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Structure−Property Relationships for Two-Photon Absorbing Chromophores: Bis-Donor Diphenylpolyene and Bis(styryl)benzene Derivatives

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Abstract: The two-photon absorption properties of a series of bis dialkylamino- or diarylamino-substituted diphenylpolyenes and bis(styryl)benzenes have been investigated. Two-photon absorption cross sections, δ, as large as 1420×10^{-50} cm^4 s/photon-molecule have been observed for molecules with this general bis-donor structure. The effect of the type and length of the conjugated chain and of dialkylamino or diarylamino substitution on the position and magnitude of the peak two-photon absorptivity is reported. The transition dipole moments for the transitions between the ground state and the first excited singlet state (M_{ge}) and between the first and second excited singlet states ($M_{ee'}$) have been estimated using experimental data from the one- and two-photon spectra. It was found that increases in chain length result mainly in an increase in M_{ge}, whereas the addition of donor end groups or going from diphenylpolyene- to phenylene-vinylene-type bridges leads primarily to an increase in $M_{ee'}$. The trends in the energy of the lowest excited singlet states and in the transition moments for the diphenylpolyene series as a function of chain length are in agreement with those calculated by quantum mechanical methods. These results furnish a link between structural features in these classes of molecules and the electronic dipole couplings and state energies that control the strength of the two-photon absorption. In bis(aminophenyl)polyenes containing up to four double bonds (m) the lowest excited singlet state is a B_u state, as opposed to the case of simple polyenes and diphenylpolyenes, for which it is an A_g state for $m > 2$. The relationship of the state ordering in these systems with the observed values of the radiative and nonradiative decay rates is also discussed.

1. Introduction

The potential for use of two-photon absorbing molecules in applications ranging from optical limiting[1−3] to three-dimensional (3D) fluorescence microscopy[4] and 3D microfabrication and optical data storage[5,6] has stimulated research on the design, synthesis, and characterization of new molecules with large two-photon absorptivities.[7,8] The ability to achieve 3D spatial resolution arises from the fact that the rate of simultaneous absorption of two photons depends quadratically on the intensity of the incident laser light. If a tightly focused beam is used, the intensity is highest at the focus and decreases quadratically with the distance (z) from the focal plane, for distances larger than the Rayleigh length. Thus, the rate at which molecules are excited decreases very rapidly (as z^{-4}) with the distance from the focus and the excitation is confined in a small volume around the focus (on the order of λ^3, where λ is the wavelength of the incident beam). The linear absorption of a material may be very weak in the wavelength range where the two-photon absorption occurs, providing the potential to excite materials at greater depth than might be possible via one-photon excitation. Additionally, since the wavelength used for two-photon excitation is roughly twice that for one-photon excitation, the influence

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of scattering on the beam intensity is greatly reduced, by about a factor of 16 (since the light scattering efficiency scales as λ^{-4}). These are clear advantages for applications such as imaging in absorbing or scattering media, like biological tissues. Also, highly transparent nonlinear absorptive materials are of great interest in optical-limiting applications.

For many applications, chromophores with large two-photon absorptivities are advantageous, because a greater degree of excitation can be obtained or lower laser intensities can be used for pumping. Thus, there is a need to develop detailed structure/property relationships for two-photon absorbing molecules in order to guide the design of molecules whereby one can systematically increase the two-photon cross section and tune the position of the two-photon absorption peak. The development of such structure/property relationships will greatly benefit the design of new materials wherein improved two-photon absorption is combined with other molecular properties or processes (for example, large fluorescence quantum yield, efficient intersystem crossing, and low oxidation potential) that make those materials suitable for given applications.

We have previously reported[7] on a design strategy for chromophores with large two-photon absorptivities. One of these chromophore designs involves symmetrically substituted conjugated molecules with the general structure D-π-D, where D indicates an electron-donor group and π is a conjugated bridge. Experimental and theoretical evidence shows that the bis-donor substituted compounds can have δ values more than 1 order of magnitude larger than the corresponding unsubstituted molecules. This enhancement in δ has been correlated with intramolecular charge transfer from the terminal donor groups to the π-bridge.[7] The magnitude of δ can thus be controlled through the modification of the molecular structure in such a way as to affect the amount of intramolecular charge transfer. Specifically, δ is increased when the conjugation length of the π-system is increased (since the charge is transferred over a longer distance) and when electron acceptors (A) are attached as side groups to the π bridge, to form molecules of general structure D-π-A-π-D (wherein the amount of charge transferred is increased).[7] Molecules based on the scheme A-π-D-π-A are also characterized by large δ (with peak absorptivities in the red and near-infrared spectral range).[7] This result provides evidence that the charge transfer is effective in enhancing the two-photon absorptivity irrespective of the direction of the transfer (from the ends to the center of the molecule or from the center to the ends).

It is known that for linear polyenes and several classes of α,ω-substituted polyenes with more than two or three double bonds, the lowest excited singlet state is the $2A_g$ state, while the one-photon-allowed $1B_u$ state lies at slightly higher energy.[9,10] This finding allows one to explain the absorptive and emissive characteristics of these molecules. We will show that the bis-donor substituted diphenylpolyenes we have prepared exhibit a different ordering of the excited states for medium-length molecules; specifically the $1B_u$ state is energetically below the $2A_g$ state for $m < 5$ (m = number of double bonds in the polyene).

We present here the results of studies aimed at understanding the two-photon spectroscopy, the ordering of electronic states, and the photophysics of D-π-D systems in which the conjugated bridge is a diphenylpolyene or a phenylene-vinylene-type chain. The issues addressed in this paper are as follows: (i) The two-photon-induced fluorescence excitation spectra for a series of systematically varied structures will be presented. (ii) The effect of pulse duration on the cross sections, as measured by two-photon-induced fluorescence excitation spectroscopy, using both nanosecond and picosecond laser pulses, will be examined for a series of substituted diphenylpolyenes. (iii) The effect of chain length, dialkylamino or diarylamino terminal groups, and type of conjugated bridge on the position and magnitude of the lowest energy two-photon absorption band will be discussed. (iv) The ordering of the lowest energy one- and two-photon-allowed excited states for these D-π-D chromophores will be discussed in comparison with similar conjugated molecules. (v) A study of the fluorescence lifetimes following either one-photon or two-photon excitation will be presented and their relationship to the ordering of the $1B_u$ and $2A_g$ states will be discussed. (vi) An examination of how the transition dipole moments between the ground state and the one-photon excited singlet state and between the one- and two-photon excited states vary with chain length, with type of bridge, and the presence of terminal donor groups will be presented. Transition moments determined from experimental spectroscopic parameters using a three-level model will be compared with those from quantum chemical calculations.

2. Experimental Section

2.a. Materials. The molecules considered in this work (Figure 1) have the general structure D-π-D, where D is a tertiary amino electron-donor group and π is a conjugated bridge. The molecules differ in the type of conjugated bridge (diphenylpolyene in compounds **1**−**6**, bis(styryl)benzene in **7**−**10**, bis(phenylbutadienyl)benzene in **11**, and bis(styrylstyryl)benzene in **12**), in the type of amino substituents (diarylamino groups (compounds **6**, **9**, **10**) or dialkylamino groups (**1**−**5**, **7**, **11**, and **12**)), and in the presence (**8**, **10**−**12**) or absence of alkoxy side groups, which can act as additional donors, on the conjugated chain. The synthetic procedures and the characterizing data for these compounds are given in the Supporting Information.

2.b. Methods. Absorption spectra were measured with a Perkin-Elmer Lambda 9 spectrophotometer, and the corrected fluorescence and fluorescence excitation spectra were obtained with a Spex Fluorolog-2 spectrofluorometer. All data reported in the tables and figures correspond to measurements performed in toluene solution, except where otherwise noted. Cyclic voltammetry was performed under argon using solutions ca. 10^{-4} M in sample and 0.1 M in $[n\text{-Bu}_4\text{N}]^+[\text{PF}_6]^-$ using a glassy carbon working electrode, a platinum auxiliary electrode, an AgCl/Ag pseudo-reference electrode, and a BAS 100B potentiostat. Potentials were referenced by the addition of ferrocene to the cell and are quoted to the nearest 5 mV relative to the ferrocenium/ferrocene couple at 0 V. High-performance liquid chromatography (HPLC) with UV−visible and mass spectrometric (MS) detection (Hewlett-Packard Series 1100 LC/MSD) was performed on compound **5**, using a C18 Alltima column (Alltech) and methanol (90%)/dichloromethane (10%) eluent.

The two-photon absorptivity, δ, of the compounds examined has been measured through the two-photon-induced fluorescence method (see section 3) using both nanosecond (compounds **1**−**5** and **7**−**12**) and picosecond (compounds **1**−**4** and **6**) laser pulses. For the nanosecond experiment, an optical parametric oscillator laser (Quanta-Ray MOPO 730), pumped by a Q-switched Nd:YAG laser, has been used as the excitation source (pulse duration ≈ 5 ns, repetition rate = 10 Hz). The wavelength range covered by this system is 430−700 and 730−2000 nm. The samples were dissolved in toluene at a concentration of 10^{-4} M. The measurements of δ were carried out relative to molecules whose two-photon properties have been well characterized in the literature (1,4-bis(2-methylstyryl)benzene in cyclohexane,[11,12]

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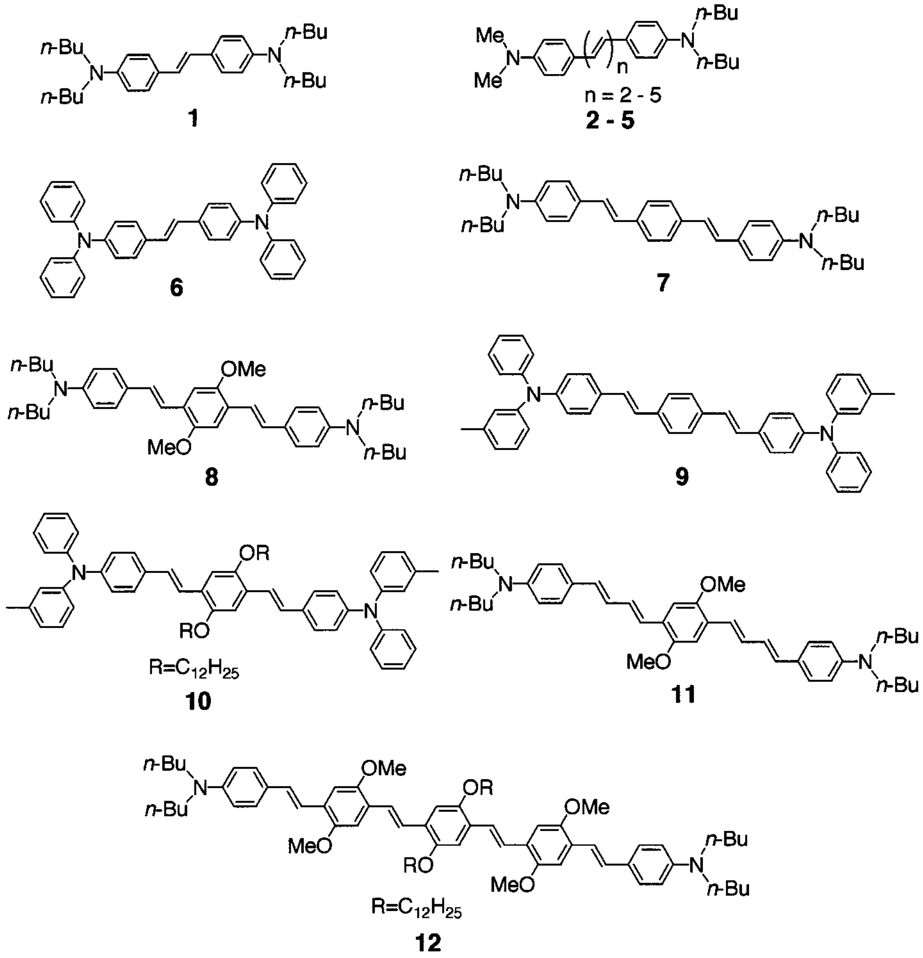

Figure 1. Molecular structure of the D-π-D chromophores considered in this work.

rhodamine B in methanol,[11] and fluorescein in water at pH = 11[11]), using a two-arm setup. In each arm, the laser beam was approximately collimated over the path length of the cuvette (1 cm) and the fluorescence was collected at a right angle with respect to the incident beam by a lens and directed to a photomultiplier tube (PMT). Proper filtering elements were used to prevent scattered light from reaching the detectors. To reduce the path length of the fluorescence emission in the solution under study and thus the effect of reabsorption, the incident beam was directed as close as possible to the window of the cell on the side where the light was collected. The effect of reabsorption of the emitted light in these conditions can be quantified as about 5% on the measured δ (slightly larger for molecules with small Stokes shift). This effect has not been explicitly included in the results reported below. The measurements were carried out in a laser intensity range for which a quadratic dependence of the fluorescence signal on the laser intensity was observed.

In the picosecond experiments, the output of a mode-locked Nd:YAG laser (Quantronix 416, repetition rate = 75 MHz, pulse duration $\approx$ 110 ps) was frequency doubled and used to synchronously pump a cavity-dumped dye laser (Coherent 702-2D, repetition rate = 3.75 MHz, pulse duration $\approx$ 3 ps). The wavelength range utilized in this study is 565−755 nm. The measurements were also performed with reference to a compound of known δ. The fluorescence was collected at a right angle to the incident beam, filtered, and focused onto a PMT. The signal from the PMT was amplified and directed to a universal counter (Hewlett-Packard 5334B). The compounds were dissolved in toluene at a concentration of 10^{-5} M.

The fluorescence lifetimes were measured using time-correlated single-photon counting. A ps laser source was used to excite fluorescence from the molecules under study through two-photon excitation (at 605 or 715 nm) or one-photon excitation (at 300 nm). The details of the experimental setup and the method of analysis of the data have been described previously.[13] The chromophores were dissolved in toluene and acetonitrile. In the case of two-photon excitation, concentrations in the range 10^{-4} to 10^{-5} M were used, while for the one-photon excitation the concentration was chosen such that the absorbance was about 0.02 for each compound.

The quantum-chemical determination of the two-photon absorption cross sections and the transition dipole moments is based on a methodology similar to that described in our previous work.[7] Calculations were performed on isolated molecules, i.e., solvent effects are neglected; however, the low dielectric constant of the solvent (toluene) used in the two-photon-induced fluorescence experiments makes this approximation reasonable. The ground-state geometries of all compounds have been calculated at the Hartree−Fock semiempirical AM1[14] level. On the basis of the optimized geometries, we have combined the intermediate neglect of differential overlap (INDO)[15] Hamiltonian with a multireference double configuration interaction (MRD-CI) scheme to describe the singlet excited states. Calculations were performed on bis(aminophenyl)polyenes similar to compounds **1**−**4**, but for which the substituents on both nitrogen atoms are methyl groups. To distinguish these systems from the experimental ones, they will be indicated with primed numbers (**1′**−**4′**). To ensure size consistency, the CI active space is made to include an increasing number of π molecular orbitals with increasing chain length (from 10 orbitals for molecule **1′** to 16 orbitals for molecule **4′**). However, for practical reasons, triple and quadruple excitations involving molecular orbitals localized within the phenylene rings were not taken into account in the CI expansion; this leads to a blue-shift of all excited states and, as a consequence, lower calculated δ values but does not affect the trends

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provided by the results. For instance, in the case of molecule **1′**, such an approach leads to $\delta = 147 \times 10^{-50}$ cm^4 s/photon-molecule, while the cross section for the same molecule was previously estimated to be of 200×10^{-50} cm^4 s/photon-molecule, when triple and quadruple excitations over the localized electronic levels were included.[7]

3. Two-Photon-Induced Fluorescence Method

For the case in which the linear absorption is negligible, the attenuation of a beam in a material due to two-photon absorption at a given time can be described by the following equation:

$$\frac{dI}{dz} = -\beta I^2 \tag{1a}$$

where I is the intensity (power per unit area) of the beam of frequency ν, z is the direction of propagation, and β is the two-photon absorption coefficient. Equivalently, eq 1a can be written in terms of the photon flux (number of photons per unit area and time, $F = I/h\nu$):

$$\frac{dF}{dz} = -\beta h\nu F^2 \tag{1b}$$

The number of photons absorbed per unit time and volume, in the two-photon absorption process, is thus $n^{(2)}{}_{\mathrm{ph}} = -dF/dz$, and, if the two-photon absorption cross section δ is defined as $h\nu\beta/C$ (C = number density of the molecules in the solution), we obtain: $n^{(2)}{}_{\mathrm{ph}} = F^2\delta C$.[16]

The number of excited molecules (per unit volume and time) is simply $^1/_2 n^{(2)}{}_{\mathrm{ph}}$, and the total density of photons, $n^{(2)}{}_{\mathrm{fl}}$, emitted per unit time is then given by:

$$n^{(2)}{}_{\mathrm{fl}} = {}^1/_2\eta n^{(2)}{}_{\mathrm{ph}} = {}^1/_2\eta F^2\delta C \tag{2}$$

with the assumption that following two-photon excitation, the molecules relax to the lowest excited singlet state, from which they fluoresce (η is the quantum yield of this emissive process). The previous expression holds when the number of excited molecules is small compared to the total number of molecules, that is, far from optical saturation. For large photon fluxes, deviations from the quadratic dependence on F predicted by eq 2 are observed. The intensity of the signal collected by a PMT detector in a two-photon-induced fluorescence measurement is $S = \Phi\ \langle n^{(2)}{}_{\mathrm{fl}}\rangle$, where Φ is the overall fluorescence collection efficiency of the experimental apparatus, which depends on the geometry of the setup, the wavelength dependence of the filters used to control the intensity and of the detector response, and the refractive index of the solution; $\langle\ \rangle$ indicates the spatial and temporal average over the laser pulses. Introducing the second-order temporal coherence term,[17] $g^{(2)} = \langle F^2(t)\rangle/\langle F(t)\rangle^2$, S can be expressed as:[11,18]

$$S = {}^1/_2\eta\Phi g^{(2)}\langle F\rangle^2\delta C \tag{3}$$

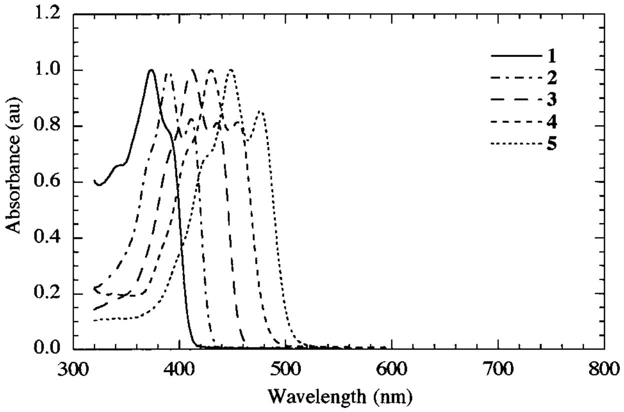

Figure 2. Linear absorption spectra of the bis(aminophenyl)polyenes **1**−**5** (in toluene).

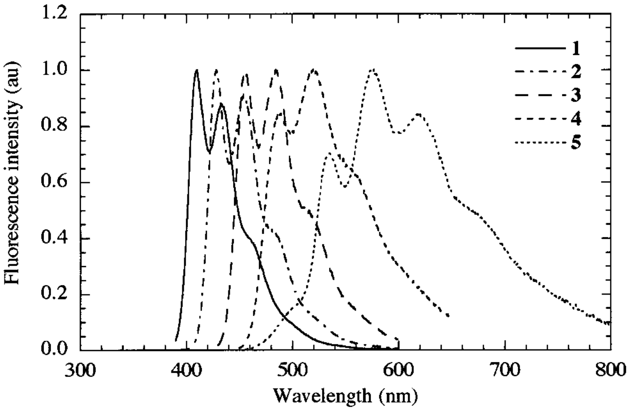

Figure 3. Fluorescence spectra of the substituted bis(aminophenyl)-polyenes **1**−**5** (in toluene) after one-photon excitation.

Using a two-arm setup, as described in the previous section, for the calibration of the intensity of the exciting beam, and using materials with known two-photon absorptivities as references, the value of δ for the sample under investigation is obtained by applying the equation:

$$\delta_{\mathrm{s}} = \frac{S_{\mathrm{s}}}{S_{\mathrm{r}}}\frac{\eta_{\mathrm{r}}\Phi_{\mathrm{r}}C_{\mathrm{r}}}{\eta_{\mathrm{s}}\Phi_{\mathrm{s}}C_{\mathrm{s}}}\delta_{\mathrm{r}} \tag{4}$$

where the subscripts s and r refer to the sample and the reference material, respectively. In this experimental setup, the collection efficiency can be expressed as $\Phi = \phi_{\mathrm{disp}} \times \phi_n$, where

$$\phi_{\mathrm{disp}} = \left[\int f_{\mathrm{fluor}}(\lambda) \times f_{\mathrm{PMT}}(\lambda) \times \prod_i T_i(\lambda)\mathrm{d}\lambda\right] \Big/ \int f_{\mathrm{fluor}}(\lambda)\mathrm{d}\lambda \tag{5}$$

is the correction factor due to the wavelength dispersion of the response functions (in eq 5, $f_{\mathrm{fluor}}(\lambda)$ is the fluorescence spectrum, $f_{\mathrm{PMT}}(\lambda)$ is the normalized PMT response, $T_i(\lambda)$ is the transmission spectrum of the ith filter used, and the integral is extended over the whole fluorescence spectrum) and $\phi_n \propto n^{-2}$ (n is the refractive index of the solution) takes into account the difference in the solid angles under which the illuminated portion of the solution is seen from the detector when the solvents for the sample and the reference solutions are different, in the limit of point sources emitting isotropically.

4. Results and Discussion

4.a. One- and Two-Photon Spectra. Figures 2 and 3 show the one-photon absorption and fluorescence spectra of the bis-(aminophenyl)polyene series (**1**−**5**). Most of these spectra exhibit vibronic structure with a progression of several peaks. The frequency of the mode progression is about 1300 cm^{-1} both in absorption and in emission, a value that is in the range of

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Table 1. Position ($\lambda^{(2)}_{\max}$, in nm) and Magnitude ($\delta_{\max}$, in 10^{-50} cm^4 s/photon-molecule) of the Peak Two-Photon Absorptivity of Bis(aminophenyl)polyenes[a]

	ns measurements		ps measurements			calculations	
compd	$\lambda^{(2)}_{\max}$	$\delta_{\max}$	$\lambda^{(2)}_{\max}$	$\delta_{\max}$	compd	$\lambda^{(2)}_{\max}$	$\delta_{\max}$
1	600	200	605	240	**1′**	484	147
2	640	260	640	230	**2′**	519	195
3	710	320	695	340	**3′**	544	219
4	730	425	695	410	**4′**	564	227
5	730	1300					
6			690	190			

[a] From two-photon-induced fluorescence measurements using nanosecond and picosecond laser pulses. The experimental uncertainty on $\delta_{\max}$ is of the order of 10−15% (25% for compound **5**, due in part to the low quantum yield).

the average of typical C−C and C═C stretching frequencies for polyenes. As is common to many series of homologous conjugated molecules, the position of the main peak in the absorption spectrum, $\lambda^{(1)}_{\max}$, shows a bathochromic shift with increasing chain length and varies over the range from 374 nm (for **1**) to 449 nm (for **5**). A more detailed analysis of the linear absorption and fluorescence spectra is given in section 4.b, together with the discussion regarding the energies of the one- and two-photon states.

Figures 4a−c display the two-photon fluorescence excitation spectra of the bis(aminophenyl)polyene chromophores **1**−**5** obtained using ns laser pulses,[19] as well as the spectra of **1**, **2**, and **6** using ps pulses. The position of the two-photon absorption maximum ($\lambda^{(2)}_{\max}$) and the peak two-photon absorptivity ($\delta_{\max}$) are summarized in Table 1 (ns results are presented for compounds **1**−**5**, ps results for **1**−**4** and **6**; the results of quantum-chemical calculations on **1′**−**4′** are also included). The $\delta_{\max}$ values obtained from the ns and ps experiments agree well with each other, indicating that these measurements are essentially independent of pulse duration, provided that the measured fluorescence signal is proportional to the square of the intensity of the exciting beam in both cases. There are, however, a few discrepancies in the spectral characteristics (band shapes and peak positions) for some of the ns and ps data, and further studies are necessary to explain these results. The rough invariance of δ with different pulse durations for two-photon-induced fluorescence measurements is in contrast with the results of nonlinear transmission measurements (NLT).[19] The values of δ for **1**−**4** obtained by NLT with ns pulses are larger by about 2 orders of magnitude than those obtained with ps pulses, although the ns NLT spectra have the same shape as the ones shown in Figure 4. During an ns pulse, the number of molecules pumped into the excited state can be large enough to give rise to substantial excited-state absorption, which appears as a contribution to the nonlinear loss. This process is a doubly resonant three-photon absorption, due to two-photon absorption followed by excited-state absorption, as opposed to a pure two-photon process. The excited-state absorption cross section was estimated to be of the order of 8 × 10^{-17} cm^2 for **1**.[19] As a consequence of the reasonably large two-photon and excited-state cross sections involved, these molecules exhibit good optical limiting properties.[19,20]

The effectiveness of the bis-donor substitution in increasing the two-photon absorptivity is evidenced by the comparison of $\delta_{\max}$ for compound **1** and for stilbene[21] (200 and ≈12 × 10^{-50} cm^4 s/photon-molecule, respectively). Upon extending the length of the polyene bridge in the bis(aminophenyl)polyenes, the position of the two-photon peak shifts toward the red, moving from 600 nm (2.07 eV) for **1** to 730 nm (1.70 eV) for **5**. For molecules with up to four conjugated double bonds (**4**), $\delta_{\max}$ increases almost linearly with chain length, consistent with the idea that the magnitude of δ is correlated to the distance over which charge may be transferred.[7] The δ for compound **5** is much larger than that for **4**, even when accounting for the larger uncertainty (± 25%) in the value for **5**. This larger value may be associated with a higher energy two-photon state than the 2A$_g$ state that has been assigned to the band observed for

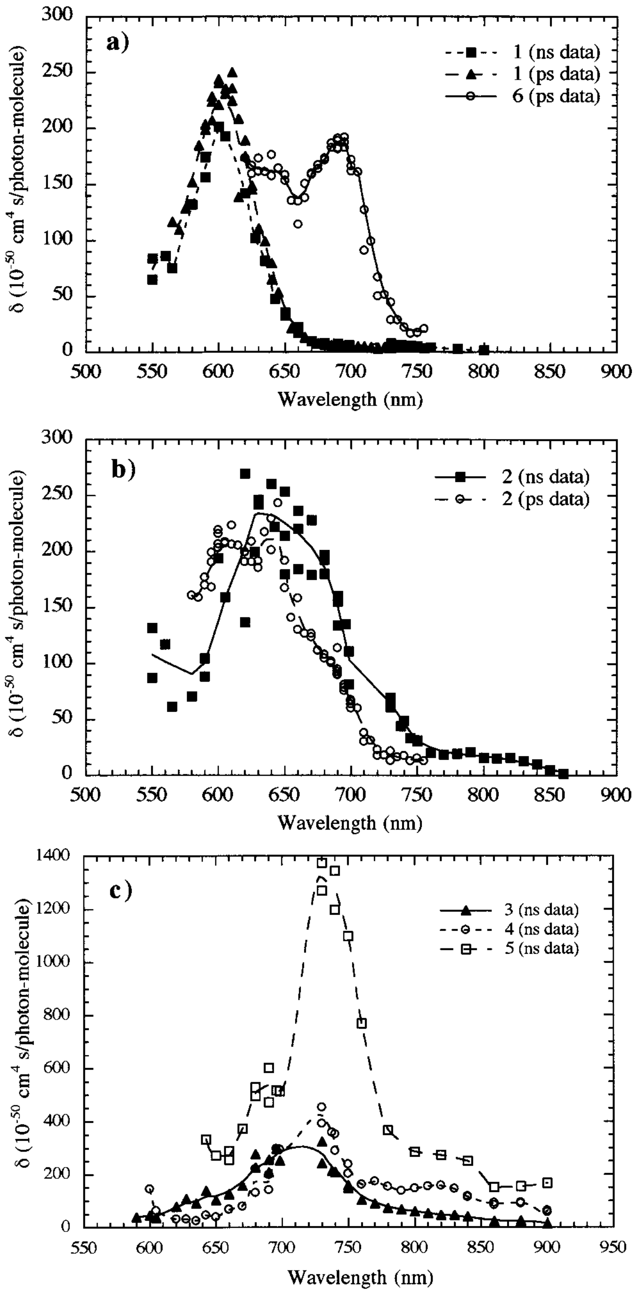

Figure 4. Two-photon-induced fluorescence excitation spectra of compounds (a) **1** (■ for ns pulses; ▲ for ps pulses) and **6** (○ for ps pulses); (b) **2** (■ for ns pulses; ○ for ps pulses); and (c) **3** (▲), **4** (○), and **5** (□) (all for ns pulses). All compounds were dissolved in toluene. The lines are provided as a guide to the eye.

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compounds **1**−**4**, as will be discussed below (section 4.b). Indeed, one would expect δ for a given two-photon state to saturate beyond some chain length because of the tradeoff between the increase in the distance over which the charge is transferred (and hence the transition length) and the decrease in the effective coupling of the terminal donors to the whole π-system (and hence a decrease of the amount of charge transferred) when the conjugated chain lengthens.[22] Such a reduction in the π-electron charge transferred from the amino moieties to the conjugated bridge in the excited state as a function of increasing chain length has been evidenced by quantum-chemical calculations on α,ω-diaminopolyenes (at the INDO/MRD-CI level of approximation).[23] The study of molecules with longer conjugation length is necessary to ascertain this point experimentally. As will be discussed in more detail in section 4.d, the increase of $\delta_{\max}$ with chain length for **1** to **5** is related mostly to an increase in the transition dipole moment between the $1A_g$ and $1B_u$ states and to a decrease of the difference between the energy of the $1A_g \rightarrow 1B_u$ transition and the energy of the incident photons at two-photon resonance (detuning energy). The values of $\delta_{\max}$ estimated from quantum-chemical calculations are in reasonable agreement with the experimental determinations, but slightly lower than the latter (Table 1). The discrepancy is partly due to the fact that the energy of the electronic states is overestimated with the choice of active space described in section 2 (recall also that the theoretical values refer to isolated molecules in a vacuum and do not include any effect of the environment).

It is interesting to compare the effect of the type of terminal amino moieties (di-*n*-butylamino or diphenylamino) on the two-photon fluorescence excitation spectrum. The two-photon absorption peak ($\lambda^{(2)}_{\max}$) is observed at 600 nm for compound **1** and 690 nm for compound **6**[19,20] (see Figure 4a; the corresponding energy difference is 0.54 eV), while the linear absorption peak ($\lambda^{(1)}_{\max}$) shifts by only 13 nm (from 374 nm for **1** to 387 nm for **6**,[20] corresponding to an energy difference of 0.11 eV). Similar values of $\delta_{\max}$ are measured for the two compounds. The analysis of the oxidation potentials for **1** and **6** (−35 and +305 mV, respectively, vs ferrocenium/ferrocene in tetrahydrofuran) shows that the diphenylamino group is a weaker donor than the dibutylamino group, due in part to the delocalization of the electrons in the nitrogen lone pair onto the terminal phenyls, in the ground state of the molecule. As a consequence, the highest occupied molecular orbital (HOMO) of **6** is actually located at slightly lower energy than that of **1**. Thus, the observed red-shift in the one- and two-photon absorption peaks must be due to a lowering of the energy of the excited electronic states involved in the transitions. This can be understood in terms of the stabilization of the partial positive charge on the nitrogen in the states that involve an intramolecular electron transfer from the nitrogen atom to the π-bridge. A larger stabilization is provided by the terminal phenyl groups, into which the positive charge can be delocalized, and it would be expected to depend on the amount of charge present on the nitrogen. The results of quantum-chemical calculations performed on bis(dimethylamino)stilbene[24] (**1′**) indicate that a larger fraction of charge is transferred from the nitrogen to the bridge in the two-photon state than in the one-photon state. Thus, the larger shift in the position of $\lambda^{(2)}_{\max}$ with respect to the shift in $\lambda^{(1)}_{\max}$ is correlated to a larger stabilization of the $2A_g$ state (see section 4.b for the assignment of this state) versus the $1B_u$ state upon replacing the dibutylamino with diphenylamino groups. The different dependence of the shift of the one-photon and two-photon bands on the molecular structure has been utilized to achieve efficient optical limiting properties over a broad wavelength range (≈200 nm) through the use of mixtures or layered structures based on these compounds.[19,20]

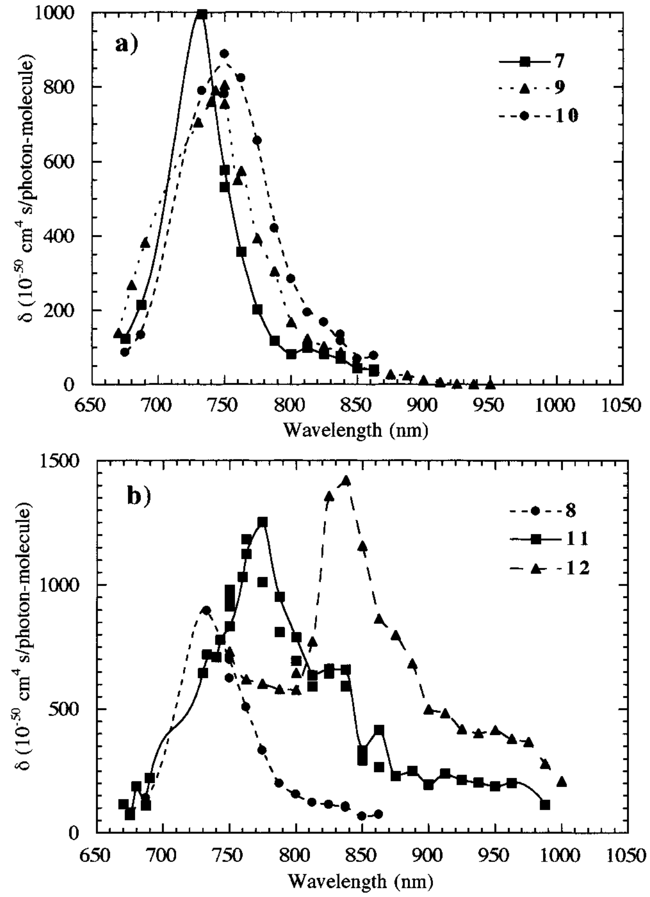

Figure 5. Two-photon-induced fluorescence excitation spectra (using ns laser pulses) for compounds (a) **7** (■), **9** (▲), and **10** (●) and (b) **8** (●), **11** (■), and **12** (▲). All compounds were dissolved in toluene. The lines are provided as a guide to the eye.

Table 2. Position ($\lambda^{(2)}_{\max}$, in nm) and Magnitude ($\delta_{\max}$, in 10^{-50} cm^4 s/photon-molecule) of the Peak Two-Photon Absorptivity of Bis(aminostyryl)Benzenes and Compounds **11** and **12**[a]

compd	$\lambda^{(2)}_{\max}$	$\delta_{\max}$	$\delta_{\max}/N$
7	730	995	155
8	730	900	140
9	745	805	125
10	745	855	130
11	775	1250	145
12	840	1420	125

[a] From nanosecond two-photon-induced fluorescence measurements. The experimental uncertainty on $\delta_{\max}$ is of the order of 10−15%. *N* is the number of double bonds in the conjugated bridge (the phenyl rings are considered equivalent to 1.5 double bonds).

The two-photon fluorescence excitation spectra, as obtained via ns measurements, of compounds **7**−**12**, which have one or more phenylene groups in the π-bridge, are displayed in Figures 5a and 5b and their peak absorptivities are summarized in Table 2. It is immediately evident that the values of $\delta_{\max}$ for the compounds in this series are larger than those for bis(aminophenyl)polyenes with comparable chain length. We have previously demonstrated that further enhancement of the two-photon response can be obtained when electron-accepting side

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groups are attached to the conjugated backbone.[7] Thus, the enhancement in δ_{max} for the bis(aminostyryl)benzenes compared to the bis(aminophenyl)polyenes suggests that the central phenylene ring in the bis(styryl)benzene bridge may be acting effectively as a weak electron acceptor. As we will show below (section 4.d), this increase of δ_{max} is mostly accounted for by an increase in the transition dipole moment between the $1B_u$ and $2A_g$ states. Also in this case, δ_{max} increases with conjugation length, both when multiple double bonds are present between the central and the terminal phenylene groups (**11**) and in the bis(styrylstyryl)benzene structure (**12**), and is largest for compound **12** (1420×10^{-50} cm^4 s/photon-molecule). It should be mentioned that δ_{max}/N, the contribution to δ_{max} per double bond (where N is the number of double bonds in the π-bridge and phenylene rings are considered equivalent to 1.5 double bonds), shows only a small variation in the whole series of compounds **7**−**12** (the values vary between 125 and 155×10^{-50} cm^4 s/photon-molecule, see Table 2), indicating that δ depends almost linearly on conjugation length among molecules with these structural designs. Also, δ_{max} increases almost linearly with chain length for the bis(aminophenyl)polyenes **1**−**4**, as mentioned above, and δ_{max}/N is about 50×10^{-50} cm^4 s/photon-molecule in the series.

Similar to the observations for **1** and **6**, red-shifts in $\lambda^{(1)}_{max}$ and $\lambda^{(2)}_{max}$ (which are larger in the case of $\lambda^{(2)}_{max}$) have been observed for compounds **7** and **8**, which bear dibutylamino donor groups, relative to compounds **9** and **10**, which have instead phenyltolylamino donor groups. In these cases, however, the red-shift is much smaller (only 3 nm in the one-photon spectrum and 15 nm in the two-photon spectrum) than in bis(aminophenyl)stilbenes. The values of δ_{max} are similar in all four compounds **7**−**10**. The oxidation potentials for compounds **7**−**10** are respectively +90, −10, +350 and +250 mV (vs ferrocenium/ferrocene in tetrahydrofuran) and show that also in this case the dibutylamino groups are slightly better donors. Because of the greater conjugation length of the bis(styryl)benzene bridge, the additional stabilization of positive charge on the nitrogen in the excited state upon adding terminal aryl groups is smaller than that in the case of the stilbene bridge. This may be responsible for the smaller shifts observed in the one- and two-photon spectra of **7**−**10** with respect to **1** and **6**. The change in oxidation potentials on going from **1** to **7** is larger than that from **6** to **9** because the relative increase in the number of rings in the molecule (and hence the stabilization of charge on the nitrogen) is larger in the former case. The influence of the alkoxy groups is the same in both dialkylamino and diarylamino compounds.

4.b. Ordering of the One- and Two-Photon States. It is well-known that the lowest excited singlet state in unsubstituted linear polyenes with $m \geq 3$ has the same symmetry as the ground state (that is A_g) while the lowest one-photon-allowed ($1B_u$) state lies at higher energy.[10,25] This deviation from the alternation between electronic levels with even and odd parity, predicted by single-electron models, is ascribed to the effect of electron correlation.[10] The presence of a low-energy A_g state is responsible for some of the anomalies observed in the absorption, fluorescence emission, and excitation spectra of these molecules,[26,27] like the large Stokes shift or the different solvent effects exhibited by the absorption and fluorescence peaks. Direct experimental evidence of the existence of an A_g level below the $1B_u$ state (which gives rise to the absorption band in the one-photon spectrum) has been obtained for a variety of compounds. This includes, for example, the observation of a low-energy weak band in the high-resolution low-temperature or gas-phase one-photon and two-photon spectroscopic studies[28,29] and the detection of a weak emission band at higher energies than the main band in the fluorescence spectrum.[30,31] This ordering of electronic levels is observed in unsubstituted polyenes (with $m \geq 3$, m = number of double bonds),[25,29] α,ω-dialkylpolyenes ($m \geq 3$),[25,32] and α,ω-diphenylpolyenes ($m \geq 2$).[10,25,31,33,34] Semiempirical INDO/MRD-CI calculations of vertical transitions predict a first excited state with A_g symmetry for polyenes ($m = 2-5$) and for some bis-donor substituted polyenes (with amino groups for $m = 2-5$ or with hydroxy and dimethylamino groups for $m = 2$).[23]

For the diphenylpolyenic molecules considered in this study (**1**−**6**), the situation is different. The relative energies of the lowest one- and two-photon levels for the bis(aminophenyl)polyenes are summarized in Figure 6a (the energies of the one- and two-photon states are derived from $\lambda^{(1)}_{max}$ and $\lambda^{(2)}_{max}$ and correspond to the energy of vertical transitions). The one-photon level corresponds to the $1B_u$ state and the two-photon level is indicated generically with nA_g in Figure 6a. The progressive and similar shifts in the position of the absorption and fluorescence maxima with chain length (see Figures 2 and 3), the relatively small Stokes shifts (of the order of 1000 cm^{-1} for **1-4**), and the large quantum yields ($\eta > 0.4$ for **1**−**4** and **6**) suggest that the electronic state responsible for the one-photon absorption and fluorescence spectra are the same and are consistent with the identification of the $1B_u$ state as the lowest excited state (S_1) for all the bis-donor substituted diphenylpolyenes containing up to four double bonds (**1**−**4** and **6**). In addition, all these molecules have rather short excited-state lifetimes ($\tau < 1.8$ ns, see Table 3). The values of the radiative (k_{rad}) and nonradiative (k_{nrad}) decay rates from the fluorescent state, as estimated from the lifetimes and the fluorescence quantum yields, are also given in Table 3. Except for molecule **5**, k_{rad} is larger than (or comparable to) k_{nrad}, as would be expected for the emission corresponding to a dipole-allowed transition ($1B_u \rightarrow 1A_g$). For compounds **1**−**3**, the two-photon fluorescence excitation spectra reported in Figures 4a and 4b extend to slightly longer wavelengths than the one-photon resonance ($2\,\lambda^{(1)}_{max}$), but negligibly small two-photon absorption is observed in that region. This is a further indication that no excited A_g state exists below the $1B_u$ one. All these observations lead to the identification of the nA_g state in Figure 6a with the $2A_g$ state for **1**−**4** and **6**. Moreover, the results of quantum-chemical calculations (Figure 6a) on molecules **1′**−**4′** show that for these systems $1B_u$ is the lowest vertical excited singlet state and $2A_g$ is the next vertical excited singlet state. Experimental and theoretical values in Figure 6a show the same trend, but the calculated energies are blue-shifted by about 1 eV, mostly because of the choice of active space to achieve size-consistency (as mentioned in section 2).

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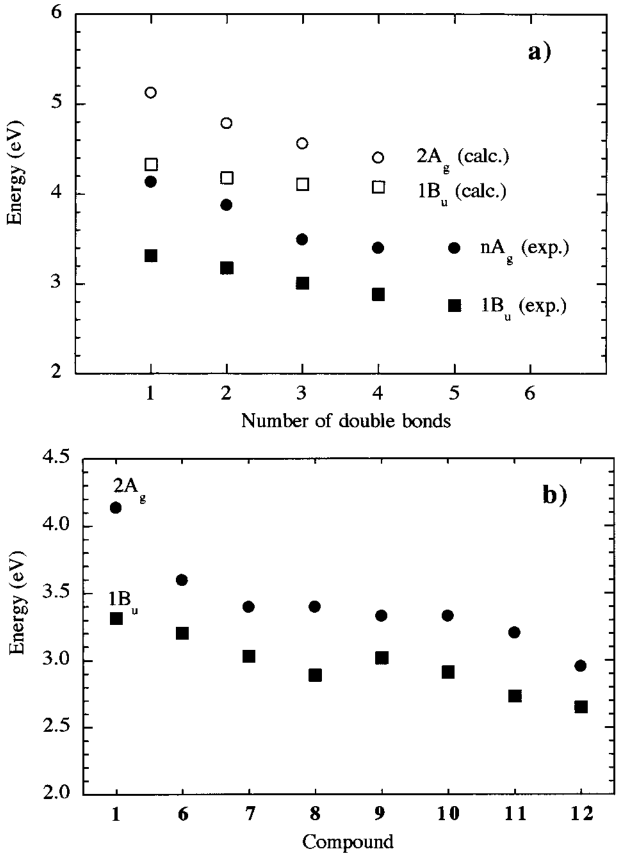

Figure 6. Relative energy of the one-photon electronic level ($1B_u$) and the two-photon level ($2A_g$ or nA_g, see text) for: (a) the bis(aminophenyl)polyenes as a function of chain length and (b) for compounds **6**−**12** (compound **1** is included for comparison). The experimental energies for the one-photon and the two-photon state correspond to $\lambda^{(1)}_{max}$ and to $\lambda^{(2)}_{max}$, respectively. In (a), solid symbols refer to experimental values for molecules **1**−**5** and open symbols to calculations for molecules **1′**−**4′**.

Table 3. Fluorescence Lifetime (τ), Fluorescence Quantum Yield η, Rate Constant for Radiative (k_{rad}) and Non-radiative (k_{nrad}) Decay for D-π-D Chromophores

compd	τ (ns) in toluene[a]	η[b]	k_{rad} (10^8 s^{-1})	k_{nrad} (10^8 s^{-1})	τ (ns) in acetonitrile[c]
1	1.55	0.90	5.81	0.65	1.60 1.54[d]
2	0.71	0.80	11.27	2.82	0.65
3	0.91	0.76	8.35	2.64	0.28
4	1.33	0.42	3.16	4.36	0.24
5	0.66	0.023	0.35	14.80	0.36
6	1.76	0.87	4.94	0.74	1.67
7		0.88			1.35
8		0.88			1.38
9		0.93			
10		0.97			1.60
11		0.12			1.01
12		0.65			

[a] Lifetime of S_1 state in toluene after two-photon excitation at 715 nm. [b] In toluene. [c] Lifetime of S_1 state in acetonitrile after one-photon excitation at 300 nm. [d] Excitation at 605 nm.

While our studies place the $2A_g$ above the $1B_u$ state for compound **4**, there is evidence of some vibronic coupling of these states in the nonnegligible two-photon activity on the red side of the two-photon peak and in the reduction in k_{rad} and increase in k_{nrad} relative to the molecules with shorter chains. The behavior of compound **5** deviates in several respects from that of the shorter substituted polyenes described above. First, the peak two-photon absorptivity is much larger for **5** than for **1**−**4** and some two-photon absorption is observed also for $\lambda > \lambda^{(2)}_{max}$. Second, the quantum yield is small ($\eta = 0.023$) and k_{rad} for **5** is much lower than k_{rad} for the shorter polyenes in the series. Moreover, the fluorescence spectrum of **5** is considerably red-shifted with respect to that of **4**, and this is responsible for a larger Stokes shift (about 2200 cm^{-1}). The fluorescence data suggests that the emitting state is either an A_g state or a mixed $1B_u/A_g$ state with a large degree of A_g character. We cannot conclude whether this A_g state is the relaxed A_g state corresponding to that observed in the two-photon spectrum at 730 nm or a lower A_g state. Given the earlier discussion of the δ value observed for **5** and the large energy gap between the two-photon state observed in absorption and the emitting state, we favor an interpretation of the two-photon absorption band as due to a higher two-photon state and the emitting state as due to or strongly involving the $2A_g$ state. Further investigations, including the measurement of the two-photon fluorescence excitation spectrum beyond 900 nm, will be carried out in order to gain insight into the assignments of these states.

The fluorescence spectrum of **5** in toluene also shows a small shoulder in the short-wavelength side of the main band (around 500 nm). While the origin of this feature has not been definitively established, evidence from HPLC with UV−visible detection, LC/MS, and excitation spectroscopy suggests that it is due to an isomer. Samples of **5** judged to be of high purity by elemental analysis and ^{1}H NMR were analyzed by HPLC, and three small peaks were separated at shorter retention times than the main peak (which accounted for 84% of the total area). LC/MS measurements showed that the masses of the species eluted were the same (in one case including one methanol molecule). Furthermore, excitation spectra obtained with emission detected at 500 and 535 nm showed some differences in peak positions and band shapes, consistent with the presence of isomers.

The above results provide evidence that bis(aminophenyl)-polyenes containing up to *four* double bonds have a first excited state (S_1) of B_u symmetry and a second excited state (S_2) of A_g symmetry, as opposed to polyenic structures of the same length but with different terminal moieties, for which $S_1 = 2A_g$ and $S_2 = 1B_u$. The correct ordering of the vertical and relaxed electronic levels for **5** has yet to be confirmed, but the data available up to now suggest that the $2A_g$ is the lowest relaxed excited state. Indeed, in the limit of long chains, the ordering of the levels is expected to become similar to that for polyenes, because of the reduced coupling between the end groups and the conjugated chain.

The $1A_g$−$1B_u$ transition energy (see Figure 6) ranges between 2.6 eV (for **12**) and 3.3 eV (for **1**) and decreases, as mentioned, with increasing conjugation length. The energy separation between the $1B_u$ and $2A_g$ states varies considerably from one compound to the other (ranging from 0.3 to 0.8 eV). Compounds **8** and **10** differ from **7** and **9**, respectively, due to the presence of alkoxy groups on the central ring. As alkoxy groups act as weak donors toward a π-system, the $1B_u$−$1A_g$ transition energy for **8** and **10** becomes smaller by 0.14 and 0.11 eV, respectively, with respect to the unsubstituted compounds (**7** and **9**) and the oxidation potentials are 100 mV smaller for **8** and **10** than for **7** and **9** (see section 4.a). The position of the $2A_g$ level is not affected by the alkoxy substitution ($\lambda^{(2)}_{max} = 730$ nm for **7** and **8**, 745 nm for **9** and **10**), probably because the larger negative charge on the bridge in the $2A_g$ state is destabilized by the presence of the alkoxy groups. Moreover, within the experimental error, δ_{max} values for the alkoxylated and unalkoxylated molecules are the same, so that the presence of alkoxy groups in the central portion of the molecule has practically no effect on the two-photon properties.

4.c. Lifetime Measurements. The fluorescence lifetimes (τ) for the compounds studied have been determined under various experimental conditions. The data presented in Table 3 demonstrate that the lifetime for **1** is the same when measured after one-photon (300 nm) or two-photon (605 nm) excitation, an indication that in both cases the molecules relax to the same electronic state (S_1), from which they fluoresce. Moreover, for compound **1**, τ is solvent independent. Large solvent effects on the lifetime are observed for **3**−**5**, but it should be kept in mind that the excitation conditions for the measurement in toluene and acetonitrile are different. Variations in the quantum yields of these compounds have also been observed in solvents of different polarity.[35] Both in toluene and in acetonitrile, τ does not vary monotonically with chain length. Most of the chromophores considered here have large fluorescence quantum yields, a characteristic that makes them interesting for applications in imaging techniques based on the detection of fluorescence. The rate for nonradiative decay (k_{nrad}) progressively increases with chain length in the series **1**−**5**. More precisely, the deexcitation in compounds **1**−**3** is dominated by the radiative decay, while in compound **4** radiative and nonradiative decays show comparable rates. Finally, for compound **5**, both a large decrease in k_{rad} and an increase in k_{nrad} with respect to **4** are observed. The large value of k_{nrad} compared to k_{rad} for **5** is consistent with the presence of an A_g state below the dipole-allowed B_u state, as discussed above (section 4.b).

4.d. Transition Dipole Moments. The two-photon cross section δ is related to the second-order hyperpolarizability γ through the following equation (for an isotropic medium):[16,36]

$$\delta = \frac{4\pi^2 \hbar\omega^2}{n^2 c^2} L^4 \mathrm{Im}\,\langle\gamma\rangle \tag{6}$$

where $\hbar$ is Planck's constant divided by 2π, n is the refractive index of the medium, c is the speed of light, L is the local field factor, and Im indicates the imaginary part of the complex quantity $<\gamma>$, the orientational average of γ. Equation 6 is written according to the definitions of electric field, polarization, and hyperpolarizability given by Butcher and Cotter.[37] The differences found in the literature[16,36] for the relationship between δ and γ are due to different conventions used. From the sum-over-states expression for γ[37] in the case where the main contributions to γ come from only two excited electronic states, and when the main element of the γ tensor is the one along the chain axis, the following simplified expression is obtained:[7,38]

$$\begin{aligned}\mathrm{Im}\,\langle\gamma\rangle &= \frac{4}{5}\,\mathrm{Im}\,\frac{M_{\mathrm{ge}}^2 M_{\mathrm{ee'}}^2}{(E_{\mathrm{ge}} - \hbar\omega - i\Gamma_{\mathrm{ge}})^2 (E_{\mathrm{ge'}} - 2\hbar\omega - i\Gamma_{\mathrm{ge'}})} \\ &\approx \frac{4}{5}\,\frac{M_{\mathrm{ge}}^2 M_{\mathrm{ee'}}^2}{(E_{\mathrm{ge}} - \hbar\omega)^2 \Gamma_{\mathrm{ge'}}}\end{aligned} \tag{7}$$

In eq 7 $M_{\alpha\beta}$ is the transition dipole moment and $E_{\alpha\beta}$ the energy for the transition between the electronic states α and β, and $\Gamma_{\alpha\beta}$ is the corresponding damping factor (half width at half-maximum), g is the ground state ($1A_g$), e is the one-photon-allowed excited state ($1B_u$), e′ is the two-photon allowed excited state ($2A_g$ or nA_g), and the approximate expression holds near the two-photon resonance ($E_{\mathrm{ge'}} \approx 2\hbar\omega$) and for a damping factor small relative to the one-photon detuning ($\Gamma_{\mathrm{ge}} \ll E_{ge} - \hbar\omega$). The energy of the electronic transitions e → g and e′ → g are derived directly from the peaks in the one- and two-photon spectra ($\lambda_{\max}^{(1)}$ and $\lambda_{\max}^{(2)}$).

The transition dipole moment M_{ge} can be calculated from the integrated strength of the $1A_g \rightarrow 1B_u$ (g → e) band in the linear absorption spectrum according to:[33,39,40]

$$M_{\mathrm{ge}} = \left[\frac{1500(\hbar c)^2 \ln 10}{\pi N_A E_{\mathrm{ge}}} \int \epsilon_{\mathrm{ge}}(\nu)\mathrm{d}\nu\right]^{1/2} \tag{8}$$

(N_A is Avogadro's number, $\epsilon_{\mathrm{ge}}(\nu)$ the extinction coefficient, in M^{-1} cm^{-1}, at the wavenumber ν, in cm^{-1}, and the integral is performed over the absorption band).

Using eqs 6 and 7, the following expression for the transition dipole moment $M_{\mathrm{ee'}}$ is obtained:

$$M_{\mathrm{ee'}} = \frac{nc(E_{\mathrm{ge}} - \hbar\omega)}{4\pi\omega L^2 M_{\mathrm{ge}}} \left(\frac{5\Gamma_{\mathrm{ge'}}\,\delta_{\max}}{\hbar}\right)^{1/2} \tag{9}$$

In this model, the actual shape of the two-photon band is not considered directly and only the peak absorptivity ($\delta_{\max}$) and the overall bandwidth ($\Gamma_{\mathrm{ge'}}$) are used.[41] In the following, we assume $\Gamma_{\mathrm{ge'}} = 0.1$ eV for all molecules, since this value is a typical damping width for conjugated organic molecules in solution. It is consistent with the bandwidth of the two-photon spectra (the full width at half-maximum for the two-photon spectra shown in Figures 4 and 5 is in the range 0.13−0.31 eV) and with the width of the vibronic features observed in the one-photon spectra (Figures 2−3). A bandwidth of this order corresponds to an electronic dephasing time ($T_2 \approx \hbar/\Gamma_{\mathrm{ge'}}$) of about 10 fs, which is shorter than but of the same order of magnitude as typical dephasing times experimentally determined for other large organic molecules (15−60 fs).[42−46] The same value of $\Gamma_{\mathrm{ge'}}$ has also been used for the quantum chemical calculations of δ presented in this paper.

The detuning energy, $\Delta E = E_{\mathrm{ge}} - \hbar\omega = E_{\mathrm{ge}} - {}^1\!/_2 E_{\mathrm{ge'}}$, is estimated from the position of the absorption peaks in the one- and two-photon spectra and ranges between 1.06 and 1.41 eV for the molecules considered in this work (see Table 4). The values of the transition moments M_{ge} obtained from eq 8 and $M_{\mathrm{ee'}}$ from eq 9 are listed in Table 4, together with the extinction

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Table 4. Summary of Optical Data and Parameters for Compounds **1**−**12**[a]

compd	$\lambda^{(1)}_{\max}$ (nm)	$\epsilon_{\max}$ (M^{-1} cm^{-1})	M_{ge} (D)	detuning energy (eV)	$M_{ee'}$ (D)
1	374	46000	7.67	1.25	5.80
2	390	65000	9.38	1.24	5.73
3	412	81000	10.9	1.26	6.17
4	430	96000	12.4	1.18	6.03
5	449	103000	12.8	1.06	9.18
6	387	47000	8.06	1.41	6.78
7	409	74000	10.7	1.33	12.1
8	429	67000	10.5	1.19	10.5
9	411	63000	10.0	1.35	12.0
10	426	65000	10.8	1.25	10.6
11	454	93000	12.8	1.13	10.2
12	468	110000	14.2	1.17	11.0
13[b]	297	31000	6.82	1.76	1.93
14[c]	350	50500	9.01	1.36	2.81

[a] Linear absorption maximum ($\lambda^{(1)}_{\max}$), extinction coefficient ϵ_{ge} at $\lambda^{(1)}_{\max}$ ($\epsilon_{\max}$), transition dipole moment M_{ge} from eq 8, detuning energy $\Delta E = E_{ge} - {}^{1}/_{2}E_{\epsilon'}$ (E_{ge} and $E_{ge'}$ are the energies of the transitions g → e and g → e′, respectively, derived from $\lambda^{(1)}_{\max}$ and $\lambda^{(2)}_{\max}$) and transition dipole moment $M_{ee'}$ from eq 9. The transition moments are expressed in debye (D). [b] *trans*-Stilbene. [c] 1,4-Bis(2-methylstyryl)benzene.

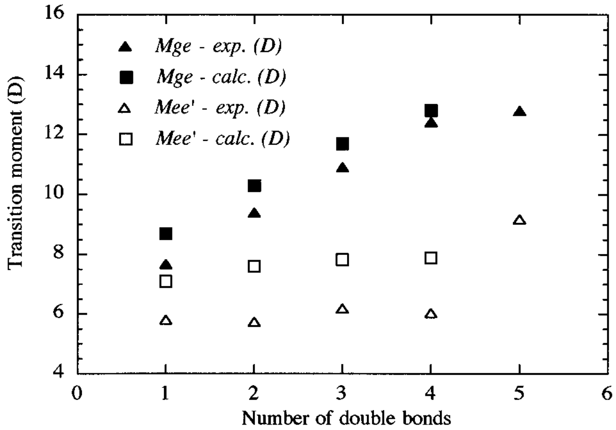

Figure 7. Transition dipole moments for compounds **1**−**5** or **1′**−**4′**: M_{ge} from eq 8 (▲) and from quantum-chemical calculations (■); $M_{ee'}$ from eq 9 (△) and from quantum-chemical calculations (□).

coefficients and the peaks of the absorption spectrum ($\epsilon_{\max}$ and $\lambda^{(1)}_{\max}$). The values of M_{ge} and $M_{ee'}$ from eqs 8 and 9 are compared with those obtained from the quantum-chemical calculations in Figure 7 for the bis(aminophenyl)polyenes. The empirical and theoretical transition dipole moments both show the same trend as the structure is varied. Considering the simplifying assumptions under which eq 9 was derived (in particular the consideration of only one intermediate state, the $1B_u$ state), the quantitative agreement between theory and experiment is quite good.

To make a comparison with compounds possessing no donor substitution, the experimental values of the transition dipole moments for stilbene (**13**) and 1,4-bis(2-methylstyryl)benzene (**14**) are also included in Table 4. On going from **13** to **1**, M_{ge} increases slightly, while $M_{ee'}$ increases by a factor of about 3. The same trend is observed when comparing **14** with **7** or **9**. These results show that the enhancement in $\delta_{\max}$ in D-π-D structures with respect to unsubstituted conjugated molecules (**13**, **14**) is correlated mainly with the increase in the transition moment $M_{ee'}$.

The data in Table 4 show that M_{ge} progressively increases with increasing chain length, and comparable values are shown by molecules with similar conjugation lengths but different backbones (compare, for example, **2** or **3** with **7**−**10**). The increase in $\delta_{\max}$ with chain length in the series **1**−**5** is due both to the increase in M_{ge} and to the decrease in the detuning energy. The increase of M_{ge} with chain length for bis(aminophenyl)-polyenes is similar to that observed in unsubstituted diphenylpolyenes,[47] but in the latter case the magnitude of the transition dipoles are smaller, due to the lower degree of charge transfer.

On the other hand, $M_{ee'}$ is almost constant with chain length in both the bis(aminophenyl)polyenes up to four double bonds (Figure 7) and in the series of compounds containing one or more phenylene rings in the conjugated bridge (**7**−**12**), but the value of $M_{ee'}$ depends critically on the type of conjugated chain. In particular, $M_{ee'}$ is much larger for the bis(styryl)benzenes and compounds **11** and **12** than for the diphenylpolyene series (about 11 and 6 D, respectively). This indicates that the probability for the transition e → e′ is greatly enhanced when a phenylene ring is present in the center of the conjugated bridge, apparently acting as an acceptor for the charge that is made available by the terminal donors. This increase in $M_{ee'}$ is responsible for the large $\delta_{\max}$ measured for the series **7**−**12** with respect to the bis(aminophenyl)polyenes.

Finally it should be noted that even if both M_{ge} and $M_{ee'}$ are larger for compound **6** than for **1**, probably due to a slightly longer effective conjugation length in the diphenylamino case, the values of δ are very similar within the experimental uncertainty. This is explained by the larger detuning for **6**, because the one- and two-photon levels are closer in this case.

5. Conclusions

We have investigated in detail the structure/property relationships for two-photon-absorbing chromophores and have confirmed that bis-donor substitution leads to an increase in the δ values, in agreement with our earlier report.[7] Increasing the length of the conjugated linker in D-π-D molecules, through use of diphenylpolyene or phenylene-vinylene-type bridges, also results in increased δ. This increase is essentially linear with chain length but depends on the type of bridge, with the phenylene-vinylenes showing the larger increase.

By making use of a three-level model, the transition moments for the $1A_g \rightarrow 1B_u$ (M_{ge}) and $1B_u \rightarrow 2A_g$ ($M_{ee'}$) transitions have been calculated from the one- and two-photon spectra. As determined experimentally and by quantum chemical calculations, the increase in δ upon bis-donor substitution of conjugated bridges has been correlated mainly with an increase in $M_{ee'}$, indicating a strong influence of the bis-donor substitution on the structure and properties of the excited states. On the other hand, the effect of increasing chain length on δ is dominated by an increase in M_{ge} and a reduction in the detuning energy.

Bis-donor substitution is also found to influence the relative ordering of the $2A_g$ and $1B_u$ states. In fact, in bis(aminophenyl)-polyenes, the $2A_g$ state lies above the $1B_u$ state at least up to $m = 4$ double bonds, in contrast with unsubstituted diphenylpolyenes or simple polyenes, for which the $2A_g$ state is observed at lower energy for $m \geq 2$.

These studies of structure/property relationships provide insight into the molecular mechanism of two-photon absorption and provide a basis upon which to examine the role of the greater degree of intramolecular symmetric charge redistribution in molecules of D-π-A-π-D and A-π-D-π-A structural types.[7]

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Supporting Information Available: Synthetic procedures and characterizing data for compounds **1**−**5** and **7**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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