population of the red-absorbing $\mathrm{bipm}^{+\bullet}$ (radical cation is coloured in blue and this means that the complementary red colour is absorbed). When the pulse is removed, two processes must be taken into account: the conversion of the neutral back into the monocation species and the conversion of this latter into the dicationic form.

$$\mathrm{bipm}^0 \rightarrow \mathrm{bipm}^{+\bullet} + \mathrm{e}^- \qquad (2.4)$$

$$\mathrm{bipm}^{\bullet+} \rightarrow \mathrm{bipm}^{2+} + \mathrm{e}^{-} \qquad (2.5)$$

These two reaction are the reverse reactions of 1.19 and 1.20 respectively. If the rate of the first reaction (2.4) is greater than the second one (2.5), the population of the absorbing monocation species keeps increasing for a while, after removing the DC electric pulse, then it decreases. The decay of neutral species into the monocation form, after the voltage removing, can actually occur by different chemical process.

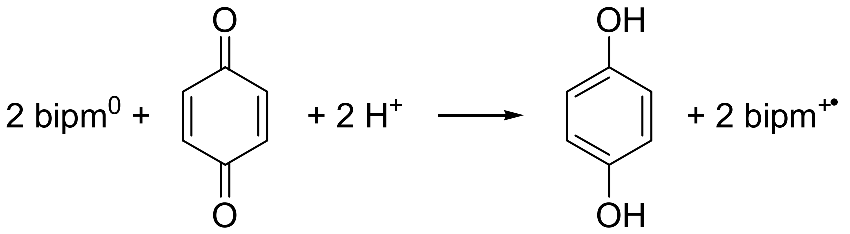


**Fig. 2.12** *Redox reduction of neutral bipyridilium to radical cationic form: The oxidizing species is the 1,4-benzoquinone formed to the anode during the charge injection process.*

One of these processes for the conversion of $\mathrm{bipm}^0$ into $\mathrm{bipm}^{+\bullet}$ is given by the reaction with the oxidized form (1,4-benzoquinone) of the anodic compound (hydroquinone), showed in figure 2.12. Another possible process could be the comproportionation reaction, but this latter mechanism related to the reaction decay of the viologen neutral form in radical cation needs more discussions. In fact, evidence for the dimer being the intermediate product of comproportionation comes from RRDE (rotated ring-disc electrode) analyses[11] and *in situ* spectroelectrochemistry[12].

The dimer is thought to have a sandwich-type structure (figure 2.13), with the two radical cations lying face to face and linked by a *π*-*π'*-bond.

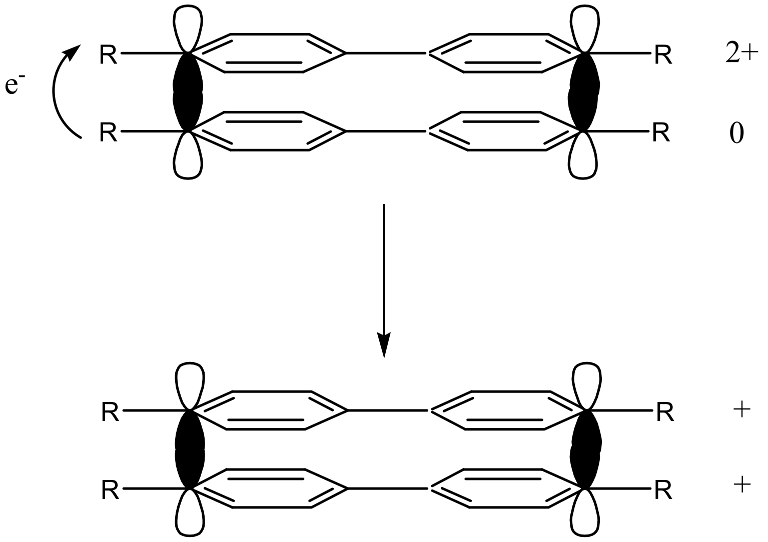


**Fig. 2.13** *Schematic diagram showing the mechanism of bipyridilium comproportionation: intramolecular electron-transfer yields a radical cation dimer, which dissociates subsequently to form monomer units.*

The transition-state complex (TS) for comproportionation is thought to have the same structure as for the dimer (above), with bipm$^{2+}$ and bipm$^{0}$ moieties being parallel to promote the electron transferring through the *π*-*π'*-bonds.

Comproportionation reaction is strictly related to the dimerization equilibrium. Our results indicate that dimer is not a stable product in the electrochromic solid film object of this study, but we suppose that factors which prevent formation of the dimer can also avoid comproportionation reaction.

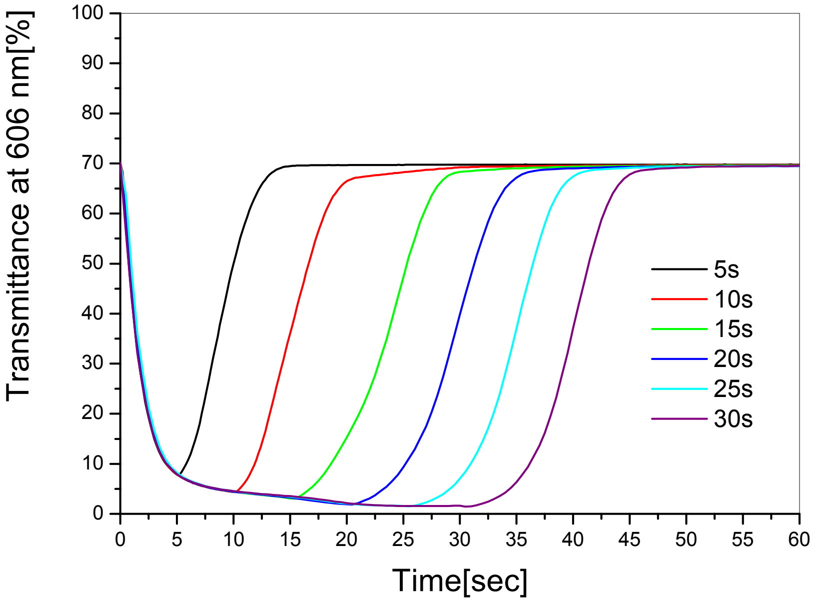


**Fig. 2.14** *Electrochromic response at 606 nanometers and 2.2 volts of a solid plastic film containing 40 wt.% poly(vinyl formal), 4 wt. %f ethyl viologen diperchlorate, 1 wt. % of hydroquinone, 55 wt. % propylene carbonate,* 60 μm thick *for increasing driving time.*

In order to show the substantial differences existing between the electrochromic response of the film presented in this research with respect to that of a fluid film obtained by dissolving analogous percentages of the same anodic and cathodic compounds into propylene carbonate, figure 2.14 and 2.15 are reported. Here several absorption curves obtained by using progressively longer driving times at 2.2 volts are shown. In the case of the fluid film (figure 2.15), the variation of driving time has an easy effect on the typical response of the film: the absorption curves reaches a constant limit value in about 3 seconds.

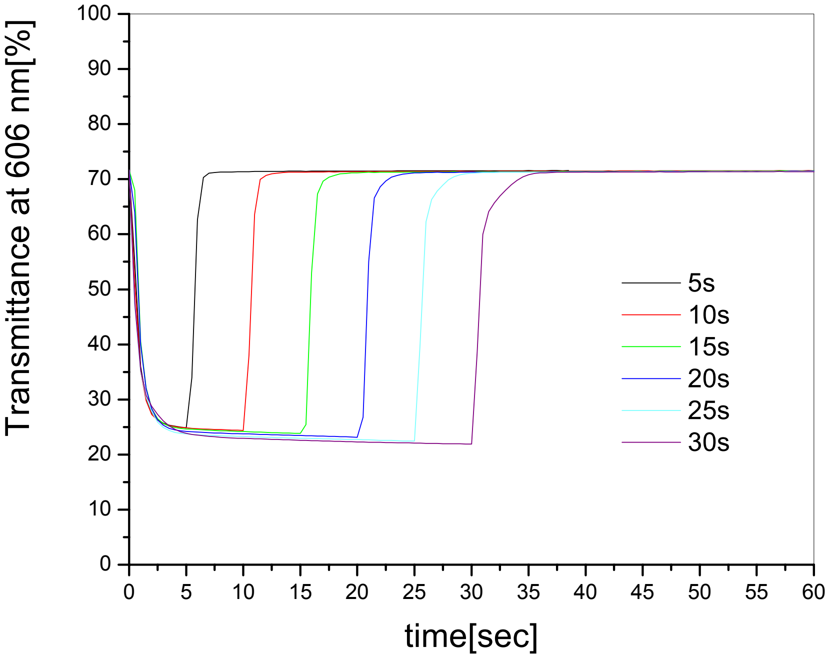


**Fig. 2.15** *Electrochromic response of a fluid film containing 4 wt. % ethyl viologen diperchlorate, 1 wt. % hydroquinone and 95 wt. % propylene carbonate, 60 µm thick for increasing driving time.*

Variations of the driving time simply increase the extent of this steady state region with constant absorption. The bleaching time is also about 3 seconds and remains constant with variation of the driving time. The trend of the absorption curves both in the colouring and bleaching regions resembles that of a mono exponential function.

In the case of the solid film (figure 2.14) the behaviour is much more complex. No stationary region appears even during longer colouring processes. Up to 25 seconds of driving time, the absorption keeps increasing with increasing of the feeding time. Only for driving times longer than 25 seconds the curves show a plateau region, where a negative slope starts to appear. For charging time above 15 seconds, the colouring curves also exhibit a flex. As stated before, the absorption increases for a short while after the voltage removing.

Figure 2.16 shows the different behaviour of contrast ratios in solution and in the plastic film. Contrast ratios at 606 nm for a liquid film and for the solid electrochromic devices are reported, as function of pulse length of the applied voltage. The pulse length plays a very important role on the contrast ratios for the electrochromic solid film, but it does not influence that of the liquid electrochromic cell. Moreover, the contrast ratios that can be obtained with a solid electrochromic device object of this study are considerable, and this is a technological improvement with respect to a traditional electrochromic device, for which the minimum transmittance values are higher than those obtained for our solid film and the colour forming process occurs only at the electrode. The behaviour of the responses observed in both the solid and fluid film need to be clarified by developing a kinetic model of the systems where the evolution time of the different species present at the electrodes is calculated, by taking into account all the factors affecting the kinetic of each raction occurring, both in the colouring and bleaching stages. Nevertheless, we can say that the differences observed in the electrochromic response of the solid film with respect to the behaviour of the fluid one, must be ascribed to differences in the chemical kinetic of the

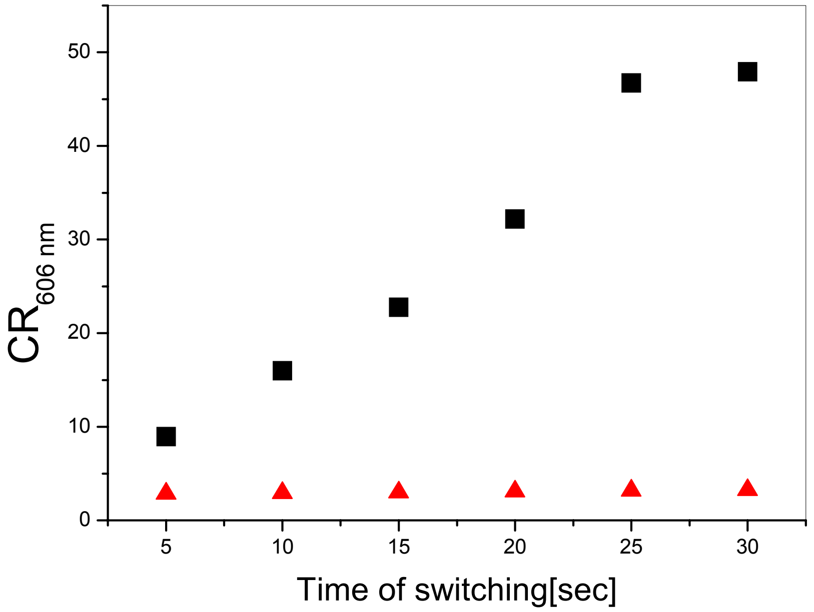


**Fig.2.16** *Comparison of contrast ratio for an electrochromic solution (▲) and for a plastic electrochromic solid film (■) as function of length of the applied voltage (2.2 volts). Chemical compositions for the samples are the same of experiment in figure 1.19 and 1.20, thicknesses of devices are the same (60 µm).*

redox process occurring in the film and at the interface between film and electrodes. These differences can arise from the slowing down of the molecular translation diffusion in the solid film, with respect to that of the fluid system. In the fluid film the fast translation diffusion rapidly assists the establishment of a stationary state, where the concentration of the monocation species doesn't change during the voltage application to the cell. In a liquid-like environment, the concentration of the neutral viologen keeps very small in the system, since the absorption curves abruptly drop immediately after the removing of the electric power supply. In fact fast translation diffusion leads to very efficient oxidation of the neutral viologen species. This effect is not observed in the solid film, because the most important contribution to charge transport is given by redox hopping. Bounded translation diffusion, occurring in limited space length, cannot be excluded of course, according to the observation that colouring and bleaching times tend to increase with increasing of the polymer matrix concentration. For long electric power supplying times the population of the neutral viologen uncoloured form becomes gradually important, and make the absorption curves decrease. Even if at short driving times a more intense contrast when compared to that of the fluid systems is observed, nevertheless it seems that the solid film cannot be exploited for usages in which a strong absorbing state needs to be kept constant for long time. This problem could be solved by using electrochromic molecules having a single coloured oxidized (anodic type) or reduced (cathodic type) state. We will show that the solid film here presented can be kept in an almost constant high-absorbing level, by applying appropriate time modulated electric driving pulses.

In order to continue to analyse the differences between the electrochromic responses of the solid film and that of a classical all-liquid EC device  several absorption curves obtained by using driving voltages of the same duration, but with progressively greater

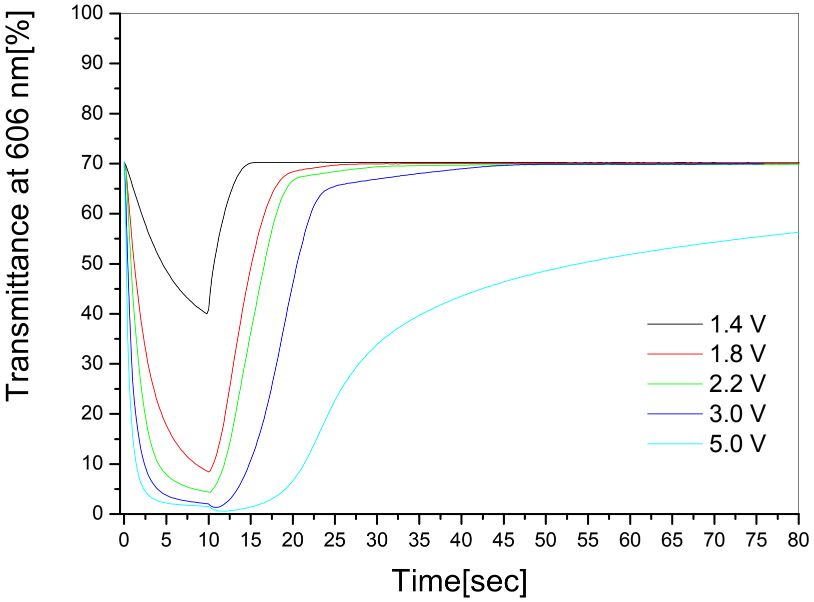


**Fig. 2.17** *Transmittance at 606 nanometers as function of time for a solid plastic film containing 40 wt.% poly(vinyl formal), 4 wt. %f ethyl viologen diperchlorate, 1 wt. % of hydroquinone, 55 wt. % propylene carbonate, 60 µm thick, with a driving voltage ten second long and with different amplitudes..*

amplitudes are shown in figure 2.17 and 2.18. What we can deduce from these two graphs is that in the solid film and also in the EC solution an increase in the voltage leads to an increase of the maximum quantity of coloured bipm$^{\bullet+}$, even if contrast ratio at the same voltage is greater for the plastic film rather than liquid EC solution, how we can see better in figure 2.19, where CR at 606 nm for the two different EC cells are reported as function of the applied voltage. This effect, as discussed before, can justified by a reduced mobility of the electrochromic molecules in the solid film, which makes more difficult the achieving of the steady state in which oxidized anodic molecules re-oxidize the blue radical cation. As a consequence, at the same voltage population of bipm$^{\bullet+}$ is greater where molecule have a smaller freedom of motion (solid film) with respect to the electrochromic solution, where are completely free to diffuse from an electrode to another. In fact just in experiments of figures 2.15 and 2.16 the transmittance curves of the fluid ECD reach a constant limit value in about 3 seconds. This behavior is not present in plastic ECD as we can see in figure 2.17. From figure 2.16 we can

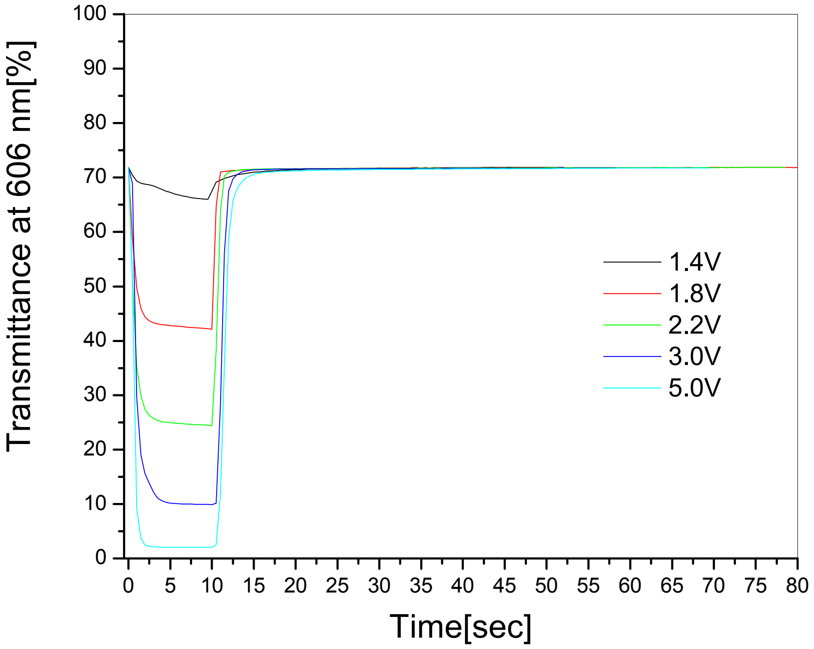


**Fig. 2.18** *Transmittance at 606 nanometers as function of time for an electrochromic solution containing 4 wt. % ethyl viologen diperchlorate, 1 wt. % hydroquinone and 95 wt. % propylene carbonate, 60 μm thick, with a driving voltage ten second long and with different amplitudes..*

deduce that a voltage of 3.0 volts ten seconds is long enough to produce in the EC solid film a contrast ratio of more than 50, so is possible to obtain very deep colourations of the electrochromic cell without causing collateral reactions of the electroactive molecules. A five volts pulse produces a contrast ratio equal to 120, that is a very high value but life of the device can be shortened. The applied voltage

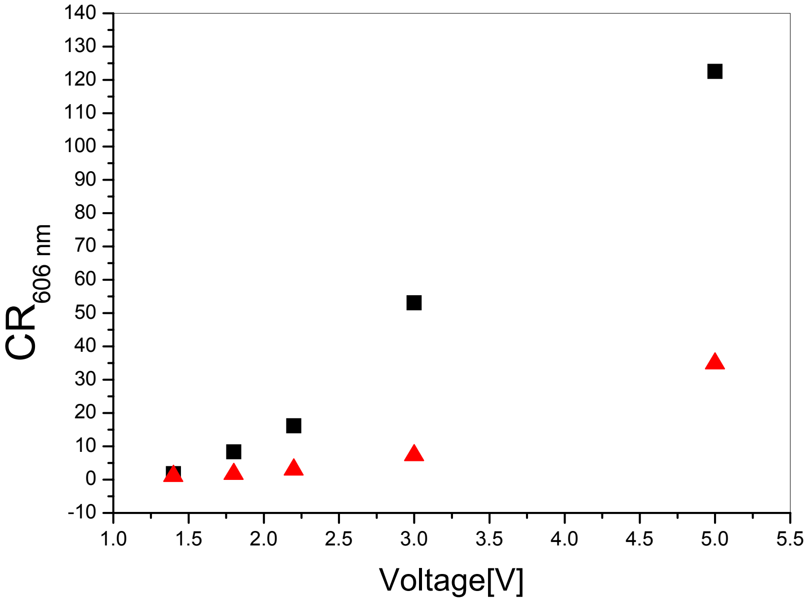


**Fig.2.19** *Comparison of contrast ratios for an electrochromic solution (▲) and for a plastic electrochromic solid film (■) as function of the applied voltage, lengths of voltages are kept constant, 10 seconds long for all the experiments. Chemical composition for the solid electrochromic film was: 40 wt.% poly(vinyl formal), 4 wt. %f ethyl viologen diperchlorate, 1 wt. % of hydroquinone, 55 wt. % propylene carbonate; instead for the electrochromic solution was: 4 wt. % ethyl viologen diperchlorate, 1 wt. % hydroquinone and 95 wt. % propylene carbonate. Cells thickness was 60 μm.*

affects also, the bleaching rates of the electrochromic device, are affected by, as we can see in the figure 2.20, where $\tau_{bl}$ (bleaching time) for our solid electrochromic film and for the electrochromic solution is plotted as a function of the applied voltages. $\tau_{bl}$ was defined as the time necessary to the EC cell to reach the 95% of the maximum transmittance value from the minimum transmittance value . This minimum was not always reached as the pulse was turned off, because for high voltages values reaction 1.20 was present. We can observe from the above graph that for the solid film bleaching times increase with the voltage amplitude, while, for the liquid system $\tau_{bl}$ remains constant. Moreover, bleaching times are approximately similar for the two kind of cells for voltages up to 3.0 volts, but reach a very large difference for a five volts pulse. This behaviour is not observed in the experiment where voltage amplitude was kept constant at 2.2 volts and duration was varied (figure 2.21), thus we can conclude that bleaching rates for the solid film increase with the voltage duration up to reach a limit value (13 seconds for a pulse length of 30 seconds) after which no further increase is possible. For electrochromic solution, on the contrary, only a small increase of $\tau_{bl}$ with pulse duration occurs.

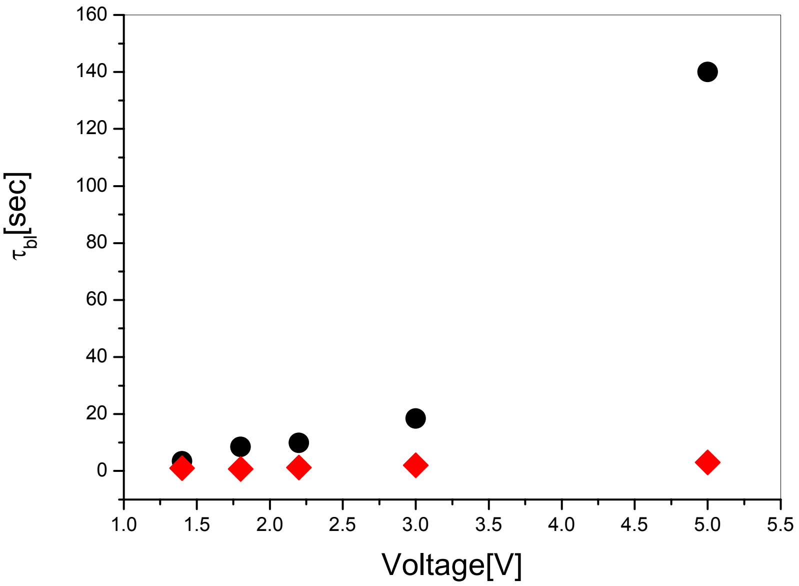


**Fig.2.20** *Bleaching times of the solid film (●) and of the liquid electrochromic cell (♦) as functions of the applied voltage. Experimental conditions, as pulses, chemical formulation, and cell thickness were the same of experiment of figure 1.23.*

From the comparison of experiment in figure 2.20 and experiment in figure 2.21 we can observe that, even for very long driving voltages, differences between the bleaching times of the two different systems are not so great, more exactly, increasing the voltage amplitude, $\Delta\tau_{bl}$ (defined as the difference between $\tau_{bl}$ of the solid system and $\tau_{bl}$ of the electrochromic solution for the same experimental conditions) increases too ($\Delta\tau_{bl}$= 137 seconds at 5 volts), while increasing the voltage duration $\Delta\tau_{bl}$ increase up to a maximum value equal to 11 seconds for an applied pulse 20 seconds long and after it tends to be constant or even to decrease. This different behaviour could be ascribed to the different concentrations in

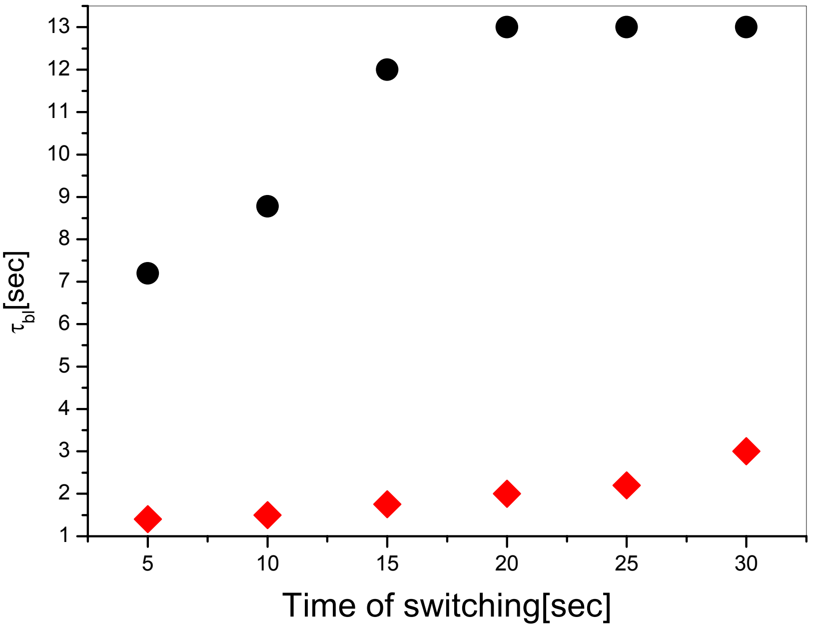


**Fig.2.21** *Comparison of bleaching rates for an electrochromic solution (♦) and for a plastic electrochromic solid film (●) as function of length of the applied voltage (2.2 volts). Compositions were: wt.% poly(vinyl formal), 4 wt. % of ethyl viologen diperchlorate, 1 wt. % of hydroquinone and 55 wt. % propylene carbonate for the plastic film, and 4 wt. % ethyl viologen diperchlorate, 1 wt. % hydroquinone and 95 wt. % propylene carbonate for the electrochromic solution. Cells thickness were 60 µm for both cells.*

bipm$^{\bullet+}$ and bipm$^0$ present in the two different electrochromic systems produced by the applied voltages. Increasing the pulse length only the population of bipm$^{\bullet+}$ increases, while the ratio bipm$^0$/ bipm$^{\bullet+}$ was constant at that voltage. On the other hand, when the voltage amplitude increases, the bipm$^0$ population increases too, as well as the ratio bipm$^0$/ bipm$^{\bullet+}$. Somehow the percentage of neutral viologen present in the electrochromic mixture is of critical importance on the spontaneous bleaching rates of the EC device. How we will see later in this chapter, the spontaneous bleaching times of this electrochromic device is strictly related to the presence of charge-transfer complexes between viologen and donor molecules. This CT complexes make easier the charge propagation inside the solid film, but the, formation of the neutral viologen species makes very unstable this complex causing a not favorable orbitals overlapping (or in other words the viologen looses its acceptor, electron poor, behaviour), and this makes the electron-transfer process inside the coloured electrochromic film slow down.

As we can deduce from experiments described in figures, the colouration and bleaching times of the solid electrochromic film are not much longer with respect to the $\tau_{col}$ and $\tau_{bl}$ for an equivalent all-liquid device. We would have expected more differences between these kinetic parameters, because, in a solid system the reduced mobility of electrochromic molecules should negatively affect the colouration and the bleaching processes. The mobility of chromophores is very important in a typical fluid electrochromic device because anodic and cathodic electrochromes need to migrate to the electrode in order to gain one or more electrons required by the chromogenic step, and they need to migrate towards the bulk of the film in order to react and to be transformed into their bleached forms. This behaviour is outlined in figure 2.22.

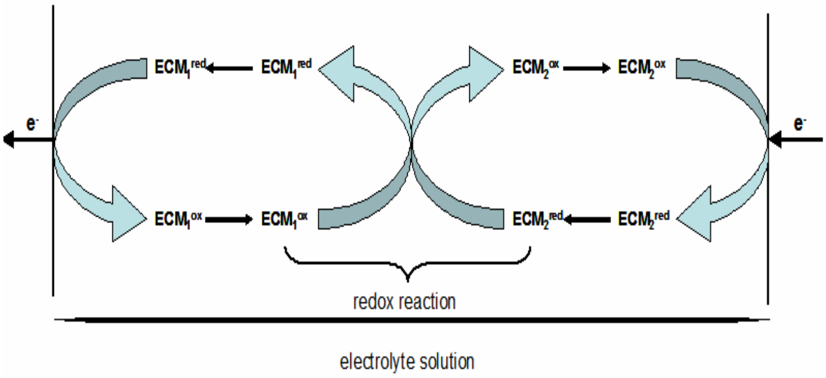


**Fig. 2.22** *Operating principle of an all-solution electrochromic device.*

We explained the fast response times of the solid electrochromic device by an electron self-exchange reaction of active redox species inside the film. This phenomenon is known to occur in redox media in which facile electron transferring moieties are present in mixed electron valency and high concentrations[13], or very slow physical diffusivities[14]. Uunder these circumstances, donor-acceptor electron self-exchange can be an important charge transport mechanism acting at rates significantly higher than that reached by the charge physical diffusion. Electron self-exchange was recognized early in chemically modified electrode as the transport mechanism for electrochemical charge through the fixed-site of redox polymer films on electrode[15]. A quantitative explanation of coupling between physical diffusion and electron self-exchange in polymeric redox materials was given for Nafion film containing a cobalt complex[16].

One of the characteristic in the polymer electrochemistry is the extremely low diffusivity of redox solutes in the polymer electrolyte.

The suppressed diffusivity enhances the importance of electron-transfer between the redox solutes in the charge transport process during electrochemical reactions according to Dahms-Ruff's equation[17]

$$D_{app} = D_{phys} + k_{ex}\delta^2 c/6 \tag{2.6}$$

where $D_{app}$ is the apparent diffusion coefficient of electroactive species, $D_{phys}$ is the physical diffusion coefficient, $k_{ex}$ is the electron self-exchange rate constant, $\delta$ is the center-to-center distance of the solute at electron-transfer, and $c$ is the sum of the concentration of the oxidized and reduced forms of the redox solute. In monomeric solvent, $D_{phys}$ of redox solute is mostly $10^{-5}$-$10^{-6}$ cm$^2$/s. Under this condition, even very fast electron self-exchange reactions contribute only in a minor way to transport, i.e. the right-hand term in equation 2.6 is small compared to $D_{phys}$. However, the situation is different for diffusion of redox solutes in polymers, where rates of physical diffusion are much smaller, yet electron self-exchange barriers, seem to be depressed. $D_{app}$ of redox solutes in polymer electrolytes is typically $10^{-9}$-$10^{-11}$ cm$^2$/s or even lower. Under these slow diffusion rates, the apparent coefficient of a redox solute having a large $k_{ex}$ may be enhanced by electron self-exchanged reaction.

About the charge propagation mechanism of the electrochromic solid film object of this work, we can conclude that it is characterized by a contribute of short range diffusion of molecules inside the film and self-exchange reaction between electroactive species. It is not possible to exclude a local motion contribute of molecules to the electrochromic mechanism, because even if the electrolyte is a solid polymeric system, molecules can preserve some degree of local mobility due to presence of some quantities of liquid plasticizer. Nevertheless, the main charge propagation mechanism is self exchange reaction in such a device, because concentration of electroactive species is enough to allow electron-transfer reaction between molecules having different redox states.

An important aspect, which needed to be explored for our ECD was the possibility to kept constant a strong absorbing state for a long time. This is an important feature for all applications which could have power consumption problems as electrochromic windows, in which electrochromic molecules must be keep in the ON (coloured) state for many hours in hot seasons. As said before, it is possible to adjust the spontaneous bleaching times of the electrochromic device simply adjusting the percentage of anodic molecules inside the chemical formulation; we will better explore this aspect later, but in the graph below (Figure 2.23) we can observe how to obtain an ECD with a “memory” effect with reduction of energy consumption is possible.

This problem could be also solved applying appropriate time modulated electric driving pulses, as it is shown in figure 2.24, which reports the data in transmittance units (100% was the transmittance of air) at 606 nanometers. The black curve shows the transmission of the solid film as a function of time for a driving voltage kept constant at 2.2 Volts. The graph highlights more evidently than previous experiments the decreasing of film absorption (increasing of transmittance) after a maximum absorption (minimum transmittance). The curve does not converge to any stationary state transmittance, at longer time, but keeps oscillating around 25% transmittance (this behaviour can be better shown when a longer time scale is used). If a pulsed (2 sec ON followed by 1 sec OFF) driving mode is applied, using a constant driving voltage until the transmittance reaches the value of 15%, the transmittance remains almost constant in time

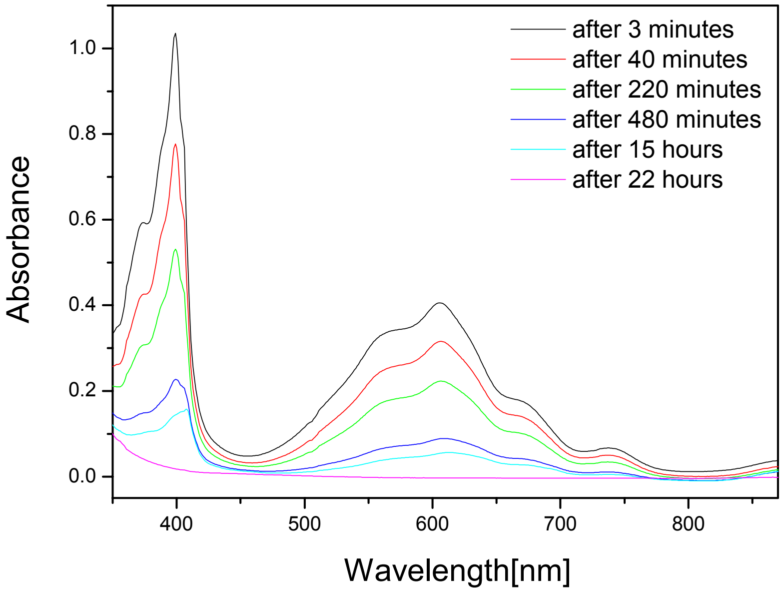


**Fig. 2.23** *UV-vis spectrum of the bleaching process for an electrochromic film having the following composition: 40 wt % poly(vinyl forma)l, 4 wt % ethyl viologen diperchlorate, 56 wt % propylene carbonate, after removing a 2.2 volts pulse ten second long.*

(variation of about 3%). Of course more stable values of absorbance could be obtained by applying tailor made driving pulse sequences. Another interesting feature of the electrochromic response of the presented solid film is that the bleaching time can be also shortened by applying to the film an off voltage having an opposite polarity to that applied during the colouring step. This effect is shown in figure 2.25.

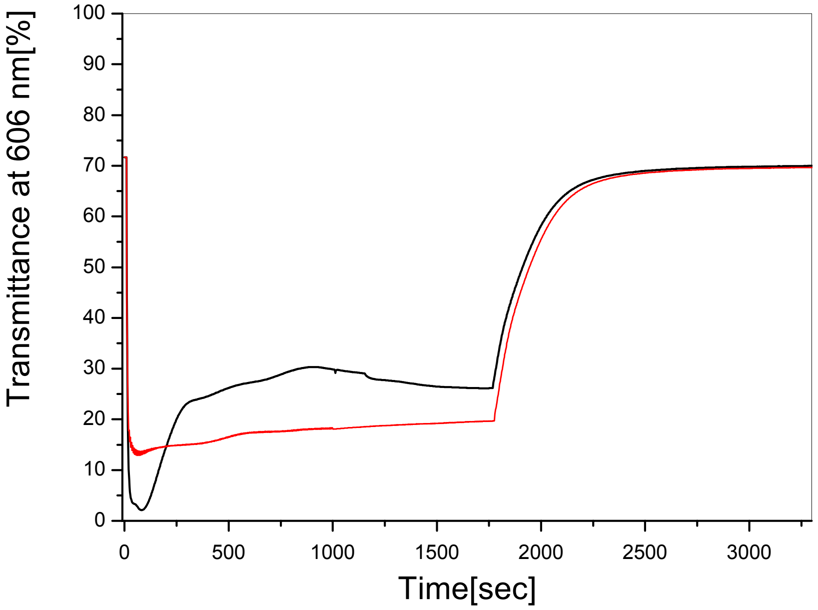


**Fig. 2.24** *Long time electrochromic response of a plastic solid film containing 40 wt.% PVF, 4 wt. % ethyl viologen diperchlorate, 1 wt. % hydroquinone and 55 wt. % propylene carbonate for two different electric driving modes. Black curve: continuous driving at 2.2 volts. Red curve modulated driving (2.2 volts 2sec ON alternated by 1 sec OFF starting from 20% transmission).*

The black curve reported in figure 2.25 was obtained from the plastic solid film, by applying a voltage of 2.2 volts for 25 seconds. The probe light going trough the sample is reduced to about 3%. Once the driving voltage has been cut out, almost 50 seconds are required to bring back the transmission to the pre-driving level. On the other hand when a counter voltage of –2.2 volts was applied (red curve), after having coloured the film for the 25 seconds with 2.2 volts, the bleaching time has been reduced to about 10 seconds.

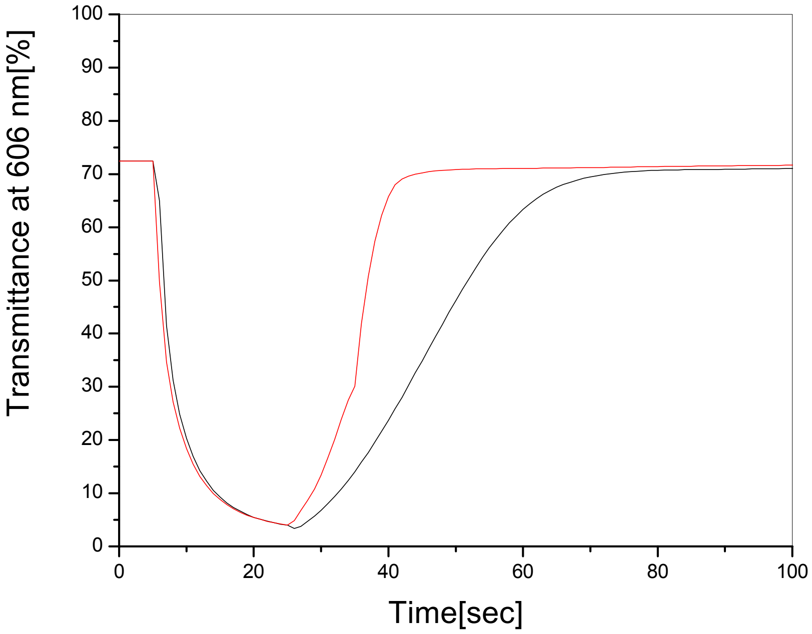


**Fig. 2.25** *Bleaching time shortening by application of a bleaching voltage. Black curve: bleaching is spontaneously achieved ( driving voltage is shut off at 25 seconds ) Red curve: bleaching is achieved under a bleaching voltage (2.2 volts with opposite polarity with respect to colouring voltage) applied at 25 seconds.*

For smaller contrast ratio values the effect of the change in polarity of the driving pulse on the bleaching time of the electrochromic device is more evident. Such a peculiarity is very important for applications which need very fast bleaching rates as electrochromic rear-view car mirrors. This kind of devices currently produced for the automotive market, has very slow relaxation times (some minutes), so the EC system object of this research could be an important improvement for the possibility to modulate bleaching times by suitable electric fields.

The duration of the bleaching voltage is very important, in fact a too long electric pulse can cause a bleaching and a successive re-colouration of the electrochromic device as we experimentally observed.

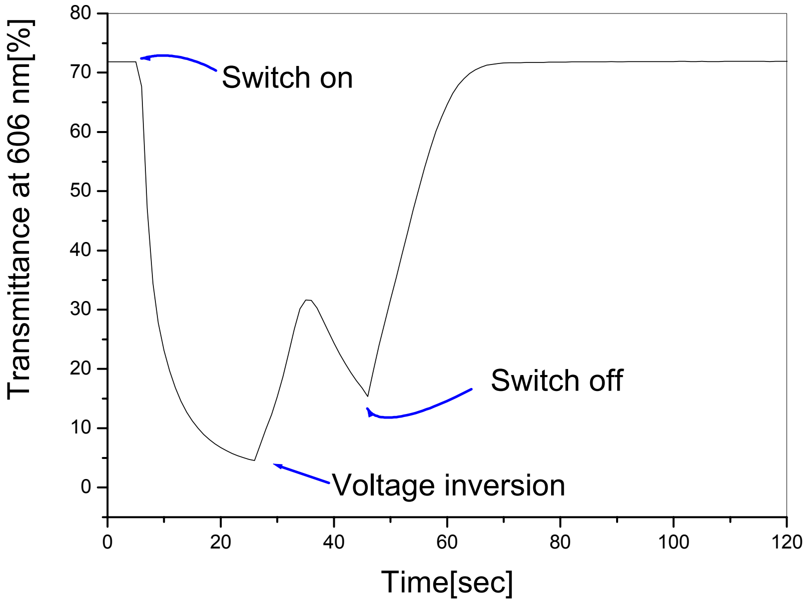


**Fig. 2.26** *Electrochromic response for an ECD during application of 2.2 volts for 20 seconds followed immediately by -2.2 volts for 20 seconds. Composition of the sample was: 40 wt.% PVF, 4 wt. % ethyl viologen diperchlorate, 1 wt. % hydroquinone and 55 wt. % propylene carbonate.*

In figure 2.26 the ON voltage applied to the sample was 2.2 volts for 20 seconds and the bleaching voltage was -2.2 volts for 20 seconds The counter voltage was immediately applied when the colouring voltage was switched off. How we can see from the graph, when the bleaching voltage was switched on the bleaching process started, but after further 10 seconds with the reverse pulse applied, there was a re-colouration of the EC device, and only when the pulse was switched off the electrochromic film recovered its initial uncoloured state in more or less 10 seconds.

Importance of reverse pulse length on bleaching times is better outlined in graph 2.27, in which behaviour of electrochromic response times for a sample having the same composition of that employed for experiment described in figure 2.24. The ECD was subjected to a set of voltages in each experiment. The colouration voltage was 2.2 volts for 20 seconds, instead bleaching pulses were -2.2 volts but with different length for every experiment. For this electrochromic formulation a voltage of -2.2 volts 7 seconds long turned out the optimal bleaching pulse ($\tau_{bl}$ 11 seconds long). Relatively long bleaching times were obtained because the driving field we used produced very high contrast ratios, in fact the minimum transmittance value obtained was 5% for all the pulse sequences.

The great importance of the bleaching voltage rate on the electrochromic response times depends on the distribution of electrochromophores in their different redox states inside the solid film after application of the ON voltage, and on the geometry of the cell. When electrons are injected inside the film (colouration process) different layers with different ratios $bipm^{2+}/bipm^{+\bullet}$ form. This ratio is small for layer near the cathode (high concentration of $bipm^{+\bullet}$) and it decreases as distance from cathode increases, according to the value of potential in every layer of the electrochromic film.

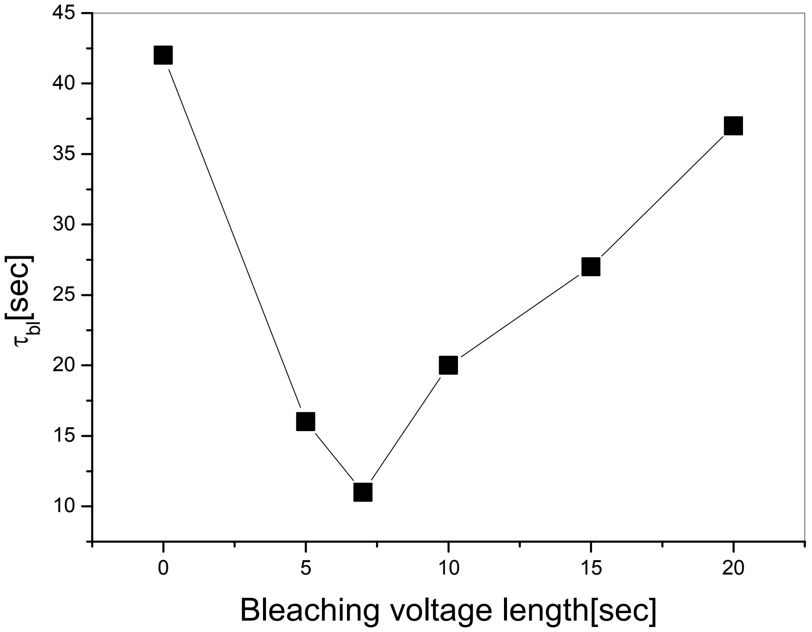


**Fig. 2.27** *Bleaching rates of the electrochromic solid film for different bleaching voltages.*

Of course, concentration of bipm$^{+\bullet}$ is zero near the positive electrode. The behaviour of the EC cell during colouration process is described in figure 2.28;

When polarity of pulse is inverted, anode changes in cathode and vice versa, all the coloured film layers give up ectrons to positive electrode (oxidation of bipm$^{+\bullet}$), at the negative electrode electrons are injected, reduction of 1,4-benzoquinone to hydroquinone occurs, but when all benzoquinone is consumed

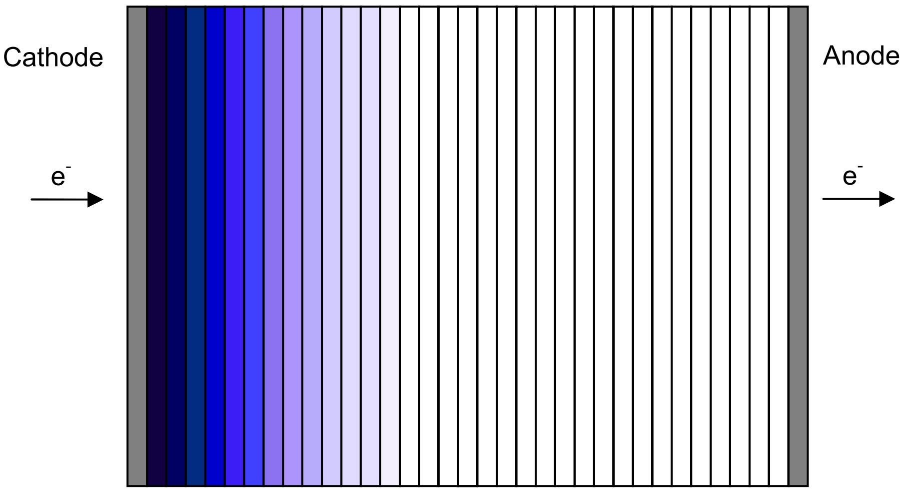


**Fig. 2.28** *Schematic representation of an electrochromic cell when electron are injected inside the film. Areas with different concentration of coloured radical cationic viologen form near the cathode by means of the electric driving field which value changes in different areas of the cell. Potential nough negative near the cathode to allow reduction of bipm*$^{2+}$*, enough positive near the anode to oxidize hydroquinone to 1,4-benzoquinone, is zero inside the film at some distance from cathode.*

dicationic viologen near the cathode starts to reduce to coloured radical viologen. So, if the reverse pulse is too long, decolouration of electrochromic layers near the anode corresponds to formation of coloured layers near cathode, just as we can see from graph in figure 2.26, when the counter voltage was applied, an initial bleaching is followed by a partial colouration of the film.

### 2.3.2 Study of the effect of CT complex formation on electrochromic response times

During this reserch a very interesting behaviour of electrochromic film object of this study was noted. Only when particular anodic substances where used, bleaching times where substantially shortened. Moreover, we experimentally observed that when these anodic molecules had been mixed with viologens to obtain an electrochromic mixture, a colour different from that of the EC substances was formed.

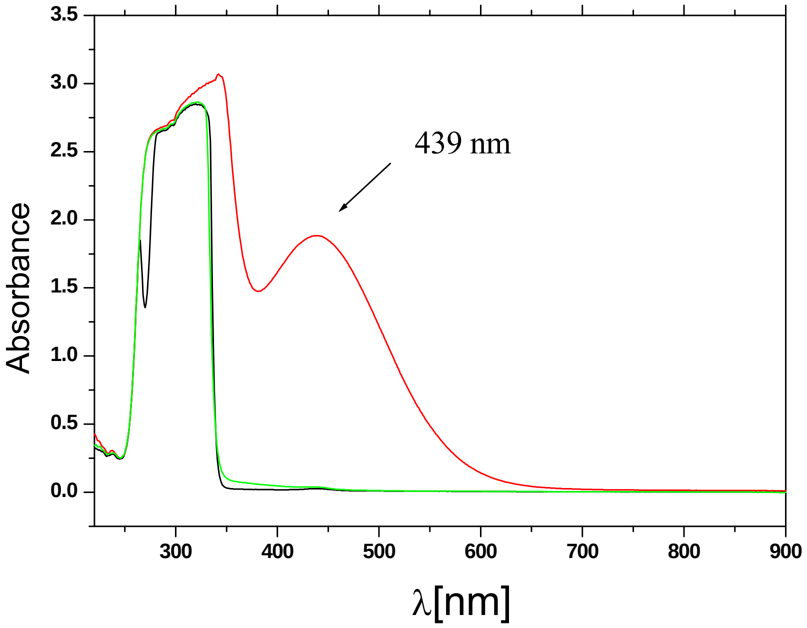


**Fig. 2.29** *UV-vis spectrum of three different solutions: ethyl viologen diperchlorate in propylene carbonate (green line), hydroquinone in propylene carbonate (black line) and a solution of both ethyl viologen diperchlorate and hydroquinone in propylene carbonate (red line).*

In particular when the anodic molecule was hydroquinone, solution colour changed from pale yellow (colour of bipm$^{2+}$) to red, more or less intense, according to the concentrations of the electrochromic species. The formation of a new dative bond was evinced by a new optical absorption band. (i.e. a new colour). From these experimental data, we ascribed decreasing in bleaching times to the formation of charge-transfer complexes between viologen, behaving as acceptor, and donor anodic molecules. It is well known in literature, as we described in paragraph 1.7 of this thesis, that viologens (electron poor molecules) are able to generate association forms with orbital and partial charge overlapping with electro-rich molecules in solution. For this reason we turn only on the effects of this phenomenon on the electrooptical properties [illegible]ur solid electrochromic film.

In figure 2.29 we can observe the UV-vis spectrum of the electrochromic solution of a mixture of hydroquinone and ethyl viologen diperchlorate in approximately [illegible]imolecolar conditions. As we can see a new and very intense optical absorption band was produced when the two species are mixed together: This new band has a maximum in absorption at 439 nanometers, and it is not present in respective absorption spectra of single electrochromic molecules.

The stoichiometry of the charge-transfer complex was checked by continuous variation method. The intensities of the absorption band at 439 nm was followed in the mixture for various molar ratio of the respective set of donor and acceptor, while the total concentration was kept constant (0.1 M). The resulting absorbances are depicted in the figure 2.30. The maximum absorbance was observed for the 1:1 molar mixture, indicating that the complex is formed by one donor molecule and one acceptor molecule.

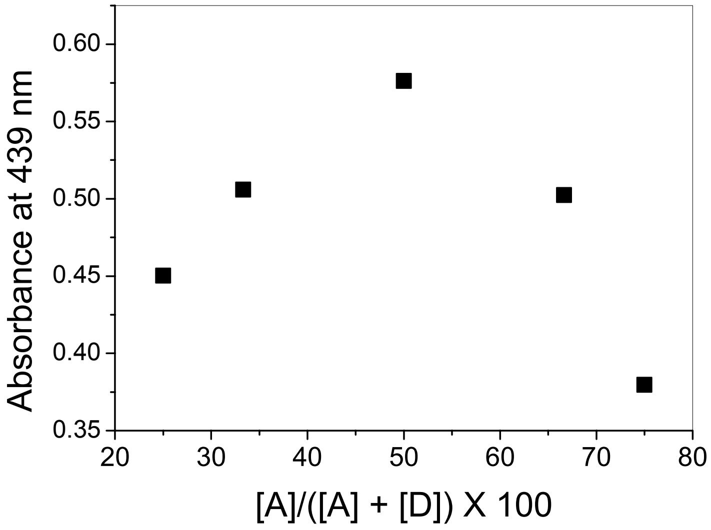


**Fig 2.30** *Absorbance at 439 nanometers for solutions of hydroquinone (donor molecule) and ethyl viologen diperchlorate (acceptor molecule) with different molar ratios in propylene carbonate as solvent. The total concentration of the mixtures was fixed at 0.1 M.*

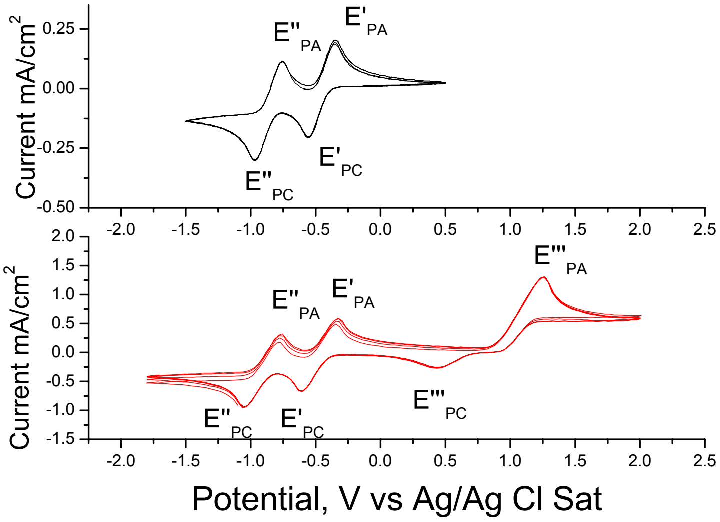


**Fig. 2.31** *Cyclic voltammetry experiment of ethyl viologen diperchlorate (EV) $1{,}5\bullet10^{-3}$ M in propylene carbonate (PC) using tetrabutylammonium perchlorate (TBAP) $1{,}5\bullet10^{-2}$ M as inert electrolyte, scan rate=10 mV/s (black curve), and cyclic voltammetry of a solution of hydroquinone and ethyl viologen diperchlorate 0.014 M in propylene carbonate TBAP, inert electrolyte 0.14 M, Sr=10mV/s, red curve.*

We performed at first a ciclic voltammetry experiment for the viologen and then for the mixture of hydroquinone (donor) and ethyl viologen diperchlorate (acceptor) (figure 2.31).Our aim was to control, if a shift in redox potentials of the chromogenic specie due to formation of the charge-transfer complex was present. From the first anodic and the first cathodic peak we calculate the standard redox potentials related to the dicationic/radical cationic viologen pair in presence and in absence of donor, according with equation 2.1. The measured values were $E_1^0 = -0.45V$ when viologen was subjected to cyclic voltammetry in absence of charge-transfer complex formation, $E_1^0 = -0.56V$ when ethyl viologen diperchlorate was mono-oxidized in presence of hydroquinone. How we can see redox potential related to the first reduction step of viologen was shifted towards more negative potentials when charge transfer complex was present. This can give evidence to a more difficult reduction caused to a stabilization of dicationic viologen due to formation of the complex.

In literature is well known[18] that dissociation of the CT complex is the rate limiting process during the process of electro-reduction of the solution-phase complex. The linearity of the graph in figure 1.8 suggests that the rate of electron-transfer is a simple factor of the rate of complex dissociation. In fact, as we can observe from the graph, increasing the dissociation constant of the complex (the CT complex is more associated) the rate constant related to the first reduction reaction of the viologen increases too, so we can deduce that complex must dissociate before the dicationic viologen being reduced to dicationic viologen. This results was confirmed by experiment of cyclic voltammetry in figure 2.31, the shift to more negative potentials for viologen first reduction step, can be attributable to a necessary dissociation of viologen.

As we can see, the redox potential shift due to formation of charge-transfer complex is not very great. This probably because the support electrolyte tetrabutylammonium perchlorate used in the ciclic voltammetry experiment partially prevents formation of charge-transfer complex. In fact we experimentally observed a reduction of the charge-transfer complex absorption band when the electrolyte was added to the electrochromic solution. This effect is well known in literature, Monk et all[19] experimentally studied the addiction of sodium chloride to a solution made of methyl viologen dication and hexacyanoferrate forming a 1:1 charge-transfer coloured complex having a $\lambda_{max}$ at 525 nm. Addition of sodium chloride to this solution causes the intensity of the colour to diminish. In this work[19] a simple model of competing equilibria was presented to account for the way the absorbance of an optical charge-transfer decreases as a function of ionic strength. The equilibrium constant K relates to CT complexation can be written as:

$$K = \frac{\alpha(A:D)}{\alpha(A)\alpha(D)} \tag{2.7}$$

Where any indication relative to the ionic charge of the acceptor (A) and donor (D) species is absent.

If the activities $\alpha$ are rewritten as the product of respective concentrations $c$ and activity coefficients $\gamma$, then equation 2.7 becomes equation 2.8

$$K = \frac{c(A:D)}{c(A)c(D)} \times \frac{\gamma(A:D)}{\gamma(A)\gamma(D)} \tag{2.8}$$

Equation 2.8 can be simplified by assuming the ionic activity coefficients to be equivalent, and using a mean ionic activity coefficient $\gamma_{\pm}$

$$K = \frac{c(A:D)}{c(A)c(D)} \times \frac{1}{\gamma_{\pm(av)}} \tag{2.9}$$

So, from the van’t Hoff isotherm

$$\Delta G = -RT \ln\left( \frac{c(A:D)}{c(A)c(D)} \times \frac{1}{\gamma_{\pm(av)}} \right) \tag{2.10}$$

and then converting to $\log_{10}$ and dissembling the K term, equation 2.11 was obtained:

$$\frac{-\Delta G}{2.303RT} = \log[A:D] - \log[A] - \log[D] - \log \gamma_{\pm(av)} \qquad \text{(2.11}$$

When an inert electrolyte is added to the solution, the ionic strength $I$ increases, causing the mean ionic activity coefficient to decrease, with a dependence described by the Debye-Hückel laws[20,21]

$$-\log_{\gamma\pm} = \frac{A\left|z^{+}z^{-}\right|\sqrt{I}}{1+\sqrt{I}} \tag{2.12}$$

Substitution of equation 2.12 in equation 2.10 yields equation 2.13:

$$\frac{-\Delta G}{2.303RT} = \log[A:D] - \log[A] - \log[D] + \frac{A\left|z^{+}z^{-}\right|\sqrt{I}}{1+\sqrt{I}} \tag{2.13}$$

Considering that the complex is the only species which absorb at the wavelength of observation and considering Beer-Lambert law (equation 1.3)
where A=0.5115 for aqueous solutions at 25°C.

$$\frac{-\Delta G}{2.303RT} = \log(Abs) - \log(\varepsilon) - \log(l) - \log[A] - \log[D] + \frac{A\left|z^{+}z^{-}\right|\sqrt{I}}{1+\sqrt{I}} \tag{2.14}$$

It was assumed that viologen is relatively weak electrolyte and is involved in separate ion-association equilibria with further ions X:

$$A + nX = AX_{n} \tag{2.15}$$

If the equilibrium constant of association is K',

$$K' = \frac{[AX_n]}{[X]^n[A]}\left(\frac{1}{\gamma_{\pm(av)}}\right)^n \tag{2.16}$$

rearranging this equation and substituting for [A], gives equation (2.17)

$$\frac{-\Delta G}{2.303RT} = \log(Abs) - \log(\varepsilon) - \log(l) - \log\left[\frac{[AX_n]}{K'[X]^n}\right] - \log[D] + (n+1) + \frac{A\left|z^+z^-\right|\sqrt{I}}{1+\sqrt{I}} \tag{2.17}$$

Equation 2.17 therefore becomes equation 2.18

$$\frac{-\Delta G}{2.303RT} + \log(\varepsilon) + \log(l) - \log K' + \log[AX_n] = \log(Abs) + \log[X]^n - \log[D] + (n+1)\frac{A\left|z^+z^-\right|\sqrt{I}}{1+\sqrt{I}} \tag{2.18}$$

in which ΔG, ε, l, K' are all constants at fixed temperature and, since the concentration of acceptor involved in ion association $[AX_n]$ is always rather small (and can therefore be assumed constant), equation 2.18 simplifies to:

$$k = \log(Abs) + n\log[X] - \log[D] + k'\sqrt{I} \qquad (2.19)$$

where k and k' here are simply collections of constants. The extent of complexation is always low, so log[D] will also be effectively constant. So, particularly when the concentration of the inert electrolyte is slight, plots of log(Abs) vs log[X] will be more or less linear for an appreciable concentration range. Furthermore, since the ionic strength I of 1:1 electrolytes is the same as the concentration c, plots of log(Abs) against log(I) will be linear also, again particularly at low [X].

In conclusion while in electrochromic mixtures we used to obtain EC devices CT complex formation has occurred, on the contrary in electrochromic solution used for cyclic voltammetry experiment CT complex formed only in small amount for the presence of tetrabutylammonium perchlorate.

As said before, the modulation of the spontaneous bleaching times of our electrochromic solid film is possible, simply adjusting the percentage of anodic donor molecule inside the chemical formulation of the EC mixture. To experimentally study this behaviour, different electrochromic samples with different ratios in hydroquinone and ethyl viologen diperchlorate were exposed to a switching voltage of 2.2 volts 30 seconds long, and transmittance at 606 nanometers was monitored as function of time. Bleaching times were extrapolated from this experiment and were plotted as a function of the molar ratio between donor (hydroquinone) and acceptor (viologen). Results are reported in graph on figure 2.32. Bleaching times are still considered as times required for the electrochromic device to recover 95% of maximum transmittance from its minimum transmittance value. From the graph we can deduce that 1:1 molar ratio produces the fastest bleaching time. In fact $\tau_{bl}$ decreased till equimolecolar amount of donor and acceptor was achieved and it slowly increased again after this minimum value.

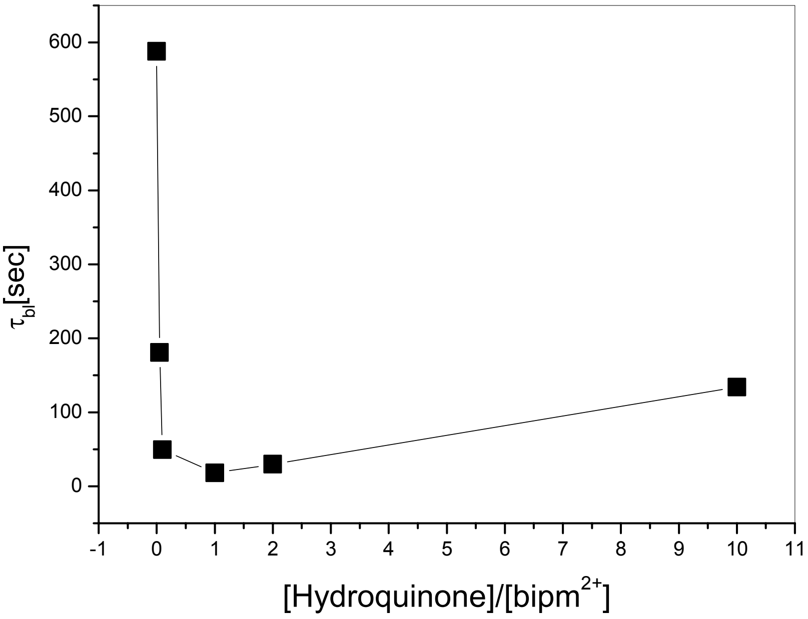


**Fig. 2.32** *Bleaching times for EC devices with 40 wt.% PVF, 55 wt. % propylene carbonate, but having different molar ratios hydroquinone-viologen. Switching voltage was 2.2 volts 30 seconds long, and thickness was 60 μm for all devices*

We can make some hypothesis on mechanism by which CT complex affects bleaching times of our solid electrochromic device. Initially, in solution, Hydroquinone and bipm$^{2+}$ interacts forming this complex, much probably oxygen negative charge of the lone pairs partially transfers on the positive charged bipyridilium rings in this 1:1

complex, as experimentally tested (figures 2.29 and 2.30). The addition of polymer blocked the molecules in this conformation, and when pulse was turned on, complex dissociated, as literature data showed[18], but molecules did not take away because of the rigidity of polymer matrix. So we have a situation in which 1,4-benzoquinone and bipm$^{\bullet+}$, which probably don't interact to form a complex, are still constrained to be close each other. Spontaneous bleaching of electrochromic device is due to recombination of oxidized anodic molecule (1,4-benzoquinone in this case) with reduced cathodic molecule (radical cationic viologen). In the absence of CT complex formation, local motion allows molecules to interact and ricombine inside the solid film. Motion is somehow impeded by polymer matrix, and consequently it can slow down the spontaneous recombination of cathode and anode and the associated bleaching process. This situation is different when the charge transfer interaction is present, in fact, as said before, 1,4-benzoquinone and viologen radical cation stay close when the pulse is turned off, no local motion is required for recombination of these two species, and spontaneous bleaching time are substantially reduced in this case, (from 588 seconds in complete absence of donor molecule, to 18 seconds when donor is in equimolecolar condition with respect to dicationic viologen).

A further experimental observation needs to be explained. When hydroquinone-viologen molar ratio overcomes 1:1 value, bleaching times start to increase, in fact $\tau_{bl}$ is equal to 134 seconds when [hydroquinone]/[bipm$^{2+}$] is 10. This is an unexpected behaviour, because increasing the hydroquinone amount in the chemical formulation, the percentage of charge transfer complex formed should increase also, and this should shorten the spontaneous bleaching times of the electrochromic film, and chemical equilibrium in equation 1.22 was shifted towards formation of AD specie. This unusual behaviour could be explained in terms of some geometrical considerations regarding 1:1 charge transfer complex of hydroquinone and dicationic viologen. In 1997 P.M.S. Monk[22] studied the effect of ferrocyanide on the performance of an heptyl viologen based electrochromic display device. Failure of such a display was caused by the comproportionation of electrogenerated $HV^0$ with $HV^{2+}$, with generation of electrochemically inert radical-cation dimer. Addition of ferrocyanide to the EC solution as an electron mediator improved the write-erase efficiency of an heptyl viologen-based device by promoting a different comproportionation mechanism that does not involve the radical-cation dimer. An inner–sphere complex in which the ferrocyanide acted as a conducting bridge between the two reacting bipyridilium redox states is shown in figure 2.33

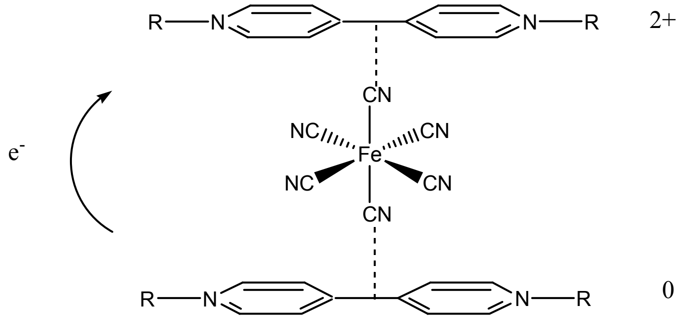


**Fig. 2.33** *Schematic representation of the comproportionation reaction in presence of ferrocyanide.*

In this last system radical cation dimer is absent during comproportionation, because the two radical cation moieties are not able to meet for the presence of the ferrocyanide bridge.

For our solid electrochromic film it can be thought a CT complex with the same spatial arrangement of donor and acceptor, where hydroquinone acts as a conducting bridge between two bipyridilium rings. In fact hydroquinone has two oxygen atoms which can transfer electronic densities to the positively charged nitrogen atoms of two different dicationic viologen molecules (figure 2.34)

This kind of spatial interaction was confirmed by the experimental observation discussed in the first part of paragraph 2.3.1, concerning formation of radical cation dimer in our solid systems. As it was said, UV-vis spectrum data showed that dimeric viologen does not form, probably by a more favourable interaction between bipm$^{2+}$ and hydroquinone compared with bipm$^{2+}$ and bipm$^{0}$.

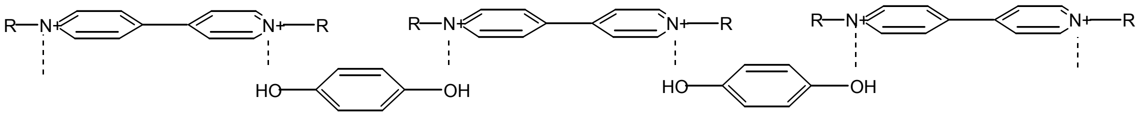


**Fig. 2.34** *Schematic representation of the charge-transfer viologen-hydroquinone complex.*

Very long charge transfer complex chains (figure 2.34) are promoted by 1:1 donor-acceptor molar ratios. In fact if electrochromic solutions are more concentrated in ethyl viologen diperchlorate, many CT aggregates are present having bipyridilium at the ends, and percentage of long charge transfer chains should be very small. The same should happen if solutions are more concentrated in hydroquinone. If short chains with the same functional groups at the ends are present, these are not able to interact forming longer CT chains (figure 2.35).

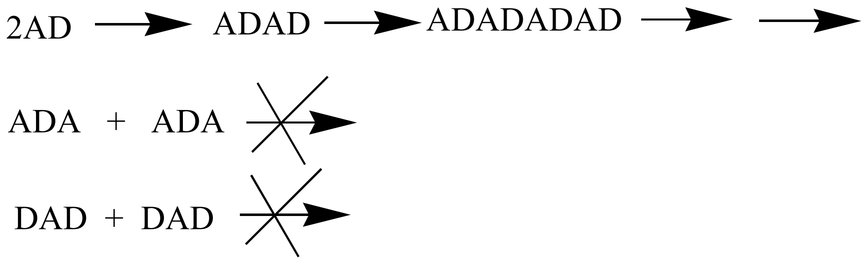


**Fig. 2.35** *Schematic representation of a situation in which acceptor (A) and donor (D) are in equimolecolar amount (first equation from the top of the figure), and of a situation in which length propagation charge transfer complex formation is prevented by acceptor or donor excesses.*

This hypothesis is in agreement with experimental observations in figure 2.32. Increasing in bleaching times for increasing molar ratio hydroquinione-ethyl viologen is shown. Longer CT chains are able to propagate charge better than shorter CT chains, with a little contribution of local motion.

In figure 2.36 the behaviour of contrast ratio of different electrochromic cells with different molar ratio donor-acceptor is shown. As we can see the contrast ratio increased with molar ratio, from a minimum value of 1.35, for electrochromic mixtures in complete absence of charge transfer complex, to a maximum value of 48.50 for hydroquinone and ethyl viologen diperchlorate in equimolecolar conditions, and after it decreases for further molar ratio increasing (CR was equal to 19.84 when molar ratio was 10). We can deduce that possibility to form long charge transfer chains is an important factor also for propagation of charge during colouration process; in fact, presence of a consistent amount of long CT chains (1:1 molar ratio) allows the reduction of a great quantity of bipm$^{2+}$. Much probably hydroquinone in CT complexes allows reduction of viologen molecules, acting as a conductive bridge between the bipm$^{2+}$ molecules near the negative electrode and those in the bulk of the film, accomplishing a more intense colouration in the device. Shorter CT chains are able to propagate charge only for short distances from the cathode, causing only very small contrast ratios.

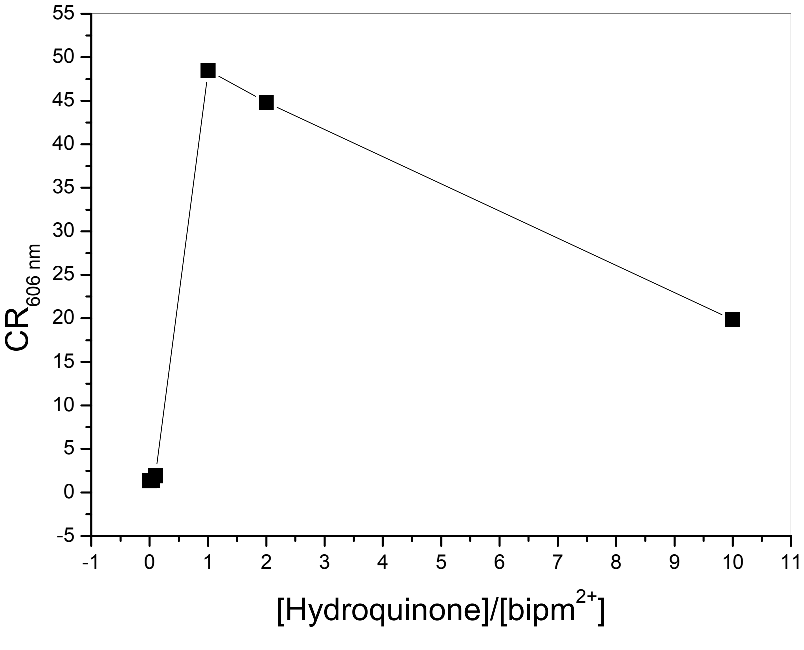


**Fig. 2.36** *Contrast ratios at 606 nanometers for EC devices with 40 wt.% PVF, 55 wt. % propylene carbonate, but having different molar ratios hydroquinone-viologen. Switching voltage was 2.2 volts 30 seconds long, and thickness was 60 μm for all devices.*

Importance of long charge-transfer complex chains on mechanism of charge propagation inside the solid electrochromic film can be outlined also by experiment described in figure 2.38, where transmittance versus time for an electrochromic cell containing charge transfer complex between pyrogallol (1,2,3-benzentriol) shown in figure 2.37, and ethyl viologen diperchlorate is reported.

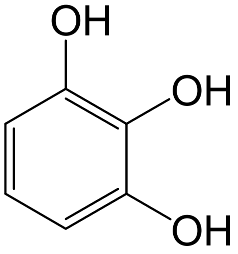


**Fig. 2.37** *Pyrogallol.*

Pyrogallol is an electron-rich substance and just like hydroquinone can give charge transfer complex formation with electro poor substances as dicationic viologens, but, the spatial arrangement of hydroxy groups on benzene ring in pyrogallol is not optimum for formation of very long CT complex chains. In fact in figure 2.36 the long decay time for these kind of systems was reported. As we can see, $\tau_{bl}$ was 1168.5 seconds with a colouration voltage of 1.8 volts applied for 5 seconds and a molar ratio pyrogallol-ethyl viologen diperchlorate of 2:1. The excess of donor in the chemical formulation must be used for the smaller association constant of the complex respect the hydroquinone-ethyl viologen diperchlorate as reported in literature[23,24] for all in solution systems. This smaller association constant together with symmetry of pyrogallol molecule, can determine the long decay times of ECD. In fact, how we can see from the graph, when the voltage was removed there was first a more rapid decolouration followed by a very slow bleaching of the ECD up to reach the initial transmittance value. This can be due to the associated radical viologen- pyrogallol quinone pair which reacts quickly at first, and to the non associated radical viologen, which need to move to reach quinone in a second moment.

The same experiment described in figure 2.32 for the solid EC film, was performed for a typical all-liquid electrochromic cell, in order to compare the effect of charge transfer complex in the two different systems.

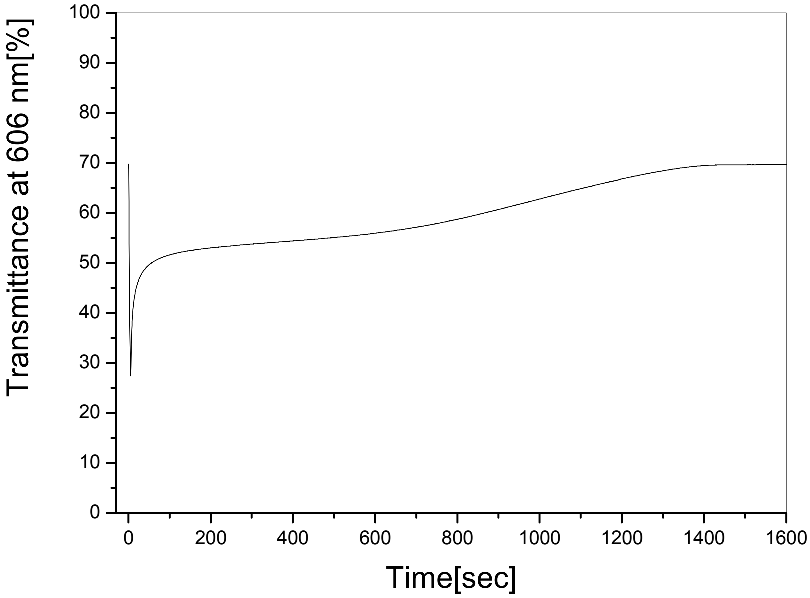


**Fig. 2.38** *Electrochromic behaviour for the pyrogallol ethil viologen perchlorate pair with 2:1 molar ratio. PVF was 40 wt. % and PC was 55 wt. %. The applied voltage was 1.8 volts for 5 seconds. The film thickness was 60 micrometers.*

2.3 volts DC for 30 seconds were applied at different electrochromic cells with no polymer content, but having different donor acceptor molar ratio. More precisely, as in experiment performed on the solid film, ethyl viologen diperchlorate percentage was kept constant, and hydroquinone amount was varied to obtain different stoichiometric ratios of the two compounds. In order to obtain the graph plotted in

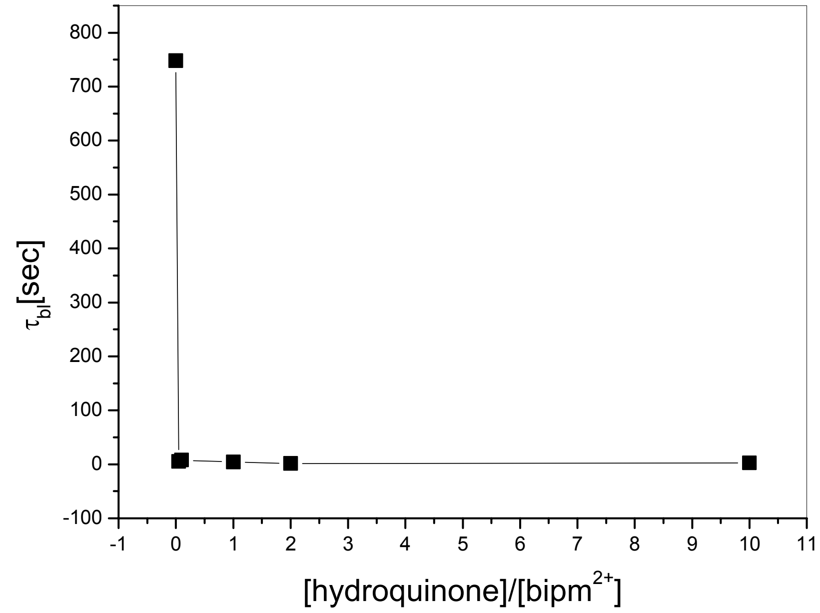


**Fig. 2.39** *Bleaching times for EC devices with 40 wt. % PVF, 55 wt. % propylene carbonate and different molar ratios hydroquinone-viologen. Switching voltage was 2.2 volts 30 seconds long, and thickness was 60 μm for all devices*

figure 2.39, at the applied voltages, transmittance at 606 nm was recorded as function of time, and bleaching times were extrapolated. How we can observe from figure 2.39, behaviour of $\tau_{bl}$ was very different from that showed for the electrochromic solid film. A great variation in spontaneous bleaching times was observed. We start from a situation of complete absence of hydroquinone ($\tau_{bl}$=748 seconds) to reach the other extreme in which very small amount of hydroquinone are present in the electrochromic solution ($\tau_{bl}$=5 seconds when [hydroquinone]/[bipm$^{2+}$]=0.05), but, further increasing in molar ratio did not produce anymore variations in bleaching times. This experimental observation can make us to hypothesize a alytical effect of the charge transfer complex on the spontaneous bleaching mechanism of the all-liquid electrochromic cell. Charge transfer chains (figure 2.34), when formed, are probably destroyed by transformation of donor and acceptor by redox reaction and by motion of molecule inside the electrochromic solution to reach the electrode when voltage is applied, so anodic and cathodic molecules are not forced to stay close each other. For this reason the completely free ability of molecules to migrate from cathode and anode towards the bulk of the liquid film to meet and react, is the only bleaching mechanism in these liquid systems.

This ability to modulate the spontaneous bleaching times of the solid electrochromic film object of this study, has a considerable technological appeal. In fact, depending on final application of the ECD, very short or long decolouration times can be required. For automotive application, for example, short decolouration times are required, whereas for solar control in buildings, the main requirement could be small power consumption. This is an important feature for electrochromic windows, for example, in which electrochromic molecules must be kept in the ON state for many hours. As said before this problem could be also solved applying appropriate time modulated electric driving pulses but stable values of absorbance could be obtained also by applying tailor made driving pulse sequences. Another possibility, which implies a smaller power consumption, is the variation of the chemical composition of the electrochromic mixture. Two factors can be changed to adjust bleaching times in order to minimize power consumption. One is, as discussed before, the amount of charge transfer complex, which is strictly related to bleaching process rate. The second one is the amount of polymer in the electrochromic film; in fact, increasing polymer percentage inside the chemical formulation, causes an increasing of bleaching times. When the rigidity of the film is raised by a greater polymer amount, electrochromic molecules have a restricted local motion, and bleaching times are increased. In figure 2.40 three different samples having different PVF contents were exposed to the same DC field (3.0 volts for 5 seconds) and transmittance versus time was recorded. As we can see spontaneous bleaching times are different for these tree electrochromic cell, $\tau_{bl}$=12.1 seconds when PVF= 30 wt. %, $\tau_{bl}$= 22.5 seconds when PVF= 40 wt. % and $\tau_{bl}$= 90 seconds when PVF=50 wt. %. An ECD having great PVF contend should be the optimum for switchable electrochromic windows which does not require short response time, particularly because high PVF or PVB percentage ensure high resistance to the glasses. Unfortunately high contrast ratio values require very long electric pulses, or high voltage values to be applied.

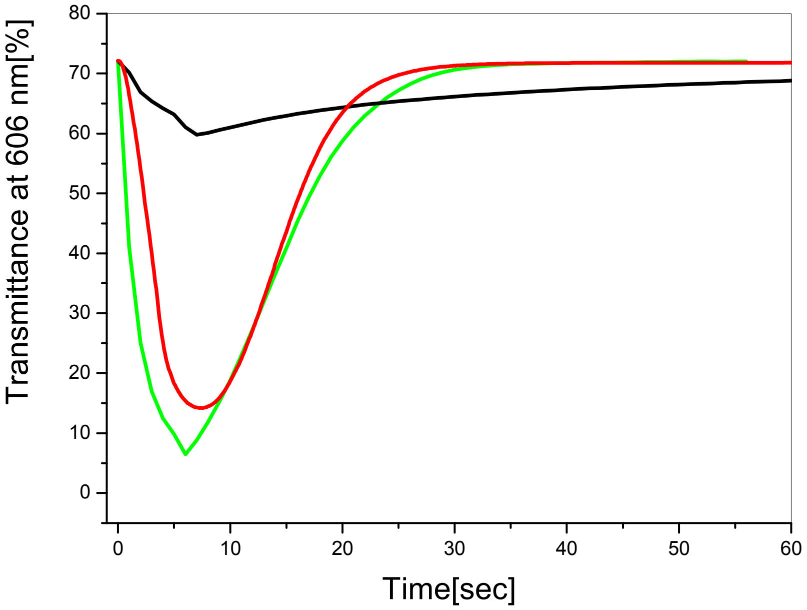


**Fig. 2.40** *Electrochromic behaviour for tree EC solid cells having the same hydroquinone-viologen molar ratio 1:1 but different PVF content. Black curve PVF=50 wt. %, green curve PVF=40 wt. % and red curve PVF=30 wt. %. Switching voltage was 3.0 volts for 5 seconds, thickness of the cells was 60 μm for the tree samples.*

### 2.3.3 Cycle Life

When an ECD is continually cycled between its coloured and bleached states, device failure can derive from physical changes in solid phases or from chemical side reactions. The cycle life is a measure of its stability, being the number of cycle possible before such failure. A major aim of device fabrication is obviously to maximize the cycle life. The cycle life is a complicated function of the colouration required in cycle: the cycle life generally decreases if wide changes in composition are required, that is, if the quantity of charge injected or removed is large.

Initially cycle life experiment was performed using our hydroquinone-viologen system, for the opportunity given by charge transfer complexes existing between donor an acceptor molecule, to adjust some properties of our electrochromic solid film, but as we are going to see, this system did not showed to be the optimum system as far as we are concerned with cycle life. Test were performed on ECDs sealed with appropriate sealer; butyl rubber based sealer were used because have a very low permeability to water.

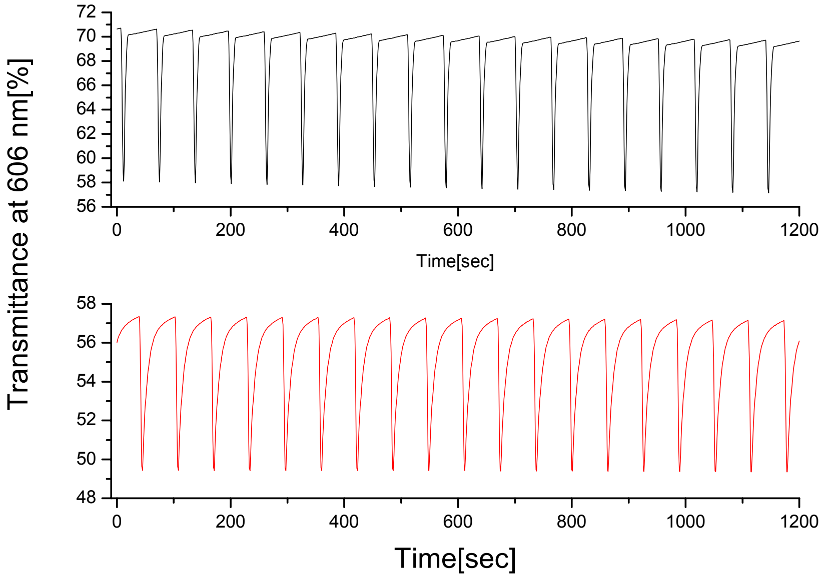
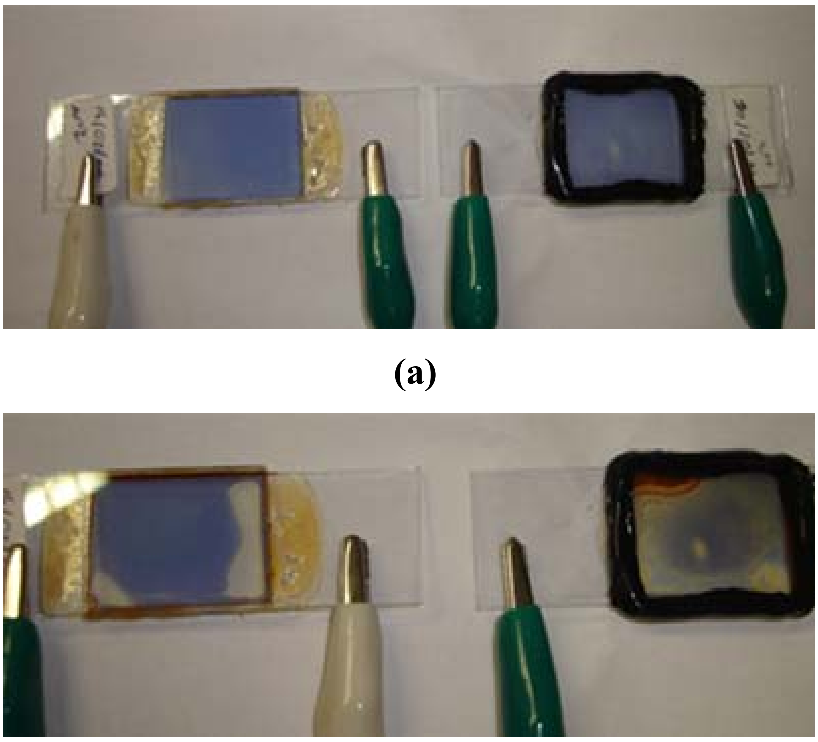


**Fig. 2.41** *Transmittance versus time before (black curve) and after 1900 electro-switching cycles (red curve) for an ECD with following composition: PVF 40 wt. %, PC 55 wt. %, ethyl viologen diperchlorate 4 wt. %, hydroquinone 1 wt. %. Pulses sequence for cycles was 1.6 volts for 5 seconds, and 58 seconds at V=0. Film thickness was 60.*

Anyway, simultaneously test on not sealed ECD were performed to observe differences between the two different sistems. In figure 1.47 transmittance curve after 1900 cycles for a sample in which electrochromophores are ethyl viologen diperchlorate and hydroquinone is shown; as we can deduce from the graph some failure of the ECD arose. The maximum transmittance value ($T_{max}$) changed from 70,62% at the first switching, to 57.18% after the 1900th cycle. Moreover, the minimum transmittance value ($T_{min}$) changed from 58.03% to 49.37%. The first reason which could be thought responsible for this decrease in transmittance values is the general loss in transparency of the electrochromic devices, observed in figure 2.42, where photographic images of the ECDs before and after the switching cycles can be seen. The second reason causing the transmittance value lowering, especially as regard $T_{max}$, is the increased spontaneous bleaching time of the electrochromic film, which is better observable in figure 2.43 were the first and the 1000th switching are reported in the same graph, and the loss bleaching rate of the ECD is evident. In the initial state 8.7 seconds were necessary to the ECD to recover its completely bleached state (100% of $T_{max}$), after 1000 switching cycles this time range was raised to 73 seconds. Increasing $\tau_{bl}$ 58 seconds between two electric pulses are no more enough to allow bleaching of the device before its re-colouration. In this situation electrons are injected inside the film before that all bipm$^{\bullet+}$ population decay in bipm$^{2+}$, creating a more and more intense colouration of the ON state (decreasing of $T_{min}$) and a residual colouration in the OFF (decreasing of $T_{max}$).

Another experimental observation which we can make from the study of graph 2.43 is the decrease of contrast ratios from 1.26 for the first cycle to 1.17 for the 1000th. These two experimental data concerning the decrease in contrast ratios and increase of bleaching times, suggest that damaging of electrochromic samples exposed to the life cycle test can be partially caused by slow hydroquinone consumption during cycling.



**(a)**

**(b)**

**Fig. 2.42** *ECD before the switching cycle (figure a )not sealed on the left, and sealed with a butylic sealer on the right, and after 1900 electrical switching (figure b).*

In fact as we seen in paragraph 2.3.2, decreasing from 1:1 to 0 the hydroquinone-viologen molar ratio in the chemical formulation of the electrochromic film, spontaneous bleaching times increase (figure

2.32), and contrast ratios for some driving voltages decrease (figure 2.36). Probably, hydroquinone takes part in some secondary not completely reversible reaction, or protons which are released from the oxidation reaction of hydroquinone to quinone are involved in some secondary process and are no more available for the re-reduction of quinone to hydroquinone. This second hypothesis should explain the yellow colour of the device after 1900 electrical switching; in fact this unwanted colouration should be due to a residual concentration of 1,4-benzoquinone which is yellow-greenish coloured.

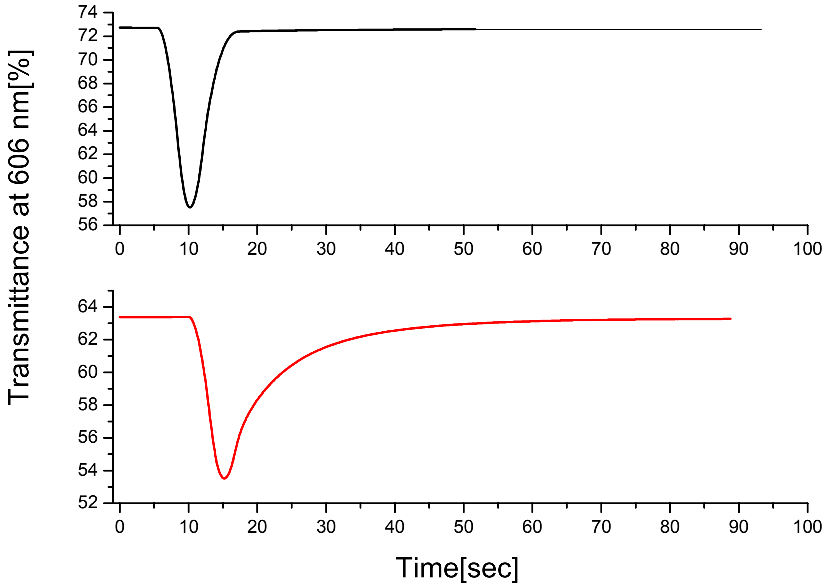


**Fig.2.43** *Electrochromic behaviour of the same electrochromic sample at the first and at the 1000th switching*

Failure of cycle life test on viologen-hydroquinone based devices, induced us to study others anodic molecules. Best results we obtained with system ethyl viologen diperchlorate-ferrocene. No protons are released during oxidation of ferrocene, which simply changes from a $Fe^{II}$ complex to a $Fe^{III}$ complex with no production of secondary species. In figure 2.44 behaviour of this cycle life test is shown. Only a very small loss in transmittance was observed (3%). This study was performed on samples having an equimolecolar amount in ferrocene and ethyl viologen diperchlorate because this formulation showed best performances. If a smaller amount in ferrocene was used bleaching times were too long, if a greater amount was used ferrocene precipitates from solution.

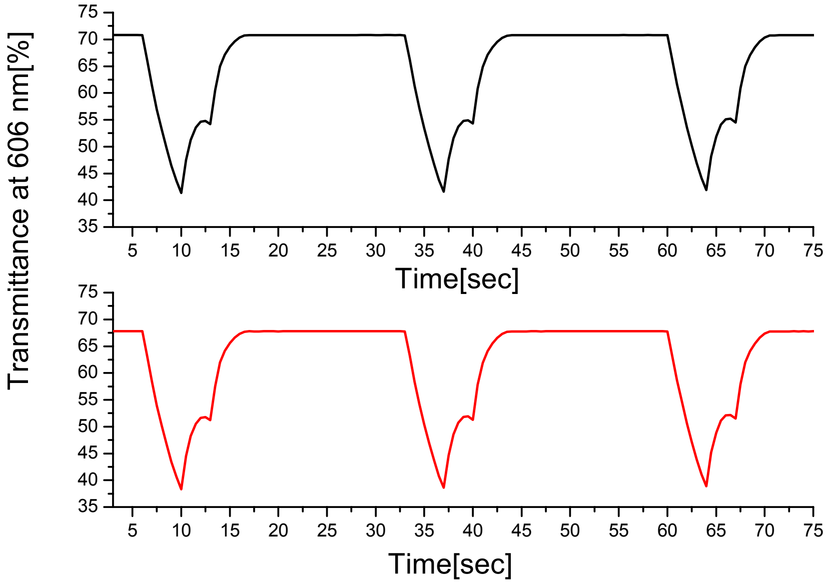


**Fig. 2.44** *Electrochromic response before (black curve) and after 65000 electro-switching cycles (red curve) for an ECD with following composition: PVF 40 wt. %, PC 54.2 wt. %, ethyl viologen diperchlorate 4 wt. %, ferrocene 1.8 wt. %. Pulses sequence for cycles was 1.8 volts for 4 seconds followed by a negative pulse -1.8 volts for 3 seconds and 20 seconds at V=0. Film thickness was 60.*

Sealed and not sealed samples showed similar behaviour in cycle life test, probably because the electrochromic polymeric film is not much permeable to water and oxygen. This is an improvement with respect to traditional liquid electrochromic films which always need to be sealed during assembling of device affecting, production costs.

**Fig. 2.45** *ECD with ethyl viologen diperchlorate and ferrocene as catodic and anodic pair after 65000 electrical switching not sealed (on the left) and sealed with a butyl sealer(on the right).*

## 2.4 Conclusions

In the first part of this research the characterization of the electrooptical properties of a new kind of solid electrochromic film was performed. This film is obtainable by simply doping preformed solid thermoplastic polymers with electrochromic molecules and plasticizers. Some innovation in preparation process and in properties make this film particularly suitable for production of large-area devices. Operational mechanisms of this ECD was studied in order to explore and to optimize electrochromic parameters such as contrast ratio and response times.

- The SEM analysis of a cross section of the EC film revealed an homogeneous and continuous structure without visible phase separation. A complete absence of porosity and channels greatly restricts the migration of the electrochromic molecules inside the film.
- The UV-vis absorption spectrum of the ECD in the ON state showed a complete absence of viologenic dimeric forms. In particular absorption bands at 350 nm, 530 nm and 900 nm typical of a dimeric viologen are substantially not present.
- High CR values can be obtained for this devices respect standard ECD for both high transmittance values in the ON state and very low transmittance values in the ON state due to colouration of many electrochromic layers near the electrode.
- Colouration decolouration process were complicated by the presence of a second redox step which slows down the bleaching process.

- Comparison of electrochromic behaviours between a standard liquid electrochromic device and this new kind of solid device revealed different charge propagation mechanisms. In particular density of electroactive molecule in the solid film is high enough to allow a charge transfer between molecules instead of migration of molecule to the electrodes. As a conseguence, the performances in CR and bleaching times of the two devices are very different.
- The time duration of the bleaching voltage was a critical factor, in fact a too long electric pulse can cause a bleaching and a successive re-colouration of the electrochromic device. This depends on the distribution of electrochromophores in their different redox states inside the solid film after application of the ON voltage, and on the geometry of the cell
- The possibility to kept constant a strong absorbing state for the ECD was also explored. This is possible both adjusting the percentage of anodic molecules inside the chemical formulation and applying appropriate time modulated electric driving pulses.
- The effect of charge-transfer (CT) complex formation on the rates of bleaching of the ECD was studied. The stoichiometry of the charge-transfer complex was checked by continuous variation method. The maximum absorbance was observed for the 1:1 molar mixture, indicating one donor molecule forms the complex with an acceptor molecule.

- The effect of CT complex formation was also folowed by cyclic voltammetry experiment. A shift in redox potentials due to formation of the CT complex was present, but it resulted to be small because the support electrolyte prevented formation of the complex.
- The shortening of bleaching times was observed to be strictly dependent from viologen donor molar ratio. The best molar ratio was 1:1. This can make us suppose that charge transfers by a long chain charge transfer complex having a sequence of alternating donor and acceptor molecules. Donor molecules which did not have geometrical requirements to promote this donor acceptor chains showed longer bleaching times.
- Bleaching times are also dependent by the polymer amount. When the rigidity of the film is raised by a greater polymer amount, electrochromic molecules have a restricted local motion, and bleaching times are increased.
- Initial life cycle tests did not give not good results for damaging of the device due to protic equilibria only after 1900 switchings. Optimization of cycle life tests was achieved using non protic anodic molecules as ferrocene (65000 switchings).

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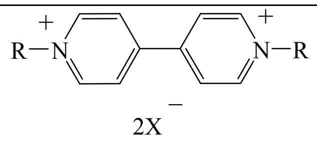
# CHAPTER 3

# ELECTROCHORIMIC PROPERTIES OF A NEW BIPYRIDINYLIUM DERIVATIVE

## 3.1 Introduction

During course of this PhD many attempts have been made to improve miscibility of viologens in poly(vinylbutanal) matrix. PVB is a technological polymer used as interlayer in safety glass, for example in windscreens, for its great adhesion ability to glassy support and its good elastic modulus[1-12]. The glass laminates are made by an interlayer PVB foil such when there is a crack in the glass the interlayer holds the pieces together and the whole structure resists to the load. For this reason to obtain an electrochromic PVB sheet is a substantial improvement in field of ECDs[13-17] in order to obtain an electrochromic window with mechanical properties similar to that of a safety glass. Generally PVB is plasticized with high boiling viscous organic solvents, as tri(ethylene glycol) bis(2-ethylhexanoate), dibutyl sebacate and so on, for this reason we have synthesized some modified viologens, with longer alkyl side chains and different functional groups in order to increase the lipophilycity of the bipyridilium salts increasing solubility in organic media. In table 3.1

some of the bipyridilium derivatives synthesized during the course of this PhD are reported. All these modified viologens have UV-vis spectrum similar to that of ethyl viologen diperchlorate shown in figure 2.6. The absorption spectrum of an electrochromic cell based on the modified viologen number four in the table below, in the ON state and in the OFF state are shown in figure 3.1. 626 nm and 421 nm are the maximum wavelengths of absorption related to the radical cation (bipm$^{+\bullet}$), the resulting colour of the film is blue.



| R | X |
|---|---|
| $-CH_2-COOH$ | $BPh_4^-$ |
| $-(CH)_5-O-CO-CH(CH_2CH_3)-(CH_2)_3-CH_3$ | $Br^-$ |
| $-(CH_2)_{11}-O-CO-(CH_2)_5-CH_3$ | $Br^-$ |
| $-(CH_2)_{11}-O-CO-CH(CH_2CH_3)-(CH_2)_3-CH_3$ | $Br^-$ |
| $-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-OH$ | $Br^-$ |
| $-(CH_2)_{11}-OH$ | $Br^-$ |
| $-(CH_2)_2-O-(CH_2)_2-O-CH_3$ | $Br^-$ |
| $-CH_2-COO-CH_3$ | $Br^-$ |
| $-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-O-CO-CH(CH_2CH_3)-(CH_2)_3-CH_3$ | $Br^-$, $Cl^-$ |
| $-(CH_2)_{11}-O-CO-CH(CH_2CH_3)-(CH_2)_3-CH_3$ | BF4-, Ph4- |

**Table 3.1** *List of modified 4,4'-bipyridilium salts synthesized in order to increase solubility of this electrochromic molecules in thermoplastic polymers.*

Surprisingly the colour in the ON state of the same electrochromic molecule obtained from a different synthetic lot turned out to be pink, how we can observe from the graph in figure 3.2 in which absorption spectrum of an electrochromic cell made with this viologen resulting from this synthetic lot is reported. As we can see the maxima wavelength are shifted to 546 nm and 342 nm.

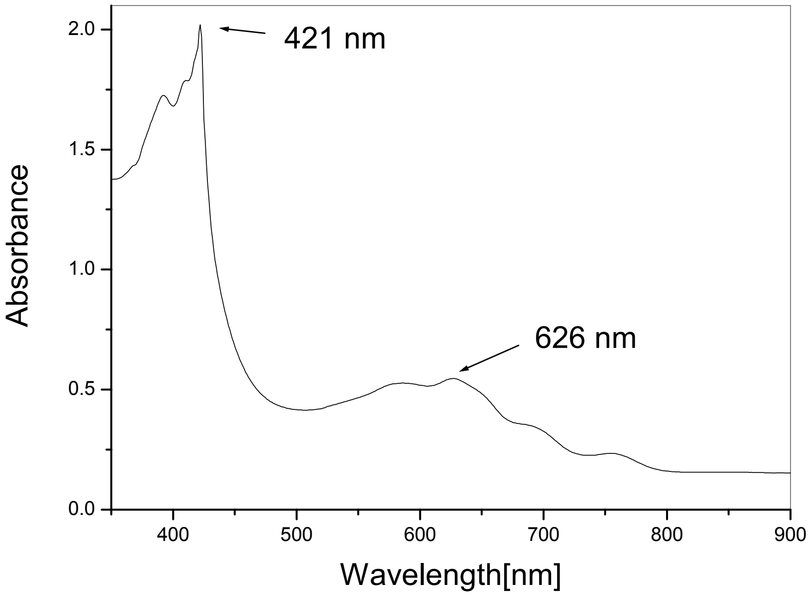


**Fig. 3.1** *UV-vis spectrum of an electrochromic film made of 40 wt% poly(vinyl butanal), 2 wt% 1,1'-di(11-Heptanoyloxyundecyl)-[4,4']bipyridinyl-1-ium dibromide 1 wt% hydroquinonee, 28.5 wt% propylene carbonate and 28.5 wt% tri(ethylene glycol) bis(2-ethylhexanoate) in the ON state.*

This very strange behaviour induced us to perform further chemical investigations (NMR, IR) about nature of this compound. From these analysis resulted a very different chemical structure compared withour expectations. In fact the last synthetic step, alchilation of the bipyridinium core, stopped to quaternization of one nitrogen atom, while the second nitrogen atom did not react with the alchilating agent.

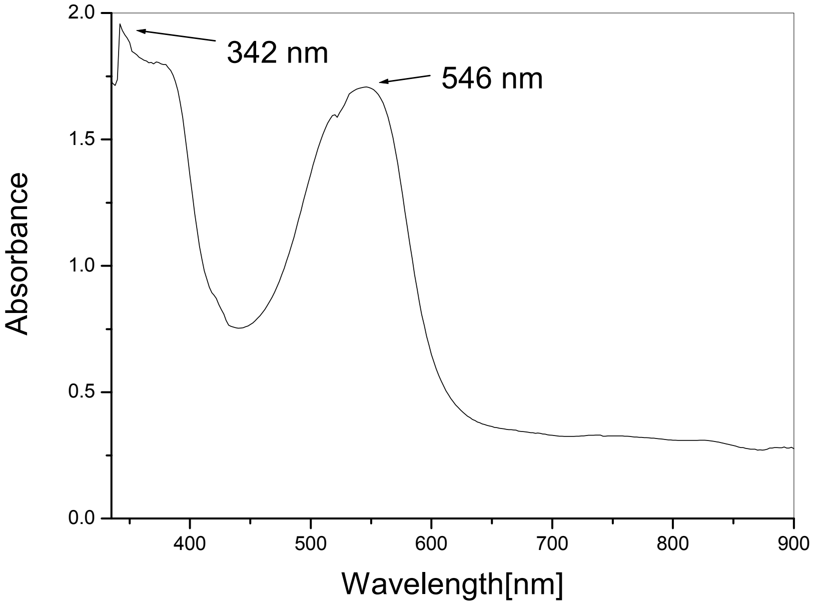


**Fig. 3.2** *UV-vis spectrum of an electrochromic film made of 40 wt% poly(vinyl butanal), 4 wt% 1-(11-Heptanoyloxyundecyl)-[4,4']bipyridinyl-1-ium bromide, 1 wt% hydroquinonee, 27.5 wt% propylene carbonate and 27.5 wt% tri(ethylene glycol) bis(2-ethylhexanoate), in the ON state.*

The structure of the compound that was produced in this second synthetic lot is shown in figure 3.3.

From literature data results that this compound is studied only as synthetic intermediate of viologenic derivatives, while its electrochromic properties were not characterized. Furthermore, spectroelectrochemical analysis of HBB showed very interesting

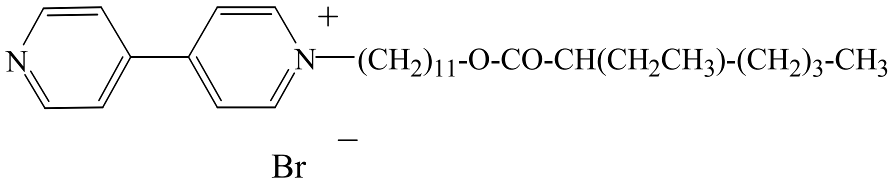


**Fig. 3.3** *Chemical structure of 1-(11-Heptanoyloxyundecyl)-[4,4']bipyridinyl-1-ium bromide (HBP) resulting from a mono-quaternization of the 4,4'-bipyridinium molecule.*

features, in fact, the shape of the absorption spectrum in the visible part is superimposable (maximum wavelength of absorption 546 nm) to the sensitivity curve of the human eye (maximum wavelength of absorption 550 nm), which can be observed figure 3.4.

Notice that sensitivity is peaked at yellow-green which is the complementary part of visible spectrum of the pink colour observed when HBB changes from the cationic form to the radicalic neutral form bipm$^{\bullet}$ . The possibility of selectively reducing the intensity of solar light according to the sensitivity of human eye make this new electrochromic molecule very attractive for anti-glare applications. In past years many attempts have been made to obtain ECDs in which absorption properties are able to reduce glare effect of sunlight[18-21]. For all these reasons we decided to perform an electrochemical characterization of the electrochromic properties of this new bipyridinylium derivative, and in this second chapter we are going to discuss the obtained results.

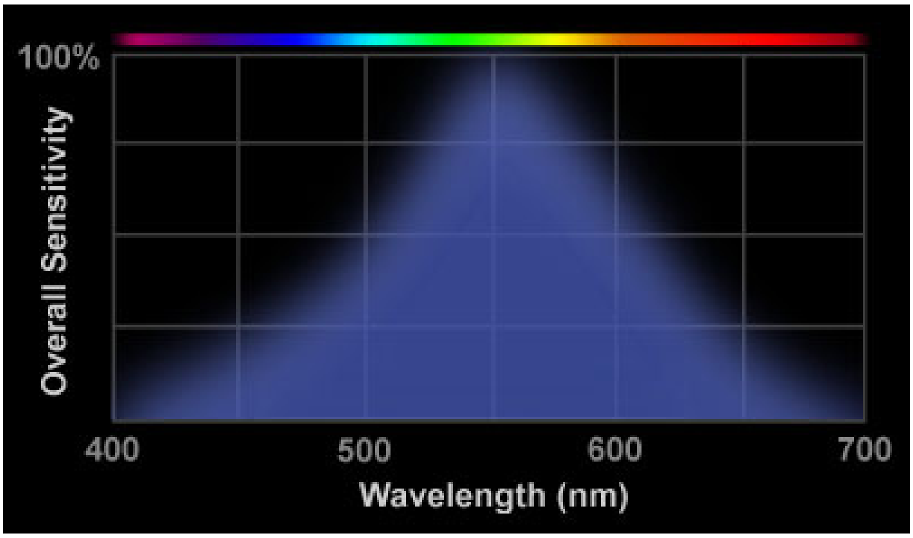


**Fig. 3.4** *The plot shows the spectral sensitivity of the human eye to the light.*

## 3.2 Experimental section

### 3.2.1 Chemicals

1-(11-Heptanoyloxyundecyl)-[4,4']bipyridinyl-1-ium bromide was synthesized in the laboratory of "New organic syntheses via organometallic catalysis" of University of Calabria.

All others chemical substances were commercially available and were used as purchased without further purification. Poly (vinyl butanal) (PVB), Poly(vinyl formal) (PVF), propylene carbonate (PC), hydroquinone, tri(ethylene glycol) 2-ethylesanoate ferrocene tetrabutylammonium hexafluorophosphate (TBAEFP) and tetrabutylammonium perchlorate (TBAP) were purchased from Aldrich Chemical.

### 3.2.2 Samples Preparation

Different electrochromic samples with different compositions and thickness were prepared according procedure described in paragraph 2.2.2 of this thesis, in order to study their electrooptical parameters and properties.

As it was said in the previous chapter, the thicknesses of the cells are controlled without additional spacer, the control of the parameters of the lamination process, as temperature and pressure applied to the pieces of conductive glass, allows to obtain the electrochromic cell of the required thickness.

### 3.2.3 Experimental setup

The oxidation/reduction behaviour of HBB was investigated by CV, in solutions of $1,5 \bullet 10^{-3}$ M of the cathodic electrochromic substance and $1,5 \bullet 10^{-2}$ M of inert electrolyte in the presence of propylene carbonate as solvent. Experiments were carried out in a three electrode system with Pt as the counter electrode, Ag/AgCl as the reference electrode, and glassy carbon as the working electrode. The potential control was achieved by means of a Amel 2049 model potentiostat/galvanostat, an Amel 568 progammable function generator with scan rate of 30 mV/sec. Measurements were carried out at room temperature.

The variation in % transmittance (% *T*) at the wavelength of maximum absorption was monitored using a YASCO V550 UV-VIS spectrophotometer, while applying a square wave potential by means of a Amel 2049 model potentiostat/galvanostat and an Amel 568 progammable function generator, the state of full transmittance (T=100%) was considered that of air (complete absence of sample) . The switching time was calculated at 95% of the full switch.

## 3.3 Results and discussion

In figure 3.5 the cyclic voltammetry experiment for HBB in propylene carbonate is reported. The following electrochemical parameters were obtained from above mentioned CV experiment: $E_{AP}$= -0.51 V, $E_{CP}$=-1.58 V the anodic and cathodic peaks respectively From these data it was possible to calculate by equation 1.25 the formal redox potential of the single redox step of this new electrochromic molecule in propylene carbonate: $E^0_1$=-1.04 V.

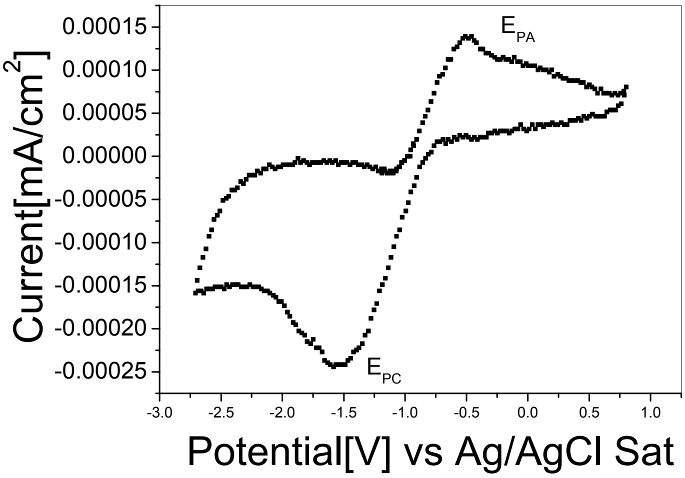


**Fig. 3.5** *Cyclic voltammetry experiment of 1-(11-Heptanoyloxyundecyl)-[4,4']bipyridinyl-1-ium 1.5•10$^{-3}$ M in propylene carbonate (PC) and tetrabutylammonium perchlorate (TBAP) 1.5•10$^{-2}$ M as inert electrolyte, scan rate=10 mV/s; working electrode: glassy carbon.*

From the CV to observe the presence of a single redox step is possible. This experimental observation is in perfect agreement with presence of a single cationic nitrogen atom which can be reduced, unlike standard viologen molecules have two different cationic nitrogen atoms which can be reduced how we can observe in the cyclic voltammetry experiment in figure 2.4. This is an important feature for HBB, in order to avoid all problems occurring during coloration process of viologens derivatives, in particular relative to the presence of a second redox step towards a neutral uncoloured form.

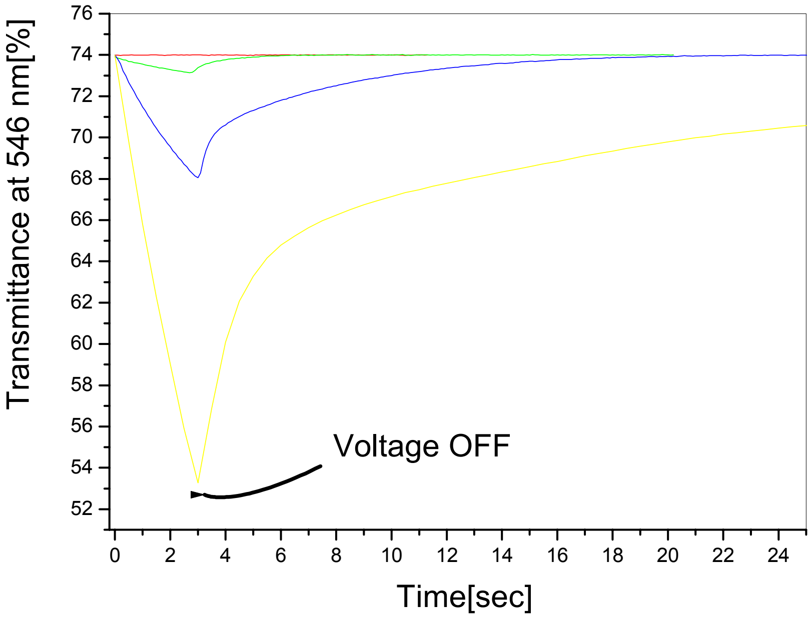


**Fig. 3.6** *Transmittance at 546 nanometers as function of time for a solid plastic film containing 40 wt.% poly(vinyl formal), 4 wt. % HBB, 1 wt. % hydroquinone and 55 wt. % propylene carbonate, with a driving voltage three second long and with different amplitude: 1.0 V (red line), 1.4 V (green line), 1.8 V (blue line) and 2.2 V (yellow line). Thickness of the film is 60 µm.*

As discussed in paragraph 2.3.1, during a colouration decolouration cycle of ethyl viologen for example, the absorption does not decrease immediately after the pulse removing, but keeps increasing for a little while because coluration increases due to the reoxidation of the neutral viologen to the radical coloured form, and then this latter specie decays into the cationic uncoloured form.

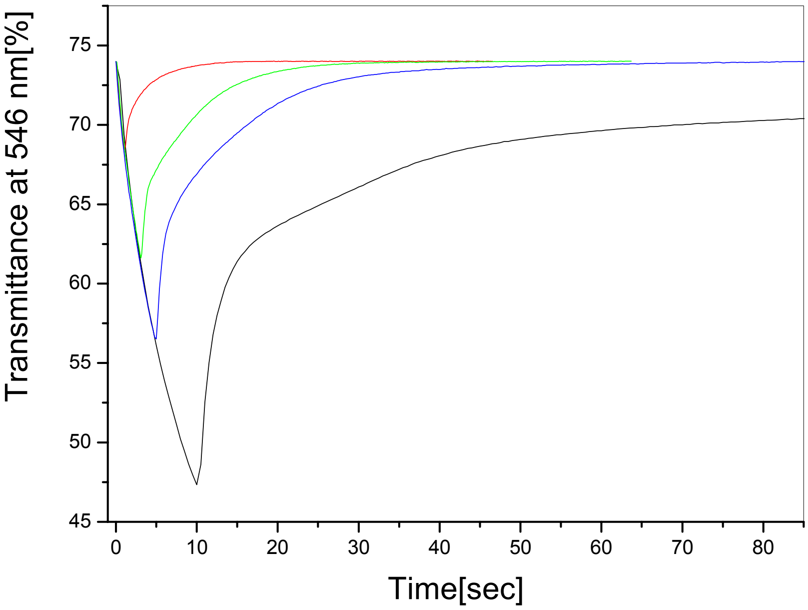


**Fig. 3.7** *Transmittance at 546 nanometers as function of time for a solid plastic film containing 40 wt.% poly(vinyl formal), 4 wt. % HBB, 1 wt. % hydroquinone and 55 wt. % propylene carbonate, with a 2.2 volts driving voltage and different lengths: 1 second (red line), 3 seconds (green line), 5 seconds (blue line) and 10 seconds (black line). Thickness of the film is 60 µm.*

This behaviour can be responsible for an increase in bleaching times of the electrochromic device. For this reason, the complete absence of a second reduction step for HBB is an interesting feature. This behaviour is confirmed by transmittance versus time experiments which can be observed in graph in figure 3.6, where DC voltages three seconds long but with different amplitudes were applied to the HBB film. How we can see, the beginning of the bleaching process was perfectly coincident with the moment in with the electric pulse is removed, no delay due to formation of a second redox step was observed. The same behaviour is observed in figure 3.7 where 2.2 volts pulses with different lengths were applied to the electrochromic film in order to check the electrochromic response of HBB. All transmittance versus time experiments were performed at 546 nanometers, which is the maximum wavelength of absorption of the radical neutral form of HBB.

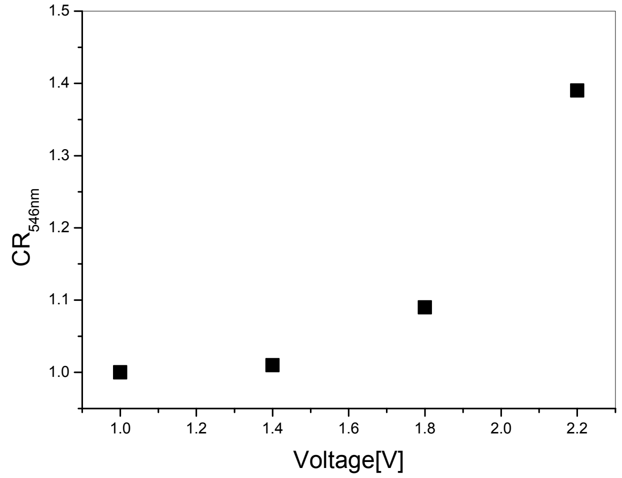


**Fig. 3.8** *Contrast ratios for a plastic electrochromic solid film as function of the applied voltage, lengths of voltages are kept constant 3 seconds long for all the experiments. Chemical composition for the solid electrochromic film was: 40 wt.% poly(vinyl formal), 4 wt. %f HBB, 1 wt. % of hydroquinone, 55 wt. % propylene carbonate. Film thicknes was 60 μm.*

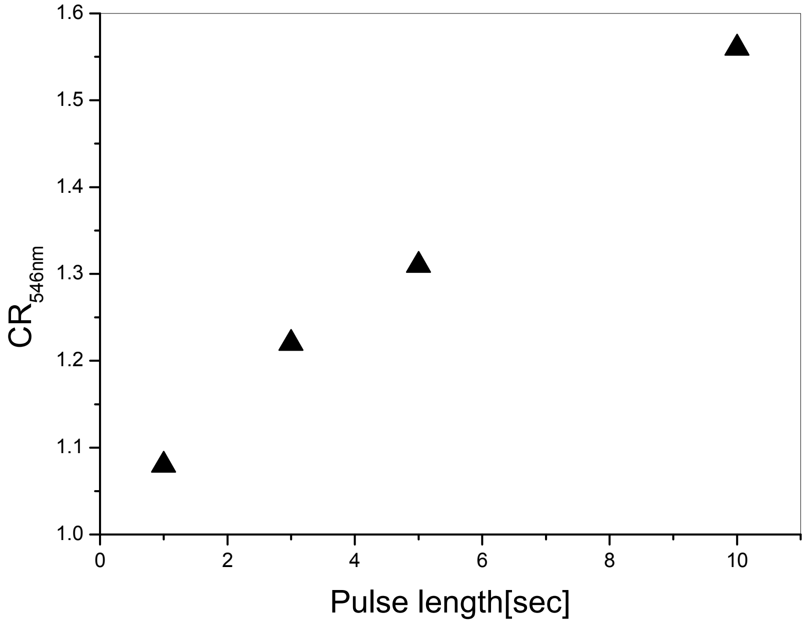


**Fig. 3.9** *Contrast ratios for a plastic electrochromic solid film as function of length of the applied voltage (2.2 volts). Chemical compositions for the samples are the same of experiment in figure 2.8. Thickness of device is 60 µm.*

For the same applied voltage, an electrochromic device made of ethyl viologen diperchlorate, one of the more studied electrochromic bipyridinium derivative, and studied by us in chapter 2, shows a greater contrat ratio with respect to an ECD made of HBB. The explanation of this behaviour could be ascribed to a smaller molar extinction coefficient value of HBB respect ethyl viologen, and, as the same time to an higher redox potential for the single mono-reduction step. In figure 3.8 and 3.9 contrast ratios of the HBB electrochromic film are reported respectively as function of the amplitude and of the length of the applied pulses. A good contrast ratio can be obtained with a 2.2 volts voltage from 3 to 10 seconds long.

In figure 3.10 bleaching times of an HBB ECD is reported as function of the length of the applied pulse. The electrochromic sample shows a substantial colouration persistence for pulse longer than 10 seconds at 2.2 volts applied.

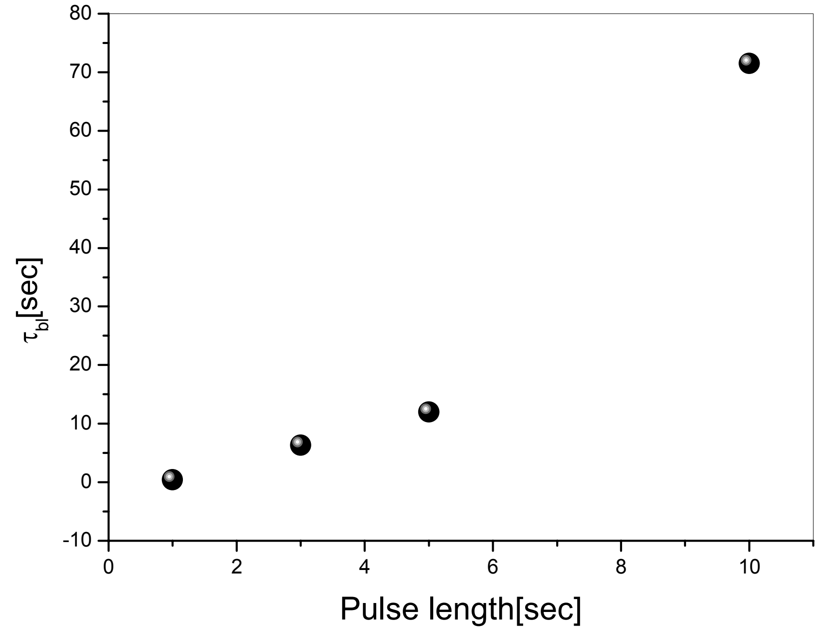


**Fig. 3.10** *Bleaching times for a plastic electrochromic solid film as function of length of the applied voltage (2.2 volts). Composition was for the plastic film: 40% wt.% poly(vinyl formal), 4 wt. % HBB, 1 wt. % of hydroquinone and 55 wt. % propylene carbonate. Cell thickness was 60 $\mu$m.*

In figure 3.11 we can observe the UV-visible absorption spectra of a solid electrochromic film based on HBB in the range 450 – 650 nanometers at different applied potentials. As we can see, 1.4 volts is the minimum voltage required to observe a minimum colouration in the ECD. Even if at lower applied potentials a band centred at 602 nanometers appeared, as we can see in figure 3.11 (the blue line which correspond to 1 volts applied voltage). The shape of the absorption spectrum at 1 volts is corresponding to that of a standard viologenic radical cation (see fig. 2.6), in fact the electrochromic device showed the presence of a second colour, blue, especially during the bleaching process, when it was electrically switched. This behaviour is attributable to the presence in the electrochromic mixture of HBB, as its protonated form in very low percentages. In fact the neutral nitrogen atom is basic and reacts with acidic impurities present in the electrochromic mixture; this protonic exchange reaction give rise to formation of a dicationic HBB molecule in which one positively charged nitrogen atom is part of an alchilated pyridinic moiety, and the second cationic nitrogen atom is part of a protonated pyridinic moiety. In the protonated form of HBB the electronic configuration of the conjugated system is very similar to that of a dicationic viologen. This justifies the resemblance of the two absorption spectra. In order to test this hypothesis, a solution of acidified HBB was prepared in propylene carbonate, a cell was filled with this electrochromic mixture, and the absorption spectrum of the HBB in the protonated form was monitored at 2.2 volts. As we can observe in figure 3.12 the shape of the absorption spectrum of the radical protonated HBB is very similar to that of a viologen radical cation, with maximum wavelengths of absorption at 602 nanometers and 388 nanometers.

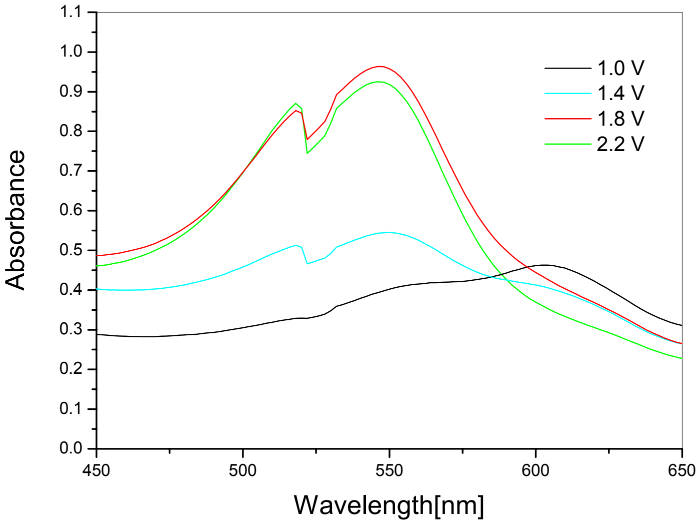


**Fig 3.11** *Absorption spectrum of an electrochromic film made of 40 wt% poly(vinyl formal), 4 wt% HBB, 1.44 wt% ferrocene, 54.46 wt% propylene carbonate, at different applied potentials.*

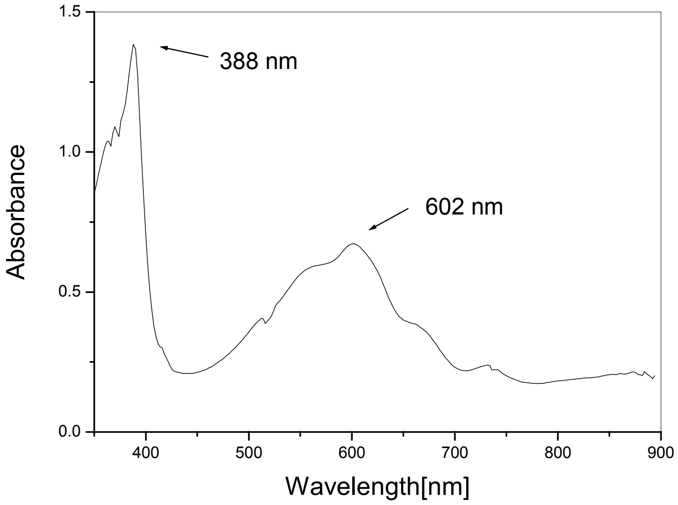


**Fig. 3.12** *UV-vis spectrum of an electrochromic cell filled with an acidified with acetic acid solution of HBB in propylene carbonate. The operating voltage is 2.2 volts, an the thickness of the cell is 60 µm.*

The formation of a second colour different from the desired pink is an unwanted feature in this kind of device, which was especially observed in the bleaching step . In figure 3.13 the electrochromic behaviour of an electrochromic device containing HBB during its bleaching process can be observed. The switching potential was 5.0 volts for 60 seconds, because at lower voltages the disappearing, during the bleaching process, of the radical cationic form of HBB protonated is too fast to record its absorption spectrum with our experimental setup. As we can see, the absorption band centred at 546 nm is no more present in the graph because it disappears in a very short time. On the contrary, as we can observe in figure 3.13, the blue colour is rather stable and persists for many seconds even if presenting very low absorbance values. The faster reoxidation of HBB respect to that of its protonated form could be explained by the easier redox step during the bleaching process of the first one. In fact when HBB changes from the coloured to the colourless form, simply, it looses an electron; on the contrary, the protonated form of HBB has two different redox states and during the colouration process a certain quantity of di-reduced neutral form forms too For this reason the bleaching step is slowed down by a two step reoxidation of the neutral form into the dicationic form with formation of an intermediate coloured radical cation; this can explain the

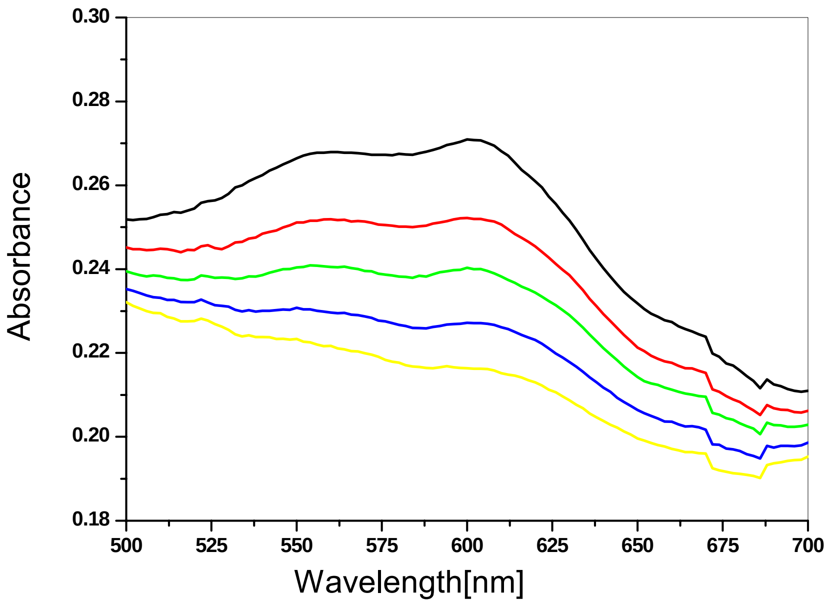


**Fig. 3.13** *Absorption spectra of an HUB solid electrochromic film during the bleaching process. The operating voltage is 5 volts for 60 seconds and the absorption spectra are monitored at different times after removing the pulse: at t=90 s (black line), t=180 s (red line), t=300 s (green line), t=540 (blue line), t=900 s (yellow line). Composition of the film was: 40 wt% poly(vinyl formal), 4 wt% HBB, 1.44 wt% ferrocene, 54.46 wt% propylene carbonate; thickness of the film was 60 µm.*

longer persistence of the blue colour with respect to the pink colour in the electrochromic device based on HBB.

In figure 3.14 the presence of the coloured protonated form of HBB during the bleaching process of a solid electrochromic film is reported at different applied potentials. The absorption spectra are all recorded 90 seconds after pulse was switched off.

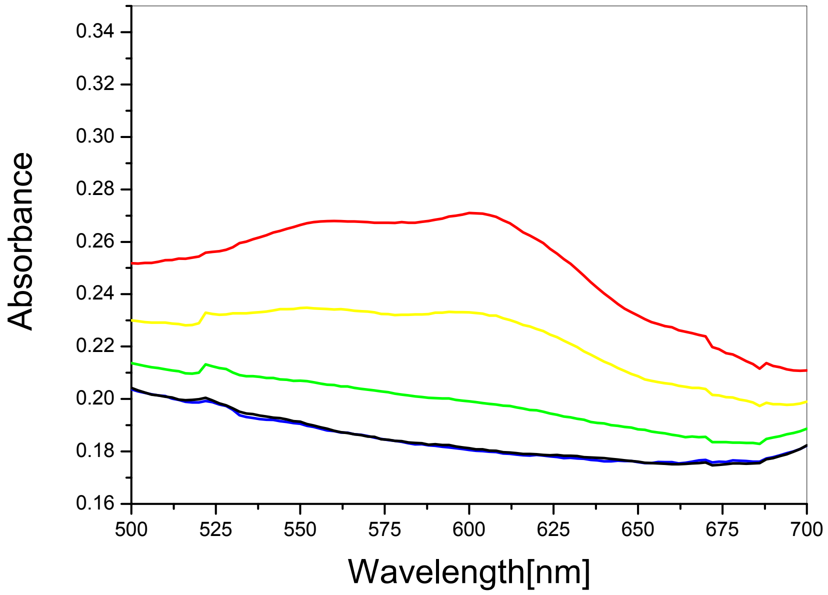


**Fig. 3.14** *UV-vis absorption spectra of an HBB electrochromic film measured at t=90 s after removing the voltage at various applied potentials 60 seconds long: 1.4 V (blue line), 1.8 V (black line), 2.2 V (green line), 3.0 V (yellow line), 5.0 V (red line). Composition of the film was: 40 wt% poly(vinyl formal), 4 wt% HBB, 1.44 wt% ferrocene, 54.46 wt% propylene carbonate; the thickness of the film was 60 μm.*

From the graph we can observe that this unwanted dual colour phenomenon is related to the applied potential, the greater is the applied potential the longer is the bleaching time of the protonated HBB form. When a voltage of 2.2 volts is applied to the film the presence of the blue colour is almost unimportant 90 seconds after the pulse has been removed. Consequently, control of the amplitude of the applied pulse is a first way to avoid the blue colour to appear. A second way to reduce formation of protonated HBB is to add in the electrochromic mixture an organic compound with basic properties, in order to compete with HBB in the protic equilibrium reactions. This molecule must have a good solubility in the plasticizer used, must be rather stable to the applied voltages and finally must have a more basic character with respect to HBB. Most of inorganic bases cannot be used for the very poor solubility in the thermoplastic polymer used to make the plastic film; organic ammine forms too intense colouration in the electrochromic mixtures of HBB. These unwanted colourations are probably due to the formation of charge transfer complexes between HBB as an acceptor and the nitrogen atom of ammines as a donor. In literature, in fact CT complex equilibriums between viologens and ammines are well known. On the contrary 4,4'-bipyridine (structure is showed in figure 3.15) is an organic base with a good solubility in the electrochromic mixture, it is electrochemically inert to the applied voltages, and it does not form charge transfer complexes with HBB absorbing in the visible region of spectrum. Furthermore the pyridinic nitrogen atoms of 4,4'-bipyridine are more basic with respect to the lone pair of neutral nitrogen of HBB, that "feels" the electron attractor effect of the positively charged nitrogen atoms across the pyridinic conjugated system and so it is less suitable for a bond with a proton. For all these reasons we thought to use 4,4'-bipyridine to reduce the presence of protonated HBB and, in this way, also the dual colour effect. Good results were obtained using this molecule in the electrochromic mixture, and in figure 3.16 the absorbance at 602 nanometers during the bleaching process are reported for different 4,4'-bipyridine amounts. As we can see, with a 2 wt.% 4,4'-bipyridine presence of blue colour 60 seconds after removing the pulse is almost unimportant and comparable with the absorption of the film in the OFF state.

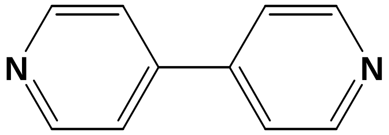


**Fig. 3.15** *Chemical structure of 4,4'-bipyridine.*

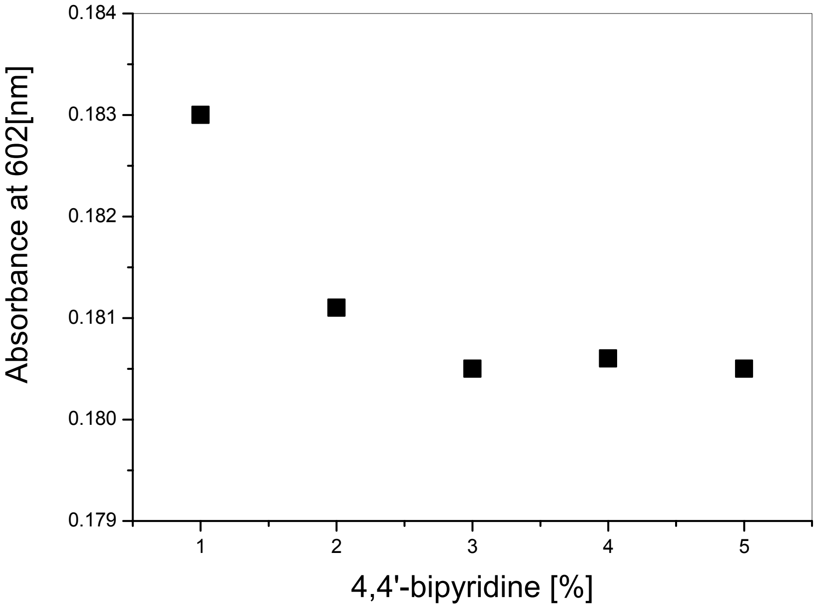


**Fig. 3.16** *Absorbance at 602 nanometers for HBB film at different amount in 4,4'-bipyridine, 60 second after removing the 5 volts electric voltage applied for 60 seconds.*

## 3.4 Conclusions

The electrochromic behaviour of 1-(11-Heptanoyloxyundecyl)-[4,4']bipyridinyl-1-ium dibromide (HBB) was explored. This new electrochromic molecule after application of a suitable voltage absorbs exactly the green-yellow part of visible spectrum, making it suitable for anti-glare applications. The characterization of the electrochromic properties of HBB was performed.

The spectroelectrochemistry and cyclic voltammetry experiment showed the presence of a single redox step for this kind of chromophore molecule. This is an important feature, in order to avoid all problems occurring during the colouration process of other viologens derivatives, in particular problems connected to the presence of a second redox step towards a neutral uncoloured form which can often be very resistant to reoxidation causing failure of device.

Devices based on HBB did not show high contrast ratio respect viologens based systems. The reason for this behaviour could be ascribed to a smaller molar extinction coefficient value of HBB, and, as the same time to an higher redox potential for the single mono-reduction step.

Some problems concerning the electrochromic performances of HBB were also studied~~,~~ in order to optimize ECD made by this molecule. In fact the electrochromic device based on HBB showed presence of a second colour, blue, especially during the bleaching process, when it was electrically switched off. This behaviour is due to the presence in the electrochromic mixture of the protonated form of HBB in very low percentages. Chemical structure and absorption spectrum  are similar to that of a standard viologen molecule. The addition to the electrochromic mixture of a competing organic base as 4,4’-bipyridine in order to compete with HBB in the protic equilibrium reactions solved this problem.

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# CHAPTER 4

## PHOTOELECTROCHROMIC BEHAVIOUR OF A SPIROOXAZINE BASED ORGANIC FILM

### 4.1 Introduction

Photoelectrochromic windows represent a special kind of switching windows. The colouring process can take place both on absorption of light or on application of an external electric field that can induce electron transfer reactions. In contrast to other photoelectrochromic devices which combine an electrochromic and a photoactive layer, we have studieda photoelectrochromic device in which the same molecule, a spirooxazine, acts as photoactive and electrochromic specie. Herein, we report our preliminary results on spectroelectrochemical and photochromic properties of the bifunctional device.

Bechinger et al.[1] have developed a photoelectrochromic system in which a dye-sensitized semiconductor electrode is combined with an electrochromic film based on $WO_3$, and recently Macchione et al.[2,3] have proposed an organic photoelectrochromic film, realized by using methylene blue, as anodic element and photoactive agent, in combination with ethyl viologen diperchlorate, as cathodic electrochromic molecule.

Our photoelectrochromic device, is based on a single self-supported polymeric active layer, laminated between two conductive glasses, in which the same molecule can change its colour from transparent to blue on absorption of light and from transparent to pink on oxidation reaction induced by an external electric field.

The innovation of our device is the use of the same molecule, dispersed in a thermoplastic polymer film, to obtain the change of colour both on absorption of light or on application of an external electric field.

Both the photochromic and electrochromic behaviour of the bifunctional polymer film have been investigated.

## 4.2 Photochromism

Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having different absorption spectra.

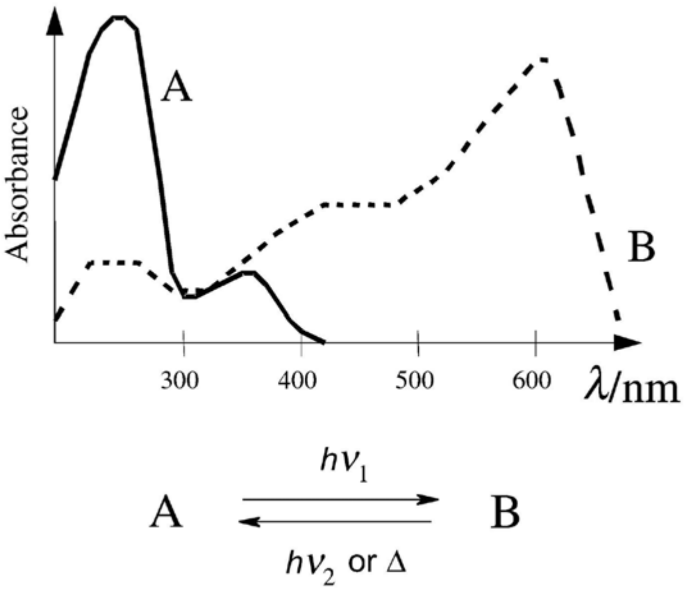


**Fig. 4.1** *The thermodynamically stable form A is transformed by irradiation into form B. The back reaction can occur thermally (Photochromism of type T) or photochemically (Photochromism of type P).*

The most prevalent organic photochromic systems involve unimolecular reactions: common photochromic molecules have a colourless or pale yellow form A and a coloured form B (e.g., red or blue). This phenomenon is referred to as positive photochromism. Other systems are bimolecular, such as those involving photocycloaddition reactions. When $\lambda_{max}(A) > \lambda_{max}(B)$, photochromism is negative or inverse.

The unimolecular processes are encountered, for example, with spiropyrans, a family of molecules that has been extensively studied. Solid photochromic spiropyrans or solutions (in ethanol, toluene, ether, ketones, esters, etc.) are colourless or weakly coloured. Upon UV irradiation, they become coloured. The coloured solutions thermally fade to their original state; in many cases, they can also be decolorized (bleached) by visible light. A few spiropyrans display negative photochromism. They are coloured in the dark and bleached by UV light. Many spiropyrans are also thermochromic (see definition below), and spectra of the colored forms are identical to those produced photochemically.

In general, the photochromic processes involve a one-photon mechanism. B is formed from the singlet ($^1A^*$) or triplet ($^3A^*$) excited states or from both. B, the photoproduct, may also be formed from an upper excited state populated by absorption of two photons.

The transition probability of populating the final state (hence of obtaining the photoproduct) depends on the product of the photon irradiances $E_{p(1)}$ and $E_{p(2)}$ of the two exciting beams.

It is, therefore, advantageous to utilize lasers emitting high photon irradiance, such as those generating picosecond or subpicosecond pulses. Two absorption processes may be distinguished:

a) simultaneous absorption of two photons via a virtual level.
b) stepwise (or sequential) two-photon absorption where the second photon absorption takes place from a real level.

The simultaneous process (a) has been successfully used for exciting photochromic molecules at specific positions inside a volume for 3D memory systems (writing process). A two-photon absorption process was also used to excite the written molecules that emit fluorescence (reading process) [4,5].

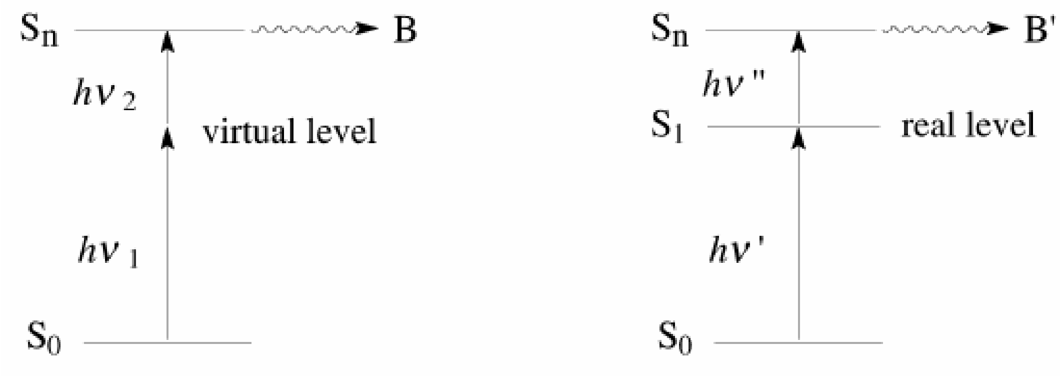
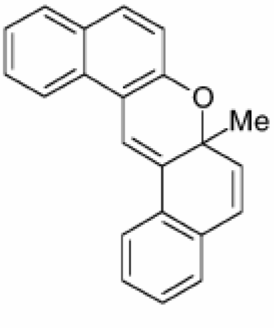
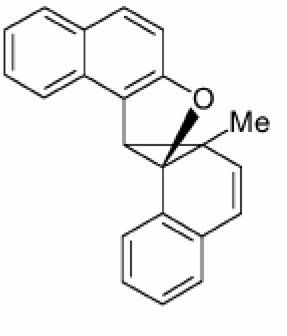


**Fig. 4.2** *Simultaneous and stepwise two photon absorption leading to product B.*

The excitation process can also proceed through a metastable intermediate (process b) as with the dinaphthopyran derivative showed in figure 4.3. It was found to isomerize to a bicyclohexene derivative via an intermediate X (not isolated). The authors used two 405-nm photons and observed that the quantum yield Φ is proportional to the square of the photon irradiance. The reverse reaction **2** → **1** was found to proceed at 334 nm[6].



**1**



**2**

**Fig. 4.3** *Dinaphtopyran derivative (1) and the bicyclohexenic form (2)resulting from a stepwise two-photon absorption.*

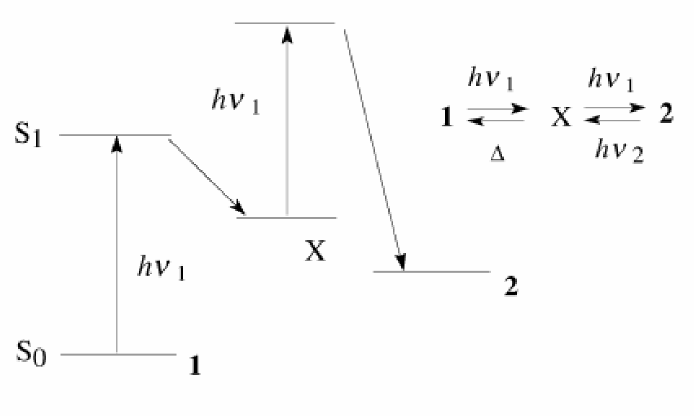


**Fig. 4.4** *Stepwise two-photon photochromic reaction.*

Colourability is the ability of a colourless or a slightly coloured (pale yellow) photochromic material to develop colouration. In dilute solutions, the initial absorbance "$A_0(\lambda)$" immediately after photolysis is proportional (proportionality constant $k$ includes the incident photon flux) to $\Phi_{col}$ (colouration quantum yield), $\varepsilon_B$ (molar absorption coefficient of the coloured form), and $c_A$ (concentration of colourless form) at a given irradiation wavelength[7].

$$A_0(\lambda) = k\Phi_{col}\varepsilon_B c_A \tag{4.1}$$

## 4.3 Chemical processes involved in organic photochromism

Electrocyclizations, whether concerted or not concerted, are 6π 6 atom processes for spiropyrans, spirooxazines, chromenes, hexa-1,3,5-

triene, diheteroarylethenes, and cyclohexa-1,3-diene systems, and 6π 5 atom processes for spirodihydroindolizines and other pyrazoline based systems. Cycloadditions are found in (2+2) cycloadditions based on valence isomerizations or in molecules with multiple bonds incorporated in or linked to aromatic systems. (4+4) Cycloadditions are found mainly in polycyclic aromatic hydrocarbons. (4+2) Cycloadditions are found, for example, in additions of singlet oxygen to aromatic compounds.

Cis-trans (E/Z) isomerizations occur in stilbenes, azo compounds, azines, thioindigoids, etc., as well as some photochromic biological receptors that are part of living systems.

Intramolecular hydrogen transfer is found in anils, benzylpyridines, aci-nitro and related compounds, salicylates, triazoles, oxazoles, metal dithizonates, and perimidinespirohexadienones.

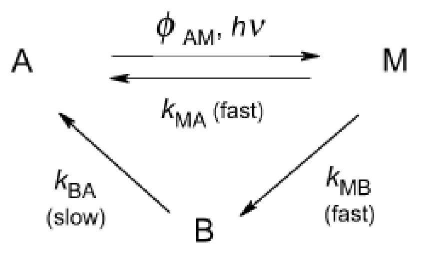
Intramolecular group transfers operate in polycyclic quinones (periaryloxyparaquinones).

Heterolytic bond cleavages occur in triarylmethanes and related systems. Homolytic bond cleavages are found in triarylimidazole dimers, tetrachloronaphthalenes, perchlorotoluene, nitrosodimers, hydrazines, etc.

Electron transfers (oxido-reduction) are photoinduced in viologens and related systems. The same compounds can also undergo electrochromism.

## 4.4 Kinetics of photochromic compounds

The determination of the photochromic parameters, such as the number, nature, and kinetic and spectral properties of the transient species formed under irradiation, is not a trivial task because the photoproducts are too labile to be isolated in many cases. As an illustration, the kinetic behavior of the unimolecular systems is considered (e.g., spiropyrans, spiroxazines, dihydroindolizines, which are of major importance for applications to ophthalmic lenses). It can be summerized in the following scheme:



(4.2)

It involves **A,** the noncoloured “closed” form, **M**, a short-lived transient species (a singlet and/or triplet excited state or a very labile photoisomer), and **B**, the long-lived but not isolable coloured “open” form.

The analysis can be performed using either pulsed or continuous irradiation methods.

a) Pulsed irradiation: Immediately after a light pulse, only M has accumulated.

b) Continuous irradiation: Using a low-power photon flux, a product such as **B** (often a photoisomer) can accumulate over time scales of $10^{-2}$–$10^{+6}$ s.

In order to estimate some relevant parameters related to photoisomer **B** (quantum yields as well as UV/visible spectra), specially designed kinetic experiments must be carried out. Under continuous monochromatic irradiation, a photochromic system can be considered to be at nonequilibrium and open. The evolution of the concentrations of the reacting species (starting compounds, photoisomers, and degradation products) can be described by an appropriate set of differential equations. The only simplifying hypothesis that is used for their establishment is that the well-stirred mixture obeys Beer's law. UV/visible multiwavelength analysis of absorbance vs. time curves recorded under continuous monochromatic irradiation provides information about the evolution of the corresponding concentrations [8]. Simulated curves obtained by numerical integration of the differential equations were generated from the kinetic scheme and compared with the experimental curves using curve-fitting procedures.

The coloration efficiency (see "colourability") is given by the absorbance $A_0(\lambda)$ at the maximum wavelength of the coloured form immediately after a pulse of radiation (t = 0). This parameter obtained under standard conditions (concentration of the closed form ca. $2.5 \times 10^{-5}$ M, in toluene solution, at 25 °C) for a series of photochromic colourless compounds such as spiropyrans, spirooxazines, chromenes, etc. (together with the maximum wavelength of their visible absorption spectra), is an indicator of their relative photochromic behaviour. Other important data are the first-order thermal decay rate constants ($k_\Delta$) and the time ($t^*_{(A_{0/2})}$), necessary to obtain half of the initial colourability after continuous irradiation (test of fatigue).

## 4.5 Spiroheterocyclic compounds

In solutions of nonpolar solvents, most spiropyrans and spirooxazines exist as ring-closed isomers, but upon dissolution in polar solvents they can undergo thermal ring opening to the corresponding merocyanine forms. The position of the established complex equilibrium depends on many factors, primarily solvent polarity, the nature of the substituents, and the concentration of the solution. Formation of the merocyanines can also be induced by irradiation of the solution in the near-UV, and equilibrium of the valence isomers is attained through the reverse dark ring-closing reaction.

The solvatochromic behaviour of spirooxazines, showing itself as pronounced changes in the position and intensity of their UV-vis absorption bands induced by variation in the polarity of a medium, may be governed by two different mechanisms. The first one is related to the shift of the equilibrium when passing from one solvent to another. One evidence for this mechanism is the redistribution of intensities of absorption bands in the spectrum of a solution containing an equilibrium mixture of the isomers or the occurrence of new bands even if only one of the isomers is present in a solutiont[9,10]. The second mechanism is inherent to the general phenomenon of solvatochromism and is related to differences in solute-solvent interactions in solvents of different polarity. Since solvent effects on absorption spectra are usually studied by measuring the longest-wavelength absorption band shifts, and since these bands in solutions of spiropyrans and spirooxazines belong to their ring-opened forms, determining the origin of these interactions requires an understanding of the structure and polarity of the merocyanines **.**

The principal reaction that governs the interconversion of valence isomers of spiropyrans and spirooxazines, is the archetypal reversible electrocyclization (figure 4.5), which is the photochromic behaviour of fulgides, diarylethenes, spiropyrans and spirooxazines.

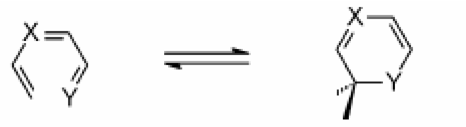


**Fig. 4.5** *Electrocyclization of spirooxazines.*

The primary step of the photochromic reaction of spiropyrans and spirooxazines is the dissociation of a C-O bond in an electronic excited state. The nature of the active excited state depends on substitution in the benzopyran and naphthoxazine rings More precisely in the photochemical ring-opening reaction of spirooxazines, as shown by transient absorption spectroscopy experiments carried out at picosecond[11,12] and femtosecond[13-15] temporal resolution, the formation of the coloured merocyanine isomers of spiroindolinonaphthoxazines derives entirely from the excited singlet state. This observation is also true for other spirooxazines, and the uninvolvement of the triplet states of spirooxazines in the principal photochemical reactionwell explains the high fatigue resistance of compounds of this class. The rate constants for C-O bond cleavage and subsequent relaxation to a metastable merocyanine in 1-butanol solution were estimated to be approximately 700 and 470 fs, respectively.[14] The final relaxation to the stable merocyanine, is presumably completed in a few hundred picoseconds. The fast kinetics of the ring-opening reaction of spirooxazines favours the efficiency of their photocolouration, which is one of the most important requirements imposed to the photochromic compounds suitable for applications in the photonics field. Other important requirements of the photochromic process are: sufficiently high quantum yields of the photoreaction, generally in the range of 0.2-0.8[15-19], and thermal stability of the photocoloured form, as assessed by the energy barrier of the back dark reaction.

## 4.6 Experimental section

### 4.6.1 Chemicals

1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3’-[3H]naphtha[2,1-b][1,4]oxazine], Poly (vinyl butanal) (PVB), Poly(vinyl formal) (PVF), propylene carbonate (PC), hydroquinone, tri(ethylene glycol) 2-ethylesanoate, tetrabutylammonium hexafluorophosphate (TBAEFP) were purchased from Aldrich Chemical and were used as purchased without further purification.

1-(11-Heptanoyloxyundecyl)-[4,4']bipyridinyl-1-ium bromide was synthesized in the laboratory of “New organic syntheses via organometallic catalysis” of University of Calabria.

## 4.6.2 Samples Preparation

A mixture of 30 wt % of poly(vinylbutyral), 4 wt % of 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3’-[3H]naphtha[2,1-b][1,4]oxazine], 1 wt % of hydroquinone, 32.5 w t% triethylenglycol 2-ethylesanoate, and 32.5 wt % of propylene carbonate, was heated at a temperature of 100°C. After cooling the mixture at room temperature, an homogenous plastic mixture, with electrochromic and photochromic properties and great adhesion ability to glassy support, was obtained.

The film was simply prepared by pressing the plastic mixture using a home-made laboratory press. The thickness of the film was 200 μm. A device based on a photoelectrochromic cell was prepared by heating the photoelectrochromic film at the temperature of softening of the plasticized thermoplastic polymer (100 – 150 °C) and laminating the film between two conductive glass supports coated with indium tin oxide. The thickness was set to about 70 μm.

## 4.6.3 Experimental Setup

Absorption spectra were recorded on a Perkin-Elmer Lambda 16 spectrophotometer and Beckman DU 7500 or HP 8453 diode-array spectrophotometers. The irradiating source, used to produce the metastable PM form, was a 150W Xe lamp.

The irradiation was carried out in a front-face geometry at an incident angle of about 30°, using all light emitted by the source at $\lambda >$ 350 nm. The color-forming kinetics was followed by monitoring the visible PM absorbance under stationary irradiation as a function of time up to photostationary state attainment. Then, exposure to light was discontinued and the kinetic rate parameter of the thermal bleaching was determined from the decrease in absorbance.

An Amel 2049 model potentiostat/galvanostat and an Amel 568 progammable function generator were used to apply a square wave potential during electrochromic measure.

The oxidation/reduction behavior of electroactive species was investigated by CV, for solutions of $1{,}5\cdot10^{-3}$ M of photoelectrochromic substances and $1{,}5\cdot10^{-2}$ M of inert electrolyte in the presence of propylene carbonate as solvent. Experiments were carried out in a three electrode system with Pt as the counter electrode, Ag/AgCl as the reference electrode, and a glassy carbon as the working electrode. The potential control was achieved by means of an Amel 2049 model potentiostat/galvanostat, an Amel 568 progammable function generator with scan rate of 30 mV/sec. Measurements were carried out at room temperature.

Morphology analysis was performed on cross sections of photoelectrochromic films, cutted after immersion in liquid nitrogen, left under vacuum for several hours in order to extract any liquid component, gold coated, and finally examined in a Leica LEO 420 scanning electron microscope.

## 4.7 Results and discussion

### 4.7.1 Photochromic behaviour

The photochromism of 1,3,3-trimethyl-spiro-(indolino-2,3'[3H]naphtho[2,1-b][1,4]oxazine) (SO), illustrated in figure 4.6, is due to the photocleavage of the C-O spiro-bond of the SO upon UV irradiation, which leads from the colourless stable closed-ring isomeric form (SO) to the coloured metastable open-ring isomer (PM), by a thermoreversible reaction. The photoinduced colour change can be explained by the extension of the conjugated system in the open-ring PM form compared with the orthogonal structure of the SO form.

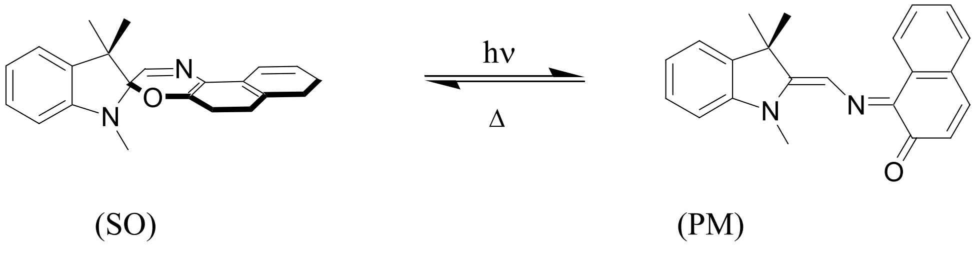


**Fig. 4.6** *Photocleavage of the C-O spiro-bound by UV irradiation.*

The absorption spectrum (from 400 to 900 nm) of the photocoloured PM form of SO in the polymer film is illustrated in figure 4.7. The maximum absorption peak is centred at 602 nm, it reveals a remarkable colour change in the film, that passes from a colourless state to a blue coloured state.

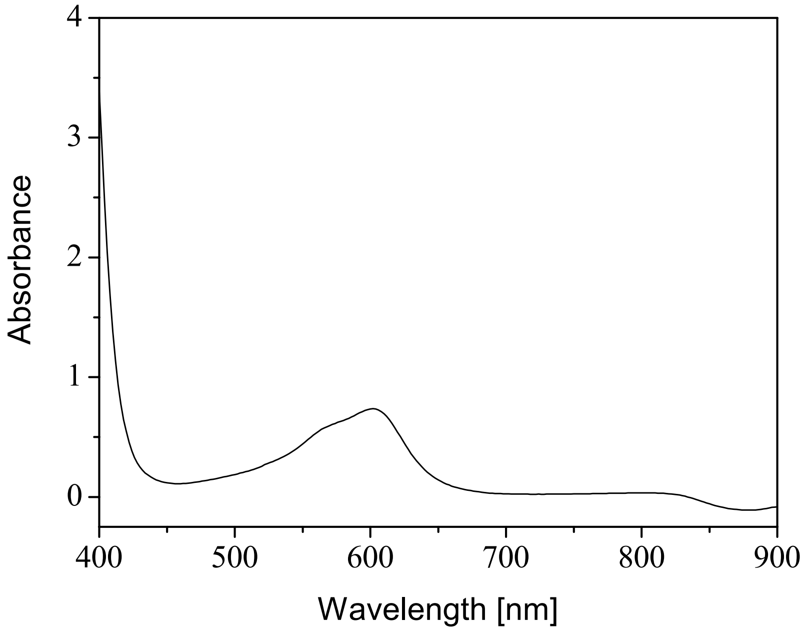
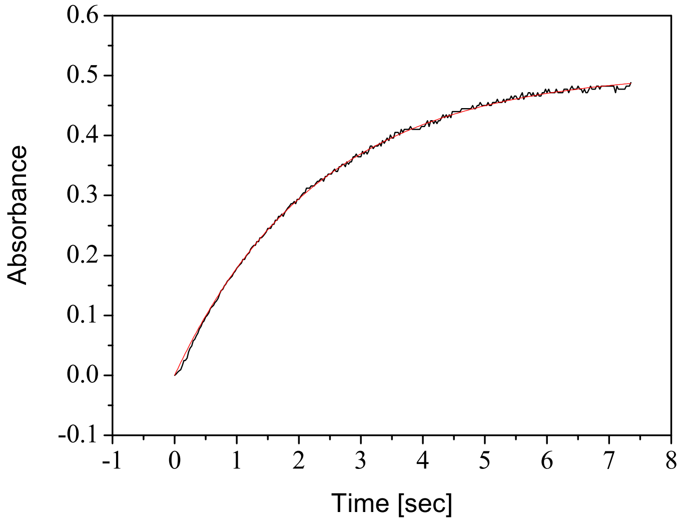


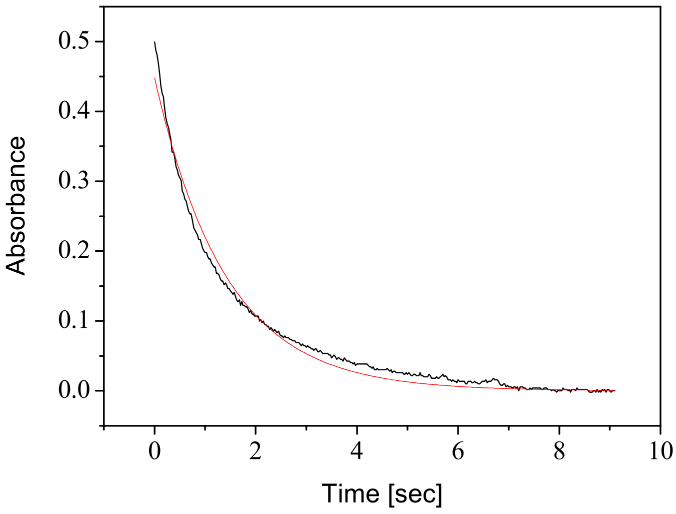
**Fig. 4.7** *Absorption spectrum of the coloured PM form obtained for a photoelectrochromic film containing SO.*

The colour-forming process, induced by steady irradiation, and the thermal bleaching of SO-1 in the polymer film have been followed at the maximum absorption and the results are reported in figure 4.8.

The kinetic parameters of the ring closure reaction have been determined by following the decrease in absorbance of the coloured form; the colour-forming kinetics have been measured by monitoring the visible PM transmittance under stationary irradiation up to photostationary state attainment.



a)



b)

**Fig. 4.8** *a) Colour-forming kinetics, and b) thermal bleaching kinetics followed at the maximum absorption for a photoelectrochromic film containing SO.*

The colour-forming and colour-bleaching kinetics are formally described by the monoexponential function of equations. 4.3 and 4.4, respectively,

$$A_{PM} = A_{PM}^{\infty}\left(1 - e^{-\alpha t}\right) \tag{4.3}$$

$$A_{PM} = A_{PM}^{\infty} e^{-k_{\Delta} t} \tag{4.4}$$

where $A_{PM}^{\infty}$, $\alpha$, and $k_{\Delta}$ can be determined by a fit procedure. $A_{PM}^{\infty}$ is the maximum absorbance of the coloured form attained at the photostationary state. The $k_{\Delta}$ parameter is the first-order kinetic constant of the bleaching process, while $\alpha$ contains experimental factors, like the intensity of the light, and property intrinsic to the system.

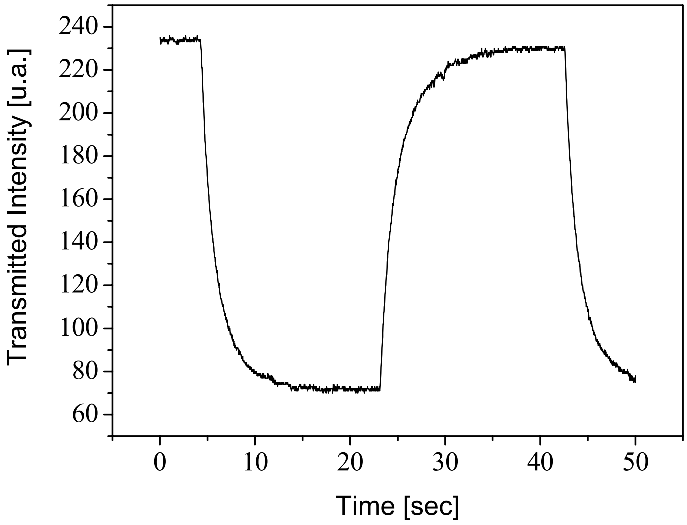


**Fig. 4.9** *Consecutive coloration-decoloration cycles carried out on a photoelectrochromic film containing SO.*

The bleaching rate, $k_{\Delta}$, and the coloration rate parameters, determined by moexponential fit of the experimental data points, are of the order of 0.7 $s^{-1}$, and 0.4 $s^{-1}$, respectively. The photoelectrochromic film has been subjected to consecutive coloration-decoloration cycles with a fairly good reversibility as can be seen in figure 4.9.

## 4.7.2 Electrochromic behaviour

In figure 4.10 is illustrated the current response signal obtained when the potential excitation signal is applied to a glassy carbon electrode immersed in propylene carbonate (PC) solution containing $1{,}5\cdot10^{-3}$ M SO-1 as the electroactive species and $1{,}5\cdot10^{-2}$ M tetrabutylammonium hexafluorophosphate (TBAEFP) as the supporting electrolyte. When the potential is scanned towards positive potential, two oxidation waves are observed at +1.19 V and +1.43 V, associated to a reversible colour change between bright yellow during the first oxidation and red during the second oxidation.

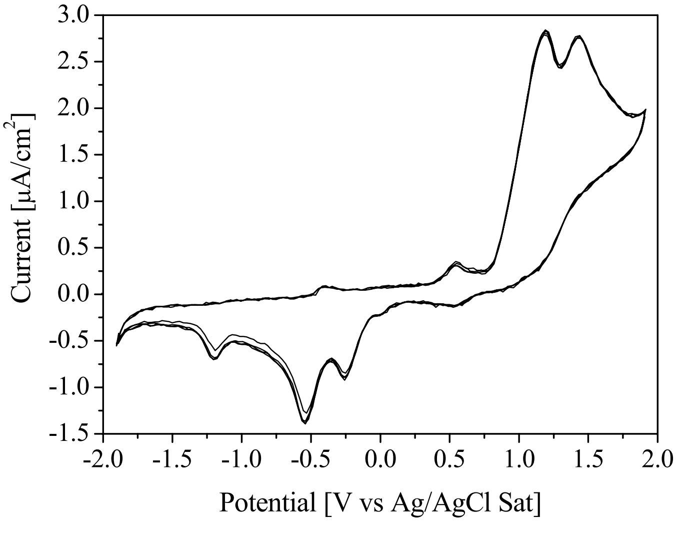


**Fig. 4.10.** *Cyclic voltammogram of $1{,}5\cdot10^{-3}$ M SO-1 in PC solution $1{,}5\cdot10^{-2}$ M TBAEFP.*

The optical properties of photoelectrochromic films were examined via spectroelectrochemistry at room temperature over the whole visible range at various applied potentials, as illustrated in figure 4.11 for a photoelectrochromic film.

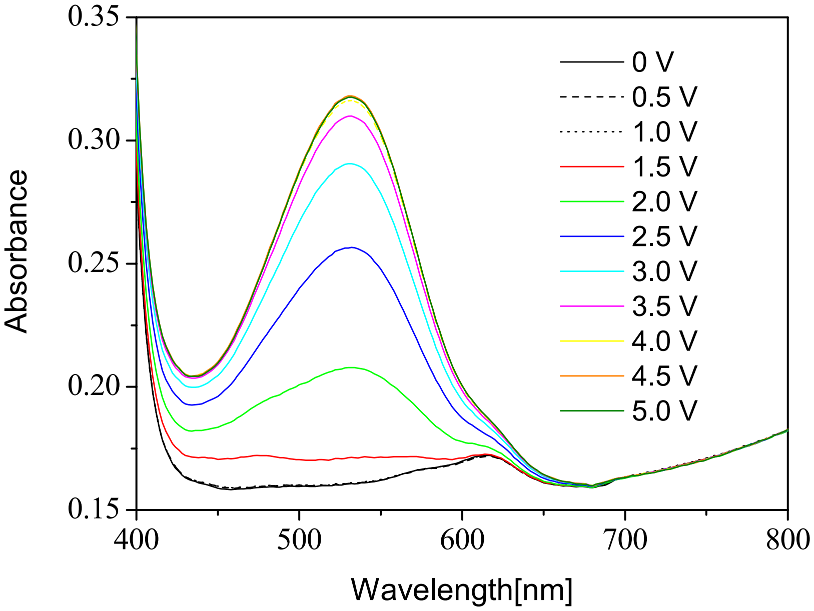


**Fig. 4.11** *Spectroelectrochemical UV-vis transmittance spectra of a photoelectrochromic film registered at various applied potential.*

Each DC pulse was 15 minutes long. When no voltage was applied, there was no particular absorption band in the spectrum (figure 4.11). Just after the application of a potential greater than 1 V a band centred at 532 nm appeared. The absorbance began to increase in intensity at more positive potentials and reached a maximum value at about 3.5 V. Such behaviour is more evident in Figure 4.12, where the maximum absorption is reported as a function of potential.

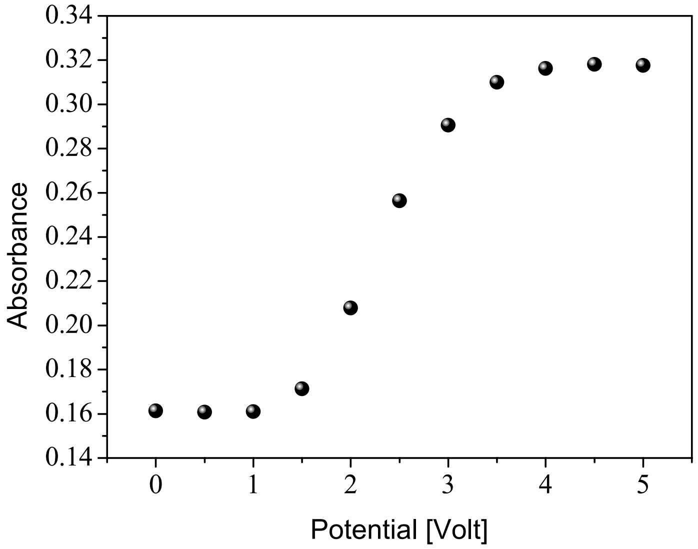


**Fig. 4.12** *Maximum absorption dependence versus applied potential for a photoelectrochromic film containing SO.*

The oxidation process changes the film appearance from bleached to coloured in some minutes. The yellow coloration observed in solution during the first oxidation step did not appear when the experiment was performed in the solid matrix; in fact, in the cyclic voltammetry experiment, the potential was scanned linearly from an initial value of -1.9 V, to a second value of +1.9 V and then back to the initial value, while in the spectroelectrochemical experiment performed on the solid film the potential was varied from 0 V to 5 V with increases of 0.5 V. The change in colour is rather stable and persists for some hours before reaching the bleached state. This behaviour is showed in figure 4.13, where the time dependence of transmittance is reported for a film subjected to a coloration-decoloration cycle at the wavelength of 532 nm. The driving voltage to reach the right coloration value was 5 V DC.

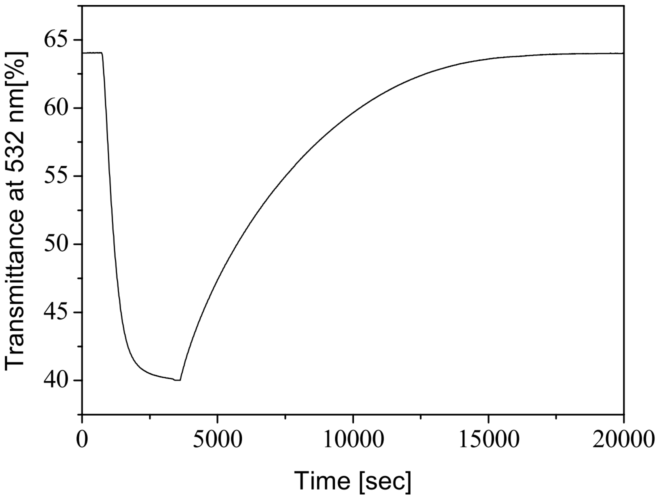


**Fig. 4.13** *Optical transmission dependence versus time of a photoelectrochromic film subjected to a colouration-decolouration cycle at the wavelength of 532 nm.*

In figure 4.14 the SEM image of the photoelectrochromic film cross section is reported. The film reveals a homogeneous and continuous structure without visible phase separation.

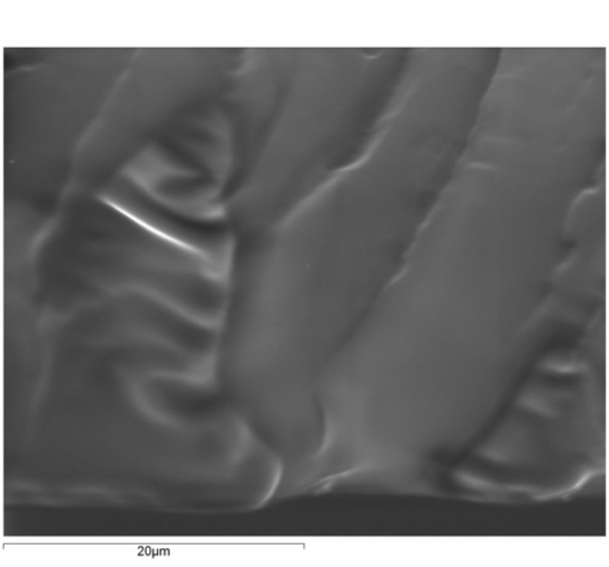


**Fig. 4.14.** *SEM image of cross section of the photoelectrochromic film.*

A complete absence of porosity and channels makes difficult the migration of the electrochromic molecules, which have to diffuse inside the plasticized polymer to reach the electrodes. For this reason the steric hindrance of the electroactive species and the rigidity of the polymer matrix strongly affect the diffusion coefficient (*Di*) and, as a conseguence the electrochromic kinetics, according to the Fick's first law for the flux $j_i$:

$$j_i = Di(\frac{\partial ci}{\partial x}) \qquad (4.5)$$

where $(\partial ci/\partial x)$ is the concentration gradient. In electrochemical processes the concentration gradient arises because some of the electroactive species is consumed around the electrode, the subsequent change in concentration causes diffusion.

Another electrochromic response times limiting factor, is the small value of the electroactive species concentration gradient near the electrodes. When the pulse is turned on, only the small amount of oxidized spirooxazine is able to react at the negative electrode, in fact SO is mainly in its reduced form ($SO_{red}$). Such a restricted quantity of electrogenerated $SO_{red}$ creates a very small value of the redox species concentration gradient, then a slow flux of molecules moves towards the electrodes.

In opposition to the electrochromic film studied in the second chapter of this research work no charge transfer complex equilibrium involving the electroactive SO is present in the photoelectrochromic film. For this reason and considering that SO is a non ionic molecule, the only colouring process which can be considered is diffusion of molecules towards electrodes, but, this mechanism is greatly slowed by the rigidity of the solid matrix

In any case, better electrochromic response times were observed when a certain amount of a good cathodic molecule as 1,1'-di(11-heptanoyloxyundecyl)-[4,4']bipyridinyl-1-ium dibromide (HBB) was added to the SO based photoelectrochromic device; in figure 4.15 the spectroelectrochemical behaviour of a film composed of 40 wt. % PVF, 4 wt. % SO, 2 wt. % HBB and 54 wt. % propylene carbonate, 60 µm thick, is shown as function of the applied voltage.

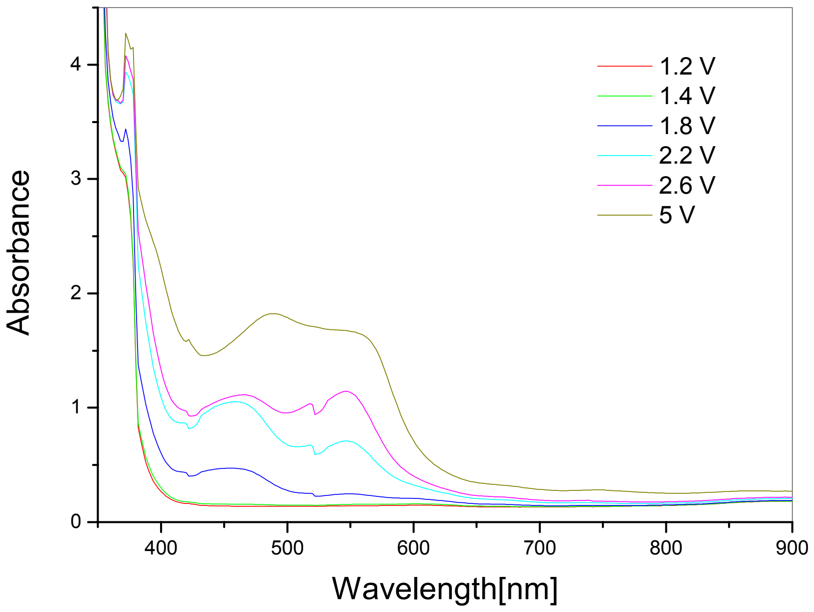


**Fig. 4.15** *Spectroelectrochemical UV-vis spectra of a photoelectrochromic film based on SO and HBB as electroactive molecules, registered at various applied potential.*

As we can observe from figure 4.15, two bands appear in the visible part of spectrum when an appropriate voltage was applied to the photoelectrochromic film. One of these bands was centered at 546 nanometers and attributable to the cathodically reduced form of HBB, the second band, centered at 456 nanometers was due to the anodical oxidation of SO. The shift of the absorption band of the coloured form of SO is due to the different polymer matrix and plasticizer used in experiments in figure 4.11and 4.15. In the first case PVB plasticized with a mixture of propylene carbonate and tri(ethylene glycol) bis-2-ethylesanoate was used. In the second case the polymer used was PVF and the plasticizer was only propylene carbonate. In any case, in order to exclude a participation of HBB to the SO electrochromic band shift, a film composed of 40 wt. % PVF, 4 wt. % SO and 56 wt. % propylene carbonate was electrically switched and the UV-vis absorption spectrum was recorded; the result is showed in figure 4.16. As we can see, the band of the spirooxazine is centred at 456 nm and the absorbance is low in intensity just like in absence of HBB.

The effect of a good cathodic molecule as HBB, on the bleaching rates and on the contrast ratio of the electrically switched SO are well observable in figures 4.17 and 4.18, were transmittances at 456 nanometers versus time and contrast ratios at the same wavelength are explored for a photoelectrochromic film based on SO and HBB as function of the applied voltages. As we can observe from these two graphs, bleaching rates are drastically decreased and contrast ratios considerable increased if compared with the experiment of the photoelectrochromic film in absence of HBB as cathodic molecule (figure 4.13). In presence of HBB the reducing species near the cathode was the bipyridinium derivative which was present in great quantity. Increasing the value of the redox species concentration gradient, then a fast flux of molecules towards the electrodes is induced. Another hypothesis to better explain relaxation time of system HBB-SO could the be formation of a inner charge transfer complex of HBB which acts as donor with the not charge nitrogen atom and as acceptor with the positively charged nitrogen atom, making easier the charge propagation mechanism inside the film. This latter mechanism needs further investigation.

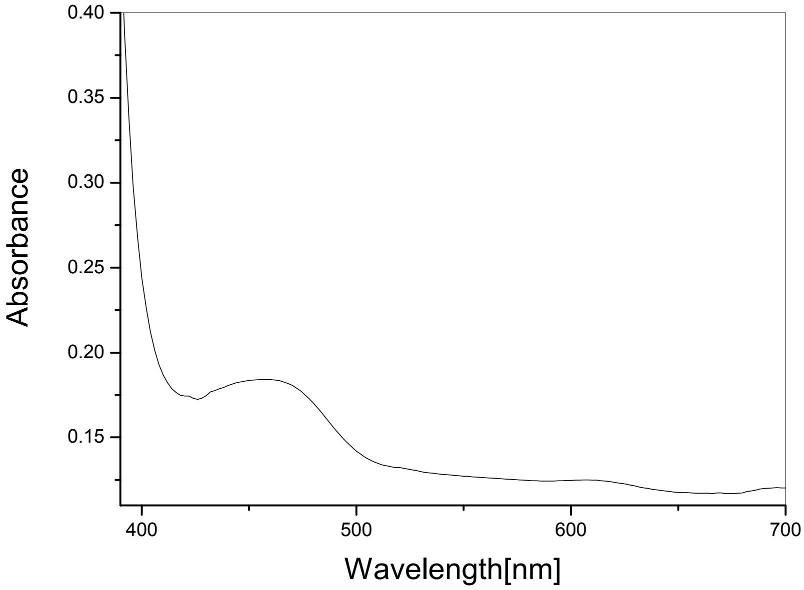


**Fig. 4.16** *UV-vis spectra of a photoelectrochromic film based on SO in PVF plasticized with propylene carbonate at 3 volts DC applied potential.*

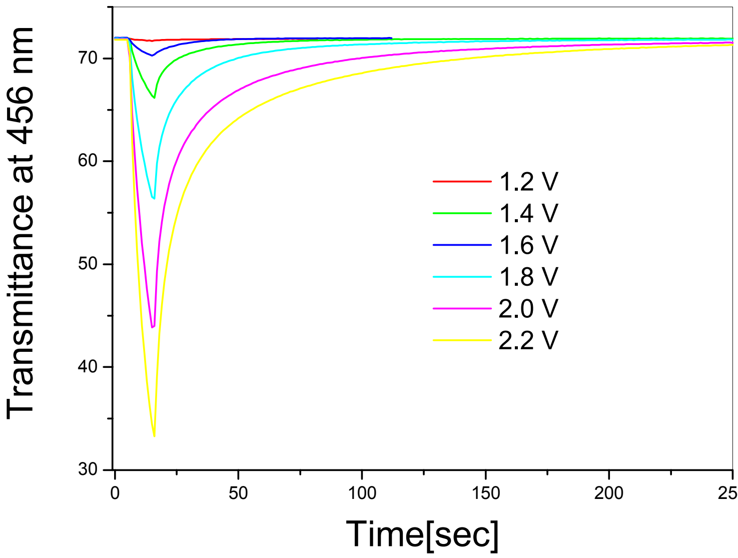


**Fig. 4.17** *Transmittance versus time as a function of the applied potential (pulse length 10 seconds in all the experiments), for a photoelectrochromic film with following composition: 40 wt. % PVF, 4 wt. % SO, 2 wt. % HBB and 54 wt. % propylene carbonate. 60 μm is thickness of film.*

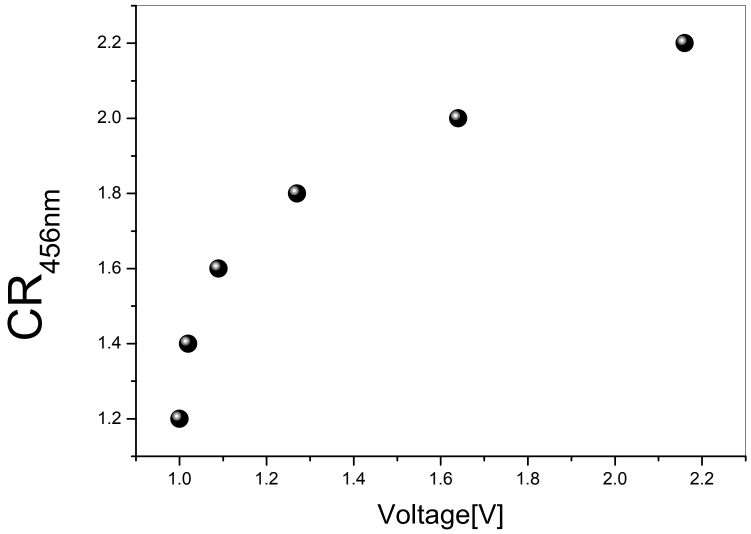


**Fig. 4.18** *Contrast ratio at 456 nanometers as a function of the increasing applied pulsed voltage, pulse length=10 seconds, for a photoelectrochromic film with following composition: 40 wt. % PVF, 4 wt. % SO, 2 wt. % HBB and 54 wt. % propylene carbonate. 60 μm is thickness of the film.*

## 4.8 Conclusions

We have realized a new photoelectrochromic device based on a spirooxazine, which acts as photoactive and electrochromic molecule. Thus the transmittance of the photoelectrochromic device can be decreased under illumination and can be increased again in the dark. Furthermore, the system can also be switched by an auxiliary external voltage. The first advantage of this new device with respect to other kinds of photoelectrochromic devices studied before is the simplicity of its fabrication, in fact simply lamination of a thermoplastic polymer layer between two pieces of conductive glasses allows to obtain the bifunctional device. The second advantage is represented by the use of a single active molecule to obtain the photochromic and the electrochromic effect. Possible limitation for the applications of such device in display technology is the long electrochromic switching time, but this electrooptical parameter can be greatly increased adding to the EC mixture a good cathodic molecule as HBB. But still, while the time constants for colouring and bleaching are fast for the photochromic reaction, some seconds are needed to reach the coloured and the bleached state for the redox electrochromic process. Work is in progress to improve the electrochromic response times.

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