



RESEARCH ARTICLE

Study UV-Visible and FTIR Characterization of ZnPc Dye using Double Solvent

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Abstract

The effects of dissolving zinc phthalocyanine (ZnPc) in two solvents, (*N,N*-dimethylformamide (DMF)/water, dimethylsulphoxide (DMSO)/water, tetrahydrofuran (THF)/water), on the absorption spectra and infrared spectra were studied using (UV-Vis) spectroscopy and FTIR spectrophotometer. Solvents affected on the photochemical and photophysical properties of ZnPc complexes. The noticed trend inside the difference of Q-band position with solvent was occasionally attributed to solvent parameters comprising aromaticity, arrange power, polarity, and refractive index. UV-V spectra analysis showed non-proof of aggregation in sol as a display through great unperturbed phthalocyanine Q band. zinc phthalocyanine emerge absorption spectra with duo essential band electron the Q band with a generality (685, 675 and 680) nm separately as well as Soret B band with an extreme of (340, 340 and 350) nm separately. Farthest potential aggregation included method is such the H-aggregation because of rise shift energy of absorption spectrum as well as provided information via the potential electrostatic allocation onto molecule zinc phthalocyanine. FTIR results showed that elevate include peaks belongs to ZnPc with the alteration in the present of the two solvent furthermore little shift toward low energy existed.

Keyword: Double solvent, Metal-Phthalocyanine dye, Energy bandgap.

Introduction

Photoelectron spectroscopy test (PES) equipping method to attractive comprehend the structures electronic of molecular and interfaces installation, absorption geometries, allocation of energy levels, and asymmetries orbital of adsorbates. Phthalocyanine dyes (Pcs) studied vastly as sensitizers due to their chemical constancy and high grade of sucking at afar red/near-IR region. Those Pcs exhibit workable advancement in energy conversion efficiencies by enough artificial adjustment [1-2].

Large types of phthalocyanines, like metal-free phthalocyanines and phthalocyanines with several metals had synthesized and now used in a broad diversity such as solar cells [3]. Phthalocyanines act as a type of organic compounds with major implementations in

diverse scopes as dyes and sensors, optical materials, solar cells, pigments, electronic devices. Through metallated phthalocyanines, (ZnPc) comprises rise (Q.Y.) of odd oxygen generation, had been utilizing in several drug delivery vehicles like nanoparticles and liposomes [4,5]. Molecules of Phthalocyanine had unusual characteristics in terms of light absorption in the far visible region of the solar spectrum at (λ 690 nm) [6].

Study several type of dyes sensitive to light in solvent double mixtures, and behavior photophysical. As photosensitizers, Pcs has the feature of top molar absorption, resistance to chemical, and photo chemical degradation. Furthermore, Pcs have absorption and emission in the about of 660-750 nm, making them sensitive to the light,

which can permeate pointedly in to living tissues. The tendency to aggregation because of molecular stacking output in low Q.Y. of $^1\text{O}_2$ and solubility limiting in watery media is the disadvantage of the dyes [7-8]. Organic solvents are familiar to decrease aggregation, whereas hydrous solvents will highly produce accumulate complexes.

On the other hand, different phthalocyanine complexes remain accumulated even in non aqueous solutions. Moreover, the sols possess an influence on the photochemical and photophysical properties of MPc complexes [9-10]. In this search, we report on the affects of a chains double solutions; *N,N*-dimethylformamide (DMF), dimethylsulphoxide (DMSO), and tetrahydrofuran (THF), with D.W. on the solubility of ZnPc dye.

The influence of dissolution on the degree of aggregation of ZnPc in hydrous solution and the affect of solvents -ZnPc interaction photophysical and photochemical properties of the photosensitizer. UV visible and FTIR

have been used to investigate the impact of varying the ratio of the solvents.

Experimental Part

Materials

Zinc phthalocyanine (ZnPc) dye, Dimethylformamide (DMF) and Dimethyl sulfoxide (DMSO), all attained from Sigma-Aldrich, and Tetrahydrofuran (THF) received from Merck-Germany. Distilled water collected from the laboratory.

Samples Preparation

A sufficient amount of ZnPc dye (5×10^{-4} M) was dissolved with two solvent in a glass bottle via utilizer a magnetic stirrer for 4 h. The solution was added dropwisely until obtaining a dark blue colloidal solution. The dissolve dye stored in a glass bottle which was wrapped with aluminum foil to avoid excitation of dye when sunlight or electrical lightening presented. The type of solvent and the ratio between the two solutions have been changing according to Table (1).

Table 1: The ratio of samples dissolved in (DMF, DMSO, and THF) and water

Sample	Solvent	
	DMF, DMSO, THF (%)	Water (%)
1	100	0
2	80	20
3	60	40
4	50	50
5	40	60

Characterization Methods

The prepared samples (Table 1) has been tested by UV absorbance using (Metertech SP-8001 UV/VIS Spectrophotometer) and Fourier Transform Infrared (FTIR) test using (Thermo- Scientific™ Nicolet™ iS™10 FTIR Spectrometer).

Results and Discussion

Study the Absorption Spectroscopy

Organic molecules of phthelocyanine and their derevatives appear characteristics optical due to the structure ring The spectra of the ZnPc in a solution of DMF/water, DMSO/water, and THF/water of various water mass percent appear in Figure 1 (a, b, & c) individually. Solvents moreover possess an influence on the photochemical and photophysical properties of MPc complexes. The interaction of a organize solvent with MPc ring rises the (HOMO) energy, causing a red-shifting of Q-band. zinc

phthalocyanine shows absorption spectra by double essential band electronic, the Q band with ultimate (685, 675 and 680) nm separately and subsequently the Soret B band with final of (340, 340 and 350) nm independently. This noticing proposes that during the previous collection of solvents, loss of symmetry occur [8]. The figure of the spectra propose the aggregation double packs: one comparable toward solutions by water mass ratio lowerthan 80% and thus the second include altogether 40% water.

One notes a faint shift to toward long wavelength for the Q band peak at water part altitude from zero to 60%. Furthermore, during this extent of water ratio, there's a decrease small through the final absorbance of this band upon the mass fraction increase. A sort of blaeching happens once the H₂O ratio boost above 40%, the Q band have a sudden reduction in

intensity and two wide little-intensity bands become broader with flat peaks at 620 nm, 750 nm. The descend variation of the ZnPc absorption ranges associated with the water mass fraction shall become official to slide alteration at the structure microscopic of the solvent.

This structural solvent alteration motivates a significant amendment of the solvent-solute interaction via aligning the zinc phthalocyanine -water interaction.

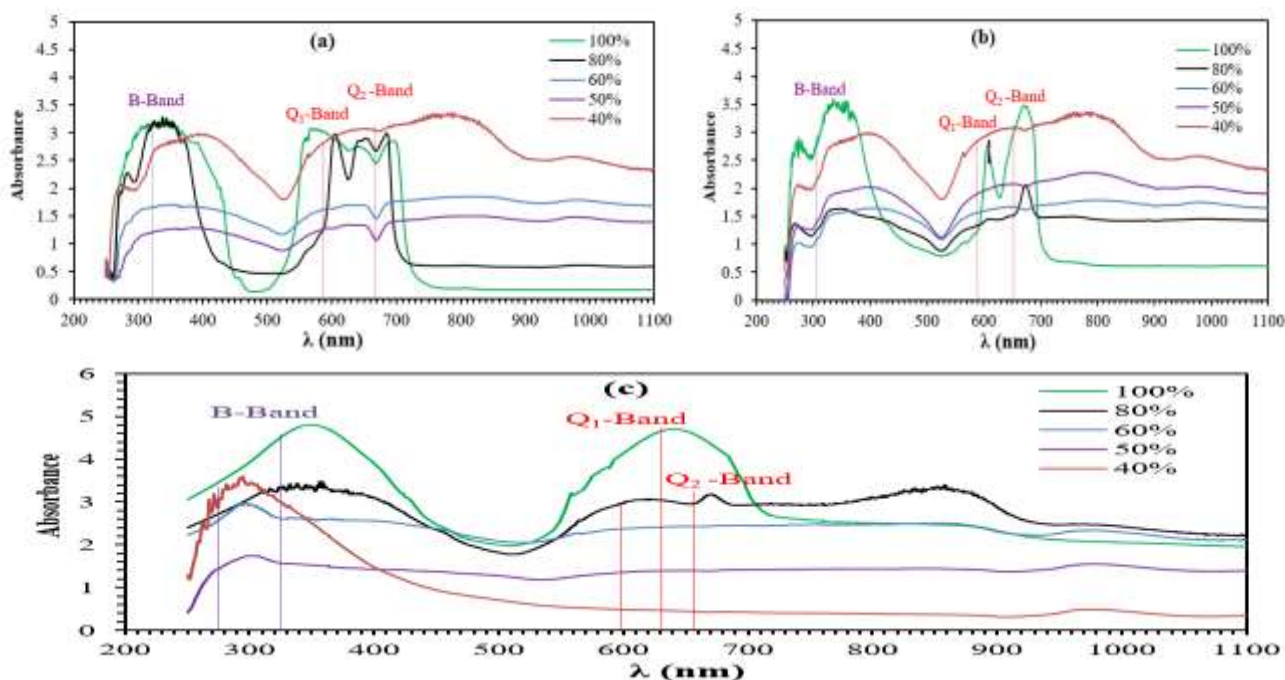


Figure 1: Absorption spectra of Zinc phthalocyanine dye in (a) DMF/H₂O, (b) DMSO/ H₂O, and THF/ H₂O, water mass percent parameter

The data is compatible with the results, point out the excess of water mass part bases a downy raise of PH [4]. The solution of absorption spectrum appear characteristic absorptions about 685 nm in the Q band region has appeared in Fig. 1(a). The other bands (Soret band) about 340 nm was observed due to the transtions from the deeper π levels to the L.U.M.O. Analysis of UV-V spectra appear no evidence of combination in solution as demonstred via a sharp unperturbed phthalocyanine Q band at 610 nm.

This result agrees with previous researches [11] The electronic absorption spectrum of ZnPc was recorded in DMSO/water solution, as shown in Figure (1.b). The DMSO /water mixture contains extremely non-ideal conducts as a result of its associative character that relies on the proportion of the two compounds. Significant deviations that occur at specific values of the water fraction into solvent mixture related to the formetion of molecular H-bond clusters such include a molecule D.M.S.O molecule and 2 molecules of H₂O or 2 molecules of D.M.S.O and one molecule of H₂O [12].

Absorption spectrum in THF/water displayed characteristic absorptions about 680 nm within Q band region, appear in Figure 1c. The peak at 680 nm for THF due to the presence of oxygen at the axial position of complexes ZnPc results in the distortion of the phthalocyanine (Pc) ring. THF contains oxygen that could react with the central Zinc of the ZnPc molecule, enhancing the distortion. From the noticing of the band at 680 nm will probably invert loss of symmetry via distortions of the metal-phthalocyanine (MPc) molecule as photolysis progressed.

The absorption maxima (Q-band) in Pcs shift towards lower energies as an outcome of the formation of molecular aggregates. The creation of aggregates may be emerging from the ability of ZnPc to create π - π accumulate structures in solution about the orientated carboxylic acid with the Zn core or with the-CN group [13]. At high water mass present the peaks are not clear-cut therefore the peaks position and the energy gap was studied only for a high concentration of ZnPc dye (80 & 100%) as depicted in Table (2).

Table 2: Absorption UV-V spectral data of ZnPc dye at several double solvents and bandgap energies (E_g)

Solvent	Ratio (%)	B-band (nm)	Q-band		Q band E_g (eV)	B band E_g (eV)
			Q ₁ peak position (nm)	Q ₂ peak position (nm)		
DMF/water	80/20	340	610	685	1.78	3.12
	100/0	340	610	700	1.73	2.84
DMSO/water	80/20	340	610	675	1.760	2.200
	100/0	340	610	675	1.780	2.980
THF/water	80/20	348	610	680	1.280	2.520
	100/0	350	640	-	1.720	2.680

The following equation can express the optical absorbance coefficient α of a semiconductor near the band edge:

Where α is the absorption coefficient, E_g is the absorption bandgap; A is constant, n rely of type transitions, n may had amount $\frac{1}{2}$, 2, $\frac{3}{2}$ and three corresponding to piable direct, piable indirect, forbedden direct and forbedden indirect transitions respectively. [13]. The bandgap energies (E_g) of ZnPc dissolved in DMF/ water, DMSO/water, and THF/water was tabulated in Table (2). The bandgap energy could be particular via extrepolation to the zero coefficients, which obtained by using equation (1)[14].

FTIR Studies

FTIR spectroscopy is an essential method in the realization of bonds and has been used to

identify and analyze the presence of the functional group and determine whether any interactions or complexation among the components. FTIR spectra in transmittance mode, for ZnPc dye dissolved in DMF/Water, DMSO/Water and THF/Water with a different ratio as illustrated in Figs. (2-4) respectively. From Fig. 2 (a & b) which describe the FTIR of ZnPc in DMF/water with a different mass percent the peak at 725 is related to C-H out of plane bending in ZnPc molecular and the peaks at 1030 and 1100 cm^{-1} are due to C-H in-plane bending in ZnPc [15].

At 1670 is a C=O stretch [16], while peaks at 2900 and 2850 C-H stretch and 2330 C-N stretch [12]. The peaks at 1395, 1450, and 1530 are CH_2 vibration; these peaks are the characteristic peaks for DMF. We can observe an increase in the peaks belong to ZnPc with the change in the ratio of the two solvent also there is a small shift toward low energy.

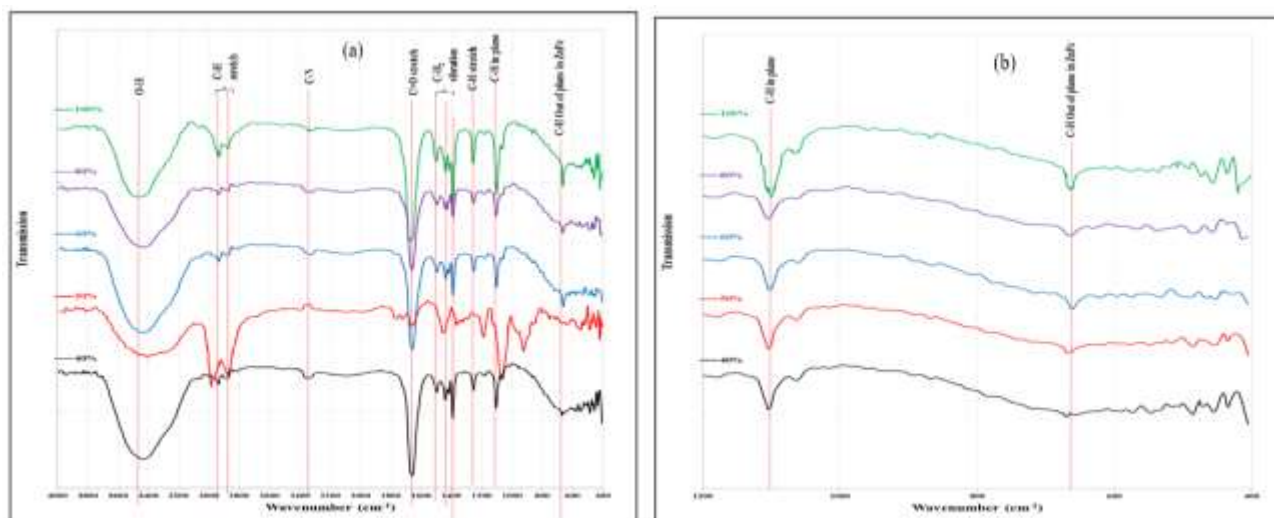
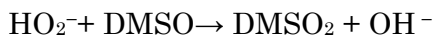


Fig. 2: FTIR spectra of ZnPc dye in binary solvent DMF/water, (a) for wavenumber range 400-4000 cm^{-1} , (b) 400-1200 cm^{-1}

Fig.3 (a & b), display FTIR spectrum which indicates the details of functional groups found in ZnPc dye. For ZnPc dye dissolved with only DMSO, extreme and sharp intense peak showed at 950 and 1020 cm^{-1} are related

S-O vibration stretching mode the characteristic of DMSO due to the alkene sp^2 C-H bend C-H stretching. The peak at (1135 cm^{-1}), is a characteristic of DMSO. The proposed the following of the reaction [17]:



However, for ZnPc dye with two solvent, the peak has been a shift to high wave number approximately 1020 cm^{-1} . The main peaks over the range ($3600\text{-}3000 \text{ cm}^{-1}$) the broadening of the band was related to O-H and N-H stretching. Peaks at 3000 and 2900 cm^{-1} related to carboxylic acid O-H stretch, and aldehyde C-H stretch nearly disappears with increase water ratio up to 60% [18] whereas the peak 1650 cm^{-1} is due to

vibration stretching of, C=O groups of carbonyl. at wavenumber 1320 and 1450 cm^{-1} correspond to the asymmetric and CH_3 bending antisymmetric, respectively [19, 20]. The modes by wavelengths of 1180 and 1191 cm^{-1} correspond to the stretching asymmetric group of SO_2 , which is the characteristic peaks for DMSO. The peak at 705 corresponds to C-H out of bending plane in ZnPc molecular [15] has appeared in Fig. 3(b). Also, one can note that there is a shift in the peaks position and an increase in the intensity of ZnPc.

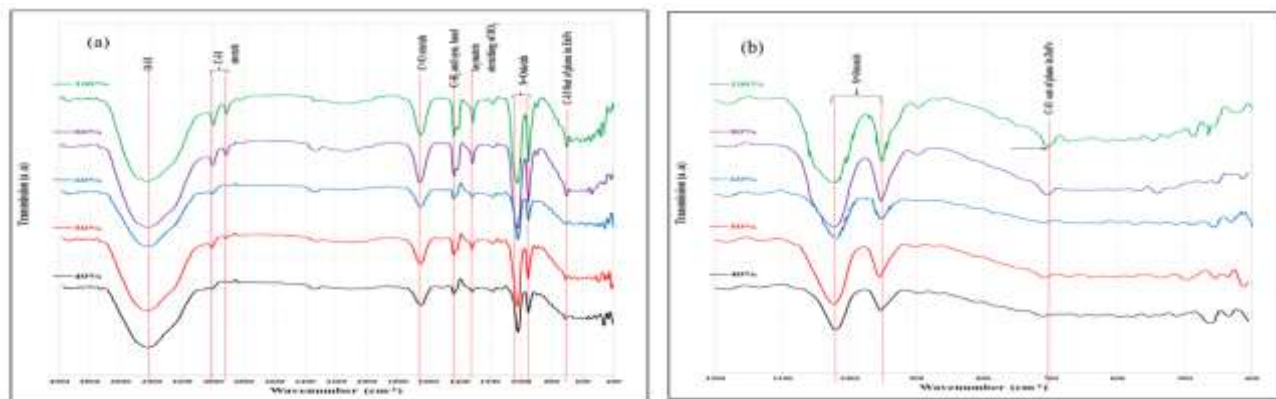


Fig. 3: FTIR spectra of ZnPc dye in binary solvent DMSO/water, (a) for wavenumber range $400\text{-}4000 \text{ cm}^{-1}$, (b) $400\text{-}1200 \text{ cm}^{-1}$

Fig. 4(a & b) shows the location of C-H in-plane bend band. There is no variation in-

band energy with a variation the mixing in binary solvent THF/Water ratio.

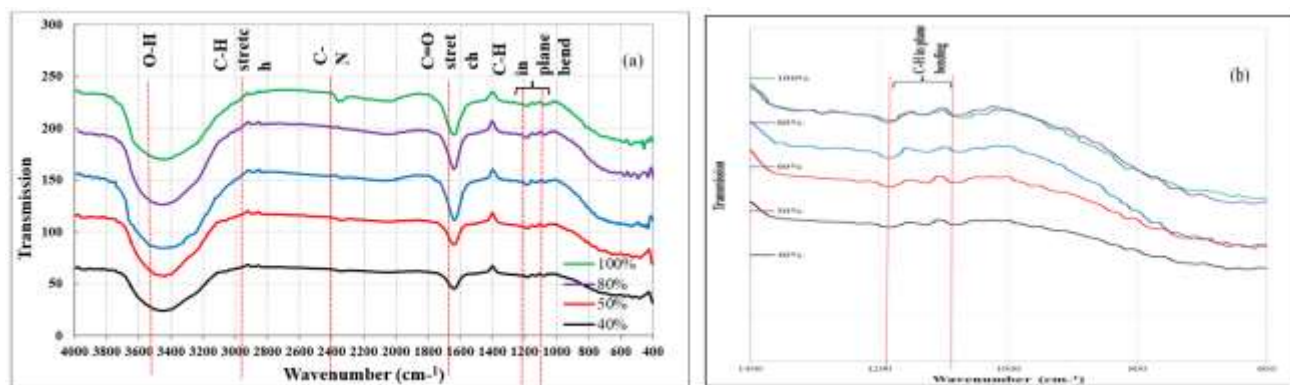


Fig. 4: FTIR spectra of ZnPc dye in binary solvent THF/water, (a) for wavenumber range $400\text{-}4000 \text{ cm}^{-1}$, (b) $400\text{-}1200 \text{ cm}^{-1}$

Conclusion

Zinc phthalocyanine ZnPc of the photophysical properties in two solvents (DMF/water, DMSO/water, and THF/water), presently informed confirm very non-ideal behavior of these two solvent mixtures. Absorption spectrum detect a dramatic

difference of intensity Q bands absorption of Zinc phthalocyanine in process for a mass water ratio more significant than 40%. This behavior has appointed for considerable modification during the solute-solvent interaction as a result of the changes in the solvent molecules assembling.

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