

Photoresponsive Azobenzene-modified Gold Nanoparticle

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Recently, inorganic nanoparticles have attracted great attention because nanoparticles exhibit interesting size-dependent physical and chemical properties due to intermediate size between single molecules and bulk materials.¹⁻⁵ Especially, the design and preparation of functional nanomaterials obtained from tunable and controlled nanoparticle self-assembly becomes one of most exciting research subject due to many practical applications using their remarkable optical, catalytical, electronic, biological, and magnetic properties, based on high surface-to-volume ratios and small size effect. Organized organic-inorganic nanohybrids can be constructed by assembling monolayers of organic molecules containing functional groups such as thiols on the three-dimensional surface of metal nanoparticles.⁶⁻⁸ The hybrid nanomaterials consisting of inorganic nanoparticle and photoactive organic molecules may provide light-controlled nano-devices.⁹⁻¹³ Incorporation of photo-switched organic molecule into inorganic nanoparticle is one of good strategies for realization of molecular device. Photo-induced *trans-cis* isomerization of organic photochromes such as diarylethenes¹⁴⁻¹⁶ and azobenzene^{17,18} could lead to the modulation of hybrid nanomaterials by external optical stimulation. In this study, we describe the preparation and photoisomerization behavior of gold nanoparticle modified with photoresponsive azobenzene-alkanethiol. This photoresponsive Au nanoparticle stabilized by self-assembled layer of azobenzene-alkanethiol may function as light-controlled nano-switch.

Azobenzene-capped gold nanoparticle was prepared as shown in Figure 1 and the detailed procedure was described in Experimental Section. FT-IR spectra show the disappearance of S-H stretching band at 2550 cm^{-1} in the azobenzene-alkanethiol stabilized gold nanoparticle. Transmission electron microscopic (TEM) image in Figure 2 showed the formation of azobenzene-alkanethiol functionalized gold nanoparticle of diameter in the range 2-3 nm. There are 45 azobenzene-alkanethiols on the gold surface, estimated from elemental analysis data (Au 78.1% (by difference); C 15.2%; H 1.6%; N 1.9%; S 2.1%) and average number of 269 Au atoms per core of 2 nm diameter.¹⁹

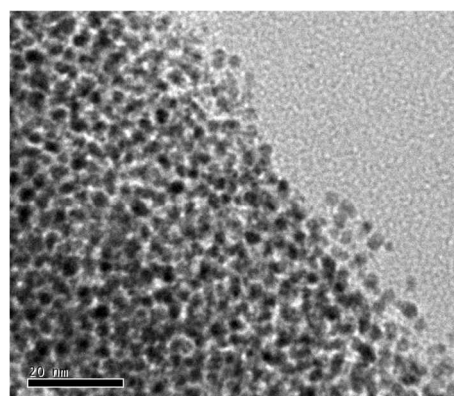


Figure 2. Transmission electron microscopic (TEM) image of azobenzene-alkanethiol functionalized gold nanoparticle.

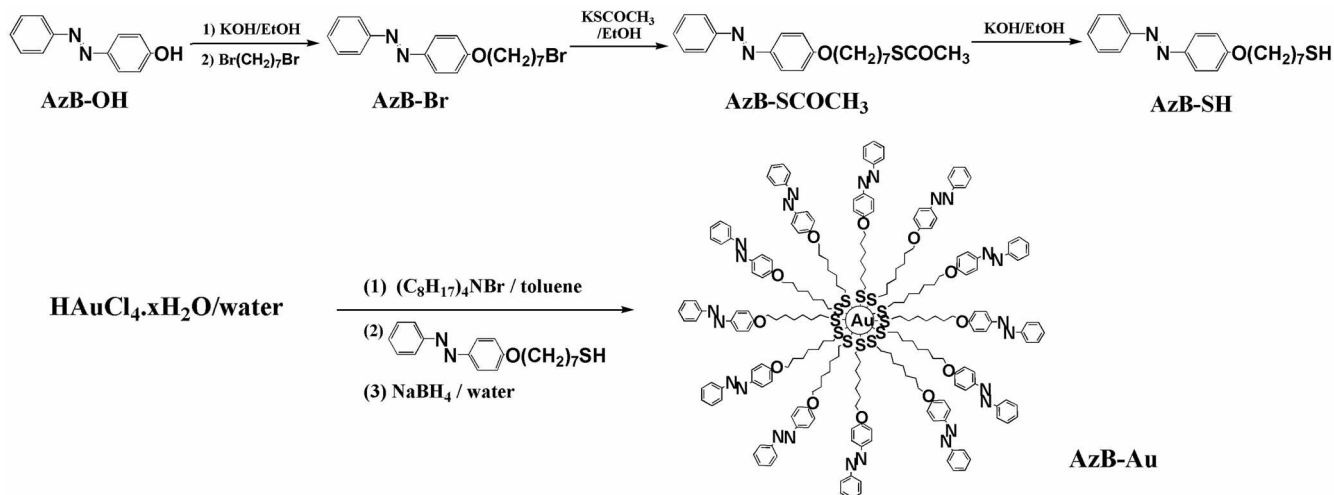


Figure 1. Preparation of azobenzene-alkanethiol functionalized gold nanoparticle.

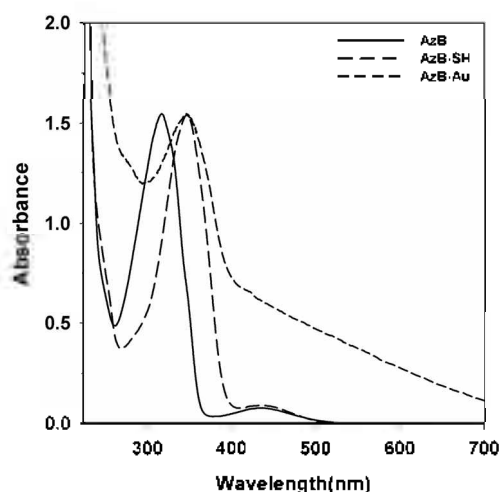


Figure 3. Absorption spectra of azobenzene-alkanethiol functionalized gold nanoparticle (AzB-Au), PhN=NPh-O(CH₂)₃SH (AzB-SH), and azobenzene (AzB) in dichloromethane.

The absorption spectra of azobenzene-capped gold nanoparticle in dichloromethane are shown in Figure 3 and absorption maximum appears at 347 nm, due to π - π^* absorption of azobenzene moiety, which is red-shifted compared with absorption band (318 nm) of azobenzene and

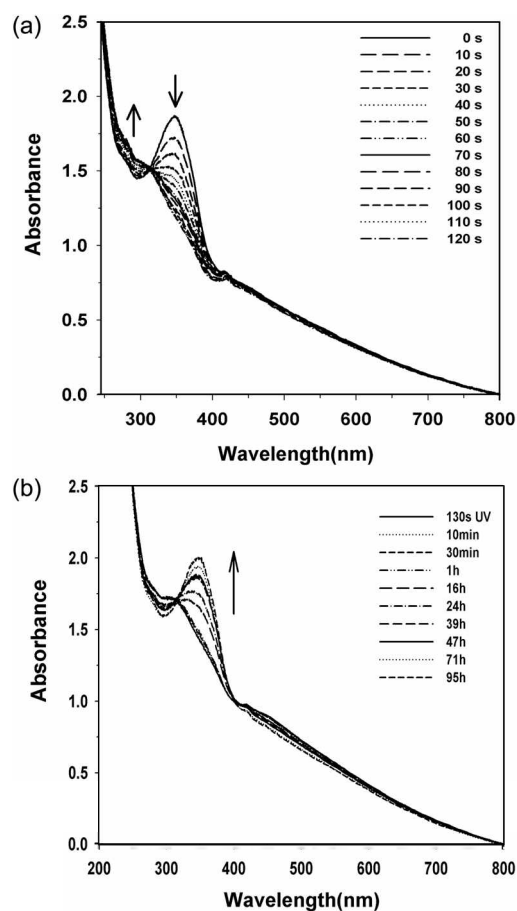


Figure 4. Absorption spectral changes of azobenzene-alkanethiol functionalized gold nanoparticle in dichloromethane (a) with irradiation time (0-120 s, 10 s interval) on irradiation at 350 nm and (b) with incubation time in the dark after 130 s irradiation at 350 nm.

similar to that (347 nm) of AzB-SH. n - π^* absorption of azobenzene moiety observed in absorption spectra of both azobenzene (434 nm) and AzB-SH (434 nm) is not observed to be obscured by bonding of azobenzene alkanethiol on Au surface.

Azobenzene anchored on gold nanoparticle accomplishes *trans*→*cis* photoisomerization upon ultraviolet irradiation and monitored by absorption spectral changes. Photogenerated *cis*-isomer reverts to *trans*-isomer when the irradiated solution is stored in the dark. In dilute solution, thermal back isomerization follows first-order kinetics. Photoirradiation was carried out in a Rayonet RPR 100 photochemical reactor equipped with 4 Southern Ultraviolet 3500 Å lamps using pyrex reaction tube in dichloromethane solution. The absorption spectral changes of azobenzene-alkanethiol functionalized gold nanoparticle in dichloromethane during 120 sec by 10 sec interval on irradiation at 350 nm were measured for monitoring the photoisomerization of azobenzene (Figure 4a). On 350 nm irradiation, absorption band at 347 nm decreases and absorption band at 434 nm increases, as

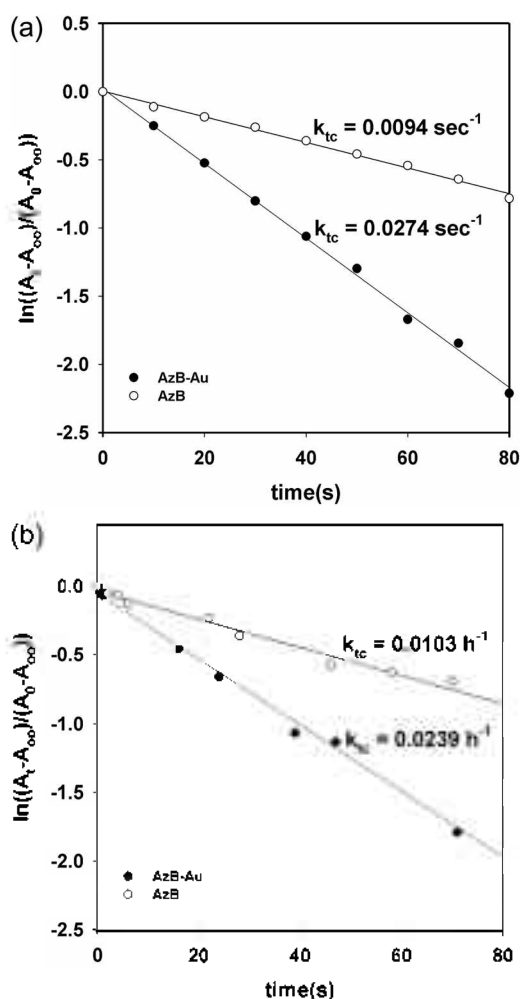


Figure 5. Plots of time versus $\ln((A_t - A_\infty)/(A_0 - A_\infty))$ for obtaining (a) the initial reaction rates $k_{t \rightarrow c}$ of *trans*→*cis* photochemical isomerization and (b) the initial reaction rates $k_{c \rightarrow t}$ of *cis*→*trans* thermal isomerization of azobenzene-alkanethiol functionalized gold nanoparticle AzB-Au and azobenzene AzB.

azobenzene moiety of azobenzene-alkanethiol functionalized gold nanoparticle converts photochemically from *trans* form to *cis* form. Similar to simple azobenzene molecule, azobenzene modified gold nanoparticle carried out very fast *trans*→*cis* photoisomerization on irradiation of 350 nm light, completed within 120 sec.

Thermal reversion of azobenzene-alkanethiol functionalized gold nanoparticle is very slow at room temperature. Thermal back isomerization followed by absorption spectral changes in dichloromethane during incubation in the dark after irradiation at 350 nm for 130 sec is shown in Figure 4b. As the irradiated solution in dichloromethane were kept in the dark, very slow reversion from *cis* form to *trans* form occur and is completed after 5 days through thermal isomerization.

Trans→*cis* photoisomerization rates $k_{t \rightarrow c}$ are calculated from the absorbance changes with irradiation time t using the following equation.

$$\ln \frac{A_{\infty} - A_t}{A_{\infty} - A_0} = -k_{t \rightarrow c} t \quad (1)$$

where A_0 , A_t , and A_{∞} represent absorbances before irradiation, at irradiation time t , and at the photostationary state gained after the prolonged irradiation, respectively.

The initial reaction rates $k_{t \rightarrow c}$ of *trans*→*cis* photochemical isomerization obtained from the plot (see Figure 5a) using equation 1 are higher for azobenzene-alkanethiol functionalized gold nanoparticle (0.027 s^{-1}) than for azobenzene (0.009 s^{-1}).

Applying the same equation, the initial reaction rates $k_{c \rightarrow t}$ of *cis*→*trans* thermal isomerization can also be estimated (see Figure 5b). Thermal reversion rate reverted to the original dark-incubated spectrum of *trans*-isomer molecule over 6 days in the dark is higher for azobenzene-alkanethiol functionalized gold nanoparticle (0.024 h^{-1}) than for simple azobenzene (0.010 h^{-1}).

Both *trans*→*cis* photochemical isomerization rate and *cis*→*trans* thermal isomerization rate become accelerate when azobenzene is anchored on metal surface. The understanding for this acceleration of isomerization in azobenzene-alkanethiol functionalized gold nanoparticle needs further work.

In summary, gold nanoparticle modified with photoresponsive azobenzene-alkanethiol molecules has been prepared and its photoisomerization behavior has been studied. Azobenzene-modified gold nanoparticle carried out very efficient *trans*→*cis* photoisomerization on irradiation of 350 nm light similar to azobenzene and reached to the photostationary state within 180 s. After the dark incubation, slow thermal back reversion to *trans* form is completed within 5 days. Both *trans*→*cis* photochemical isomerization rate and *cis*→*trans* thermal isomerization rate become faster when azobenzene is anchored on metal surface.

Experimental Section

Synthesis. The synthetic procedure of azobenzene-

alkanethiol functionalized gold nanoparticle is shown in Figure 1. Williamson ether synthesis reaction of 4-hydroxyazobenzene and 1,7-dibromoheptane, thioesterification with potassium thioacetate, and subsequent base deprotection afforded $\text{PhN=NPh-O}(\text{CH}_2)_7\text{SH}$.

Synthesis of $\text{PhN=NPh-O}(\text{CH}_2)_7\text{Br}$ (AzB-Br): To a solution of 4-hydroxyazobenzene (AzB-OH, 1.0 g, 5 mmol) in deoxygenated EtOH (50 mL) was added a solution of KOH (10 mL, 0.5 M, 5 mmol) in deoxygenated EtOH. After refluxing the mixture for 30 min, a solution of 1,7-dibromoheptane (0.86 mL, 5 mmol) in deoxygenated EtOH (20 mL) was added dropwise for 30 min to the reaction mixture and the resulting solution was refluxed for an additional 5 hours. As the solution cooled, it became cloudy with a KBr precipitate. The reaction mixture was concentrated and extracted with benzene and diethyl ether. The combined organic extract was washed with water, dried over magnesium sulfate and filtered. The solvent was evaporated. The crude mixture was purified with silica gel column chromatography eluted with a 1:9 ether/hexane. An orange crystalline solid was isolated (0.65 g, yield 35%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.28-1.43 (m, 6H, $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{CH}_2\text{-Br}$), 1.74-1.83 (m, 4H, $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{CH}_2\text{-Br}$), 3.36 (t, 2H, $J = 6.4 \text{ Hz}$, $-\text{O}(\text{CH}_2)_6\text{CH}_2\text{-Br}$), 3.98 (t, 2H, $J = 6.4 \text{ Hz}$, $-\text{OCH}_2(\text{CH}_2)_6\text{-Br}$), 6.93 (d, 2H, $J = 8.9 \text{ Hz}$, phenyl), 7.31 (d, 1H, $J = 7.1 \text{ Hz}$, phenyl), 7.43 (t, 2H, $J = 7.2, 7.7 \text{ Hz}$, phenyl), 7.80 (d, 2H, $J = 7.4 \text{ Hz}$, phenyl), 7.83 (d, 2H, $J = 8.9 \text{ Hz}$, phenyl) ppm. MS m/z 374 (M^+).

Synthesis of $\text{PhN=NPh-O}(\text{CH}_2)_7\text{SCOCH}_3$ (AzB-SCOCH₃): To a solution of $\text{PhN=NPh-O}(\text{CH}_2)_7\text{Br}$ (AzB-Br, 0.38 g, 1 mmol) in deoxygenated EtOH (50 mL) was added potassium thioacetate (0.12 g, 1.1 mmol). After refluxing the mixture for 24 hr, the solvent was evaporated. The crude mixture was purified with silica gel column chromatography eluted with a 1:9 ether/hexane. An orange crystalline solid was isolated (0.15 g, yield 41%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.15-1.20 (m, 8H, $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{-SCOCH}_3$), 1.75 (q, 2H, $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{-SCOCH}_3$), 2.26 (s, 3H, $-\text{SCOCH}_3$), 2.81 (t, 2H, $J = 7.3 \text{ Hz}$, $-\text{O}(\text{CH}_2)_6\text{CH}_2\text{-SCOCH}_3$), 3.96 (t, 2H, $J = 6.5 \text{ Hz}$, $-\text{OCH}_2\text{-}$), 6.93 (d, 2H, $J = 8.9 \text{ Hz}$, phenyl), 7.37 (d, 1H, $J = 7.0 \text{ Hz}$, phenyl), 7.43 (t, 2H, $J = 7.0, 7.4 \text{ Hz}$, phenyl), 7.81 (d, 2H, $J = 7.2 \text{ Hz}$, phenyl), 7.84 (d, 2H, $J = 8.9 \text{ Hz}$, phenyl) ppm. MS m/z 370 (M^+).

Synthesis of $\text{PhN=NPh-O}(\text{CH}_2)_7\text{SH}$ (AzB-SH): To a solution of $\text{PhN=NPh-O}(\text{CH}_2)_7\text{SCOCH}_3$ (AzB-SCOCH₃, 0.11 g, 0.3 mmol) in deoxygenated EtOH (30 mL) was added a solution of KOH (0.7 mL, 0.5 M, 0.4 mmol) in deoxygenated EtOH. After stirring the mixture for 1 hr, a solution of NH_4Cl (1.5 mL, 1.0 M, 1.5 mmol) in deoxygenated water was added. The resulting solution was concentrated and extracted with diethyl ether. The ether solution was washed first with water and then with saturated aqueous NaCl solution, dried over magnesium sulfate and filtered. The solvent was evaporated. The crude mixture was purified with silica gel column chromatography eluted with a 1:9 ether/hexane. An orange solid was isolated (0.04 g, yield 41%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.41-1.61 (m, 8H,

-OCH₂CH₂(CH₂)₄CH₂-SH), 1.76 (q, 2H, *J* = 7.4 Hz, -OCH₂-CH₂-), 2.47 (q, 2H, *J* = 7.3 Hz, -O(CH₂)₆CH₂-SH), 3.97 (t, 2H, *J* = 6.5 Hz, -OCH₂-), 6.93 (q, 2H, *J* = 6.9 Hz, phenyl), 7.38 (d, 1H, *J* = 6.5 Hz, phenyl), 7.43 (d, 2H, *J* = 7.4 Hz, phenyl), 7.81 (q, 2H, *J* = 7.9 Hz, phenyl), 7.83-7.85 (q, 2H, *J* = 7.0 Hz, phenyl) ppm. MS *m/z* 328 (M⁺).

Preparation of azobenzene-capped gold nanoparticle (AzB-Au): A solution of HAuCl₄·3H₂O (0.53 g, 1.6 mmol) in water (40 mL) was mixed with a solution of tetraoctylammonium bromide (1.44 g, 2.6 mmol) in toluene (140 mL). The two-phase mixture was vigorously stirred until all the tetrachloroaurate was transferred into the organic layer and PhN=NPh-O(CH₂)₇SH (AzB-SH, 8.8 mg, 2.7 mmol) was added to the organic layer. A freshly prepared solution of sodium borohydride (2.8 g, 75 mmol) in water (140 mL) was slowly added with vigorous stirring. After the further stirring for 3 hrs, the organic layer was separated and the solution was filtered and washed with acetonitrile. A dark brown solid was obtained (0.16 g).

Spectroscopic measurements. ¹H NMR spectra were measured on a 400 MHz Bruker Avance 400 NMR spectrometer in chloroform-*d*. Mass spectra were obtained on Micro-mass (UK) Platform II GC/LC-Mass Spectrometer. IR spectra were measured on Midac Prospect FT-IR spectrometer. TEM image was obtained on JEM-2010 (JEOL, 200 kV) TEM. Elemental analysis was accomplished with Leco CHNS-932. Absorption spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. Steady-state fluorescence spectra were recorded on a SLM-Aminco AB2 luminescence spectrophotometer. Photoirradiation was carried out in a Rayonet RPR 100 photochemical reactor equipped with Southern Ultraviolet 3500 Å lamps using pyrex reaction tube in dichloromethane solution. Reaction progress of photoisomerization on UV irradiation and reverse thermal isomerization in the dark was monitored by change of absorption spectra.

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