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Photochromic properties of diarylethenes having 2,4-diphenylphenyl substituents in the amorphous and PMMA films

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Abstract

1,2-Bis[5-methyl-2-(2,4-diphenyl)phenyl-4-thiazolyl]perfluorocyclopentene **1a** and 1,2-bis-[2-methyl-5-(2,4-diphenyl)phenyl-3-thienyl]perfluorocyclopentene **2a** were synthesized and their photochromic performance was examined in the bulk amorphous states. Compounds **1a** and **2a** formed stable amorphous bulk solid at room temperature and the glass transition temperatures (T_gs) of them were observed at 77 °C. The conversions in the photostationary states were evaluated to be 88% and 90% in the amorphous films prepared from the closed-ring isomers **1b** and **2b**. The values are higher than that of 1,2-bis[2,4-dimethyl-5-(2,4-diphenyl)phenyl-3-thienyl]perfluorocyclopentene **3** (74%). Photochromic reactions of these compounds were also examined in poly(methyl methacrylate) (PMMA) films. The conversion ratios of **1** and **2** (91% for both compounds) in the PMMA films are also higher than that observed in **3** (80%). The photocyclization quantum yields of **1a**, **2a**, and **3a** are the same, while the photocycloreversion quantum yields of **1b** and **2b** are lower than that of **3b**. The higher conversions of **1** and **2** are attributed to the lower photocycloreversion quantum yields, which were caused by the decrease in the steric hindrance between 4-position of the aryl groups and perfluorocyclopentene ring.

Keywords: Photochromism; Diarylethene; Amorphous film; PMMA film

1. Introduction

Photochromic compounds have attracted much attention because of their potential ability for optical memory media and photo-optical switching devices [1,2]. For the practical applications the photochromic reaction should take place in solid states, such as in polymer matrices, sol–gel glasses or bulk amorphous states [3]. Among them bulk amorphous photochromic materials are the most promising for the practical use because of their optical transparency and capability to form thin films by a spin-coating method [4–17]. In previous papers [14,16], we showed that introduction of 2,4-diphenylphenyl groups to diarylethene derivatives are effective to stabilize the amorphous state. When the diphenylphenyl groups are introduced at both sides of bisbenzothienylethene, the highest T_g of 127 °C is observed. The conversion ratio from the open- to the closed-ring isomers in the amorphous state is strongly dependent on the structure of the diarylethenes. When the methyl groups at 4-position of the thiophene rings of diarylethene are eliminated, the conversion ratios dramatically increase. The conversion ratios of 1,2-bis[2-methyl-5-[4-*N*,*N*-bis-(4-methylphenyl)amino]phenyl-3-thienyl]perfluorocyclopentene and 1,2-bis[2,4-dimethyl-5-[4-*N*,*N*-bis(4-methylphenyl)amino]phenyl-3-thienyl]perfluorocyclopentene having bulky diphenylamino groups are reported to be 35% and 77% in the amorphous films, respectively [8,10]. In this study, amorphous diarylethenes **1** and **2** having 2,4-diphenylphenyl group have been synthesized, and their photochromic properties have been compared with that of 1,2-bis[2,4-dimethyl-5-(2,4-diphenyl)phenyl-3-thienyl]perfluorocyclopentene **3** in order to know the effect of the methyl substituents at the 4-position. (Scheme 1) Furthermore, we have investigated the photochromic reactions of these compounds in poly(methyl methacrylate) (PMMA) films.

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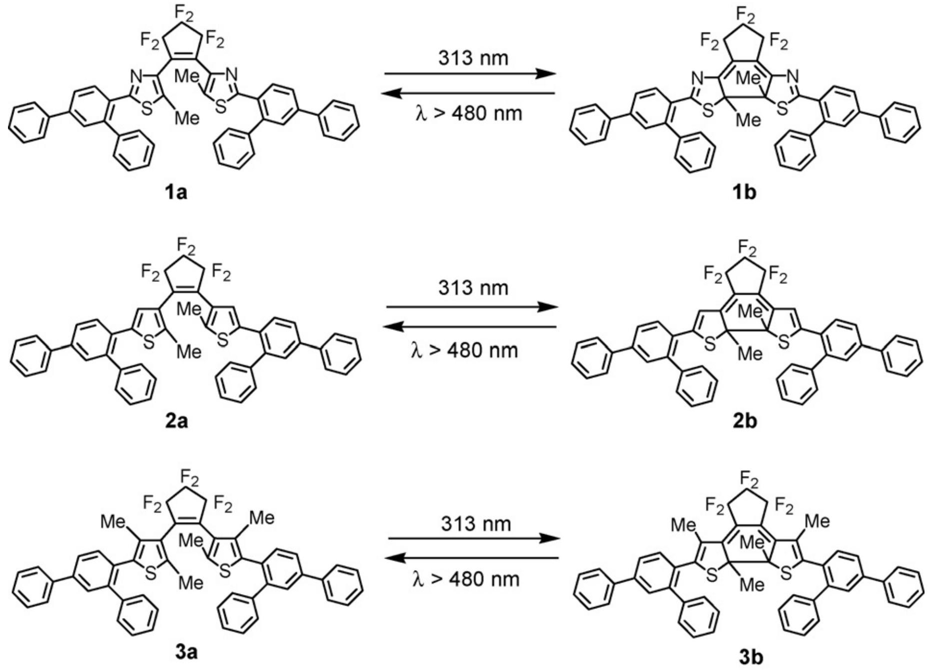

Scheme 1.

2. Experimental

2.1. General

HPLC was performed on a Hitachi L-7100 liquid chromatography coupled with a Hitachi L-7400 spectrophotometeric detector. ^{1}H NMR spectra were recorded on a Varian Gemini 200 instrument. Mass spectra were measured with a Shimadzu GCMS-QP5050A gas chromatography-mass spectrometer. Absorption spectra record on a Hitachi U-3500 absorption spectrophotometer. Photoirradiation was carried out using an Ushio 500 W superhigh-pressure mercury lamp or an Ushio 500 W xenon lamp. Monochromatic light was isolated by passing the light through a cutoff filter (UV-27) and monochromator (Ritsu MC-10N). The thickness of the films were measured by Alpha-Step 500. The differential scanning calorimetry (DSC) measurement was carried out using a Perking Elmer, Pyris 1 apparatus. The measurement was carried out at a heating rate of 5 °C/min. Poly(methyl methacrylate) (PMMA) ($M_w = 10{,}000$) was used as polymer matrix.

2.2. Synthesis

2.2.1. 5-Methyl-2-(2,4-diphenyl)thiazole (*4*)

To a solution of 5-methylthiazole (1.9 g, 19 mmol), iodo-*m*-terphenyl (2.3 g, 6.5 mmol) [18], $PdCl_2(PPh_3)_2$ (1 g, 1.42 mmol), and CuI (150 mg, 0.79 mmol) in dry DMSO (50 mL) was added TBAF (27 mL of 1 M THF solution, 27 mmol) under an argon atmosphere. The resulting solution was degassed via five freeze–pumo–thaw cycles and heated in an oil bath (65 °C). The solution was stirred at that temperature for 3.5 days, and then distilled water was added. The product was extracted with diethyl ether, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane, 1:9) to afford to 1.5 g (70%) of **4** as a colorless crystal: mp 128–129 °C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.35$ (d, $J = 1.2$ Hz, 3H), 7.7–7.3 (m, 13H), 8.08 (d, $J = 8.4$ Hz, 1H). MS $m/z = 326$ (M^+). Anal. Calcd. For $C_{22}H_{17}NS$: C 80.70, H 5.23, N 4.28%. Found: C 81.00, H 5.29, N 4.51%.

2.2.2. 4-Bromo-5-methyl-2-(2,4-diphenyl)thiazole (*5*)

Bromine (0.7 g, 4.8 mmol) was added to a stirred solution of **4** (1.6 g, 4.9 mmol) in CS_2 (15 mL). The mixture was stirred at room temperature for 36 h and extracted with ethyl acetate. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The reduced was purified by column chromatography (ethyl acetate/hexane, 1:9) to afford 400 mg (20%) of **5** as colorless solid: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.25$ (s, 3H), 7.71–7.30 (m, 12H), 8.17 (d, $J = 8.2$ Hz, 1H). MS $m/z = 406$ (M^+). Anal. Calcd. For $C_{22}H_{16}BrNS$: C 65.03, H 3.97, N 3.45%. Found: C 65.17, H 4.05, N 3.71%.

2.2.3. 1-[5-Methyl-2-(2,4-diphenyl)-4-thiazolyl] perfluorocyclopentene (*6*)

To a stirring solution of **5** (780 mg, 1.9 mmol) in 7.5 mL THF was slowly added dropwise 1.6 M *n*-BuLi in hexane (1.3 mL, 2.00 mmol) at −80 °C under an atmosphere of argon. After the mixture had been stirred for 15 min at −80 °C, perfluorocyclopentene (0.3 mL, 2.10 mmol) in dry THF (2 mL) was added. The reaction mixture was stirred at −80 °C for 1 h, and then distilled water was added. The product was extracted with diethyl ether, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane, 1:9) to afford to 400 mg (41%) of **6** as a colorless solid: mp 90–91 °C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.36$ (d,