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**INSIGHT INTO THE NONLINEAR  
ABSORBANCE OF TWO RELATED  
SERIES OF TWO-PHOTON  
ABSORBING CHROMOPHORES  
(Preprint)**

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# Insight into the Nonlinear Absorbance of Two Related Series of Two-Photon Absorbing Chromophores

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## Abstract

A comprehensive photophysical study has been carried out on two series of two-photon absorbing dyes. Looking at a series of structurally related chromophores provides insight into what controls the linear and nonlinear photophysical properties. These materials consist of an electron withdrawing benzothiazole group connected to a diphenylamine via a fluorene group. Within the series there are one-arm (dipolar), two-arm (quadrupolar), and three-arm (octupolar) versions of each dye. The one photon properties were studied using steady-state absorption, steady-state and time resolved emission, femtosecond transient absorption, and nanosecond transient absorption. The two-photon properties were studied using femtosecond Z-scan and nanosecond nonlinear transmittance. On the basis of a two photon assisted excited state absorption model we show that the excited state absorption from both the singlet and triplet excited states contributes to the overall nanosecond nonlinear absorption in these materials. In this study we determined that increasing the number of branches from one to three on the chromophore results in an increase in the overall nanosecond nonlinear absorption due to an increase in the excited state absorption.

## Introduction

The development of two-photon absorbing materials is a growing area of research as evidenced by the numerous publications in the past fifteen years.<sup>1,2</sup> There are a host of uses for two photon absorbers that include use in optical data storage,<sup>3</sup> frequency upconverted lasing,<sup>4</sup> nonlinear photonics,<sup>5</sup> microfabrication,<sup>6</sup> fluorescence imaging,<sup>7</sup> and photodynamic therapy<sup>8</sup>. Two photon absorbers provide an advantage by exciting in the lower energy near IR region resulting in the higher energy photophysical properties. Another advantage is that a two photon absorption process only turns on at high energy levels allowing for more control in various applications.

We recently reported on the one photon photophysical properties of a two-photon absorbing chromophore named AF455 in various solvents.<sup>2(n)</sup> In this study the two-photon assisted excited-state

absorption model was used as a basis for using the measured one-photon photophysical properties to understand why the nanosecond effective two-photon absorption cross section is much larger than the femtosecond intrinsic two-photon absorption cross section. Since then a more detailed manuscript has been published that concludes that excited singlet-singlet and triplet-triplet absorption are the dominant sources of nonlinear transmittance loss in the nanosecond regime, and that the chief role of two-photon absorption is to populate these states.<sup>9</sup> Based on this finding we have increased our efforts to design materials with large  $S_1$ - $S_n$  and  $T_1$ - $T_n$  absorption in the same spectral region as the two-photon absorption to increase the overall nonlinear absorption in a material.

In this study we focus our efforts on understanding the one-photon photophysical properties of two series of two-photon dyes that have previously been separately published.<sup>2(d,e,g,i,k,l,m,o,p)</sup> The structures are shown in Figure 1. All molecules contain an electron donating diphenylamine/triphenylamine conjugated through a fluorene center and an electron withdrawing benzothiazole. The two series each consist of a dipolar (one-arm), quadrupolar (two-arm), and octupolar (three-arm) chromophore. The AF270 series only differs to the AF240 series by an additional phenyl group (triphenylamine) between the central fluorene and the nitrogen of the amine. Recently in collaboration with computational work the one photon absorption properties of these molecules were published<sup>2(p)</sup> but to our knowledge a complete photophysical study has never been completed. In this paper we systematically compare the one-photon and two-photon photophysical properties within the series of chromophores to identify structure property relationships based on a dipolar vs. quadrupolar vs. octupolar species. We also want to show that the kinetics and spectral properties obtained via one-photon excitation are needed to understand the differences of two-photon absorption in the femtosecond and nanosecond domains.

## Experimental

**Synthesis.** The synthesis of all materials has previously been described.<sup>2(p)</sup>

**General Techniques.** Ground state UV/Vis absorption spectra were measured on a Cary 500 spectrophotometer. Emission spectra were measured using a Perkin Elmer model LS 50B fluorometer. Time correlated single photon counting (Edinburgh Instruments OB 920 Spectrometer) was utilized to determine singlet state lifetimes. The sample was pumped using a 70-picosecond laser diode at 401 nm. Emission was detected on a cooled microchannel plate PMT. Data was analyzed using a reconvolution software package provided by Edinburgh Instruments. Ultrafast pump-probe transient absorption measurements using a 1-mJ, 100 fs pulse at 400 nm at a 1 kHz repetition rate obtained from a diode-pumped, Ti:sapphire regenerative amplifier (spectra Physics Hurricane) were performed. The 800 nm beam was split and sent through a frequency doubler to create 400 nm light. The split beam was delayed and then focused into a sapphire plate to generate a white light continuum. The white light was then overlapped with the pump beam in a 2-mm quartz cuvette and then coupled into a CCD detector. Details of the ultrafast system are described elsewhere.<sup>2(n)</sup> Nanosecond transient absorption measurements were carried out using the third harmonic (355-nm) of a Q-switched Nd:YAG laser (Quantel Brilliant, pulse width ca. 5 ns). Pulse fluences of up to 8 mJ cm<sup>-2</sup> at the excitation wavelength were typically used. A detailed description of the laser flash photolysis apparatus has been published earlier.<sup>10</sup>

Fluorescence quantum yields were determined using the actinometry method previously described.<sup>10</sup> Quinine sulfate was used as an actinometer with a known fluorescence quantum yield of 0.55 in 1.0 N H<sub>2</sub>SO<sub>4</sub>.<sup>11</sup> All samples were excited at 350 nm with a matched optical density of 0.1. The molar absorption coefficient of the chromophore singlet excited state was determined using the method of relative actinometry utilizing C<sub>60</sub> in toluene.<sup>12</sup> The samples had matched OD at the exciting wavelength of 400 nm. The molar absorption coefficient of the triplet excited state was determined using the method of singlet depletion, which has been described previously.<sup>10</sup> Quantum yields for intersystem crossing were determined using the method of relative actinometry with a benzophenone actinometer.<sup>10</sup> Matched optical densities of the AFX molecule and benzophenone at 355 nm were utilized in each determination.

The femtosecond two-photon absorption cross-sections were measured using the open aperture z-scan technique<sup>13</sup> with the concentrations of the samples in THF at 0.02 M unless otherwise noted. For these experiments we used a Spectra-Physics Hurricane Ti:Sapphire laser operating at 800 nm with a repetition rate of 1 kHz and pulse duration of 105 fs. Both the temporal and spatial profiles of the laser beam were Gaussian. In the z-scan technique a thin sample, meaning the pathlength through the sample is much less than the Rayleigh range of the optical path, translates in and out of the focus of a laser beam and the transmission of the laser through the sample is recorded as a function of position along the optical axis (z-axis). Z-scans were collected at various laser fluences for each sample and the transmission profiles were fit to determine the two-photon absorption coefficient ( $\beta$ ) and from that the two-photon absorption cross-section ( $\sigma_2$ ). This procedure is described later in the manuscript. For our system the Rayleigh range was approximately 6 mm and pathlength of the samples was 1 mm for which the thin sample approximation was valid. On-axis intensity was measured with a Si photodiode and the laser beam profile was monitored with a WinCAD CCD array and software package from DataRay. Careful measurement of the on-axis laser intensity is necessary to get an absolute value for the two-photon absorption coefficient. To mitigate the effects of laser intensity fluctuations the laser beam is split into two arms, one for the sample ( $D_s$ ) and the other for the reference ( $D_r$ ) and the recorded transmission is the quotient of the two detectors ( $D_s/D_r$ ).

Nanoscecond nonlinear transmittance measurements were performed with an optical parametric oscillator tuned to 800 nm. The pulse was Gaussian shaped with  $\tau_L = 3.2$  ns. The beam was focused with an  $f = 50$  cm lens into the sample. Over the length of the sample (1 mm) the beam was essentially collimated. The beam shape was slightly elliptical, with a geometric-mean  $1/e^2$  radius  $w \approx 18.4 - 18.9$   $\mu\text{m}$ , assuming an approximately Gaussian beam shape. The energy was varied, and incident and transmitted energies were measured with energy meters. To rule out the effects of self-focusing-defocusing we placed a large-area ( $\sim 1$  cm<sup>2</sup>) detector near the exit of the sample to collect all transmitted energy. We also looked for stimulated backscattering by rotating the sample slightly to avoid Fresnel

reflected light and measuring 180°-scattered light with an energy meter. At an incident pulse energy of 124  $\mu\text{J}$ , we measured  $\sim 2$  nJ of backscattered light. This would correspond to  $< 2 \times 10^{-5}$  efficiency for stimulated scattering, which can be considered negligible compared with the nonlinear absorption loss.

## Results.

### One-Photon Properties

**Ground-State Absorbance.** Figure 1 shows the structure of each of the chromophores identified as AF240, AF287, AF380, AF270, AF295, and AF350. Structurally all of these materials are similar except for the number of arms attached. Each arm consists of a D- $\pi$ -A motif. A single arm is identified as dipolar, two arms are quadrupolar, and three arms are octupolar. Between the AF240 and AF270 series the only difference is the addition of a phenyl ring between the fluorene and the nitrogen. To gain insight on the effect of altering the structure, ground state absorption spectra (bold line) were measured in THF and are shown in Figure 2. The intensity of each material has been quantified. A slight red-shift in the peak maximum is observed for both the AF240 and AF270 series with increasing branches (Table 1). A recent theoretical study of these two series of materials revealed that the strong absorption centered at 400 nm is due to an intramolecular charge transfer (ICT) absorption from the triphenylamine to the benzothiazole.<sup>2(p)</sup> The red shift within the series is attributed to stabilization of the LUMO. An interesting thing to note is the blue shift in the peak of the AF270 series relative to the AF240 series. The calculations also showed that in the quadrupolar and octupolar species the first and second excited state are energetically close lying transitions that result in significant overlap.<sup>2(p)</sup> Therefore the maximum peak may be due to the  $S_0$ - $S_2$  transition. In addition the spectra lose sharpness because of vibrational broadening from the solvent.

**Steady-State Emission.** Also shown in Figure 2 is the fluorescence spectrum (dashed line) of each chromophore in THF. The fluorescence spectra were obtained at room temperature in air saturated THF and through a series there is only a minimal red-shift with increasing conjugation. However, a significant Stokes shift in the fluorescence is observed for all six chromophores (Table 1). The origin of

this red-shift was explored in great detail recently by us and it is due to emission from a lower energy ICT (intramolecular charge transfer) state.<sup>2(n)</sup> Upon vertical excitation to the excited state a great deal of vibrational relaxation and solvent reorganization results in a stabilized lower energy state. The degree of the ICT state that is formed is dependent on the solvent and its ability to stabilize the state. In this case we are working with a relatively polar solvent THF with a dielectric constant of 7.6. Therefore we assume that significant ICT state will be formed and stabilized by solvent. The fluorescence quantum yields obtained in air saturated THF are given in Table 1. The trend observed is that the quantum yield decreases slightly from dipolar to octupolar in both series.

Phosphorescence data for each chromophore was obtained at 77 K in MeTHF and the data is shown in Figure 2 (solid line). Approximately 20% MeI was added to each sample to enhance the formation of the triplet excited state. As with the fluorescence data there is only a slight red-shift in the emission with increased branches for the two series. We determined the triplet excited state energy from the blue edge of the phosphorescence spectra. This data is given in Table 1 along with the phosphorescence maximum.

***Time Resolved Excited State Properties.*** Time resolved absorption was utilized to gain insight on both the decay kinetics and the spectral properties of the chromophores. Shown in the two left panels of Figure 3 are quantified transient absorption spectra of all chromophores in air saturated THF following 100 fs excitation at 400 nm. In each of the chromophores we observe a transient at approximately time zero that shifts to form a new species in less than 3 ps. The specific lifetime for this change is given in Table 2 as  $\tau_1$ . This change is attributed to solvent reorganization and stabilization of the ICT state. The trend observed is that with increasing branches to the chromophore the lifetime is longer. Therefore in the larger octupolar materials it takes more time for the solvent to reorganize around the chromophore to stabilize the charge transfer. There are steric hindrances in the octupolar and quadrupolar species that are not as prevalent in the dipolar chromophores. We did not observe a fast relaxation from upper state levels to the  $S_1$  level in any of these materials but this is because at 400 nm we are exciting directly into the  $S_1$  level of the material so any relaxation is only vibrational and undetectable with this method. For

the AFX transient at approximately time zero we were able to quantify the spectra using  $C_{60}$  in toluene as an actinometer.<sup>12</sup> These results are given in Table 1. For both series we found that the molar absorption coefficient at the peak for the dipolar species is largest then followed by the octupolar and finally the quadrupolar.

In addition to measuring the steady state fluorescence we also looked at the time resolved fluorescence using time correlated single photon counting exciting at 400 nm. The lifetimes obtained are given in Table 2 as  $\tau_2$ . The lifetimes in air saturated THF show no trend with structure differences. They are all around 2 ns.

Nanosecond laser flash photolysis was utilized to obtain the  $T_1$ - $T_n$  excited state spectra of each chromophore in deoxygenated THF. Upon 355 nm excitation the spectra obtained are shown in the right panel of Figure 4. Unfortunately due to a small intersystem crossing quantum yield (Table 1) the transient spectra are noisy. We were able to quantify the spectra using the method of singlet depletion. For the AF240 series we observed a red-shift in the transient species along with an increase in the overall molar absorption coefficient. This follows the trend observed for the ground state absorbance spectra indicating an increase in the overall conjugation in the quadrupolar and octupolar chromophores. In the AF270 series the peak maximum is shifted to the blue relative to the AF240 series. Similar to the  $S_1$ - $S_n$  data there are two peaks in the region from 450 – 1000 nm. With increasing branches a slight red shift in the  $T_1$ - $T_n$  spectra is observed as well as an increase in the molar absorption coefficient. Of the two series, the AF270 series has the larger molar absorption coefficient due to increased conjugation through the additional phenyl ring.

All materials in deoxygenated THF were found to decay biexponentially upon 355 nm excitation. The respective lifetimes are given in Table 2 as  $\tau_3$  and  $\tau_4$ . A shorter decay with a lifetime around 100  $\mu$ s was observed followed by a long lived transient ranging from 500  $\mu$ s to 1 ms. Looking at the spectral details at time zero overlaid with the longer lived transient (data not shown) there is a difference in the spectra indicating a new transient is being formed. Based on our previous study of AF455 it is possible that the

new transient is due to an ICT state formed via the triplet excited state.<sup>2(n)</sup> The triplet excited state lifetime measured in air saturated THF is also given in Table 2. A trend observed under air saturated conditions is that the lifetime is typically longer in the dipolar species and then becomes shorter with increasing arms. The same trend is not observed under deoxygenated conditions.

**Femtosecond Two Photon Absorption.** In an open aperture z-scan measurement the decrease in transmission as the sample approaches the focus is directly proportional to nonlinear absorption processes (two-photon absorption, etc.). The shape of the transmission profile follows Equation 1 for a Gaussian temporal profile of the incident laser pulse:

$$T = \frac{1}{\sqrt{\pi}q_0} \int_{-\infty}^{+\infty} \ln[1 + q_0 \exp(-x^2)] dx \quad (1)$$

where  $q_0 = \beta I_0 L(1 + z^2/z_0^2)^{-1}$ ,  $L$  is the sample thickness (1 mm),  $I_0$  is the on-axis laser intensity,  $z$  is the position on the optical axis with respect to the focus of the beam and  $z_0$  is the Rayleigh length, typically 6 mm for our system. By fitting the experimental data with Equation 1, values of the two-photon absorption coefficient ( $\beta$ ) were obtained as a function of  $I$  for each AFX chromophore studied. In Figure 4 these data are plotted for each dye studied and the two-photon absorption cross-section was determined by the y-intercept of the linear relationship between on-axis intensity ( $I$ ) and  $\beta$ :<sup>14</sup>

$$\beta_{eff}(I) \propto \sigma_{TPA} + \sigma_{ESA} I. \quad (2)$$

The slope of the line is proportional to the excited-state cross-section ( $\sigma_{ESA}$ ). To get the TPA cross-section in recognizable units ( $\text{cm}^4/\text{GW}$ ), the cross-section is simply divided by Avagadro's number ( $N_0$ ) and the concentration of the sample ( $d$ ) in mol/mL as shown by Equation 3:

$$\sigma_2 = \sigma_{TPA} / N_0 d \quad (3)$$

**Nanosecond Nonlinear Transmission.** Shown in Figure 5 are the nonlinear transmission plots for all six chromophores in air saturated THF pumping at 800 nm with various energies. The samples were prepared to be around 0.02 M except for AF287, which was made to be 0.0099 M due to solubility limits. Measurements were made using a 1 mm quartz cuvette. Using the measured  $\sigma_2$  values in Table

3, we calculated the NLT for each material and compared these calculations with the data shown in Figure 5. The calculation is based on an analytical effective three-photon absorption model of two-photon-induced excited state absorption that was previously described in detail.<sup>9</sup> The energy transmittance for a sample of thickness  $L$  in this model is given by

$$T = \frac{T_0^2}{\sqrt{\pi} p_0} \int_{-\infty}^{\infty} \ln \left\{ \left[ 1 + p_0^2 \exp(-2x^2) \right]^{1/2} + p_0 \exp(-x^2) \right\} dx \quad (4)$$

where  $p_0 = (2\gamma T_0^2 I_0^2 L)^{1/2}$ ,  $T_0$  is the linear transmittance of the sample, and  $\gamma$  is the effective three-photon absorption coefficient.  $\gamma$  is directly proportional to the product of  $\sigma_2$  and an effective excited state absorption cross section, which is a linear combination of the  $S_1$ - $S_n$  and  $T_1$ - $T_n$  cross sections. The theory in Figure 5 is determined using no adjustable parameters. In addition, the data in Figure 5 were fit with adjustable parameters to an effective TPA model, using Equation 1 with  $z = 0$ , i.e., the sample was at the beam focus. This fit is given in Table 3 for comparison to the literature.

## Discussion.

As stated in the introduction of this paper there is interest in systematically comparing the one- and two-photon photophysical properties within a series of chromophores to identify structure property relationships. Understanding structure property relationships provides the tools needed to gain insight into molecular design and engineering of better nonlinear materials. The importance of the singlet and triplet excited state in the nanosecond nonlinear absorption is high as previously reported<sup>9</sup> so we want to focus our efforts on understanding these properties and ways to improve on them. It is important to show that the kinetics and spectral properties obtained via one-photon excitation are needed to understand the differences of two-photon absorption in the femtosecond and nanosecond domains.

**One-Photon Spectral Properties.** Addition of branches to the AF240 and AF270 molecules results in only a slight red shift in all of the spectral data obtained indicating that the degree of conjugation is limited. In the ground state spectral data and the triplet excited state data a trend is observed that the molar absorption coefficient becomes larger with increased branches to the material. This is consistent

with increased chromophore density or an additive effect from the extra chromophores. In fact with each addition of an arm the molar absorption coefficient is nearly doubled or tripled that of the dipolar species. It is interesting to note that the  $S_1$ - $S_n$  data does not follow the same trend. There is a slight red-shift in the data from 550 – 650 nm for AF270 (595 nm), AF295 (595 nm), and AF350 (615 nm) but in this case the dipolar material has the largest molar absorption coefficient followed by AF350 with AF295 the smallest. In the AF240 series we observe a blue shift in the  $S_1$ - $S_n$  absorption maximum from AF240 (623 nm) to AF287nm (603 nm). The AF380 then red-shifts back slightly to 617 nm. Also the spectra are different for the quadrupolar species compared to the two dipolar AF240 and AF270. Theoretical calculations show that the  $S_1$  and  $S_2$  state of AF295, AF287, AF380 and AF350 are nearly degenerate<sup>2(p)</sup> so perhaps excited state absorption is occurring from both states resulting in different spectral characteristics than for AF270 and AF240. Comparing the singlet excited state spectra of the AF240 series and the AF270 series reveals that their spectral characteristics are also different. The AF240 series only has one major peak while the AF270 series has two. It is surprising that addition of one phenyl group to the AF270 results in such different characteristics in the singlet excited state but has only a small effect on the  $S_0$ - $S_1$  and  $T_1$ - $T_n$  data.

Structure property relationships are the key to understanding how to design new nonlinear absorbing materials. Looking at the spectral details of these two series of closely related materials reveals that increasing the number of arms results in enhanced absorption intensity in both the ground state and triplet excited state spectra. The effect of red-shifting is only minimal with this addition. Comparing the two series with the AF270 having an additional phenyl ring, it would be expected that the AF270 series would be more conjugated and therefore more red-shifted but looking at the figures and the data in Table 1 this is not always the case. Previous calculations determined that in the quadrupolar and octupolar species the first and second excited state are energetically close lying transitions that result in significant overlap.<sup>2(p)</sup> This would justify the blue shift in the quadrupolar and octupolar species but not for the dipolar species. The fact that the ground state absorbance of AF240 is red-shifted relative to

AF270 tells us that the charge transfer state ( $S_0$ - $S_1$ ) for AF240 is more stabilized than for AF270 in THF. Perhaps the addition of the phenyl group results in a weaker charge transfer from the nitrogen to the benzothiazole because of increased distance from the donor and acceptor.

**Kinetic Pathways.** Table 2 summarizes all of the kinetic decays observed for each material under various conditions. Upon excitation the excited material quickly reorients itself with the solvent to form a solvent stabilized ICT state that is evident by both the fluorescence Stokes shift and the new species evolved in the femtosecond transient absorption data. The octupolar materials take the longest for the solvent to reorganize ( $\sim 2.7$  ps), which is because of steric hindrance of the bulkier chromophore and the ability of the solvent to get their. The second lifetime is dual decay from both the  $S_1$  state (localized excited state- LE) and the ICT state to form either the triplet excited state or to reform the ground state by giving off light through fluorescence or heat through internal conversion. We have not determined in this study to what extent the solvent stabilized ICT state is formed but we do not believe it to be 100%. A detailed study with various solvents would verify this.<sup>15</sup> Upon formation of the triplet excited state we monitored the decay in both air saturated and deoxygenated conditions. Under air saturated conditions the lifetimes are in the nanosecond range, which is typical of most triplet excited states. The observed trend is that the larger molecules decay faster in the presence of air. Under deoxygenated conditions two lifetimes were found. Overlaying the spectra at different times indicates the formation of a new species. We believe this new species to also be a solvent stabilized ICT state formed from the triplet excited state but we are unable to confirm this at the time.

**Two-Photon Assisted Excited State Absorption.** For many two photon absorbing materials there is a discrepancy in the two photon absorption cross-sections obtained by differing pulse widths. A dramatic enhancement in the nanosecond regime has been observed repeatedly in many materials and has been termed the effective two-photon cross-section. This enhanced loss in the nanosecond nonlinear data has been attributed to excited state absorption but never experimentally confirmed.<sup>16,17</sup> Recently we were able to show that the enhancement in the nanosecond nonlinear absorption of AF240 and AF350 is

strongly due to excited state absorption from both the singlet and triplet excited states.<sup>9</sup> We assume that for other materials in the AFX family the same would be true.

For the AF240 and AF270 series a comparison is made to predict, which material will have large nanosecond nonlinear absorption. This is based on a two-photon-assisted excited-state absorption model where two photons are needed to promote the electron to the singlet manifold and then a third photon is absorbed to either promote to higher  $S_n$  levels or following intersystem crossing to higher  $T_n$  levels. There are several parameters that are critical in nonlinear absorption of a material and are shown in Equation one as the attenuation of the intensity  $I$  as light propagates through a sample. Equation 5 incorporates the loss in transmittance due to absorption from the  $S_1$ - $S_n$  and  $T_1$ - $T_n$  upper excited states.

$$\frac{\partial I}{\partial z} = -\sigma_2 N_{S0} I^2 - \sigma_S N_{S1} I - \sigma_T N_{T1} I \quad (5)$$

In this equation  $N_{S0}$ ,  $N_{S1}$ , and  $N_{T1}$  are the number densities of molecules and  $\sigma_2$ ,  $\sigma_S$ , and  $\sigma_T$  are the cross-sections in the  $S_0$ ,  $S_1$ , and  $T_1$  states, respectively. The triplet quantum yield ( $\Phi_T$ ) is also another important parameter because it determines the number density of molecules in the triplet excited state ( $N_{T1}$ ) so it also must be considered. The critical data has been compiled in Table 3 for comparison. The Sum column shows the triplet quantum yield multiplied by the triplet excited state cross-section because the concentration of triplet excited state is limited by this value.

Qualitatively comparing the data it is evident that the contribution from the  $S_1$ - $S_n$  state at 800 nm is largest from the octupolar AF350 however this is not the case for the  $T_1$ - $T_n$ . The material with the largest triplet contribution is the octupolar AF380 followed by AF287 and AF295. Based on the fs TPA cross sections given in Table 3 the octupolar materials have the largest cross section values at 800 nm. Therefore simply based on a comparison of these values we predict that AF287, AF350, and AF380 will have the largest nonlinear absorption in the nanosecond time regime followed closely by AF295. We utilize the effective two-photon cross-section fit to the data in Figure 5 for comparison of the materials among themselves as well as to the literature. Given in Table 3 are the effective two photon cross-

sections obtained by fits to Equation 1 with  $z = 0$ , when the sample is at the focus, allowing the TPA cross section to float as a variable parameter. The effective TPA cross-sections reveal that AF287, AF350, and AF380 do have the largest nonlinear absorption as we predicted.

In addition to the qualitative comparison we also performed a theoretical fit based on the parameters given in Table 3. The data is shown in Figure 5 and is based on Equation 4 and is determined with no adjustable parameters.<sup>9</sup> While the overlap of the experimental and theoretical data is not good for every material it shows the large contribution of the excited state to the overall nonlinear absorption. We are just beginning to understand the various processes involved in nonlinear absorption and hope in the future to improve on the theoretical model including other possible excited state absorptions and possible thermal effects. It is true for these materials that the largest nonlinearities arise from AF287 and the octupolar materials as predicted by the linear properties. This proves that measuring the  $S_1$ - $S_n$  and  $T_1$ - $T_n$  properties of a material is a good linear tool that provides much information about the nonlinear absorption of a material.

## **Conclusions.**

Structure property relationships of materials are the key to understanding the nonlinear absorbance properties of this class of materials. It also guides the pathway for new materials in the future. In the AF240 and AF270 series we have shown that the effect of adding arms to the material resulted in the octupolar materials having the largest ground state and triplet excited state absorption of the series. While intersystem crossing is small in all materials it is certainly important to the overall absorbance nonlinearity. Also the  $S_1$ - $S_n$  absorption is a key property in predicting the nonlinear response. The collective union of these properties results in a solid prediction of a material's nonlinear response.

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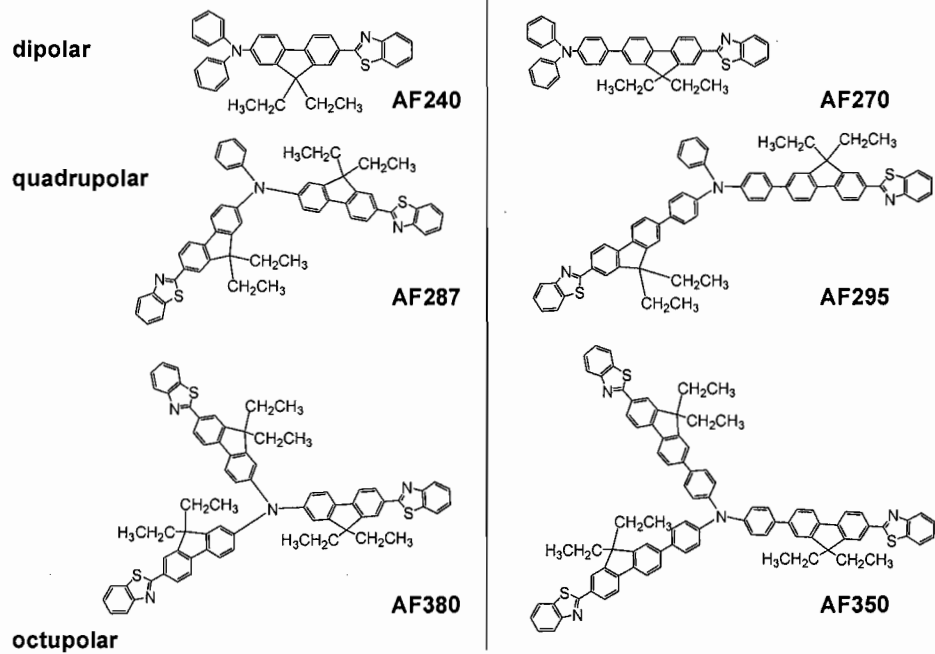


Figure 1. Shown are the structures of the AF240 series and the AF270 series. The dipolar molecules are AF240 and AF270. Quadrupolar are made up of two branches and are AF287 and AF295. AF380 and AF350 are octupolar containing three branches.

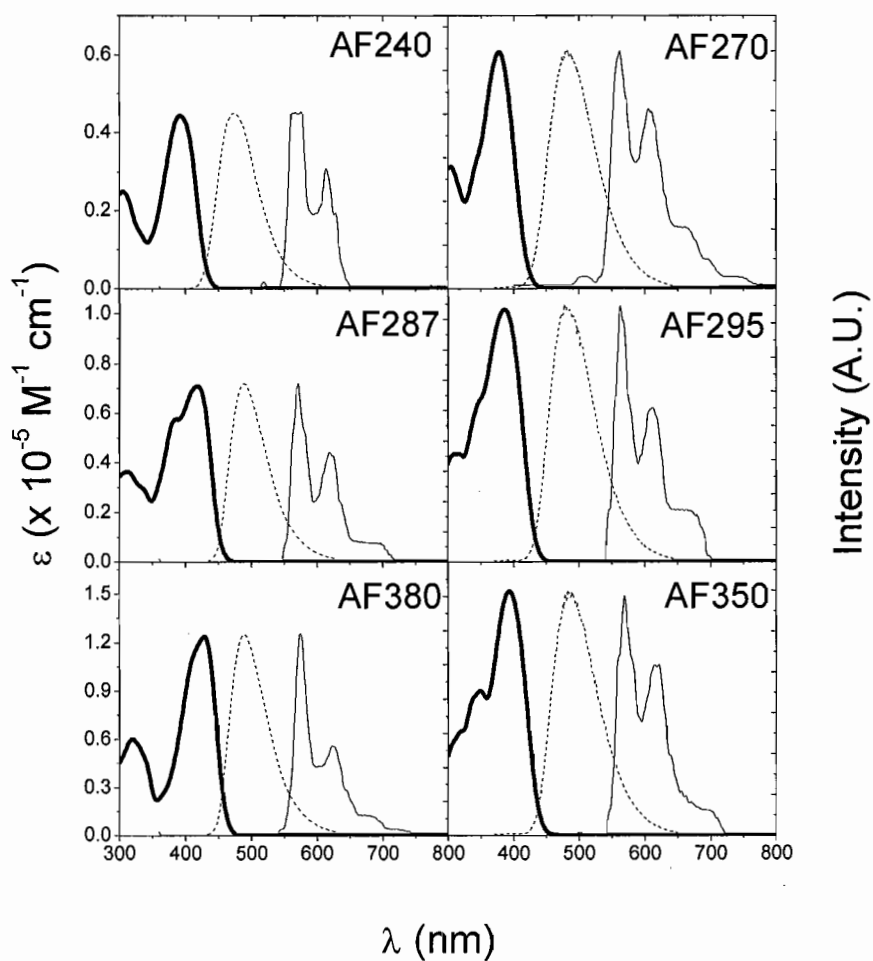


Figure 2. Absorbance (bold), fluorescence (dotted), and phosphorescence (solid) spectra of AF240, AF287, AF380, AF270, AF295, and AF350 in air saturated THF. Fluorescence spectra obtained exciting at 350 nm at room temperature. Phosphorescence measurements were done at 77K in MeTHF exciting at the absorbance peak of each material.

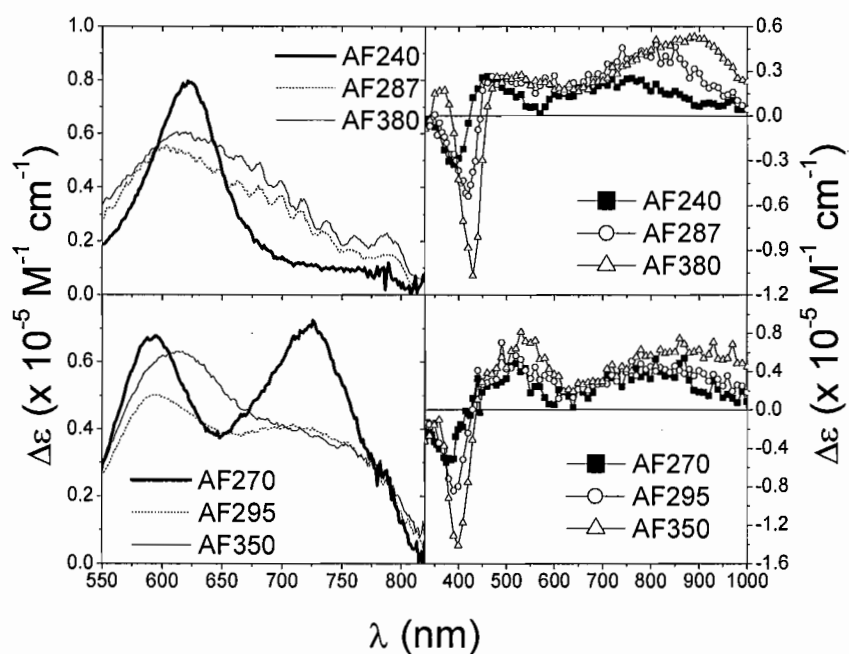


Figure 3. Shown in the two left panels are the quantified  $S_1$ - $S_n$  spectra of AF240, AF287, AF380, AF270, AF295, and AF350 in air saturated THF obtained immediately following a 100 fs 400 nm pulse. Molar absorption coefficients were obtained using  $C_{60}$  as an actinometer. In the two right panels are the quantified  $T_1$ - $T_n$  spectra of all materials in deoxygenated THF obtained upon 355 nm excitation. Samples were deoxygenated by the freeze pump thaw method. Molar absorption coefficients were obtained by using the method of singlet depletion.

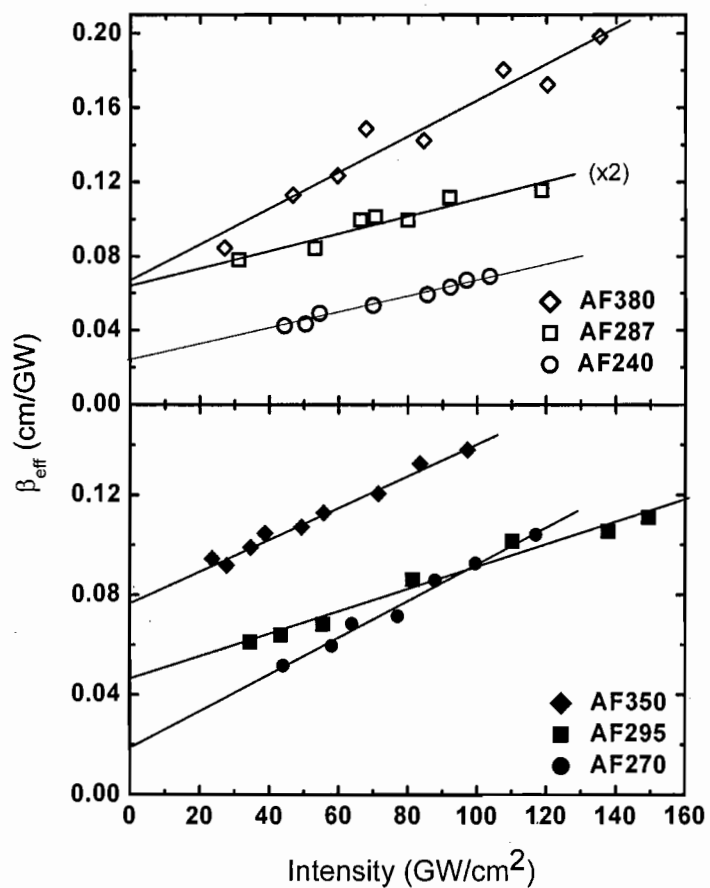


Figure 4. Plots of  $\beta_{\text{eff}}$  as a function of on-axis laser intensity for AF-X dyes as indicated in the foreground of the panels. Lines through the points are fits to Equation 2 in the text. Y-intercepts are proportional to the intrinsic two-photon absorption cross-section ( $\sigma_2$ ). For AF287 the data was multiplied by two because of the half concentration.

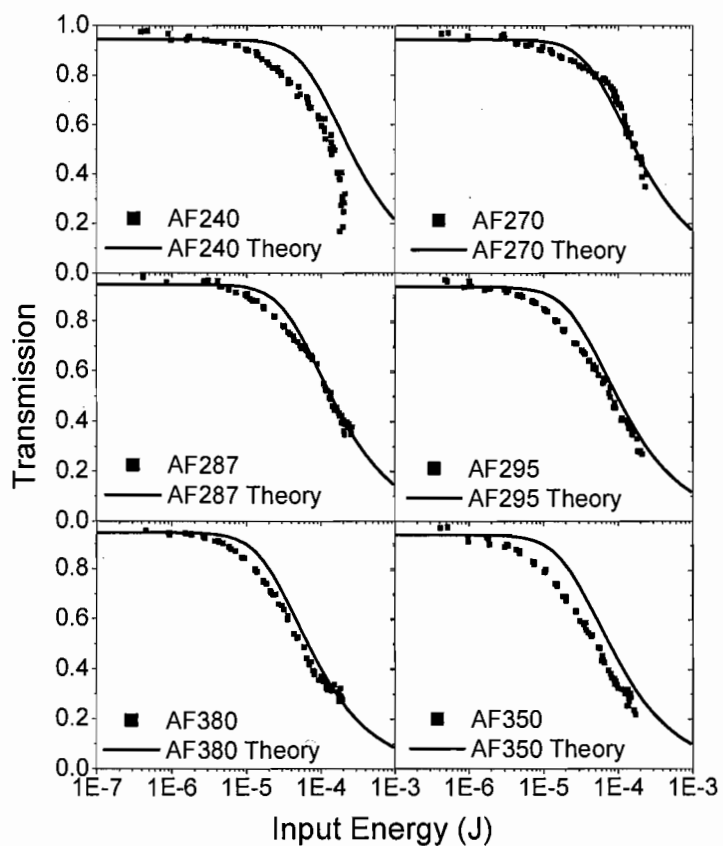


Figure 5. Nanosecond nonlinear transmission data for AF240 (0.0206 M), AF287 (0.0099 M), AF380 (0.0201 M), AF270 (0.0198 M), AF295 (0.0202 M), and AF350 (0.0195 M) in air saturated THF as a function of laser pulse energy at 800 nm. Also shown is theoretical data calculated using an analytical effective three-photon absorption model based on the properties given in Table 3.

**Table 1. Summary of Photophysical Properties in THF**

	AF240	AF287	AF380	AF270	AF295	AF350
$Abs_{max}$	392 nm	418 nm	429 nm	377 nm	386 nm	393 nm
$\epsilon$ ( $M^{-1} cm^{-1}$ )	44400 $\pm$ 2200	70900 $\pm$ 1300	123700 $\pm$ 900	60700 $\pm$ 1600	101700 $\pm$ 2800	152100 $\pm$ 2700
$Fl_{max}$	473 nm	481 nm	489 nm	483 nm	483 nm	486 nm
$\Phi_{flair}$ saturated	0.649	0.609	0.516	0.765	0.701	0.594
Stokes Shift	0.54 eV	0.39 eV	0.35 eV	0.72 eV	0.64 eV	0.61 eV
$Ph_{max}$	569 nm	571 nm	575 nm	561 nm	563 nm	569 nm
$E_T$	2.23 eV	2.22 eV	2.19 eV	2.26 eV	2.25 eV	2.23 eV
$S_1-S_n$ max	623 nm	608 nm	618 nm	725 nm	595 nm	610 nm
$\epsilon$ ( $M^{-1} cm^{-1}$ )	78800 $\pm$ 3900	54600 $\pm$ 4000	60100 $\pm$ 2000	70500 $\pm$ 3500	50200 $\pm$ 2500	62500 $\pm$ 3100
$T_1-T_n$ max <sup>a</sup>	760 nm	810 nm	890 nm	520 nm	520 nm	530 nm
$\epsilon$ ( $M^{-1} cm^{-1}$ ) <sup>a</sup>	25100 $\pm$ 1300	47900 $\pm$ 2400	53000 $\pm$ 2700	48300 $\pm$ 2400	56700 $\pm$ 2800	81200 $\pm$ 4100
$\Phi_{ISC}$ air saturated	0.064 $\pm$ 0.007	0.074 $\pm$ 0.004	0.130 $\pm$ 0.039	0.031 $\pm$ 0.005	0.050 $\pm$ 0.002	0.035 $\pm$ 0.003

a) deoxygenated by three freeze pump thaw cycles

**Table 2. Excited State Kinetics of AF240 and AF270 Series in THF**

	$\tau_1$ (air saturated)	$\tau_2$ (air saturated)	$\tau_3$ (air saturated)	$\tau_3$ (deoxygenated)	$\tau_4$ (deoxygenated)
AF240	0.93 ps	2.03 ns	227 ns	97 $\mu$ s	$\sim$ 1 ms
AF287	1.92 ps	1.88 ns	211 ns	135 $\mu$ s	503 $\mu$ s
AF380	2.53 ps	1.85 ns	112 ns	87 $\mu$ s	943 $\mu$ s
AF270	1.35 ps	1.89 ns	444 ns	123 $\mu$ s	539 $\mu$ s
AF295	1.98 ps	1.88 ns	151 ns	140 $\mu$ s	452 $\mu$ s
AF350	2.71 ps	1.99 ns	152 ns	113 $\mu$ s	438 $\mu$ s

**Table 3. Comparison of One Photon and Two Photon Properties in THF at 800 nm (unless noted)**

	fs TPA	S <sub>1</sub> -S <sub>n</sub>	T <sub>1</sub> -T <sub>n</sub>	Φ <sub>T</sub>	Sum	ns TPA
	σ <sub>2</sub> (10 <sup>-20</sup> cm <sup>4</sup> /GW)	σ (cm <sup>2</sup> )	σ (cm <sup>2</sup> )	air saturated	Φ <sub>T</sub> *σ <sub>T1-Tn</sub>	σ <sub>2</sub> (10 <sup>-20</sup> cm <sup>4</sup> /GW)
AF240	0.185 ± 0.015	1.45 x 10 <sup>-17</sup>	7.45 x 10 <sup>-17</sup>	0.064	0.48 x 10 <sup>-17</sup>	50 ± 8 39.3 ± 0.59 <sup>b</sup>
AF287	0.495 ± 0.038	4.39 x 10 <sup>-17</sup>	15.9 x 10 <sup>-17</sup>	0.074	1.18 x 10 <sup>-17</sup>	99 ± 15
AF380	0.634 ± 0.016 0.39 ± 0.04 <sup>a</sup>	6.08 x 10 <sup>-17</sup>	17.2 x 10 <sup>-17</sup>	0.130	2.24 x 10 <sup>-17</sup>	119 ± 18 92 ± 14 <sup>c</sup>
AF270	0.146 ± 0.005 0.20 ± 0.02 <sup>a</sup>	4.93 x 10 <sup>-17</sup>	15.3 x 10 <sup>-17</sup>	0.031	0.47 x 10 <sup>-17</sup>	29 ± 5
AF295	0.315 ± 0.014 0.31 ± 0.03 <sup>a</sup>	5.80 x 10 <sup>-17</sup>	16.6 x 10 <sup>-17</sup>	0.050	0.83 x 10 <sup>-17</sup>	78 ± 12
AF350	0.489 ± 0.054 0.53 ± 0.05 <sup>a</sup>	6.91 x 10 <sup>-17</sup>	22.0 x 10 <sup>-17</sup>	0.035	0.76 x 10 <sup>-17</sup>	139 ± 21 96 ± 14 <sup>c</sup>

<sup>a</sup> He, G.S. et al. *J. Chem. Phys.* **2004**, *120*, 5275. 790 nm; 140 fs pulse width

<sup>b</sup> Kannan, R. et al. *Chem. Mater.* **2001**, *13*, 1896. 800 nm; 8 ns pulse width

<sup>c</sup> Kannan, R. et al. *Chem. Mater.* **2004**, *16*, 185. 800 nm; 8 ns pulse width

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