Ink-jet Printing for the Fabrication of a Flexible Electrochromic Device Based on the Water-Soluble Viologen-Functionalized Dendrimer

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ABSTRACT

This paper reports the preparation of an ink-jet printed flexible electrochromic device based on a water-soluble viologen-functionalized dendrimer. Polyamidoamine (PAMAM) dendrimers were modified with different concentrations of 1-1 bis(propylamine)-4,4'-bipyridylium dibromides to obtain solution-processable electrochromic materials ($K_{1/2}$ and K_1). FTIR, NMR, and elemental analyses are used to characterize synthesized viologens. Moreover, their electrochemical properties were investigated using cyclic voltammetry in an electrolyte solution consisting of 0.1 M HCl to find the optimum viologens. The low-cost ink-jet printer was used to print the prepared water-soluble electrochromic inks onto the ITO coated PET substrate to form desired transparent patterns. The electrolyte was applied on the printed electrochromic ink to make a sandwich with another ITO coated PET to prepare the electrochromic devices (ECD). By applying an electrical potential (0 to -2 V), the transparent ECD's color changed from colorless to blue. The color changes for the optimum ECD (K_1), which had more viologen units on the dendrimer, was accompanied by an optical contrast of 47% and $311.5 \text{ cm}^2 \text{ C}^{-1}$ coloration efficiency at 600 nm.

Keywords : Viologen, Electrochemistry, Ink-jet printing, Flexible polymers, Dendrimers

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1. Introduction

Electrochromism is a phenomenon in which the material's optical properties such as reflectance, transmittance, and absorbance are changed reversibly by applying a burst of charge. This phenomenon is associated with an electrochemically induced oxidation-reduction reaction in an electrochromic (EC) material [1,2]. The main classes of EC materials are the transition metal oxides, Prussian blue, metal coordination complexes, viologens, fullerenes dyes, and conducting polymers. A fabricated thin film of such EC materials was incorporated as a component of the EC device. Standard EC devices combine distinct

layers between two transparent substrates (glass or PET). These different layers consist of optically transparent conductive oxide layers, typically indium-tin-oxide (ITO) as the electrodes coated on glass or PET substrate on either side of the device. The electrochromic (redox-active) material was printed on one of the conductive electrode substrates. A transparent conductive electrolyte (a pure ion conductor) in which an electron transfer occurs is characteristically located in the middle of the EC device, adjoining electrochromic material film, and conductive electrodes on the transparent conductive oxide coated glass or PET (Fig. 1). The device is typically sealed with the epoxy polymer and other sealants to avoid any leakage of electrolyte from the device.

In this study, the EC materials were synthesized based on the 4,4'-bipyridinium, known as viologen. Advantages such as derivation with a short switching time, high stability, low-cost, and good applicability

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Fig. 1. Layers together in the electrochromic device (ECD).

make these materials greatly desired [3,4]. There are three types of EC materials; types I, II, and III. The materials can be designed appropriately, such as to have different solubility levels, electrochemical properties, and a variety of colors. Type I viologen materials are soluble in their redox state. Type II viologen materials are soluble typically in their colorless state and produce a solid-colored film at the electrode surface after the electron transfer. Type III viologen materials are solid in all redox states during usage. Researchers have developed various viologen-functionalized materials [5-7] such as viologen-modified nano-crystals [8-12], viologen nano-composite [13], polymers containing viologen [14,15], dialkyl and diaryl viologens [3,12,16-24], viologen-functionalized hyper-branched and viologen-functionalized dendrimer [16,25-28], which have different solubility and EC device efficiency.

The efficiency of an EC device using aqueous viologen materials such as methyl viologens (type I) would be low since both the di-cationic and radical-cation states are very soluble [2,29]. Alternatively, neither small-molecule viologens nor the linear polymeric viologen derivatives are appropriate for fabricating an EC film, due to the high crystallinity of small-molecule viologens that produce opaque films and low solubility within linear polymeric viologen derivatives in most solvents, in particular, water [30]. It is necessary to design a viologen derivative to overcome such disadvantages for the application in flexible EC devices.

Previous studies [13,14,16,25-28,31,32] have proven that using the bulky substituents instead of flat molecules in 4,4'-bipyridyl was a more efficient method to synthesize water-soluble EC materials

without the crystallinity issues [4,33-35]. Therefore, in this study, the macromolecule PAMAM dendrimers [36,37] were selected to prepare novel water-soluble EC functional materials by attaching a viologen chromophore to end groups of polyamidoamine dendrimer branches. The main reasons for choosing these dendrimers are their relatively well-defined nanometer-scale sizes, good water-solubility, and the ability to be functionalized. Viologen-functionalized dendrimer materials consist of soluble dicationic species and soluble radical, cationic species.

EC materials are typically fabricated onto a substrate via a number of methods such as vacuum evaporation [38], sputtering [39], dipping or spray deposition [40], electrodeposition [41], electrochemical oxidation, chemical vapor deposition (CVD) [42], spin coating [43], screen printing, and ink-jet printing [43,44]. Research into the fabrication of various viologen-functionalized materials has focused overwhelmingly on high-temperature, vacuumed, and other conventional processes. In contrast, considerably less attention has centered on the printing processes. In this line of research, we look into the ink-jet printing technique as a non-contact printing method to deposit a variety of materials as droplets directly onto the substrate. For this purpose, a viologen-functionalized dendrimer was used as an ink-jet ink to print onto a flexible film with minimal wastage of materials. A computer program controls the print and allows accurate replication with the ability to change images quickly and inexpensively. These features are difficult to achieve by using other methods.

Due to health and environmental concerns, solvent-based inks have been replaced by water-based inks to develop inks with better performance, lower printing costs, and less damage to both operator and environment. In this study, an attempt was made to prepare a water-based EC ink that can be fabricated onto flexible substrates by an ink-jet printer. The flexibility of the substrate permits soft handling and reduces the occurrence of damage during transport. The substrate is also lightweight, can be rolled, and is relatively thin, which makes it suitable for incorporation into windows (construction), sunroofs (automobiles), and even curved glass surfaces (household wares). The present study was conducted to identify the application of ink-jet printing technology as a replacement for high-temperature processes and other conventional methods in the manufacture of

flexible EC devices. Smart water-based inks as an environmental bonus were printed on the flexible ITO-coated PET to make EC devices.

2. Experimental

2.1 Materials

In this study, 4,4'-bipyridine was provided by Alfa Aesar Company. 3-Bromo propylamine hydrobromide 98% was supplied by Sigma-Aldrich Company, and 2,4,6-trichloro-s-triazine (cyanuric chloride) was purchased from Merck Company, Germany. The preparation of ethylenediamine core poly-amidoamine dendrimer of (PAMAM G2) is described within reference [45]. DuPont Company, Germany, provided polymethyl methacrylate. Propylene carbonate and a binary mixture of ethylene poly(oxide) and propylene poly(oxide) (PEO-PPO) were purchased from Fluka Company, Germany. The polyethylene glycol 200, isopropyl alcohol, lithium perchlorate, tetrahydrofuran (THF), and all the other chemicals used during this work were chosen as they are laboratory grade, being received from Merck Company, UK. The Sigma-Aldrich Company, USA, provided the indium tin oxide (ITO) coated polyethylene terephthalate (PET) with a surface resistivity of $60 \text{ W}\cdot\text{sq}^{-1}$ and thickness of 127 nm.

2.2 Instrument and equipment

The prepared EC ink was ink-jet printed using an Epson Stylus Photo P50 printer. The pH, surface tension, and viscosity of the prepared water-based inks were characterized using 827 pH Metrohm meters (Herisau/Switzerland), Tensiometer K100MK2 (Hamburg, Germany), and Brookfield DVII (New Jersey, USA), respectively. The prepared ink was filtered through 0.45 and the $0.2\mu\text{m}$ Sartorius Minisart filter (Göttingen, Germany). Static contact angle (θ) and surface energy of the substrate were measured by a Kruss G40-type contact angle measuring system using distilled water as the probe liquid at temperature and humidity of 25°C and 30%, respectively. For this purpose, a small drop of distilled water (2-3 mL) was exposed to the surface of the substrates. The test was done in triplicate, and the average of the measurements was reported. An image analysis system (G2/G40) was used to calculate the contact angle values. Thin-layer chromatography (TLC) was performed using aluminum plates coated with silica gel

60 F254 (Merck) as a stationary phase and a mixture of isobutanol: n-propanol: ethyl acetate: water in the ratio 2:4:1:3 as the mobile phase. The developed plates were visualized under both short and long-wavelength ultraviolet light (254 nm, 365 nm). The Fourier transformed infrared spectroscopy (FTIR) spectrums of synthesized electrochromic dyes were recorded on Bruker (IFS-48) (Bruker Optik GmbH, Germany), in the range of 400 to 4000 cm^{-1} . The synthesized electrochromic dyes were characterized by proton nuclear magnetic resonance (^1H NMR) spectra, which were recorded on a Bruker-SY200-250 MHz spectrometer analyzer. The gel permeation chromatography (GPC) was performed on a Shimadzu 6-A with the column model Waters Ultrahydrogel 250, which was fitted by water as the mobile phase (flow rate $1 \text{ mL}\cdot\text{min}^{-1}$) and PEG as standard material to determine the molecular weight of previously synthesized PAMAM dendrimer. Elemental analyses for carbon, hydrogen, nitrogen, and sulfur were carried out at the Central Laboratory, Tehran University, on an Eager 300 for EA1112. In the cyclic voltammetry, a three-electrode method was adapted with platinum wire, glassy carbon (3 mm diameter), and Ag/AgCl as the counter, working, and reference electrodes, respectively. A cyclic voltammetry experiment was performed by cycling the potential of a working electrode and measuring the resulting current. In the preparation process for the CV experiment, a glassy carbon as a working electrode was polished with a $1 \mu\text{m}$ and $0.1 \mu\text{m}$ $\gamma\text{-Al}_2\text{O}_3$ polishing cloth for 5 minutes. Polishing was followed with 3 minutes of sonication in water to ethanol mixture (1:1). Background voltammograms were obtained in 0.1 M HCl saturated electrolyte by cycling the potential between 0 to -1.4 V . Absorbance measurements at I_{max} using UV Ikon 923 Double Beam UV/Visible spectrometer (Saint-Quentin-Yvelines, France) determined the electrochromic characterizations of novel ECDs that contain newly synthesized viologen-functionalized dendrimer.

2.3 Layer preparation by ink-jet printing

Epson Stylus Photo P50 ink-jet printer was used to print a solid square pattern by the water-based ink formulation containing 100 g/dm^3 synthesized viologen-functionalized dendrimers (K_1 or $K_{1/2}$), 50 g/dm^3 polyethylene glycol 200, and 300 g/dm^3 isopropyl alcohol. The inks were made up to 1 dm^3 with de-ion-

Fig. 2. The preparation scheme of 1-1-bis(propylamine)-4,4'-bipyridylium dibromide (v^{2+}).

ized water. Epson Stylus Photo P50 ink-jet printer operated using a piezoelectric squeeze mode print head that squirts ink droplets through a nozzle with a 65- μm opening. Printing was carried out at pH=6 using a buffer solution to prevent damage to the print-head and cartridge. The prepared inks were filtered by 0.45 μm and 0.2 μm filters to prevent the nozzles clogging. The ink-jet printing substrate was an ITO coated PET. The ITO coated PET was cleaned using an ultrasonic bath in de-ionized water, isopropyl alcohol, acetone, and methanol, respectively. The methanol is an effective solvent and provides a higher surface energy substrate. Finally, the cleaned ITO coated PET dried at 60°C for 2 hours before loading inside the printing system.

During the preparation of ink-jet printing of flexible ITO coated PET substrates, a new and cleaned cartridge was filled with filtered formulated ink. Subsequently, the filled cartridge was located inside the printer. The printed ITO coated PET dried at 130°C for 30 minutes.

2.4 Electrolyte preparation

Within electrolyte preparation, polymethyl methacrylate (PMMA) (0.36 g), lithium perchlorate LiClO_4 (0.33 g), a binary mixture of ethylene poly(oxide) and propylene poly(oxide) (PEO-PPO) (0.21 g), and propylene carbonate (PC) (1.75 g) were mixed with 4 mL of THF and followed by stirring for about 4 hours to obtain transparent uniform lightly viscous gel [46]. The prepared gel electrolyte was used as an ion conductor layer between the counter and working electrodes in the EC device.

3. Results and Discussion

3.1 Electrochromic dyes synthesis and characterization

3.1.1 Synthesis of 1-1-bis(propylamine)-4,4'-bipyridylium (v^{2+})

The 1-1-bis(propylamine)-4,4'-bipyridyl viologen derivative (Fig. 2) was synthesized via the reaction of 3-bromo propylamine hydrobromide with 4,4'-bipyri-

Fig. 3. a) ^1H NMR spectra of (v^{2+}), b) FT-IR spectra of (v^{2+}).

dine in an aqueous solvent. Thus, 3-bromo propylamine hydrobromide (0.2 mol, 43.78 g), and 4,4'-bipyridine (0.1 mol, 15.619 g) dissolved in 200 mL distilled water, and the pH of the solution adjusted to 5 via the addition of dilute hydrochloric acid. The reaction mixture was refluxed at 100°C for 2 hours to yield a pale yellow solution. During the reaction, the pH value of the solution was adjusted with Na_2CO_3 . The mixture stirred at pH 5 with control by TLC, and the resulting yellow product, 1-1-bis(propylamino)-4,4'-bipyridyl viologen derivative, was precipitated from the solution via the addition of acetone. The powder was dried at 40°C in a vacuum oven overnight, Yield: 44.5 g (75% yield). The product was homogeneous as judged by TLC, ^1H NMR (250 MHz; D_2O , ppm): 2.5 (E), 3.1 (D), 4.8 (F), 8.5 (B), and 9.1 (A) (Fig. 3a).

FT-IR (KBr , $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$): 3697 (-OH water), 3065 (-CH aromatic), 2987 (-CH aliphatic), 1643 (-NH), 1562 ($\text{C}=\text{C}$ aromatic resonance), 1474 (-CH ali-

phatic), and 1279 (aromatic amine) (Fig. 3b)

Regularly, the product is an isolate containing an impurity. Mole In (MI) represents the weight in grams of the synthesized material, in question within 1 mol of "pure" synthesized material. The MI and purity were determined by elemental analysis. Calc. for $C_{16}H_{24}N_4$: C, 70.56%; N, 20.59%. Found: C, 55.8%; N, 16.6%, corresponded to purity 79.5%, MI=342.

3.1.2 Synthesis of PAMAM- triazine

In the first step, the purity and MI of the PAMAM

dendrimer have been calculated using gel permeation chromatography (GPC): Calc for $C_{142}H_{288}N_{58}O_{28}$ =3256, Found MI:3565 that corresponded to purity (91%).

Surface-primary amino groups of PAMAM G2 dendrimer was used as nucleophile agents to react with different molar ratios of 2,4,6-trichloro-s-triazine (1:8 and 1:16 of PAMAM G2 to 2,4,6-trichloro-s-triazine). A suspension of freshly 2,4,6-trichloro-s-triazine, which cooled in an ice bath added drop-wise into a solution of PAMAM dendrimer at 0°C and pH~5-6. It was possible to substi-

Fig. 4. The second and third steps of synthesis of viologen-functionalized dendrimer.

tute a first triazine chlorine atom with the surface primary amino functions that are conducting to PAMAM-triazine derivatives (Fig. 4). Reaction progress was followed by the release of hydrochloric acid and the reduction of pH, which was controlled by adding Na_2CO_3 . The mixture was stirred at pH~5-6 with control via TLC. Finally, the dendrimer surface was modified using alternative ratios of 2,4,6-trichloro-s-triazine that were highly reactive, thus, forcing the next step to be initiated immediately.

3.1.3 Synthesis of PAMAM-triazine - $\text{V}^{2+}((\text{V}^{2+})_x(\text{NH}_2)_{16-x})$

1-1-bis(propylamino)-4,4'-bipyridylum (v^{2+}) dissolved in de-ionized water with different molar ratios 8:1 and 16:1 of v^{2+} to PAMAM G2, and then introduced drop-wise into the PAMAM-triazine reaction mixture. The amino groups in v^{2+} as nucleophile

agents reacted with PAMAM-triazine at 40°C and pH~5-6. The pH of the reaction was controlled by adding Na_2CO_3 . The reaction mixtures were stirred overnight, followed by isolating the colored yellow powder by acetone. The powder was placed in the freeze dryer at -37°C overnight. The products with molar ratios 16:1 and 8:1 of v^{2+} to PAMAM G2 were called K_1 and $\text{K}_{1/2}$, respectively.

^1H NMR (250 MHz; D_2O , ppm): 2.1 (G), 2.5 (H,E), 2.7 (K), 3.1 (D), 3-3.5 (I), 4.8 (F), 8.5 (B), 9.1 (A) (Fig. 5a and Fig. 5b). The percentage of terminal amino groups of the dendrimer was calculated by integrated ^1H NMR intensities, wherein functionalized viologens were 82% of the dendrimer branches in K_1 and 40% in $\text{K}_{1/2}$. ^1H NMR spectrum of dendrimers exhibited significantly broadened peaks. FT-IR (KBr, $\tilde{\nu}$ max/ cm^{-1}): 3429 (hydrogen bonds), 3285 (-NH), 3064 (-CH aromatic), 2966 (-CH aliphatic),

Fig. 5. a) ^1H NMR spectra of K_1 in D_2O , b) ^1H NMR spectra of $\text{K}_{1/2}$ in D_2O

Fig. 5. c) FT-IR of spectra K_1 (line) and $K_{1/2}$ (dash).

1645 (-NH-C=O amide), 1550 (C-C=C aromatic resonance), 1433 and 1365 (-CH aliphatic), 1275 (aromatic amine), 584 (C-Cl) (Fig. 5c).

MI and purity by elemental analysis for $K_{1/2}$: Calc. for $C_{294}H_{464}N_{114}O_{28}Cl_8$, C, 55.8%; N, 25.2%. Found: C, 33.8%; N, 15.27%, corresponds to purity 60.5%, MI=10452.

MI and purity by elemental analysis for K_1 : Calc. for $C_{448}H_{640}N_{170}O_{28}Cl_{16}$, C, 56.96%; N, 25.33%. Found: C, 34.1%; N, 14.14%, corresponds to purity 57.9%, MI= 16234

3.2 Cyclic voltammetry

The cyclic voltammetry (CV) measurements were performed to examine the existence of the reversibility and redox behavior of newly synthesized viologen derivatives.

The CVs of viologen-functionalized dendrimers (K_1 and $K_{1/2}$) illustrate in Fig. 6a-Fig. 6b. The electrochemical parameters are given in Table 1. As it can be seen, both CVs exhibited oxidation-reduction waves. A sharp peak appeared with a peak potential wave of $E = -0.67$ V for K_1 , corresponding to the first reduction of dicationic viologen (V^{2+}) to mono-cation radical (V^{+}) as deep-blue color. Doubly reduced viologen (V^{2+}) at -1.0 V was formed according to the color changes from deep blue to a colorless state. The first oxidation occurred at -0.91 V with a change of colorless to blue during the formation of mono-cation radical (V^{+}).

As expected, $K_{1/2}$ showed the same CV with peak potential wave of $E = -0.65$ V, corresponding to the first reduction of di-cationic viologen (V^{2+}) to mono-

Table 1. Electrochemical parameters for K_1 and $K_{1/2}$

Sample	E^{R1} (V)	E^{R2} (V)	E^{OX1} (V)	E^{OX2} (V)	ΔE_p (mV)
K_1	-0.67	-1.0	-0.91	0.54	90
$K_{1/2}$	-0.65	-0.99	-0.91	0.57	80

cation radical (V^{+}) as deep-blue color. Doubly reduced viologen (V^{2+}) at -0.99 V formed according to color changing from deep blue to colorless state as the same as K_1 . The first oxidation occurred at -0.91 V with a change of colorless to blue during the formation of mono-cation radical (V^{+}). Detrimental changes did not observe for the initial and second reduction and oxidation potentials. These results show that the origins of redox potential are related to the same molecule of viologen on dendrimer.

As expected, a transition from a deep blue to a colorless state occurred during the second oxidation related to the oxidation of mono-cation radical to dication (V^{2+}) form.

The values of peak potential separation (ΔE_p) for K_1 and $K_{1/2}$ were 90 mV and 80 mV, respectively. Suggesting that the electron transfers in K_1 and $K_{1/2}$ were quasi-reversible [47-49].

The voltammograms also were recorded by changing the scan rates from 0.05 Vs^{-1} to 0.5 Vs^{-1} (Fig. 6c). The peak current ratios (I_{pc}/I_{pa}) ranging from 0.05 Vs^{-1} to 0.5 Vs^{-1} were found to be very near to unity, which implies that the system was quasi-reversible for both K_1 and $K_{1/2}$. Increasing peak current at the same condition for K_1 concerning $K_{1/2}$ has approved the addition of more viologen units on the dendrimer, which

Fig. 6. Cyclic voltammogram of the viologen-functionalized dendrimer $(V^{2+})_x(NH_2)_{16-x}$, a) K_1 and b) $K_{1/2}$ in aqueous 0.1 M HCl at a glassy carbon working electrode, scan rate varies from 0.05 to 0.5 Vs^{-1} , c) Plot of peak current vs. SQRT of scan rate for the first oxidation and reduction peaks.

is responsible for the production of more reduction and oxidation currents.

As can be seen in Fig. 6c, the peak currents for both redox processes (I_{pa} , I_{pc}) were found to increase linearly with the square root of the scan rate, suggesting that a diffusion control reaction was involved [50].

3.3 The ink wettability on the ITO coated PET substrate

The wettability of the ink on a substrate depends on the substrate's surface energy and the ink's surface tension. Therefore, before starting to develop the ink-jet inks, the surface energy of the substrate should be considered to prepare an ink with lower surface tension than the substrate's surface energy[50].

The surface energy values of the ITO coated PET calculated according to equations (1) and equation (2), which are known as the equations of state as proposed by Li and Neumann [51].

$$W_A = \gamma_{sv}(1 + \cos\theta) \quad \text{Equation (1)}$$

$$W_A = 2(\gamma_{lv}\gamma_{sv})^{1/2} \exp[-\beta(\gamma_{lv} - \gamma_{sv})^2] \quad \text{Equation (2)}$$

where γ_{lv} and γ_{sv} are surface tension of water and surface energy of the substrate, respectively. θ is a water contact angle and b is 0.0001247 ± 0.000010 (mJ/m^2)⁻². The work of adhesion (W_A) was first calculated according to equation (1) (Young's equation). Surface energy (γ_{sv}) was then calculated using equation (2).

Based on Fig. 7, the water contact angle on the ITO coated PET is 79.5° . According to the above equations, the surface energy values of ITO coated PET was 35.8 mNm^{-1} . Correspondingly, the surface tension of the prepared inks plays significant roles in the wettability of the ink onto the substrate and in the decomposition of the ink into precise drops through the printer's nozzle. The surface tension values of the formulated inks were 29.9 mNm^{-1} and 30.1 mNm^{-1} , respectively. The results were within the values of commercial ink-jet ink ($28\text{-}31 \text{ mNm}^{-1}$) and lower than the obtained surface energy of the substrate (35.8 mNm^{-1}).

3.4 The viscosity of electrochromic ink-jet printing inks

The viscosity of the prepared ink mainly affects the

Fig. 7. The water contact angle on the ITO coated PET.

Fig. 8. Rheology behavior of inkjet inks at different shear rate.

rheological performances within the capillary nozzles of the printer. Fig. 8 shows the variation of viscosities along with shear rates for the prepared water-soluble inks on a logarithmic scale. As can be seen, the viscosity of the inks remained almost unchanged by increasing the shear rate, demonstrating that the inks behave as a Newtonian fluid [52]. Consequently, the viscosity value for the ink-jet ink was 1.8 mPa.s , which is within the acceptable range for ink-jet printing ink.

3.5 Electrochromic properties of electrochromic devices

The flexible EC devices are assembled in a multi-layer structure due to investigate the electrochromic properties of synthesized EC material as an active printed layer in an EC device. First, the homogeneous and thin layers of EC materials based on novel water-soluble viologen-functionalized dendrimers ($K_{1/2}$ and K_1) ink-jet printed on the ITO coated PET substrate. Then, the electrolyte that was previously prepared was spilled onto the printed EC film to facilitate the

movement of ions between each electrode. Subsequently, an extra ITO coated PET substrate was used as a counter electrode placed on top of it and combined in a sandwich structure (Fig. 1). The connection was reinforced using a clip with dimensions of $2.5\text{ cm} \times 3.5\text{ cm}$. The electrolyte inside the device needed not to contain air bubbles, because their presence may interfere in the measurements.

Then, the EC device color changes were examined by UV-Vis spectroscopy (Fig. 9a and Fig. 9b) at various applied potentials. In the initial state (0 V), when

the viologen di-cation formed, the prepared EC devices were colorless. By applying the potential, the electrochemical reduction obtained in the formation of the radical cation and EC device color changes from the transparent to blue occurred (Fig. 9c) with the absorption of broadband centered at $\lambda_{\text{max}} = 550\text{ nm}$ and 600 nm for $K_{1/2}$ and K_1 , respectively. By increasing the applied potential from -1 V to -1.5 V and -2 V , color absorption intensity in λ_{max} increased. The absorption at $\lambda_{\text{max}} = 600\text{ nm}$ for K_1 indicates the formation of viologen cation radical monomers,

Table 2. Electrochromic properties of K_1 and $K_{1/2}$ devices

Sample	$\lambda_{\text{max}}^{\text{a}}$ /nm	A_{b}	$\Delta\%T$	A^{c} (mA)	$(T_{\text{C}})^{\text{d}}$	$(T_{\text{b}})^{\text{e}}$	ΔOD^{f}	$(EE)^{\text{g}}$ Cm^2C^{-1}
$K_{1/2}$	550	0.97	38.6	6	%40.6	%79.2	0.66	192.5
K_1	600	1.60	47.0	5	%32.2	%79.2	0.89	311.5

^aWavelength of absorption maximum ^bAbsorbance at 0.0001 mol/L ^cElectrical current ^dColored Transmittance, ^eBleached Transmittance, ^fOptical density(DOD) = $\log[T_{\text{bleached}}/T_{\text{colored}}]$, where T_{bleached} and T_{colored} are the maximum transmittance in the neutral and oxidized state, respectively, ^g Electrochromic Efficiency, ^h

Fig. 9. a) Absorption spectra for ECD ($K_{1/2}$) in different potential b) absorption spectra for ECD (K_1) in different potential.

Fig. 9. c) Absorption spectra for ECD K₁(line) and K_{1/2} (dash) in different potential.

while its associated species or dimeric forms are at $\lambda_{\max} = 550 \text{ nm}$ [25]. A great way to assess the insertion/extraction film is to compare spectral coloration efficiencies, CE (λ), for the visible region.

Coloration efficiency is defined as the amount of electronic charge (Q), which is necessary to produce an optical density change (ΔOD), equation (3).

$$\eta(\lambda) = \frac{\Delta OD}{Q}, \Delta OD = \log \frac{T_b}{T_c} \quad \text{Equation (3)}$$

$\Delta OD (\lambda_{\max})$ is the change in transmitted optical density at the maximum wavelength (single-pass) because of charge density Q ($\text{cm}^2 \text{C}^{-1}$) inserted to the T_b (bleached transmittance value) and T_c (colored transmittance value). The best prepared EC device's coloration efficiency (η) or electrochromic efficiency (EE) was $311.5 \text{ cm}^2 \text{C}^{-1}$ at 600 nm in -2 V potential. The redox process was reversible, and the coloration-decoloration switching time was 5 seconds. Color contrast for the prepared EC device was the transmittance change from 79.2% (0 V) to 32.2% (-2 V) at $\lambda_{\max} = 600 \text{ nm}$ ($\Delta T = 47\%$), Table 2.

The obtained results were comparable to previous reports [8,20,53-59]. However, the switching time value was longer than that obtained in the ECD based on type II electrochromic materials. This difference was due to the diffusional limitation of the solution based viologen- functionalized dendrimer system.

4. Conclusions

Water-soluble novel electrochromic materials were prepared based on viologen-functionalized dendrimer

(K₁ and K_{1/2}). From the cyclic voltammetry (CV) measurement results, the best synthesized viologen-functionalized dendrimer that had more viologen units on the dendrimer was K₁. The water-based ink-jet inks that contained the novel synthesized electrochromic materials (K₁ and K_{1/2}) were ink-jet printed onto the ITO coated PET to make flexible EC devices. The EC devices with a gel polymeric electrolyte based PMMA showed a change in color from colorless to blue of various intensities at the increasingly applied potential. The EC device demonstrated acceptable electrochromic properties with switching time 5 seconds in alternate cycles. The results of the K₁ and K_{1/2} electrochromic properties proved that the EC device was prepared by K₁ to be the optimal device. The color changes of the optimal EC device showed an optical contrast of 47% and a coloration efficiency of $311.5 \text{ cm}^2 \text{C}^{-1}$ at 600 nm. The transmittance of the EC device at 600 nm can be changed reversibly from 79.2% (bleached) to 32.2% (darkened), with applied potentials of 0 and -2 V, respectively. Therefore, a water-based electrochromic ink-jet ink that has no contamination to humans, and no environmental risk was formulated and successfully printed to prepare flexible electrochromic devices. Assembling an all-polymeric flexible electrochromic device in the form of a film, opens the perspective of applying these films on a flat or curved substrate.

Compliance with ethical standards

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Conflict of interest

The authors declare that they have no conflict of interest (financial or non-financial).

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