Refractive index and Urbach tail of 2,7dichlorofluorecsien(DCF) dye

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Abstract:

2,7 Dichlorofluorecsien (DCF) dye thin films are deposited on glass substrates by spin coating. In this study the optical properties of the thin films were studied. The reflectance and transmittance spectrophotometric measurements have been done in the spectral range from 300nm to 800nm. The transmittance of the prepared thin films is 96% in the long wavelength >550nm and the reflectance is 9%. Determination of the optical constants such as refractive index(n=1.65), absorption coefficient(α),optical energy gap (Eg=2.18eV) ,Urbach tail(ΔE_t=0.135eV) and dielectric constant in real and imaginary parts(ε_1,ε_2) in this wavelength range has been evaluated. Optical and electrical conductivities (σ_{opt} , σ_e) of the films have been done. Further, normal dispersion of the refractive index has been analyzed in terms of single oscillator model of free carrier absorption to estimate the dispersion and oscillation energy.

Keywords: Dichlorofluorecsien dye, Optical properties, Urbach tial.

معامل الأنكسار وذيول يورباخ لصبغة 2,7 داي كلورو فلورسين (DCF)

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الخلاصة:

تم دراسة الخواص البصرية لاغشية رقيقة من صبغة 7,2داي كلورو فلورسين المحضرة بطريقة البرم على قواعد من الزجاج.تم دراسة الخصائص البصرية للاغشية المحضرة.تم قياس كل من طيفي الانعكاسية والنفاذية عند مدى الاطوال الموجية من 300nm الى 800nmحيث كانت قيمة النفاذية تصل الى 96% عند الاطوال الموجية الطويلة >500nm بينما كانت نسبة الانعكاسية 9% حسبت الثوابت البصرية مثل معامل الانكسار(n=1.65)،معامل الامتصاص(α)،فجوة الطاقة البصرية(Eg=2.18eV)،ذيول يورباخ(ΔE_t=0.135eV) وثابت العزل بجزيئيه الحقيقي والخيالي عند الاطوال الموجية المذكورة .تم حساب التوصيلية الضوئية والتوصيلية الكهربائية على التوالي. معامل الانكسار الاعتيادي وباستخدام نموذج المذبذب الاحادي لامتصاص الحاملات الحرة لحساب ثوابت طاقة التذبذب.

الكلمات المفتاحية: داي كلورو فلورسين، الخواص البصرية،ذيول يورباخ.

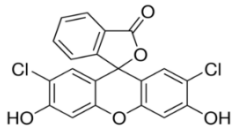
1. Introduction

DCF is an organic dye of the fluorescein family, formed by the substitution at the 2 and 7 positions of chloride. DCF is a probe that is trapped within cells and is easily oxidized to fluorescent dichlorofluorescein. This method measures the ability of compounds to prevent the formation of DCF by 2,2'-Azobis (2-amidinopropane) dihydrochloride (ABAP) - generated peroxyl radicals in human hepatocarcinoma HepG2 cells [1] .The optical absorption ,particularly ,studying the shape and shift of the absorption edge, is a very useful technique for understanding the basic mechanism of light-induced transitions in crystalline and non-crystalline materials ,as well as providing information about the band structure[2].Dyes have poor mechanical properties for example at the unstable high temperature ,since these dyes are needed any electronic device, percentages of them should be taken when preparing thin films. So one of the methods that benefit from dyes advantages is additive of dyes to polymers [3], because polymers have many appropriate characteristics such as thermal stability , good mechanical properties (strain ,stress and flexibility) and can prepare it as with any desirable shape and size[4]. In the present work we studied the optical constants of DCF by adding amount of dye to poly vinyl pyrrolidone (PVP) to enhance the adhesive to prepare thin film. Many optical constants are calculated such as energy gap, refractive index, extinction coefficient , real and imaginary parts of dielectric constant ,optical and electrical conductivity and by using the Wemple - DiDomenico (WD) single oscillator model we were calculated the dispersion parameters.

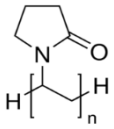
2. Experimental Work

Preparation of thin films

Thin film of DCF is prepared by dissolving 0.004g of DCF in 10ml of ethanol as a solvent .A 0.1g of PVP was dissolved in 5ml of ethanol .The solutions is shi;r by magnetic stirrer at room temperature for 2 hrs . Glass substrates taken was washed thoroughly with an agent solution . Thin films are prepared using the spin-coating technique , a small amount of the organic dye solution is dropped on the substrate . The transmittance (T) and reflectance spectra(R) of this dye were measured by using a double beam spectrophotometer type schmidzu-1800 spectrophotometer at range of 300-800nm at normal incident and at room temperature. The thickness of the polymeric samples were measured by electronic external micrometer by INSIZE Co.,LTD.



2,7Dichlorofluorscie n dye



Polyvinylpyrrolidone (PVP)

d

3. Result and Discussion:

1- Optical measurements

Figure(1) shows the transmittance and reflectance spectra of DCF thin films. The figure demonstrates that the film has a high transparency in wavelength >550nm , while the maximum value of reflectance R up to 9%.

The optical absorption coefficient (α) is calculated from transmission data as follows [5].

$$\alpha = \frac{1}{d}\ln\frac{1}{T} \text{ ----------(1)}$$

where T and d are the transmittance and thickness of DCF samples respectively.

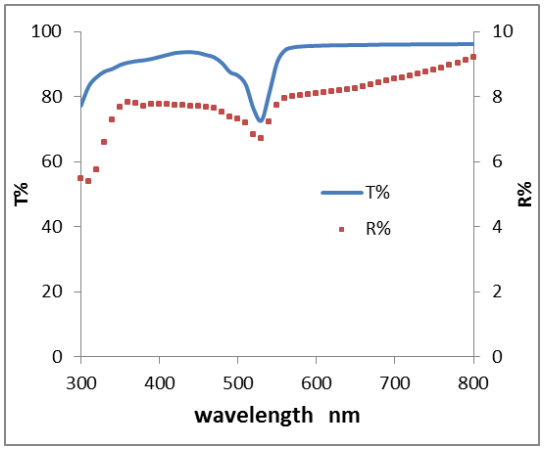


Fig. 1 : The relationship between transmittance and reflectance spectra of DCF dye films.

The thickness of films are kept within 1μm range .The extinction coefficient k is calculated from the values of α and λ by using the following formula:

$$k = \frac{\alpha\lambda}{4\pi} \text{ ----------(2)}$$

Where λ is the wavelength . Figure (2) shows both the excitation coefficient k and refractive index n on the wavelength of DCF films, The n value are estimated using the following equation [6]:

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - K^2} \qquad (3)$$

The extinction coefficient k measured as a wavelength in the range of 300-800nm ,from figures(2) k is increased with increasing in the wavelength ,while the refractive index n is decreases slightly.

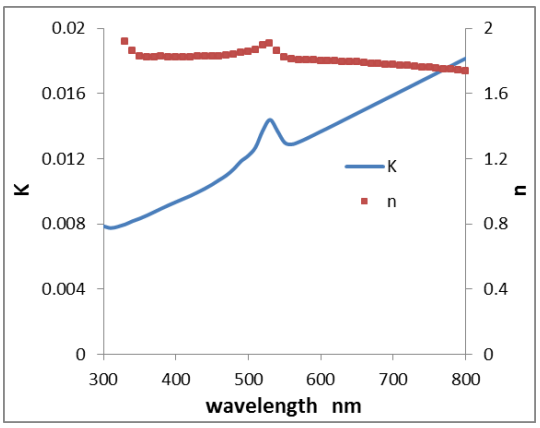


Fig. 2 : The relationship between k , n and wavelength of DCF dye films.

2-Calculation of optical energy gap

The absorption spectrum at the high energy region > 2 eV .Figure (3) is related to the π-π* transition conjugated system[7].

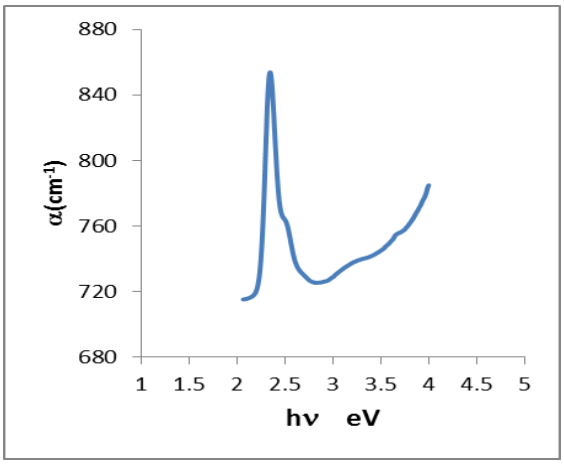


Fig. 3 : The relationship between α and hν of DCF dye films.

According to Tauc's relation ,the photon energy dependence of the absorption coefficient can be described by[8,9]:

$$\alpha h\upsilon = \alpha_o (h\upsilon - E_g)^r \qquad (4)$$

Where α_o is a parameter that depends on the transition probability ,E_g is the optical energy gap,E_p is the phonon energy

where (+) represents absorbance (-) represents emission. r is an index which

can be assumed to have values of 1/2,3/2,

2 and 3 depending on the nature of the electronic transition. r = 1/2 for allowed direct transition ,3/2 for forbidden direct transition and r = 3 for forbidden indirect transition ,and r =2 refers to indirect allowed transition. The Absorption coefficient for the direct transition takes the values of $\alpha \geq 10^4 cm^{-1}$, while the absorption coefficient for indirect transition takes the values of $\alpha \leq 10^4 cm^{-1}$ [10]. Figure (4)shows$(\alpha h\nu)^{1/2}$ versus hν of DCF thin film.

The intercept of the straight lines with the photon energy axis yield the value of the optical band gap. The value of the indirect allowed optical energy gap is about 2.18eV .On the other hand , the optical transitions due to photons of energy hν<Eg , related to the presence of localized tail states in the forbidden gap.

The width of this tail is called,Urbach tail which is an indicator of the defect levels in the forbidden band gap.

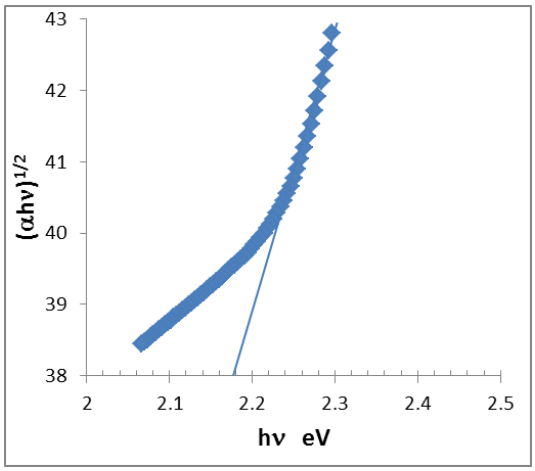


Fig. 4: The relationship between $(\alpha h\nu)^{1/2}$ and hν of DCF dye films.

The width of Urbach tail is calculated by the following equation [11]:

$$\alpha(\nu) = \alpha_o e^{\frac{h\nu}{\Delta Et}} \qquad (5)$$

Where α_o is a constant and ΔE_t is the Urbach energy , it can be evaluated as the width of the localized states .The value of ΔE_t is estimated from Figure(5) , by plotting lnα versus the photon energy and taking the reciprocals of the slope of the linear portion in the lower photon energy of the curve .The value of Urbach energy are 0.135meV.

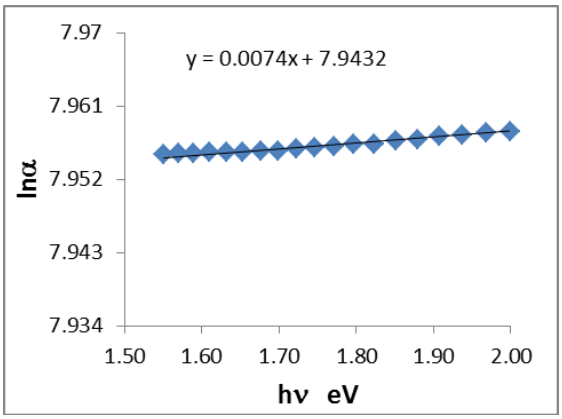


Fig. 5: The relationship between lnα and hν of DCF dye films.

$$\varepsilon_1 = n^2 - k^2 \qquad (6)$$

$$\varepsilon_2 = 2nk \qquad (7)$$

Figure(6) shows the relationship between the real (ε_1) , the imaginary (ε_2) parts and the photon energy. It is clear that the value of ε_1 is large due to the polar groups in dye refers to Cl atom , while ε_2 is decrease with increase in photon energy.

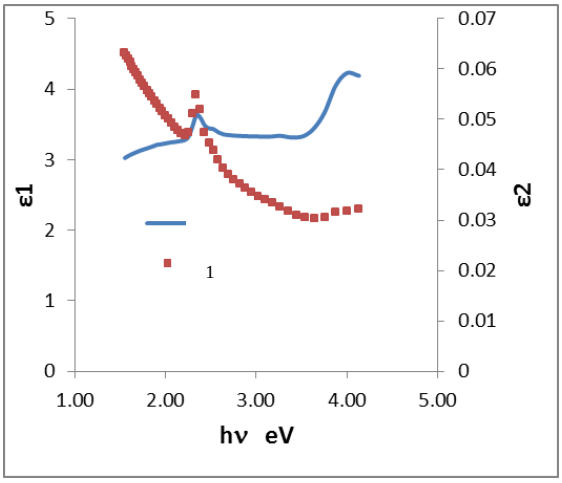


Fig. 6: The relationship between ε_1 , ε_2 and hν of DCF dye films.

The optical and the electrical conductivities of a material are given by the following relation respectively [13]

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \qquad (8)$$

$$\sigma_e = \frac{2\lambda\sigma_{opt}}{\alpha} \qquad (9)$$

where c is the speed of light .

Figure (7) show the relationship between the optical conductivity σ_{opt} ,the electrical conductivity σ_e and the photon energy . The optical conductivity $\sigma_{Opt.}$ increases with increasing the photon energy and at the high photon energy > 2eV increment is an analogue to the α spectrum while electrical conductivity σ_e decrease with photon energy .The refractive index, *n* is obtained according to the single effective oscillator equation used by Wemple and DiDomenico [14].According to this model, the only contribution to the dispersion of dielectric constant is due to interband transition and assumed that each electron behaves as an oscillator so:

$$n^2 - 1 = \frac{E_o E_d}{(E_o^2 - E^2)} \qquad (10)$$

where the dispersion energy E_d is the interband optical transition and can be considered as a parameter that relate the charge distribution within unit cell and the chemical bonding . E_o is usually considered as an " average" energy gap (E_g^{WDD}) and is empirically related to the lowest direct Tuac energy gap (E_g^T) . Accordingly one can develop some relationships between the dispersion parameters:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \qquad (11)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \qquad (12)$$

Where M_{-1} , M_{-3} are the moment of the optical spectra . Figure(8) shows the relationship between $(n^2\text{-}1)^{-1}$ and the photon energy $(h\nu)^2$ which yield the straight line for normal behavior. The slope $(E_o E_d)^{-1}$ and the intercept with the vertical axis is equal to (E_o/E_d).The value of E_o , E_d , n(o) , ε(o) , M_{-1} and M_{-3} were presented in table (1)

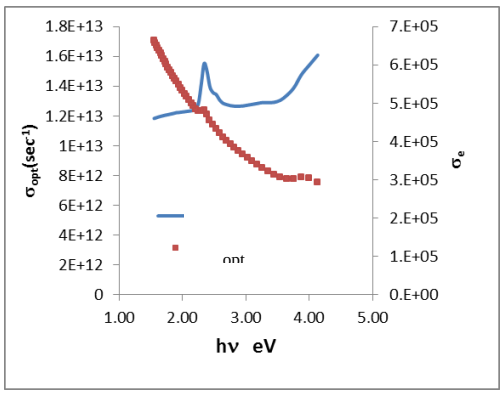


Fig.7:The relationship between σ_{opt},σ_e and hν of DCF dye films.

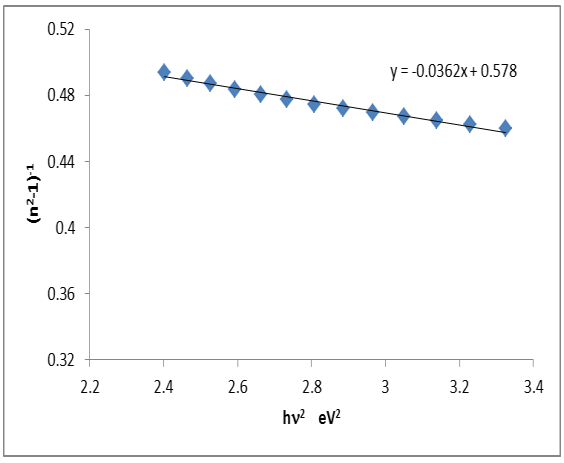


Fig. 8 : The relationship between $(n^2\text{-}1)^{-1}$ and $(h\nu)^2$ of DCF dye films.

The nonlinear optical properties provide several means to control light with light change the frequency of light , amplify one source of light . According to Frumer [15],the Miller rule is very convenient for visible ,nonlinear and near

infrared frequencies, which are related for the third order of nonlinear polarizability parameter $\chi^{(3)}$ as shown in figure 9, the so-called nonlinear optical susceptibility, and the linear optical susceptibility, $\chi^{(1)}$ are related through the following equation:

$$\chi^{(3)} = A(\chi^{(1)})^4 = A[E_o E_d / 4\pi(E_o^2 - (h\nu)^2]^4 = A/(4\pi)^4 (n^2-1)^4 \quad (13)$$

where A is equal to 1.7×10^{-10}.

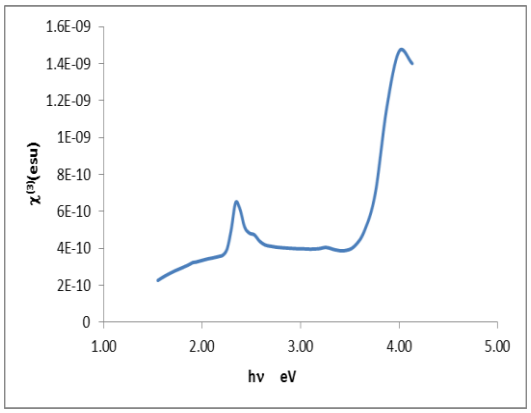


Fig. 9 : The relationship between $\chi^{(3)}$ and hν of DCF dye films

Table 1 : Optical parameters of DCF dye thin films

Parameters	Value
$E_g^{Opt}(eV)$	2.18
$\Delta E_t\ (meV)$	0.135
$E_\circ(eV)$	3.99
$E_d(eV)$	6.91
$M_{-1}(eV)^2$	1.73
$M_{-3}(eV)^2$	0.10
$n_\circ$	1.65
$\varepsilon_\circ$	2.73
$\chi^3(0)(esu)$	$6.01\text{x}10^{-14}$

4. Conclusions

2,7Dichlorofluoresien thin films have been deposited on glass substrate by the spin coating . The DCF thin films . The indirect optical band gap of the films were found about 2.18eV.The values of M_{-1} and M_{-3} are high which indicates that the studied sample have high polarization. Simple semiempirical relation based on generalized Miller´s rule allows an estimation of nonlinear susceptibility (χ^3) or from the dispersion energy and the energy of effective oscillator of the Wemple-DiDomenico model.

The conductivity $\sigma_{Opt.}$ and electrical conductivity σe were increased with increasing photon energy that related to electronic transitions.

5. Reference

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