All-in-one Dual-Band Electrochromic Devices Based on Viologen Derivative

Hengzhi Zhang, Jixun Gong, Chunyang Jia *

National Key Laboratory of Electronic Thin Films and Integrated Devices, School of Integrated Circuit Science and Engineering, University of Electronic Science and Technology of China, Chengdu 611731, P. R. China

* Corresponding Author Email: cyjia@uestc.edu.cn

Abstract. A viologen derivative, 1- (4- (trifluoromethyl) benzyl) -4- (4- (1- (4-vinylbenzyl) pyridin-1-ium-4-yl) phenyl) pyridin-1-ium (FBPCV), with modulation properties in the Visible/near-infrared dual-band was prepared, and further cross-linking and polymerization with poly (ethylene glycol) diacrylate to produce electrochromic device (ECD) in the gel state. The trifluoromethyl group is introduced to increase the π-conjugation of the viologen to enhance its spectra modulation range and to avoid dimerization of the viologen by using the repulsion of the fluorine atoms. The maximum transmittance modulation of FBPCV-ECD in the visible/near-infrared dual-band reaches 74.25 % and 67.15 %, respectively, and its good stability enables it to maintain the initial transmittance modulation range of 91.3 % after 5000 cycles, which is a good prospect for the application of electrochromic smart windows.

Keywords: Electrochromic, all-in-one, viologen, dual-band.

1. Introduction

Materials that exhibit a reversible color shift in response to an applied potential difference are designated as electrochromic materials (ECMs). These materials are classified into two principal categories: inorganic ECMs and organic ECMs. The former includes transition metal oxides, Prussian blue, etc., while the latter contains small molecules (viologen, quinones, tetrathiafulvalene, etc.) together with conductive polymers. This material with its special properties can be used to construct various types of electrochromic devices (ECDs), e.g. anti-glare mirrors, bionic skins, encryption devices, etc., along with EC smart windows, which have attracted a lot of attention in recent years [1].

Among the EC materials, viologen, a 4-4′-bipyridine and its derivatives, has been widely investigated for the manufacture of EC smart windows due to its low driving voltage, fast response time and excellent designability [2]. Since the coloring state of viologen typically depends on the substituent group attached to the pyridine nitrogen, its electronic structure and spectra properties can be precisely tuned through the introduction of functional group modifications, leading to designable EC properties. For instance, Ho et al [3]. prepared poly (butyl viologen) and achieved a modulation rate of 72.2% at 545 nm based on Prussian blue pairs of electrodes. Liou et al [4]. synthesized a bipolar ECM containing viologen-arginine triphenylamine and prepared an integrated smart window achieving a large modulation range of 96% at 724 nm. Ferrocene is widely used in all-in-one ECD preparation due to its high solubility, low operating voltage and high stability, Ho et al [5]. based on this introduced trifluoromethyl into the viologen molecule, synthesized 1, 1′-bis (3, 5-bis (trifluoromethyl) -benzyl) -4, 4′-bipyridine-1, 1′-diium and prepared an all-in-one smart window containing ferrocene electrolyte, which achieves a modulation of 63.5% at 605 nm Range. While Viologen-based EC smart windows excel at regulating in the visible light band, their ability to regulate in the infrared (IR) band remains more limited, which results in less than optimal regulation of indoor temperatures, as the near-infrared (NIR) band is the main source of heat energy in solar radiation.

Herein, in response to the above problems, viologen derivatives 1-benzyl-4- (4- (1- (4-vinylbenzyl) pyridin-1-ium-4-yl) phenyl) pyridin-1-ium (BBPCV) and 1- (4- (trifluoromethyl) benzyl) -4- (4- (1-

(4-vinylbenzyl) pyridin-1-ium-4-yl) phenyl) pyridin-1-ium (FBPCV) with dual-band modulation effects were prepared, and further cross-linking and polymerization with poly (ethylene glycol) diacrylate to produce all-in-one ECDs. Experiments proved that these two ECDs not only exhibited excellent visible light electrochromic performance, but also performed well in NIR modulation, providing new material options for further practical applications of smart windows.

2. Experimental

2.1. Materials

1, 4-Di (4-pyridyl) benzene, Benzyl bromide, 4- (Trifluoromethyl) benzyl bromide, Ferrocene, Poly (ethylene glycol) diacrylate, 2-Hydroxy-2-methylpropiophenone, Trimethylolpropane trimethacrylate, Ammonium hexafluorophosphate were purchased from Shanghai Macklin Biochemical Co., Ltd. 1- (chloromethyl) -4- vinylbenzene, N,N-Dimethylformamide, Ethyl acetate, Acetone, Methanol, Ethanol anhydrous, lithium perchlorate were purchased from Kelong Chemical Co. Glasses with ITO layer (15 Ω/□) were cut into rectangles (3 cm × 3 cm). After rinsing with deionized water, ethanol and isopropanol respectively and ultrasonication for 5 min, then dried, and immersed it in ethanol for use.

2.2. Synthesis of Viologen Derivatives

Synthesis of BPCV: 5 g of 1, 4-Di (4-pyridyl) benzene and 1.14 g of 1- (chloromethyl) -4-vinylbenzene were added to 100 ml of DMF and stirred at 100 °C for 12 hours. After cooling, the solution was dried by repeated rinsing with ethyl acetate to remove the solvent, yielding a yellow solid BPCV. (1H NMR (600 MHz, DMSO-d6) δ 9.65 (dd, J = 47.2, 6.4 Hz, 2H), 9.51 – 9.30 (m, 2H), 9.01 – 8.96 (m, 2H), 8.76 – 8.66 (m, 2H), 8.05 – 7.95 (m, 2H), 7.69 – 7.53 (m, 4H), 7.20 – 7.05 (m, 2H),6.76 (ddd, J = 17.6, 11.0, 1.6 Hz, 1H), 6.10 (d, J = 10.0 Hz, 2H), 5.91 (d, J = 17.6 Hz, 1H), 5.33 (d, J = 11.0 Hz, 1H).).

Synthesis of BBPCV: 3.49 g BPCV, 5.13 g benzyl bromide were added to 100 ml DMF and stirred for 12 h at 100 °C. After cooling, the solution was added to 500 ml of acetone to produce a white precipitate, which was washed repeatedly with acetone and dried to remove the solvent to give a pale-yellow solid.

Anionic displacement: The pale-yellow solid obtained above was dissolved in methanol and added to saturated aqueous ammonium hexafluorophosphate solution and stirred for 24 h. A white precipitate was obtained. A white solid was obtained by filtration and washed repeatedly with methanol to convert chloride and bromide ions to hexafluorophosphate ions. Drying to remove solvent to obtain BBPCV (1H NMR (600 MHz, DMSO-d6) δ 9.32 (t, J = 6.5 Hz, 4H), 8.66 (dd, J = 7.0, 1.9 Hz, 4H), 8.32 (s, 4H), 7.65 – 7.55 (m, 6H), 7.51 – 7.43 (m, 3H), 6.76 (dd, J = 17.6, 10.9 Hz, 1H), 5.93 – 5.84 (m, 5H), 5.33 (dd, J = 10.9, 0.9 Hz, 1H).

Synthesis of FBPCV: 3.49 g of BPCV, 4.78 g of 4-(Trifluoromethyl) benzyl bromide were added to 100 ml of DMF and stirred at 100 °C for 12 hours. After cooling to room temperature, filter and dry the solvent to obtain a pale-yellow solid, according to the above steps for anion substitution, drying to remove the solvent, to obtain FBPCV. (1H NMR (600 MHz, DMSO-d6) δ 9.31 (dd, J = 12.6, 6.2 Hz, 4H), 8.76 – 8.58 (m, 4H), 8.33 (d, J = 6.6 Hz, 4H), 7.84 (d, J = 34.9 Hz, 2H), 7.58 (s, 4H), 7.09 (s, 2H), 6.76 (dd, J = 17.6, 10.9 Hz, 1H), 6.00 – 5.82 (m, 5H), 5.34 (d, J = 10.9 Hz, 1H).)

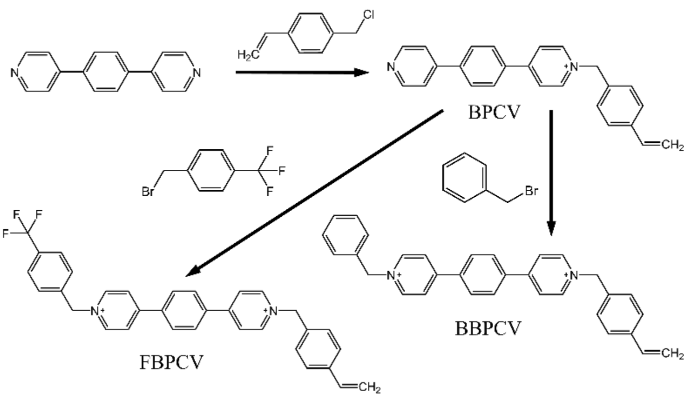

Figure 1. Synthesis pathways of BBPCV and FBPCV

2.3. Fabrication of the ECD

Add 0.03 g of BBPCV/FBPCV, 0.01 g of ferrocene with 0.05 g of lithium perchlorate to 1 ml of DMF and stir until it is completely dissolved. Then 1 g of poly (ethylene glycol) diacrylate, 0.1 g of trimethylolpropane trimethacrylate with 0.005 g of 2-Hydroxy-2-methylpropiophenone were added sequentially, and stir again until well dissolved and mixed. The hybrid solution was infused in a device consisting of two ITO sheets and cured with UV to obtain a solid-state all-in-one ECD.

2.4. Characterization

The ECM components and molecular structure were qualitatively analyzed using a Fourier transform infrared spectrometer (Nicolet iS5 Thermo Fisher Scientific, USA) as well as a nuclear magnetic resonance spectrometer (Bruker-600 Bruker Technologies GmbH, Germany). The electrochemical characterization and testing of ECD was carried out using an electrochemical workstation (CHI660E Shanghai Chenhua Instrument Co., Ltd.). A UV/Vis spectrophotometer was used for spectra response and modulation analyses of ECD (SP60 X-Rite USA).

3. Results and Discussion

The FTIR results are shown in Fig. 2 (a), where the absorption peaks of FBPCV and BBPCV at 1637 cm-1 exhibit a redshift compared to BPV, which usually is interpreted as an increase in the number of C=C bonds, thus confirming the successful access of the vinyl double bond. In addition, the FBPCV added a new C-F bond absorption peak at 729 cm-1 [5], reflecting the successful introduction of 4-(Trifluoromethyl) benzyl bromide. Subsequently, BBPCV and FBPCV were assembled into 3 × 3 cm ECDs for electrochemical and spectra response and modulation analyses. The electrochemical redox properties of the ECDs were investigated by cyclic voltammetry. As shown in Fig. 2 (b) and (c), two pairs of redox peaks were displayed within -0.5~1.8 V. The first pair of peaks was due to the reversible redox reaction between the divalent cation (V2+) and the radical cation (V+·) of the viologen derivative. The second pair of oxidation peaks is due to the reversible redox reaction between the radical cation (V+·) of the viologen derivative and the neutral, fully reduced state (V0).

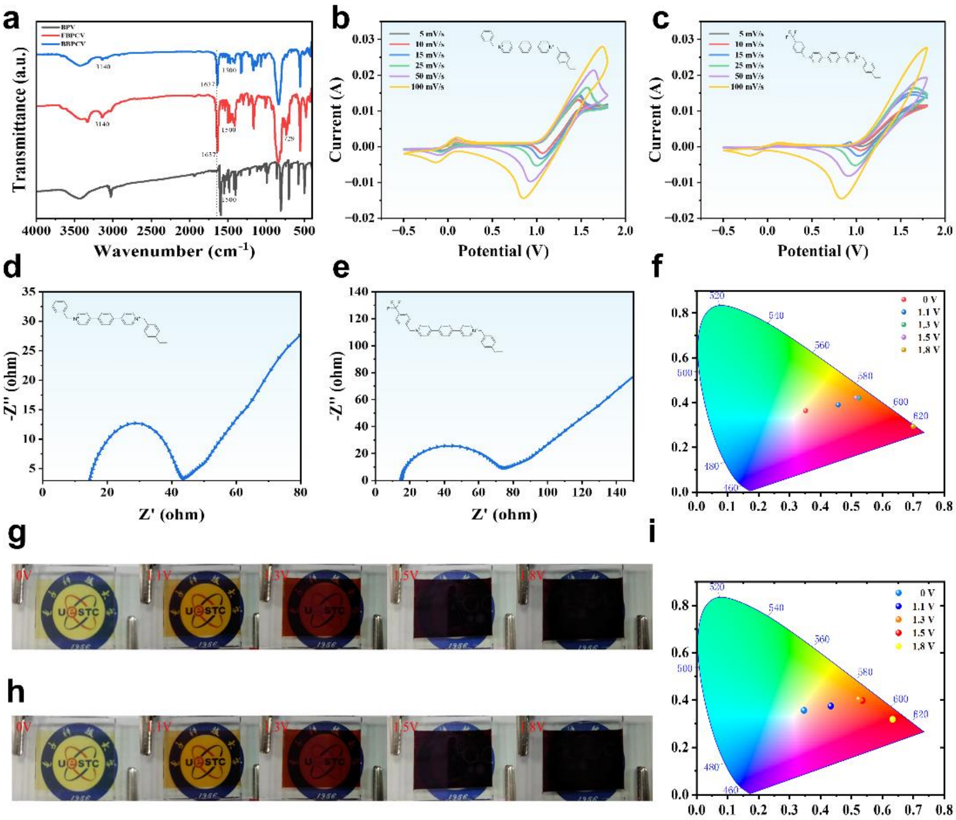

Figure 2. (a) FTIR spectrum of ECMs. Cyclic voltammetry testing of ECDs: (b) BBPCV-ECD and (c) FBPCV-ECD. EIS curves: (d) BBPCV-ECD and (e) FBPCV-ECD. Color change of ECDs: (g) BBPCV-ECD and (h) FBPCV-ECD and the corresponding chromaticity diagram: (f) BBPCV-ECD and (i) FBPCV-ECD.

In the electrochemical impedance spectroscopy (EIS) curves shown in Fig. 2 (d) and (e) (Frequency 5 mv, interval 100 KHz to 0.01 Hz), the semicircle in the high-frequency region corresponds to the charge-transfer impedance between the electrode and the electrolyte, while the slope of the straight line in the low-frequency region correlates with the diffusion process of the ions. The system resistance and charge transfer resistance of BBPCV-ECD is lower than that of FBPCV-ECD, and the low slope of FBPCV-ECD in the low-frequency region indicates a slower ion diffusion, confirming that the introduction of trifluoromethyl methane effectively reduces the dimerization of viologen and contributes to the improvement of the stability of ECD.

As shown in Fig. 2 (g), the colors of the prepared BBPCV-ECD were light yellow, orange, orange-red and dark red at 0 V, 1.1 V, 1.3 V and 1.5 V, respectively. In contrast, the FBPCV-ECD is lighter in color at 0 V and exhibits orange and dark red at 1.1 V and 1.3 V voltages, respectively (Fig. 2 (h)). Both ECDs exhibit a deep red color at 1.8 V. As observed from the chromaticity diagram, the BBPCV-ECD color (Fig. 2 (f)) is slightly darker compared to the FBPCV-ECD (Fig. 2 (i)).

The transmittance variations of the ECDs were tested by a visible-NIR spectrophotometer, as shown in Fig. 3 (a) and (b), where both ECDs exceeded 70 % in the maximum transmittance variation, and the transmittance exceeded 80 % in the bleached state (0 V), i.e., good transparency. The maximum transmittance change of BBPCV-ECD reaches 78.82 % at 780 nm, demonstrating a wide visible modulation range, and a transmittance change of 64.32 % is observed at 1120 nm, indicating its excellent NIR transmittance modulation capability. The maximum transmission change of FBPCV-ECD is 74.25 % at 980 nm and 67.15 % at 1120 nm, which proves that it also possesses the modulation effect in the NIR band.

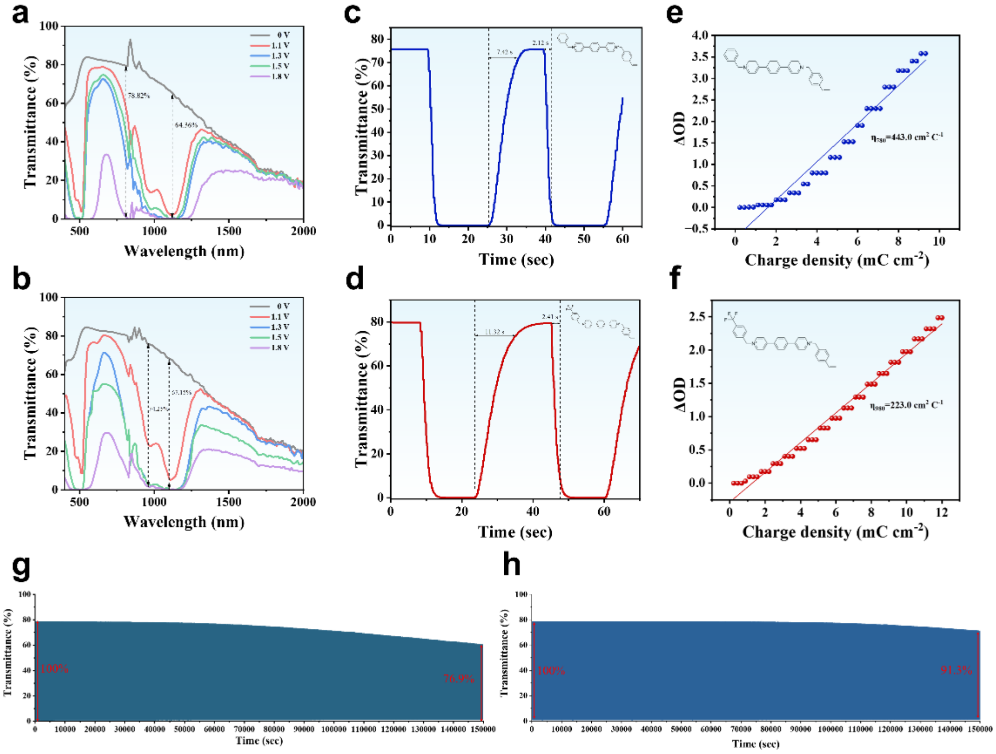

Figure 3. Visible/NIR transmittance modulation of ECDs: (a) BBPCV-ECD and (b) FBPCV-ECD. Response speed of ECDs: (c) BBPCV-ECD and (d) FBPCV-ECD. Coloring efficiency of ECDs: (e) BBPCV-ECD and (f) FBPCV-ECD. Stability of the spectra modulation rate of the ECDs. Spectra modulation variations of ECDs: (g) BBPCV-ECD and (h) FBPCV-ECD.

The spectrophotometer was used in conjunction with the electrochemical workstation to set the coloring and fading voltages to a two-potential step of 1.8 V and -0.3 V, respectively, and 780 nm and 980 nm were selected to record the response times (time taken to reach 90% of the difference in spectra contrast between the coloring and fading states) of the BBPCV-ECD and the FBPCV-ECD, respectively. As shown in Fig. 3 (c) and (d), the coloring time and fading time of BBPCV-ECD are 2.12 s and 7.42 s, respectively, and the coloring time and fading time of FBPCV-ECD are 2.41 s and 11.32 s, respectively, and the two ECDs have an extremely fast response. The coloring efficiencies of the two ECDs were calculated, as shown in Fig. 3 (e) and (f), and the coloring efficiencies of BBPCV-ECD and FBPCV-ECD were 443 cm2 C-1 and 223 cm2 C-1, respectively.

Finally, the stability of the ECDs after repeated coloring and fading was investigated by long-time step cycling. The spectral transmittance modulation range at 780 nm of the BBPCV-ECD was reduced to the original 76.9 % after 5000 cycles at a step voltage of 1.8 V versus -0.3 V (Fig. 3 (g)). Similarly, the spectral modulation range of FBPCV-ECD at 980 nm was still maintained at 91.3 % (Fig. 3 (h)), which demonstrated a significant performance enhancement due to the introduction of trifluoromethyl group into FBPCV, and the strong electronegativity of fluorine can effectively inhibit the dimerization of viologen, which significantly improves the stability of the material.

4. Conclusions

In this paper, two viologen derivatives, BBPCV and FBPCV, were successfully designed and synthesized with 1,4-Di(4-pyridyl) benzene as the core, and their electrochromic properties were investigated. Specifically, BBPCV-ECD and FBPCV-ECD can achieve a transition from the pale yellow (0 V) to the deep red (1.8 V) with a maximum transmittance change of more than 70% in both cases, realizing a dual-band modulation of visible and NIR dual-band. Among them, FBPCV can effectively inhibit the dimerization of viologen due to the introduction of strong electronegativity fluorine, and FBPCV-ECD shows excellent stability, and still maintains a transmittance modulation range of 91.3 % after 5000 cycles, which is a good prospect for the application of electrochromic smart windows.

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