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Designed Synthesis of Multi-Electrochromic Systems Bearing Diaryl Ketone and Isophthalates

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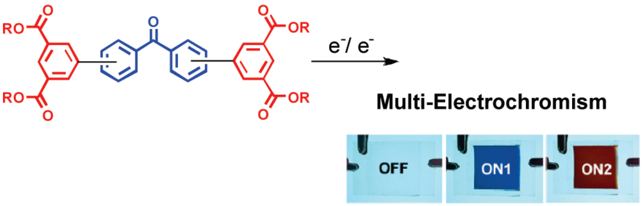

New multi-electrochromic systems have been developed through the combination of a diaryl ketyl radical system with isophthalate-based electrochromic materials. The location of the isophthalate group in compounds is very critical to obtaining different colors in the multi-electrochromism.

Organic electrochromic materials have attracted special attention due to their unique advantages over their inorganic counterparts.[1] First, organic materials possess the flexibility necessary for flexible device fabrications. Second, compared to inorganic materials, they display diverse and clear colors with a relatively narrow absorption band.

During the past decade, the related studies have focused on polymeric organic materials.[2] Usually, redox reactions of conducting organic polymers result in a change in the absorption band in the visible light range. By changing the electronic structure of the monomers, the electrochromic properties of the polymers are tuned.[2,3] Furthermore, more than two monomers can be incorporated into conducting polymers to induce multi-electrochromism.[4]

Recently, single molecular electrochromic materials have attracted significant attention given their ability to be chemically engineered onto nanosized electrode materials.[5] For ultimate full-color displays, the combination of several independent molecular electrochromic materials displaying the different colors is needed. Usually, the related devices have been fabricated based on a multilayer structure in which each layer contains distinct colors.[6] Comparatively, if the materials can show multicolors depending on applied potentials, the structure of the device can be more effectively designed. One can easily speculate that the combination of several different molecular electrochromic systems could generate more advanced systems. However, compared to the conducting polymer-based electrochromic systems, the single molecular engineering of electrochromic systems has been sparsely explored.

The ketyl radical system, with an anionic radical of the general structure $[C-O]^{\cdot -}$, has been well recognized in organic chemistry for a long time.[7] One of the most famous ketyl radical systems can be formed by the one-electron reduction of benzophenone. Our research group has studied the reductive inorganic and organic electrochromic systems including isophthalate derivatives.[8] In this study, we report on the molecular engineering of multi-electrochromic systems through combination of the diaryl ketyl radical and isophthalate systems (Scheme 1).

A series of new molecular electrochromic systems bearing the diaryl ketones and isophthalates have been designed. As shown in Chart 1, the diaryl ketyl radical system was connected to the isophthalate unit. The target electrochromic compounds in Chart 1 were prepared following Scheme 2. Although, in addition to the compounds in Chart 1, the bis(isophthalate) compounds, bearing 2,6-anthracene-9,10-dione, 3,3′-benzil, and 5,5′-di(2-thienyl)methanone as bridges, were also prepared; they were excluded from the study due to solubility problems.

First, **EC1** was prepared by coupling with isophthalic acid and successive esterification[9] (Scheme 2). The central methylene group was then oxidized to a carbonyl group using CrO_3.[10] For improvement of solubility in organic media and ultimate attachment of compounds to electrode materials through olefin

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(1) (a) Grätzel, M. *Nature* **2001**, *409*, 575. (b) Hünig, S.; Langels, A.; Schmittel, M.; Wenner, H.; Perepichka, I. F.; Peters, K. *Eur. J. Org. Chem.* **2001**, 1391. (c) Porter, W. W.; Vaid, T. P. *J. Org. Chem.* **2005**, *70*, 5028. (d) Sprutta, N.; Siczek, M.; Latos-Grażyński, L.; Pawlicki, M.; Szterenberg, L.; Lis, T. *J. Org. Chem.* **2007**, *72*, 9501. (e) Lanzo, J.; Benedittis, M. D.; Simone, B. C.; Imbardelli, D.; Formoso, P.; Manfredi, S.; Chidichimo, G. *J. Mater. Chem.* **2007**, *17*, 1412. (e) Ito, S.; Morita, N. *Eur. J. Org. Chem.* **2009**, 4567. (f) Sinan, M.; Ghosh, K.; Goswami, S. *J. Org. Chem.* **2010**, *75*, 2065. (g) Reczek, J. J.; Rebolini, E.; Urbach, A. R. *J. Org. Chem.* **2010**, *75*, 2111.

(2) (a) Mortimer, R. J.; Dyer, A. L.; Reynolds, J. R. *Displays* **2006**, *27*, 2. (b) Beaujuge, P.; Ellinger, S.; Reynolds, J. R. *Nat. Mater.* **2008**, *7*, 795.

(3) (a) Patra, A.; Wijsboom, Y. H.; Zade, S. S.; Li, M.; Sheynin, Y.; Leitus, G.; Bendikov, M. *J. Am. Chem. Soc.* **2008**, *130*, 6734. (b) Beaupré, S.; Dumas, J.; Leclerc, M. *Chem. Mater.* **2006**, *18*, 4011.

(4) Argun, A. A.; Aubert, P.-H.; Thompson, B. C.; Schwendeman, I.; Gaupp, C. L.; Hwang, J.; Pinto, N. J.; Tanner, D. B.; MacDiarmid, A. G.; Reynolds, J. R. *Chem. Mater.* **2004**, *16*, 4401.

(5) Cummins, D.; Boschloo, G.; Ryan, M.; Corr, D.; Rao, S. N.; Fitzmaurice, D. *J. Phys. Chem. B* **2000**, *104*, 11449.

(6) Kobayashi, N.; Miura, S.; Nishimura, M.; Urano, H. *Solar Energy Mater. Solar Cells* **2009**, *92*, 136.

(7) Selected references: (a) Thum, C. C. L.; Khairallah, G. N.; O'Hair, R. A. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 9118 and references therein. (b) Inui, M.; Nakazaki, A.; Kobayashi, S. *Org. Lett.* **2007**, *9*, 469. (c) Sakamoto, M.; Cai, X.; Fujitsuka, M.; Majima, T. *Chem.—Eur. J.* **2006**, *12*, 1610.

(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.; Son, S. U. *J. Mater. Chem.* **2009**, *19*, 7959. (d) Sharmoukh, W.; Ko, K. C.; Ko, J. H.; Jung, I. G.; Noh, C.; Lee, J. Y.; Son, S. U. *Org. Lett.* **2010**, *12*, 3226.

(9) Mazik, M.; König, A. *Eur. J. Org. Chem.* **2007**, *10*, 3271.

(10) Xu, G.; Micklatcher, M.; Silvestri., M. A.; Hartman, T. L.; Burrier, J.; Osterling, M. C.; Wargo, H.; Turpin, J. A.; Buckheit, R. W.; Cushman, M. *J. Med. Chem.* **2001**, *44*, 4092.

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SCHEME 1. **Formation of the Ketyl Radical (a); Reduction of Isophthalate Derivatives (b); Design of New Electrochromic Compounds through Combination of Both Systems (c)**

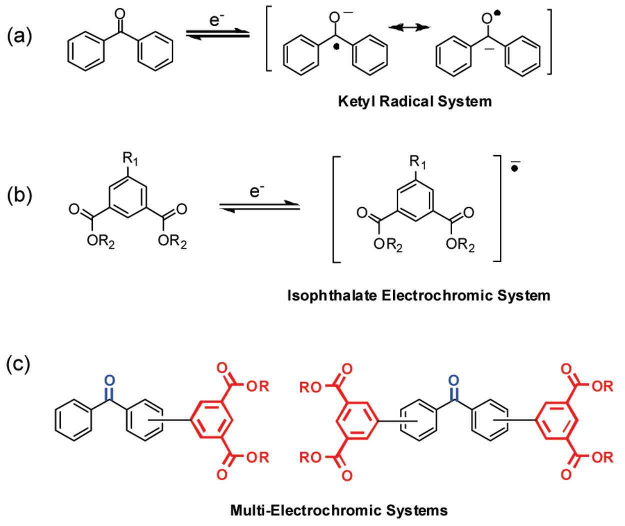
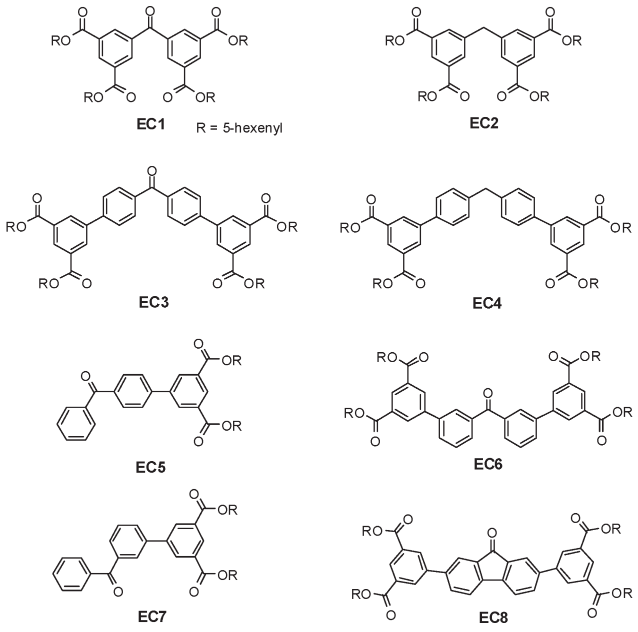


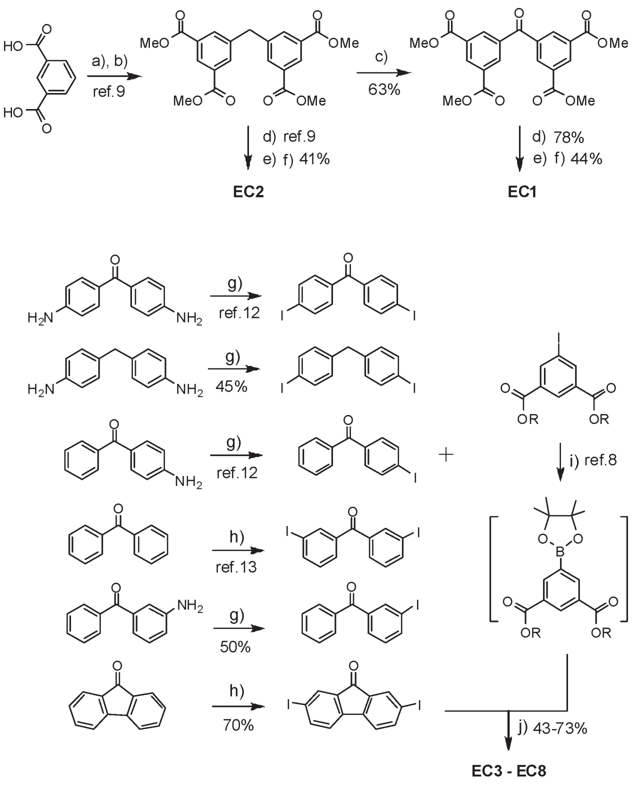
CHART 1. **Electrochromic Compounds Used in This Study**



metathesis chemistry,[11] 5-hexenyl groups were introduced into the ester groups instead of methyl groups. Actually, **EC1** can be regarded as a derivative of both benzophenone and diisophthalates. To test the effects of the carbonyl groups in the bridge of the two isophthalate groups, **EC2**, possessing a methylene bridge, was also prepared.

As shown in Scheme 2, **EC3**−**EC8** bearing 4,4′-benzophenone, 4-benzophenone, 3,3′-benzophenone, 3-benzophenone, and 2,7-fluoren-9-one were prepared. First, 4,4′-diiodobenzophenone, 4-iodobenzophenone, and 3-iodobenzophenone were prepared by respective iodination of 4,4′-diaminobenzophenone, 4-aminobenzophenone, and 3-aminobenzophenone.[12]

SCHEME 2. **Synthetic Pathways for EC1−EC8**[a]



[a](a) CH_2O, 20% Oleum, 120 °C, 6 h; (b) MeOH, HCl, reflux, 0.5 h; (c) CrO_3, Ac_2O, rt, overnight; (d) NaOH, MeOH, reflux, 8 h, then HCl; (e) $SOCl_2$, reflux, 6 h; (f) 5-Hexen-1-ol, CH_2Cl_2, pyridine, rt, 6 h; (g) $NaNO_2$, 10% HCl, H_2O, KI, rt, overnight; (h) $KMnO_4$, I_2, AcOH, Ac_2O, H_2SO_4, 70 °C, 4 h; (i) Bis(pinacolato)diborane, K_2OAc, $Pd(OAc)_2$, DMF, 90 °C, 4 h; (j) $Pd(OAc)_2$, K_2CO_3, DMF, 90 °C, 4−12 h.

3,3′-Diiodobenzophenone and 2,7-diiodofluoren-9-one were prepared by direct iodation of benzophenone and fluorenone.[13] Then, these iodoarenes were coupled with 5-pinacolatoboron-isophthalates by palladium catalysis. Moreover, to elucidate the role of the carbonyl group in the bridge of **EC3**, **EC4** was prepared by coupling with bis(4-iodophenyl)methane.

Next, electrochemical and electrochromic properties of the prepared compounds (**EC1**−**EC8**) were investigated by cyclic voltammetry (CV) and *in situ* UV/visible absorption spectroscopy (Table 1; Figures 2, S1, and S2 in the Supporting Information). Compound **EC1** showed simple reversible *one-electron reduction* behavior at −1.76 V (versus Ag/Ag^+). The expected second reduction peak by isophthalate groups was not observed in the electrochemical test range of the solvent, implying that the second reduction needs a much higher voltage due to the close electronic communication between the central carbonyl group and two isophthalates. Compared to benzophenone, showing a one-electron reduction peak at −2.14 V (versus Ag/Ag^+), the reduction peak of **EC1** at −1.76 V was significantly shifted in a more positive direction due to the electron-withdrawing effect of the four ester groups. As has been well documented, the ketyl radical of benzophenone is quite sensitive and unstable.[7] Benzophenone showed a pale blue-green color *via* reduction; the

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[11] Noh, C. H.; Son, S. U. U.S. Patent US-2009097096, 2009.

[12] Takalo, H.; Hanninen, E.; Kankare, J. *Acta Chem. Scand., Ser. B: Org. Chem. Biochem.* **1988**, *B42*, 662.

[13] (a) Lulinski, P.; Krassowska-Swiebocka, B.; Skulski, L. *Molecules* **2004**, *9*, 595. (b) Xu, J.; Zheng, H.; Liu, H.; Zhou, C.; Zhao, Y.; Li, Y.; Li, Y. *J. Phys. Chem. C* **2010**, *114*, 2925.

TABLE 1. **Electrochemical and Electrochromic Properties**

compounds	reduction potential[a] (V, vs Ag/Ag^+) first (ON1)	reduction potential[a] (V, vs Ag/Ag^+) second (ON2)	UV/vis max. abs. (nm) first	UV/vis max. abs. (nm) second
EC1	−1.76	–	462	–
EC2	−2.28[b]	–	434	–
EC3	−1.95	−2.34	589	507
EC4	−2.30[b]	–	507	–
EC5	−2.05	−2.47	567	510
EC6	−2.03	−2.43	519	505
EC7	−2.14	−2.41[b]	529	501
EC8	−1.51	−2.06[b]	530	575

[a]Redox potential vs Ag/Ag^+(reference electrode), 0.20 M tetrabutylammonium hexafluorophosphate as supporting electrolyte in acetonitrile, ITO glass as the working electrode, and platinum as the counter electrode. [b]Quasi-reversible peaks.

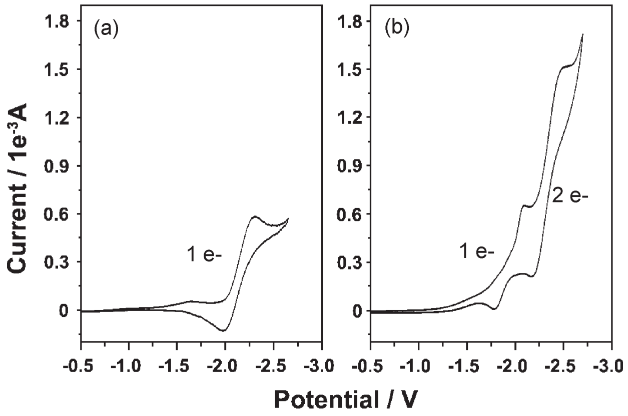

FIGURE 1. Cyclic voltammograms of benzophenone (a) and **EC3** (b).

displayed color, however, immediately disappeared. In comparison, **EC1** showed a stable color change from colorless to yellow-orange (max. absorbance at 462 nm) through reduction, due to the stabilization effect of the anionic radical by the four electron-withdrawing ester groups.

Compound **EC2**, having a methylene bridge between two isophthalates, showed a quasi-reversible *two-electron reduction* peak at −2.28 V (versus Ag/Ag^+) and a color change from colorless to yellow (max. absorbance at 434 nm), which corresponds to the typical isophthalate-based electrochromism.[8a] Considering the electrochemical properties of **EC1** and **EC2**, it is noteworthy that the benzophenone analogue underwent reduction more easily than the isophthalates. Although multi-electrochromism was not observed, it was clear that the existence of the carbonyl group had a crucial effect on the electrochromic properties of **EC1**.

Compounds **EC3** and **EC5**−**EC8** showed interesting multi-electrochromic behaviors. According to the CV studies presented in Figure 1, **EC3** demonstrated the two-step reduction process with the first one-electron reversible reduction peak at −1.95 V and the second two-electron reversible reduction peak at −2.34 V. Interestingly, the corresponding color changes were from colorless to vivid blue (max. absorption peak at 589 nm) and then red (max. absorption peak at 507 nm) (Figure 2). The potential difference between the two reduction processes was 0.39 V, and the clear color difference enables **EC3** as a promising multi-electrochromic material. Compared to **EC3**, **EC4**, containing the 4,4′-biphenylmethane as a bridge instead of 4,4′-benzophenone, showed a two-electron reversible reduction peak at −2.30 V and a color change from colorless to red with maximum absorption peaks at 507 nm. This confirmed again that the existence of the carbonyl group played a key role in the multi-electrochromic performance.

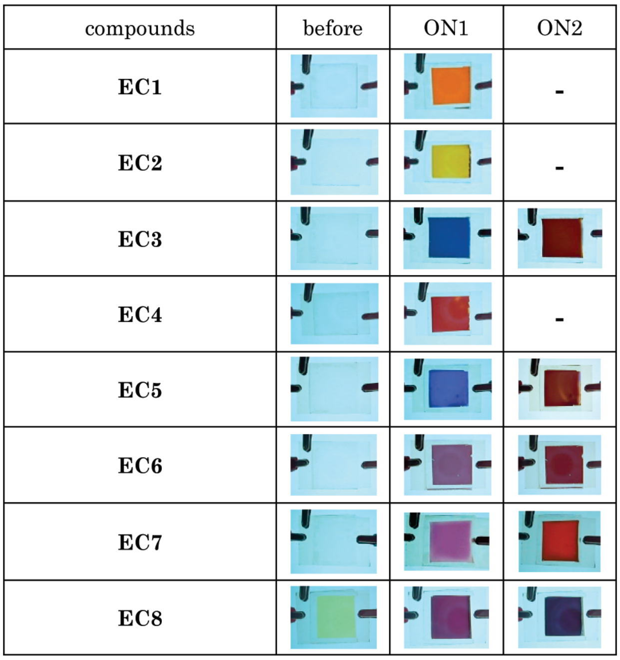

FIGURE 2. Photographs of the displayed colors of **EC1-8** before and after the power supply.

EC5 displayed very similar multi-electrochromism with **EC3**. Due to the existence of one isophthalate group, it showed two-step one-electron reduction peaks with a color change from colorless to vivid blue (max. absorption peak at 567 nm) and then red (max. absorption peak at 510 nm).

Compounds **EC6**−**EC8** demonstrated the two-step reduction process, and the displayed colors are quite dependent on the chemical structure of compounds[14] (Table 1 and Figure 2). The color difference between the first and the second reduced species will be an important factor in multi-electrochromism. In this regard, a comparison of the displayed colors by **EC3** with those by **EC6** was interesting. Compound **EC6**, containing a 3,3′-benzophenone as a bridge instead of 4,4′-benzophenone, showed very similar electrochemical behavior to that of **EC3** with one-electron reduction at −2.03 V and a two-electron reduction process at −2.43 V. However, the difference between the displayed colors by **EC6** was not as big as that by **EC3**; first, violet-red (max. absorbance at 519 nm) and, second, dark-red (the maximum absorbance at 505 nm), respectively (Figure 3). It is worth noting that the second colors of **EC3** (507 nm) and **EC6** (505 nm) were nearly identical and, furthermore, very similar to those of the reduced **EC4** (507 nm) and 5-phenyl-isophthalate (506 nm)[15](Figure S3).

To understand the color difference of the first reduced species of **EC3** and **EC6**, a computational calculation was conducted on the reduced forms by one electron. As shown in Figure 3c, the natural bond orbital (NBO) charge in a model compound of the reduced **EC3** by one electron is more

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(14) In the case of **EC8**, the multielectrochromism resulted from the two-step reduction of the central fluoren-9-one moiety.

(15) 5-Phenyl-isophthalate showed the maxium absorption peak at 506 nm by one-electron reduction in ref 8a.

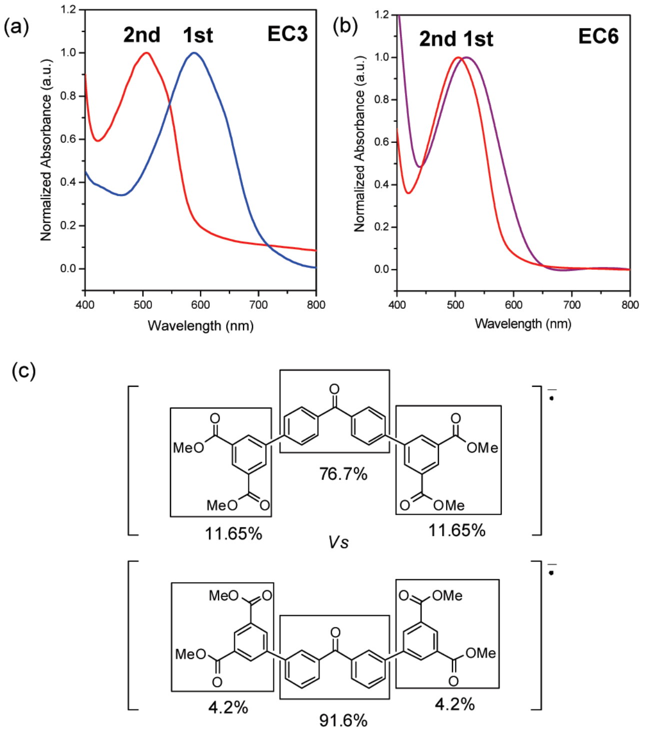

FIGURE 3. UV/vis absorption spectra of the first and second reduced species of **EC3** (a) and **EC6** (b) by one and three electrons. The calculated NBO charge distribution in the model compounds of the reduced **EC3** and **EC6** by one electron (c).

effectively delocalized than that of a model compound of the reduced **EC6**.[16] This resulted in a red shift of the absorption band of the reduced **EC3** by one electron, compared to the reduced **EC6**. Actually, the more effective delocalization of anionic radicals is an efficient strategy to obtain the red-shifted absorption bands in diverse reductive electrochromic systems.[8a,b] Figure 4 shows the reversible multi-electrochromic performances of **EC3** in a sandwich-type device,[8a,17] displaying blue and red color with a supply of 2.4 and 3.0 DC voltages respectively.

In conclusion, this work verified that the combination of the ketyl radical system with the isophthalate electrochromic system is a successful strategy to obtain a multi-electrochromic system. Interestingly, the location of the isophthalate group is very critical to obtaining different colors in the multi-electrochromism. Also, we believe that more diverse molecular multi-electrochromic systems can be designed through the combination of isophthalate with other redox systems.

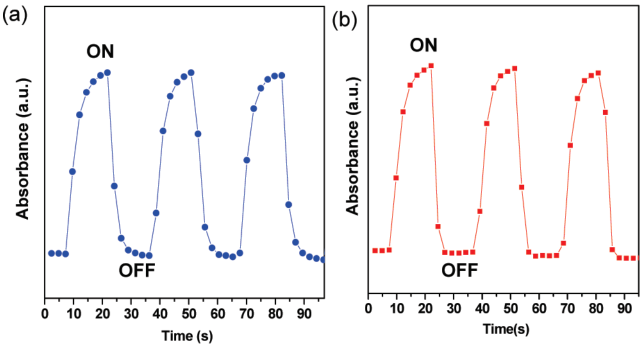

FIGURE 4. Multi-electrochromic performance of **EC3**; blue color display (589 nm) with 2.4 (DC)V (a); red color display (507 nm) with 3.0 (DC)V.

Experimental Section

Synthesis of EC3. To a DMF (20 mL) solution of di-5-hexenyl 5-pinacolatoboron-isophthalate[8] (0.30 g, 0.66 mmol), 4,4′-diiodobenzophenone[12] (0.12 g, 0.28 mmol), palladium acetate (12 mg, 0.053 mmol), and potassium carbonate (0.50 g, 3.6 mmol) were added. The reaction mixture was heated at 90 °C for 4 h. Then, the reaction mixture was extracted using ethylacetate and brine and then dried over $MgSO_4$. After the solvent was evaporated, the product was isolated with 42% yield by column chromatography using a mixture of hexane and ethylacetate (10:1) as eluent. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 8.70 (s, 2H), 8.51 (s, 4 H), 7.97 (d, J = 8.4 Hz, 4H), 7.80 (d, J = 8.4 Hz, 4H), 5.80 (m, 4H), 5.03 (d, J = 14 Hz, 4H), 4.98 (d, J = 6.9 Hz, 4H), 4.41 (t, J = 6.9 Hz, 8H), 2.14 (q, J = 7.2 Hz, 8H), 1.82 (q, J = 7.2 Hz, 8H), 1.58 (q, J = 7.2 Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 195.6, 165.8, 143.3, 140.8, 138.4, 137.2, 132.5, 131.9, 130.9, 130.2, 127.4, 115.1, 65.7, 33.4, 28.2, 25.4; HRMS (FAB) calcd for $[M + H]^+$, $C_{53}H_{59}O_9$, 839.4159; found, 839.4163.

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Supporting Information Available: Synthetic procedures and characterization data of new compounds, details of calculation, and additional UV and CV data. This information is available free of charge via the Internet at http://pubs.acs.org.

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[16] See the Supporting Information for a detailed procedure of calculation.

[17] Unfortunately, the reduced species have no bistability.