

Effect of Peripheral Substitution on the Thermal and Optical Properties of Metal Phthalocyanine- A Comparative Study

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Abstract: Suitability of metal phthalocyanine for wide range of material science applications depends upon its thermal stability and optical properties. In present study we substituted 4-(phenyl) thiazole moieties on to the peripheral positions of metal phthalocyanine ($M = \text{Cu, Ni, Co}$) through amide linkages. Which intern prepared by the one pot condensation reaction between tetracarboxy metal (II) phthalocyanines with 2-amino-4-(phenyl) thiazole in optimized experimental conditions. Synthesized metal complexes characterized by various spectral techniques like ¹H NMR, Mass spectra, IR and UV-Visible spectroscopic techniques. Thick films of average thickness 10 μm are prepared onto glass substrates by doctor's blade method using dispersions of synthesized compound in acetone. Optical band gap evaluated by Kubelka-Munk Model for solid state diffuse reflectance spectra recorded for thick films. Thermal stability of newly synthesized phthalocyanine complexes were investigated by means of thermogravimetric analysis (TGA). On basis of the TGA data, the kinetic and thermodynamic parameters such as activation energy (E_a), order of reaction (n), entropy change (ΔS), free energy (ΔG), enthalpy (ΔH) and frequency factor (A) were calculated using Broido's method. Comparative study of results with reported compounds revealed that, introduction of heterocyclic pendants into the MPc core results in improved thermal stability, fine-tuning of the position of the Q-band with decrease in band gap, indicating effective electronic communication between the two different ring systems with MPc core with improved thermal stability.

Keywords: Substituted metal(II)Phthalocyanine; 2-amino-4-(phenyl)thiazole; Solid state Diffuse Reflectance Spectra; Broido's method; Kubelka-Munk Model

1. INTRODUCTION

Phthalocyanines are planar, macrocyclic aromatic compounds, which are isoelectronic with porphyrin molecule consisting of 4 isoindole units linked together by nitrogen atoms. Phthalocyanine (Pc) and metallophthalocyanines (MPcs) have been intensively studied during last few years because of their electrical and optical properties as well as their chemical and thermal stability [1–4]. Generally phthalocyanines (Pcs) were a class of organic semiconductor with alternate single-double bond structure [5]. Phthalocyanines absorb light on either side of blue-green region; hence its complexes were used as photoconductors. Metal phthalocyanines (MPc's) have gained considerable attention in recent years because they have been successfully applied in many applications such as optical logic display devices [6], electrotopography, solar cells [7,8], sensitizers color filters [9] and optical recording [10]. Peripheral substitution for core metal phthalocyanine proved to be best method improve its physico-chemical properties and applicability. Relatively few studies have focused on the heterocycle substituted MPc's although there is evidence that they may exhibit properties suitable for gas sensing applications [11]. It has also been shown that the heterocycle substituted MPc's exhibit remarkable optical properties and thermal stability over a larger temperature range compared to unsubstituted MPc's [12]. It has been suggested that, the UV-VIS spectrum obtained for (Pcs) originates from the molecular orbital within aromatic 18 π electron system and from overlapping on central metal ions. In present study we investigated the basic properties of heterocycle substituted metal phthalocyanines such as absorption, transmission, etc. [13] to get the optical absorption coefficient (a), extinction coefficient (k), refractive index (n) and their dependence on wavelength of the incident radiation to valuable information on the basic electronic parameters of these materials.

2. EXPERIMENTAL

2.1 Synthesis of Tetra(4-phenyl-1,3-thiazole-2-amide)M(II)phthalocyanine:

Title complexes prepared by one pot condensation reaction between tetracarboxy metal (II) phthalocyanines with 2-amino-4-(phenyl) thiazole in optimized experimental conditions. Synthesized metal complexes characterized by various spectral techniques like ¹H NMR, Mass spectra, IR and UV-Visible spectroscopic techniques [14].

2.2 Optical measurements

Band gap energy of the synthesized compounds was determined by recording reflectance spectra in solid state. Thick films of average thickness 10 μm are prepared onto glass substrates by doctor's blade method using dispersions of synthesized compound in acetone. The optical reflectance was measured by using a UV-Visible-NIR Ocean optics–HR 4000 spectrophotometer type, light source; DT-MINI-2-GS, Jaz detector (in the spectral range of 200-900 nm with a scan step of 2 nm. A reference BaSO₄ surface was used throughout the measurements [15].

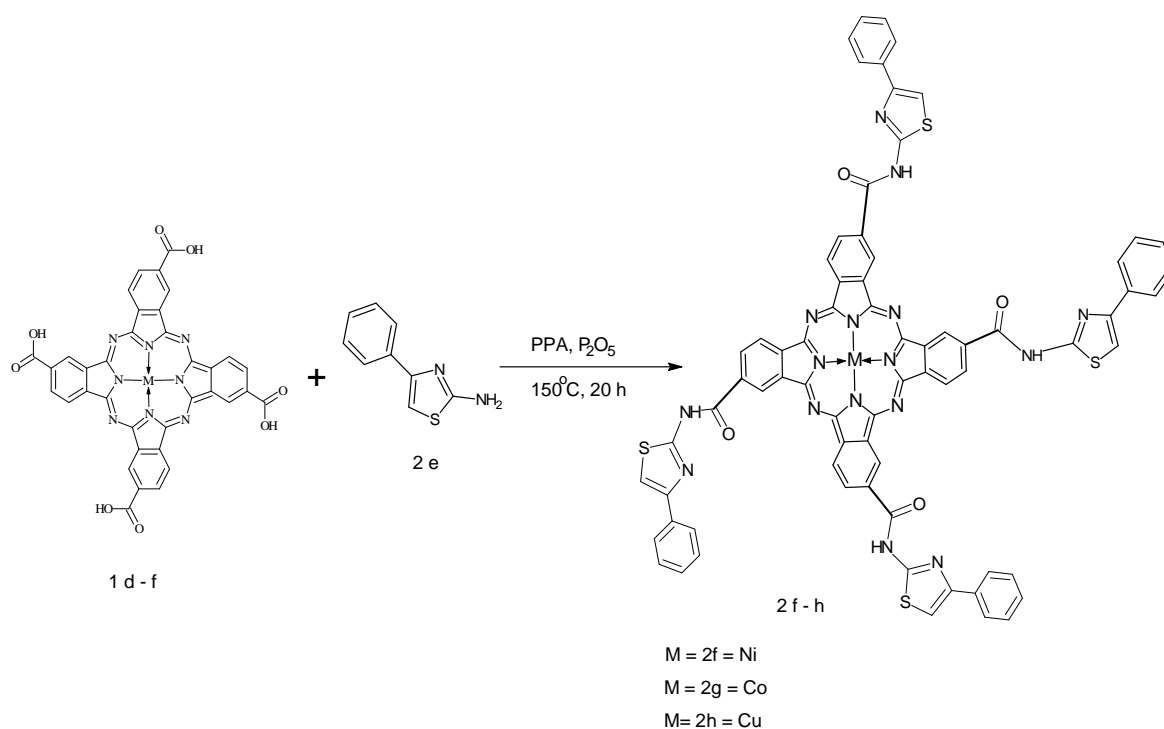


Figure 1: Synthetic route for the preparation of Tetra(4-phenyl-1,3-thiazole-2-amide)M(II)phthalocyanine

2.3 Thermogravimetric analysis

The dynamic thermogravimetric analyses were carried out in oxidizing atmosphere for synthesized compounds using SHIMADZU TA-60WS Thermal analyzer in the temperature range 30- 800°C with heating rate of 10°C/min. The typical TG curves of the phthalocyanine complexes are given in figure 6.

3. RESULTS AND DISCUSSION

3.1 Method for calculation of energy of band gap

UV-Vis spectra were recorded for complexes in range 200 to 800 nm showed characteristic bands in the range 320-340 nm, 620-630 nm and 680-685 nm representing B and Q band respectively. Split of Q band gives the evidence for the peripheral substitution of phenyl thiazole, thiadiazole through amide bond. Because of extended conjugation by heterocycle substitution bathochromic shift is observed in comparison with unsubstituted metal phthalocyanine. UV-Visible data presented in table 1, figure 2.

Table 1: UV-Visible spectral and optical band gap data of compound 2(f-h).

Compound	max (in nm)	Molar extinction coefficient	Band gap (eV)
2f	350.2	30.0X10 ³	-
	618.05	14.55 X10 ³	2.521
	670.20	12.30 X10 ³	1.654
2g	340.15	18.44 X10 ³	-
	640.11	13.52 X10 ³	2.802
	692.32	20.05 X10 ³	2.102
2h	328.20	18.32 X10 ³	-
	612.10	10.33 X10 ³	1.894
	686.05	19.02 X10 ³	1.361

When a light beam impinges on a thick film deposited on a substrate, multiple reflections and absorbance occur at the two boundary surfaces of the system. Kubelka-Munk Model is used to determine the band gap energy for synthesised compounds [16]. Assuming that the simultaneous reflection, absorption and scattering occurs in thick film, the expression of R, K and S is given by Kubelk-Munk,

$$K/S = \frac{F(R)}{1-R} = \frac{(1-R)^2}{2R} \quad (1)$$

Where, K is the unit absorption coefficient, S is the unit scattering coefficient, R is the reflectance co-efficient, absorption co-efficient is also defined as

$$K = 2.303.A/d \quad (2)$$

A is the absorbance; d is the thickness of the sample. Relating equation (1) and (2),

$$[F(R).hv]^n = [F(R).E]^n = (h\nu - E_g)^n = B(h\nu - E_g)^n \quad (3)$$

Where, R and $F(R)$ are experimentally determined by reflectance spectra

$$(h\nu - E_g)^n = -E_g \cdot hv + B \cdot h\nu \quad (4)$$

$$y = mx + c$$

Where, $h\nu$ is the photonic energy, n depends on the electron transition (direct $n = 2$ or indirect $n = 1/2$). E_g is the value of the optical band gap corresponding to transitions indicated by the value of n. The factor B depends on the transition probability and can be assumed to be constant within the optical frequency range. Tauc plots of $(h\nu - E_g)^n$ vs $h\nu$ near the absorption edge of the Q- and B-bands for the thick films produce a linear fit over a wider range in $h\nu$ as shown in Figure 3-5. The band gap is obtained by extrapolating the linear part of the graphics to the axis of the abscissa.

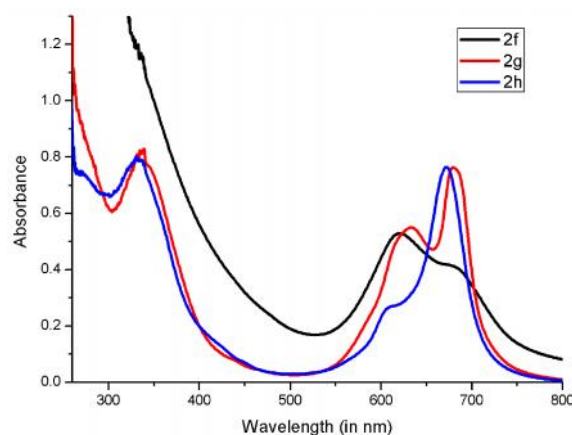


Figure 2: UV-Visible spectra of compound 2 (f-h)

Results revealed that, extended π -conjugation due to heterocycle substitution results in decrease in optical band gap energy in comparison with unsubstituted metal phthalocyanine [17,18].

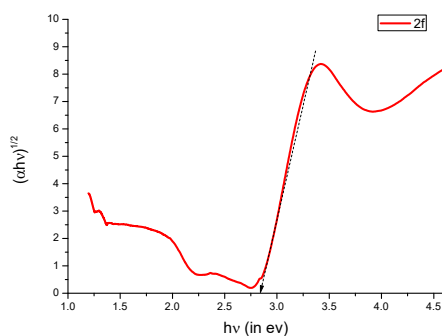


Figure 3: $(\alpha hv)^{1/2}$ vs $h\nu$ plots for compound 2f

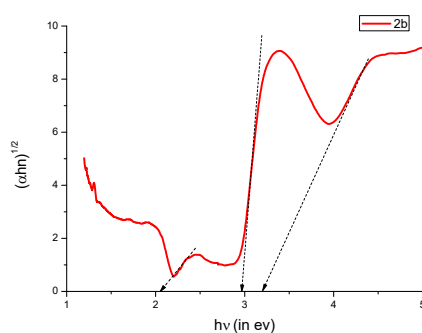


Figure 4: $(\alpha hv)^{1/2}$ vs $h\nu$ plots for compound 2g

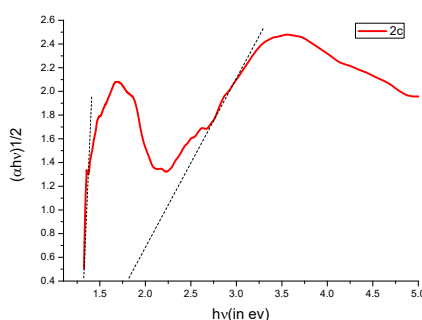


Figure 5: $(\alpha hv)^{1/2}$ vs $h\nu$ plots for compound 2h

3.2 Calculation of Kinetic parameters

Analysis of thermogravimetric curves and the corresponding data represented in Table 2. Data reveals that the complexes undergo decomposition in three steps. First step degradation which takes place in temperature region 30-110°C; which results in weight loss of 2.3-3.0% was observed for all the complexes, corresponding to the loss of free moisture. All complexes displayed weight loss in the range 250-372 °C, which corresponds to the loss of heterocycle substituent present on the peripheral positions of complexes. Even though, there was a weight loss corresponding to substituent in second step degradation, no sharp weight loss was observed. The

major weight loss was observed for all the complexes in the temperature range 450-800°C corresponding to oxidative degradation of phthalocyanine moiety.

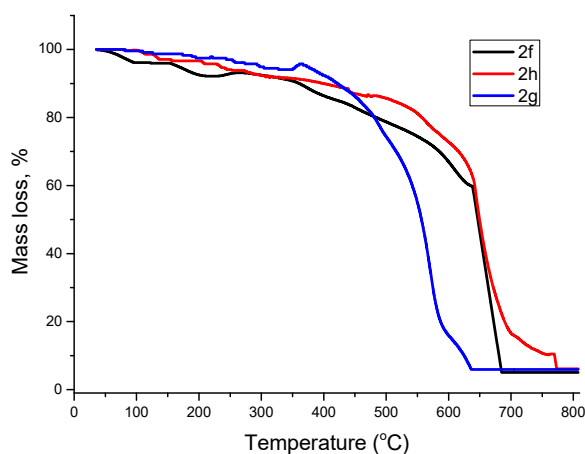


Figure 6: TGA curves for compounds 2(f-g)

DTA results revealed that all degradation steps are exothermic in nature. The final undecomposed products were found to be corresponding metal oxides.

In the present investigation, the general thermal behavior of the synthesized phthalocyanine complexes in terms of stability ranges, peak temperatures and values of kinetic parameters, are discussed. Broidos graphical procedure is used for the straight line decomposition portion of the thermogravimetric analytical curves to evaluate activation energies[16]. The graphical plots of $\ln[\ln(1/y)]$ vs $10^3/TK^{-1}$ obtained for compounds 2(g-h) are presented in Fig. 9-10. The value of 'y' represents the fraction of compound remained at the temperature T (K). A plot of $\log(a/a-x)$ vs time is also shown in figure 7-8.

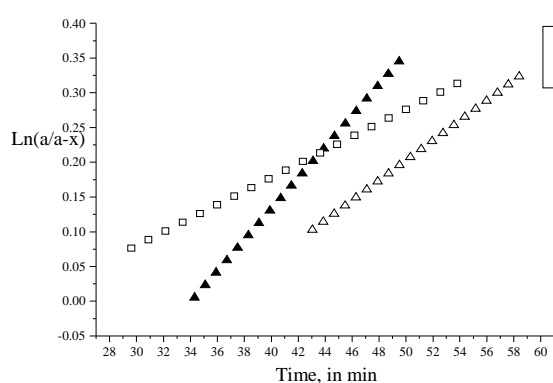


Fig 7. Plots of $\ln(a/a-x)$ vs time for first step degradation of the phthalocyanine complexes 2(a-c).

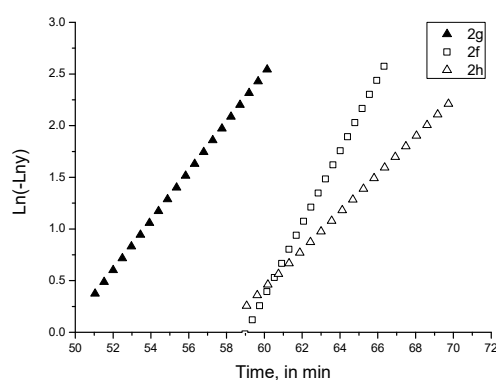


Figure 8: Plots of $\ln(a/a-x)$ vs time for second step degradation of the phthalocyanine complexes 2(a-c).

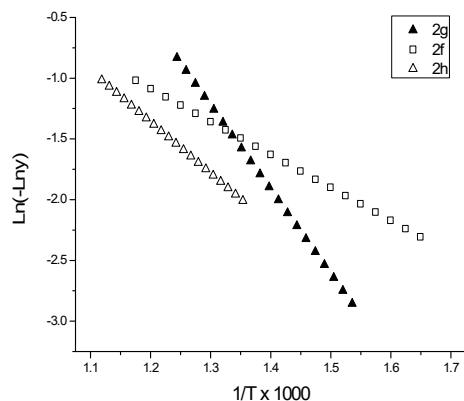


Figure 9: Ln(-Ln y) vs 1000/T plots for first step degradation using Broido method.

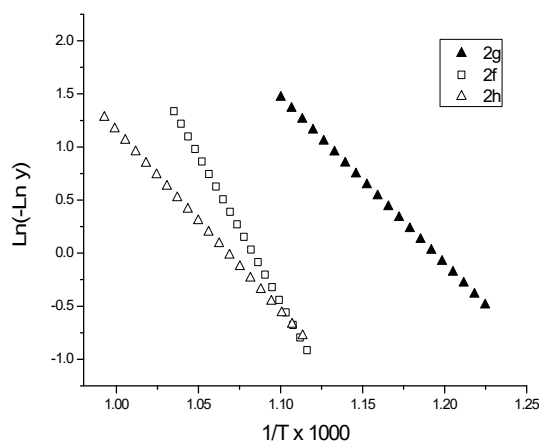


Figure 10: Ln(-Ln y) vs 1000/T plots for second step degradation using Broido method

Where ‘a’ is the initial weight loss of the sample taken and (a-x) is the weight of the sample left after time t. The plots indicate that all the three complexes degrade through a first order process. The slopes of the plots are determined and used to evaluate the activation energies of complexes and the data presented in table 2. The activation energies are in the order 55 to 150 KJ mol⁻¹ the thermodynamic properties like enthalpy (ΔH), entropy (ΔS), free energy (ΔG) and frequency factor (A) are calculated using the standard equation.

$$\Delta H = E_a - RT$$

$$\Delta S = \Delta H/T - 19.15 \log T/K - 197.57$$

$$\Delta G = \Delta H - T\Delta S$$

$$A = RT/Nhe^{\Delta S/R}$$

Where R= gas constant, T= degradation temperature in K, K= rate constant, N= Avogadro’s number, h= plank’s constant. The kinetic and thermodynamic parameters obtained for the degradation of these complexes are summarized in Table 2.4. The first order rate constant is determined based on the weight change with time in the linear degradation portion of the thermodynamic curve and used for the evaluation of entropy change. The mechanism of degradation found to be same for all the synthesized complexes.

Table 2: kinetic and thermodynamic parameters of synthesised compounds.

Compound	Decomposition range (°C)	DTA (°C)	E _a (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹)	A (s ⁻¹)
2g	370-530	452	57.67	61.42	126570	-279.89	3.92X10 ¹⁶
	540-630	587.5	130.47	135.35	154230	-262.29	6.14X10 ¹⁵
2f	330-580	451.5	22.57	26.32	129523	-286.82	9.02 X10 ¹⁶
	620-690	660.5	230.73	236.22	171896	-259.89	5.18 X10 ¹⁵
2h	470-620	542	35.16	39.67	154584	-285.14	8.85 X10 ¹⁶
	640-730	680.5	141.56	147.22	180966	-265.72	1.07 X10 ¹⁶

4. CONCLUSION

The data of the absorption spectra obtained verifies that heterocyclic substitution having marked effect on position and nature of Soret band Q-band. Extended π - π conjugation extended due to heterocycle substitution resulted in decrease in optical band gap energy in comparison with unsubstituted metal phthalocyanine. Degradation kinetic studies help to know about its thermal stability and suitability of synthesized complexes for wide range of applications.

5. REFERENCES

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