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Designed Synthesis of Ferrocenylanthraquinones and Their Bifunctional Electrochromic Properties

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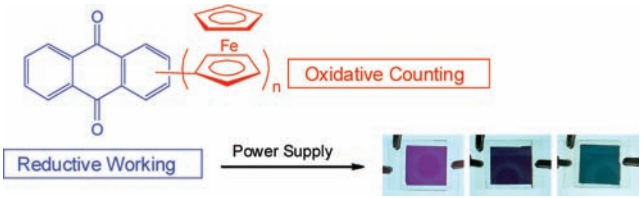
ABSTRACT



New bifunctional electrochromic systems were developed by combination of reductive anthraquinone with oxidative ferrocene redox systems. The resultant ferrocenylanthraquinones demonstrated enhanced stability in electrochromic performance through the concomitant reductive electrochromism and oxidative counting action. The displayed colors were dependent on the position of the ferrocenyl group.

Electrochromism, reversible color change depending on the power supply, is a very promising phenomenon with ultimate application in display devices.[1] Usually, electrochromism-based displays require a relatively low operating voltage with a good color contrast, even at wide angles.[2] Electrochromism has been observed not only in organic materials[3] but also in inorganic systems.[4] Generally, in the case of inorganic materials, the range of the displayed colors and the methods of color control are quite limited. However, organic materials offer great advantages over inorganic ones in color diversity due to the relative ease of chemical modification.

Nevertheless, in addition to color diversity, the stability of organic systems is another very important issue, and more efforts are required to improve the stability by designing new electrochromic systems. Usually, oxidation or reduction of electrochromic materials forms active anionic or cationic radical species that can be irreversibly transformed into other organic species. To maintain the cationic or anionic radical species, the generated charge should be efficiently compensated for through reversible counting materials.[5] In addition, the appropriate counting action enables the lowering of the operating voltage of electrochromic devices.

Benzophenone and anthraquinones are redox-active species.[6] In particular, anionic radical species can be formed

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(1) (a) Grätzel, M. *Nature* **2001**, *409*, 575. (b) Rosseinsky, D. R.; Mortimer, R. J. *Adv. Mater.* **2001**, *13*, 783. (c) Mortimer, R. J.; Dyer, A. L.; Reynolds, J. R. *Displays* **2006**, *27*, 2. (d) Beaujuge, P.; Ellinger, S.; Reynolds, J. R. *Nat. Mater.* **2008**, *7*, 795.

(2) Monk, R. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism and Electrochromic Devices*; Cambridge University Press: Cambridge, 2007.

(3) Recent example: (a) Nishida, J.-I.; Miyagawa, T.; Yamashita, Y. *Org. Lett.* **2004**, *6*, 2523. (b) Yamazaki, T.; Murata, Y.; Komatsu, K.; Furukawa, K.; Morita, M.; Maruyama, N.; Yamao, T.; Fujita, S. *Org. Lett.* **2004**, *6*, 4865. (c) Sortino, S.; Conoci, S.; Yildiz, I.; Tomasulo, M.; Raymo, F. M. *J. Mater. Chem.* **2006**, *16*, 3171. (d) Deng, J.; Song, N.; Zhou, Q.; Su, Z. *Org. Lett.* **2007**, *9*, 5393. (e) Areephong, J.; Logtenberg, H.; Browne, W. R.; Feringa, B. L. *Org. Lett.* **2010**, *12*, 2132.

(4) Granqvist, C. G. *Handbook of Inorganic Electrochromic Materials*; Elsevier: Amsterdam, 1995.

(5) The counting materials are charge-balancing ones on the counter electrode for electrochemical reactions on working electrode. Recent example of inorganic counting materials: Gillaspie, D.; Norman, A.; Tracy, C. E.; Pitts, J. R.; Lee, S.-H.; Dillon, A. *J. Electrochem. Soc.* **2010**, *157*, H328.

10.1021/ol101168w

via one-electron reduction. To make the reduction process stable and reversible, the generated negative charge should be efficiently compensated for by the positive charge. Ferrocene is well-known for its stable and reversible one electron oxidation reaction.[7] Our research group has studied the new stable organic and inorganic electrochromic materials.[8] In this work, we report the synthesis of bifunctional and stable electrochromic systems through combination of anthraquinones and ferrocenes (Figure 1a,b). It can be expected that in single-layer sandwich-type electrochromic devices, via power supply, the ferrocenyl group will be oxidized to assume the role of a counter material on the anode as the anthraquinone portion will be reduced to show electrochromism on the cathode and the charges compensated for by each other (Figure 1c).

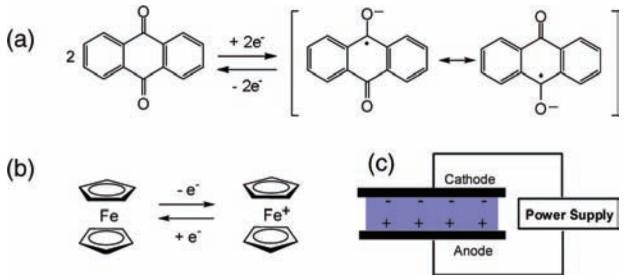


Figure 1. Redox reactions of anthraquinone (a) and ferrocene (b); cartoon of a single-layer electrochromic device (c).

Figure 2 shows the compounds used in this work. Actually, we started from the combination of ferrocene systems with a well-known ketyl radical system based on diaryl ketone. Three benzophenone derivatives having ferrocenyl groups at the 3-, 4-, or the 4,4′-position were designed. In addition, two monoferrocenylanthraquinones and three bisferrocenylanthraquionones were designed.

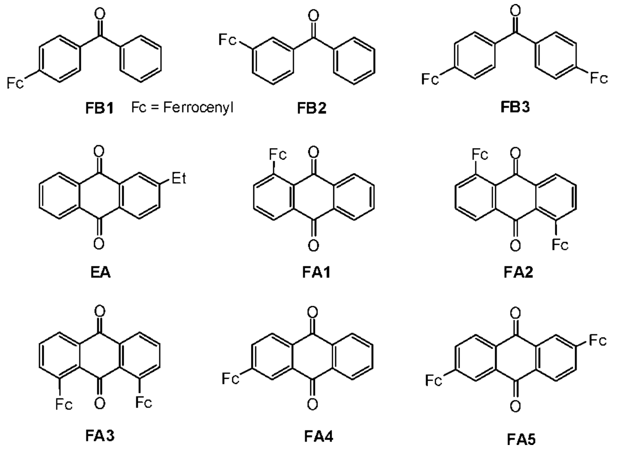
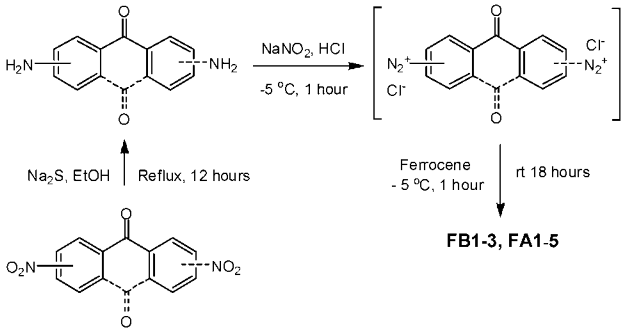


Figure 2. Compounds used in this work.

For preparation of the target compounds, the ferrocenyl group was successfully introduced to the benzophenone or anthraquinone via coupling of the corresponding aryl diazonium salts with ferrocene.[9] As shown in Scheme 1, diazonium salts were prepared in situ from the corresponding aryl amines via reaction with sodium nitrite under acidic conditions. 1,8-Bisferrocenylanthraquinone is not available commercially and was prepared from the corresponding nitroarene by reduction using Na_2S.[10] All compounds were stable under air and purified by flash column chromatography.

Scheme 1. Synthetic Pathway for Ferrocenylbenzophenones (**FB**) and Ferrocenylanthraquinones (**FA**)



Next, the electrochemical behavior of each compound was investigated by cyclicvoltammetry using a conventional three-electrode cell assembly. Each compound (5 mM) was dissolved in *N*-methylpyrrolidone (NMP) containing 0.10 M tetrabutylammonium tetrafluoroborate. The working and counting electrodes were glassy carbon and platinum wire, respectively. An Ag/Ag^+ reference electrode was used. Table 1 summarizes the electrochemical properties of the all compounds studied in this work.

Ferrocenylbenzophenones (**FB1-3**) showed *irreversible* reduction peaks between −2.08 and −2.17 V (versus Ag/Ag^+) and reversible oxidation peaks at +0.27 V. The unstability of the generated ketyl radicals resulted in poor electrochromic performance.[11] In contrast, ferrocenylanthraquinones showed stable electrochemical properties. As revealed in cyclovoltammograms in Figure 3a,c, 1-ferroce-

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(6) (a) Qiao, W.; Zheng, J.; Wang., Y.; Zheng, Y.; Song, N.; Wan, X.; Wang, Z. Y. *Org. Lett.* **2008**, *10*, 641. (b) Zheng, Y.; Zheng, J.; Dou, L.; Qiao, W.; Wan, X. *J. Mater. Chem.* **2009**, *19*, 8470. (c) Thum, C. C. L.; Khairallah, G. N.; O'Hair, R. A. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 9118, and references cited therein.

(7) Togni, A.; Hayashi, T. *Ferrocenes*; Wiley-VCH: Weinheim, 1995.

(8) (a) Sharmoukh, W.; Ko, K. C.; Ko, J. H.; Nam, H. J.; Jung, D.-Y.; Noh, C.; Lee, J. Y.; Son, S. U. *J. Mater. Chem.* **2008**, *18*, 4408. (b) Sharmoukh, W.; Ko, K. C.; Park, S. Y.; Ko, J. H.; Lee, J. M.; Noh, C.; Lee, J. Y.; Son, S. U. *Org. Lett.* **2008**, *10*, 5365. (c) Park, S. Y.; Lee, J. M.; Noh, C.; Son, S. U. *J. Mater. Chem.* **2009**, *19*, 7959.

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(10) Dahan, A.; Ashkenazi, T.; Kuznetsov, V.; Makievski, S.; Drug, E.; Fadeev, L.; Bramson, M.; Schokoroy, S.; Rozenshine-Kemelmakher, E.; Gozin, M. *J. Org. Chem.* **2007**, *72*, 2289.

(11) It should be noted that electrochromism has been defined in reversible electrochemical systems.

Table 1. Electrochemical and Electrochromic Properties

compd	potential[a] (V, vs Ag/Ag+) oxidation	reduction	UV/vis max abs (nm) before	after
ferrocene	+0.17 (rev)			
FB1	+0.27 (rev)	−2.12 (irrev)	506	
FB2	+0.27 (rev)	−2.17 (irrev)	436	
FB3	+0.27 (rev)	−2.08 (irrev)	520	
FA1	+0.24 (rev)	−1.21 (rev)	580	568
FA2	+0.24 (rev)	−1.30 (rev)	530	584
FA3	+0.24 (rev)	−1.32 (rev)	482	582
FA4	+0.30 (rev)	−1.14 (rev)	564	575
FA5	+0.30 (rev)	−1.16 (rev)	555	592

[a] Redox potential vs Ag/Ag$^+$ (reference electrode) determined in a conventional three electrodes cell by using 0.10 M tetrabutylammonium hexafluorophosphate as supporting electrolyte in NMP, glassy carbons as the working electrode, and platinum as the counter electrode.

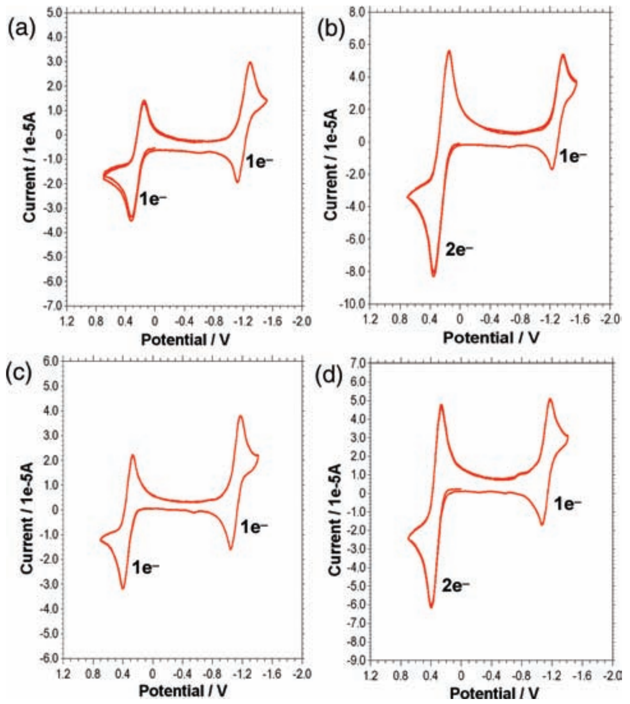

Figure 3. Cyclic voltammograms of **FA1** (a), **FA2** (b), **FA4** (c), and **FA5** (d).

nylanthraquinone (**FA1**) and 2-ferrocenylanthraquinone (**FA4**) showed one-electron reversible reduction peaks at −1.21 and −1.14 V (versus Ag/Ag$^+$) and one-electron reversible peaks at +0.24 and +0.30 V, respectively. In the case of 1,5-bisferrocenylanthraquinone (**FA2**) and 2,6-bisferrocenylanthraquinone (**FA5**), nearly identical patterns were observed with those of **FA1** and **FA4**, except the two-electron oxidation peaks due to two ferrocenyl groups (Figure 3b,d). Overall, ferrocenylanthraquinones possess reversible oxidation and reduction processes.

Interestingly, compared with the oxidation and reduction peaks of **FA1**−**3** having a ferrocenyl group at the 1-postion of anthraquinone, those of **FA4** and **FA5** were shifted by 0.06−0.18 V toward the positive potential direction. These observations imply that HOMOs and LUMOs of **FA1**−**3** are less stable than those of **FA4**−**5**, possibly due to the steric repulsion between the ferrocenyl group at 1-position and carbonyl (see the HOMOs and LUMOs of **FA1** and **FA4** in Figure S1, Supporting Information).

Considering the reversible electrochemical behaviors of ferrocenylanthraquinones, their electrochromic performances were studied using a sandwich-type cell. Two indium tin oxide (ITO) electrodes were attached with Surlyn tape.[12] Then, ferrocenylanthraquinones (50 mM) in NMP were carefully injected into the space between the two electrodes with a syringe. Table 1 and Figure 4 summarize the electrochromic properties of the ferrocenylanthraquinones (**FA1**−**5**).

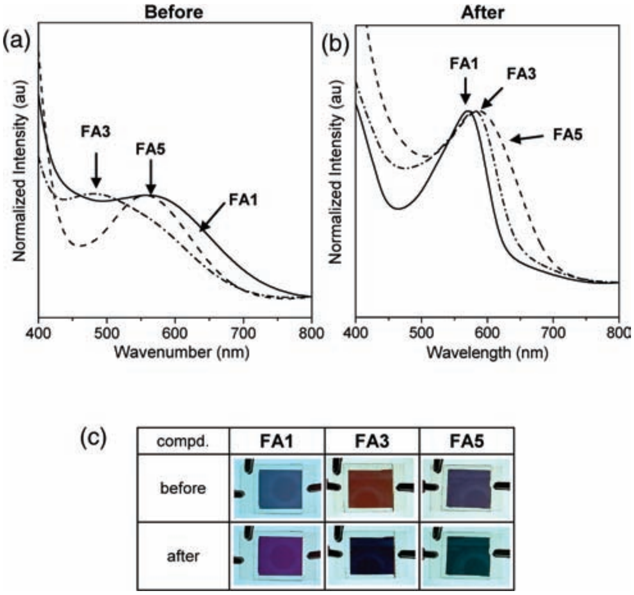

Figure 4. UV/vis absorption spectra of **FA1**, **FA3**, and **FA5** before (a) and after (b) power supply and photographs (c) of the color change of **FA1**, **FA3**, and **FA5**.

All ferrocenylanthraquinones showed very stable color changes via the power supply (see the movie showing the color change of **FA1** in the Supporting Information) As shown in Figure 4a−c and Table 1, with the power supply, monoferrocenylanthraquinones **FA1** and **FA4** displayed violet and blue colors with respective maximum UV/vis absorption peaks at 568 and 575 nm. Bisferrocenylanthraquinones **FA2** and **FA3** showed deep blue colors with maximum absorption peaks at 584 and 582 nm, respectively. The **FA5** displayed green color (maximum absorption peak at 592 nm) with the power supply. Overall, both the original colors and the displayed ones with a power supply were significantly dependent on the position and number of the ferrocenyl groups.

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(12) See the recent reports in ref 8 by our group for detailed procedures for fabrication of simple single-layer electrochromic cells.

Besides the displayed colors themselves, the color difference between the original color and the displayed one with a power supply is another important factor in display applications. The observed trend in the color difference is that with an increase of the number of ferrocenyl groups, the displayed colors with a power supply and the original ones were relatively and respectively red-shifted and blue-shifted, resulting in an increase in the maximum absorption peak difference between the original color and the displayed one with a power supply from 11 to 100 nm. Interestingly, time-dependent density functional theory (TD-DFT) calculations revealed that the original color of **FA1** and the displayed one by reduction have a different origin. The original color of **FA1** resulted from the photoinduced intramolecular charge transfer from the ferrocenyl group to anthraquinone. Comparatively, the displayed color of the reduced species of **FA1** resulted from transition from HOMO to LUMO+6, maintaining the major electron density distribution in anthraquinone. (Figure S2, Supporting Information) According to these observations, although the synthetic route has yet to be developed, we expect that tris- or tetrakis-ferrocenylanthraquinones will be additional promising electrochromic materials.

To investigate the positive effects of counting ferrocenyl groups in the electrochromic performance of anthraquinone, comparison experiments with **FA1** and 2-ethylanthraquinone (**EA**) were conducted.[13] The **EA** showed one electron-reversible reduction peaks at −1.18 V resulting in a color change with a maximum absorption peak at 545 nm. In the sandwich-type device, **EA** showed electrochromism at 3.4 V (DC). First, the electrochromic operating voltage of **FA1** was significantly lowered to 2.0 V (DC) due to the appropriate counting action of the ferrocenyl group. Second, as shown in Figure 5, the clearly enhanced stability of the electrochromic system was observed in **FA1**, compared with that of **EA**.

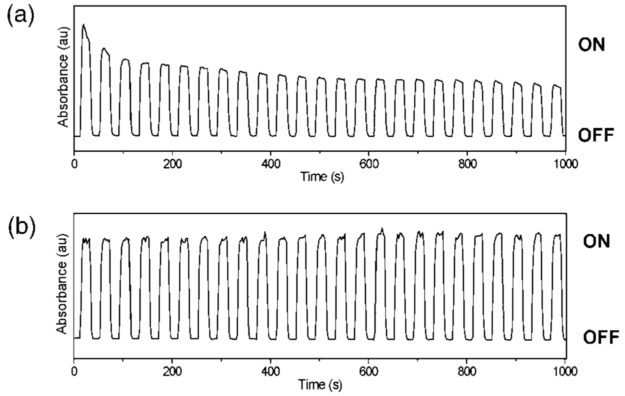

Figure 5. Electrochromic performance of 2-ethylanthraquinone at 545 nm (a) and **FA1** at 568 nm (b).

In conclusion, bifunctional electrochromic materials were prepared by combination of reductive anthraquinone and oxidative ferrocene redox system. The resultant ferrocenyl-anthraquinone displayed different electrochromic performances depending on the number and position of the ferrocenyl groups. Furthermore, based on the design strategy presented herein, we believe that more diverse multifunctional electrochromic systems could be designed for single-layer electrochromic devices through diverse combination of other redox systems.

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Supporting Information Available: Experimental procedure for preparation of new compounds, their characterization data, and a movie showing electrochromism of **FA1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Unfortunately, the simple anthraquinone is insoluble in NMP. Thus, 2-ethylanthraquinone was used without additional counter materials.