Journal of Photochemistry and Photobiology A: Chemistry 285 (2014) 44–51

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photochromism and fluorescence properties of 1,2-bis(2-alkyl-1-benzothiophene-3-yl)perhydrocyclopentenes

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ARTICLE INFO

Article history:
Received 30 December 2013
Received in revised form 11 March 2014
Accepted 9 April 2014
Available online 19 April 2014

Keywords:
Photochromism
Diarylethene
Benzothiophene
Substitution effect
Fluorescence

ABSTRACT

Three 1,2-bis(2-alkyl-1-benzothiophene-3-yl)perhydrocyclopentenes with different alkyl chain lengths (methyl, ethyl, and propyl) at the reactive carbons were synthesized, and their photophysical properties were compared with those of 1,2-bis(2-alkyl-1-benzothiophene-3-yl)perfluorocyclopentenes. The structures of the perhydrocyclopentenes were analyzed by X-ray crystallography, and their cyclization/cycloreversion reaction and fluorescence quantum yields, and fluorescence lifetimes were measured by steady-state spectroscopy and the time-correlated single photon counting method, respectively. From these results, we found the following three differences between perhydrocyclopentenes and perfluorocyclopentenes. (1) For the closed-ring isomers, the absorption bands of the perhydrocyclopentenes (around 450 nm) shifted to a shorter wavelength than those of the perfluorocyclopentenes (around 530 nm) because of the acceptor nature of the perfluorocyclopentene moiety. (2) The cyclization/cycloreversion quantum yields of the perhydrocyclopentenes were slightly larger than those of the perfluorocyclopentenes in hexane. (3) Interestingly, the fluorescence of both the open- and closed-ring isomers was observed only for the perhydrocyclopentenes, and the lifetimes of the closed-ring isomers were estimated to be <30 ps. The fluorescence of the closed-ring isomers of the perhydrocyclopentenes was mainly due to the suppression of nonradiative deactivation from the excited state directly to the ground state compared with the perfluorocyclopentenes.

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1. Introduction

Various types of photochromic compounds have so far been synthesized in an attempt to apply them to optoelectronic devices [1–3]. Among these compounds, diarylethene derivatives are the most promising candidates for such applications because of their photofatigue resistance and thermal irreversibility [3–19]. Diarylethenes have two aryl moieties, thiophene and benzothiophene rings, which are bound to a cycloalkane moiety. The cycloalkane moiety has a crucial function of controlling physical properties such as the absorption spectra and cyclization/cycloreversion quantum yields, and so on.

Among the diarylethene derivatives of various cycloalkenes, we focused on a perhydrocyclopentenes (PHCs) and a perfluorocyclopentenes (PFCs). Some groups have already synthesized bis(thienyl)cyclopentenes in which the fluorine substituents on the central cyclopentene ring were replaced by hydrogens [20,21]. 1,2-Bis(2-methylthien-3-yl)cyclopentene and 1,2-bis(2,5-dimethylthien-3-yl)cyclopentene do not exhibit reversible photochromism [20]. However, PHCs having thiophene rings with substituted groups (such as aryl, formyl, and carboxyl groups) at the 5-position are isomerized to the stable closed-ring isomers upon UV irradiation. Given that the substituents at the 5-position allow π-conjugation of the thiophene system, the PHCs may exhibit reversible photochromism. On the basis of this concept, several interesting studies have recently been reported on these PHCs [22–24]. Zao et al. reported that the differences in absorption and fluorescence between two isomers (open- and closed-ring isomers) can be discriminated by the photoswitching in living cells in an

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http://dx.doi.org/10.1016/j.jphotochem.2014.04.007
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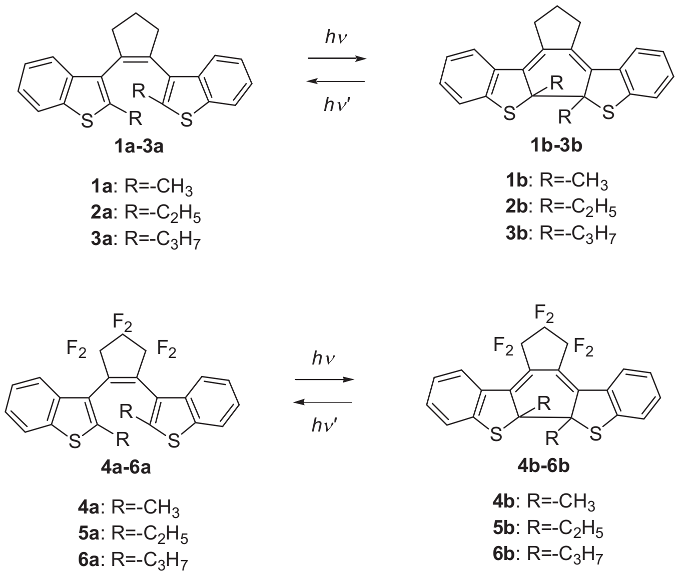

Scheme 1. Photochromic diarylethenes with perhydrocyclopentene (PHC) and perfluorocyclopentene (PFC).

aqueous solution [22]. In addition, the changes in pK_a between open- and closed-ring isomers were observed in a mixed solvent of water and acetonitrile [23]. The diarylethenes with methyl substituents introduced on cyclopentene at the 3- and 5-positions exhibited high cyclization quantum yields compared with the analog PHCs [24]. The substituent effect of fluorine and hydrogen atoms on the cyclopentene ring will affect cyclization and/or cycloreversion quantum yields, fluorescence properties, and reaction dynamics.

In addition, from the fundamental viewpoint of excited-state dynamics, Hania et al. have reported the difference in the cyclization reaction dynamics between 1,2-bis(2-methyl-5-phenylthien-3-yl)perhydrocyclopentene (HPT) and 1,2-bis(2-methyl-5-phenylthien-3-yl)perfluorocyclopentene (FPT) by means of ultrafast transient spectroscopy. HPT undergoes a slower cyclization reaction than FPT [25]. This is because the electronic level shifts near the conical intersection between the S_1 and S_0 potential energy surfaces according to the results of a theoretical calculation. That is, the introduction of a PHC or PFC moiety may play an important role in changing the electronic excited-state potential surface and the fundamental investigation of the reaction dynamics in bis(thienyl)ethenes. Unfortunately, there have been few reports on the photochromic properties of closed-ring isomers of diarylethene derivatives with a PHC moiety and their cycloreversion reaction dynamics, although they are possibly alternatives to derivatives with a PFC.

Along the above lines, we have synthesized three diarylethene derivatives **1a–3a** with PHC as the main molecular frame, and studied their photochemical and physical properties by conventional steady-state spectroscopy and the time-correlated single photon counting method. The PFC derivatives **4a–6a** were also synthesized and examined to compare their properties with those of **1a–3a**. On the basis of the experimental results for the reaction and fluorescence quantum yields and the fluorescence profiles, we discuss the differences between PHCs and PFCs (Scheme 1).

2. Experimental

2.1. General

The solvents used were spectrograde and were purified by distillation before use. Absorption spectra were measured using a spectrophotometer (Shimadzu, UV-2100PC). A mercury lamp (Ushio, 500 W) was used as the light source. Light of an appropriate wavelength was isolated by passing it through a monochromator (Ritsu MC-10N) or through a UV-29, UV-31, UV-36, or Y-44 filter. The same mercury lamp was used as the light source in fatigue resistance experiments, and the appropriate wavelength was isolated by passing through the light 254 nm band-pass and Y-44 filters. A portable UV lamp (As One Corp., SLUV-4) was used as the light source in an experiment on photochromism in the single-crystalline phase. Diarylethene crystals were observed using an OPTI-POL 2POL (Nikon) polarizing microscope. The cyclization quantum yields were determined by comparison with the photocyclization rate of **4a** in hexane using a conventional procedure [26-28]. The cycloreversion quantum yields were also measured using **4b** in hexane as a reference. Fluorescence spectra were measured with a Hitachi F-2500 spectrometer. The fluorescence quantum yields at 254 nm were determined using anthracene in ethanol ($\Phi = 0.30$) as a reference. The fluorescence quantum yields at 436 nm were determined using fluorescein in sodium hydroxide solution ($\Phi = 0.90$) as a reference.

Fluorescence time profiles for the closed-ring isomers of the PHC derivative **1b–3b** in hexane were measured using a time-correlated single photon counting system. As an excitation laser pulse, a 468 nm picosecond pulsed laser (PLP10-047, Hamamatsu) was employed with a repetition rate of 50 MHz. An avalanche photodiode (PDF series, MPD) and a counting board (SPC-130, Becker & Hickl GmbH) were used for signal detection. Sharp cut filters (O-52, HOYA) were placed in front of the avalanche photodiode to detect weak fluorescence in the range of more than 520 nm and avoid the scattering of excitation light. The instrumental response time was 100 ps, which was determined by the FWHM of scattered light from a colloidal solution.

^{1}H-NMR data was recorded on a JEOL ECP400 (400 MHz) or JEOL ECA (600 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. Mass spectra were obtained using a Shimadzu Parvum gas chromatography-mass spectrometer and a JEOL MS-700 mass spectrometer. X-ray crystallographic analysis was carried out using a Bruker SMART CCD X-ray diffractometer. HPLC was carried out using a Shimadzu LC-10AD liquid chromatography system coupled with a Shimadzu SPD-10AV spectrophotomeric detector. A silica gel column (Wako Wakosil-5SIL) was used to analyze the diarylethene isomers. Optimized molecular structures were calculated at the B3LYP/6-311 + G(d, p) levels using the Gaussian 09 program [29].

2.2. Materials

The materials 2-ethyl-1-benzothiophene (CAS no. 1196-81-2), 2-propyl-1-benzothiophene (CAS no. 16587-32-9), and 3-bromo-2-ethyl-1-benzothiophene (CAS no. 64860-32-8), which cannot be obtained as commercial reagents, were synthesized as described in the supplementary data. 1,2-Bis(2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene (**4a**) [12], 1,2-bis(2-ethyl-1-benzothiophene-3-yl)perfluorocyclopentene (**5a**) [26], and 1,2-bis(2-propyl-1-benzothiophene-3-yl)perfluorocyclopentene (**6a**) [26] were synthesized according as described in the literature.

2.2.1. Preparation of 1,2-bis(2-methyl-1-benzothiophene-3-yl)cyclopentene (*1a*)

To a stirred THF solution (40 mL) containing 3-bromo-2-methyl-1-benzothiophene **7** (2.0 g, 8.81 mmol), 6.05 mL of 1.6 M butyllithium hexane solution (9.68 mmol) in dry THF (40 ml) was slowly added at −80 °C, and the solution was stirred for 15 min at −80 °C. Then, the solution was slowly added dropwise to trimethyl borate (1.37 g, 13.2 mmol), and the resulting solution was stirred for

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