

Dendrimer molecules with record large two-photon absorption cross section

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We report what is to our knowledge a record high value for an intrinsic two-photon absorption (TPA) cross section, $\sigma_2 = 11 \times 10^{-47} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$, measured with femtosecond pulses in a new dendrimer molecule comprising 29 repeat units of 4,4'-bis(diphenylamino)stilbene chromophore. We measure the dependence of TPA on excitation wavelength in three consecutive generations of the dendrimer and show that the maximum σ_2 value increases faster than the total number of stilbene chromophores. This result indicates that it is possible to obtain even larger σ_2 values in higher generations of this dendrimer family. © 2001 Optical Society of America

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Two-photon absorption (TPA) is a third-order nonlinear optical process in which two photons are absorbed simultaneously, such that the energy of the molecule excitation is equal to the sum of the energies of the photons, $E = h\nu_1 + h\nu_2$. Because of the nonlinear dependence of absorption on illumination intensity, TPA may be used to increase the spatial storage density of optical memory^{1,2} or to improve the spatial resolution of lithographic microfabrication³ and scanning fluorescence microscopy.⁴ TPA may also be used for optical power limiting^{5,6} and photodynamic therapy with an improved depth of light penetration.⁷ Unfortunately, all the above-mentioned potential applications suffer from a drawback that a majority of known organic molecules (as well as most inorganic materials) have very small values of nonlinear absorption cross section, typically $\sigma_2 \sim 1 \text{ GM}$ (1 GM = $10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$). As a result, even with high-intensity pulsed laser illumination ($I \sim 10^9 \text{ W cm}^{-2}$), the probability of exciting a molecule by simultaneous absorption of two photons remains inefficiently small.

Recently, the applications of TPA received new emphasis because of the chemical synthesis of organic molecules with high σ_2 value, which is 10^2 – 10^3 times larger than that of conventional dyes.⁸ An increase of σ_2 value in new molecules has been achieved by extension of the π -conjugation length and by introduction of electron-donating (D) and (or) electron-accepting (A) groups at the chain termini and throughout the conjugation sequence. The highest value reported so far, to our knowledge, is $\sigma_2 \approx 4000 \text{ GM}$, which corresponds to D–A–D- and A–D–A-type structures.⁸ To facilitate practical applications will require new TPA molecules with an even larger nonlinear absorption cross section. One may achieve this goal by designing three-dimensional molecules called dendrimers, which comprise many repeating units of a TPA-active chromophore. In comparison with the linear-chain molecules, TPA dendrimers have several important advantages: (1) owing to the special treelike building principle of a dendritic structure, the size of a

dendrimer molecule can be increased by addition of successive generations of the same-type dendrons through a divergent methodology or by attachment of chromophore dendrons to a central core unit through a convergent methodology; (2) the resulting three-dimensional structure allows a very high packing density of chromophores per unit volume, with the number of chromophores increasing exponentially with dendrimer size; (3) dendrimers exhibit high photochemical and thermal stability along with good processibility, which allows preparation of thin polymer films, fibers, and bulk polymers doped with these monodisperse macromolecules; (4) dendrimers can be chemically modified to combine several functionalities. For example, the energy of photons absorbed in different branches of a dendritic structure can be funneled to a special reaction unit placed at the core of the molecule.^{9,10}

In this Letter we present intrinsic (femtosecond) σ_2 values for a new type of TPA-active dendrimer macromolecule built from a D– π –D-type chromophore, 4,4'-bis(diphenylamino)stilbene (DPAS).⁶ The chemical structure of the parent molecule and three generations of dendrimers is shown in Fig. 1. The parent molecule contains only one stilbene chromophore, whereas in the dendrimers the number of stilbene units increases almost exponentially with generation number: 5 for G-0, 13 for G-1, and 29 for G-2. Note that even higher generations are possible if one follows the same chemical iterative principle. Linear optical absorption and emission spectra, along with picosecond time-resolved emission kinetics of this new dendrimer family, were reported in our recent paper.¹¹ Here we investigate their nonlinear TPA properties by accurately following the TPA spectra of all the molecules and comparing their TPA cross sections at spectral maximum positions.

Our experimental setup comprised a Ti:sapphire femtosecond oscillator (Coherent MIRA 900) with 100–200-fs pulse duration and a 76-MHz repetition rate. We also used a regenerative Ti:sapphire amplifier with the same pulse duration (after compressor)

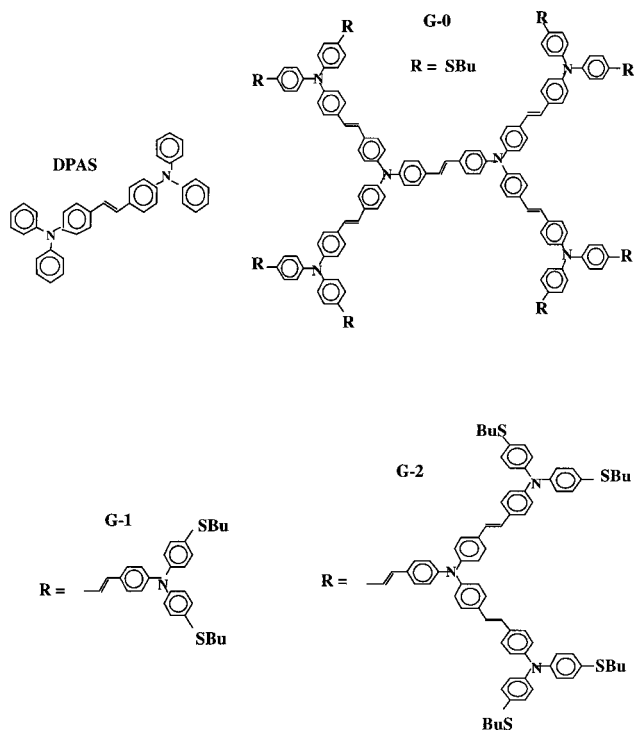


Fig. 1. Chemical structure of three generations of dendrimers, G-0, G-1, and G-2, and the DPAS parent chromophore molecule.

and a 1-kHz repetition rate. Fluorescence intensity was measured with a digital CCD camera (Xillix Microimager), and spectra were measured with a Jobin-Yvon TRIAX 550 spectrometer. For sample preparation, the molecules were dissolved in dichloromethane in a standard 2-mm-thick spectroscopic cell. A fresh solution was prepared for every experiment.

In our experiment we employed the fundamental wavelength of the femtosecond Ti:sapphire laser for two-photon excitation and the second harmonic of the same laser for one-photon excitation. In both cases, the beam was slightly focused with an $f = 500$ mm lens onto the sample through a pinhole placed in front of the lens. A stack of colored-glass filters cut off scattered laser light.

For the measurement of the relative TPA cross section we used a fluorescence method¹² in which the fluorescence signal intensities obtained from two-photon excitation of unknown and reference molecules at the same conditions are compared. The relative TPA cross

section of an unknown compound is then proportional to its fluorescence emission intensity divided by the fluorescence quantum yield.

We checked that, upon two-photon excitation, the fluorescence spectra of all the substances are the same as those obtained with one-photon excitation. Therefore the same electronic state is responsible for emission after either one- or two-photon excitation. For DPAS, the absolute value of the fluorescence quantum yield was reported to be 0.87.¹³ Fluorescence yields for all dendrimers are measured by a standard one-photon excitation procedure, relative to DPAS, and are presented in Table 1.

Figure 2 shows the dependence of the TPA cross section on laser wavelength for three dendrimer generations and for the parent DPAS molecule. To obtain these spectra we normalized the fluorescence signal to inverse pulse duration¹² at each wavelength of the Ti:sapphire femtosecond oscillator. Since the spectral peaks for all three dendrimers lie in the region 710–715 nm, we measured the fluorescence signal at 714 nm for all the molecules at equal conditions. Then the signal was normalized to the fluorescence quantum yield and the molar concentration of a particular molecule. We calculated absolute σ_2 values for the dendrimers by taking $\sigma_2 = 325$ GM as a reference, which was measured previously with picosecond pulses for the DPAS peak value.¹⁴ The peak TPA cross sections for our dendrimers are presented in Table 1.

The highest intrinsic σ_2 values measured previously with 100-fs excitation pulses of which we are aware, $\sigma_2 = 3700$ GM, belongs to a substituted bis(styryl)benzene.⁸ The cross section of our G-2 dendrimer, $\sigma_2 = 11 \times 10^3$ GM, is three times greater, thus presenting, to our best knowledge, the record high value for a monodisperse organic macromolecule. We emphasize here that, for nanosecond pulses, even higher effective cross sections were reported (see, for example, Ref. 15), but they included an absorption from the excited-state populated after the direct TPA process.¹⁶ Although we have also found some contribution of excited-state absorption when we use 76-MHz repetition-rate pulses from the oscillator, this absorption can be avoided by use of 1-kHz repetition-rate pulses from the amplifier. So the record value of σ_2 mentioned above, as well as all other σ_2 values presented in Table 1, corresponds to intrinsic TPA.

TPA maximum of G-1 and G-2 dendrimers in Fig. 2 is clearly redshifted with respect to DPAS. This

Table 1. One-Photon (Linear) and Two-Photon (TPA) Peak Positions (λ_{\max}), Absolute Fluorescence Quantum Yields (η), and Peak TPA Cross-Section Values of DPAS and the Dendrimers

Molecule	Number of Stilbenes	λ_{\max} (nm)		η	σ_2 (GM) ^a
		Linear	TPA		
DPAS	1	392	690 ^b	0.87	325 ^b
G-0	5	416	705 ± 10	0.52	2800
G-1	13	413	714 ± 2	0.81	4500
G-2	29	419	713 ± 2	0.55	11,000

^aThe error of measurement of σ_2 is 10%.

^bObtained from the data in Ref. 14.

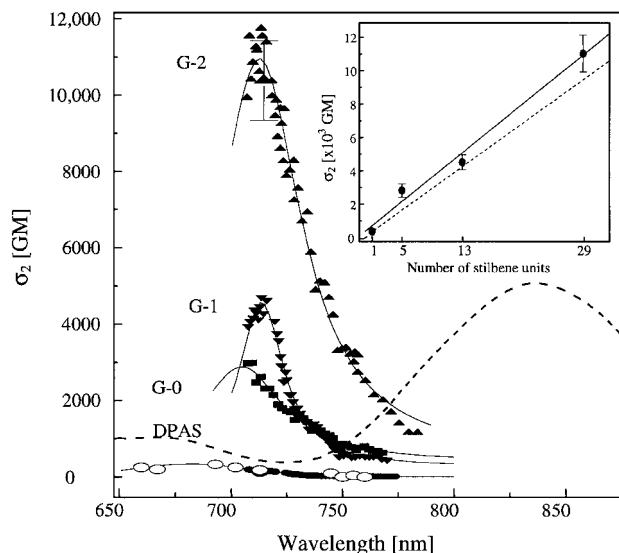


Fig. 2. TPA spectra of G-0 (squares), G-1 (downward triangles), and G-2 (upward triangles) dendrimers. Solid curves, Lorentzian fit to experimental data. The TPA spectrum of the parent molecule DPAS is presented for comparison (filled circles). Open ovals, data from Ref. 14. Dashed curve, rescaled linear absorption of G-2. The real wavelength for this spectrum is one-half the abscissa value. Inset, dependence of the peak TPA cross section on the total number of stilbene moieties in a dendrimer molecule. Solid line, the best linear fit. Dashed line, thermodynamic limit of a collection of noninteracting chromophores.

shift, as well as a similar redshift in the linear absorption,¹¹ suggests either dipole-dipole-type¹⁷ or π -conjugation-type¹⁸ interaction between the dendrimer's branches.

The inset of Fig. 2 shows the TPA peak cross section for one dendrimer molecule as a function of the total number of stilbene moieties, N . As one can see, the dependence is very close to linear. Although the peak position for the G-0 dendrimer is not accurately defined, we can estimate it by fitting the experimental spectrum to a model Lorentzian distribution. It is interesting that the lowest estimate for σ_2 is still eight times higher than that of DPAS, whereas the number of stilbenes in G-0 is only five times higher. We have drawn in the same plot a dashed line for $\sigma_2 = 325 N$, which corresponds to the case when cross sections of dendrimer-constituent stilbenes simply add together. Here we again notice evidence of a cooperative effect between segments in the G-0 dendrimer, which saturates in higher generations. In previous studies of oligomer¹⁷ and dendrimer¹⁸ molecules containing TPA chromophores, the authors also observed an increase of molecular TPA cross sections with the number of chromophores per molecule, but the cross sections were measured at only one wavelength.

In conclusion, we have studied two-photon absorption spectra in three generations of dendrimers based on 4,4'-bis(diphenylamino)stilbene repeat units. The peak femtosecond two-photon cross section increases almost linearly with the number of chromophores in

a dendrimer but jumps when going from the parent DPAS molecule to the first, G-0 generation. For the largest dendrimer studied, G-2, the cross section of 11×10^3 GM is to our knowledge the highest intrinsic value obtained so far for an organic molecule. We have also shown that these new dendrimers possess high quantum yields of fluorescence, which is important for several applications.

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