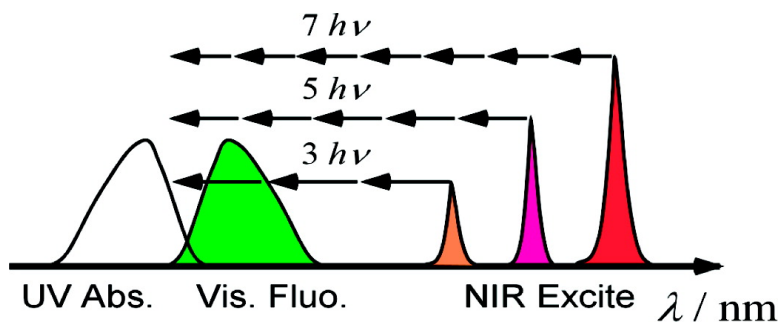


High-Order Multiphoton Fluorescence of Organic Molecules in Solution by Intense Femtosecond Laser Pulses

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High-Order Multiphoton Fluorescence of Organic Molecules in Solution by Intense Femtosecond Laser Pulses

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Multiphoton absorption is one of the most fundamental nonlinear processes induced by lasers. Two-photon¹ fluorescence microscopes² are now becoming indispensable tools in biology and medicine because of their high three-dimensional spatial resolution, selectivity, and sensitivity. Fluorescence,³ lasing,⁴ and fluorescence microscopes⁵ utilizing a four-photon absorption process have been reported; however, fluorescence emission after multiphoton absorption of organic molecules higher than five photons has been mentioned only once without any experimental details.⁶ No one knows how many photons can be absorbed to electronically excite molecules in a nonresonant way without passing intermediate states in solution. The highest-order absorption process will achieve the maximum penetration depth, the minimum confined volume, the highest damage threshold, the minimum influence of scattering, etc. These advantages will be very useful for imaging biological tissues, inspection of defects in semiconductors, and also for three-dimensional fabrication such as lithography and high-density optical memories. Thus, we tried to find the maximum order of the multiphoton process as a step toward developing an ultimate-order multiphoton detection method such as a microscope. We investigated what we believe to be the first case of five and possibly seven-photon fluorescence from organic molecules in solution by using NIR femtosecond laser pulses.

High intensity ultrafast laser enabled us to ionize atoms and molecules by multiphoton or tunneling mechanism in the gas phase.⁷ It is possible to generate excited states and also ionize molecules with a burst of infrared laser pulses using free electron lasers.⁸ However, the latter comprises thermal processes, the penetration depth is too shallow, and there is little selectivity. The accessible wavelengths for the multiphoton process by NIR light are limited by the absorption of solvent, solute, and cell. Figure 1 shows the absorption spectra of *p*-terphenyl and acetonitrile-*d*₃ (MeCN-*d*₃). The vertical arrows indicate the probable multiphoton transitions at the excitation wavelength. The energy and number of photons are represented by the length and number of arrows, respectively. The heights of the dotted lines represent the 0–0 transition energy of S₁ and S₂ levels. It is clear that the longest excitation wavelength free from solvent absorption is 2 μm, and we can expect a seven-photon process. Energetically, it is possible to select the order of multiphoton processes by choosing the excitation wavelength if there are no intermediate states. On the other hand, the excess energy is different for the different processes schematically depicted in Figure 1. Excess energy depends on the lowest energy of S₁ (3.95 eV), the photon energy, and the multiphoton order. When we used 400, 795, 1300, 1500, and 2000 nm for excitation, the excess energy was 2.2, 0.73, –0.14, 0.18, and 0.39 eV, respectively. The wide laser spectrum centered at 1300 nm allowed for the four-photon absorption process. Although huge differences in the excess energies were present, the emission spectra originating from 2, 3, 4, 5, and 7 photon absorption processes were identical to the ordinary one photon fluorescence spectrum obtained by mercury

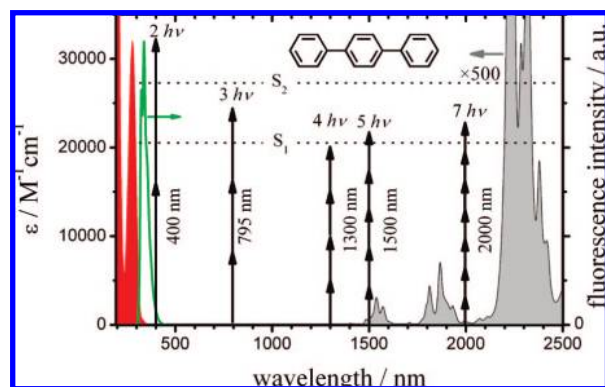


Figure 1. Absorption spectra of *p*-terphenyl (red) and MeCN-*d*₃ (gray). Vertical arrows indicate the excitation laser wavelengths (horizontal position) and energy (vertical scale). The 0–0 transition energies of the S₁ and S₂ levels are indicated by the dotted horizontal lines. The fluorescence spectrum of *p*-terphenyl (green) is also shown. Absorption of MeCN-*d*₃ above 1000 nm is multiplied by 500.

lamp irradiation. The absence of an excess energy effect was simply understood by the well-known Kasha's rule. In the case of two- and perhaps three-photon processes, the molecule would be excited to the S₂ state.

Definitive characterization of a simultaneous four-photon absorption process by the fringe-resolved autocorrelation method,⁹ and also a four-photon scanning microscope¹⁰ with a Cr:forsterite laser of 35 fs at 1.26 μm were reported by Matsuda et al. They clearly showed the absence of an intermediate state such as a triplet state during the four-photon absorption process of aromatic molecules such as anthracene. We confirmed the order of the multiphoton processes by laser intensity dependence experiments up to five-photon absorption as shown in Figure 2. Fluorescence intensities were proportional to the cubic, quartic, and quintic of laser energy depending on the wavelengths. Although the laser intensity dependence experiments were difficult, energy conservation requires that the seven photons emit fluorescence with 2000 nm pulse irradiation. We examined a variety of molecules such as biphenyl, *p*-terphenyl, 2,2'-dimethyl-*p*-terphenyl, *p*-quarterphenyl, anthracene, pyrene, diphenylamine, and *L*-tryptophan; all the molecules emitted multiphoton fluorescence. White light centered at 510 nm with a spectral width of 160 nm (fwhm) was observed above threshold energy. No photochemical reactions of solvent and solute were observed below the threshold of white light generation.

Although the electric-dipole transition dominated in the multiphoton process,¹¹ both even and odd order transitions were provided. The possibility of a five-photon absorption process of anthracene was indisputably denied under the consideration of parity,⁶ but it was observed by femtosecond pulses. This is because the parity selection rule is strict in the cases of atoms, while vibronic interaction allows molecules to couple two states by breaking their

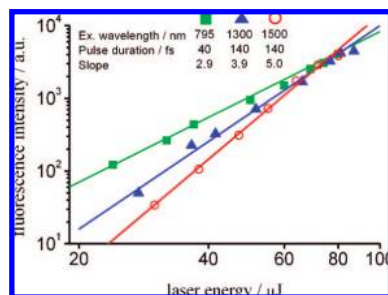


Figure 2. The correlation between fluorescence intensity (at 340 nm) of *p*-terphenyl in MeCN-*d*₃ and laser energy. The excitation wavelengths, pulse durations, and slopes of the log–log plot are indicated.

Table 1. Multiphoton Absorption Cross Section σ_n ($\text{cm}^{2n} \text{s}^{n-1} \text{ photon}^{1-n}$) of *p*-Terphenyl in MeCN-*d*₃

λ (nm) ^a	n^b	σ_n^c	σ_n^d
795	3	1.1×10^{-84}	3.7×10^{-80}
1300	4	2.6×10^{-116}	7.6×10^{-112}
1500	5	1.4×10^{-149}	3.8×10^{-144}

^a Excitation wavelength. ^b Order of multiphoton process. ^c Absorption cross section assuming the ideal focusing geometry. ^d Absorption cross section assuming the white light generation threshold as $1 \times 10^{13} \text{ W cm}^{-2}$.

symmetry. The correlation between excited-state symmetry and the photon order¹² is very interesting. In addition, the great enhancement of the multiphoton coupling of a pair of nearly degenerate upper excited states with the ground state (3-level system) were investigated.¹³ Excitation of molecules to broad vibrational levels because of the wide spectral width of femtosecond pulses may be the case. For many species, the multiphoton process, especially the transition to the continuum (ionization), is well described by considering their single-photon ionization cross section at the VUV region,¹⁴ but this method's application to transitions to the discrete levels has not been proved. The excited-state produced by electron–hole recombination may not contribute below the white light (filament) generation threshold, because filament formation is an index of solvent ionization; that is, the filaments are created by the balancing between self-focusing by nonlinear refractive index n_2 and defocusing by plasma (electrons).

We evaluated the multiphoton (3–5) absorption cross section of *p*-terphenyl by the transmittance measurements. Usually, ideal laser focus parameters are used for intensity determination in the cross-section evaluation for multiphoton absorption. However, the laser beam can be easily self-focused accompanied with pulse shape distortion when we use intense femtosecond laser pulses, especially in condensed media. The pulse shape distortion and focusing diameter in solution have not been accurately estimated yet because they differ by the penetration depth and intensity. Thus, we chose two ways to determine the laser intensity for cross-section evaluation: using an ideal focusing geometry including focusing length correction on wavelength or using the filamentation (white light generation¹⁵) threshold¹⁶ as an index of intensity. The filament created by the propagation of femtosecond laser pulses in bulk transparent media has become a subject of considerable interest. Though the threshold intensity of filament generation in condensed material has not been well determined, we used $1 \times 10^{13} \text{ W cm}^{-2}$ as estimated in methanol¹⁶ for the evaluation of the absorption cross sections. The results are summarized in Table 1. The results using

the latter method were about 4 orders of magnitude larger than that using the ideal focusing parameters. The intensity at the focus was estimated to be $10^{14} \text{ W cm}^{-2}$ using the ideal focusing parameters; however, many organic molecules even in the gas phase are ionized at the intensity of $10^{13} \text{ W cm}^{-2}$, and the ionization potential is smaller in solutions of even a few eV. These considerations suggest that the evaluation by an ideal focusing parameter has already failed and should be inspected. A four-photon cross section has rarely been reported, and the values evaluated under the ideal focusing assumption can be compared. The four-photon cross section in a $\text{cm}^8 \text{ s}^3 \text{ photon}^{-3}$ unit of ZnS, naphthalene crystal, anthracene crystal, and (7-benzothiazol-2-yl-9-didecylfluorene-2-yl)-diphenylamine in hexane was 2.0×10^{-111} ,¹⁷ 1.9×10^{-121} ,¹¹ 4.0×10^{-115} ,⁹ and 8.1×10^{-109} ,¹⁸ respectively. The four-photon cross sections obtained in this study were within the range of reported figures. It was surprising that the order of the obtained cross section decreased by about 10^{33} as the order of the multiphoton process increased. As the most important dye today, continuous efforts toward the improvement of the two-photon absorption cross section through modifications of the molecular structure are underway.¹⁹ Our results indicated that the efforts on two-photon absorption cross section improvement would also be valid for the increase in the higher-order absorption cross sections.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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