



Synthesis, Spectral and Thermal degradation Kinetics studies of Benzimidazole substituted Metal phthalocyanine through oxadiazole Bridge (M=Co,Ni,Cu)

Tantry Rajesh N., Jathi Keshavayya*, Harish M.N.K., Angadi Shoukat Ali R, and Chinnagiri Keerthi Kumar T.

¹Dept. of Studies and Research in Chemistry, Kuvempu University, Janna Sahyadri, Shankaragatta-577451, Shimoga District, Karnataka, INDIA

Available online at: www.isca.in, www.isca.me

Received 12th August 2013, revised 26th October 2013, accepted 17th November 2013

Abstract

In this study, new type of benzimidazole substituted metal Phthalocyanine complexes connected by oxadiazole bridge were prepared by the acid catalysed melt condensation of hydrazides with tetracarboxy metal Phthalocyanine in the presence of PPA. Which in turn, tetracarboxy metal Phthalocyanines and 2-(2-substituted-1H-benzimidazol-1-yl)acetohydrazide were synthesized by suitable modification of reported procedure. Novel dark green coloured 1,8,15,22-Tetra-[1-(1,3,4-oxadiazol-2-ylmethyl)-1H-benzimidazole] M(II) Phthalocyanine (M=Co,Cu,Ni) were characterized by elemental analysis, UV-Vis and IR-Spectroscopic techniques. 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.

Keywords: Phthalocyanines, 1, 3, 4—Oxadiazole, Benzimidazole, electronic, IR, PPA, TGA.

Introduction

Phthalocyanines are synthetic macromolecules having structural similarities with natural pigments of life, the porphyrins, such as chlorophyll and haemoglobin. After the accidental discovery in 1928, phthalocyanines showed its commercial importance as colorants next to pervasive azo dyes. Phthalocyanine ligand has a heteroaromatic π system and readily forms complexes with many group and transition metals. The azo-nitrogen and peripheral benzene rings impart chemical and thermal stability to the ligand¹⁻⁴.

Phthalocyanines have been used as materials for numerous technological applications, such as photovoltaic solar cells, electrophotography, molecular electronics, Langmuir-Blodgett films, electrochromism in display devices, gassensors, liquid crystals, nonlinear optics and medical applications⁵⁻¹³. Recently, many research articles published on synthesis of substituted metal phthalocyanine, because their properties can be extensively modified by varying the metal and peripheral substituents¹⁴⁻¹⁷.

Heterocyclic compounds having widespread application both in medicinal and material science¹⁸⁻²¹. Among various heterocycles, 1,3,4-oxadiazole derivatives are planar, electron deficient and having high charge carrying mobility. These attractive properties of 1,3,4-oxadiazole derivatives utilised in photo-electronic devices, organic light emitting devices and organic electronics²²⁻²⁵. Earlier reports showed introduction of aryl-1,3,4-oxadiazole subunits onto the peripheral positions of Pc, resulted in increased solubility and semiconducting properties²⁶⁻²⁸. Therefore, in this contribution, we attached the

Benzimidazole-1,3,4-oxadiazole moieties onto electron-rich Pc, which would endow the synthesized symmetrical tetra-[1-(1,3,4-oxadiazol-2-ylmethyl)-1H-benzimidazole] M(II) Phthalocyanine (4a-c) with new properties and better performances of the devices fabricated with it. Synthesised compounds characterised by elemental analysis, FT-IR, solid-state UV-Vis spectroscopy, along with X-ray diffraction (XRD). Optical and thermal stability were evaluated by using UV-Visible and thermal analyses respectively.

Material and Methods

Materials: 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. Tetracarboxymetalphthalocyanine (3 a-c) and benzimidazol-1-yl acetohydrazide were prepared according to the described procedure with suitable modifications²⁹⁻³⁰.

Synthesis of benzimidazol-1-yl acetate(1): Ethylchloroacetate (0.07mol) was added to a solution of dry acetone (25ml) containing 1H-benzimidazole (0.006 mol). Reaction mixture was refluxed for 10-12 h after adding anhydrous K_2CO_3 (0.024 mol). After completion of reaction acetone was removed by distillation and residue was recrystallized from ethanol. The purity of the compound was evaluated by thin layer chromatography. Yield 70%, mp 178–180°C (Found: C, 64.67; H, 5.91; N, 13.70. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72%). [IR (KBr) ν_{max}/cm^{-1}]: 1632 (–C=N), 1150 (–C–N),

1745 (–C=O ester), 1460 (–N–CH₂)cm⁻¹; ¹H NMR (CDCl₃) δppm: 3.70 (s, 2H, –N–CH₂), 4.21(q, 2H, –COOCH₂CH₃), 1.32 (t, 3H, –COOCH₂CH₃), 8.50 (s, 1H, –N=CH), 7.72–7.90 (m, 4H, Ar–H); EI-MS: 205 (M⁺ +1).

Synthesis of benzimidazol-1-yl acetohydrazide (2): To a solution of compound 1 (0.003 mol) dissolved in dry methanol (25ml), 99% hydrazine hydrate (0.02 mol) was added and the mixture was refluxed for 4-5h. Solid obtained after cooling reaction mixture was filtered and washed with small quantity of cold methanol to give the compound 2. The purity of the compound was evaluated by thin layer chromatography. Yield 70%, mp 200–202°C (Found: C, 56.82; H, 5.29; N, 29.43. Calcd for C₉H₁₀N₄O: C, 56.83; H, 5.30; N, 29.46%). [IR (KBr) ν_{max}/cm⁻¹]: 1645 (–C=N), 1122 (–C–N), 1680 (–C=O amide), 1461 (–N–CH₂)cm⁻¹; ¹H NMR (CDCl₃) δppm: 3.62 (s, 2H, –N–CH₂), 8.40 (s, 1H, –N=CH), 8.10 (m, 3H, –CONHNH₂), 7.60–8.00 (m, 4H, Ar–H); EI-MS: 191 (M⁺ +1).

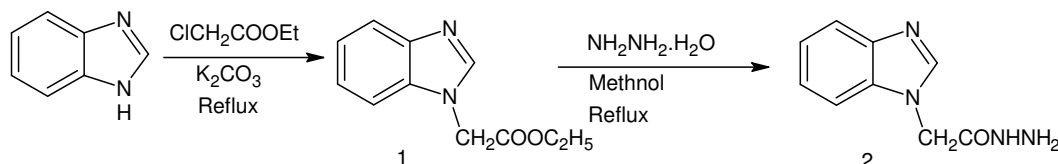
Synthesis of 1,3,4-oxadiazol-2-ylmethyl-1H-benzimidazole substituted M (II) Phthalocyanine (4a-c): Tetracarboxymetal phthalocyanine (3a-c) (0.0128 mol) and benzimidazol-1-yl-hydrazide (7) (0.0027 mol, 0.5g.) were stirred into preheated PPA (100 g) containing 10 g P₂O₅ at 100°C in a three necked round bottom flask containing mechanical stirrer, condenser and thermometer for 1h and then maintained at 150°C for 20h under nitrogen atmosphere. The reaction mixture was allowed to cool to 100°C and quenched with ice cold water and filtered. The

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.

1,8,15,22-Tetra-[1-(1,3,4-oxadiazol-2-ylmethyl)-1H-benzimidazole] Ni(II)Phthalocyanine (4a): Yield 60%, (Found: C, 62.0; H, 2.81; N, 24.5. Calcd for C₇₂H₄₀N₂₄NiO₄: C, 63.40; H, 2.96; N, 24.65%). [IR (KBr) ν_{max}/cm⁻¹]: 1665 (–C=N), 1160 (–C–N), 1468 (–N–CH₂), 1530(–C–O), 1090, 930, 834, 725 (Pc skeleton vibration); UV-Vis (solid state) λ_{max}/nm 359.5, 435, 608, 740.0.

1,8,15,22-Tetra-[1-(1,3,4-oxadiazol-2-ylmethyl)-1H-benzimidazole] Co(II)Phthalocyanine (4b): Yield 65%, (Found: C, 63.0; H, 2.89; N, 24.4. Calcd for C₇₂H₄₀N₂₄NiO₄: C, 63.40; H, 2.96; N, 24.65%). [IR (KBr) ν_{max}/cm⁻¹]: 1670 (–C=N), 1138 (–C–N), 1470(–N–CH₂), 1536(–C–O), 1092, 935, 830, 721 (Pc skeleton vibration); UV-Vis (Solid state) λ_{max}/nm 345.8, 433.8, 615, 710.2.

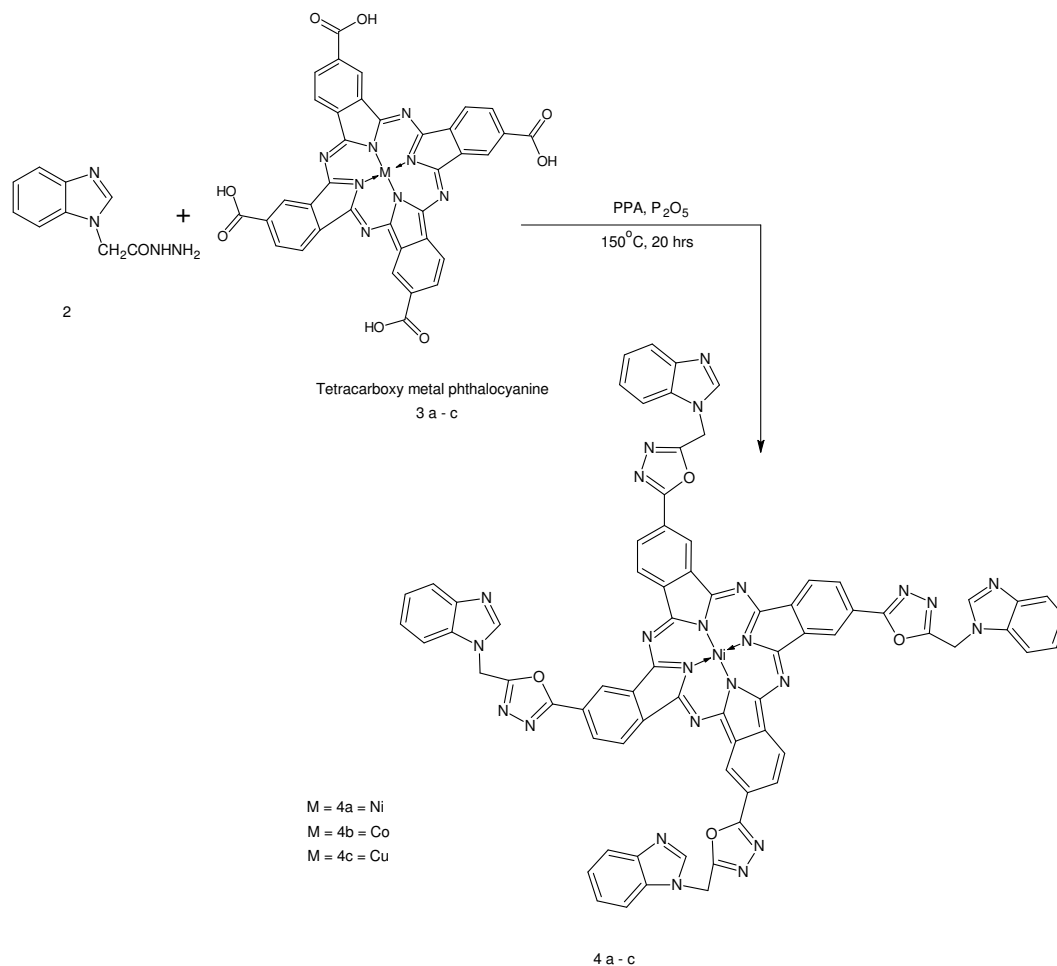
1,8,15,22-Tetra-[1-(1,3,4-oxadiazol-2-ylmethyl)-1H-benzimidazole] Cu(II)Phthalocyanine (4c): Yield 75%, (Found: C, 62.8; H, 3.01; N, 23.9. Calcd for C₇₂H₄₀N₂₄NiO₄: C, 63.40; H, 2.96; N, 24.65%). [IR (KBr) ν_{max}/cm⁻¹]: 1675 (–C=N), 1155 (–C–N), 1475(–N–CH₂), 1532(–C–O), 1085, 935, 830, 728 (Pc skeleton vibration); UV-Vis (Solid state) λ_{max}/nm 351.4, 482.05, 590.3, 780.



Scheme-1
Synthesis of benzimidazol-1-yl acetohydrazide(2)

Table-1
Elemental analysis, yield and solubility data of compounds 1,2,3a-c,4a-c

Compound	Emperical Formula	M.wt g/mol	Colour	Yield (%)	Content(Calculated)found			solubility
					% C	% H	% N	
1	C ₁₁ H ₁₂ N ₂ O ₂	204.22	White	72	(64.69)	(5.92)	(13.72)	Acetone
					64.82	6.20	13.32	
2	C ₉ H ₁₀ N ₄ O	190.20	White	60	(56.83)	(5.30)	(29.46)	Chlorofom
					57.02	5.92	29.12	
3a	C ₃₆ H ₁₆ N ₈ NiO ₈	747.25	Green	65	(57.86)	(2.16)	(15.00)	DMF
					58.13	2.03	15.11	
3b	C ₃₆ H ₁₆ N ₈ CoO ₈	747.49	Bluishgreen	75	(57.84)	(2.16)	(14.99)	DMSO
					58.32	2.47	14.62	
3c	C ₃₆ H ₁₆ N ₈ CuO ₈	752.10	Violet blue	70	(57.49)	(2.14)	(14.90)	DMSO
					58.03	2.63	13.43	
4a	C ₇₂ H ₄₀ N ₂₄ NiO ₄	1363.93	Bottle green	55	(63.40)	(2.96)	(24.65)	Insoluble
					63.92	3.24	24.13	
4b	C ₇₂ H ₄₀ N ₂₄ CoO ₄	1364.17	Bottle green	60	(63.39)	(2.96)	(24.64)	Insoluble
					64.02	3.41	24.12	
4c	C ₇₂ H ₄₀ N ₂₄ CuO ₄	1368.79	Bottle green	65	(63.18)	(2.95)	(24.56)	Insoluble
					63.73	3.01	24.33	



Scheme-2

Synthetic route for preparation of 1,3,4-oxadiazol-2-ylmethyl-1H-benzimidazole substituted M (II) Phthalocyanine(4a-c)

Analyses: Elemental analyses (C, H, and N) were performed using a Thermo finnigan, FLASHEA 1112 elemental analyzer. ¹H NMR Varian 200 MHz spectrometer using DMSO as solvent, chemical shift are given in ppm relative totetramethylsilane (TMS). Electron impact mass spectra were recorded on a Jeol, JMS, DX-303 mass spectrometer. Solid state electronic absorption spectra were recorded on USB 4000 Ocean Optics UV-Visible spectrophotometer in the range 200–800 nm. IR spectra (4000–400 cm⁻¹) were recorded as KBr pellets on Bruker FT-IR Spectrophotometer. Thermogravimetric analysis (TG/DTG) was carried out in the temperature range from 25 to 600°C in air atmosphere using Shimadzu TGA 50H thermal analyser, at heating rate of 10°C/min.

Results and Discussion

Bottle green coloured 2,9,16,23–tetra (1,3,4-oxadiazol-2-ylmethyl-1H-benzimidazole) metal (II) Phthalocyanine (4a-c) were obtained in good yield and purity by melt condensation of compound 3a-c with hydrazide (2) using PPA as condensing agent. The elemental analyses for carbon, hydrogen and nitrogen and gravimetric methods for metals are in good

agreement with thecalculated values and consistent with the proposed structure, table-1.

IR absorption spectra: The entire complexes showed broad peak observed in the range 3436-3493 cm⁻¹is assigned to the hydrogen bonding formed between the nitrogen atoms of the phthalocyanine macromolecule and H-atom of moisture observed on the KBr pellets during palletisation³¹. The very weak signal observed in the range2344-2360 cm⁻¹is due to C-H stretching at the periphery of the phthalocyanine moiety. In comparison with FT-IR spectra of tetracarboxy metal phthalocyanine (3a-c) characteristic C=O peak at 1697 cm⁻¹of –COOH group has disappeared in compounds 4a-c, along with these changes new characteristic bands at region 1603–1614 and 1528–1530 assigned for C=N and C-O of oxadiazole, coupled with C=N and C=C in plane skeletal vibrations of the Pc core. Peaks observed at 1672 cm⁻¹, 1155 cm⁻¹ and 1473 cm⁻¹ were assigned to the characteristic stretching vibrations of –C–N, –C=N and –N–CH₂ respectively for benzimidazole ring at the periphery of Pc core. 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.

UV-Visible spectral studies: Optical study of compounds 4a-c films was carried in the range 200-800 nm for the films deposited at room temperature. Solid state UV-Visible Absorption spectra are obtained directly from the spectrometer, absorption maxima were recorded in table-2, figure-1.

The value of absorption coefficient (α) was calculated for all the films which provides valuable information about the inter band transition and hence the energy band structure of the materials. Band gap of the synthesised compounds were tabulated in table-3.

Table-2
Solid-state electronic absorption data of 4a-c

Compound	Peaks λ_{max} (nm)
4a	359.5, 435, 608, 740.0
4b	345.8, 433.8, 615, 710.2
4c	351.4, 482.05, 590.3, 780

Table-3
Optical band gap data for compound 4a-c

Compound	Peaks λ_{max} (nm)	Band Gap(eV)
4a	608.0	1.974
	740.0	1.461
4b	615.0	1.974
	710	1.444
4c	590	1.974
	780	1.446

Thermodynamic and Kinetic studies: Thermogravimetric analysis results of title compounds were presented in table-4, figure-2. Thermogram shows decomposition of the complexes occurs in three distinct steps and char residue is found to be in the range of 7-5% corresponding to their metaloxides. At 110-120°C initial weight loss of 1-2% was observed for all the complexes corresponding to the loss of free moisture. All the complexes shown a weight loss of 20-22% in the temperature range of 160-300°C which corresponds to the loss of benzimidazole moiety of the macromolecule. Decomposition of oxadiazole bridge will not be distinct in all the complexes, it is varying from 15-35% at temperature range 260-400°C. Gradual and major decomposition of 40-45% observed in temperature range of 400-580°C corresponding to the oxidative degradation of phthalocyanine moiety. The observed thermal stabilities of metal complexes in air was in the order of 4b>4c>4a.

Degradation mechanism, kinetic and thermodynamic parameters of the synthesised complexes have been evaluated by Broido's graphical method for straight line decomposition portion of the thermodynamic analytical curve³². Energy of activation (E_a) were calculated by the slope of $\ln(-\ln y)$ versus $1/T$, where y is the fraction of the complex undecomposed. Since plots of $\ln(a/a-x)$ versus time, gives straight line for all the three stage degradation steps, this indicate degradation follows first order kinetics, where a is the initial weight of sample taken and $(a-x)$ is the weight of sample left after time t , The thermodynamic properties like change in enthalpy (ΔH), entropy (ΔS), free energy (ΔG) and frequency factor (A) are calculated using the standard equations as explained elsewhere and data presented in table-5, figure- 3 to 8.

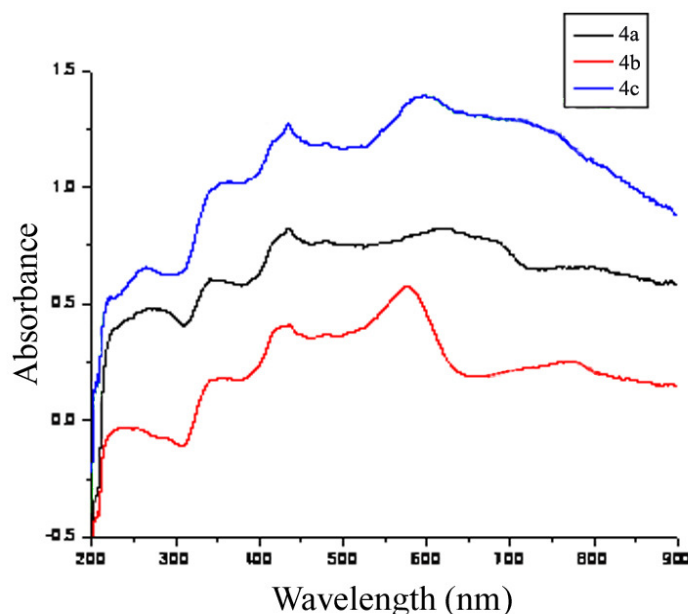


Figure-1
Solid state UV-Visible spectra for compounds 4a-c

Table-4
TGA Data of the complexes

Compound	Decomposition Temp °C	Mass Loss		Probable mode of decomposition and fragment lost
		% found	% calculated	
4a	166-259	35	34	4 Benzimidazole group
	262-349	13	23	4 oxadiazole group
	355-559	42	40	Pc moiety
4b	156-257	22	34	4 Benzimidazole group
	258-400	35	23	4 oxadiazole group
	410-536	34	40	Pc moiety
4c	180-280	23	34	4 Benzimidazole group
	290-340	37	23	4 oxadiazole group
	350-545	35	40	Pc moiety

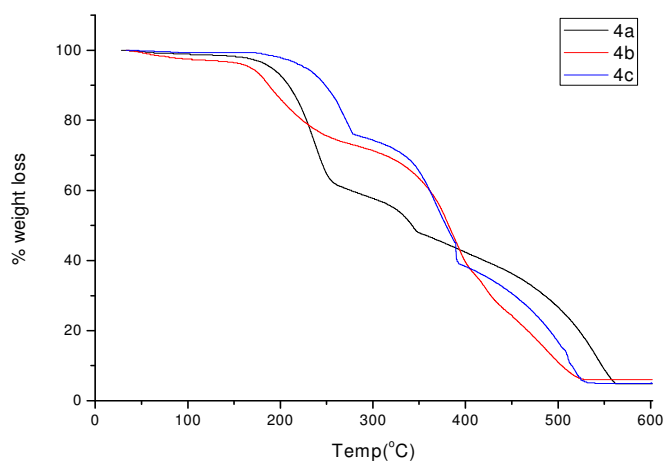


Figure-2
TGA pattern of compound 4a-c

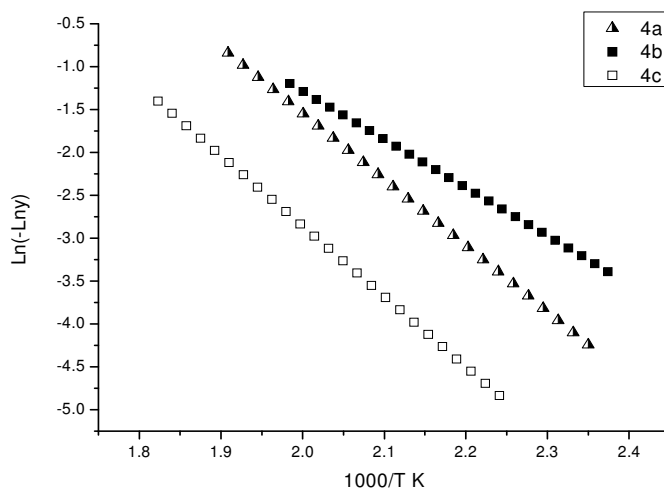


Figure-3
Plots of $\ln(-\ln 1/y)$ vs. $1000/T$ K plots for the first step decomposition of compound 4a-c, using Broido method

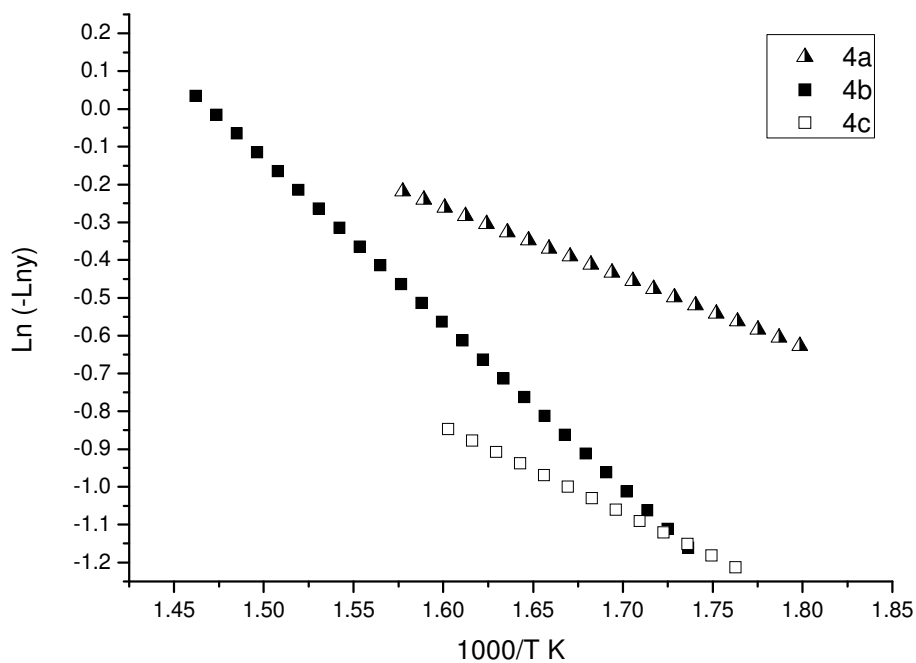


Figure-4
Plots of $\ln(\ln 1/y)$ vs. $1000/T$ K plots for the second step decomposition of compound 4a-c, using Broido method

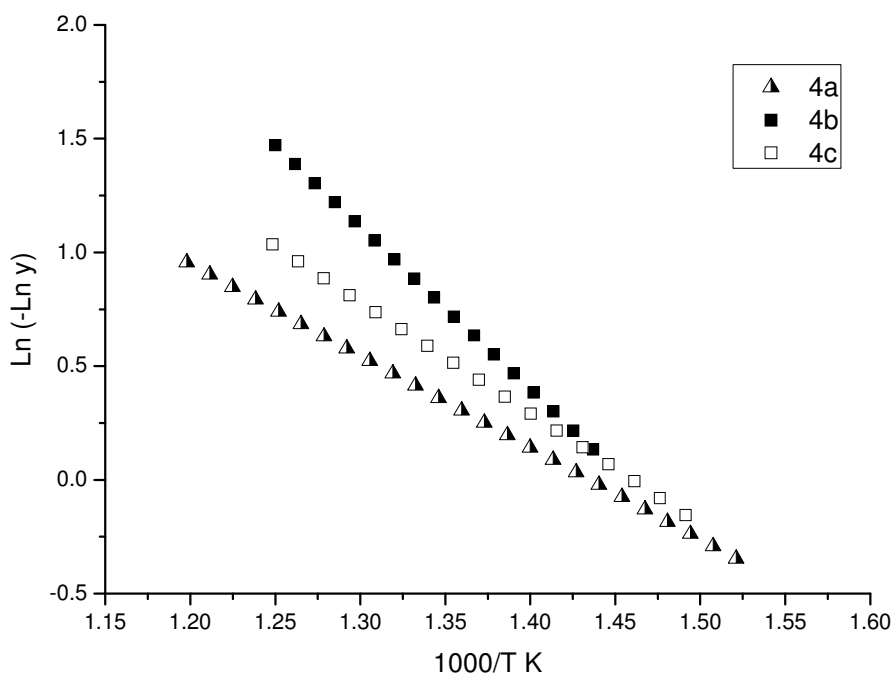


Figure-5
Plots of $\ln(\ln 1/y)$ vs. $1000/T$ K plots for the third step decomposition of compound 4a-c, using Broido method

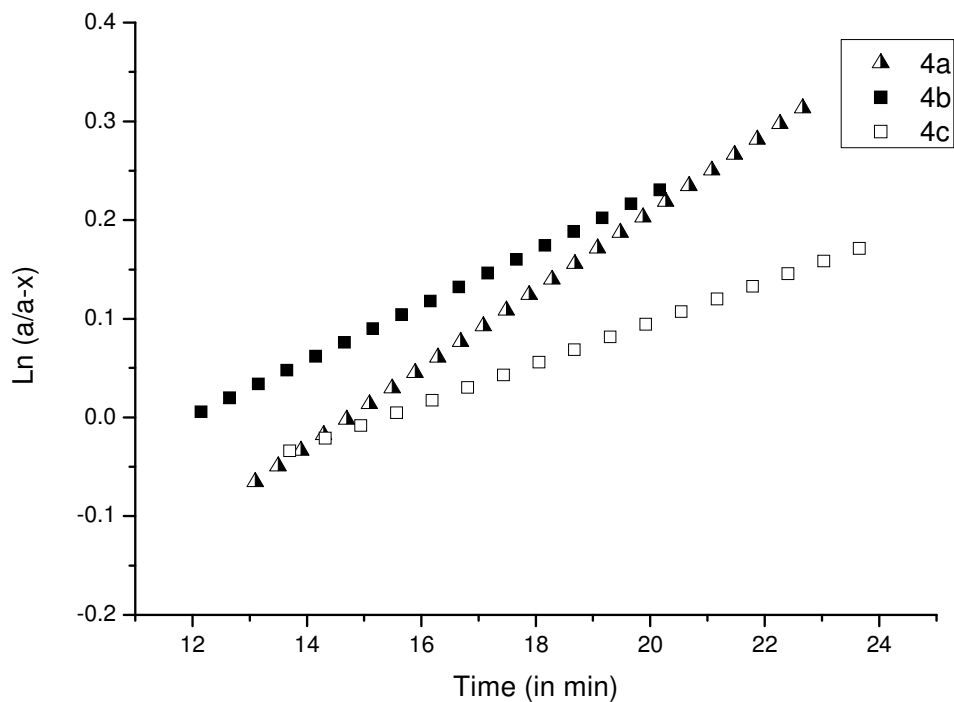


Figure-6
Plots of $\log(a/a-x)$ vs time for the first step decomposition of compound 4a-c

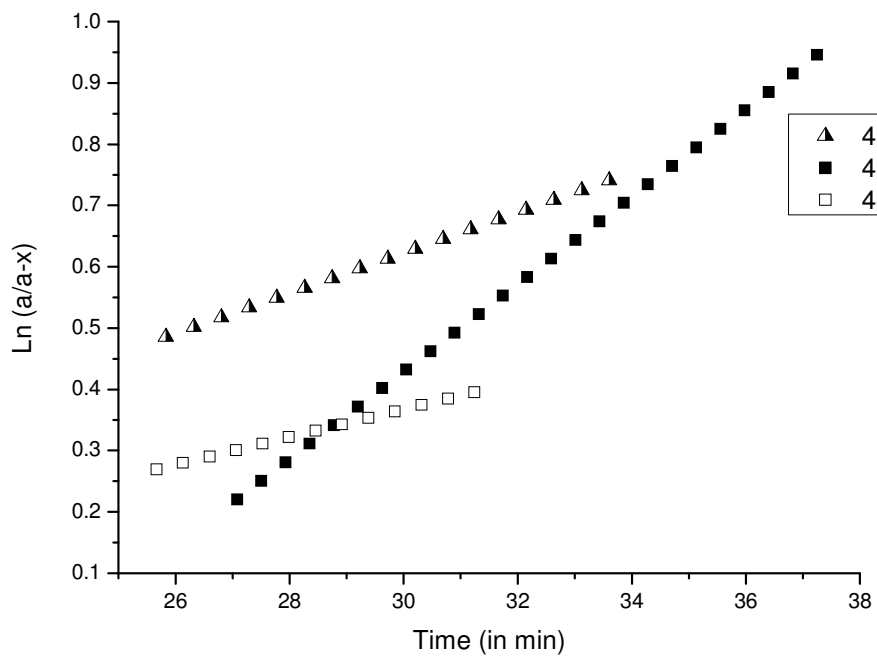


Figure-7
Plots of $\log(a/a-x)$ vs time for the second step decomposition of compound 4a-c

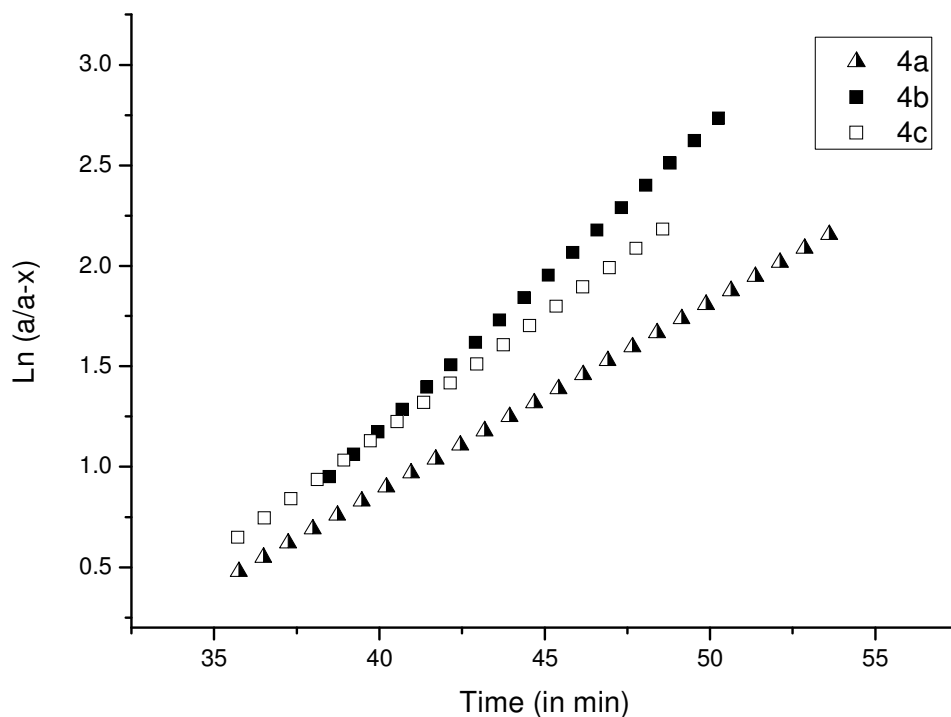


Figure-8
 Plots of $\ln(a/a-x)$ vs time for the third step decomposition of compound 4a-c

Table-5
 Kinetic and thermodynamic parameters

Compound	Decomposition range(in k)	E_a (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1})	ΔG (kJ mol^{-1})	A (s^{-1})
4a	423-523	64.12	68.06	-275.52	130.518	2.43×10^{-19}
	553-633	15.36	20.29	-279.06	165.6512	4.66×10^{-19}
	653-835	33.53	39.72	-272.19	202.6549	2.56×10^{-19}
4b	419-503	46.71	50.55	-278.21	128.4288	3.27×10^{-19}
	573-683	36.27	41.50	-273.05	171.6493	2.40×10^{-19}
	693-803	59.50	65.72	-268.22	200.8222	1.60×10^{-19}
4c	443-548	68.22	72.35	-281.33	139.64	5.12×10^{-19}
	565-623	19.00	23.94	-282.17	167.8647	6.79×10^{-19}
	667-801	40.64	46.74	-270.07	198.2978	1.96×10^{-19}

XRD Studies: Degree of crystallinity of synthesised compounds was studied qualitatively using X-ray diffraction studies. The powder X-ray diffraction pattern of synthesized metal (II) phthalocyanines are obtained using Cu- K α radiation ($\lambda = 1.542 \text{ \AA}$) taken through a range of 2θ angles $6-70^\circ$. The X-ray diffraction pattern showed in figure-9 and summarized data presented in table-6, clearly indicating the crystal line nature of the samples. Spectrum shows sharp peaks at lower angles with maximum intensity and broad peaks with

minimum intensity in higher angles. The observed patterns of title complex showed broadening of the peaks with diffused intensity in comparison with unsubstituted parent phthalocyanines. The broadening may be due to the presence of substituents and which seems to play an important role in the stacking of the metal phthalocyanine derivatives. Quantities such as 2θ angles, intra planar spacing (d), crystallite size were calculated using standard equation's³³.

Table-6
Powdered XRD data for complexes 4a-c

Sl.No.	Complex compound (Code name)	2 θ (degress)	Lattice spacing (d) (Å ^o)	Relative Intensity	crystallite size
1.	4 a	12.5419	7.0579	22.0	584 nm
		17	5.21575	36.4	
		18.68	4.75029	80.6	
		20.2785	4.37929	28.0	
		22.3044	3.9859	30.2	
		26.6	3.35118	100	
		41.4	2.18102	15.1	
2.	4 b	12.9	6.86277	15.3	492 nm
		17.2488	5.14107	73.2	
		18.96	4.68076	38.5	
		21.8865	4.06105	33.7	
		26.6745	3.34199	100	
		33.4655	2.67772	13.0	
		44.6	2.03169	12.2	
3.	4 c	15.4145	5.74847	60.1	512 nm
		18.96	4.68076	35.4	
		22.3014	3.98643	52.0	
		24.02	3.70496	100	
		27.28	3.26917	85.7	
		31.9065	2.80491	22.4	
		56.86	1.61933	8.6	

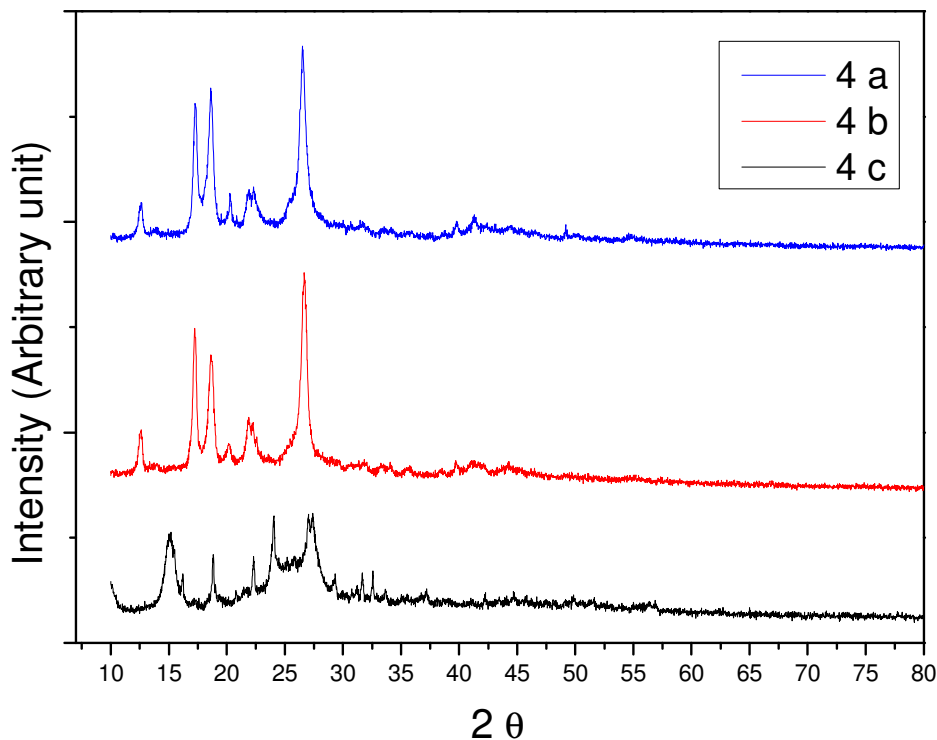


Figure-9
Powder XRD patterns for compounds 4a-c

Conclusion

Here we are reporting convenient and cast effective methodology for the synthesis of heterocyclic substituted metal phthalocyanine. Synthesised compounds showed decreased band gap and greater thermal stability in comparison with the earlier oxadiazole substituted metal phthalocyanine. Synthesised compounds may be useful for optical sensor and charge-carrier semiconducting materials with high chemical and thermal stabilities.

Acknowledgement

The authors thank to Dr. Fasiulla, 'Manipal Institute of technology' for providing (TGA) thermogravimetric analytical data.

References

1. Dent C.E., Instead R.P. and Lowe A.R., Phthalocyanines, Part VI, The structure of the phthalocyanines, *J. Am. Chem. Soc.*, **1**, 1033-1039 (1934)
2. Myers J.F., Rayner Canham G.W. and Lever A.B.P., Higher oxidation level phthalocyanine complexes of chromium, iron, cobalt and zinc. Phthalocyanine radical species, *Inorg. Chem.*, **14**, 461 (1975)
3. Moser F.M. and Tomas A.L., The Phthalocyanines, *CRC Press, Boca Raton, FL*, (1983)
4. McKeown N.B., Phthalocyanine Materials: Synthesis and Structure and Function, *Cambridge University Press*, (1998)
5. Walter M.G., Rudine A.B. and Wamser C.C., Porphyrins and phthalocyanines in solar photovoltaic cells, *J. Porhp. Phtha.*, **14**, 759-792 (2010)
6. Loi M.A., Neugebauer H., Denk P., Brabec C.J., Sariciftci N.S., Gouloumis A., Vázquez P. and Torres T., Long-lived photoinduced charge separation for solar cell applications in phthalocyanine-fulleropyrrolidine dyad thin films, *J. Mater. Chem.*, **13**, 700-704 (2003)
7. Kadish K., Smith K.M., Guillard R. (Eds.), The Porphyrin Handbook, *Academic Press, Boston*, 15-20 (2003)
8. Guillaud G., Simon J. and Germain J.P., Metallophthalocyanines Gas sensors, resistors and field effect transistors, *Coord. Chem. Rev.*, **178**, 1433 (1998)
9. Cook M.J., Dunn A.J., Daniel F.M., Hart R.C.O., Richardson R.M., Roser S.J., Fabrication of ordered Langmuir-Blodgett multilayers of octa-n-alkoxy phthalocyanines, *Thin Solid Films*, **159**, 395-404 (1988)
10. Duro J.A., G. De la Torre, Barberá J., Serrano J.L. and Torres T., Synthesis and Liquid-Crystal Behavior of Metal-Free and Metal-Containing Phthalocyanines Substituted with Long-Chain Amide Groups, *Chem. Mater.*, **8**, 1061 (1996)
11. De la Torre G., Torres T. and Lopez F.A., The phthalocyanine approach to second harmonic generation, *Adv. Mater.*, **9**, 265 (1997)
12. Van Lier J.E., D. Kessel (Ed.), Photodynamic Therapy of Neoplastic Diseases, vol. 1, *CRC Press, Boca Raton, FL*, 279-290 (1990)
13. Ümit Salan, Nagao Kobayashi, Özer Bekaroğlu, Effect of peripheral substitution on the electronic absorption and magnetic circular dichroism (MCD) spectra of metal-free azo-coupled bisphthalocyanine, *Tetrahedron Lett.*, **50**(49), 6775-6778 (2009)
14. Fasiulla K.R. Reddy Venugopala, Keshavayya J., Moinuddin Khan M.H. Anitha and Vittala Rao Synthesis, Structural Investigations and Antifungal Studies on Symmetrically Substituted Metal (II) Octa-1-(3-chlorophenyl) Methanimine Phthalocyanine, *Res. J. of Chem. Sci.*, **1**(9), 29-36 (2011)
15. Rashidi N.A. and Berad B.N., Synthesis of some Novel 1,3,4-Oxadiazole derivatives, *Res. J. of Chem. Sci.*, **2**(ISC-2012), 10-12 (2013)
16. Jain N.C., Pilgrimage of Phthalocyanine Macromolecule Phthalocyanine Dyes (Part-II), *Res. J. Chem. Sci.*, **2**(1), 1-6 (2012)
17. Venugopala Reddy K.R., Keshavayya J., Kumara Swamy B.E., Harish M.N.K., Mallikarjuna H.R. and Sherigara B.S., Spectral and electrochemical investigation of octanitro substituted metal phthalocyanines, *Dyes Pigments*, **80**, 1-5 (2009)
18. Jones G., Jackson W.R., Choi C. and Bergmark W.R., Solvent effects on emission yield and lifetime for coumarin laser dyes, Requirements for a rotatory decay mechanism, *J. Phys. Chem.*, **89**, 294-300 (1985)
19. Jiang C., Yang W., Peng J., Xiao S. and Cao Y. High-Efficiency, Saturated Red-Phosphorescent Polymer Light-Emitting Diodes Based on Conjugated and Non-Conjugated Polymers Doped with an Ir Complex, *Advanced Mater.*, **16**, 537 (2004)
20. Tokito S., Suzuki M., Sato F., Kamachi M. and Shirane K., High-efficiency phosphorescent polymer light-emitting devices, *Organic Electronics*, **4**, 105 (2003)
21. Risko C., Zojer E., Brocorens P., Marder S.R. and Bredas J.L., Bis-aryl substituted dioxaborines as electron-transport materials: a comparative density functional theory investigation with oxadiazoles and siloles, *Chem. Phys.*, **313**, 151 (2005)
22. Janietz S., Anlauf S. and Wedel A., A New Class of Organosoluble Rigid-Rod, Fully Aromatic Poly (1,3,4-

- oxadiazole)s and Their Solid-State Properties, 2, Solid-State Properties, *Macromol. Chem. Phys.*, **203**, 433 (2002)
23. Zhan X., Liu Y., Wu X., Wang S. and Zhu D., New Series of Blue-Emitting and Electron-Transporting Copolymers Based on Fluorene, *Macromolecules*, **35**, 2529 (2002)
24. Ichikawa M., Kawaguchi T., Kobayashi K., Miki T., Furukawa K., Koyama T. and Taniguchi Y. Bipyridyloxadiazoles as efficient and durable electron-transporting and hole-blocking molecular materials, *J. Mater.Chem.*, **16**, 221 (2006)
25. Zhang Y.D., Jespersen K.G., Kempe M., Kornfield J.A., Barlow S., Kippelen B. and Marder S.R., Columnar Discotic Liquid-Crystalline Oxadiazoles as Electron-Transport Materials, *Langmuir*, **19**, 6534 (2003)
26. Harish M.N.K., Keshavayya J., Venugopala Reddy K.R., Mallikarjuna H.R., Shoukat Ali R.A. and Rajesh T., Decorating nickel phthalocyanine periphery by aryl-1,3,4-oxadiazole pendants: synthesis, characterization, and conductivity studies, *J. Coord. Chem.*, **63**, 4050 (2010)
27. Chen S., Liu Y., Xu Y., Sun Y., Qiu W., Sun X. and Zhu D., Langmuir-Blodgett film of new phthalocyanine containing oxadiazol groups and its application in field-effect transistor, *Synthetic Mat.*, **156**, 1236 (2006)
28. Harish M.N.K., Keshavayya J., Venugopala Reddy K.R., Mallikarjuna H.R., Designing nickel phthalocyanine periphery by alkyl chain via [1,3,4]-oxadiazole, *J. Coord. Chem.*, **64**, 2075-2087 (2011)
29. Song X., She Y., Ji H. and Zhang Y., Highly Efficient, Mild, Bromide-Free and Acetic Acid-Free Dioxxygen Oxidation of *p*-Nitrotoluene to *p*-Nitrobenzoic Acid with Metal Phthalocyanine Catalysts, *Org. Process Res. Dev.*, **9**, 297 (2005)
30. Ansari K.F. and Lal C., Synthesis, physicochemical properties and antimicrobial activity of some new benzimidazole derivatives, *Eur. J. Med. Chem.*, **44**, 4028-4033 (2009)
31. Fasiulla M.H., Moinuddin Khan, Harish M.N.K., Keshavayya J. and Venugopala Reddy K.R., Synthesis, spectral, magnetic and antifungal studies on symmetrically substituted metal(II) octaimino phthalocyanine pigments, *Dyes Pigments*, **76(2)**, 557-563 (2008)
32. Venugopala Reddy K.R., Keshavayya J. and Seetharamappa J., Synthesis, spectral, magnetic and thermal studies on symmetrically substituted metal (II) 1,3,8,10,15,17,22,24-octachloro phthalocyanines, *Dyes Pigments*, **59(3)**, 237-244 (2003)
33. Fasiulla, Venugopala Reddy K.R., Moinuddin Khan M.H. and Keshavayya J., Synthesis, Spectral, Magnetic Susceptibility and Antifungal Studies On Symmetrically Substituted Metal (II) Octafurylmethanimine Phthalocyanine, *Der.Pharma. Chemica.*, **3(2)**, 392-403 (2011)