

## Fabrication and Photochromism of High-density Diarylethene Monolayer Immobilized on a Quartz-glass Substrate

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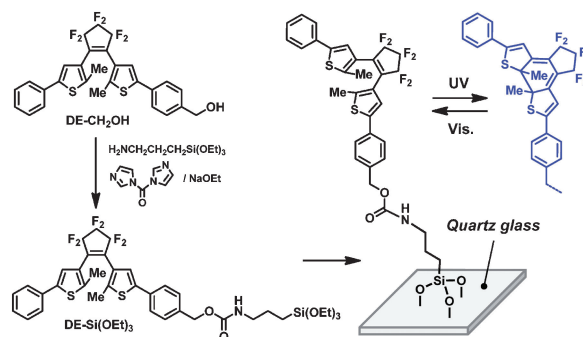
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Diarylethene monolayer was fabricated on a quartz-glass substrate using a silane coupling technique. The coupling agent was easily prepared from a diarylethene with a hydroxy group and 3-aminopropyltriethoxysilane. It was found that the chromophore was introduced in high density on the substrate and still exhibited reversible photochromism with relatively high conversion upon photoirradiation despite being constrained on the quartz-glass surface.

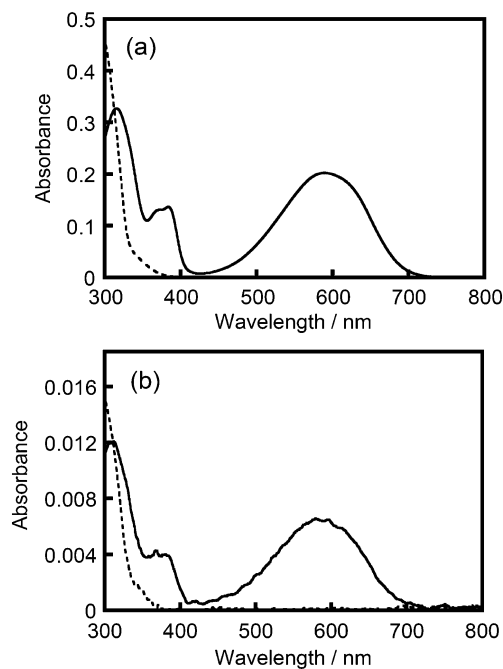
Photochromic compounds show reversible changes in physical and chemical properties such as their color, refractive indices, dielectric constants, and geometric structures along with their reversible isomerizations upon photoirradiation.<sup>1</sup> Diarylethene, one of the most attractive photochromic compounds, has been considered to be potentially useful for various optoelectronic and switching devices because of high thermal stability, fatigue resistance, high sensitivity, high response, and high reactivity not only in a solution but also even in the solid state such as polymer matrix, amorphous state, and crystalline phase.<sup>2–9</sup> Recently, various types of diarylethenes that show photochromism in the crystalline phase have been used to control surface properties, morphology, and shape.<sup>10–13</sup> However, there have been few studies on a photochromic diarylethene monolayer fixed on a glass or quartz substrate. Only azobenzene and spiropyran immobilized on a glass or silicon wafer have been reported.<sup>14,15</sup> A Langmuir–Blodgett film of diarylethene has already been reported.<sup>16</sup> In this case, the chromophore is not fixed by a covalent bond on a substrate. If diarylethene is immobilized on a glass surface as a monolayer, it can be useful as a photofunctional substrate to control physical properties of the surface with high thermal stability, fatigue resistance, and high sensitivity by photoirradiation, which leads to various types of applications relating to adsorption, adhesion, dewetting, lithography, and biomedical engineering. Here, we fabricated a simple diarylethene monolayer fixed on a quartz-glass surface in high density by a basic silane coupling (Scheme 1), and examined the photochromic reactivity as a light-controllable glass substrate.

The silane coupling agent with a diarylethene moiety (DE–Si(OEt)<sub>3</sub>) was prepared by formation of an urethane bond between a diarylethene with a hydroxy group (DE–CH<sub>2</sub>OH)<sup>20</sup> and 3-aminopropyltriethoxysilane in the presence of 1,1'-carbonyldiimidazole and sodium ethoxide.<sup>19</sup> A quartz-glass substrate was cleaned by treatment with a piranha solution (concentrated sulfuric acid (70%) and 30% aqueous hydrogen peroxide (30%)) at 100 °C for 1 h before use.<sup>21</sup> The cleaned and dried quartz-glass substrate was soaked in a glacial acetic acid solution of DE–Si(OEt)<sub>3</sub>. The treated substrate was washed with toluene and the unreacted coupling agent was removed by sonication in toluene several times, and then the substrate was dried under vacuum.<sup>22</sup>

Figure 1 shows absorption spectra of DE–Si(OEt)<sub>3</sub> in toluene and the diarylethene moiety immobilized on the quartz glass

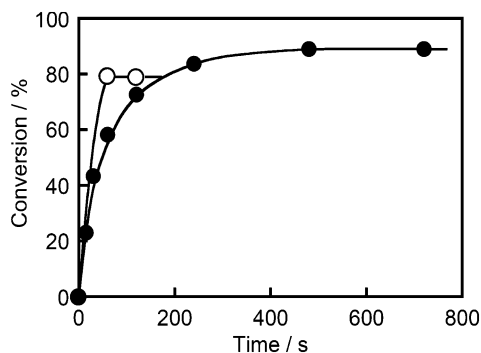


**Scheme 1.** Synthetic scheme of a diarylethene monolayer immobilized on a quartz glass surface. This figure shows that the diarylethene chromophore is immobilized by the formation of three Si–O bonds with the quartz-glass surface. Actually, the immobilization may include the connection with one or two Si–O bonds as shown in Refs. 17–19.



**Figure 1.** Absorption spectra of (a) DE–Si(OEt)<sub>3</sub> in toluene (1.3 × 10<sup>-5</sup> M) and (b) diarylethene monolayer fabricated on a quartz glass before photoirradiation (dotted line) and in the photostationary state upon irradiation at 313 nm (solid line).

before photoirradiation and in the photostationary state upon irradiation at 313 nm. A new absorption band appeared at 588 nm and the absorption band disappeared by irradiation with visible



**Figure 2.** Time-conversion curves of DE-Si(OEt)<sub>3</sub> in toluene (●) and diarylethene monolayer fabricated on a quartz glass (○) upon irradiation at 313 nm.

**Table 1.** Absorbance at the isosbestic point ( $A_{312}$ ) and the absorption maximum ( $A_{588}$ ), and cyclization conversion of DE-Si(OEt)<sub>3</sub> in toluene and the diarylethene monolayer in the photostationary state upon irradiation at 313 nm

Sample	$A_{312}$	$A_{588}$	$A_{588}/A_{312}$	Conversion / %
DE-Si(OEt) <sub>3</sub> in toluene	0.32	0.20	0.63	90
Diarylethene monolayer	0.012	0.0066	0.55	79

light both in the solution and on the quartz glass. The shape of the spectra in Figures 1a and 1b is very similar to each other. These results indicate that the chromophore in DE-Si(OEt)<sub>3</sub> was not decomposed during fabrication of the monolayer in glacial acetic acid, the agent was successfully fixed on the quartz glass, and the diarylethene chromophore exhibited reversible photochromism both in the solution and on the quartz glass upon alternating irradiation with UV and visible light.

The cyclization conversion of DE-Si(OEt)<sub>3</sub> in the photostationary state in toluene upon irradiation at 313 nm was estimated to be 90% from NMR and absorption spectroscopy as shown in Figure 2. Since the spectral shape of the diarylethene moiety immobilized on the quartz glass is almost the same as that in the solution, the diarylethene chromophore is randomly arranged even on the glass surface and the cyclization conversion of the diarylethene moiety fixed on the quartz glass can be estimated by a comparison of absorbance at the isosbestic point ( $A_{312}$ ) with that at the absorption maximum ( $A_{588}$ ) in the photostationary state upon irradiation at 313 nm. Table 1 shows  $A_{312}$ ,  $A_{588}$ , a ratio of  $A_{588}$  to  $A_{312}$ , and the cyclization conversion both in toluene and of the diarylethene monolayer in the photostationary state. The conversion in the photostationary state was determined to be 79% by the following calculation;  $90 \times 0.55/0.63$ . The time-conversion curve of the monolayer upon irradiation at 313 nm is also shown in Figure 2. It was found that the diarylethene monolayer immobilized on the quartz glass can undergo the cyclization reaction with relatively high cyclization conversion.

The coverage of the diarylethene-coupling agent on the quartz-glass surface can be estimated by comparing the absorption spectra. The molar absorption coefficient of the closed-ring form of DE-Si(OEt)<sub>3</sub> at 588 nm in toluene was determined to be  $17200 \text{ M}^{-1} \text{ cm}^{-1}$ . Assuming that the coefficient in the solution is the same as that fixed on the quartz glass, the number of molecules

per unit area in the diarylethene monolayer can be determined using Lambert-Beer's law. Absorbance of the monolayer on both sides of the quartz glass at 588 nm is 0.0066 as shown in Figure 1b and Table 1, which means that the absorption of one monolayer is 0.0033. The molecule per unit area can be readily calculated to be 1.5 molecules per square nanometer by dividing 0.0033 by the molar absorption coefficient.<sup>22</sup> This value corresponds to a quarter of the value derived from the theoretical close packing.<sup>23</sup> However, taking into account the size of the diarylethene moiety (ca. 1.5 nanometers in the long axis), it is considered that 1.5 molecules per square nanometer are a substantially high value and the chromophores are closely packed in the monolayer.

In conclusion, we succeeded fabrication of a diarylethene monolayer fixed on a quartz-glass surface by silane coupling. The resulting monolayer exhibited reversible photochromism upon alternating irradiation with UV and visible light. The cyclization conversion of the diarylethene moiety immobilized on the substrate was relatively high in spite of the close-packed structure as much as 1.5 molecules per square nanometer on the surface. The method to fabricate the photochromic monolayer can be useful for development of light-controllable thin film devices on the substrate.

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- Caution!** Piranha solution is potentially explosive and highly corrosive, and should be handled with extreme caution.
- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
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