

# A Highly Efficient Silole-Containing Dithienylethene with Excellent Thermal Stability and Fatigue Resistance: A Promising Candidate for Optical Memory Storage Materials

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## S Supporting Information

**ABSTRACT:** Diarylethene compounds are potential candidates for applications in optical memory storage systems and photoswitchable molecular devices; however, they usually show low photocycloreversion quantum yields, which result in ineffective erasure processes. Here, we present the first highly efficient photochromic silole-containing dithienylethene with excellent thermal stability and fatigue resistance. The photochemical quantum yields for photocyclization and photocycloreversion of the compound are found to be high and comparable to each other; the latter of which is rarely found in diarylethene compounds. These would give rise to highly efficient photoswitchable material with effective writing and erasure processes. Incorporation of the silole moiety as a photochromic dithienylethene backbone also was demonstrated to enhance the thermal stability of the closed form, in which the thermal backward reaction to the open form was found to be negligible even at 100 °C, which leads to a promising candidate for use as photoswitchable materials and optical memory storage.

Photoswitchable materials have been widely used in photo-switching, optical recording, and sensing devices.<sup>1,2</sup> High stability and efficiency are two major prerequisites for smart materials.<sup>3</sup> Among photoswitchable materials, photochromic materials are the most widely explored. Of these, spiropyran is most commonly used; however, common problems with spiropyran-based smart materials include the presence of efficient thermal reversible pathways and the loss of reversibility brought about by photodegradation or photooxidation.<sup>4</sup> Meanwhile, research on photochromic diarylethene compounds has received much attention because of the distinguishable absorption spectra, changes in emission intensity, and other differences in physicochemical properties between the open and closed forms. These properties have made diarylethene compounds potential candidates for applications in optical memory storage systems and photoswitchable molecular devices.<sup>1,2</sup> Although some of the photochromic diarylethenes showed excellent thermal stability and fatigue resistance,<sup>3</sup> they usually show low photocycloreversion quantum yields<sup>1</sup> that result in inefficient photoinduced ring-opening processes and slow photoresponses, which limit their potential use and efficiency in photoswitchable devices. To be a promising candidate of optical memory storage systems and photo-

switchable molecular devices, the photochromic materials should have high and comparable photocyclization and photocycloreversion quantum yields with excellent thermal stability and fatigue resistance. While there have been many efforts to derivatize diarylethenes, especially dithienylperfluorocyclopentenes, to tune their photophysical and photochromic behaviors, studies on the design and synthesis of different types of diarylethene backbones with high photoswitching efficiency and high thermal stabilities are relatively less explored. Most works mainly focus on modifications at the substituted aryl groups of diarylethenes.<sup>1–3</sup>

Various researchers have shown that incorporation of heterocycles into the bridging part of the diarylethene backbone, instead of derivatizing the pendants of the dithienylperfluorocyclopentene core, can enrich the photochromic and photophysical behaviors,<sup>5–10</sup> such as enhancement of efficiency of the photochromic system by stabilizing the photoactive antiparallel conformation for the photochromic reaction.<sup>6</sup> The most commonly studied heterocycles include pyrroles, thiophenes, indoles, thiazoles, imidazoles, and others.<sup>1–3,5–10</sup> Recently, various versatile photochromic compounds, such as imidazolium salts and ionic liquids,<sup>3d,7e,8b</sup> *N*-heterocyclic carbenes,<sup>7e,8b,c</sup> pyridylimidazoles,<sup>7d</sup>  $\beta$ -diketonates,<sup>8a,9c</sup> and phospholes,<sup>9e</sup> were prepared to demonstrate the possibility of tunable photochromism. However, incorporation of these heterocycles usually shows less thermally stable closed forms, and the resistance to photofatigue is not as good as the dithienylperfluorocyclopentene derivatives, possibly due to the relatively higher aromaticity of these heterocycles.<sup>1–3,5–9</sup> Among the heterocycles, siloles have been less extensively studied but have attracted increasing interest due to their unique low-lying lowest unoccupied molecular orbital (LUMO) level associated with the  $\sigma^*-\pi^*$  conjugation between the  $\sigma^*$  orbital of the silylene moiety and the  $\pi^*$  orbital of the endocyclic 1,3-butadiene.<sup>11</sup> Apart from the low-lying LUMO level, the  $\pi$ -electrons of siloles are mainly localized on the C=C bonds of the butadiene unit with only a slightly higher aromaticity than cyclopentadiene; exploitation of this interesting property has gained much less attention.<sup>12</sup> We believe that by utilizing this unique characteristic of siloles, the designed photochromic diarylethenes may readily give rise to some excellent photochromic properties as well as excellent thermal stability and fatigue resistance.<sup>13</sup> To the best of our

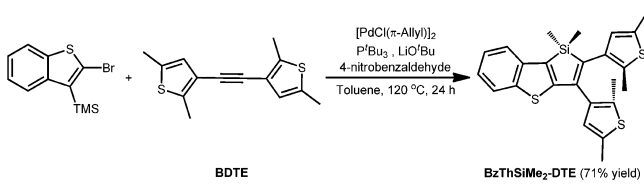
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knowledge, although silole-containing materials have attracted growing interest and have been studied by many groups, use of the silole moiety as the heterocyclic backbone for photochromic dithienylethenes has not been reported.<sup>14</sup> Herein, we report the syntheses of a silole-containing dithienylethene. Rich and promising photochromic properties of the compound were observed and investigated in detail. Insights into the electronic structure of the compound and the nature of its excited states have also been provided by computational studies.

By modification of a synthetic pathway for the synthesis of siloles reported in the literature,<sup>15</sup> the target compound was prepared in one single step by the intermolecular coupling reaction of 2-silylaryl bromide with 1,2-bis(2,5-dimethylthiophen-3-yl)ethyne (BDTE) associated with the C(sp<sup>3</sup>)-Si bond cleavage in the trimethylsilane group, as shown in Scheme 1. BDTE was prepared by the iodination of 2,5-dimethylth-

### Scheme 1. Synthesis of BzThSiMe<sub>2</sub>-DTE



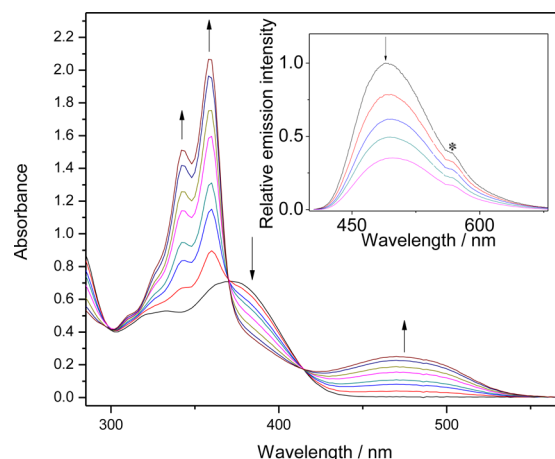
iophene, followed by Sonogashira coupling with ethynyl-trimethylsilane and subsequent deprotection of the trimethylsilyl group. Finally, Sonogashira coupling between 3-iodo-2,5-dimethylthiophene and 3-ethynyl-2,5-dimethylthiophene produced the target compound in good yield. With BDTE, the target compound could be prepared in one step via a Pd-mediated coupling reaction. By utilizing this synthetic pathway and BDTE, silole-containing dithienylethenes can be readily synthesized and functionalized without the need for tedious synthesis and modification of the dithienylethene framework.

BzThSiMe<sub>2</sub>-DTE was characterized by <sup>1</sup>H NMR spectroscopy, mass spectrometry, and elemental analysis and was structurally determined. The <sup>1</sup>H NMR spectrum of the compound revealed that the two dimethylthienyl moieties can freely rotate at room temperature in solution medium, which probably results from the lack of steric bulk on the thiophene rings. Distances between the reactive carbon atoms on the dithienylethenes are 3.571 and 3.609 Å, which indicate that the compound in the crystal form is able to undergo photochemical cyclization in the solid state.<sup>16</sup>

BzThSiMe<sub>2</sub>-DTE is found to dissolve in benzene to give a pale yellow solution with two intense absorption bands at ~332 and 371 nm (Figure S1; Table S1). The intense absorption bands are tentatively assigned as intraligand π-π\* transitions of the benzo[*b*]silole moiety mixed with π-π\* transitions of the peripheral dimethylthienyl moieties. Upon photoexcitation at room temperature, the compound displays intense greenish-yellow luminescence at ~491 nm, with a fluorescence quantum yield of ~0.14 in degassed benzene solution.

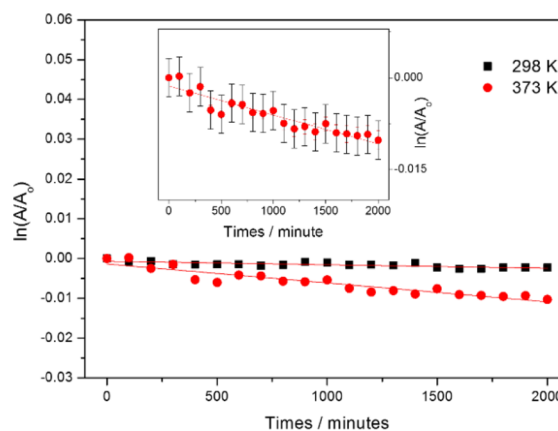
Upon photoexcitation at the π-π\* absorption of BzThSiMe<sub>2</sub>-DTE in degassed benzene, BzThSiMe<sub>2</sub>-DTE undergoes photocyclization, and the solution turns to orange color with the emergence of a low-energy absorption band at ~474 nm. Two well-defined isosbestic points at ~370 and 415 nm are observed, which indicate a clean conversion from the open to closed form.<sup>1,7-9</sup> The UV-vis absorption spectral changes upon photoirradiation of BzThSiMe<sub>2</sub>-DTE in degassed benzene are

shown in Figure 1. The significant bathochromic shift in the closed form relative to its open form is mainly due to the increase



**Figure 1.** UV-vis absorption spectral changes of BzThSiMe<sub>2</sub>-DTE in benzene upon irradiation at 370 nm. Inset shows the plot of emission change upon irradiation at 370 nm; asterisk represents an instrumental artifact.

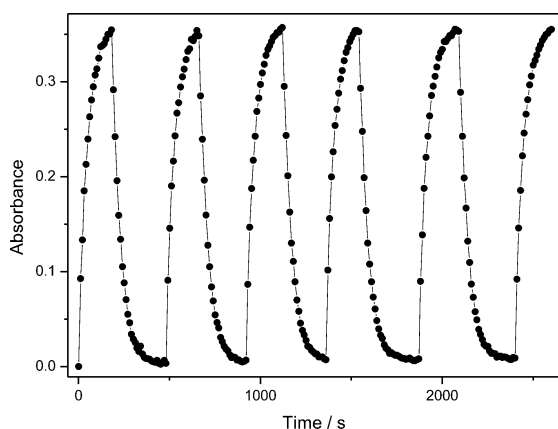
in planarity and extended π-conjugation across the 8a,8b-dimethyl-1,8-thia-as-indacene moiety (Figure S2).<sup>7-9</sup> The thermal stability of the closed form is excellent, and the thermal back-reaction into the open form is found to be negligible (<2%) at 100 °C for 2000 min (Figure 2) and comparable to the



**Figure 2.** A plot of  $\ln(A/A_0)$  versus time for the absorbance decay of BzThSiMe<sub>2</sub>-DTE at 474 nm at 25 and 100 °C in argon-flushed 1,2-dichlorobenzene solution.  $A$  denotes absorbance at time  $t$ ;  $A_0$  denotes initial absorbance; solid lines represent theoretical linear fits. Inset shows the expanded plot of  $\ln(A/A_0)$  versus time for the absorbance decay of BzThSiMe<sub>2</sub>-DTE at 474 nm at 100 °C in argon-flushed 1,2-dichlorobenzene solution.

thermally stable dithienylperfluorocyclopentenes.<sup>1</sup> The decay rate constant for BzThSiMe<sub>2</sub>-DTE is estimated to be  $4.75 \times 10^{-6} \text{ min}^{-1}$ , and the calculated half-life is found to be around 101 days at 100 °C. To the best of our knowledge, this is one of the best thermally stable photochromic compounds.<sup>1-3,7-10</sup> It should be noted that the closed form can return completely back to the open form via photoirradiation at the lowest energy band of the closed form with no signs of decomposition during the thermal conversion measurement. As a result, the open form can only be regenerated by photoexcitation.

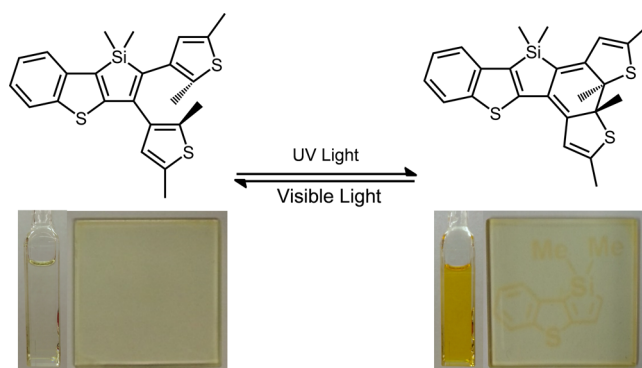
The quantum yields for both photocyclization and photocycloreversion processes also were determined. A high photocyclization quantum yield of  $\sim 0.48$  and a photocycloreversion quantum yield of  $\sim 0.42$ , which are comparable to each other and seldom observed in photochromic dithienylperfluorocyclopentene systems, were obtained.<sup>1–3,7–9</sup> Interestingly, the photocyclization quantum yield is close to the maximum value of 0.5 that can be achieved for a 1:1 mixture of antiparallel and parallel conformers in photochromic diarylethene systems, while the photocycloreversion quantum yield is much higher than that commonly observed in other photochromic diarylethene systems, which is usually  $< 0.1$ .<sup>1–3,7–10</sup> With high photocycloreversion quantum yield and excellent thermal stability, the compound can undergo effective photoinduced ring-opening processes. Large quantum yields in both the photocyclization and photocycloreversion represent an important property to increase the efficiency of photochromic-based molecular memory devices.<sup>17</sup> In addition, the conversion at the photostationary state of **BzThSiMe<sub>2</sub>-DTE** is determined to be  $\sim 66\%$ . Besides excellent thermal stability, fatigue resistance represents another important parameter commonly used to evaluate the performance of photochromic materials.<sup>1</sup> Photochromic materials could lose their photochromic reactivities through side reactions of the closed form; thus, photochromic compounds should have a high fatigue resistance to be employed for different practical applications. **BzThSiMe<sub>2</sub>-DTE** shows high fatigue resistance as demonstrated in Figure 3 and Figure S3.



**Figure 3.** UV–vis absorbance changes of **BzThSiMe<sub>2</sub>-DTE** at 474 nm on alternate excitation at the isosbestic wavelength of 370 nm and the absorption maximum of the closed form at 474 nm over five cycles in degassed benzene solution at 298 K.

**BzThSiMe<sub>2</sub>-DTE** can undergo fully reversible photochemical ring-opening and ring-closing processes without photochemical side reactions in more than five cycles under both degassed and nondegassed conditions. It should be mentioned that the ring-closing process of the cycle is monitored upon irradiation at the isosbestic wavelength until the photostationary state is reached, which demonstrates the excellent fatigue resistance of the compound.

In addition, a thin poly(methyl methacrylate) (PMMA) film of **BzThSiMe<sub>2</sub>-DTE** was spin-coated on a quartz plate to study the photochromic properties in rigid medium. The quartz plate was covered with a patterned mask and exposed to light; the uncovered area undergoes color change, as shown in Figure 4. Moreover, the emission intensity was shown to be quenched during the photoirradiation process (Figure 1), which is



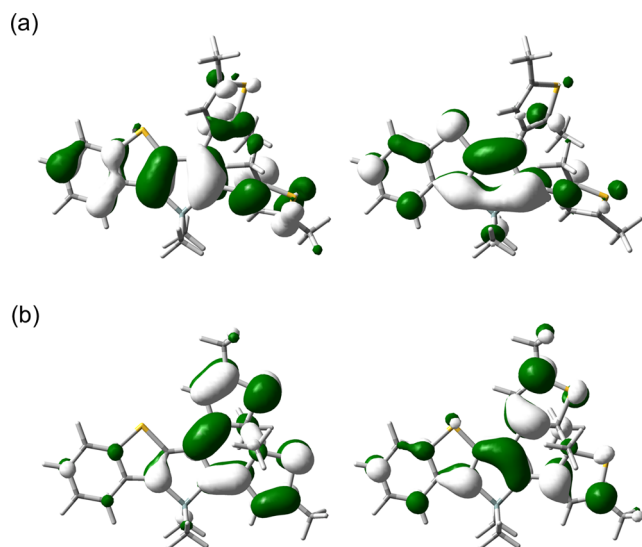
**Figure 4.** Color change of **BzThSiMe<sub>2</sub>-DTE** in benzene and in PMMA film upon photoirradiation at 298 K.

attributed to the generation of the non-emissive closed form and the depletion of the open form.<sup>7–9</sup> Apart from conversion to the non-emissive closed form, the absorption band of the closed form occurs at the same region as the emission band of the open form, which leads to possible reabsorption as well as energy transfer quenching.<sup>1,7–9</sup>

Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations were performed to gain further insight into the electronic structures and origins of the electronic transitions of the open and closed forms. The thermal stability of the closed form is governed by the ground-state energy difference between the two forms. The smaller the energy difference, the larger is the activation energy for cycloreversion. The energy difference between the open and closed form for **BzThSiMe<sub>2</sub>-DTE** is very small, in which the open form is more stable than the closed form by  $0.3 \text{ kcal mol}^{-1}$ . Such a small energy difference will result in **BzThSiMe<sub>2</sub>-DTE** having excellent thermal stability.

On the basis of the TDDFT calculation (Table S2), the low-energy absorption band for the open form is attributed to the HOMO  $\rightarrow$  LUMO excitation, which can be assigned as mainly  $\pi-\pi^*$  transition of the benzo[*b*]silole moiety mixed with the  $\pi-\pi^*$  transition of the peripheral dimethylthiophenes. It is noted that a contribution from the  $\sigma^*$  orbital of the exocyclic Si–C bonds to the LUMO is found (Figure 5). However, the lower energy absorption band for the closed form is attributed to the  $\pi-\pi^*$  transition predominantly localized on the condensed thiophene moiety.

In conclusion, a highly efficient photochromic silole-containing dithienylethene derivative was synthesized and characterized. The photophysical, photochromic, and electrochemical properties were studied and found to be strongly influenced by the silole backbone. Robust fatigue resistance was observed in the present system, which suggests that incorporation of silole moiety into the diarylethene backbone can effectively stabilize the closed form of the compounds to eliminate photochemical side reactions during the ring-opening and ring-closing processes. Most interestingly, the similar aromaticity and energy level of the open form and closed form of the photochromic siloles give rise to negligible thermal cycloreversion and high photocycloreversion observed in this novel compound. Together with these attractive features, it is believed that this silole-containing photochromic compound would act as excellent alternatives for dithienylperfluorocyclopentenes in optical memory storage and photoswitching material, and the present work would provide further insights into future design of new thermally stable and fatigue-resistant photochromic compounds.



**Figure 5.** Spatial plots (isovalue = 0.03) of HOMO (left) and LUMO (right) for the open form (a) and closed form (b) of BzThSiMe<sub>2</sub>-DTE.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Experimental section; crystal structure determination, characterization, and photophysical data; computational details; synthetic procedures; selected singlet–singlet transition and structural parameters; electronic absorption spectra; perspective view; and Cartesian coordinates of optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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