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Author(s)	Masuda, Takuya; Irie, Masahiro; Uosaki, Kohei
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Photoswitching of Electron Transfer Property of Diarylethene-Viologen Linked Molecular Layer Constructed on a Hydrogen-Terminated Si(111) Surface

Takuya Masuda,[a,b] Masahiro Irie,[c] and Kohei Uosaki [a,b,d*]

[a] Physical Chemistry Laboratory, Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810 (Japan)

[b] Network Center for Molecular and System Life Sciences, Graduate School of Science, Hokkaido University, Sapporo 060-0810 (Japan)

[c] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581 (Japan)
Present address: Department of Chemistry, Rikkyo University, Toshima-Ku, 3-34-1 Nishi Ikebukuro, Tokyo 171-8501 (Japan)

[d]International Center for Materials Nanoarchitectonics Satellite (MANA), National Institute of Material Science (NIMS), Sapporo 060-0810 (Japan)

* corresponding author

Kohei Uosaki

Phone: +81-11-706-3812

Fax: +81-11-706-3440

E-mail: uosaki@pcl.sci.hokudai.ac.jp

Abstract

An organic monolayer with diarylethene and viologen moieties as a photochromic and an electroactive group, respectively, was constructed on a hydrogen-terminated Si(111) surface by sequential surface reactions. Photoswitching behaviour of electron transfer from the Si electrode to viologen moiety, larger and smaller current after UV and visible irradiation, respectively, was observed. This photoswitching behaviour can be explained by change in molecular conductivity of diarylethene moiety, which separates Si surface and viologen moiety, induced by ring closing and opening UV and visible irradiation, respectively.

Introduction

Controlling optical and electrical properties has attracted much attention because of its potential applications for molecular electronic devices such as memories and switches. One possible way to construct such devices is incorporation of molecular layers with a photochromic unit on solid surfaces.

Diarylethene is considered to be one of the most promising photochromic units because of its thermally irreversibility and extremely high fatigue durability.[1] Diarylethene has two isomers as shown in Scheme 1. One is an open-ring isomer (**1a**) formed by visible

irradiation and the other is a closed-ring isomer (**1b**) formed by UV irradiation. Photoswitching of optical, electrical and electrochemical properties of the diarylethenes has been demonstrated in single crystalline phase,[2,3] polymer,[4] solution[5] and molecular thin films.[6, 7] Recently, molecular conductivities of diarylethenes were measured in single molecular level using break junctions and huge difference in conductivities between the two isomers was reported.[8-10]

Although surface immobilization of diarylethene moiety is essential for useful application, only few groups have reported the introduction of diarylethene derivatives into surface molecular layers via covalent bond because of difficulty in synthesis of molecule with surface attachment, linker and diarylethene moieties.[11-21]

Recently, we reported a construction of mono- and multi-viologen layers on Si(111) surface, by sequential surface reactions, i.e., layer-by-layer growth, without loosing their electron mediation capability. [22, 23] This method can be utilized for constructing other tailor-made organic molecular layers with multiple functional components by building up various molecules as building blocks. Moreover, as far as the practical applications are concerned, functional molecular layers constructed on a Si surface via Si-C covalent bond have a distinct advantage over those formed on other solid surfaces because of their extremely high stability and potential hybridization with the advanced

silicon technology.

Here, we constructed an organic molecular layer with viologen and diarylethene moieties as an electron acceptor and a photochromic unit, respectively, on a H-Si(111) electrode by sequential chemical reactions and demonstrated photoswitching of electron transfer from the Si electrode to viologen moiety by utilizing photoinduced ring opening/closing of diarylethene moiety, which is present between the Si electrode and viologen moiety.

Experimental Details

Ultrapure nitrogen (99.9995 %) and argon (99.999 %) were purchased from Air-Water. Ultrapure-grade sulfuric acid and potassium chloride and reagent-grade sodium sulfate, hydrochloric acid, hydrofluoric acid, hydrogen peroxide, benzene, ethanol, potassium tetrachloroplatinate (II), 1-bromobutane, 1, 4-dibromobutane, 4-vinylbenzylchloride (4VBC), 4-methylstyrene (4MS) and 4, 4'-bipyridine from Aldrich, ultrapure-grade methylene chloride (dichloromethane) and DMF from Dojin Laboratory and special grade (for semiconductor industries) ammonium fluoride from Morita Chemical were used as received except for 4VBC and 4MS, which were purified by vacuum distillation before use. Water was purified using a Milli-Q system (Yamato, WQ-500). The Ag and

Pt wires used as the reference electrodes and counter electrodes were purchased from Nilaco.

Si(111) substrate (n-type; P-doped, 1-10 Ω cm), which was obtained from Shin-Etsu Semiconductor, was treated by sequential immersion of the sample in freshly prepared sulfuric acid and hydrogen peroxide (2: 1 by volume) at 60 °C for 20 min, in aqueous solution of 0.5 % hydrofluoric acid at room temperature (RT) for 5 min and in freshly prepared RCA solution (water/hydrogen peroxide/hydrochloric acid, 4: 1: 1 by volume) at 80 °C for 20 min. After these treatments, the sample was immersed in deaerated aqueous solution of 40 % ammonium fluoride for 5 min to obtain a monohydride-terminated surface, that is, H-Si(111).[24, 25]

X-ray photoelectron spectra (XP spectra) were obtained using a Rigakudenki model XPS-7000 X-ray photoelectron spectrometer with monochromic Mg-Kα radiation at 25–300 W.[26] Photoelectron were collected at 0° from the surface normal, i. e., take-off angle of 90°.

Electrochemical measurements were performed in a three electrode electrochemical cell equipped with a quartz window in front of the working electrode.[22, 23, 27] A Ag/AgCl electrode, a Pt wire, and the Si(111) substrates were used as a reference, a counter, and a working electrode, respectively. A potentiostat (Hokuto Denko, HA-501G) was used to

control the potential of working electrode and a function generator (Hokuto Denko, HB-111) was used to provide an external potential. Cyclic voltammograms (CVs) were recorded on an X-Y recorder (Graphtec, WX-1200). 0.1 M Na_2SO_4 aqueous solution prepared by Milli-Q water and sodium sulfate was used as an electrolyte solution was. UV and visible light were provided by a Hg lamp (Ushio, USH-250D) through a band path filter (Melles Griot, Center Wavelength: 340.3 nm, Bandwidth: 8.7 nm) and a 500 W Xenon lamp (Ushio, UXL-500-D) through an IR cut filter (Toshiba, IRA-20) and a UV cut filter (Sigma Koki), respectively. Intensities of UV and visible light measured by an optical power meter (Melles Griot) were 150 μW cm^{-2} and 50 mW cm^{-2}, respectively.

Results and Discussion

Constriction and characterization of molecular layers: Freshly prepared H-Si(111) surfaces were sequentially reacted with various molecules as shown in Scheme 2. After each modification step, the surface composition was characterized by XPS. The H-Si(111) surface was illuminated with 254 nm light (≈3.2 mW cm^{-2}) for 8 h in deaerated solution containing 4VBC and 4MS (mole fraction of 1: 20) (Step (i) in Scheme 2) to form a mixed monolayer of 4-ethylbenzylchloride (EBC) and

1-ethyl-4-methyl-benzene (EMB). We denote the monolayer terminated Si as EBC-Si, although majority of the monolayer is of EMB group. Figure 1 (a) shows XP spectrum of the EBC-Si(111)surface. In wide scan spectrum (Fig. 1 A (a)), peaks corresponding to Si 2p, Si 2s, C 1s, and O 1s peaks were observed around 100 eV, 150 eV, 285 eV, and 530 eV, respectively.[26] A narrow scan spectrum in the Si 2p region (Fig. 1 B (a)) showed only a peak of Si(0) at 99.4 eV and no peak due to oxidized Si around 103 eV,[26] confirming the formation of a densely-packed mixed molecular layer of 4VBC and 4MS on the Si(111) surface via Si-C covalent bonds without formation of silicon oxide. No peak was observed in N 1s and F 1s regions (Fig. 1 C and D (a)).

The EBC-Si(111) surface was reacted with diarylethene (**1a**) in an acetonitrile solution containing 10 mM diarylethene under Ar atmosphere at reflux temperature for 12 h (step (ii) in Scheme 2) and then reacted with either 1, 4-dibromobutane or 1-bromobutane in neat liquid at 80 °C for 12 h (step (iii) in Scheme 2) to yield Br-DAE- or H-DAE-Si(111) surface, respectively. At the H-DAE-Si(111) surface (Fig. 1 A, C and D (b)), N 1s and F 1s peaks appeared around 400 eV and 688 eV corresponding to quaternary nitrogen and fluorine species of diarylethene, respectively,[26] showing attachment of the DAE moieties. The absence of a peak due to Si(IV) around 103 eV shows that oxide formation was inhibited by the organic monolayer (Fig. 1 B (b)).

The Br-DAE-Si(111) surface was further reacted with 4, 4'-bipyridine (BPY) in a BPY saturated benzene solution at 80 °C for 12 h (Step (iv) in Scheme 2). Finally, the substrate was reacted with 1-bromobutane in a neat liquid at 80 °C for 12 h (Step (v) in Scheme 2) to yield a V^{++}-DAE- Si(111) surface, which has viologen and diarylethene moieties. N 1s increased by attachment of the viologen moiety, whereas F 1s decreased due to attenuation of emitted photoelectron, by formation of upper layer (Fig. 1 C and D (c)). Appearance of a small peak due to Si(IV) around 103 eV and growth of O 1s peak at 532 eV implies that the Si surface is slightly oxidized during this step (Fig. 1 A and B (c)). Thus, a viologen-diarylethene linked molecule was synthesized at a H-Si(111) surface.

Electrochemical characteristics of V^{++}-DAE- Si(111) surface: Figure 2 (a) shows CVs of the n-type V^{++}-DAE-Si(111) surfaces in a 0.1 M Na_2SO_4 aqueous solution at a scan rate of 50 mV s^{-1} after UV (blue line) and visible (red line) irradiations. A cathodic peak corresponding to the reduction of viologen moieties to viologen radical cation ($V^{++}/V^{+\bullet}$) was observed around -0.55 V. The peak potential is in good agreement with that reported previously at viologen-modified n-type Si(111) electrode.[23] A second cathodic peak corresponding to the reduction of viologen radical cation to di-radical ($V^{+\bullet}/V^{\bullet\bullet}$) was also observed around -0.9 to -1.0 V when scan limit was extended to more negative

potential. In the present experiment, however, potential scan was reversed at -0.8 V because di-radical formation may result in decomposition of the viologen moiety.[28] Background current around -0.8 V should include the second reduction wave of viologen and hydrogen evolution reaction. It is clear that the current at the cathodic peak around -0.55 V is higher after UV irradiation than after visible irradiation, suggesting the closed-ring isomer generated by UV irradiation and the open-ring isomer generated by visible irradiation acted as a mediator and a barrier for electron transfer from the Si electrode to viologen moiety. The former and latter are considered to be "on" and "off" states, respectively. This result is consistent with previous result obtained by break junction measurements using similar molecule that the open-ring isomer has higher resistance than that of the closed-ring isomer.[8, 9] Since n-Si(111), in which majority carrier is electron, is used as an electrode substrate and cathodic processes are under investigation, photo-excitation of Si substrate generating electron-hole pairs does not affect the electrochemical response.

Figure 2 (b) shows the baseline-corrected peak current around -0.55 V after UV (blue circles) and visible light irradiation (red circles), indicating that the two states were repeatedly inter-converted with an average of observed on/off ratio of ca. 3.2.

There is a possibility that cathodic current can be observed only in the closed-ring state,

in which two pyridinium groups behave as one viologen moiety acting as electron acceptor, not in the open-ring state, in which two pyridinium groups are isolated.[5] If this model is valid, cathodic peak should be observed even at a viologen-free DAE-modified, i.e., H-DAE-, Si(111) electrode after UV irradiation. Figure 3 shows CVs of the H-DAE-Si(111) electrode in a 0.1 M Na_2SO_4 aqueous solution in relatively wide potential range at a scan rate of 50 mV s^{-1} after (blue) UV and (red) visible irradiation. Although background current slightly changed, no cathodic peak was observed after UV irradiation, indicating that the photoswitching of the electron transfer is not caused by change in redox property of the diarylethene molecule itself but modulation of electron transport property of diarylethene. The redox peak of the diarylethene moiety was not observed may be because the redox takes place at more negative potential than -0.8 V and the redox peak overlaps with current due to hydrogen evolution.

Most of the previous studies on photoswitching of conductance of diarylethene moiety were performed on a gold electrode and the reversibility of switching was rather low due to the quenching of the excited state of the open-ring isomer at by plasmon band of gold.[8, 9] Nuckolls and his colleagues reported that while the conductance can be photoswitched reversibly in the case of pyrrole-based diarylethene placed in a nano gap

of carbon nanotubes, thiophen-based diarylethene in the same arrangement resulted in "non-reversible" switching because the use of long π-conjugating material, such as carbon nanotube, as a terminal electrode often decreases the quantum yield for opening reaction.[1, 10] Reversible photoswitching of thiophene-based diarylethene was achieved in the present system because neither quenching the open-ring isomer at excited state by plasmon band of gold nor lowering of quantum yield for opening reaction took place because Si was used as an electrode.

Figure 4 shows the schematic energy diagram of the present system. HOMO and LUMO levels of diarylethene at the closed- and open-ring states were obtained from theoretical calculation for similar molecule by Huang et al.[29] HOMO and LUMO levels were located around 5.9 and 4.6 eV at closed-ring state and 6.6 and 3.4 eV at open-ring state, respectively. Conduction band edge of the Si(111) electrode was determined by electrochemical impedance measurement of H-Si(111) electrode, assuming that the flat band potential is equal to the conduction band edge. The value obtained electrochemically was then converted to vacuum scale using the absolute potential of standard hydrogen electrode of 4.44 eV.[30] Peak potential of the reduction of viologen moieties to viologen radical cation ($V^{++}/V^{+\bullet}$) converted to vacuum scale, 4.09 eV, was used as an energy level of viologen moiety. Alignment of Fermi level of Si

electrode with respect to HOMO and LUMO is a predominant factor for molecular conductance[31, 32] Theoretical study for the similar molecule system showed that the closed-ring isomer has two significant transmission pathways contributed by HOMO and LUMO on both sides of Fermi level of Si electrode (Fig. 4 (a)), while the open-ring isomer lacks any significant transmission pathway within a wide energy window (Fig. 4 (b)).[29] The higher peak current at the closed-ring isomer should be attributed to the existence of LUMO located relatively close to the Fermi level in the present system. The open-ring isomer serves as a barrier for electron transfer reaction.[33]

Conclusion

We have constructed an organic molecular layer with diarylethene and viologen moieties as a photochromic and an electroactive group, respectively, on a hydrogen-terminated Si(111) surface and demonstrated its reversible photoswitching function of electron transfer from the Si electrode to viologen moiety.

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Figure captions

Scheme 1. Schematic illustration of photochromic reaction of the diarylethene.

Scheme 2. Schematic illustration of sequential surface modification steps. Step (i): Irradiation of UV (254 nm, 3.2 mW cm^{-2}) in a mixed solution of 4VBC and 4MS (1:10, 1:20 and 1:50 by mole fraction) under Ar atmosphere at room temperature for 6 h. Step (ii): Refluxing in an acetonitrile solution of 10 mM diarylethene (1a) for 12 h, and then immersion into neat 1, 4-dibromobutane at 80 °C for 12 h. Step (iii): Refluxing in a benzene solution saturated with 4, 4'-bipyridine for 12 h, and then immersion into neat 1-bromobutane at 80 °C for 12 h.

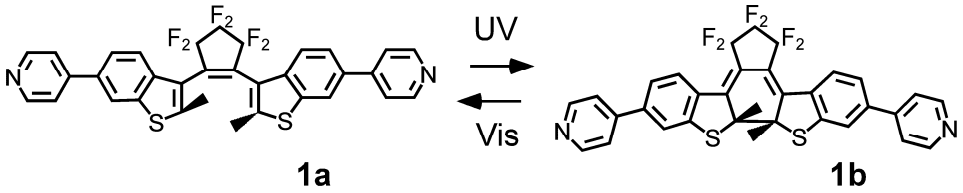
Figure 1. Wide scan (A) and narrow scan XP spectra in the region of the (B) Si 2p, (C) N 1s and (D) F 1s for (a) EBC-Si(111), (b) H-DAE-Si(111) and (c) V^{++}-DAE-Si(111) surfaces.

Figure 2. (a) CVs and (b) current densities at cathodic peak of the V^{++}-DAE-Si(111) electrode in an aqueous solution of 0.1 M Na_2SO_4 after UV (blue) and visible (red)

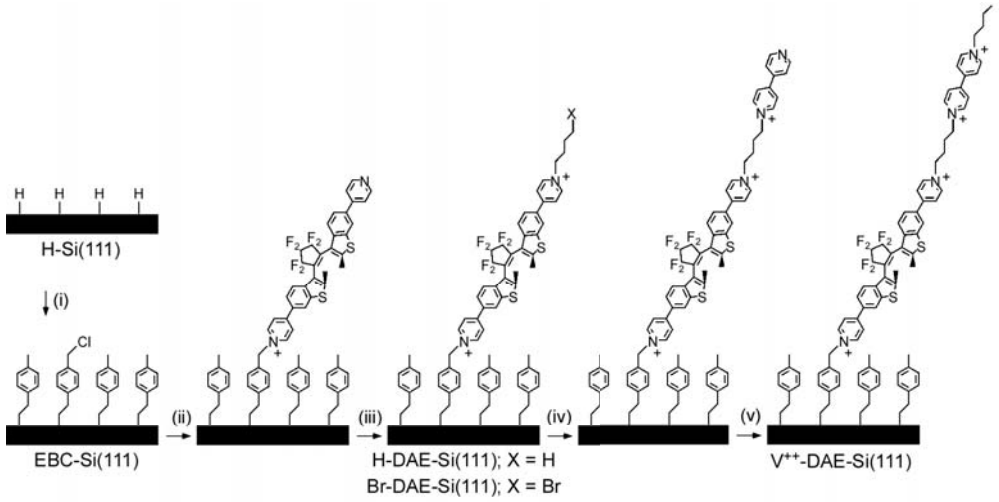
irradiation. Scan rate: 50 mV s^{-1}.

Figure 3. CVs of the H-DAE-Si(111) electrode in a 0.1 M Na_2SO_4 aqueous solution after UV(blue) and visible (red) irradiation. Scan rate: 50 mV s^{-1}.

Figure 4. Schematic energy diagram of the present system in "on" (a) and "off" (b) states.



Scheme 1



Scheme 2

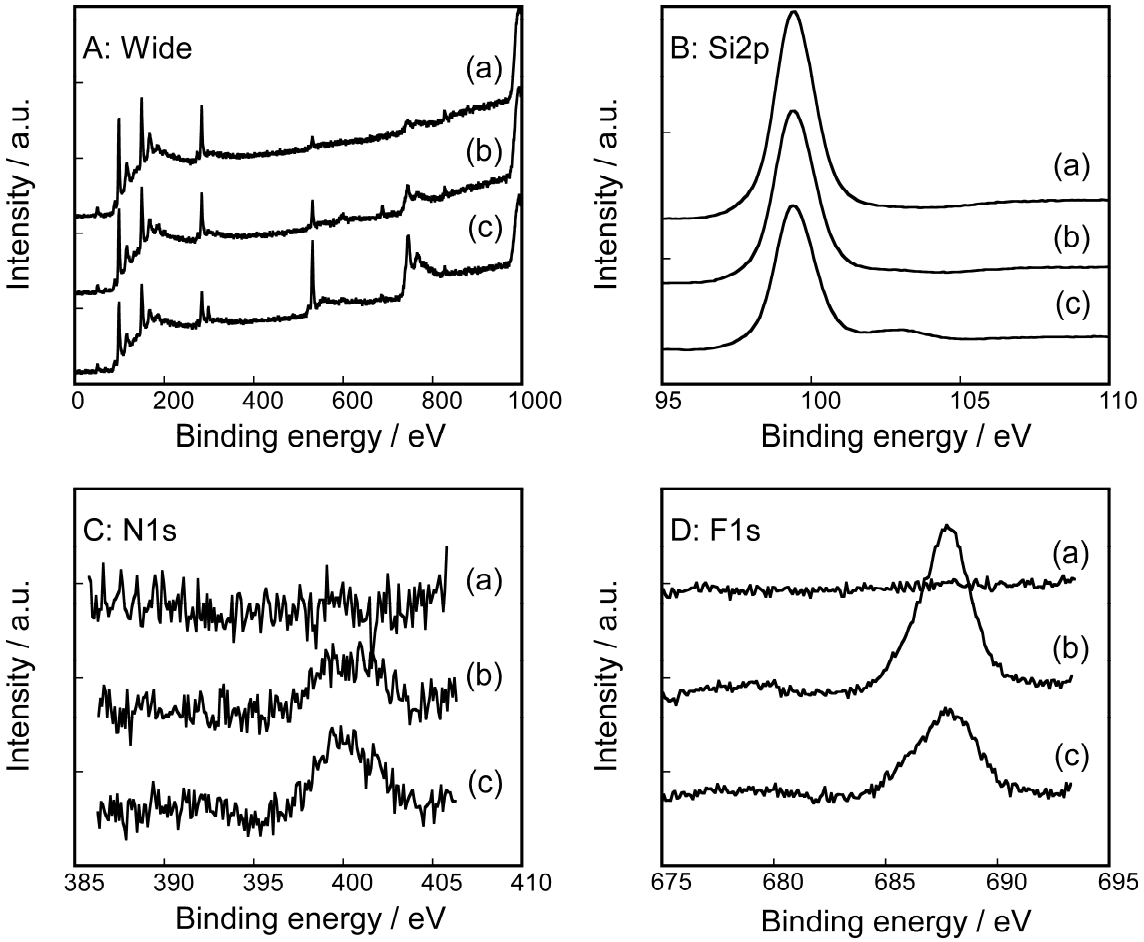


Figure 1

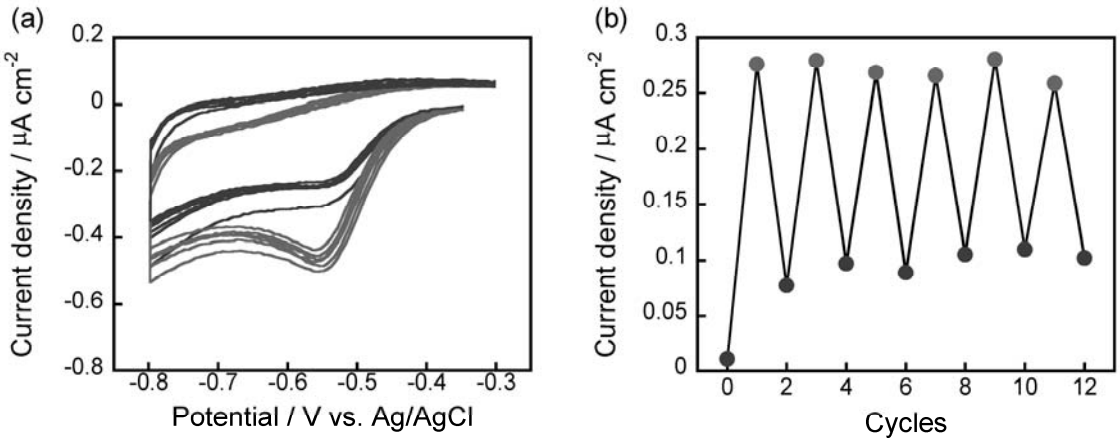


Figure 2

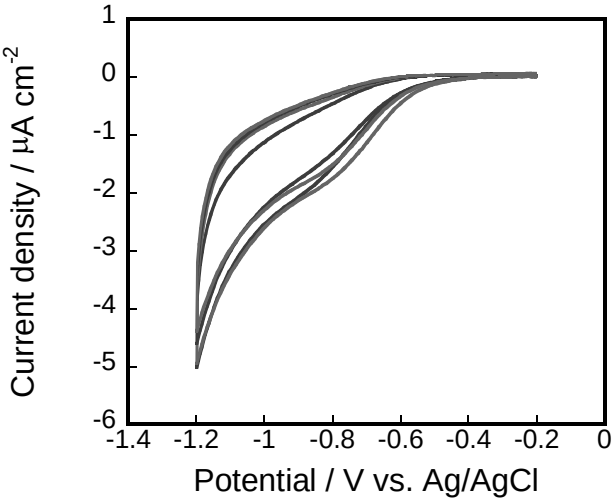


Figure 3

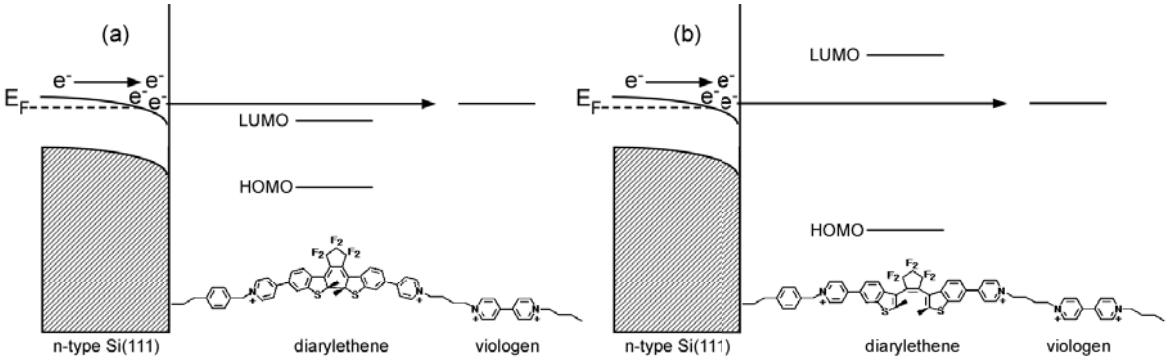


Figure 4