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Short Communication

Synthesis and Photochromic Activity of a New Diarylethene Bearing Benzo[b]Thiophene Unit

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Abstract. The synthesis of new photochromic compound 3-[2-(3,5-*bis* methoxymethoxymethylthiophene-2-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl]-2-methyl-benzo[b]thiophene is reported. In multistep synthesis from 2,4-dibromothiophene, benzo[b]thiophene was synthesized. This product exhibited photochromic properties upon irradiation with ultraviolet and visible light.

Keywords: photochromism, photomemory, photocyclization, coupling reaction

Photochromism is the term used for a reversible photo induced transformation of a molecule between two isomers whose absorption spectra are distinguishably different (Dürr and Bouas-Laurent, 1990). The chemical bond reconstruction *via* photo excitation induces not only the change of absorption spectra but also refractive indices, fluorescence spectra, oxidation/reduction potentials, chiral properties and so on (Irie and Uchida, 1998). The quick change of these properties induced by the photoexcitation has been attracting much attention (Hossain *et al*., 2005a; 2005b; de Jong *et al*., 2003; Myles and Branda, 2002; Delaire and Nakatani, 2000; Matsuda and Irie, 2000; Hanazawa *et al*., 1992) from the view points of the application to optoelectronic devices such as memories and switches.

In this study novel photochromic compound 3-[2-(3,5-*bis*-methoxy-methoxymethylthiophene-2-yl)-3,3,4,4,5,5-hexafluoro-cyclopent-1-enyl]-2-methylbenzo[b] thiophene (**9**) has been designed and synthesized. It shows unique photochromic behaviours upon irradiation with UV light.

Absorption spectra were measured with an absorption spectrophotometer (Hitachi, U-3310). ^{1}H-NMR spectra were recorded on a FT-NMR, JEOL-AL300, spectrometer at 270 MHz. All chemical shifts are given in ppm relative. IR spectra were recorded with a FT-IR, 2000, Perkin-Elmer spectrometer. Mass spectra were taken on JEOL JMS-GCMATE II (EI, 70 ev). Photo irradiation was carried out by using a 500 W super high pressure mercury lamp and monochromic light was obtained by passing it through a monochromator (JOBIN YVON). The samples were not degassed.

The newly synthesized compound 3-[2-(3,5-*bis*-methoxymethoxymethylthiophene-2-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl]-2-methyl benzo[b] thiophene (**9**) is shown in (Scheme 1). Compound (**9**) was prepared in five steps from the commercially available 2, 4-dibromothiophene (**1**). Compound (**2**) and (**3**) have been synthesized according to the known procedure (Mitsumori *et al*., 1995).

2, 4-Diformylthiophene (2). To a solution of 1.45 g of 2,4-dibromo thiophene (**1**) (6.06 mmol) in 300 mL of ether was added dropwise 25.2 mL of a solution of tert-butyllithium in hexane (1.7 M) at -78 °C. The mixture was stirred for 10 min and then 4.7 mL of N,N-dimethyl formamide was added. After stirring for 1 h, dry/acetone bath was removed and the reaction mixture was allowed to warm gradually to room temperature. A yellow oil obtained by usual work-up was purified by silica gel column chromatography (*n* hexane:ethyl acetate = 3:1) to afford 0.69 g of white solid of 2,4-diformylthiophene 2 (81% yield). m.p 79-80 °C. IR (KBr): 1688, 1658 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) 9.98 (d, 1H), 9.95(s, 1H), 8.45 (dd, 1H), 8.17 (d, 1H) Anal calcd for $C_6H_4O_2S$: C; 51.42; H; 2.88; S; 22.88, Found: C, 51.66, H, 3.17, S, 22.94.

2,4-dihydroxymethylthiophene (3). A mixture of 0.68 g of 2,4-diformylthiophene (**2**) (4.73 mmol) in 15 mL of EtOH was added to 0.4 g of $NaBH_4$ (11.7 mmol) in an ice bath. After stirring for 3 h, ice bath was removed and the reaction mixture was allowed

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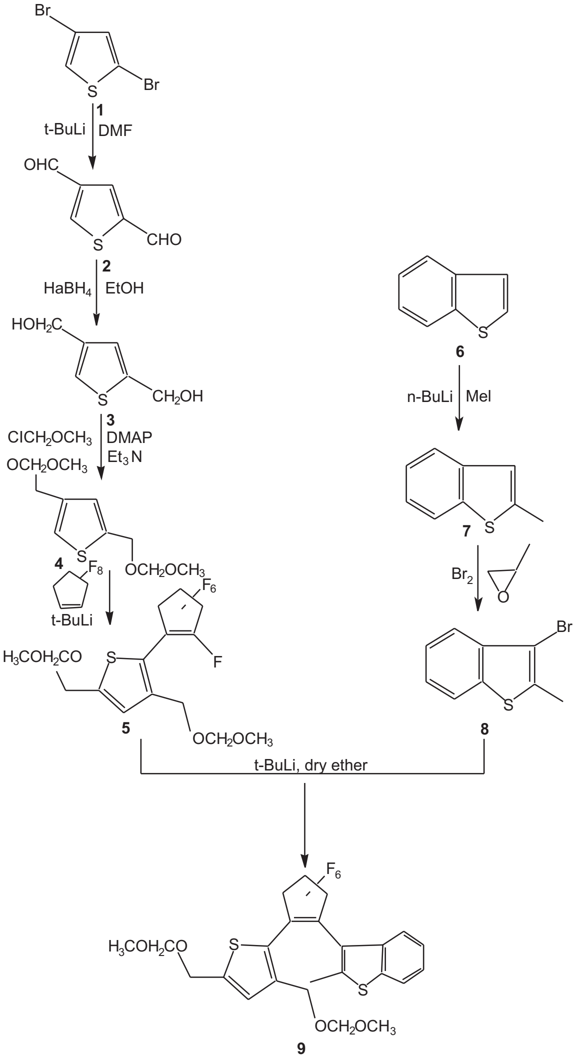
*Author for correspondence; E-mail: mkhossain73@yahoo.com to warm gradually to room temperature. The organic phase was washed with brine, dried over Na_2SO_4 and the solvent was evaporated *in vacuo*. Recrystallization of the residue from hexane afforded (0.68 g, 98%) (**3**) as yellow prisms (hexane), mp 40-41 °C, ^{1}H-NMR (270 MHz, $CDCl_3$) 7.17 (s, 1H), 7.01(s, 1H), 4.82 (d, 2H), 4.64 (d, 2H), 1.76 (d, 2H), 1.61 (d, 2H).

Compound (**4**) was prepared from the treatment of 2, 4-dihydroxymethyl thiophene (**3**) with chloromethylmethyl ether and DMAP in Et_3N. Compound (**4**) treated with octafluorocyclopentene and t-BuLi in THF to form (**5**). Compound (**7**) and (**8**) have been synthesized according to the known procedure (Irie, 2000).



Scheme 1. Newly synthesized compound.

The coupling reaction of 3-(2,4-*bis*-methoxymethoxymethylthienyl)heptafluorocyclopentene (**5**) with 3-bromo-2-methylbenzothiophene (**8**) was carried out under high dilution condition (Takeshita and Tashiro, 1991) to afford the benzo[b]thiophene (**9**). Purification of (**9**) was carried out by silica gel column chromatography. The structure of benzo[b]thiophene (**9**) was determined by ^{1}H-NMR, mass spectroscopy and elemental analysis.

Figure 1, illustrates the absorption change of 3-[2-(3,5-*bis*-methoxymethoxymethylthiophene-2-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl]-2-methyl-benzo[b] thiophene (**9**) in hexane.

Upon irradiation with 366 nm light a colourless hexane solution of (λ_{max} = 500 nm) of (**9a**) (4.010^{-5} M) afforded a yellow solution with a new absorption at 450 nm (Scheme 2).

This new band is ascribed to the closed ring form of (**9b**). When the yellow solution was irradiated with visible light at wavelength longer than 460 nm, the spectrum returned to the initial one. The reversible photoisomerization indicate that the 3-[2-(3,5-*bis*-methoxymethoxymethylthiophene-2-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl]-2-methylbenzo[b]thiophene (**9**) is photochromic.

Synthesis of new asymmetric diarylethene bearing a benzo[b]thiophene unit has been demonstrated. The photochromic performance is exhibited upon irradiation with UV-Vis light.

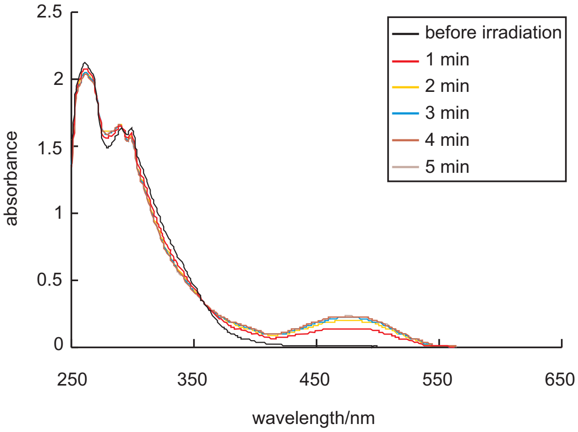
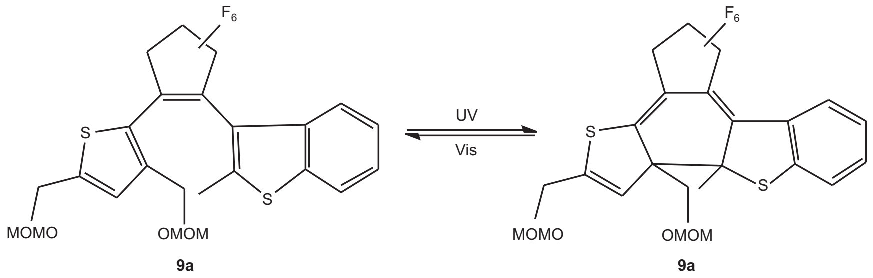


Fig. 1. Absorption spectral change of (**9a**) (4.0× 10^{-5} M) in hexane upon irradiation with 366 nm light.



Scheme 2. The open and closed ring form of compound 9.

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