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Electrochromism of a Fused Acceptor–Donor–Acceptor Triad Covering Entire UV–vis and Near-Infrared Regions

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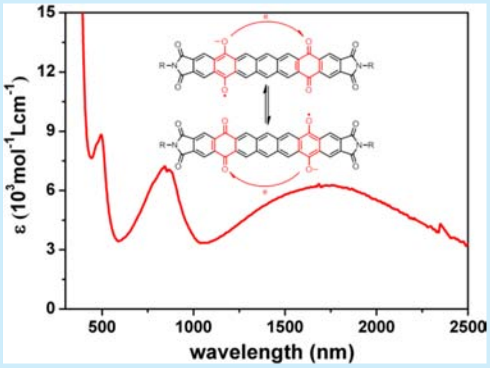
S *Supporting Information*

ABSTRACT: A novel fused acceptor–donor–acceptor (A–D–A) type panchromatically electrochromic compound was synthesized. It exhibited intensive absorption bands covering entire UV–vis and near-infrared regions upon reduction to the radical anionic state, owing to the simultaneous presence of $\pi^*-\pi^*$ transitions and intervalence charge transfer.



Organic electrochromic materials operating within both UV–vis and near-infrared (NIR) regions have attracted increased attention due to their potential applications in many fields such as smart windows and military camouflage, as well as the advantages over their inorganic counterparts of low cost, large area flexibility, good solution processability, and high color contrast.[1] In comparison with the well-investigated anodically electrochromic materials (e.g., poly(triarylamine)s, conjugated polymers),[2] cathodically active materials are less approached although they are in high demand as complementary layers to enhance corresponding device performance. This is probably due to the instability of a radical anion and the lack of reliable molecular design strategy,[3] especially an efficient way to achieve intensive absorptions in the NIR region through small molecules. Many mechanisms, including a stacking-induced optical band,[4] a $\pi^*-\pi^*$ transition,[5] and an intervalence charge transfer (IV-CT) band,[6] have been proposed to generate NIR electrochromism. Among them, the IV-CT band from mixed-valence (MV) compounds is of significant importance since it can dramatically extend the absorption range to the long-wavelength NIR range.[6] The radical anions of a series of diquinone-based compounds are known to absorb light up to 2 μm.[7] However, the rigid anthracene and tetrathiafulvalene fused bridges make them difficult to dissolve in common solvents. In addition, the absorptions in the NIR region are weak.

Anthraquinone imide (AQI) derivatives, including both quinone and imide motifs, represent another kind of NIR cathodically electrochromic materials.[8] With the addition of one electron, the resultant radical anions display intensive absorptions of $\pi^*-\pi^*$ transitions ranging from 780 to 1400 nm, depending on the electronic nature of substituents on the aromatic ring. It was envisioned that the employment of an AQI chromophore as an electron-deficient unit to build a fused acceptor–donor–acceptor (A–D–A) molecule would cause stronger electronic coupling than quinone alone and thereafter result in panchromatic electrochromism by a combination of $\pi^*-\pi^*$ transitions and an IV-CT band. Moreover, the imide groups containing flexible alkyl chains could cause it to become easily dissolved in common solvents. Herein, the synthesis and electrochromism of a fused weak A–D–A molecule **6a** containing two AQI units were reported (Scheme 1). Upon one-electron reduction, it was expected that the IV-CT between each side of the long conjugated molecule could further extend and enhance the NIR absorption.

The synthesis of **6a** started with the imidization of maleic anhydride and substituted aniline (Scheme 1). The subsequent Diels–Alder reaction followed by dehydrogenation and oxidation produced the key intermediate, dienophile **5**.[9] The target **6a** was obtained by another Diels–Alder reaction of **5** with 1,2,4,5-tetrakis(dibromomethyl)benzene.[10] The introduction of alkyl chains enabled **6a** to dissolve readily in apolar or less polar solvents such as toluene, CH_2Cl_2, $CHCl_3$, and THF, but not in strong polar solvents such as CH_3CN, acetone, DMF, DMSO, and CH_3OH. The model compound **6b**, containing only one AQI unit, was also prepared and characterized for comparison (for more synthetic details, see Supporting Information).

Cyclic voltammetry is an effective tool to investigate the MV phenomenon owing to the distinguishing redox behaviors between localized and delocalized compounds. The cyclic voltammogram (CV) of **6a** in CH_2Cl_2 solution (with 0.1 M

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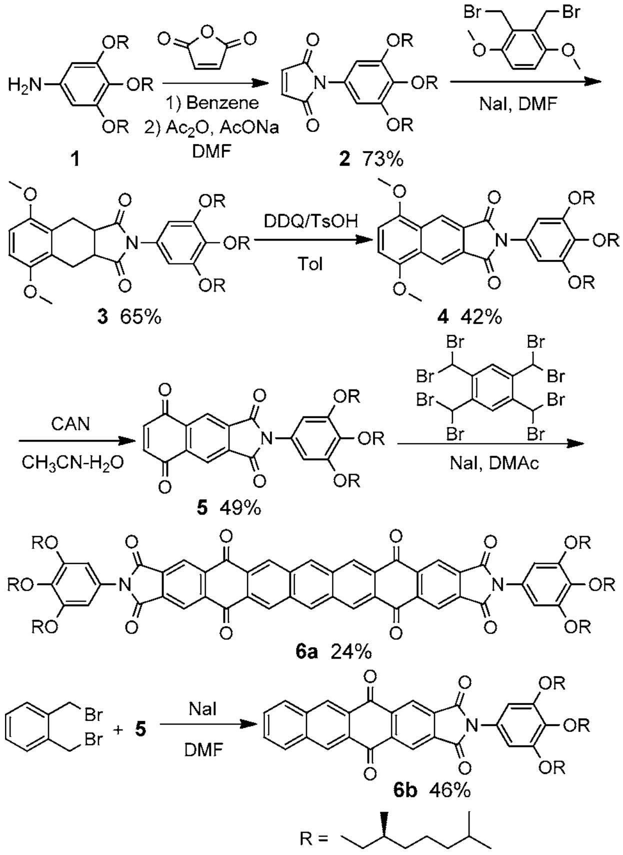
Scheme 1. Synthetic Routes of Molecules 6a and 6b



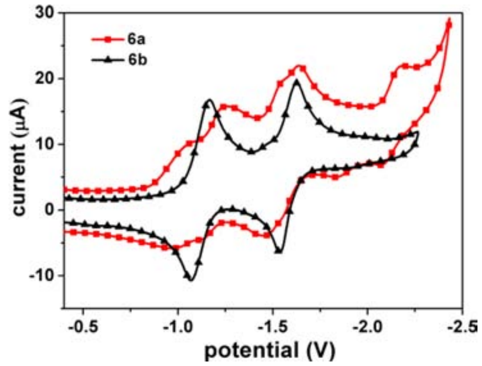


Figure 1. CVs of **6a** and **6b** in CH_2Cl_2/TBAP (0.1 M) at ambient temperature, scan rate of 100 mV/s, Pt disk as working electrode, potentials vs Fc/Fc$^+$.

Table 1. Electrochemical Properties and Corresponding Energy Levels of 6a and 6b[a]

entry	E_{r1} (V)	E_{r2} (V)	ΔE^b (V)	$E_{LUMO}{}^c$ (eV)	$E_{HOMO}{}^d$ (eV)	$E_{LUMO}{}^d$ (eV)
6a	−0.97	−1.15	0.18	−3.83	−6.71	−3.91
6b	−1.11	−1.55	0.44	−3.69	−6.84	−3.58

[a] $c = 4 \times 10^{-4}$ mol/L in CH_2Cl_2/TBAP (0.1 M) vs ferrocene at 100 mV/s, and only the first two reduction potentials were listed. [b] $\Delta E = E_{r1} - E_{r2}$. [c] Found $E_{LUMO} = -(E_{r1} + 4.8)$ (eV).[12] [d] Calculated E_{HOMO} and E_{LUMO} were obtained from Gaussian calculations at the B3LYP/6-31+G(d) level.

TBAP) exhibits multiple redox potentials mainly due to the various redox centers and large conjugation length (Figure 1).[7a,11] The first two reduction potentials of **6a** are −0.97 and −1.15 V (Table 1, Figure S1), respectively. They are attributed to the reductions of quinones since a quinone accepts an electron more easily than an imide.[9] The single peak in the electron paramagnetic resonance (EPR) spectrum of one-electron reduced species of **6a** coincides with such a speculation (Figure S2). This is also confirmed by the fact that other AQIs[8a,f] and **6b** (Figure 1) display only two reversible one-electron reductions of the quinone with no reduction wave of the imide moiety. As shown in Table 1, the redox potential splitting ΔE between the first and second reduction processes for **6a** is 0.18 V, much smaller than 0.44 V for **6b**, and is in the range of the value 0.12−0.25 V of similar MV diquinones reported by Miller,[7a] illustrating the MV nature of **6a**. That is, as one electron is added, the electron is localized at only one side of **6a**, making it easier for the extra electron to be added onto the other side without too much Coulomb repulsion.

Spectroelectrochemical measurements were carried out using an OTTLE cell[13] in CH_2Cl_2 solutions to probe the electrochromic properties of **6a** and **6b** (Figure 2). Before reduction, similar to **6b**, **6a** exhibits weak intramolecular charge transfer (ICT) bands in the visible region (500 nm) and strong $\pi-\pi^*$ absorptions in the ultraviolet region, demonstrating the A−D−A characteristic of **6a** (Figure 2a).

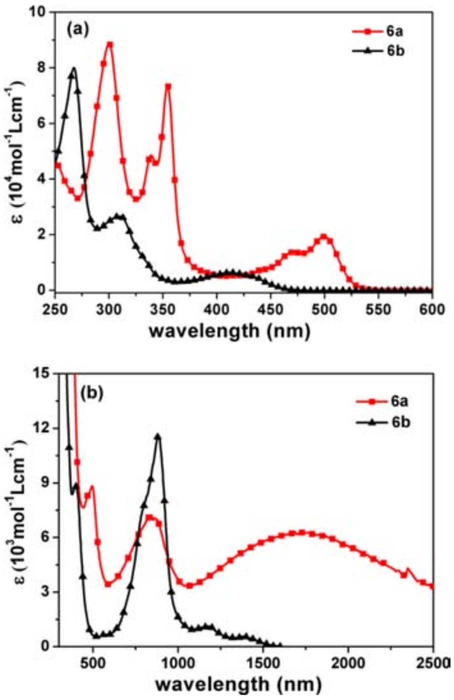


Figure 2. UV−vis and NIR spectra of **6a** and **6b** in CH_2Cl_2 solutions in different states: (a) neutral state; (b) radical anionic state.

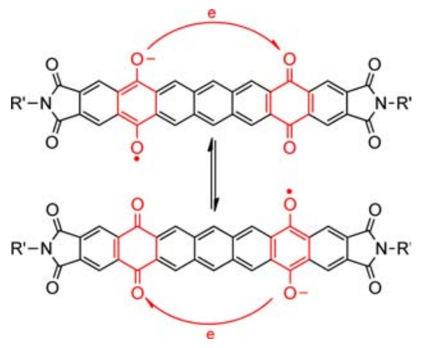
Upon one-electron reduction, the ICT band of **6a** gradually decreases, accompanied by increasing absorption bands covering the entire UV−visible and NIR regions. The **6a** radical anions display two main groups of absorption bands in the NIR region: the one peaked at 860 nm arising from the $\pi^*-\pi^*$ transition is similar to the NIR absorptions of AQIs[8c,f] and the **6b** radical anion (Figure 2b, black line), and the other nearly Gaussian-shaped broad one centered at 1720 nm corresponds to the IV-CT band.[6] According to Hush theory,[14] the electronic coupling (V) between two redox sites can be estimated from the IV-CT band using the equation:

$$V = \frac{0.0206}{d}\sqrt{\tilde{\nu}_{\max}\tilde{\nu}_{1/2}\varepsilon}$$

where $\tilde{\nu}_{\max}$ is the band energy of IV-CT in cm^{-1}, $\tilde{\nu}_{1/2}$ is the half-height bandwidth of the IV-CT band in cm^{-1}, ε is the maximum molar extinction coefficient of the IV-CT band in M^{-1} cm, and d is the effective distance between two redox sites in Å, which can be obtained from semiempirical calculation. The electronic coupling is calculated to be 1000 cm^{-1}, which is less than half of the IV-CT band energy (5813 cm^{-1}). This further classifies the **6a** radical anion as an anionic class II MV compound according to the Robin–Day classification.[15] Notably enough, by combining $\pi^*-\pi^*$ transitions with the IV-CT band, **6a** is capable of cathodically panchromatic electrochromism with considerable molar absorption coefficients at the small molecular level.

The schematic diagram of IV-CT is displayed in Scheme 2. When one electron is added on to **6a**, a little perturbation from the solvent effect or ion-pairing effect causes the electron to be localized at one side of the molecule.[16] There are two fates for the localized electron under external light: the transition at the same side of the molecule brings about $\pi^*-\pi^*$ transition, and an optically induced charge transfer from one side to the other side results in IV-CT.[17] In comparison with the work of Miller and Hudhomme,[7] we suppose that the expanded conjugation length and high electron affinity would make it easier for the perturbation and charge transfer to occur and, thus, result in the enhanced IV-CT band.

Scheme 2. Schematic Diagram of IV-CT Character of 6a Radical Anion in CH_2Cl_2



Furthermore, the **6a** film coated on ITO glass was dipped into CH_3CN/TBAP (0.1 M) solution to characterize the stability of the electrochromic process (Figure S3). With the increasing cycles of potentials between −1.0 and 0.0 V, the color change ratio decreases gradually. Nevertheless, the decreased stability is expected, since the radical anion is sensitive to the trace oxygen and water in solution.[3] More factors should be taken into account to enhance the electrochromic stability.

Gaussian calculations[18] in both neutral and radical anionic states were performed to better understand the experimental observations. In the neutral states, the simulated energy levels (Table 1), the electronic distributions (Figure S4), and the absorption spectra (Figure S5 and Table S1) are all in good agreement with experimental findings. The electron of LUMO orbitals is mainly distributed in the electron-withdrawing quinone and imide units. In the radical anionic states, the calculated results of **6b** are in good agreement with our experimental results that the maximum absorption wavelength is ascribed to $\pi^*-\pi^*$ transition (Figures S6, S7 and Table S2). For the **6a** radical anion, calculations at different levels were conducted (Figure 3). At the UB3LYP/6-31+G(d) level, the single occupied molecular orbital (SOMO) presents a delocalized structure, which is in conflict with the MV character verified by experimental results. This can be explained by the fact that DFT calculation often overemphasizes the stabilization provided by delocalization.[19] The calculation at the UHF/6-31+G(d) level provides a localized electron. Despite the possibility of overlocalizing the electron due to the lack of correlation,[20] it is still meaningful to qualitatively interpret the experimental results. More comprehensive calculations regarding this MV compound are still ongoing in our laboratory.

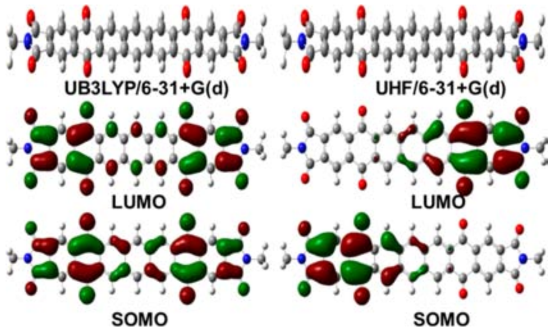


Figure 3. Optimized geometries and frontier MOs of **6a** radical anion obtained at the UB3LYP/6-31+G(d) and UHF/6-31+G(d) level, respectively.

In conclusion, we reported a novel anionic Class II MV compound based on AQI. Due to the fused A–D–A structural characteristic, intensive absorption bands covering entire UV–vis and NIR wavelength ranges arising from a combination of $\pi^*-\pi^*$ transitions and IV-CT were achieved upon one-electron reduction. This work provides a promising strategy to design panchromatically electrochromic materials by combining various transitions into one molecule. The absorption at long wavelengths could be further enhanced by adjusting the relative strength of the donor and acceptor. Molecules based on AQI with enhanced cathodically electrochromic stability are currently in development in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, NMR spectra, and computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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