

**Synthesis and Characterization of New Zinc phthalocyanine - dodecyl succinic
Anhydride Benzoic groups**

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Abstract

In this study a newly synthesized molecules of 4,4',4''-tri-(dodecyl succinic anhydride)-4'''-(5-amino salicylic acid) Zinc phthalocyanine (I), tetra-(5-amino salicylic acid)zinc phthalocyanine(E) and 4,4',4''-triamino-4'''-nitro Zinc phthalocyanine (S). The reaction of 4- nitro Phthalonitrile and 4- amino Phthalonitrile with ZnCl₂ in the presence of dimethyl amino ethanol afforded 4,4',4''-triamino-4'''-nitro Zinc phthalocyanine.

This product was reacted with 5-amino salicylic acid to yield tetra-(5-amino salicylic acid)zinc phthalocyanine. After that, a dodecyl succinic anhydride was added on amine group of benzoic rings to afford 4,4',4''-tri-(dodecyl succinic anhydride)-4'''-(5-amino salicylic acid) Zinc phthalocyanine. The synthesized compounds were further recrystallized using different solvents. The newly synthesized phthalocyanine was characterized using UV-Visible spectroscopy, ¹H NMR and FT-IR spectroscopy.

Keywords: zinc phthalocyanine; dodecyl succinic anhydride, 5-amino salicylic acid.

1. Introduction

Phthalocyanine is an intensely blue-green-colored, macrocyclic aromatic compound that is widely used in dyes. It is a planar heterocyclic aromatic and tetra-azo derivative of four isoindole units in which connected by four nitrogen atoms forming an internal 16-membered ring as carbon and nitrogen alternate atoms system have 18 p-electron [1]. It is widely used as colorants and have been recognized as most stable organic colourants due to its extensive structural resonance stabilization. It has resistant to almost all acids, alkalis, oxidizing and reducing agents[2-4], (Figure 1). The peripheral and non-peripheral positions on the benzenoid ring of phthalocyanines can be substituted with many other functional groups to impart new properties.

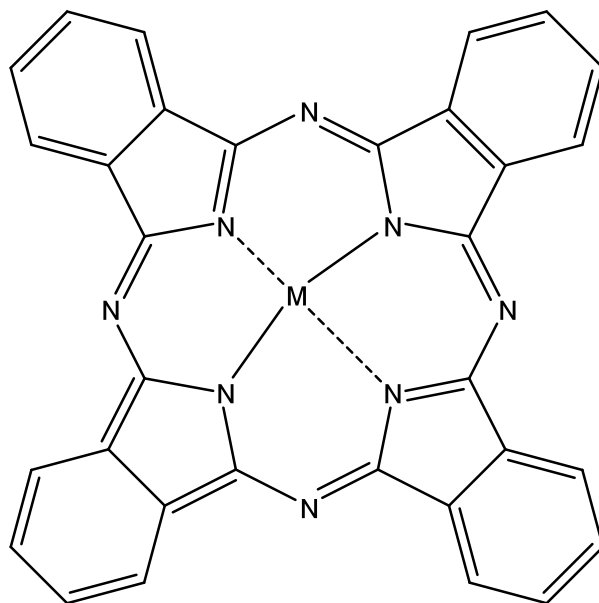
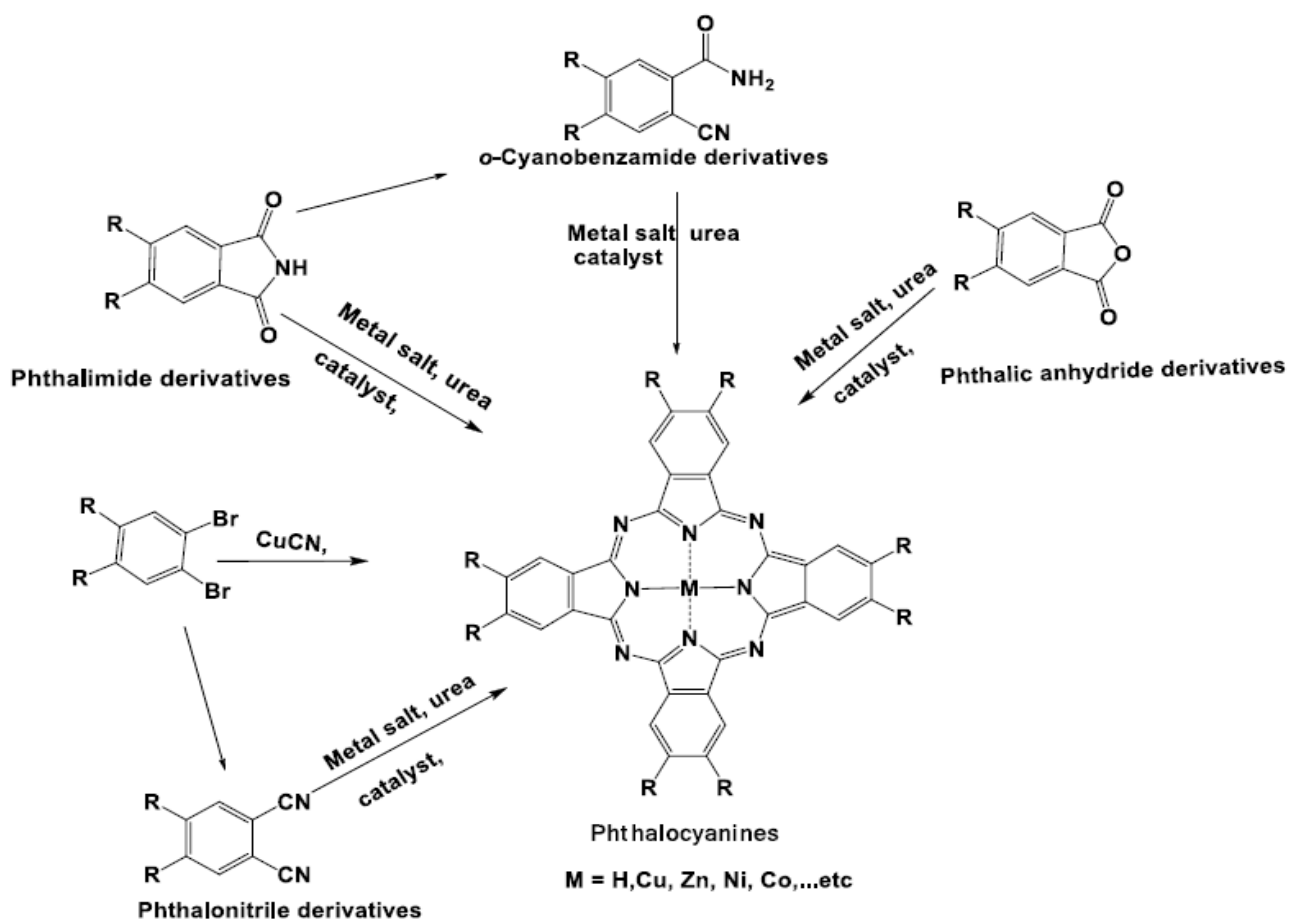


Figure 1. The structures of phthalocyanines

Phthalocyanine (Pc) and their substituted derivatives (Pcs) in the last years were intensively studied for photodynamic therapy for cancer [5-6]. In the phthalocyanine ring, both hydrophobic and hydrophilic groups are useful for the best rendering in tumor selectivity [7]. It has been used in many applications depending on the substitution in the peripheral position. The properties of their optical, electrical and thermal stability[8] is determine its application as such field-effect transistors, gas sensors, optical limiters, optical recording materials and solar cells[9]. It can be created by different ways according to the type of Pc to be synthesized; metal-free, metal, symmetrical or asymmetrical Phthalocyanine. Created Pc based on many factors: temperature (to facilitate melting of the precursor and rapid cyclotetramerization), precursor metal salt (metals, sulphates, halides, metal salts and oxides), solvent (high boiling point solvents), base and catalyst. Phthalocyanines is formed through cyclotetramerization of phthalonitrile precursors, phthalimide, phthalic acids, phthalic anhydrides in the presence of a metal salt and Pcs of metal-free (Scheme 1).



Scheme 1: Schematic description for the created routes of metallophthalocyanines from different routes.

In this study a new zinc and carboxylic phthalocyanines and Zn carboxylic- dodecenyphthalocyanines were Synthesized and characterization as presented in Figure 2.

Synthesis of compounds U, S, E and I

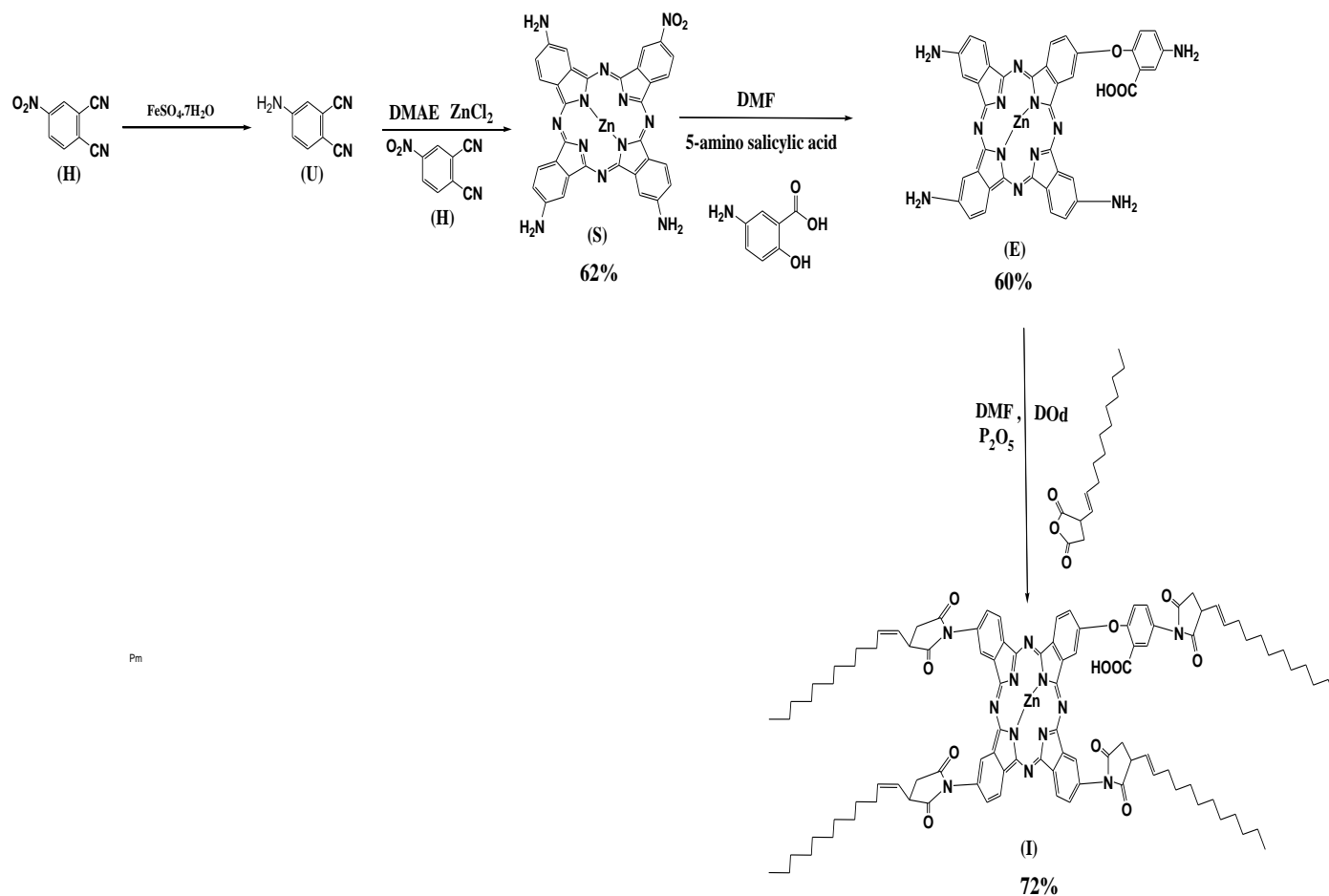


Figure 2. Syntheses of compounds S, E and I

2. Experimental

Synthesis of 4,4',4''-triamino-4'''-nitro Zinc phthalocyanine (S)

A mixture of 4-nitro phthalonitrile (0.19g, 1mmol, eq= 0.322), 4-amino phthalonitrile (0.5g, 3mmol) and ZnCl_2 (0.16g, 1.173 mmol, eq= 0.34) in 2ml dimethylaminoethanol (DMAE), were stirred at 185°C for 2h under nitrogen atmosphere. The product was cooled to the room temperature and washed with water and ethanol. The precipitate was purified by column chromatography over silica gel using a mixture of (DMF: n-hexane)(50:10). afforded green precipitate (0.46g, 62%) of the compound (S), TLC $R_f = 0.59$ (DMF: DCM: n-hexane)(7:2:1).

Synthesis of tetra-(5-amino salicylic acid)zinc phthalocyanine (E)

A mixture of compound (S) (0.5g ,0.74mmol) and 5-Amino-2-hydroxybenzoic Acid (0.229g) and then K₂CO₃ (0.103 g) in DMF (10 mL) was heated at 70°C and stirred for 9h under nitrogen atmosphere, after that K₂CO₃ (0.103g) was added and stirred 9h. Then the mixture was cooled to the room temperature, and 1N HCl was added. The mixture was filtered and the precipitate was purified by column chromatography over silica gel using a mixture of (DMF: n-hexane) (4:1) as eluent, afforded green precipitate (0.08g, 13.51%) of compound (E) ,TLC R_f= 0.7 (DMF:DCM: n-hexane)(6:3:1).

Synthesis of 4,4',4''-tri-(dodecanyl succinic anhydride)-4'''-(5-amino salicylic acid) Zinc phthalocyanine (I)

Dodecanyl succinic anhydride (0.275 g, 1.032 mmol) and (E) (0.2 g, 0.258 mmol) were dissolved separately in DMF (10 mL) to yield solutions (1) and (2), respectively. Solution (1) was added dropwise into solution (2) to give solution (3). which heated kept at 30°C and stirred for 2h. P₂O₅ (0.08 g, 0.571 mmol) was dissolved in H₂SO₄ (5 mL) and DMF (10 mL) was added dropwise into solution (3) and the mixture was stirred at 70°C for 2 hours. The mixture was cooled in the ice bath and added cold water afforded green precipitate. The formed precipitate was filtered and washed with distilled water. Afforded green precipitate (0.09 g, 19.73%) of compound (I), TLC R_f = 0.73 (DCM: n-hexane) (4:1).

3- Results and discussion

4-Amino phthalonitrile (U) was prepared by mixing 2.2 g FeSO₄.7H₂O and 1g of 4-nitrophthalonitrile (H) its FT-IR spectrum is given in Figure (3). Physical properties, FT-IR is identical with the reported in the literature[18]. FT-IR spectrum of (U) Figure(4) shows the appearance of NH₂ peaks at 3477 cm⁻¹ and 3377 cm⁻¹, C–H of aromatic 3045 cm⁻¹, nitrile group at 2236 cm⁻¹ and –C–C– of aromatic at 1456 cm⁻¹ that prove to conversion 4-nitro phthalonitrile to 4-amino phthalonitrile.

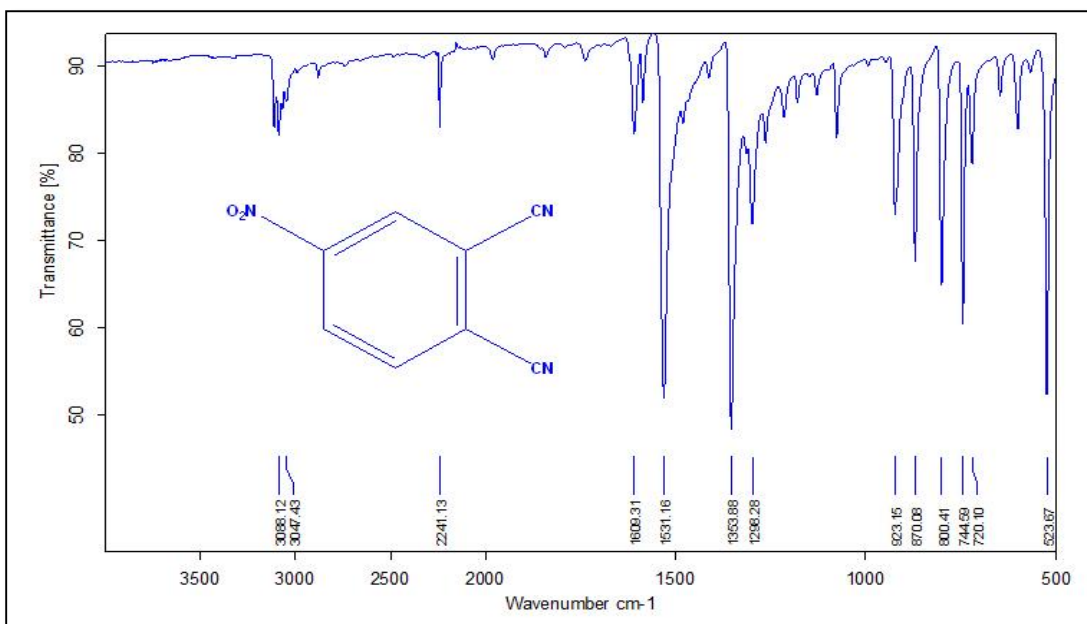


Figure 3. FT-IR spectrum of compound (H).

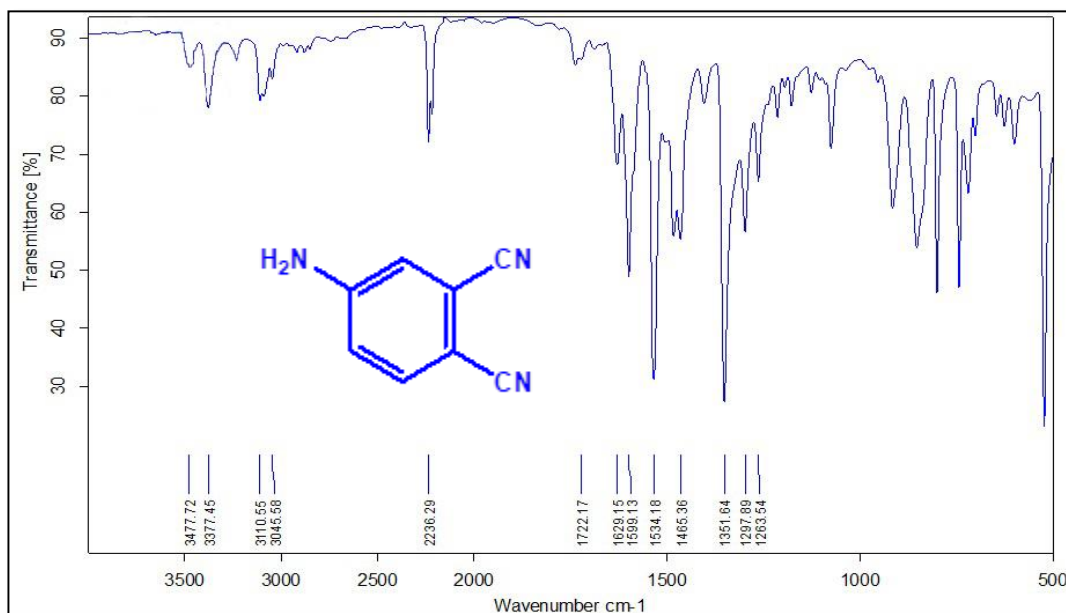


Figure 4. FT-IR spectrum of 4-amino phthalonitrile (U)

The UV – visible spectrum of 4-amino phthalonitrile (U) shows by the appearance absorption bands at (320) nm in Figure (5).

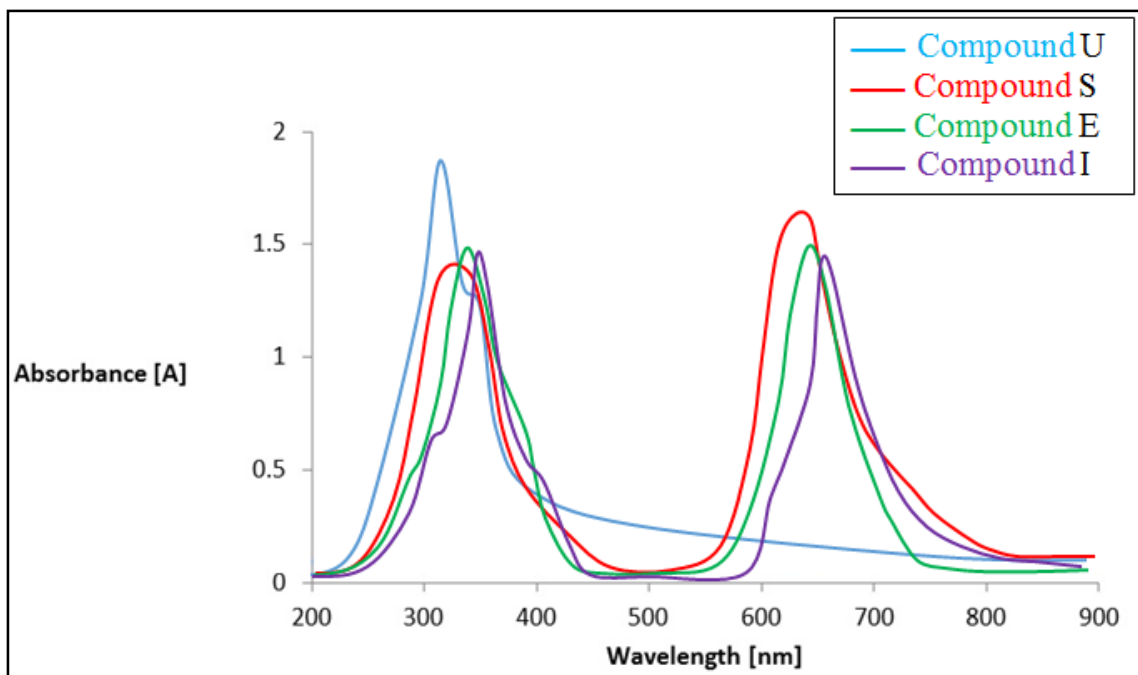


Figure 5. UV – Visible spectrum of compound U, S, E and I recorded in DMF (1×10^{-4} M).

Compound 4,4',4''-triamino-4'''-nitro zinc phthalocyanine (S) was prepared by mixing (3.49 mmol) of 4-amino phthalonitrile, (1.09 mmol) 4-nitro phthalonitrile and (1.17 mmol) of $ZnCl_2$. FT-IR spectrum of compound (S) Figure (6) in comparison with 4-amino phthalonitrile and 4-nitro phthalonitrile, shows peaks at 3247 cm^{-1} for NH_2 , C–H of aromatic at 3164 cm^{-1} and $-C=C-$ of aromatic at 1588 cm^{-1} , C–N at 1316 and aromatic group at 826 cm^{-1} . Disappearance of nitrile group band at 2236 cm^{-1} confirms conversion of 4,4',4''-triamino-4'''-nitro zinc phthalocyanine (S).

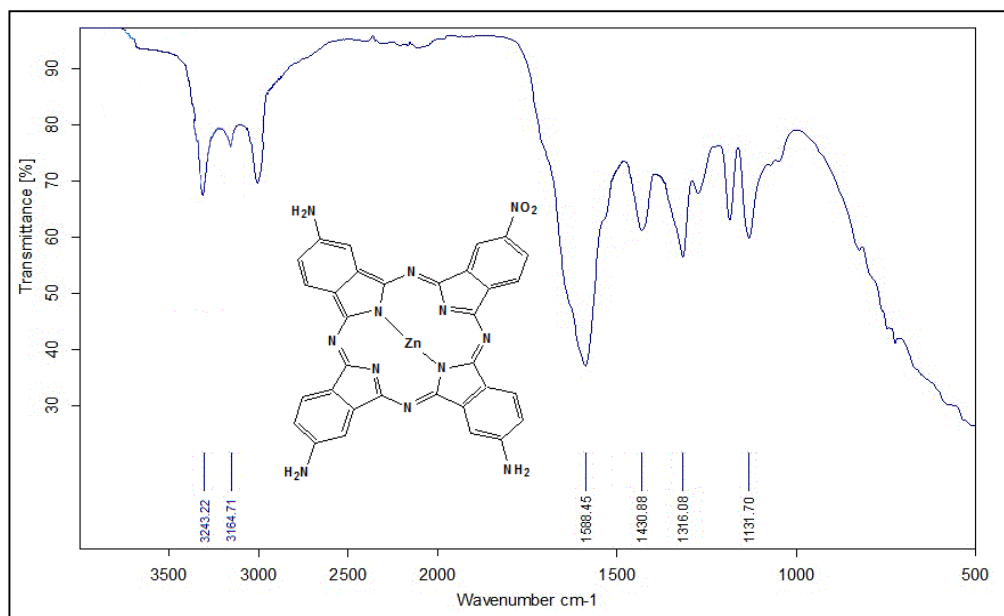


Figure 6. FT-IR spectrum of compound (S)

^1H NMR of Compound (S) Figure (7) shows the peaks (7 and 7.9) ppm of (12H, Pc-CH) and a broad singlet peak at 6.7 ppm of NH_2 proton

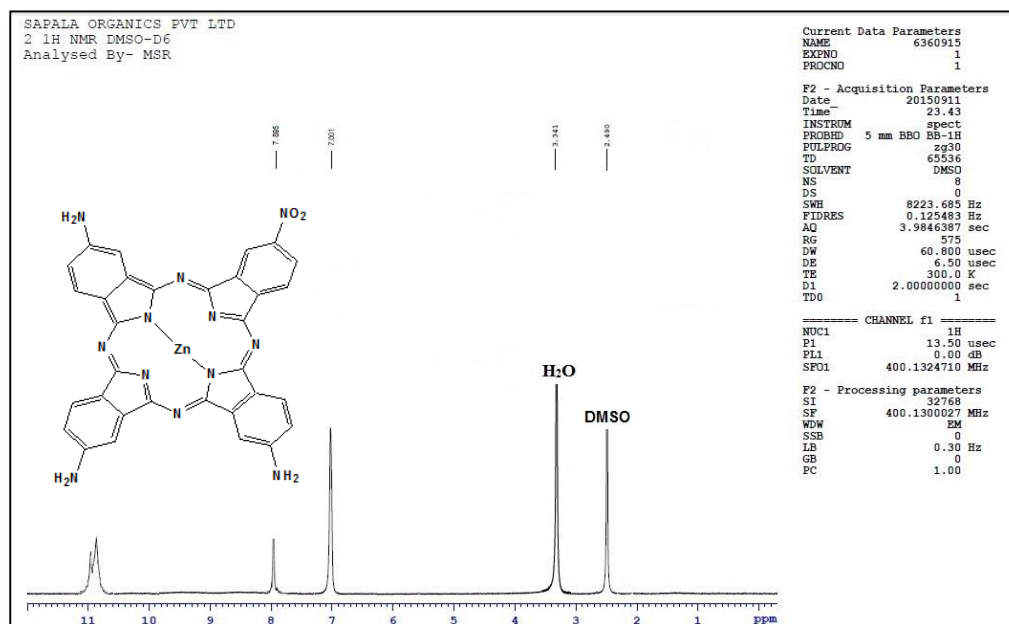


Figure 7. ^1H NMR spectrum of compound (S)

The UV – Visible spectrum of compound (S) Figure (5) shows of two absorption bands , the first at (380.35) nm which is called B or soret – band and the second at the (669.71) nm which is called Q – band which is near to IR region, corresponds to an optically determined band gap energy (1.77 eV).

FT-IR spectrum of compound 4,4',4'' -triamino-[5-Amino-2-hydroxybenzoic Acid] zinc phthalocyanine (E) Figure (8) shows appearance peaks at 3389 cm^{-1} and 3291 cm^{-1} for NH_2 , C–H of aromatic at 3189 cm^{-1} , O–H of carboxylic acids at 2976 cm^{-1} , C=O of carboxylic acids at 1675 cm^{-1} , –C=C– stretch of aromatic at 1588 cm^{-1} , C–O at 1131 cm^{-1} and aromatic group at 876 cm^{-1} Disappearance of NO_2 band at 1291 cm^{-1} , 1524 cm^{-1} confirm linking of 4,4',4'' -triamino-4'''-nitro zinc phthalocyanine (S) with 5-amino salicylic acid.

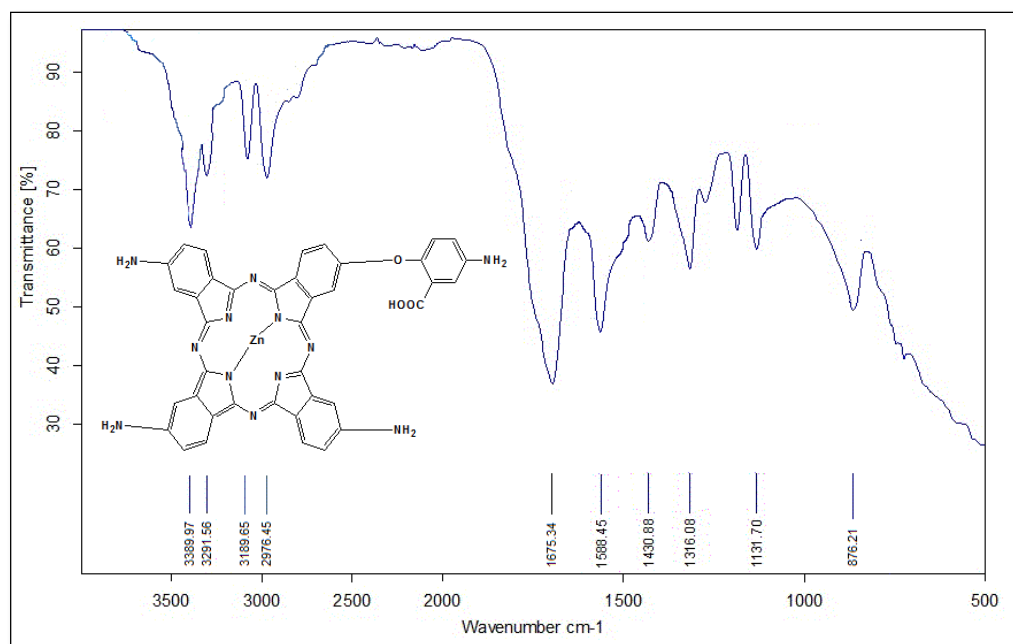


Figure 8. FT-IR spectrum of compound (E)

^1H NMR of (E) Figure (9) shows OH protons of carboxylic acid at (10.689) ppm, 7.112 ppm of (12H , Pc-CH) , 8.145 ppm of (12H , benzoic rings) and NH_2 protons at 5.792 ppm.

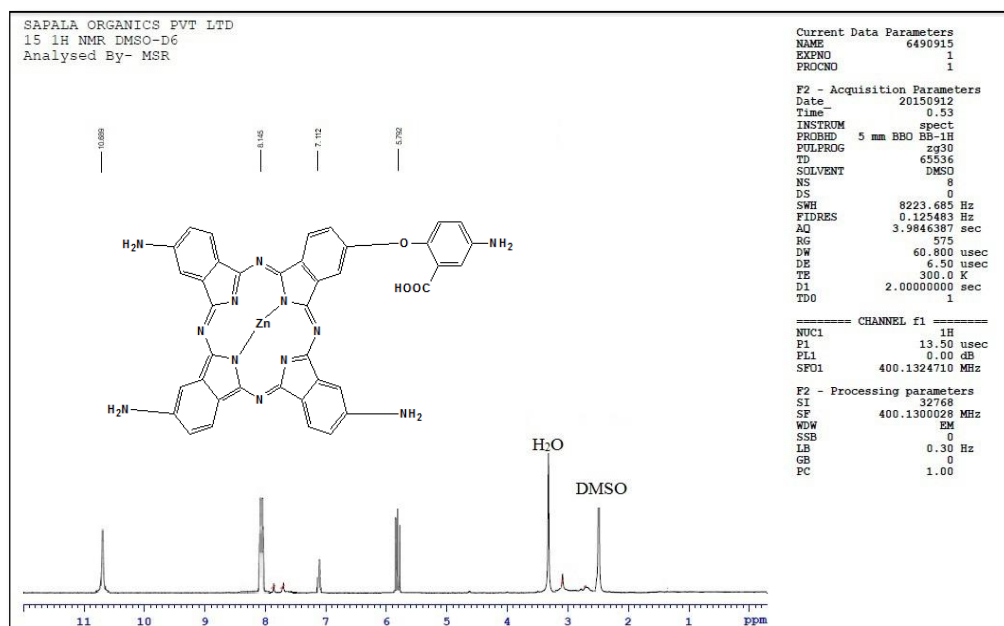


Figure 9. ^1H NMR spectrum of compound (**E**)

The UV – Visible spectrum of compound (**E**), Figure (5) shows of two absorption bands , the first at (359.25) nm which is called B or soret – band and the second at the (666.7) nm which is called Q – band which is near to IR region, corresponds to an optically determined band gap energy (1.77 eV).

FT-IR spectrum of compound (**I**), Figure (10) shows disappearance of NH_2 peaks at 3389 cm^{-1} and 3291 cm^{-1} , shows O–H of carboxylic acids at $(2798)\text{ cm}^{-1}$, C–H stretch aromatic at 3187 cm^{-1} , C-H aliphatic at 2957 cm^{-1} , C=O of carboxylic acids at 1679 cm^{-1} , C=C aliphatic at 1646 cm^{-1} , C=O at 1765 cm^{-1} , – C=C– stretch aromatic at 1491 cm^{-1} , C-N at 1163 cm^{-1} , C–O ether at 1082 cm^{-1} , and aromatic group at 798 cm^{-1} confirmed linking dodecanyl succinic anhydride with (**E**).

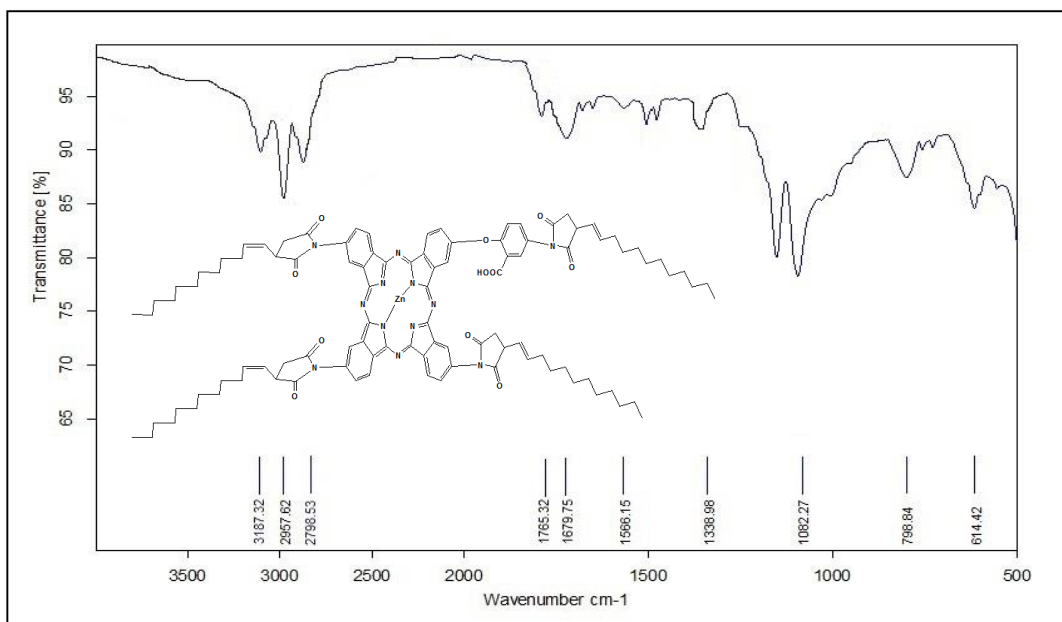


Figure 10. FT-IR spectrum of compound (**I**)

^1H NMR spectrum of compound (**I**), Figure(11) shows appearance OH protons for carboxylic acid at (11.28) ppm, (5.14) ppm of alkene, (6.65, 7.11) ppm of (12H , Pc-CH), (8.42) ppm of (12H , benzoic rings) , (0.74) ppm of CH_3 proton and (2.34) ppm of CH_2 proton.

The UV – Visible spectrum of compound (**I**), Figure (2) shows of two absorption bands , the first at (359.25) nm which is called B or soret – band and the second at the (666.7) nm which is called Q – band which is near to IR region, corresponds to an optically determined band gap energy (1.77 eV).

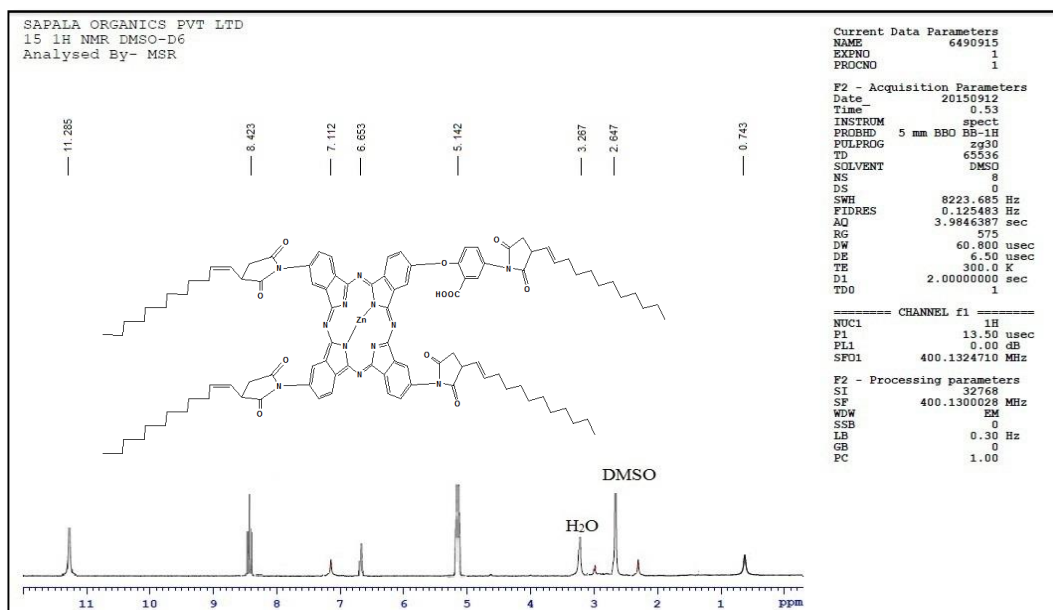


Figure 11. ^1H NMR spectrum of compound (I)

Table (1) Physical properties of compounds *U*, *S*, *E* and *I*

Compound	Chemical formula	M.Wt (g/mol)	Color	Melting point(m.p)	Yield%	TLC(R_F)
U	$\text{C}_8\text{H}_5\text{N}_3$	143.15	brown	179-181°C	51%	0.57 (Ethanol-Hexane) (2:1)
S	$\text{C}_{32}\text{H}_{18}\text{N}_{12}\text{O}_2\text{Zn}$	667.95	Green	>300 °C	62%	0.52 (DCM:n-hexane) (4:1)
E	$\text{C}_{39}\text{H}_{24}\text{N}_{12}\text{O}_3\text{Zn}$	774.08	Green	>300 °C	60%	0.64 (DMF:DCM:n- hexane) (6:3:1)

I	C ₁₀₃ H ₁₂₀ N ₁₂ O ₁₁ Zn	1767.52	Green	>300 °C	72%	0.73 (DCM:n-hexane) (4:1)
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Conclusion

Zinc, copper, and nickel phthalocyanines have been successfully synthesised using a new nitro and amino phthalonitrile precursors. The photophysical and photochemical properties associated with the molecules synthesised in this work have been determined. All the phthalocyanines are soluble in common organic solvents such as DMF, DMSO, THF and DCM. The ¹H NMR and FT-IR of all the synthesized phthalocyanines displayed characteristic bands proving the formation of the desired Pc from the starting material. The UV-vis spectra shows that these new compounds have strong absorptions towards the NIR region between 646 and 720 nm

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