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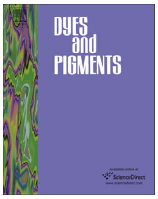

# Photochromism of diarylethene derivatives having benzophosphole and benzothiophene groups

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ABSTRACT

Asymmetric diarylethene derivatives having benzophosphole and benzothiophene groups at the aryl moieties were synthesized and their photochromic properties were examined. Three diarylethene derivatives, **1** having benzophosphole and benzothiophene groups, **2** having benzophosphole *P*-oxide and benzothiophene groups, and **3** having benzophosphole *P*-oxide and benzothiophene *S*,*S*-dioxide groups, were synthesized by appropriately controlled oxidation of benzophosphole and benzothiophene groups. Diarylethenes **1**–**3** underwent photochromic reactions in acetonitrile as well as in the powder solid state upon alternate irradiation with ultraviolet (UV) and visible light. The closed-ring isomer of diarylethene **3** emitted fluorescence with a quantum yield of 0.05 in acetonitrile solution. The fluorescence quantum yield dramatically increased up to 0.55 in the solid state.

## 1. Introduction

Photochromism is defined as a reversible transformation of a molecule between two isomers having different absorption spectra upon photoirradiation [1]. The photochromic molecules have the potential for applications to various photonics devices, such as optical memories and optical switches [2–6]. Among various photochromic compounds, diarylethene is one of the most promising candidates for the applications because of its outstanding performance, such as thermally irreversibility, fatigue resistance, and high reactivity in the solid state [7,8]. Photochromic properties of diarylethene derivatives depend on their aryl moieties. So far, diarylethene derivatives having heteroaryl groups, such as thiophene [9], benzothiophene [10], furan [11], benzofuran [12], pyrrole [13], indole [14], thiazole [15], oxazole [16], imidazole [17], isooxazole [18], pyrazole [19], pyridine [20], and benzosilole [21], have been synthesized and examined.

Recently, phosphole derivatives have attracted considerable attention as organic electronic materials. The phosphole derivatives show low aromaticity and narrow HOMO–LUMO gaps [22–27]. These properties can be modulated by changing the substituent on the phosphine atom [28,29]. Some of the phosphole derivatives exhibit aggregation induced emission (AIE) [30–32]. These characteristic features of the phosphole derivatives were successfully utilized in organic light-emitting diodes (OLEDs) [33–35] and organic field-effect transistors (OFETs) [36–39]. When integrating the phosphole skeletons into diarylethene derivatives, their photochromic performance is expected to be further extended. However, reports on diarylethene derivatives having phosphole groups are rare [40–42]. It has been reported that diarylethenes having phosphole skeletons at the central ethene bridges exhibit photoswitching of fluorescence [41].

Here we report on photochromic diarylethene derivatives **1**–**3** having benzophosphole skeletons at the aryl moieties (Scheme 1). The derivatives have asymmetric structures in which benzophosphole and benzothiophene groups are connected to the central perfluorocyclopentene bridge. Appropriately controlled oxidation of the aryl moieties afforded three diarylethene derivatives, **1** having benzophosphole and benzothiophene groups, **2** having benzophosphole *P*-oxide and benzothiophene groups, and **3** having benzophosphole *P*-oxide and benzothiophene *S*,*S*-dioxide groups. Short alkyl chain substituents (ethyl and *n*-propyl) were introduced

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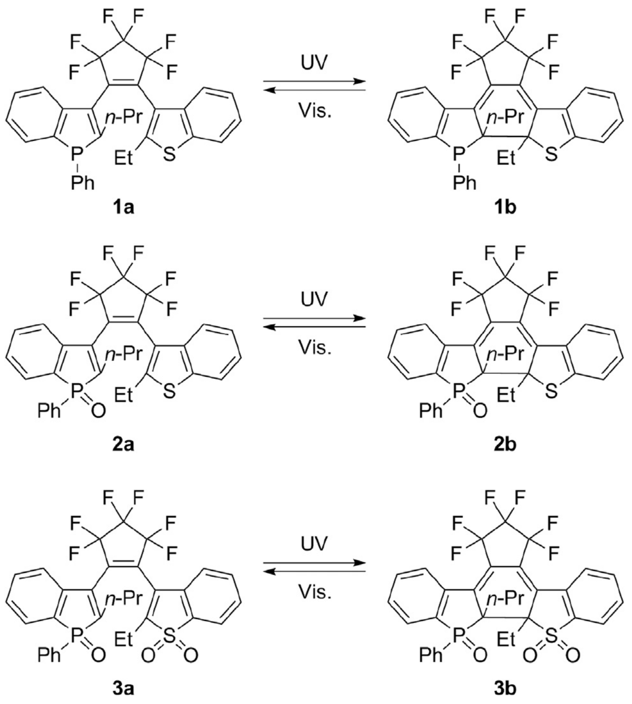


**Scheme 1.** Photochromism of diarylethenes **1**–**3** having benzophosphole and benzothiophene groups.

at the reactive carbons, because diarylethene derivatives having benzothiophene *S*,*S*-dioxide groups improved their fluorescent properties by introduction of ethyl or *n*-propyl substituents [43–47]. Photochromic and fluorescent properties of **1**–**3** have been examined in solutions as well as in the solid state.

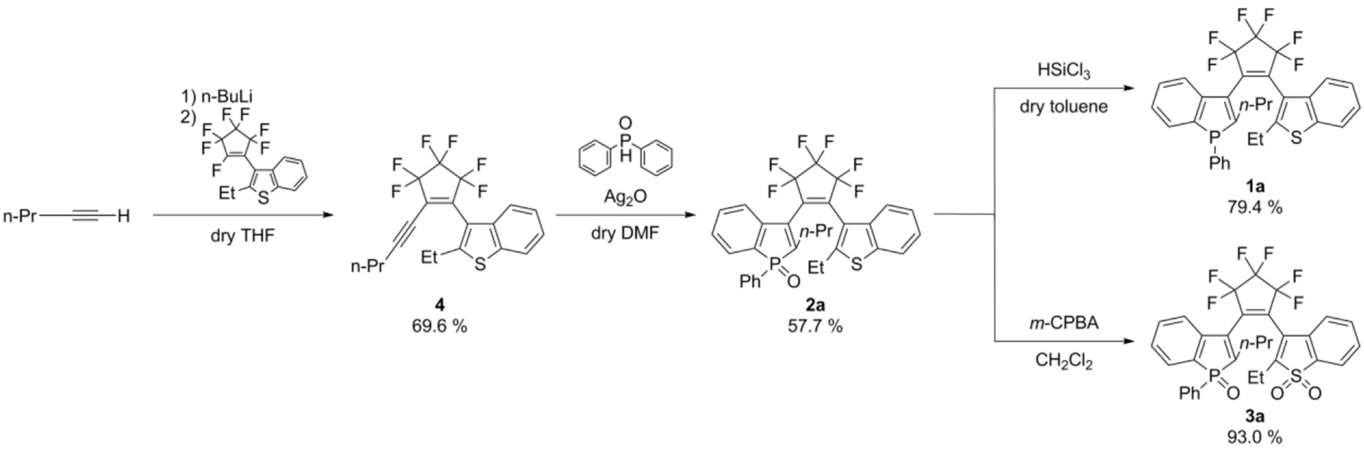
## 2. Experimental section

### 2.1. General

All reagents used for syntheses were purchased from Kanto Chemical Co., Inc., Tokyo Chemical Industry Co., Ltd., Wako Pure Chemical Industries, Ltd., and Sigma–Aldrich Co. LLC and were used without further purification. Solvents used for spectroscopic measurements were purchased from Kanto Chemical Co., Inc. and were of guaranteed reagent grade. Diarylethenes synthesized were subjected to spectroscopic measurements after purification by GPC for **1**–**3** (Japan Analytical Industry LC-908, Jaigel-2H ϕ20 mm × 600 mm and Jaigel-2.5H ϕ20 mm × 600 mm, chloroform, 3.5 mL/min) and further purification by HPLC for **2** and **3** (Hitachi L-6250 pump system and L-7400 UV–visible detector, Wakosil 5SIL ϕ20 mm × 250 mm, hexane:ethyl acetate = 60:40 (**2**) and 45:55 (**3**), 20 mL/min). $^1$H and $^{31}$P NMR spectra were measured with a Bruker Biospin Avance 400 spectrometer (400 MHz) and a JEOL ECX 400 P spectrometer (162 MHz), respectively. Tetramethylsilane (TMS) was used as an internal standard for $^1$H NMR. 85% Phosphoric acid ($H_3PO_4$) was used as an external standard for $^{31}$P NMR. For clarity of analysis, the NMR spectra were measured for one of diastereomers of the closed-ring isomer which were isolated by HPLC (Hitachi L-6250 pump system and L-7400 UV–visible detector, Wakosil 5SIL ϕ20 mm × 250 mm, hexane:ethyl acetate = 60:40 (**2**) and 45:55 (**3**), 20 mL/min). Mass spectra based on the electron impact (EI) ionization method were measured with a Shimadzu GCMS-QP2010Plus mass spectrometer. High-resolution mass spectra based on the direct-analysis-in-real-time (DART) ionization method were measured with a JEOL JMS-T100LP mass spectrometer.

Absorption spectra in solutions were measured with a Hitachi U-4100 absorption spectrophotometer. Photoirradiation was carried out by using a 500 W xenon short-arc lamp (Ushio, SX-UI501XQ) or a 300 W xenon light source (Asahi Spectra, MAX-302). Monochromic light was obtained by passing the light through a monochromator (Jobin Yvon, H-10 UV or Ritsu Oyo Kogaku, MC-10N). Fluorescence spectra in solutions were measured with a Hitachi F-2500 fluorescence spectrophotometer. Fluorescence spectra in powder solids and fluorescence quantum yields were measured with a Hamamatsu C9920-02G absolute PL quantum yield measurement system.

Fluorescence lifetimes were measured with a time-correlated single-photon-counting (TCSPC) system. Experimental setup for the TCSPC was described previously [48]. Briefly, a Ti:sapphire oscillator (Spectra Physics, Tsunami) was utilized as a pulsed light source. The operation wavelength, pulse width and repetition rate were tuned to be 820 nm, 70 fs, 80 MHz, respectively. The fundamental output of the laser was frequency doubled in a type I BBO crystal and the generated second harmonics centered at 410 nm was introduced into samples. The repetition rate was reduced down to 8 MHz by using an electro-optic modulator (Conoptics, Model 350) and the excitation power to the samples was typically 1.4 μW at 8 MHz. The detection of the fluorescence at the magic



**Scheme 2.** Syntheses of **1a**–**3a**.