

Study of nonlinear absorption in a dye doped polymer film due to frequency up-converted fluorescence

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Abstract

Nonlinear absorption study is performed in 4-[4-(Dimethylamino)styryl]-1- docosyl pyridinium bromide (DASPB) doped in PAMA-PA polymer film at linear absorbing region using cw, nanosecond and picosecond 532 nm laser beams and in two photon absorbing region using pico-second 800 nm, 900 nm and 1,000 nm laser beams. The linear transmission of dye in PMMA-PA film was about 10 %. The nonlinear absorption properties leading to optical limiting using 532 nm pico second and nano second pulses are studied. From the results, it can be noted that at very low input intensity, linear transmission is preserved, with increase in input intensity DASPB starts to contribute to saturation absorption which increases the transmission above linear level, and at higher intensities the excited state frequency up-converted fluorescence (nonlinear absorption) starts to contribute and it dominates with further increase in intensity. This kind of behavior has interesting applications in optical limiting and optical switching.

Nonlinear absorption process is basic principle used in Optical limiters which are the devices designed to have high transmittance for low intensity inputs (such as in images) while blocking the transmittance for high intensity laser beams. Since the development of the first lasers in the late 60's passive optical limiters has been built and tested to protect optical sensors against laser-induced damage. The first optical limiters for cw lasers were based on thermal lensing in absorbing liquids, i.e. heating reduced the index causing thermal blooming resulting in a beam that was no longer focused in an imaging system. Then, two-photon absorption, self-focusing in Kerr liquids, nonlinear scattering from carbon particle suspensions (i.e. diluted India ink) and among other processes have been suggested for pulsed laser sources.[1] Typically, it is desirable for a limiter to keep its transmitted focusable energy below about 1 mJ even for inputs up to many millijoules, while maintaining a linear transmittance of approximately 50%. The definition of focusable energy depends on the particular type of system the limiter is to protect. While it is relatively easy to provide protection against a single wavelength, the wide availability of tunable high-power laser sources demands that a practical limiter work over a broad wavelength band. The device itself must also have a high damage threshold[2-3]. To meet all these demanding specifications research has progressed on two fronts. The first is to synthesize and characterize new limiting materials, while the other is to design new optical devices that maximize the range of protection using available materials.

In this paper we have studied the third order optical properties of dye-doped polymer by considering an example of an organic dye 4-[4-(Dimethylamino)styryl]-1- docosyl pyridinium bromide, doped in a polymer matrix Polymethyl methacrylate methacrylic acid (PMMA-MA). We have studied the nonlinear properties like the two photon induced fluorescence and optical limiting capability of DASPB in Methyl methacrylate – methacrylic acid co-polymer (PMMA-MA) matrix. The linear absorption, single photon fluorescence, two

photon induced fluorescence behavior are studied. The intensity dependent nonlinear absorption at various wavelengths and optical limiting behavior are studied using a pico second laser beam.

One of design strategy is proposed recently by Albota et.al [4], dealing with molecules based on benzene ring as π -center which is attached symmetrically by either electron-donor (D) or electron-acceptor (A) through various lengths of conjugated connectors; D- π -D or A- π -A. They concluded that σ is increased by increasing the length of conjugation; change with the D/A strength and the extent of symmetric intramolecular charge-transfer (CT) from the D ends to the π -center or vice versa, meaning that symmetric charge redistribution effectively occurs upon excitation of such symmetric molecules. A similar approach was made in designing molecules by Reinhardt [5] and his coworkers. dealing with benzene ring as π -center which is symmetrically coupled with two electron acceptor (A- π -A) or asymmetrically with D and A (D- π -A), respectively. There is no clear effect of structural symmetry on σ values, although increasing conjugation length of π -center brings about a significant improvement of the value. In fact, an asymmetric structure, D- π -A. This seems to suggest that there must be more crucial molecular factors other than structural symmetry involved. In this study we have considered dye molecule as 4-[4-(Dimethylamino)styryl]-1- docosyl pyridinium bromide with π centre is used.

Commercially available DASPb (Aldrich Chemical Co.) is purified by recrystallization twice with spectrograde ethanol and by vacuum sublimation. The purity is determined spectroscopically. Purified chloroform is used as the solvent. To prepare the film, Polymethyl methacrylate – methacrylic acid was used as polymer matrix. The thin films of DASPb doped in PMMA-MA is prepared using hot press technique. Thin films of variable thickness are obtained between two glass slides. The molecular structure of DASPb is shown in Figure 1. A charge-transfer in between the aromatic moiety (electron donor) and bromine unit (electron acceptor) can be proposed to explain large χ^3 value measured using Z-scan technique. The linear absorption spectrum of DASPb in chloroform is measured on a VARIAN Cary UV-vis-IR recording Spectrophotometer by using quartz cuvette with one cm path length as well as doping it in Polymethyl methacrylate methacrylic acid (PMMA-MA) film. The Figure 2 shows the linear absorption spectrum of a DASPb in chloroform with solute concentration of $d_0 = 0.0001$ mol/L, in which the solvent influence is not included. The spectral curve has shown that there is a strong absorption band with peak absorption located at 478 nm with a bandwidth of 100 nm, a medium absorption peaked at 270 nm with a bandwidth of 80 nm and no linear absorption is observed in entire spectral range of 580 to 2000 nm except IR absorption between 1200 nm to 1600 nm.

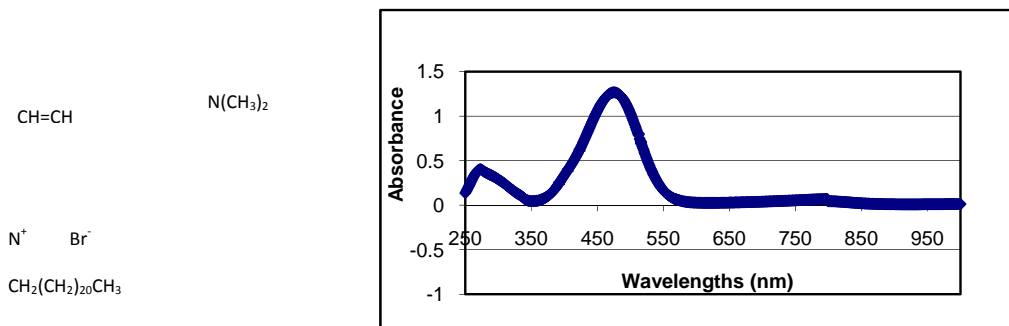


Fig.1 : Molecular structure of DASPb.

Fig.2 : Linear absorption spectrum of DASPb in PMMA-MA matrix.

The single photon fluorescence spectrum of the sample is measured using a spectral fluophotometer (Rf 50000U from Schmadza) with the spectral resolution of 1 nm. The peak wavelength of the single-photon induced fluorescence was 610 nm with a bandwidth of 60 nm (Figure 3). Figure 4 corresponds to single photon fluorescence when DASPb is excited at 532 nm using an Nd:YAG laser beam.

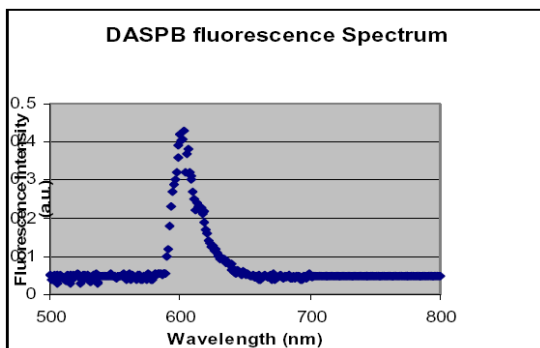


Fig.3 : One photon induced emission spectrum.

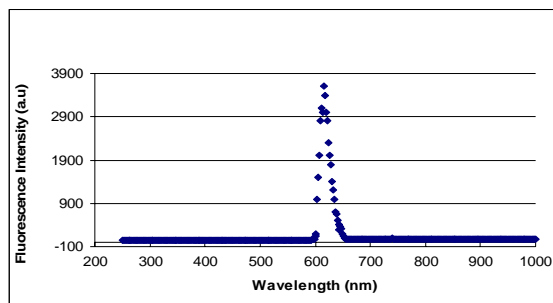


Fig.4 : One photon induced fluorescence at 532 nm.

From absorption spectrum of DASPb, we can see that there is no linear absorption in the entire spectral range from 580 nm to 1800 nm except the fact that IR radiation between 1,200 nm to 1,600 nm is strongly absorbed by DSAPB solution. It has been observed that this dye shows quite strong frequency upconverted fluorescence when exposed to near IR and IR laser beam above 700 nm. This suggests that a very strong TPA process may occur inside the sample. The TPA induced emission spectrum of 0.0005 mol/L DASPb in chloroform with 1 cm path length excited with 1064 nm laser beam is shown in Figure 5. In the measurement of the upconversion efficiencies, VIS cutting filters were used to cut transmitted pump energy. Comparing Figure 5 with Figure 4, we can see that the TPA induced emission spectrum of DASPb with much higher concentration has a red-shift as compared to that in much lower concentration single photon absorption study. This can be explained by re-absorption of Dye material [6].

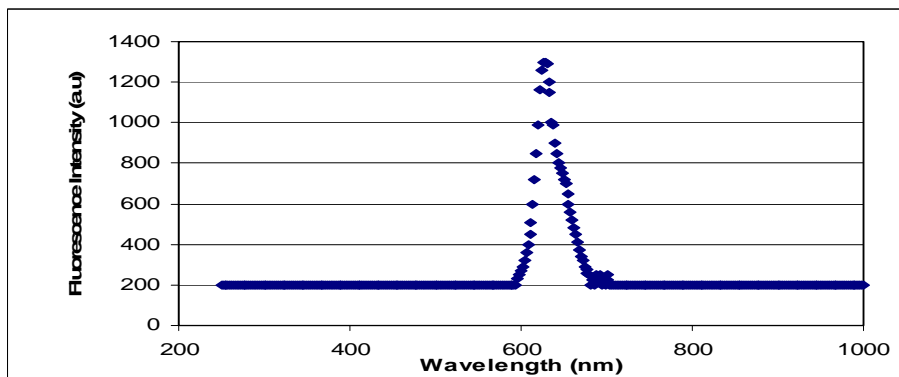


Fig. 5 : Two-photon induced emission spectrum of DASPb at 1.06 μm irradiation.

The linear transmission of dye in the form of film was about 10 %. The optical limiting curves using 532 nm pico second and nano second pulses are shown in Figure 6 and Figure 7 respectively. Optical limiting study is performed in two photon absorbing region using pico-second 800 nm, 900 nm and 1,000 nm laser beam (Figure 8). From the figures it can be noted that at very low input intensity, linear transmission is preserved, with increase in input intensity DASPb starts to contribute to saturation absorption which increases the

transmission above linear level and at higher intensities the excited state absorption starts to contribute and it dominates with further increase in intensity. This kind of behavior has interesting applications in Optical switching [7].

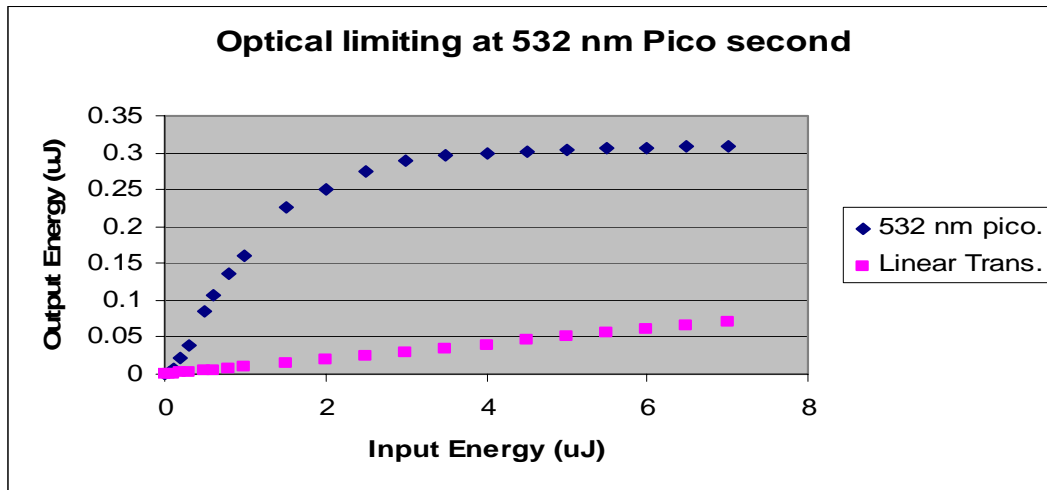


Fig. 6: Optical limiting behavior at 532 nm pico second pulses.

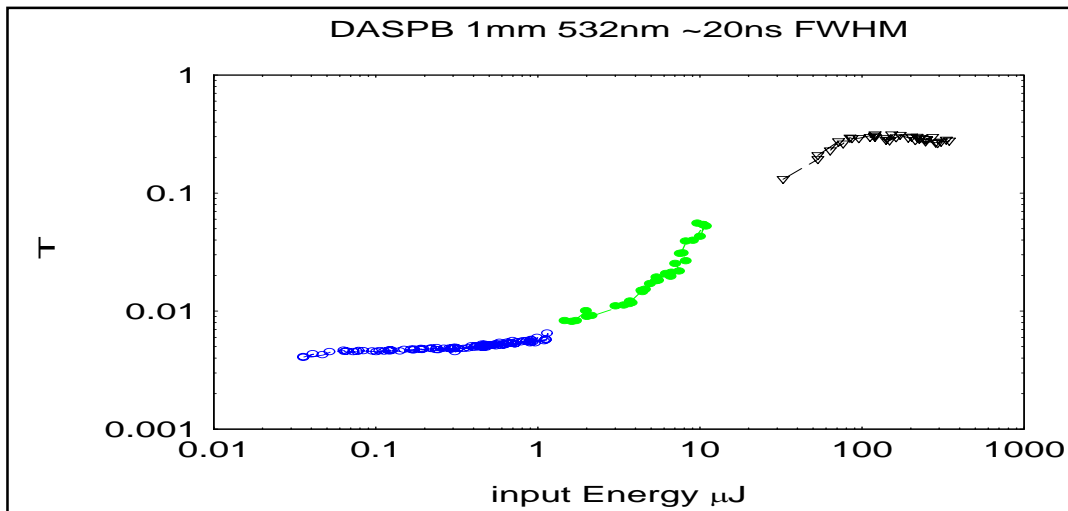


Fig. 7 : Optical limiting behavior of DASPb at 532 nm nano second pulses.

In conclusion, we have characterized the nonlinear optical properties of DASPb in PMMA-MA polymer matrix at its linear absorbing region and linear transmitting region. We found that the type of nonlinear absorption due to frequency up-converted fluorescence depends on the intensity of input beam. In linear absorption region, at lower intensity, the dye has shown saturation absorption and with increase in input intensity, the excited state absorption due to frequency up-converted fluorescence became prominent. This mechanism contributed to optical limiting behavior in absorbing region of the dye. In non-absorbing region, the two photon induced fluorescence along with excited state absorption contributed for optical limiting. More detailed understanding of the behavior in entire spectral region in terms of different nonlinear processes require further investigation. Efforts are under way to study the two-photon pumped cavity lasing using this dye doped

polymer material. Based on the result, it is expected that DASPB dye doped polymers are going to be the next practice as effective nonlinear material for future optical limiting and optical switching devices.

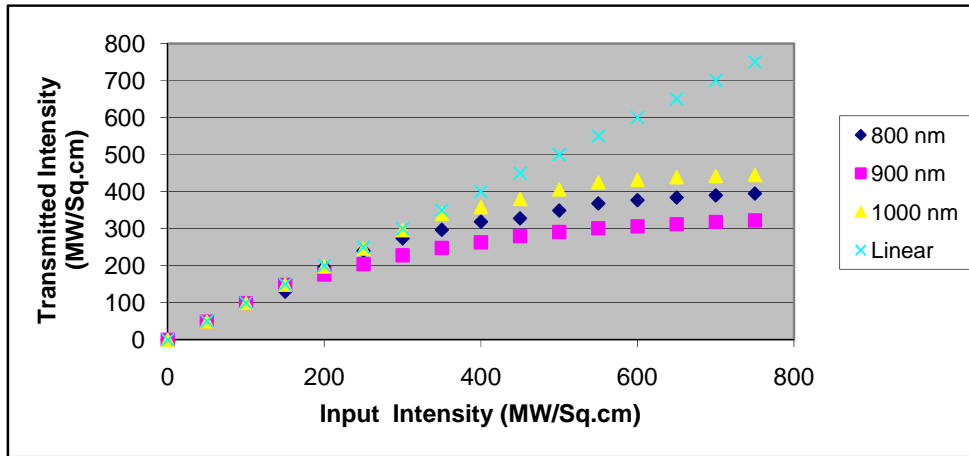


Fig. 8 : Optical limiting behavior of DASPB at 800 nm, 900nm and at 1000 nm.

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