

Study of Two-Photon Absorption Spectral Property of a Novel Nonlinear Optical Chromophore Using Femtosecond Continuum

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The degenerate two-photon absorption (TPA) spectrum has been studied for a novel organic chromophore (AF389) that exhibits extremely high TPA cross-section values around the ~ 800 nm range in both nanosecond and femtosecond domains. To measure the direct degenerate TPA spectrum of AF389 in the femtosecond regime, we have developed a new technique that is based on the use of a single continuum-generation beam as an intense coherent white-light source for TPA excitation. The different spectral components of the input continuum beam are spatially dispersed and then pass the sample through different pathways so that nondegenerate TPA processes among different spectral components can be avoided. Our results show that the TPA spectrum of AF389 is different from the linear absorption spectrum on the scale of absorbing photon energy. There is a significant blue shift of the absorption peak position for the TPA spectrum with respect to the linear absorption spectrum, indicating that the transition pathways are different for the TPA and linear absorption processes.

1. Introduction

In recent years, multiphoton excitation related studies have generated a great deal of attention and interest in the research community. This trend is particularly enhanced by the recent progress in developing novel and efficient two-photon-absorption (TPA) active materials that have led to a series of new applications, such as TPA-based frequency upconversion lasing,¹ optical power limiting, reshaping and stabilization,² 3-D data storage,³ 3-D scanning microscopy,⁴ and 3-D optical circuiting and microfabrication.⁵

Most of recently developed two-photon absorbing materials are various organic chromophores in either the solution phase or doped-matrix solid phase and exhibit much larger TPA cross-section values than the common commercial dyes. However, the measurements of TPA cross-section values for these new compounds were mostly performed at either a single wavelength or few discrete wavelengths of laser radiation. For the purposes of molecular design and application considerations, it is necessary to know the cross-section value as a function of excitation wavelength in a wide spectral range. Usually, two approaches can be employed to reach this goal. The first is to use a pulsed and tunable laser source (such as dye laser, optical parametric generator (OPG), or Ti:sapphire laser) to measure the nonlinear transmissivity of tested samples as a function of the tunable wavelength.⁶ This method is very time consuming because of the slow spectral tuning process and the nature of multipoints measurement. For materials exhibiting two-photon excited fluorescence, an alternative approach is to measure TPA-induced fluorescence intensity as a function of excitation wavelength.⁷

The advantage of this technique is its higher sensitivity for detecting fluorescence signals and a much lower requirement for intensity levels of tunable laser sources. The disadvantage is that the final TPA cross-section spectrum can be extracted only with the assumption that the quantum yield of TPA-induced fluorescence as a function of excitation wavelength is known.

Very recently, a continuum-generation technique has been successfully used to measure the nondegenerate TPA spectra for organic chromophore solutions.⁸ In this work a pump–probe two-beam configuration was employed: a weaker white continuum light (450–750 nm) was employed as a probe beam along with a stronger 1210 nm laser beam to excite the nondegenerate TPA process in the sample medium. In this case, the most critical requirement is to ensure a synchronous arrival, at the sample position, of the monochromatic pump pulse and the probe pulses with different spectral components. It is difficult to meet this requirement because of frequency chirping taking place in continuum generation.

In this Letter we report a new technique to measure the direct degenerate TPA spectra, which is based on using a single intense continuum beam with no need for any spectral scanning or wavelength tuning mechanism. In this approach, a powerful continuum beam is spectrally dispersed by a prism or a grating and then focused into the sample. Since different spectral components of the continuum beam pass through different areas of the sample, the nondegenerate TPA processes among these different spectral components can be avoided. Furthermore, the frequency chirping effect among different spectral components of the continuum has no influence on our TPA spectral measurement.

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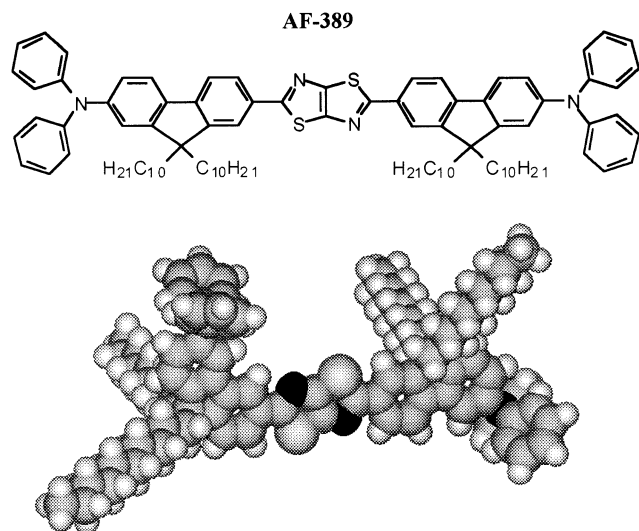


Figure 1. Chemical structure (upper) and three-dimensional model (lower) of chromophore AF-389.

2. Chromophore AF389 and Its Linear Optical Properties

Our early work on two-photon absorbing (TPA) molecules with the structural motif, A- π -core- π -A, where the electron accepting group (A) is 2-benzothiazolyl and the π -core is the electron-rich 3,4-dialkyloxythiophene or its dimer indicated that they had relatively low effective two-photon cross-sections in comparison with their asymmetric (A- π -D) analogues, for which diphenylamine or its derivatives served as the electron-donating (D) group.^{9,10} However, a number of symmetrical, quadrupolar molecules with D- π -core- π -D structural motif have been reported to exhibit impressively large TPA cross-sections at various wavelengths in the visible to near-IR regions.¹¹ The π -cores of these systems are typically highly polarizable oligo-enes, electron-rich oligo-phenylenevinyls, or π -electron-rich heterocyclic functions such as dithienothiophene or *N*-methylpyrrole. More recently, Huang et al. reported a A- π -core- π -A system with a very large femtosecond cross-section, where A is π -deficient oxadiazole and the π -core is a spiro-bifluorene.¹² As we are interested in the utilization of π -deficient heterocyclics as the essential building blocks for our AFX family of two-photon chromophores, we have designed and synthesized a D- π -core- π -D type chromophore with thiazolothiazole as the π -deficient core and the diphenylamino moieties as the electron-donating termini. This chromophore, {7-[5-(7-(diphenylamino)-9,9-didecylfluorene-2-yl)-1,3-thiazolo(5,4-*d*)-1,3-thiazole-2-yl]-9,9-didecylfluorene-2-yl}diphenylamine (designated as AF-389), exhibits the largest effective TPA cross-section among the AFX chromophores characterized to date. The chemical structure of AF-389 and its three-dimensional model are shown in Figure 1. It was synthesized via a double palladium-catalyzed amination¹³ of the precursor dibromide, 2,5-bis(7-bromo-9,9-didecylfluorene-2-yl)-1,3-thiazolo(5,4-*d*)-1,3-thiazole, with diphenylamine. The precursor dibromide was prepared from the condensation of commercially available dithiooxamide (rubeanic acid) and the previously reported 7-bromo-9,9-didecylfluorene-2-carbaldehyde.¹⁴ The details for the synthesis and characterization of AF-389 as well as the related benzobisthiazole- and bibenzothiazole-based AFX chromophores will be reported in a separate paper.

AF-389 is highly soluble in tetrahydrofuran (THF); therefore, its solution in THF with a higher concentration (0.02 M) is employed for TPA cross-section and spectral measurements. The linear absorption spectrum for a 1 cm path-length solution of

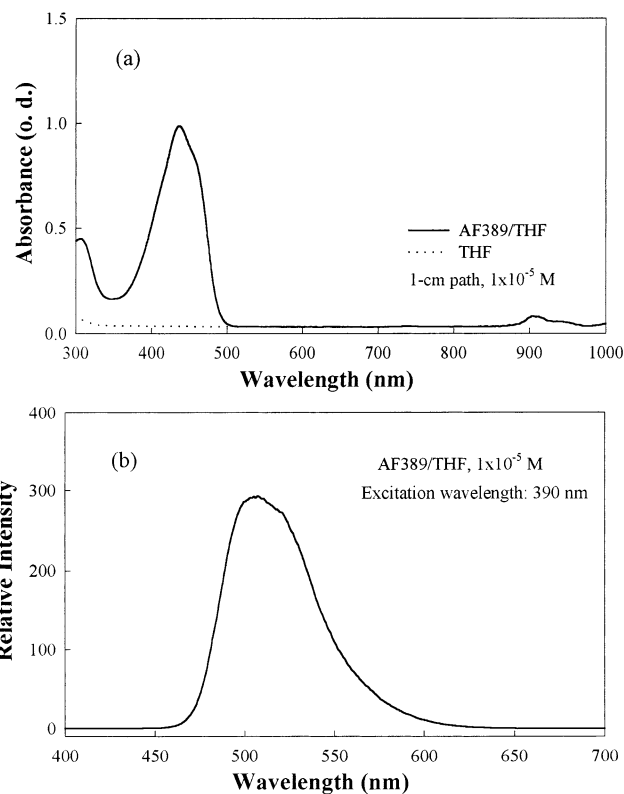


Figure 2. (a) Linear absorption spectra for AF-389 solution in THF (solid line) and for the pure solvent (THF) (dotted line). (b) Fluorescence emission spectrum of AF-389 solution in THF using one-photon excitation at wavelength of 390 nm.

AF389 in THF with low concentration (1×10^{-5} M) is shown in Figure 2a. One can see that the major linear absorption band is located at ~ 470 nm with a bandwidth of ~ 75 nm; the linear absorption in the spectral range from 550 to 1000 nm is practically nonexistent for the solute; the weak absorption around 900 nm is due to the solvent (THF). The latter feature makes the TPA spectral measurement in this range much simpler and easier. In other words, any intensity-dependent nonlinear absorption occurring in this spectral range can be readily measured on the basis of the procedure described in the following section. AF-389 solution in THF is highly fluorescent upon excitation with wavelengths that are located within the linear absorption band. As an example, the one-photon induced fluorescence spectrum of this solution, excited at 390 nm wavelength, is shown in Figure 2b, exhibiting a broad emission band in the 480–540 nm range.

3. TPA Cross-Section Measurement

It is observed in our experiment that a strong fluorescence emission can be seen from the AF-389 solution of high concentration excited by either a nanosecond- or a femtosecond-pulsed IR laser beam of wavelength around 800 nm. This observation implies that AF-389 is a chromophore strongly two-photon absorbing in this wavelength region. The TPA cross-section value of a sample solution can be experimentally determined for a given excitation wavelength by measuring its nonlinear transmissivity as a function of the input light intensity.¹⁰ The effective and intrinsic TPA cross-section values for AF-389 in THF are $\sigma_2 = 235(\pm 15\%) \times 10^{-20}$ cm⁴/GW measured by using ~ 800 nm and ~ 8 ns dye-laser pulses, and $\sigma_2 = 1(\pm 15\%) \times 10^{-20}$ cm⁴/GW measured by using ~ 790 nm and ~ 140 fs Ti:sapphire laser pulses, respectively.

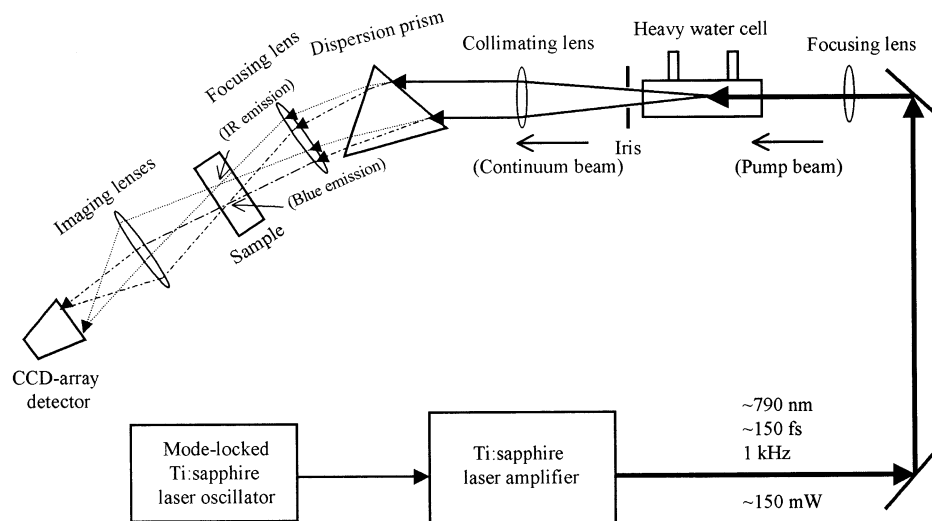


Figure 3. Experimental setup for degenerate TPA spectral measurement using a single intense continuum-generation beam.

4. TPA Spectrum Measurement

Our experimental setup for degenerate TPA spectrum measurement is shown in Figure 3. Heavy water was chosen as the transparent nonlinear medium to provide continuum generation because of its high efficiency and stability compared with other commonly used solvents or liquids.¹⁵ The pump source for continuum generation was a focused ultra-short pulsed laser beam provided by a Ti:sapphire laser oscillator/amplifier system with the following output parameters: pulse duration ~ 140 fs, wavelength ~ 790 nm, repetition rate 1 kHz, and available average power up to ~ 150 mW (or pulse energy up to $150 \mu\text{J}$). The output continuum-generation beam from the heavy-water cell was collimated first and passed through a dispersion prism, then focused via an $f = 10$ cm lens into the center of a 1 cm path quartz cuvette filled with either the AF-389/THF solution or pure THF solvent. With this particular arrangement, different spectral components of the continuum beam were spatially separated from each other at the sample position and only degenerate TPA from the same spectral component could take place. The intensity distribution of the dispersed continuum spectrum at the sample position can be further imaged through a camera lens set at the surface of a CCD array detector. By comparing the recorded continuum spectrum passing through a chromophore solution sample to that passing through the pure solvent sample, the attenuation of different spectral components due to the investigated chromophore can be readily determined. Since the relative spectral intensity distribution of the input continuum is known, the relative TPA cross-section value as a function of wavelength can be determined accordingly if the linear absorption in the measured spectral range is known or negligible. Furthermore, if we know the absolute value(s) of the TPA cross-section at one (or several) wavelength position(s), the whole measured TPA spectrum can be calibrated into an absolute scale of cross-section values.¹⁶

5. Final Result and Discussion

Figure 4 shows the obtained degenerate TPA spectral curve (solid line) of AF-389 solution in THF on an absolute scale of cross-section. The optical path length and concentration of the sample solution used for this measurement were 1 cm and 0.02 M, respectively. The measured spectral range is from 550 to 1000 nm. The long-wavelength end is limited by the spectral-response range of the used CCD detector, while the short wavelength end is limited by the relatively low intensity levels

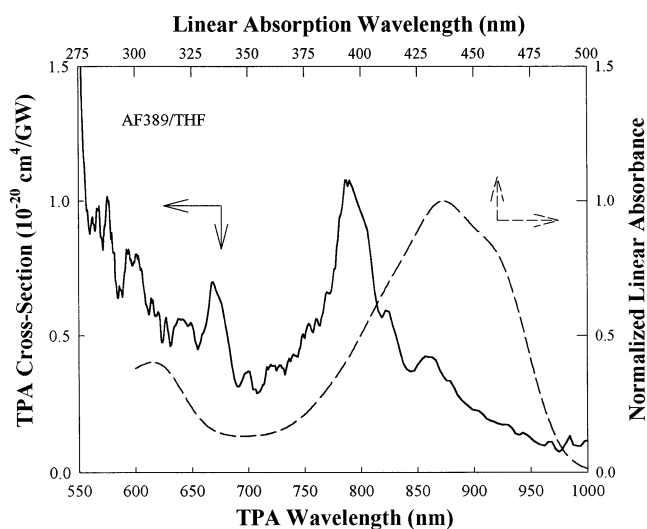


Figure 4. Absolute TPA spectrum (solid line) and normalized one-photon absorption spectrum (dashed line) of AF-389 solution in THF.

of the input continuum spectrum in this range, which causes a lower signal-to-noise ratio. For comparison, the normalized linear (one-photon) absorption spectrum is also shown in Figure 4 by a dashed-line curve.

Three salient features can be seen in Figure 4. The first is that for the AF-389 solution in THF there is a TPA spectral peak around the ~ 800 nm range. The second is that the two-photon absorption spectrum is not in coincidence with the one-photon absorption spectrum in the same scale of the absorbed photon energy. Finally, there is a remarkable blue shift for the TPA peak around 800 nm with respect to the one-photon absorption peak around 435 nm. The latter two features imply that the molecular absorptive-transition pathways for one- and two-photon excitation are essentially different for the chromophore system we studied. Thus, the two-photon excitation generates an excited state that is different from that generated by a single-photon excitation. Considering the symmetric (D- π -core- π -D) nature of the chromophore, such a result is not unexpected.

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