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Linear Response of Multiphoton Reaction: Three-Photon Cycloreversion of Anthracene Biplanemer in Solution by Intense Femtosecond Laser Pulses

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The photocycloreversion of anthracene photodimers and biplanemer in solution was investigated by nonresonant intense femtosecond laser pulses. Cycloreversion of biplanemer showed a pseudolinear response to laser intensity whereas the formation of anthracene from photodimer was proportional to the cubic of laser intensity. The unusual intensity dependence of biplanemer was explained in terms of the sum of three-photon intramolecular cycloreversion and the recovery of reactant by a two-photon intramolecular cyclodimerization. The coexistence of high- and low-order multiphoton processes within the same laser pulse originated in the spatial distribution of the laser intensity. We observed white light emerging from the sample solution; however, the effect of solvated electrons was not observed in the present system. The saturation of both the photoreaction and white light due to a volume effect was observed at high intensity.

Introduction

Multiphoton chemistry is one of the most attractive reaction schemes in photochemistry. Generally speaking, two types of multiphoton excitations can generate reactive excited or continuum states. They are (1) sequential multiphoton absorption via intermediate states, which are initially formed by the first photon absorption, and (2) simultaneous multiphoton absorption without passing intermediate states. The former can be achieved by a single laser pulse or a sequence of multiple laser pulses, and the lifetime of the intermediate states should be sufficient to allow second photon absorption. The possible intermediate states are radicals,[1] electronically excited states such as S_1 and T_1,[2] and also vibrationally excited S_0.[3,4] The use of multiphoton chemistry enabled us to enhance and control the reaction yield,[5] and to explore the reaction from a higher excited state.[6] Resonant-enhanced multiphoton ionization combined with supersonic jet expansion is one of the successful techniques for isomer selective detection by multiphoton chemistry. In contrast, an intense single laser pulse is used for simultaneous multiphoton excitation. At moderate intensity, nonresonant two-photon absorption[7] is one of the most fundamental nonlinear processes induced by lasers, and two-photon fluorescence microscopy is now used as an indispensable technique in biology and medicine due to the high three-dimensional spatial resolution, as nonresonant laser pulses can penetrate bulk material and be tightly focused.

Nonresonant multiphoton and/or tunnel ionization have been the main focus of most femtosecond intense laser studies in the gas phase.[8] Multiply charged atomic ions with large kinetic energy are formed by Coulomb explosions of large organic molecules above 10^{16} W cm^{-2}.[9] As for the molecular ions, C_{60}^{12+} is the highest charged state ever observed,[10] and a quadruply charged state is the maximum charge state in the case of common hydrocarbons.[11] However, chemical reactions in response to the use of such high intensity laser have rarely been reported, which is partly due to the low density of molecules in the gas-phase experiments. Chemical reactions, and especially fusion reactions of high-density cations, have been observed for organic molecules in the solid phase around 10^{13} W cm^{-2}.[12] In contrast to gas-phase experiments, several nonlinear phenomena are important in condensed mediums due to the high density of molecules such as self-focusing by the Kerr effect, nonresonant multiphoton excitation, and ionization followed by white light generation and filamentation.[13–15] Several processes are expected to occur simultaneously in the condensed phase, and the first competing events are photochemical reaction and ionization. We investigated five- and possibly seven-photon fluorescence from organic molecules in solution using NIR femtosecond laser pulses.[16] A further increase in laser intensity results in the generation of white light, which is an index of self-focusing and solvent ionization. We have observed the reduction of europium ions by solvated electrons whenever white light appears.[17] Ionization of liquid followed by excited state formation due to the electron−hole recombination process has come to occupy an important position in high-intensity laser chemistry such as VUV laser[18] and X-ray generation.[19] However, there remain a number of questions that need to be answered in the intermediate intensity range, where there is a transition to both excited and continuum states. We examined well-known photocycloreversion of anthracene photodimers (An1, An2) and biplanemer (An3), as shown in Scheme 1, which has attracted much interest in relation to diabatic/adiabatic processes in photochemistry.[20–22] The characteristic feature of these reactions is that the absorption spectra of reactant and product are remarkably distinctive. We initially induced three-photon cycloreversion of An1, An2, and An3, and investigated the effects of backward cyclodimerization (2An → An1, 2An′ → An2, An4 → An3) on the total reaction yield. The competition between these two processes with a one-color and single-laser
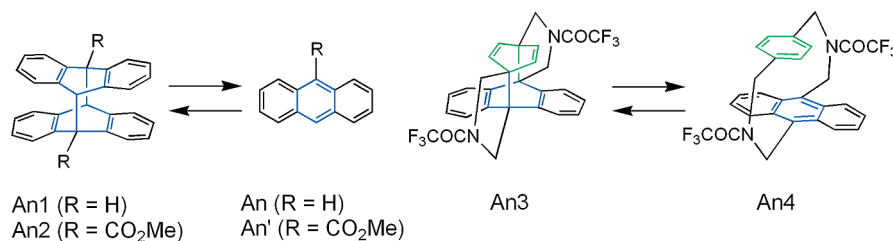
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SCHEME 1: Cycloreversion and Cyclodimerization of Anthracene Photodimer (left) and Biplanemer (right)

An1 (R = H)   An (R = H)   An3   An4
An2 (R = CO$_2$Me)   An' (R = CO$_2$Me)

pulse excitation resulted in the pseudolinear response of An4 formation against laser intensity. The equilibrium between the high- and low-order multiphoton process is one of the key issues in developing multiphoton chemical reactions in fluid solution. We observed the white light emerging from the sample solution; however, the effect of solvated electron was not observed in the present system. The saturation of both photoreaction and white light due to volume effect was observed at high intensity.

Experimental Section

The structures of 5,6,11,12-tetrahydro-5,12[1′,2′]:6,11[1″,2″]-dibenzenodibenzo[*a*,*e*]cyclooctene (An1, anthracene photodimer), 5,12[1′,2′]:6,11[1″,2″]-dibenzenodibenzo[*a*,*e*]cyclooctene-5,11(6H,12H)-dicarboxylic acid dimethyl ester (An2), 6,7,11,12-tetrahydro-6,11-bis(trifluoroacetyl)-5*H*,10*H*-4b,12a[1′,2′]-benzeno-7a,9a-ethenobenzo[3,4]cycloocta[1,2-*c*:5,6-*c*′]dipyrrole (An3), and 2,3,4,9,10,11-hexahydro-3,10-bis(trifluoroacetyl)-1,12[1′,2′]-benzeno-5,8-etheno-3,10-benzodiazacyclotetradecine (An4) are shown in Scheme 1. Anthracene (An, Nacalai, zone refined) was used as received. 9-Anthracenecarboxylic acid methyl ester (An′) was prepared by esterification of 9-anthracenecarboxylic acid (Aldrich). An3 and An4 were synthesized as reported.[23] Methanol, dichloromethane, and acetonitrile (spectral grade, Nacalai) were used as received. Anthracene photodimer contains 0.11% (An1) and 0.03% (An2) of the corresponding anthracene, respectively.

The absorption spectra were measured with a Hitachi U-3500 spectrophotometer or a Shimadzu UV-3600 spectrophotometer. The steady-state fluorescence spectra were measured with Hitachi F-4500T and F-7000 spectrofluorometers. Instrumental response was corrected by rhodamine B in ethylene glycol. Multiphoton laser photolysis was performed by a 0.5 TW all-diode-laser-pumped Ti:sapphire laser system (Thales laser, alpha 100/XS, 100 Hz, >15 mJ, 800 nm). Pulse duration (40 fs) was measured by a single shot autocorrelator (Thales laser, TAIGA). The same optical elements, such as focusing lens, beam splitter, and neutral density filter, were placed in front of the autocorrelators to have the same group velocity dispersion. The laser energy was attenuated by the combination of a half-wave plate and plate polarizers. The laser energy was further attenuated by a reflection-type neutral density filter (Sigma Koki). A part of the laser beam was reflected by a beam splitter at a small incident angle and laser pulse energy was measured with an integrating sphere (Labsphere, Spectralon coating) and a calibrated Si pin-photodiode. The laser beam was focused onto anthracene photodimers (An1, An2) and biplanemer (An3) solution using a plano-convex quartz lens with a focusing length of 200 mm. Reactants (An1, An2, An3) in solution (200 μL) in a glass sample cell (ϕ = 5 mm, t = 0.42 mm) were stirred with magnetic stirrer during laser irradiation at a constant speed at 296 K. An1 (3.7 × 10^{-4} M) and An2 (2.2 × 10^{-4} M) dissolved in dichloromethane and An3 (1.2 × 10^{-4} M) dissolved in acetonitrile were photolyzed. Batch-type experiments were carried out in all experiments. The laser beam after the sample was collected by an integrating sphere (Labsphere, Spectralon coating), and the spectrum was measured with a fiber-coupled spectrometer (Ocean Optics, USB2000). The reactants do not have absorption above 300 nm; therefore, the amount of photoproduct (An, An′, An4) was quantitatively determined by measuring the fluorescence intensity by selective excitation of photoproducts by spectrofluorometer. Excitation wavelengths of 359 (An), 364 (An′), and 392 nm (An4) were used for the fluorescence measurements. The fluorescence intensity of the sample in the dark (control) was subtracted. Fluorescence intensities were linearly proportional to the concentration of An, An′, and An4 between 1 × 10^{-7} and 5 × 10^{-6} M, respectively. Backward cyclodimerizations were negligible during the fluorescence measurements.

Results and Discussion

Linear and Nonlinear Responses of Overall Multiphoton Photolysis. Multiphoton photolysis of An1, An2, and An3 was carried out with a 40-fs pulse centered at 800 nm. The amount of photoproduct (An, An′, An4) was determined by its fluorescence measured with a spectrofluorometer after irradiation of laser pulses. Figure 1a shows the fluorescence spectra of anthracene (An) before and after the laser irradiation (3 × 10^4 shots) onto An1 solution at different laser intensities. As stated in the Experimental Section, An1 contains 0.11% An (4.1 × 10^{-7} M An in 3.7 × 10^{-4} M An1). The photoproduct produced in a very tiny laser focus volume was diluted by stirring, allowing us to avoid a further complicated photoreaction. The total reaction yield was kept below 1%. The fluorescence spectral shapes after the laser pulse irradiation were identical and independent of the laser intensity. No byproduct was detected by the fluorescence measurements with excitation at other wavelengths. Figure 1b shows the time evolution of An formation from An1 at different laser intensities. The formation of An from An1 was linearly proportional to the number of laser pulses at any of the laser intensities examined. Although saturation of the photoreaction was not observed, we limited the exposure of An1 solution to laser pulses for 5 min (3 × 10^4 shots) to keep the reaction yield below 1% at the maximum laser intensity. Figure 1c shows the correlation between An concentrations after 3 × 10^4-shot exposure of An1 to laser pulses and the initial concentrations of An1 at different laser intensities. An formation was linearly dependent on the initial concentration of An1. On the basis of these findings, the linearity of anthracene formation with the irradiation time and the initial concentration of An1 was confirmed. Figure 2 shows the An yield produced from two different initial concentrations of An1 as a function of the laser intensity. As the laser intensity increased, the An yield increased steeply until reaching the saturation region. After the saturation region, it again increased gently. The observable range of the steep region is limited by both the detection limit
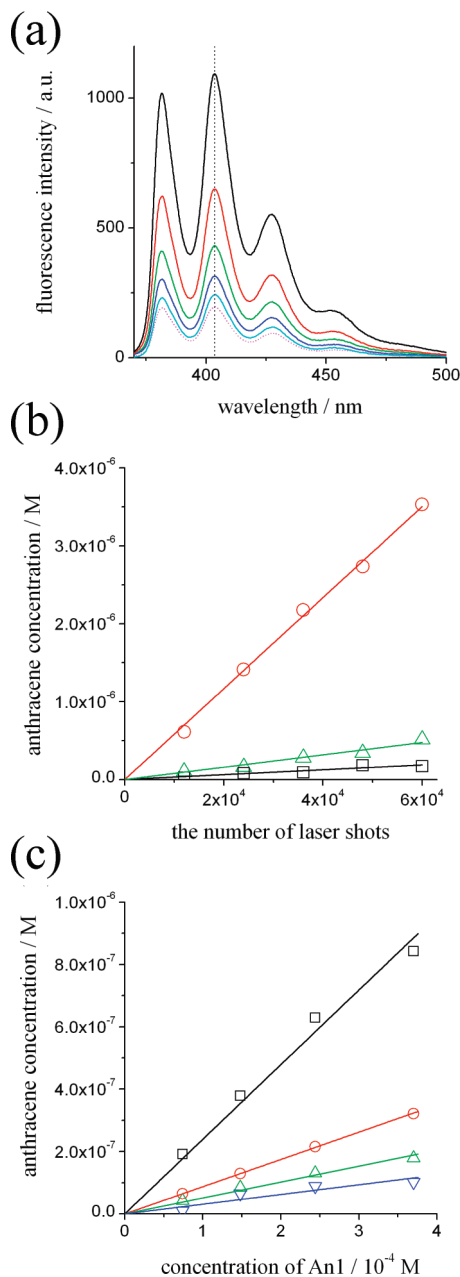
Cycloreversion of Anthracene Biplanemer in Solution

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Figure 1. (a) Fluorescence spectra of anthracene excited at 359 nm before (dotted line) and after (solid lines) the laser irradiation (3×10^4 pulses) onto An1 solution (3.7×10^{-4} M in dichloromethane). Laser intensities from top to bottom are 25×10^{12}, 15×10^{12}, 9.0×10^{12}, 5.7×10^{12}, and 3.3×10^{12} W cm^{-2}, respectively. The vertical dotted line indicates the wavelength for the determination of anthracene concentration. (b) Time evolution of anthracene concentration produced from An1 in dichloromethane (3.7×10^{-4} M). Anthracene concentration was determined by its fluorescence intensities. Laser intensities are 24×10^{12} (circle), 5.2×10^{12} (triangle), and 2.6×10^{12} W cm^{-2} (square), respectively. The solid lines are best fitted by the linear function. (c) The correlation between anthracene concentration after the exposure of An1 in dichloromethane to laser pulses (3×10^4 pulses) and the initial concentration of An1. Anthracene concentration was determined by its fluorescence intensities. Laser intensities are 12×10^{12} (square), 5.4×10^{12} (circle), 3.9×10^{12} (triangle), and 2.2×10^{12} W cm^{-2} (inverted triangle), respectively. The solid lines are best fitted by the linear function.

of An, as we kept total reaction yield below 1%, and the saturation. It is difficult to derive the slope of the plot; however, the slope of the steep region cannot be described by one and two. Therefore, we concluded that the steep region has a slope

of three; in other words, the amount of An was proportional to the cubic of the laser intensity below the saturation region. We cannot exclude the possibility of a higher order process, including the excitation of solvent, because the absorption of An1 and solvent is not well-separated. However, the contribution of solvent would be negligible because the product yield was linearly proportional to the initial concentration of An1, even at the maximum laser intensity. 9-Anthracenecarboxylic acid methyl ester (An′) was produced by the laser irradiation onto An2, and its yield showed the same tendency against the laser intensity. It should be noted that the slope of the steep region was independent of the concentration of An1, whereas different slopes (1.0 and 1.5) were obtained in the saturation region. Low initial concentrations of An1 (Figure 2a) resulted in a smaller slope. In panels a and b of Figure 2, the laser intensity dependencies of the transmitted laser intensities observed at 700 nm are also shown. As we increased the laser intensity, the spectral shape of the transmitted laser pulse broadened and was widely spread across the visible region, as shown in Figure 3. The broadened emission is called "white light". The shape of the white light was strongly dependent on the laser intensity, and was independent of the concentrations of An1. As the laser intensity increased, the intensity of white light increased steeply until reaching the saturation region. After the saturation region, it again increased gently. The intensity of white light was proportional to the cubic of the laser intensity below the saturation region. In contrast to An formation, the slopes of white light intensity above the saturation region were 1.5 and independent of the concentration of An1.

The yield of An4 from An3 was also determined by fluorescence measurements after the laser irradiation; however, it was linearly proportional to the laser intensity, as shown in Figure 2a. It was interesting that the saturation of product yield was only slightly observed in the case of An3 at the intensity where saturation was clearly observed for An1 (Figure 2) and An2. The discrepancy from the linear dependence was observed above 5×10^{12} to 6×10^{12} W cm^{-2}. The laser intensity dependencies of product formation indicated initially that photochemical reactions require three-photon absorption for An1 and An2, and one-photon absorption for An3. However, the latter result is unexpected because An3 is transparent at the laser wavelength utilized (800 nm). The absorption spectra of An3 and An4 are shown in Figure 4. It is obvious that three-photon absorption of the 800-nm pulse is necessary to access the lowest excited singlet (reactive) state of An3. In contrast, the photo-product An4 has absorption maxima at around 400 nm. Thus, we can excite An4 by two-photon absorption of the 800-nm pulse and reproduce An3. The coexistence of high- and low-order multiphoton processes can be explained in terms of the spatial distribution of the laser intensity. The three-photon process should occur at the center of the laser focus where the laser intensity is maximum, whereas the two-photon process can occur at the wing of the laser focus. Contrary to An1 and An2, cycloreversion and cyclodimerization occur intramolecu-larly in the case of An3 and An4, both of which have a bridged structure connected by alkyl chains that do not dissociate during photoreactions. An4 would react intramolecularly at the wing of the laser focus when the next laser pulse triggers a two-photon reaction through the low repetition rate of the laser pulses (100 Hz). Therefore, the observed pseudolinear response of intramolecular cycloreversion of An3 against laser intensity is understood to be the sum of three-photon forward intramolecular cycloreversion of An3 and two-photon backward intramolecular cyclodimerization of An4. The different laser intensity depend-
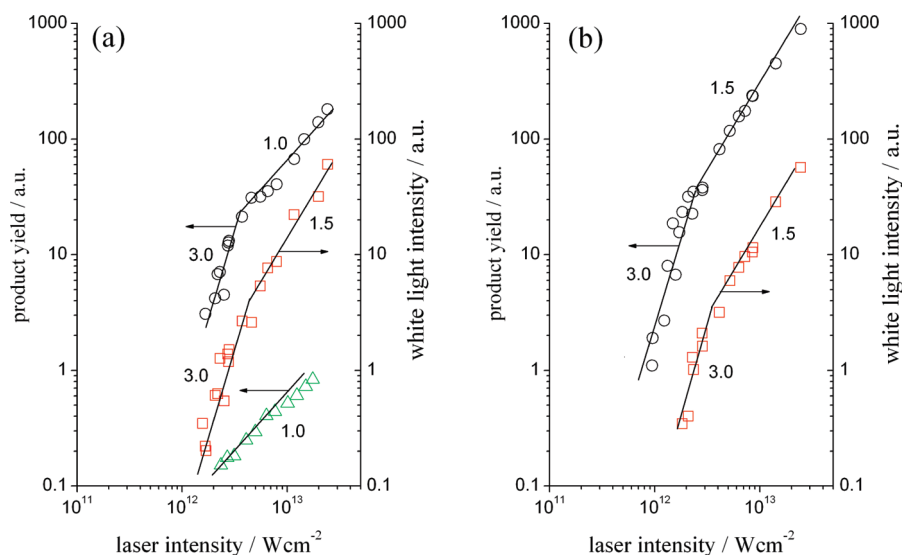
Figure 2. Laser-intensity dependencies of the An yields (circle) from An1 (a, 7.4×10^{-5} M; b, 3.7×10^{-4} M) and An4 yields (triangle) from An3 (1.2×10^{-4} M in acetonitrile) as determined by their fluorescence intensities. The white light (square) intensities observed at 700 nm are also plotted. The lines having slope 1.0, 1.5, and 3.0 are shown to guide the eyes.
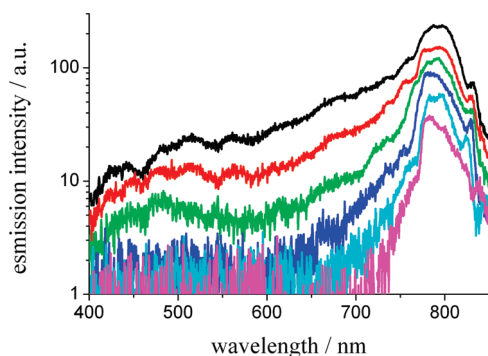

Figure 3. Emission spectra of the laser pulse after the transmitting glass cell with An1 solution in dichrolomethane. Laser intensities from top to bottom are 25×10^{12}, 14×10^{12}, 8.6×10^{12}, 5.2×10^{12}, 2.8×10^{12}, and 1.8×10^{12} W cm^{-2}, respectively.
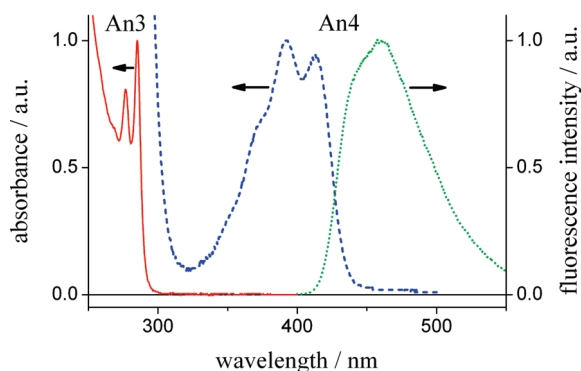

Figure 4. Absorption spectra of An3 (solid line, 1.2×10^{-4} M) and An4 (dashed line, 3.0×10^{-5} M), and the fluorescence spectrum of An4 (dotted line, 3.0×10^{-5} M) in acetonitrile. The spectra are normalized to unity for comparison.

encies between An1 and An3, as shown in Figure 2a, can be attributed to a backward reaction. Two-photon backward cyclodimerization of An (An′) would be negligible for several reasons, including the absorption coefficient, concentration, and reaction quantum yield. The small two-photon absorption cross section of anthracene was reported,[24] and three-photon fluorescence was observed in separate experiments when the An solution was solely excited by 800 nm. Supposing that two-

photon absorption of anthracene (An, An′) by a broad laser pulse at 800 nm is possible, the bimolecular reaction is almost negligible due to the low concentrations (below 4×10^{-6} M) of An (An′).[25] An (An′) is diffused into bulk from the center of the laser pulse and has very little chance of colliding with another anthracene, even though it is excited at the wing of the laser pulse. The cycloreversion is a one-way process in the case of An1 and An2 under our experimental conditions. Things to be emphasized are that the three-photon reaction controlled the overall reaction in all the molecules examined. The coexistence of high- and low-order multiphoton processes within the same laser pulse depending on the spatial distribution of the laser intensity was more clearly and visibly shown by the multiphoton reversible photochromic reaction of diaryl ethene fixed on the solid surface.[26] It is interesting to see the cycloreversion of An1 (An2) in the crystalline phase because the absorption spectrum of An shifts to a longer wavelength in the solid phase, and thus a two-photon reaction could be expected.

Saturation of the Three-Photon Reaction and White Light Generation. As the laser intensity increased, saturation of both the product yield and white light intensity was observed (Figure 2). In the case of photoreaction by ordinal steady-state light sources, saturation could be explained in several ways, including consumption of reactant and reabsorption and successive reaction by the products such as endoperoxide formation. An excimer of anthracenes, which absorbs 800-nm photons,[27] would be formed adiabatically after the cleavage of An1. However, the possibility of saturation due to further excitation of excimer followed by decomposition was excluded because the pulse duration of the laser is much shorter than the time scale of excimer formation (2.5 ns at 293 K[28]). In contrast to photoreaction by ordinal steady-state light sources, ionization of the solute or solvent and the volume effect would be key issues related to saturation under intense laser fields. Two possibilities, reabsorption and consumption, were excluded based on the experimental results shown in Figure 1. Thus, we will discuss the ionization and volume effect as the origin of saturation. To examine the ionization, we first determined the laser intensity of the ionization. The ionization potential of molecules in the liquid phase became lower than that in the gas phase due to the stabilization. As a result, the energy gap between the lowest
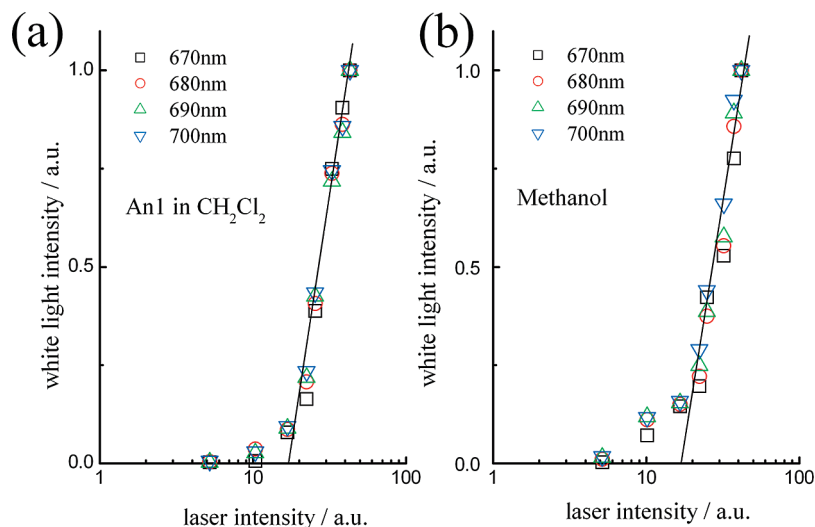
Figure 5. Normalized white light intensity from (a) An1 in dichloromethane and (b) methanol observed at different wavelengths as a function of laser intensity (arbitrary units). The white light intensities were monitored at several wavelengths indicated.

excited state and the continuum level narrowed. The competition between excited state formation and ionization was expected to be easier in both the liquid and solid[12] phases than in the gas phase. The ionization potentials of organic liquid have been studied by photoelectron spectroscopy and photoconductivity. The lowering of ionization potential compared with that measured in the gas phase is approximately 1 eV for a liquid surface by the former method,[29,30] and approximately 1.6 eV for nonpolar liquids by the latter method.[31] Significant lowering of the ionization potential (about 6 eV) of associated liquids such as water and alcohol has also been reported, and excess electron formation by the photoexcitation of methanol followed by proton transfer and ejection of electrons from excited methoxy ions has been proposed.[32] It is not easy to evaluate the laser intensity where ionization takes place in the case of solute compared with solvent, as the ionization of solvent accompanied by white light and filament has been well-studied.[13−15] We have observed the reduction of europium ion by solvated electrons generated by intense nonresonant femtosecond pulses.[17] The reduction of europium ion occurred when the white light was generated in methanol solution by 800-nm pulse irradiation. As the white light generation and reduction of europium ion was strongly correlated, the generation threshold of white light was found to be an index of solvent ionization. Once the ionization of solvent takes place, the filament is created by the propagation of femtosecond laser pulses in bulk transparent media. Filament formation is a result of the balance between self-focusing by the nonlinear refractive index and defocusing by plasma (electrons). White light is generated when the self-focusing is stopped by free-electron generation.[33,34] Figure 5 shows the laser-intensity dependencies of the white light intensity. The white light intensities were monitored at several wavelengths, and we determined the threshold intensity of white light generation as the point at which the emission intensity (linear scale), extrapolated back from the high-intensity linear portion of the curve, intersects the intensity axis (logarithmic scale). The threshold intensity of white light generation was independent of the observed wavelength and was not observed without sample solution under the same intensity condition. It should be noted that the variation of transmitted laser intensity at around the fundamental wavelength (800 nm) is complicated and therefore not suitable for evaluating the threshold intensity. The threshold intensities of white light generation and spectra were virtually the same among reactant solution and solvent.

We therefore used the white light generation threshold to evaluate the laser intensity. Although the threshold intensity of white light generation in condensed material has not been well-established, we used 1×10^{13} W cm^{-2} as estimated in methanol[35] for filament generation. The laser intensity evaluated by the white light generation threshold was 0.29 times smaller than that obtained by using the ideal focusing parameters. It should be noted that the above method could not always be applied for a liquid sample. Although ionization and free-electron generation occurred, white light emerging from a thin liquid layer (60 μm) of *n*-octane was not observed below 2×10^{14} W cm^{-2} by 400-nm pulse.[36] We used dichloromethane and acetonitrile as solvents; as such, ionization of the solute should occur at the white light generation threshold because the ionization potential of solute is lower than that of solvent. As a result, a variety of chemical reactions initiated by ionization of solute and solvent, and reduction by solvated electrons could occur. Cation radical formed by ionization followed by deprotonation presumably occurs. Another possible reaction is electron capture and protonation of anion radicals. Regardless, the contribution of solvent is a key issue in determining the final products. Direct excitation of ruthenium complex[37] by femtosecond pulses initiating oxidation, reduction, and solvated electron formation has been reported. The hydrogen abstraction from solvent by successive excitation of radicals has also been reported.[38]

We can determine the laser intensity by measuring the white light generation threshold, as mentioned above; however, we observed white light below the saturation intensity of product (Figure 2). In addition, as shown in Figure 2, the saturation intensities of the photoreaction and the white light were close. It is important to consider whether the origin of saturation of product formation and white light intensity is identical or not. We now discuss and interpret the origins of the saturation behavior by volume effect. The slopes of product formation above the saturation region depend on the concentration of reactant, whereas that of white light was independent of the concentration of reactant. For the case of white light generation, where solvent plays a role, the possible reason for the saturation was a volume effect. As we detected the white light by an integrating sphere, a full-volume experiment, white light generated at the whole focal region along the beam propagation axis was exposed to the detector; the white light above saturation intensity was expected to increase as the Gaussian focal volume

grew with the $I^{3/2}$ rate (I represents laser intensity).[39] In the case of ionization in the gas phase, an attempt was made to minimize this volume effect by extracting the ions through a slit smaller than the confocal length to restrict the volume results in the slope of the saturation region to less than 1.5.[40] In contrast to white light, the slope of product formation above the saturation region depended on the concentration of reactant. The smaller slope in the diluted condition could be explained in terms of a similar volume effect. If sufficient concentrations of reactant existed, the slope would be 1.5, as in the case of the full-volume experiments in the gas phase. However, the product yield per unit volume is small if the concentration of reactant is not sufficient. The similar saturation intensities between the photoreaction and the white light indicated that the photoreaction and white light generation suffered the same volume effect.

We have observed the reduction of europium ion by solvated electrons generated by intense nonresonant femtosecond pulses.[17] The reduction of europium ion occurred when the white light was generated in methanol solution by 800-nm pulse irradiation. Ionization of the solute or solvent should occur as the white light was generated in this study; however, definitive evidence for the reduction of product (An, An′, An3) was not found. We need a more appropriate system such as a Birch reduction to investigate the correlation between the photoreaction of organic molecules initiated by multiphoton absorption and reduction by solvated electrons accompanying white light. We are currently preparing such experiments. The chemical reaction initiated by intense femtosecond laser pulses, including photoreaction from the excited state, oxidation (ionization), and reduction by solvated electrons depending on the laser intensity, is quite interesting. Identification of the final products and a detailed study of the subsequent reaction will open up a new field of photochemical reactions in the white light region initiated by intense laser pulses.

Supporting Information Available: Plot of the laser intensity vs spatial distribution of laser pulse. This material is available free of charge via the Internet at http://pubs.acs.org.

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