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Syntheses and optoelectronic properties of four photochromic dithienylethenes

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Abstract—Four photochromic dithienylethene compounds, 1,2-bis(2-methyl-5-naphthalene-3-thienyl)perfluorocyclopentene **1a**, 1,2-bis[2-methyl-5(*p*-fluorophenyl)-3-thienyl]perfluorocyclopentene **2a**, 1,2-bis[2-methyl-5(*p*-ethoxyphenyl)-3-thienyl]perfluorocyclopentene **3a**, and 1,2-bis[2-methyl-5(*p*-*N*,*N*-dimethylaminophenyl)-3-thienyl]perfluorocyclopentene **4a** were synthesized, and their optoelectronic properties, such as photochromism in solution as well as in poly-methylmethacrylate (PMMA) amorphous films, fluorescences and electrochemical properties were investigated in detail. These dithienylethenes have shown good photochromic behavior both in solution and in PMMA amorphous film. All of them exhibited relatively strong fluorescence and gave a bathochromic shift upon increasing concentration in THF. The irreversible anodic oxidation of **1a**, **2a** and **4a** was observed by performing cyclic voltammetry experiments.

1. Introduction

Organic photochromic materials have attracted much attention, because of their potential application to optical memory media and optical switches.[1–6] Among various types of photochromic compounds,[3,4,7] diarylethene derivatives,[4,8,9] bearing two thiophene-derived groups are the most promising because of their excellent thermal stability of both isomers,[3,10–12] fatigue resistant character,[13,14] rapid response,[15–17] and high reactivity in the solid state.[18,19]

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 C_2 symmetry.[20,21] The photoinduced cyclization and cycloreversion reactions can only proceed in a conrotatory mode by alternate irradiation with UV and visible light only from the anti-parallel conformation.[3,22] The photogenerated closed-ring isomers show colors with broad absorption bands in the visible region, and they can regenerate the open-ring isomers on irradiation with appropriate wavelengths of visible light. The two isomers of the dithienylethenes differ from each other not only in their absorption spectra, but also in many physical and chemical properties, such as fluorescence spectra, oxidation/reduction potentials and refractive indices, etc.[5,23,24] The most important difference is that while the π-systems of two aryl rings are separated in the open-ring isomer, the π-conjugation is delocalized, throughout the molecule in the closed-ring isomer.[25] By far, many dithienylethenes derivatives and their optoelectronic properties were reported.[3,26,27] Dithienylethenes bearing phenyl groups on the end are of special interest, because the end group can be substituted by electron donating group or electron withdrawing group. These groups inevitably influence the optoelectronic properties of corresponding diarylethenes. To the best of our knowledge, flurophenyl, ethoxyphenyl, and *N*,*N*-dimethylaminophenyl except naphthyl[28] substituted dithienylethenes have not been reported till now. Their syntheses are helpful both for, the preparation of new photochromic diarylethenes and for the understanding of substitution effect of corresponding products. On the basis of this idea, some novel photochromic dithienylethenes materials were developed which exhibit good photochromism, fluorescent, and electrochemical properties.

In this paper, four photochromic dithienylethenes compounds, 1,2-bis(2-methyl-5-naphthalene-3-thienyl)perfluorocyclopentene **1a**, 1,2-bis[2-methyl-5(*p*-fluorophenyl)-3-thienyl]perfluorocyclopentene **2a**, 1,2-bis[2-methyl-5(*p*-ethoxyphenyl)-3-thienyl]perfluorocyclopentene **3a**, and 1,2-bis[2-methyl-5(*p*-*N*,*N*-dimethylaminophenyl)-3-thienyl]perfluorocyclopentene **4a** (Scheme 1) were synthesized, and their optoelectronic properties, such as UV–vis absorption spectra, fluorescence spectra, and electrochemical properties were investigated in detail. Among the four compounds,

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Keywords: Dithienylethene; Photochromism; Fluorescence; Electrochemical properties.

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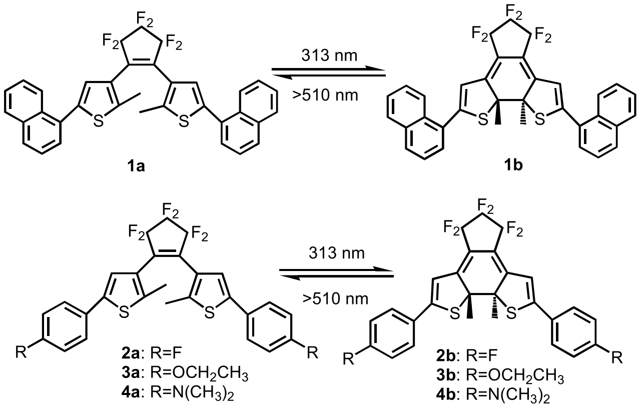

Scheme 1.

2a, **3a**, and **4a** are new compounds. Although **1a** was reported by Irie group,[28] its fluorescence and electrochemical properties had not been reported.

2. Results and discussion

2.1. Photochromism of dithienylethenes

Figure 1 showed the absorption spectral changes of **4a** in hexane (5.0×10^{-5} mol dm^{-3}) and in PMMA amorphous (10% w/w) by photoirradiation, respectively.

In hexane solution, the absorption maximum of compound **4a** was observed at 322 nm ($\varepsilon=3.86\times10^{4}$ dm^{3} mol^{-1} cm^{-1}) (Fig. 1a). Upon irradiation with 313 nm light, the color of the hexane solution turned blue, in which the absorption maximum was observed at 602 nm ($\varepsilon=1.75\times10^{4}$ dm^{3} mol^{-1} cm^{-1}). The blue solution turned colorless, upon irradiation with visible light ($\lambda>510$ nm). The quantum yields of cyclization and cycloreversion reactions of **4** in hexane solution were 0.80 (313 nm) and 0.013 (570 nm) at room temperature, respectively. In the PMMA amorphous film, dithienylethene **4a** also showed good photochromic property, as shown in Figure 1b. Upon irradiation 313 nm light, the color of **4a** PMMA film ($\lambda_{\max}=340$ nm) changed from colorless to blue with the appearance of a new broad absorption band at $\lambda_{\max}=646$ nm, which was assigned to the formation of the closed form **4b**. The colored PMMA film can invert to colorless, on irradiation of appropriate visible light ($\lambda>510$ nm). The red shift of the ring-closed form of **4a** in PMMA film in comparison with those in hexane solution can be ascribed to the stabilization of molecular arrangement in solid state.[29] The spectral changes of dithienylethenes **1a**, **2a**, and **3a** were similar to that of **4a**. Their absorption spectral properties were summarized in Table 1. These data indicated that both the maxima wavelengths of ring-open and ring-closed isomers increased, when an electron-donating group was introduced into the 4- and 4′-positions of the benzene rings. The maxima wavelengths of all compounds in solution were less than those in PMMA amorphous film. When the 4- and 4′-positions of the benzene rings were substituted by an electron-donating group, the value of the cyclization quantum also increased, but that of the cycloreversion quantum was irregular.

2.2. Fluorescence of ditheinylethenes

The fluorescence excitation and emission spectra of **1a**, **2a**, **3a**, and **4a** ($C=1.0\times10^{-5}$ mol dm^{-3}) in hexane at room temperature were illustrated in Figure 2. All of them exhibited good 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 313 nm UV light.[30] From this figure, one can clearly see that the hexane solutions of compound **1a**, **2a**, **3a**, and **4a** showed relatively strong fluorescence at 380, 345, 340, and 455 nm when excited at 300, 285, 245, and 327 nm, respectively.

The concentration dependence of fluorescence and excitation spectra of **2a** was measured in THF solution at room temperature, as shown in Figure 3. When these solutions at 1.0×10^{-6}, 1.0×10^{-5}, 1.0×10^{-4}, and 1.0×10^{-3} mol dm^{-3} were excited at 290 nm, the maximum emission arose at 311, 343, 357, and 403 nm, respectively (Fig. 3b). Because the relative fluorescence intensity of the solution containing **2a** at a concentration of 1.0×10^{-3} mol dm^{-3} is too low comparing to the Y-axis value, the excitation and emission peaks cannot be observed (dash dot lines in Fig. 3). From Figure 3, we can see that both excitation and

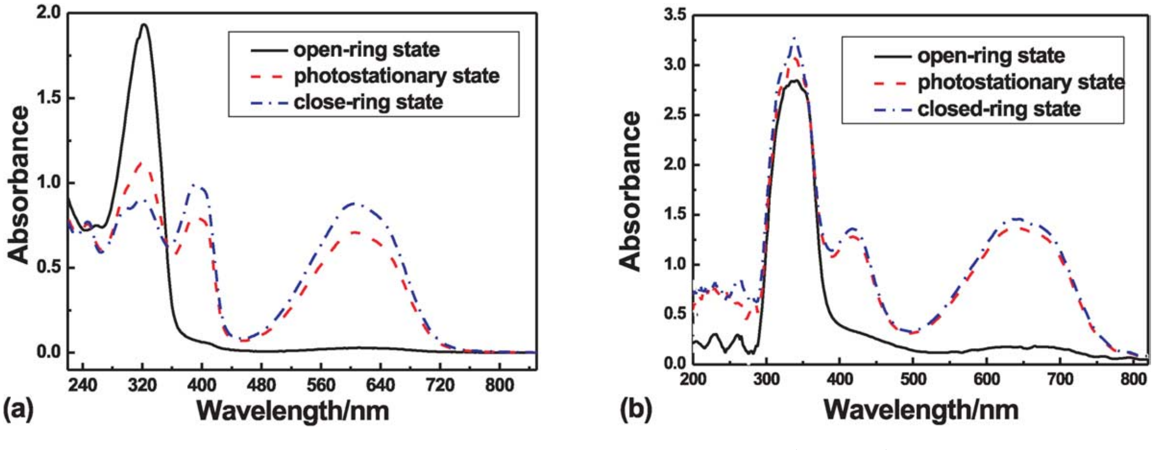

Figure 1. Absorption spectra of compound **4** in hexane and PMMA amorphous film. (a) in hexane (5.0×10^{-5} mol dm^{-3}); (b) in PMMA amorphous film (10% w/w).