

# Modulation of the Photochromic Property in an Organoboron-Based Diarylethene by a Fluoride Ion

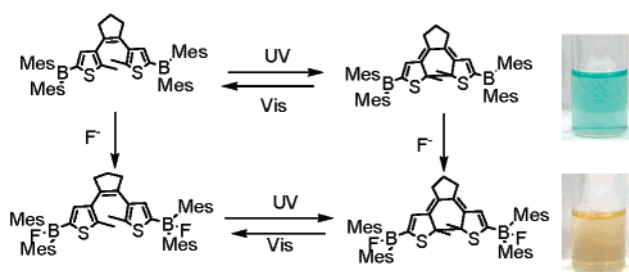
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## ABSTRACT



Organoboron-based diarylethene was successfully synthesized and exhibited photochromic property. Furthermore, its photochromic property can be modulated by a fluoride ion. The absorption maximum of the photostationary state shifted from 655 to 490 nm upon addition of a fluoride ion. The modulation mechanism is attributed to the special Lewis acid–base interaction between a trivalent boron atom and a fluoride ion.

Photochromic materials have recently received remarkable attention for their potential applications of optoelectronic devices such as optical memories and photoinduced switches.<sup>1</sup> Diarylethene derivatives are the most promising candidates for their notable thermal irreversible photochromic behavior and outstanding fatigue resistance.<sup>2</sup> The open and closed isomers of diarylethenes have not only different absorption spectra but also many different physical and chemical properties such as photoluminescence,<sup>3</sup> refractive index,<sup>4</sup>

electrical carrier injection, and transport characteristics.<sup>5</sup> These differences have been utilized to control their functions such as electrical conductivity,<sup>6</sup> alignment of liquid crystals,<sup>7</sup> light-driven organogelators,<sup>8</sup> and photocontrolled release and uptake.<sup>9</sup>

For practical applications, modulation of photochromic property is indispensable. The conventional approaches have been used by controlling their conformations (parallel or antiparallel),<sup>10</sup> changing the acid strength,<sup>11</sup> tuning the intramolecular proton transfer,<sup>12</sup> and coordinating with metal ions.<sup>13</sup> For example, Lehn et al.<sup>11</sup> reported a proton-gated photochromic reaction. At low and high pH values, the relative rates of photocyclization were found to be 1 and 0.003, respectively. Irie et al.<sup>10</sup> described the reactivity control of diarylethenes by introducing intralocking arms, which were able to form hydrogen bonds or a disulfide linkage. Recently, they<sup>12</sup> also investigated the modulation

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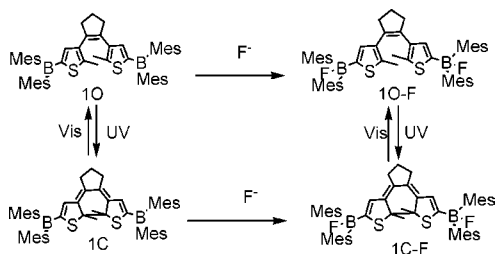
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of the photochromic property of diarylethenes by esterification and a hydrolysis reaction.

Generally, organoboron compounds bearing  $\pi$ -conjugated groups have a unique LUMO on a boron atom in which the  $\pi$ -conjugation is divergently extended through the vacant p-orbital of the boron atom. Physical and chemical properties of organoborons are modified as the vacant p-orbital of the boron atom is disturbed. Tamao et al. and Gabbai et al.<sup>14</sup> have reported organoborons as colorimetric and fluorogenic sensors for a fluoride ion, respectively. Recently, our group has also reported the two-photon fluorescent sensors derived from boranes for a fluoride ion by means of the special Lewis acid–base interaction between a boron atom and a fluoride ion.<sup>15</sup> In this communication, we synthesized a diarylethene derivative 1,2-bis-(5'-dimesitylboryl-2'-methylthieny-3'-yl)-cyclopentene (**1**) (Scheme 1) by introducing the dimesityl-

**Scheme 1.** Concept of Photochromic Property Modulated by a Fluoride Ion



boryl group and found that the photochromic property was modulated by a fluoride ion.

Compound **1** was prepared from 1,2-bis-(5'-chloro-2'-methylthieny-3'-yl)cyclopentene<sup>16</sup> in a one-step reaction with

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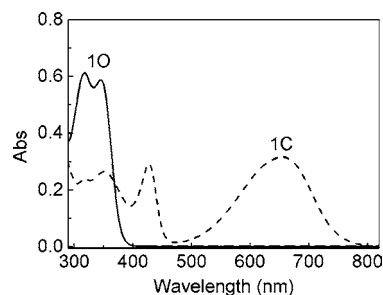
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dimesitylboron fluoride (FBMes<sub>2</sub>) in 75% yield. The structure was identified with <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS spectra (Supporting Information), and X-ray single-crystal diffraction.

The absorption spectra for the open (**1O**) and closed (**1C**) ring isomers at the photostationary state are shown in Figure 1. The open isomer in THF solution was colorless, and its



**Figure 1.** UV–vis absorption spectra. Solid line: **1O** ( $2.0 \times 10^{-5}$  M) in THF solution. Dashed line: the photostationary state of **1O**.

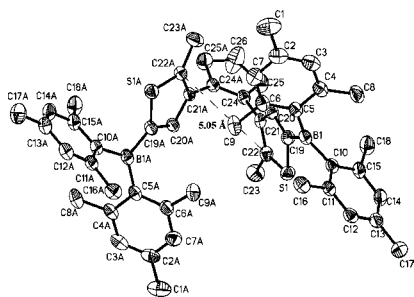
absorption maximum was at 344 nm assigned to the  $\pi \rightarrow \pi^*$  transition of the 5-dimesitylboryl-2-methylthienyl group (Figure 1). Upon illumination at a wavelength of 365 nm of light, the colorless solution of **1O** turned green quickly, and new absorption bands centered at 428 and 655 nm were observed with a clear isosbestic point at 368 nm. The photocyclization reaction was monitored by <sup>1</sup>H NMR. The signals of the methyl proton of thiophene were shifted to a lower magnetic field from 1.90 to 2.21 ppm. After 30 min illuminating, the increase in the absorbance leveled off. The conversion from **1O** to **1C** in the photostationary state was calculated to be about 94% by <sup>1</sup>H NMR spectra. The closed isomer (**1C**) was completely reverted to its open isomer (**1O**) by photoexcitation with visible light of a wavelength greater than 500 nm. The cyclization and cycloreversion quantum yields<sup>17</sup> were determined to be 0.27 irradiating with 365 nm and 0.063 irradiating with 650 nm, respectively.

The single crystal of **1O** was obtained by recrystallization from dichloromethane/acetonitrile. The ORTEP drawing is shown in Figure 2, which indicated that **1O** was packed in a distorted antiparallel conformation in the crystal. The distance between the two reactive carbons was 5.05 Å, which is too large to photocyclize in the single crystal according to the literature.<sup>18</sup> This is verified by the fact that irradiating a single crystal of **1O** with 365 nm of light for 24 h resulted in no observable color change. In the crystal state, it was completely symmetrical, and the boron atom adopted a trigonal planar geometry ( $\Sigma(\text{C}–\text{B}–\text{C}) = 360.7^\circ$ ), as expected

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**Figure 2.** ORTEP drawing of **10** (30% ellipsoid). H atoms omitted for clarity.<sup>20</sup>

from previous work on the structurally characterized dimesitylboryl group.<sup>19</sup>

The reaction between the boron atom (Lewis acid) and the fluoride ion (Lewis base) has been reported in some systems.<sup>21</sup> Herein, the interaction between a boron atom of **10** and a fluoride ion was investigated by <sup>1</sup>H and <sup>19</sup>F NMR spectra.<sup>22</sup> Upon addition of a *n*-Bu<sub>4</sub>NF salt (TBAF, as a source of a fluoride ion) in CDCl<sub>3</sub> solution, large shifts were observed for the signals of the thienyl proton (from 7.18 to 6.41 ppm), the phenyl proton (from 6.79 to 6.51 ppm), and the methyl proton (from 1.90 to 1.82 ppm). Moreover, the signal from <sup>19</sup>F NMR was upshifted to –162.1 ppm from –114.5 ppm of the free fluoride ion. These facts suggested a strong affinity of the boron atom for the fluoride ion. Upon complexation of the boron atom with the fluoride ion, the electron negativity increased, resulting in the increasing shield effects of the boron atom and the upshift of the proton signal. Furthermore, the methyl proton's peak of the dimesitylboryl group was split into multiplets due to the coupling interaction between the fluoride ion and the methyl proton of the dimesityl group.

The binding property of **10** with the fluoride ion was also investigated by UV–vis absorption spectra. When TBAF was added to the THF solution of **10**, the absorbance centered at 344 nm of **10** was decreased gradually and then reached the saturation after a total addition of about 3 equiv of the fluoride ion (Figure 3). These facts indicated that the strong B–F interaction resulted in sp<sup>3</sup> hybridization of the boron atom and subsequently interrupted the extended p–π conjugation between 2-methylthienyl groups and dimesitylboryl groups, thereby causing a dramatic change in the photo-physical properties.

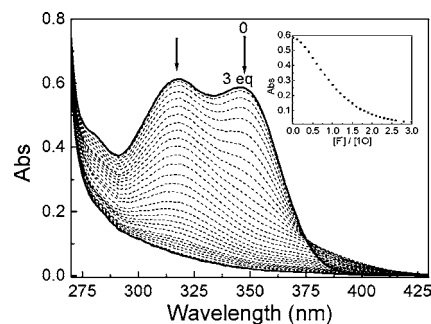
The geometry structure of the closed-ring isomer **1C** was computationally optimized with density functional theory

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(20) Crystal data for C<sub>51</sub>H<sub>58</sub>B<sub>2</sub>S<sub>2</sub>: fw = 756.71, monoclinic (C2/C), a = 14.231(3) Å, b = 11.851(2) Å, c = 27.763(6) Å, α = 90°, β = 90.34(3)°, γ = 90°, V = 4682.2(16) Å<sup>3</sup>, ρ<sub>calcd</sub> = 1.073 g cm<sup>-3</sup>, Z = 4, μ = 0.145 mm<sup>-1</sup>, R1 [I > 2σ(I)] = 0.0459, wR2 [I > 2σ(I)] = 0.1330, R1 (all data) = 0.0665, wR2 (all data) = 0.1468, GOF = 1.046. The CCDC number of compound **10** is 296303.

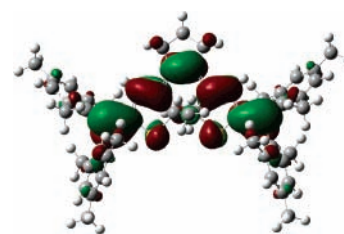
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**Figure 3.** Changes in UV–vis absorption spectra of **10** ( $2.0 \times 10^{-5}$  M) in THF solution upon addition of 0.1–3.0 equiv of TBAF. Inset: plots of absorbance at 344 nm as a function of [F<sup>-</sup>]/[**10**].

with exchange correction functionals of B3LYP based on the 3-21+G\* set. The examination of the DFT orbitals revealed that the p<sub>z</sub> orbitals of the boron atom contributed to the LUMO of **1C** (Figure 4), which was close to the

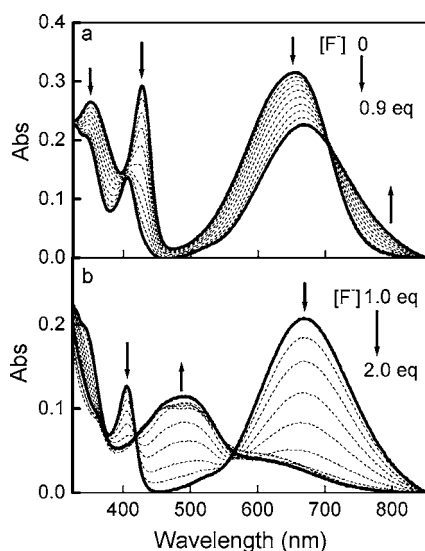


**Figure 4.** DFT orbital picture of LUMO in **1C**.

observed other organoborons bearing two dimesitylboryl groups.<sup>23</sup> Therefore, any events disrupting the LUMO should greatly affect the absorption spectra of **1C**. In the case of **1C**, the combination of the fluoride ion, which generates anionic charge on the boron atom, should change the conjugation of the dipole moment of diarylethene and the dimesitylboryl substituent, so it could be expected that the absorption property of **1C** was modulated upon addition of the fluoride ion.<sup>14b</sup>

The modulation of the photochromic property of **1C** by a fluoride ion was recorded by UV–vis absorption techniques. Figure 5 showed the changes in absorption spectra of the photostationary states (PSS) irradiated with 365 nm when TBAF was added in THF solution. Upon addition of less than 1.0 equiv of TBAF, the absorption maximum of PSS was red shifted from 655 to 670 nm with an isobestic point of 705 nm (Figure 5a); consequently, the absorption edge was greatly red shifted. However, when more than 1.0 equiv of TBAF was added, the absorption maximum of PSS was blue shifted to 490 nm (Figure 5b), and the solution turned from green to orange. It was attributed to the formation of

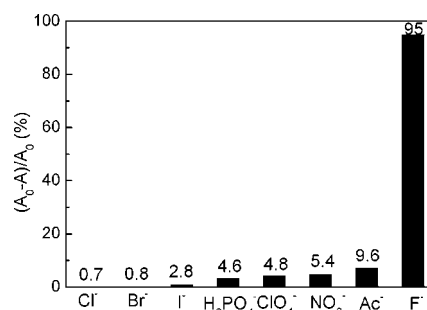
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**Figure 5.** Changes in UV-vis absorption spectra of **1** in PSS ( $2.0 \times 10^{-5}$  M) in THF solution upon addition of (a) 0.1–0.9 equiv and (b) 1.0–2.0 equiv of TBAF.

a fluoride adduct with photochromic property. Furthermore, the solution turned colorless completely by photoexcitation with visible light at 490 nm, which was in agreement with the observation that the THF solution of a bis(fluoride) adduct of **10** ( $[\mathbf{10F}_2]^{2-}$ ) turned orange upon illumination with UV (254 nm) light.

As depicted in Figure 6, the fluoride binding property of **10** is remarkably selective. **10** showed scarcely any response with other halide ions and weak complexation with  $\text{AcO}^-$ ,  $\text{NO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{ClO}_4^-$ . The high selective binding property of **10** to a fluoride ion is coincident with the previous work on other organoboranes.<sup>14,15</sup> Generally, the high selectivity of the fluoride ion can be probably attributed to two factors. First, the trivalent boron atom and the fluoride ion are a typical Lewis acid and base, respectively; therefore, they have very strong affinity.<sup>21</sup> Second, with sterically congested surroundings around the central boron atom (Figure 2), four *o*-methyls on the two mesityls, just like a



**Figure 6.** Comparison of the percent decrease of absorbance of **10** ( $2.0 \times 10^{-5}$  M) in THF solution at 344 nm in the presence of 3 equiv of different ions.

“cage”, only allow a small “base” such as a fluoride ion to break through this “cage” and react with the boron atom. In addition, this steric effect has also been noted by other researchers in their previous work.<sup>2c,3a,b,14,15</sup>

In summary, we have synthesized an organoboron-based diarylethene derivative **1** and demonstrated the modulation of its photochromic property by a fluoride ion. The interaction of a boron atom with a fluoride ion caused obvious spectral changes of **1** in both open-ring and closed-ring form. Moreover, the structural feature of dimesitylboryl groups benefits the high selectivity of the fluoride ion. The results provide a useful design strategy for the tuning of photochromic properties for further applications.

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**Supporting Information Available:** Synthetic and experimental details, CIF of **10**, and computational chemistry of **1C**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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