Synthesis of novel photochromic dithienylethenes and investigation on their optoelectronic properties

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ABSTRACT

Four novel photochromic dithienylethenes compounds, 1,2-bis[2-methyl-5(p-fluorophenyl)-3-thienyl]perfluorocyclopentene (1a), 1,2-bis[2-methyl-5(p-ethoxyphenyl)-3-thienyl]perfluorocyclopentene (2a), 1,2-bis[2-methyl-5(p,N,N-dimethylaminophenyl)-3-thienyl]perfluorocyclopentene (3a) and 1,2-bis(2-methyl-5-naphthalene-3-thienyl)perfluorocyclopentene (4a) were synthesized. Their optoelectronic properties, such as photochromism in solution as well as in PMMA amorphous, fluorescence and electrochemistry properties were systematically investigated. These dithienylethenes have shown good photochromic behavior both in solution and in PMMA amorphous film. All of them exhibited relatively strong fluorescence. With the increase of their concentration in a THF solution, their fluorescence spectra showed a bathochromic shift. The irreversible anodic oxidation of 1a, 3a and 4a occurred when performing cyclic voltammetry tests. Moreover, dithienylethene 1a showed remarkable multi-color electrochromic properties during the anodic polarization. In addition, photo-mode multi-step optical storage using 2a and 3a as recording medium was performed successfully.

Keywords: Dithienylethene, photochromism, fluorescence, electrochemistry, multi-step optical storage.

1. INTRODUCTION

In recent years, optical memory and molecular device applications have motivated much concern in organic photochromism.1 Especially, molecular units that allow the reversible modulation of a given electronic property, for instance, conjugation by an external trigger such as light, electricity or magnetism, are of potential interest as materials for optoelectronic devices.2 Photochromic materials which characteristically exhibit two different chemical forms reversibly transformed from one to the other upon irradiation with appropriate wavelengths light can be used for such devices. Among the many known photochromic compounds, diarylethenes bearing two thiophene-derived groups have received the most attention because of their good thermal stability in both isomers, remarkable fatigue resistant character, high sensitivity and rapid response.3-6

Generally, the open-ring isomers of dithienylethenes in solution have two conformations, namely, parallel conformation with the two thiophene-rings in mirror symmetry and anti-parallel conformation with them in C2 symmetry.7,8 The photoinduced cyclization and cycloreversion reactions can proceed only in a conrotatory mode by alternate irradiation with UV and visible light only from the anti-parallel conformation.9,10 The photogenerated closed-ring isomers show some colors with broad absorption bands in the visible region, and they can regenerate the open-ring isomers on irradiation with appropriate wavelengths visible light. The two isomers of the dithienylethenes differ from each other not only in their absorption spectra, but in many physical and chemical properties, such as fluorescence spectra, oxidation/reduction potentials and refractive indices, etc.11-13 The most important difference is that while π-systems of the two aryl rings are separated in the open-ring isomer, the π-conjugation is delocalized throughout the molecule in the closed-ring isomer.14 On the basis of this idea, we are developing some novel photochromic dithienylethenes materials that exhibit good photochromism, fluorescence characters and electrochemistry properties.

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In this paper, we synthesized four novel photochromic dithienylethenes compounds, 1,2-bis[2-methyl-5(p-fluorophenyl)-3-thienyl]perfluorocyclopentene 1a, 1,2-bis[2-methyl-5(p-ethoxyphenyl)-3-thienyl]perfluorocyclopentene 2a, 1,2-bis[2-methyl-5(p-N,N-dimethylaminophenyl)-3-thienyl]perfluorocyclopentene 3a and 1,2-bis(2-methyl-5-naphthalene-3-thienyl)perfluorocyclopentene 4a (Scheme 1), and investigated their optoelectronic properties systematically, such as UV-Vis absorption spectra, fluorescence spectra and electrochemistry properties, and discussed their applications on the multi-step optical storage.

![Scheme 1. Photochemical interconversion of 1a, 2a, 3a and 4a](image)

2. METHODOLOGY

2.1. Experimental section

\[ \text{Br}_{2} + \text{R} \xrightarrow{\text{Pd}(	ext{PPh}_3)_4, \text{Na}_2\text{CO}_3 \text{ aq.}} \text{R} \]

\[ \text{Br}_{2} + \text{(HO)B} \xrightarrow{\text{Pd}(	ext{PPh}_3)_4, \text{Na}_2\text{CO}_3 \text{ aq.}} \text{R} \]

\[ \text{Br}_{2} + \text{C}_{10} \text{H}_{12} \xrightarrow{\text{BuLi, -80°C}} \text{C}_{12} \text{H}_{12} \]

![Scheme 2. Reagents and conditions](image)

\(^1\text{H}\) NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with CDCl\(_3\) as the solvent and tetramethylsilane as an internal standard. The absorption spectra were measured using a PerkinElmer Lambda-900 UV/VIS/NIR spectrometer. Photo-irradiation was carried out using SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet, and BMH-250 Visible lamp. Light of appropriate wavelengths was isolated by different light filters. The quantum yields were determined by comparing the reaction yields of the dithienylethenes in hexane against 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane. Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer. Electrochemical examinations were performed in a one-compartment cell by using a Model 263 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control at room temperature. Platinum-electrodes (diameter 0.5 mm) served as working electrode and counter electrode. A platinum wire as a...
quasireference electrode. It was calibrated using the ferrocene (Fc/Fc+) redox couple which has a formal potential $E_{1/2} = +0.35$ V vs. platinum wire. The typical electrolyte was acetonitrile (5 ml) containing 0.1 mol/L LiClO$_4$ and $4 \times 10^{-3}$ mol/L dithienylethene. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments.

The 1,2-bis(3-thienyl)perfluorocyclopentene derivatives, 1,2-bis[2-methyl-5(p-fluorophenyl)-3-thienyl]perfluorocyclopentene (1a), 1,2-bis[2-methyl-5(p-ethoxyphenyl)-3-thienyl]perfluorocyclopentene (2a), 1,2-bis[2-methyl-5(p-N,N-dimethylaminophenyl)-3-thienyl]perfluorocyclopentene (3a) and 1,2-bis[2-methyl-5-naphthalene-3-thienyl]perfluorocyclopentene (4a) were prepared by the method shown in Scheme 2. Experimental details were described as following.

3-Bromo-2-methyl-5-(p-fluorophenyl)thiophene (6). 6 was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid (5) ($\delta$ 3.53 g; 16.0 mmol) with 4-bromofluorobenzene (2.87 g; 16.0 mmol) in the presence of Pd(PPh$_3$)$_4$ (208 mg; 0.43 mmol) and Na$_2$CO$_3$ (6.36 g; 60 mmol) in tetrahydrofuran (THF) (80 mL containing 10% water) for15 h at 70°C. 6 was purified by column chromatography on SiO$_2$ using hexane/chloroform (2:1) as the eluent and 3.9 g obtained as buff solid in 71% yield: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.48 (s, 3H), 7.05 (s, 1H), 7.31-7.53 (m, 4H).

3-Bromo-2-methyl-5-(p-ethoxylphenyl)thiophene (7). 7 was prepared by a method similar to that used for 6 and obtained as white solid in 72% yield: m.p. 108~110°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.42 (t, 3H), 4.09 (q, 2H), 6.95 (s, 1H), 7.05-7.49 (q, 4H).

3-Bromo-2-methyl-5-(p-(N,N-dimethylamino)phenyl)thiophene (8). 8 was prepared by a met hod similar to that used for 6 and obtained as buff solid in 79% yield: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.37 (s, 3H), 2.98 (s, 6H), 6.93 (s, 1H), 7.24-7.45 (q, 4H).

3-Bromo-2-methyl-5-naphthylthiophene (9). 9 was prepared by a method similar to that used for 6 and obtained as yellow oil in 83% yield: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.47 (s, 3H), 7.76 (s, 1H), 7.50-8.24 (m, 7H).

1.2-Bis(2-methyl-5-fluorophenyl-3-thienyl)perfluorocyclopentene (1a). To a stirred solution of 6 (2.71 g; 10.0 mmol) in THF was added dropwise a 2.5 mol/L $n$-BuLi solution (4.0 mL; 10.0 mmol) at -78°C under nitrogen atmosphere. Stirring was continued for 30 min at the low temperature. Perfluorocyclopentene (0.68 mL; 5.0 mmol) was slowly added to the reaction mixture at -78 °C, and the mixture was stirred for 2.5 h at that temperature. The reaction was stopped by the addition of water. The product was extracted with ether. The organic layer was washed with 1 N HCl solution and water. The organic layer was dried over MgSO$_4$, filtrated, and evaporated. The crude product was obtained as buff solid in 71% yield: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.48 (s, 3H), 7.05 (s, 1H), 7.31-7.53 (m, 4H).

1.2-Bis(2-methyl-5-p-ethoxylphenyl-3-thienyl)perfluorocyclopentene (2a). 2a was prepared by a method similar to that used for 1a and obtained as baby blue solid in 51% yield: mp. 101~103°C; MS m/z (M$^+$) 609; $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 2.38 (s, 6H), 2.38 (s, 6H), 4.05 (q, 4H), 6.98 (s, 2H), 7.15-7.58 (q, 8H).

1.2-Bis(2-methyl-5-p-(N,N-dimethylamino)phenyl-3-thienyl)perfluorocyclopentene (3a). 3a was prepared by a method similar to that used for 1a and obtained as cyan solid in 55% yield: mp. 140~142°C; MS m/z (M$^+$) 606; $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 2.17 (t, 12H), 2.97 (s, 6H), 6.73 (s, 2H), 7.25-7.43 (q, 8H).

1.2-Bis(2-methyl-5-naphthyl-3-thienyl)perfluorocyclopentene (4a). 4a was prepared by a method similar to that used for 1a and obtained as baby blue oil in 67% yield: MS m/z (M$^+$) 620; $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 2.20 (s, 6H), 6.99 (s, 2H), 7.02-8.25 (m, 14H).

2.2. Film preparation and optical recording

Two different photochromic dithienylethenes, 2a and 3a, were used as the recording media. The recording films were prepared by solubilizing ultrasonically 100 mg PMMA and 10 mg molecule 2a or 10 mg 3a in chloroform (1 ml), and
then spin-coating the solution on a glass substrate with a spin rotation speed 1500 rpm. The recording medium structure is as shown in Figure 1 with a perfect aluminum reflective layer. Multi-step optical storage was carried out by bleaching with 650 nm pulsed laser. The reflective light intensity was detected by a photosensitive detector, and the output was transformed into voltage. The reflectivity of a film with only the reflective aluminum layer was used as standard of 100%. Before recording, they were initiated by UV light in order to make sure that the colorless open forms were entirely converted to the color closed forms, correspondingly, both of them turned from colorless to blue.

Figure 1. Structure of an optical memory film. The recording layer contains photochromic molecules.

3. RESULTS AND DISCUSSION

3.1. Photochromism of dithienylethenes

![Absorption spectral changes of compound 1 in hexane and PMMA amorphous film](image)

Figure 2. Absorption spectral changes of compound 1 in hexane and PMMA amorphous film

Figure 2 show the absorption spectral changes of 1a in hexane ($3.0 \times 10^{-5}$ mol.dm$^{-3}$) and in PMMA amorphous (10% w/w) by photoirradiation, respectively. In hexane solution, the absorption maximum of compound 1a was observed at 190 nm ($\varepsilon = 6.5 \times 10^{4}$ dm$^{3}$.mol$^{-1}$.cm$^{-1}$) and 280 nm ($\varepsilon = 3.2 \times 10^{4}$ dm$^{3}$.mol$^{-1}$.cm$^{-1}$) (shown in Figure 2 (a)). Upon irradiation with 254 nm light, the colorless hexane solution of compound 1a turned violet blue, in which the absorption maximum was observed at 570 nm ($\varepsilon = 6.3 \times 10^{3}$ dm$^{3}$.mol$^{-1}$.cm$^{-1}$). The colored isomer 1b was stable and could be isolated, and its absorption spectrum is also shown in Figure 2 (a). The violet blue solution returned to a colorless one on irradiation with visible light ($\lambda > 500$ nm). The quantum yields of cyclization and cycloreversion reactions of 1 were determined in hexane solution to be 0.58 (313 nm) and 0.025 (570 nm) at room temperature, respectively. In the PMMA amorphous film, dithienylethene 1a has also shown good photochromic property. Its absorption spectral changes were shown in Figure 2 (b). Upon irradiation 313 nm light, the colorless 1a PMMA film ($\lambda_{max} = 310$ nm) turned blue with a new broad
absorption band at $\lambda_{\text{max}} = 590$ nm appeared, which was assigned to the formation of the closed form 1b. The colored PMMA film can invert to colorless on irradiation of appropriate wavelength visible light ($\lambda > 500$ nm). The spectral changes of dithienylethenes 2a, 3a and 4a were similar to that of 1a, and their absorption spectral properties were summarized in Table 1.

Table 1. The absorption spectral properties of dithienylethenes 1, 2, 3 and 4 in hexane and PMMA film

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}, o}$/nm ($\varepsilon$/dm$^3$.mol$^{-1}$.cm$^{-1}$)</th>
<th>$\lambda_{\text{max}, c}$/nm ($\varepsilon$/dm$^3$.mol$^{-1}$.cm$^{-1}$)</th>
<th>$\Phi_o$</th>
<th>$\Phi_c$</th>
</tr>
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<tr>
<td>Hexane</td>
<td>PMMA film</td>
<td>Hexane</td>
<td>PMMA film</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>280 (3.2×10$^4$)</td>
<td>310</td>
<td>570 (6.3×10$^4$)</td>
<td>590</td>
</tr>
<tr>
<td>2</td>
<td>290 (4.1×10$^4$)</td>
<td>321</td>
<td>584 (8.7×10$^4$)</td>
<td>604</td>
</tr>
<tr>
<td>3</td>
<td>322 (3.1×10$^4$)</td>
<td>340</td>
<td>598 (1.4×10$^4$)</td>
<td>638</td>
</tr>
<tr>
<td>4</td>
<td>280 (4.9×10$^4$)</td>
<td>292</td>
<td>570 (7.9×10$^4$)</td>
<td>580</td>
</tr>
</tbody>
</table>

a Absorption maxima of open-ring isomers. b Absorption maxima of closed-ring isomers. c Quantum yields of open-ring and closed-ring isomers, respectively.

3.2. Fluorescence of dithienylethenes

Figure 3. Fluorescence and excitation spectra of 1a, 2a, 3a and 4a (C = 10$^{-5}$ mol/L) in hexane at room temperature. Figure 3 shows fluorescence and excitation spectra of 1a, 2a, 3a and 4a (C = 1.0×10$^{-5}$ mol/L) in hexane at room temperature. All of them exhibited fluorescence at different wavelength in hexane solution excited by their respective excitation wavelength, and their fluorescence intensity decreased along with the photochromism from open-ring form to closed-ring form upon irradiation with 254 nm UV light. From figure 3 it can be clearly seen that the hexane solutions of compound 1a, 2a, 3a and 4a showed relatively strong fluorescence at 345, 305, 455 and 380 nm when excited at 285, 245, 250 and 300 nm, respectively.

The concentration dependence of fluorescence and excitation spectra of 1a was measured in THF solution at room temperature, as shown in Figure 4. When the THF solutions of 1a at various concentrations (from 10$^{-6}$ to 10$^{-3}$ mol/L) were monitored at the same wavelength light (345 nm), the excitation peaks were observed at 291, 298, 315 and 329 nm, respectively (Figure 4(a)). Similarly, when these solutions at various concentrations were excited at 290 nm, the emission peaks were appeared at 311, 343, 357 and 403 nm, respectively (Figure 4(b)). Because the relative fluorescence intensity of the solution containing 1a at a concentration of 10$^{-3}$ mol/L is too small and the value of y-axis is too high, the excitation and emission peaks can’t be observed (dash dot lines in Figure 4). Moreover, the concentration effect on the excitation and fluorescence spectra of 2a, 3a and 4a were also investigated, and the
excitation and fluorescence maxima of the four dithienylethenes in various concentration were summarized in Table 2. From these data, it can be reasonably concluded that both the fluorescence and excitation spectra of the four compounds showed remarkable concentration dependence. They both showed a red shift and the relative intensity of the emission spectra decreased rapidly with an increase in concentration. This results imply that molecular aggregation and fluorescence quench may take place due to increasing in concentration of the four compounds. 18

![Excitation spectra](image1)

![Emission spectra](image2)

(a) Excitation spectra, monitored at 345 nm.
(b) Emission spectra, excited at 290 nm.

**Figure 4.** Fluorescence and excitation spectra of 1a in THF at room temperature.

**Table 2.** Fluorescence properties of 1a, 2a, 3a and 4a at room temperature in various concentrations at 10⁻⁵ mol/L.

<table>
<thead>
<tr>
<th>Conc.(mol/L)</th>
<th>λ\text{max (nm)}\textsuperscript{a}</th>
<th>λ\text{max (nm)}\textsuperscript{b}</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>1a</td>
<td>2a</td>
</tr>
<tr>
<td>1×10⁻⁶</td>
<td>291</td>
<td>286</td>
</tr>
<tr>
<td>1×10⁻⁵</td>
<td>298</td>
<td>290</td>
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<tr>
<td>1×10⁻⁴</td>
<td>315</td>
<td>—</td>
</tr>
<tr>
<td>1×10⁻³</td>
<td>329</td>
<td>—</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Excitation maxima, monitored at 345, 310, 310 and 385 nm for 1a, 2a, 3a and 4a, respectively; \textsuperscript{b} Fluorescence maxima, excited at 290, 290, 285 and 300 nm for 1a, 2a, 3a and 4a, respectively; “—” no spectrum peak.

The solvent effect on the fluorescence and excitation spectra of 1a, 2a, 3a and 4a were also investigated. Figure 5 shows fluorescence and excitation spectra of 1a (C = 1.0×10⁻⁵ mol/L) in different solvents at room temperature, and Table 3 summarizes the fluorescence and excitation maxima of these four dithienylethenes in various solvents at room temperature. From these data, it can be clearly seen that the solvent effect on the excitation and fluorescence spectra is relatively complex. For dithienylethene 1a and 2a, their excitation and fluorescence spectra exhibit irregular and the peak maxima change in a narrow range of wavelength with an increase in solvent polarity. This indicates that the solvent effect on fluorescence property of dithienylethene 1a and 2a was not significant. On the contrary, the fluorescence spectra of compound 3a and 4a showed remarkable solvent dependence. The fluorescence maximum of 3a was observed between 452 and 517 nm and that of 4a appeared between 379 to 394 nm in all solvents. It indicates that the fluorescence spectra of 3a and 4a showed a systematic red shift with an increase in solvent polarity. In addition, the excitation maximum of 3a exhibited a blue shift and that of 4a appeared ruleless.
Figure 5. Fluorescence and excitation spectra of 1a (C = 10^{-5} \text{ mol/L}) in various solvents at room temperature.

Table 3. Fluorescence properties of 1a, 2a, 3a and 4a at room temperature in various solutions at 10^{-5} \text{ mol/L}.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>1a</th>
<th>2a</th>
<th>3a</th>
<th>4a</th>
<th>1a</th>
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</table>

\(^a\) Excitation maxima, monitored at 345, 340, 360, 385 nm for 1a, 2a, 3a and 4a, respectively; \(^b\) Fluorescence maxima, excited at 290, 235, 260 and 300 nm for 1a, 2a, 3a and 4a, respectively; “—“ no spectrum peak.

3.3. Electrochemistry of dithienylethenes

Figure 6. The anodic polarization curves of diarylethene 1, 4 and 3.

It was reported that some diarylethenes can not only perform ring opening and closing by UV or visible light irradiation, but also can be realized by electrochemical or chemical oxidation, i.e., electrochromic. \(^{12, 19}\) Therefore, the
The cyclic voltammograms of 1a and 1b were illustrated in Figure 7 (a). As can be seen from this figure, there is no apparent cathodic waves during the potential scan cycles. This implies that the anodic oxidation of 1a is irreversible and other electrochemical reactions may also occur together with the electrochromic reaction. At the same time, the anodic currents decreased rapidly cycle by cycle, indicating the concentration of 1a in the electrolyte also decreased, further proving the electrochemical reaction of 1a. On the other hand, the anodic oxidation of 1b also observed similar phenomenon. This certified the occurrence of other electrochemical reactions, in accordance with the anodic oxidation of 1a. The possible reactions may involve the oxidation of thiophene or benzene ring in both ring-open and ring-closed form and radical cations may be formed and coupling between two radical cations may occur. They lead to the decrease the concentration of the reactant thus result in the decreases of anodic current. Similar phenomena were also observed for 3a, 3b, 4a and 4b (Figure 7 (b) and (c)). However, the electrochromic properties of 3a and 4a were also not very clear in comparison with that of 1a during the potential scan cycles. The electrochromic properties of 1a may find other applications for diarylethenes.

### 3.4. Optical recording properties

Semiconductor laser light (650 nm) was introduced into the Multi-wavelength and Multi-step Optical Storage System\(^{17}\) to write eight-step marks by bleaching. Before performing the multi-step experiments, the best recording condition (writing time) of different recording material must be determined by testing again and again. The writing and readout conditions for 2a and 3a are summarized in Table 4. According to the writing time shown in Table 4, eight-step signals were
recorded on the two photochromic recording films, respectively. The distance between the two vicinity marks is 8 micron. The readout wavelength and power is the same as that of writing process. Figure 8 showed the intensity of all recording signals at the speed of 5×10⁻⁴ m/s, and Figure 9 showed the relationship of the writing time (t) and the intensity of each signal vs. the zero-step signal (∆V). The results show that the maximum ∆V between the recorded dot and unrecorded region is greater than 3.5 V, which the voltage difference is very important to enhance the memory density of multi-step optical recording. The signal base line is not smooth because of the coarse surface of the recording film. In order to distinguish the two curves well, we move rightward the signal curve of 3a to a half unit along horizontal-axis direction in Figure 8.

**Table 4. Writing/readout conditions for 2a and 3a**

<table>
<thead>
<tr>
<th>Write/read Power (mW)</th>
<th>Step number</th>
<th>Writing time (ms)</th>
<th>2a</th>
<th>3a</th>
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<td></td>
<td>7</td>
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</tbody>
</table>

**Figure 8.** Eight-step optical storage using 2a and 3a as recording medium, respectively.

**Figure 9.** ∆V-t curve of eight-step recording signals using 2a and 3a as recording medium, respectively.

From the two figures, it can be concluded that the two materials are very sensitive responding to 650 nm recording laser, and the recording multi-step signals are provided with high S/N ratio. The relationship between ∆V and t shows very good linear indicating that multi-step optical storage can be carried out by controlling the writing time of each step signal using photochromic diarylenes as recording materials. Because the recording processes are based on a photo-mode recording method, the power of the recording laser can be very low, which are the most different from the CD-R or CD-RW pits based on a heat-mode recording method. After recording, the closed-ring isomers 2b and 3b in the recorded region were converted unequally to the open-ring isomers 2a and 3a based on writing time.

**4. CONCLUSIONS**

We have successed in synthesizing four novel photochromic dithienylethenes with good photochromism both in solution and in PMMA amorphous film by photoirradiation. Their fluorescence and electrochemical characteristics in solution were investigated by fluorescence spectra and cyclic voltammetry, respectively. When the concentrations of them were increased in solution, the phenomenon of fluorescence quench took place and the fluorescence spectra
maxima exhibited a significant bathochromic shift. The solvent effect on the fluorescence of the four compounds is relatively irregular. The irreversible anodic oxidation of 1a, 3a, and 4a in acetonitrile containing LiClO₄ as the supporting electrolyte was initiated at 0.83, 0.82 and 0.96 V, respectively. It should be noted here that dithienylethene 1a showed remarkable multi-color electrochromic properties during the anodic polarization while 3a and 4a showed no obvious electrochromism. Finally, using compound 2a and 3a as recording medium, we have implemented successfully a photo-mode multi-step optical storage. This is the first example of multi-step optical recording using photochromic dithienylethene materials.

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