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Near-Infrared Continuous-Wave Light Driving a Two-Photon Photochromic Reaction with the Assistance of Localized Surface Plasmon

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Abstract: We demonstrate that a photochromic reaction can be driven by irradiation from a weak, near-infrared continuous-wave (NIR-CW) laser light. A two-photon ring-opening photochromic reaction of a diarylethene (DE) derivative can be induced by irradiation with a NIR-CW laser light (λ = 808 nm). An ultrathin polymer film doped with DE in its closed form was coated onto a gold-nanoparticle-integrated glass substrate. Upon irradiation of the sample with a CW laser at low fluence (0.1−4.0 W/cm^2), we could clearly observe bleaching of the DE (ring-opening reaction). Following the IR irradiation, the bleached absorption could be reversibly recovered by applying UV irradiation (ring-closing reaction). We verified that the yield of the photochromic ring-opening reaction of the DE was proportional to the square of the irradiation fluence. The origin of this NIR-CW-induced two-photon photochromic reaction is an "enhancing effect" that acts on the electromagnetic field (localized surface plasmon) of the gold nanoparticles. The DE interacts with the surface plasmon and receives energy from two photons, which excites it to a state from which the ring-opening reaction can be initiated.

Introduction

Multiphoton absorption, which was first predicted by Goppert-Mayer,[1] is a representative nonlinear optical process with respect to the intensity of the incident light. Multiphoton phenomena are quite important, not only in terms of fundamental photoscience but also for various potential applications involving nanofabrication using ultrafast laser pulses, ultra-high-density optical memory, ultra-high-resolution optical microscopy, energy up-conversion, and so on. The most common approach for inducing successive multiphoton absorption is to irradiate a material with short light pulses whose peak intensity (W/cm^2) is quite high. The precise control of multiphoton absorption has been also explored using a variety of light sources.[2] It has been accepted that normal continuous-wave (CW) light does not (in general) induce successive multiphoton absorption. A second approach for inducing multiphoton absorption is the development of a material or molecule that possesses a high cross-section of multiphoton absorption.[2,3]

A novel method for achieving multiphoton absorption is based on controlling the reaction field. A material that is capable of localizing light within itself would serve as a reaction field, which can be used to increase the cross-section for multiphoton absorption. For instance, Ye and Ishikawa et al. demonstrated that the two-photon fluorescence of a dye could be enhanced by a factor of >100 in the presence of one-dimensional photon crystals compared with its fluorescence in a solution.[4,5] We also reported that the two-photon fluorescence of a dye could be considerably enhanced in a microcavity (microsphere).[6] Both of these results are based on a light-confinement effect with high Q values.

In addition to these nano/micro materials (photon crystal and microspheres), nanosized particles of noble metals could be a third candidate for light-localizing materials due to surface plasmon effects.[7,8] When nanoparticles of a noble metal such as gold or silver are irradiated with light, a localized surface plasmon could be excited, and the electromagnetic field of the light would be strongly localized around the nanostructure of the metal.[7,8] Very recently, Ueno and Misawa et al. demonstrated the two-photon polymerization of a photoresist polymer (SU-8) on gold nanoblocks arranged regularly on a glass substrate by irradiation with an incoherent CW light (halogen lamp).[9] They concluded that the two-photon absorption of incoherent light by the resist was due to enhancement of the electromagnetic field of the incident light by surface plasmons localized in the nanogaps between adjacent gold nanoblocks. Other groups have also reported the enhancement of polymerization[10,11] and photochemical isomerization[12] around metal

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nanoparticles based on the surface plasmon of the particles. It is noteworthy here that the resonant one-photon plasmon absorption of Au nanoparticles has been applied to the photochemistry of biosystems by El-Sayed's group[13,14] and to photocatalytic reactions by other groups.[15,16]

Such plasmon-assisted two-photon absorption would be quite fruitful if the concept could be established and applied to various general photochemical processes such as photochromism, photocatalysis, and solar energy conversion. Indeed, if near-infrared (NIR) light could be used to drive a solar battery or a photocatalytic reaction, a new channel would be opened for the next generation of photochemical applications. In the work by Ueno et al., the occurrence of polymerization was not confirmed by chemical analysis but simply by scanning electron microscopy observations.[9] In order to establish the use of plasmon-assisted photochemistry, a more detailed experimental approach is required. Spectroscopic approaches and the dependence of photochemical yield on light intensity should be explored in more detail. In particular, the plasmon-assisted two-photon process should be further explored with the aim of gaining insight into representative well-defined photochemistry beyond the simple photopolymerization reaction.

In order to address this issue, we demonstrate a two-photon photochromic reaction induced by localized surface plasmons in the present study. The photochromic ring-opening reaction (bleaching reaction) of a diarylethene (DE) derivative was successfully induced by irradiation with NIR-CW light. DE is well-known as a representative photochromic compound that was developed by Irie's group.[17] DE undergoes reversible ring-opening and -closing reactions induced by visible and UV light irradiation, respectively (see Figure 1). It is noteworthy here that DE was designed as a molecule that is very resistant to thermal ring-opening and -closing reactions.[17−19] Here, we aimed to demonstrate a two-photon ring-opening reaction that could be induced by NIR-CW laser irradiation. For DE (as shown in Figure 1) it was concluded that the origin of the two-photon chemical reaction was enhancement of the electromagnetic field of the incident light induced by a localized surface plasmon of the gold nanoparticles.

Materials and Methods

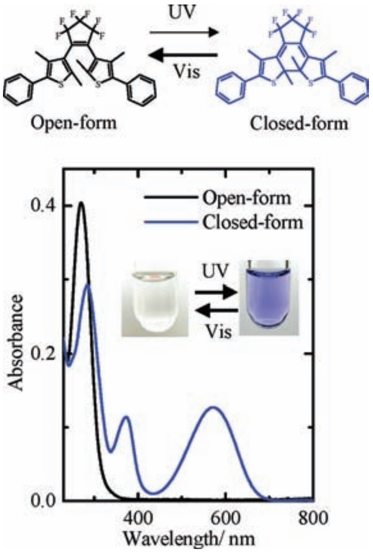

Figure 1. Molecular structures of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene (abbreviated here as diarylethene, DE). DE undergoes a reversible photochromic reaction as indicated. Absorption spectra of DE in open and closed forms are also displayed.

The essential details of the method that was used to integrate Au nanoparticles onto a glass surface are analogous to those reported in a previous study[20] and resemble those in works published by other groups.[21,22] The reported procedures were modified in the present study. Glass substrates (Matsunami Glass, S-0314) were soaked in an aqueous solution of SO_4/H_2O_2 (7:3, v/v) and dried to render their surfaces hydrophilic. The glass substrates were then soaked using an ethanol solution of 3-aminopropyltrimethoxysilane, washed with ethanol, and dried. The resulting glass substrates, modified with the silane coupling agent, were soaked in a colloidal solution of Au (BB International; diameter of Au nanoparticles = 20 nm) and dried to fix the Au nanoparticles on the substrate. The optical properties (absorption wavelength) of the Au-nanoparticle-integrated substrates were dependent on the soaking time (t_s) in the Au colloidal solution; the details are described later. The surface morphologies of the substrates were observed using atomic force microscopy (AFM; Seiko Instruments SPA400/SPI3800NM microscope). Surface-enhanced Raman scattering (SERS) spectra were measured with a confocal Raman microscope, as reported in our previous papers.[23−25]

1,2-Bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene (Figure 1, Tokyo Kasei, abbreviated as DE) and poly(methyl methacrylate) (PMMA, Aldrich, $M_w \approx 1.2 \times 10^5$) were dissolved in acetonitrile (Wako). The concentrations of DE and PMMA in the solution were 7.0×10^{-3} M and 1.0 wt %, respectively. The solution was then spin-coated (2 s for 400 rpm and then 30 s for 1200 rpm) onto one of the glass substrates described above to form a thin polymer film. The film thickness was 15 nm, which was less than the diameter of the Au nanoparticles. The concentration of DE was set to 1.3 mol/L in the PMMA film. Therefore, a large proportion of the DE in the film could interact with the Au nanoparticles. Also, a similar DE-doped film was coated onto a plain glass substrate (without Au nanoparticles), which was used as a reference. The DE (closed form)-doped PMMA film that was coated onto the substrate was irradiated using a CW laser diode light (Spectra Physics, CWA0400-SXD-808-30-E, wavelength = 808 nm) in a dark room. The 808-nm light was defocused in the irradiation, and the incident angle was normal to the surface. The photochemical ring-opening reaction of the DE was monitored by absorption spectroscopy using a Hitachi U-3300 spectrometer.

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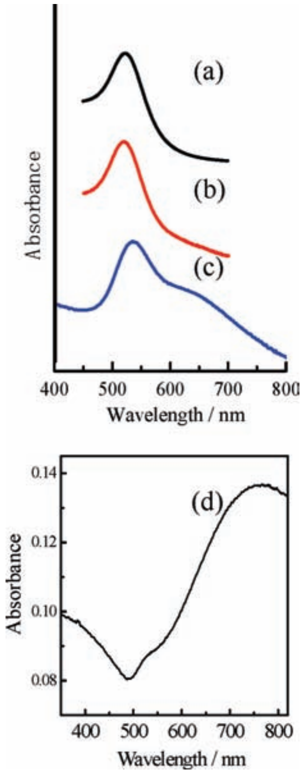

Figure 2. Absorption spectra of Au-nanoparticle-integrated substrates and the mother colloidal solution of Au nanoparticles: (a) mother colloidal solution, (b) type-I substrate, (c) type-II substrate, and (d) type-II substrate optimized for the present two-photon experiment.

Au-Nanoparticles-Integrated Substrates. Prior to describing the present work on CW-NIR-light-induced two-photon photochromism, it is necessary to characterize the substrates that were used for the reaction. We prepared two types of Au-nanoparticle-integrated substrates. Substrates of type-I, which were prepared with a t_s of several hours, exhibited a red coloration (similar to that of the mother Au colloidal solution), while type-II substrates, which were prepared with a t_s of about one day, were blue in color. Their respective absorption spectra are shown in Figure 2, together with that of the mother colloidal solution. The type-I substrate exhibited an absorption band due to the surface plasmon of the Au nanoparticles, which was also seen in the spectrum of the mother colloidal solution. This means that no interactions occur that are dependent on the Au nanoparticles with the type-I substrates. On the other hand, the type-II substrates exhibited a broad shoulder absorption band extending to the near-infrared region (600−900 nm), implying the presence of electronic interactions among the Au nanoparticles.

Corresponding to the absorption spectra, the surface morphologies of the substrates were obviously different from each other. On the type-I substrates (Figure 3a), the Au nanoparticles were arranged homogeneously on the glass surface: each nanoparticle could be seen distinctly in the AFM image. In contrast, Au nanoparticles were inhomogeneously aggregated on the type-II substrates (Figure 3b, corresponding to Figure 2c), suggesting interactions among the nanoparticles. While the size of Au nanoparticles in the mother colloidal solution was almost monodisperse, the size of Au nanoparticles is observed to be rather dispersed in the type-II substrate. This is because of formation of dimer-like, trimer-like, and oligomer-like aggregates that produce “nano-gaps” among adjacent nanoparticles around which electromagnetic fields of incident light would be much enhanced (details are described latter).

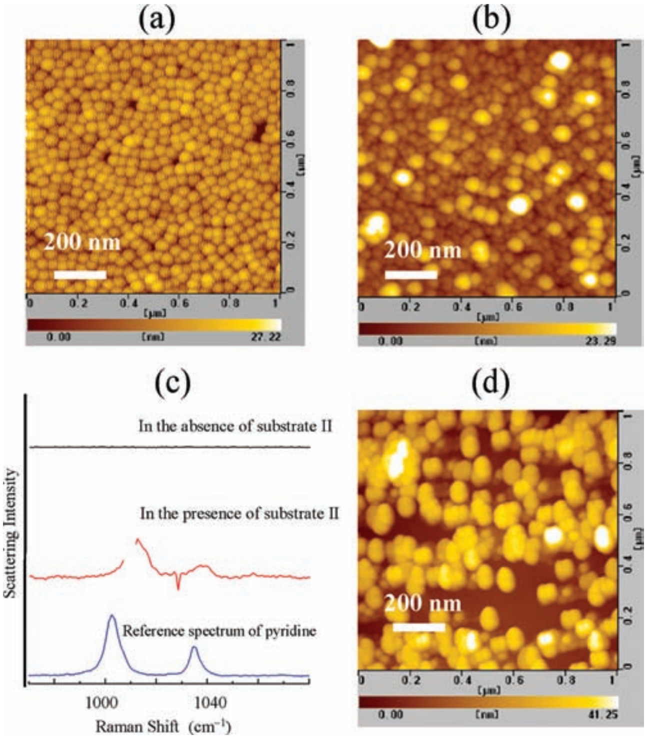

Figure 3. Representative AFM images of (a) type-I substrate and (b) type-II substrate. (c) SERS spectrum of pyridine (1.0 mM aqueous solution) in the presence of a type-II substrate. (d) A representative AFM image of an optimized type-II substrate.

The plasmon properties of a material should be reflected in the SERS spectra of molecules that are adsorbed onto the material. To examine the plasmon properties of the different substrate types, we conducted Raman spectroscopy on an aqueous solution of pyridine (1.0 mM) in the presence of type-I and type-II substrates, and the results are shown in Figure 3c. The reference Raman spectrum shown in Figure 3c (bottom spectrum) was obtained by measuring for neat pyridine without using any substrate. For the type-I and type-II substrates, aqueous pyridine solution (1.0 mM) was dropped onto the substrates, and then the Raman microspectroscopy was carried out for the samples. As a matter of course, it was quite difficult to detect any Raman scattering signal from the aqueous pyridine solution in a normal cell without the substrate (in the absence of the substrate, Figure 3c, top spectrum. When the surface plasmon band of the Au nanoparticles was excited at 532 nm, neither the type-I nor the type-II substrates yielded SERS signals that were characteristic of pyridine. By contrast, strong SERS signals characteristic of pyridine were clearly observed from the type-II substrate (Figure 3c, middle spectrum) when the broad shoulder band was excited ($\lambda = 633$ nm).

By integration of these results, we consider that the broad absorption band around 600−900 nm that was observed for the type-II substrate can be assigned to the absorption of a “gap mode” among the nanoparticles.[26,27] In the nanometer-scale gaps between the metal particles, strong dipole−dipole interactions are induced by light irradiation, leading to the absorption of incident light. Furthermore, upon light irradiation, the electromagnetic field is localized and is greatly enhanced at the nanogaps due to localized surface plasmons.[26,27] Such effects would be enhanced when the type-II substrates are excited at the gap-mode band. In Figure 2d, the gap-mode absorption spectrum for a type-II substrate prepared under optimized conditions is shown. Here, “optimized” means the largest absorption of gap-mode bands that were prepared in the

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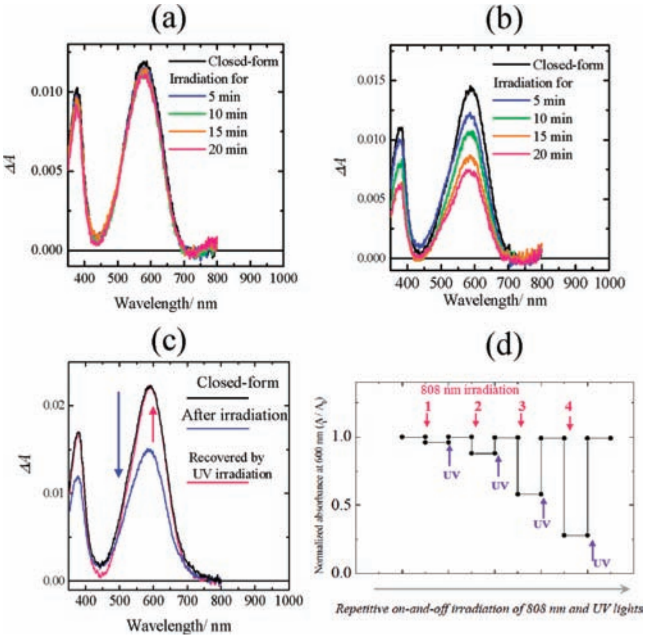

Figure 4. Effects of CW 808 LD light irradiation onto sample films (PMMA doped with DE) on (a) type-I substrate and (b) type-II substrate. Irradiation time is given in the figures. (c) Recovery reaction (reversible backward ring-closing reaction). Spectra in red, blue, and black correspond to the sample before irradiation, after 3 W/cm^2 irradiation (15 min) at 808 nm, and then after UV irradiation. (d) Trace of absorption change at 600 nm induced by repetitive on-and-off irradiation with 808 nm and UV lights. The absorption was normalized as A_t/A_0, where A_t is absorbance after irradiation and A_0 is the initial absorbance. The duration 808 nm irradiation was 15 min, and its light intensity at 808 nm was 1.0 W/cm^2 for **1**, 1.7 W/cm^2 for **2**, 3.0 W/cm^2 for **3**, and 4.0 W/cm^2 for **4**.

present study. The surface morphology (a representative AFM image) of the optimized substrate is displayed in Figure 3d, where dimer-like through oligomer-like aggregates of Au nanoparticles can be clearly realized, as previously suggested. Upon excitation of this strong gap-mode absorption, the incident electromagnetic field would be much enhanced. The type-II substrate offers two advantages: (i) it is easy to prepare using simple wet chemistry, and (ii) it is also possible to prepare a wide substrate with dimensions on a cm × cm scale, since the preparation procedures are based not on a complicated nanofabrication method such as electron beam lithography but on a simple wet chemistry technique. In the following study, we used the optimized type-II substrates for all the experiments.

Two-Photon Ring-Opening Reaction of DE Based on a Localized Plasmon. We examined the two-photon ring-opening reaction of DE (closed form) in PMMA coated on a plain glass substrate and on a type-II substrate by NIR-CW laser irradiation ($\lambda = 808$ nm), which can just excite the gap band. The results obtained using a plain glass substrate as a reference are shown in Figure 4a. The absorption spectra seen in the figure were obtained by subtraction of the spectrum of the substrate itself (Figure 2) from the observed spectrum of the sample at each irradiation time. Before irradiation, two bands can be observed around 470 and 580 nm, and these can be safely assigned to the absorption spectrum of the closed form of DE. Any decrease in the absorbance should correspond to the occurrence of the ring-opening reaction. Thermal degradation reaction such as oxidation is readily distinguishable by examining the recovery reaction (i.e., ring-closing reaction) upon UV light irradiation of the present 808-nm-iradiated samples. As can be seen in Figure 4a, the absorption spectrum was scarcely affected, even at high-power irradiation ($I_p = 3.0$ W/cm^2) at 808 nm. This is quite normal, since DE in its closed form has no absorption at all at 808 nm. No chemical reaction proceeded in films coated on a glass substrate upon 808 nm irradiation.

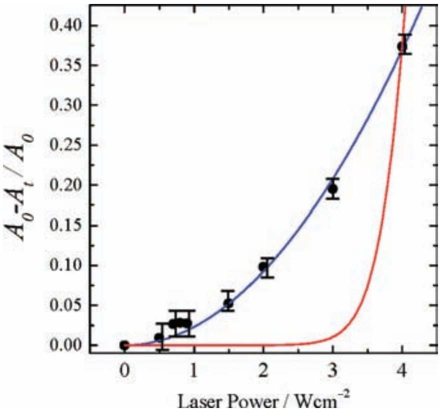

Figure 5. Reaction yields as a function of irradiation intensity. The blue curve is a “best fit” using a quadratic function for the observed data points. The red curve is a simulated result based on eq 1 (see text).

In Figure 4b, the results of irradiation experiments are also displayed for a sample using the type-II substrate. As can be clearly seen in the figure, the absorption band due to the closed form of DE (370 and 580 nm) obviously decreased with irradiation time ($\leq$15 min). After the absorbance had been decreased by the 808 nm irradiation, we confirmed that the band recovered to its starting value by irradiation with UV light (UV lamp, irradiation for several minutes), and this cycle could be achieved repetitively. As a representative example, in Figure 4c we display an absorption spectrum of DE in its closed form, formed by the recovery reaction upon UV irradiation. In Figure 4d, we show a trace of absorption change switched by repetitive on-and-off irradiation with 808 nm and UV light irradiation. As can be seen in the figure, absorption at 600 nm dropped upon 808 nm irradiation and recovered upon UV irradiation. This cycle proceeded repetitively, and it is obvious that the absorption drop and recovery are due to the ring-opening and ring-closing reactions, respectively. Namely, the present bleaching reaction (Figure 4b) is ascribed not to degradation but to the photochromic reaction induced by two-photon absorption.

These results indicate that 808 nm CW light irradiation can induce the ring-opening reaction of DE adjacent to the Au nanoparticles. This photochromic ring-opening reaction can even be induced when I_p is as weak as 0.1 W/cm^2, although it then takes several hours to realize the ring-opening reaction. It is noteworthy here that observation of the increase in the absorbance due to the product, DE in its open form ($\lambda < 350$ nm), would reinforce our conclusion of the occurrence of a two-photon ring-opening reaction. However, it was rather difficult to measure that wavelength region ($\lambda < 350$ nm) due to the strong absorption of Au itself.

Since DE has no significant absorption at 808 nm, the ring-opening reaction could be induced by two-photon absorption, assisted by a localized surface plasmon. The direct evidence for two-photon absorption is that the yield of the photochemical reaction is proportional to the square of the intensity of the excitation light. In Figure 5b, the yield of the ring-opening reaction (Figure 4 b) is plotted against irradiation power I_p. Here, the yield of the reaction is defined as $\Phi = (A_0 - A_t)/A_0$, where A_0 and A_t are the integrated absorbance of DE before irradiation (initial absorbance integrated from 450 to 750 nm) and that after 15 min of irradiation, respectively. As can be seen in the figure, the dependence on irradiation power (I_p) of the reaction yield (Φ) was well-fitted by a quadratic function (solid blue line in the figure), which verified that Φ was proportional to the square of I_p.

Another possible mechanism for the ring-opening reaction observed here is a photothermal effect, by which the ring-opening reaction would be accelerated by heat released upon gap-mode excitation at 808 nm. The thermal ring-opening reaction of DE was investigated in detail by Kobatake and Irie et al.[18,19] DE is a thermally stable compound, and the half-life of DE in the closed form at room temperature is $t_{1/2} = 3.1 \times 10^5$ years.[19] The rate constant k for the thermal ring-opening reaction of DE follows Arrhenius's relationship:

$$k(T) = A \exp(-E_a/RT(I_p)) \qquad (1)$$

where the pre-exponential factor is $A = 1.5 \times 10^{13}$ and the activation energy is $E_a = 149$ kJ/mol according to Kobatake et al.[19] In Figure 4b, the half-life of DE in the closed form was $t_{1/2} = 15$ min at $I_p = 3.0$ W/cm^2. On the assumption that this reaction proceeds *photothermally* (assuming that all of the absorbed photon energy is converted into heat), we can evaluate the yield of the thermal ring-opening reaction on the basis of eq 1 and the reported values. Here, $T(I_p)$ is the temperature of a type-II substrate elevated by laser irradiation, defined as $T(I_p) = T_{room} + cI_p$, where T_{room} is room temperature and c is a constant that can be obtained from the relationship whereby $t_{1/2} = 15$ min at $I_p = 3.0$ W/cm^2; $t_{1/2} = 15$ min corresponds to $T = 200$ °C at $I_p = 3.0$ W/cm^2. The simulated curve that predicts a laser power dependence of the reaction yield on the basis of a *photothermal* mechanism and eq 1 is also displayed in Figure 5 (solid red line). As can be clearly recognized in Figure 5, the simulated curve deviates significantly from the observed results. Thus, we can exclude any photothermal contribution from the present ring-opening reaction.

With respect to the two-photon photochromism of DE, Miyasaka et al. have reported that the ring-opening photochromic reactions of diarylethene derivatives are markedly accelerated by two-photon excitation in the visible region.[28,29] Two-photon absorption can break the selection rules on parity, as follows. The gerade−gerade and ungerade−ungerade optical transitions that are forbidden in one-photon absorption are allowed in two-photon absorption. Therefore, two-photon absorption might lead to a specific excited state that is hidden in one-photon absorption. The electronic structure of the specific state would possibly have a character that is different from that of the normal S_1 state of a molecule. According to the report by Miyasaka et al. concerning DE derivatives, such a specific character of the two-photon excited state should be favorable for ring-opening reactions.[28,29] Such effects would presumably contribute to the present two-photon ring-opening reaction of DE, enhanced by localized surface plasmons.

Concluding Remarks

We can safely conclude that the ring-opening reaction of DE in the closed form that was observed here is promoted by two-photon absorption due to an enhanced electric field (localized surface plasmon) induced by gap-mode excitation. The DE interacts with the surface plasmon and receives photon energy, which excites it to an S_1 state whose electronic structure might be expected to differ from that of the normal one-photon-produced S_1 state. The present work clearly demonstrates a plasmon-assisted two-photon chemical reaction. The merits of the present NIR-CW-induced two-photon photochromic reaction should be noted: (i) low photon cost because NIR-LED or NIR-LD are extensively available; (ii) mild irradiation with low-energy photon of NIR light, avoiding photodegradation; and (iii) efficient reaction from a one-photon-forbidden excited state that is peculiar to the two-photon absorption.

The application of such a plasmon-assisted two-photon process would have an impact on many relevant research fields, since it would enable us to utilize sunlight in the near-infrared region to promote photocatalytic reactions and solar energy conversion by designing processes involving plasmonic substrates.

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