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Molecular Design and Preparation of Bis-isophthalate Electrochromic Systems having Controllable Color and Bistability

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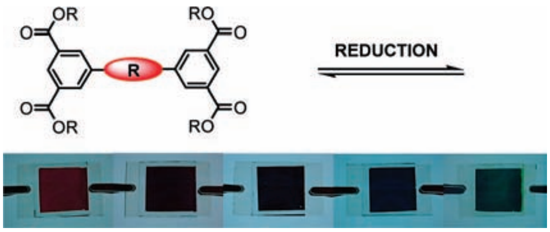
ABSTRACT



New electrochromic systems based on bis-isophthalates were designed and prepared. They showed electrochromism behavior by two-electron reduction. The displayed colors showed greatly enhanced bistability and were dependent on the length of the conjugated bridge between the two isophthalate groups. We believe that the connection of two electrochromic systems with a conjugated bridge is a good basic strategy to obtain new bistable electrochromic systems.

Recently, the electrochromism of organic molecules has become an academically and industrially important issue.[1] During the past decade, diverse organic electrochromic systems have been developed, including organic conducting polymers in which the cationic radical species formed via oxidation have usually shown color in the visible light range.[2] Compared to oxidation-inducd electrochromism, reduction-induced electrochromism is relatively rare.[3] Most studies have focused on *N*,*N*′-disubstituted viologen derivatives, which have been applied for industrial purposes such as smart windows and diverse mirror devices.[4] Usually, they have displayed a blue color via one-electron reduction to form radicals.

Two-electron-based electrochromic systems also have been developed.[5] Usually, the examples in the literature have focused on the oxidative breaking of covalent bonds via two-electron oxidation to form dications. It has been suggested

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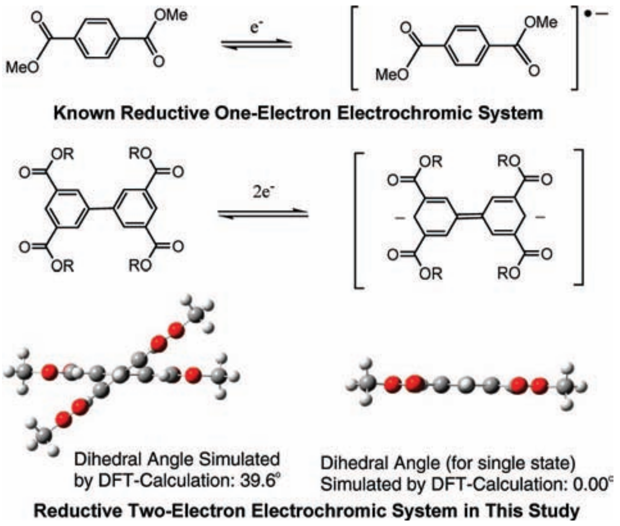
that the more stable (bistable) color species could be obtained in these two-electron systems because dications are believed to be more stable than the cationic or anionic radical species. The stability of colored species via redox reaction is another important issue because if the displayed color can be maintained after power is off, electricity and the cost of operating devices can be saved.[6] Thus, to obtain more diverse colors with bistability, more diverse organic electrochromic systems need to be developed.

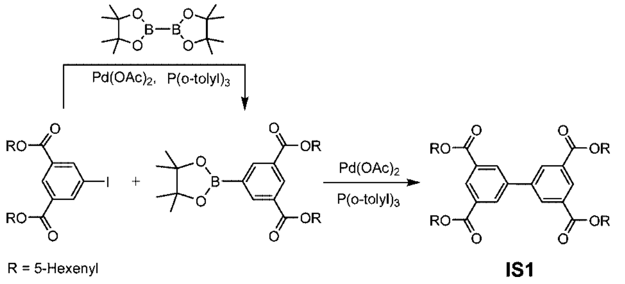
Our research group has studied the electrochromism of isophthalates via one-electron reduction to form anionic radicals.[7] However, the displayed color immediately disappeared after power off as a result of the instability of radical species, like the known case of dimethyl terephthalate (Scheme 1). In our ongoing efforts to develop new electrochromic systems that are more bistable and can be tailored to control the displayed colors, we designed two-electron systems based on bis-isophthalates with the help of density functional theory (DFT) calculation.[8] If two isophthalate groups were connected by a conjugated bridge, the generated radicals in each part could be coupled to form a more stable quinoid dianion, like Chichibabin's hydrocarbon.[9] In the case of the singlet diradical form, it was theoretically anticipated that the dihedral angle (39.6°) between two arenes was decreased to be coplanar via two-electron reduction.[8] The color can be dependent on the length of the conjugated systems. In this regard, bis-isophthalate systems having diverse conjugated bridges were designed and prepared.

Scheme 1. Electrochromism of Dimethyl Terephthalate and Bis-isophthalate Derivatives



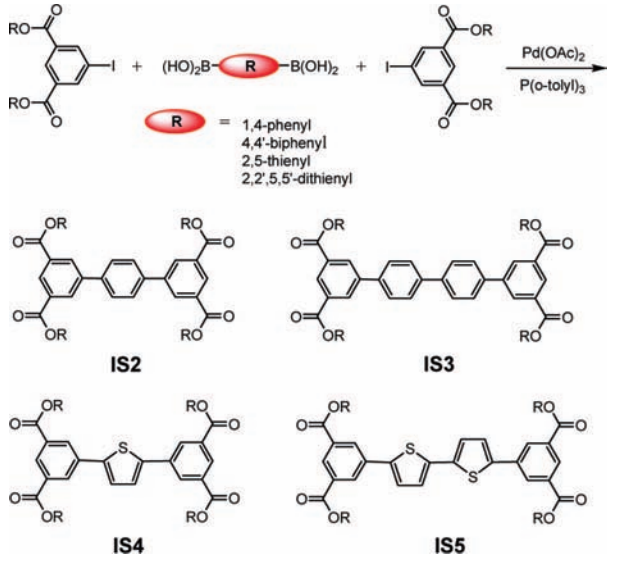
Scheme 2 shows the synthetic route for the preparation of simple bis-isophthalates; **IS1** was prepared via Suzuki coupling between 5-pinacolatoborane-substituted isophthalate and 5-iodo-isophthalate. The 5-pinacolatoborane-substituted isophthalate could be prepared in situ via coupling between the 5-iodo-isophthalate and bis(pinacolato)diborane.[10] Terminal double bond groups were introduced in each ester group for possible further modification.

Scheme 2. Synthesis of Bis-isophthalate Derivative **IS1**



For the longer conjugated bridge groups between two isophthalates, the benzene (**IS2**), biphenyl (**IS3**), thienyl (**IS4**), and dithienyl groups (**IS5**) were introduced by coupling of two 5-iodo isophthalates with the corresponding diboronic acids. (Scheme 3) The synthesized bis-isophthalates were fully characterized by ^{1}H NMR, ^{13}C NMR, and high resolution mass spectroscopy.

Scheme 3. Synthesis of Bis-isophthalates **IS2**, **IS3**, **IS4**, and **IS5**



A *p*-terphenyl group was introduced into the bridge by coupling between 5-pinacolatoborane isophthalate (Scheme 4) and diiodo-*p*-terphenyl, which was prepared via iodation of *p*-terphenyl using iodine in acidic solution.[11]

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(6) This has been described as "bistability" or "memory effect" in electrochromism.

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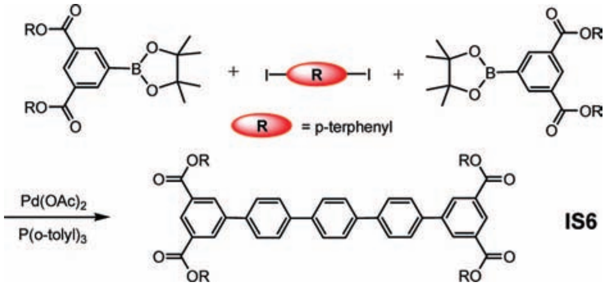
Scheme 4. Synthesis of Bis-isophthalates **IS6**



The two-electron reduction processes of **IS1**, **2**, **3,** and **6** were studied by cyclic voltammetry. Monoisophthalate shows reversible one-electron reduction.[7] Each compound (5 mM) was dissolved in *N*-methylpyrrolidone (NMP) containing 0.2 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$). As shown in Figure 1, **IS1** showed two separated reduction peaks, indicating that the second reduction needs higher energy than first one and, therefore, that the two isophthalate rings are electronically well connected. With increasing length of the conjugated bridge, the two reduction peaks became more overlapped. In case of **IS3**, which has biphenyl as bridge, one redox peak was observed. The height of the reduction peak indicated a correspondence to the two-electron reduction process. With increasing length of the connector, reduction of each isophthalate ring occurred at nearly the same position. As expected, the cyclic voltammogram of **IS6**, which has a terphenyl bridge, showed nearly the same shape as that of **IS3**. (table 1).

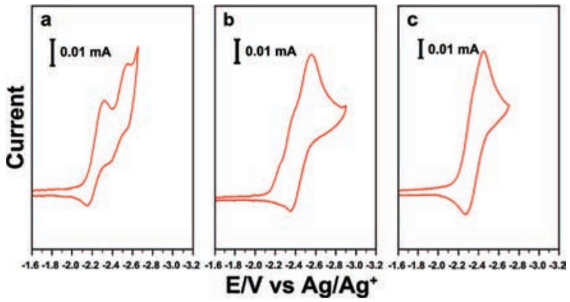


Figure 1. Cyclic voltammograms of bis-isophthalate derivatives **IS1** (a), **IS2** (b), and **IS3** (c).

To investigate the bridge-length-dependent electrochromic behavior of the bis-isophthalates, each compound (0.20 M) was dissolved in NMP containing 0.20 M TBAPF$_6$ as a supporting electrolyte. This solution was injected into the sandwich-type ITO glass cells. The DC voltage was gradually applied to these cells. The displayed color was characterized by UV−vis absorption spectroscopy. As shown in Figure 2, **IS1** showed a reddish color with a maximum absorption peak at 533 nm. The color displayed by **IS2** can be described as violet with a maximum absorption peak at 542 nm. The reduction of **IS3** showed a dark blue color, which was shifted to violet and blue colors as the bridge became longer. Interestingly, **IS6** showed nearly the same UV absorption peak (573nm) as **IS3** (572 nm), indicating the limitation in controlling the color via bridge-length control. However, we could move the absorption peaks in the red direction by introducing a thienyl group in the bridge.

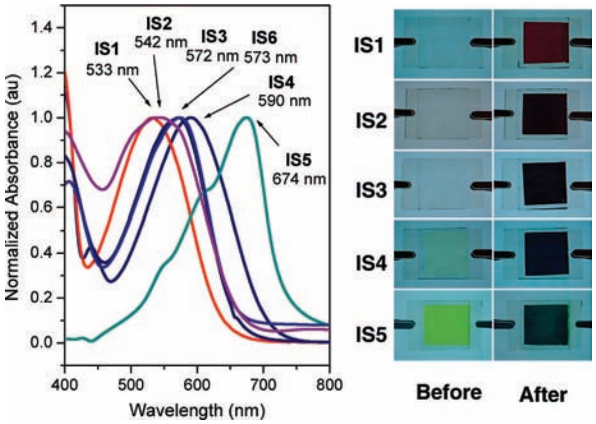


Figure 2. UV−visible spectra and photos of displayed colors before and after voltage supply.

Table 1. Redox Potentials of Compounds in Cyclic Voltammetry and Maximum UV−vis Absorption Peak

compounds	redox potential[a] vs Ag/Ag$^+$ (V)	max abs (nm)
IS1	−2.24, −2.48	533
IS2	−2.46	542
IS3	−2.36	572
IS4	−2.06, −2.36	590
IS5	−2.18, −2.49	674
IS6	−2.36	573

[a] Redox potential vs Ag/Ag$^+$ (reference electrode) determined in a conventional three-electrode cell by using 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte in *N*-metylpyrrolidone, ITO glass as the working electrode, and platinum as the counter electrode.

Interestingly, **IS4** showed a deep blue color with a maximum absorption peak at 592 nm. In cyclic voltammetry, **IS4** showed two separated reduction peaks, indicating a facile electronic communication between the two isophthalate groups (Table 1 and Figure S1, Supporting Information). It is noteworthy that the thiophene ring is popular in designing organic electronic systems due to its excellent performance in electron transfer.[12] The two-electron reduction of **IS5** showed a display of green color with a maximum UV−vis absorption peak at 674 nm. According to the cyclic voltammogram of **IS5**, the two isophthalate groups were still electronically communicating well (Table 1 and Figure S1, Supporting Information). According to these observations,

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it was concluded that the displayed color is highly dependent on the length of the conjugated bridge and the ability of electronic communication.

Next, we tested the stability of the colored species of bis-isophthalates. We gradually supplied −3.2 V to the ITO working electrode and then suddenly stopped the voltage supply. **IS1** exhibited a promising memory effect as shown in Figure 3a, which shows the time-dependent color intensity change of **IS1**.

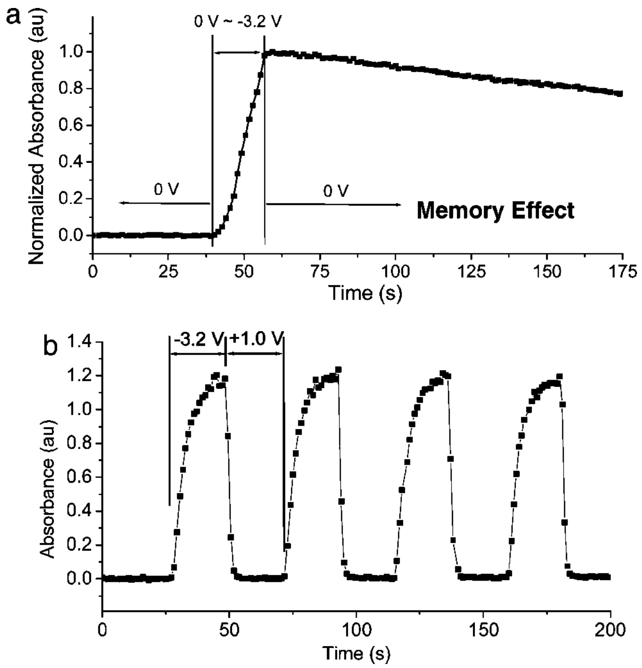

Figure 3. Change of color intensity of **IS1** after power off (a) and with switching voltage between −3.2 V and +1.0 V for 22 s, respectively (b).

It took around 300 s for half-intensity to be obtained. In sharp contrast, the similar color as was formed by the one-electron reduction of dimethyl terephthalate to form an anionic radical disappeared rapidly. The gradual color quenching process resulted from the recombination of reduced bis-isophthalates and oxidized ferrocene species through electrolyte solution. Thus, we believe that the efficient separation of working and counter materials by heterogenization will greatly extend the lifetime of colored species. To remove that displayed color, we applied a positive potential (+1.0V) to the working electrode, which resulted in the immediate disappearance of color. Figure 3b shows the reversible switching of color with the help of the contemporary redox reaction by ferrocene.[13] The memory effect of the displayed color after power off was also dependent on the bridge length. With increasing conjugated bridge length from **IS1**, through **IS2** to **IS3**, the memory effect was shortened (see Supporting Information).

In conclusion, new electrochromic systems based on bis-isophthalates were designed and prepared. They showed electrochromism behavior by two-electron reduction. The displayed colors showed greatly enhanced bistability and were dependent on the length of the conjugated bridge between the two isophthalate groups. The color change was reversible in the presence of the contemporary redox system, ferrocene. The study results suggested that the connection of two electrochromic systems with a conjugated bridge is a good basic strategy to obtain bistable electrochromic systems. We believe that this method can be applied to the design of more diverse electrochromic systems.

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Supporting Information Available: Experimental procedure for the preparation of new compounds and their characterization data, and manipulation procedure of two ITO electrodes cells. This information is available free of charge via the Internet at http://pubs.acs.org.

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