

Photochromism of Diarylethene-capped Gold Nanoparticles

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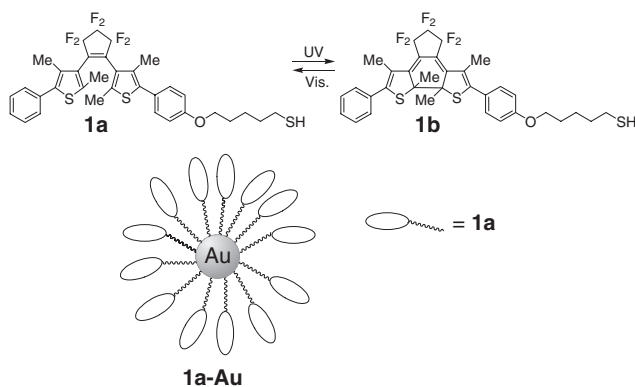
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(Received January 9, 2004; CL-040037)

Diarylethene-capped gold nanoparticles were synthesized by a self-assembled monolayer (SAM) technique and the photochemical behavior was studied. The average diameter of the particles was determined to be 1.1 nm from TEM image. The synthesized nanoparticles showed reversible photochromic reactivity regardless of the presence of the surface plasmon band.

Photochromic diarylethenes undergo reversible cyclization/cycloreversion photoreactions upon alternate irradiation with UV and visible light.¹ Diarylethene is considered as a candidate for molecular switching devices because the π -conjugated chain lengths of the open- and closed-ring isomers are significantly different.² For the realization of the molecular scale photonics or electronics,³ metal-molecule junction is essential. SAM on gold surface is one of the robust techniques to make covalent metal-organic bonds.⁴ Diarylethene-capped gold nanoparticles can work as a junction of π -conjugated organic molecule and electroconductive metal particle. Herein we would like to report the synthesis of diarylethene-capped gold nanoparticles and the photochemical behavior of the nanoparticles.



Scheme 1. Photochromism of thiol **1** and schematic drawing of **1a-Au**.

We prepared diarylethene **1a**. Diarylethene **1a** has one terminal thiol group and a pentamethylene alkyl chain is introduced to separate the diarylethene and the gold nanoparticle. The synthesis of **1a** was performed via phenol-terminated diarylethene. The structure of thiol **1a** was confirmed by NMR, high-resolution mass spectroscopy and elemental analysis.⁵

Gold nanoparticles capped with thiol **1a** (**1a-Au**) were synthesized as follows.⁶ A solution of hydrogen tetrachloroaurate(III) hydrate in water was added to a solution of tetraoctylammonium bromide in toluene. A solution of thiol **1a** in toluene was added to the mixture. Then a solution of sodium borohydride in water was added to the mixture. After stirring, organic

layer was separated and concentrated. The toluene solution of the residue was added to ethanol and centrifuged. The precipitation was collected, redissolved in toluene and ethanol, sonicated, and centrifuged. This cycle was repeated three times and finally dried in vacuo. **1a-Au** was obtained as a black powder.⁷

IR measurement of **1a** and **1a-Au** was carried out. Both spectra were basically similar. In the region where only the diarylethene has signals ($1500\text{--}1700\text{ cm}^{-1}$), the peak positions are exactly the same. In the C-H stretching region, the peak became sharp with incorporation in the gold nanoparticle. The peak positions (2921 and 2851 cm^{-1}) suggested that the alkyl chain adopts *trans* conformation.⁸

Figure 1a shows the transmission electron micrograph (TEM) image of **1a-Au**. The particles are spherical and two-dimensionally dispersed. Figure 1b shows the histogram of the diameter of the nanoparticles. The average diameter of **1a-Au** was 1.1 ± 0.2 nm. From the average diameter and the data of elemental analysis, the number of molecules attached to one Au nanoparticle was estimated to be around 15.

Figure 2a shows absorption spectra of **1** along with photochromic reactions in toluene. Upon irradiation with 313-nm light, **1a** underwent a photochromic reaction. The colorless solution of **1a** became blue-purple and the absorption maximum was

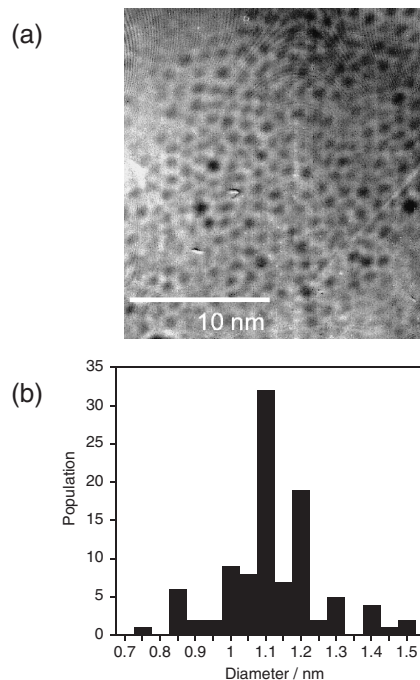


Figure 1. (a) TEM image of **1a-Au** (125 kV). Sample was placed on a carbon-coated copper grid. (b) Histogram of the diameter of the nanoparticles.

observed at 578 nm. The color change is due to the generation of the closed-ring isomer **1b**. The conversion under irradiation with 313-nm light was 87%. Upon irradiation with 578-nm light the closed-ring isomer **1b** returned to the open-ring isomer **1a** and the blue-purple solution became colorless.

Toluene solutions of **1-Au** also showed photochromic reactivity by irradiation with 313 and 578 nm lights (Figure 2b). The absorption spectra of **1a-Au** showed surface plasmon band around 520 nm. Despite the existence of the absorption in visible region, the photochromic reactions was not prohibited.⁹ Diarylethenes are known to undergo a cyclization reaction in less than 10 ps.¹⁰ It is also reported the energy transfer efficiency is decreased in smaller size particles.¹¹ The fast reaction and small particle size favor the photocyclization reaction. The absorption maximum of **1b-Au** was estimated from the difference spectrum before and after irradiation. The absorption maximum was 578 nm, indicating that the origin of the color is the closed-ring isomer **1b**.

In conclusion we have prepared gold nanoparticles covered with photochromic diarylethenes. The nanoparticles underwent photochromic reactions in spite of the existence of the Au surface plasmon absorption. The effects of the metal-chromophore

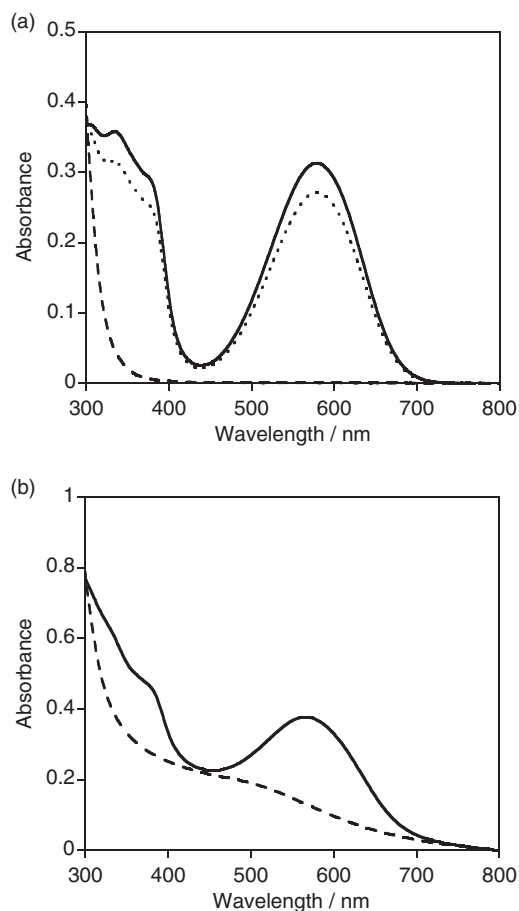


Figure 2. (a) Absorption spectral change of **1** in toluene: open-ring isomer (dashed line); closed-ring isomer (solid line); in the photostationary state under irradiation with 313-nm light (dotted line). (b) Absorption spectral change of **1-Au** in toluene: open-ring isomer (dashed line); in the photostationary state under irradiation with 313-nm light (solid line).

distance and the size of the nanoparticle on the photoreactivity are under investigation.

This work was supported by PRESTO, JST and a Grant-in-Aid for Scientific Research (S) (No. 15105006) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. The measurement of TEM was made using HITACHI H-7000 microscope at the Center of Advanced Instrumental Analysis, Kyushu University.

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- Analytical data for **1a**: ¹H NMR (200 MHz, CDCl₃) δ 1.36 (t, J = 7.6 Hz, 1H), 1.50–1.90 (m, 6H), 2.00–2.11 (m, 6H), 2.25–2.38 (m, 6H), 2.57 (q, J = 7.2 Hz, 2H), 3.98 (t, J = 6.4 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 7.25–7.40 (m, 7H); IR (Ge ATR) 2935, 1608, 1514, 1341, 1275, 1248, 1145, 1114, 1056, 988 cm⁻¹; UV-vis (hexane) λ_{max} 272 nm; FAB HRMS (m/z) [M]⁺ Found 666.1528, Calcd for C₃₄H₃₂F₆OS₃ 666.1519; Anal Found: C, 61.36; H, 4.99%. Calcd for C₃₄H₃₂F₆OS₃: C, 61.24; H, 4.84%. Corresponding closed-ring isomer **1b**: UV-vis (toluene) λ_{max} 335, 373 (sh), 578 nm.
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- Analytical data for **1a-Au**: IR (Ge ATR) 2921, 2851, 1608, 1514, 1342, 1274, 1259, 1145, 1112, 1055, 988 cm⁻¹; UV-vis (toluene) λ_{max} 515 (sh) nm; Anal. Found: C, 32.66; H, 3.11%.
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