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Reversible On/Off Conductance Switching of Single Diarylethene Immobilized on a Silicon Surface

Kazuki Uchida, Yoshinori Yamanoi, Tetsu Yonezawa, and Hiroshi Nishihara*

Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Supporting Information

ABSTRACT: The chemical functionalization of hydrogen-terminated silicon(111) surfaces with photochromic diarylethene using an ethylene anchoring group was achieved. Conductive atomic force microscopy measurements showed the current changes on modified silicon electrodes caused by light-induced isomerization of the diarylethene between an open form and a closed form.

Photochromism is the photochemical process by which a photoactive compound transitions between two isomers having different absorption spectra.[1] Among the various photochromic compounds, diarylethenes are promising photoswitchable molecules because both isomers are thermally stable and fatigue resistant, and the photoinduced transition is highly reversible, sensitive, and responsive.[2] The functionalization of surfaces using diarylethenes has been suggested as a method for information strorage,[3] optical switching,[4] and the design of optoelectronic devices.[5] Despite much progress, photochromic studies of diarylethenes with switching units linked to the electrode surface have posed several challenges, and few reports describe attempts to switch the conductance of electrode surface-bound molecules using light.[6] A major hurdle to such studies has been the difficulties associated with synthesizing surface modified organic molecules.

Modification of silicon surfaces with organic groups via hydrosilylation has attracted much attention.[7] The hydrosilylation reaction offers mild reaction conditions for producing high-quality monolayers that are more stable than those formed on other commonly used substrates. Recently, we reported the immobilization of gold nanoparticles on hydrogen-terminated silicon(111) surfaces using the thermal hydrosilylation reaction.[8] Although Uosaki described the diarylethene connected to a silicon surface via viologen derivatives linkers,[9] the direct attachment of diarylethene has not been reported. Here, we report the direct immobilization of diarylethene having an acetylene moiety onto a silicon surface via a π-conjugated system, and we describe electrical characterization studies using conductive AFM. The closed form of diarylethene on a silicon surface is expected to exhibit better electrical conductance than the open form. We refer to the two forms as the on (closed) and off (open) states of the switch.

Photochromic diarylethene molecule **1o** was prepared in three steps from 2,4-dibromo-3,5-dimethylthiophene.[10] This molecule bears an acetylene moiety at the terminus for bonding to the hydrogen-terminated silicon surface. The synthesis is outlined in Scheme 1. Treatment of 2,4-dibromo-3,5-dimethylthiophene with *n*-BuLi and subsequent reaction with tri*n*-butylborate provided a boronic ester intermediate, which was reacted with (4-iodophenylethynyl)trimethylsilane in the presence of a palladium catalyst to provide **2** in 91% yield. Introduction of **2** to 1-(2,4-dimethyl-5-phenyl-3-thienyl)heptafluorocyclopentene[11] gave compound **3** in 73% yield. Deprotection of the trimethylsilyl group proceeded using K_2CO_3 in an ether-ethanol mixture to afford the desired unsymmetrical diarylethene **1o** in 95%.[12]

Scheme 2 shows the photochromic reaction between the open-ring isomer **1o** and the closed-ring isomer **1c**. π-Conjugation extended over the entire molecule in the closed form, whereas it was restricted to each half of the molecule in the open form. The molecule photoisomerized from an open form **1o** (colorless) to a closed form **1c** (deep blue) in 78% yield upon exposure to UV light (313 nm). The reverse transition to the open form was driven by exposure to visible light (578 nm).

Next, we sought to determine the extent to which the transition between isomers occurred on the silicon surface and to measure the differences in the electrical conductance of the two forms (Figure 1a). The photochromic diarylethene **1o** was anchored onto a hydrogen-terminated silicon(111) surface via a thermal hydrosilylation reaction.[8] Anchoring of the molecule to the silicon surface was ensured by the ethylene anchoring group.[13] The resulting surface was characterized by measuring the water contact angle as well as by AFM, after sonicating the silicon wafers in a nonpolar solvent (toluene) and a polar solvent (ethanol) for 10 min.

Water contact angle measurements provide a simple and direct method for evaluating surface modifications. The water contact angle on the hydrogen-terminated silicon(111) surface was 89° in agreement with previously reported data.[14] The contact angle decreased to 66° upon SAM formation (Figure 1b), indicating that the surface was terminated with close-packed phenyl groups.[15] AFM images of the modified surface showed that the fully formed monolayer was continuous (see Supporting Information). Holes extending to the silicon substrate were not observed at this resolution. Accordingly, we concluded that a highly packed monolayer was prepared using this process.

The current−voltage ($I-V$) curves of the modified layer were evaluated by forming a junction with the metallic tip of a conductive AFM instrument. Typical $I-V$ curves are presented in Figure 1 for the **1o-Si** SAM and after irradiation at 313 nm (for 0.5 h), which switched the molecules to the ring-closed form, **1c-Si**. The closed form corresponded to the more conductive state and the

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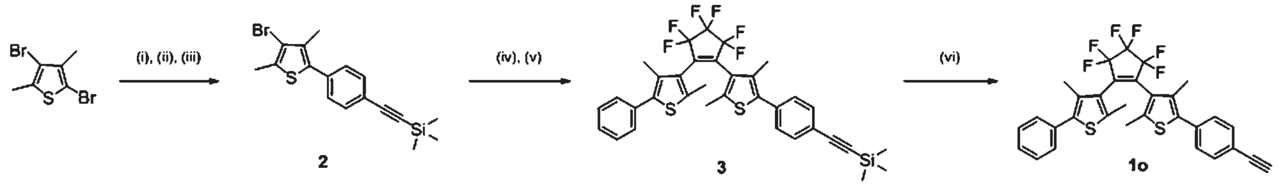
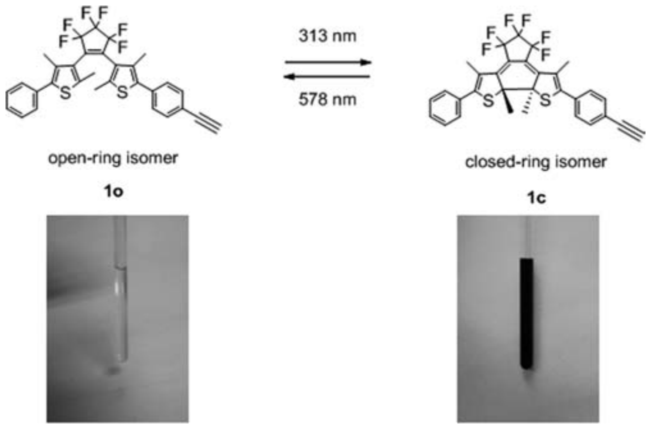
Scheme 1. Synthetic Route of Ethynyldiarylethene 1o[a]



[a] Reagents and conditions: (i) *n*-BuLi, THF, −78 °C; (ii) $B(O(n\text{-}Bu))_3$, −78 °C to rt; (iii) (4-iodophenylethynyl)trimethylsilane, $Pd(PPh_3)_4$, Na_2CO_3, THF-H_2O, reflux, 91% (in 3 steps); (iv) *n*-BuLi, THF, −78 °C; (v) 1-(2,4-dimethyl-5-phenyl-3-thienyl)heptafluorocyclopentene, −78 °C to rt, 73% (in 2 steps); (vi) K_2CO_3, ether-ethanol, rt, 95%.

Scheme 2. Photochromic Reaction between Open-Ring Isomer 1o and Closed-Ring Isomer 1c



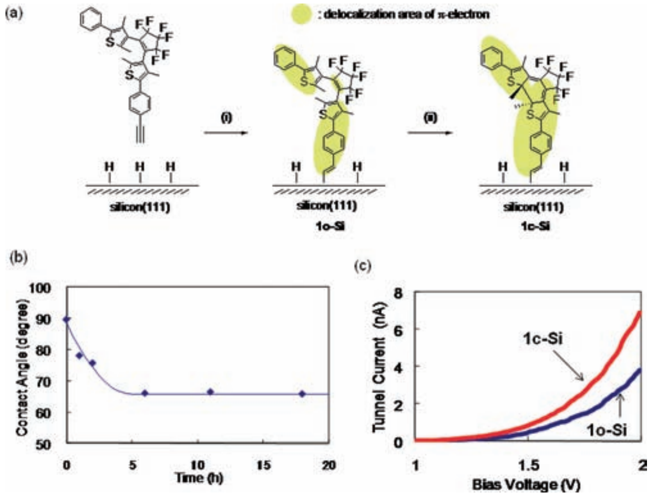


Figure 1. (a) Diarylethene switch bound through a C═C bond to Si(111). Reagents and conditions: (i) toluene, reflux, 18 h. (ii) 313 nm, 0.5 h. (b) Progress of the hydrosilylation reaction over time during the formation of the **1o-Si** SAM, measured by water contact angle. (c) Typical current−voltage (*I*−*V*) curves measured by conductive AFM on the **1o-Si** SAM immediately after its formation and following irradiation at 313 nm for 0.5 h (**1c-Si** SAM).

open form corresponds to the less conductive state (Figure 1c). These measurements allowed us to associate the ring open form with the off state and the ring closed form with the on state.

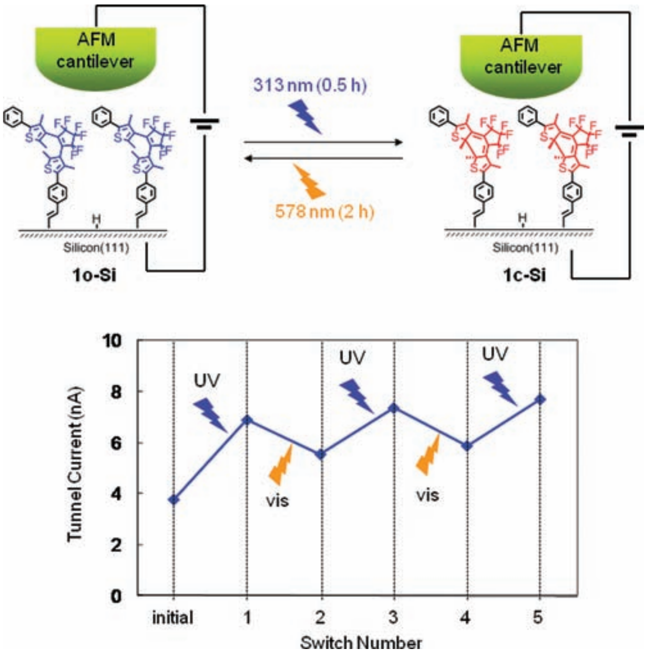


Figure 2. Current changes of the **1o-Si** and **1c-Si** surfaces due to photoisomerization by alternate photoillumination with UV and visible light. Tunnel current on a silicon(111) surface modified with ethynyldiarylethene after 313 and 578 nm photoillumination, which was measured by conductive AFM at a voltage of 2 V.

We investigated the influence of alternating photoillumination on the current changes of **1-Si** under a fixed tip bias of 2 V (Figure 2). During UV (313 nm) illumination, the initial current of the silicon surface increased. Irradiation of the **1c-Si** SAM with visible light (578 nm) for 2 h restored the **1o-Si** surface, and the current decreased near the value for the initial state. After this process, the UV light-induced increase and the visible light-induced decrease in current were repeated without attenuation. The stability of the response over time was attributed to the high stability of the covalent attachment to the silicon surface through the anchoring π-conjugated group. This experiment showed that the structure−property relationships were preserved upon self-assembly of the switch on Si(111).

In conclusion, we designed and synthesized a new diarylethene bearing an acetylene moiety at the terminus, and we demonstrated light-controlled reversible conductance switching of the monolayers prepared on silicon surfaces. This system underwent photochemically reversible current changes upon alternate irradiation with UV and visible light, which drove a reversible photocyclization reaction. Understanding the interplay between the molecular structures and the switching properties can provide firm design principles for the creation of optoelectronics devices. The reversibility of switching was directly related to π-conjugation between the switching unit and the substrate.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{1}H and ^{13}C NMR spectra of **1o**, UV−vis spectra of **1o** and **1c**, and AFM images of **1o-Si** and **1c-Si** surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

nisihara@chem.s.u-tokyo.ac.jp

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