ORGANIC
LETTERS

2008
Vol. 10, No. 4
641−644

Efficient Synthesis and Properties of Novel Near-Infrared Electrochromic Anthraquinone Imides

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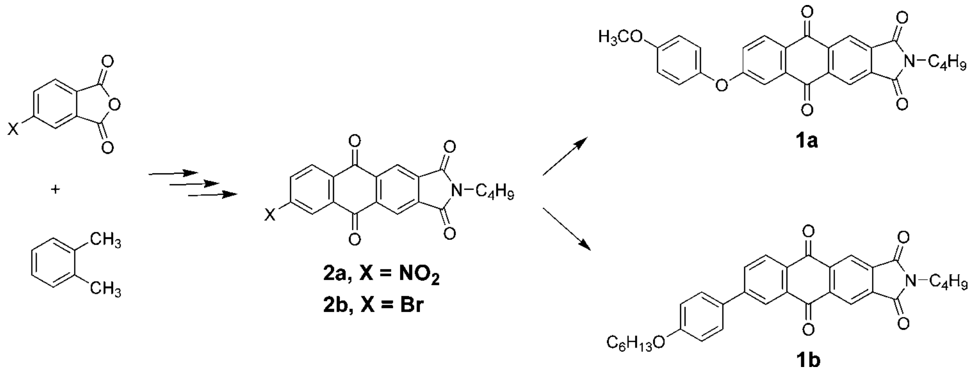
Received December 13, 2007

ABSTRACT



An efficient synthesis of novel near-infrared electrochromic 6-substituted (NO_2, Br) anthraquinone imides, i.e., 2a and 2b, was established. Bearing functional groups suitable for further structural modifications by nucleophilic substitution reaction and various metal-catalyzed coupling reactions (e.g., Suzuki coupling), 2a and 2b were easily transferred to 1a by reaction with 4-methoxyphenol and 1b by reaction with 4-hexyloxyphenylboronic acid, respectively. These new imides are electrochromic and absorb intensely in the near-infrared range of 700–1600 nm upon electrochemical reduction.

Electrochromic (EC) materials are known to have wide applications in fields such as smart windows, variable reflectance mirrors, and information display and storage devices.[1] Currently, most studies with EC materials are concerned with optical changes in the visible spectral region; meanwhile, near-infrared (NIR)-absorbing EC materials are receiving more attention due to their potential applications in optical communications,[2] biomedicals,[3] camouflage materials in warfare,[4] and thermal control and thermal emission detectors for spacecraft.[5]

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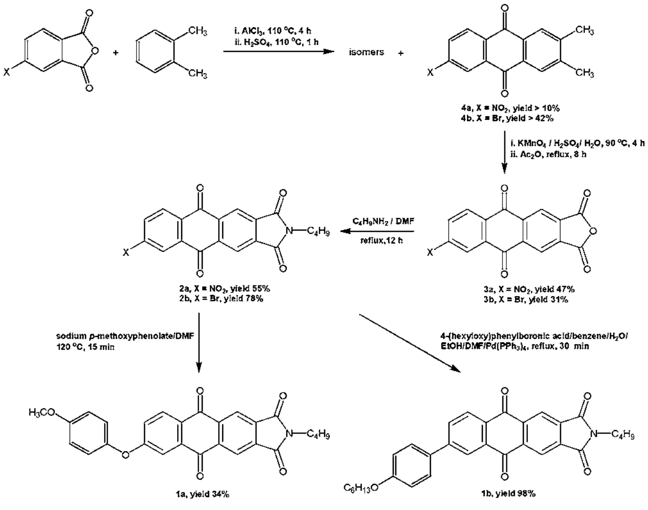
10.1021/ol703001s CCC: $40.75 © 2008 American Chemical Society
Published on Web 01/19/2008

Up to now, various types of NIR electrochromic materials have been developed, including transition-metal complexes,[6] viologens, conjugated polymers,[7] aromatic diquinones,[8] and aromatic imides.[9] Among them, we are particularly interested in anthraquinone imides (AQIs). Upon electrochemical reduction to the state of radical anion, they strongly absorb in a range of 700−1200 nm, which has much less optical interference for tissue and other biological studies. Difficulties with the synthesis of functionalized AQIs hamper further exploration of AQIs as NIR electrochromic materials in various applications. To the best of our knowledge, there is still no AQI bearing functional groups on the anthraquinone moiety that could tune the electrochromic properties.[10] Herein, we report an efficient synthesis of a new type of anthraquinone imides bearing the functional groups (i.e., nitro and bromo groups) at the 6-position on the anthraquinone moiety, i.e., *N*-butyl-6-nitroanthraquinone-2,3-dicarboxylic imide (**2a**) and *N*-butyl-6-bromoanthraquinone-2,3-dicarboxylic imide (**2b**). The high reactivity of the nitro and bromo groups, due to the activation effect of electrodeficient quinone unit, allows for easy functionalization through the nucleophilic substitution reaction and metal-catalyzed coupling reaction (e.g., Suzuki coupling). In this regard, two new modified anthraquinone imides, i.e., *N*-butyl-6-(4-methoxyphenoxy)anthraquinone-2,3-dicarboxylic imide (**1a**) and *N*-butyl-6-(4-hexyloxyphenyl)anthraquinone-2,3-dicarboxylic imide (**1b**) were synthesized by reacting **2a** with 4-methoxyphenol and **2b** with 4-hexyloxyphenylboronic acid, respectively. All the intermediates and compounds were fully characterized by spectroscopic means.

Cyclic voltammetry of these imide compounds showed two one-electron reduction processes, corresponding to the radical anion and dianion states of anthraquinone imide, respectively. Upon reduction to the radial anion, all compounds exhibited intense absorptions in the NIR range.

Scheme 1. Synthetic Route of Target Molecules



For the synthesis of 6-substituted anthraquinone imides (i.e., **2a**, **2b**, **1a**, **1b**), important intermediates, i.e., **3a** and **3b**, were first prepared via a multistep synthetic route as shown in Scheme 1. Friedel−Crafts acylation of *o*-xylene with 4-nitro (or bromo)-phthalic anhydride in the presence of anhydrous aluminum chloride, followed by ring-closure reaction using sulfuric acid yielded 6-substituted-2,3-dimethylanthraquinones. Due to the monosubstitution, four isomers could be expected in the first acylation step and three isomers after the cyclization. Although effort was initially made to separate all four isomers from the first acylation step, it turned out to be time-consuming and inefficient. Thus, isolation and purification were carried out on 6-nitro-2,3-dimethylanthraquinone (**4a**) and 6-bromo-2,3-dimethylanthraquinone (**4b**). Column chromatography was inefficient in separation of **4a** from other isomers. Three recrystallizations from toluene resulted in a mixture of needlelike and grainlike crystals, which were confirmed to be the three isomers, **4a**, 6-nitro-1,2-dimethylanthraquinone, and 7-nitro-1,2-dimethylanthraquinone from the proton NMR and mass spectroscopic studies. Fortunately, it was found that the needlelike crystals had a much better solubility in dichloromethane than the other grainlike crystals. Thus, the crystalline mixture was further treated with dichloromethane, followed by removal of solvent and recrystallization from toluene again, to yield pure **4a** (mp = 220.8−222.0 °C) in an overall yield of 10% based on 4-nitrophthalic anhydride (not including the recovered product). The ^{1}H and ^{13}C NMR spectra (Figures S1 and S2) confirmed its correct structure. The residue after removal of **4a** contained a mixture (mp = 162.3−166.1 °C) of roughly equal amounts of the other two isomers as indicated by ^{1}H and ^{13}C NMR spectra (Figures S3 and S4). The separation and purification of **4b** was relatively easier. Recrystallization from acetic acid and petroleum ether (1/1, v/v) 4 to 5 times yielded pure **4b** (mp = 194.8−196.0 °C) in an overall yield of 42%. Its structure was confirmed by NMR and mass spectroscopy and elemental analysis.

The oxidation of **4a** and **4b** was accomplished by using $KMnO_4$ in an acidic solution.[11] The resulting diacids were

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[10] There are a few articles concerning the substitution of anthraquinone-2,3-dicarboxylic anhydride (**AQA**). However, with these limited published methods, only 5-nitroanthraquinone-2,3-dicarboxylic acid or the mixtures of different isomers of nitro-substituted **AQA** can be obtained, and no **AQI** with functional groups on the aromatic ring has ever been reported. (a) Gundermann, K. D.; Klockenbring, G.; Röker, C.; Brinkmeyer, H. *Liebigs Ann. Chem*. **1976**, 1873. (b) Borisov, A. V.; Maizlish, V. E.; Shaposhnikov, G. P. *Russ. J. Gen. Chem*. **2005**, *75*, 1151. (c) Sun, S. S.; Desper, J. *Tetrahedron* **1998**, *54*, 411.

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readily purified by dissolution in aqueous ammonia solution followed by acidification.

6-Nitro-/bromo-substituted anthraquinone imides, i.e., **2a** and **2b**, were then prepared by imidization of the corresponding anhydrides (refluxing the diacids in acetic anhydride) with *n*-butyl amine (Scheme 1). Due to the activation effect of the electron-deficient benzoquinone unit, the nitro and bromo groups should have high reactivity toward nucleophilic substitution reaction and metal-catalyzed coupling reaction (e.g., Suzuki coupling), which allows for further modification. Thus, **1a** was first prepared in a moderate yield of 34% by reacting **2a** with 4-methoxyphenol. Caswell and co-workers[12] reported that *N*-substituted phthalimide could activate the 3-nitro group, but the nucleophilic substitution yields were very low, possibly due to the imide hydrolysis. The Suzuki coupling reaction of **2b** with 4-hexyloxyphenylboronic acid was also carried out to give a 6-aryl-substituted anthraquinone imide (**1b**) in 98% yield. Substitution at the 6-position with different electron-donating and -withdrawing groups is expected to tune the redox and NIR electrochromic properties of anthraquinone imides.

The redox properties of the new **AQI** derivates were investigated by cyclic voltammetry in CH_2Cl_2 and tetra-*n*-butylammonium perchlorate (TBAP) as an electrolyte (Figure 1). Reduction potentials were measured relative to the internal standard ferrocene/ferricenium (Fc/Fc+) (Table 1). For the three compounds, **1a**, **1b**, and **2b,** two reduction waves were revealed, indicating the formation of stable radical anions and dianions, respectively. However, the CV curve of **2a** exhibited three reduction processes. According to electron effect, **2a**, which has the strongest acceptor nitro is reduced at the highest potential ($E^o_{red1} = -0.82$ V, $E^o_{red2} = -1.32$ V), **2b** at $E^o_{red1} = -0.99$ V, $E^o_{red2} = -1.49$ V, **1b** at $E^o_{red1} = -1.07$ V, $E^o_{red2} = -1.51$ V, whereas **1a** shows the lowest potentials ($E^o_{red1} = -1.07$ V, $E^o_{red2} = -1.53$ V). In addition, the substituted effect of nitro causes the carbonyl in imide moiety to be reduced at $E^o_{red3} = -1.86$ V. From the above discussion we find that electron effect of substituted groups can strongly influence the electrochemical properties of **AQI**. These results indicate that the electron structure of **AQI** can be efficiently tuned by introducing different substituted groups.

Table 1. Electrochemical Properties[a] of the AQI Derivates

cmpd	E^o_{red1} (V)	E^o_{red2} (V)	E^o_{red3} (V)
2a	−0.82	−1.32	−1.86
2b	−0.99	−1.49	−
1a	−1.07	−1.53	−
1b	−1.07	−1.51	−

[a] $c = 5 \times 10^{-3}$ mol/L in CH_2Cl_2/TBAP (0.1 M) vs Fc/Fc^+ at 100 mV/s.

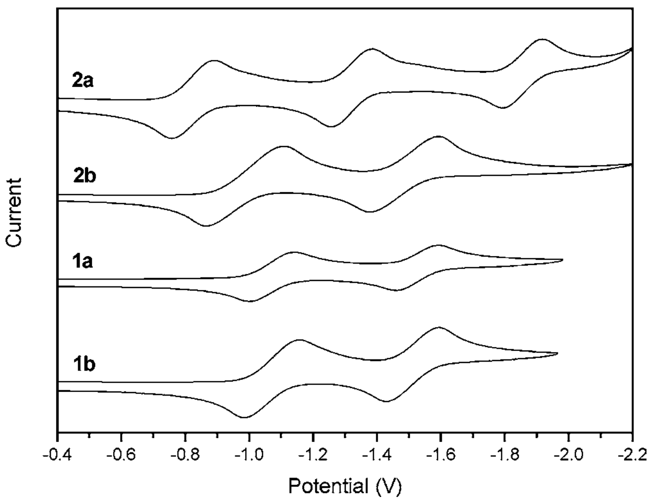

Figure 1. Cyclic voltammograms of AQI derivates in CH_2Cl_2/TBAP (0.1 M) at room temperature, scan rate of 100 mV/s, Pt disk working electrode, potentials vs Fc/Fc^+.

Spectroelectrochemical work was done on the **AQI** derivatives in order to investigate their NIR EC properties. Figures 2 and 3 illustrate the spectroelectrochemical spectra of **2a** and **2b** in dichloromethane containing 0.1 M TBAP. Upon one-electron reduction to radical anions, intense NIR absorptions appeared in the range of 700−1600 nm with maximal peaks at 863 and 1267 nm for **2a**, whereas in the range 700−1100 nm the peak for **2b** centered at 808 nm. These NIR absorptions can be attributed to $\pi^*-\pi^*$ (SOMO → LUMO) transitions of the radical anions of the imides.[9a] Further reduction to dianions resulted in the disappearance of the NIR absorptions and the appearance of new absorption bands at 522, 672 nm for **2a** and 447 nm for **2b**. Spectroelectrograms of other two **AQI** derivates, **1a** (Figure S17) and **1b** (Figure S18) are similar to the spectrum of **2b**. But the maximal absorption wavelengths are different. In anionic state, the NIR absorption centered at 810 and 827 nm for **1a** and **1b**, respectively. Otherwise, when they were reduced

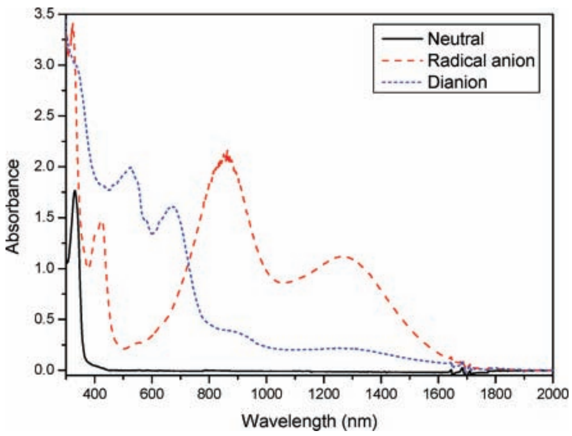

Figure 2. UV/vis/NIR absorption spectra of **2a** (10^{-3} M containing 0.1 M TBAP) and its electrochemically generated radical anion and dianion in CH_2Cl_2.

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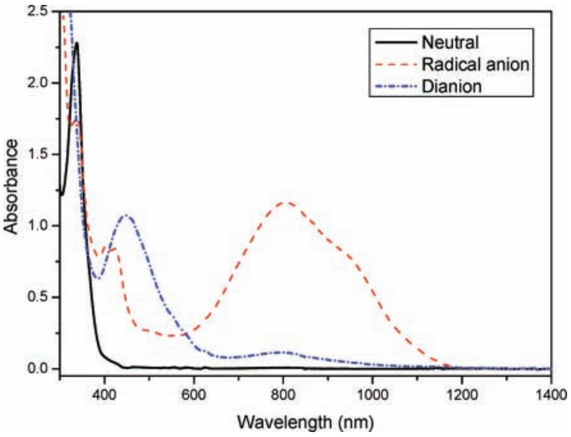

Figure 3. UV/vis/NIR absorption spectra of **2b** (10^{-3} M containing 0.1 M TBAP) and its electrochemically generated radical anion and dianion in CH_2Cl_2.

into dianionic state, a new absorption band appeared at 524 nm for **1a** and 541 nm for **1b**. Simultaneously, the absorption in NIR region disappeared. The above results proved that the electrochromic wavelength range of **AQI** could be modulated by substitution on the ring and by extending the conjugating length. Strong electron-withdrawing substituents led to a large red-shift in the absorption of anions. Increasing the conjugating length of the molecule had a similar effect.

In conclusion, we have established an efficient method for the syntheses of 6-nitro (and bromo)-substituted anthraquinone imides and demonstrated further functionalizations through the nitro displacement and Suzuki coupling reactions. The new anthraquinone imides are redox active and NIR electrochromic in a range of 700−1600 nm and potentially useful as an NIR tag for tissue and other biological studies.

Acknowledgment. This work was financially supported by the National Distinguished Young Scholar Fund (No. 20325415), the Research Fund for Doctoral Program of Higher Education of MOE (No. 20060001029), and the China Postdoctoral Science Foundation (No. 20060390357).

Supporting Information Available: Synthesis and characterization for all the key intermediates and target molecules (including NMR spectra), and spectroelectrochemical spectra of **1a** and **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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