



Synthesis and Characterization of Tetraformamido [2-amino-5-(phenyl)thiazole] substituted metal Phthalocyanines

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Abstract

Title compound were synthesised by the simple method by the melt condensation of the tetracarboxy metal phthalocyanine with 2-amino-5-phenyl thiazole. Proposed method is better method for the synthesis of heterocycles substituted soluble metal phthalocyanine. Soluble phthalocyanine obtained in good yield and purity was characterized by various spectral techniques like ¹H NMR, Mass spectra, IR and UV-Visible spectroscopic techniques.

Keywords: Phthalocyanines, amide linkage, phenyl thiazole, Electronic, IR; PPA.

Introduction

In recent years many publications were published on synthesis and studies on heterocyclic substituted metal phthalocyanine¹⁻⁸. Even though it is showing remarkable properties in comparison with the unsubstituted metal phthalocyanine, its applicability is limited in material science because of its insolubility⁹⁻¹⁵. Science 5-phenyl thiazole is planar, substitution of these moieties will not alter the aggregation behaviour of metal phthalocyanine. Here we report the promising approach for the synthesis of soluble heterocyclic substituted metal phthalocyanine through the amide bond¹⁶. Since synthesised compounds soluble in common organic solvent structural characterization became easier.

Material and Methods

1,2,4-Benzene tricarboxylic anhydride and Benzimidazole were purchased from Aldrich and other chemicals were obtained from Merck (India), Spectrochem and used without purification. All solvents used were dried and purified before use. Tetracarboxy metal phthalocyanine (3 a-c) was prepared according to the described procedure.

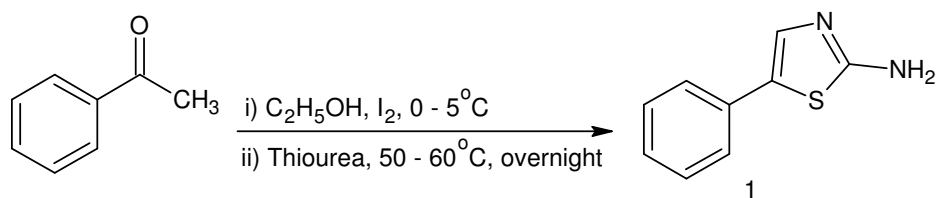
Synthesis of 2-amino 5-phenyl thiazole (1): To a solution of acetophenone (0.0083mol) dissolved in ethanol (20 ml) add Iodine (0.0332) under cold condition, stir for 15 to 20 min. To the above mixture add thiourea (0.01665), maintain the reaction mixture under 50-60°C for overnight. Filter the slurry obtained after concentration of reaction mixture by distillation then washed with plenty of water. White colour compound obtained recrystallized by ethanol. Reaction progress and purity of compound monitored by TLC. Yield 85%, mp 150–153°C (Found: C, 57.34; H, 4.12; N, 14.8 Calcd for C₉H₈N₂S: C, 61.34; H, 4.58; N, 15.90%). IR (KBr): 1583 (–C=N), 3455, 3329 (–NH₂), 682 (C–S–C), 1059 (N=C–S–C=N) cm⁻¹; ¹H NMR (CDCl₃) δ ppm: 5.10 (s, 2H, –NH₂), 6.72 (s, 1H, –C–H thiazole), 7.25–7.76 (m, 4H, Ar–H); EI-MS: 177.2 (M⁺ + 1).

Synthesis of Tetraformamido-(2-amino-5-phenylthiazole) substituted metal Phthalocyanines: Tetracarboxy metal phthalocyanine (3a-c) (0.0128 mol) and 2-amino-5-phenylthiazole (7) (0.0027 mol, 0.5g.) were stirred into preheated PPA (100 g) containing 10 g P₂O₅ at 100°C in a three necked round bottom flask containing mechanical stirrer, condenser and thermometer for 1h and then maintained at 150°C for 20h under nitrogen atmosphere. After cooling reaction mixture to 100°C, quenched with ice cold water and filtered. Product obtained was repeatedly treated with 0.1N sodium hydroxide solution followed by water, hot acetic acid, 10% sodium bicarbonate solution, water, and acetone to get 4a-c. Yield and solubility was recorded (table-1).

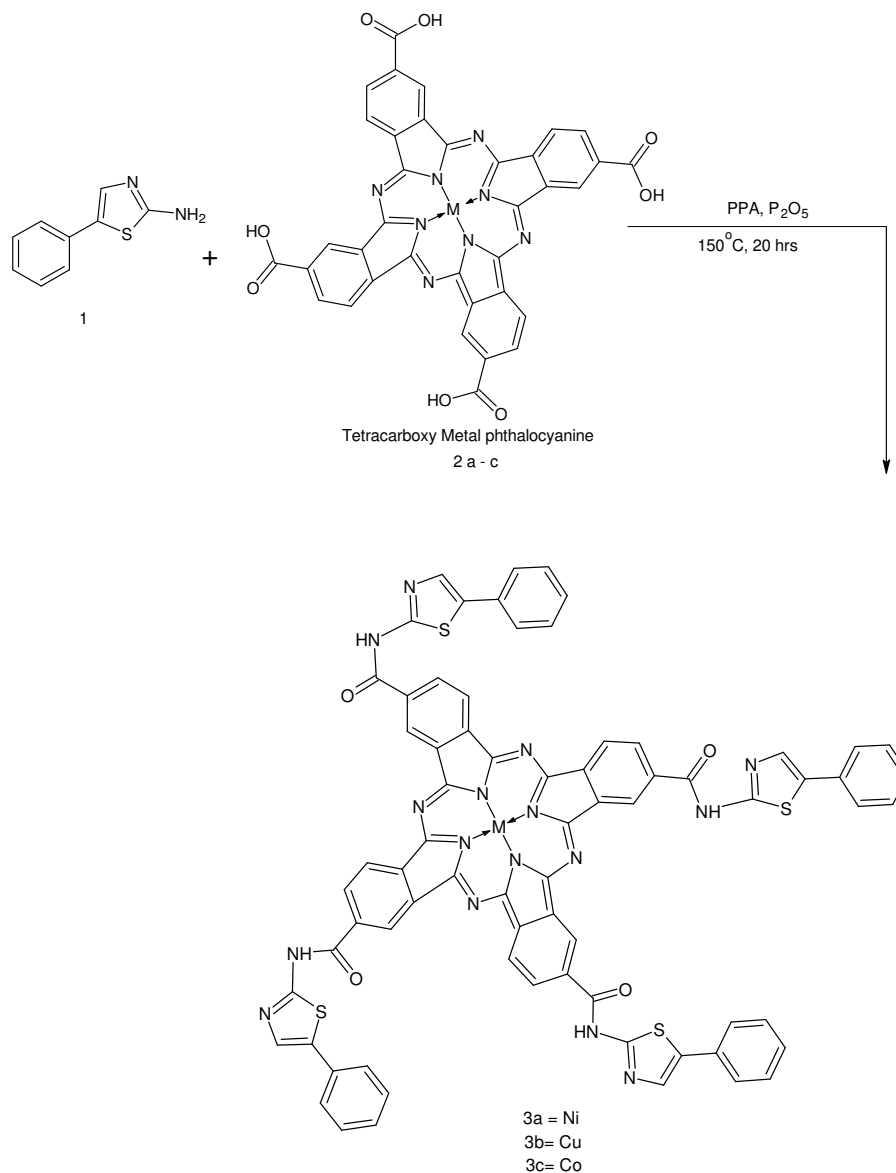
2,9,16,23-Tetraformamido [2-amino-(5-phenyl) thiazole] Nickel (II) Phthalocyanine: Yield 60%, (Found: C, 62.10; H, 2.90; N, 16.32. Calcd for C₇₂H₄₀N₁₆NiO₄S₄: C, 62.66; H, 2.92; N, 16.24%). [IR (KBr) ν_{max}/cm⁻¹]: 1613(C=O), 3423, 2904(–NH), 1521(C=N), 1086(N=C–S–C=N), 1239, 1086, 842, 733 (Pc skeleton vibration); UV-Vis (DMSO) λ_{max}/nm: 322.73, 620.37, 682.65; ¹H NMR (DMSO) δ ppm: 7.2–8.9 (m, 36H, Ar–H), 7.9 (s, 4H, –NH); EI-MS: 1381.9 (M⁺ + 1).

2,9,16,23-Tetraformamido [2-amino-(5-phenyl) thiazole] Cobalt (II) Phthalocyanine: Yield 65%, (Found: C, 63.0; H, 2.95; N, 16.12. Calcd for C₇₂H₄₀N₁₆CoO₄S₄: C, 62.65; H, 2.92; N, 16.24%). [IR (KBr) ν_{max}/cm⁻¹]: 1632(C=O), 3483, 2921(–NH), 1526(C=N), 1090.0(N=C–S–C=N), 1240, 1080, 848, 741 Pc skeleton vibration); UV-Vis (DMSO) λ_{max}/nm: 334.01, 606.61, 672.05; EI-MS: 1381.1 (M⁺ + 1).

2,9,16,23-Tetraformamido [2-amino-(5-phenyl) thiazole] Copper (II) Phthalocyanine: Yield 70%, (Found: C, 63.1; H, 2.88; N, 16.10. Calcd for C₇₂H₄₀N₁₆CuO₄S₄: C, 62.44; H, 2.91; N, 16.18%). [IR (KBr) ν_{max}/cm⁻¹]: 1640(C=O), 3490, 2928(–NH), 1535(C=N), 1092.0 (N=C–S–C=N), 1242, 1082, 850, 741 Pc skeleton vibration); UV-Vis (DMSO) λ_{max}/nm: 338.07, 633.68, 681.07; EI-MS: 1381.1 (M⁺ + 1).



Scheme-1
Synthesis of 2-amino 5-phenyl thiazole



Scheme-2
Synthetic route for preparation of Tetraformamido(2-amino-5-phenylthiazole)substituted metal Phthalocyanines (3a-c)

Table-1
Elemental analysis, yield and solubility data of compounds 1, 2a-c, 3a-c.

Sl. No.	Compound	Emperical Formula	M.wt g/mol	Colour	Yield (%)	Content (Calculated) found			solubility
						% C	% H	% N	
1.	1	C ₉ H ₈ N ₂ S	176.23	White	85	(61.34) 57.34	(4.58) 4.12	(15.90) 14.8	Ethanol
2.	2a	C ₃₆ H ₁₆ N ₈ NiO ₈	747.25	Green	65	(57.86) 58.13	(2.16) 2.03	(15.00) 15.11	DMF
3.	2b	C ₃₆ H ₁₆ N ₈ CoO ₈	747.49	Bluishgreen	75	(57.84) 58.32	(2.16) 2.47	(14.99) 14.62	DMSO
4.	2c	C ₃₆ H ₁₆ N ₈ CuO ₈	752.10	Violet blue	70	(57.49) 58.03	(2.14) 2.63	(14.90) 13.43	DMSO
5.	3a	C ₇₂ H ₄₀ N ₁₆ NiO ₄ S ₄	1380.14	Bottle green	60	(62.66) 62.10	(2.92) 2.90	(16.24) 16.32	DMSO
6.	3b	C ₇₂ H ₄₀ N ₁₆ CoO ₄ S ₄	1380.38	Bottle green	65	(62.65) 63.0	(2.92) 2.95	(16.24) 16.12	DMSO
7.	3c	C ₇₂ H ₄₀ N ₁₆ CuO ₄ S ₄	1384.99	Bottle green	70	(62.44) 63.1	(2.91) 2.88	(16.18) 16.10	DMSO

Analyses: Elemental analyses (C, H, and N) were performed using a Thermo finnigan, FLASHEA 1112 elemental analyzer. ¹H NMR Varian 300 MHz (CDCl₃ solvent) and Bruker 400 MHz spectrometer using DMSO as solvent, chemical shift are given in ppm relative to tetramethylsilane (TMS). Electron impact mass spectra were recorded on a Jeol, JMS, DX-303 mass spectrometer. Solid state electronic absorption spectra were recorded on USB4000 Ocean Optics UV-Visible spectrophotometer in the range 200–800 nm. Liquid state UV-Visible spectra recorded in Shimadzu UV-Vis spectrophotometer. IR spectra (4000–400 cm⁻¹) were recorded as KBr pellets on Bruker FT-IR Spectrophotometer.

Results and Discussion

Bottle green coloured 2,9,16,23-Tetraformamido [2-amino-(5-phenyl) thiazole] Metal (II) Phthalocyanine (3a-c) were obtained in good yield and purity by melt condensation of compound 2a-c with 2-amino 5-phenyl thiazole(1) using PPA as condensing agent. The elemental analyses for carbon, hydrogen and nitrogen and gravimetric methods for metals are in good agreement with the calculated values and consistent with the proposed structure, Table-1. Further synthesised compounds were characterized by ¹H NMR, LC-MS and IR spectroscopic techniques.

IR absorption spectra: Spectra of all synthesised compounds showed diffused peak in the range 3420 – 3490 cm⁻¹ representing –NH group of amide bond, that was previously not observed in tetracarboxy metalphthalocyanines (2a-c), along with this –C=O stretching frequency in IR spectra of tetracarboxymetalphthalocyanines (2a-c) at 1700 cm⁻¹ shifted to lower frequency range 1685 cm⁻¹ this clearly indicate the substitution of thiazole through amide bond. The very weak signal observed in the range 2344-2360 cm⁻¹ is due to C-H stretching at the periphery of the phthalocyanine moiety. In comparison with FT-IR spectra of tetracarboxy metal phthalocyanine (3a-c) new peaks observed in product spectra's

in the range 1520-1535 cm⁻¹ and 1080-1090 cm⁻¹ corresponding to the –C=N and N=C-S-C=N functionalities of thiazole moiety. All the remaining bands observed in the range 1201-1284, 1041-1180, and 596-875 cm⁻¹ can be assigned to various characteristic skeletal vibrations of the phthalocyanines. IR spectrum shown in figure-1.

¹H NMR Spectra: The ¹H spectra of diamagnetic complex (3a) shows diffused broad peak at δ 7.9 due to presence of –NH group of amide bond, which is absent in starting material ¹H NMR spectra. Other than this multiplet peak at δ 8.2-7.6 due to aromatic protons. The positions of the peaks will support much evidences for the proposed structure of the title compound. ¹H NMR of compound of synthesised compounds shown in figure-3-4.

Electronic absorption spectra: UV-Vis spectra were recorded in range 200 to 800 nm using DMSO as solvent. All the complexes 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 through amide bond. Because of extended conjugation by heterocyclic substitution bathochromic shift is observed in comparison with TcPc. UV-Visible data presented in table-2, figure-5.

Table-2
UV-Visible spectral data

Compound	λ max (in nm)	Molar extinction coefficient
3 a	341.23	27.0X10 ³
	621.05	13.25 X10 ³
	683.30	10.30 X10 ³
3b	337.85	20.64 X10 ³
	633.91	13.75 X10 ³
	681.52	19.05 X10 ³
3c	330.40	19.82 X10 ³
	607.96	6.65 X10 ³
	672.27	19.06 X10 ³

Mass spectral studies: Mass spectrum of synthesised compounds (3a-c) shown molecular ion peak at m/z 1380.9, 1384.8 and 1381 for 3a, 3b and 3c. This supports the proposed structure of the compound. LC-MS mass spectrum shown in figure-2, and EI-MS spectrum shown in figure-6-8.

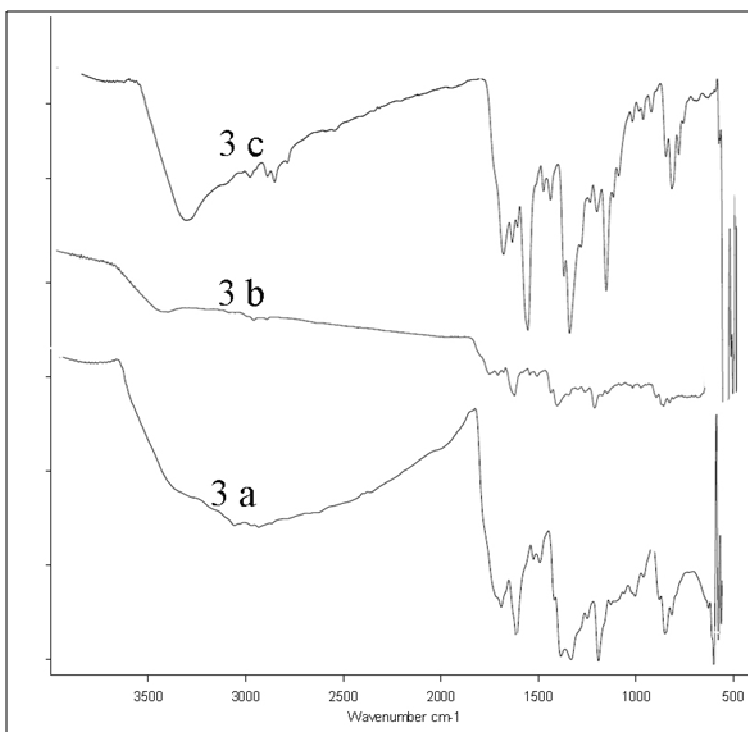


Figure-1
IR absorption spectra of compound 3a-c

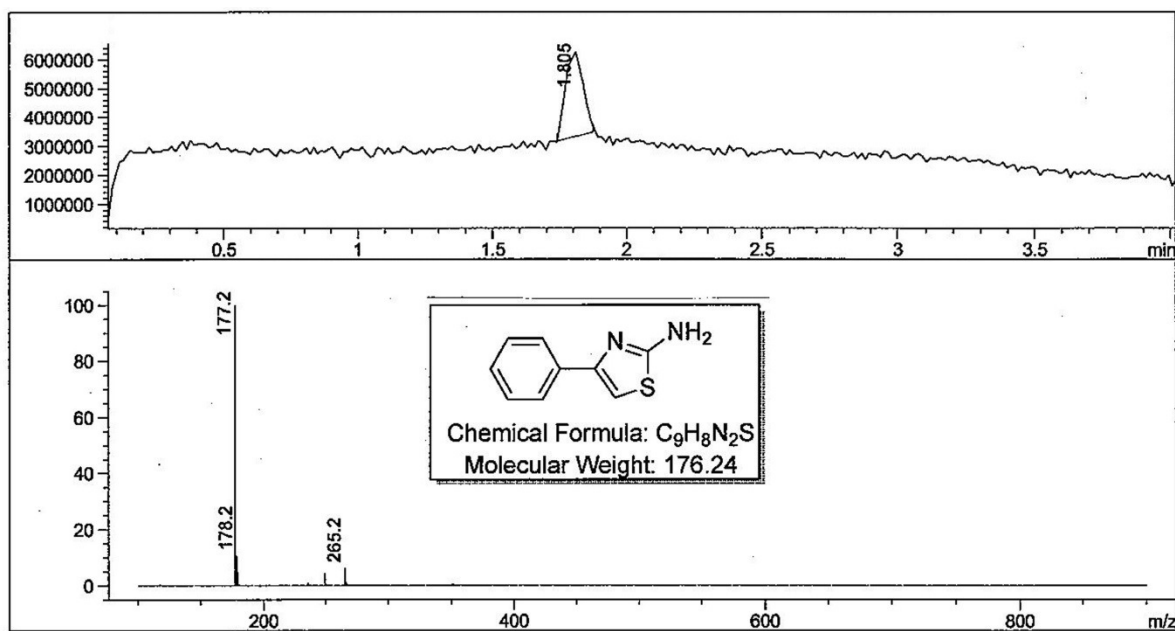


Figure-2
LC-MS pattern of compound 1

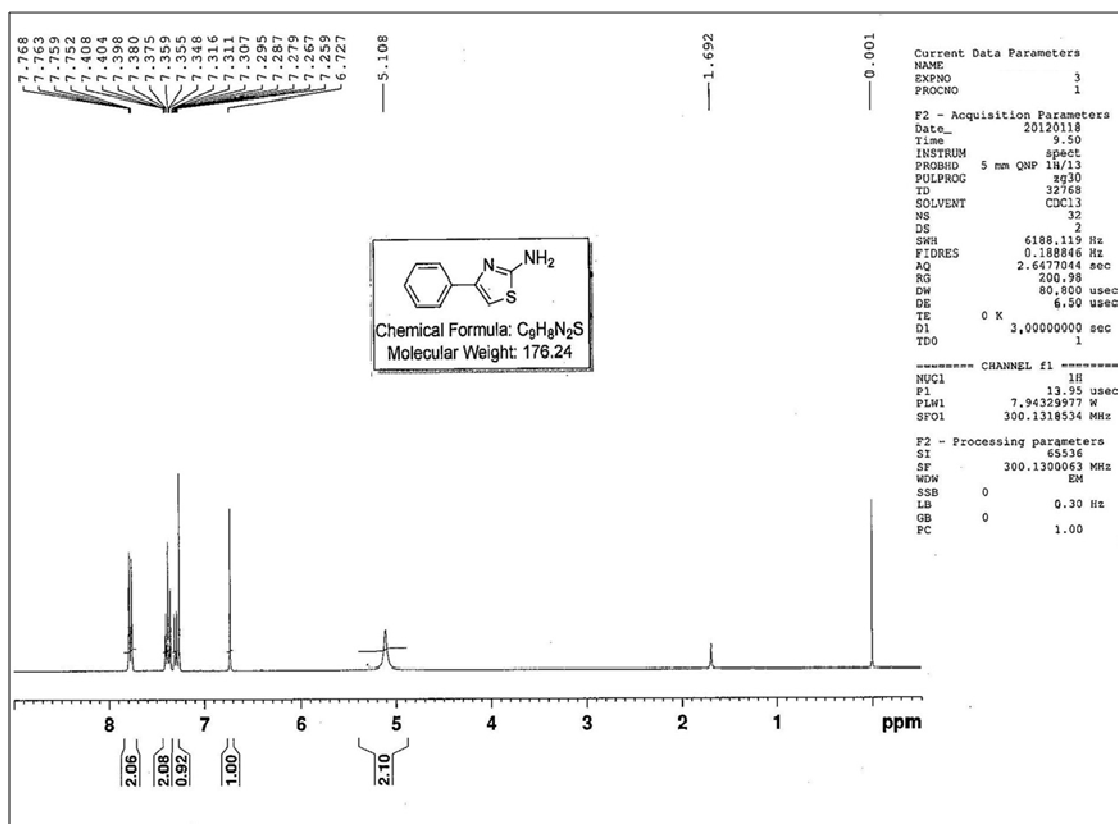


Figure-3
 1H NMR of compound 1

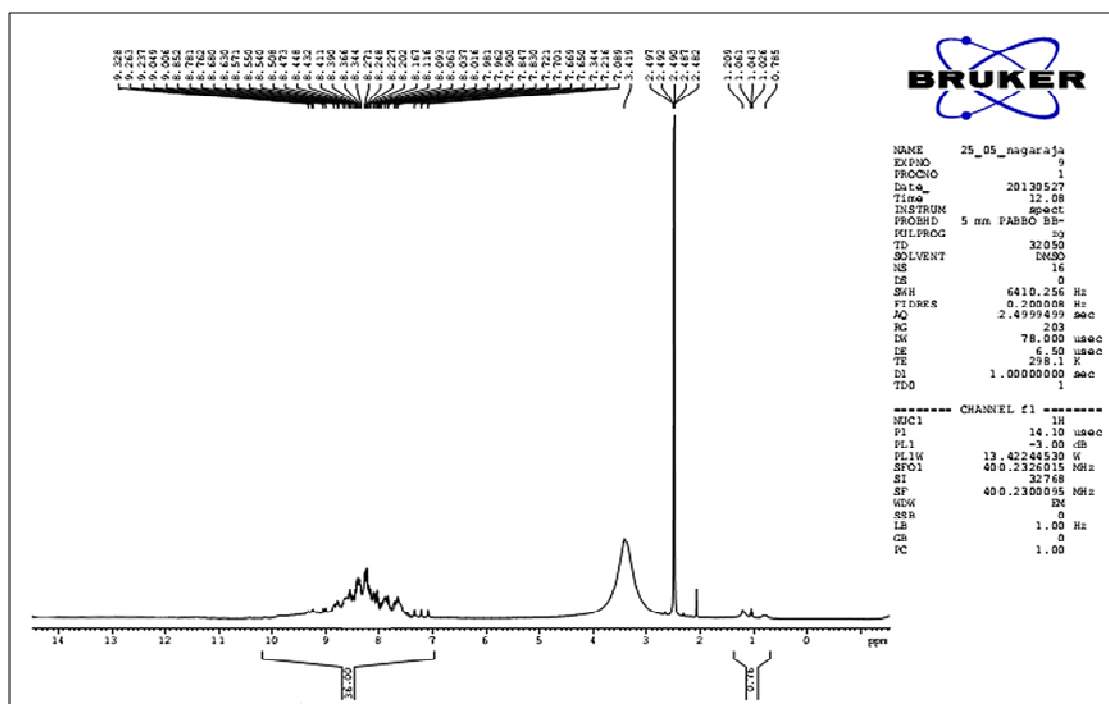


Figure-4
 1H NMR of compound 3a

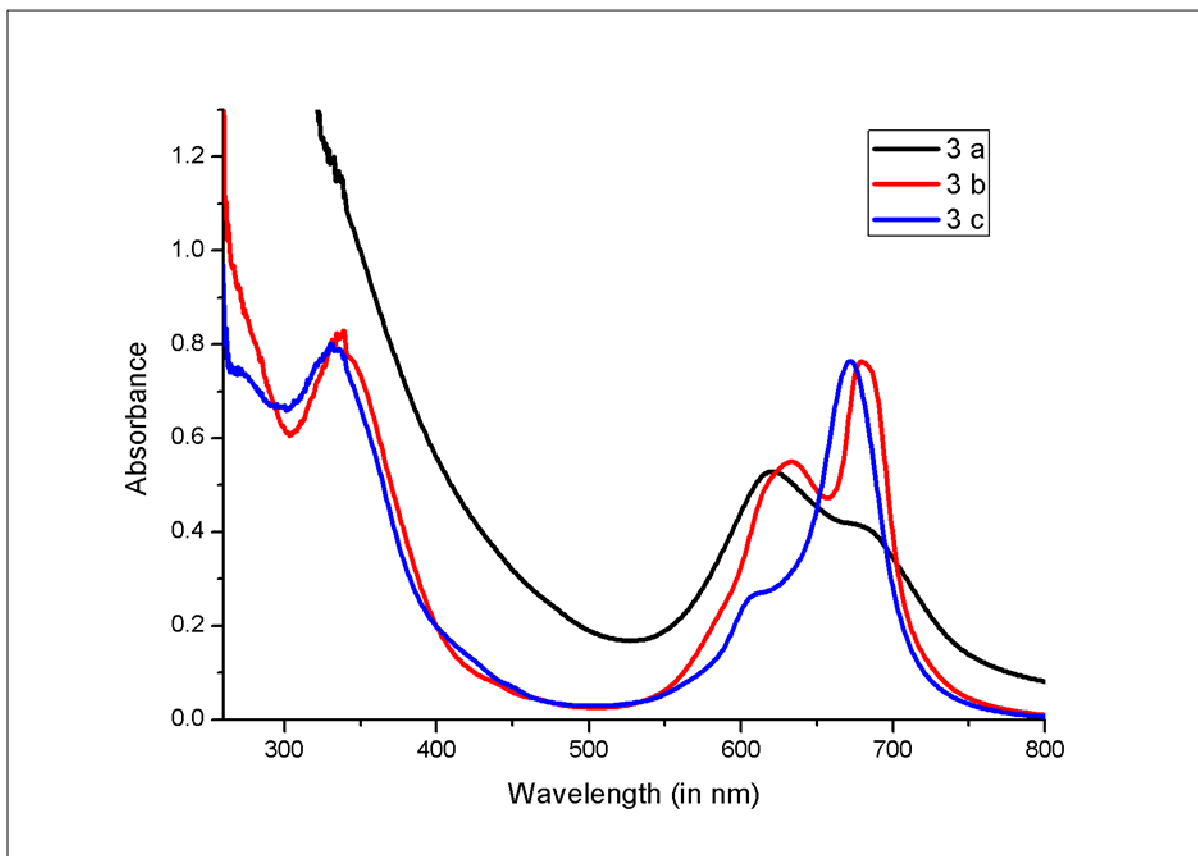


Figure-5
UV-Visible spectrum of compound 3a-c

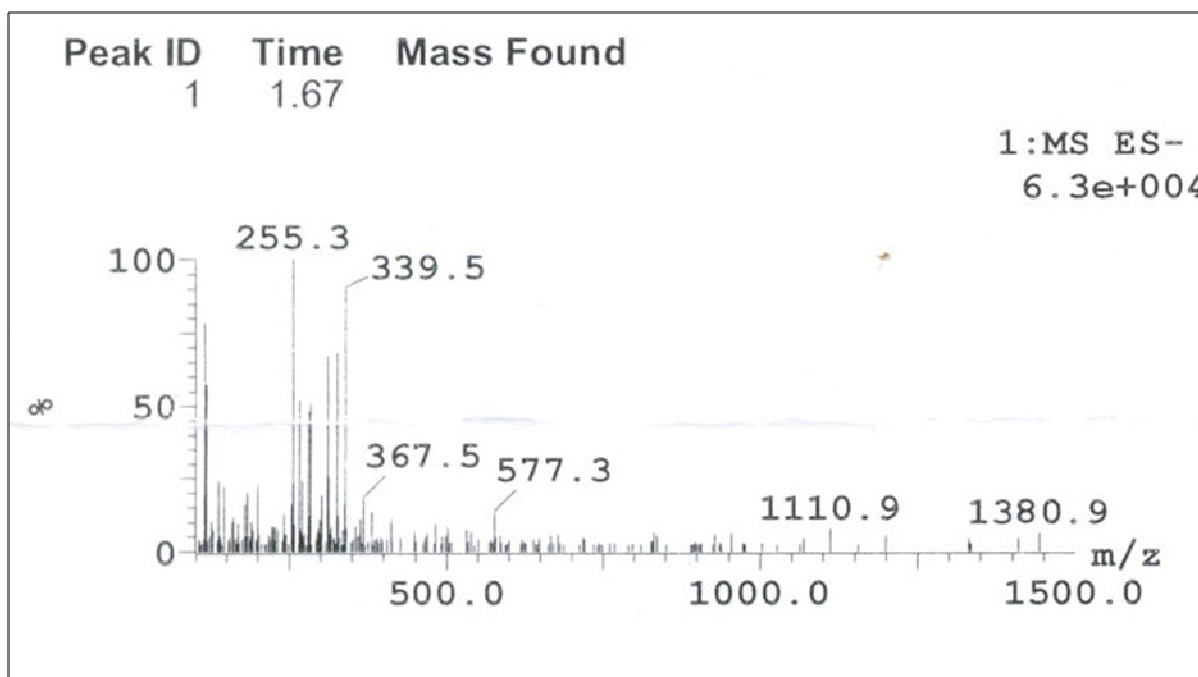


Figure-6
EI-MS pattern of compound 3a

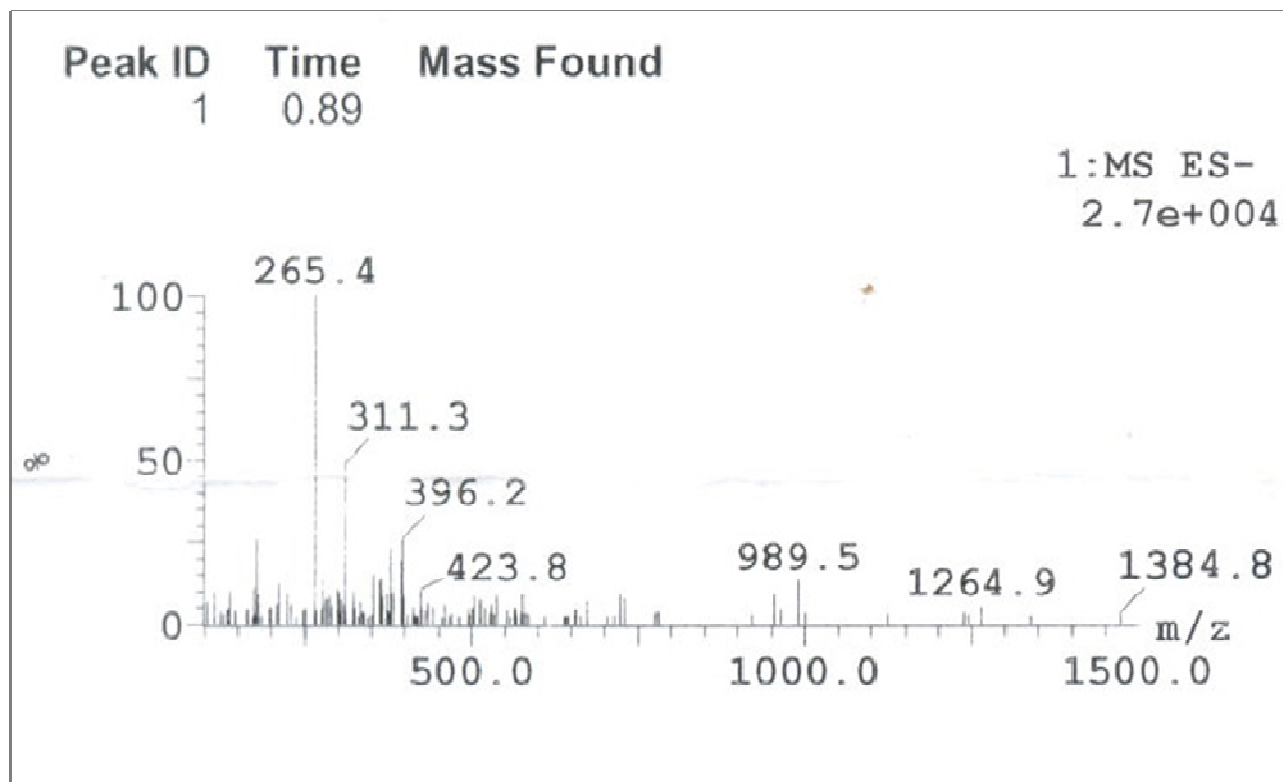


Figure-7
EI-MS pattern of compound 3b

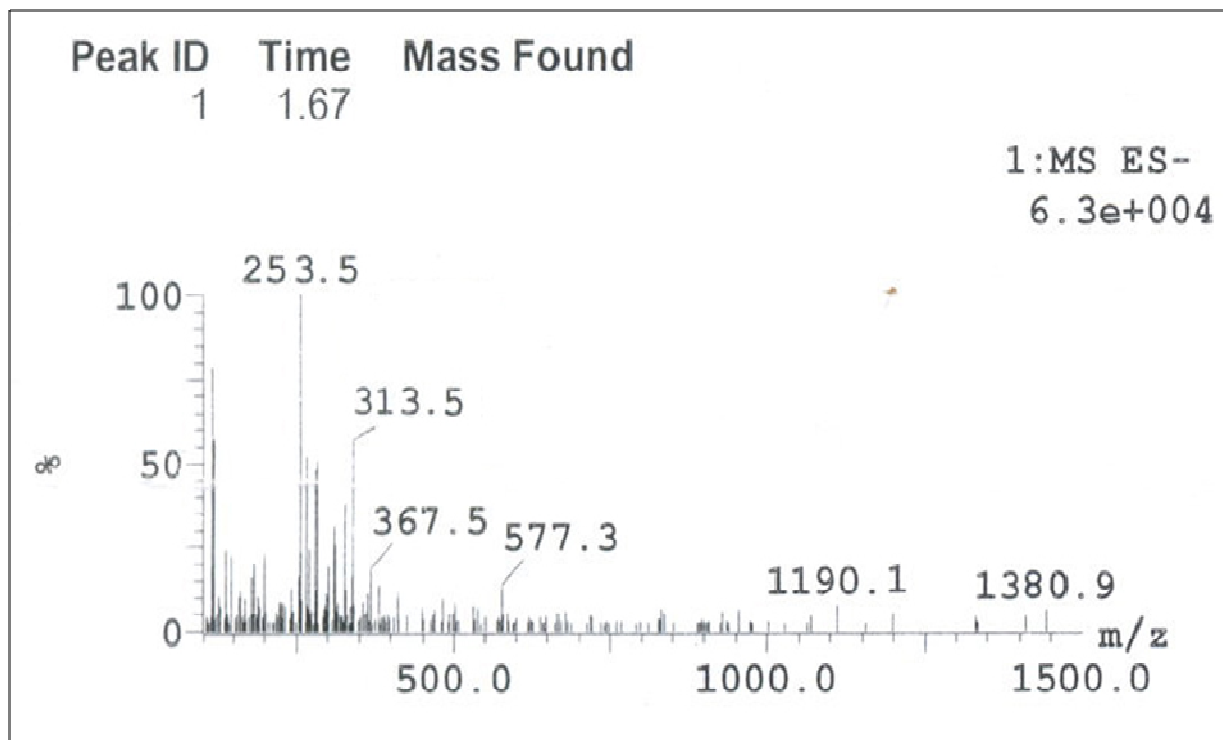


Figure-8
EI-MS pattern of compound 3c

Conclusion

Synthetic route adopted for the preparation of compounds 3a to 3c given good yield with purity. Structural characterization of synthesised compounds were easier because compounds soluble in common organic solvents. Compounds showing red shifted absorption maximum along with increased absorptivity in comparison with unsubstituted metal phthalocyanine. Since compounds were thermally stable enough to use in different material science application.

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