Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 80 (2009) 1–5
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Spectral and electrochemical investigation of octanitro substituted metal phthalocyanines

K.R. Venugopala Reddy [a,*], J. Keshavayya [b,2], B.E. Kumara Swamy [a,1], M.N.K. Harish [b,3], H.R. Mallikarjuna [b,3], B.S. Sherigara [a,1]

[a] Department of Studies in Industrial Chemistry, Kuvempu University, Jnana Sahyadri, Shankaraghatta 577 451, Shimoga District, Karnataka, India
[b] Department of Studies in Chemistry, Kuvempu University, Jnana Sahyadri, Shankaraghatta 577 451, Shimoga District, Karnataka, India

Received 13 May 2007; received in revised form 3 January 2008; accepted 3 January 2008
Available online 1 February 2008

Abstract

A simple and convenient method has been developed for the synthesis of 1,3,8,10,15,17,22,24-octanitrophthalocyanine derivatives MPcON's [M = Fe(III)Cl, Zn(II), Co(II), Cu(II) and Ni(II)]. The compounds were prepared from 3,5-dinitrophthalic acid in the presence of ammonium chloride, urea and catalytic quantity of ammonium molybdate in nitrobenzene solvent; the complexes were characterized by elemental analysis, electronic and IR spectra and powder XRD. The electrochemical redox properties of the complexes were studied using glassy carbon and platinum electrodes in non-aqueous media employing tetra butyl ammonium perchlorate as supporting electrolyte.

Keywords: Octonitrophthalocyanines; Synthesis; Spectral studies; Electrochemical studies

1. Introduction

The redox properties of phthalocyanines (Pcs) are related to most of their industrial applications [1,2]. The earlier interest in metal phthalocyanines was mainly because of their importance as dyes and pigments [3–5]. Recently, intensive research is focused on producing the phthalocyanines for catalysts [6], photosensitizers [3], photoconductors [3–6], thermally stable polymers [7–12] and for photodynamic therapy of cancer [13]. Versatile properties like electrical conductivity, thermal stability, catalytic properties, photoconductivity and chemical resistance of these complexes are mainly influenced by the nature of the central metal ions and substitutents present on the periphery of the phthalocyanine ring.

The aromatic 18π electron system of Pcs with the usual two negative charges enables oxidation and reduction on the macrocycle prior to any redox process on the central metal ions such as Ni(II), Cu(II), Fe(III) and Co(II), because the energies of photo-excitation and oxidoreduction processes can be compared while both are occurring on the highest energy orbitals [14].

A limiting factor for the solution studies on Pcs is the insolubility of the parent compound. Peripheral substitutions with bulky substitutents or the use of donor solvents capable of binding to axial positions of the central metal ion are the two generally adopted practical ways to overcome the hindrance. In continuation of our previous work on synthesis and structural investigations of various symmetrically tetra- and octa-substituted phthalocyanines [15–23], the literature survey reveled that no reports are available on the electrochemical study of octanitro phthalocyanines of Cu(II), Co(II), Ni(II), Zn(II) and Fe(III)Cl. In this paper we report the electrochemical studies on the aforesaid complexes.

2. Results and discussion

The elemental analyses of the MPcON's are given Table 1. The C, H, N and metal analyses confirm that the stoichiometry

* Corresponding author. Tel.: +91 08282 256228; fax: +91 08282 256255.
E-mail addresses: venuleena13@yahoo.com (K.R. Venugopala Reddy), jkeshavayya@rediffmail.com (J. Keshavayya).
[1] Tel.: +91 08282 256228; fax: +91 08282 256255.
[2] Tel.: +91 08282 256308; fax: +91 08282 256255.
[3] Tel: +91 08282 656308; fax: +91 08282 656255.

0143-7208/$ - see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.dyepig.2008.01.010

Table 1
Elemental analysis and spectral data of 1,3,8,10,15,17,22,24-octanitrophthalocyanines of Cu(II), Co(II), Ni(II), Zn(II) and Fe(III)

Complex, color	Empirical formulae (formula weight)	UV–visible absorption λ nm (log ε)	IR spectral data (cm^{-1})	Elemental analysis (%) found (calc.)	Yield (%)
CuPcON, dark green	$C_{32}H_8N_{16}O_{16}Cu$ (935.50)	217 (4.04), 304 (4.40), 470 (4.14), 682 (4.05)	3447, 1636, 1543, 1352, 1114, 917, 752	C, 40.23 (41.05); H, 0.84 (0.86); N, 23.70 (23.94); Cu, 6.65 (6.70)	55
CoPcON, dark green	$C_{32}H_8N_{16}O_{16}Co$ (930.93)	216 (3.96), 281 (4.26), 450 (3.79), 680 (3.64)	3441, 1626, 1528, 1476, 1347, 1264, 1109, 747	C, 40.50 (41.27); H, 0.85 (0.87); N, 23.97 (24.06); Co, 6.26 (6.32)	55
NiPcON, dark green	$C_{32}H_8N_{16}O_{16}Ni$ (930.70)	214 (4.12), 257 (4.48), 318 (4.41), 468 (4.20), 690 (4.03)	3426, 1616, 1533, 1341, 1269, 1119, 850, 747, 602	C, 40.50 (41.27); H, 0.93 (0.85); N, 23.90 (24.06); Ni 6.18 (6.30)	55
ZnPcON, dark green	$C_{32}H_8N_{16}O_{16}Zn$ (937.38)	214 (4.20), 316 (4.11), 468 (4.04), 680 (4.11)	3430, 1641, 1631, 1635, 1347, 1269, 669, 560	C, 40.45 (40.96); H, 0.91 (0.85); N, 24.0 (23.89); Zn, 6.86 (6.97)	45
FePcON, green with brown tinge	$C_{32}H_8N_{16}O_{16}Fe$ (963.35)	216 (4.24), 318 (4.10), 460 (4.04), 695 (4.12), 612 (4.72)	3440, 1660, 1476, 1357, 1274, 855, 793, 669	C, 39.86 (40.38); H, 0.83 (0.86); N, 23.25 (24.04); Fe, 6.23 (6.03); Cl, 3.85 (3.75)	45

of the complex is 1:4 for metal to ligand and the values are in agreement with the suggested structure as shown in Fig. 1. Even though isomers could be formed theoretically they couldn't be separated. The literature survey reveals that during the synthesis of octa-substituted phthalocyanine complexes, the statistical isomers are formed [16]. The title complexes exist as a mixture of 1,3,8,10,15,17,23,25-, 1,3,9,11,15,17,23,25- and 1,3,9,11,16,18,22,24-isomers. In our case we accept that the statistical isomers do exist but we couldn't separate them. All the complexes are highly colored, air stable, non hygroscopic and soluble in polar solvents.

3. Experimental

3.1. General

Tetra butyl ammonium perchlorate and 2-methyl benzoic acid were purchased from Lancaster Company and used as received. Sulfuric acid and dimethylsulfoxide used are of AR grade.

The electrochemical experiments were carried out using potentiostat provided with data acquisition PC interface card fabricated at Analytical Chemistry Division, Bhabha Atomic Research Center, Trombay, India, compatible with an IBM personal computer and coupled to printer.

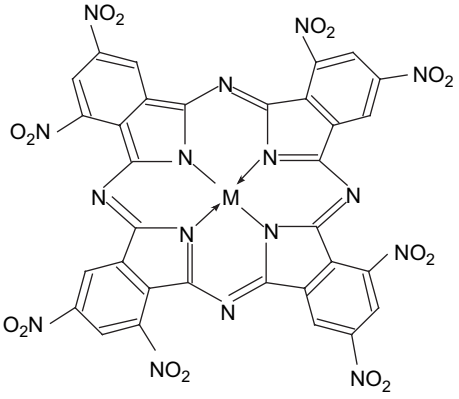

Fig. 1. The proposed structure of metal 1,3,8,10,15,17,22,24-octanitrophthalocyanines, MPcON's where M = Fe(III)Cl, Zn(II), Cu(II), Co(II) and Ni(II).

4. Electrochemistry

4.1. At glassy carbon electrode

The redox activity of metal octanitro phthalocyanines was studied in the potential range +0 to −2.0 V versus the ferrocene–ferrocenium redox system in dimethylsulfoxide solvent. The complexes of Cu(II), Co(II), Zn(II) showed four reduction and oxidation reversible peaks corresponding to PC_1, PC_2, PC_3 and PC_4 reduction and oxidation peaks, resulting from four step ring reduction and ring oxidation of phthalocyanine moiety as given in Fig. 2. (Tetra butyl ammonium perchlorate, which was used as supporting electrolyte, is a strong oxidizing agent and its use requires caution.) The analysis of cyclic voltammetric response with the scan rate varying from 0.02 to 0.2 V s^{-1} gives the evidence for a reversible one-electron reduction. Table 2 summarizes the electrode potentials for the most significant redox change of the above moiety. In general, the more polarizing the central metal ions, the easier is to

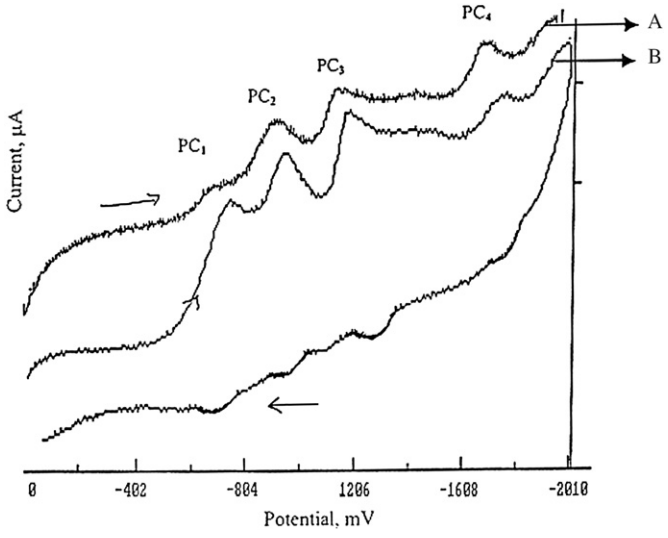

Fig. 2. Typical voltammogram of CuPcON, CoPcON and ZnPcON rings at 295 K in 0.1 M tetra butyl ammonium perchlorate, sweep rate = 50 mV s^{-1}: (A) linear sweep voltammetry, (B) cyclic voltammetry.

Table 2
Effects of scan rates on reduction of the phthalocyanine moiety (0.2 mM) in dimethylsulfoxide and 0.1 M TBAP at glassy carbon electrode

Scan rate (volts)	$\nu^{1/2}$	i_{pc} (μA)				Peak potential (mV)				$i_{pc}/\nu^{1/2}$			
		i_{pc1}	i_{pc2}	i_{pc3}	i_{pc4}	E_{pc1}	E_{pc2}	E_{pc3}	E_{pc4}	$i_{pc1}/\nu^{1/2}$	$i_{pc2}/\nu^{1/2}$	$i_{pc3}/\nu^{1/2}$	$i_{pc4}/\nu^{1/2}$
0.005	0.0707	26.1	33.0	39.9	40.5	738	934	1172	1763	369.1	466.7	562.9	572.8
0.01	0.1000	36.9	46.6	56.3	57.2	740	936	1175	1764	369.0	466.0	563.0	572.0
0.02	0.1414	52.3	66.0	79.7	81.0	739	936	1176	1765	369.4	466.7	563.6	572.8
0.05	0.2236	82.6	104.2	126.1	128.1	740	937	1177	1766	369.7	466.0	563.9	572.8
0.1	0.3162	116.9	147.4	178.3	181.0	741	939	1179	1767	369.0	466.1	563.8	572.4
0.2	0.4472	165.2	209.0	252.0	256.2	742	941	1182	1769	369.0	466.9	563.0	572.4

reduce the ring, and the more difficult to oxidize the ring as reflected in the less prominent oxidation peaks, corresponding to the reduction peaks. A linear plot of these quantities, the first reduction and oxidation potentials verses *Ze*/*r* has been obtained for many MPc species [17]. In the case of Ni(II) and Fe(III) complexes, the observed peaks correspond only to the metal reduction forming Ni(II)/Ni(I) and Fe(III)/Fe(II) as shown in Fig. 3. The reported differences between the forward and backward peaks, which if compared with the values of 62 mV for a purely one-electron transfer, can provide a rough evaluation of degree of reversibility of one-electron addition. It is observed at a scan rate of 0.05 V s^{-1}, where the complex of Ni(II) and Fe(III) exhibited a pair of cathodic and anodic peaks representing the Ni(II)/Ni(I) and Fe(III)/Fe(II) couple. The ratio of anodic to cathodic peak height is almost 1. However, its height increases with the increase in the square root of scan rate ($\nu^{1/2}$). The $i_{pc}/\nu^{1/2}$ value for cathodic peak is 29.11 and 30.45 at 0.05 V s^{-1}. It is almost constant for other scan rates as illustrated in Table 3. This establishes that the electrode process is a diffusion-controlled one [24]. Both the peaks take broad shape as the scan rate is increased. Besides, the cathodic peak shifted to more negative potential while anodic peak shifted to more anodic peak potential. These characteristic features are consistent with the reversibility of Ni(II) and Fe(III) ions.

Mechanism:

$$Ni(II) + e \rightleftharpoons Ni(I)$$

$$Fe(III) + e \rightleftharpoons Fe(II)$$

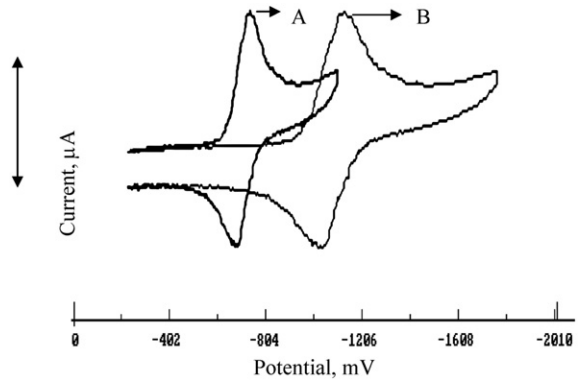

Fig. 3. Cyclic voltammograms of (A) FePcONCl and (B) NiPcON at a scan rate 100 mV s^{-1} at glassy carbon electrode.

4.2. At platinum electrode

The redox activity of metal octanitro phthalocyanines was studied in the potential range +0 to −2.0 V versus the ferrocene−ferrocenium redox system in dimethylsulfoxide. The complexes of Co(II) and Zn(II) showed two reversible reduction and oxidation peaks corresponding to PC_1 and PC_2 which reflect on the two-step ring reduction and oxidation of the phthalocyanine moiety (Fig. 4). Table 4 summarizes the electrode potentials for the most significant redox changes of the ring. The complexes Cu(II), Ni(II) and Fe(III) show only the metal reduction forming Cu(II)/Cu(I), Ni(II)/Ni(I) and Fe(III)/Fe(II) (Fig. 5). The reported differences between the forward and backward peaks, which if compared with the value of 60 mV for a purely one-electron transfer, can provide a rough evaluation of degree of reversibility of one-electron addition. It is observed that at the scan rate of 0.05 V s^{-1}, where the complex of Cu(II), Fe(III) and Ni(II) exhibited a pair of cathodic and anodic peaks representing the Cu(II)/Cu(I), Fe(III)/Fe(II) and Ni(II)/Ni(I) couples respectively. The ratio of anodic to cathodic peak height is found to be almost 1. However, its height increases with the increase in the square root of scan rate ($\nu^{1/2}$). The $i_{pc}/\nu^{1/2}$ values for cathodic peak are 24.64, 29.06 and 31.75 at 50 mV s^{-1}. It is almost constant for other scan rates as illustrated in Table 4. This establishes that the electrode process is diffusion-controlled [24]. Both the peaks take a broad shape as the scan rate is increased. Besides, the cathodic peak is found to shift to more negative potential while anodic peak to more positive peak potential. These characteristic features are consistent with the reversibility of Cu(II), Ni(II) and Fe(III), respectively.

Mechanism:

$$Cu(II) + e \rightleftharpoons Cu(I)$$

$$Ni(II) + e \rightleftharpoons Ni(I)$$

$$Fe(III) + e \rightleftharpoons Fe(II)$$

Table 3
Cyclic voltammetric data of Fe(III) and Ni(II) complexes at glassy carbon electrode

Scan rate ν (V s^{-1})	Complexes						i_{pc} (μA)		$i_{pc}/\nu^{1/2}$	
	Fe(III)			Ni(II)						
	E_{pc} (mV)	E_{pa} (mV)	ΔE_p (mV)	E_{pc} (mV)	E_{pa} (mV)	ΔE_p (mV)	Fe(III)	Ni(II)	Fe(III)	Ni(II)
0.05	510	450	60	820	761	59	6.51	6.81	29.11	30.45
0.1	514	456	58	826	768	58	9.21	9.81	29.12	30.67
0.2	520	460	60	830	770	60	13.21	13.48	29.53	30.14

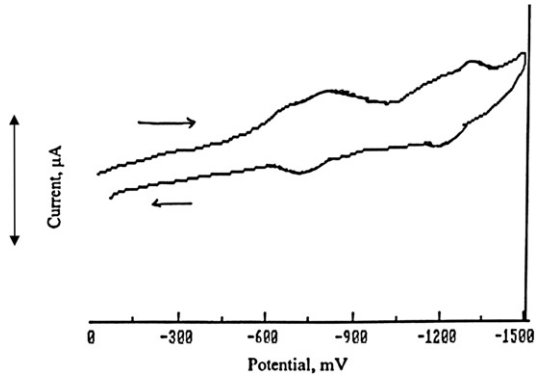

Fig. 4. Typical cyclic voltammograms of ring and CoPcON and ZnPcON complexes at 295 K in 0.1 M tetra butyl ammonium perchlorate, sweep rate = 50 mV s^{-1}.

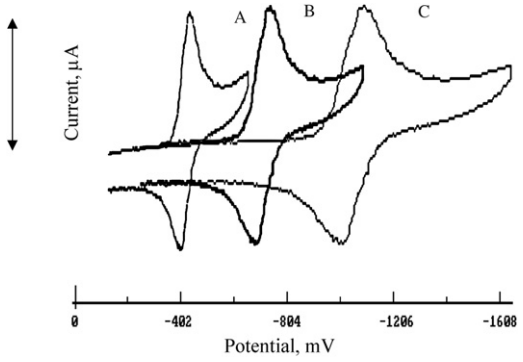

Fig. 5. Cyclic voltammograms of (A) CuPcON, (B) FePcONCl and (C) NiPcON complexes at a scan rate 100 mV s^{-1} at platinum electrode.

4.3. Effect of addition of water

A drop of water was added, to know whether the substitutents NO_2 undergo reduction or not. But on adding water, reduction of ring disappears, there is no reduction of the phthalocyanine moiety and there was no reduction of $-NO_2$ group.

4.4. Effect of sulfuric acid concentration

The complex (0.2 mM) undergoes reduction in the presence of 9 M sulfuric acid i.e. the reduction of NO_2 to NH_2 and the corresponding voltammogram is given in Fig. 6. As the concentration of sulfuric acid increases, the corresponding cathodic peak potential decreases towards the positive direction [25]. This indicates that reduction becomes easier at higher concentration of sulfuric acid as shown in Fig. 7.

4.5. Effect of sweep rate

To see the effect of sweep rate on the cathodic reduction of the complexes, the concentration was kept at 0.2 mM in 9 M sulfuric acid. The cyclic voltammetric behavior of CuPcON was studied by varying the sweep rate from 2 mV s^{-1} to 200 mV s^{-1}. The i_{pc} value was found to increase linearly with the square root of sweep rate ($\nu^{1/2}$) and the current function values ($i_{pc}/\nu^{1/2}$) are found to be constant and this observation suggests that the process is diffusion-controlled as suggested by earlier workers [24–27]. The peak potential E_{pc} was found to shift in the cathodic direction with increase in sweep rate indicating the irreversible nature of the electrode reaction [28].

Table 4
Effect of scan rates on reduction of ring (0.2 mM) at platinum electrode in dimethylsulphoxide and 0.1 M TBAP

Scan rate (volts)	$\nu^{1/2}$	i_{pc} (µA)		Peak potential		$i_{pc}/\nu^{1/2}$	
		i_{pc1}	i_{pc2}	E_{pc1}	E_{pc2}	$i_{pc1}/\nu^{1/2}$	$i_{pc2}/\nu^{1/2}$
0.005	0.0707	2.30	3.5	725	1264	32.53	49.50
0.010	0.1000	3.21	4.96	726	1266	32.1	49.60
0.020	0.1414	4.62	7.0	728	1267	32.67	49.50
0.050	0.2236	7.30	11.1	729	1268	32.64	49.64
0.100	0.3162	10.2	15.5	730	1270	32.25	49.01
0.200	0.4472	14.5	22.1	732	1272	32.42	49.41

4.6. Effect of concentration

Cyclic voltammograms were recorded for complexes in the various concentrations ranging from 0.1 mM to 1.0 mM. The cathodic peak current i_{pc} was found to increase linearly with increase in concentration of the complex. It was also observed that the peak potential shifted towards more negative values which is in agreement with the earlier reports [29].

5. Electrochemical measurements

The electrochemical cell consists of a glass container with a cap having holes for introducing electrodes and nitrogen. The cell is maintained oxygen free by passing nitrogen over the solution. The reference electrode was saturated calomel electrode (SCE), which was often isolated from the solution by salt bridge to prevent contamination by leakage from the reference electrode. The auxiliary and working electrodes are platinum foil and glassy carbon respectively and they are placed directly into the solution. Since the limiting (or peak) current in any type of voltammetry is temperature dependent, the cell was themostated for the required temperature (295 K).

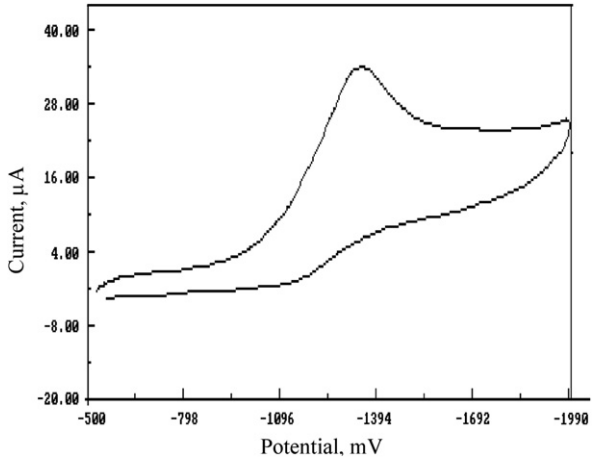

Fig. 6. Typical cyclic voltammogram of CuPcON complex (2 mM) at 295 K in 9 M sulfuric acid, sweep rate = 50 mV s^{-1}.

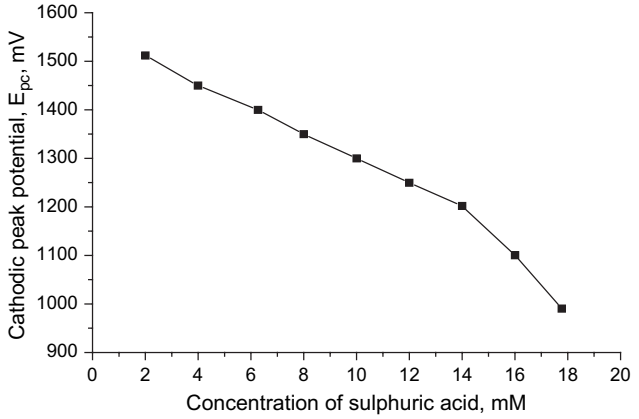

Fig. 7. Dependence of cathodic peak potential of CuPcON complex on concentration of sulfuric acid, sweep rate = 50 mV s^{-1}. Temp. 295 K.

5.1. Pre-treatment of the glassy carbon electrode

Before each measurement, the surface of glassy carbon electrode was polished with alumina on an alumina-polished pad for 60 s and then rinsed with purified water. The solution of supporting electrolyte was placed in the cell and several potential sweeps applied to obtain a low background. The complex is then added and the first potential sweep was registered.

6. Conclusion

The redox activity of Co(II) and Zn(II) showed two reversible reduction and oxidation peaks corresponding to Pc(-1) and Pc(-2) which reflects on the two step ring reduction and oxidation of the phthalocyanine moiety. The peak potential E_{pc} was found to shift in the cathodic direction with increase in sweep rate indicating the irreversible nature of the electrode reaction. The complex undergoes reduction of NO_2 to NH_2 and as the concentration of sulfuric acid increases, the corresponding cathodic peak potential decreases towards the positive direction, which indicated that reduction becomes easier at higher concentration of sulfuric acid. In DMSO the redox behavior of all the three complexes are quasi reversible

Acknowledgements

The authors are thankful to the chairman, department of Industrial Chemistry for providing the basic laboratory facilities. One of the authors(KRVR) thanks UGC, India for the award of FIP-Teacher Fellowship.

References

[1] Lenzoff CC, Lever ABP. Phthalocyanines, properties and applications, vol. 3. USA, Weinhiem: VCH Publishers; 1993.
[2] Bhugn IB, Lexa D, Saveant JM. Homogeneous catalysis of electrochemical hydrogen evaluation by iron(0) porphyrins. J Am Chem Soc 1996;118(16):3982–3.
[3] Venkataraman K. The chemistry of synthetic dyes, vol. 2. New York: Academic Press; 1957.
[4] Moser FH, Thomas AL. Phthalocyanine compounds. New York: Reinhold Publishing Corporation; 1963.
[5] Potins SP, Dharuwala AP. Paintindia 1969;21.
[6] Wynne KJ, Davidson JB. U.S. Patent 4,132,842; Jan 3, 1977.
[7] Griffith JR, O'Rear JG. U.S. Patent 4,056,560; Nov 1, 1977.
[8] Marks TJ, Kundallkar BR, Lin LS, Schock KF, Jr. IMB. In: Symposium on the structure and properties of highly conducting polymers and graphite. Sanjose; 1979.
[9] Nohr RSM, Kuznesof P, Wynne KJ, Kenny ME, Siebenman PG. High conducting linear stacked polymers: iodine doped fluoroaluminium and fluorogallium phthalocyanines. J Chem Soc 1981;103:4371–6.
[10] Moser FH, Thomas AL. The phthalocyanines, vols. 1 and 2. Boca Raton: CRC Press; 1983.
[11] Achar BN, Fohlen GM, Parker JA. Studies on heat-resistant thermosetting phthalocyanine polymers. J Appl Polym Sci 1984;29(1):353–9.
[12] Achar BN, Fohlen GM, Parker JA. U.S. Patent 4,522,755; June 11, 1985.
[13] Cook MJ, Chambrier I, Cracknell SJ, Mayes DA, Russel DA. Octa-alkyl zinc phthalocyanines – potential photosenstisers for use in photodynamic therapy of cancer. Photochem Photobiol 1995;62:988–94.
[14] Myers JF, Canham Rayner GW, Lever ABP. Higher oxidation level phthalocyanine complexes of chromium, iron, cobalt and zinc. Phthalocyanine radical species. Inorg Chem 1975;14(3):461–8.
[15] Samoshekarappa MP, Keshavayya J. Synthesis, magnetic, spectral and thermal studies on metal(II) 1,8,15,22-tetranitrophthalocyanines. Synth React Inorg Met Org Chem 1999;29(5):767–83.
[16] Lever ABP, Leznoff CC. Phthalocyanine properties and applications, vol. 1. New York: VCH Publications; 1989.
[17] Samoshekarappa MP, Keshavayya J. Synthesis and structural studies of metal(II) 1,8,15,22-phthalocyanine tetraamines. J Saudi Chem Soc 1999;3(2):113–9.
[18] Venugopala Reddy KR, Keshavayya J. Synthesis, magnetic, spectral and thermal studies on metal 1,3,8,10,15,17,22,24-octanitrophthalocyanines. Turk J Chem 2002;26:573.
[19] Venugopala Reddy KR, Keshavayya J. Synthesis of symmetrically substituted octobromo phthalocyanine pigments and their characterization. Dyes Pigments 2002;53:187–94.
[20] Samoshekarappa MP, Keshavayya J. Synthesis and spectral investigation of tetranitro-, tetraamino-, tetrahydroxy-, and tetracyanophthalocyanide Iron(III)chloride. Synth React Inorg Met Org Chem 2001;31(5):811–27.
[21] Venugopala Reddy KR, Keshavayya J. Synthesis, magnetic, spectral and thermal studies on metal(II) 1,3,8,10,15,17,22,24-octaaminophthalocyanines. Synth React Inorg Met Org Chem 2002;32(7):1235.
[22] Achar BN, Fohlen GM, Parker JA, Keshavayya. Synthesis and structural studies of metal (II) 2,9,14,23-phthalocyanine tetraamines. Polyhedron 1987;6(6):1463–7.
[23] Bhandari JM. Studies on synthesis and characterization of metal phthalocyanines. Mysore: University of Mysore; 1992.
[24] Lever ABP, Minor PC. Inorg Chem 1981;26:4015.
[25] Herovsky J, Rute J. Principles of polarography. New York: Academic Press; 1965.
[26] Kumaraswamy BE, Sherigara BS, Yashoda MP, Jayadevappa H, Sundaresan R. Electrochemical behavior of furfuraldoxime and furildioxime at glassy carbon electrode: a cyclic voltammetry. Indian council of chemists; 2004.
[27] Siddalingaiah AHM, Naik SG, Sherigara BS, Kumara Swamy BE. Spectral characterization and electrochemical investigation of some divalent transition metal complexes of di(4-flurophenyl)carbazone. J Mol Struct (Theochem) 2002;582:69.
[28] Ramanathan E, Kannan PSM, Thangavelu S, Udupa KS. Voltammetric behaviour of phenylglyoxylic acid on glassy carbon electrode. Bull Electrochem 1988;4(4):65.
[29] Ghoniem MM, Issa RM, Issa YM, Mansour IA, Tawfik. Voltammetric studies of some formagan compounds in buffer solutions. Bull Electrochem 1998;14(1):9.