

Synthesis, characterization, and Optical properties of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) thin films prepared by spin-coating method

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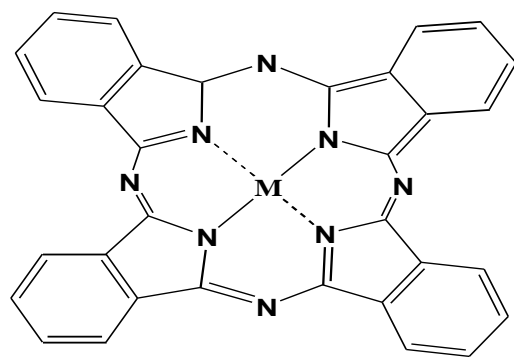
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ABSTRACT: In the present work a thin film of new 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) (300–900 nm) have been prepared by spin-coating technique and studied the optical properties. The optical properties and optical constants have been investigated means of transmittance and reflectance spectra were measured in the wavelength range (300-900) nm. The optical energy gap E_g was estimated from the absorption coefficient values using Tauc's procedure. The optical absorption spectra shows that the absorption mechanism is a direct allowed transition. The oscillator energy E_o , dispersion energy E_d and other parameters have been determined by the Wemple–DiDomenico method.

Keywords: Optical properties, phthalocyanine copper (II), Refractive index, optical energy gap.

INTRODUCTION

In recent years, studies on optical properties of polymers with different optical properties have attracted much attention due to their applications in optical devices [1]. Phthalocyanines (Pcs.) and their analogues have been investigated in detail for many years, especially with regard to their properties as dyes, pigments and colours. In the last 20 years phthalocyanine chemistry is undergoing a renaissance because phthalocyanines and many of their derivatives exhibit singular and unconventional physical properties interesting for applications in materials science. Thus in addition to basic research the interest in phthalocyanines has been recently expanded into applied fields such as photovoltaic, electrochromism, optical data storage, laser dyes, liquid crystals chemical sensors and photosensitizers for photodynamic therapy [2,3].



Metallophthalocyanine

EXPERIMENT

Material

Phthalic anhydride, Sulphuric acid, nitric acid, acetic anhydride, ammonium molybdate tetrahydride, HCl, NaOH, sodium polysulphide and Thionylchloride were purchased from Aldrich chemical company.

Synthesis

Preparation of nitro phthalic acid [4].

3- nitrophthalic acids were prepared by nitration of phthalic anhydride as following:-

Phthalic anhydride (50g, 5 mole) was dissolved in 50ml of conc. Sulphuric acid at 75°C, then 21 ml of fuming nitric acid was added with vigorous stirring at 90°C. 15 ml of sulphuric acid was added dropwise for 1 hr, then 90 ml of nitric acid was added at 90°C with vigorous stirring for 3 hours. After cooling, the mixture was filtered to remove the excess of nitric acid and sulphuric acid. The crude product washed several times with distilled water. Pale yellow powder were obtained m.p 220°C (lit. 220 °C) yield 40%.

Preparation of nitro phthalic anhydrided [5]

3- nitro phthalic acid (0.1 mole) was added to acetic anhydride (20 g , 0.19 mole) and the mixture was refluxed for 1 hour . After cooling, the mixture was filtered and the solid product washed several times with absolute ethanol yield 90%.

Preparation of complex: copper (II) phthalocyanine[5]

CuCl₂ (0.504 gm , 8 mmole) , 3-nitrophthalic phthalic anhydride (4.73 g , 32 mmole) , ammonium molybdate tetrahydride (0.2 g) m ammonium chloride (0.5 g , 9 mmole)

and excess of urea (30g , 0.5 mole) were grounded and placed in 250 ml round bottom flask containing 100 ml of nitrobenzene. The temperature of the stirred reaction mixture was increased gradually to 185°C and maintained it for 5 hours. The hot mixture was filtered and the precipitate washed with ethanol repeatedly to remove the nitrobenzene. The solid product was dried and added to 200 ml of 1 N HCl and then refluxed for 1 hour, cooled to room temperature and filtered. The solid precipitate added to 200 ml of 1 N NaOH and reflux the solution for 1 hour, filtered and washing with distilled water to obtain brown crystals of copper (II) phthalocyanine yield 85%.

Preparation of complex: copper (II) – 3,3',3'',3'''-tetraaminophthalocyanine[6]

To a suspension of complex (10 mmole) in 45 ml of water added to (9.6 g, 40 mmole) of sodium polysulphide in 25 ml of distilled water in 20°C. The mixture was stirred at 20°C with vigorous stirring for 24 hrs. After cooling, the mixture was added to 50 ml of 1N HCl and stirred for 30 min. Then the solid precipitate was collected by centrifuge. The collected precipitated was added to 50ml of 1 N NaOH and stirred for 30 min. The result solid was collected by centrifuge and washing with distilled water. Blue solid of

copper (II) – 3,3',3'',3'''-tetraaminophthalocyanine was obtained yield 87% .

Preparation of poly (1, 4-diaminobenzen phthalate) [7]

Thionylchloride (8 mmole) in 50 ml of chloroforme added to 1,4-phenylenediamine (4 mmole) in (50 ml) chloroforme and conc. HCl (0.2 ml) dropwies in 250 ml round bottom flask. The temperature of the stirred reaction mixture was (-5°C). The mixture was filtered and the precipitate washed with ethanol. The solid product was dried, to obtain white crystals of poly (1, 4-diaminobenzen phthalate) yield 85%.

Preparation of copper (II) – 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine[8]

To a suspension of poly (1, 4-diaminobenzen phthalate) (10 mmole) in 25 ml of chloroforme added to (2 mmole) of copper (II) – 3,3',3'',3'''-tetraaminophthalocyanine in 25 ml of chloroforme in 25°C . The mixture was stirred at 25°C with vigorous stirring for 5 hours. Then the solid precipitate was collected by centrifuge and washing with chloroforme. Blue solid of copper (II) – 3,3',3'',3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine was obtained yield 87% .

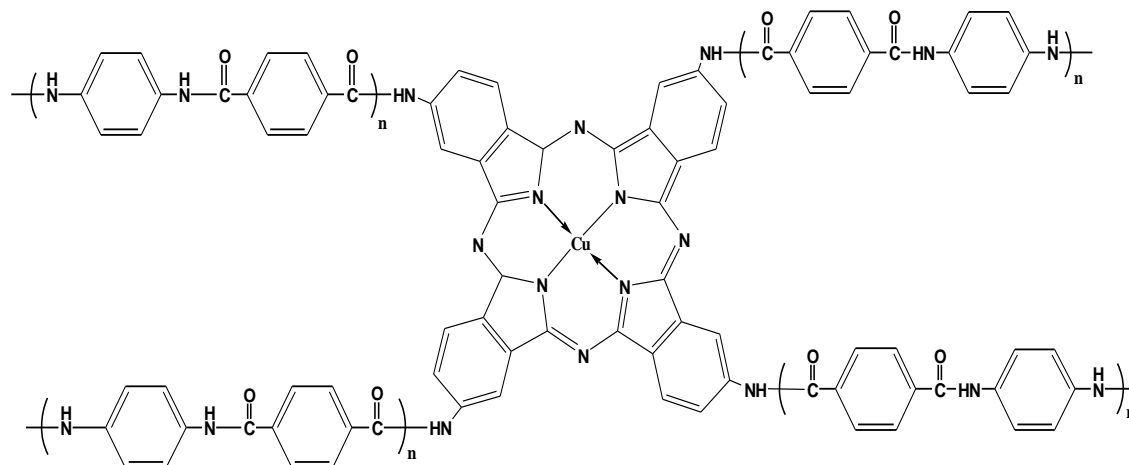


Figure (1) Show the chemical structure of copper (II)- of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine[2] .

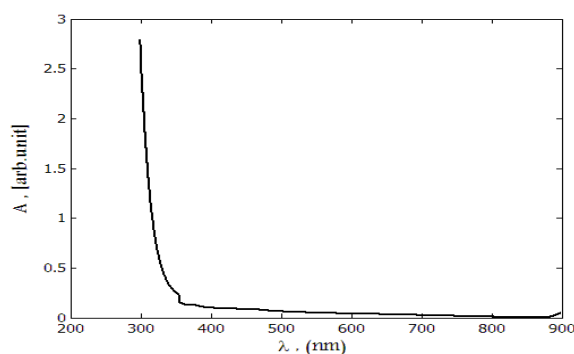


Figure (1) Absorbance as a function of wavelength for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

Measurement

The measurements of absorbance and transmittance spectra of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) thin film in the wavelength range (300-900) nm were carried out using UV-VIS Recording Spectrophotometer (UV-CE7200-Aquarius). The optical absorption (A) and reflectance spectra(R) were analyzed to determine the optical constants such as refractive index (n), extinction coefficient (k), and absorption coefficient (α).

Analysis of the absorption coefficient was also carried out to determine the optical band gap and nature of transitions. The thickness of prepared films was measured (0.7 μm).

Result and Discussion

The study of materials by means of the optical absorption provides a simple method for explaining some features concerning the band structure and energy gap. The absorption spectra of the 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) was recorded in the wavelength range of 300–900 nm and is given in Figure (2). The optical parameters related to the spectrum are given in table 1.

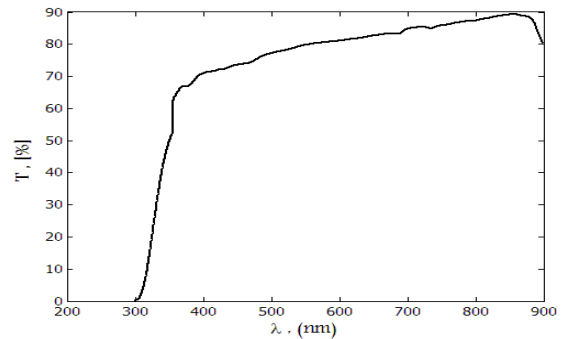


Figure (2) Optical transmittance spectra as a function of wavelength for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

Table 1: optical parameters of the 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) thin film.

$E_g^{Opt} (eV)$	$E_o (eV)$	$E_d (eV)$	E_o / E_g^{Opt}	n_o	$B (cm.eV)^{-1}$	$\alpha(0) cm^{-1}$	$\lambda_o (nm)$	ϵ_o
3.94	7.9373	12.59	2.01	1.608	1.8×10^{12}	0.0111	228.04	2.58

The absorption coefficient (α) can be calculated from observed absorbance data using Beer Lambert's formula ($\alpha = 2.303(A/d)$), where A is the optical absorbance and d is the film thickness. The extinction coefficient can be obtained from the relation ($k = \alpha\lambda/4\pi$), where λ is the wavelength of the light. The reflection can be determined by using the following relation [9]:

$$T = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \quad (1)$$

Where T is the transmittance, R the reflectance and d is the film's thickness. Fig. (2) Shows the variation of absorption coefficient as a function of wavelength of the light in the rang (300-900) nm. It is clear that, the absorption coefficient (α) decrease as the wavelength increases. This is due to an increase Permeability class in the range of wavelength. Figures (3&4) show the dependence of the optical transmission and reflection, on wavelength respectively. The data from transmission and reflection spectrum are used to calculate absorption coefficient by using equation (1).

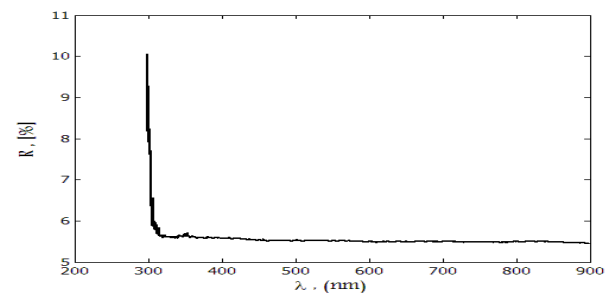


Figure (3) Optical reflectance spectra of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

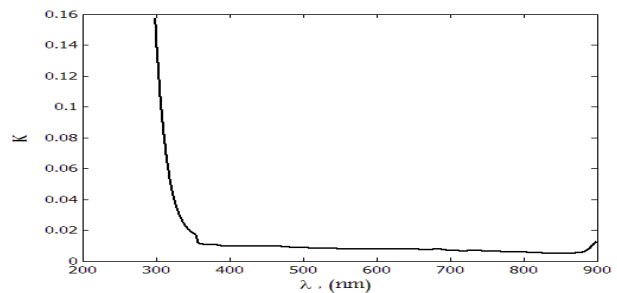


Figure (4) Extinction coefficient (k) as a function of wavelength for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

The extinction coefficient represents the amount of attenuation of an electromagnetic wave that is traveling in material, where it values depends on the density of free electrons in the material and also on the structure nature. The values of extinction coefficient are directly related to the absorption of light. It can be noticed that there is a decrease of extinction coefficient with increasing wave length. Figure(5) shows the extinction coefficient (k) for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) thin films as a function of wavelength in the rang (300-900) nm [10].

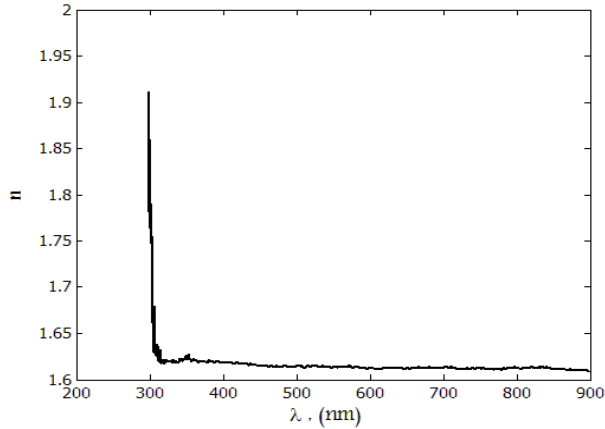


Figure (5) The variation of the refractive index (n) vs. photon energy for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

The refractive index (n) of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) thin film as functions of wavelength is shown in Figure (6).

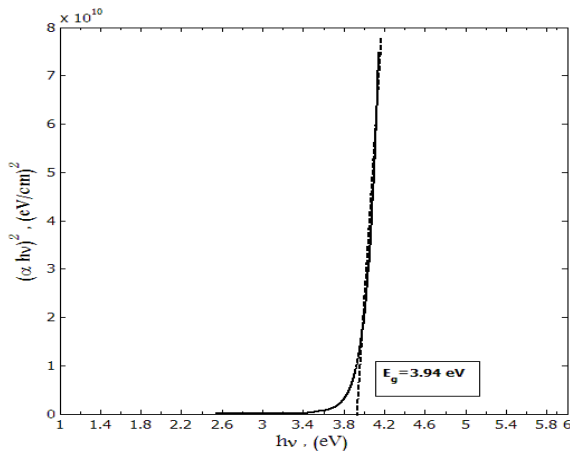


Figure (6) Plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) near the absorption edge for for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

It can be seen that refractive index decreases with the increasing of wavelength. The decrease obtained in the

value (n) is due to that some interactions take places between photons and electrons. The refractive index changes with the variation of the wavelength of the incident light beam due to these interactions, in anther word, one is the optical loss caused by absorption and scattering, which decreases the amplitudes of the transmission intensity oscillations at shorter wavelengths, in this work it can be neglected because of the highly transparent of 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) thin film. In the determination of refractive indices for the 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II) thin film, the main loss arises from the transmission measurement procedures, such as small difference of light spot sizes and apertures [11]

The relation between the absorption coefficient α , and optical band gap E_g , is given by the following relation [12].

$$\alpha = \frac{B(h\nu - E_g)^r}{h\nu} \quad (2)$$

Where B is an energy-independent constant ($h\nu$) is the photon energy and E_g is the indirect optical band gap (Tauc gap) and r determine the type of transition. The parameter r has value $(1/2)$ for direct allowed transition and 2 for indirect allowed transition [13].

The energy gap values depends in general on the film crystal structure, the arrangement and distribution of atoms in the crystal lattice, also it is affected by crystal regularity. The energy gap (E_g) value is calculated by extrapolation of the straight line of the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) as shown in figure (7).

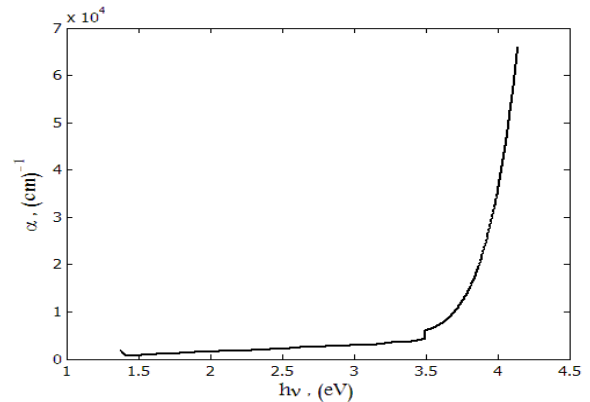


Figure (7) Variation of the absorption coefficient (α) against the photon energy ($h\nu$) for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

The optical absorption coefficient near the fundamental absorption edge is found to be exponentially dependent on the incident photon energy and obeys the empirical Urbach rule [14]

$$\alpha = \alpha_0 \exp(h\nu / E_u) \quad (3)$$

Where α_0 is constant and E_u is the Urbach energy and it can be evaluated as the width of the localized states. The variation of α vs photon energy is given in figure (7). The value of E_0 was calculated from figure (8).

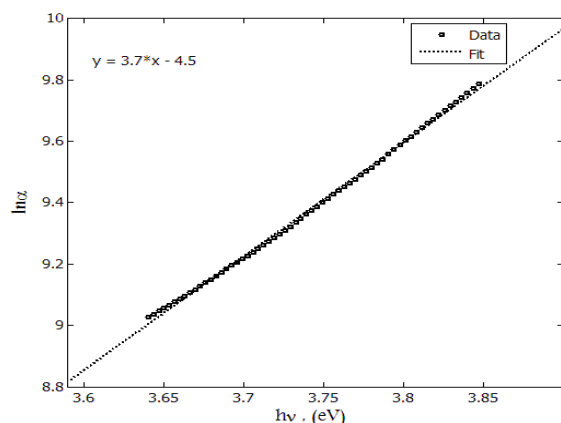


Figure (8) Variation of the $(\ln \alpha)$ against the photon energy $(h\nu)$ for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

The exponential dependence of α on photon energy for the compound indicates that it obeys Urbach's energy equation. An electronic transition between localized states in the band edge tails is valid in this compound. The exponential dependence of the optical absorption coefficient with photon energy may arise from the electronic transitions between the localized states, which tail off in the band gap [10]. Figure (9) shows the variation of the $(\ln \alpha)$ against the photon energy $(h\nu)$ for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

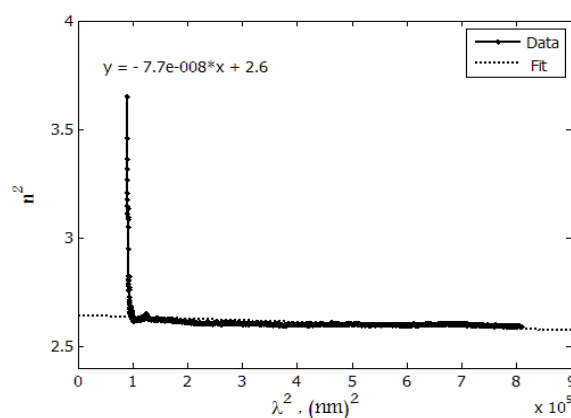


Figure (9) the plots of the variations of (n^2) vs λ^2 for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

According to the single oscillator model proposed by Wemple and DiDomenico [15-17] have analyzed refractive index data below the inter-band absorption edge using the single effective oscillator equation.

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2} \quad (4)$$

Where, n is the refractive index, E_o is the average excitation energy for electronic transitions, and E_d is the so-called dispersion energy. The latter quantity measures the average strength of the interband optical transitions.

Curving $(n^2 - 1)^{-1}$ vs $(h\nu)^2$ and (λ^{-2}) allows the determination of the oscillator parameters by fitting a straight line to the points figure (10&11).

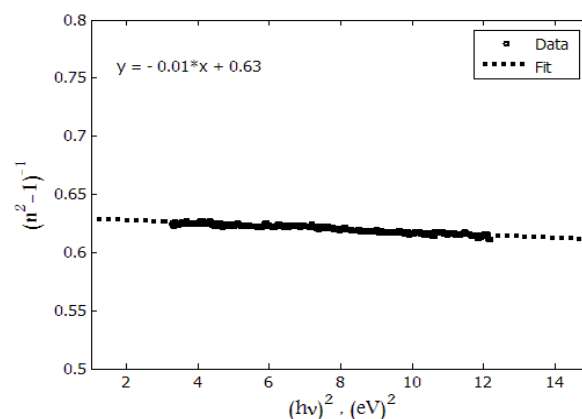


Figure (10) The plots of the variations of $(n^2 - 1)^{-1}$ vs. $(h\nu)^2$ for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

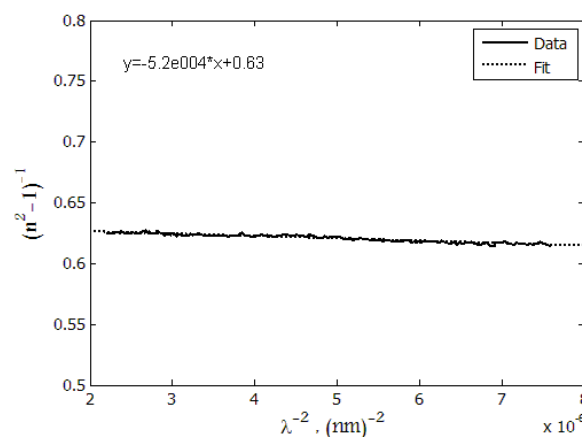


Figure (11) the plots of the variations of $(n^2 - 1)^{-1}$ vs λ^{-2} for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

The real part of the permittivity ϵ_1 and the imaginary part of the permittivity ϵ_2 can be calculated by the following relations [18,19]:

$$\epsilon_1 = n^2 - k^2 \quad (5)$$

$$\epsilon_2 = 2nk \quad (6)$$

Figures (12&13) show the relation between ϵ_1 , ϵ_2 and photon energy.

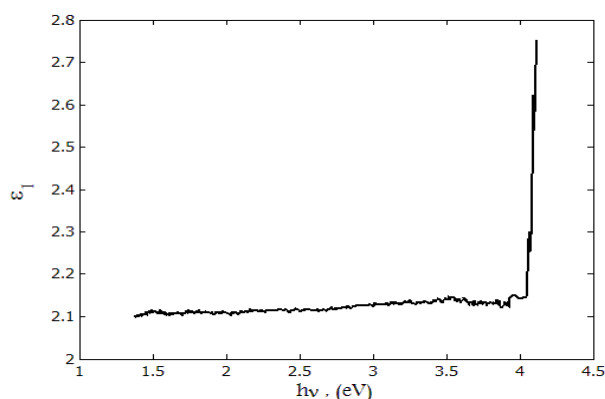


Figure (12) the plots of the variations ϵ_1 vs $h\nu$ for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

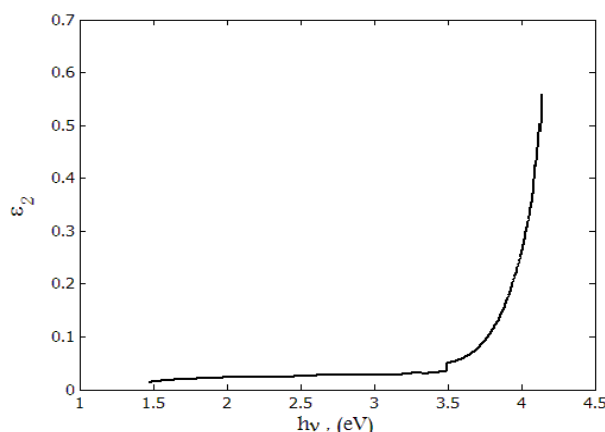


Figure (13) the plots of the variations ϵ_2 vs $h\nu$ for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

The dissipation factor ($\tan \delta$) is a measure of loss rate of power of a mechanical mode, such as an oscillation in a dissipation system. The dissipation factor ($\tan \delta$) can be calculated by this relation [20]

$$\tan \delta = \epsilon_2 / \epsilon_1 \quad (7)$$

The dielectric relaxation time τ can be calculated by using the relation [20, 21]

$$\tau = \epsilon_\infty \epsilon_1 / \omega \epsilon_2 \quad (8)$$

$$\text{As } \omega = 2\pi \frac{c}{\lambda}$$

Where, c is the speed of light.

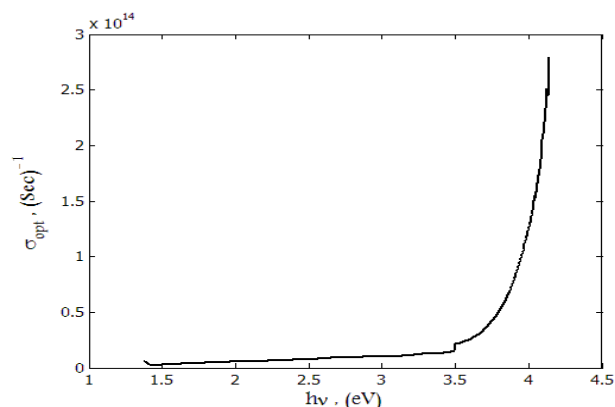


Figure (14) the plots of the variations Optical Conductivity vs $h\nu$ for 3, 3', 3'', 3'''-tetra poly (1, 4-diaminobenzen phthalate) phthalocyanine copper (II).

Figure (14) shows the variation of optical conductivity with incident photon energy. The optical conductivity is determined by using the relation [22]:

$$\sigma = \frac{\alpha mc}{4\pi} \quad (9)$$

The optical conductivity directly depends on the absorption coefficient and was found to increase sharply for higher energy values due to the large absorption coefficient for these values.

Conclusions

The dependence of the absorption coefficient (α) on photon energy ($h\nu$) was determined in the spectral range from (300–900 nm). The variation of the absorption coefficient and the optical gap are reported. The allowed direct transitions were found to be responsible for interband transitions. The optical constant as a function of incident photon energy, indicated that the refractive index, extinction coefficient, real part of permittivity, imaginary part of permittivity and the optical conductivity show their maximum values near absorption edge.

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