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Uncovering Coherent Domain Structure in a Series of π-Conjugated Dendrimers by Simultaneous Three-Photon Absorption

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We study three-photon absorption (3PA) in a series of 4,4′-bis(diphenylamino) stilbene-based dendrimers and show that the cross section of the nonlinear absorption scales faster than in a linear fashion with the molecular size, which is a manifestation of the cooperative enhancement effect. The coherent domain structure is deduced from 3PA cross section values for all of the dendrimers in the series. It is found that, in terms of largest coherence domain size, the optimum dendrimer generation is 4-arm G-0. Molecular 3PA cross section, $\sigma_3 = 10^{-79}$ cm^6 s^2, is obtained for 4-arm G-2 dendrimer generation, which is, to our best knowledge, one of the largest intrinsic σ_3 values measured for any organic molecule.

The advance of high-peak-intensity near-IR femtosecond lasers has transformed the simultaneous three-photon absorption from a rare nonlinear optical process, interesting only from a fundamental point of view, into a practical tool with a number of intriguing applications, including upconversion lasing,[1] optical power limiting,[2] and ultrahigh-resolution microscopy.[3] It can be expected that under special circumstances, such as local field enhancement by nanoparticle surfaces,[4] and in spectral regions where the two-photon absorption (2PA) remains relatively weak, the process of three-photon absorption (3PA) can actually dominate over 2PA already at pulse peak intensities of $1-10$ GW/cm^2. New applications of the 3PA may be facilitated in the future by designing molecules with enhanced nonlinear-optical response, similar to that, currently developed for 2PA.

On the other hand, measuring the 3PA cross section, σ_3, and its wavelength dependence in conjugated macromolecules can yield unique information about various intrinsic molecular parameters, not accessible by traditional spectroscopy techniques. In this paper, we use 3PA to study the length of electronic delocalization, alternatively called coherence domain size, in a series of complex dendrimer generations.

In our previous papers,[5] we demonstrated that the cross section of both 2PA and 3PA in a series of 4,4′-bis(diphenyl-amino) stilbene-based dendrimers increases faster than the number of chromophores−dendrimer building blocks. Such cooperative enhancement of the nonlinear absorption can be explained by electronic delocalization, which increases with the number of π electrons in the system. However, we also observed that if the dendrimer exceeds some critical size, typically generation G-0, then the enhancement effect saturates and the nonlinear cross section transforms into almost linear dependence on the number of chromophores (or π electrons).

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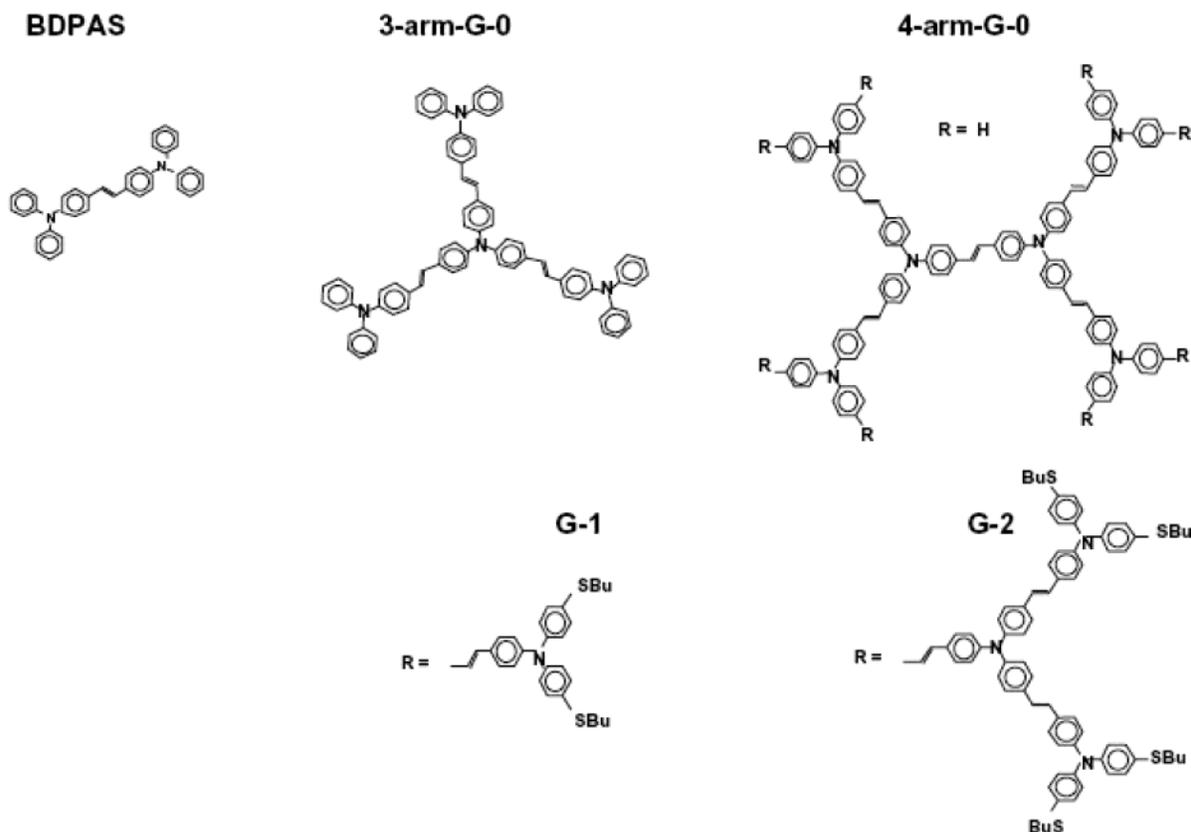
Figure 1. Chemical structure of molecules studied.

Although it was clear that the coherent interaction of π electrons plays decisive role in cooperative enhancement, the size and the structure of the underlying coherence domains in dendrimers could not be determined straightforwardly from only 1PA and 2PA measurements. Besides presenting a fundamental interest, the knowledge of the properties of these domains is crucial for the design of macromolecules with nonlinear-optical response optimized for various applications listed above.[6]

In this paper we show, for the first time, that 3PA can be employed as a very efficient technique for determining the size and number of coherence domains in dendrimers. Indeed, we observe that, in the dendrimers under study, the elementary act of three-photon transition occurs from the ground state and terminates into the lowest one-photon-allowed singlet state ("nonresonant" 3PA). In this case, the process of nonlinear absorption can be described by a two-level approximation, which leads to the cubic dependence of σ_3 on the one-photon transition oscillator strength. Therefore, this process turns out to be extremely sensitive to small changes of the linear oscillator strength of each separate coherent domain. By using this model and measuring σ_3 in a series of dendrimers with known linear absorption properties, we calculate the size of coherence domains in each of the dendrimer generations.

The laser system used in our experiments was described in detail previously.[7] Briefly, it comprised a Ti:sapphire regenerative amplifier (CPA-1000, Clark MRX), which was operated at 1-kHz repetition rate and produced 150-fs duration 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. 3PA spectra were measured by detecting the relative fluorescence intensity at different OPA excitation wavelengths, while maintaining constant photon flux. The absolute σ_3 value was measured at a

wavelength corresponding to the maximum of 3PA, and then the whole spectrum was scaled according to this value. The absolute 3PA cross section was obtained by comparing the intensity of the fluorescence signal under three- and one-photon excitation, where for the last we used the strongly attenuated second harmonic of the Ti:sapphire amplifier at around 392 nm. A known diameter small pinhole was placed in front of the sample, which guaranteed the "flat-hat" beam profile and also the constancy of excitation volume and geometry upon one- and three-photon excitation. The 3PA cross-section is obtained in this case from the relation

$$\sigma_3 = \frac{3\sqrt{3}}{4} \frac{\pi^3}{\ln 2} \frac{\nu_3{}^3 \langle I_1 \rangle}{\nu_1 \langle I_3 \rangle^3} \frac{F_3}{F_1} \frac{C_1}{C_3} h^2 r_0{}^4 \tau^2 R^2 \sigma_1$$

where ν is the optical frequency (Hz), $\langle I \rangle$ is the average intensity (W), F is the relative fluorescence signal intensity, C is the concentration (M), h is the Plank's constant (J s), r_0 is the beam radius (cm), τ is the pulse duration (fwhm, s), R is the laser repetition rate (Hz), and σ_1 is the 1PA cross section at the wavelength of one-photon excitation (cm²). Indexes 1 and 3 correspond to one- and three-photon excitation, respectively.

The samples were prepared as dichloromethane solutions with the concentration of ca. 5×10^{-5} M and 10^{-6} M for 3PA and 1PA measurements, respectively. The quantum chemical calculations were performed with the Hyperchem 7 software package. Geometry optimization was accomplished with the AM1 method and for spectral calculations, we employed the ZINDO/S method.

Figure 1 presents the structure of zeroth, first, and second generation dendrimers along with parent BDPAS chromophore. All these molecules can be viewed as members of a homologous series composed of individual triphenylamine and stilbene
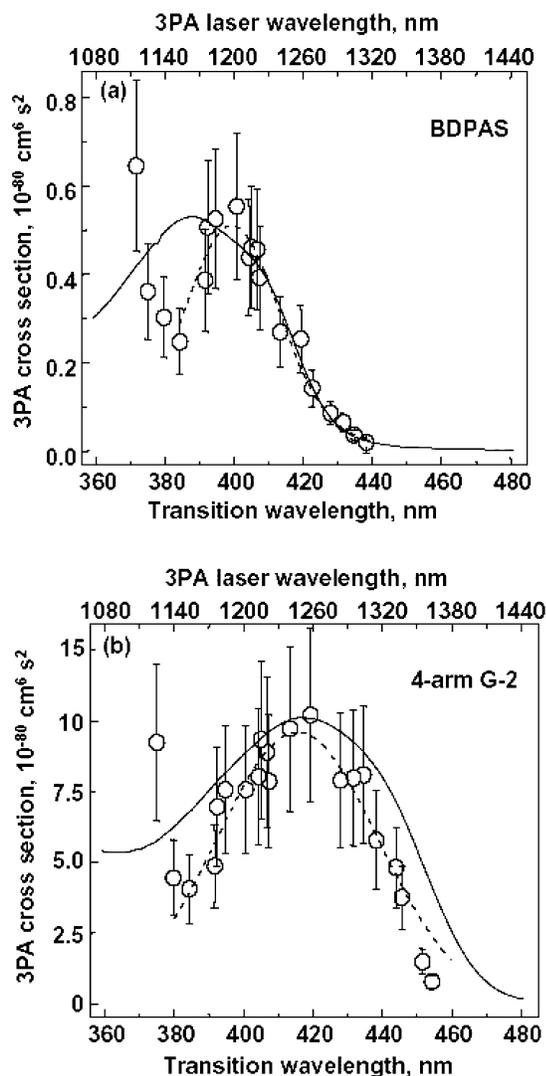
Figure 2. Absolute three-photon spectra of BDPAS and 4-arm-G-2 dendrimer in dichloromethane (symbols). Dashed curves: Gaussian fits to 3PA bands. Solid curves: one-photon absorption spectra. The abscissa shows transition wavelength, which is one-third of excitation wavelength in case of three-photon absorption.

building blocks. Several recent studies[5,8] have highlighted that π-electron conjugation in these structures is facilitated by unusual sp^2 hybridization of branching nitrogen atoms.

Figure 2 presents the measured 3PA spectra, along with the corresponding linear (one-photon) absorption spectra in the region of the lowest one-photon absorption band, for the parent BDPAS molecule and the largest 4-arm G-2 dendrimer. The lower wavelength scale shows the 1PA transition wavelength, which corresponds to one-third of the 3PA illumination wavelength (upper scale). It is evident that the 3PA spectrum generally follows the profile of the 1PA spectrum, and that maxima of both spectra virtually coincide. This is not surprising because, independently of molecular symmetry, 1PA and 3PA obey the same parity selection rules. This behavior also corroborates our earlier observation that there are no two-photon-allowed levels in a gap below the depicted absorption band. Otherwise, the 3PA spectrum would be shifted due to the 2PA intermediate resonance. The high value of the quantum yield of fluorescence[5a] along with the results of our quantum-mechanical calculations, presented below, serve as a further support that there are no intermediate dark singlet states in the series of dendrimers under study.

With this information in hand, we measured σ_3 for each molecule at an excitation wavelength, corresponding to 3PA maximum wavelength. The results are presented in Table 1. For comparison, our data are shown along with literature values for other organic molecules, where σ_3 fluorescence measurements have been previously performed.

We note that here we do not bring to comparison the results obtained with nonlinear transmission measurements, such as the Z-scan technique, essentially because in the latter case the σ_3 value is usually overestimated, especially when ps or ns pulses are used. This discrepancy is caused by excited-state absorption, which can accompany 3PA at high excitation intensity, and which is usually difficult to separate from initial 3PA.[18]

Comparison to previous literature values shows that already BDPAS has a particularly large σ_3 value. With the increase of the dendrimer size, we observe a drastic increase of σ_3. For 4-arm G-2 molecule, $\sigma_3 = 10^{-79}$ cm^6 s^2, which is, to our best knowledge, one of the largest values measured so far for any organic molecule with a fluorescence technique. Only in the

TABLE 1: Three-Photon Absorption Cross Sections of Organic Molecules[a]

molecule	$\sigma_3\,\varphi$ (10^{-82} cm^6 s^2)	φ	σ_3 (10^{-82} cm^6 s^2)	λ_{ex}, nm	pulse duration/rep. rate
1-chloronaphthalene (neat liquid)	0.2[9]			1064	5 ps
naphthalene	0.19[10]	0.16[11]	1.2	694	~10 ns
(crystal)		0.4[12]	0.47		
anthracene	4.8[10]	0.8[12,13]	6.0	1064	~10 ns
(crystal)		0.7[11]	6.9		
fura-2 + Ca^{2+}	3[3a]	0.49[14]	6	1000	~100 fs/82 MHz
fura-2 free	2[3a]	0.23[14]	9	1000	~100 fs/82 MHz
indo-1 + Ca^{2+}	0.6[3a]	0.56[14]	1	1000	~100 fs/82 MHz
indo-1 free	0.2[3a]	0.37[14]	0.5	1000	~100 fs/82 MHz
DAPI free	0.025[3a]	0.043[15]	0.6	1000	~100 fs/82 MHz
dansyl	0.03[3a]			1000	~100 fs/82 MHz
tryptophan	0.02[3b]	0.12[16]	0.2	710	~200 fs/76 MHZ
dopamine	0.004[3b]			710	~200 fs/76 MHZ
serotonin	0.07[3b]			710	~200 fs/76 MHZ
dimethy-POPOP			$10^{3\,[17]}$	1064	cw
BDPAS			5×10^1	1175	100 fs/1 kHz
3-arm-G-0			1.5×10^2	1235	100 fs/1 kHz
4-arm-G-0			4×10^2	1235	100 fs/1 kHz
4-arm-G-1			5×10^2	1235	100 fs/1 kHz
4-arm-G-2			1×10^3	1235	100 fs/1 kHz

[a] The product of the 3PA cross section, σ_3, times the fluorescence quantum efficiency, φ, originally measured for a number of systems is presented in the second column. When data on φ are available from literature (third column), the σ_3 is calculated and presented in the fourth column.
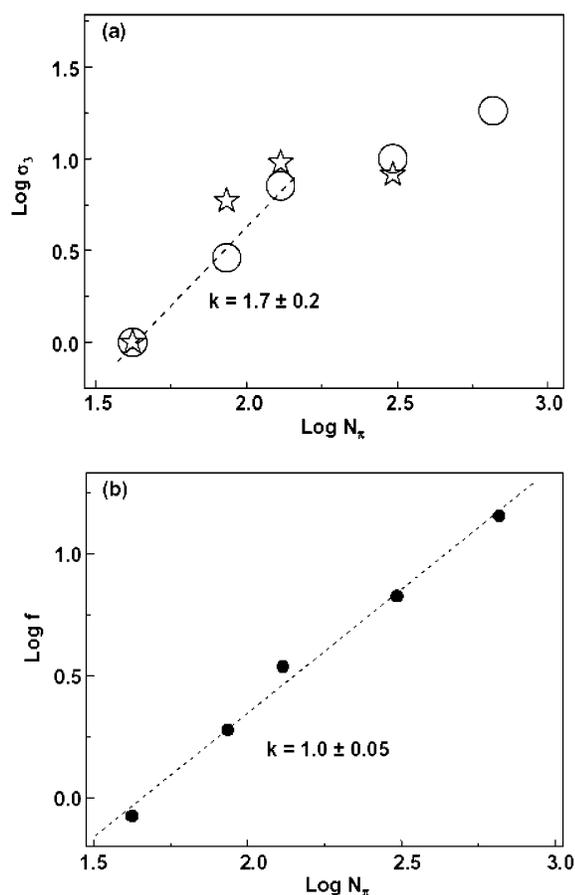
Figure 3. (a) Double logarithmic plot of relative 3PA cross section versus the number of π electrons in the molecule; circles, experiment; stars, quantum chemical calculations. For the first three molecules, the scaling law is nonlinear (dashed line has a slope 1.7). (b) Double logarithmic plot of 1PA oscillator strength versus the number of π-electrons in molecule; circles, experiment; line, linear regression. Linear scaling law corroborates with a unity slope of linear regression.

dimethyl-POPOP molecule was a comparable large value reported; however, it was measured to an accuracy of an order

of magnitude.[17] We estimate an error (standard deviation) of our measurement of the absolute σ_3 values of dendrimers to be 30%, and the error of relative (with respect to BDPAS) σ_3 values in a series to be 20%.

We now turn to the analysis of the scaling behavior of the spectral maximum value of σ_3 in the series of dendrimers. Figure 3a presents a double-logarithmic plot of this value versus the total number of π electrons, N_π, in the molecule. One can see that σ_3 scales according to the power law, $\sigma_3 \propto N_\pi^a$ with $a = 1.7 \pm 0.2$, when going from parent (BDPAS) to 4-arm G-0 dendrimer and then levels off showing saturation at higher generations. The higher-than-linear power law at lower generations implies that there exists an inter-branch coupling, at least up to G-0 generation. A similar conclusion has recently been drawn from 2PA measurements in the same series of dendrimers[5b] and has been attributed to sp[2] hybridization of nitrogen in the triphenylamine branching unit, allowing π conjugation across it. Here we will use the nonlinear scaling of σ_3 to estimate the size of effective coherence domain (conjugation length) in each dendrimer molecule.

Table 2 summarizes the key parameters of the linear absorption spectra of this particular series of molecules. With the increase of molecular size, the absorption maximum gradually shifts to the red. Figure 3b shows that the oscillator strength, calculated by integrating the area of the corresponding peak in the 1PA spectrum, increases linearly with the total number of π electrons. Such linear scaling of 1PA is not exceptional and was proven experimentally[19] and theoretically[20] for different homologous series of π-conjugated oligomer and polymer systems. It is important to note that, independently of whether the monomers (or building blocks) are conjugated or not, the oscillator strength will scale linearly. This circumstance precludes the determination of the coherence length from solely 1PA data.

Our model of coherent domains in a dendrimer is as follows. Assume that a dendrimer comprises a number μ uncoupled domains, each of which contains (on average) m coherently coupled π electrons ($N_\pi = \mu m$). Assume also that BDPAS contains only one such domain with m_0 coherently coupled electrons. Since we observe that the overall oscillator strength

TABLE 2: One- and Three-Photon Absorption Parameters for the Dendrimers Studied[a]

| molecule | N_π | calculation (several first singlet − singlet OPA transitions) | | | | experiment | | | | |
		λ_m, nm	f_m	$f = \sum_m f_m$	$\sum_m (f_m^3)/(n_m^4)$	λ, nm	f	σ_3 (relative values)	m/m_0	σ_3/N_π (relative values)
BDPAS	42	345	1.45	1.45	1	389	0.85	1	1	1
3-arm G-0	86	359	2.29	3.80	5.9	412	1.90	2.7 ± 0.5	1.14 ± 0.11	1.29
		358	1.51							
4-arm G-0	130	360	2.18							
		353	1.84	6.15	9.5	417	3.45	7.1 ± 1.4	1.32 ± 0.13	2.29
		347	2.13							
4-arm G-1	306	294	3.23							
		293	0.15							
		289	0.43							
		288	0.64							
		285	2.47	8.25	8.4	413	6.72	10 ± 2	1.12 ± 0.11	1.37
		281	0.30							
		279	0.76							
		264	0.15							
		254	0.12							
4-arm G-2	658					419	14.3	18 ± 4	1.03 ± 0.10	1.12

[a] N_π is the total number of π electrons in the molecule, λ_m is the calculated maximum of one-photon transition, f_m is the oscillator strength of the corresponding transition, λ is the wavelength of experimental one-photon peak, f is the corresponding oscillator strength, σ_3 is the relative (with respect to BDPAS) 3PA cross section in maximum, m/m_0 is the relative size of average coherent domain in the dendrimer. The experimental error of relative σ_3 values is 20%. This presents a main contribution to an experimental error of m/m_0, which is estimated to be ~10% by using the square root dependence of m/m_0 on $\sigma_3/\sigma_{3,0}$ (7). The value σ_3/N_π (last column) represents a 3PA enhancement factor, relative to BDPAS.

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scales linearly with the number of π electrons, $f \propto N_\pi$, we can conclude that inside each domain, possessing oscillator strength f_m, this latter value also scales linearly with the number of π electrons

$$f_m \propto m \qquad (1)$$

As a result, we can write for the total number of π electrons in a dendrimer

$$\mu m \propto f \qquad (2)$$

According to our spectroscopic data presented above in Figure 2, there are no intermediate states between the ground and final levels, which, along with high oscillator strength value, $f_m \sim 1$, justifies using a simple two-level model for describing the 3PA within each domain. Under these conditions, one obtains a simple expression for the maximum 3PA cross section within each coherent domain[10]

$$\sigma_{3,m} \propto \frac{f_m^3}{\nu_m^4} g_m(0) \qquad (3)$$

where ν_m, and $g_m(0)$ are the central frequency and normalized spectral shape function in the maximum of the corresponding three-photon $0 \rightarrow f$ transition within the mth domain. Then, the total 3PA cross section per dendrimer will be

$$\sigma_3 \propto \sum_m \frac{f_m^3}{\nu_m^4} g_m(0) \qquad (4)$$

Because our model implies that all domains are of equal size, it is reasonable to suggest that $\nu_m = \nu$ and $g_m(0) = g(0)$ are the same for each domain. Then the above equation yields

$$\sigma_3 \propto \frac{g(0)}{\nu^4} \sum_m f_m^3 = \frac{g(0)\mu f_m^3}{\nu^4} \qquad (5)$$

By using (1), we get

$$\mu m^3 \propto \frac{\nu^4 \sigma_3}{g(0)} \qquad (6)$$

To check the validity of two-level approximation, and of the basic for our model eq 4, we carried out quantum-mechanical calculations of 1PA spectra of all of the molecules studied here, up to 4-arm G-1 dendrimer. The corresponding wavelengths and oscillator strengths are presented in Table 2. The main qualitative result of these calculations is that, whereas in BDPAS the first S_0-S_1 electronic transition is well isolated from the others and polarized along the N−N stilbene axis, in all other molecules this transition is split into a number of close-lying transitions, with different polarizations. We assign these transitions to absorption in decoupled coherent domains, discussed above. The number of these transitions (multiplicity of splitting) increases with the size of the molecule. Quantitatively, we have calculated the value $\sum_m(f_m^3)/(\nu_m^4)$ (we assume here $g(0)$ to be constant) for all of the molecules relative to BDPAS and presented it in Table 2 and in Figure 3a. A reasonably good correlation between the relative values of calculated $\sum_m(f_m^3)/(\nu_m^4)$ and experimental σ_3 serves as a confirmation of our model (eq 4).
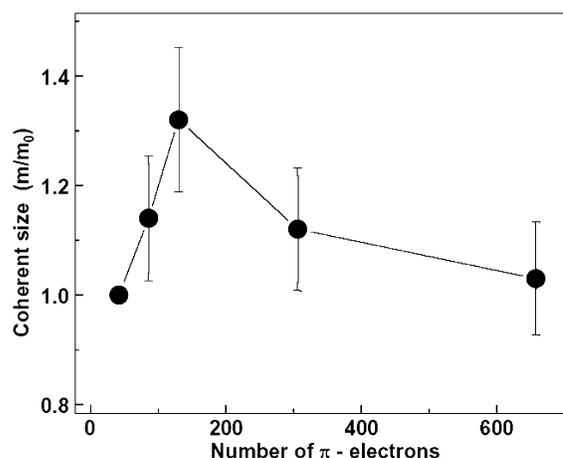
Figure 4. Dependence of relative (to BDPAS) size of coherent domain on the number of π electrons in the dendrimer.

Now we can estimate the size of coherent domains, relatively, for example, to BDPAS, in each dendrimer by solving the system of eqs 2 and 6

$$\frac{m}{m_0} = \left(\frac{\nu}{\nu_0}\right)^2 \sqrt{\frac{\sigma_3}{\sigma_{3,0}} \frac{f_0}{f} \frac{g_0(0)}{g(0)}} \qquad (7)$$

where index 0 corresponds to the values obtained for BDPAS. We observe only very little (less than 5%) variation in $\nu^2/[g(0)]^{1/2}$ value (a lowering of ν is compensated by a broadening of TPA-transition) within the series of molecules studied. Therefore, disregarding a variation in $\nu^2/[g(0)]^{1/2}$ and substituting all of the known values into (7), we obtain coherent domain sizes in each dendrimer relative to BDPAS. These results are shown in Figure 4 and Table 2.

We see that, compared to BDPAS, the average domain size increases in 3-arm G-0 and 4-arm G-0 by ca. 14 and 32%, respectively,[21] and then it reduces in G-1 and becomes almost equal to that of BDPAS in G-2 dendrimer. This behavior can be explained if we assume that lower-generation dendrimers remain generally planar, which allows the conjugation length to increase. The planarity is lost in G-1 and G-2 generation dendrimers,[5b] which leads to a sudden decrease of the conjugation size. We note, however, that our model gives only a simplified picture, where all domains are of the same size. In reality, the size of the domains can vary inside one dendrimer. Such variation manifests itself, for example, in a difference of oscillator strengths obtained by quantum-chemical calculations and shown in Table 2.

By substituting the above m/m_0 values into the relation

$$\mu = \frac{N_\pi}{N_{\pi,0}} \frac{m_0}{m} \qquad (8)$$

we obtain the effective number of domains per dendrimer, which gives 1.9, 2.4, 6.6, and 15.6, for 3-arm G-0, 4-arm G-0, 4-arm G-1, and 4-arm G-2, respectively. Note that there is a good correspondence between these numbers and the number of low-lying singlet electronic transitions calculated by the ZINDO/S method (Table 2), at least for the first three molecules, i.e., 2, 3, and 9. The value obtained for 4-arm G-2 is close to the number of peripheral dendrons (16) in this molecule, which probably statistically determine the absorption (linear and nonlinear) of the whole molecule in the spectral maximum, similarly to the case of electronically decoupled dendrimers.[22]

In conclusion, we have demonstrated that 3PA in BDPAS-based dendrimers scales in a nonlinear fashion with the molecular size, which is a manifestation of cooperative enhancement effect. One of the largest absolute values of the molecular 3PA cross section is obtained for 4-arm G-2 dendrimer generation. Within a conjugated domain, 3PA scales as a third power of the domain size. The coherent domain structure is deduced from 3PA measurement for all of the dendrimers in the series. It is found that, in terms of the largest coherence domain size, 4-arm G-0 is the optimum dendrimer generation. The described method of determining coherence domain size may be applicable also to other complex molecular nano-systems, such as J aggregates, π-conjugated polymers, and others.

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