5-Substituted isophthalate-based organic electrochromic materials

W. Sharmoukh,[a] Kyoung Chul Ko,[a] Ju Hong Ko,[a] Hye Jin Nam,[a] Duk-Young Jung,[a] Changho Noh,[b] Jin Yong Lee*[a] and Seung Uk Son*[a]

Received 21st May 2008, Accepted 7th July 2008
First published as an Advance Article on the web 4th August 2008
DOI: 10.1039/b808638a

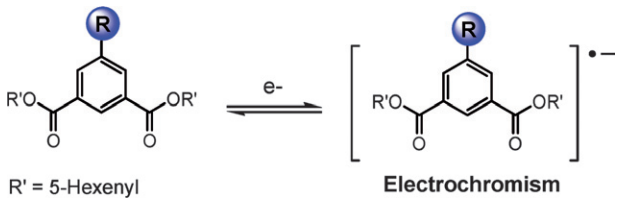
A new series of isophthalate-based electrochromic materials were prepared. The functional groups at the 5-position of isophthalate have a significant influence on the observed color. In particular, an electrochemically active nitro group induced a multi-color display, indicating that further electrochromic properties could be manipulated using more diverse 5-substituted isophthalate derivatives.

Introduction

Electrochromism is an interesting phenomenon defined as color display dependence on applied voltage.[1] Academic, as well as industrial research interests have been focused on electrochromic materials for their broad application in such commercial products as smart windows, diverse displays, and mirror devices.[2] In the case of application for electrochromic paper, organic materials are very promising candidates where reduction or oxidation of the neutral organic compound to its radical species induces the desired color change.[3] There have been extensive studies on the electrochromism of conducting organic polymers.[3c] The polymer-based devices have many advantages in processing. However, a drawback of these is their relatively slow response time, which is limited by ion transport or electron-migration rate within polymeric materials.[3d]

Several privileged organic molecules such as viologen and phenothiazine derivatives are known to show electrochromism.[4] Recently, the new structured devices have been developed by attaching these materials onto the surface of nanostructured semiconductor films, which showed very fast response times.[5] In this regard, more organic electrochromic compounds should be developed for display of diverse colors.

Compared to viologen and phenothiazines, less attention has been paid to the 1,4-terephthalate derivatives.[6] Moreover, as far as we are aware, there is no report on the electrochromism of 1,3-isophthalates, which attracted our attention because functional groups can be easily introduced at the 5-position of these. Our research group has prepared the diverse 5-substituted isophthalate compounds and investigated their electrochromic behavior (Scheme 1). In this paper, we report new isophthalate-based electrochromic materials and the facile control of their electrochromic properties by changing the functional group at the 5-position.



Scheme 1 Electrochromism of 5-substituted isophthalate derivatives.

Experimental

Materials and apparatus

Isophthalic acid, pyridine and boronic acids were purchased from Aldrich Chemical Company, Inc., and used as supplied. Palladium acetate was purchased from Strem Chemicals. 5-Hexene-1-ol, tetrabutylammonium hexafluorophosphate and tritolylphosphine were purchased from TCI (Japan). Thionyl chloride was purchased from Samchun Chemical Company (Korea). γ-Butyrolactone (Aldrich), methylene chloride (Samchun) and DMF (Samchun) were freshly distilled before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 300 MHz spectrometer. High resolution mass spectra of new compounds were obtained using a Jeol JMS 700 spectrometer at Korea Basic Science Institute (Daegu).

General synthetic procedure for M1, 7–10

Isophthalic acid (6.0 mmol) was dissolved in 3 mL (41 mmol) of thionyl chloride in a 50 mL Schlenk flask. The reaction mixture was heated for 3 hours under reflux. Then, the solution was cooled to room temperature and the excess thionyl chloride was removed under vacuum. The oily product was dried under vacuum for 1 hour. Methylene chloride (20 mL) was added to dissolve the oily product. 5-Hexen-1-ol (2.16 mL, 18 mmol) and pyridine (1.94 mL, 24 mmol) were added at 0 °C. The reaction mixture was stirred for 3 hours at 0 °C. After reaction, the reaction mixture was extracted using methylene chloride and aqueous ammonium chloride solution. The filtered solution was dried using $MgSO_4$ and evaporated. The product was separated *via* column chromatography using a mixture of hexane and ether (12 : 2) as eluent.

[a]*Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea. E-mail: sson@skku.edu; Fax: +82 031-290-4572; Tel: +82 031-299-5932*
[b]*Samsung Advanced Institute of Technology (SAIT), Suwon 440-600, Korea*

General synthetic procedure for M2–6

5-Iodo-isophthalate **M10** (0.22 mmol), aryl boronic acid (29 mg, 0.24 mmol), palladium acetate (5.0 mg, 0.022 mmol), potassium carbonate (0.15 g, 1.1 mmol) and tritolylphosphine (13.3 mg, 0.044 mmol) were added to 20 mL of DMF. The reaction mixture was heated at 90 °C for 4 hours. After reaction, the reaction mixture was extracted using methylene chloride and aqueous solution of sodium chloride and then, dried using $MgSO_4$. The product was separated *via* column chromatography using mixture of hexane and ether (12 : 1) as eluent.

Characterization data of new compounds

M1; 56% isolated yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.21 (d, $J = 7.8$ Hz, 2H), 7.52 (t, $J = 7.5$ Hz, 1H), 5.80 (m, 2H), 5.03 (d, $J = 14$ Hz, 2H), 4.96 (d, $J = 6.9$ Hz, 2H), 4.34 (t, $J = 6.6$ Hz, 4H), 2.12 (q, $J = 6.9$ Hz, 4H), 1.79 (q, $J = 6.9$ Hz, 4H), 1.54 (q, $J = 6.9$ Hz, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 138.3, 133.7, 130.9, 130.7, 128.6, 114.9, 65.3, 33.3, 28.2, 25.3 ppm. HRMS (EI) calc. for $C_{20}H_{26}O_4$ 330.1831, found 330.1827.

M2; 90% isolated yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.45 (s, 2H), 7.66 (d, $J = 6.9$ Hz, 2H), 7.47 (m, 3H), 5.82 (m, 2H), 5.06 (d, $J = 14$ Hz, 2H), 4.97 (d, $J = 6.9$ Hz, 2H), 4.41 (t, $J = 6.6$ Hz, 4H), 2.14 (q, $J = 6.9$ Hz, 4H), 1.83 (q, $J = 6.9$ Hz, 4H), 1.55 (q, $J = 6.9$ Hz, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 142.0, 139.3, 138.4, 132.4, 131.6, 129.4, 129.2, 128.3, 127.4, 115.1, 65.5, 33.4, 28.3, 25. ppm. HRMS (EI) calc. for $C_{26}H_{30}O_4$ 406.2144, found 406.2144.

M3; 76% isolated yield,^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.39 (s, 2H), 7.62 (d, $J = 8.7$ Hz, 2H), 7.17 (t, $J = 8.7$ Hz, 2H), 5.83 (m, 2H), 5.04 (d, $J = 14$ Hz, 2H), 4.98 (d, $J = 6.9$ Hz, 2H), 4.39 (t, $J = 6.6$ Hz, 4H), 2.14 (q, $J = 7.2$ Hz, 4H), 1.84 (q, $J = 6.9$ Hz, 4H), 1.58 (q, $J = 6.9$ Hz, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 140.9, 138.3, 135.4, 132.1, 131.6, 129.3, 129.0, 116.2, 115.9, 115.1, 65.5, 33.4, 28.2, 25.4 ppm. HRMS (EI) calc. for $C_{26}H_{29}O_4F$ 424.2050, found 424.2047.

M4; 91% isolated yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.41 (s, 2H), 7.61 (d, $J = 6.9$ Hz, 2H), 7.00 (d, $J = 6.9$ Hz, 2H), 5.81 (m, 2H), 5.04 (d, $J = 15$ Hz, 2H), 4.99 (d, $J = 7.0$ Hz, 2H), 4.40 (t, $J = 6.9$ Hz, 4H), 3.86 (s, 3H), 2.15 (q, $J = 6.9$ Hz, 4H), 1.84 (q, J = 6.9 Hz, 4H), 1.59 (q, $J = 7.2$ Hz, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 159.9, 141.5, 138.4, 131.8, 131.4, 128.7, 128.4, 115.1, 114.5, 65.4, 55.4, 33.4, 28.2, 25.4 ppm. HRMS (EI) calc. for $C_{27}H_{32}O_5$ 436.2250, found 436.2249.

M5; 70% isolated yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.51 (s, 2H), 7.74 (s, 4H), 7.65 (d, $J = 7.5$ Hz, 2H), 7.48 (t, $J = 7.2$ Hz, 2H), 7.40 (t, $J = 7.2$ Hz, 1H), 5.84 (m, 2H), 5.05 (d, $J = 14$ Hz, 2H), 4.98 (d, $J = 6.9$ Hz, 2H), 4.40 (t, $J = 6.6$ Hz, 4H), 2.15 (q, $J = 7.2$ Hz, 4H), 1.84 (q, $J = 7.2$ Hz, 4H), 1.57 (q, $J = 7.2$ Hz, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 141.6, 141.3, 140.6, 138.5, 138.2, 132.3, 131.7, 129.5, 129.1, 127.9, 127.8, 127.3, 115.3, 65.6, 33.5, 28.4, 25.5 ppm. HRMS (EI) calc. for $C_{32}H_{34}O_4$ 482.2457, found 482.2452.

M6; 89% isolated yield ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.43 (s, 2H), 7.46 (d, $J = 3.6$ Hz, 1H), 7.36 (d, $J = 5.1$ Hz, 1H), 7.12 (dd, $J = 3.6$, 5.0 Hz, 1H), 5.84 (m, 2H), 5.07 (d, $J = 14$ Hz, 2H), 4.98 (d, $J = 6.9$ Hz, 2H), 4.40 (t, $J = 6.6$ Hz, 4H), 2.14 (q, $J = 6.9$ Hz, 4H), 1.84 (q, $J = 6.9$ Hz, 4H), 1.57 (q, $J = 6.9$ Hz, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 142.1, 138.3, 135.2, 131.6, 130.7, 129.1, 128.4, 126.2, 124.5, 115.1, 65.5, 33.4, 28.1, 25.3 ppm. HRMS (EI) calc. for $C_{24}H_{28}O_4S_1$ 412.1708, found 412.1707.

M7; 43% isolated yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.02 (s, 2H), 5.81 (m, 2H), 5.01 (d, $J = 15$ Hz, 2H), 4.96 (d, $J = 6.9$ Hz, 2H), 4.32 (t, $J = 6.9$ Hz, 4H), 2.45 (s, 3H), 2.14 (q, $J = 6.9$ Hz, 4H), 1.80 (q, $J = 6.9$ Hz, 4H), 1.53 (q, $J = 6.9$ Hz, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 138.7, 138.4, 134.4, 130.9, 128.0, 115.1, 65.3, 33.4, 28.3, 25.4, 21.3 ppm. HRMS (EI) calc. for $C_{21}H_{28}O_4$ 344.1987, found 344.1991.

M8; 61% isolated yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.73 (s, 2H), 5.82 (m, 2H), 5.03 (d, $J = 14$ Hz, 2H), 4.97 (d, $J = 6.9$ Hz, 2H), 4.36 (t, $J = 6.6$ Hz, 4H), 3.88 (s, 3H), 2.12 (q, $J = 6.9$ Hz, 4H), 1.79 (q, $J = 6.9$ Hz, 4H), 1.54 (q, $J = 6.9$ Hz, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 159.7, 138.4, 132.2, 122.9, 119.3, 115.1, 65.5, 55.9, 33.4, 28.2, 25.4 ppm. HRMS (EI) calc. for $C_{21}H_{28}O_5$ 360.1937, found 360.1936.

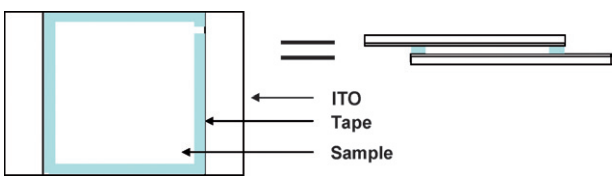
M9; 58% isolated yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.99 (s, 2H), 8.93 (s, 1H), 5.79 (m, 2H), 5.04 (d, $J = 14$ Hz, 2H), 4.95 (d, $J = 6.9$ Hz, 2H), 4.38 (t, $J = 6.9$ Hz, 4H), 2.14 (q, $J = 7.0$ Hz, 4H), 1.79 (q, $J = 6.9$ Hz, 4H), 1.54 (q, $J = 6.9$ Hz, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 148.5, 138.1, 135.8, 132.8, 128.1, 115.2, 66.3, 33.3, 28.1, 25.2 ppm. HRMS (EI) calc. for $C_{20}H_{25}O_6N_1$ 375.1682, found 375.1677.

M10; 67% isolated yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.51 (s, 2H), 5.78 (m, 2H), 5.00 (d, $J = 13$ Hz, 2H), 4.96 (d, $J = 6.9$ Hz, 2H), 4.36 (t, $J = 6.6$ Hz, 4H), 2.10 (q, $J = 6.9$ Hz, 4H), 1.78 (q, $J = 6.9$ Hz, 4H), 1.50 (q, $J = 7.0$ Hz, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 142.4, 138.3, 132.6, 129.9, 115.1, 93.5, 65.7, 33.3, 28.1, 25.3 ppm. HRMS (EI) calc. for $C_{20}H_{25}O_4I$ 456.0797, found 456.0797.

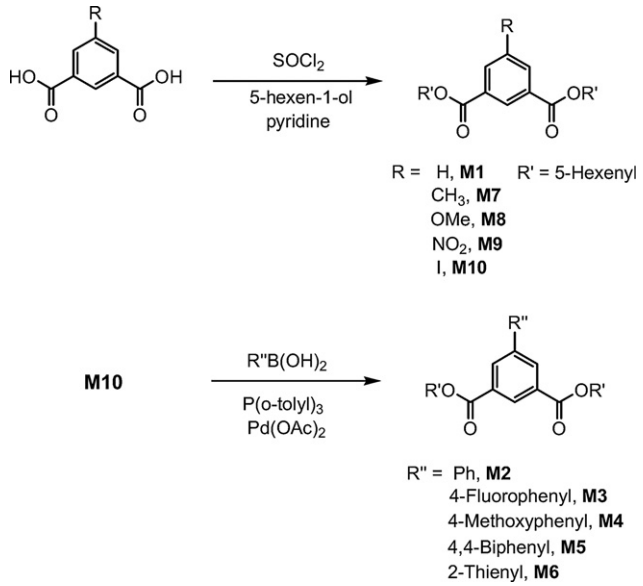
UV-visible spectroscopy and cyclic voltammetry

The UV-visible spectra were recorded using Jasco V630 and Ocean Optics USB4000 spectrometer. Cyclic voltammetry measurements were carried out using a CH instruments model CHI600 potentiostat. Conventional three electrodes assembly was used under nitrogen to record cyclic voltammograms. The working electrode was an ITO-coated glass electrode. The counter-electrode was a platinum wire, and $Ag/AgNO_3$ (Ag/Ag^+) was used as the reference electrode. The scan rate was 100 mV s^{-1}. The 0.20 M anhydrous tetrabutylammonium hexafluorophophate ($TBAPF_6$) solution in distilled γ-butyrolactone was used as a supporting electrolyte. The 5 mM solutions of each compound were used for measurement.

Preparation of sandwich-type two ITO electrodes cells



The electrochromic cells were prepared using two ITO-coated glass electrodes, which were sandwiched by Surlyn tape. The solution was injected into the cell using a syringe.



Scheme 2 Synthesis of 5-substituted isophthalate derivatives.

Results and discussion

Diverse 5-substituted isophthalate derivatives used in this study were prepared *via* esterification of 5-substituted isophthalic acids or Suzuki coupling between 5-iodo-isophthalate and diverse boronic acids (Scheme 2). All compounds were fully characterized by ^{1}H and ^{13}C NMR and high resolution mass spectroscopy. 5-(2-Thienyl)-isophthalate has a pale yellow color and other compounds are colorless in their neutral state.

First, cyclic voltammeric analysis was conducted for each sample (5 mM) to understand the electrochemical behavior. 0.2 M Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was used as the supporting electrolyte in γ-butyrolactone. As summarized in Table 1, the compounds showed reversible reduction peaks in range of −2.5 to −2.90 V (*vs.* Ag/Ag^+) with a scan in the negative direction (100 mV s^{-1}). At these reduction potentials, we could observe a color on the surface of the working electrode (ITO glass) (Fig. 1). In comparison, there was no change of color with a scan in the positive direction (0–3 V *vs.* Ag/Ag^+). This means that isophthalate derivatives in this study generate colored species *via* reduction. Similarly, it has been reported that electrochromism of 1,4-terephthalate derivatives resulted from the formation of the anionic radical *via* electrochemical reduction.[6]

Table 1 Redox potentials of compounds in cyclic voltammetry and applied voltage for color display

Compounds R′ =	Redox potential[a] *vs.* Ag/Ag^+/V	Applied DC voltage[b]/V
H, **M1**	−2.68 (rev)[c]	5.05
Ph, **M2**	−2.55 (rev)	5.14
4-Fluorophenyl, **M3**	−2.58 (rev)	5.20
4-Methoxyphenyl, **M4**	−2.62 (rev)	5.54
4,4-Biphenyl, **M5**	−2.57 (rev)	4.38
2-Thienyl, **M6**	−2.63 (rev)	5.15
CH_3, **M7**	−2.72 (rev)	5.32
OMe, **M8**	−2.61 (rev)	5.21
NO_2, **M9**	−1.88, −2.71, −2.81 (rev)	4.17, 5.19
Nitrobenzene	−2.04, −3.08	4.38, 5.27

[a] Redox potential *vs.* Ag/Ag^+(reference electrode) determined in a conventional three electrodes cell by using 0.2 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte in γ-butyrolactone, ITO glass as the working electrode, and platinum as the counter electrode.[b] Applied DC voltage for color displays from sandwich-type ITO electrode cells, 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte in γ-butyrolactone.[c] Reversible peak.

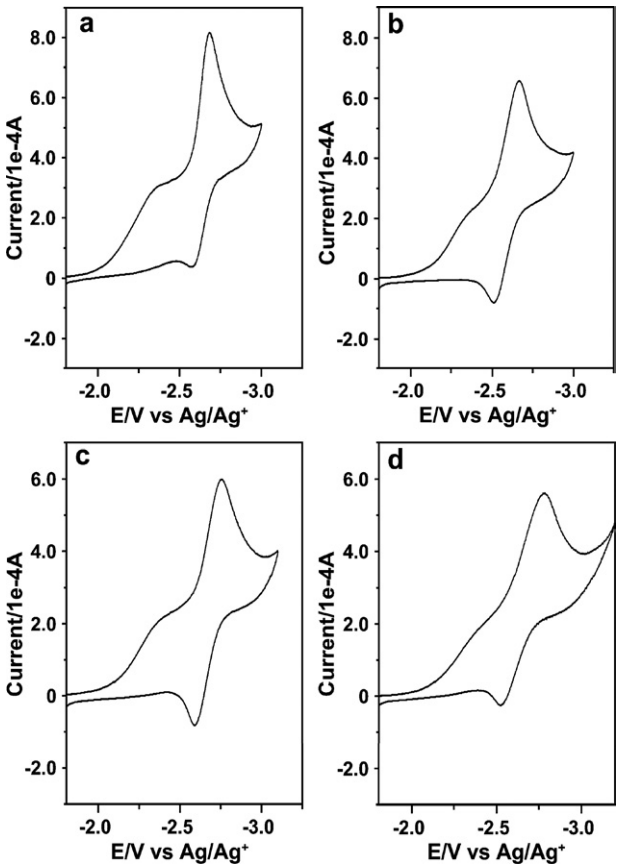


Fig. 1 Representative cyclic voltammorgrams of **M1** (a), **M2** (b), **M7** (c) and **M8** (d).

We prepared solution-based simple electrochromic devices using sandwich-type indium tin oxide (ITO)-coated glass electrodes.[6b] Each sample (0.225 M) was dissolved in γ-butyrolactone, containing 0.2 M $TBAPF_6$ as the electrolyte. The DC voltage was slowly provided to the cells (from 0 to 6 V, 100 mV s^{-1}). The displayed colors of isophthalate derivatives *via* supply of DC voltage are summarized in Fig. 2 and Fig. 3.

As expected, isophthalate derivatives (**M1**–**M8**) displayed diverse colors. It is evident that a functional group in the 5-position has a significant influence on the electronic surroundings of the reduced species. In case of **M1** (5-H), **M7** (5-Me) and **M8** (5-OMe), the colored species showed maximum absorption peak at 450, 449 and 445 nm, respectively. When the functional groups were monoarenes, the maximum absorption peaks were red-shifted to 509 (**M2**), 512 (**M3**) and 530 nm (**M6**). The colored species by **M5** (5-4,4′-biphenyl) showed the maximum absorption peak at 568 nm (Fig. 3). Considering the

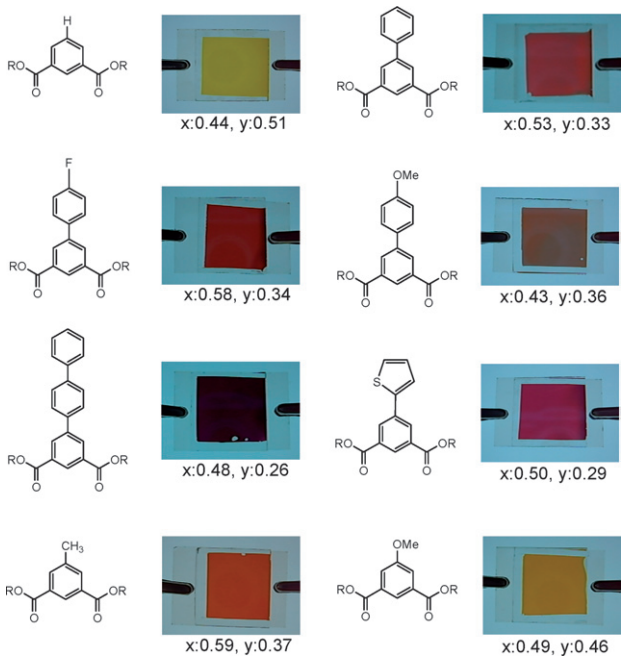


Fig. 2 Electrochromism of 5-substituted isophthalate derivatives (with the computed coordinates in the CIE chromaticity diagram).

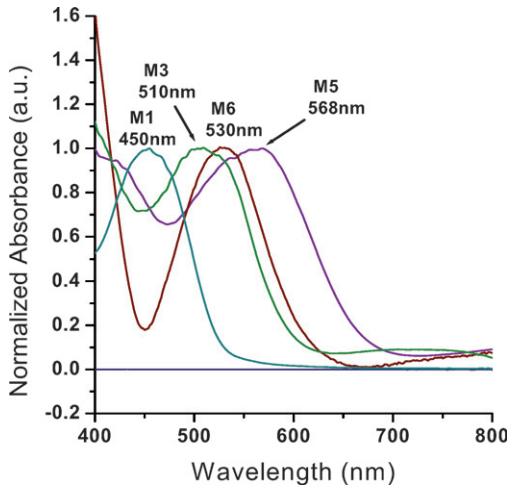


Fig. 3 Representative UV-visible absorption spectra of the reduced species of **M1, M3, M5** and **M6**.

length of conjugated system, the trend of the resultant color could be rationalized; as the conjugated system is longer, the maximum absorption peak is more red-shifted. Based on this speculation, we believe that the color can be controlled by properly choosing a functional group at 5-position. It is noteworthy that *more than two hundred kinds* of boronic acid are now commercially available.

The trend of the observed color of reduced species was rationalized by time-dependent density functional theory (TDDFT) calculations.[7] The excitation properties (transition energies and oscillator strengths) of the reduced species of **M1**, **M3** and **M5** by one electron were calculated. The HOMO–LUMO energy gaps

Table 2 The comparison of calculated absorption peak based on time-dependent density functional theory (TDDFT) with the experimentally observed ones

Compounds	Calculated abs[a]/nm	Observed abs[b]/nm
M1	476	450
M3	537	510
M5	562	568

[a] The calculation was conducted based on B3LYP/6-31+G* method.[b] Experimentally observed UV-visible absorption peaks.

for the reduced species of **M1**, **M3** and **M5** as the representatives were calculated to be 723.2, 893.4 and 1265.6 nm, respectively. As the conjugated system was longer by introducing a substituent at 5-position, the HOMO–LUMO energy gap became smaller. It should be pointed out that not only the HOMO–LUMO transition but also the other orbital transitions have contributed to the absorption in the visible region. As a matter of fact, from the TDDFT calculations of the reduced species of **M1**, HOMO–LUMO + 10 transition was shown to give a significant contribution to the absorption at 476.4 nm. Nevertheless, the HOMO–LUMO energy gap gives the consistent trend that shows more red-shifted absorption peak when the conjugated system is longer. Table 2 summarizes the calculated absorption peaks in the visible region along with the experimentally observed maximum visible absorption peak. The calculated absorption maximum peak positions in the visible region are in good agreement with the experimental results.

Another interesting feature is the electronic structures of the molecular orbitals (MO). Fig. 4 shows the MOs that are involved in the maximum absorption peak in visible region for **M1**. It was found that the LUMO and LUMO + 10 show the electron density localized at the central conjugated systems, as seen in Fig. 4. The MOs between LUMO and LUMO + 10 were not involved in the absorption process, which means that the transitions from HOMO to the orbitals between LUMO and LUMO + 10 are not involved in the absorption. It is very interesting to find that the electron densities are mostly distributed over the two ester moieties in the MOs between LUMO and LUMO + 10. This may be responsible for the quite pure colors for the 5-substituted isophthalate derivatives investigated.

Next, we were curious about what would happen if an electrochemically active group was introduced at the 5-position. Considering the functional-group-dependent color, multicolor displays can be expected.

Anionic radicals of aromatic nitro compounds have been a very important electrochemical research subject, in part because of their role in the unique functions of organic aromatic nitro compounds,[8] such as the activity of commercial drugs and

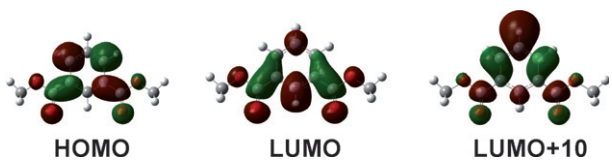
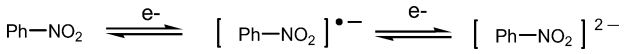


Fig. 4 Calculated HOMO, LUMO and LUMO + 10 of the reduced species of **M1**.



Scheme 3 Known reduction process of nitrobenzene.

pesticides, both based on the nitro aromatic radical species.[9] Thus, reduction of aromatic nitro compounds has been electrochemically characterized.[10] Until now, it has been known that two reduced species can be generated step-by-step with two electrons as shown in Scheme 3. The first reduced species is an anionic radical that can undergo further reduction to form the dianion.

Considering this multi-step reduction process of nitrobenzene, we prepared the 5-nitro-isophthalate, **M9**, and investigated its electrochromism behavior. As shown in Fig. 6a, the cyclic voltammogram of 5 mM **M9** in a 0.2 M $TBAPF_6$ solution in γ-butyrolactone showed the multi-step reduction process at −1.88, −2.71 and −2.81 V (*vs.* Ag/Ag^+) (Table 1). As well-documented, in the case of nitrobenzene, nearly the same pattern was observed for the two reduction peaks with their shift to more negative potentials of −2.04 and −3.08 V (*vs.* Ag/Ag^+), denoting that reduction of nitrobenzene requires higher energy than that of **M9**.[10] It should be noted that **M9** has two additional electron-withdrawing ester groups. Thus, the first two reduction peaks of **M9** can be attributed to the formation of the anionic radical and dianion, respectively, as with nitrobenzene.

M9 and nitrobenzene (0.225M) were dissolved in γ-butyrolactone, containing 0.2 M $TBAPF_6$ as the electrolyte and added to the electrochromic cells. And then, the DC voltage was slowly provided to the cells (from 0 to 6 V, 100 mV s^{-1}). As shown in current–voltage curves of **M9** and nitrobenzene in Fig. 6b and 6c, two redox peaks were observed. In the case of **M9**, vivid blue, then red appeared at 4.17 and 5.19 V, respectively (Fig. 5).[11] In contrast, simple nitrobenzene did not show any detectable color change in a range of 0–6 V, which reveals that two ester groups play an important role in electrochromism. Considering Fig. 6b and 6c, we assigned the blue and red species as the anionic radical and dianion, respectively. The reason why two distinct colors were generated is unknown at this stage and further work on the computational approach is needed. However, we believe that this discovery opens the door not only to diverse spectroelectrochemical approaches for the study of nitro radicals and dianions academically, but also to the development of multi-color display devices.[12]

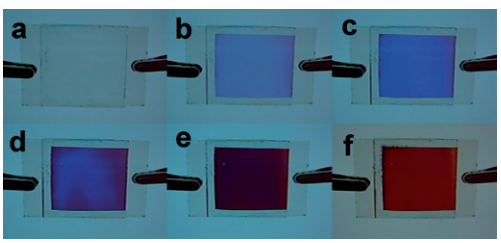


Fig. 5 Multicolor display of 5-nitro-isophthalate derivative with a supply of DC voltage; before voltage application (a), colors of the first reduced species (b, c) and the second reduced species (d–f).

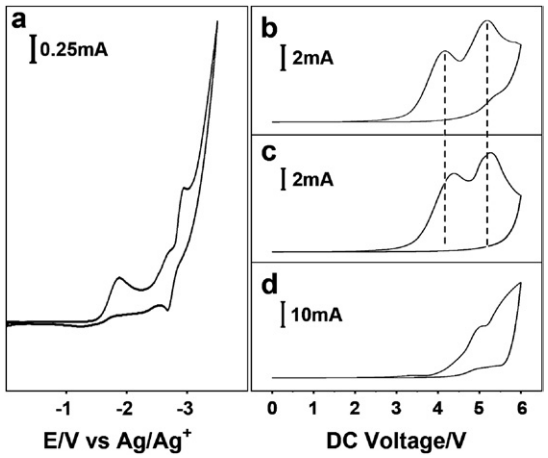


Fig. 6 Cyclic voltammogram of 5-nitro-isophthalate derivative, **M9** with Ag/Ag^+ reference electrode and scan rate of 100 mV s^{-1} (a), *I–V* curves of sandwich-type two ITO electrodes cells of 5-nitro-isophthalate derivatives, **M9** (b), nitrobenzene (c), and isophthalate derivatives, **M1** (d).

Fabrication of device

For practical use, all-solid-state devices are preferable to the solution-based ones due to technical problems, such as leakage of electrolyte solution. Thus, we fabricated the quasi-solid devices using poly(vinylpyrrolidone)-based gel electrolyte.[13] A mixture of 3.33 g of 1-vinyl-2-pyrrolidinone (30 mmol), 0.031 g of *N*,*N*′-methylenebisacrylamide (0.2 mmol), 0.99 g of 1-methyl-2-pyrrolidinone (10 mmol), 4.6 mg of ammonium persulfate (0.02 mmol), 1.2 mg of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine

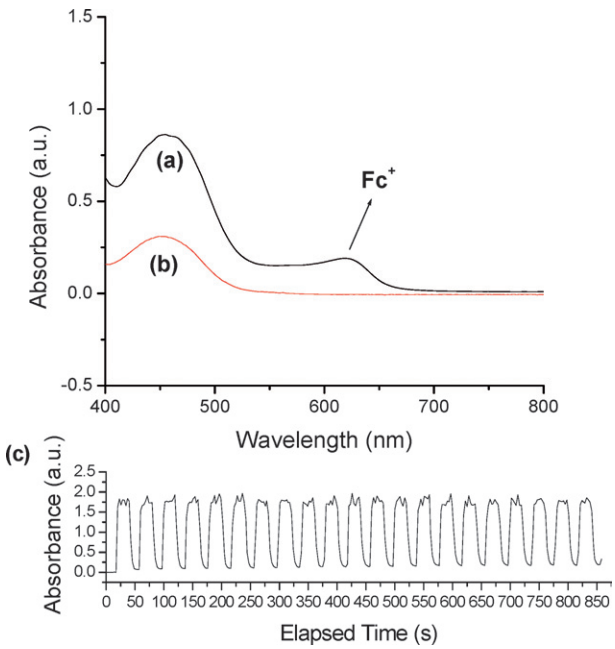


Fig. 7 UV-visible spectra of the colored species by **M1** in gel-electrolyte-based quasi-solid device (a) and in solution-based device. (b) The intensity change of UV-visible absorption peak at 450 nm by applying a potential step (0.00–3.6 V) to the gel-electrolyte-based quasi-solid device using **M1** (c).

(0.01 mmol), 0.068 g of tetrabutylammonium hexafluorophosphate (0.2 mmol), ferrocene (0.2 mmol) and the coloring material (0.2 mmol, **M1**) was injected into the cell *via* syringe. Then, the cell was gently heated at 40 °C for 12 h to induce the gelation of solution. The colored species in this device showed maximum absorption peak at 452 nm, which is nearly same with that by **M1** in solution-based device. With help of contemporary redox reaction of ferrocene (charge compensation *via* oxidation), the electrochromic performance was quite reversible (Fig. 7).

Conclusion

A new series of isophthalate-based electrochromic materials were prepared. The functional groups at the 5-position of isophthalate have a significant influence on the observed color. In particular, the electrochemically active nitro group induced multi-color, indicating that further electrochromic properties could be manipulated using more diverse 5-substituted isophthalate derivatives.

Acknowledgements

This work was supported by the Samsung Research Fund, Sungkyunkwan University, 2007. JHK is grateful for a grant from the Korean Research Foundation (MOEHRD) (KRF-2005-005-J11901). JYL acknowledges the financial support by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korean Government (MEST) (No. R11-2008-012-03002-0).

References

1 M. Grätzel, *Nature*, 2001, **409**, 575.
2 D. R. Rosseinsky and R. J. Mortimer, *Adv. Mater.*, 2001, **13**, 783.
3 (*a*) P. Anderson, R. Forchheimer, P. Tehrani and M. Berggren, *Adv. Funct. Mater.*, 2007, **17**, 3074; (*b*) R. J. Mortimer, A. L. Dyer and J. R. Reynolds, *Displays*, 2006, **27**, 2; (*c*) S. A. Sapp, G. A. Sotzing and J. R. Reynolds, *Chem. Mater.*, 1998, **10**, 2101; (*d*) S. Beaupré, J Dumas and M. Leclerc, *Chem. Mater.*, 2006, **18**, 4011.
4 (*a*) D. Corr, U. Bach, D. Fay, M. Kinsella, C. McAtamney, F. O'Reilly, S. N. Rao and N. Stobie, *Solid State Ionics*, 2003, **165**, 315; (*b*) M. O. M. Edwards, T. Gruszecki, H. Pettersson, G. Thraisingham and A. Hagfeldt, *Electrochem. Commun.*, 2002, **4**, 963; (*c*) M. Felderhoff, S. Heinen, N. Molisho, S. Webersinn and L. Walder, *Helv. Chim. Acta*, 2000, **83**, 181.
5 D. Cummins, G. Boschloo, M. Ryan, D. Corr, S. N. Rao and D. Fitzmaurice, *J. Phys. Chem. B*, 2000, **104**, 11449.
6 (*a*) K. Nakamura, Y. Oda, T. Sekikawa and M. Sugimoto, *Jpn. J. Appl. Phys.*, 1987, **26**, 931; (*b*) H. Urano, S. Sunohara, H. Ohtomo and N. Kobayashi, *J. Mater. Chem.*, 2004, **14**, 2366, also refer to experimental details in the ESI for the preparation of devices.
7 The DFT calculations with B3LYP exchange functionals with 6-31+G* basis sets were carried out to optimize the structures of the reduced species of M1, M3 and M5 using a suite of Gaussian 03 programs. (Frisch, *et al.*, *Gaussian 03*, revision A1; Gaussian Inc.: Pittsburgh, PA, 2003). Then, at the optimized geometries, TDDFT calculations have been performed to obtain their excitation properties.
8 (*a*) H. Kojima and A. J. Bard, *J. Am. Chem. Soc.*, 1975, **97**, 6317; (*b*) W. R. Fawcett and A. Lasia, *J. Phys. Chem.*, 1978, **82**, 1114; (*c*) R. A. Petersen and D. H. Evans, *J. Electroanal. Chem.*, 1987, **222**, 129; (*d*) B. G. Chauhan, W. R. Fawcett and A. Lasia, *J. Phys. Chem.*, 1977, **81**, 1476; (*e*) W. R. Fawcett, M. Fedurco and M. Opallo, *J. Phys. Chem.*, 1992, **96**, 9959; (*f*) B. Kwiatek and M. K. Kalinowski, *J. Electroanal. Chem.*, 1987, **226**, 61; (*g*) C. Kraiya, P. Singh and D. H. Evans, *J. Electroanal. Chem.*, 2004, **563**, 203; (*h*) A. Kapturkiewicz and M. Opallo, *J. Electroanal. Chem.*, 1985, **185**, 15; (*i*) G. Pezzatini and R. Guidelli, *J. Electroanal. Chem.*, 1979, **102**, 205.
9 (*a*) P. Mořkovská, M. Hromadová, L. Pospíšil and S. Giannarelli, *Langmuir*, 2006, **22**, 1896; (*b*) C. R. Worthing and D. Phil, *The Pesticide Manual*, British Crop Protection Council, Hampshire, UK, 1987.
10 G. L. McIntire, *J. Electrochem. Soc.*, 1981, **128**, 427C.
11 In *N*-methylpyrrolidone (NMP) solution, blue, then red color appeared at 3.11 and 4.40 V (DC voltage).
12 (*a*) A. A. Argun, P.-H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, N. J. Pinto, D. B. Tanner, A. G. MacDiarmid and J. R. Reynolds, *Chem. Mater.*, 2004, **16**, 4401; (*b*) G. Sonmez, C. K. F. Shen, Y. Rubin and F. Wudl, *Angew. Chem., Int. Ed.*, 2004, **43**, 1498; (*c*) N. Kobayashi, S. Miura, M. Nishimura and H. Urano, *Sol. Energy Mater. Sol. Cells*, 2008, **92**, 136; (*d*) S. Hünig, M Kemmer, H. Wenner, F. Barbosa, G. Gescheidt, I. F. Perepichka, P. Bäuerle, A. Emge and K. Peters, *Chem.–Eur. J.*, 2000, **6**, 2618.
13 H. Tsutsumi, Y. Nakagawa and K. Tamura, *Sol. Energy Mater. Sol. Cells*, 1995, **39**, 341.