المؤتمر العلمي السنوي الثالث والعشرون الموسوم
(مؤتمر كلية التربية الأساسية في مجال العلوم الصرفة)
والمنعقد تحت شعار (بالبحث العلمي الرصين نرتقي ونتعلم ونتقدم)
للمدة 29_30 /4/ 2024

Spectroscopic Properties Of Copper-Phthalocyanine (Cupc) Dye

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Abstract:
The absorption and fluorescence spectra of the dye Copper-phthalocyanine (CuPc) in Dioxane solvent were separately studied under normal conditions at room temperature for three concentrations.($2x10^{-4}$, $1x10^{-4}$and $5x10^{-5}$) M.

The intensities of the absorption and fluorescence spectra are increasing with the increase of the concentration which agrees with Beer – Lambert Law.

Phthalocyanine molecules (CuPc) have two absorption bands in the visible and ultraviolet region of the spectrum. The higher energy band, occurring at around 350 nm, is generally known as the B-band. The lower energy band, occurring at around 650nm, is generally known as the Q-band.

The measurement shows that the Absorption and Fluorescence spectrum have shifted to short wavelengths (Blue Shift).

Additionally, the quantum efficiency increases with the decrease in concentration.

Keywords: Organic dye, Absorption, Fluorescence, Quantum efficiency.

1.Introduction

Organic compounds are divided into two main groups: hydrocarbons and their derivatives. They are further categorized based on their structure, Convert into compounds that are saturated and unsaturated. Unsaturated compounds are distinguished at minimum by double or triple chemical bonds must be present. The bonds greatly affect the chemical properties of these compounds[1]. When there are two double bonds, they are referred to as conjugated. Conjugated dual bonds cause molecules to Capture light at specific wavelengths. greater than 200nm. True the dyes are compounds that strongly absorb light in the visible spectrum. [1].

Phthalocyanine is one of the organic dyes that are commonly used in various applications. It is a macro-cyclic compound that The text possesses distinct physical and chemical characteristics, The material exhibits exceptional thermal stability and remarkable sensitivity. Its molecular formula is

$C_{32}H_{18}N_8$, and it is a flat molecule composed of an inner porphyrin ring with four benzene rings located symmetrically at the four corners. the center of the molecule, there is a pair of hydrogen atoms that can be replaced by various metals, such as copper. There are different types of Phthalocyanine, including metal-free, symmetrical, and asymmetrical, and they can be prepared using various methods, depending on factors such as the precursor, solvent, catalyst, and temperature.

Phthalocyanine is commonly recognized as a blue-green pigment due to its strong absorption of light in the UV region of the spectra. [5].

Some researchers are currently focusing on the synthesis of copper phthalocyanine due to its importance in industrial applications[7,8].

The Phthalocyanine molecule is a versatile compound with various industrial applications, such as pigment, organic dyes, catalysts, semiconductors, solar cells, photoreceptors, gas sensors, and diodes [2,3]. Typically, it behaves as a p-type semiconductor [9]. The CuPc has three different The crystallographic phases include α-metastable, β-stable, and x-crystal phases.The outcome is contingent upon the deposition conditions, atomic orientation, and crystal arrangements [10,11].CuPc is a prominent choice for organic pigments in various applications [12].

2.Exbermantal

The materials have been chosen in search it is Copper –Phthalocyanine dye and Dioxane solvent.

Copper-phthalocyanine (CuPc) is a type of cyanine dye with a molecular formula of $C_{32}H_{16}N_8Cu$ and a molecular weight of 575.5 gm/mol. It contains 90% dye content and its chemical formula is shown in Figure (1). Three different concentrations of CuPc have been prepared: $2x10^{-4}$ M, $1x10^{-4}$ M, and $5x10^{-5}$ M.

The molecular formula and weight of the organic solvent (1,4 Dioxane) with a purity of 99.99% (spectra grade) was used in the current study The chemical formula for the compound is $C_4H_8O_2$, and its molar mass is calculated as the molecular weight (88.11 gm/mol) [19].

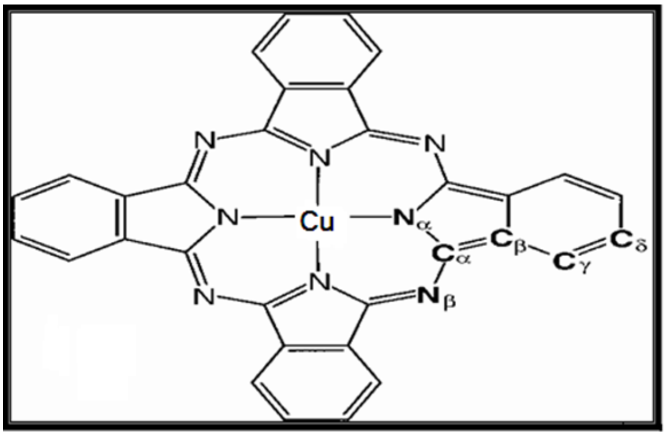


Figure (1): Copper-Phthalocyanine molecule [13]

3. Solution preparation

The solvent concentration solution is prepared by accurately measuring the required material by Utilizing a balance that has a sensitivity of 10^{-4} gm, various concentrations are subsequently prepared according to the given equation:

$$W = \frac{M_W \times V \times C}{1000} \quad \text{….(1)}$$

Where W weight of the dissolved dye (gm)
M_W Molecular weight of the dye (gm/mol)
V the volume of the solvent (ml)
C the dye concentration (mol/l)

The solutions that have been prepared are diluted based on the equation provided below: $C_1 V_1 = C_2 V_2$…..(2)

Where
C_1 primary concentration
C_2 new concentration
V_1 the volume before dilution
V_2 the volume after dilution

Three concentrations are prepared for CuPc the concentrations are 2×10^{-4} M, 1×10^{-4} M, 5×10^{-5} M.

5.Results and Discussion

In this section, the results of the sample preparation for studying the impact of concentration and solvent on the quantum efficiencies of Copper-Phthalocyanine dye will be present .The absorption and fluorescence spectra of the dye that was dissolved in Dioxane were analyzed.

6.UV absorption spectra around (350nm)

The absorption spectra of the solvent , as shown in Fig.(2), indicates that there is no absorption spectrum present in the CuPc region, to show the absorption of the dye only. In Figure (3), It is evident that the enhancement in absorption intensity fluctuates in accordance with the rise in concentration, by the Beer-Lambert law. The CuPc dye's absorption spectrum in the solvent, as illustrated in Fig. (3), indicates that this dye exhibits a wide range of absorption across various wavelengths of 300 to 400 nm[14]. Additionally, it's worth noting he absorption spectrum bandwidth at the midpoint intensity (λFWHM) diminishes with decreasing concentration.

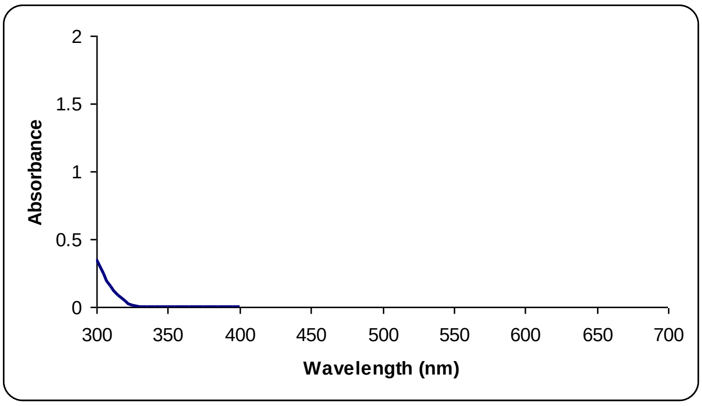
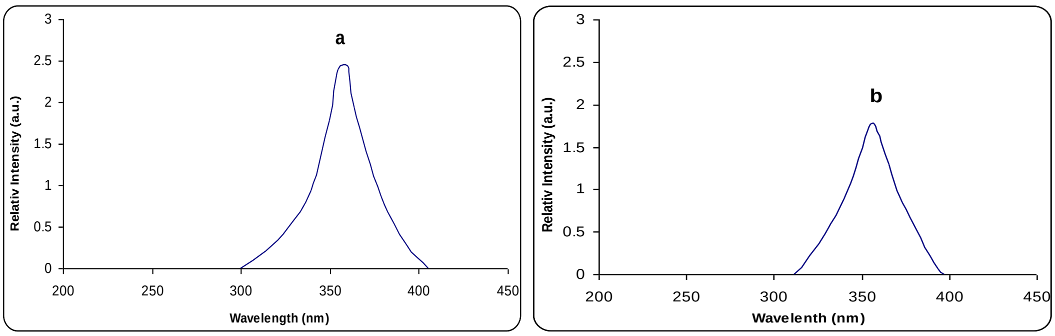


Figure (2): Absorbance of Dioxane solvent

Changing the concentration has a direct impact on the maximum wavelength of the absorption spectrum (λmaxabs). For example, when the concentration is at $2x10^{-4}$ M, the peak absorption is observed at 360 nm. Then, a blue shift occurs, moving the peak to 358 nm at a concentration of $1x10^{-4}$ M and further to 355 nm at $5x10^{-5}$ M. This decrease in concentration also results in a reduction in The absorption's relative intensity value can be rewritten as the relative value of absorption intensity, thus narrowing the spectrum range.



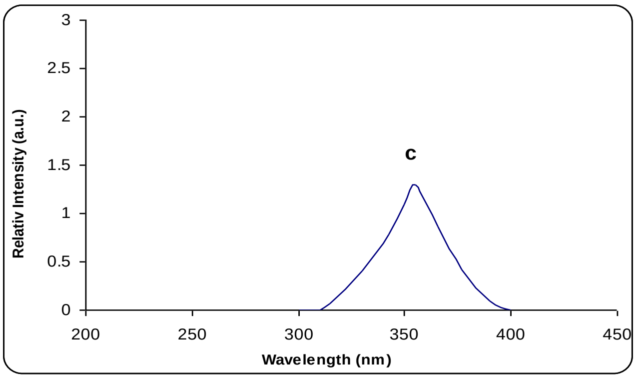


Figure (3): Absorption spectra of CuPc dye dissolved in Dioxane (a) $2x10^{-4}$M(b) $1x10^{-4}$M (c) $5x10^{-5}$M

Table (1) shows the results of CuPc dye absorption in dioxane at room temperature for varying concentrations..

Table (1):The CuPc dye's absorption spectra.

Absorption Spectrum Dye : CuPc Solvent: Dioxane At Room Temp.				
Concentration (mol/liter)	Relative Intensity (a.u.)	λ_{max}abs (nm)	Band Width $\Delta\lambda$ (nm)	$\Delta\lambda_{max}$ (FWHM) (nm)
$2x10^{-4}$	2.5	360	100	60
$1x10^{-4}$	1.8	358	90	52
$5x10^{-5}$	1.3	355	80	33

Through the study of absorption spectra, we have observed that the intensity of the absorption increases the greater number of molecules present. This aligns with the principles of the Beer-Lambert law. Furthermore, the peak of the absorption shifts towards longer wavelengths (Red Shift) due to the higher Electric dipole moment of the higher energy level., compared to the ground state.

7.Fluorescence spectra within the ultraviolet (UV) range

We observed the fluorescence spectrum of the CuPc dye, which is shown in Figure 4. The dye has a wide range of wavelengths (310-380) nm. We noticed that bandwidth of the fluorescence spectruawith moderate intensity. (ΔλFWHM) decreases with a decrease in concentration. Also, the intensity increases with an increase in concentration. The fluorescence spectrum reflects the absorption spectrum.

The impact of altering the concentration becomes apparent when determining the maximum wavelength of the fluorescence spectrum ($\Delta\lambda_{maxflu}$).. When concentration is ($2x10^{-4}$)M, the highest peak of fluorescence is at (350) nm. The spectrum undergoes a transition towards shorter wavelengths (blue shift) at a wavelength of 347 nm when concentration is 1x10-4 M. Subsequently, it reaches its maximum intensity at 340 nm for the most minimal concentration of 5x10-5 M. This is accompanied by a the decrease in relative intensity of fluorescence and a narrowing of the spectra range.

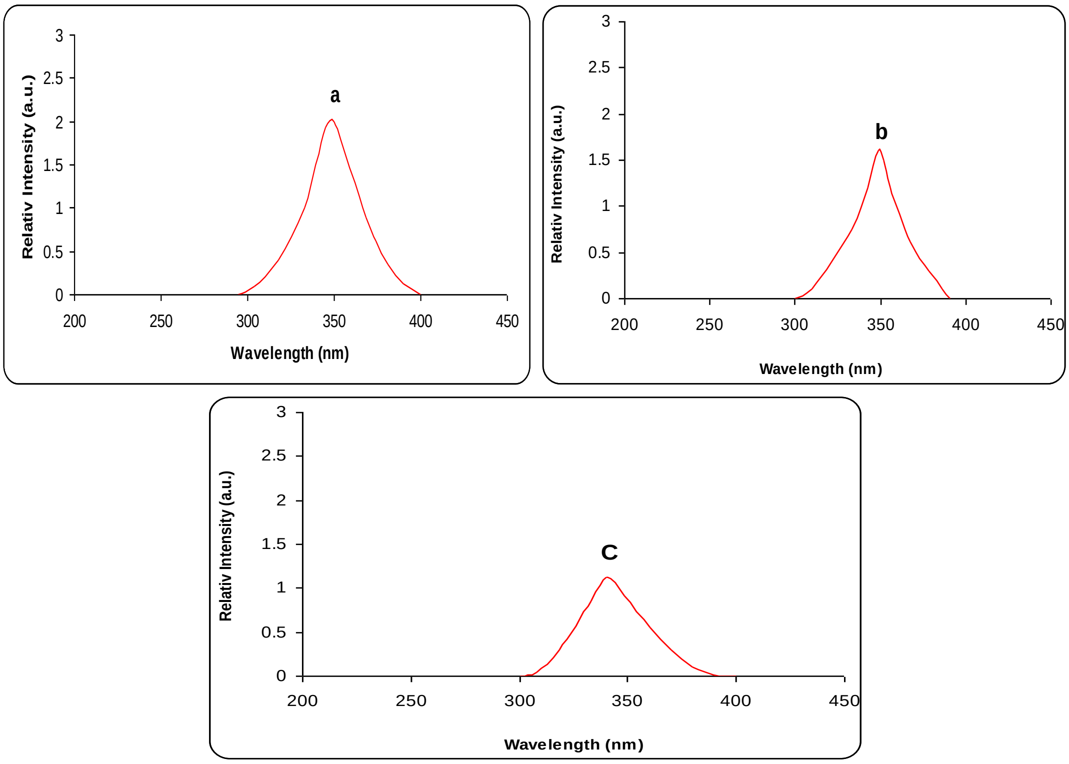


Figure (4):Fluorescence spectra of CuPc dye dissolved in Dioxane (a) $2x10^{-4}$M (b) $1x10^{-4}$M (c) $5x10^{-5}$M

Table (2) displays (CuPc) dye's fluorescence at room temperature in different Dioxane concentrations.

Table (2):The fluorescence spectra for CuPc dye

Fluorescence Spectrum Dye : CuPc Solvent: Dioxane At Room Temp.				
Concentration (mol/liter)	Relative Intensity (a.u.)	λ_{max}flu (nm)	Band Width $\Delta\lambda$ (nm)	$\Delta\lambda_{max}$ (FWHM) (nm)
$2x10^{-4}$	2	350	95	55
$1x10^{-4}$	1.6	347	94	50
$5x10^{-5}$	1.1	340	90	45

The fluorescence peak shifts towards longer wavelengths (Red Shift) with an increase in concentration. This is because higher concentration leads to energy loss from non-radiative transitions, such as internal conversion (IC) and intersystem crossing (ISC). The fluorescence spectrum in figure (4) shows that the peak shifts towards the blue region due to the non-linear properties of the copper phthalocyanine molecule. This change in polarization arises from the interaction with the exciting photon.

8. Calculation Important Parameters for Organic Dye CuPc

We have calculated some parameters of organic dye CuPc which are used in the research, by using some mathematical equations for these parameters and an approximation, in accordance with the following steps:

a- The determination of the Fluorescence Quantum Efficiency

The quantum efficiency of the dye is estimated by determining Utilize the supplied formula and software (MATLAB 6.5) to calculate the integrals of the relative absorption and fluorescence spectra curves., where a dilute solution of the dyes.

By employing equation (3) to compute the quantum efficiency, of CuPc dye in Dioxane solvent, as follows[15]:-

$$q_{FM} = \frac{\textbf{Area under the Curve of the relative Fluorescence}}{\textbf{Area under the Curve of the relative Absorption}} \quad ....(3)$$

b- Calculation the Einstein Coefficient For Spontaneous Emission

Einstein coefficient is calculated from the relation[16] :

$$A_E = K_{FM} = 2.88x10^{-9}\bar{\upsilon}^2 n^2 \int \varepsilon(\bar{\upsilon})d\bar{\upsilon} \quad .....(4))$$

And its unit (sec^{-1})

Where:

$\bar{v}$: is the wave number at mid band of the extinction coefficient

n: is the refractive index of the solvent

$\int \varepsilon(\bar{\upsilon})d\bar{\upsilon}$: is the area under the curve of the molar extinction coefficient (ε), it is a function for the wave number $\bar{v}$.

c- Calculation of the radiative Life Time

Radiative lifetime has been calculated by using relation (5) and (4)[17].

$$\tau_{FM} = \frac{1}{K_{FM}} \quad .....(5)$$

Where:

τ_{FM}: is the radiative lifetime and its unit (sec) and (τ_{FM}) indirect proportion

d- Calculation the Fluorescence lifetime

The Fluorescence lifetime has also been calculated by using relation(6)[18].

$$\phi_{FM} = \frac{\tau_F}{\tau_{FM}} \quad .....(6)$$

If we know the life time for the excited singlet state and fluorescence quantum yield then we can calculate the radiative lifetime, and since values of the quantum efficiency are less than or equal to one then (τ_{FM}>T_F)[15].

Table (3) shows the values of the parameters (q_{FM}, A_E, τ_{FM}, τ_F) of CuPc dye at different concentrations, as follows:

Table (3):Shows the parameters (q_{FM}, A_E, τ_{FM}, τ_F) of CuPc dye

Dye	Concentration (Molar)	Fluorescence Quantum Efficiency(q_{FM})	Einstein coefficient for spot. Emission (A_E) sec^{-1}	Radiative lifetime(τ_{FM}) ns	Fluorescence Life Time (τ_F) ns
CuPc	$2x10^{-4}$	52%	194453	2.5071	1. 3036
	$1x10^{-4}$	73%	66352	5.1426	3.7540
	$5x10^{-5}$	83%	15976	6.2593	5.1952

After comparing certain parameters with existing literature, it is clear that these results offer a comprehensive understanding of the mechanism of action. It has been concluded that the impact of the solvent on the Molar coefficient (ε) decreases as the concentration increases. The values of these parameters for the dye used at a concentration of 5x10-5 M for the UV are:
Quantum Efficient q_{FM} = 83%
Radiative lifetimeτ_{FM} = 6.2593 ns
Fluorescence lifetimeτ_F =5.1952 ns

10. Conclusions

Through studying thespectra of absorption and fluorescence, along with the relationship between the Molar extinction coefficient and wavenumber, and calculating related parameters, the following conclusions have been drawn:
Phthalocyanine molecules (CuPc) exhibit two absorption bands in the visible and ultraviolet regions of the spectrum. The higher energy band, occurring at around 350 nm, is commonly referred to as the B-band. The lower energy band, occurring at around 650 nm, is known as the Q-band.
As the concentration of the dye used in the research (CuPc) increases, the peaks of the absorption and fluorescence spectra shift towards longer wavelengths, within the studied range of 300-700 nm.
From the fluorescence spectrum, it has been observed that the fluorescence peak shifts towards the blue region due to the non-linear properties of copper phthalocyanine molecules, which causes a change in polarization resulting from the interaction with exciting photons. The overlap between absorption and fluorescence increases with concentration.

The quantum efficiency (qFM) value increases with decreasing concentration of the dye solution (CuPc), which also increases the Radiative lifetime (τFM) to be greater than the fluorescence lifetime (τF).

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مستخلص البحث:

لقد تمت دراسة أطياف الإمتصاص والفلورة للصبغة العضوية نوع الفثالوسيانين-نحاس(CuPc) في المذيب الدايوكسان، وتحت ظروف طبيعية عن(درجة حرارة الغرفة) وللتراكيز الثلاثة , ($5x10^{-5}$, $1x10^{-4}$, $2x10^{-4}$) مولاري. إن الشدة النسبية لطيفي الإمتصاص والفلورة تزداد مع زيادة التركيز وهذا ينطبق مع قانون بير – لامبرت. ان جزيئة الفثالوسيانين(CuPc) تمتلك حزمتي امتصاص في المنطقة المرئية وفوق البنفسجية من الطيف،حزمة الطاقة العالية تقع عند حوالي 350 نانومتر،وتعرف عموما باسم حزمة-B.بينما حزمة الطاقة الواطئة فتقع عند حوالي 650 نانومتر،وتعرف عموما باسم حزمة-Q.وقد بينت النتائج تأثير نقصان التركيز في إزاحة أطياف الإمتصاص والفلورة إلى الأطوال الموجية القصيرة (Blue Shift).دلت الدراسة لأطياف الإمتصاص والفلورة للصبغة العضوية (CuPc) بأن علاقة الكفاءة الكمية تتناسب عكسياً مع زيادة التركيز.