Studying the nonlinear optical properties of organic dyes after Dissolved in Methanol and Epoxy Resin

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Abstract. In this paper, some linear optical properties such as (absorbance and transmittance) of an organic dye (Calcein -W) in Methanol and Epoxy resin with different concentration were studied by using UV/VIS spectrum. Nonlinear optical properties of Calcein –W anesthetized in epoxy resin matrix using different concentrations (5*10⁻⁵, 1*10⁻⁴, 5*10⁻³, 1*10⁻³ mol/l) at ambient temperature were studied by using open and closed aperture of Z-scan technique, with continuous wave from Neodymium-doped Yttrium Garnet (Nd: YAG (CW)) laser beams of 532 nm wavelength as an excitation source. The “nonlinear refractive index” (n2), ”nonlinear absorption coefficient” (β) of Calcein –W doped film is experimentally determined.

Keywords: Organic dye, Z-Scan, Optical properties, Nonlinear properties.

1. Introduction
The selection of dye is an important parameter which influences in the dye sensitized solar cell (DSSC) efficiency. The sensitizers are generally chosen to have functional groups such as–COOH, etc. to get stable adsorption on the semiconductor layer. The semiconductor bulk in DSSCs can be considered as a charge transporter while the photosensitive dyes are providing the photoelectrons are [1]. Parameters of optical properties such as absorption, transmittance, etc. are important for artificial a solar cell [2].

Also organic dyes are in general appealing for examining non-linear optical properties in order to understand the viewpoint of their photo-physics and their applications [3]. Nonlinear optics is interested in the influences and phenomena that happened when the response of a material system to an utilized optical field rely in a nonlinear way on the strength of the optical field. Usually, nonlinear optics is noticed with only laser light which have enough intense to adjust the optical properties for the system of used material [4].

A review of the literature showed that several researchers have studied the linear and nonlinear properties of organic dyes; Yathisha R. O. and co- worker 2020, selected a dye sensitized Cr–ZnO and Ni–CdO nanoparticles before and after sensitization with Trypan Blue (TB), SPADNS (SPD) and Evans Blue (EB) for the applications of DSSCs. They were examined through X-ray diffraction...
(XRD), cyclic voltammetry, and UV–Visible. The results display that there are improved in the absorption edge of nanoparticles toward the longer wavelength side [5].

Ali F H and co- worker 2017,mixed two organic dyes Rhodamine B and Methyl violet dissolved in ethanol and examined through UV-VIS spectrophotometer. The results display that the mixture solution of laser dyes boost the optical properties compared with samples before mixing[6].

Alhamdani AH and co-workers 2017, studied the nonlinear optical properties of doped organic dye (Rhodamine 6G) with Aluminum oxide nanoparticle. They were examined by using Eclipsing Z-scan technique. They observed a proportional relationship between nonlinear optical properties and nanoparticle concentration [7].

Keta R N and co- workers 2019, produced cold plasma by using plane "Dielectric Barrier Discharge" and treated prepared organic dye doped polymeric films. They were examined by using Z-Scan technique. They concluded that increasing of plasma exposure time gives perfect indication on the polymer internal structure [8].

Dyed doped polymer films are attracting researchers because of its enhanced efficiency and reasonable mechanical properties to manufacturing beneficial devices [9]. No recorded researches were found dealing with the same research topic related to nonlinear properties of calcium-W dye. Z-scan technique was utilized to demonstrate the nonlinear properties for calcium-W anesthetized films with epoxy resin.

The sensitive single-beam utilized in this technique is active to measure each of optical nonlinear refractive index and optical nonlinear absorption coefficient.

2. Experimental pat:
2.1. Materials
Calcein W (Fluorescein iminodiacetic Acid) with molecular formula (C₃₀H₂₈N₂O₁₃) and molecular weight (624.570) as orange-brown solid from (Fisher Scientific Company) was used, Methanol (CH₃OH) (99.9%) was used as a solvent from (Scharlau, Spain), and Epoxy resin from "CLEVER EPOXY TP (A), Polyurethane systems clever polymers and construction chemicals INC." (Istanbul, Turkey) was used.

2.2 Synthesis of organic dye
Figure (1), shows the "Mannich condensation" method for preparing Calcein [10].

![Synthesis of Organic Days](image)

2.3 Synthesis of dye doped in epoxy resin:
Known weight of Calcein -W was dissolved in Methanol, which was diluted to prepare the required concentrations (5*10⁻³, 1*10⁻⁴, 5*10⁻⁴, 1*10⁻³ mol/l).

The membrane was prepared by taking a specific volume of Epoxy mixture (A) and (B) mixed in the ratio (3: 1) ,and mixing it with a certain volume of dye solution dissolved in Methanol to prepare the required concentrations , then poured into molds and left at room temperature until it dries. Thickness of the prepared samples is 1 mm.
3. Results and discussion

3.1 linear optical properties

The absorption and transmittance spectra were recorded for both the calcein-W dye solution in methanol and for the epoxy resin films using a "UV- VIS-T60 PG" spectrophotometer device. The spectra are shown in Figures (2 and 3). The absorbance of Calcein-W in Methanol at (481nm) for concentration \(5 \times 10^{-5}\) is (0.261) and for concentration \(1 \times 10^{-3}\) at (479nm) is (0.893) which means that the increasing in concentration of Calcein-W dye solution allow to increase the absorption intensity. The spectral parameters are shown in Table 1.

![Figure 2](image2.png)

**Figure 2.** Absorption spectrum of Calcein-W resolves in methanol at various concentrations.

![Figure 3](image3.png)

**Figure 3.** Transmittance spectrum of Calcein-W resolves in methanol at various concentrations.
Table 1. Some linear parameters of Calcein-W resolve in Methanol at various concentrations.

| Concentration | $\text{ABS}_\text{max.}$ Wavelength (nm) |ABS Intensity | FWHM (nm) | Transmittance Wavelength (nm) | Transmittance (T %) |
|---------------|--------------------------------------|--------------|-----------|-------------------------------|--------------------|
| $5 \times 10^{-5}$ | 481 | 0.261 | 32.4792 | 481 | 53.4 |
| $1 \times 10^{-4}$ | 490 | 0.3 | 38.5315 | 493 | 42.5 |
| $5 \times 10^{-4}$ | 479 | 0.663 | 39.3031 | 479 | 21.7 |
| $1 \times 10^{-3}$ | 479 | 0.893 | 48.9636 | 479 | 12.9 |

Figures (4 and 5) show the absorption and transmittance spectrum of Calcein-W doped Epoxy resin at various concentrations respectively. We observe the maximum absorption peak value for Calcein-W/Epoxy resin was greater than that in Methanol. That means the presence of Calcein-W, boost the absorbance of the "composite films" and modify the optical behavior. The features of the dye spectral in Epoxy resin rely on their intermolecular influence between Calcein molecule and the Epoxy resin molecules.

The absorbance of Calcein-W in Epoxy resin at (513nm) for concentration ($5 \times 10^{-5}$) is (0.089) and for concentration ($1 \times 10^{-3}$) at (522nm) is (3.514), Table 2 show the spectral parameters of dye doped at various concentrations.

Figure 4. Absorption spectrum of Calcein-W in epoxy resin at various concentrations.
Figure 5. Transmittance spectrum of Calcein-W in epoxy resin at various concentrations.

Table 2. Some linear parameters of Calcein-W in epoxy resin at various concentrations.

| Concentration | ABS
max Wavelength (nm) | ABS Intensity | FWHM (nm) | Transmittance Wavelength (nm) | Transmittance (T %) |
|---------------|----------------------|---------------|-----------|-------------------------------|---------------------|
| 5*10^-5       | 513                  | 0.089         | 18.0657   | 513                           | 81.3                |
| 1*10^-4       | 514                  | 0.423         | 21.1198   | 513                           | 38                  |
| 5*10^-4       | 514                  | 1.801         | 40.2419   | 513                           | 4.2                 |
| 1*10^-3       | 522                  | 3.514         | 55.0277   | 518                           | 1.8                 |

3.2. Nonlinear properties:
A (532 nm) wavelength (Nd: YAG (CW)) laser beams was utilized as the light exporter. Transmittance of the nonlinear samples medium was measured toward the centric area over the axial trend which represents the trend of the laser beam diffused. The lens used in the setup has a focal length equal to (10) cm.

The "nonlinear absorption coefficient" of (Calcein –W) shows that the material has a demeanor of two photon absorption, the reason for this is consequent to alteration in the intensity of the laser; which is outcome of alteration in the laser intensity that obtain at the waist of the influential beam on Calcein -W dye.

Figure (6) shows the "z-scan" of Calcein -W dye in thin Epoxy resin film. From the curve of the aperture Z-scan we can infer the appearance of the inductive absorption behavior of the resin dye films. The steeper in the curve of the open aperture z-scan display the transmittance limiting efficiency of the Calcein-W doped epoxy films.
The transmittance minimum acquired for Calcein-W anesthetized epoxy film is about 0.0338 for dye concentration (5*10^{-5} mol. /l), and (0.0027) for dye concentration (1*10^{-4}mol. /l). The amounts of nonlinear absorption coefficient are listed in table (3) which has been obtained using the following equation formula [11]:

\[ q_o(Z) = I_0 L_{eff} \beta \left( 1 + \frac{Z^2}{Z_0^2} \right)^{-1} \]  

(1)

Where: Z: the placement of sample, L_{eff}: effective thickness, I_0: Intensity at focus z = 0.

**Figure 6.** The open aperture / Z-scan of Calcein-W anesthetized epoxy resin at various concentrations.

**Figure 7.** The setup of close aperture z-scan.

**Figure (7)** shows a closed aperture z-scan set up, and the closed aperture Z-scan plot between Z and normalized transmittance for Calcein-W dye anesthetized in various concentrations is shown in Figure (8). The noted peak amplitude pursued by valley amplitude of normalized transmittance curve in the plot of closed aperture Z-scan for doped dye (5*10^{-5}, 1*10^{-4}) shows that the refractive nonlinearity sign is
negative (i.e. self-defocusing), because the sample act as a negative lens and dissipates the laser beam, the "non-linear refractive index" value of concentrations (5*10^-4, 1*10^-3) is positive, denote that the Calcein film at these concentrations conduct as a lens to compile the laser beam. Table (3) shows the "nonlinear refractive index" values which has been obtained using the following equation formula [12]:

\[ n_z = \Delta \Phi_0 \left( I_0 L_{eff} K \right)^{-1} \]  

(2)

Where :- \( k \): the wave number, and, \( \Delta \Phi_0 \): the nonlinear phase shift

**Figure 8.** Close aperture Z-scan of the Calcein-W anesthetized epoxy resin at various concentrations.

**Figure 10.** Relationship between various concentrations of Calcein-W in epoxy resin and nonlinear refractive index.

**Figure 9.** Relationship between various concentrations of Calcein-W in epoxy resin and nonlinear absorption coefficient.
Table 3. The nonlinear parameters of Calcein-W in epoxy resin at various concentrations.

| Concentration (mol/l) | Absorption intensity at wavelength (532nm) | Absorption coefficient (cm⁻¹) | Effective length (cm) | Nonlinear Transmittance at Z=0 | nonlinear absorption coefficient (cm/mW) | Difference between the transmittance of the peak and the valley | Nonlinear phase shift 10⁻⁵ | Nonlinear refractive index (cm²/mW) 10⁻² |
|-----------------------|--------------------------------------------|-------------------------------|----------------------|--------------------------------|------------------------------------------|-------------------------------------------------|-------------------------|---------------------------------------|
| 5*10⁻⁵                | 0.023                                      | 1.0593                        | 0.7058               | 0.0338                          | 0.2728                                   | 0.0194                                          | 1.0415                  | 8.81                                  |
| 1*10⁻⁴                | 0.025                                      | 1.1515                        | 0.6849               | 0.0214                          | 0.2847                                   | 0.0152                                          | 0.8134                  | 7.09                                  |
| 5*10⁻⁴                | 0.123                                      | 5.6653                        | 0.1764               | 0.0172                          | 1.1102                                   | 0.0024                                          | 0.1306                  | 4.419                                 |
| 1*10⁻³                | 0.404                                      | 18.6082                       | 0.0537               | 0.0027                          | 3.6991                                   | 0.0006                                          | 0.0358                  | 3.977                                 |

4. Conclusion:
The spectral characteristics (Absorption; Transmittance) of Calcein -W dye were studied in Methanol and Epoxy resin. Nonlinear studies display that the nonlinear refractive index exhibits negative when Calcein-W dye doped with Epoxy resin at concentration (5*10⁻⁵, 1*10⁻⁴) mol/l ;and positive at dye doped Epoxy with concentration (5*10⁻⁴, 1*10⁻³) mol/l.

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