

# Understanding perceived color through gradual spectroscopic variations in electrochromism

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**Abstract:** A bias-dependent in situ Raman scattering and UV–Vis absorption spectroscopic change has been correlated with the corresponding color change of an electrochromic device in an attempt to explain how to understand the relationship between actual perceived color and its absorption/transmittance spectra. For this, the bias across an electrochromic device was increased gradually, rather than abruptly turning ON and OFF, to see subtle variations in Raman and absorption spectra due to bias. Raman scattering establishes that viologen changes its oxidation state reversibly between two redox species ( $EV^{2+}$  to  $EV^{+\bullet}$ ) as a result of bias-induced dynamic redox process. A gradual variation in Raman and absorption spectra, which shows maximum absorption corresponding to the yellow light, accompanies similar variation in color change of the device as visible by naked eye. These spectroscopic results are correlated with the perceived blue color, in the reflected light, by the eye to understand the actual reason behind this. Maximum absorption of yellow light by the device resulting in blue appearance has been explained using the concept of additive and subtractive primary colors.

**Keywords:** Viologen; Raman spectroscopy; Electrochromism; UV–Vis

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## 1. Introduction

Color is a qualitative term assigned for a wavelength (or frequency) when perceived by eye, which is nothing but an optical device. It is a fascinating term that sounds trivial but is not so easy to understand due to complications introduced by concepts of primary–secondary colors (different in additive and subtractive modes). This further gets complicated if one wants to correlate the color appearance with its corresponding spectroscopic manifestations. It has been attempted here to fill the gap between the color perceived and corresponding spectral observations through an example of electrochromic device. Various materials, organic and inorganic, change color on application of electrical bias mainly due to change in their oxidation state

and are known as electrochromic (EC) materials [1–8]. Members of inorganic electrochromic materials include different oxides of metals (i.e., tungsten, vanadium) showing multiple oxidation states [9–14]. On the other hand, the organic electrochromic counterparts [15–19] include various conjugated polymers and bipyridine’s derivatives and are very suitable for “all-organic” electrochromic devices (ECDs). The bias-induced color switching of electrochromic materials originates from the fact that absorption/transmittance properties vary with the oxidation state of the molecular species present in the material. Ethyl viologen, one of the widely used electrochromic materials, in the  $EV^{2+}$  state is colorless, whereas its radical cationic form ( $EV^{+\bullet}$ ) appears blue due to different absorbance in visible spectrum.

Search of various electrochromic materials and various fabrication paradigms, in terms of composition and design of device, is going on, and there are several ECDs available that can be used according to one’s requirement. Apart from the technology part, the science and explanation of

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the perceived color are not very clearly mentioned in the literature. Thus, it needs a vivid way of understanding along with a generalized approach, adopting which one can understand the perceived color from an electrochromic material in particular and from any material in general. Various spectroscopic techniques including UV–Vis [20–23], Raman scattering [24–28], FTIR [29, 30] and XPS [31] are very handy in identifying the origin of such bias-induced color switching. Usually, spectroscopic techniques are capable of identifying the species present (and their oxidation state) and correlating them with the absorption properties while explaining the color switching. The available literature usually deals with such materials by considering them to be in either of the color states as if they are binary counterparts and investigates electrochromic materials in their corresponding ON and OFF (say) states exclusively. However, the concepts about color switching will be complete if one can understand the transient behavior of material while changing its state from one to the other oxidation state. This can be done by spectroscopically investigating subtle changes by gradually changing the bias to see whether the color transition is gradual or abrupt.

In this paper, a careful explanation of the origin of perceived color as a result of bias-induced color switching, taking place in viologen-based electrochromic device, has been provided using bias-induced in situ Raman scattering and UV–Vis spectroscopy. The in situ Raman spectra recorded from a simple ECD at very close intervals of voltages reveal transformation of one type of chemical species, responsible for transparent behavior of device in OFF state, into the other type of species which are responsible for the colored state. Raman scattering also reveals that the color switching is reversible and so is the oxidation state which returns back to the transparent state on removal of the bias. In other words, the reversible color change is accompanied by the reversal of corresponding chemical species. Bias-dependent absorbance spectroscopy has been employed to analyze the blue color that is perceived to the eyes when the device is in the ON state. An absorption maximum at  $\sim 590$  nm has been analyzed in the framework of additive as well as complementary primary color schemes to understand the blue appearance of the ON device.

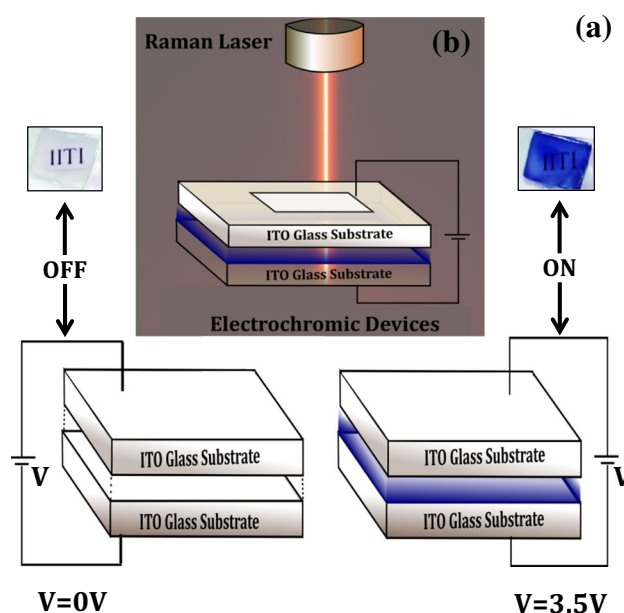
## 2. Experimental details

All the chemicals used for the device fabrication were purchased commercially and used as-received which includes ethyl viologen dication (98%, Sigma-Aldrich), polyethylene oxide (PEO, Alfa Aesar) and acetonitrile (ACN, anhydrous, 99.8%, Sigma-Aldrich). The

active layer in the ECD was used by preparing an electrochromic gel using 4 wt% ethyl viologen dication [EV(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>] and 5 wt% polyethylene oxide (PEO) dissolved in acetonitrile. Prepared solution was filtered using 0.45- $\mu$ m PTFE filter (Axiva<sup>TM</sup>). The film of electrochromic gel has been obtained on an ITO-coated conducting transparent electrode using spin coating (1200 rpm up to 2 min). After spin coating, second ITO electrode was laminated on spin-coated substrate face to face. The extreme part of both the electrodes is connected with copper tape to make connections with external power supply. All the optical absorption measurements were taken using Cary-60 UV–Vis spectrophotometer (Agilent). In situ Raman spectroscopy was carried out using LAB-RAM-HR spectrometer (Horiba-JY) using a 633 nm excitation wavelength.

## 3. Results and discussion

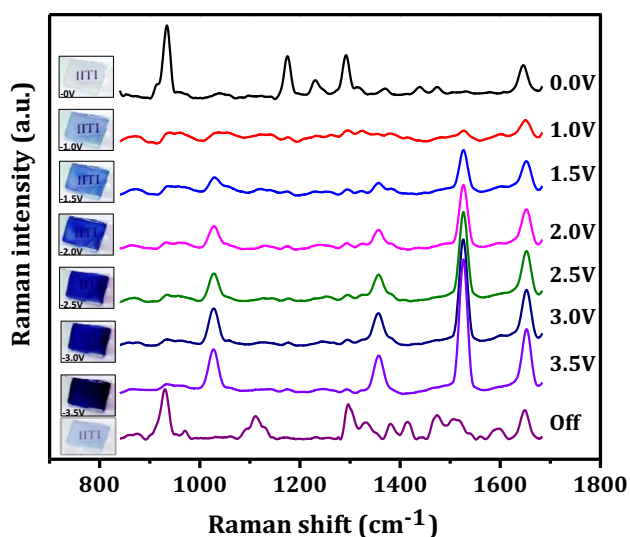
Figure 1a shows the schematic of the simplest electrochromic device, in crossbar geometry, which has been used in the present study. As mentioned above, the device has been fabricated by simply sandwiching the electrochromic layer (EV + PEO) in between two transparent conducting ITO electrodes. It is important here to mention that the device shown here has been fabricated for spectroscopic studies to understand the origin of perceived



**Fig. 1** (a) Schematic of electrochromic device in the simplest geometry, showing bias polarity arrangement, along with actual photograph of the device in OFF and ON states. (b) Schematic to show arrangement in which Raman scattering experiments have been carried out

color and is not complete from performance point of view. A complete device will need at least a layer consisting of counterions to support the redox process in electrochromic active layer. The schematic also shows that the active layer changes color on application of bias. Bias polarity will have little effect on color change as the device shown here is symmetric in nature. The corresponding actual photographs (Fig. 1a) of the device are also showing color switching from transparent to blue color. The photographs of the device have been taken which is kept on a white paper on which the text “IITI” is written. It is very important to realize that the blue color is perceived when a white light enters the device, passes through the electrochromic layer, and reflects back from the white paper and reaches the eye.

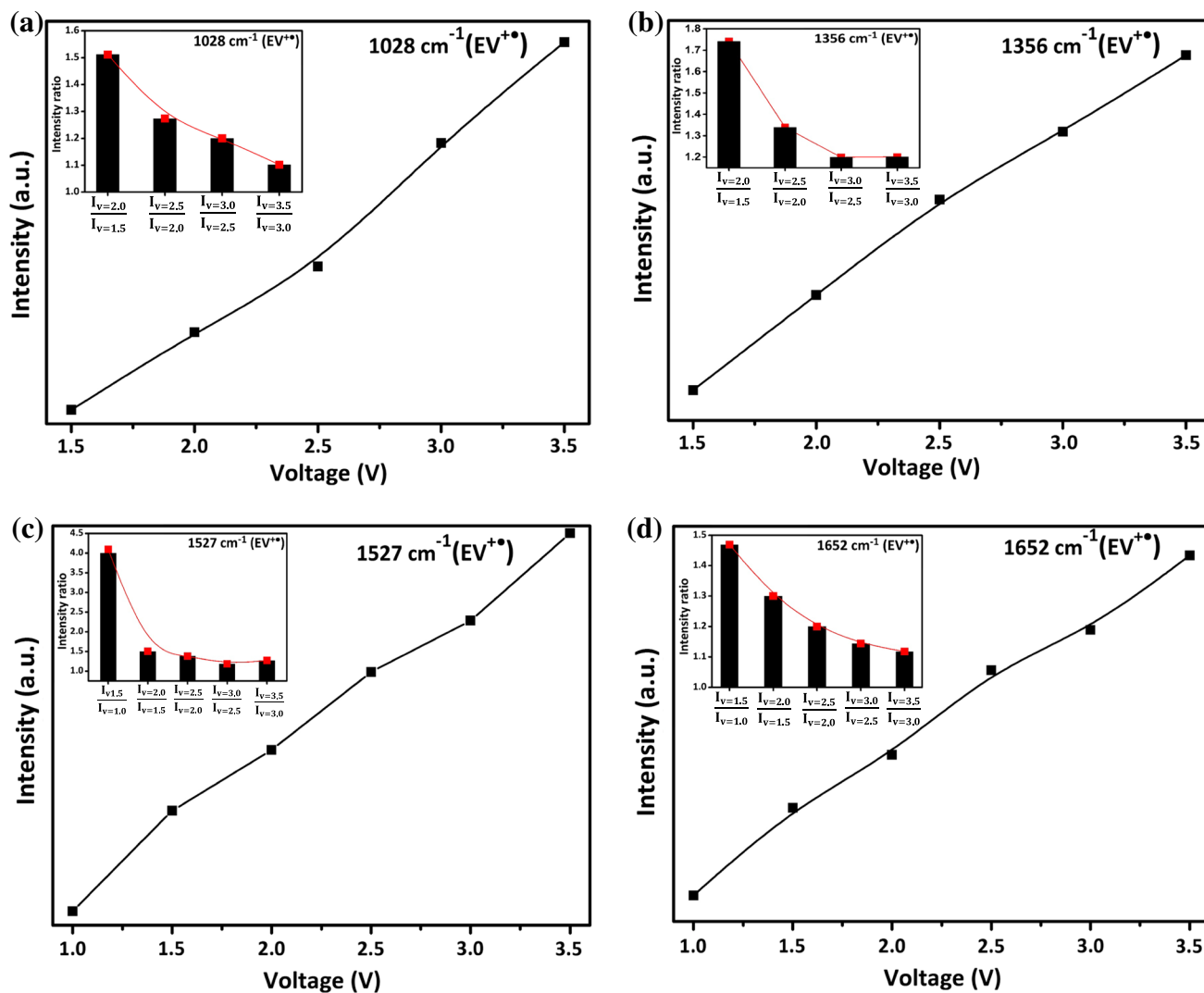
This will be discussed in detail later on. It is understood that the viologen in its  $EV^{2+}$  and  $EV^{\bullet+}$  states is responsible for transparent and colored (blue) states, respectively, as identified using Raman scattering in combination with transmission spectra [25, 26, 28, 32, 33]. Figure 1b depicts the geometry in which Raman scattering measurements have been taken. Though not discussed much and not reported properly in the literature, practically the bias-induced color change in a viologen-based ECD is not abrupt, but rather is gradual. A transmittance measurement can tell the basic properties of the material but may not correlate directly to the color perceived to the eye and thus needs explanation so that the color change can be understood as per the intuition. This has been carried out through gradual bias-dependent Raman spectroscopic study and its correlation with absorption spectrum and color change.



**Fig. 2** Absolute bias-dependent in situ Raman spectra from the electrochromic device along with the corresponding actual photographs of the device

Bias-dependent in situ Raman spectra from a prototype ECD, designed for the present study, are shown in Fig. 2 along with the corresponding actual photographs of the device. It is evident from Fig. 2 that some Raman peaks disappear as a result of bias and simultaneously some new peaks appear which is clear indication of bias-induced change in chemical structure of material present in the device which can be understood as follows. Viologen is known to be present in three different oxidation states ( $EV^{2+}$ ,  $EV^{\bullet+}$  and  $EV^0$ ), and they exhibit their typical Raman signature [25] as summarized in Table S1 in the supporting information (SI). These peaks in the Raman spectra correspond to different vibrational modes (Table S2 in the SI). It is clear from Raman spectra recorded with 1 V bias (Fig. 2) that minute peaks at  $1527\text{ cm}^{-1}$  appear which is accompanied by the disappearance of several peaks, present when recorded from the OFF device. The tiny peak at  $1527\text{ cm}^{-1}$ , observed for  $EV^{\bullet+}$  state (Table S2), means that formation of  $EV^{\bullet+}$  has initiated after application of 1 V bias. Though the device is still transparent, a slight bluish tint is apparent in the actual photograph (Fig. 2). This peak becomes more and more prominent on increasing the bias voltage from 1 to 3.5 V. Since the Raman peak intensity directly corresponds to the density of species available for that mode, increasing peak intensity means the presence of more number of  $EV^{\bullet+}$  molecule under higher bias. Furthermore, on increasing bias beyond 1.5 V, couple of more Raman modes starts appearing in the Raman spectra (Fig. 2) at  $1028\text{ cm}^{-1}$  and  $1356\text{ cm}^{-1}$  which arise due to  $EV^{\bullet+}$  [25]. Similar to the  $1527\text{ cm}^{-1}$  Raman mode, intensity of these two peaks also increases with the increase in voltage. Since the  $1028\text{ cm}^{-1}$  and  $1356\text{ cm}^{-1}$  modes also belong to the  $EV^{\bullet+}$  form of viologen, an increased density of reduced viologen species ( $EV^{\bullet+}$ ) is confirmed as discussed above. The bias-induced gradual conversion of  $EV^{2+}$  to  $EV^{\bullet+}$  is accompanied by gradual color change from transparent (0 V) to opaque dark blue (3.5 V) through sky blue (1.5 V).

In addition to the above-mentioned peak appearing and disappearing, frequency of one of the Raman modes changes on application of bias. A Raman peak visible at  $1643\text{ cm}^{-1}$ , when the device is in OFF state, shifts to  $1654\text{ cm}^{-1}$  under application of bias (1.5 V to 3.5 V). This can be understood as follows. The Raman peaks at  $1028\text{ cm}^{-1}$  and  $1654\text{ cm}^{-1}$  (both present in the device when biased) are the vibrational modes of the restructured molecule after the reduction in viologen which leads to the formation of  $EV^{\bullet+}$ . The appearance of the  $1028\text{ cm}^{-1}$  peak, which corresponds to the ring breathing mode, in ON state, indicates that the addition of one electron to the LUMO results in a weakening of the C–C ring [27]. Considerable electron density addition to the viologen molecule leads a significant upshift of the frequency. The



**Fig. 3** Bias-dependent increase in intensity of various Raman modes corresponding to  $EV^{+\bullet}$  along with relative intensities as a function of bias (insets)

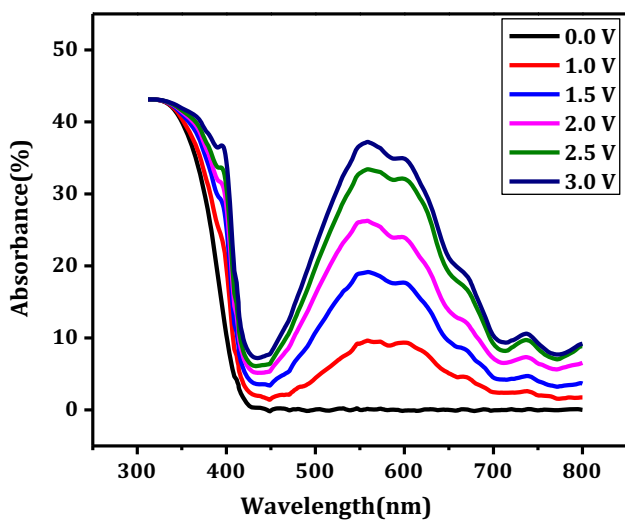
strong band at  $1643\text{ cm}^{-1}$  reflects C–C inner-ring vibrations. The upshift of the resonance-enhanced mode at  $1654\text{ cm}^{-1}$  for ON state, as compared to  $1643\text{ cm}^{-1}$  for OFF state, reflects the dominant contributions of the C–C ring vibrations and minor contributions of the inter-ring C–C [34].

The above-mentioned bias dependence of Raman spectral features and color switching is reversible on removing the bias while turning the device OFF. On removal of bias from the ON device, Raman modes at  $1025\text{ cm}^{-1}$ ,  $1356\text{ cm}^{-1}$  and  $1527\text{ cm}^{-1}$  disappear meaning absence of  $EV^{+\bullet}$  in the OFF device. In addition, as a signature of  $EV^{2+}$ , Raman modes at  $932\text{ cm}^{-1}$  and  $1296\text{ cm}^{-1}$  get reinstalled when device is turned OFF as evident from Fig. 2 (bottom-most spectrum). Furthermore, the  $1654\text{ cm}^{-1}$  peak (present in ON device) shifts a bit toward  $1643\text{ cm}^{-1}$ . When the device is in ON state, the density of

$EV^{+\bullet}$  ions in the device is increasing with increasing the bias voltage. This can be seen quantitatively from Fig. 3 which shows increase in Raman peak intensity with increasing the voltage corresponding to Raman modes of  $1028\text{ cm}^{-1}$ ,  $1356\text{ cm}^{-1}$ ,  $1527\text{ cm}^{-1}$  and  $1652\text{ cm}^{-1}$ , respectively, in Fig. 3(a)–(d). More ions generated, as evident from Fig. 3, result in decreasing transparency of the device (Fig. 2). Inset in Fig. 3(a) shows the change in relative intensity of  $1028\text{ cm}^{-1}$  Raman mode at a given bias with respect to a smaller bias voltage. An asymptotic behavior (insets) can be seen indicating almost conversion of species from  $EV^{2+}$  to  $EV^{+\bullet}$  at higher voltages. Similar variation corresponding to other  $EV^{+\bullet}$  Raman modes can be seen in insets in Fig. 3(b)–(d). The presence of more numbers of ions in the device at higher voltages (ON) is giving the opaque nature of the device.

From the above discussion in the context of Fig. 3, it is established that the colored (opaque) state of the device is obtained by bias-induced dynamic reduction in  $EV^{2+}$ , which is present in transparent virgin device, resulting in  $EV^{+\bullet}$ -rich device reversibly. It has been reported that  $EV^{2+}$  and  $EV^{+\bullet}$  have different optical properties (absorption/transmission); hence, it gives different appearances. A neat experiment must be designed to correlate the perceived color of the device and its optical properties. It is important here to understand that an ECD is not emitting light on its own; thus, the appearance of the device will depend on the optical source in which it is being observed and the arrangement of light source, device and observer. If the observer and source are in the same direction of the device, then the light that comes after reflection from the device (top and/or bottom surface) decides the appearance. On the other hand, if the light source and observer are on the opposite sides of the device, perceived color can be explained by looking at the transmittance spectrum. Images shown in Fig. 2 have been recorded in the situation as in the first case discussed above, and thus, transmittance spectrum will not be conclusive and may lead to confusion while understanding the observed color.

In situ absorbance spectra from the electrochromic device have been recorded (Fig. 4) under different bias voltages with the gradual increase from 0 to 3.5 V. The absorption spectrum corresponding to the OFF device (0 V) has been used as the base line so that absorbance with respect to the OFF state can be seen to understand the effect of bias on the absorbance of the device in ON state. The unprocessed spectrum for OFF device is shown in Figure S1 in the SI. Figure 4 clearly shows an increase in



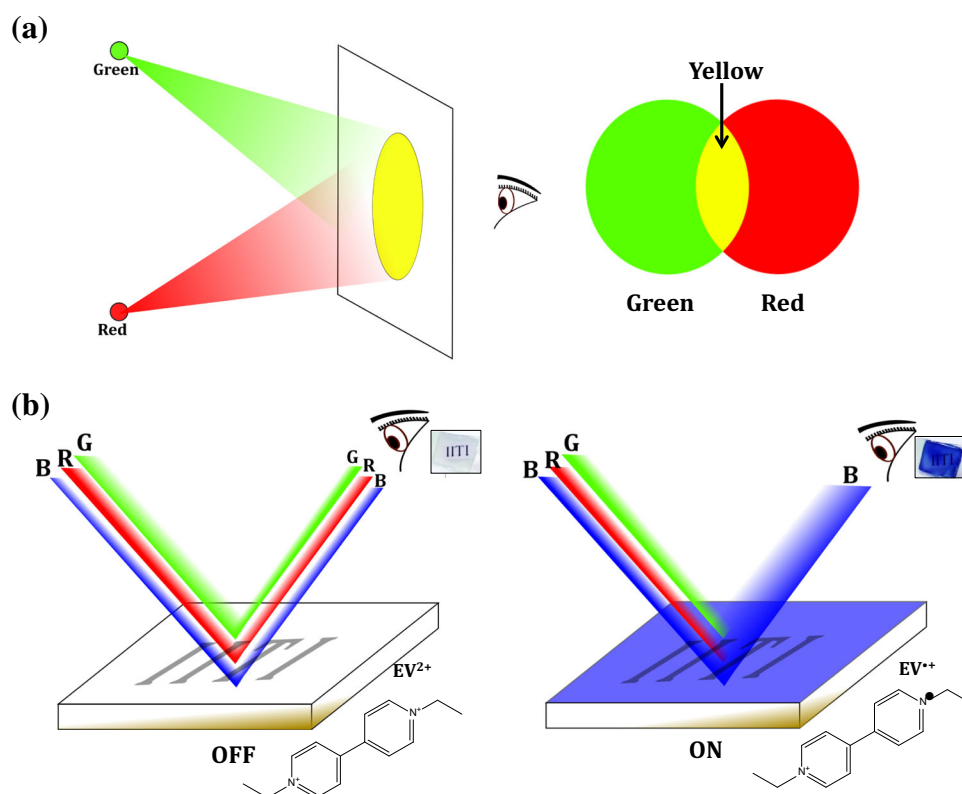
**Fig. 4** In situ bias-dependent absorbance spectra from electrochromic device. The spectra have been presented relative to the spectrum corresponding to the OFF device (transparent state)

the absorbance of 590 nm wavelength (yellowish). It is also evident that the absorbance increases with increasing the bias voltage without changing the peak position ( $\lambda_{max}$ ). An unchanged peak position with respect to bias means that the species present in the device, which is  $EV^{+\bullet}$  as evident established using Raman spectroscopy (Fig. 2), is not changing. Secondly, an increase in maximum absorbance value with voltage means that the concentration of  $EV^{2+}$ , which is responsible for the blue color, is increasing. Both of these observations are consistent with the Raman results as shown in Fig. 2. Figure 3 draws the constraints under which the origin of blue color of ON device needs to be understood and explained. It is not very straightforward to say that an absorption of yellow color ( $\sim 590$  nm) means the appearance of blue color ( $\sim 400$  nm) to the eye and hence needs proper explanation especially by considering the situations under which the observations have been made.

Before starting the explanation of blue color, it is important to reiterate the fact that the color perceived depends on the visible wavelength ( $s$ ) that reaches the eye by whatever means. It is the combination of the reaching wavelengths that decide the resultant color that is perceived. While correlating the absorbance spectra in Fig. 4 with the observed blue color, concept of additive primary colors (RGB or red–green–blue) and subtractive primary colors (CMY or cyan–magenta–yellow) will be used. Yellow, the color which is being absorbed by the ON device (Fig. 4), is the combination of primary additive wavelengths corresponding to red and green colors as depicted schematically in Fig. 5a. Since the device is kept on an “IITI” printed white paper, the subtractive color scheme needs to be considered. This situation is analogous to a color printer where the combination of primary colors CMY is used to get the desired ink color when printed. The electrochromic layer, consisting of  $EV^{2+}$ , absorbs red and green colors of the visible light (in which the device is being observed) while penetrating through ECD and reflecting back from the white paper. After red–green getting absorbed, only blue color remains and reaches the eye to be perceived as blue which is the case. This is depicted schematically in Fig. 5b. The colors perceived for intermediate voltages (1 V to 3 V) are obtained when the extent of red–green colors is absorbed only in smaller proportions due to a lesser number of absorbing species,  $EV^{+\bullet}$  present in the device under an insufficient bias. With the increase in bias, increasing  $EV^{+\bullet}$  concentration enables the electrochromic layer to absorb red–green component up to more extent, thus resulting in more pure blue component (Fig. 5b). In contrast, no color change will be observable if the device is kept on a non-reflecting surface like black paper.



**Fig. 5** (a) Schematic to show that yellow color is composed of green and blue colors and (b) origin of perceived blue color from an ON device when seen under white light illumination



#### 4. Conclusions

In summary, bias-dependent in situ Raman scattering and UV–Vis absorption spectroscopic investigation is found to be helpful in better understanding of the perceived color induced by application of voltage in an electrochromic device. On gradually increasing the voltage (in steps of half a volt), Raman modes change in terms of appearance of some modes at the cost of some other modes due to change of species in the electrochromic active layer. The viologen changes its oxidation state reversibly from  $EV^{2+}$  to  $EV^{+\bullet}$  as a result of bias-induced dynamic reduction in viologen. A gradual increase in the Raman intensity of corresponding  $EV^{+\bullet}$  modes is observed which reveals that concentration of  $EV^{+\bullet}$  increases gradually as device starts turning ON. After removing the bias, the redox process reverses itself to reinstall the  $EV^{2+}$  state back. The redox-induced gradual increase in  $EV^{+\bullet}$  concentration is followed by a gradual increase in the absorbance corresponding to  $\sim 590$  nm wavelength which means that yellow color is absorbed more as compared to the other wavelengths of the visible spectrum. Maximum absorption corresponding to yellow wavelength, a combination of red and green, means the availability of blue color to be perceived by the eye when the device is in ON state.

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