

**A novel 1,1'-bis-[2-(1H-indole-3-yl)-ethyl]-4,4'-bipyridinium
diperchlorate (viologen) for a high contrast electrochromic device**

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Indian Institute of Technology Hyderabad
As part of the requirements for the degree of**

Master of Science

By

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
DEPARTMENT OF CHEMISTRY
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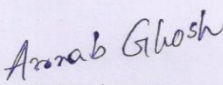
Declaration

I hereby declare that the matter embodied in this report is the result of investigation carried out by me in the Department of Chemistry, Indian Institute of Technology Hyderabad under the supervision of **Dr. M. Deepa**.

In keeping with general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.


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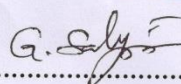
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This thesis entitled "A novel 1,1'-bis(2-(1H-indol-3-yl)ethyl)-4,4'-bipyridinium diperchlorate (viologen) for a fast bleaching and high contrast electrochromic device" by **Arnab Ghosh** is approved for the degree of Master of Science from IIT Hyderabad.


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Abstract

A new organic electrochromic material, 1,1'-bis-[2-(1H-indole-3-yl)-ethyl]-4,4'-bipyridinium diperchlorate (viologen) was synthesized by di-quaternization of 4,4'-bipyridyl using 3-(2-bromoethyl)-indole under the assistance of microwave irradiation with high yields and in short reaction times. The compound (IEV) was characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and FTIR spectroscopic methods. Thermal decomposition temperature of indole viologen perchlorate is above 300°C . An electrochromic device, containing IEV salt in N,N-Dimethylformamide (DMF) and 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)-imide (ionic liquid) as electrolyte was constructed, where Prussian blue was used as counter electrode. IEV is a cathodically coloring organic electrochromic material and thus the device underwent reversible transitions between transparent and deep blue hues; the color change was accompanied by an excellent optical contrast (57% at 605 nm), a large coloration efficiency of $533\text{ cm}^2\text{ C}^{-1}$ at 605 nm and switching times of $\sim 2\text{ s}$. The device was subjected to repetitive switching between the colored and bleached states and was found that almost no loss in redox activity up to 2000 cycles, ratifying its suitability for electrochromic window/display applications.

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1. Introduction:

Viologens are di-quaternized salts of 4,4'-bipyridyl and they exhibit significant color change upon reduction to radical cations by application of an electric current or voltage [1,2]. This color change is reversible as the change in direction of current results decoloring of the colored species. Thus viologens are incorporated in electrochromic devices (ECDs) and they find applications in smart windows, glare reduction mirrors and high contrast displays [3-5]. Viologens are dissolved in the electrolyte [6] for use in an electrochromic device (ECD). In electrolyte solution they exist in the dicationic form which is generally colorless [7]. In an electrochromic device, they are reduced to radical cations, at the cathode, by an electrochemical reaction. The colored radical cation is insoluble in the electrolyte and appears in the form of a colored layer over the transparent conducting electrode surface. They easily revert to the soluble and colorless dicationic form, by reversing the applied potential [6]. Although conventional N,N'-dimethyl- or N,N'-diheptyl-4,4'-bipyridinium salts have been exhaustively reconnoitered for electrochromic applications [16], even commercially [14,17], nevertheless very high optical contrast [6,7] (> 40 %), ultra high coloration efficiencies [9] (> 300 cm² C⁻¹) in the visible region and fast switching between colored and bleached states (~2 s, for areas greater than 2 cm²) [10,11] are very much desirable for electrochromic devices. The need for developing new viologens stems from the fact that traditional viologens like di-heptyl viologen [14] are planar molecules, and when reduced to radical cations, they re-arrange themselves on the electrode surface to form a stack like assembly, wherein each molecule lies directly above the other [13,15]. Such a compact structure is resistive to oxidation and within a few cycles, the redox process becomes irreversible and the device acquires a permanently colored state. To circumvent this, bulky substituents are attached to the N,N'- positions of the bipyridyl, which coerce the radical cation out of planarity, prevent re-arrangement [12,13] thus inhibit stacking and make the process reversible. To address these issues, we synthesized a new viologen, which showed an extremely high contrast, good color uniformity, fast response time and high coloration efficiency. A novel derivative of viologen salt containing the indole moiety connected by an ethyl unit was synthesized and characterized. For practical purpose we used Prussian blue for anodically coloring materials.

2. Experimental:

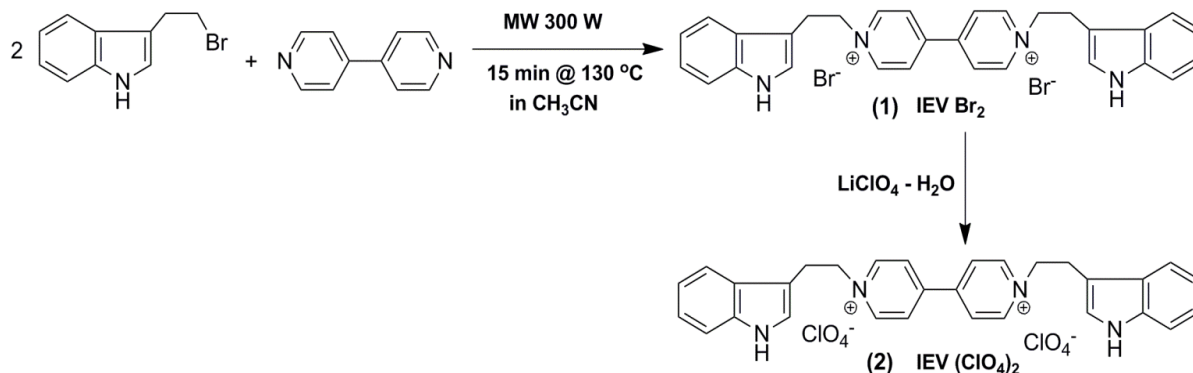
2.1 Materials

4,4'-bipyridyl, 3-(2-bromoethyl)-indole were procured from Sigma Aldrich. Potassium ferricyanide ($K_3[Fe(CN)_6]$), iron(III)chloride ($FeCl_3$), acetonitrile, N,N-dimethylformamide (DMF), 1-Ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)-imide ($EtMeIm^+Im^-$), hydrochloric acid (35% HCl), acetone, ethanol and were procured from Merck. Ultrapure water (resistivity 18.2 M Ω cm) obtained through the Millipore Direct-Q 3 UV system was used as the solvent. Fluorine doped tin oxide ($SnO_2:F$ or FTO) coated glass substrates were purchased from Pilkington (sheet resistance: 14 Ω sq $^{-1}$) and used after cleaning with 10 % HCl, soap solution and distilled water and acetone.

2.2 Synthesis of 1,1'-bis-[2-(1H-indole-3-yl)-ethyl]-4,4'-bipyridinium diperchlorate(2)

3-(2-bromoethyl)-indole (0.3 g, 1.3 mmol), 4,4'-bipyridyl (0.07 g, 0.5 mmol) and dried acetonitrile (2.5 mL) were irradiated in a quartz vessel of 10 mL in a microwave reactor at 300 Watts for 15 min at 130 °C. The precipitate was filtered and well washed by plenty of acetonitrile to remove unreacted reactants and dried under vacuum at room temperature. This viologen salt (**1**) is a deep brown powder. Yield (0.22 g, 81%). Melting point: Decomposed at 305°C. The characterization data of the product is given below: IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3172, 3004, 2853, 1633, 1551, 1498, 1340, 1221, 1168, 1022, 816, 748, 701 & 632 cm^{-1} . 1H NMR : (DMSO- d_6 , 400 MHz): δ (ppm)=10.97 (d, 2H, Ar-NH), 9.11-9.13 (d, 4H, Ar-H, J=7.2 Hz), 8.54-8.56 (d, 4H, Ar-H, J=6.8 Hz), 7.51-7.53 (d, 2H, Ar-H) 7.36-7.37 (d, 2H, Ar-H), 7.14-7.15 (d, 2H, Ar-H), 7.08-7.10 (m, 2H, Ar-H), 6.94-6.98 (m, 2H, Ar-H), 4.92-4.95 (t, 4H, N-CH $_2$), 3.42-3.45 (t, 4H, Ar-CH $_2$) ppm. ^{13}C NMR (DMSO- d_6 , 100 MHz): δ =148.99 (s, 2C Ar-C), 146.01 (d, 4C, Ar-CH), 136.55 (s, 2C, Ar-C), 127.07 (s, 2C, Ar-C), 126.60 (d, 4C, Ar-CH), 124.57 (d, 2C, Ar-CH), 121.92 (d, 2C, Ar-CH), 119.24 (d, 2C, Ar-CH), 118.43 (d, 2C, Ar-CH), 112.12 (d, 2C, Ar-CH), 108.66 (s, 2C, Ar-C), 62.06 (t, 2C, 2 \times N-CH $_2$), 27.27 (t, 2C, 2 \times N-CH $_2$ -CH $_2$) ppm. HR-MS (ESI+) m/z calculated for $[C_{30}H_{28}Br_2N_4] = [M+Na]^+$: 625.057; found: 625.060. The viologen of perchlorate salt (IEV) was obtained by re-precipitation of IEV-Br $_2$ (~50 mM) in an aqueous solution of 0.3 M LiClO $_4$. The precipitate was filtered and washed with

plenty of water, ethanol and dried under vacuum at room temperature, yields a brownish orange solid powder (2). HR-MS (ESI+) m/z calculated for $[C_{30}H_{28}Cl_2N_4O_8] = [M+Na]^+$: 665.118; found: 665.116.



Scheme 1: Synthesis of IEV-(ClO₄⁻)₂

2.3 Fabrication of electrochromic device with IEV-perchlorate salt

For preparing an electrochromic device, 10mM of IEV-(ClO₄)₂ solution was prepared by dissolving it (IEV-salt) in the electrolyte solution containing N,N-Dimethylformamide (DMF) and EtMeIm⁺Im⁻ ionic liquid (in 1:1 volume ratio). All the contents were sonicated for 10 minutes. Prussian blue films were grown from a solution of 10 mM K₃[Fe(CN)₆] and 10 (mM) FeCl₃ in 0.01 N HCl in a three electrode cell, using Ag/AgCl/KCl as reference electrode by applying a fixed potential of +1.5 V for 300 sec. to a SnO₂:F coated glass substrate. Films were washed in a solution of 0.01 N HCl and deionized water mixed in a 2:3 volume ratio and stored in air. An acrylic adhesive tape (0.64 mm thick and 3 mm wide) was applied along the four edges of the blank FTO coated glass substrate (cathode) and two 1 to 2 mm wide openings were grafted in the tape along one edge and the complementary electrode (PB) was then placed above this electrode and thus a cavity was created between two electrodes. Except for the two openings, the remainder of this assembly was sealed with an epoxy. Here the acrylic tape was employed as the spacer, which prevented the shorting of the two electrodes and also held the device assembly together. The electrolyte solution containing the IEV-(ClO₄)₂ salt was injected into the device. A transparent, pale yellowish colored device encompassing the solution based electrolyte was

obtained and all the edges were sealed with epoxy. The device, hereafter is referred to as the IEV-PB device.

2.4 Instrumentation techniques

Microwave synthesis was carried out in a CEM Discover system. Thermo-gravimetric analysis (TGA, TA instruments, Q600) were carried out for IL (liquid) and IEV salt (solid powder) from 30 – 500 °C temperature with 10°C/minute ramp rate under N₂ atmosphere. Cyclic voltammetry (CV) for the devices and linear sweep voltammetry (LSV) for the electrolyte were performed on an Autolab PGSTAT 302N Potentiostat/Galvanostat coupled with a NOVA 1.9 software. The optical density and transmittance of the device was measured *in-situ*, on a Shimadzu UV-Visible-NIR 3600 spectrophotometer under dc potentials of different magnitudes (applied for a 60 s duration). Electrochromic switching response of the device was performed under a square wave potential and at a fixed monochromatic wavelength, in kinetic mode.

3. Results and discussion:

3.1 Electrolyte and IEV-diperchlorate salt characteristics

3.1.1 Thermogravimetric analysis (TGA)

TGA plots of the liquid electrolyte [N,N-Dimethylformamide (DMF) + 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)-imide (ionic liquid)] and IEV salt (solid powder) in the 30–500 °C temperature range are shown in Fig. 3.1.1. The figure shows the weight losses in the samples as a function of temperature. For pristine ionic liquid, a plateau was observed till 400°C, indicating that the ionic liquid EtMeIm⁺Im⁻, is highly stable even at high temperatures and therefore can be incorporated in an electrochromic device. The IEV-(ClO₄)₂ salt (solid) decomposed at ~300°C, which illustrates its suitability for any electrochemical device application. Hence the ECD based on the electrolyte can be stable from ambient temperatures to ~ 90°C. The IEV salt completely dissolves in the solution based electrolyte to yield a pale yellow transparent solution, indicating good compatibility with organic solvents like DMF and the ionic liquid.

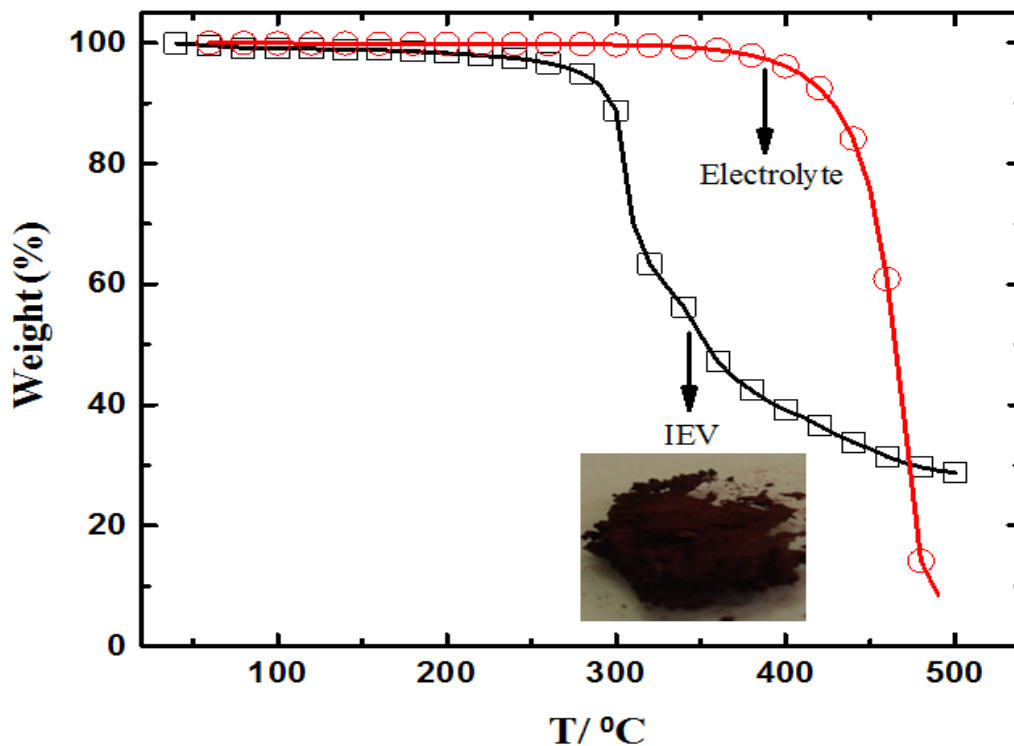


Figure 3.1.1 TGA curves for the liquid electrolyte [*N,N*-dimethylformamide + *1*-Ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)-imide (ionic liquid)] and IEV-(ClO₄)₂ salt.

3.1.2 Linear Sweep Voltammetry (LSV)

The linear sweep voltammogram of the electrolyte is shown in Fig. 3.1.2 and the electrolyte was observed to be electrochemically inert in the voltage range of -2 V to $+2$ V, indicating a potential stability window of about ~ 4 V, which is adequate for electrochromic device application. Since the electrolyte is optically transparent in the 400-800 nm wavelength region, it can be employed for fabricating transmissive electrochromic devices.

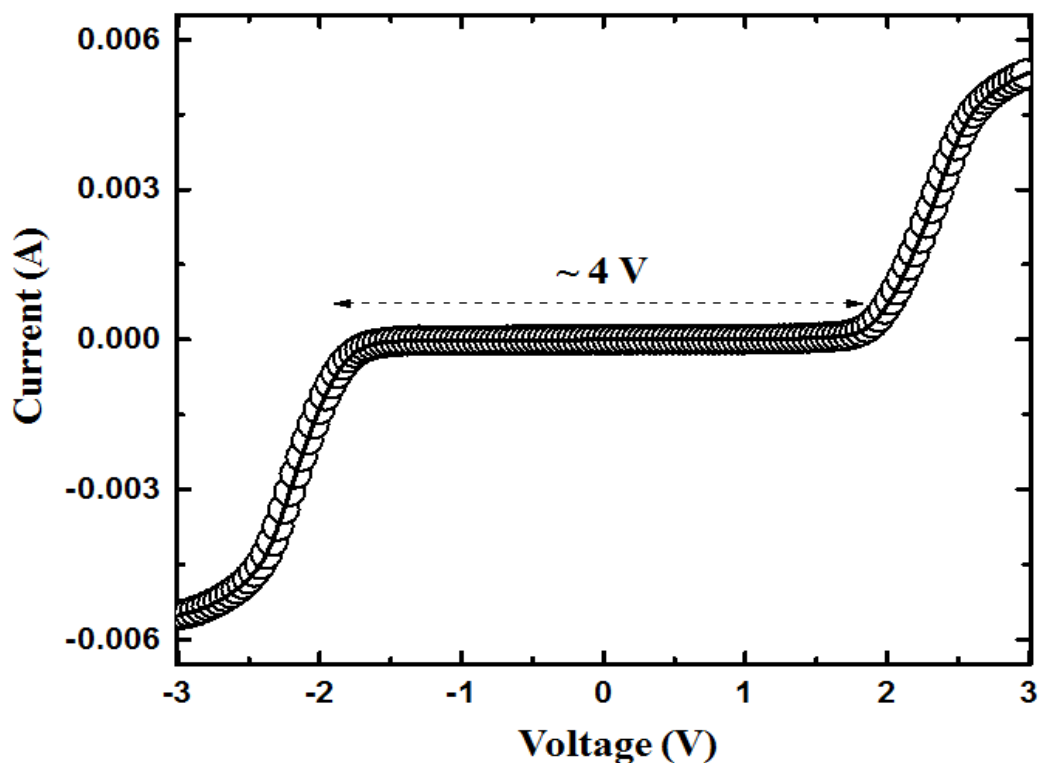


Figure 3.1.2 LSV plot of the *1-Ethyl-3-methylimidazolium [bis-(trifluoromethylsulfonyl)-imide + DMF]* liquid electrolyte recorded at the scan rate 20 mV/s.

3.1.3 Conductivity study of the electrolyte

The ionic conductivity of the electrolyte IL-DMF was found to be 4.6 mS.cm^{-1} at room temperature and it varied considerably with temperature from 30 to 50°C ; and there on conductivity varied insignificantly as it is increased from 8.2 to 8.7 mS.cm^{-1} on raising temperature from 40 to 70°C in steps of 10°C (Fig. 3.1.3). Previously, electrochromic devices employing ionic liquid based electrolytes in combination with organic solvents like methanol, N,N-dimethylformamide exhibited good ionic conductivities in the range of $5\text{-}20 \text{ mS.cm}^{-1}$ at 20°C , which is comparable to our observed value. The increase in the conductivity values are due to increased dissociation of ionic liquid and also due to the high polarity of DMF. These high conductivity values make the electrolyte as a good transport medium.

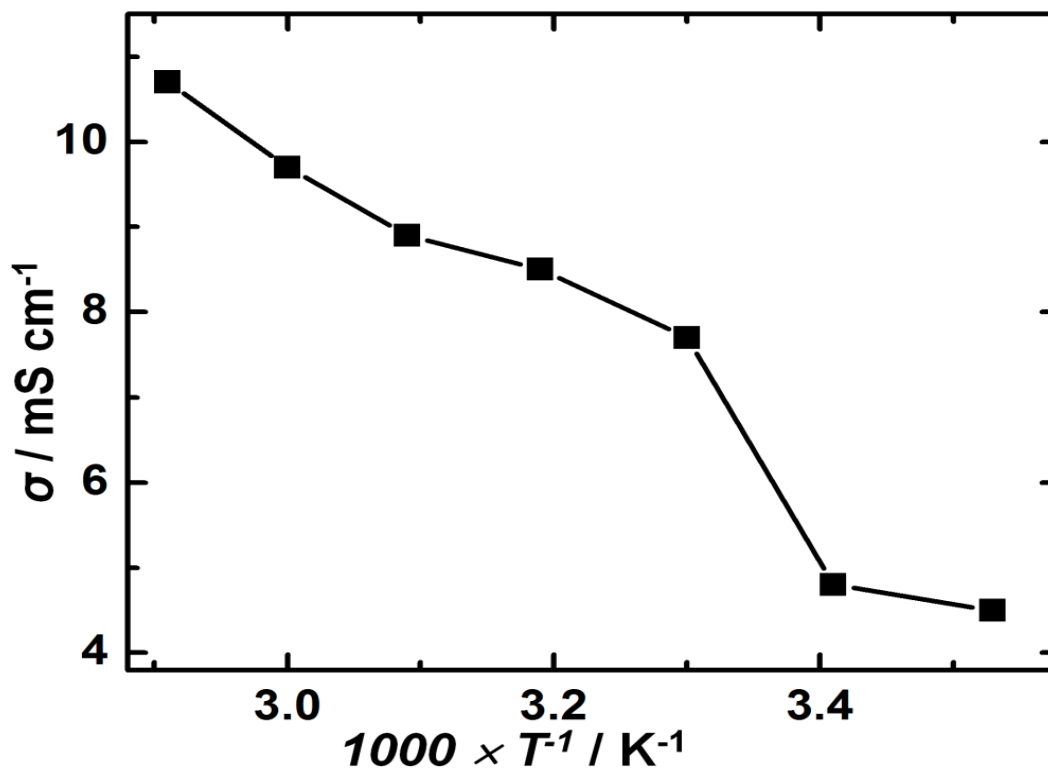


Fig. 3.1.3 Ionic conductivity *versus* the reciprocal absolute temperature curve for *1-Ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)-imide* + DMF liquid electrolyte.

3.2 Cyclic Voltammetry (CV)

3.2.1 Cyclic Voltammetry study for IEV-(ClO₄)₂ solution

The cyclic voltammograms for 10mM of IEV-(ClO₄)₂ solution in IL+ DMF were recorded within potential limits of -0.8 V to +0.2 V and between -1.2 V to and +0.2 V respectively [Fig. 3.2.1(a) and 3.2.1(b)]. The first reduction peak observed at -0.48 V [Fig. 3.2.1(a)] is assigned to formation of deep violet radical cation salt on the FTO surface, which is followed by re-oxidation to the di-cation and its dissolution in the electrolyte at -0.36 V, in the reverse sweep. The one electron oxidation and reduction reaction occurs as shown in the first step of the following equation (1).

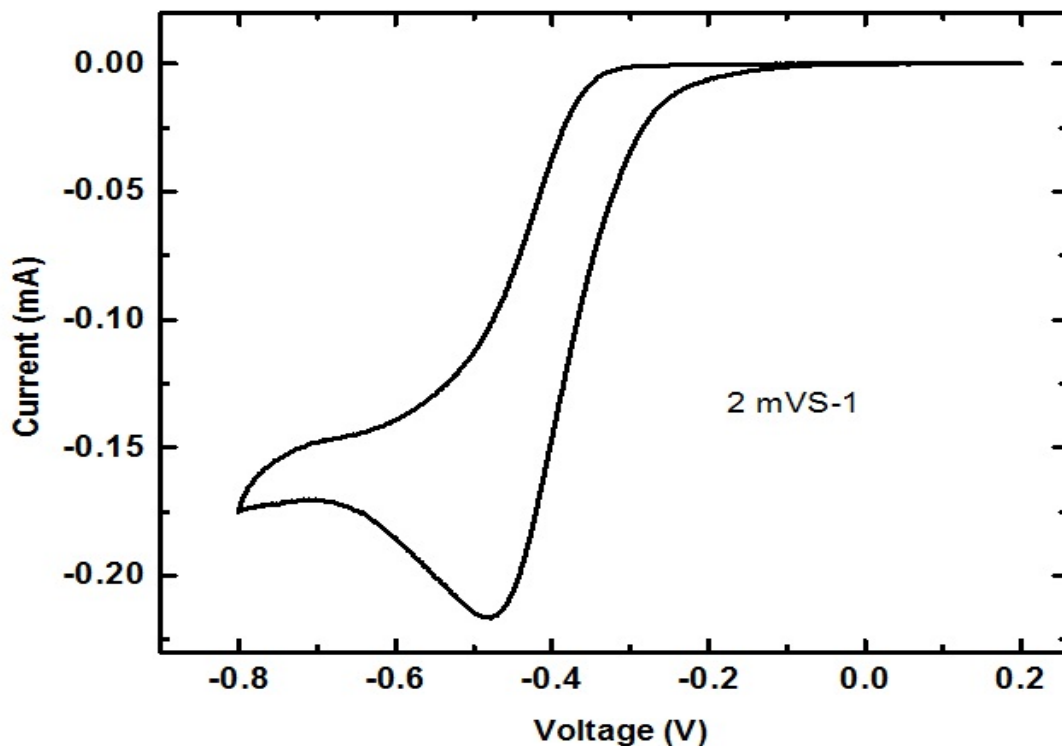
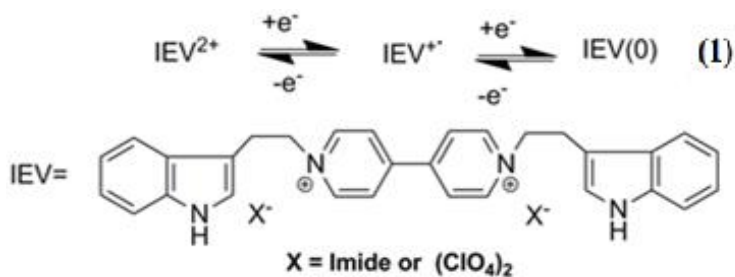


Figure 3.2.1(a) Cyclic voltammogram of IEV-(ClO₄)₂ (10mM) in (DMF+IL) recorded between +0.2 V and -0.8 V versus Ag/AgCl/KCl at a scan rate of 2 mV/s.

The cyclic voltammogram shown in Fig. 3.2.1(b) illustrates the two redox states of the IEV salt. We observed a second reduction peak at -0.94 V. These two peaks correspond to monovalent radical cation formation followed by formation of the neutral viologen, upon further increasing the reduction potential, as shown in the second step of equation (1). In the anodic branch, the first oxidation peak at -0.80V corresponds to radical cation formation and the second peak at -0.38 V is attributed to the di-cation formation.

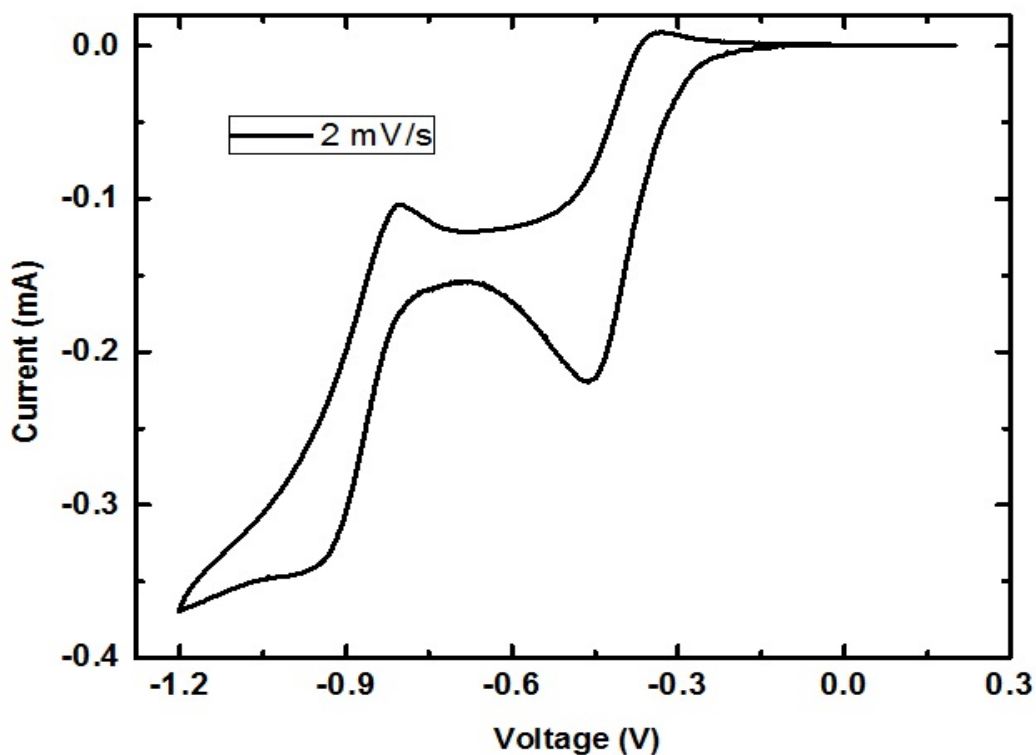


Figure 3.2.1(b) Cyclic voltammogram of IEV-(ClO₄)₂ (10mM) in (DMF+IL) recorded between +0.2 V and -1.2 V versus Ag/AgCl/KCl at a scan rate of 2 mV/s.

Since the reversible transition between deep violet and colorless hues was easily achieved within the voltage limits of -0.8 V to +0.2 V, the effect of scan rate on the redox response of the IEV-(ClO₄)₂ salt was examined within these limits [Fig. 3.2.1(c)]. With increasing the scan rate (from 2 to 100 mV/sec.), the oxidation peak shifts towards the less negative potential, the reduction peak shifts towards more negative potentials and the peak separation increases.

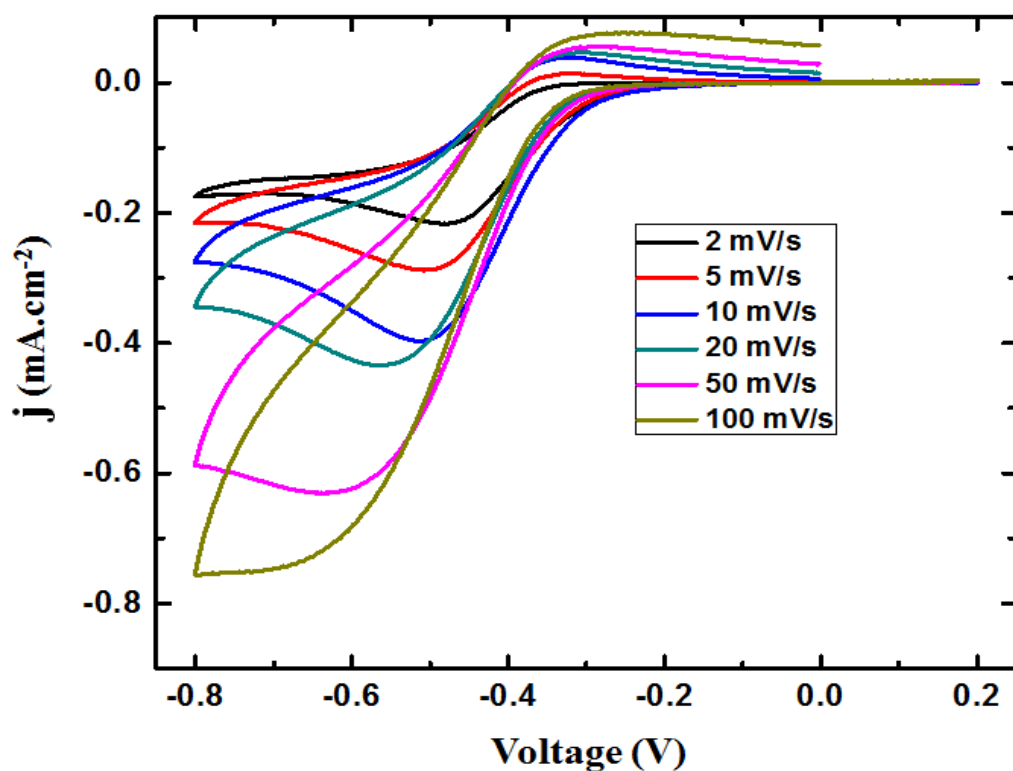


Figure 3.2.1(c) Cyclic voltammogram of IEV/ (DMF+IL) solution recorded between +0.2 V and -0.8 V versus Ag/AgCl/KCl at different scan rates of 2, 5, 10, 20, 50 and 100 mV/s.

3.2.2 Cyclic Voltammetry study for the IEV-(ClO₄)₂/PB device

Cyclic voltammograms for the IEV-(ClO₄)₂/PB device were recorded within potential range of ± 1.5 Volt at the scan rate of 2 mV/s (Fig. 3.2.3). Here, the first reduction peak observed at -0.72 Volt which is followed by re-oxidation to the di-cation at -0.48 V, in the reverse sweep. The effect of scan rate (from 2 to 100 mV/s) on the redox response of the IEV-(ClO₄)₂/PB device was also examined within these limits.

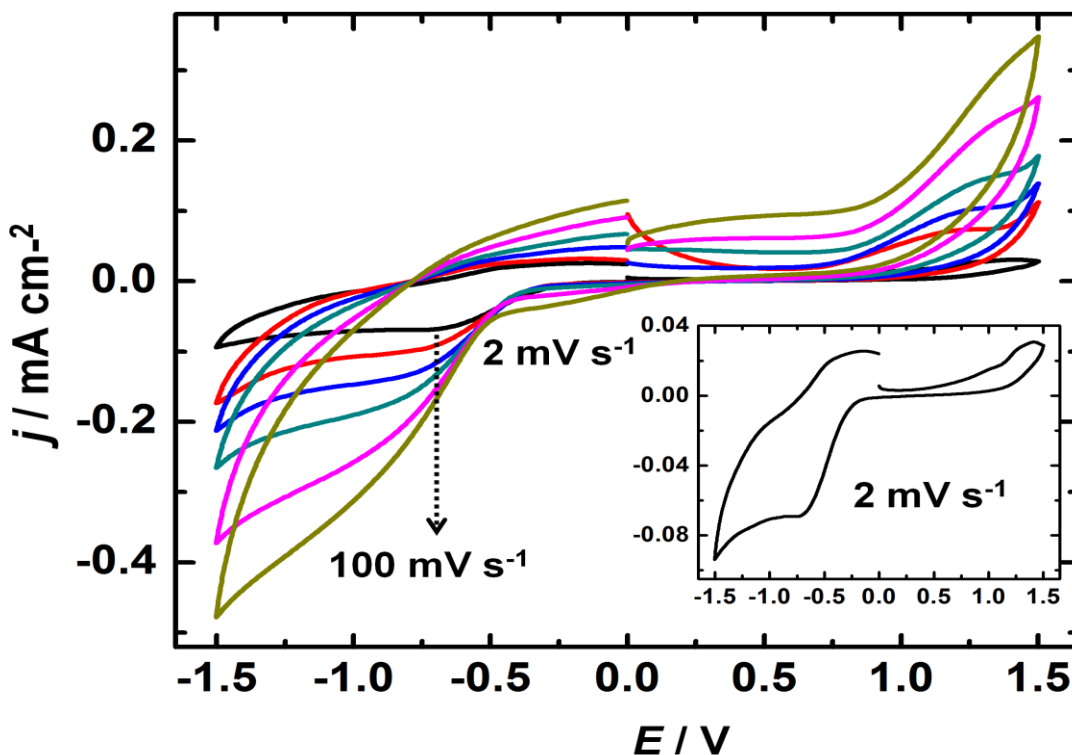


Figure 3.2.2 Cyclic voltammograms for the IEV-(ClO₄)₂/PB device were recorded between +1.5 V and -1.5 V at different scan rates of 2, 5, 10, 20, 50 and 100 mV/s

3.3 Spectroelectrochemistry of IEV-(ClO₄)₂/PB device

3.3.1 Absorption study for the device

The UV-Visible absorption spectra of IEV/ (DMF+IL) /PB device was measured under different reduction potential (applied to the blank electrode) in the range of -0.4 V to -2.0V and under the oxidation potential of +0.5 V to +1.6 V. Upon applying reduction potentials to the device, initially a blue film of IEV radical cation (which is insoluble in the electrolyte) was formed on the FTO surface. With increasing the negative potential number of IEV radical cations increases and hence the color intensity also increases (turns to violet). So, with increasing the negative potential absorption peak of the colored film formed on the FTO surface gradually increases (at 605 nm) which is shown in Fig. 3.3.1. Whilst reduction of IEV²⁺ to IEV⁺ occurs at the cathode, at the anode the Prussian white (PW) oxidizes to form Prussian blue (PB).

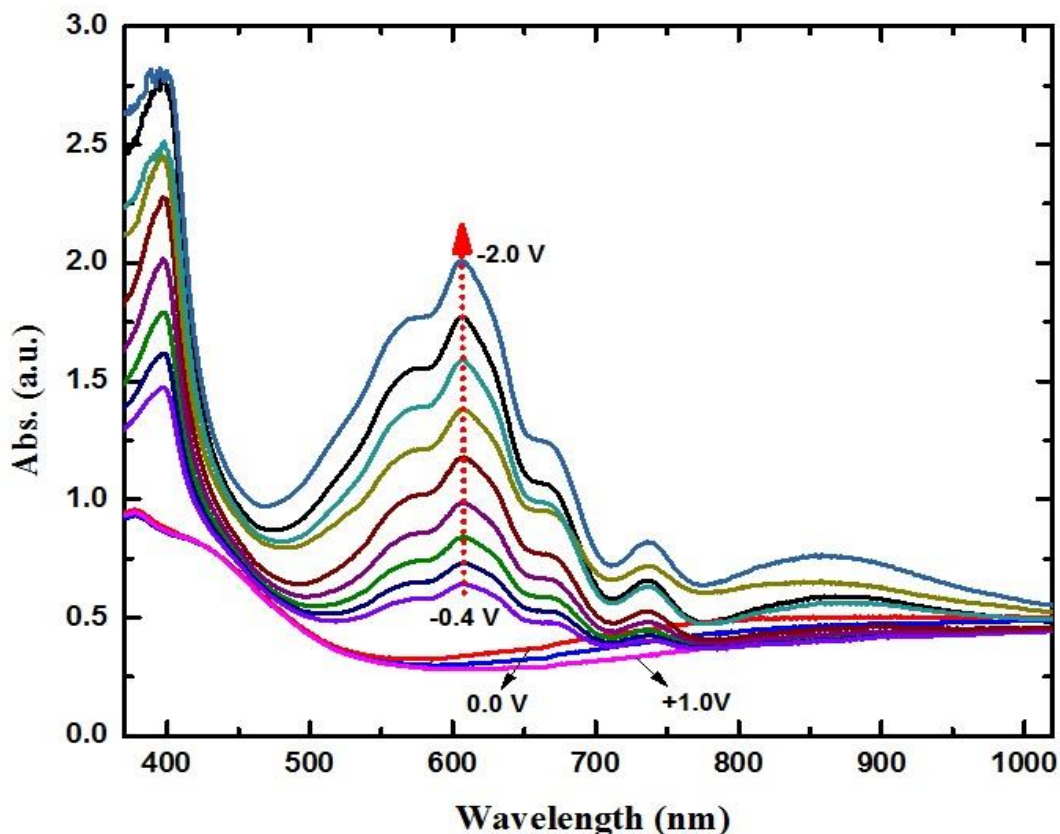


Figure 3.3.1 Absorption spectra of IEV/ (DMF+IL) /PB device recorded under reduction potentials between -0.4 V to -2.0 V and under oxidation potentials of +0.5 V to +1.0 V.

3.3.2 Transmittance study for the device

The UV-Visible transmittance spectra for the same IEV/ (DMF+IL) /PB device was also measured under the potential range between +0.5 to +1.0 V and between -0.4 V to -2.0 V [Fig. 3.3.2(a)]. Upon applying the negative potentials to the blank FTO the IEV^{2+} get reduced and colored. Hence with increasing the amount of negative potential, transmittance peak at 605 nm gradually decreases. Whilst with applying the positive potentials to the same FTO, the reduced species get re-oxidized and color intensity decreased. At +1.5 V (when it is applied to blank FTO), the device shows its maximum transmittance ~66% (at 605 nm). Thus the maximum transmission modulation [$dT = T(+1.5\text{V}) - T(-2.0\text{V})$] offered by the device is (66% – 8%) = 58% which is sufficient for electrochromic window applications. The digital photographs of the device at various potentials are shown in Fig. 3.3.2(b).

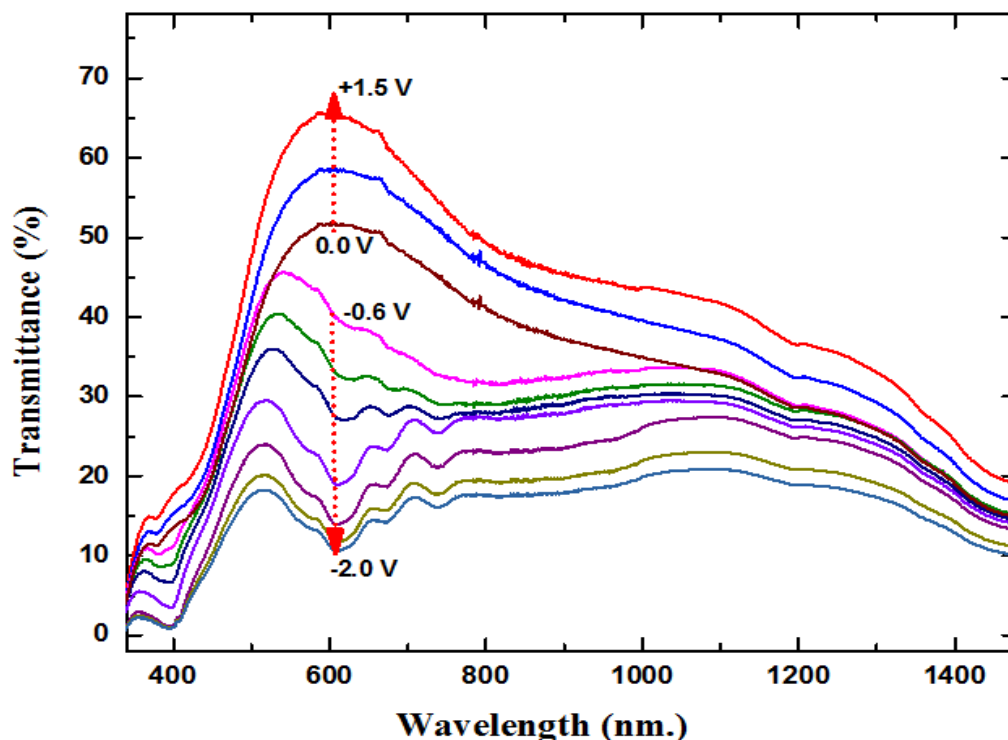


Figure 3.3.2(a) Transmittance spectra of IEV/ (DMF+IL) /PB device recorded under reduction potentials between -0.6 V to -2.0 V and under oxidation potentials of +0.5 V to +1.0 V.

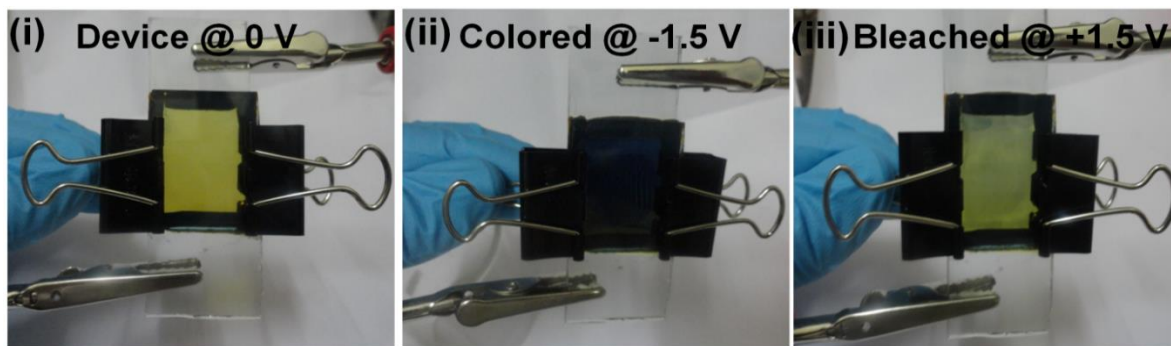


Figure 3.3.2(b) Digital photographs of electrochromic device in (i) as fabricated device (ii) fully colored (deep violet) state (at -1.5 V) and (iii) fully bleached state (at +1.5 V).

3.3.3 Coloration Efficiency

When a series of voltages (from -0.5 to -2.0 V) are applied, the device gets colored; the values of injection charge were determined by chronoamperometry [15] and these values were used for plotting the optical density change *versus* the inserted charge per unit area (Q/A) shown in Fig.

3.3.3. The slope of this plot yields the coloration efficiency (CE) of the device at a monochromatic wavelength. Coloration efficiency at 605 nm was therefore calculated to be $533 \text{ cm}^2 \text{ C}^{-1}$ at around -2.0 V for the IEV/ (DMF+IL) /PB device.

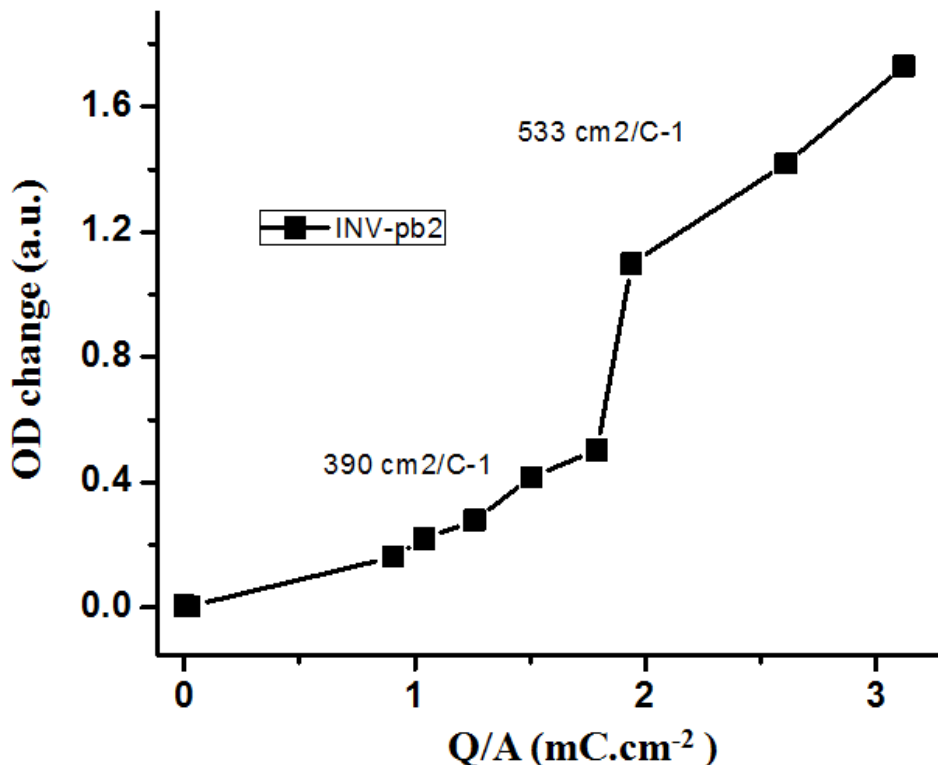


Figure 3.3.3 OD change *versus* intercalated charge per area (Q/A) plot at the monochromatic wavelength of 605 nm for the IEV/ (DMF+IL) / PB device within the voltage range between -0.5 V to -2.0 V .

3.3.4 Switching Kinetics

The color-bleach characteristic for the IEV/ (DMF+IL) / PB device was recorded at half-cycles corresponding to 3 s, 5 s and 10 s and by switching potentials of $\pm 1.5 \text{ V}$ (Fig. 3.3.4). The kinetic responses were recorded at the wavelength 605 nm at which maximum absorption occurs. Coloration time, defined as the time required for the device to acquire 90% of the total absorption change was observed to be 2.3 s, 3.7 s and 7.2 s for the step times of 3 s, 5 s and 10 s respectively. Bleaching time, defined as the time taken by the device to undergo a 90% decrease (of the complete absorption change) was 2.4, 3.4 and 7.4 s for the step times of 3, 5 and 10 s respectively.

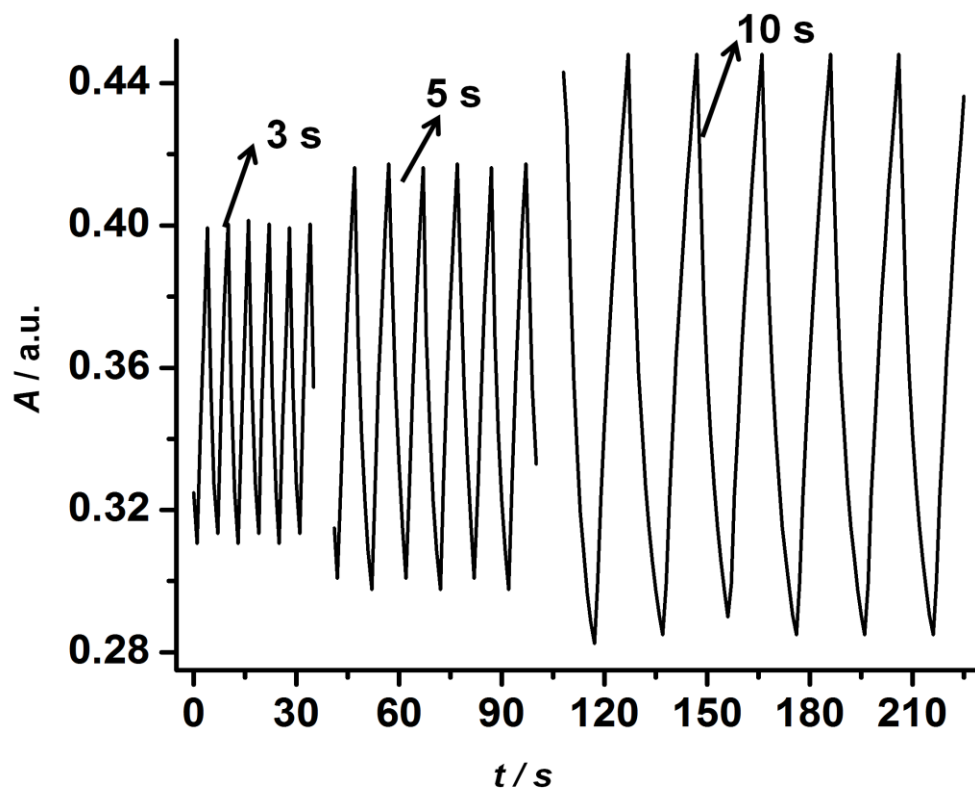


Figure 3.3.4 Normalized absorbance *versus* time curves for the IEV/ (DMF+IL) / PB device at the monochromatic wavelength of 605 nm, under a square wave dc potentials of ± 1.5 V, for the step times of 3, 5 and 10 s respectively.

3.3.5 Stability Studies for the IEV/ (DMF+IL) / PB device

The capability of the IEV/ (DMF+IL) / PB device to resist deterioration upon repeated cycling between the transparent and blue states was examined by cyclic voltammetry and multi-step chronoamperometry. The device was subjected to continuous cycling at a scan rate of 100 mV/s, between +0.2 V to +1.0 V and the CV plots for the 1st, 1000th and 2000th cycles are displayed in Fig. 3.3.5(a). The shift of cathodic peak current is negligible, indicating that the IEV-(ClO₄)₂ salt based device can endure repetitive reversible color change between transparent and deep violet color without undergoing degradation.

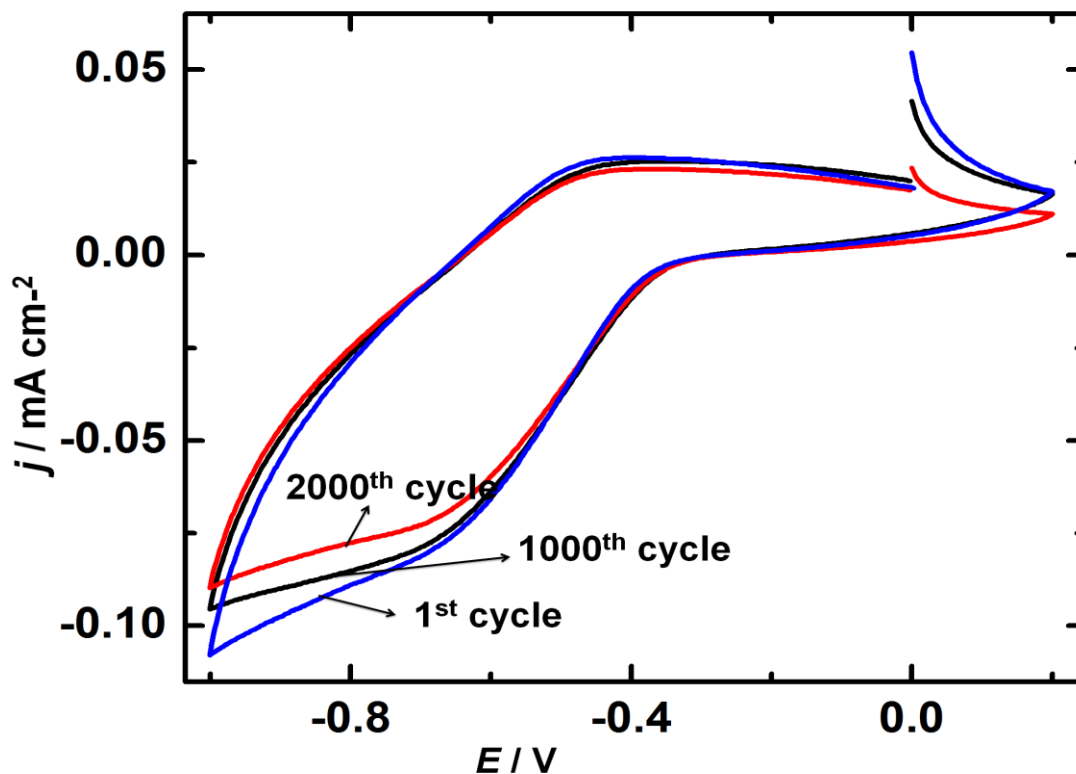


Figure 3.3.5(a) Cyclic voltammograms for the IEV/ (DMF+IL) /PB device within the potential range of +0.2 V to -1.0 V at a scan rate of 10 mV/s for 1st, 1000th and 2000th cycles.

To re-affirm the cycling stability of the device, color-bleach kinetics measured with a step time of 5 s under an applied potential of ± 1.5 V for 2000 times in absorbance mode at λ_{max} of 605 nm [Fig. 3.3.5(b)]. The absorbance change (ΔA) offered by the device in the 1st cycle is 0.92 and after 2000 cycles, (ΔA is 0.76). The device shows high stability up to 2000 cycles since 82.6% of the original optical density change is retained.

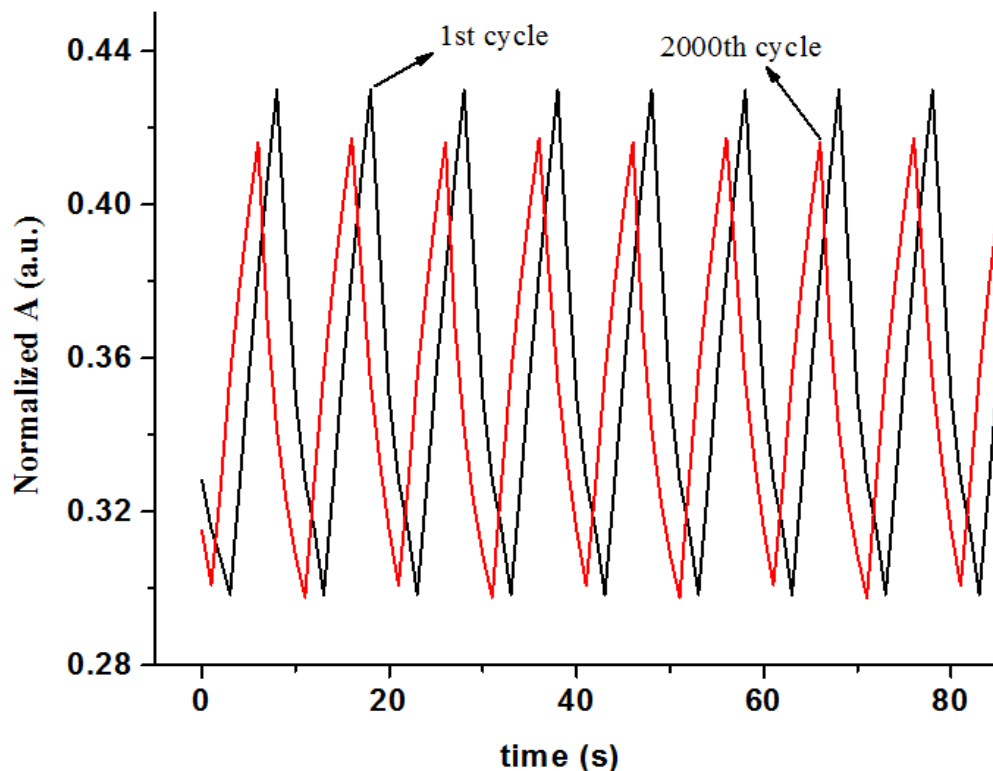


Figure 3.3.5(b) Color-bleach plots of (i) 1st cycle and (ii) 2000th cycle for the IEV/ (DMF+IL) /PB device with a step time 5 s under the applied potential of ± 1.5 V (at 605 nm).

4. Conclusions:

A novel 1,1'-bis-[2-(1H-indole-3-yl)-ethyl]-4,4'-bipyridinium diperchlorate (viologen) (IEV) was synthesized and characterized. The viologen was incorporated in an electrochromic device, by dissolving it in a liquid electrolyte of [N,N-Dimethylformamide (DMF) + 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)-imide (IL)] having good ionic conductivity, good thermal stability (up to 150^oC) and wide electrochemical potential stability range (of ~ 4 V) and moderately high optical transparency in the visible region. The device exhibited reversible switching between colorless and deep violet states with high transmission modulation of 58% at 605 nm. The device showed an outstanding coloration efficiency of 533 cm².C⁻¹ and rapid response time of ~ 2 s. The high electrochemical activity of IEV-(ClO₄)₂ salt (viologen) was retained even after 2000 repeated switches between the transparent and colored states. The excellent performances this new viologen opens up avenues to develop various indole based derivatives of 4,4'- bipyridyl, for applications in both transmissive and reflective ECDs.

References:

- [1] P.M.S. Monk, R.J. Mortimer, D.R. Rosseinsky, *Electrochromism and Electrochromic Devices*, Cambridge University Press, Cambridge, UK, 2007.
- [2] D.R. Rosseinsky, R.J. Mortimer, *Adv. Mater.* 13 (2001) 783.
- [3] T. -H. Kuo, C.-Y. Hsu, K. -M. Lee, K. -C. Ho, *Solar Energy Mater. Solar Cells* 93 (2009) 1755.
- [4] R. Cinnsealach, G. Boschloo, S.N. Rao, D. Fitzmaurice, *Solar Energy Mater. Solar Cells* 55 (1998) 215.
- [5] R.J. Mortimer, *Chem. Soc. Rev.* 26 (1997) 147.
- [6] P.M.S. Monk, *The Viologens: Physicochemical Properties, Synthesis and Applications of the Salts of 4,4'-Bipyridine*, J. Wiley & Sons: Chichester, U.K., 1998.
- [7] R.J. Mortimer, *Electrochim. Acta* 44 (1999) 2971.
- [8] H.J. Kim, J.K. Seo, Y.J. Kim, H.K. Jeong, G.I. Lim, Y.S. Choi, W.I. Lee, *Solar Energy Mater. Solar Cells* 93 (2009) 2108.
- [9] G. Wang, X. Fu, J. Huang, C. Wu, L. Wu, Q. Du, *Org. Elec.* 12 (2011) 1216.
- [10] R.J. Mortimer, T.S. Varley, *Chem. Mater.* 23 (2011) 4077.
- [11] S.Y. Choi, M. Mamak, N. Coombs, N. Chopra, G. A. Ozin, *Nano Lett.* 4 (2004) 1231.
- [12] V. Jain, M. Khiterer, R. Montazami, H.M. Yochum, K.J. Shea, J.R. Heflin, *Appl. Mater. Interfaces* 1 (2009) 83.
- [13] C.W. Hu, K. M. Lee, K. C. Chen, L. C. Chang, K. Y. Shen, S. C. Lai, T. H. Kuo, C. Y. Hsu, L. M. Huang, R. Vittal, K. C. Ho, *Solar Energy Materials & Solar Cells* 99 (2012) 135.
- [14] Y. Rong, S. Kim, F. Su, D. Myers, M. Taya, *Electrochim. Acta* 56 (2011) 6230.
- [15] Rambabu Sydam, Melepurath Deepa, Amish G. Joshi, *Org. Elec.* 14 (2013) 1027-1036.
- [16] J.C. Evans, C.C. Rowlands, C.R. Morris, *J. Chem. Soc. Perkin Trans. II* 9 (1987) 1375.
- [17] P.R. Somani, S. Radhakrishnan, *Mater. Chem. Phys.* 77 (2002) 117.