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Improvement of Nonlinear Optical Properties for Mixture Laser Dyes Doped PMMA

Zainab F. Mahdi

Institute of Laser for Postgraduate Studies, University of Baghdad, Baghdad, Iraq

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Abstract: The spectral characteristics and the nonlinear optical properties of the mixed donor (C-480) acceptor (Rh-6G) have been determined. The spectral characteristics are studied by recording their absorption and fluorescence spectra. The nonlinear optical properties were measured by z-scan technique, using Q-switched Nd: YAG laser with 1064 nm wavelength. The results showed that the optimum concentration of acceptor is responsible for increasing the absorption and the emission bandwidth of donor to full range and to 242 nm respectively by the energy transfer process, also the efficiency of the process was increased by increasing the donor and acceptor concentration. The obtained nonlinear properties results of the mixture C-480/ Rh-6G showed a negative nonlinear refractive index and reverse saturation absorption. All the nonlinear optical parameters are linearly dependent with concentration. The origin of optical nonlinearity in the dye may be attributed to laser-heating induced nonlinear effect. Results show that mixture of laser dyes are effective nonlinear optical materials as compared to individual laser dyes.

Introduction

Organic dyes have various applications in many scientific branches due to their high fluorescence quantum yield and broad gain bandwidth [1]. The wide bandwidth makes them particularly suitable for tunable ultrafast pulse generation [2]. In order to achieve better laser performance such as higher lasing efficiency, wider wavelength tunibility and simultaneous multi-color generation, laser dyes must be mixed by varying the donor/acceptor concentration via fluorescence resonance energy transfer (FRET) from the excited donor molecule (D) to the acceptor molecule (A). FRET provides the structural information of a complex media also it has wide applications in the field of Physics, Chemistry and Biology [3].

Some parameters that require increasing the rate of excitation energy transfer depend upon (i) the quantum yield of emission of donor, (ii) the extent of overlap of the emission spectrum of donor and the absorption spectrum of acceptor, (iii) the light absorbing ability of the acceptor. (iv) the concentration of the acceptor molecule[4].

Mixture laser dyes are promising compounds for nonlinear optical applications because they exhibit strong nonlinear-optical behavior**.** Materials with nonlinear optical properties are under investigation due to their applications in optical communications, image processing, switching, 3D data storage and optical limiting [5].

The z-scan method has gained rapid acceptance by nonlinear optics community as a standard technique because it has several advantages. It has simple alignment set up. Under certain conditions, it is possible to isolate the nonlinear refractive index and nonlinear absorption. Both the magnitude and the sign of nonlinear refractive index can be determined .The data analysis are quick and simple, making it a good method for screening new nonlinear materials. Z-scan can determine both the real and the imaginary parts of susptibility. The technique is also highly sensitive, capable of resolving a phase distortion of λ/300 in samples of high optical quality. Finally the z-scan method can also be modified to study nonlinearities on different time scales [6, 7].

Xanthenes and Coumarin families showed high nonlinear properties especially C-480 and Rh-6G [8]. Therefore, these laser dyes and their mixture were chosen in the present study.

The objective of this work is to study the absorption and fluorescence spectra of mixture C-480 as a donor and Rh-6G as an acceptor at different concentrations also measuring the nonlinear optical parameter of this mixture via z-scan experiment at 1064 nm at different intensities.

Experimental work

Two well known groups of laser dyes, Coumarin 480 as a donor and Rh-6G as an acceptor were used .Both of them were supplied from Lambda Physics. These two laser dyes were dissolved in chloroform solvent (spectroscopy grade) at different concentrations. The analytic concentrations of the five solutions examined are 10^{-5} M, 5x 10^{-5} M, 10^{-4} M, 5x10^{-4} M and 10^{-3} M. A 1:1 (v/v) pair donor and acceptor solution was mixed to produce five series. At each series, there is single donor concentration with five concentrations of the acceptor. All five series are doped in PMMA (from, ICI, England) at room temperature .The absorption and fluorescence spectra of C- 480/ Rh- 6G and their mixture were recorded by a UV–VIS–NIR spectrophotometer (SP3000) and SL 147 spectrophotometer.

Figure 1 shows the experimental z-scan setup. It consists of a 30 ns Q-switched Nd: YAG laser operating at 1064 nm wavelength with two energies of 34 mJ and 54mJ. Laser pulse energy was measured by the (DPSS 1830C) detector. The laser beam passes through a lens of 300 mm focal length. A 6 μm thin sample was moved through the beam waist of laser beam along the z axis distance using a translating stage. The transmitted laser beam was splitted via a beam splitter, a reflected laser beam from beam splitter was sent to a first joule meter (D1). This arrangement represents an open –aperture z-scan to measure nonlinear absorption properties. The transmitted laser beam from beam splitter was sent through an aperture (iris) which clips roughly half of the beam intensity. After the aperture, a second energy meter detects the remainder of the beam. The normalized transmittance through an aperture in the far field is monitored as a function of the sample position with respect to the focal position .This arrangement represents a closed –aperture z-scan to measure nonlinear refractive index properties. The power densities of the laser were 63 MW/cm^2 and 100 MW/cm^2.

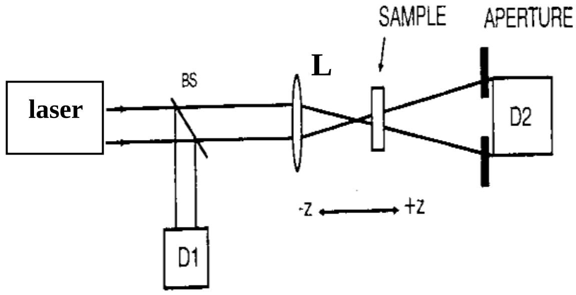

Fig. (1): Schematic diagram of a single beam z-scan setup: L: Lens; S: Sample; A: Aperture; D_1, D_2: Detectors; BS: Beam Splitter

Results and Discussion

The absorption and fluorescence spectra of C-480 (donor)/Rh -6G (acceptor) system in PMMA are shown in Figure 2. Due to large overlap zone of the donor fluorescence with the acceptor absorption there is a high possibility of excitation energy transfer between them.

At 10^{-4} M concentration, the maximum absorption and fluorescence for C-480 was at 350 nm and 465 nm respectively yielding Stoke shift of about 115 nm .The absorption and fluorescence peaks for Rh-6G was at 530 nm and 560 nm respectively that yielding Stokes shift of 30 nm. From Figure 2, less overlap in the absorption and fluorescence bands of C-480 / Rh-6G was observed. This is suitable for a gain material's efficiency since there will be less self absorption of the fluorescence emission by the dye in addition both molecules are highly planar. Two molecules have high fluorescence efficiencies of 0.95 for Rh -6G and 0.8 for C-480.

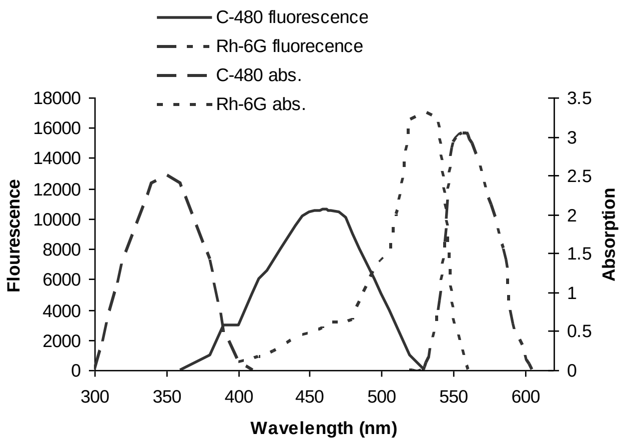

Fig. (2): Absorption and Fluorescence spectra of Rh-6G and C-480

Absorption and fluorescence parameters of C-480 and Rh-6G at 10^{-4} M concentration are tabulated in Table 1

Table (1): Absorption and fluorescence parameters of donor and acceptor at 10^{-4} M concentration

Laser dyes	λ_{max}Abs. nm	$FWHM_{abs}$ nm	λ_{max} Emin. nm	$FWHM_{ems}$ nm
10^{-4} M C-480	350	105	465	120
10^{-4} M Rh-6G	530	115	560	51

The absorption spectra of C-480/Rh-6G mixture at different concentrations for five series showed that increasing the acceptor dye concentration step by step , decreases the absorption peak intensity of the donor .An extended band covered donor and acceptor region at each series of donor was observed at 10^{-4} M of acceptor. This behavior is shown in Figure 3. Similar observation of the fluorescence spectra for the mixture can be observed. The donor fluorescence intensity spectra for C-480 decreased and emission maximum is shifted gradually toward the blue end to maximum 15 nm of the donor spectrum. Meanwhile, the acceptor emission intensity peak for Rh-6G was increased and slightly red shifted to maximum 60 nm. Similar observation of the fluorescence spectra for the mixture can be observed. The donor fluorescence intensity spectra for C-480 decreased and emission maximum is shifted gradually toward the blue end to maximum 15 nm of the donor spectrum.

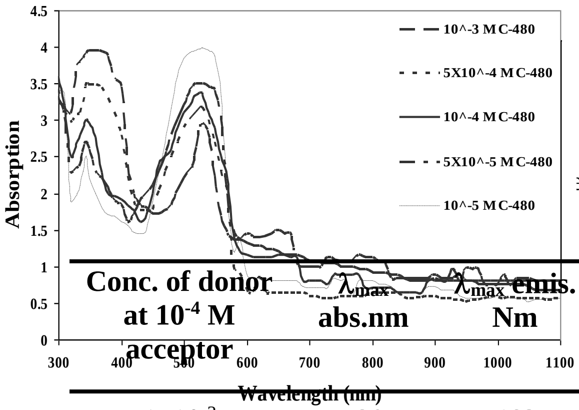

Fig. (3): The absorption spectra of mixed laser dyes at 10^{-4} M of Rh-6G

Meanwhile, the acceptor emission intensity peak for Rh-6G was increased and slightly red shifted to maximum 60 nm.

Again due to the energy transfer from donor to acceptor as direct excitation the fluorescence spectra were extended to a wide range as in Figure 4. FWHM of the mixture laser dyes emission at 10^{-4} M of acceptor generally increased with increasing concentration of the donor.

The maximum FWHM of mixture was equal to 242 nm at 10^{-4} M donor concentration. Two peaks of emission for both donor and acceptor appeared .This demonstrates that the gain of each dye can be adjusted to about equaled values by changing the concentration. The efficiency of energy transfer (E) was calculated from Equation1 [4]:

$$E = 1 - F_{DA}/F_{D} \qquad (1)$$

where $\mathbf{F_{DA}}$ **,** $\mathbf{F_D}$ are the fluorescence intensity of the donor in the presence and absence of acceptor respectively .

Absorption and fluorescence parameters of PMMA mixture laser dyes at 10^{-4} M acceptor concentration for different donor concentration are listed in Table 2.

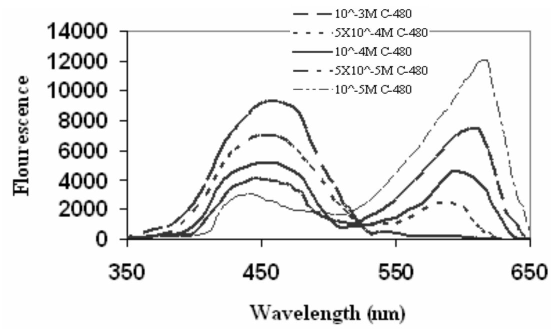

Fig. (4): The fluorescence spectra of mixed laser dyes at 10^{-4} M of Rh-6G .

...ers of PMMA mixture laser dyes at 10^{-4} M acceptor

Conc. of donor at 10^{-4} M acceptor	λ_{max} abs.nm	λ_{max} emis. Nm	FWHM Abs. nm	FWHM Emin. Nm	Efficiency of energy transfer
1×10^{-3}	529	463	full range	148	0.143
5×10^{-4}	530	460	full range	217	0.333
1×10^{-4}	530	457	full range	242	0.505

From Table 2, the efficiency of energy transfer at 10^{-4} M concentration of the acceptor increased with increasing donor concentration. This is also due to the increase of the overlap between donor and acceptor. Nonlinear properties of PMMA doped mixture of C480/Rh-6G were obtained for all series at 10^{-4} M concentration of acceptor for 63 MW/cm^2 and 100 MW/cm^2 power densities at 1064 nm. Figure 5 and Figure 6 show the profile of transmittance difference in closed aperture z-scan .A peak-valley structure in the profile indicates the negative effect of refractive nonlinearity i.e., self-defocusing. The defocusing effect is attributed to the thermal nonlinearity resulting from the absorption of radiation at 1064 nm.

The localized absorption of a tightly focused laser pulse propagating through an absorbing dye medium produces a spatial distribution of temperature, density gradients in the dye sample, therefore; it has a larger nonlinear phase shift consequently larger value of the peak-to-valley transmittance.

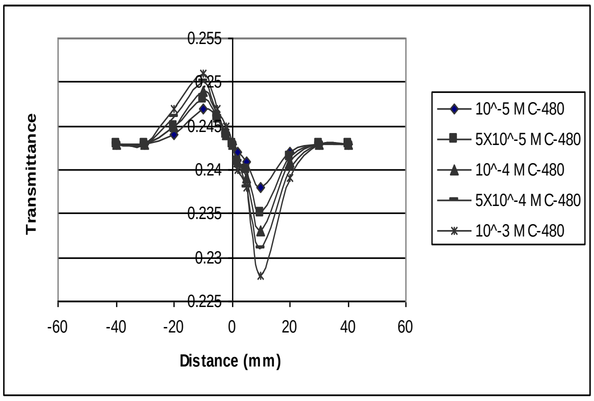

Fig. (5): closed aperture z-scan of mixture laser dyes at 10^{-4} M of Rh-6G at

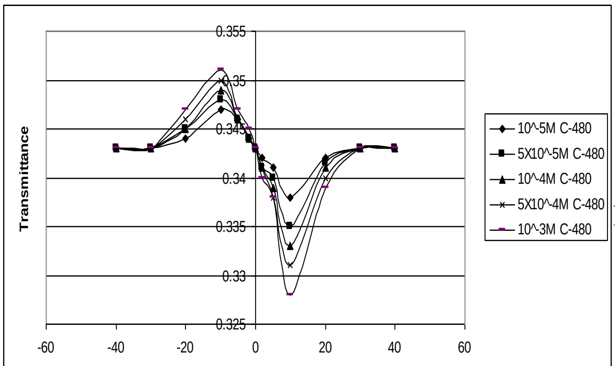

Fig. (6): closed aperture z-scan of mixture laser dyes at 10^{-4} M of Rh-6G at 100 MW/cm^2

63 MW/cm^2

Consequently, a spatial variation of nonlinear refractive index which acts as a thermal lens will result in a severe phase distortion of the propagating beam. The effect of power densities on the peak-to-valley transmittance can be shown in Figure 5 and Figure 6. Also High peak densities lead to an increase in the transmittance difference and finally increase nonlinear refractive index. Also these figures show an increase of vally transmittance according to peak transmittance. This refers to the contribution of positive absorptive nonlinearity which is mostly due to reverse saturable absorption (RSA).

Investigation has been carried out for the dependence of nonlinear refractive index on concentration of the donor at 10^{-4} M of acceptor at 63 MW/cm^2 and 100 MW/cm^2. The nonlinear refractive index n_2 increased with increasing donor concentration as in Figure 7. This may be attributed to the fact that the number of the dye molecules increases when the concentration increases and more particles get thermally agitated resulting in an enhanced effect. Also the refractive indices increased with increasing the intensity at the same concentration.

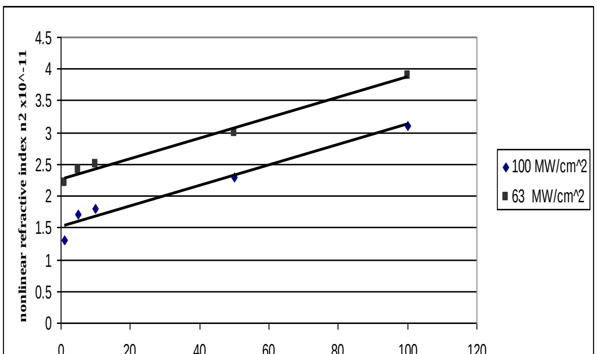

Fig. (7): Nonlinear refractive index at different concentration of donor at 100 MW/cm^2 and 63 MW/cm^2 power densities

The transmittance profile at open-aperture (OA) z-scan experiment shows reverse saturation absorption (RSA) as in Figure 8 and Figure 9 .Transmittance increased for 10^{-4} M concentration of the acceptor with increasing concentration of the donor at 63 MW/cm^2 and 100 MW/cm^2. The absorptive nonlinear behavior that was found in open aperture (OA) z-scan is in agreement to those obtained from closed-aperture (CA) z-scan. This confirmed the fact that, a single CA profile is sufficient to elucidate all the optical nonlinear parameters. All those results are in a good agreement with Tripathy and Bisht work which depends on closed aperture results to get optical nonlinear parameters [9].

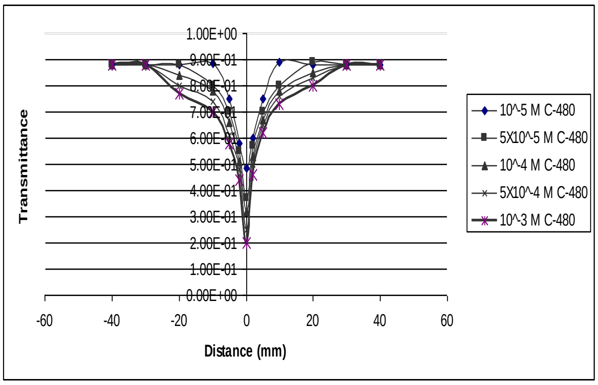

Fig. (8): open aperture z-scan of different concentration of donor at 10^{-4} M acceptor at 63 MW/cm^2

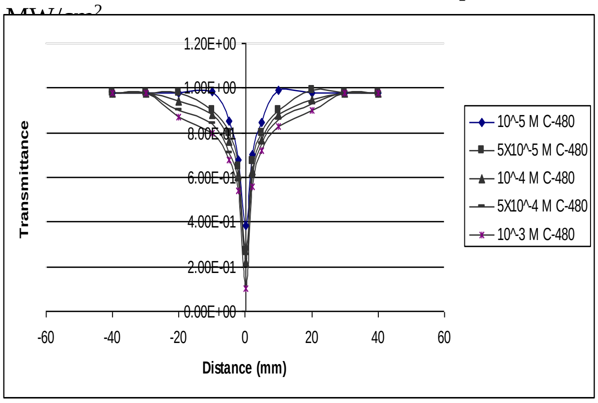

Fig. (9): open aperture z-scan of different concentration of donor at 10^{-4} M acceptor at 100 MW/cm^2

The linear dependence of nonlinear absorption coefficient β on the optimum mixture of acceptor at different concentrations of donor at incident intensity 63 MW/cm^2 and 100 MW/cm^2 are shown in Figure 10

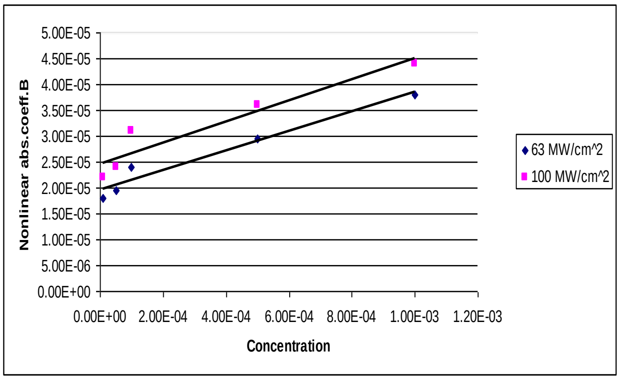

Fig. (10): Nonlinear absorption of different concentration of donor at 100 MW/cm^2 and 63 MW/cm^2 power densities

The third order nonlinear susceptibility $\chi^{(3)}$ at 10^{-4} M concentration of acceptor increases with increasing donor concentration at 63 MW/cm^2 and 100 MW/cm^2 as in Figure 11 .All results of n_2 , β and $\chi^{(3)}$ show a direct relation with concentration.

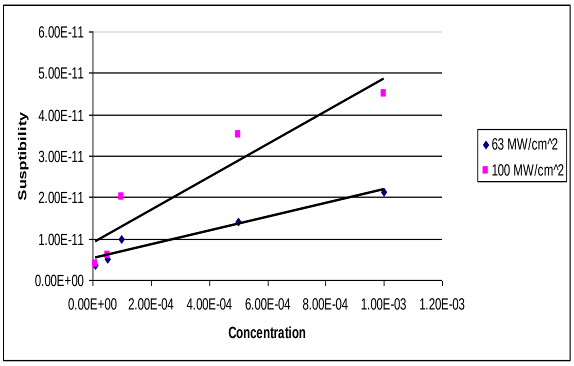

Fig. (11): Susptibility of different concentration of donor at 63 MW/cm^2 and 100 MW/cm^2 power densities

bandwidth of C-480 and Rh-6G individually at the same concentration. Thermally induced refractive index changes are responsible for nonlinear refractive index variations. Finally mixture laser dyes are promising materials for applications in nonlinear optical devices.

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تحسين الخواص البصرية اللاخطية لخليط الصبغات الليزرية المشوبة ببولي ميثل ميثا أكرليت

زينب فاضل مهدي

معهد الليزر للدراسات العليا , جامعة بغداد , بغداد, العراق

الخلاصة في هذا البحث تم تحديد الخواص الطيفية والخواص البصرية اللاخطية لخليط من مانح (كومارين – 480) ومتقبل (رودامين – 6 ج) درست الخواص الطيفية بتسجيل اطياف الامتصاص والانبعاث أما الخواص البصرية اللاخطية فتم قياسها بواسطة تقنية المسح على المحور الثالث باستخدام ليزر نديميوم – ياك بعرض نبضة 10 نانوثانية عند الطول الموجي 1064 نانومتر . بينت النتائج بأن تراكيز مثالية للمستقبل هي المسؤولة عن زيادة عرض المدى الطيفي للامتصاص للمانح الى اقصى مدى والانبعاث الى 242 نانومتر باستخدام تقنية انتقال الطاقة . أظهرت النتائج ان كفاءة انتقال الطاقة تزداد بزيادة تركيز المانح والمستقبل . اوضحت النتائج بأن معامل الانكسار اللاخطي يكون سالب بينما معامل الامتصاص اللاخطي هو الامتصاص المشبع المعكوس كما ان العوامل البصرية اللاخطية تتناسب خطيا مع التركيز. بينت ملخصات النتائج بأن خليط الصبغات يعتبر مادة لاخطية مؤثرة مقارنة بالصبغات المنفردة .