All-in-one Dual-Band Wide Optical Modulation Electrochromic Films

Tairan Wang, 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. The electron-withdrawing property of the six-unit ring containing three nitrogen atoms in the structure of 2, 4, 6-tris (4-pyridyl)1,3,5-triazine was utilized to form with bipyridine salts two new viologen derivatives, 4, 4', 4''- (1, 3, 5-triazin-2, 4, 6-triyl) tris -1- (but-3-enyl) pyridine) (TPBET) and 4, 4', 4''- (1, 3, 5-triazine-2, 4, 6-triyl) tris 1-(4-vinylbenzylpyridine) (TPSET) were prepared as electrochromic devices (ECDs) with dual-band wide optical modulation. The maximum transmittance modulation of the prepared ECDs in the visible/near-infrared bands reaches 82.46 % and 78.31 %, respectively, and its good stability enables it to maintain the initial transmittance modulation range of 91.6 % after 1,000 cycles, which brings a good prospect for the application of electrochromic smart windows.

Keywords: Electrochromic, high stability, viologen, dual-band regulation.

1. Introduction

With the increasingly severe global climate change problem, low-carbon development has become an irreversible trend. As an advanced building energy-saving technology, electrochromic smart windows have received a lot of attention in recent years due to their unique function in regulating indoor light and temperature [1, 2]. Through its ability to dynamically regulate solar and thermal radiation, electrochromic smart windows can not only significantly reduce the energy consumption of buildings, but also improve the comfort of the living and working environment. In addition, they reduce reliance on traditional air conditioning and lighting systems, further reducing energy consumption and carbon emissions. Among many electrochromic materials, viologen as an organic small molecule is considered as one of the potential materials to commercialize electrochromic smart windows due to its easy synthesis, low cost, and easy modification [3].

Nevertheless, the irreversible aggregation of radical cations (also known as dimerization) during the switching process of viologen coloring states results in a gradual deterioration of redox reversibility. This is reflected in the narrowing of the regulation range and the reduction of the response speed, representing the most significant obstacle to the rapid development and wide application of viologen-based ECDs. Various strategies have been employed to prevent the dimerization of viologen, including the design of asymmetric structures, the introduction of polymer matrices, and other methodologies. Wu et al. proposed a strategy to achieve an optical modulation rate of 62% in the visible region through the synergistic dual network interaction of poly (ionic liquid) and poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). Meanwhile, the synergistic dual-network interaction of PVDF-HFP was realized with high cyclic stability, which could inhibit the irreversible aggregation of radical cations during electrochemical processes [4]. Kao et al. prepared a violet gel based on poly (methyl methacrylate) (PMMA). The interaction between the PMMA chains and the violet gel prevented the dimerization of the violet gel and possessed more than 60% optical modulation in the visible region [5]. Although there are many reports on electrochromic smart windows, there are still fewer studies that can extend the modulation range to the near-infrared region. Most of the heat of sunlight is concentrated in the near-infrared region, so it is meaningful to realize dual-band modulation of smart windows.

To address the above issues and improve the environmental utility of ECDs, a series of viologen molecules with improved conjugated structures and multiple reaction sites were synthesized through the rational design of the structure of viologen molecules centered on triazine. The abundance of reactive sites allows for the occurrence of numerous progressive color changes. The enhancement of the conjugated structure results in a coloring state close to black, with a minimum transmittance of 0.03% in the visible region and 0.01% in the NIR region. In the meantime, the prepared ECDs exhibit excellent modulation ranges in both the visible and NIR regions. The modulation range in the visible region is 76.12%, and in the NIR region is 82.71%.

2. Experimental

2.1. Materials

2, 4, 6-Tris (4-pyridyl) 1, 3, 5-triazine, 4-Bromo-1-butene, 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

Preparation of electrochromic material TPBET: In a 100 ml beaker, 2.49 g of 2, 4, 6-tris (4-pyridyl) 1, 3, 5-triazine (TPT) (8 mmol), 1.14 g of 4-bromo-1-butene (24 mmol) were added, and the reaction was heated up to 100 ℃ with DMF as solvent and stirred for 24 h. After cooled down to room temperature, the black solution and off-white precipitate were obtained. After cooling to room temperature, the black solution and gray-white precipitate were obtained. After the precipitate was filtered off by suction filtration, the black solution was poured into 800 ml of acetone to obtain a yellow-brown precipitate, which was washed repeatedly with acetone and dried to remove the solvent, and the yellow-brown solid TPBET was obtained. (^{1}H NMR (600 MHz, DMSO-d6) δ 9.77-9.34 (m, 4H), 5.93 (ddt, J = 17.1, 10.8, 6.6 Hz, 1H), 5.19-4.80 (m, 4H), 2.84 (p, J = 7.1 Hz, 2H).).

Preparation of electrochromic material TPSET: In a 100 ml beaker, add 2.49 g of 2, 4, 6-tris (4-pyridine) 1, 3, 5-triazine (TPT) (8 mmol), 3.64 g of 4-chloromethylstyrene (24 mmol), and use DMF as the solvent, raise the temperature to 100 ℃, stirring the reaction for 24 h. After cooling to room temperature, the brownish-black solution was obtained, and then poured into 800 ml of acetone to obtain a black precipitate. After cooling to room temperature, a brownish-black solution was obtained, and the solution was poured into 800 ml of acetone to obtain a black precipitate, which was washed repeatedly with acetone and dried to remove the solvent, and a black solid TPSET was obtained. (^{1}H NMR (600 MHz, DMSO-d6) δ 9.83 – 9.75 (m, 2H), 9.62 – 9.51 (m, 2H), 7.69 (d, J = 8.1 Hz, 2H), 7.58 (dd, J = 8.3, 2.0 Hz, 2H), 6.76 (dd, J = 17.6, 11.0 Hz, 1H), 6.13 (s, 2H), 5.93 – 5.89 (m, 1H), 5.35 – 5.31 (m, 1H).).

2.3. Fabrication of the ECDs

0.03 g of TPBET/TPSET, 0.01 g of ferrocene and 0.05 g of lithium perchlorate were added to a 25 ml beaker, and 1 ml of DMF was added with thorough stirring and ultrasonic for 10 min until they were completely dissolved. Add 1 g of PEGDA, 0.1 g of trimethylolpropane trimethacrylate and 0.005 g of 2-hydroxy-2-methylpropiophenone to the beaker sequentially. It was stirred thoroughly until it was well mixed. The mixed solution was perfused in a device consisting of two pieces of ITO and crosslinked with UV curing. The all-solid-state integrated electrochromic device was obtained.

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 FT-IR characterization of TPBET and TPSET is shown in Fig. 1a, comparing the infrared absorption peaks of TPT, TPBET and TPSET, the characteristic absorption peak of C=C(Ar) at 1500 cm^{-1} and the Ar-H stretching vibration peak at 3140 cm^{-1}, compared to TPT, the absorption peaks of TPBET and TPSET at 1637 cm^{-1} are significantly red-shifted and the intensity of the characteristic absorption peak is significantly enhanced. Compared with TPT, the absorption peaks of TPBET and TPSET at 1637 cm^{-1} are significantly red-shifted and the intensity of the characteristic absorption peaks is significantly enhanced, which can be analyzed as the increase of C=C, indicating the successful connection of the vinyl double bond. It can be proved that TPBET and TPSET were successfully synthesized. Cyclic voltammetry was further used to investigate the electrochemical redox properties of TPBET and TPSET. As shown in Fig. 1b and Fig. 1c, the cyclic voltammetry characteristics of the electrochromic films were tested by cyclic voltammetry scanning in the range of -0.5 to 1.8 V. Three redox pairs can be clearly seen in the figure. The appearance of the first redox pair is due to the reversible redox reaction between the trivalent cation (V^{3+}) and the divalent radical cation ($V^{\cdot 2+}$) of the violet essence derivatives. The second redox pair is due to the reversible redox reaction between the divalent radical cation ($V^{\cdot 2+}$) and the monovalent radical cation ($V^{\cdot\cdot +}$) of the violet essence derivative. The appearance of the third redox pair is due to a reversible redox reaction between the monovalent radical cation ($V^{\cdot\cdot +}$) of the violet essence derivative and the neutral, fully reduced state (V^0).

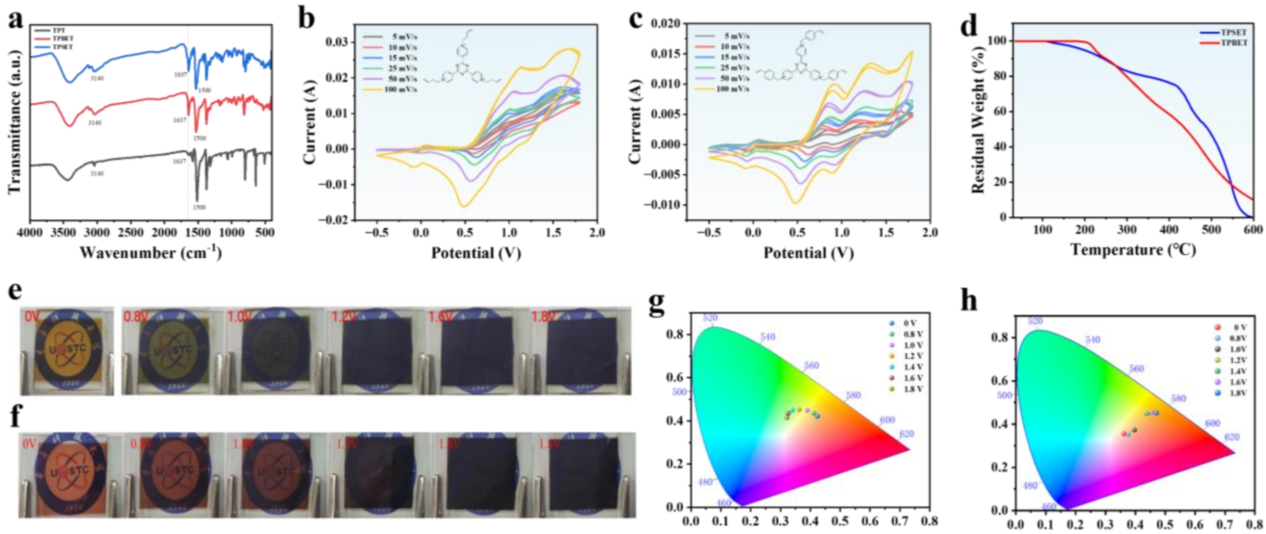

Figure 1. (a) FT-IR spectra of TPBET and TPSET. CV curve of (b) TPBET and (c) TPSET. (d) TG analysis plot of TPBET vs TPSET. Digital photographs at different voltages (e) TPBET and (f) TPSET. CIE spectra of (g)TPBET and (h)TPSET.

The thermal stability of TPBET was compared with that of TPSET, as shown in Fig. 1d. The initial weight loss temperature of TPBET was slightly higher than that of TPSET, and the residual amount of TPSET was higher in the interval from 300 ℃ to 500 ℃. Therefore, it can be judged that TPBET has better thermal stability in the middle and low temperature intervals, while TPSET has better thermal stability in the high temperature interval. As shown in Fig. 1e and Fig. 1f, in cyclic voltammetry tests, the TPBET electrochromic film changes from light yellow (0 V), gradually to black (1.8 V), and the TPSET electrochromic film changes from light red (0 V), gradually to black (1.8 V). In order to further investigate the color properties of the two electrochromic films, the color was tested by color product testing, and the chromaticity diagrams of the films at different voltages were plotted according to the color value coordinates (Fig. 1g and Fig. 1h), and it can be seen that there is a great change in the color value coordinates with the change of voltage.

In order to gain a deeper understanding of the modulation effect of the films in the dual wavelength band, the trend test of the transmittance of the films at different voltages was carried out. Fig. 2a and Fig. 2b show the transmittance modulation of the films at various voltage levels in the wavelength range from 400 nm to 2000 nm. Both electrochromic devices (ECDs) have a maximum transmittance change of more than 75 % and a transmittance of more than 80 % in the bleached condition, showing good transparency for both at 0 V. The TPBET has a maximum transmittance change of 81.5 % at 780 nm, demonstrating a wide range of visible light modulation. In addition, a transmittance changes of 76.46 % is observed at 1000 nm, which indicates that it also has excellent NIR transmittance modulation capability. TPSET has a maximum transmittance change of 82.46 % at 780 nm and a transmittance change of 78.31 % at 1000 nm, which demonstrates that it also possesses the dual-band modulation effect of both the visible light and the near infrared. In summary, both ECDs can realize effective dual-band modulation in the visible and near-infrared regions, and both of them have very high transmittance modulation ranges in dual-band, among which the optical modulation performance of TPSET is more excellent, and it realizes the transmittance of less than 1 % in the whole band in the wavelength range of 400-1750 nm, which shows significant dual-band transmittance modulation effect. Electrochromic devices assembled with TPBET and TPSET films, respectively, were subjected to multipotential step test. The coloring voltage was set to 1.8 V, while the fading voltage was -0.3 V. The response time of the TPBET film at 780 nm wavelength was initially tested to show a coloring time of 2.99 s and a fading time of 11.03 s (Fig. 2c). The same test method was applied to the TPSET film, which showed a coloring time of 2.59 s and a fading time of 10.15 s at 780 nm (Fig. 2d). This indicates that both electrochromic films have a fast response. A series of continuous cyclic tests were performed on electrochromic films at room temperature using a combined test method of an electrochemical workstation and a UV spectrophotometer. The step voltages were set to 1.8 V (coloring) and -0.3 V (fading). After 1000 cycle tests, the optical modulation change of TPBET was maintained at 88.4 % (Fig. 2e), while that of TPSET was maintained at 91.6 % (Fig. 2f). This shows that the TPSET has a slight advantage in optical modulation stability compared to the TPBET.

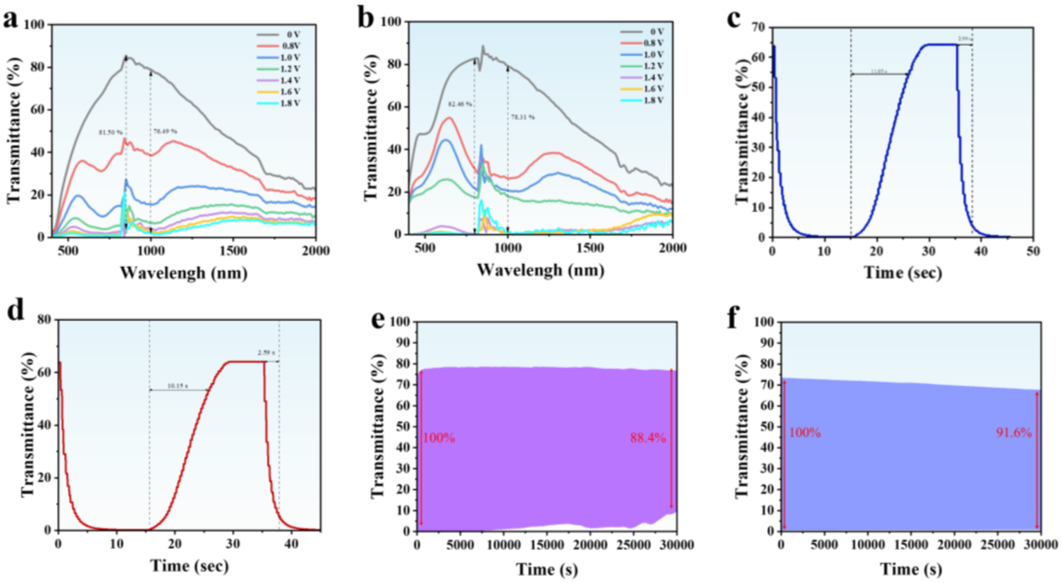

Figure 2. Optical transmittance plots of (a) TPBET and (b) TPSET. Response time plots of (c) TPBET and (d) TPSET. Cyclic stability of (e) TPBET and (f) TPSET.

4. Conclusions

Two electrochromic materials, TPBET and TPSET, have been synthesized with 2, 4, 6-tris (4-pyridyl) 1, 3, 5-triazine as the center, and the synthesized ECDs have reached more than 80 % at 780 nm and more than 75 % at 1000 nm, among which the optical modulation of TPSET is more superior, and it has achieved a full band transmittance of less than 1 % in the wavelength band of 400-1750 nm, showing a remarkable dual-band transmittance modulation effect. In the 400-1750 nm band, the optical modulation performance of TPSET is more excellent, and the transmittance of the whole band is less than 1 %, which shows a remarkable dual-band transmittance modulation effect. At 780 nm, the coloring time of the TPBET film is 2.99 s and the fading time is 11.03 s. The coloring time of the TPSET film is 2.59 s and the fading time is 10.15 s. The coloring time of the TPSET film is 2.59 s and the fading time is 10.15 s. Both electrochromic films have good electrochromic modulation response and can effectively perform electrochromic modulation.

References

[1] J. Chen, G. Li, T. Jiang, S. Wang, H. Hu, Z. Bai, D. Shi, M. Chen, J. Guan, G. Tan, Y. Long, Zwitterionic hydrogel smart windows: Radiative cooling, privacy protection and energy savings, Nano Energy. Vol. 123 (2024), p. 109386.

[2] X.-H. Li, C. Liu, S.-P. Feng, N.X. Fang, Broadband Light Management with Thermochromic Hydrogel Microparticles for Smart Windows, Joule Vol. 3 (2019), p. 290-302.

[3] M. Chen, X. Zhang, W. Sun, Y. Xiao, H. Zhang, J. Deng, Z. Li, D. Yan, J. Zhao, Y. Li, A dual-responsive smart window based on inorganic all-solid-state electro- and photochromic device, Nano Energy Vol. 123 (2024), p. 109352.

[4] X. Wu, Q. Fan, Z. Bai, Q. Zhang, W. Jiang, Y. Li, C. Hou, K. Li, H. Wang, Synergistic Interaction of Dual-Polymer Networks Containing Viologens-Anchored Poly (ionic liquid) s Enabling Long-Life and Large-Area Electrochromic Organogels, Small Vol. 19 (2023), p. 2301742.

[5] S.-Y. Kao, H.-C. Lu, C.-W. Kung, H.-W. Chen, T.-H. Chang, K.-C. Ho, Thermally Cured Dual Functional Viologen-Based All-in-One Electrochromic Devices with Panchromatic Modulation, ACS Appl. Mater. Interfaces Vol. 8 (2016), p. 4175-4184.