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The synthesis and electrochemical properties of cathodic–anodic composite electrochromic materials

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ABSTRACT

A series of electrochromic materials were synthesized by incorporating the cathodic material viologen with anodic materials phenothiazine, indole, morpholine, pyrrole and carbazole, respectively. Their electrochemical and electrochromic properties were investigated by cyclic voltammetry and UV–Visible spectrophotometer. Electrochromic devices based on these compounds were fabricated with an active area of 2 cm × 4 cm which exhibited colorless-wine-blue multicolor electrochromism. Their color and bleach reversibility was excellent with high coloration efficiency after 100 cyclic voltammetry. The response times for the coloring and bleaching processes were less than 150 ms and 2 s respectively, and the dominant response speed significantly exceeded that of viologen alone. Their remarkable electrochromic behaviour and high stability render these electrochromic materials excellent candidates for applications in electrochromic devices.

1. Introduction

Electrochromism (EC) results from the generation of different electronic absorption bands in the visible region, which corresponds to the changes between at least two redox states [1]. Electrochromic materials (ECMs) change their optical properties immediately after the potential pulse that decreases across the pulse period for both the oxidation process (anodic coloration) and the reduction process (cathodic bleaching). This interesting property has been largely studied for different technological applications, such as mirrors of vehicles [2,3], electrochromic displays [4,5], smart windows [6–8], earth-tone chameleon materials [9,10] and ink-jet printers [11]. These applications have led to a demand for new materials with improved electrochromic responses. Many different types of materials have been described and used in the construction of electrochromic device (ECD), such as inorganic systems based on transition metal oxides (e.g., WO_3, V_2O_5, and IrO_2) [12,13] and organic systems based on anthraquinone [14,15], aromatic imides [16,17], and conjugated polymers [18,19].

Among the numerous materials for organic systems, viologen has been extensively focused as cathodic ECM [20,21]. The previous report regarding the pairing cathode with anode electrochromic material was published by H.Byke [22,23], and this composite ECM which exhibited better electrochromic character than single viologen. However, only a few papers have reported fully about the cathode-anode composite ECMs due to a number of problems and challenges that still need to be solved. For example, those ECMs had insufficiently fast response times to be considered for the applications and cycle lives were probably also too low.

With this feature, a series of novel ECMs were synthesized by incorporating cathodic material viologen with anodic materials phenothiazine [24], indole, morpholine, pyrrole and carbazole, respectively. And the films of these ECMs were investigated by measuring the changes in ECDs charge, optical and electrochemical methods. Furthermore, the electrochromic coloration and response times of the ECDs were also investigated.

2. Experimental

2.1. General

All manipulations involving air-sensitive reagents were performed in an atmosphere of dry argon. The chemicals and reagents, unless otherwise specified, were purchased from Aldrich, Acros, and TCI Chemical Co. and used as received. All the solvents were further purified before use. All new compounds were characterized by

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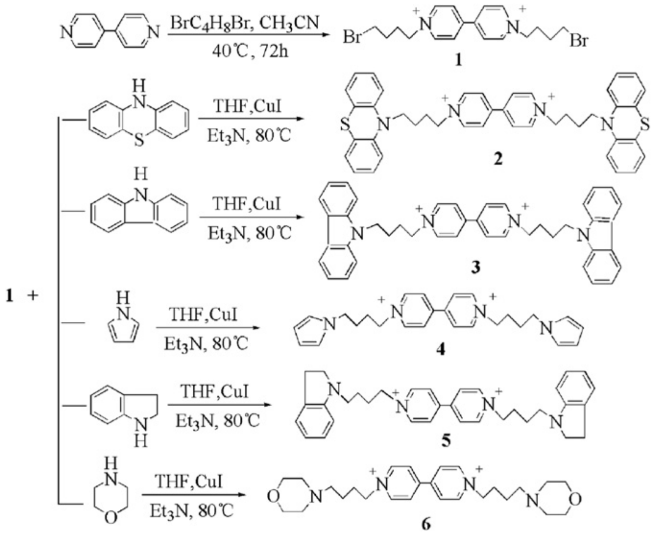
^{1}H NMR, ^{13}C NMR and MS. ^{1}HNMR spectra were measured on a Bruker AV300 (300 MHz) spectrometer at the ambient temperature with tetramethylsilane (TMS) as an internal standard. ^{13}CNMR spectra were recorded on Bruker AV300 (75 MHz) spectrometer at the ambient temperature and chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard. Atmospheric pressure chemical ionization mass spectra were obtained on a Bruker HCT Mass Spectrometer. Elemental analyses were performed on a Costech ECS 4010 instrument; values agreed with the calculation. UV spectra were performed on a Unico UV-4802H UV–visible spectrophotometer connected to a computer. Cyclic voltammetry was carried out on a CHI 650B electrochemical workstation at a scan rate 100 mV/s with platinum as counter wire electrodes and saturated calomel electrodes (SCE) as reference electrodes. The solutions were made in deionized water containing 0.1 M KCl and were degassed with argon prior to electrochemical work.



Scheme 1. Synthetic route of compounds **1**–**6**.

2.2. *General procedure for the synthesis of compounds **2**–**6***

4, 4′- bipyridine dihydrate (0.78 g, 5 mmol) was dissolved in 10 mL acetonitrile and 1,4-dibromobutane (8.76 g, 15 mmol) was added dropwise and the ensuing solution was stirred at 40 °C for 72 h under nitrogen. The reaction was monitored by thin layer chromatography (TLC). At the end of this period, the mixture was cooled to room temperature. The crude product was filtered and dried in vacuum for 12 h to obtain yellow solid **1**.

To a mixture of **1** (0.64 g, 1.5 mmol), Et_3N (6 mL) and CuI (0.2 g, 1 mmol) in 15 mL THF, phenothiazine (0.64 g, 3.2 mmol) was added and the mixture was stirred at 80 °C for 24 h under nitrogen. After cooling to room temperature, the reddish yellow colored solid **2** was obtained by filtration. The crude product was purified using silica gel column chromatography, eluting with petroleum ether/ethyl acetate = 10/1. Following the same approach, compound **3, 4, 5** and **6** were also synthesized by product **1** with the carbazole (0.53 g, 3.2 mmol), pyrrole (0.22 g, 3.2 mmol), indole (0.38 g, 3.2 mmol) and morpholine (0.28 g, 3.2 mmol), respectively.

2.2.1. *1, 1′-bis-(4-bromo-butyl)-[4, 4′]bipyridinyl (**1**)*

Yield: 88%. M.p.: 215.5 °C, δ_H (300 MHz, D_2O): 9.07 (d, $J = 6.5$ Hz, 4H), 8.50 (d, $J = 6.3$ Hz, 4H), 4.68 (t, $J = 7.3$ Hz, 4H), 2.04 (m, 4H), 1.80 (t, $J = 6.5$ Hz, 6H). δ_C (75 MHz, D_2O): 151.5, 149.0, 138.0, 128.9, 127.1, 126.8, 118.2, 47.4, 33.0, 30.1, 25.2. FT-IR (KBr, cm^{-1}): 2920(s), 2852 (s), 1636(s), 1556(m), 1509(m), 1467(m), 1450(m), 1379(m), 835(s), 721(m). Anal. Calc. for $C_{18}H_{24}N_2Br_4$: C, 36.77; H, 4.11; N, 4.76. Found: C, 36.98; H, 4.30; N, 4.91. MS (*m*/*z*): 588.1 (M^+).

2.2.2. *1,1′-bis-(4-phenothiazinyl -butyl)-[4,4′]bipyridinyl (**2**)*

Yield: 73%. M.p.: 287.2–287.6 °C, δ_H (300 MHz, D_2O): 8.96 (d, $J = 3.18$ Hz, 2H), 8.75 (d, $J = 5.22$ Hz, 2H), 8.39 (d, $J = 2.91$ Hz, 2H), 7.89 (d, $J = 2.4$ Hz, 2H), 7.14 (t, $J = 7.44$ Hz, 4H), 6.89 (q, $J = 7.79$ Hz, 4H), 3.52 (t, $J = 7.1$ Hz, 2H), 2.25 (d, $J = 3.36$ Hz, 4H), 2.20 (d, $J = 3.89$ Hz, 2H). δ_C (75 MHz, D_2O): 149.1, 145.5, 142.6, 127.3, 126.2, 122.9, 60.3, 59.8, 33.1, 29.3, 28.4. FT-IR (KBr, cm^{-1}): 3420 (s), 3022 (s), 2867 (s), 1594, 1571, 1457 (m), 1364 (m), 1286 (m), 1249 (m), 839 (s), 748 (m). Anal. Calc. for $C_{42}H_{40}N_4S_2Br_2$: C, 61.17; H, 4.89; N, 6.79. Found: C, 61.21; H, 4.95; N, 6.83. MS (*m*/*z*): 824.5 (M^+).

2.2.3. *1,1′-bis-(4-carbazolyl -butyl)-[4,4′]bipyridinyl (**3**)*

Yield: 86%. M.p.: 266.4 °C, δ_H (300 MHz, D_2O): 8.92 (d, $J = 3.02$ Hz, 2H), 8.73 (d, $J = 2.0$ Hz, 2H), 8.53 (s, 1H), 8.36–8.34 (m, 3H), 7.49–7.40 (m, 4H), 7.24 (t, $J = 6.47$ Hz, 4H), 3.50 (t, $J = 5.7$ Hz, 2H), 2.21 (t, $J = 9.79$ Hz, 4H), 1.92(q, $J = 3.96$ Hz, 2H). δ_C (75 MHz, D_2O): 149.4, 145.1, 127.4, 125.5, 122.6, 115.5, 66.7, 46.2, 33.1, 29.9, 25.7. FT-IR (KBr, cm^{-1}): 3423 (s), 3043 (s), 2360 (m), 1716 (s), 1637, 1558, 1486 (m), 1353 (m), 1252 (m), 834 (s), 762 (m). Anal.

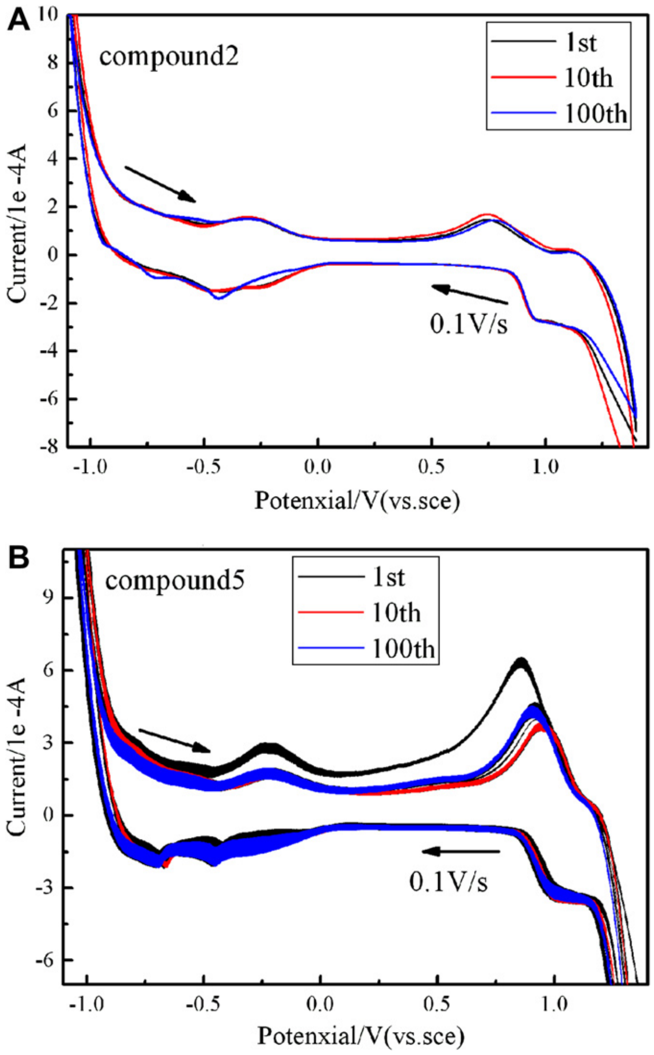


Fig. 1. Cyclic voltammetry of (A) compound **2** and (B) compound **5** in deionized water/KCl (0.1 M) at room temperature, Pt disk working electrode. The first, 10th and 100th cycles are shown and the scan rate is 100 mV/s.

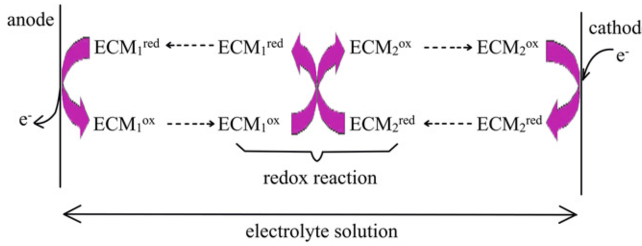


Fig. 2. The mechanism of cathode-anode composited electrochromic compound.

Calc. for $C_{42}H_{40}N_4Br_2$: C, 66.32; H, 5.30; N, 7.37. Found: C, 66.41; H, 5.52; N, 7.44. MS (*m*/*z*): 760.1 (M^+).

2.2.4. 1,1′-bis-(4-pyrroly-butyl)-[4,4′]bipyridinyl (4)

Yield: 63%. M.p.: 237.2 °C, δ_H (300 MHz, D_2O): 8.93 (d, $J = 2.02$ Hz, 2H), 8.74–8.66 (m, 3H), 8.52 (s, 1H), 8.37 (d, $J = 3.6$ Hz, 2H), 6.63 (d, $J = 8.16$ Hz, 2H), 3.89 (q, $J = 2.56$ Hz, 2H), 3.41 (q, $J = 2.94$ Hz, 2H), 1.95 (d, $J = 3.17$ Hz, 2H), 1.82 (d, $J = 3.36$ Hz, 2H). δ_C (75 MHz, D_2O): 150.0, 148.4, 126.0, 122.1, 118.4, 108.0, 56.8, 36.2, 30.5, 29.4. FT-IR (KBr, cm^{-1}): 3420 (s), 3028 (s), 2361 (m), 1637, 1556, 1456 (m), 1363 (m), 1273 (m), 835 (s), 718 (m). Anal. Calc. for $C_{26}H_{32}N_4Br_2$: C, 55.73; H, 5.76; N, 10.00. Found: C, 55.81; H, 5.90; N, 10.28. MS (*m*/*z*): 560.1 (M^+).

2.2.5. 1,1′-bis-(4-indolyl -butyl)-[4,4′]bipyridinyl (5)

Yield: 86%. M.p.: 257.6 °C, δ_H (300 MHz, D_2O): 9.10 (d, $J = 2.93$ Hz, 2H), 8.57 (d, $J = 2.2$ Hz, 2H), 6.90 (d, $J = 3.4$ Hz, 2H), 6.55 (d, $J = 3.6$ Hz, 2H), 3.50 (t, $J = 6.17$ Hz, 2H), 3.26–3.12 (m, 2H), 2.22 (t, $J = 7.22$ Hz, 2H), 1.98–1.89 (m, 4H), 1.22 (d, $J = 3.48$ Hz, 2H). δ_C (75 MHz, D_2O): 151.0, 149.5, 143.6, 128.8, 124.8, 113.0, 60.8, 53.8, 49.1, 33.7, 28.0. FT-IR (KBr, cm^{-1}): 3423 (s), 3000 (s), 2361 (m), 1684, 1556, 1450 (m), 1389 (m), 1312 (m), 813 (s), 742 (m). Anal. Calc. for $C_{34}H_{40}N_4Br_2$: C, 61.45; H, 6.07; N, 8.43. Found: C, 61.49; H, 6.42; N, 8.59. MS (*m*/*z*): 664.1 (M^+).

2.2.6. 1,1′-bis-(4-morpholinyl-butyl)-[4,4′]bipyridinyl (6)

Yield: 71%. M.p.: 238.2 °C δ_H (300 MHz, D_2O): 8.93 (d, $J = 2.74$ Hz, 2H), 7.88 (d, $J = 7.74$ Hz, 2H), 4.66 (t, $J = 7.23$ Hz, 2H), 4.46 (d, $J = 3.2$ Hz, 2H), 3.49 (t, $J = 5.99$ Hz, 2H), 2.20 (d, $J = 8.16$ Hz, 6H), 1.92 (d, $J = 2.96$ Hz, 2H). δ_C (75 MHz, D_2O): 149.2, 148.5, 142.5, 129.1, 71.4, 56.8, 51.6, 32.5, 28.4. FT-IR (KBr, cm^{-1}): 3420(s), 3021 (s), 2360 (m), 1638, 1559, 1449 (m), 1363 (m), 1256 (m), 834 (s), 716 (m). Anal. Calc. for $C_{26}H_{40}N_4O_2Br_2$: C, 52.01; H, 6.71; N, 9.33. Found: C, 52.18; H, 6.84; N, 9.47. MS (*m*/*z*): 600.2 (M^+).

3. Results and discussion

3.1. Outlook of the synthesized compounds

The preparation of the target cathode–anode composite compounds **1, 2, 3, 4, 5** and **6** are shown in Scheme 1. The structures of novel compounds were characterized by a combination of $^1H/^{13}C$NMR, IR, elemental analysis and MS spectral data. Compound **2** and **5** demonstrated the most excellent electrochromic characters. In particular, the response times of ECD with **2** and ECD with **5** were less than 150 ms and 180 ms respectively, both much faster than that of ECD with **3**, **4** or **6**.

3.2. Cyclic voltammetry and electrochemistry

In order to study the present electrochromic mechanism, electrochemistry and spectroscopic response have been analyzed by cyclic voltamm for compound **2** and **5**. The full scan-range cyclic voltammetry curves are shown in Fig. 1, from which two couples of redox waves are observed. The cyclic voltammetry data are recorded simultaneously during 100 cyclic voltammetry experiments, compound **2** (Fig. 1A) and **5** (Fig. 1B) show excellent electrochemical reversibility and stability after more than 100 cycles in both electrolytes.

Fig. 2. shows the mechanism of cathode-anode composite electrochromic compound [25]. In the curve of compound **2**, the first anodic peak at −0.25 V, corresponds to the reaction between +1 and zero valent nitrogens of viologen part of compound **2**, and this can be expressed as follows:

$$\underset{(\text{colored})}{\text{viologen}} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \underset{(\text{colored})}{\text{viologen}^+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \underset{(\text{colorless})}{\text{viologen}^{2+}}$$

The second anodic peak at 0.75 V probably relates to the phenothiazine parts, which are good electron-donor due to the presence of electron-rich sulfur and nitrogen heteroatoms, as can be illustrated below:

$$\underset{(\text{colorless})}{\text{phenothiazine}} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \underset{(\text{colored})}{\text{phenothiazine}^+}$$

The mechanism of compound **2** can be expressed as follows:

$$\underset{(\text{colorless})}{\text{viologen}^{2+}} + \underset{(\text{colorless})}{\text{phenothiazine}} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \underset{(\text{colored})}{\text{viologen}^+} + \underset{(\text{colored})}{\text{phenothiazine}^+}$$

3.3. Cathode-anode composite ECDs

The most common electrochromic device configuration is a solid EC device (Fig. 3A). In this configuration, a thin film cathode electrochromic material layer and an anode electrochromic material counter electrode layer are separated by a polymer electrolyte and ion conducting layer. In this paper, new cathode-anode composite compounds **2**–**6** are introduced as electroactive layers based on conductive polymers which work without separating cathode or anode ECM. This method simplifies the classic six-layer sandwich configuration into a four-layer sandwich (Fig. 3B).

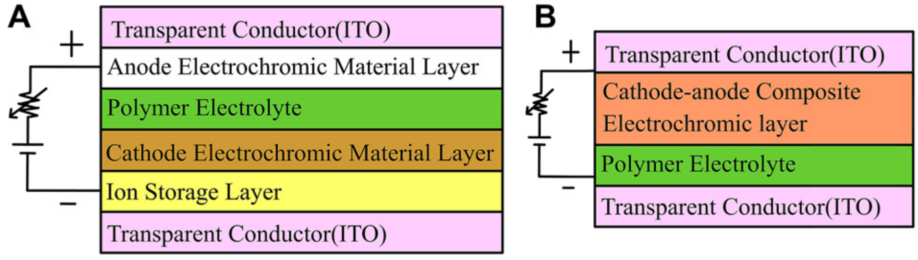


Fig. 3. Structure of EC device (A) common electrochromic device, (B) cathode-anode composited compounds electrochromic device.

According to previous works [26], the electrochromic properties and applications of cathode and anode ECMs have been widely described. In this work, we prepared the device with cathode-anode composite compounds **2**–**6**. A propylene carbonate solution of P(MMA-VAC-LiAA)/$LiClO_4$ polymer electrolyte was deposited onto an ITO [27]. The solid ECD was constructed with multilayer device structure consisting of ITO glass//cathode-anode composite ECMs//polymer electrolyte//ITO glass. The thickness of ECD was 4 mm.

3.4. Optical properties

Fig. 4. shows photograph of 2 cm × 4 cm ECD with compound **2** as ECM (Fig. 4A) and compounds **3**–**6** (Fig. 4B) in the bleached (0 V) and different colored state when 2 and −2 V are applied. When a 2 V potential is applied between the ECM layers, the color of ECD changes from colorless to dark blue. It is worth noting that a wine colored film of compound **2** is observed when applying −2 V potential, and it switches to blue when 2 V potential is applied. The color change is due to the reduction of viologen at the cathode part of compound **2** whereas the other phenothiazine at the anodic part is oxidized. Once the potential is switched again to 0 V, the device recovers its original transparent aspect, proving that the electrochromic device works satisfactorily. The ECD presents a chromatic

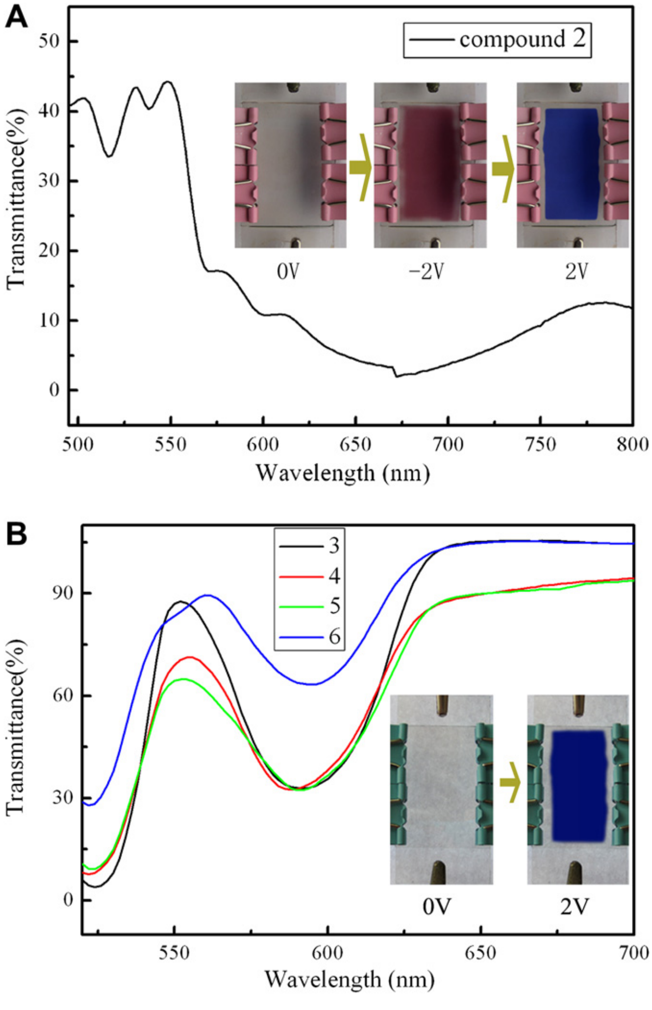


Fig. 4. Optical characterization of ECD of (A) compound **2** (B) compounds **3**–**6**. ECDs were described by applying 2 V, and typical photograph of 2 cm × 4 cm electrochromic devices in the transparent state (0 V) and colored state (±2 V).

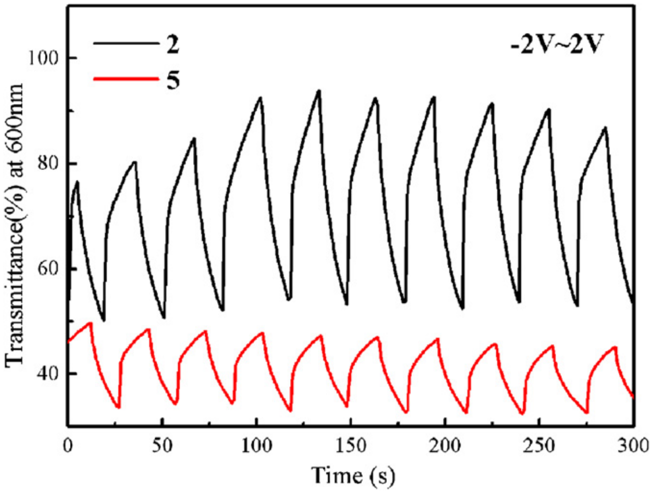


Fig. 5. Electric current and absorbance at 600 nm of the electrochromic device of compound **2** and **5** under subsequent double potential steps between −2 and 2 V.

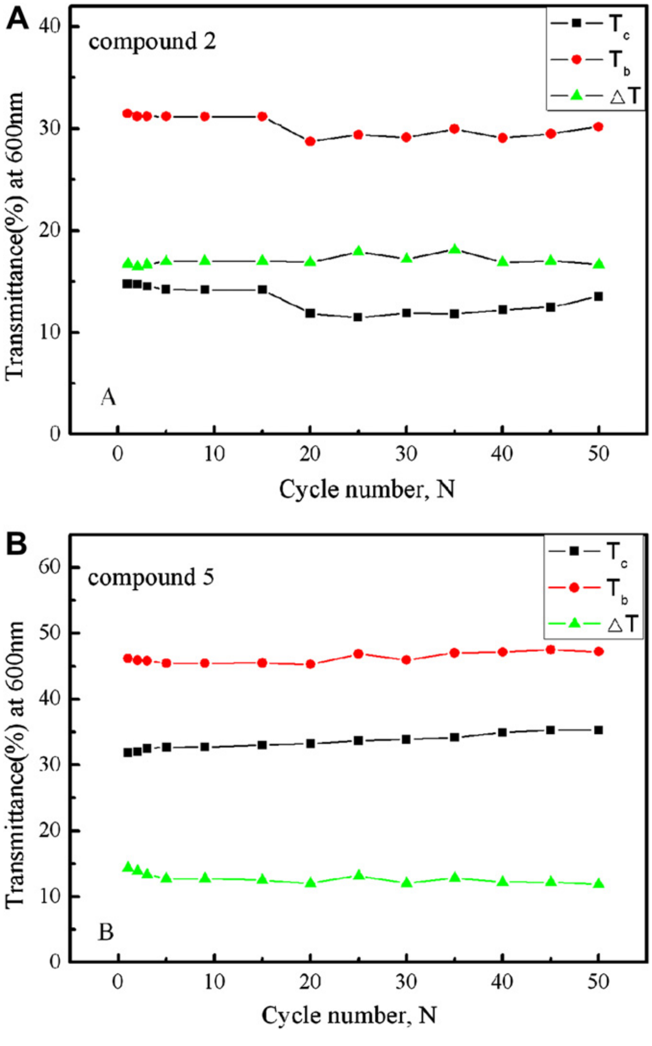


Fig. 6. The ECD transmittance values of (A) compound **2** (B) compound **5** at bleached state (Tb), darkened state (Tc), and the transmittance change (ΔT) at 600 nm as a function of cycle number.

contrast in all the visible range with a maximum at 600 nm between 0 and 2 V.

The dynamic optical behaviour of the device is measured at the wavelength of 600 nm, which is selected as the reference wavelength for the next studies due to the maximum value of optical contrast in the device. Fig. 5. shows the optical response to potential steps between −2 and 2 V for a given ECD. Taking transmittance attenuation and response time into consideration, 15 s is chose as the step time as well as the sampling time for both the coloring and bleaching processes. Due to a faster charge movement in the reduction reaction, T % of ECD of compound **5** is around 50% larger than of ECD of compound **2** layer.

The coloration efficiency, optical memory and cycle stability are important parameters to characterize an ECD. The cycling stability data for ECDs operated at electrochromic voltages (±2 V) are shown in Fig. 6. It can be seen that the ECDs are able to be colored reversibly for at least 50 cycles of (±2 V). Moreover, the optical performance ΔT % of ECD with **2** (Fig. 6A) is higher than ECD with **5** (Fig. 6B) in process of applying cycles. The transmittance attenuation increased is observed from dark state (Tc) of ECD with **2** after applying 15 cycles, while the Tc values of ECD with **5** improves smoothly. The optical performance of the ECD decays slowly after 50 cycles as a whole. This might imply the occurrence of stable reversible redox reactions of compounds **2** and **5**.

4. Conclusion

In conclusion, a series of novel cathodic-anodic composite ECMs were synthesized in this paper. Their color and bleach reversibility was excellent with high coloration efficiency after 100 cyclic voltammetry cycles. The ECDs exhibited colorless-wine-blue multicolor electrochromism. Furthermore, the dominant response speed significantly exceeded single viologen. It was discovered that the cathodic-anodic composite ECMs remarkably influenced both coloring response time and the optical performance of the present system. The cathodic-anodic composite ECMs may open new avenues in the development of advanced electrochromic devices.

Acknowledgements

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References

[1] Rosseinsky DR, Mortimer RJ. Electrochromic systems and the prospects for devices. Advanced Materials 2001;13(11):783–93.
[2] Argun AA, Aubert PH, Thompson BC, Schwendeman I, Gaupp CL, Hwang J, et al. Multicolored electrochromism in polymers: structures and devices. Chemistry of Materials 2004;16(23):4401–12.
[3] Sonmez G. Polymeric electrochromics. Chemical Communications 2005;42:5251–9.
[4] Monk PMS. The effect of ferrocyanide on the performance of heptyl viologen-based electrochromic display devices. Journal of Electroanalytical Chemistry 1997;432(1–2):175–9.
[5] Bange K. Colouration of tungsten oxide films: a model for optically active coatings. Solar Energy Materials and Solar Cells 1999;58(1):1–131.
[6] Rauh RD. Electrochromic windows: an overview. Electrochimica Acta 1999;44 (18):3165–76.
[7] Kim Yuna, Do Jaekwon, Kim Eunkyoung, Clavier Gilles, Galmiche Laurent, Audebert Pierre. Tetrazine-based electrofluorochromic windows: modulation of the fluorescence through applied potential. Journal of Electroanalytical Chemistry 2009;632(1–2):201–5.
[8] Piccolo A, Pennisi A, Simone F. Daylighting performance of an electrochromic window in a small scale test-cell. Solar Energy 2009;83(6):832–44.
[9] Mudigonda DSK, Meeker DL, Loveday DC, Osborn JM, Ferraris JP. Compositional control of electrochromic properties in copolymers of N-vinylcarbazole and N- phenyl-2-(5’-vinyl-2’-thienyl)-5-(2’’-thienyl) – pyrrole. Polymer 1999;40:3407–12.
[10] Brotherson ID, Mudigonda DSK, Ocborn JM, Belk J, Chen J, Loveday DC, et al. Tailoring the electrochromic properties of devices via polymer blends, copolymers, laminates and patterns. Electrochimica Acta 1999;44 (18):2993–3004.
[11] Peters AT, Freeman HS. Color chemistry: the design and synthesis of organic dyes and pigments. Barking, Essex: Appl Sci Publ Ltd; 1991. 193–195.
[12] Hasanain Fatima, Wang Zhi Yuan. The synthesis and characterization of near-infrared absorbing, electrochromic polyimides containing a dinuclear ruthenium complex in the polymer main chain. Dyes and Pigments 2009;83 (1):95–101.
[13] Sauvet K, Rougier A, Sauques L. Electrochromic WO_3 thin films active in the IR region. Solar Energy Materials & Solar Cells 2008;92(2):209–15.
[14] Sui BL, Fu XK. The copper(I) iodide accelerated synthesis of mono- and bis-benzylsubstituted 1- and 2-aminoanthraquinones. Dyes and Pigments 2009;83(1):1–6.
[15] Yijun Zheng, Jia Zheng, Letian Dou, Wenqiang Qiao, Xinhua Wan. Synthesis and characterization of a novel kind of near-infrared electrochromic polymers containing anthraquinone imide group and ionic moieties. Journal of Materials Chemistry 2009;19(44):8470–7.
[16] Todd EK, Wang S, Wan XH, Wang ZY. Chiral imides as potential chiroptical switches: synthesis and optical properties. Tetrahedron Letters 2005;46 (4):587–90.
[17] Liou Guey-Sheng, Fang Yi-Kai. Electrochemical behavior of N, N, N’, N’- tetraphenyl-1,4- phenylenediamine moiety on novel aromatic polyamides and their electrochromic properties. Dyes and Pigments 2007;74(2):273–8.
[18] Argun AA, Berard M, Aubert PH, Reynolds JR. Back-side electrical contacts for patterned electrochromic devices on porous substrates. Advanced Materials 2005;17(4):422–6.
[19] Aubrey AL, Grenier CRG, Reynolds JR. A poly(3,4-alkylenedioxythiophene) electrochromic variable optical attenuator with near-infrared reflectivity tuned independently of the visible region. Advanced Functional Materials 2007;17(9):1480–6.
[20] Son Young-A, Park Young-Min, Choi Myung-Sik, Kim Sung-Hoon. Synthesis of hetero-bi-functional dye having photochromism and electrochromism. Part 1: characteristics and its sensing properties. Dyes and Pigments 2007;75 (2):279–82.
[21] Jiang QL, Fu XK, Chen ZJ. The synthesis of 1-ethyl-1’- (4-vinylbenzyl)-4, 4’-bipyridinium chloride and iodide and its electrochromic property. Chinese Chemical Letters 2006;17(11):1447–50.
[22] Byker HJ. United States Patent, 5336448. 1994.
[23] Byker HJ. Electrochromics and polymers. Electrochimica Acta 2001;46 (13–14):2015–22.
[24] Simokaitiene J, Grazulevicius JV, Jankauskas V, Rutkaite R, Sidaravicius J. Synthesis and properties of glass-forming phenothiazine and carbazole adducts. Dyes and Pigments 2008;79(1):40–7.
[25] Mortimer Roger J. Organic electrochromic materials. Electrochimica Acta 1999;44(18):2971–81.
[26] Wenqiang Qiao, Jia Zheng, Yufeng Wang, Yijun Zheng, Naiheng Song, Xinhua Wan, et al. Efficient synthesis and properties of novel near-infrared electrochromic anthraquinone imides. Organic Letters 2008;10 (4):641–4.
[27] Liu SJ, Fu XK, Niu LD. Preparation and characterization of electrolytes based on P(MMA-VAC -LiAA). Journal of Functional Materials 2009;40(12): 2115–8.