Photochromism of Diarylethenes on Gold and Silver Nanoparticles

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Gold and silver nanoparticles capped with photochromic diarylethene ligands were prepared and their photochromic performance was investigated. Although the quenching of cyclization reactions by the metal particles took place to some extent, the diarylethene on the nanoparticles underwent reversible photochromic reactions by irradiation with UV and visible light.

Photochromic compounds, which undergo reversible photoisomerizations, inherently have bistability such that the compounds can be utilized as switching units in molecular-scale optoelectronic devices.[1] Diarylethenes have been extensively studied because this series of compounds have highly sensitive, thermally stable, and fatigue resistant photochromic characteristics.[2] In order to fabricate practical devices, molecule–electrode contacts are indispensable, and several methods have been designed to attach organic molecules to metal surfaces. Among them, self-assembled monolayers (SAM) on metal surfaces have advantages in terms of facile preparation and stability of the junctions.[3] However, metals are known to quench readily the electronic excited states of the molecule placed on their surfaces.[4] This problem must be solved in order to perform photochemical reactions on metal surfaces.

Metal nanoparticles are of interest in multidisciplinary fields because the physical properties of the nanoparticles are different from those of the bulk state.[5] The introduction of facile preparation methods by Brust et al.[6] accelerated the study on the nanoparticles of noble metals. Photophysical properties of the metal nanoparticles are also different from the bulk state. For example, plasmon absorption is clearly observed depending on the size of the particles. Gold nanoparticles have a surface plasmon resonance absorption band at around 520 nm,[7] while silver nanoparticles have a surface plasmon resonance absorption at around 420 nm, which is shorter than that of gold nanoparticles.[8] Some of the gold and silver nanoparticles are reported to exhibit fluorescence.[9] The interplay between the plasmon absorption and the photochemical property of ligand is an attractive subject, and chromophore-functionalized metal nanoparticles have been extensively studied.[10]

Photochemical properties of photochromic dyes on the surface of metal nanoparticles should also be affected by the metal. Gold nanoparticles capped with azobenzene[11] and spiropyran[12] have been prepared and their photochromic reactivity was examined. In this paper, in order to investigate the photochromic reactivity on metal nanoparticles in detail, diarylethene-capped gold and silver nanoparticles were prepared, and the effect of the plasmon absorption on the photochromic reactivity was studied.[13]

Results and Discussion

Design and Synthesis of Ligand 1a. In order to investigate the photochromic reaction of diarylethenes on the gold and silver nanoparticles, there are two points to consider for the molecular design: 1) distance between the chromophore and the metal nanoparticle and 2) size of the metal nanoparticles.

Figure 1 shows the diarylethene derivative **1a** used in this experiment. Diarylethene **1a** has a thiol unit, which forms self-assembled monolayer on the metal nanoparticle core. Methyl groups are introduced at the 3-positions on thiophene ring to increase fatigue-resistance. The distance between the diarylethene moiety and the metal nanoparticle was five methylene units to decrease the quenching effect by the metal surface.[14] To examine the dependence of the photochromic reactivity of diarylethene **1a** on the core size of the nanoparticle, different sizes of the nanoparticles were prepared by changing the molar ratio between metal source and ligand **1a**.

Scheme 1 shows the synthetic route to diarylethene **1a**. Hydroxy-terminated diarylethene **4** was synthesized using methoxymethyl protecting group. Bromoalkyl group was introduced by Williamson ether synthesis, and the final alkanethiol derivative **1a** was synthesized by the reaction with hexamethyldisilathiane and tetrabutylammonium fluoride. The structure of ligand **1a** was confirmed by NMR, IR, and high-resolution mass spectroscopy and elemental analysis.

Photochromism of Ligand 1a. Ligand **1a** showed a photochromic reaction in ethyl acetate by alternative irradiation with 313 and 578 nm light (Fig. 2). Upon irradiation with 313 nm light, ligand **1a** underwent a photochromic reaction in ethyl acetate to give blue-purple solution. The blue-purple color is due to the formation of the closed-ring isomer **1b**. The absorption maximum was observed at 577 nm. The conversion under irradiation with 313 nm light was 81%. Upon irradiation with 578 nm light, the colored solution turned colorless. The quantum yield of the cyclization (313 nm) and cycloreversion (517 nm) reactions were measured using 1,2-bis(benzothiophen-3-yl)hexafluorocyclopentene as a reference,[15] and the cyclization and cyclereversion quantum yields were determined to be 0.41 and 0.023, respectively.

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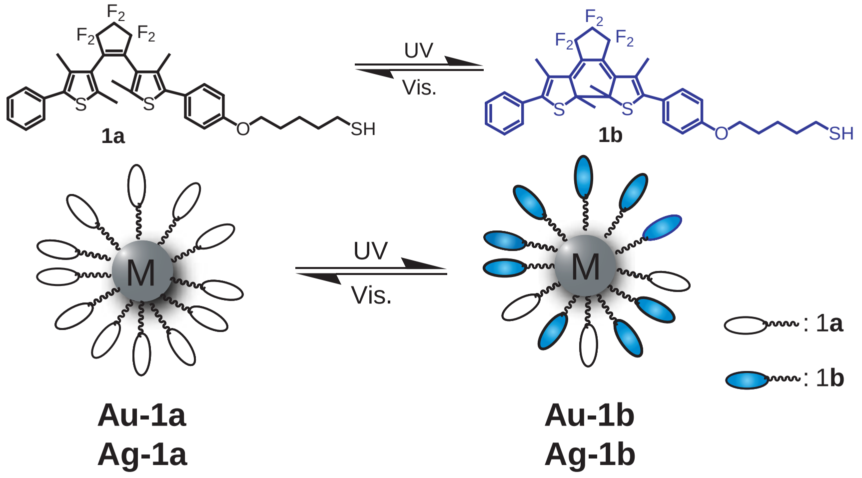
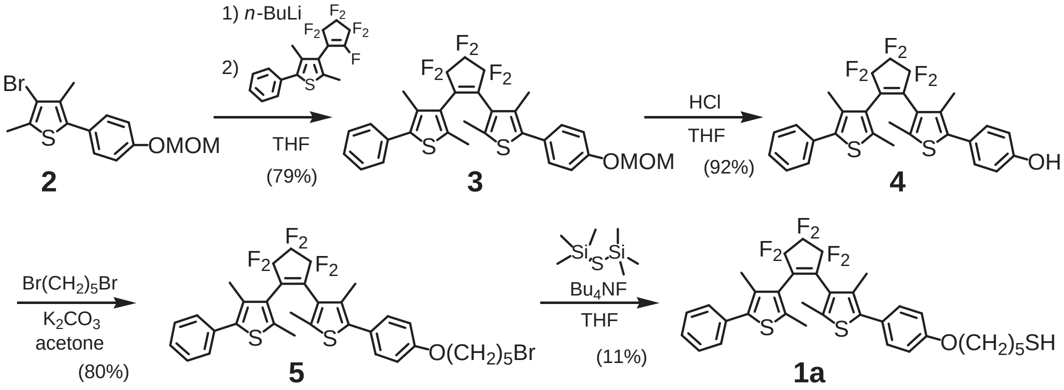


Fig. 1. Photochromic reactions of diarylethene **1** and **Au–** and **Ag–1**.



Scheme 1. Synthesis of ligand **1a**.

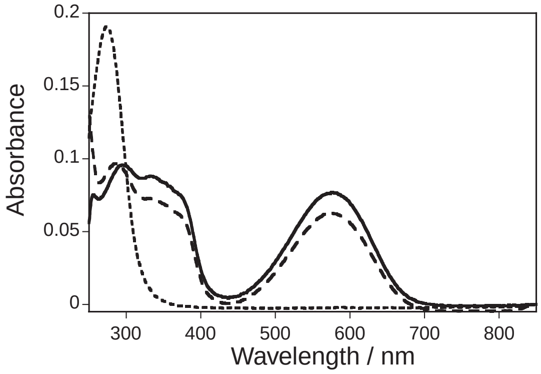


Fig. 2. Photochromic reaction of ligand **1a** in ethyl acetate (6.5 µmol L^{-1}). Dotted line denotes the open-ring isomer; solid line denotes the closed-ring isomer; dashed line denotes the spectrum in the photostationary state under irradiation with 313 nm light.

Preparation and Characterization of Gold and Silver Nanoparticle. Gold nanoparticles capped with thiol **1a** (**Au–1a**) were prepared by the Brust and Schiffrin protocol.[6] Silver nanoparticles (**Ag–1a**) were synthesized by Kim's method which is a modification of the Brust's protocol.[16] Nanoparticles of different sizes were prepared by changing the molar ratio between diarylethene **1a** and metal source. Stoichiometric ratio for preparing gold and silver nanoparticles were changed as Au or Ag:**1a** = 1:1 and 3:1. Four kinds of nanoparticles, **Au–1a(1:1)**, **Au–1a(3:1)**, **Ag–1a(1:1)**, and **Ag–1a(3:1)** were prepared with molar ratios of Au:**1a** = 1:1, Au:**1a** = 3:1, Ag:**1a** = 1:1, and Ag:**1a** = 3:1, respectively. The nanoparticles were soluble in chloroform, ethyl acetate, and toluene.

To measure the particle size, transmission electron microscopy (TEM) and dynamic light scattering (DLS) measurements were performed. TEM samples were prepared by dropping a toluene or ethyl acetate solution on a carbon-coated copper grid. Figure 3 shows the TEM images of **Au–** and **Ag–1a**. The size distribution of the particles is moderately polydisperse. The particles are well separated from each other due to the diarylethene monolayers. Figure 4 shows the histograms of the diameter of gold and silver nanoparticles **Au–** and **Ag–1a** based on TEM images. The average diameter of **Au–1a(1:1)**, **Au–1a(3:1)**, **Ag–1a(1:1)**, and **Ag–1a(3:1)** were 2.2 ± 0.3, 3.2 ± 0.4, 1.2 ± 0.2, and 6.7 ± 1.5 nm, respectively (Table 1).

Dynamic light scattering (DLS) measurements were also carried out in ethyl acetate to get further information on the particle size (Fig. 5). While TEM image reflects only diameter of silver core, DLS measurement reflects Brownian movement of silver core and diarylethene monolayer; therefore, the particle size measured by DLS was larger than that of TEM image. The number-average diameter of **Ag–1a(1:1)** and **Ag–1a(3:1)**

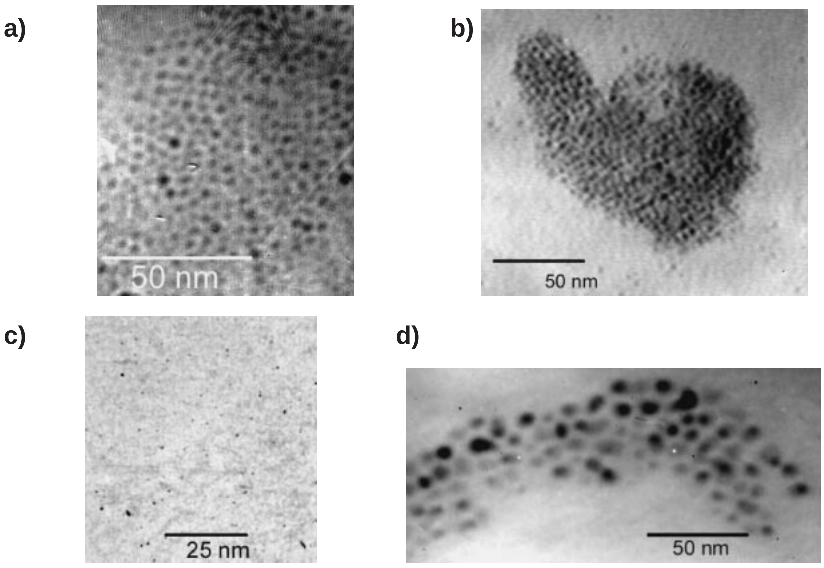


Fig. 3. TEM images of a) **Au–1a(1:1)**, b) **Au–1a(3:1)**, c) **Ag–1a(1:1)**, and d) **Ag–1a(3:1)**.

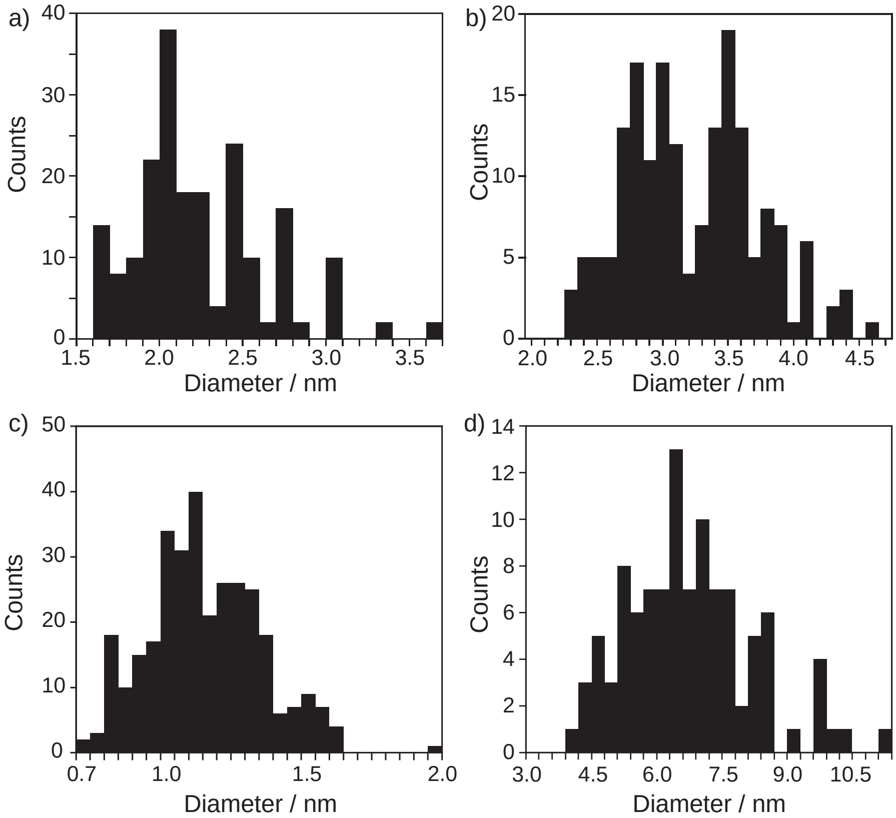


Fig. 4. Core size histograms of a) **Au–1a(1:1)**, b) **Au–1a(3:1)**, c) **Ag–1a(1:1)**, and d) **Ag–1a(3:1)** obtained from the TEM images (Figs. 3a–3d).

determined by DLS measurement were 3.6 and 9.0 nm, respectively. This result agreed with the particle size difference observed in TEM images.

In order to investigate the packing of the diarylethene molecules on the metal nanoparticles, IR spectra of diarylethene-capped gold and silver nanoparticles were measured. The spectra of gold and silver nanoparticles are similar to that of ligand **1a** itself, indicating that diarylethenes definitely capped the gold and silver nanoparticles. The spectrum of ligand **1a** has peaks at 2864 and 2935 cm^{-1} originating from alkyl C–H asymmetric and symmetric stretching mode, respectively. On the other hand, **Au–1a(1:1)**, **Au–1a(3:1)**, **Ag–1a(1:1)**, and **Ag–1a(3:1)** have peaks at 2852–2857 and 2921–2928 cm^{-1}. The shift to lower wavenumber suggests that diarylethenes on the metal nanoparticles adopted on all-*trans* conformation and were packed more regularly than free **1a**.[17]

Table 1. Diameters and Optical Properties of Gold and Silver Nanoparticles Capped with Diarylethene **1**

Entry	TEM (Diameter/nm)	DLS (Diameter/nm)	Plasmon absorption λ_{max}/nm	Absorption maxima of the closed-ring isomer λ_{max} /nm[a)]	IR stretching/cm^{-1}
1	N/A	N/A	N/A	577	2864, 2935
Au–1a(1:1)	2.2 ± 0.3[b)]	N/A	520	578	2852, 2921
Au–1a(3:1)	3.2 ± 0.4	N/A	520	582	2856, 2926
Ag–1a(1:1)	1.2 ± 0.2	3.6	none	573	2855, 2926
Ag–1a(3:1)	6.7 ± 1.5	9.0	435	574	2857, 2928
Au–1b′	2.9 ± 0.7	N/A	520	582	N/A
Ag–1b′	11.4 ± 3.6	N/A	422	573	N/A

a) Measured by subtracting the spectra before and after irradiation. b) The value in Ref. 13 is revised.

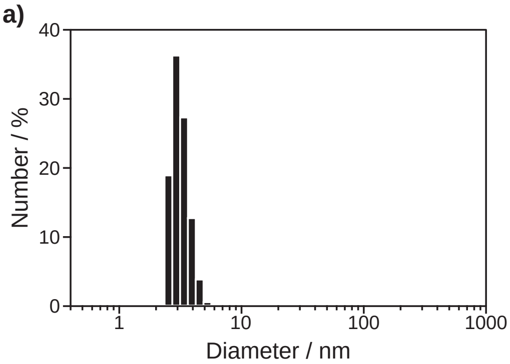


Fig. 5. DLS histograms of a) **Ag–1a(1:1)** and b) **Ag–1a(3:1)**.

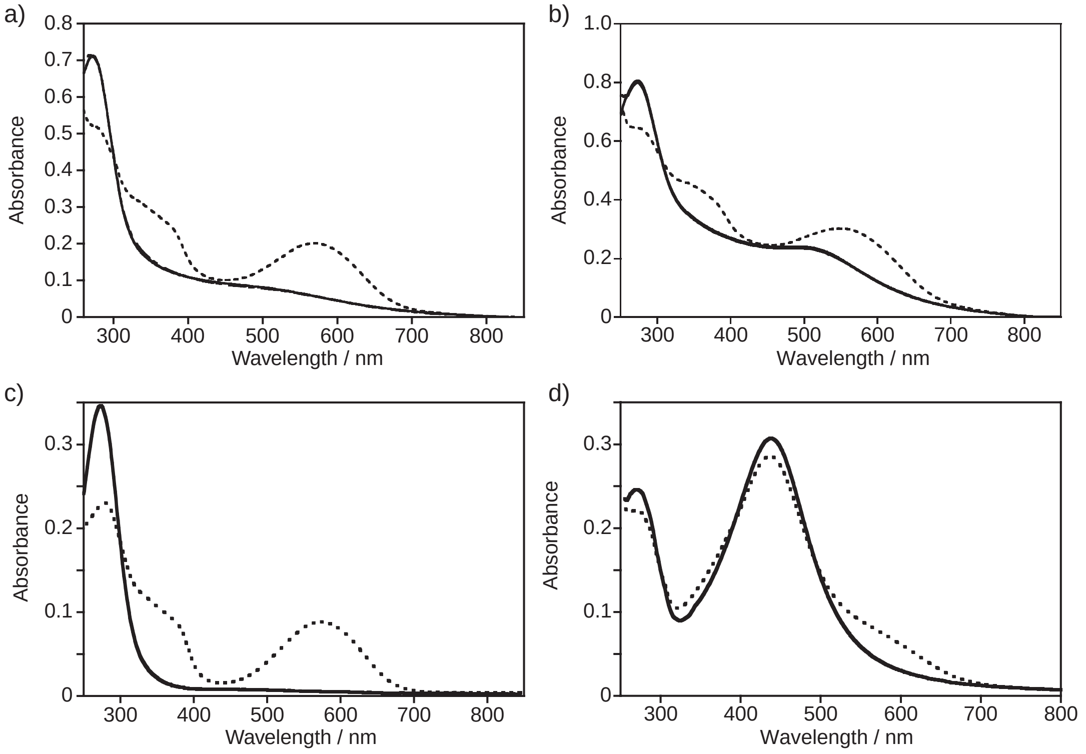


Fig. 6. Absorption spectra of a) **Au–1a(1:1)**, b) **Au–1a(3:1)**, c) **Ag–1a(1:1)**, and d) **Ag–1a(3:1)** in ethyl acetate. Solid lines denote the open-ring isomer. Dotted lines denote the photostationary state under irradiation with 313 nm light.

Photochromism of Gold and Silver Nanoparticle. All of the metal nanoparticles capped with diarylethenes underwent photochromic reactions by irradiation with UV and visible light in ethyl acetate (Fig. 6). The red-brown solution of gold nanoparticles **Au–1a** turned red-purple upon irradiation with 313 nm light, which is due to the formation of the closed-ring

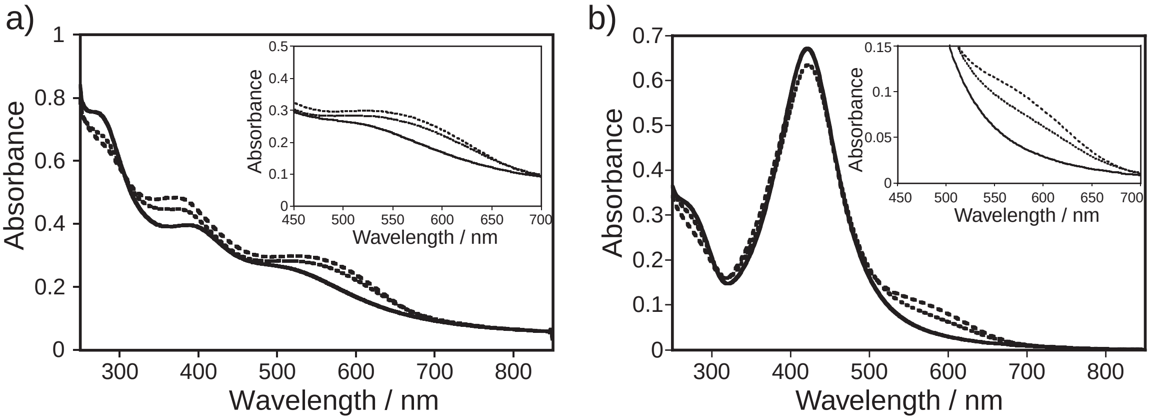


Fig. 7. Absorption spectra of a) **Au–1b′** and b) **Ag–1b′** in ethyl acetate: the open-ring isomer (solid line); the closed-ring isomer (dashed line); in the photostationary state under irradiation with 313 nm light (dotted line). Inset shows expansion from 450 to 700 nm.

isomer. For silver nanoparticles **Ag–1a**, the color changed from pale brownish yellow to greenish yellow. In both cases, the solution returned back to original color after irradiation with 578 nm light. Although **Ag–1a(3:1)** has a strong plasmon absorption peak at 435 nm, the sample underwent a photochromic reaction.

The optical properties of the gold and silver nanoparticles capped with diarylethenes are summarized in Table 1. The plasmon absorption intensity decreases when the particles size becomes small. **Ag–1a(1:1)** did not show any distinctive plasmon absorption because the size of this nanoparticle was very small.[7] The absorption maxima of the closed-ring isomer was not strongly dependent on the metal element nor the particle size.

Gold and silver nanoparticles were prepared using the closed-ring isomer **1b**. By this method, nanoparticles capped with only the closed-ring isomers (**Au–1b′** and **Ag–1b′**) were prepared. The closed-ring isomer was separated by HPLC from a mixture of the closed- and the open-ring isomer, and the preparation of the nanoparticle was performed in the dark. The size distributions of the nanoparticles are listed in Table 1. Figure 7 shows the photochromic behavior of **Au–** and **Ag–1b′**. The conversion was estimated as 74 and 64% for gold and silver nanoparticles, respectively. The conversion gives information concerning the ratio of the cyclization and the cycloreversion quantum yields,[18] and the lower conversion as compared to that of the free ligand indicates that the cyclization quantum yield is suppressed due to the metal. Although the conversion was suppressed by the metal, it was proved in this study that a photochromic reaction takes place on the surface of noble metal nanoparticles.

The photochromic reactivity revealed that the cyclization reaction was more effectively quenched than the cycloreversion reaction. In the case of **Ag–1a(3:1)** and **Ag–1b′**, a strong plasmon band was observed between the absorption maxima of the open- and the closed-ring isomer. Provided that quenching occurs by an energy-transfer mechanism, the cyclization reaction should be quenched more effectively than the cycloreversion reaction. The gold nanoparticles have a plasmon band at a longer wavelength than silver nanoparticles, which can explain the stronger quenching by the silver nanoparticles (74% vs 64%). Many fluorophores are reported to lose the fluorescent properties on the surfaces of metal nanoparticles.[19] However, the cyclization reaction of diarylethenes (<10 ps) is a much faster phenomenon than fluorescence ($\approx$ca. several ns). This fast reaction is the main reason why the photochromic reaction took place on the surface of noble metal nanoparticles.

Conclusion

Gold and silver nanoparticles capped with diarylethene were synthesized by Brust and Kim's method. The particle sizes of gold and silver nanoparticles were determined by TEM and DLS measurement, and from the IR spectra diarylethene capped the gold and silver nanoparticles and were densely packed. The metal nanoparticles underwent photochromic reactions by irradiation with UV and visible light. Although the quenching of the cyclization reaction was observed, the photochromic reaction of diarylethene occurred reversibly on the gold and silver nanoparticles.

Experimental

Materials. IR spectra were recorded on a Perkin-Elmer Spectrum One instrument by ATR method. ^{1}H NMR spectra were recorded on Varian Gemini 200 instruments. UV–vis spectra were recorded on a Hitachi U-3500 spectrophotometer. Mass spectra were obtained on JEOL JMS-GCmate II. Melting points were not corrected.

All reactions were monitored by thin-layer chromatography carried out on 0.2-mm E. Merck silica-gel plates (60F-254). Column chromatography was performed using silica gel (Kanto, 63-210 mesh).

1-[5-(4-Methoxymethoxyphenyl)-2,4-dimethyl-3-thienyl]-2-(2,4-dimethyl-5-phenyl-3-thienyl)hexafluorocyclopentene (3): To a solution of 3-bromo-5-(4-methoxymethoxyphenyl)-2,4-dimethylthiophene (**2**)[20] (4.32 g, 16 mmol) in dry THF (45 mL) was added 1.6 M *n*-BuLi (11 mL, 17.6 mmol) at -70 °C. After the mixture was stirred for 1 h, a solution of 1-(2,4-dimethyl-5-phenyl-3-thienyl)heptafluorocyclopentene[21] (1.05 g, 2.76 mmol) in dry THF (8 mL) was added. The reaction mixture was stirred at -70 °C for 2 h, and then the solution was allowed to warm up to room temperature, quenched by water, extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica, hexane:$CHCl_3$ = 9:1) gave diarylethene derivative **3** (1.20 g, 79%) as a brown wax. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.00–2.11 (m, 6H), 2.28–2.38 (m, 6H), 3.49 (s, 3H), 5.20 (s, 2H), 7.05 (d, 2H, $J = 8.6$ Hz), 7.22–7.44 (m, 7H). MS(FAB) (m/z) $[M]^+$ 608. Anal. Calcd for $C_{31}H_{26}F_6O_2S_2$: C, 61.31; H, 4.33%. Found: C, 61.17; H, 4.31%.

1-[5-(4-Hydroxyphenyl)-2,4-dimethyl-3-thienyl]-2-(2,4-dimethyl-5-phenyl-3-thienyl)hexafluorocyclopentene (4): To a solution of derivative **3** (2.2 g, 3.61 mmol) in THF (40 mL) was added conc. HCl (9.2 mL) and stirred for 6.5 h. After the addition of water, the mixture was extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica, $CHCl_3$) gave phenol derivative **4** (1.88 g, 92%) as a green wax. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.04–2.10 (m, 6H), 2.32–2.38 (m, 6H), 4.85 (s, 1H), 6.85 (d, 2H, $J = 8.0$ Hz), 7.21–7.40 (m, 7H). MS(FAB) (m/z) $[M]^+$ 564. Anal. Calcd for $C_{29}H_{22}F_6OS_2$: C, 61.33; H, 4.04%. Found: C, 61.69; H, 3.93%.

1-[5-(4-Bromopentyloxyphenyl)-2,4-dimethyl-3-thienyl]-2-(2,4-dimethyl-5-phenyl-3-thienyl)hexafluorocyclopentene (5): To a solution of derivative **4** (1.11 g, 1.97 mmol) in acetone (30 mL) was added K_2CO_3 (0.27 g, 1.97 mmol) and 1,5-dibromopentane (0.53 mL, 3.94 mmol). After the mixture was refluxed under argon atmosphere K_2CO_3, it was filtrated and then concentrated. After the addition of water, the mixture was extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica, $CHCl_3$) gave bromoalkane derivative **5** (1.13 g, 80%) as a yellow wax. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.58–2.00 (m, 6H), 2.00–2.22 (m, 6H), 2.24–2.46 (m, 6H), 3.45 (t, 2H, $J = 6.6$ Hz), 3.99 (t, 2H, $J = 6.2$ Hz), 6.90 (d, 2H, $J = 9$ Hz), 7.20–7.42 (m, 7H). MS(FAB) (m/z) $[M]^+$ 712. Anal. Calcd for $C_{34}H_{31}BrF_6OS_2$: C, 57.46; H, 4.43%. Found: C, 57.22; H, 4.38%.

1-{5-[4-(5-Mercaptopentyloxy)phenyl]-2,4-dimethyl-3-thienyl}-2-(2,4-dimethyl-5-phenyl-3-thienyl)hexafluorocyclopentene (1a): To a solution of derivative **5** (200 mg, 0.28 mmol) in THF (0.56 mL) was added a mixture of hexamethyldisilathiane (142 µL, 0.672 mmol, 2.4 equiv) and tetrabutylammonium fluoride (178 µL, 0.616 mmol, 2.2 equiv). After the mixture was stirred for 2 days at room temperature, water was poured into the reaction vessel. The mixture was extracted with CH_2Cl_2, washed with aqueous NH_4Cl and brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica, hexane:$CHCl_3$ = 2:1) and then GPC ($CHCl_3$) and HPLC (Kanto chemical mightysil Si60 250-20, hexane:EtOAc = 9:1) gave thiol **1a** (20 mg, 11%) as a blue wax. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.35 (t, 1H, $J = 7.8$ Hz), 1.50–1.90 (m, 6H), 2.02–2.10 (m, 6H), 2.30–2.36 (m, 6H), 2.57 (q, 2H, $J = 6.8$ Hz), 3.98 (t, 2H, $J = 6.4$ Hz), 6.89 (d, 2H, $J = 8.8$ Hz), 7.26 (d, 2H, $J = 8.6$ Hz), 7.29–7.42 (m, 5H); IR (Ge ATR) 2935, 1608, 1514, 1341, 1275, 1248, 1145, 1114, 1056, 988 cm^{-1}; UV–vis (EtOAc) λ_{max} (ε/M^{-1} cm^{-1}) 274 (2.9×10^4) nm, closed-ring isomer **1b** 577 (1.2×10^4) nm; HRMS (FAB) (m/z) $[M]^+$ calcd for $C_{34}H_{32}F_6OS_3$: 666.1528. Found 666.1519. Anal. Calcd for $C_{34}H_{32}F_6OS_3$: C, 61.36; H, 4.99%. Found: C, 61.24; H, 4.84%.

Preparation of Metal Nanoparticles. Gold Nanoparticles Capped with Thiol 1a (Au–1a(1:1)): A solution of hydrogen tetrachloroaurate(III) hydrate (9 mg, 21.9 µmol) in ultrapure water (18.2 MΩ cm, 0.76 mL) was added to a solution of tetraoctylammonium bromide (56 mg, 102 µmol) in toluene (5 mL) and the mixture was vigorously stirred for 10 min. A solution of thiol **1a** (16 mg, 24 µmol) in toluene (2 mL) was added to the mixture. Then, a solution of sodium tetrahydroborate (9 mg, 230 µmol) in water (0.58 mL) was slowly added to the mixture. After stirring, the organic layer was separated and concentrated. The toluene (3 mL) solution of the residue was added to ethanol (20 mL) and centrifuged (0 °C, 6000 rpm, 40 min). The precipitate was collected, redissolved in toluene and ethanol, sonicated, and centrifuged again. This cycle was repeated three times, and the precipitate was finally dried in vacuo. **Au–1a** was obtained as a black powder. Nanoparticles of different sizes were prepared by similar method by changing the molar ratio between $HAuCl_4$ and **1a** to 3:1. IR (Ge ATR) 2921, 2851, 1608, 1514, 1342, 1274, 1259, 1145, 1112, 1055, 988 cm^{-1}; UV–vis (toluene) λ_{max} 515 (sh) nm.

Silver Nanoparticles Capped with Thiol 1a (Ag–1a(1:1)): A solution of tetraoctylammonium bromide (73 mg, 0.13 mmol) in chloroform (5 mL) was added to a solution of $AgNO_3$ (5.1 mg, 0.03 mmol) in ultrapure water (18.2 MΩ cm, 1 mL), and then, the solution was stirred vigorously for 1 h. Then, a solution of ligand **1a** (20 mg, 0.03 mmol) in chloroform (2 mL) was added. In a separate flask, a solution of $NaBH_4$ (13 mg, 0.34 mmol) in ultrapure water (18.2 MΩ cm, 1 mL) was placed, and then, it was slowly added to reaction vessel. After stirring for 3 h, the aqueous phase was removed and the organic phase was concentrated. The residue was dissolved in a small amount of chloroform and poured into ethanol (30 mL) and then, the precipitated particles were collected by filtration. The precipitate was again dissolved in small amount of chloroform and poured into ethanol, and then the precipitated particles were collected by filtration. This cycle was repeated using methanol and hexane to remove excess thiol and phase transfer reagent. **Ag–1a(1:1)** was obtained as a black powder. Nanoparticles of different sizes were prepared by changing the molar ratio between $AgNO_3$ and ligand **1a** to 3:1. The silver nanoparticles can be dissolved in chloroform, ethyl acetate, and toluene. IR (Ge ATR) 2926, 2855, 1607, 1514, 1471, 1444, 1341, 1275, 1249, 1191, 1145, 1114, 1055, 1033, 988, 878, 859, 830, 758, 697 cm^{-1}.

Photochemical Mesurement. Absorption spectra were measured on a spectrophotometer (Hitachi U-3500). Photoirradiation was carried out using a USHIO 500 W super high-pressure mercury lamp or a USHIO 500 W xenon lamp. Mercury lines of 313 and 578 nm were isolated by passing the light through a combination of band-pass filter (UV-D33S) or sharp-cut filter (Y-50) and monochromator (Ritsu MC-20L).

Condition for the separation of the closed-ring isomer **1b** was as follows. Pump: Hitachi L-2420; Detector: Hitachi L-2130 (detective wavelength: 313 nm); Column: Mightysil (Kanto Chemical Co., Inc.) 250–4.6 mm; Eluent:hexane:CH_2Cl_2 = 3:1.

TEM Measurement. TEM measurement was performed on a Hitachi H-7500 instrument. The measurement was performed at 100 kV. TEM samples were prepared by placing a drop of ethyl acetate or toluene solution of **Au–** and **Ag–1a** onto carbon-coated copper grid.

DLS Measurement. Particle size distribution was measured on Malvern Zetasizer Nano-ZS particle sizer equipped with 633 nm laser as light source, using a fixed angle (173°). The samples were filtered by using a MILLIPORE Millex membrane filter (0.20 µm) before measurement. The samples were kept 25 °C during measurement.

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