Spectroscopic Properties of Organic Dye for Visible region

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Abstract

This study focuses on the Spectroscopic Properties of Copper phthalocyanine dye solution ,with an emphasis on evaluating its Quantum efficiency and Radiative life time.

The solution was prepared using a powder of Copper-phthalocyanine (CuPc) It has the formula $C_{32}H_{16}N_8Cu$ which it dissolves in organic solvents such as Dioxane.

The fluorescence and absorption spectra were analyzed using UV-VIS spectroscopy.

The results indicated significant increases in quantum efficiency and radiative lifetime, with values of 59%, 65%, and 74% for quantum efficiency, and 3.1802, 5.9717, and 7.6244 for radiative lifetime. In particular, these increases occurred as the concentration rate decreased.

Keywords: CuPc, Absorption, Fluorescence, Organic dye.

Introduction

Organic compounds from ancient times are used for the prevention and treatment of human ailments. They are an important part of human civilization, used as health supplements, foods, nutraceuticals, and in the treatment of various human diseases [1].

The compounds are separated into two categories: saturated and unsaturated. The unsaturated compounds differ from the former because they have at smallest amount one double or triple bond. These manifold bonds affect spectroscopic characteristics in addition to having a profound impact on chemical reactivity.

Typically, organic compounds with no double or triple bonds absorb at wavelengths shorter than 160 nm. Since this energy is bigger than the separation energy of the majority of chemical bonds, photochemical

breakdown is possible to take place, making these compounds unsuitable for use as laser active media .

The rotational symmetry of electrons' wave functions connection with the bond direction—the line joining the two nuclei—defines each bond in an unsaturated compound. Double (and triple) bonds contain both π electrons and δ bonds. The electrons of a carbon or heteroatom have a rotational symmetry the length of a line through the nucleus that is standard to the plane occupied by the three electron orbitals. π bond is formed by the maximal side overlap of the π-electron orbitals when their symmetry axes are parallel[17].

The two double bonds are mentioned to as conjugated. Compounds that contain conjugated double bonds are capable of absorbing light at wavelengths exceeding 200nm. All substances that qualify as dyes, defined as compounds exhibiting significant absorption in the visible spectrum, contain multiple conjugated double bonds. The essential mechanism that regulates light absorption in compounds containing conjugated double bonds remains unchanged; irrespective of the particular area of the spectrum in which these compounds display their longest wavelength absorption band, whether in the visible, near-infrared, or near-ultraviolet range[2].

Phthalocyanine is one of the organic dyes. The macrocyclic compound phthalocyanine (Pc) has π-electrons. It has high sensitivity, distinct chemical and physical characteristics, and thermal stability [3, 4]. The planar molecule $C_{32}H_{18}N_8$ has four benzene rings symmetrically positioned at each of its four corners and an inner porphyrin ring. A pair of hydrogen atoms sits at the middle of the molecule, we can replaced the two central hydrogen atoms by a metal, such as Copper [5]. There are several methods for preparing Pc, based on its type, such assymmetrical, metal-free, or asymmetrical Pc. The precursor, solvent, catalyst, and temperature all play a role in the synthetic process. PC are commonly recognised as blue-green pigments because of their physically powerful absorption of light in the visible region of the spectra. [6,7].

Phthalocyanines are macrocyclic compounds that exhibit a striking blue/green color and form coordination complexes with various the ions

ofmetal at the middle of the molecule. Because of the importance of CuPc dye in industrial applications,a number of researchers have focused on it in their studes [8, 9].

Stains,diodes, catalysts,gas sensors, semiconductors, organic dyes, photoreceptors, andsolar cells are just a few of the industrial applications for phthalocyanine molecules [3, 4]. In general, PC acts like a p-type semiconductor [10]. Depending on the atomic direction, crystal structures, and deposition conditions, the CuPc exhibits three distinct crystallographic phases: theβ-stable,α-metastable, and x-crystal phases [11- 13].
injecting contact is difficult for organic compounds especially for Phthalocyanine (H_2Pc). Both injecting and blocking contact we can make it by metal electrodes [14].Phthalocyanine (H_2Pc) has measurement polarizated and non-polarizated can conclude that evaporation gold film exhibits gap in the injecting on (p-type) for (H_2Pc) film, while if put mineral rod such as (silver or aluminum) occur obstruction for the electronic injecting [15].
The aim of this study is to investigate the absorption and fluorescence characteristics of the dye in the visible region of the electromagnetic spectrum, as well as to examine the effect of concentration variation on its absorbance and fluorescence properties, with calculation of the quantum efficiency and the lifetime.

2. Experimental Work and Preparation of Solution

The molecule phthalocyanine ($C_{32}H_{18}N_8$) is made up of four benzene rings that are symmetrically arranged at each of its four corners and a central porphyrin ring. Many industrial processes, such as gas detectors, solar cells, photoreceptors, catalysts, pigments, and organic dyes, use phthalocyanine molecules as active media[16].
Copper-phthalocyanine (CuPc) powder is blue and readilyIt has the formula $C_{32}H_{16}N_8Cu$ and 575.5 gm/mol is represent a molecular weight. It dissolves in organic solvents such as dioxane. Figure (1) shows the chemical formula for this dye, which belongs to the cyanine family.The organic solvent has a molecular weight of 88.11 g/mol and the$C_4H_8O_2$is the molecular formula. It is known scientifically as 1,4-Dioxane. The concentration of pure dioxane

used in this study is 99.99% (spectra grade).

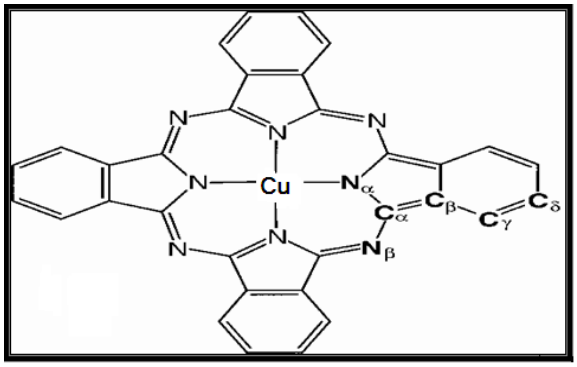


Fig. (1): phthalocyanine molecule [16]

To make a solvent solution of concentration, a suitable amount of the material is weighed using a Mettler balance with a sensitivity of 10^{-4}gm.The following formula is used to prepare various concentrations:

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

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

The following formula is used to dilute the prepared solutions:

$$C1\ V1 = C2\ V2 \quad (2)$$

Where
C1 is the primary concentration, C2:The new concentration
V1: is the volume prior to dilution, V2 : is the volume following dilution.

Three concentrations are made from CuPc dye, this was achieved by dissolving (2 g)of the dye in (100 mL) of the solvent. The solution was then thoroughly shaken until complete dissolution of the dye in the solvent was observed. This procedure yielded the first concentration, and upon dilution according to the dilution equation, the second and third concentrations were obtained.

3. Result

3. 1 Absorption spectra in visible region around (650 nm)

Through the examination of the absorption range of CuPc dye in Dioxane, we have noted that it exhibits a broad spectrum of wavelengths ranging from 590 to 680 nm. The absorption peak at approximately 650 nm occurs at the highest concentration of ($2x10^{-4}$) M. Subsequently, this peak shifts towards shorter wavelengths, known as a blue shift, reaching (647) nm at a first concentration. Finally, at the lowest concentration of ($5x10^{-5}$) M, the peak is observed at (640) nm. This is displayed in figure (2).

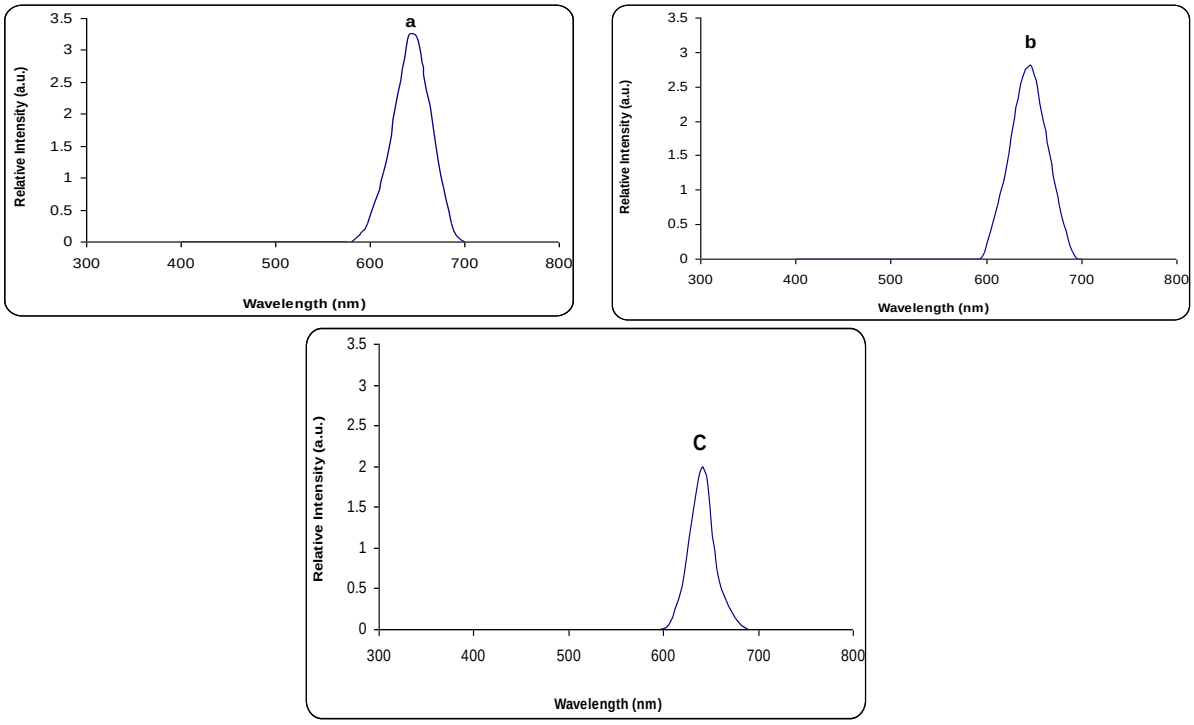


Figure (2):Absorption spectra of the dye (a)**$2x10^{-4}$M (b) $1x10^{-4}$M (c) $5x10^{-5}$M**

Table (1) shows the result of changing concentrations of Copper-Phthalocyanine dye (CuPc) dissolved in Dioxane on absorption band.

Table (1): Absorption spectra of CuPc dye

Concentration (mol/liter)	Relative Intensity (a.u.)	λ_{max}abs (nm)	Band Width $\Delta\lambda$ (nm)	$\Delta\lambda_{max}$ (FWHM) (nm)
$2x10^{-4}$	3.2	650	120	60
$1x10^{-4}$	2.8	647	110	45
$5x10^{-5}$	2	640	90	35

The increase in dye absorption intensity improves focus because there are more molecules present, which increases the probability of absorption at the used concentrations. According to the Beer-Lambert law, this is correct. Because the excited state's dipole moment is greater than the ground state's, the concentration of dye solution increases, causing a red shift—a shift of the absorption peak towards long wavelengths—and an expansion of the spectral range. As the concentration increases, we have observed activities that resemble the UV absorption spectra shifting to the red region because the excited state have a higher dipole moment more than the ground state.

3.2 **Fluorescence spectra in visible region**

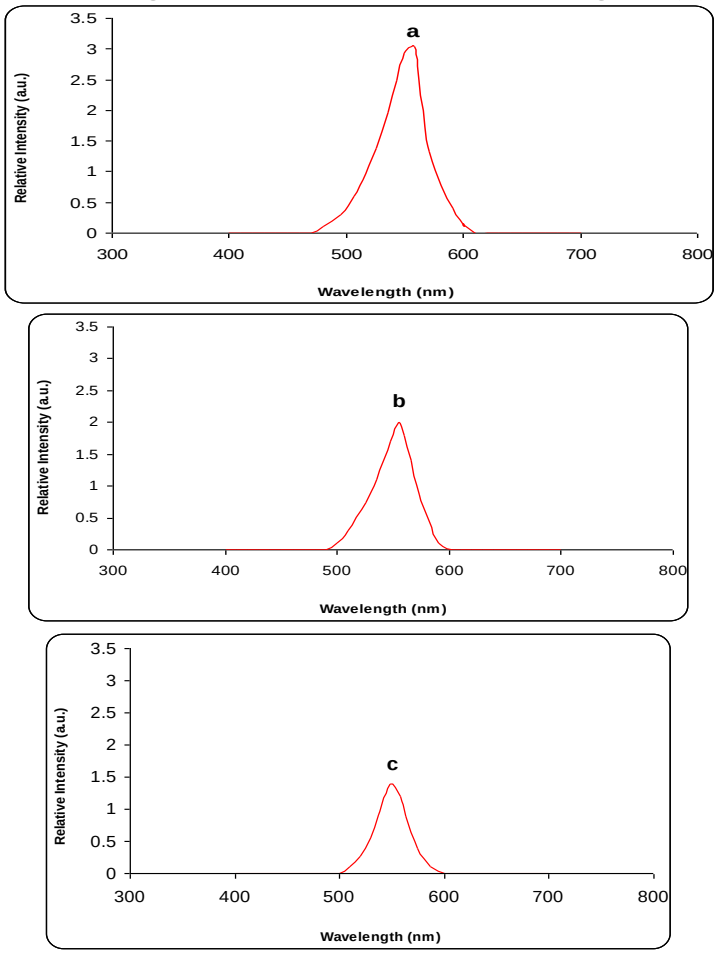
Upon examining the fluorescence spectrum of CuPc dye in dioxane, we discovered that it exhibits a broad range of wavelengths (480-600 nm).

When figuring out the maximum wavelength that corresponds to the highest intensity of the fluorescence spectrum (λmaxflu), the effect of fluctuating concentration is evident. We find that when the concentration is lowered, the maximum fluorescence peak, which is located at a wavelength of (560) nm with a concentration of ($2x10^{-4}$) M, shifts towards shorter wavelengths (blue shift) to (555) nm. Additionally, figure (3) illustrates how the peak moves to (550) nm at the lowest concentration of ($5x10^{-5}$) M, along with a drop in the relative fluorescence intensity.

The peak of fluorescence is shifted (Red Shift) with increasing concentration, due to increase the collision between the molecules and loss of the energy by non-raditivily (ISC-IC) transition.

From the spectrum of fluorescence, it has been observed that the peak of the fluorescence is shifted to the blue region because of a non-linearity properties of copper pthalocyanine molecule, which cause a change in the polarization resulting from the interaction with exciting photon.

The overlapping among absorption spectrum and fluorescence were increased with increasing concentration as shown in figure (3).



Figure(3) :Fluorescence spectra of dye

Table (2):Fluorescence spectra of CuPc dye

Concentration (mol/liter)	Relative Intensity (a.u.)	λ_{max}flu (nm)	Band Width $\Delta\lambda$ (nm)	$\Delta\lambda_{max}$ (FWHM) (nm)
$2x10^{-4}$	3	560	140	55
$1x10^{-4}$	2	555	110	45
$5x10^{-5}$	1.4	550	100	30

4- Calculation Parameters for Organic Dye CuPc

In accordance with the following procedures, we have computed several organic dye CuPc parameters that are utilised in the study using a few mathematical formulas for these parameters as well as an estimate:

a. Calculation of the Fluorescence Quantum Efficiency

Using a diluted solution of the dyes and (MATLAB 6.5)software, we estimate the dye's quantum efficiency by calculating the areas under the curves of the relative absorption spectra and fluorescence. The quantum efficiency of CuPc dye can be determined using equation (3) as below[18]:

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

b. Einstein Coefficient

The Einstein coefficient is determined from the relation[19] :

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

And its unit (sec^{-1})

Where:

$\bar{v}$: is represent the wave number.

n: isrepresent the refractive index of the solvent

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

c. Radiative Life Time

Radiative life time is determined by apply the equations (5) , (4)[20].

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

Where:

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

d. Fluorescence Life Time

Fluorescence life time were calculate by using relation(6)[21].

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

we can calculate the radiative lifetime when noted that the fluorescence quantum yield and life time for the excited singlet state, and while the quantum efficiency values are equal or under to one then (τ_{FM}>T_F)[18].the following table show the value of the(A_E, q_{FM}, τ_{FM}, τ_F) of dye:

The results of the parameters provide a the device of action when compared to the corpus of literature[22,23]. The molar coefficient (ε) has been found to have a lesser effect as concentration increases. The following parameters' standards for the (visible) at $5x10^{-5}$ M concentrations:

Quantum Efficient q_{FM} = 74%

Radiative life time τ_{FM} = 7.6244ns

Fluorescence life time τ_F = 5.6420ns

Table (3): The (A_E, q_{FM}, τ_{FM}, τ_F) of 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	$2x10^{-4}$	59%	33650	3.1802	1.8763
	$1x10^{-4}$	65%	11462	5.9717	3.8816
	$5x10^{-5}$	74%	11462	7.6244	5.6420

10. Conclusions

The experimental results presented in Table (3) clearly demonstrate the effect of concentration on the photophysical properties of the CuPc organic dye. As the dye concentration decreases from 2×10^{-4} M to 5×10^{-5} M, a noticeable increase in the fluorescence quantum efficiency (q_{FM}) is observed, rising from 59% to 74%. This behavior can be attributed to the reduction of intermolecular interactions at lower concentrations, which minimizes self-quenching effects and suppresses non-radiative energy transfer between dye molecules.

In addition, the radiative lifetime (τ_{FM}) shows a systematic increase with decreasing concentration, increasing from 3.1802 ns to 7.6244 ns. This increase indicates a reduction in non-radiative decay channels and enhanced stability of the excited state at lower concentrations.

Consequently, the excited molecules have a longer probability to undergo radiative transitions, which contributes to the observed enhancement in fluorescence efficiency.

Similarly, the fluorescence lifetime (τ_F) increases significantly with dilution, from 1.8763 ns at higher concentration to 5.6420 ns at the lowest concentration. This trend further confirms that concentration quenching and molecular aggregation play a major role at higher concentrations, shortening the excited-state lifetime through non-radiative processes.

Moreover, the Einstein coefficient for spontaneous emission (A_E) exhibits higher values at higher concentrations, reflecting the influence of intermolecular effects and possible re-absorption phenomena. At lower concentrations, the reduced (A_E) values are consistent with the dominance of intrinsic radiative processes of isolated dye molecules.

Overall, the results in Table (3) confirm that dilution of the CuPc dye solution leads to enhanced fluorescence performance, characterized by higher quantum efficiency and longer radiative and fluorescence lifetimes. These findings are consistent with the suppression of aggregation, self-quenching, and re-absorption effects at lower concentrations, thereby improving the radiative emission properties of the dye.

Copper phthalocyanine (CuPc) absorption bands are located in the visible portion of the spectrum, commonly known as the "Q-band" and located at about 650 nm.

The fluorescence and absorption peaks shift to the longer wavelengths in the 300–700 nm range under investigation as the concentration of the dye used in the study (CuPc) increases.The interference between fluorescence and absorption increased with concentration.

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