

Percolation-type Photoswitching Behavior in Conductance of Diarylethene–Silver Nanoparticle Networks

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A silver nanoparticle network interlinked by photochromic diarylethene dithiophenols was fabricated and its photoreactive and conductive properties were investigated. The network showed reversible changes in absorption spectra and conductance by photoirradiation. The results indicate the percolation-type behavior.

Research on “molecular electronics” is dramatically being advanced using traditional and new methods such as STM¹ and nanogapped electrodes.² Network structures composed of stimuli-responsive molecules and metal nanoparticles attract increasing attention.³ Diarylethene derivatives can be regarded as a single molecular photoswitch because π -conjugation length of both isomers is interconverted by UV and visible light.⁴ Feringa et al. reported the three orders of magnitude conductance change of single diarylethene molecule.⁵ We have reported the conductance photoswitching of a network composed of diarylethene dithiophenols and gold nanoparticles.⁶ Among many metal nanoparticles, silver nanoparticles have unique optical properties such as enhancement of local electromagnetic field, resulting in enhanced Raman scattering⁷ and photoemission.⁸

Herein, we report on the reversible conductance photoswitching of a diarylethene–silver nanoparticle network induced by photochromism of diarylethenes. The percolation-type behavior will be discussed.

As photochromic linkers, benzothiophene diarylethene thiophenols **1** and **2** were synthesized (Figure 1).⁹ This type of

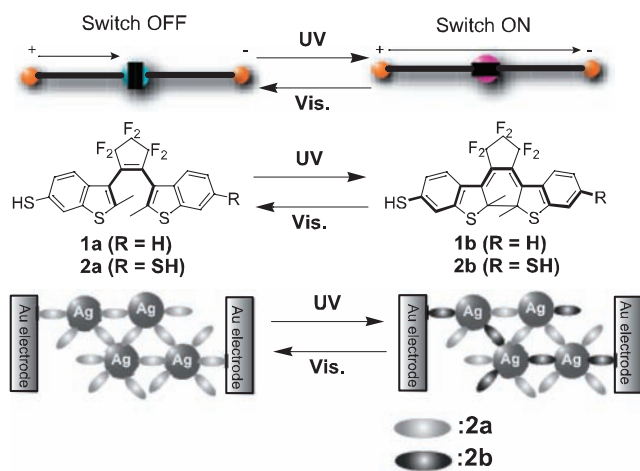


Figure 1. Molecular structure of compounds **1** and **2**. Schematic illustration of silver nanoparticle network **Ag-2**.

diarylethene has high cycloreversion quantum yield ($\Phi_{CO} = 0.35$).¹⁰

Photochromic absorption spectral changes were observed for ligands **1a** and **2a** in toluene solution (Figure S1).¹¹ The colorless solution turned red under irradiation with 313-nm light, indicating the formation of the closed-ring isomers **1b** and **2b**. The absorption maxima of the closed-ring isomers are located at 532 and 541 nm for **1b** and **2b**, respectively. These colored solutions went back to colorless under irradiation with 578-nm light.

Ag nanoparticles capped with monothiol **1a** (**Ag-1a**) were prepared according to the procedure of Kim which is a modification of Brust's method.¹² The silver nanoparticles were soluble in organic solvents. The prepared **Ag-1a** was observed by a transmission electron microscope (TEM), and the average diameter was determined to be 9.1 ± 3.4 nm (Figure S2).¹¹ IR spectroscopy also supported that **1a** is attached to Ag nanoparticles because the spectrum of **Ag-1a** is similar to that of **1a** (Figure S3).¹¹ In order to study the photochromic properties of **Ag-1a**, absorption spectra were measured in toluene solution. As shown in Figure S4,¹¹ surface plasmon band appeared around 480 nm. When this solution was irradiated with 313-nm light, a new band originating from the closed-ring isomer appeared. When this solution was irradiated with 578-nm light, the new band disappeared. Absorption maximum of the closed-ring isomer is located at 582 nm, which is shifted to longer wavelength by 50 nm in comparison with the maximum of **1b**.

Preparation of the interlinked **Ag-2a** network was performed according to a previously reported method.⁶ The Ag nanoparticles protected by tetraoctylammonium bromide (TOAB) were firstly prepared, and then the dithiol was mixed to make the network. From the TEM images, the diameter of TOAB-protected silver nanoparticles was determined to be 8.5 ± 2.0 nm (Figure S5).¹¹ The absorption spectra of **Ag-2a** were measured in KBr matrix (Figure 2). The network has broadened absorption from the visible to near-infrared region instead of the clear plasmon absorption at 480 nm that is observed for **Ag-1a**.

When the network is irradiated with 313-nm light, not only an absorption band originating from the closed-ring isomer (absorption maximum: 590 nm) but also a broad band spread in the near-infrared region (>650 nm) were observed. Changes of both bands were confirmed to be reversible by irradiation with UV and following with visible light. This reversible absorption change in the near-infrared region may suggest that the intensity of plasmon coupling is switched by photochromic reaction of interlinked diarylethenes.¹³ This phenomenon was not discerned in the case of Au nanoparticle networks.

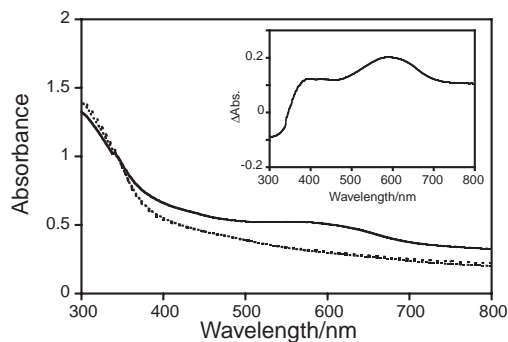


Figure 2. a) Absorption spectra of **Ag-2**: dashed line, before irradiation; solid line, after UV irradiation; dotted line, after visible light irradiation. Inset: difference absorption spectra between those measured before and after UV irradiation.

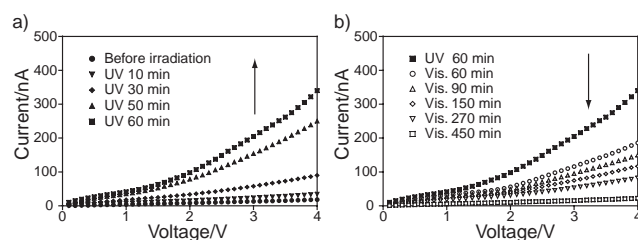


Figure 3. Conductance photoswitching behavior of **Ag-2a** network on the interdigitated electrode: a) upon irradiation with UV light; b) upon irradiation with visible light.

Ag-2a was prepared on an interdigitated gold electrode (NTT-AT, 5 μm gap) in order to investigate the conductance change by photoirradiation. The fabricated network was stable against applied voltage from 0 to 4 V. Upon irradiation with UV light, an increase of conductance was observed. After UV irradiation for 60 min, the conductance became around 18 times larger than the initial value as shown in Figure 3. The increased conductance returned to the initial value after irradiation with visible ($\lambda > 560$ nm) light for 450 min. This switching behavior can be explained by the photochromic reaction between “OFF-state” (open-ring isomer) and “ON-state” (closed-ring isomer).

In order to investigate the mechanism of conductance photoswitching, the time profiles of the conductance and the absorbance were measured at different stages of the photochromic reaction. Figure 4a shows the time profile of the increase of the absorbance at 590 nm of **Ag-2** network. The absorbance at 590 nm has a linear relationship with the population of the closed-ring isomer. The plot shows that the reaction rate is larger at the beginning and gets smaller as the reaction proceeds. This is a normal photochemical reaction. On the other hand, the time profile of the conductance showed a different behavior (Figure 4b). The reaction rate is smaller at the beginning and gets larger as the reaction proceeds. The difference of the two time profiles suggests that the increase of the conductance does not directly reflect the content of the closed-ring isomer but can be explained by the percolation model.¹⁴ The network is not completely connected by the closed-ring isomer at the initial stage of the photochromic reaction, but as the

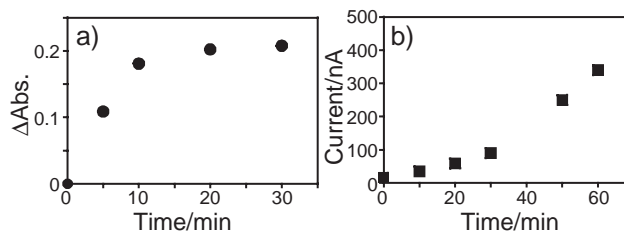


Figure 4. Time profiles of the photoinduced change of **Ag-2** network. a) Plot of difference absorbance at 590 nm. b) Plot of current value measured at applied voltage of 4 V.

reaction proceeds the closed-ring isomers make the conducting path between the interdigitated electrodes.

In conclusion, we have demonstrated 18-fold reversible change in conductance of a diarylethene–Ag nanoparticle network by photoirradiation. The time profiles of absorbance and conductance indicate the percolation-type behavior.

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- 9 The synthesis of **1** and **2** will be published elsewhere. **1a**: ¹H NMR (400 MHz, TMS) δ 2.17 (s, 1.9H), 2.20 (s, 1.9H), 2.46 (s, 1.1H), 2.47 (s, 1.1H), 3.46 (s, 0.4H), 3.55 (s, 0.6H), 7.15–7.71 (m, 7H); HRMS (m/z) [M]⁺ Calcd for C₂₃H₁₄F₆S₃: 500.0162, found: 500.0156. **2a**: ¹H NMR (400 MHz, TMS) δ 2.16 (s, 3.8H), 2.44 (s, 2.2H), 3.49 (s, 0.8H), 3.56 (s, 1.2H), 7.08–7.50 (m, 6H); HRMS (m/z) [M]⁺ Calcd for C₂₃H₁₄F₆S₄: 531.9882, found: 531.9872.
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