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Individual and Collective Modes of Surface Magnetoplasmon in Thiolate-Protected Silver Nanoparticles studied by MCD Spectroscopy

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**Energy dispersive X-ray (EDX) spectroscopic analyses for various Ag nanoparticle samples.**
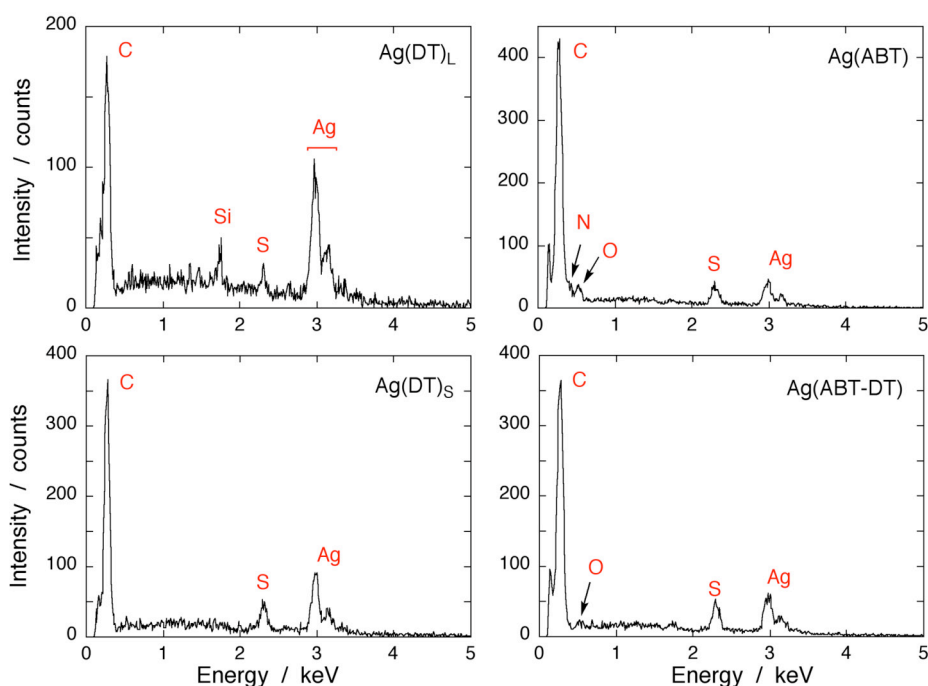
Fig. S1. Typical EDX spectra of Ag(DT)$_L$, Ag(DT)$_S$, Ag(ABT), and Ag(ABT-DT).

In order to examine whether the surface oxidation of the present Ag nanoparticle samples occurs or not, we carried out elemental analysis using energy dispersive X-ray (EDX) spectroscopy with excitation by an electron beam at 6.0 kV. Fig. S1 shows EDX spectra of various Ag nanoparticle samples. Note that the substrates we used were Si wafers that were

surface-cleaned by treating with HF solution to remove the oxide layers. In both $Ag(DT)_L$ and $Ag(DT)_S$, peaks of C, Ag, and S were only identified, indicating that surface oxidation is unlikely. On the other hand, for the Ag(ABT), peaks of C, N, O, S and Ag were detected. The element O comes from the ABT ligand itself having amide groups, since the atomic ratio of C/N/O/S quantitatively obtained is approximately 15.6/ 2.3/ 0.98/ 1 (the ratio is normalized to the sulfur content), which is close to the theoretical value of 15/ 3/ 1/ 1 based on its molecular formula. This means that surface oxidation is also unlikely. In the Ag(ABT-DT) sample, a very small amount of oxygen is found, which comes from the ABT moiety on the nanoparticle surface of mixed-monolayers. The element N was hard to detect due to its weak intensity of characteristic X-ray generation. On the basis of the experimentally obtained atomic ratio of C/O/S of 12.0/ 0.22/ 1, the real molar ratio of the surface mixed-monolayer of ABT/DT can be calculated as ~0.2 (1/4).

**MCD signals to normalized to absorbance for the $Ag(DT)_L$ and $Ag(DT)_S$ samples.**
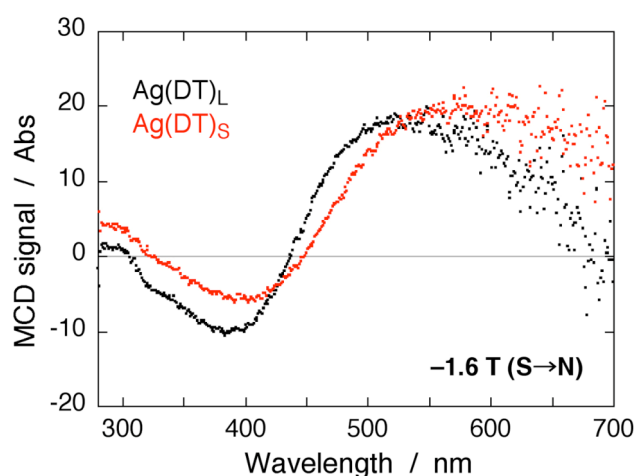
Fig. S2. Normalized MCD signals to the absorbance under an applied magnetic field of –1.6 T. Black and red dots indicate the data for $Ag(DT)_L$ and $Ag(DT)_S$, respectively.

We examined the MCD signals normalized to absorbance under an applied magnetic field of –1.6 T. Fig. S2 shows the results on the $Ag(DT)_L$ and $Ag(DT)_S$ samples. Black and red dots indicate the data for $Ag(DT)_L$ and $Ag(DT)_S$, respectively. We found that the normalized response of the high-energy portion only increased with an increase in the size of the nanoparticles, but that of the low-energy portion was almost constant.

**Deconvolution of absorption and MCD spectra of Ag(DT)$_S$ using three Lorentzian components.**

Typical fits of MCD as well as electronic absorption spectra of Ag(DT)$_S$ using three Lorentzian components (three-Lorentzian-band description) are shown in Fig. S3. We found a moderate agreement *only* for either MCD or absorption spectrum as represented in Fig. S3a or S3b, respectively, indicating that satisfactory fitting of the two spectra is difficult within the model. For the excellent agreement between the measure and calculated spectra, at least (one) additional Lorentzian component is requisite. In the four-band description, two components can be reasonably assigned to the surface magnetoplasmonic modes and other two are due to interband transitions originated from the imaginary part of the dielectric function of silver.
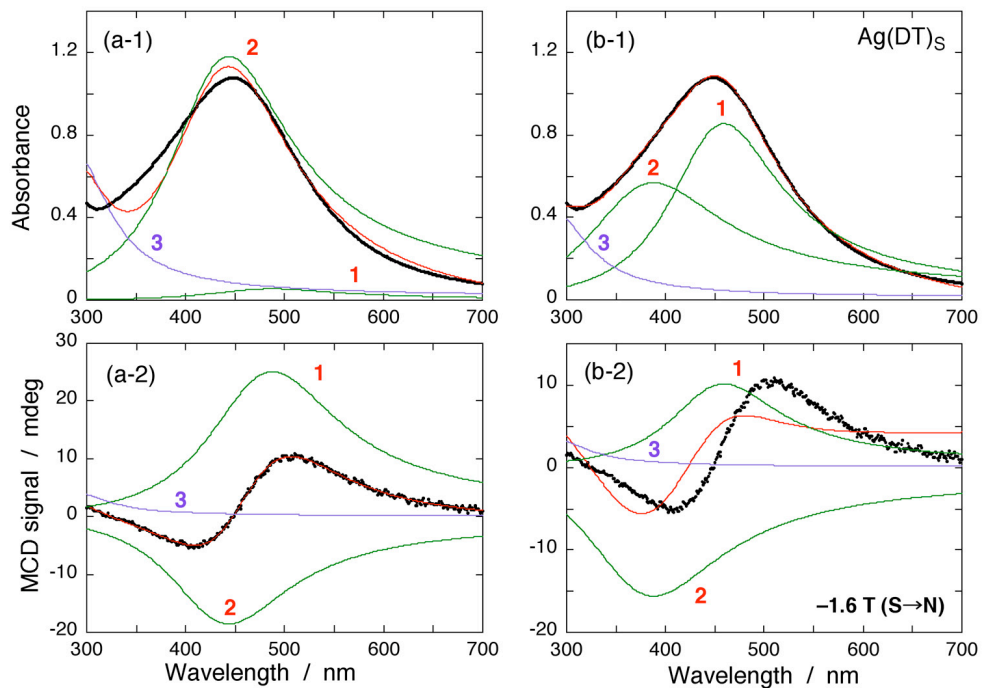
Fig. S3. Lorentzian fits of the electronic absorption and MCD spectra of Ag(DT)$_S$ using three components (three-Lorentzian-band description).

IR spectroscopic changes upon photoisomerization.

IR spectral analysis can elucidate the surface chemical properties of the Ag nanoparticle samples. We focused on vibrational information on the C–C stretching modes of benzene moieties and amide functions (C=O stretch and N–H bending) in the ligand that can be observed as characteristic peaks in the 1200–1700 cm^{-1} region. Fig. S4 shows the IR absorption spectra of Ag(ABT) before and after UV irradiation. Fig. S4b is the magnified spectra in the region of 1200–1700 cm^{-1}. Spectra were measured using a KBr pellet method. Strong bands at 1630 cm^{-1} (C=O stretching) and 1537 cm^{-1} (N-H bending) are assigned to amide I and II, respectively.[1] Peaks at 1603 and 1576 cm^{-1} are C–C stretching modes of benzene rings that are assigned as ν_{8a} and ν_{8b} based on the Wilson notation, respectively.[2] Two other C–C stretching modes of benzene rings at around 1490 cm^{-1} are assigned as ν_{19a} and ν_{19b}. The peak at around 1294 cm^{-1} is due to a coupling of vibrations of N–H bending and C–N stretching. We found that, upon UV-irradiation, the spectral changes were quite small, but with a close inspection, the ν_{8a} mode of benzene rings was significantly enhanced, indicating that environments of benzene rings in the ligands are modified upon UV-irradiation and thus the occurrence of photoisomerization of azobenzene moieties without decomposition.
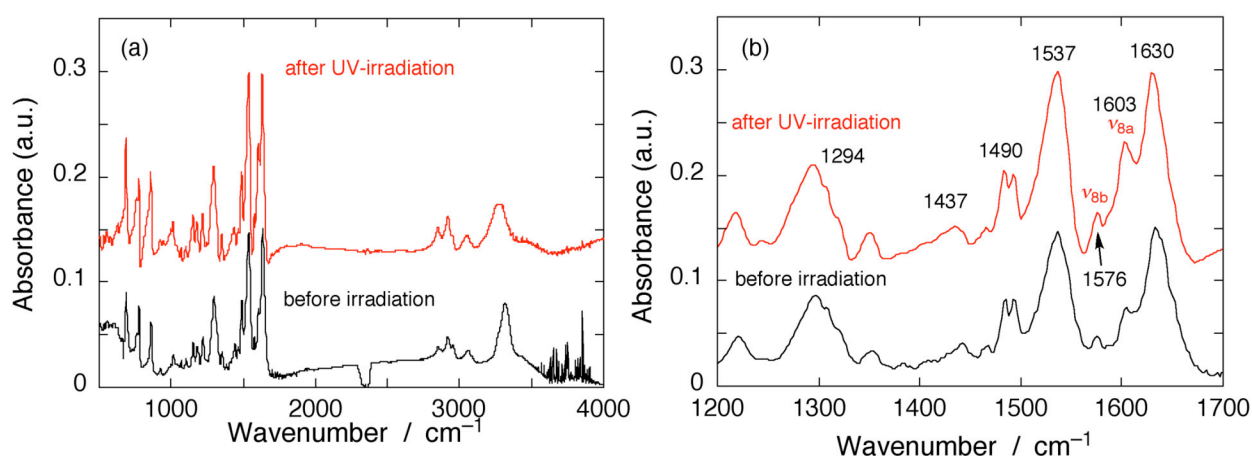
Fig. S4. IR absorption spectra of Ag(ABT) before and after UV-light irradiation.

Thermal *cis*-to-*trans* relaxation of azobenzene moieties on Ag(ABT) nanoparticle sample: Spectroscopic characterization.
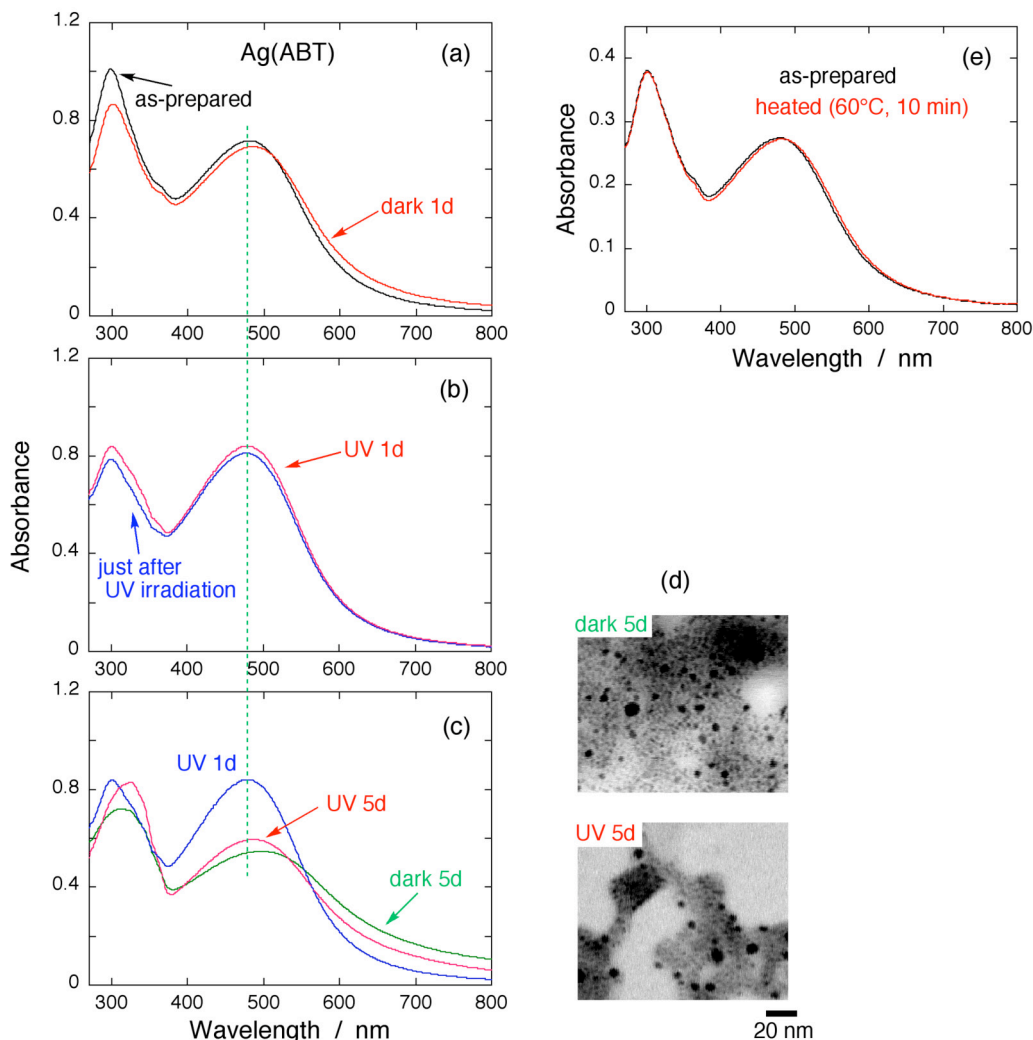

Fig. S5. (a)–(d) Absorption spectral changes of Ag nanoparticle samples as a function of storage time. The samples examined are Ag(ABT) in the presence and absence of UV-light irradiation (3 min). Then the samples are stored in dark at room temperature. (e) Heating effect on the absorption of Ag(ABT).

We examined thermal *cis*-to-*trans* back reaction of azobenzene in the Ag(ABT) sample. After UV-light (365 nm) irradiation of Ag(ABT) in DMF for 3 min, the sample was stored in dark for 1–5 days (Figs. S5b and S5c). For comparison, thermal stability of as-prepared Ag(ABT) (no UV irradiation) was also examined (Figs. S5a and S5c). In the absence of UV irradiation, the plasmonic peak became broad and exhibited a slight red shift in 1–5 days (see "dark 1d" and "dark 5d" in Figs. S5a and S5c, respectively), suggesting that further aggregation occurred

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between the Ag nanoparticles. The STEM image was in good agreement with this behavior. On the other hand, when the UV-irradiated Ag(ABT) sample was kept for 1–5 days (see "UV 1d" and "UV 5d" in Figs. S5b and S5c, respectively), similar spectral changes were observed in the plasmonic region; however, further nanoparticle aggregation was obviously slower than that occurred for the sample without photoisomerization. Note that this behavior is not substantially due to the thermal (or heating) effect since the sample heating (60°C, 10 min) only caused a slight red shift of the plasmonic peak (Fig. S5e; the examined specimen is different form that shown in Fig. S5a), which is in contrast to the behavior under UV irradiation as shown in Fig. 4b in the main text. Then, *cis*-form of ABT ligands on the Ag nanoparticles can make the aggregation rate reduce, which is probably due to a large free volume of the ligands. Note here that *cis*-to-*trans* conversion can be confirmed by the spectroscopic change at 350–300 nm.

UV-vis absorption spectra of Ag nanoparticles in the presence/absence of a magnetic field of 1.6T.
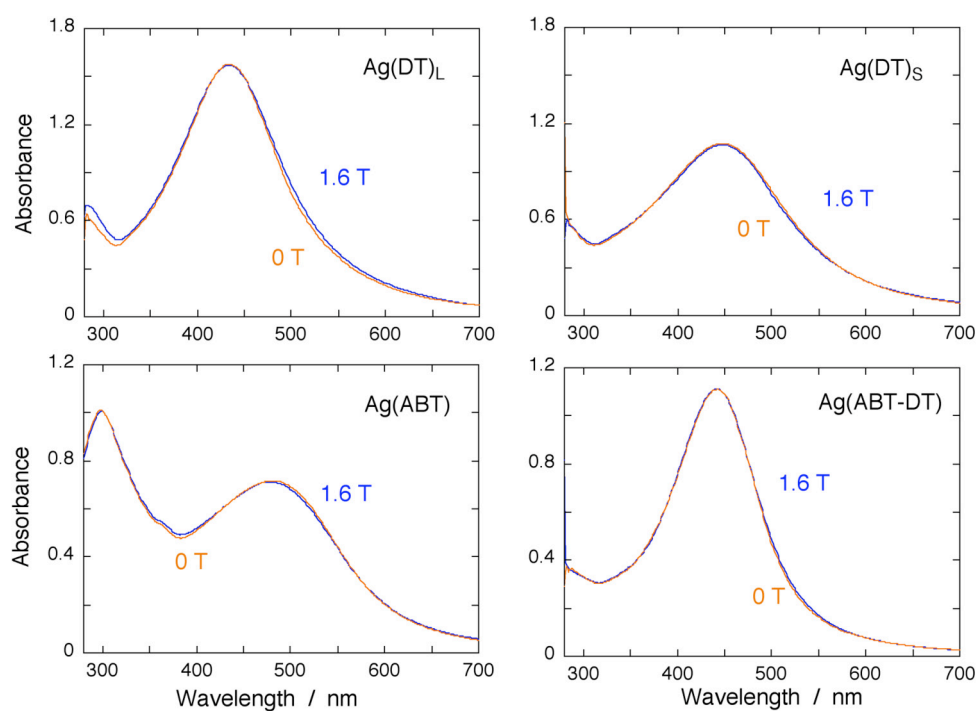
Fig. S6. Absorption spectra of various Ag nanoparticle samples in the presence/absence of magnetic field of 1.6 T.

Fig. S6 shows absorption spectra of $Ag(DT)_L$, $Ag(DT)_S$, Ag(ABT), and Ag(ABT-DT) nanoparticle samples in the presence/absence of a magnetic field of 1.6 T. They were basically very similar with each other.

References

1.   L. M. Siewierski, W. J. Brittain, S. Petrash, and M. D. Foster, *Langmuir*, 1996, *12*, 5838.

2.   K. Rajalingam, L. Hallmann, T. Strunskus, A. Bashir, C. Wöll and F. Tuczek, *Phys. Chem. Chem. Phys.*, 2010, *12*, 4390.