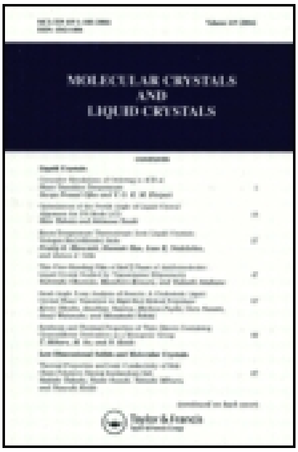

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Self-Organization of Gold Nanoparticles Coated with a Monolayer of Azobenzene Liquid Crystals

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A gold nanoparticle having a monolayer of azobenzene liquid crystal (LC) was synthesized. The size of the gold nanoparticle obtained was 4.7 nm in average diameter, and it was soluble in common non-polar organic solvents such as toluene and dichloromethane. We confirmed that the reversible photochemical and thermal isomerization of the azobenzene could take place on the surface of the gold nanoparticles in analogy with free azobenzenes in solutions. Furthermore, a 1-dimensional self-organization of the nanoparticle was observed by transmission electron microscopy. However, a gold nanoparticle without LC molecules never showed such self-organization. Therefore, we conclude that the self-organization of the gold nanoparticle is based on the liquid crystallinity of the organic ligands attached on their surface.

Keywords Gold Nanoparticle; Liquid Crystal; Azobenzene; Self-Organization; Photochromism

1. Introduction

Recently, metal nanoparticles have been expected to be applicable to novel materials for electronics, photonics, and magnetic devices due to their unique properties based on quantum size effects [1, 2]. In terms of application, we need to control the spatial arrangement and distribution of the nanoparticles. To date, 1-dimensional, 2-dimensional or 3-dimensional arrangements of the various metal nanoparticles have been achieved by the "top-down" methods, such as nanolithography, template synthesis methods, and so on [1–5].

Liquid crystals (LCs) are one of the self-organized materials and show long-range order, cooperative effects, and anisotropic natures in optical and electrical properties. Therefore, the arrangements of the metal nanoparticles by means of the LCs have been also investigated, and the spontaneous arrangements of the nanoparticles have been accomplished by using a rod-like LC and discotic LC molecules [6–8].

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Since the LCs also show fluidity, we can easily control the phase structure of LCs as well as the direction of their molecular orientation by external stimuli such as an electric field and light. Here, we can expect that the spatial arrangement and distribution of the metal nanoparticles can be controlled with the external stimuli. In this study, therefore, we synthesized gold nanoparticles with azobenzene LC ligands on their surface.

Azobenzene LCs are photochromic compounds that show the reversible *trans-cis* photoisomerization by irradiation with light and are also known as a photoresponsive LCs [9]. It has been demonstrated that the LC phase structure, the direction of the molecular alignment and the distribution of the photoresponsive molecules in the LC phase can be controlled by the photochromic reaction of the azobenzene mesogens [9]. Hence, when the azobenzene LCs were introduced to gold nanoparticles, the 1-, 2- or 3-dimensional arrangements spontaneously appeared and we might also control those self-organized structure of the gold nanoparticles by light. In this article, we report a preparation and characterization of the gold nanoparticles covered with a monolayer of azobenzene LCs, and the self-organization behavior of gold nanoparticles is discussed.

2. Experimental

Materials

Structures of the gold nanoparticles and azobenzene liquid crystals are shown in Figure 1. We synthesized gold nanoparticles with azobenzene LCs and azobenzene model compounds to evaluate liquid crystallinity of the ligands. We introduce a thiol group to one end of azobenzene LCs to link them with gold nanoparticles through an Au–S covalent bond. The azobenzene compounds were synthesized and purified by the conventional method. The gold nanoparticles were synthesized through modification of the method reported by Brust *et al.* [10, 11] In this study, tetrachloroaurate (III) ion was reduced to Au(0) under the presence of surfactant (tetraoctylammonium bromide). The bare gold nanoparticles obtained by the reduction were treated with the corresponding azobenzene compounds having thiol group to

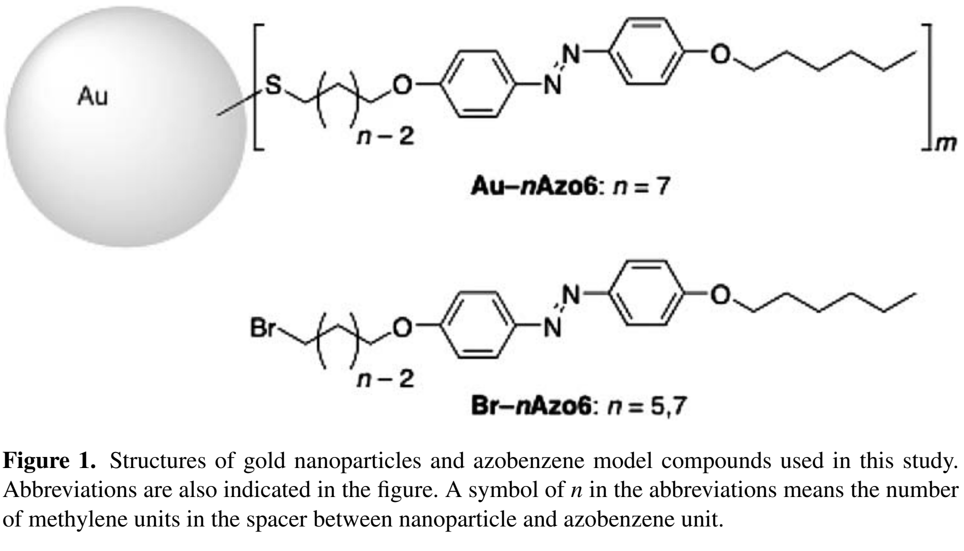

Figure 1. Structures of gold nanoparticles and azobenzene model compounds used in this study. Abbreviations are also indicated in the figure. A symbol of *n* in the abbreviations means the number of methylene units in the spacer between nanoparticle and azobenzene unit.

cover them with the azobenzene LCs. The formation of gold nanoparticles with azobenzene LC ligands was confirmed by NMR and transmission electron microscopy (TEM).

Characterization of the Azobenzene LCs

LC behavior was examined by polarizing microscopy (Olympus Model BX51) equipped with a hot-stage (Instec HCS302 hot-stage and mK1000 controller). Thermodynamic properties of LCs were determined by differential scanning calorimetery (DSC, Perkin Elmer Diamond DSC) at a heating and cooling rate of 1.0°C/min. At least three scans were performed for each sample to check reproducibility.

Single-crystal X-ray structure analyses were carried out at 296 (2) K, using a Rigaku AFC-5*R* diffractometer with graphite-monochromated Cu Kα radiation. The intensity data were corrected for Lorentz and polarization effects. Other details are summarized in the supplementary crystallographic data (CCDC 787170-787171). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Self-Organization of Gold Nanoparticles

Self-organization structures of the gold nanoparticles were observed by TEM. Gold nanoparticles were dissolved in an organic solvent at a concentration of $\sim 10^{-3}$ mol/L based on the azobenzene moiety and a small portion of this solution ($\sim 1\ \mu$L) was casted on a carbon-supported TEM grid. The solvent was slowly evaporated at ambient temperature, and then it was removed completely under vacuum. The resultant samples were observed with TEM (JEOL JEM-3100FEF, 300 kV).

3. Results and Discussion

LC Behavior of Azobenzenes

It was observed with a polarizing microscope that both azobenzene compounds used in this study showed LC phase. Phase sequences of the azobenzene LCs are summarized in Table 1. As listed in the table, **Br-5Azo6** showed monotropic N phase in a very narrow temperature range. On the other hand, **Br-7Azo6** exhibited enantiotropic S and N phases in much wider temperature range. The single-crystal X-ray structure analysis revealed that the molecule of **Br-5Azo6** is centrosymmetric with a disorder at the terminal of alkyl chains because the size of the bromine atom is very similar to that of the methyl group (Figure 2(a)).

Table 1. Phase sequence of azobenzene LCs

Sample	Phase Transition Temperature (°C)[a,b]
Br-5Azo6[c]	Cr 105 N 108 I
Br-6Azo6	Cr 53 S 106 N 112 I

[a]Abbreviations: Cr, crystalline; S, smectic; N, nematic; I, isotropic. [b]Determined in the cooling process. [c]The N phase was observed only in the cooling process, but this compound exhibited no LC phase in the heating process.

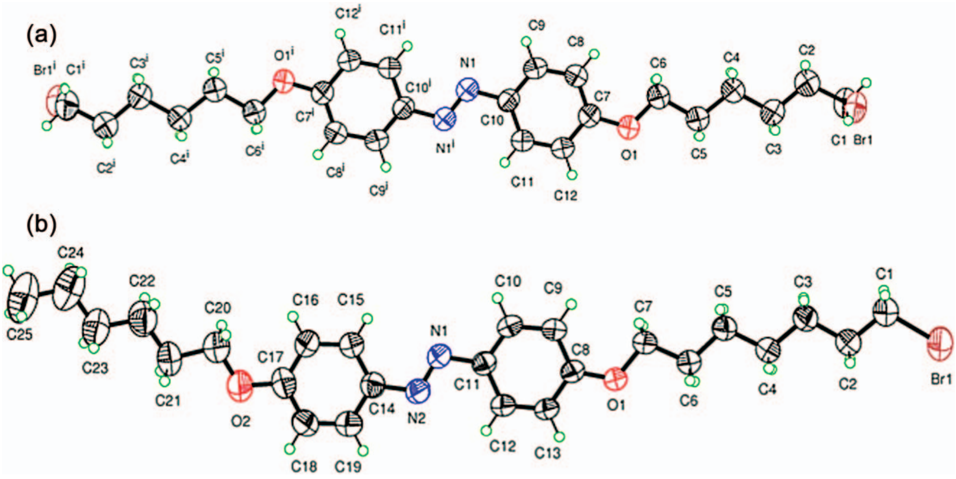

Figure 2. Molecular structures of azobenzene LCs. The superscript *i* of the atomic label refers the equivalent position related to the inversion center. Displacement ellipsoids are drawn at the 50% probability level. (a), **Br-5Azo6**; (b), **Br-7Azo6**.

Therefore, the crystalline phase in **Br-5Azo6** is stable and it shows high melting point. It can be considered that in **Br-5Azo6** the monotropic N phase in the narrow temperature range results from the stability of the crystalline phase. However, the molecular structure of **Br-7Azo6** is asymmetric (Figure 2(b)), and the lack of the symmetry destabilizes the crystal structure in **Br-7Azo6**. In consequence of instability of the crystalline phase, the melting point became lower in **Br-7Azo6**. For this reason, we consider that **Br-7Azo6** shows the enantiotropic LC phases in the wide temperature range. From those results, we employed **Br-7Azo6** as the azobenzene LC ligand for the gold nanoparticle.

Characterization of the Gold Nanoparticles

The gold nanoparticle synthesized in this study was soluble in common organic solvents such as toluene and dichloromethane, but they are insoluble in polar solvents. We can determine the size of the gold nanoparticles in **Au-7Azo6** by TEM observation. Figure 3 shows the histogram of the diameter of **Au-7Azo6** obtained from the TEM image. The histogram indicates the unimodal distribution of the size of nanoparticles and the estimated average diameter was 4.7 nm.

Figure 4 shows the UV-Vis absorption spectra of **Au-7Azo6**. The absorption spectrum exhibited their absorption maxima at around 360 nm and at around 450 nm in the non-irradiated dichloromethane solution of **Au-7Azo6**, and those absorption bands are attributable to the π-π^* absorption and n-π^*absorption, respectively. In addition, a small broad absorption band also appeared at a wavelength of ~550 nm. It is known that nanometer-scale gold particles show the absorption band with absorption maximum of >500 nm, depending on the size of the particles, and this absorption band can be assigned to the surface plasmon resonance of the gold nanoparticles [1]. From this absorption band, therefore, the formation of the gold nanoparticles was also confirmed.

Irradiation of the solution of **Au-7Azo6** with UV light at 366 nm induced a significant decrease in the absorbance at the π–π^* band and increase in it at the n–π^* band. This clearly indicates that the *trans-cis* photoisomerization of the azobenzene moiety takes place even

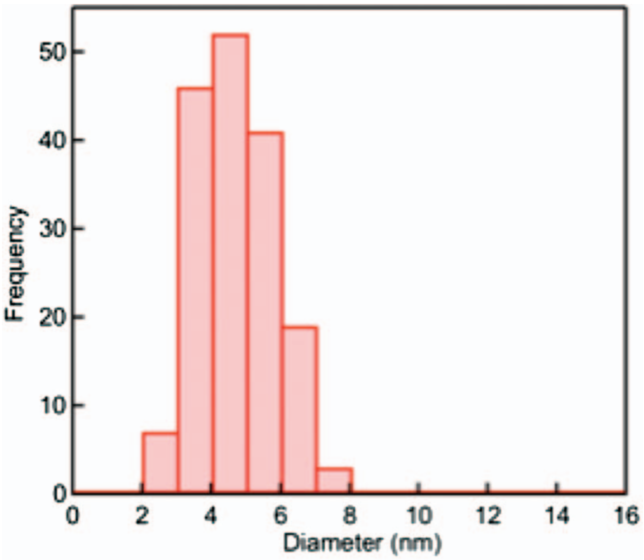

Figure 3. Histogram of the diameter of **Au-7Azo6**. The diameter was obtained by TEM.

on the surface of the gold nanoparticles. Furthermore, when the irradiated solution was kept in the dark at room temperature, the absorption spectrum recovered to the initial shape with showing the isosbestic points, meaning that the thermal *cis-trans* back isomerization occurred. Thus, we can conclude that the azobenzenes immobilized on the surface of the

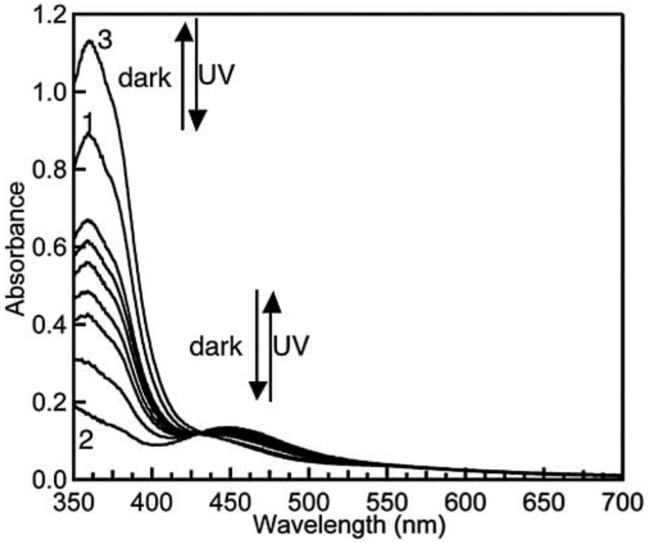

Figure 4. Absorption spectra of **Au-7Azo6** in dichloromethane. The concentration of the solution was 4.8 × 10^{-5} mol/L based on azobenzene units. 1: non-irradiated sample, 2: just after irradiation with UV light at 366 nm, 3: sample kept in the dark at room temperature for 64 h after irradiation. The non-irradiated sample contains significant amount of the *cis* isomer, because the sample was prepared under ordinary room light.

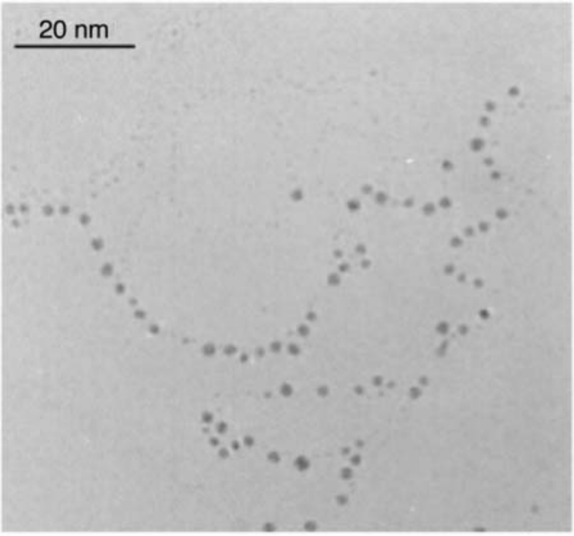

Figure 5. TEM image of **Au-7Azo6**. The TEM sample was prepared from toluene solution.

gold nanoparticles shows reversible photochromic reaction as well as free azobenzene molecules in solutions.

Self-Organization of Gold Nanoparticles

A TEM image of **Au-7Azo6** is shown in Figure 5. The TEM sample in the figure was prepared from a toluene solution. As shown in the figure, a 1-dimentional self-organization of the gold nanoparticles appeared. The nanoparticles are arranged in lines at the same spacing; the interparticle spacing was about 3 nm. In this case, the molecular length of the azobenzene LC ligand between thiol and the opposite methyl group is 2.9 nm, which was obtained from the structure optimized by the B3LYP/6-31G(d,p) level density functional theory (DFT) calculations [12]. Namely, the interparticle spacing in the self-organized structure is very similar to the molecular length of the azobenzene LC. Thus, we conclude that the nanoparticles are organized with the aid of azobenzene LC molecules attached on their surface.

We also observed the TEM images of a gold nanoparticle bearing 1-dodecanethiol instead of azobenzene LCs as a model of the gold nanoparticles without liquid-crystalline molecules. In this nanoparticle, we could never observe the liner 1-dimensional self-organization. Therefore, it may be concluded that the 1-dimensional organization observed in **Au-7Azo6** is due to the liquid crystallinity of the azobenzene molecules.

4. Conclusion

In this study, the photochromic azobenzene LCs was attached on the gold nanoparticles. It became clear that the same photo- and thermal isomerization behavior as the free azobenzenes in solutions was observed even on the surface of the gold nanoparticles. Spontaneous 1-dimensional organization of the nanoparticle with the azobenzene LC was observed with TEM, and the interparticle spacing in the organization was very close to the molecular length of the azobenzene LC. However, the gold nanoparticle without LC molecule never showed such self-organization. Those results suggest that the self-organization of the gold nanoparticle results from the liquid crystallinity of the ligand. From the results reported here, we can expect that the photochemical control of the self-organization structure of the gold nanoparticles may be realized based on the photochromic reaction of the azobenzene LC ligands. Further studies on the control of the self-organized structure of the nanoparticles by photoirradiation are in progress.

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