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Linear Optical Properties of Organic Dye Doped Poly Methyl Methacrylate and Titanium Dioxide Nanoparticle

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Abstract:

In this paper (absorption and fluorescence) spectral properties of organic laser dyes for Aurintricarboxylic Acid compound (s) have been investigated, dissolved in Dimethyl sulfoxide (DMSO) prepare($10^{-4}$and 10^{-5}) at (25^0c) temperature. The experimental results show to an increase the intensities of absorption with the concentration increasing, this result which are found in agreement with Beer – Lambert law, these results have been also point out to shift in the absorption spectral range and fluorescence with a expansion in the direction of short wavelength with high energy, the quantum yield of the dissolved compound (s) in Dimethyl sulfoxide DMSO has been calculated for thin film for pure dye and use polymer (PMMA) with dye and use Titanium dioxide nanoparticle with dye and polymer with thickness (100, 120 and 140) nm respectively, radiative lifetime for thin film with dye add polymer and thin film with dye add polymer and nanoparticle become less when we compare with pure dye also quantum efficiency increase when we use polymer and nanoparticle, thus we can use this material as laser active media .
Keywords: *linear optical , absorption and fluorescence , organic dyes*

I. Introduction

Organic dye doped with polymers are a great deal of concern in last century , due to their great effect in many important employment such as optical store, optical convert, optical limiting, signal processing, holography and nonlinear optics application processing, photoelectric devices add to various type of nonlinear photonic devices**[1-3].** Solid-state dye laser have been organic dye molecules essential distributed in a highly solid homogenous matrix, many of substance which have been consumed as solid hosts for organic laser dyes such as, (polymers - glasses - organically changing silicates or nano-composites). An example. of such polymer pure form poly methyl methacrylate (PMMA) [4] . commonly ,the solid host substance used as suitable in solid-state of organic dyes laser. This material should be have highly transparent to the pump laser and organic dye laser and solid-state dye laser wavelengths. Polymeric matrices hosts

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have been some major feature over other host substance materials because simple prepare and cheap to produce [5]. Special properties of Poly(methyl methacrylate) such as low density, ability to form intricate shapes, high quality mechanical strength versatile, electrical properties, and few manufacturing cost made them promising materials that have been successfully in matrix's host matrices for dyes use with some fluorescent dyes have been used in dye lasers for active media [4,6]. If the light pass with organic dye the optical parameter observed in solid state matter use as three part, reflection, absorption, and transmission [7]. The beam of light have intensity I_O when incident the surface of the solid material must combine the sum of the intensities of the transmitted, absorbed, and reflected beams, we can represent by a symbol (I_T, I_A, and I_R) respectively [8,9].

$$I_O = I_T + I_A + I_R \quad \textbf{(1)}$$

Where: I_O: total intensity , I_T: transmission intensity , I_A: absorption intensity, and

I_R: reflective intensity

$$T + A + R = 1 \quad \textbf{(2)}$$

Where T:transmission , A: absorption,and R: reflective

Different properties can be used to identical the optical parameter of organic dye . Specially the refractive index n_0, absorbance, or refractivity, absorption coefficient, are know as the ratio of the refracted to incident intensity and absorbed to incident intensity ,respectively [10].
The linear absorption coefficient (α_o) and the linear refractive index(n_o) can be define as transmittance spectrum calculated from the following equations [10]:

(3)

$$n_o = \frac{1}{T} + [(\frac{1}{T^2} - 1)]^{1/2} \quad \textbf{(4)}$$

t: is the sample thickness .

$$T_f = \frac{a \ \times \tau_{fRB}}{a_{RB}} \quad \textbf{(5)}$$

Where a: area under fluorescent curve, τ_{fRB}:livetime for Roadmen dye and a_{RB}: area under fluorescent curve Roadmen dye.

Quantum yield is an important property of a fluorophore and is essential for the characterization of novel fluorescent probes. The fluorescence quantum yields the ratio of photons absorbed to photons emitted through fluorescence[11] .

$$\emptyset_F = \frac{\int \mathbf{F(v)dv}}{\int \in \mathbf{(v)dv}} \quad \textbf{(6)}$$

Where $\emptyset_F$: Quantum yield, $\int F(v)dv$:area under fluorescent curve and $\int \in (v)dv$: area under absorbance curve.

$$T_{FM} = \frac{T_F}{\emptyset_F} \quad \textbf{(7)}$$

Where T_{FM}: lifetime of radiative time .

The effect of solvent on the absorption and fluorescence characteristics of organic materials has been a subject of interesting research .
In this study, the optical parameter such as absorption coefficient α_0, refractive index n_0 of pure dye and with doped polymers were study by know the information about spectroscopic absorbance and transmittance spectroscopy .
We present the influence of Aurintricarboxylic dye compound (s) on the optical parameter of poly methyl methacrylate(PMMA) polymeric substance (guest - host system). Poly methyl methacrylate (PMMA) was a transparent plastic material with very high solidity, durability, and flexibility[12].
Nanostructure materials are. a new type of materials that exhibit unique properties and feature in

different fields Synthesis of nanoparticles in matrixes such as polymer films are main interest in several optical, nonlinear optical, and sensor applications [13].

II. Materials and Samples Preparation

The compound (S) dye was obtained from (Aurintricarboxylic Acid) with a chemical molecular formula of $C_{39}H_{44}N_6O_6$ and its chemical structure is show in Figure(1).We can preparation the essential dyes by use 17 mL litter of concentrated (H_2SO_4) were mixed with (10 gm. ,0.014mol) of solid potassium nitrate. After solution is complete, began to add slowly 20 g. (0.014mol) of salicylic acid with slowly moving . The blending , should be light(red to brown) colour. And by twisted an ice-salt container . Add (1.95 g, 0.065 mol) of formaldehyde is bit by bit with vastly vigorous stirring. A bout 100 g of mash ice is then mixed , the stirring should be vigorous with the addition. The mixture of the flask are stirred until the dye of aurintricarboxylic acid has disintegrated into very small parts of dye[14].From Aurintricarboxylic Acid (1.18g , 0.002 mol) have been mixed with Benzidine (0.46g , 0.005 mol) ,the mixture has been refluxed for 3 hours with increase temperate from (50-300) ^{0}C with continuous stirring. The precipitate has been filtered and washed wit 100 mL.

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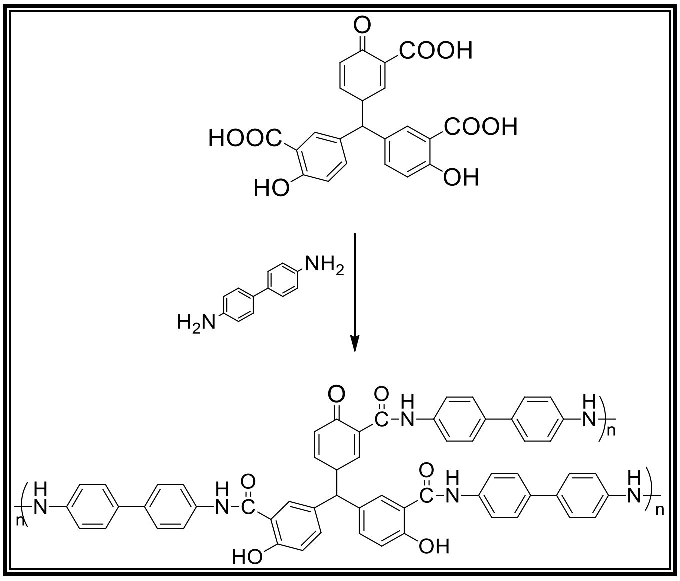

Fig: 1 Scheme diagram of procedure for the preparation Aurintricarboxylic compound (S)

Poly methyl methacrylate (PMMA) polymer was purchased from (ICI, England) and used as add up at material for organic laser dye because its perfect optical properties. The molecular formula of PMMA is ($C_5O_2H_8$),it is highly amorphous with average M_w of about 8400(g/mol), and (G_T)glass transition temperature about 105(°C).

Polymer (PMMA) is an aromatic polymer consist of the aromatic monomer styrene, asolution of hydrocarbon that is mainley manufactured from petroleum by the chemical manufacture . PMMA is a thermoplastic materail and one of the most excessively used type of plastic.

The thin films of compound (s), were prepared on a clean glass slide via drop casting method , with solution at concentration (10^{-4}and10^{-5}) M for each of them, and dried at room temperature for (3) days, the thickness of these thin films is about (100-140) nm.

Thin films of dye doped polymer preparation by use drop casting method, at concentration (10^{-4}and10^{-5}) M. Polymer is prepared as liquid dissolving the required amount of (PMMA) (seven(g) in 100 mL of Dimethyl sulfoxide solvent). A require amount of dye solution was added to polymer solution and put the mixture on the stirrer by a magnetic stirrer at room temperature to get a homogenous mixture. Films were shaped by drying polymer dye liquid on a glass films at room temperature 25 ^{0}C. After this stage ,we add nanoparticles to dye doped with polymer.

mixture (dye, TiO_2 and polymer PMMA)get together to prepare thin films by distributed the mixing to dry on a glass at room temperature. This process was repeated at each dyes.

The dye, nanoparticles and PMMA thin films were made by dropping method. The solution of the (PMMA) polymer was prepared by solubility 7 gm of PMMA polymer in 100 mL of DMSO solvent. The compound added to ($10^{-4}$and 10^{-5}) M dyes solution. Different weight of nanoparticles powder (0.1) wt % have been added and stirred by magnetic stirrer at (25) temperature to get a uniform material.

III. Results and Discussion

The Table(1) include some physical properties for compound (s), molecular formula (M.F) ,molecular weight (M.Wt) , color, and melting point(M.P).

The crystal structures of compound prepared have been studied by using X-ray diffraction instrument type (DX-2700).X-ray diffractometer instrument has been used to examine the mode of X-ray diffraction of all compounds that were prepared. The examination was carried out at the laboratories of Physics, College of Basic Education - Babylon University . Wavelength: 1.5405 Ǻ; Voltage: 40 kV; Current: 30mA; Scan Type: Continuous; Source: CuK_α. Figure (2) illustration XRD diffractometer.

dye	Molecular Formal	M_w (g/mol)	Color	Melting Point (°C)
Compound(S)	$C_{39}H_{44}N_6O_6$	920	Black	129

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Characteristic of the crystal structure using x-ray diffraction (XRD) of the Aurintricarboxylic Acid compound (s) , distance between planers(d), Full Width, at Half Maximum, (FWHM), and crystalline size (G)are shown in Tables (2).

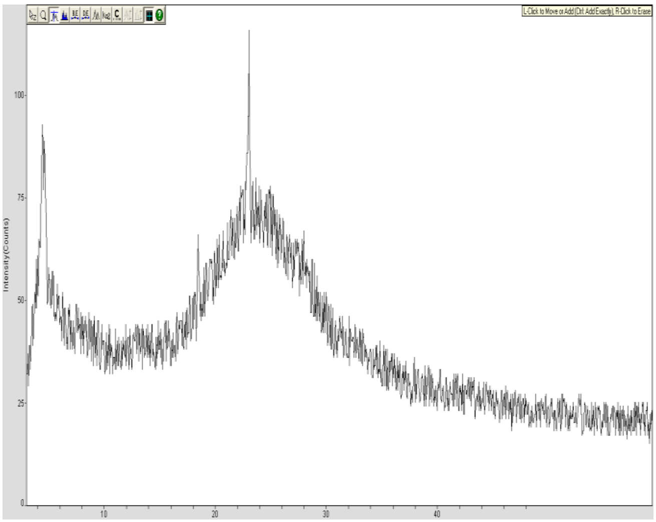
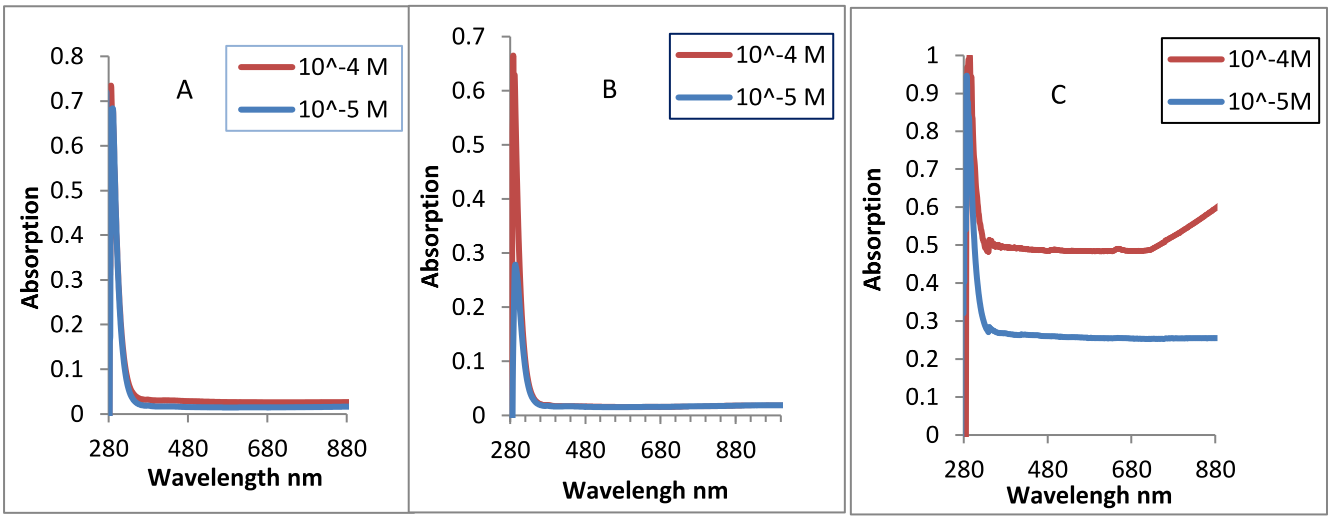


Figure (2) : XRD spectrum of compound (S).

Table (3) show optical properties linear absorption coefficient(α_0) ,linear refractive index(n_0), lifetime fluoresce(τ_f), lifetime radiative (τ_{fm}) for different type of thin film of compound (s) pure dye , dye with polymer ,dye with polymer and nanoparticle with concertation(10^{-4}and10^{-5})M for each type ,the result show decrease of lifetime radiative (τ_{fm}) with increase the value of refractive index(n_0) when we add polymer and nanoparticle to the material.

Figure (3) show the absorption spectra for compound (S) pure , compound (S) with PMMA and compound (S) with PMMA plus nanoparticle TiO_2 with different concentration(10^{-4}and10^{-5})M was compared ,the figure show that spectra have one band, in uv region which is called B-band, we can observed that absorption spectrum and the fluorescence spectrum shifted to shorts wavelength with increasing the concentration this shift obtain because increasing the number of molecules per volume unit .

influencing the detection of imperfections in software items versus other industrial items are appeared in the accompanying table.



Figure(3): The absorption spectrum of compound (S),A:Compound (S) pure, B: Compound (S) +PMMA, C: Compound (S) +PMMA+Nano

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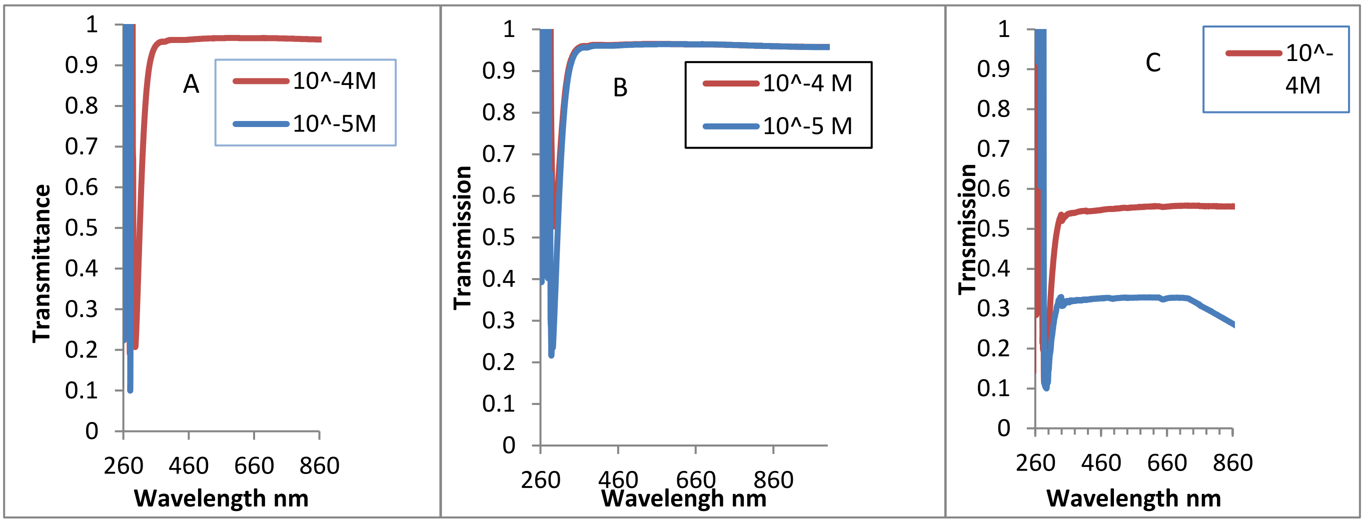
Material	C mole/litter	α_0 cm^{-1}	n_0	τ_f ns	τ_{fm} ns
Compound (s) pure	10^{-4}	0.068	1.454	24	50
	10^{-5}	0.055	1.148	25	44
Compound (s) +PMMA	10^{-4}	0.008	1.151	2.612	5.712
	10^{-5}	0.007	1.131	3.823	3.912
Compound (s) +PMMA+TiO2	10^{-4}	0.487	1.756	5.411	9.435
	10^{-5}	0.345	1.321	5.523	9.345



Figure(4): The transmission spectrum of compound (S),A:Compound (S) pure, B: Compound (S) +PMMA, C: Compound (S) +PMMA+Nano

Figure (5) show fluorescence and emission spectrum has more importance to give information about the optical energy band gap excitons and energy level .As it happened in the absorption spectra , at high concertation fluorescence intensity reach a limiting value ,several factors related to the phenomenon of re-absorption and re-emission, with increasing dye concentration the formation of dimmer and aggregates decrease the fluorescence emission.

Table (4) appear the change in the wavelength of absorption and fluorescence to obtain stock shift (nm) , we can note the quantum efficiency increase when add polymer and TiO_2 nanoparticle because when we add polymer or nanoparticle the thickness of thin film will increase and that led to make molecular of (DMSO) system to move freely in the new host material but thin film with less volume restricted molecular moving and led to consist dimmers and aggregation which have perfect properties.

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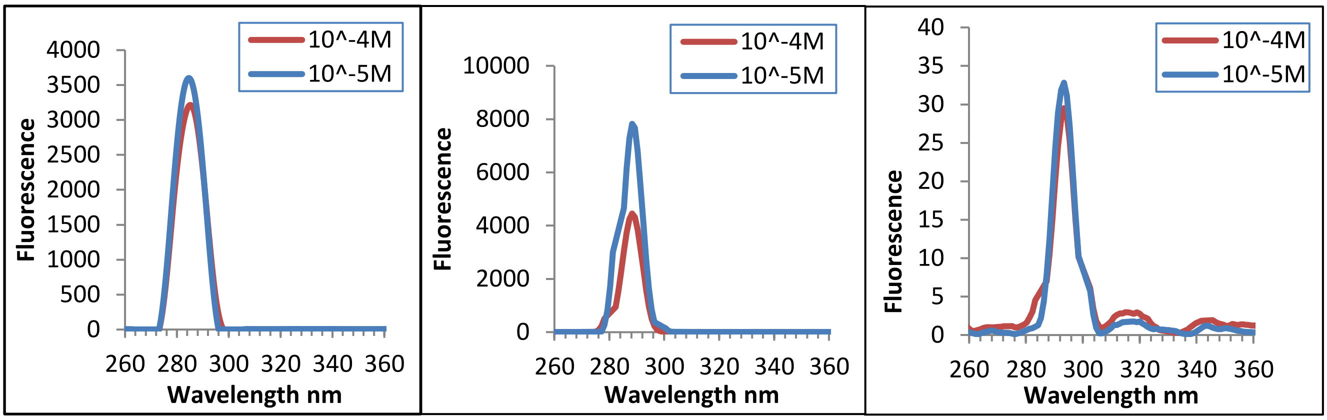

Figure(5): The flouresoence spectrum of compound (S),A:Compound (S) pure, B: Compound (S) +PMMA, C: Compound (S) +PMMA+Nano

Material	C mole/litter	λabsλ (nm)	λfluo (nm)	Stock Shift (nm)	Quantum Efficiency qfm
Compound (s) pure	**10^{-4}**	**274**	**285**	**11**	**53%**
	10^{-5}	**275**	**283**	**8**	**56%**
Compound (s) +PMMA	**10^{-4}**	**287**	**288**	**1**	**45%**
	10^{-5}	**263**	**287**	**24**	**98%**
Compound (s) +PMMA+Nano	**10^{-4}**	**292**	**294**	**2**	**57%**

VII:CONCLUSION

In this experimental work, we have investigated the effects of dye concentration on the optical properties of pure dye ,dye doped PMMA, and dye with PMMA pulse TiO_2 prepare as thin films. Using transmittance and absorption spectrum, linear absorption coefficient(α_0) ,linear refractive index(n_0), lifetime fluoresce(Ʈ$_f$), lifetime radiative

(Ʈ$_{fm}$) led to enhance the optical properties of PMMA and TiO_2 nanoparticle by increase refractive index with quantum yield and reduce lifetime radiative according to increase thickness of thin film by adding host material to give the molecular of dye more space moving to get films consider a promised materials as active laser media as well as we can use this material in photo device .

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