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**DEVELOPMENT OF NOVEL TWO-
PHOTON ABSORBING
CHROMOPHORES**



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14. ABSTRACT There has been much interest in the development of two-photon absorbing materials and many efforts to understand the nonlinear absorption properties of these dyes, but this area is still not well understood. A computational model has been developed in our lab to understand the nanosecond nonlinear absorption properties that incorporate all of the measured one-photon photophysical parameters of a class of materials called AFX. We have investigated the nonlinear and the photophysical properties of the AFX chromophores including the two-photon absorption cross-section, the excited state cross-section, the intersystem crossing quantum yield, and the singlet and triplet excited state lifetimes using a variety of experimental techniques that include UV-visible, fluorescence and phosphorescence spectroscopy, time correlated single photon counting, ultrafast transient absorption, and nanosecond laser flash photolysis. The model accurately predicts the nanosecond nonlinear transmittance data using experimentally measured parameters.					
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Development of novel two-photon absorbing chromophores

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ABSTRACT

There has been much interest in the development of two-photon absorbing materials and many efforts to understand the nonlinear absorption properties of these dyes but this area is still not well understood. A computational model has been developed in our lab to understand the nanosecond nonlinear absorption properties that incorporate all of the measured one-photon photophysical parameters of a class of materials called AFX. We have investigated the nonlinear and photophysical properties of the AFX chromophores including the two-photon absorption cross-section, the excited state cross-section, the intersystem crossing quantum yield, and the singlet and triplet excited state lifetimes using a variety of experimental techniques that include UV-visible, fluorescence and phosphorescence spectroscopy, time correlated single photon counting, ultrafast transient absorption, and nanosecond laser flash photolysis. The model accurately predicts the nanosecond nonlinear transmittance data using experimentally measured parameters. Much of the strong nonlinear absorption has been shown to be due to excited state absorption from both the singlet and triplet excited states. Based on this understanding of the nonlinear absorption and the importance of singlet and triplet excited states we have begun to develop new two-photon absorbing molecules within the AFX class as well as linked to other classes of nonlinear absorbing molecules. This opens up the possibilities of new materials with unique and interesting properties. Specifically we have been working on a new class of two-photon absorbing molecules linked to platinum poly-ynes. In the platinum poly-yne chromophores the photophysics are more complicated and we have just started to understand what drives both the linear and non-linear photophysical properties.

Keywords: Two-photon absorbers, two-photon assisted excited state absorption, AFX, Pt TPA dyes

1. 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, we give just a few.¹ There are a host of uses for two photon absorbers that include use in optical data storage², frequency upconverted lasing³, nonlinear photonics⁴, microfabrication⁵, fluorescence imaging⁶, and photodynamic therapy.⁷ 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.

An important measurement associated with the two photon absorbers is the two photon cross-section (σ_2) determination. There has been much debate over the differences in the cross-sections measured dependent on the pulse width of the exciting laser. The nanosecond cross-sections are often several orders of magnitude larger than those obtained using a femtosecond pulse.⁸ Excited state absorption is believed to enhance the two photon cross-section measurements in the nanosecond regime and was first reported by Kleinschmidt et al. back in 1974.⁹ Since then the enhanced nanosecond cross-section has thus been termed an effective two-photon cross-section.¹⁰

There has been an interest in understanding the differences in the two pulse regions but to our knowledge no one has independently identified and characterized these excited states and then used this information to theoretically predict or model nanosecond nonlinear absorbance measurements. We recently reported 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.¹¹ Based on this finding we have increased our efforts to develop 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.

Recently we have focused on understanding the key elements of the one-photon photophysical properties of various materials via structure property relationships. Specifically we are interested in the class of AFX dyes that have been studied for nearly ten years now by the Air Force and vary slightly but all maintain a similar D- π -D, A- π -A, and D- π -A (D = donor, A = Acceptor) design with fluorene serving as the π group.¹² We have intensively studied several of the AFX materials but in this proceeding we will only touch on some of our findings on what linear aspects of a material drive the nanosecond nonlinear absorbance. In addition we will also present a new class of TPA materials based on a Pt center that are designed based on their T_1 - T_n absorption properties.

2. EXPERIMENTAL

General Techniques. 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.¹³ 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 1 mJ cm⁻² at the excitation wavelength were typically used. A detailed description of the laser flash photolysis apparatus has been published earlier.¹⁴

The molar absorption coefficient of the chromophore singlet excited state was determined using the method of relative actinometry utilizing C₆₀ in toluene.¹⁵ 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.¹⁴ Quantum yields for intersystem crossing were determined using the method of relative actinometry with a benzophenone actinometer.¹⁴ Matched optical densities of the AFX molecule and benzophenone at 355 nm were utilized in each determination.

Nanosecond 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 ($\sim 1 \text{ cm}^2$) 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 μJ , we measured ~ 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.

3. RESULTS AND DISCUSSION

As mentioned earlier we determined that both the S_1 - S_n and T_1 - T_n absorption characteristics are very important to the nanosecond nonlinear absorption as well as the two photon absorption properties.¹¹ Also we should note that the ability of the excited state to intersystem cross to the triplet state from the singlet state also has a large part in the nanosecond nonlinear absorbance. Therefore in this paper we will only focus on an overview of our findings on the linear parameters and how they relate to the nanosecond nonlinear absorbance data. Shown in Figure 1 are the structures of the AFX dyes that we have recently studied. There are three classes of materials that make up these dyes – the dipolar, quadrupolar, and octupolar. The dipolar molecules contain a simple D- π -A model while the quadrupolar and octupolar are just an extension of this design with either two or three arms, respectively.

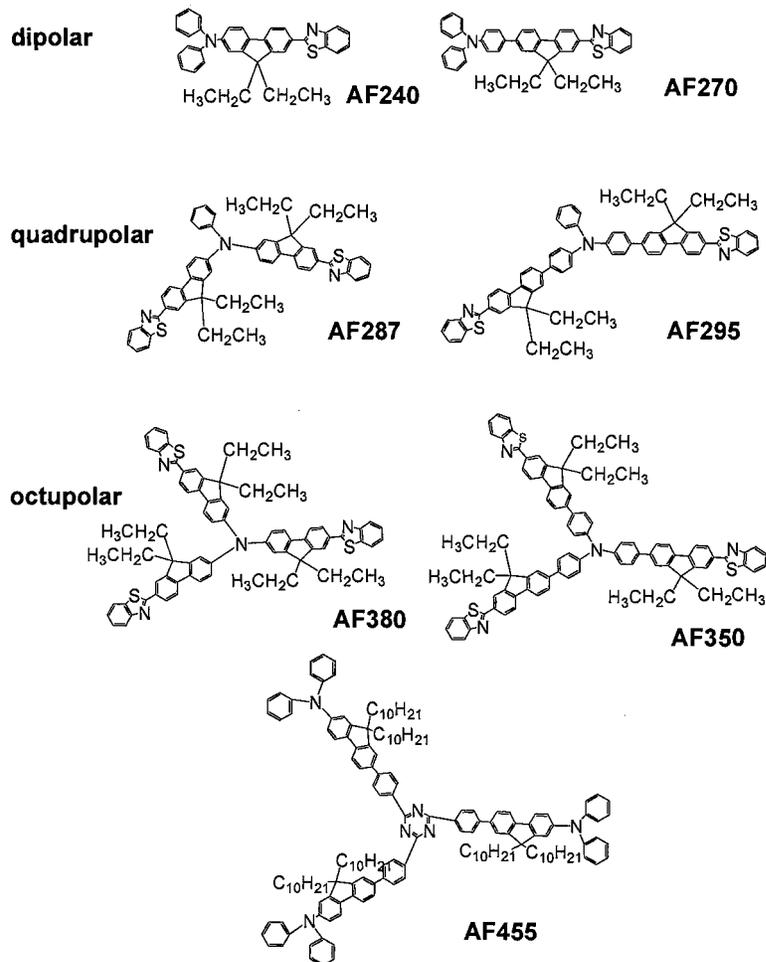


Figure 1. Structures of AFX materials. The dipolar species are AF240 and AF270, quadrupolar are AF287 and AF295, and octupolar are AF380, AF350, and AF455.

Initially we did a detailed study on AF455 in various solvents.¹⁶ What we observed is that the photophysical properties of AF455 are markedly different in a polar solvent relative to a non-polar solvent. We attribute this difference to the ability of the solvent to stabilize an intramolecular charge transfer (ICT) complex that is formed upon excitation to the excited state. Shown in Figure 2 are the S_1 - S_n absorption spectra of AF455 in air-saturated hexane, benzene, THF, and 2-propanol upon 400 nm excitation. The data shown was obtained 1.68 ps following the laser pulse. In our detailed publication we showed that this correlates to the time when the ICT state becomes stabilized.¹⁶ A few things to notice

are that in more polar solvents we see a blue-shift in the spectrum and also a new species that forms in the 450 nm region. We attribute this new species to the formation of the solvent stabilized ICT state.

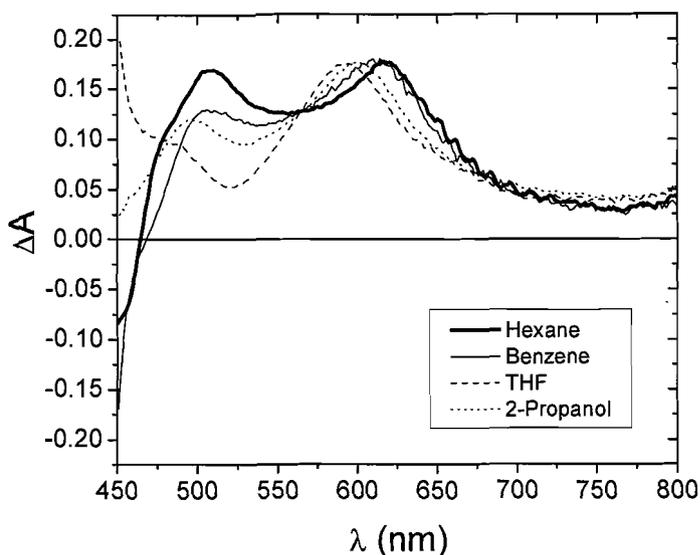


Figure 2. S_1-S_n absorption data of AF455 in air-saturated Hexane – 41.5 μM (bold solid), Benzene – 53.9 μM (solid), THF – 67.9 μM (dashed), and 2-Propanol – 38.3 μM (dotted) upon 400 nm excitation with a 93 fs pulse. Data shown is ~ 2 ps after the laser pulse.

Shown in Figure 3 are the T_1-T_n absorption spectra in the four solvents. A trend observed with solvent is that we see a red-shift in the peak maximum with increasing polarity. It is also important to note that the molar extinction coefficient is very similar in all solvents with only a slightly smaller value in THF. The intersystem crossing quantum yield is also an important parameter in nanosecond nonlinear absorption because it determines how many singlet excited states actually make it to the triplet excited state in a given time. For AF455 all of the ISC yields are fairly small but we do observe a difference in solvent. For AF455 under air saturated conditions we determined Φ_{ISC} as 0.075 ± 0.004 in hexane, 0.030 ± 0.002 in benzene, 0.060 ± 0.003 in THF, and 0.058 ± 0.003 in 2-propanol.

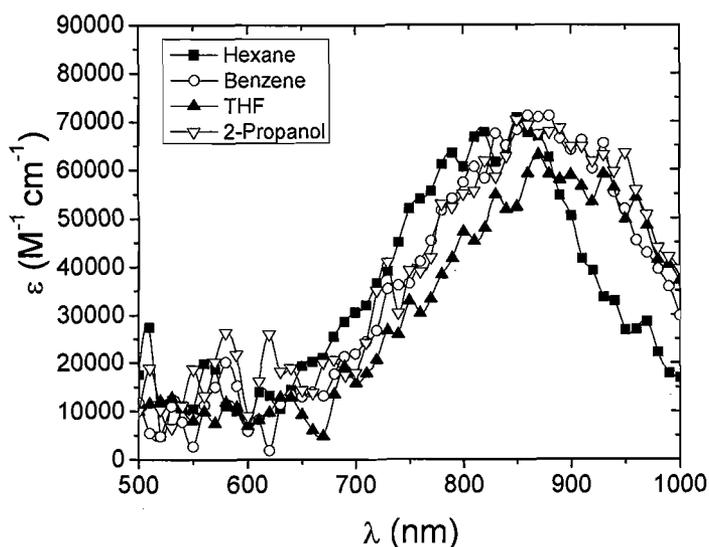


Figure 3. T_1-T_n absorption data of AF455 in Hexane ($8.3 \mu\text{M}$), Benzene ($8.8 \mu\text{M}$), THF ($9.2 \mu\text{M}$), and 2-Propanol ($8.5 \mu\text{M}$) upon 355 nm excitation. Data shown immediately following the laser pulse.

While the shift in either the S_1-S_n or the T_1-T_n is not large it certainly makes a difference in the nanosecond nonlinear absorption data along with the differences in the intersystem crossing quantum yield. Shown in Figure 4 are three nonlinear transmittance scans taken for 0.02 M AF455 in THF, benzene, and hexane under air-saturated conditions exciting at 800 nm. For a qualitative comparison it is interesting to note that we observe the largest nonlinear

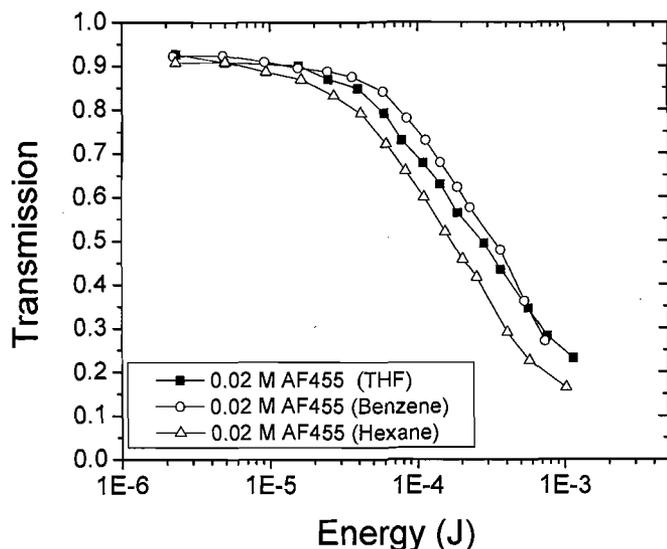


Figure 4. Nanosecond nonlinear absorbance data of 0.02 M AF455 in air saturated Hexane, Benzene, and THF with 800 nm excitation.

transmittance change in hexane, followed by THF and then benzene. This trend correlates very well with the differences in the intersystem crossing quantum yields (0.075 – hexane, 0.030 – benzene, and 0.060 – THF). In benzene, the smallest triplet quantum yield has the smallest turnover in the transmission. At 800 nm both the S_1-S_n and T_1-T_n cross-

sections are very similar in all solvents. We should note that the data collected in the 800 nm region for the S_1 - S_n absorption is difficult to measure because this is the fundamental wavelength of the Ti:sapphire laser used in the experiments. A cut-off filter is used to eliminate the strong 800 nm light, making the measured absorbance values noisy. At this time the two photon cross sections have not been measured in the various solvents but has been reported for AF455 in THF as $0.51 \times 10^{-20} \text{ cm}^4/\text{GW}$ at 790 nm.^{12(f)} It would be interesting to see if there is a large change in the intrinsic cross section with solvent. Perhaps this is driving the differences in the nanosecond data with only a small contribution from the small changes in the intersystem crossing quantum yields.

From this initial study with AF455 we realized that the S_1 - S_n and T_1 - T_n excited state properties are important for the nanosecond nonlinear absorbance so we decided to look at the same properties in other materials and qualitatively correlate the data with the nanosecond NLA data. The next two series that we studied each include a dipolar, quadrupolar, and octupolar chromophore.¹⁷ The AF240 series includes AF240, AF287, AF380 and differs from the AF270 series by one phenyl group between the amine and the fluorene bridging group. The AF270 series is made up of AF270, AF295, and AF350. Both series structures are given in Figure 1. Shown in Figure 5 are the S_1 - S_n absorption data of all six chromophores obtained in air saturated THF. All samples were excited at 400 nm with a 93 fs pulse. The data shown in Figure 5 was obtained immediately following the laser pulse and is considered time zero. Again we should point out that the data in the region of 800 nm is noisy due to a cut-off filter used to remove the residual 800 nm light. A couple of things to note in this data is that in the AF240 series there is only one peak for each material where in the AF270 series we observe a double peak around 580 nm and then again around 740 nm. It is surprising that addition of one phenyl group to the AF270 results in such different characteristics in the singlet excited state. Another thing to note is that the spectra of AF240 and AF270 are shaped differently than their larger counterparts. Theoretical calculations show that the S_1 and S_2 state of AF295, AF287, AF380 and AF350 are nearly degenerate so perhaps excited state absorption is occurring from both states resulting in different spectral characteristics than for AF270 and AF240.¹⁸

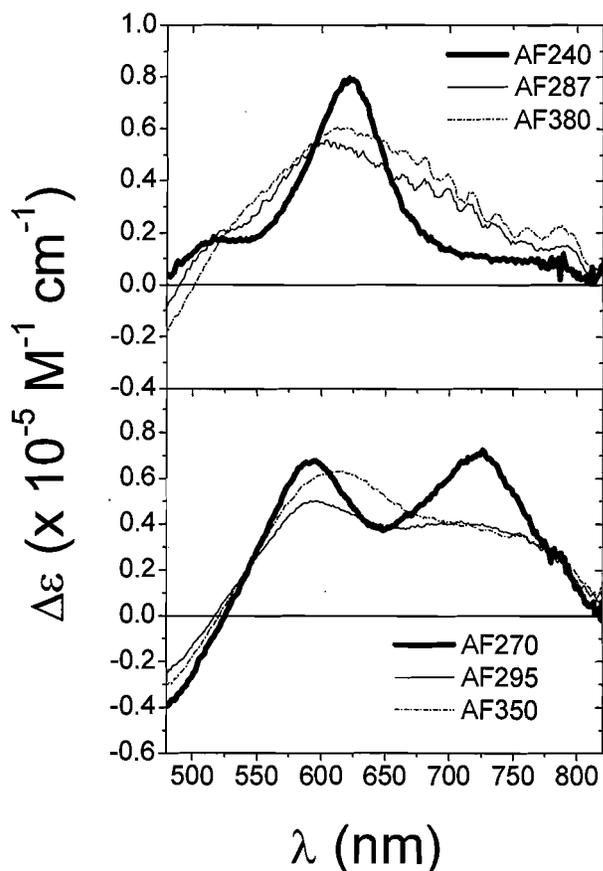


Figure 5. S_1 - S_n data of AF240 (117.3 μM), AF287 (74.4 μM), AF380 (60.6 μM), AF270 (138.1 μM), AF295 (55.4 μM), and AF350 (33.9 μM) in air saturated THF upon 400 nm excitation.

The triplet absorption spectrum for each chromophore is shown in Figure 6 in deoxygenated THF. The two things that are most noticeable are that with increasing arms a red-shift is observed in both series as well as an increase in the triplet extinction coefficient. In 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 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 500 – 1000 nm. We also determined the intersystem crossing quantum yields for all six chromophores and were found to be rather small under air saturated conditions. We found the following for AF240 – 0.064 ± 0.007 , AF287 – 0.074 ± 0.004 , AF380 – 0.130 ± 0.039 , AF270 – 0.031 ± 0.005 , AF295 – 0.050 ± 0.002 , and AF350 – 0.035 ± 0.003 . There is no clear trend in the values except that intersystem crossing is larger in the AF240 series.

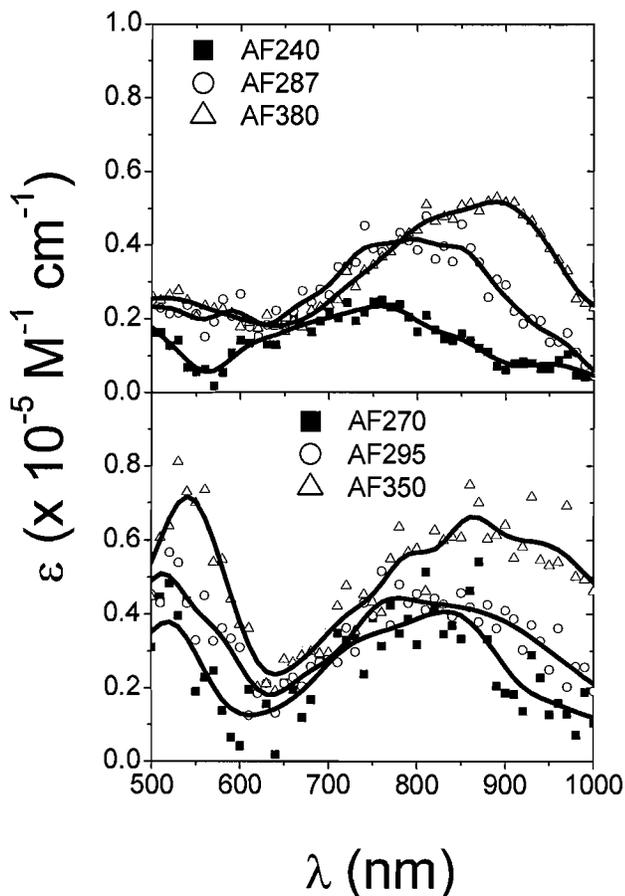


Figure 6. Upon 355 nm excitation the T_1 - T_n absorption spectra are shown for AF240 (25 μM), AF287 (7.3 μM), AF380 (11.2 μM), AF270 (4.8 μM), AF295 (4.1 μM), and AF350 (3.1 μM) in deoxygenated THF.

Lastly with this series of materials we would like to qualitatively correlate our findings for the S_1 - S_n , T_1 - T_n and Φ_{ISC} with the nanosecond NLA data. As expected the NLA data shown in Figure 7 follows the trend of the excited state data. In this series of materials it is expected that the S_1 - S_n absorption plays a larger role than the T_1 - T_n because of the small intersystem crossing quantum yields. We observe an enhancement in the NLA at 800 nm with increased branches or arms. One thing to note in Figure 7 is that AF287 was prepared at half the concentration of the others (0.0097 M) due to

solubility problems and is evident when comparing the data. Qualitatively between the two series there does not appear to be much of a difference in the NLA results. This is not a surprise because the NLA is obtained at 800 nm and at this

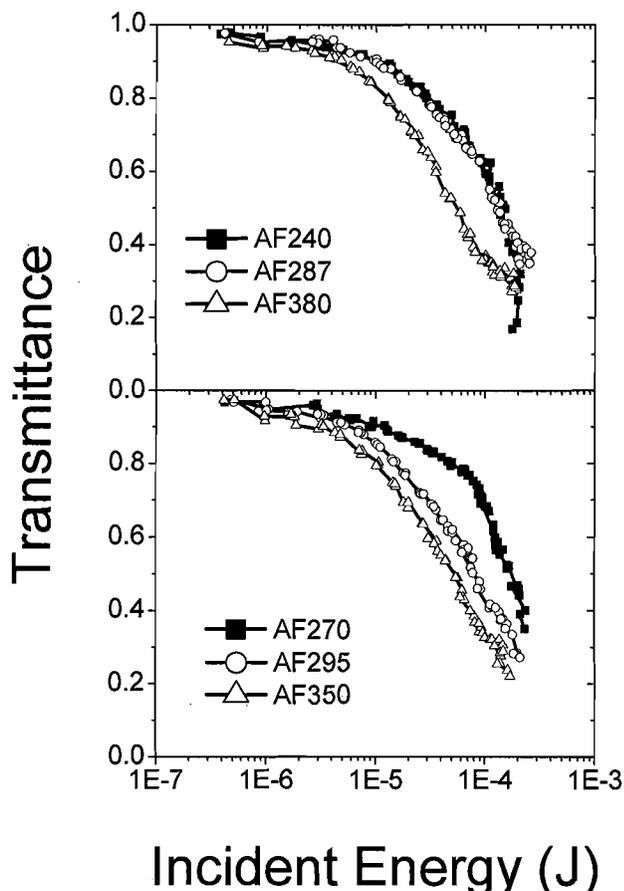


Figure 7. Nanosecond nonlinear absorption of AF240, AF287, AF380, AF270, AF295, and AF350 in air saturated THF upon 800 nm excitation. All samples are 0.02 M except AF287 that is 0.0097 M.

wavelength the largest difference is observed in the triplet excited state spectra but between the two series the data is similar. We have also determined the femtosecond cross-sections for both series at 800 nm and found that they increase with the number of arms and they also tend to be larger for the AF240 series.^{17,19} In this structure property relationship comparison it is evident that the largest drivers in the nanosecond nonlinear transmittance data are the intrinsic two photon cross sections and the triplet excited state absorbance. The triplet excited state has the largest extinction coefficient in the 800 nm region but a small intersystem crossing quantum yield. At 800 nm the singlet excited state cross-section is relatively small and similar for all six chromophores. Therefore it appears that to enhance nanosecond nonlinear absorbance at 800 nm we need to increase intersystem crossing to the triplet excited state.

We determined the best way to increase intersystem crossing would be to add a heavy atom to the AFX chromophore. Based on our vast knowledge of a class of Pt poly-yne dyes^{14,20} we decided to link an AFX chromophore to a Pt poly-yne.²¹ The resulting structures are shown in Figure 8.

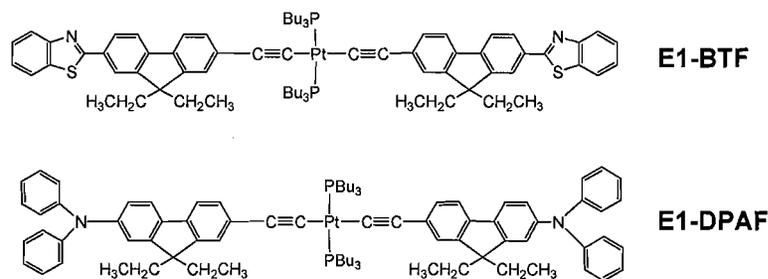


Figure 8. Structures of Pt-containing two photon dyes E1-BTF and E1-DPAF.

Both dyes consist of a Pt core linked to either a benzothiazole fluorene (BTF) or a diphenylamine fluorene (DPAF) group. In Figure 9 are the S_1 - S_n absorption spectra of both materials. The data has been quantified. The most evident result from this data is the large difference in the intensity between the BTF ligand versus the DPAF ligand. We see a large increase for the BTF ligand in the region from 550 nm to 750 nm. At this time we do not understand why there is such a discrepancy in the two materials. The benzothiazole group is an electron accepting group while the diphenylamine is typically electron donating. Perhaps the Pt interacts with the benzothiazole increasing overlap of the S_1 and higher S_n orbitals. There is also evidence in the literature that the benzothiazole group and the electron rich fluorene form a charge transfer state.²² Perhaps this is enhancing the overlap as well in E1-BTF.

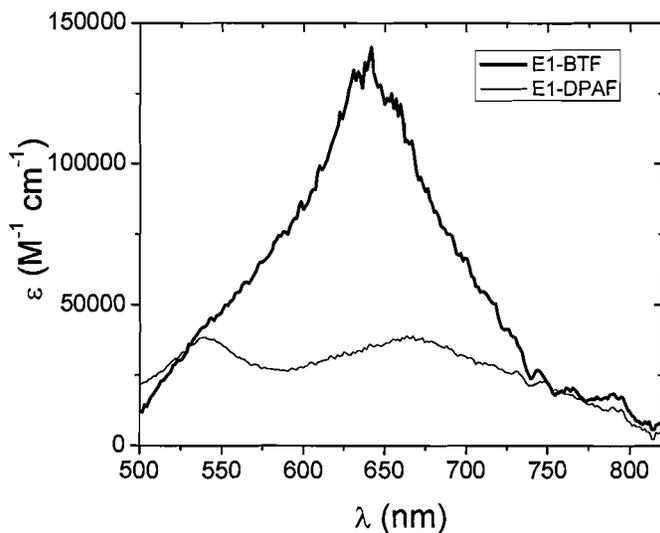


Figure 9. S_1 - S_n absorption of E1-BTF (32.3 μ M) and E1-DPAF (123 μ M) in air saturated benzene. Samples were excited at 400 nm.

We also observe similar results for the T_1 - T_n absorption as shown in Figure 10. The extinction coefficient for E1-BTF is nearly three times larger in the triplet excited state than E1-DPAF. Again we see a large enhancement in the overlap of the T_1 and T_n orbitals for E1-BTF. The intersystem crossing yield on both materials is near unity with E1-BTF – 0.95 ± 0.02 and E1-DPAF – 0.94 ± 0.03 . This is not surprising due to the heavy atom effect of the central platinum. Due to the fast intersystem crossing in these materials the major contribution to the nanosecond nonlinear absorption is due to the triplet excited state.

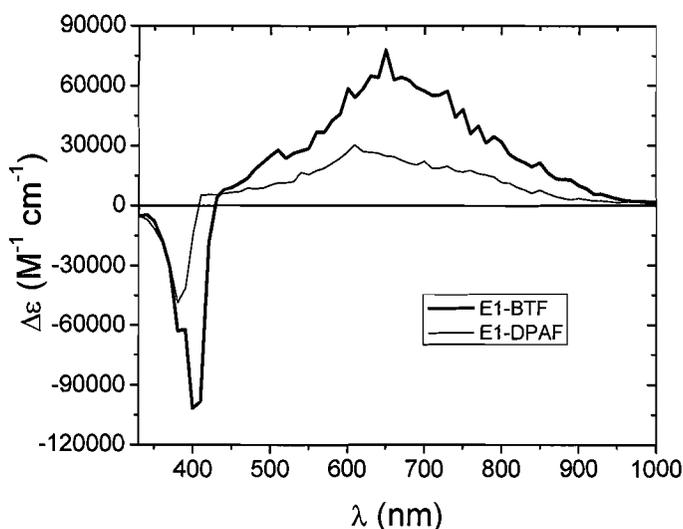


Figure 10. T_1 - T_n absorption of E1-BTF (5.9 μM) and E1-DPAF (2.5 μM) in deoxygenated benzene. Chromophores were excited at 355 nm.

Shown in Figure 11 is the nonlinear absorbance data of E1-BTF and E1-DPAF upon 800 nm excitation. At this wavelength the E1-BTF material is clearly a better nonlinear absorber. This is what was expected based on the excited state absorption data. At 800 nm the T_1 - T_n excited state cross-sections is much larger for E1-BTF. Also the intrinsic two photon cross-section of each material in benzene was determined to be nearly four times larger in E1-BTF than E1-DPAF at 800 nm.²¹ Still there are questions of why the benzothiazole group results in such differences over the diphenylamine group. This will be answered with theoretical calculations in the future.

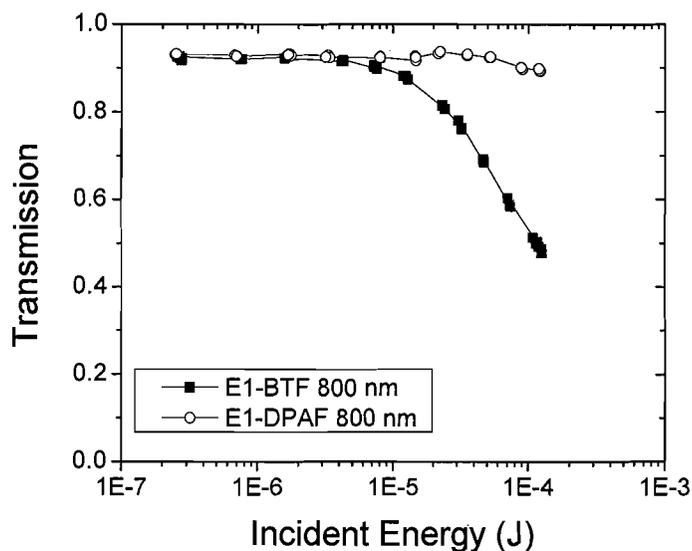


Figure 11. Nanosecond nonlinear absorption data of 0.02 M E1-BTF and 0.02 M E1-DPAF in air saturated benzene upon 800 nm excitation.

In the past our group has worked on a three-level model to describe the nonlinear transmission.¹¹ This model is given in detail in an accompanying paper for many of the same materials presented here.¹⁹ The results from the accompanying

paper further confirm many of the results printed here and how important the singlet and triplet excited states are in nanosecond nonlinear transmittance changes.

4. CONCLUSIONS

Overall this research has provided us with decent insight into some of the linear factors that are responsible for nanosecond nonlinear absorbance. We have determined that the S_1 - S_n , T_1 - T_n absorption, and the intersystem crossing yield are all important factors. We also showed that by qualitatively comparing these parameters we qualitatively correlate the one-photon data to the nanosecond NLA data. In the future we will expand on this by actually implementing a theoretical model for a comparison to the experimental data. Designing new chromophores based on these findings will help to increase the performance of our materials in the future.

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