



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.

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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., WO₃, V₂O₅, and IrO₂) [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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^1H NMR, ^{13}C NMR and MS. ^1H NMR spectra were measured on a Bruker AV300 (300 MHz) spectrometer at the ambient temperature with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR 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 Unicou 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.

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**)

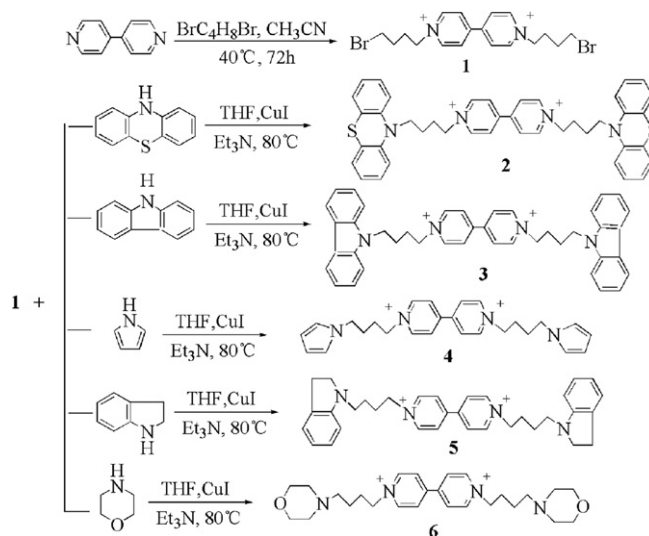
Yield: 88%. M.p.: 215.5 °C, δ_{H} (300 MHz, D_2O): 9.07 (d, $J = 6.5$ Hz, 4H), 8.50 (d, $J = 6.3$ Hz, 4H), 4.68 (t, $J = 7.3$ Hz, 4H), 2.04 (m, 4H), 1.80 (t, $J = 6.5$ Hz, 6H). δ_{C} (75 MHz, D_2O): 151.5, 149.0, 138.0, 128.9, 127.1, 126.8, 118.2, 47.4, 33.0, 30.1, 25.2. FT-IR (KBr, cm^{-1}): 2920(s), 2852(s), 1636(s), 1556(m), 1509(m), 1467(m), 1450(m), 1379(m), 835(s), 721(m). Anal. Calc. for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{Br}_2$: 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 $\text{C}_{42}\text{H}_{40}\text{N}_4\text{S}_2\text{Br}_2$: 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.



Scheme 1. Synthetic route of compounds 1–6.

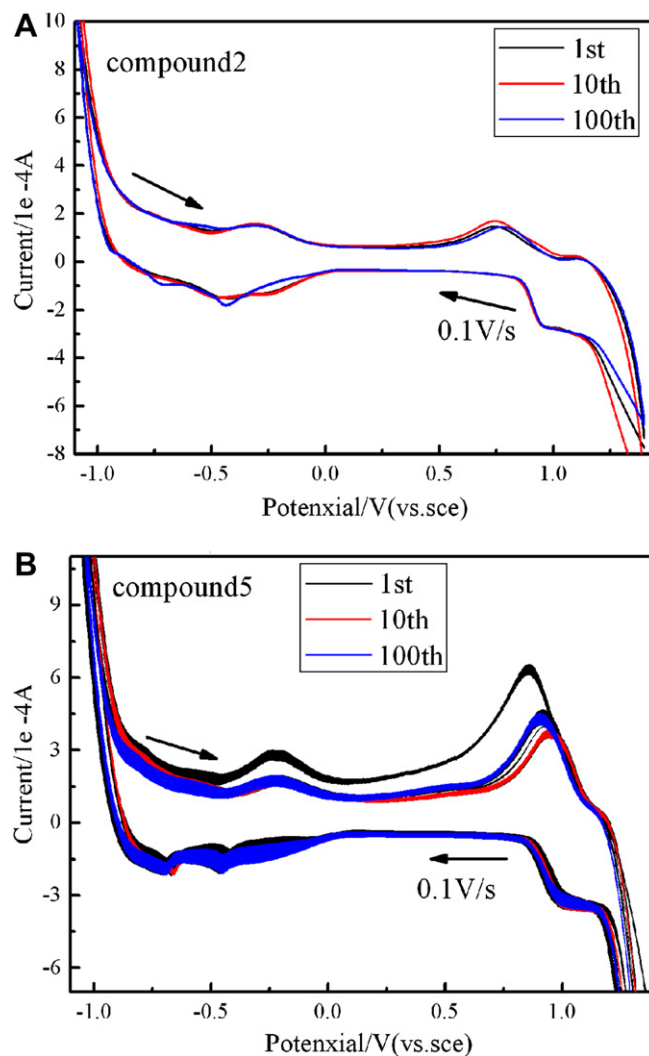


Fig. 1. Cyclic voltammetry of (A) compound **2** and (B) compound **5** in deionized water/KCl (0.1 M) at room temperature, Pt disk working electrode. The first, 10th and 100th cycles are shown and the scan rate is 100 mV/s.

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