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Novel application of 1-/2-phenyl substituted 9, 10-anthraquinones in solid electrochromic devices

Binglin Sui · Xiangkai Fu

Abstract 1-/2-phenyl substituted 9,10-anthraquinones were synthesized via Suzuki coupling reactions of 1-/2-iodo-9,10-anthraquinones with benzeneboronic acid. They are efficient and reversible electrochromic materials and their solid electrochromic devices were prepared. When reduced, the device color of 1-phenyl-9,10-anthraquinone shifts from yellow to claret while that of 2-phenyl-9,10-anthraquinone switches from yellow-green to a dark blue-purple. Their different characteristics and behaviors in electrochromic devices are only determined by the different substituted positions of the phenyl group. They are potentially to be widely applied in commercial application for the excellent behaviors plus the inexpensive starting materials and short synthetic routes.

Keywords Phenylanthraquinones · Electrochromism · Electrochromic materials · Solid electrochromic devices · Resonance structures

Introduction

Electrochromic (EC) materials are currently attracting much interest in academia and industry for both their fascinating spectroelectrochemical properties and their commercial applications [1–5]. A great deal of research regarding these materials has focused on the applications of light-modulating devices, such as smart windows, variable reflectance mirrors, and information display and storage devices [6–12]. Among the materials, organic chromophores have merits suitable for these displays because of their low-driving voltage, high contrast, flexible switching, color-mixing capability, and simple device setup [13].

Various types of electrochromic materials have been developed, including transition-metal complexes [14–16], conjugated polymers [17–20], viologens [21–24], aromatic diquinones [25–26], and aromatic imides [27–30]. Anthraquinone derivatives are efficient and interesting electrochromic materials but haven't received much attention except a few reports about polyanthraquinones and anthraquinone imides [31–35]. Herein, we report a more efficient synthesis of 1-/2-phenyl-9,10-anthraquinones (PAQs) through the diazotization–Sandmeyer and Suzuki coupling reactions and discuss their different characteristics and behaviors in cyclic voltammograms (CV) and electrochromic devices. They are redox active because the phenyl-substituted group extends the degree of conjugation of anthraquinone. So, they are efficient and reversible electrochromic materials. When reduced, the device color of 1-phenyl-9,10-anthraquinone shifts from yellow to claret while that of 2-phenyl-9,10-anthraquinone switches from yellow-green to dark blue-purple.

Experimental

General Data All manipulations involving air-sensitive reagents were performed in an atmosphere of dry argon. All chemicals and reagents, unless otherwise specified, were purchased from Aldrich, Acros, and TCI Chemical and used as received. All the solvents were further purified before use. All new compounds were characterized by ^1H NMR, ^{13}C NMR, MS, and IR. ^1H NMR spectra were measured on a Bruker AV300 (300 MHz) spectrometer at

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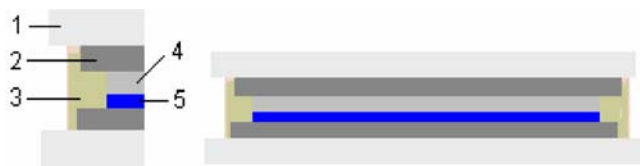e-mail: fxk@swu.edu.cn

Fig. 1 Structure of the transparent solid EC devices. *1* glass, *2* ITO, *3* insulating epoxy resin, *4* gel electrolyte, *5* PAQs films

the ambient temperature with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on Bruker AV300 (75 MHz) spectrometer at the ambient temperature with $CDCl_3$ as the solvent. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($CDCl_3$ at 77 ppm). Melting points were determined by differential scanning calorimetry (TA Q100) at a heating rate of 10 °C/min under Ar atmosphere. Atmospheric pressure chemical ionization mass spectra (APCI-MS) were obtained on a Bruker HCT mass spectrometer. Infrared spectroscopic measurements were performed in the range of 4,000–400 cm^{-1} on a Bruker Tensor 27 FT-IR spectrometer. Cyclic voltammetry was carried out on a CHI 650B electrochemical workstation at a scan rate of 100 mV/s with platinum wire and saturated calomel electrodes (SCE) as the counter and reference electrodes, respectively. The solutions were made in CH_2Cl_2 containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) and were degassed with argon prior to electrochemical work. Spectroelectrochemical data were performed on a Unico UV-4802H UV-visible spectrophotometer connected to a computer in an optical transparent thin layer cell.

General procedure for the synthesis of iodoanthraquinones A sample of aminoanthraquinone (0.45 g, 2.0 mmol) was

added in portions with stirring to concentrated sulfuric acid (5 mL). To this solution, maintained at a temperature of 10 to 15 °C, was added dropwise the solution of sodium nitrite (0.15 g, 2.2 mmol) in concentrated sulfuric acid (1 mL) under argon. The diazonium salt solution resulted was stirred for further 2 h and then poured into adequate amount of ice. The precipitate formed was passed through a glass filter and dissolved in water (25 mL) at room temperature while still wet and the solution was filtered from the impurities to yield a brownish filtrate. A solution of potassium iodide (0.4 g, 24.0 mmol) in water (1 mL) was then dropwise added. After the resulting reaction mixture was stirred at room temperature for 5 h, a solution of $Na_2S_2O_3$ was added to remove I_2. The crude product was collected by filtration and purified by silica gel column chromatography, eluting with hexane/methylene chlorideB=1/1.

1-Iodoanthraquinone (1) Yield: 87% M.p.: 204–205 °C; δ_H (300 MHz, $CDCl_3$): 8.24–8.44 (m, 4 H), 7.80 (s, 2 H), 7.39 (t, $^3J_{HH}$=7.5 Hz, 1 H); δ_C (75 MHz, $CDCl_3$): 181.8 (C=O), 181.4 (C=O), 148.6, 135.8, 134.5, 134.0, 133.8, 132.6, 132.2, 128.3, 127.7, 126.7, 93.2; FT-IR (KBr, cm^{-1}): 1,676 (s), 1,590 (m), 1,566 (m), 1,314 (s), 1,264 (s), 1,156 (m), 1,104 (m), 948 (m), 806 (m), 702 (s); MS (*m/z*): 334.1 (M^+).

2-Iodoanthraquinone (3) Yield: 85% M.p.: 172–173 °C; δ_H (300 MHz, $CDCl_3$): 8.59 (s, 1 H), 8.25 (s, 2 H), 8.11 (d, $^3J_{HH}$=7.9Hz, 1 H), 7.96 (d, $^3J_{HH}$=7.9 Hz, 1 H), 7.80 (s, 2 H); δ_C (75 MHz, $CDCl_3$): 182.5 (C=O), 181.8 (C=O), 143.0, 136.2, 134.4, 134.3, 133.9, 133.2, 132.9, 132.4, 128.6, 127.3, 127.2, 102.2; FT-IR (KBr, cm^{-1}): 3,062 (w), 1,674 (s), 1,568 (s), 1,321 (s), 1,289 (s), 1,163 (m), 925 (m), 897 (m), 849 (m), 707 (s); MS (*m/z*): 334.1 (M^+).
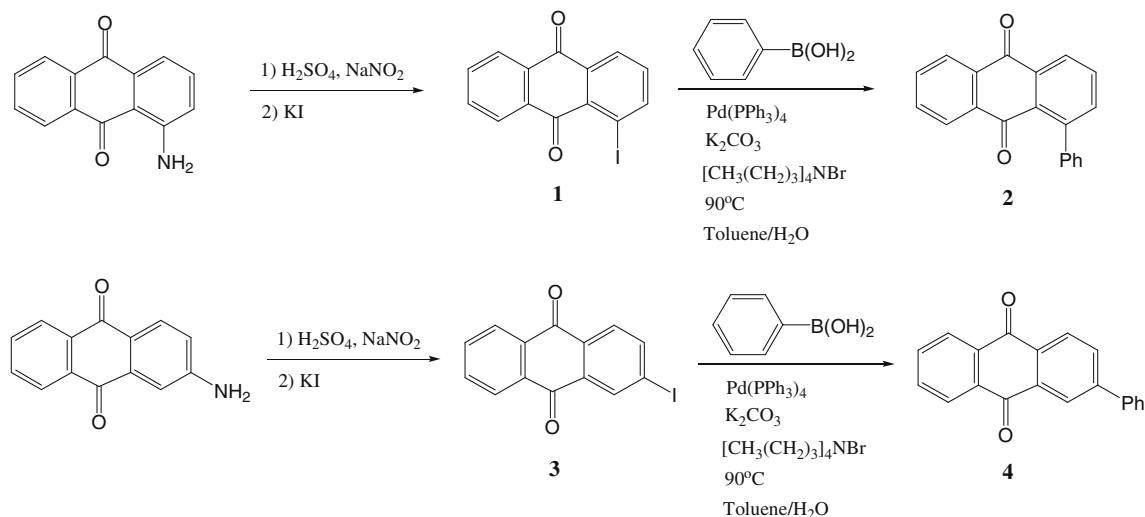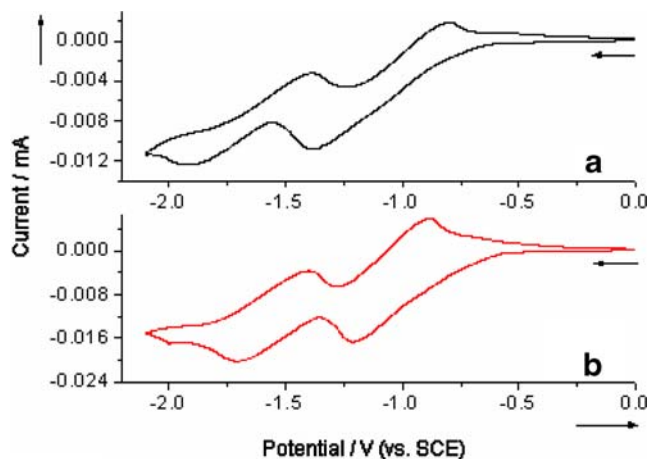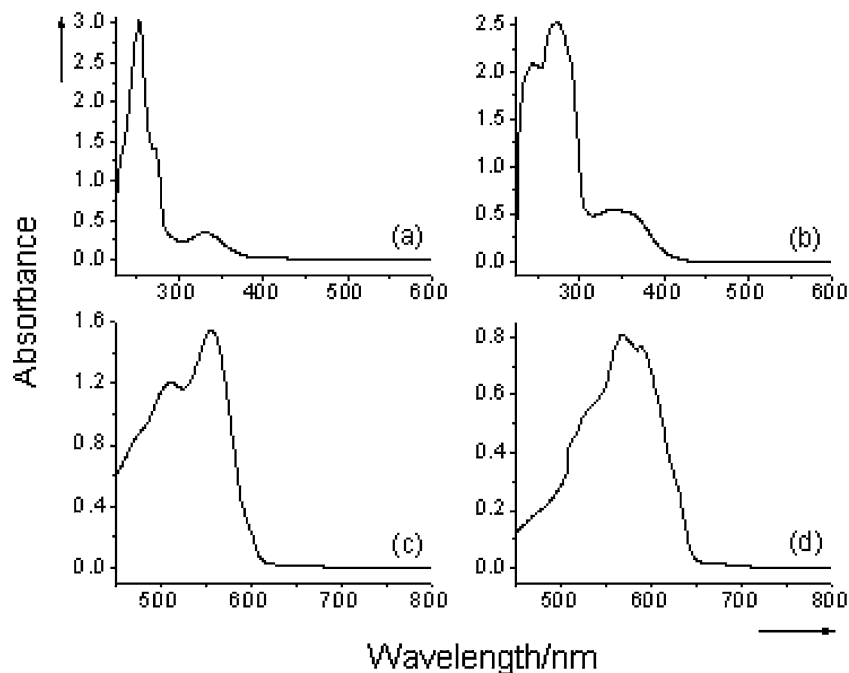

Scheme 1 Synthetic route of target molecules

Fig. 2 Cyclic voltammetry of **a** **2** (5.0×10^{-3} M) and **b** **4** (5.0×10^{-3} M) in CH_2Cl_2/TBAP (0.1 M) at room temperature, scan rate of 100 mV/s, Pt disk working electrode (a radius of 4 mm)

General procedure for the synthesis of phenylanthraquinones To a stirred mixture of benzeneboronic acid (0.15 g, 1.2 mmol) and iodoanthraquinone (0.33 g, 1.0 mmol) in toluene (3.5 mL) was added a 2 M aqueous potassium carbonate solution (2.5 mL) followed by the addition of phase-transfer agent tetra-*n*-butylammonium bromide (0.32 g, 1.0 mmol). The mixture was bubbled with argon for 15 min. Then, tetrakis(triphenylphosphine)palladium(0) [Pd(PPh$_3$)$_4$] (0.05 g, 0.04 mmol) was added, and the mixture was bubbled with argon for an additional 10 min. The mixture was vigorously stirred at 90 °C for 24 h under argon. After the mixture was cooled to room temperature, it was diluted with chloroform and washed with water (3×5 mL).

The organic layer was dried over $MgSO_4$ and evaporated. The crude product was collected by filtration and purified by silica gel column chromatography, eluting with hexane/methylene chloride=1/1.

1-Phenylanthraquinone (2) Yield: 98% M.p.: 178–179 °C; δ_H (300 MHz, CDCl$_3$): 8.37 (d, $^3J_{HH}$=7.2 Hz, 1 H), 8.25 (s, 1 H), 8.10 (s, 1 H), 7.73 (s, 3 H), 7.59 (d, $^3J_{HH}$=6.9 Hz, 1 H), 7.44 (s, 3 H), 7.30 (s, 2 H); δ_C (75 MHz, CDCl$_3$): 183.3 (C=O), 183.2 (C=O), 144.3, 141.9, 137.7, 134.7, 134.5, 134.2, 133.6, 132.8, 132.7, 130.8, 128.0, 127.9, 127.3, 127.2, 126.7; FT-IR (KBr, cm^{-1}): 3,098 (w), 3,061 (w), 1,673 (s), 1,593 (m), 1,577 (m), 1,319 (s), 1,275 (s), 1,159 (m), 949 (m), 789 (m), 760 (m), 707 (s); MS (*m/z*): 284.3 (M$^+$).

2-Phenylanthraquinone (4) Yield: 96% M.p.: 158–159 °C; δ_H (300 MHz, CDCl$_3$): 8.50 (s, 1 H), 8.31–8.35 (m, 3 H), 7.80 (d, $^3J_{HH}$=7.7 Hz, 1 H), 7.78 (s, 2 H), 7.70 (d, $^3J_{HH}$=6.8 Hz, 2 H), 7.44–7.50 (m, 3H); δ_C (75 MHz, CDCl$_3$): 183.1 (C=O), 182.8 (C=O), 146.7, 138.8, 134.1, 134.0, 133.8, 133.6, 133.5, 132.3, 132.1, 129.1, 128.8, 128.0, 127.3, 127.2, 127.1, 125.5; FT-IR (KBr, cm^{-1}): 3,063 (w), 3,035 (w), 1,675 (s), 1,593 (s), 1,330 (s), 1,308 (s), 1,161 (w), 931 (m), 906 (m), 859 (w), 709 (s); MS (*m/z*): 284.3 (M$^+$).

Preparation of the gel electrolyte The gel electrolyte used for electrochromic devices was prepared using LiClO$_4$:ACN:PMMA:PC in the ratio of 3:70:7:20 by weight. After the dissolution of LiClO$_4$ in ACN, poly(methyl methacrylate) (PMMA), (M, 350,000) was added into the solution. Vigorous stirring and heating was applied to dissolve

Fig. 3 UV-vis absorption spectra of PAQs in CH_2Cl_2 at room temperature in neutral and radical anion states. **a** **2** (3.0×10^{-4} M containing 0.1 M TBAP) in neutral state; **b** **4** (1.5×10^{-4} M containing 0.1 M TBAP) in neutral state; **c** **2** (3.0×10^{-4} M containing 0.1 M TBAP) in radical anion state; **d** **4** (1.5×10^{-4} M containing 0.1 M TBAP) in radical anion state
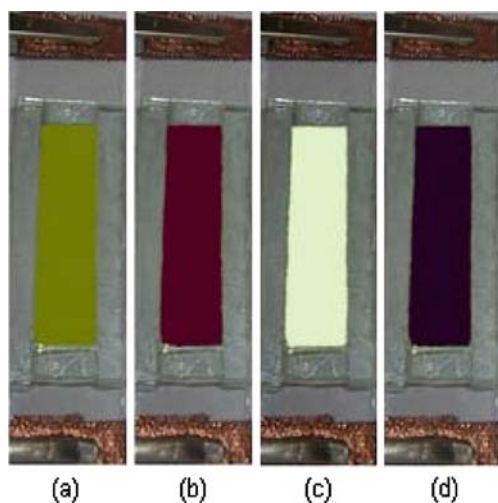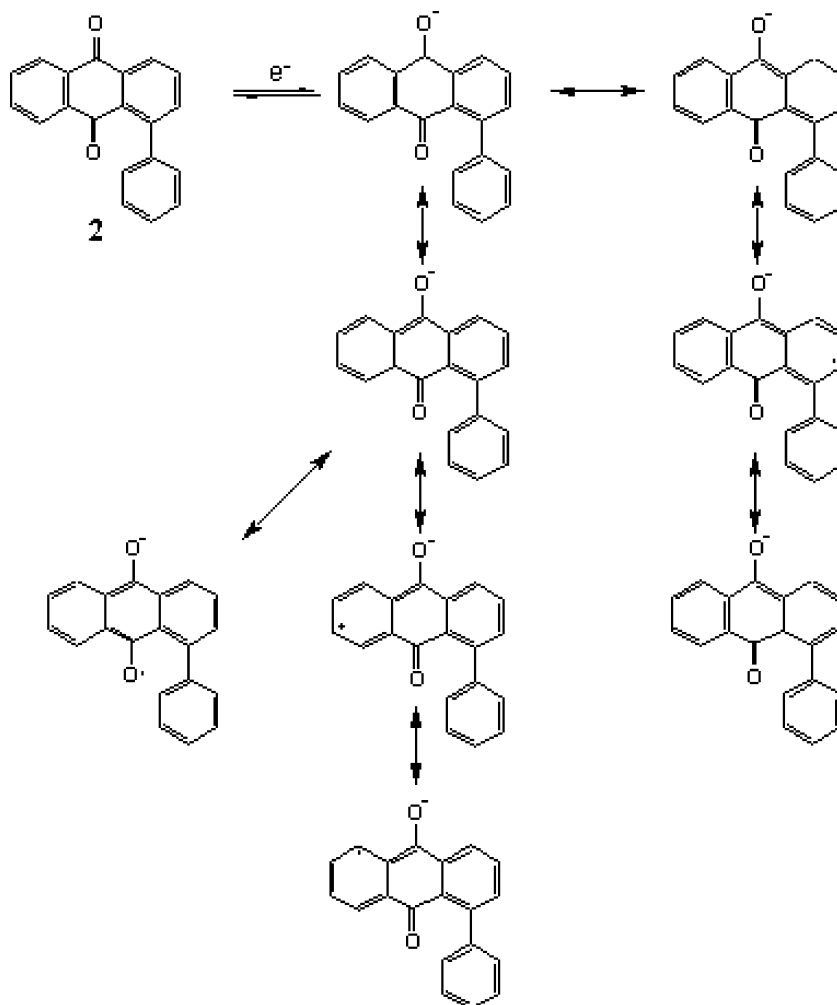
Fig. 4 Photographs of EC devices in neutral and redox states. **a 2** in neutral state, **b 2** in redox state at a potential of −3.5 V, **c 4** in neutral state, **d 4** in redox state at a potential of −3.0 V

PMMA. Propylene carbonate (PC), as plasticizer, was introduced to the reaction medium when all of the PMMA was completely dissolved. The mixture was stirred and

heated until the highly conducting transparent gel was produced [36].

EC devices fabrication The PAQs were dissolved in a solution of polyvinyl formal (PVF) polymer in THF. Then the mixture was spread on ITO/glass (10 Ω) by spin-coating and dried in vacuum desiccator. The gel electrolyte was spread on ITO/glass (10 Ω) by spin-coating to make the counter electrode. Electrochromic devices with PAQs on ITO/glass (10 Ω) and the corresponding counter electrode were laminated together at elevated temperature and pressure. The edges of the devices were sealed with an insulating epoxy resin (Fig. 1). Electrical contacts were produced by applying an electrically conducting copper tape onto overlapping ITO/glass areas. The operation area was about 3.5 × 1 cm^2.

Results and discussion

The synthetic procedure for all derivatives is outlined in Scheme 1. The synthesis of phenylanthraquinones (**2** and **4**)

Scheme 2 Resonance structures and electron delocalization of **2** in radical anion state

was accomplished through the Suzuki coupling reaction between benzeneboronic acid and iodoanthraquinones (**1** and **3**). The preparation of intermediates (**1** and **3**) via the diazotization–Sandmeyer reaction is very important. There was a report about the preparation of 1-iodoanthraquinone that carried out in water and concentrated hydrochloric acid [37]. But it isn't the most useful method for the synthesis of iodoanthraquinones because of the poor solvation of aminoanthraquinones in concentrated hydrochloric acid. The basicity of aminoanthraquinones is too weak owing to two electron-attracting groups (carbonyl) were attached to the amido substituted aromatic ring. Thus, the stronger concentrated sulfuric acid was used instead of concentrated hydrochloric acid as the solvent to get a solution rather than a suspension. Meanwhile, the sodium nitrite was also dissolved in concentrated sulfuric acid instead of water before adding into the solution for the poor stability of diazonium salt in water. As a result, products with the high yield were obtained.

The redox properties of the PAQs were investigated by CV in CH$_2$Cl$_2$ and TBAP as an electrolyte in an electrochemical cell (Fig. 2). Reduction potentials were measured relative to the internal SCE. No product of the reduction of the PAQs adheres to the electrode surface in the proceeding of the whole experiment. For the two PAQs, two reduction waves were revealed, indicating the formation of stable radical anions and dianions, respectively. 1-PAQ is reduced at the higher potential $\left(E_{red1}^0 = -1.39\text{V}, E_{red2}^0 = -1.92\text{V}\right)$ and 2-PAQ shows the lower potential $\left(E_{red1}^0 = -1.21\text{V}, E_{red2}^0 = -1.71\text{V}\right)$. These data are quite different from that of the unsubstituted anthraquinone which has only one redox peak under the same conditions. So, the board CVs are specific to PAQs. The above data suggest that the positions of substituted groups can strongly influence the electrochemical properties of anthraquinone derivatives. These results indicate that the electron structure of anthraquinone derivatives can be efficiently tuned by introducing substituted groups at different substituted positions.

The spectrochemical properties of the PAQs were determined by UV-vis in dichloromethane. Figure 3a, b shows the normalized UV-vis absorptions of 1-PAQ and 2-PAQ, respectively. Two distinct absorption bands are observed. The strong absorption peaks of **2** at 253 nm while **4** at 245 nm, the shoulder peaks of **2** at 272 nm while
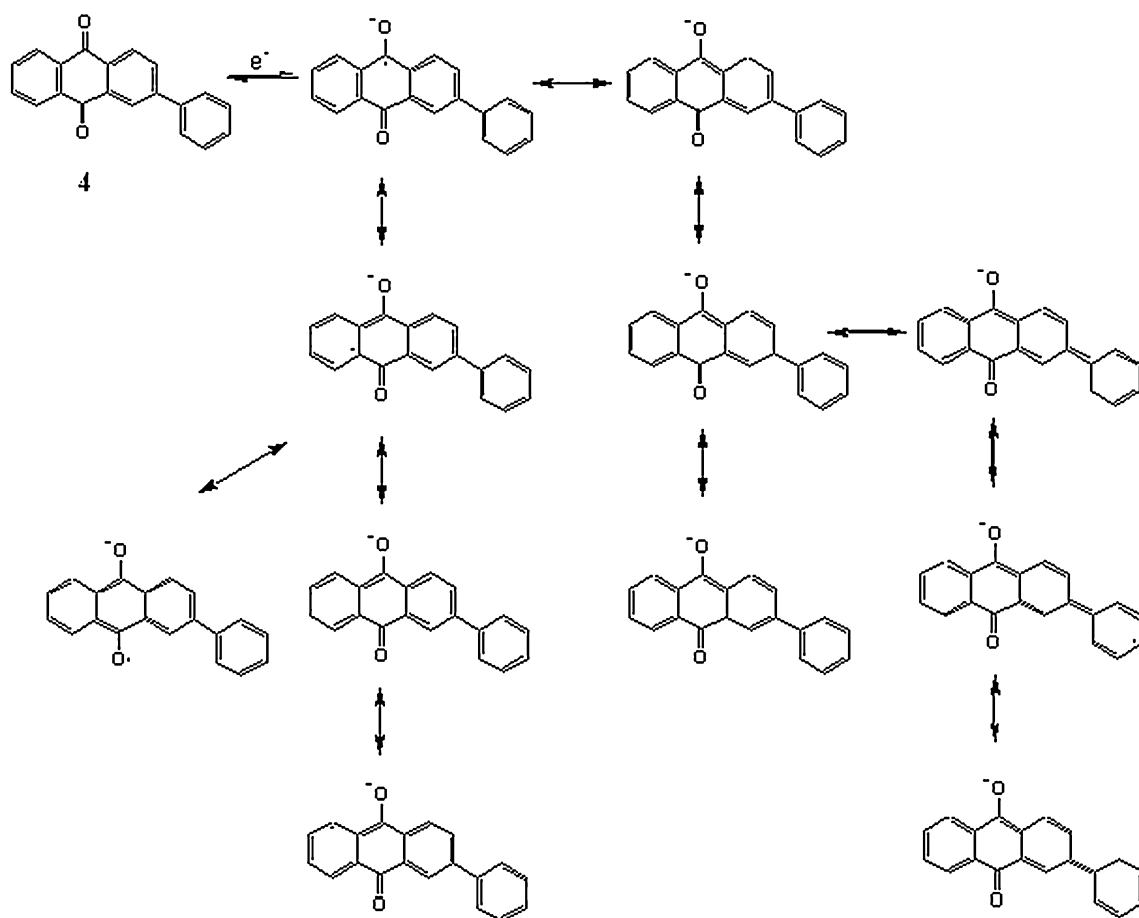
Scheme 3 Resonance structures and electron delocalization of **4** in radical anion state

4 at 274 nm, and side peaks of **2** at 331 nm while **4** at 340 nm are assigned to K band, B band, and R band, respectively. The small distinction is induced just by the different substituted positions of the phenyl group. Spectro-electrochemical work was done on the PAQs in order to investigate their EC properties (Fig. 3c, d). When the PAQs were reduced to radical anions, the UV-vis absorptions appeared in the range of 450–600 nm with maximal peaks at 511 and 556 nm for **2**, whereas in the range of 450–650 nm with maximal peaks at 567 and 586 nm for **4**. In the neutral state, **2** is yellow (Fig. 4a) while **4** is yellow-green (Fig. 4c). When a potential of −3.5 V is applied to **2**, the device color shifts to claret (Fig. 4b) as a result of a reduction, whereas **4** switches to a dark blue-purple (Fig. 4d) at a potential of −3.0 V. They return to the original state after withdrawing the potentials. The applied potentials for coloration are high because the coloration voltage of EC devices is controlled by the gel electrolyte and concentration of PVF besides the redox properties of electrochromic materials. The response time of both EC devices is 450 ms. The number of EC circulation for the EC devices was over 10^5.

According to the above results and resonance theory [38], we can deduce that, in the radical anion state, **4** is in a higher degree of electron delocalization than **2**. Schemes 2 and 3 particularly depict the resonance structures and electron delocalization of **2** and **4** in the radical anion state, respectively. The radical electron can delocalize to the phenyl group in **4** but it can't in **2**.

Conclusions

In summary, 1-/2-phenyl substituted 9,10-anthraquinones were synthesized through the diazotization–Sandmeyer and Suzuki coupling reactions. It has been shown that they are efficient and reversible electrochromic materials and their solid electrochromic devices were prepared. When reduced, the device color of 1-phenyl-9,10-anthraquinone shifts from yellow to claret while that of 2-phenyl-9,10-anthraquinone switches from yellow-green to dark blue-purple. They are potentially to be widely applied in commercial application for the excellent behaviors plus the inexpensive starting materials and short synthetic routes.

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