



Isomer effect on the near-infrared electrochromism of anthraquinone imides



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ABSTRACT

To deeply explore the interplay between molecular structure and near-infrared electrochromism of anthraquinone imides, two pairs of unsubstituted isomers (**1a** and **1b**) and nitro-substituted isomers (**11a** and **11b**) of anthraquinone imides were synthesized, in which the molecules **1a** and **11a** took more linear shapes than **1b** and **11b**. Cyclic voltammetry and spectroelectrochemistry were combined to investigate their electrochemical properties. Cyclic voltammetry showed that **1b** and **11b** revealed decreased first reduction potentials and low cyclic stability compared to their isomers, indicating that the isomerization weakened the stabilization effect. Upon one-electron reduction, both the absorption wavelengths and absorption intensities of radical anions were greatly dependent on the structures of isomers. The radical anions of **1a**, **11a**, and **11b** illustrated NIR absorptions peaked at 820, 1260, and 1380 nm, respectively, but that of **1b** exhibited only weak absorption in the visible region centered at 660 nm. Gaussian calculations suggested that the electrons were delocalized over the whole molecular skeletons of **1a** and **11a** radical anions, but the effective conjugation length was interrupted on the imide section in both **1b** and **11b**. The isomer effects on the effective conjugation length and electron density distribution were considered to rationalize the different electrochromic behaviors.

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1. Introduction

Near-infrared (NIR) electrochromic (EC) materials have been attracting considerable attention for their promising applications in military and civilian fields [1–4]. Despite the fact that the most extensively explored NIR EC materials are inorganic compounds, including transition metal oxides [5,6] and transition metal complexes [7–9], organic EC compounds with NIR absorptions are emerging as potential alternatives due to their several advantages, such as tunable structure, solution-processability, fast response, and high color contrast ratio [10–12]. Actually, in the past decade, a large number of p-type materials, including poly(triarylamine)s [13,14] and conjugated conducting polymers [15–17], have been investigated as NIR EC materials. Nevertheless, in comparison with the well-investigated organic anodically NIR EC materials, cathodically EC materials are relatively less concerned, mainly owing to the limited number of n-type materials, low long-term stability of radical anions, and undefined

structure-property relationship.[18] With the development of material science, it is urgent to develop cathodic materials to form complementary circuits with the available anodic ones. Besides, cathodic materials can be operated at relatively low voltages, which can avoid the degradation problem of materials at high potentials. Aromatic imides [19–21] and aromatic quinones [22–25] are two kinds of cathodically active systems that display intense absorptions in the telecommunication wavelength range (i.e., 1310 and 1550 nm) upon one-electron reduction. For example, a NIR optical band arising from the excitation of π -electrons along the stacks appears when reduced naphthalene diimides form ordered π -stacks in solution [26] or gel [19]. Concerning the diquinone compounds, the effects of substituent structure, number of quinone motif, and EC mechanism on the radical anionic absorptions have also been systematically investigated by Miller and co-workers [23–25]. However, the tedious synthetic routes and poor solubilities hamper their further practical applications.

Recently, a novel kind of cathodically NIR EC materials named anthraquinone imides (AQIs) [27–34], simultaneously containing the advantages of quinone and imide units, were reported by our group. Unsubstituted AQIs [28] or AQIs substituted with electron-donating groups [32] exhibit intensive NIR absorptions

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peaked at around 820 nm in their radical anionic states arising from $\pi^*-\pi^*$ transitions. The substitution with electronegative groups remarkably red-shifts the radical anionic absorptions [28,33]. The introduction of AQI chromophores into helical polymers [29,34], liquid crystalline compounds [30], and low molecular mass organic organic gelators [31] demonstrate interesting electrochemically triggered chiroptical switching properties. However, most of these systems exhibit NIR electrochromism only at around 820 nm, which is far shorter than the telecommunication wavelength range. It is desired to deeply understand the structure-property relationship and tune the radical anionic absorptions of AQIs. Isomer effect has been known to possess important influence on the performances of photoelectric materials, such as organic solar cells and organic thin film transistors [35–38]. It functions by affecting the electron density distributions and the closely related intramolecular or intermolecular interactions. But no work has been reported concerning with the isomer effect on the NIR electrochromism of AQIs as well as other organic n-type NIR EC materials.

To achieve this objective, four AQI derivatives, i.e., N-(1-hexylheptyl)anthraquinone-2,3-dicarboxylic imide (**Ia**), N-(1-hexylheptyl)anthraquinone-1,2-dicarboxylic imide (**Ib**), N-(1-hexylheptyl)-6-nitro-anthraquinone-2,3-dicarboxylic imide (**IIa**), and N-(1-hexylheptyl)-6-nitro-anthraquinone-3,4-dicarboxylic imide (**IIb**) were synthesized (Chart 1). Among them **Ia** and **Ib**, **IIa** and **IIb** are isomers, respectively. Their electrochemical properties were investigated by cyclic voltammetry and spectroelectrochemical methods. With the addition of one electron, both the absorption wavelengths and absorption intensities varied a lot between different isomers. Density-functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed to rationalize the isomer effect observed.

2. Experimental

2.1. Materials

All chemical reagents were of analytical grade and purchased from J&K, Aldrich, Acros, and TCI Chemical Co. Dichloromethane (DCM) and N-dimethylformamide (DMF) were dried and distilled over CaH₂, and stored over 0.4 nm molecular sieves prior to use. Other chemicals were used without further purification. 9,10-Anthraquinone-2,3-dicarboxylic anhydride [27], 9,10-anthraquinone-1,2-dicarboxylic acid [39], and N-(1-hexylheptyl)amine [40] were prepared according to the reported procedures. 6-Nitro-9,10-anthraquinone-dicarboxylic anhydrides were synthesized with the published procedure of 6-nitro-9,10-anthraquinone-2,3-dicarboxylic anhydride [28].

2.2. Characterizations

¹H NMR, ¹³C NMR, and heteronuclear multiple bond coherence (HMBC) spectra were measured on a Bruker AVANCE III (400 MHz)

spectrometer at ambient temperature with CDCl₃ as the solvent. Chemical shifts in ¹H NMR and ¹³C NMR were recorded in ppm with tetramethylsilane as a standard. High-resolution mass spectra were recorded on a Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer. Elemental analyses were performed on an Elementar Vario EL instrument.

UV-vis-NIR absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. The cyclic voltammetry and differential pulse voltammetry measurements were carried out on a CHI840B electrochemical workstation in CH₂Cl₂ solutions containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte. A three-electrode assembly was used with a platinum disk as working electrode, a platinum wire as counter electrode, and a silver wire as pseudo-reference electrode. All the experimentally measured redox potentials were calibrated externally using a solution of ferrocene (Fc/Fc⁺). Spectroelectrochemical measurements were carried out on a Hitachi U-4100 spectrophotometer connected to electrochemical workstation in an optical transparent thin layer (OTTLE) cell [41]. Before every electrochemical measurement, the solution was degassed with nitrogen to exclude the trace oxygen.

2.3. Computational methods

The Gaussian calculations were performed with the Gaussian 09 program package [42]. The geometries of all AQI molecules in both the neutral and radical anionic states were fully optimized using Kohn-Sham Density Functional Theory (DFT) based on the Becke's three parameter hybrid functional B3LYP with the 6-31+G(d, p) basis set [43] and followed by vibrational-frequency calculations to confirm that real minima were obtained. To simplify the calculations, the methyl group was employed to replace the long alkyl chain. For radical anions, the corresponding spin-unrestricted approach was used. The frontier molecular orbital (MO) energy levels were calculated based on the optimized structures. TD-DFT was employed to simulate the vertical transitions of the first 10 states at the UB3LYP/6-31+G(d, p) level. In all cases, the solvation effects were considered using the polarizable continuum model (PCM) with CH₂Cl₂ as the solvent. In addition, the orbital pictures were prepared using GaussView [44].

2.4. Synthesis

2.4.1. N-(1-hexylheptyl)anthraquinone-2,3-dicarboxylic imide (**Ia**)

9,10-Anthraquinone-2,3-dicarboxylic anhydride (0.28 g, 1.0 mmol), anhydrous DMF (12 mL), and N-(1-hexylheptyl)amine (0.22 g, 1.1 mmol) were successively added into a 50 mL three-necked flask under nitrogen. After stirring for 1 h at room temperature, the mixture was heated to reflux for 4 h. After cooling to room temperature, the solution was poured into a dilute hydrochloric acid solution (100 mL). The precipitated solids were filtrated and washed with methanol. After drying, the product was purified by chromatography (silica gel, petroleum

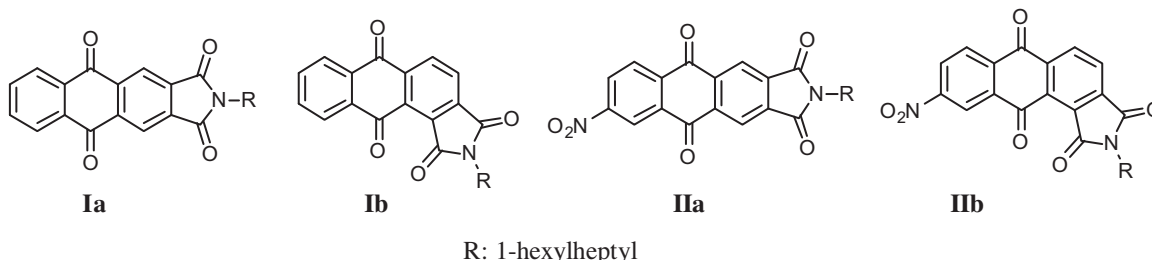


Chart 1. Chemical structures of four AQI molecules.

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