Strong Cooperative Enhancement of Two-Photon Absorption in Dendrimers

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We present, for the first time, unambiguous spectroscopic evidence of strong cooperative enhancement of two-photon absorption (TPA) in a series of dendritic macromolecules. The maximum TPA cross section increases in proportion to N^2, where $N = 2, 4, 6$ is the number of constituent identical chromophore units. We show that the enhancement is facilitated by the quasi-planar structure, which allows direct interbranch conjugation throughout the molecule.

Molecular dendrimers constitute a new class of organic nanostructures with multibranched fractal geometry.[1] Due to an exponential rise of the number of branches (dendrons) with generation number, a dendrimer can form a compact structure in three dimensions, such that its effective geometric size is less than that of the corresponding linear polymer. The dendrimers constructed from optically active blocks (chromophores) show several intriguing physical properties, including efficient light harvesting,[2] electroluminescence,[3] and optical power limiting.[4] However, nonlinear optical features of dendrimers, especially scaling of the third-order molecular polarizability, γ, with generation number were not systematically studied yet.[5] A primary reason is that in a majority of optical dendrimers, a coherent electronic molecular wave function did not span the area larger than just one dendron, because it was blocked at branching centers, possessing unfavorable chemical structure.[2] It is known, however, that it is this delocalization that governs cooperative enhancement of nonlinear optical response of polymers.[6,7]

In this paper we study an enhancement of two-photon absorption (TPA) in a series of dendrimers (see Figure 1 for structures) with an amino-branching unit, which allows efficient π-electron delocalization. The choice of two-photon absorption for studying cooperative response in dendrimers was motivated by both fundamental and application reasons. From a fundamental point of view, due to its resonant character, the TPA response is more transparent for theoretical description. Indeed, it is often sufficient to retain only one single term in a second-order perturbative treatment of the TPA cross section, σ_2, within the three-level approximation (see for example ref 8). From the point of view of applications, strong TPA enhancement in nanometer-size volume can make possible such emerging techniques as two-photon near-field microscopy,[9] ultrahigh-density optical memory,[10] two-photon micro- and nanolithography,[11] and holography.[12]

We note that in some papers[13] the effect of cooperative enhancement of σ_2 in multibranched molecules has been claimed. However, the TPA cross section was measured only at one wavelength. It is easy to show that such measurements fail to reveal any real TPA-scaling dependence, because in the presence of conjugation between chromophores, the TPA spectrum gradually shifts to lower frequencies with increasing number of chromophores, which makes it impossible to follow the scaling law at one particular wavelength. The apparent enhancement was subsequently explained in terms of the (trivial) change in strength of vibronic TPA transitions.[14] In this Letter we present, for the first time, unambiguous spectroscopic evidence of strong electronic cooperative enhancement of two-photon absorption (TPA) in a series of dendritic macromolecules.

Our laser system comprised a Ti: Sapphire regenerative amplifier (CPA-1000, Clark MRX), which was operated at 1-kHz repetition rate and produced 150-fs pulses at 0.8 mJ energy per pulse. These pulses were parametrically down-converted using an optical parametric amplifier, OPA (TOPAS, Quantronix), which yielded 100-fs pulses in the wavelength range from 1100 to 1600 nm. TPA spectra of molecules were obtained as fluorescence excitation spectra by tuning the OPA and taking the second harmonic of the signal beam. These relative spectra, obtained at constant photon flux, were normalized to an absolute σ_2 value, measured at the spectral maximum. Absolute TPA cross section values were obtained by comparing fluorescence intensity under one- and two-photon excitation (see ref 15 for details).

Linear one-photon absorption spectra of the three molecules (Figure 2, right) show a small but systematic red shift, when going from **2** to **4** and further to **6**. This fact alone immediately suggests a particular coupling between the constituent chromophores in **4** and **6**. All three spectra exhibit a similar, slightly asymmetric shape. We attribute this shape to overlapping vibronic transitions, because fluorescence spectra are mirror-symmetrical to absorption ones.[16]

Crystallographic data on triphenylamine[17] and BDPAS[18] as well as quantum-mechanical calculations[19] indicate that the three N−C bonds of the triphenylamine group in triphenylamine-containing compounds lie in one common plane. Also, according to crystallographic data,[18] in BDPAS two NC$_3$ planes are parallel to each other. Furthermore, quantum mechanical calculations and linear optical spectroscopy[19,20] confirm continuity of the π-conjugation all the way through the nitrogen atom within triphenylamine and related molecules. Such unusual behavior is credited to the sp^2-hybridization[20] of nitrogen, leading to an

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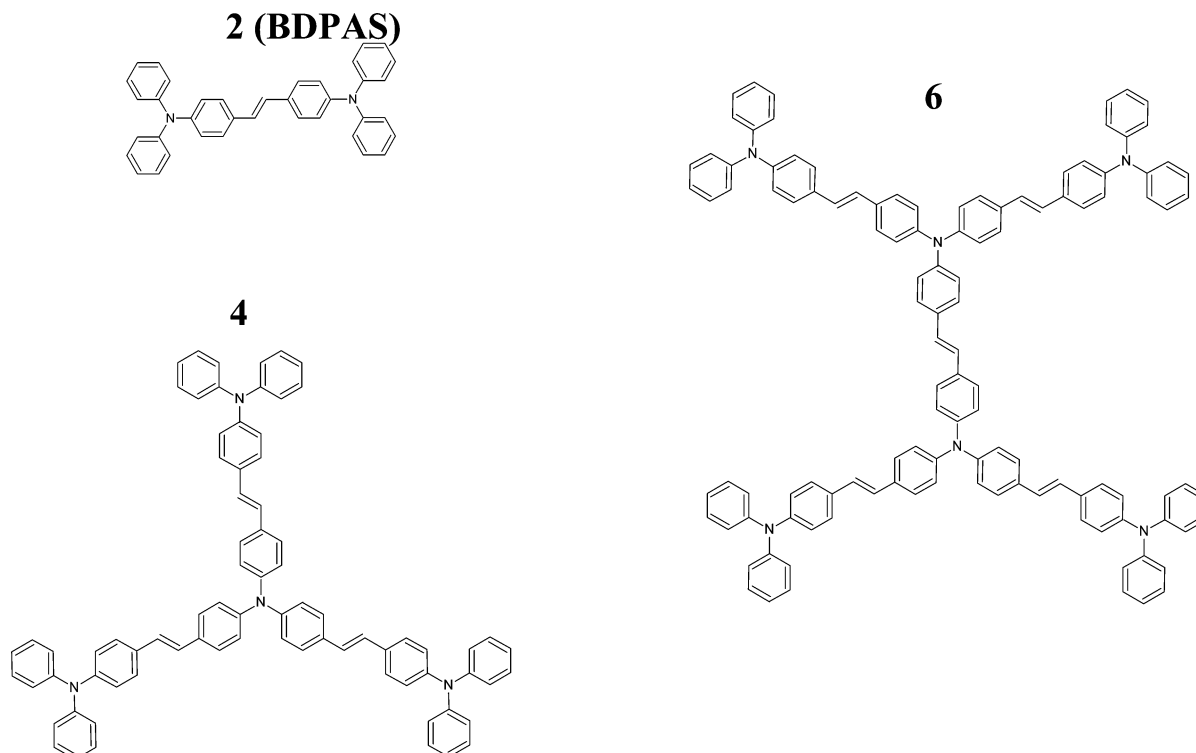
2 (BDPAS)

6

4

Figure 1. Molecular structures of the main three compounds studied: (a) parent chromophore, 4,4′-bis(diphenylamino)stilbene (BDPAS), **2**; (b) three-branch G-0 dendrimer, **4**; (c) four-branch G-0 dendrimer, **6**. All these compounds were characterized by high-field ^{1}H and ^{13}C NMR spectra, as well as mass spectrometry. No aggregation effects were observed over a wide concentration range, typically 10^{-2} to 10^{-5} M in either polar or nonpolar solvents.
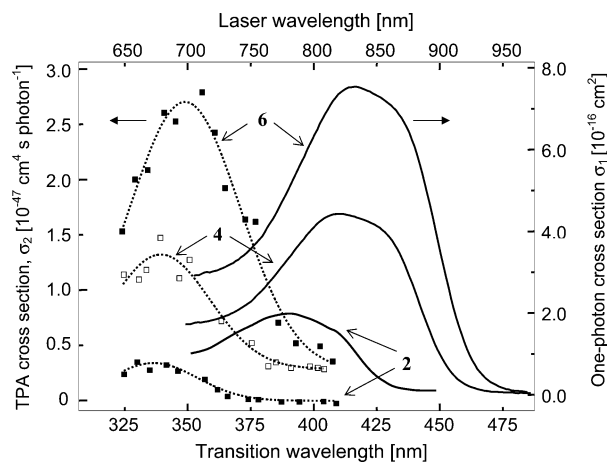
Figure 2. Absolute two-photon abortion spectra (dashed curves, left) and linear absorption spectra (solid curves, right) of **2**, **4**, and **6**. Notice different vertical axis units for left- and right-hand spectra.

interaction between the nonpaired electron in the nitrogen atom and the π-electrons in the neighbor conjugated units.[20]

The maximum linear cross section σ_1 increases by a factor of 2.1 and 3.8, when going from **2** to **4** and **6**, respectively (see Table 1). This implies that the linear absorption cross section σ_1 is proportional to the number of triphenylamine moieties, rather than that of stilbene moieties, because in the latter case σ_1 would rise in proportion: 1:3:5. Therefore, in what follows we consider the triphenylamine moiety as an elementary chromophore in the dendrimers under study.

Two-photon absorption spectra of **2**, **4**, and **6** are shown in the left of Figure 2. The spectra of **4** and **6** are slightly shifted to longer wavelengths (340 and 347 nm, respectively) with respect to **2** (335 nm). The fact that one- and two-photon transition maxima do not coincide in all three molecules suggests that either, because of the centrosymmetrical structure, the corresponding selection rules are mutually exclusive or, alternatively, the vibronic transition in TPA borrows most of the intensity from the pure electronic transition. The first explanation is most probable because the first TPA transition of the parent compound, **2**, is assigned to a pure electronic $1A_g \rightarrow 2A_g$ type.[21] From the similarity of TPA spectra of **4** and **6** to **2**, we assume that in **4** and **6** we also deal with the same pure electronic transition.

The TPA cross section values measured for all three molecules in their corresponding maxima are presented in Table 1. The value obtained for BDPAS, $\sigma_2 = 320$ GM, is close to

TABLE 1: Linear and Two-Photon Absorption Maximum Wavelengths and Corresponding Cross Sections of Molecules Studied

no. of chromo-phores, N	one-photon λ_{max}, nm	two-photon λ_{max}, nm	$10^{16}\sigma_{1,max}$, cm^2 (10% error)	$\sigma_{2,max}$ GM (15% error)	σ_2/N GM
2	389	335	2.0	320	160
4	412	340	4.2	1300	320
6	417	347	7.6	2700	460
14	413	347	13	4500	320
30	419	345	29	11000	370

[a] The last column presents the TPA cross section per one chromophore.

that measured before in ref 21. The values measured for the other two molecules, namely, $\sigma_2 = 1300$ (for **4**) and $\sigma_2 = 2700$ GM (for **6**) compare well with other strong TPA absorbers.[8] We note here that all the results presented in this paper correspond to intrinsic σ_2 values, i.e., those measured with the fluorescence method in the femtosecond regime, and therefore not affected by excited-state absorption.

The most important experimental result is that the σ_2 value rises in proportion 1:4:8 in the series **2−4−6**. We emphasize that this behavior is very close to $\sigma_2 \propto N^2$ scaling, namely 1:4:9 proportion, where N is the number of triphenylamine groups. In this way, our current result presents the first unambiguous evidence of cooperative enhancement of two-photon absorption (TPA) in organic systems.

This result can be qualitatively explained in the framework of three-level approximation of TPA. If the energies of two photons are the same (degenerate case), their combined energy equals the maximum of two-photon transition, and photon energy detuning from real one-photon transition energy is much larger than the broadening of this transition, the TPA cross section reads (see, for example, ref 8)

$$\sigma_2 \propto \frac{(E_{f0}/2)^2 M_{i0}^2 M_{fi}^2}{(E_{i0} - E_{f0}/2)^2 \Gamma_{f0}} \tag{1}$$

Subscripts 0, i, and f refer to the ground, intermediate, and final excited state, respectively, Γ_{f0} is the line width of the two-photon transition. E_{nm} and M_{nm} are the energy difference and the transition dipole moment between the states n and m, respectively. If the experimental values, E_{i0}, E_{f0}, and Γ_{f0}, measured for **2**, **4**, and **6**, are inserted into eq 1, then the corresponding variation of the expression is 10% at the most. On the other hand, the one-photon cross section ($\sigma_1 \propto M_{i0}^2$) grows linearly with the number of chromophores (Table 1). If one supposes that one-photon cross section of the absorption from the excited state f ← i also grows linearly with N, then the $\sigma_2 \propto N^2$ dependence observed in our experiment follows.

The semiempirical CNDO/S calculations of σ_2 in linear chain oligomers[22] give the $\sigma_2 \propto N^a$ law with $a = 1.9-3.6$, depending on oligomer structure and number of intermediate states considered. Ab initio response theory calculations for several other series of oligomers result in a power law again with $a = 4-7$, depending on the oligomer chemical structure.[23] Exponent values a larger than 2, theoretically predicted in these papers, can at least in part result from a much stronger resonance enhancement (decrease of denominator in (1)) in those cases.

We would like to note that the N dependence of the resonant Im γ value, which is proportional to σ_2 should, generally speaking, differ from the N dependence of the far-off-resonant Re γ value, studied in refs 6 and 7. However, if the contribution of TPA to the complex γ is considerable, e.g., due to an accidental TPA resonance near the working frequency, then the Re γ and Im γ values will scale in the same way. This is suggested to be the case in a series of π-conjugated porphyrin oligomers,[24] where the Re $\gamma \propto N^2$ law was measured and explained by nearby TPA resonance.

All the above evidence clearly suggests that the observed N^2 enhancement of σ_2 in dendrimers is due to interchromophore coupling via extended π-conjugation. It is also worth noting that similar scaling behavior ($\propto N^2$) can be observed in molecular aggregates and dendrimers with dipole−dipole coupling (Frenkel excitons).[5,25] However, this kind of cooperativity takes place only in a very narrow spectral region, close to one-photon resonance, $\Delta\omega \sim V/\hbar$, where $\Delta\omega$ is the laser detuning from the
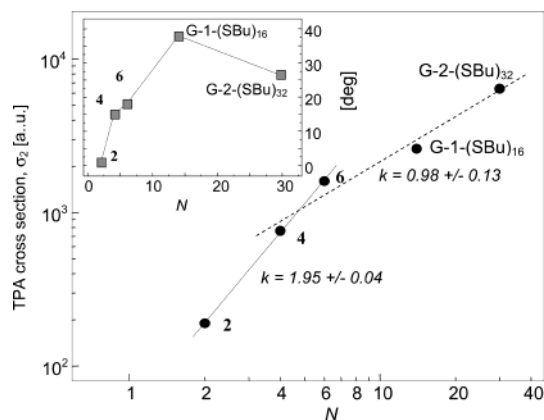

Figure 3. Dependence of maximum TPA cross section on the number of chromophore units in a dendrimer (in double logarithmic scale). Inset: dependence of the dihedral angle θ between the two NC_3 planes adjacent to the core stilbene unit on the number of chromophores in a dendrimer.

resonance and V is the (dipole−dipole) coupling strength.[25] Because for molecular aggregates $V \sim 1000$ cm^{-1}, at most, our probe photon energy is certainly out of one-photon resonance ($\Delta\omega \sim 11\,000$ cm^{-1}). The cooperative enhancement in TPA within the excitonic model is related to the two-exciton transition, which occurs at a transition energy almost twice that of the one-photon transition. Such a ratio in the two- and one-photon transition energies is not observed in our experiments as well, and, therefore, we assign the effect of cooperativity to the electronic (π-conjugation) coupling between chromophores.

We note that the linear absorption spectra of all three molecules show very similar vibronic features (Figure 2) and that the detuning, $E_{i0} - E_{f0}/2$, is more than 10 times as large as the entire width of the absorption band. This allows us to conclude that the vibronic interaction does not contribute significantly to the TPA scaling law.

Finally, the last intriguing issue is whether a further increase of molecule size, i.e., proceeding to higher dendrimer generations, would retain the cooperative effect or not. An answer to this question can be found in Figure 3, where current data are plotted together with our earlier measurements[26] for structurally related, but larger, four-branch G-1 and G-2 generation dendrimers. The plot shows that for $N > 6$, the N^2 dependence turns over into a linear one, which is an evidence of saturation. This effect could manifest itself, for example, if the initially quasi-planar core of the dendrimer would be deformed, as the molecule becomes larger in size. To verify this hypothesis, we present in Figure 3, inset, the results of computer simulations of the molecular structures (HyperChem software, MM+ force field method) of the relevant dendrimers, where we calculated the dihedral angle θ between the two NC_3 planes on both sides of the core stilbene unit. Because the bridging stilbene segments are nearly straight, the angle θ can be considered a characteristic measure of the degree of planarity of the core and, presumably, the entire molecule. We find an almost monotonic increase of θ with increasing N, such that the largest change occurs when going from **6** to G-1-(SBu)$_{16}$, where θ suddenly increases from 17 to 38°. This large change is associated with a transformation from a quasi-2D to a globular 3D structure. We think that, as a result, the total degree of conjugation diminishes, which explains why the σ_2 value calculated per one chromophore decreases, as compared to **6**; see last column of Table 1. It is interesting to note that the present behavior is distinctly different from what has been observed in 1D polymers, where the

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absolute value of γ per one monomer also saturates, but does not decrease with increasing length of the polymer chain.[6,7]

In conclusion, we have observed a strong cooperative effect in TPA absorption of nanometer-size molecular dendrimers and showed that it is connected to an effective π-conjugation between constituent branches. The peak TPA cross section increases quadratically with the number of chromophores in a dendrimer. As compared to linear chain oligomers and polymers, the dendrimers are space-saving nanostructures, because their geometrical radius increases more slowly with the number of building blocks. Therefore, the demonstration of such cooperativity offers the possibility of a large two-photon absorption concentrated in an extremely small (nanometer) volume, which can be used in a wide range of photonic applications.

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