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The Synthesis, Characterization and the Study of Optical Properties to Blends (4-NH$_2$)$_4$ PcCu Complex with Florescence and Rhodamine-B Dyes

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1. Abstract

Four types of complexes derivatives from (4-NH$_2$)$_4$ PcCu and two types of dyes (florescence and rhodamine-B) were prepared by condensation method. The prepared complexes were diagnosed by FTIR and UV.Visible spectrophotometry. The optical properties of the prepared complexes were measured. The optical band gap E$_g$ was determined. The analysis of the optical absorption data indicates that the optical band gap E$_g$ was indirect transitions.

Key Words: Substituted phthalocyanines, Dyes phthalocyanines and photochemical phthalocyanines.

2. Introduction

Phthalocyanines (Pcs) are a common class of organic semiconductor compound which have received considerable attention from scientists because of their potential applications in a variety of fields. It was found that (Pcs) have many attractive properties: the availability of high purity due to the ease of crystallization and sublimation, extraordinary thermal and chemical stability; attractive optical properties; and a large number of available compounds [1].

Some of the most important applications of these organic molecules are in The fabrication of Photovoltaic devices [2-5] , Photo detectors [6] , organic transistors[1,7] electro photography , colour filters [8], organic electroluminescence devices [9-11]

, sensors [12, 13] , logic display devices [14] and laser dyes.

Absorption spectra display the existence of strong absorption band in the visible light range caused by the π- π^* transition s of the conjugated macro cycle of 18 π–electrons. For most metallophthalocyanines (MPcs), five transition bands, labeled as Q, B, N, L and C bands, were identified. Some MPcs may miss one or two of these bands [15].

There are two general forms of phthalocyanines, which are metal free Pc (H$_2$Pc) and various metal substituted form phthalocyanines. Metal free phthalocyanine contains two hydrogen atoms in the center of molecule where the various metallophthalocyanines occur when the hydrogen atoms are replaced by a single metal atom [16]. One of the

metallophthalocyanines is copper phthalocyanine (PcCu), which is a P–type semiconductor and has the advantage of being sufficiently stable towards chemicals and heat treatment [17].

3. Experimental
A. Chemicals:

Phthalic anhydride (99%) (Merk), urea (99.9%) (Fluka), ammonium molybdate (98%) (RDH), $CuSO_4.5H_2O$ (99.5%) (Merk), hydrochloric acid [Sp.gr. 1.191] (36.5%) (BDH), nitric acid [Sp.gr. 1.42] (98%) (BDH), sulfuric acid [Sp.gr. 1.834] (97%) (APP), diethey ether (99%) (Scharlau), ethanol (99.9%) (Scharlau), acetone (99.5%) (GCC), nitrobenzene (99%) (Scharlau), $Na_2S.9H_2O$ (38%) (Merk), florescence dye (99.9%) (Fluka) and rhodamine-B dye (99.9%) (RDH).

B. Instruments:
1. FTIR-Infrared spectrophotometer (8400s) made by (SHIMADZU) the range $(4000-400 cm^{-1})$.
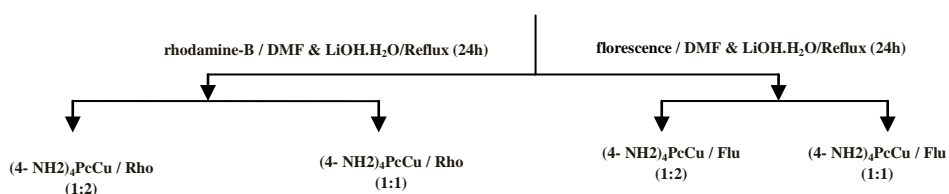2. UV-Visible spectrophotometer made (Thermo Spectronic–Heλ_{10}Sα) the range (200-900 nm).
3. Thickness Measurement (CT200-521) (Electronic Digital outside Micrometer).

C. Preparation Methods:

In this paper, we report on the effect of Rhodamine –B and Florescence on optical properties of the (PcCu) films.

In the present research the $(4-NO_2)_4$ PcCu was prepared from 4-nitrophthalic acid. The product $(4-NO_2)_4$ PcCu is reduced to $(4-NH_2)_4$ PcCu by using certain reducing agent mainly, $Na_2S.9H_2O$. The compound of $(4-NH_2)_4$ PcCu reacted with two types of dyes florescence and rhodamine-B by [1:1] and [1:2] mole ratio for $(4-NH_2)_4$ PcCu: dyes) respectively as shown in Scheme (1), [18-20].

rhodamine-B / DMF & LiOH.H$_2$O/Reflux (24h)   florescence / DMF & LiOH.H$_2$O/Reflux (24h)

(4- NH2)$_4$PcCu / Rho
(1:2)

(4- NH2)$_4$PcCu / Rho
(1:1)

(4- NH2)$_4$PcCu / Flu
(1:2)

(4- NH2)$_4$PcCu / Flu
(1:1)

Scheme 1. Preparation of the phthalocyanine complexes

The UV.Visible solution samples were prepared by dissolving the complexes in DMF solvent to obtain on concentration equal $(1\times10^{-5}M)$ and measured the absorption at (200-900nm).

The films were prepared by cast method from dissolving (0.035g) (4-NO$_2$)$_4$ PcCu and dyes in (10ml) DMF solvent with stirring at (100°C) for (1 hour), the mixture was filtrated (3 times) to obtain on homogeneous solutions .The PVC polymer solution was prepared by dissolving (1g) in (10ml) DMF solvent with stirring at (90°C) for (1 hour), after that the solutions were mixed. (0.5ml) from mixture was casted on the glass bases and dried by heat to make the film, and then the optical properties were measured.
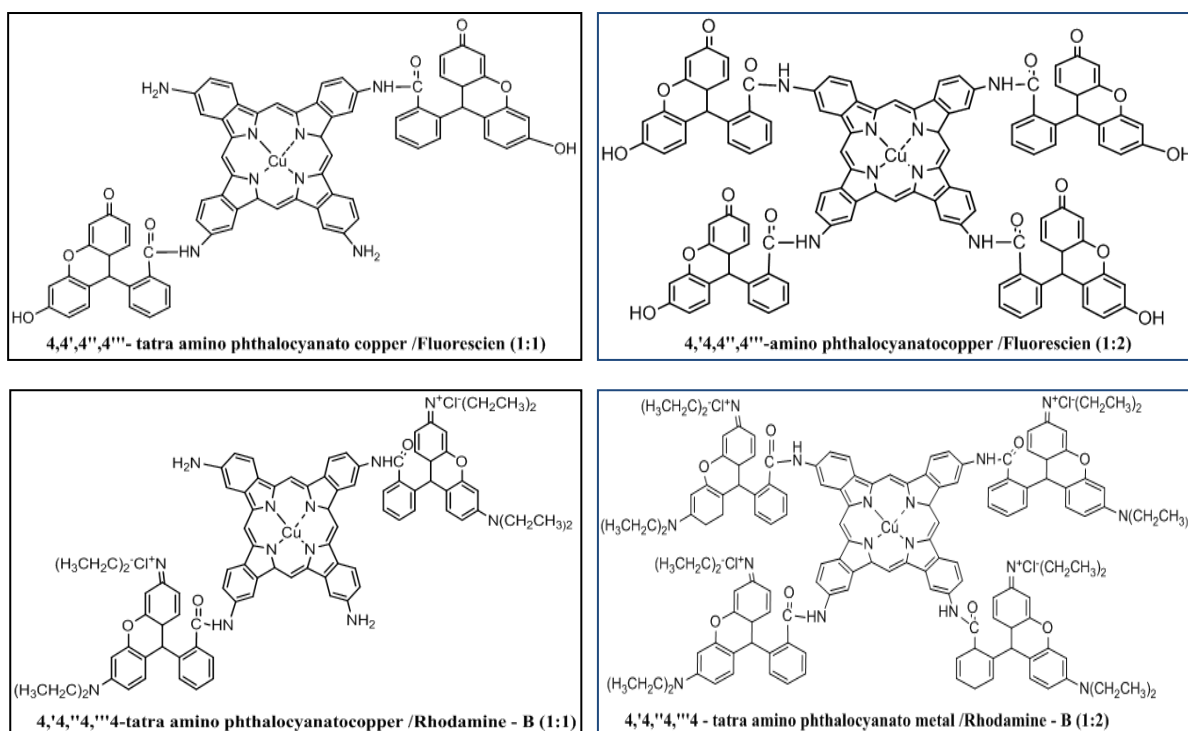
**Figure (1): Structure of phthalocyanine complexes**

4. Results and Discussion

Figure (2a) the IR-spectrum of $(4\text{-NH}_2)_4$ PcCu shows the characteristic broad N-H asymmetric stretching band at 3448cm^{-1} and symmetric stretching at 3419cm^{-1}. The bands at 1614cm^{-1} are attributed to the N-H bending vibration [21].

Figures (2b and 2d) show the IR-spectra for $(4\text{-NH}_2)_4$ PcCu/ flourescien and rhodamine–B dye in mole ratio [1:1] (Pc: dye), it shows bands at 1740 cm^{-1} and 1664 cm^{-1} which are attributed to the carbonyl stretching vibration asymmetric and symmetric respectively [22], in addition to the O-H stretching at 3460 cm^{-1} and O-H bending at 1477 cm^{-1}. The complexes showed N-H asymmetric stretching at 3448 cm^{-1} and symmetric at 3419 cm^{-1} respectively and the bending vibration at 1617cm^{-1}[21]. The bands at 1253 cm^{-1} and 1095 cm^{-1} are attributed to the C-N and C-O brands respectively [21].

Figures (2c and 2e) show similar characteristic peaks for $(4\text{-NH}_2)_4$ PcCu/ flourescien and rhodamine–B dye in mole ratio [1:2] (Pc: dye) to 1:1 mole ratio as the above complexes, but N-H group disappeared in the spectra due to the contact of the active groups in the dyes and the O-H group broad band at 3444-3550 cm^{-1} which may be attributed to stretching vibration and the bending vibration at 1479 cm^{-1}. It shows band at 3100 cm^{-1} and 3020 cm^{-1} which are attributed to asymmetric and symmetric stretching of C-H group respectively. The bands at 600-800cm^{-1} are attributed to the C-H bending vibration [21], in addition to the C-H stretching aliphatic asymmetric and symmetric at 2930cm^{-1} and 2890cm^{-1} respectively and the bending vibration at 1617cm^{-1}[14]. The bands at 1140-1000, 960-945, 830-810, 770-745, 740-720, 600-500 and 400-300cm^{-1} appeared in spectra of the studied compounds assigned to the phthalocyanine skeletal vibrations [22] as shown in Table (1).
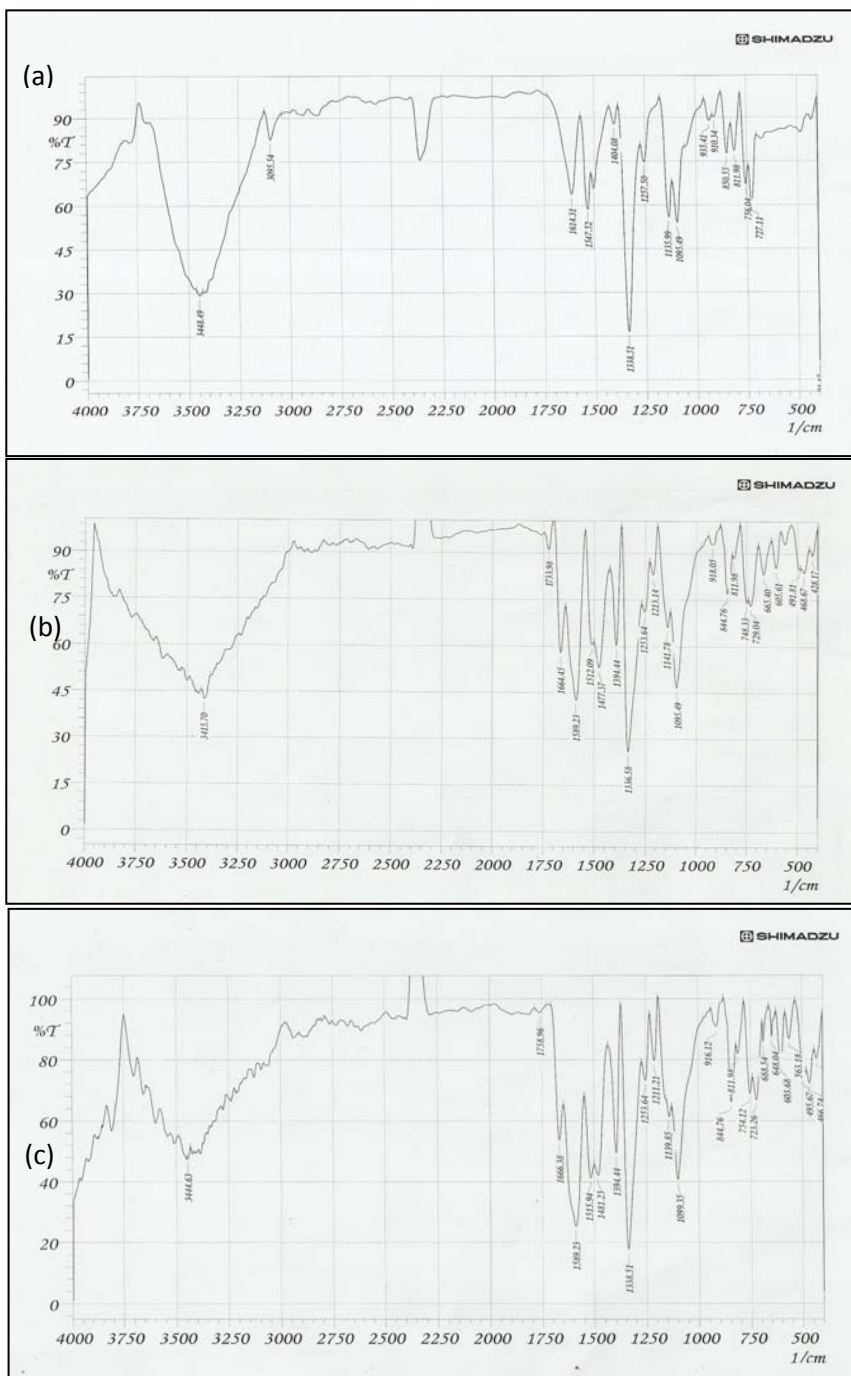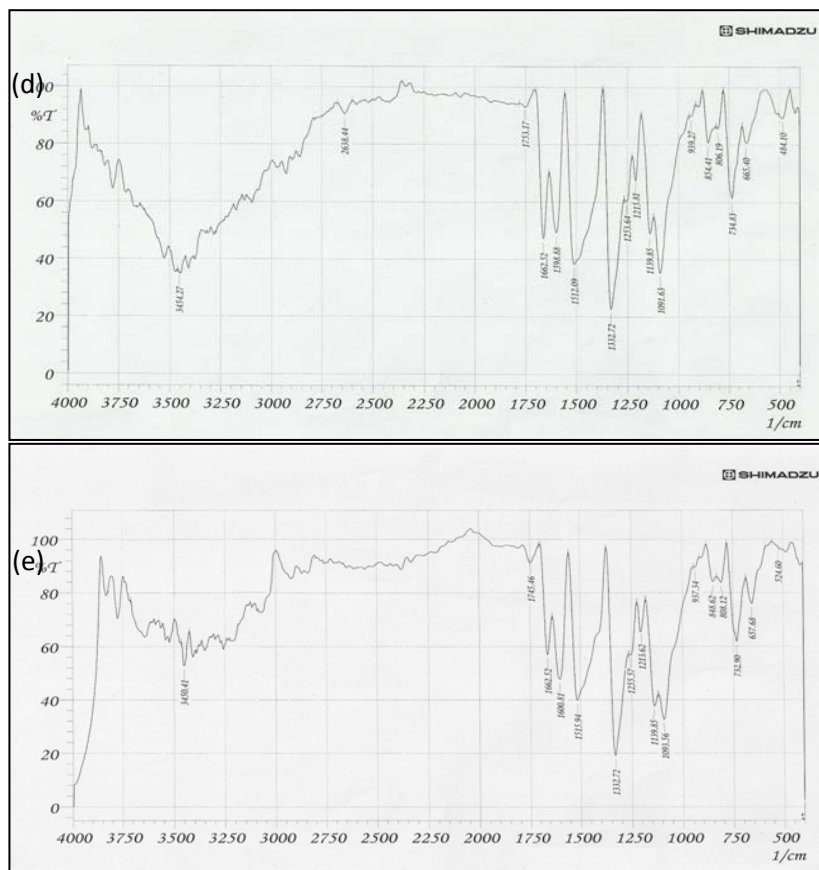
Figure (2): I.R-spectrum of a: (4-NH₂)₄ PcCu, b: (4-NH₂)₄ PcCu /Florescence (1:1), c: (4-NH₂)₄ PcCu /Florescence (1:2), d: (4-NH₂)₄ PcCu /Rodamine-B (1:1), e: (4-NH₂)₄ PcCu / Rodamine-B (1:2) as KBr disc

Table (1) The Infra-red absorption data of phthalocyanines complexes

No.	Compounds	Frequencies (cm^{-1})
1	**4, 4', 4'', 4'''-tetranitrophthalocyaniato Cupper (II)**	3095 (m) , 1612 (m) ,1525 (s) , 1404 (w) , 1338 (s) 1257 (w) , 1134 (m) , 1093 (m) , 933 (w) , 848(m) , 910 (m) , 756 (m) , 723 (m) , 487 (m) .
2	**4, 4', 4'', 4'''-tetraminophthalocyaniato Cupper (II)**	3448 (s) , 3417 (s) , 3095 (s) , 1612 (s) ,1547 (s) , 1404 (w) , 1338 (s) , 1255 (w) , 1134 (m) , 1093 (m) , 933 (w) ,910 (w) , 848(m) , 811 (m) , 756 (m) , 727 (m) , 487 (m) .
3	**4, 4', 4'', 4'''-tetraminophthalocyaniato Cupper (II) with florescence (1:1)**	3448 (s) , 3414 (s) , 3094 (s) , 1734 (w) , 1664 (s) ,1589 (s) , 1512 (m) , 1477 (m) , 1338 (s) , 1253 (w) , 1213 (w) , 1141 (w) , 1095 (s),918 (w) , 844(w) , 811 (m) , 748 (s) , 729 (m) , 665 (w) , 468 (m) .
4	**4, 4', 4'', 4'''-tetraminophthalocyaniato Cupper (II)with florescence (1:2)**	3450 (s) , 3088 (s) , 3094 (s) , 1758 (w) , 1666 (s) ,1589 (s) , 1515 (m) , 1481 (m) , 1338 (s) , 1253 (w) , 1211 (w) , 1139 (w) , 1099 (s) , 916 (w) , 844(w) , 811 (m) , 754 (s) , 723 (s) , 688 (w) , 495 (m) .
5	**4, 4', 4'', 4'''-tetraminophthalocyaniato Cupper (II) with rhodamine (1:1)**	3418 (s) , 2910 (m) , 2638 (w) , 1753 (w) , 1662 (s) ,1598 (s) , 1512 (m) , 1332 (s) , 1253 (w), 1139 (w) , 1091 (s) , 939 (w) , 854(w) , 809 (w) , 734 (s) , 665 (w) , 484(m) .
6	**4, 4', 4'', 4'''-tetraminophthalocyaniato Cupper (II) with rhodamine (1:2)**	2930 (m) , 2885 (m) , 1745 (m) , 1662 (s) ,1600 (s) , 1515 (s) , 1332 (s) , 1255 (w), 1139 (w) , 1093 (s) , 937 (w) , 848(w) , 808 (w) , 732 (s) , 657 (m) , 524 (m) .

s: strong,   m: medium,   w: weak

Figure (3a) and Table (2) shows the absorption spectra for $(4-NH_2)_4$ PcCu compound, it shows Q-band and B-band at (680 nm) and(284 nm) respectively [14]. The Q-band and B-band for $(4-NH_2)_4$ PcCu/ florescence mole ratio [1:1] (Pc: dye) at (672nm) and (280nm) respectively, are blue shifted -18 nm and -4 nm comparing with the $(4-NH_2)_4$ PcCu compound may be attributed to the presence of the two unreacted amine groups which lead to reduce the delocalization on the phthalocyanine rings. While the complex of $(4-NH_2)_4$ PcCu/ florescence mole ratio [1:2] (Pc: dye) at (668nm) and (280nm)

respectively, are blue shifted -22 nm and -4 nm compared with the$(4-NH_2)_4$ PcCu compound which may be attributed to the reaction of the amine groups with dye which leads to reduce delocalization on the phthalocyanine rings [22, 23].

Figure (3b) and Table (2) show the behavior of Q and B-bands of $(4-NH_2)_4$ PcCu / rohdamine-B mole ratio [1:1] and [1:2] (Pc: dye) complexes respectively, which have a similar general behavior to $(4-NH_2)_4$ PcCu/ florescence mole ratio [1:1] and [1:2] (Pc: Dye) which can be attributed to the same reasons as for $(4-NH_2)_4$ PcCu.

Table (2) Absorption bands of phthalocyanines complexes in DMF solvent

No.	Compounds	Q-band λ_{max}(nm)	B-band λ_{max}(nm)
1	4, 4', 4'', 4'''-tetranitrophthalocyaniato Cupper (II)	680	284
2	4, 4', 4'', 4'''-tetraminophthalocyaniato Cupper (II)	672	280
3	4, 4', 4'', 4'''-tetraminophthalocyaniato Cupper (II) with florescence (1:1)	668	280
4	4, 4', 4'', 4'''-tetraminophthalocyaniato Cupper (II)with florescence (1:2)	674	281
5	4, 4', 4'', 4'''-tetraminophthalocyaniato Cupper (II) with rhodamine (1:1)	670	273
6	4, 4', 4'', 4'''-tetraminophthalocyaniato Cupper (II) with rhodamine (1:2)	680	284

The Q-band showed two shoulder peaks with wavelengths of 605 nm and 705 nm. The two maxima peaks are separated by 100 nm as show in Figure (4a).

The intensity of the first peak of the Q-band is larger than that of the second peak.

This behavior is assigned to the first π- π^* transition on the phthalocyanine macrocycle (high energy peak). The low energy peak has been variously explained as a second π-π^* transition [24].
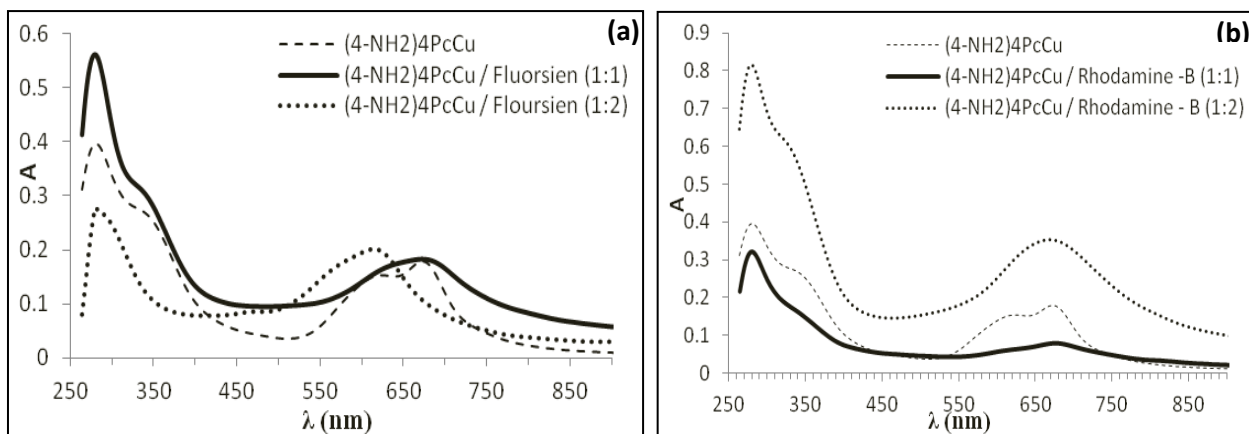
Figure (3) : U.V – visible absorption spectra for 1*10⁻⁵ M of (a) (4- NH₂)4 PcCu, (4- NH₂)4 PcCu /Florescence 1:1) (4-NH₂)4 PcCu /Florescence (1:2) PcCu , (b) (4- NH₂)4 PcCu, (4- NH₂)4 PcCu/ Rohadmine-B (1:1) and (4- NH₂)4 PcCu / Rohaamine-B (1:2) solution in DMF Solvent
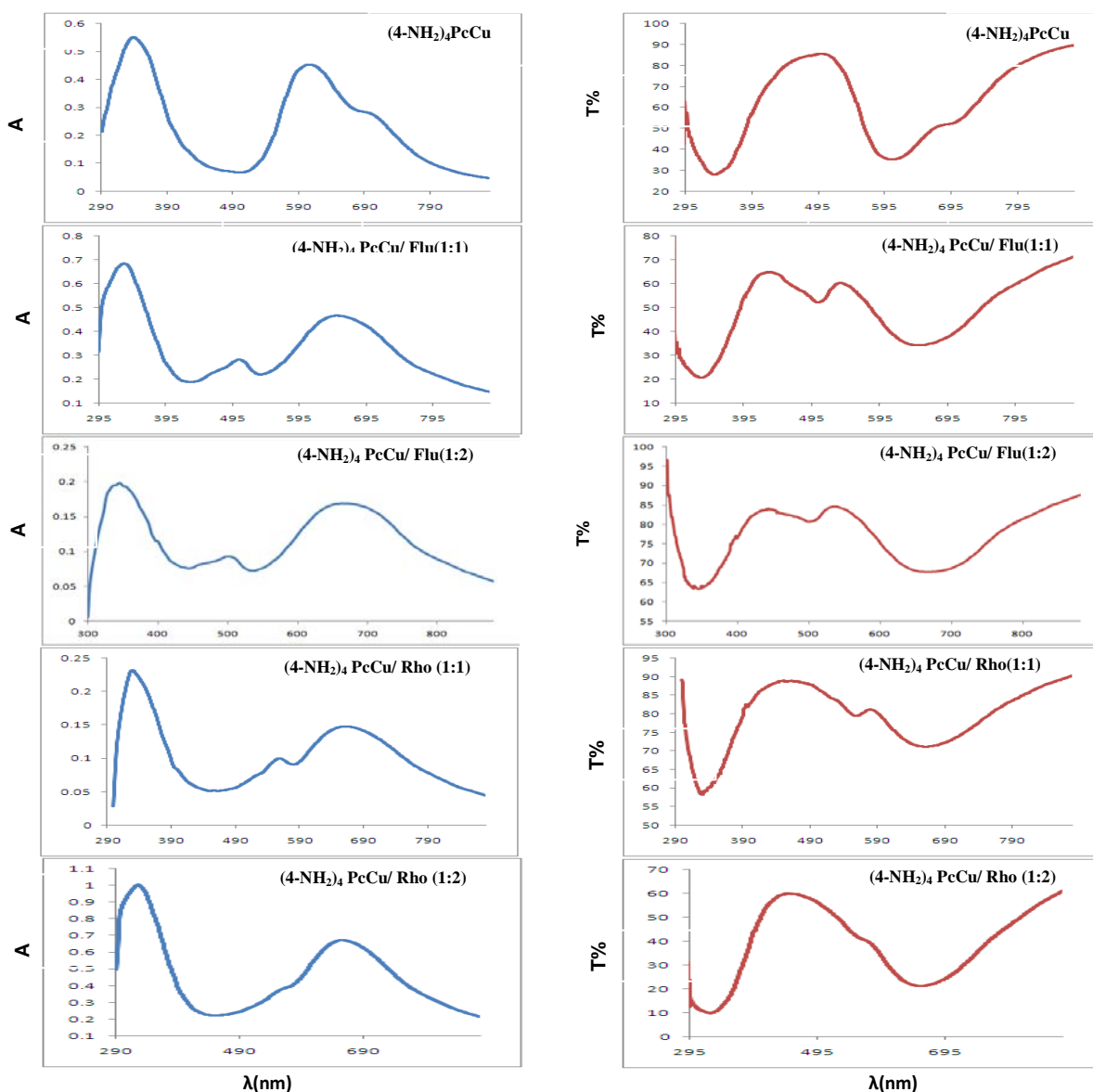

Figure (4): U.V–Visible absorption spectra of (a) (4- NH₂)₄ PcCu, (b) 4- NH₂)₄ PcCu /Florescence (1:1) , (c) (4- NH₂)₄ PcCu /Florescence (1:2) PcCu, (d) (4- NH₂)₄ PcCu / Rohadmine-B (1:1) and   (e) (4- NH₂)₄ PcCu / Rohaamine-B (1:2) thin films

The one electron theory of Bardeen [25] was applied to obtain the information about direct or inter – band transitions, this theory has been used to analyze the absorption edge data of molecular solids such as phthalocyanine derivatives [26]. The absorption coefficient (α) is related to the photon energy hυ by the equation:

$$\alpha h\upsilon = \alpha_\circ (h\upsilon - E_g)^n \ \dots \ (1)$$

E_g is the optical band gap, $\alpha_\circ$ and n are constant. The values of n are 1/2, 2, 3/2, 1/3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively, depending on the nature of the band to band electronic transition and profile of the electron density in the valance and conduction bands.

The parameter (α) can be calculated from the optical transmittance spectra (T) using the relation[27]

$$\alpha = (1/d) \ \ln(1/T)$$

where d is the thickness of the prepared films which are about (20 μm).

In the case of indirect transition, n take the value 2. The value of the optical energy gap E_g is obtained plotting $(\alpha h\upsilon)^{1/2}$ Vs hυ in the high absorption range followed by extrapolating the linear region of the plot $(\alpha h\upsilon)^{1/2} = 0$. This extrapolated value is used to define the so called optical gap. The energies gaps for the samples are given in Figure (5) and Table (3). Our results showed that the optical band gaps E_g dependent only on the addition of the florescence dye which gives a good results compared with the others complex films.
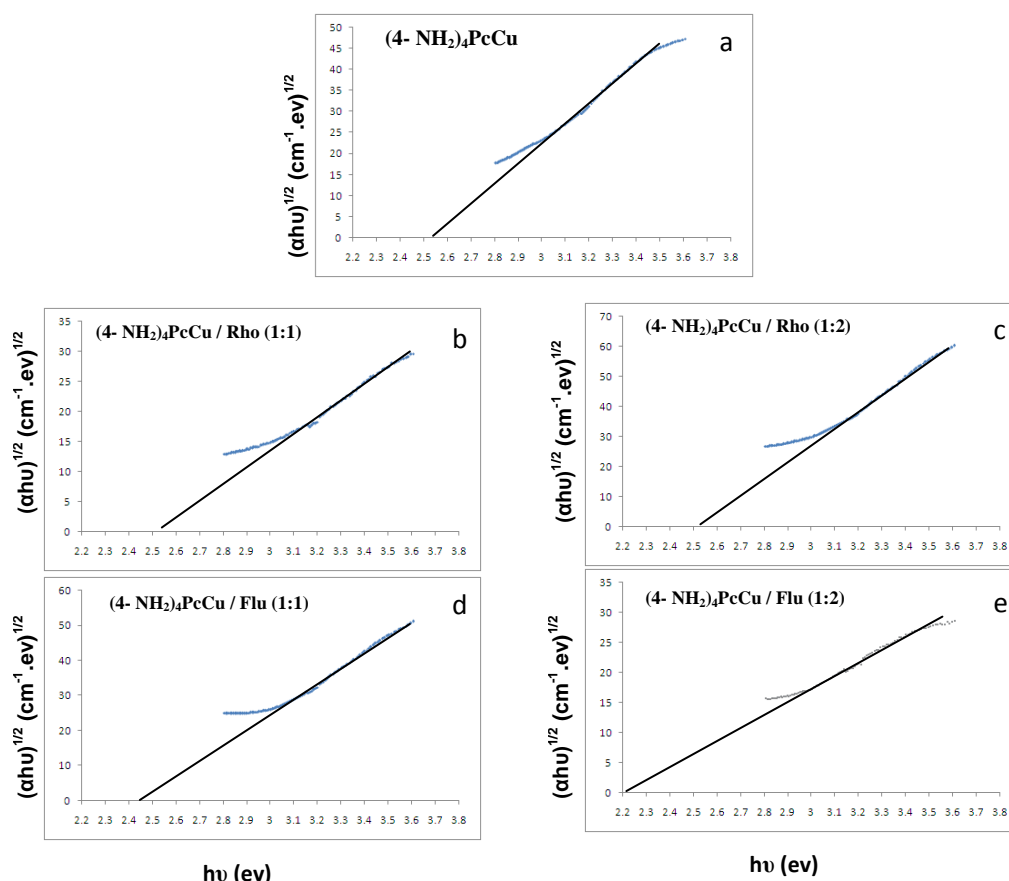

Figure (5): Plot of (αhυ)1/2 vs. hυ for PcCu complexes thin film

Table (3): The optical band gap, Eg values for the complexes of PcCu

Complexes	Optical band gab, E_g (±0.02 ev)
(4-NH$_2$)$_4$PcCu	2.53
(4-NH2)4PcCu / rhodamine (1:1)	2.52
(4-NH2)4PcCu / rhodamine (1:2)	2.52
(4-NH2)4 PcCu/ florescence (1:1)	2.45
(4-NH2)4 PcCu/ florescence (1:2)	2.22

5. Conclusion

In this present study of the derivative complexes form (4-NH$_2$)$_4$ PcCu and fluorescence have high optical properties compared with derivative complexes form (4-NH$_2$)$_4$ PcCu and rohdamine-B. In addition to, the (4-NH$_2$)$_4$ PcCu/ florescence mole ratio [1:2] (Pc: dye) is more optical compared with (4-NH$_2$)$_4$ PcCu/ florescence mole ratio [1:1] (Pc: dye) by the values of E_g, as shown in Table (3). The type of optical transition responsible for optical absorption was indirect transitions.

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