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Properties and Application of a Novel Unsymmetrical Photochromic Diarylethene

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Abstract. A new unsymmetrical photochromic diarylethene, 1-(2-methyl-5-phenyl-3-thienyl)-2-(2-n-butyl-5-(1,3-dioxolane)-3-thienyl)perfluorocyclopentene (1a), was synthesized and its optoelectronic properties, such as photochromism in solution as well as in poly-methylmethacrylate (PMMA) amorphous films and fluorences were investigated. The photochromic reaction kinetics was also studied. Using diarylethene 1b/PMMA film as recording medium and a linearly polarized 633 nm laser diode for recording and readout, polarization multiplexed image recording can be carried out in this film, which illustrated that the diarylethene can be potentially used as holographic optical recording medium.

1. Introduction

Photochromic diarylethenes exhibit reversible variations in their physicochemical properties when stimulated by light and are amongst the most promising candidates for photoelectronic applications such memories and switches because of their thermo-irreversible and fatigue-resistant photoisomerization performances[1]. This photoinduced change is not limited to the color or absorption spectra, as the change occurs between two different molecules with different physical and chemical properties[2,3]. Derivatives of diarylethenes, especially those with thiophene rings, are currently being investigated as candidates for switches in molecular electronic devices, or for other applications, because of their photochromic properties[4]. The important features of this class of molecules are the good fatigue resistance, fairly high photocyclization quantum yields, high reversibility of the forward and reversed photo processes triggered by irradiation with light of different wavelengths and thermal stability of the products[5]. The majority of the research work has been devoted to the development of new molecules and investigative studies into their fundamental properties, and the results obtained have contributed to a broad understanding of the effects of substituents on the photochromism of diarylethenes[6]. Up to date, design and synthesis of new Photochromic compounds which is an active area of research[7]. In this paper, we synthesized a new diarylethene 1-(2-methyl-5-phenylthiophene-3-y1)-2-(2-nbutyl-5-(1,3-dioxolane) thiophene-3-y1) perfluorocyclopentene. Its photochromic reactivity and fluorescence were investigated in detail.
2. Experiments

2.1. Synthesis of diarylethene 1a
The synthetic route for diarylethene 1a was shown in Scheme 2 and its synthetic steps based on the similar procedure of Pu et al[8,9]. It optoelectronic properties, such as UV–Vis absorption spectra, fluorescence spectra were investigated in detail. Diarylethene 1a was characterized by $^1$H NMR spectroscopy. NMR spectra were recorded on Bruker AV400 (400MHz) spectrometer with CDCl$_3$ as the solvent. $^1$H NMR (400MHz, CDCl$_3$): 1.14(d, 3H, -CH$_3$), 1.31 (s, 2H, -CH$_2$),1.53 (s, 2H,-CH$_2$), 2.48(d, 3H, -CH$_3$),2.68 (s, 2H, -CH$_2$), 4.01 (s, 4H, -CH$_2$-CH$_2$),6.89 (d, 1H, Ar-H),7.25((d, 1H, Ar-H),7.32 (d, 1H, Ar-H),7.39 (s, 2H, Ar-H), 7.53(s, 2H, Ar-H).

2.2. Preparation of PMMA film
First of all, one hundred milligram of PMMA was dissolved in 1 ml chloroform, which was stirred ultrasonically to make it homogeneous. Samples were obtained by dissolving ultrasonically 10 mg of compounds 1 with 1 ml of the PMMA solution, respectively, and the solution was spin-coated on a glass substrate with a spin rotation speed of 1500 rpm.

3. Results and Discussion

3.1. Photochromic in solution and in PMMA film
Figure 1a shows absorption spectral changes of 1 in hexane solution ($2 \times 10^{-5}$ mol $\cdot$ L$^{-1}$). The hexane solution of the open-ring isomer 1a was colorless without absorption in the visible region. The absorption maximum of its colorless open-ring isomer 1a was observed at 285nm ($= 1.43 \times 10^3$ mol $\cdot$ L$^{-1}$ $\cdot$ cm$^{-1}$). Upon irradiation with UV light ($= 297$ nm), the colorless solution turned violet. Isomer 1b has an absorption maximum at 522 nm ($= 4.45 \times 10^3$ mol $\cdot$ L$^{-1}$ $\cdot$ cm$^{-1}$) in the visible region. Upon irradiation with visible light ($> 500$ nm), the violet solution of 1b was completely bleached, and the absorption spectrum returned to that of 1a[10]. The quantum yields of cyclization and cycloreversion reaction of diarylethene 1 were 0.19 and 0.000086 at room temperature. Similarly, the color of dithienylethene 1a in PMMA film (10% w/w) changed from colorless to violet with the appearance of a new broad absorption band at $\lambda_{max} = 568$ nm upon irradiation 297 nm light. The colored PMMA film can invert to colorless, upon irradiation appropriate visible light ($ > 500$ nm)[11].

Figure 1. Absorption spectral changes of compound 1a :(a) in hexane and (b) in PMMA.
3.2. Photochromic reaction kinetics in hexane solution
As shown as in Figure 2, the photochromic cyclization/cycloreversion kinetics of diarylethene 1a in hexane solution was determined by UV-Vis spectra upon alternating irradiation with UV and appropriate wavelength visible light at room temperature. It can be seen that the relationships between the absorbance and exposure time have good linearity upon irradiation with 297 nm UV light suggesting that the cyclization processes of 1a belong to the zeroth order reaction when open-ring isomer changed to closed-ring isomer. The slope of every line in Figure 2a represents the reaction rate constant \( k \) of diarylethene 1a in hexane solution. So all \( k \) of cyclization process \( (k_{oc}, 10^{-3}) \) of diarylethene 1a can be easily obtained, which is 2.01 s\(^{-1}\) in hexane solution. As shown in Figure 2b, during the cycloreversion of 1b, the relationship between –Log(Abs) and exposure time also behave perfect linearity, indicating that the cycloreversion process belong to the first order reaction. The \( k \) of cycloreversion \( (k_{co}, 10^{-3}) \) process of 1b can be easily obtained, which is 16.69 s\(^{-1}\) in hexane solution.

![Figure 2](image2.png)

**Figure 2.** The cyclization/cycloreversion kinetics of compound 1a in hexane solution

3.3. Fluorescence of diarylethene
The fluorescence spectra of diarylethenes 1a in hexane at room temperature is illustrated in Figure 3. We could clearly see that the fluorescent emissions of 1a was at 356 nm when excited at 297 nm. When it arrived at photostationary state, the emission intensities of diarylethenes 1a was quenched to ca 51%. The fluorescence was efficiently quenched when the diarylethene unit converts from the open- to closed-ring form. The fluorescence intensity gradually decreased in proportion to the conversion from 1a to 1b[12].The back irradiation with visible light of wavelength longer than 450 nm regenerated the open-ring forms and recovered the original emission spectra. Otherwise, the average times of “on” and “off” state shortened in proportion to the reciprocal power of radiated light by changing the power of the UV and visible light, indicating that the switching effect is perfect in hexane solution.

![Figure 3](image3.png)

**Figure3.** Fluorescence spectral of 1a in hexane

![Figure 4](image4.png)

**Figure4.** Readout patterns from the film
3.4. Photoinduced anisotropy and polarization multiplexed image recording

With a linearly polarized 633 nm laser diode in the experimental setup[13,14], the evaluation of potential of photochromic diarylethene as a polarization holographic medium by recording and reading the holograms in a real-time operation is investigated. Using diarylethene 1b/PMMA film as recording medium. Two patterns are written on and readout successfully. To observe and measure the photoinduced anisotropy, diarylethene 1b/PMMA film is placed between two orthogonal polarizes P and A. Two patterns are written on 1b/PMMA film by a linearly polarized 633 nm laser diode. Readout patterns with the three types of polarization holographic optical recording are shown in Figure 5. The first pattern is written with the beam polarization at 0 deg (Figure 5a), while the second was written with the beam polarization at 45 deg (Figure 5c). After writing, the patterns are readout with the sample placed between two orthogonal polarizers P and A. If the polarization of P is 22.5 deg from the horizontal direction, both the vertical polarization light and horizontal polarization light patterns can pass through the A-diarylethene-P system. Thus, the readout pattern is like Figure 5b. The results demonstrate that the diarylethene compound has attractive properties for polarization holographic optical recording.

In conclusion, diarylethene 1a changed the color from colorless to violet upon irradiation with 297 nm UV light, in which absorption maxima were observed at 522 nm in hexane and at 568 nm in PMMA. The cyclization processes of 1a belong to the zeroth order reaction and the cycloreversion process belong to the first order reaction. The \( k \) of cyclization process (\( k_{oc} \), \( 10^{-3} \)/cycloreversion (\( k_{co} \), \( 10^{-3} \)) process of 1 can be easily obtained, which are 2.01 s\(^{-1}\)/16.67 s\(^{-1}\) in hexane solution. Diarylethene 1a showed relatively strong fluorescence intensity in hexane solution. Polarization multiplexed images was performed successfully in diarylethene 1b/PMMA film, the results demonstrated that the compound was very sensitive responding to 633 nm recording laser, and the recorded holographic images have good contrast, which illustrated that the diarylethene can be potentially used as holographic optical recording medium.

Acknowledgment

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