

Observation of Isomerization of an Azobenzene Derivative in Gold Nanoparticle Aggregates Using SERS

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Photoisomerization has fascinated scientists for decades.¹ The light-induced molecular motion provides important information on the dynamics of molecules on the excited-state potential energy surfaces. It also has a wide range of applications including optical switches, light-driven devices, and erasable writing media.^{2,3} Azobenzene represents the most widely studied photochromic molecule. *Trans*-Azobenzene is more stable than its *cis* counterpart due to less steric hindrance. Electronic transition of *trans*-Azobenzene to S_1 ($\lambda_{\text{max}} = 449$ nm) or S_2 ($\lambda_{\text{max}} = 317$ nm) states leads to the isomerization to *cis*-Azobenzene with a quantum yield of 0.25 and 0.10, respectively.^{4,5} So far, many experimental and theoretical studies have been performed on the dynamics of photoisomerization of azobenzene.⁶⁻⁹

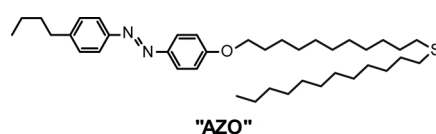
Novel metal nanoparticles and their aggregates provide unique environments for studying photochemistry.¹⁰ They act as an electron source for photo-induced charge transfer which opens a new reaction pathway in addition to the regular photochemistry of adsorbates on their surfaces. Furthermore, surface-enhanced Raman scattering (SERS) from nanoparticle aggregates provides extremely high sensitivity that allows one to probe submonolayer coverage of molecules.

Despite many attractive properties of metal nanoparticle aggregates, studies on the photoisomerization of azobenzene are rare.^{11,12} The reason is probably that it is difficult to produce stable aggregates that maintain their morphologies during the period of experiments without precipitation. Another reason is a difficulty in probing the isomerization in aggregates. Since the absorption of gold or silver nanoparticles is so large that it overwhelms the absorption of azobenzene,¹³ UV-Vis absorption spectroscopy typically used to probe the isomerization in solution is inadequate for studying the isomerization in aggregates.

In this communication, we report the observation of photoisomerization of an azobenzene derivative in gold nanoparticle (AuNP) aggregates using SERS. We synthesize an azobenzene derivative that can induce the formation of AuNP aggregates by adsorbing onto the surface of AuNPs. By the addition of a carefully controlled amount of the azobenzene derivative, we produce stable AuNP aggregates. SERS allows us to probe the *trans*-*cis* isomerization of the azobenzene derivatives.

The molecular structure of the synthesized azobenzene derivative ("AZO") is given below. AZO consists of a photo-sensitive azobenzene moiety and a long alkyl chain spacer group that provides a room for isomerization of the azobenzene

moiety when adsorbed on the surfaces of AuNPs (Supporting Information).



We first characterized photochemical properties of AZO in solution. The synthesized AZO is predominantly in the *trans* form with an absorption at 349 nm. Fig. 1(a) shows that upon irradiation at 365 nm (3 mW/cm^2) for 30 min, the 349-nm band vanishes and the absorption at 446 nm rises (Lamp ON), indicating that the photoisomerization from *trans* to *cis* has occurred. When we turn off the lamp and measure the UV-Vis absorption

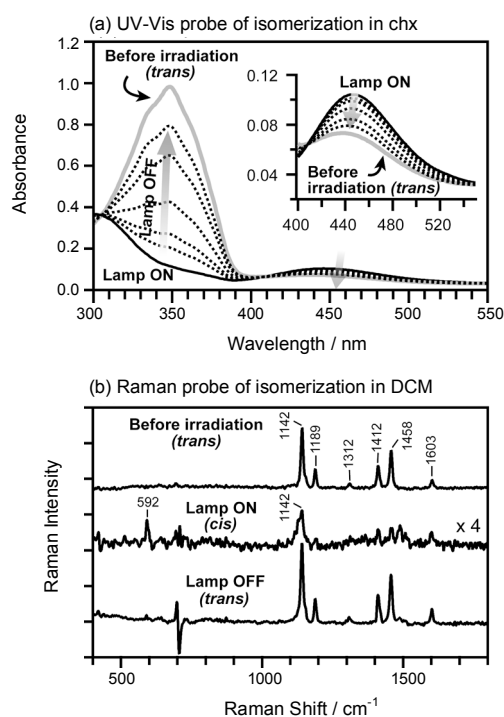


Figure 1. (a) UV-Vis absorption spectra of AZO in cyclohexane (23 μM) before irradiation, after irradiation at 365 nm for 30 min (Lamp ON), and after the subsequent lamp-off for 4, 8, 16, 32, and 60 min. (b) Raman spectra of AZO in dichloromethane (1 mM) before irradiation, after irradiation for 30 min (Lamp ON) and after the subsequent lamp-off for 3 h. The solvent spectra have been subtracted.

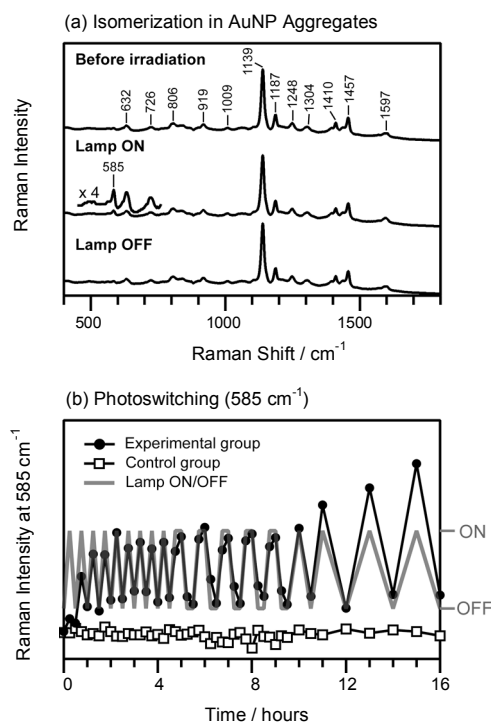


Figure 2. (a) SERS spectra of AZO in AuNP aggregates before irradiation, after irradiation at 365 nm for 50 min, and after the subsequent lamp-off for 50 min. (b) The change of the Raman intensity at 585 cm⁻¹ (*cis* band) of the experimental and control group as the 365-nm lamp is switched on and off repeatedly. The control group is the sample taken from the same batch as the experimental group, but subject to no irradiation.

spectra as time elapses, the 349-nm *trans* band is gradually restored and the 449-nm *cis* band becomes subdued, suggesting that the back-isomerization by a room light slowly occurs.¹⁴

Raman spectra measurements for more concentrated solution of AZO in dichloromethane (1 mM) show that upon irradiation at 365 nm, the overall Raman intensity decreases and a new band at 592 cm⁻¹, assigned to the mixed CNNC and CCCH torsional mode of the azobenzene moiety in the *cis* form, appears.⁹ Because other bands are either weak or overlapped with the *trans* bands, the 592-cm⁻¹ band is an important signature of isomerization. Termination of the irradiation gives rise to the Raman spectrum of the *trans* isomer (Lamp OFF).

We prepared AuNPs with an average diameter of 40 nm by the citrate-reduction of Au³⁺ ions, following the method developed by Frens and coworkers.¹⁵ Adsorption of AZO onto the surface of AuNPs via the formation of a Au-S bond induces the aggregation of AuNPs.¹⁶ Addition of 0.8 μM of AZO produces stable AuNP aggregates without precipitation for at least 16 h (Supporting Information). A new absorption band at ~800 nm arising from the dipolar coupling of surface plasmons between individual AuNPs in the aggregates offers an opportunity for the SERS probe of the isomerization because the surface plasmon absorption is resonant with our Raman excitation laser (785 nm).¹⁷

Indeed, Raman spectra obtained from the aggregates are greatly enhanced as shown in Fig. 2(a). Note that the spectrum

is produced by only 0.4 μM of AZO used to form the aggregates. The SERS spectrum of *trans*-AZO from the AuNP aggregates is similar to the Raman spectra of AZO in solution except that more low frequency bands are observed for the former.

Upon irradiation at 365 nm (3 mW/cm²) for 50 min, the characteristic *cis* Raman band appears at 585 cm⁻¹, indicating that the isomerization of AZO has occurred in the aggregates. Since other Raman peaks from the *trans* are still observed, the isomerization quantum yield seems rather low. When we leave the sample under a room light after the irradiation, *cis*-AZO isomerizes back to the *trans* form (Lamp OFF).

The photoisomerization reaction in AuNP aggregates is highly reversible. We demonstrate the photoswitching of AuNP aggregates in Fig. 2(b). We turned on and off the lamp repeatedly and measured the Raman intensity of the signature *cis* band at 585 cm⁻¹. Figure 2(b) shows that the Raman intensity at 585 cm⁻¹ increases as the lamp is turned on and decreases as the lamp is switched off. As the irradiation time is lengthened (10 ~ 16 h region), the Raman intensity increases exponentially. In contrast, the Raman intensity of the control group without irradiation remains unchanged, indicating that the signal change we observed is indeed from photoreaction, not from any effects of aggregation.

Further quantitative investigations on the isomerization rate and the effect of other experimental parameters on the rate are underway in our laboratory.

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Supporting Information. Experimental method and Raman spectral assignments are available via the internet at <http://www.kcsnet.or.kr/bkcs>.

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