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Gas Chromatographic Technique Employed for Catalytic Investigation of Novel Phthalocyanines

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The primaquine substituted Fe(II) phthalocyanine (PQFePc) and Co(II) phthalocyanine (PQCoPc) catalysts were prepared by using amide linkage method. The physical and chemical properties have been investigated by FTIR, mass, UV-Vis, TGA, XRD and elemental analysis. The catalytic oxidation of benzyl alcohol was determined by PQFePc and PQCoPc complexes by varying parameters like temperature, oxidant/catalytic ratio and substance/catalyst ratio. The optimization of catalytic oxidation reaction has been effectively achieved for the determination of benzyl alcohol (Bzalc) to benzaldehyde (Bzald). The PQCoPc and PQFePc exhibited excellent catalytic behaviour for the oxidation of benzyl alcohol obtaining high yield and good selectivity.

Keywords: Primaquine, Catalytic oxidation, Benzyl alcohol, Phthalocyanines.

INTRODUCTION

The invention of phthalocyanine has dragged greater attention in various technological applications due to its solubility in organic solvents and water [1]. Phthalocyanine exhibits good chemical, electrochemical and physical properties by suitable modifications in the structure [2]. The phthalocyanines are widely used in the field of sensors, supercapacitors, electrocatalytic, catalytic studies [3-7], semiconductors, nonlinear optical materials, liquid crystals, molecular conductors, nanotechnology [8-13], photosensitizers [14] and in addition, as a catalyst in the chemical reactions [15-17]. Primaquine ligand is an 8-aminoqunoline derivative in the Class-I of the biopharmaceutical classification system [18]. Primaquine phosphate salt exhibits antiparasitic activity which acts on the secondary tissue schizonts and hypnozoites, which reveals the outstanding activity of exo-erythrocytic antimalarial agent [19]. In this view, we have chosen primaquine compound for the substitution with phthalocyanine ring for further studies.

In recent years, researchers in both academia and chemical industries have focused on improving the catalytic process by which benzyl alcohol is transformed into benzaldehyde [20,21]. The benzaldehyde is an important raw material for the preparation of dyestuff, perfumery and agrochemical sectors [22,23].

Earlier, Aktas *et al.* [24] reported the benzyl alcohol oxidation using fluoro-substituted iron(II), cobalt(II) phthalocyanines has determined the oxidation of benzyl alcohol to benzaldehyde using *tert*.-butyl hydroperoxide (tBuOOH, TBHP) as oxidant. The determination of new material for the detection of highly effective benzyl alcohol to benzaldehyde is an never ending process in this context, primaquine substituted Fe(II) phthalocyanine (PQFePc) and Co(II) phthalocyanine (PQCoPc) complexes were synthesized. These complexes characterized by mass, FTIR, UV-visible, XRD, elemental analysis and thermogravimetric methods. A novel gas chromatographic (GC) technique has been adopted for the catalytic oxidation of benzyl alcohol with PQFePc and PQCoPc catalysts. The catalytic activities of PQCoPc and PQFePc were confirmed by varying the parameters such as temperature, oxidant/catalytic ratio and substance/catalyst ratio. The overall results revealed that the synthesized compounds act as good catalyst for oxidation of benzyl alcohol into benzaldehyde reaction.

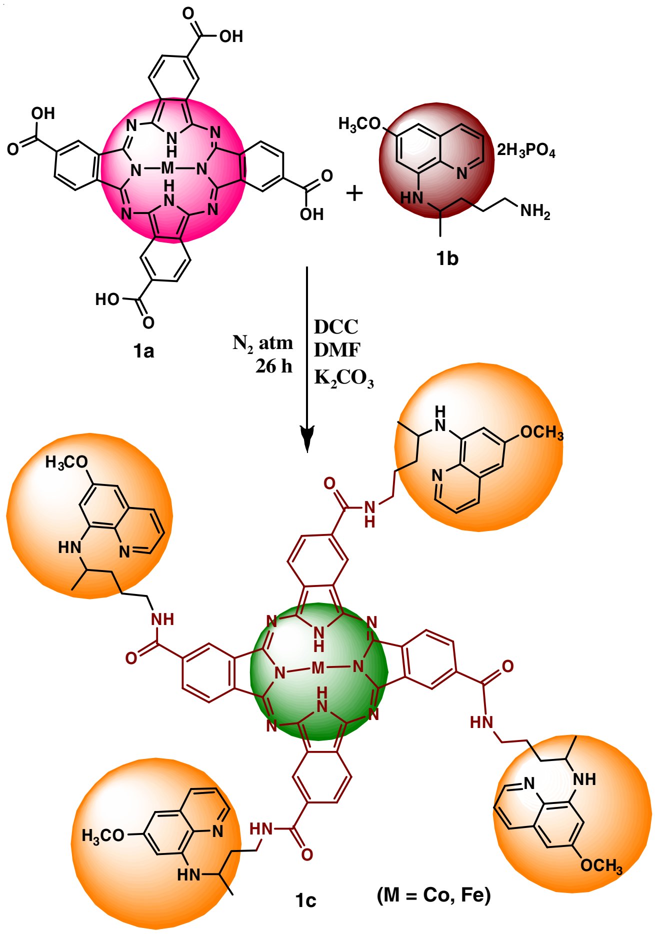
EXPERIMENTAL

All the utilized chemicals, solvents and reagents were procured for the Sigma-Aldrich Chemie GmbH, Sternheim, Germany. Nitrogen atmosphere was used during the reaction. A few chemicals like NaOH, HCl, KOH were prepared by using oxygen-free distilled water. The primaquine substituted Fe(II) phthalocyanine (PQFePc) and Co(II) phthalocyanine (PQCoPc) were synthesized by following the procedure reported earlier [25,26].

The FT-IR measurements were carried out on a Perkin Elmer-1600 FTIR instrument on A Perkin-Elmer Lambda 25 instrument was used to record UV-vis spectra. The crystal structure evaluation was carried out on Bruker D8 diffractometer Cu*K*α radiation source and the thermal stability of PQFePc and PQCoPc was investigated by thermogravimetric analysis using STA6000 system in the 20 to 1000 ºC temperature range with the sweep rate of 20 ºC min^{-1} under blowing rate of 20 mL min^{-1} oxygen and GC Agilent technologies 7820A equipment was used for GC measurement.

Synthesis of primaquine bisphosphate substituted Co(II) phthalocyanine (PQCoPc): A mixture of primaquine bisphosphate (0.07 mmol) with tetracarboxy-Co(II) phthalocyanine (CoTcPc) (0.0175 mmol), K_2CO_3 (0.06 mmol), DCC (15 mg) and DMF 40 mL in 250 mL round bottom flask was agitated under N_2 atmosphere for 26 h at 28 ºC (**Scheme-I**). The obtained green coloured material was then filtered and washed with warm water as well as ethanol and finally rinsed with oxygen-free distilled water then dried at 45 ºC (yield = 45%).

Synthesis of primaquine bisphosphate substituted Fe(II) phthalocyanine (PQFePc): A mixture of primaquine bisphosphate (0.06 mmol), tetracarboxylic-Fe(II)-phthalocyanine (FeTcPc) (0.015 mmol), K_2CO_3 (0.05 mmol), N,N′-dicyclohexylcarbodiimide (DCC, 15 mg) and DMF 40 mL in 250 mL round bottom flask was agitated under N_2 atmosphere for about 26 h at 28 ºC (**Scheme-I**). The resulting green coloured material was filtered and washed by ethanol and distilled water. At the last, the obtained PQFePc complex was dried at 45 ºC (yield = 55 %).



Scheme-I: Preparation route of PQCoPc and PQFePc complexes

Oxidation of benzyl alcohol: The oxidation reaction was conducted by using a thermostat schlenk vessel fitted with a stirrer and a condenser. Initially, oxygen was removed by passing nitrogen gas into the mixture containing benzyl alcohol (2.12 mol), catalyst (2.12 mol) and solvent (0.02 L). Later this mixture was stirred (2-3 min) in a Schlenk's vessel maintained at 50 ºC. The oxidant *tert*.-butyl hydroperoxide (TBHP, 2.23 mol) was added to this mixture with constant stirring. The samples (0.0006 L) were drawn at regular time intervals; at least twice, each sample was injected into GC (1.5 µL each time). The obtained products, consumed substrates and conversion were monitored by GC method.

RESULTS AND DISCUSSION

Elemental analysis: Vario EL (III) CHNS analyzer used for elemental analysis of the synthesized compounds. The primaquine, PQCoPc and PQFePc complexes, were examined by decomposing a well known quantity of the complexes mixed with H_2SO_4 and HNO_3, followed evaporation and calcinations. The results are shown in Table-1.

Mass spectral studies: The mass by charge ratio [M+2] of prepared compounds was measured by mass spectra Fig. 1. The theoretical value of PQFePc was found to be 1697.75 and

TABLE-1
ELEMENTAL ANALYSIS OF THE LIGAND AND ITS METAL COMPLEXES

Ligand/ complexes	m.f.	m.w.	Colour	Elemental analysis (%): Calcd. (found)				
				C	H	N	O	M
Ligand	$C_{15}H_{21}N_3O$	259.35	Violet blue	69.47 (69.45)	8.16 (8.12)	16.20 (16.21)	6.17 (6.12)	–
[Co(L)$_4$]	$C_{95}H_{92}N_{20}O_8Co$	1698.67	Green	67.09 (67.08)	5.45 (5.42)	16.47 (16.45)	7.53 (7.51)	3.46 (3.44)
[Fe(L)$_4$]	$C_{95}H_{92}N_{20}O_8Fe$	1697.75	Green	67.21 (67.18)	5.46 (5.44)	16.50 (16.47)	7.54 (7.52)	3.29 (3.28)

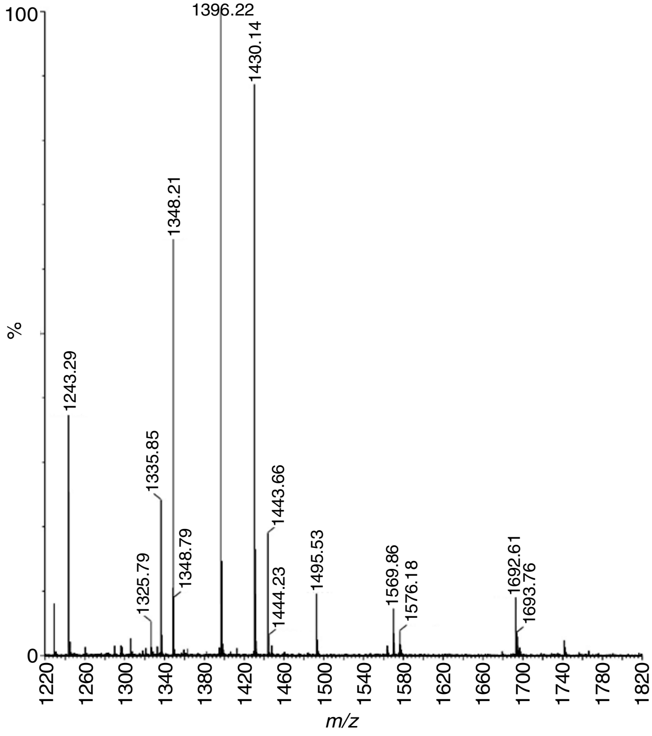


Fig. 1. Mass spectra of PQFePc complex

the experimental result is 1693.76. It clearly shows the confirmation of the prepared compound.

FT-IR spectral studies: The FTIR spectra confirmed the functional groups present in the range between 4000 to 600 cm^{-1} [27]. The FTIR spectra of the PQCoPc and PQFePc (Fig. 2a-b) shows the broad and intense peak in the range of 3600 to 3000 cm^{-1} (–OH and –NH$_2$). The peaks at 3420.43 and 3432.72 cm^{-1} corresponds to –COOH group of CoTcPc and FeTcPc, respectively appears in the range of 3300 to 2500 cm^{-1}. However in Fig. 2a (line blue) and 2b (line brown), the peak for –COOH group disappears with the appearance of new peak pertaining to amide group formation (PQCoPc) at 3327.65 cm^{-1} and (PQFePc) at 3334.54 cm^{-1}(-CONH). The presence of narrow peak between 2932 and 2878 cm^{-1} is due to the vibration of C–H bond. Finally, the bands at 2236 cm^{-1}, 1653 cm^{-1} corresponds to C=C group, whereas 1629.29 and 1616.36 cm^{-1} corresponds to C-O group. Moreover, the peaks at 1242.72 and 1239.33 cm^{-1} corresponds to –C-N group, while the peaks at 1082 and 1084.54 cm^{-1} corresponds to the C=N group, respectively.

UV-visible spectral studies: The UV-Vis spectra of the PQCoPc, CoTcPc PQFePc and FeTcPc complexes exhibits a well distinguished two strong absorption Q and B bands in the range of 300-800 nm (Fig. 3). The Q-band was observed at 680-720 nm, which is due to the excitation of the electrons from π to π* (HOMO to LUMO) level in the complexes, similarly, the B-band was observed at 300-350 nm [28,29]. The lower state electronic absorption spectra of the compounds showed characteristics absorption Q-band region at 687.13 nm for PQCoPc compound, 711.54 nm for CoTcPc compound, 707.98 nm for PQFePc compound and 699 nm for FeTcPc compound in DMF. The B-band absorption of phthalocyanines of PQCoPc, CoTcPc, PQFePc and FeTcPc were observed at 384.80, 374.29, 319.86 and 328.95 nm, respectively [28,29]. These findings demonstrate that the aggregation behaviour was satisfactory in the DMF solvent.

Thermal studies: Fig. 4 represents the TGA plots of the PQCoPc and PQFePc complexes involves two-step reactions. In the first step, the PQCoPc and PQFePc undergo degradation and decomposition of the substituents take place at the temperature range of 150-300 ºC, while in the second step, phthalocyanine ring is broken, finally, metal is converted into metal oxide at 500-550 ºC [29]. The PQCoPc and PQFePc complexes exhibited a good thermal stability upto nearly 550 ºC, confirms that the melting points of the PQCoPc and PQFePc complexes are greater than 500 ºC. Consequently, the PQCoPc and PQFePc complexes are used in electrochemical and chemical reactions.

XRD studies: The diffraction patterns of PQCoPc and PQFePc complexes (Fig. 5a-b) shows the broad peaks with different diffused intensity, where the intensity of peak increases by primaquine group. The less intense and short peaks were observed at 2θ values of 12º, 13º, 21º, 35º, 36º, 38º, 48º and 55º for PQCoPc and 13º, 14º, 16º, 20º, 35º, 37º, 38º, 50º and 55º

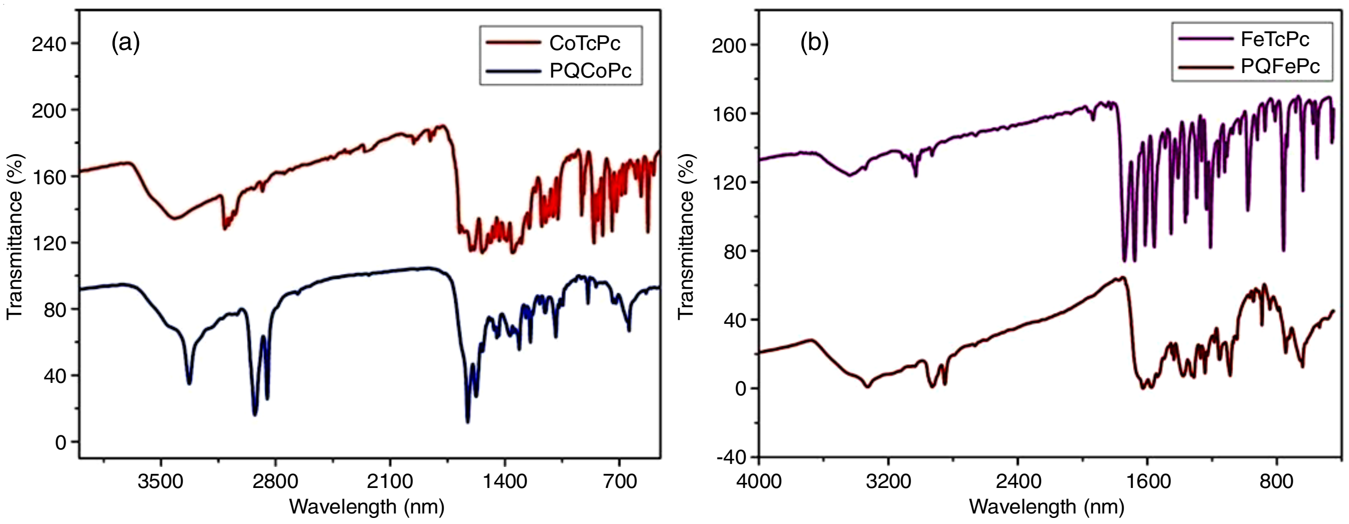


Fig. 2. FT-IR spectra of (a) PQCoPc with CoTcPc complex (b) PQFePc with FeTcPc complex

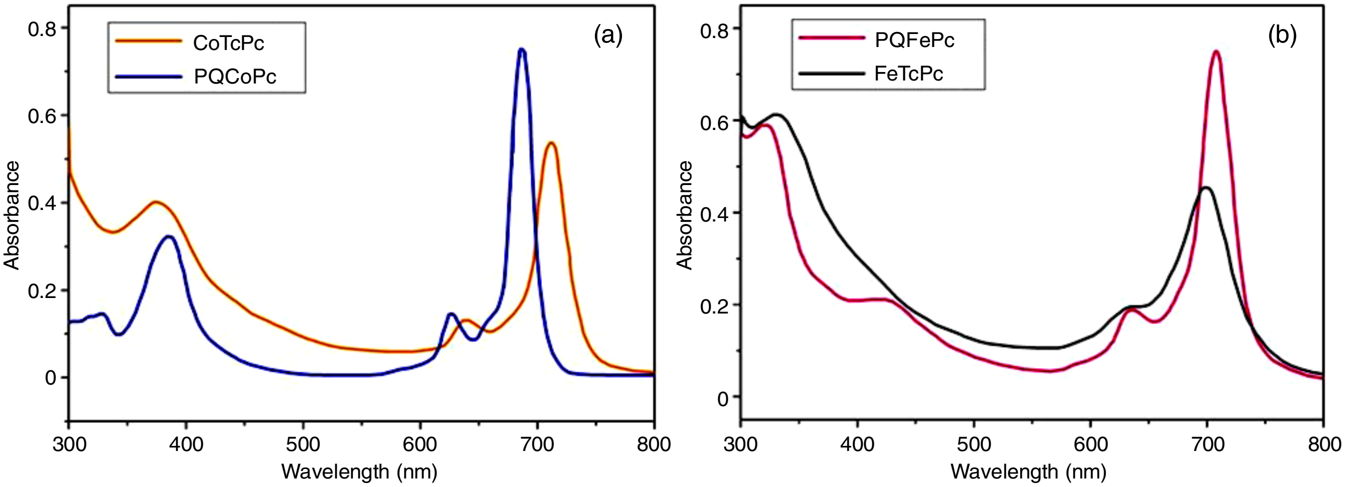


Fig. 3. UV-visible spectra of (a) PQCoPc with CoTcPc complex (b) PQFePc with FeTcPc complex

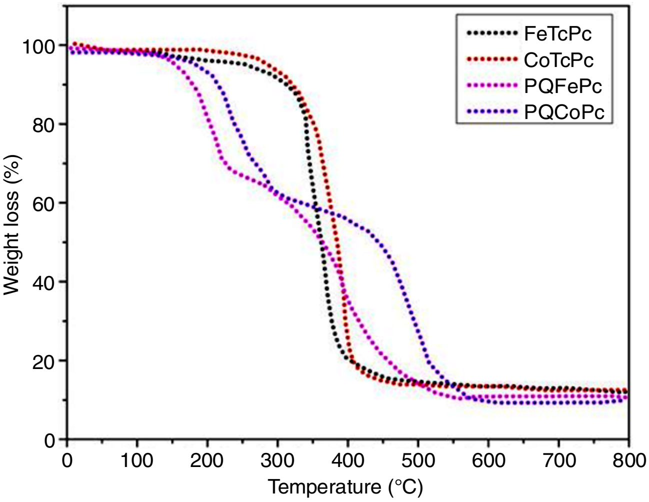


Fig. 4. TGA plots of PQCoPc, PQFePc, CoTcPc and FeTcPc complexes

for PQFePc. The high intense and sharp peaks were observed at 2θ values of 11°, 27°, 28°, 30° and 45° for PQCoPc and 12°, 27°, 28°, 30° and 46° for PQFePc. This indicates that PQCoPc and PQFePc complexes were crystalline nature.

Aggregation behaviour of PQCoPc complex: The aggregation behaviour of PQCoPc was studied by the UV-Vis absorption method. This complex exhibited good aggregation because of its 18π-electron structure. The major factors affecting the aggregation are concentration, temperature, solubility and substituents. The two types of aggregation observed are H-type and J-type [30]. The PQCoPc complex exhibited less of J-type aggregation but more of H-type aggregation in solvents.

The PQCoPc complex aggregation studies were performed by using different concentrations of DMF solvents (Fig. 6a). The Q-band intensity increased with the concentration of DMF solvent. The PQCoPc complex aggregation studies were performed by using different solvents like DMSO, EtOAc, $CHCl_3$, THF and DMF (Fig. 6b). The Q-band intensity increased with DMF solvent. The aggregation studies of the PQCoPc complex were measured in the concentration range from 12×10^{-6} to 6×10^{-6} mol dm^{-3}. The PQCoPc complex exhibited high coordinating ability and solubility in DMF and DMSO solvents. Therefore, more aggregation took place in these two solvents but less aggregation was observed in EtOAc and $CHCl_3$ solvents.

The above overall results showed that the aggregation of PQCoPc complex was better in DMF solvent. It increased the

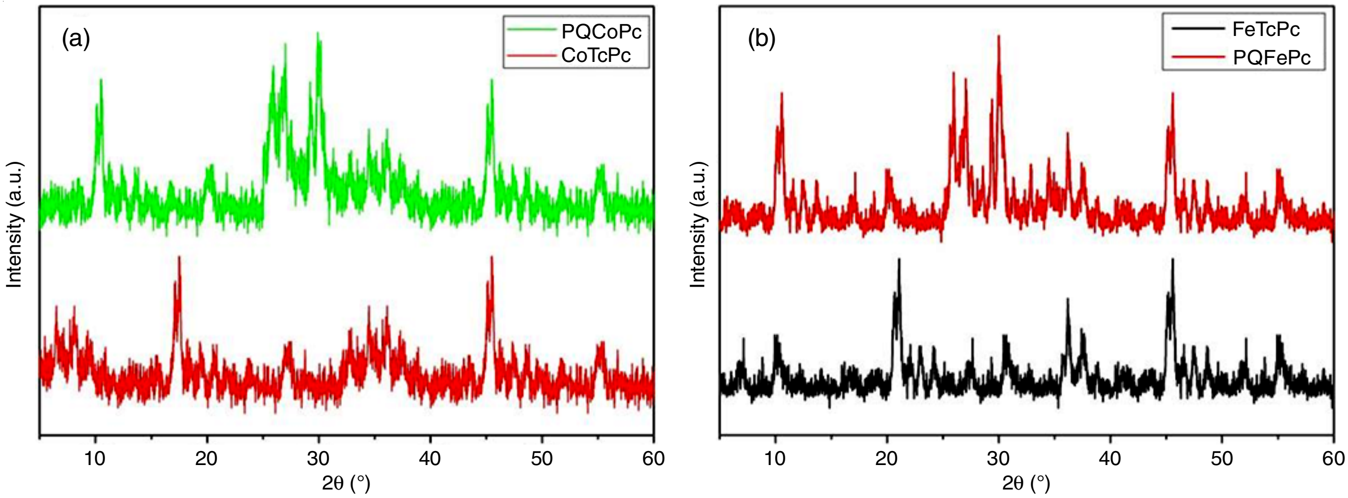


Fig. 5. P-XRD spectra of (a) PQCoPc with CoTcPc complex (b) PQFePc with FeTcPc complex

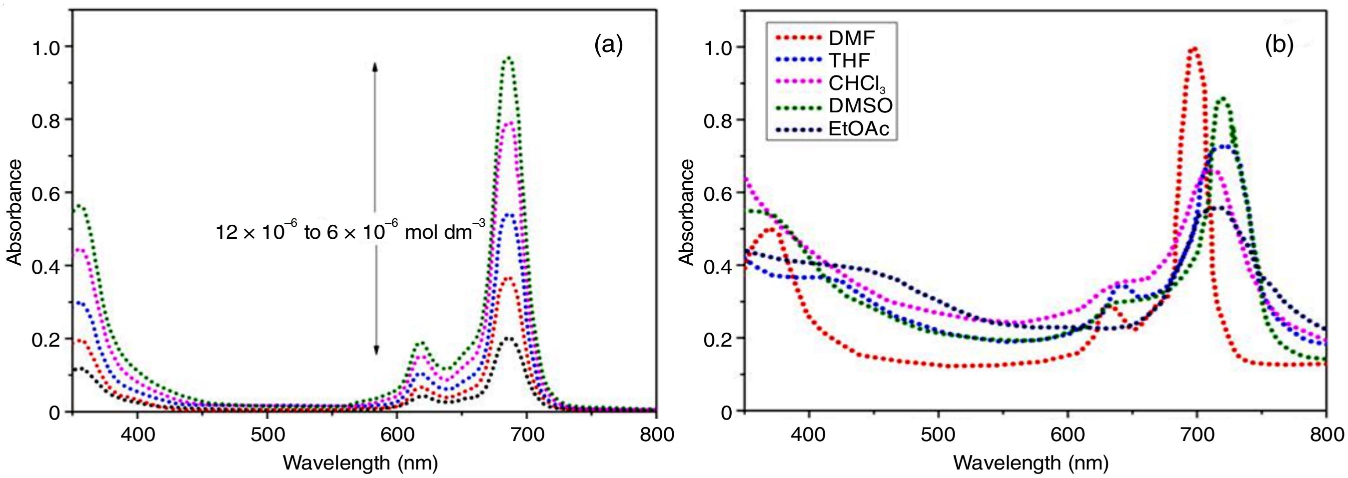


Fig. 6. Aggregation behaviour of (a) DMF solvents with different concentration (b) PQCoPc with different solvents (DMF, THF, $CHCl_3$, DMSO and EtOAC)

absorption of Q-band by an increase of the concentration of DMF solvent.

Catalytic studies: Oxidation of benzyl alcohol was performed in presence of PQCoPc and PQFePc complexes as catalysts using gas chromatographic method and applied by various parameters of catalytic oxidation reactions *e.g.*, the percentage conversion and selectivity of products have been studied. The catalytic oxidation was performed by using various oxidants and auxiliary chemicals to reach good yields. In the oxidation reaction, benzyl alcohol was converted into various organic products. The major product is benzaldehyde (Bzald) and the minor products are benzoquinone (BzQn) and benzoic acid (BzAc). The peripherally substituents play an important role in the catalytic reaction [24].

The catalytic oxidations of benzyl alcohol to benzaldehyde were carried out in the presence and absence of PQCoPc and PQFePc catalysts and suitable oxidant at 50 ºC (Table-1). The catalytic oxidation reaction was found to give low yield of benzaldehyde in absence of catalyst. But, in presence of catalyst, an excellent yield (98%) was recorded after 3 h. There is no product formed (Table-2) when the catalytic oxidation was performed in absence of an oxidant. These results proved that the oxidation of benzyl alcohol, PQCoPc and PQFePc catalyst and oxidants are required and the present synthesized compounds have important role in the oxidation of benzyl alcohol.

Effect of substrate concentration: The transformation of benzyl alcohol to benzaldehyde was increased with the continuous reaction and yielded maximum conversion of 98% for PQCoPc and 95% for PQFePc after the reaction continued for 210 min and remains ideal with a slight increase as shown in Table-1. On the other hand, as the reaction precedes further oxidation of benzaldehyde to benzoic acid leads to decreased selectivity. From these results, 210 min was chosen as the optimal reaction time for conversion and selectivity of catalytic oxidation reaction of benzaldehyde to benzoic acid.

The conversion of benzyl alcohol to various organic products by uneven addition of the substrate/catalyst in a molar ratio varying from 600 to 1600 at 45 ºC is shown in Table-2. The obtained data shows that as the substrate/catalyst ratio is increased, the conversion of benzyl alcohol was found to decrease. The high mass of the substrate and low mass of the catalyst exhibits low conversion of benzyl alcohol due to fewer catalytic sites. From these result, it can be concluded that 600/1 substrate/catalyst ratio is ideal for the efficient conversion of benzyl alcohol (98% for PQCoPc and 95% for PQFePc) when compared to ratios reported in the previous studies [31,32].

Effect of oxidants concentration: Table-3 shows oxidation effects of benzyl alcohol with PQCoPc and PQFePc with the varied molar ratio of substrate/oxidant. If the ratio of TBHP/benzyl alcohol was increased from 0.83 to 3.3, the conversion

TABLE-2
OXIDATION OF BENZYL ALCOHOL WITH PQCoPc AND PQFePc BY VARYING OF QUANTITY OF SUBSTRATE

Substrate/ catalyst	Catalyst	Aldehyde (Bzald)	Quinine (BzQn)	Acid (BzAc)	Total conv. (%)	TON (mole of product/mole of catalyst)	TOF (h^{-1}) (mole of product/ mole of catalyst × time)
600/1	1c	82	8	8	98	584	196
	2c	79	9	7	95	566	190
800/1	1c	66	8	7	81	642	214
	2c	70	9	7	86	682	228
1000/1	1c	58	8	6	72	712	238
	2c	55	9	7	71	702	234
1200/1	1c	48	6	6	60	710	238
	2c	46	7	6	59	698	234
1600/1	1c	33	5	6	46	722	242
	2c	33	6	5	44	690	230
600/1	Absence of catalyst	–	–	–	–	–	–

TABLE-3
OXIDATION OF BENZYL ALCOHOL WITH PQCoPc AND PQFePc WITH VARIOUS AMOUNTS OF OXIDANTS

Oxidant/ catalyst	Catalyst	Aldehyde (Bzald)	Quinine (BzQn)	Acid (BzAc)	Total conv. (%)	TON (mole of product/ mole of catalyst)	TOF (h^{-1}) (mole of product/ mole of catalyst × time)
500/1	1c	84	5.9	8.1	98	584	196
	2c	83	4.3	7.7	95	566	190
800/1	1c	79	3.2	3.8	86	500	168
	2c	74	4.2	4.8	83	518	174
1200/1	1c	76	2.7	2.3	81	476	160
	2c	70	3.2	3.8	77	464	156
1600/1	1c	61	6.3	4.7	72	380	128
	2c	59	4.9	4.1	68	362	122
2000/1	1c	54	7.6	7.4	69	308	104
	2c	50	5.1	4.9	60	260	88
Without oxidant	Without catalyst	–	–	–	–	–	–

rate of benzyl alcohol was decreased from 98% to 52% for PQCoPc and 95% to 44% for PQFePc complexes. When the substrate and oxidant ratio increased to 0.83 benzyl alcohol conversion reaches 98% for PQCoPc and 95% for PQFePc, it exhibits high turnover number (TON) and turnover frequency (TOF) values of 584, 196 for PQCoPc and 566, 190 for PQFePc, respectively. The above result corroborates that a decrease in benzyl alcohol conversion rate is inversely related to the amount of TBHP oxidant [33]. The PQCoPc selectivity for benzaldehyde is 84%, while the PQFePc's selectivity is 83% at this oxidant content. Therefore, all these results revealed that the molar ratio of TBHP:benzyl alcohol of 0.83 was ideal with high conversion rate and selectivity.

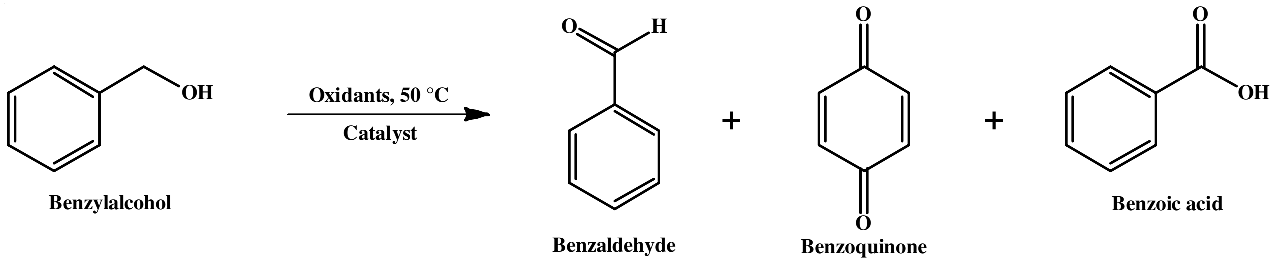
Effect of temperature: The oxidation of benzyl alcohol was performed at various temperatures ranging from 25 to 90 ºC in the presence of PQCoPc and PQFePc catalysts. A drastic change was observed in the conversion of benzyl alcohol (Table-4). It can be observed that as the temperature increased from 25 to 50 ºC, the rate of conversion of benzyl alcohol increases from 61% to 98% for PQCoPc and 58% to 95% for PQFePc. When temperature was increased above 50 ºC, benzaldehyde selectivity was found to be decreased slightly. This decrease in selectivity of benzaldehyde can be attributed, as before, to the loss of benzyl alcohol [24]. Therefore, 50 ºC is the ideal temperature for producing a good yield of benzaldehyde.

Oxidant effect: The catalytic oxidation of benzyl alcohol (**Scheme-II**) was conducted with PQCoPc and PQFePc by various oxidants hydrogen peroxide (H_2O_2) and *meta*-chloroperbenzoic acid (*m*-CPBA), which produces fewer yields of both PQCoPc and PQFePc complexes as shown in Table-5. The reaction of PQCoPc and PQFePc yields brown products from green colour in the presence of *m*-CPBA and H_2O_2. The colour changes due to PQCoPc and PQFePc were degraded immediately with H_2O_2 and *m*-CPBA. All of these findings suggest that TBHP is an effective oxidant for selectively converting benzaldehyde. In the presence of TBHP oxidant, the colour of both complex becomes light green from green.

The PQCoPc catalyst showed good catalytic effect with the highest conversion, TON and TOF values compared with the PQFePc catalyst. The catalytic activity also varies with the

TABLE-4
OXIDATION OF BENZYL ALCOHOL WITH PQCoPc AND PQFePc BY VARYING OF TEMPERATURE

Temp. (°C)	Catalyst	Aldehyde (Bzald)	Quinine (BzQn)	Acid (BzAc)	Total conv. (%)	TON (mole of product/ mole of catalyst)	TOF (h^{-1}) (mole of product/ mole of catalyst × time)
25	1c	56	3	2	61	356	120
	2c	50	5	3	58	392	132
50	1c	83	8	7	98	584	196
	2c	81	7	7	95	566	190
70	1c	62	5	3	70	368	124
	2c	55	7	6	68	362	122
90	1c	46	4	2	52	302	102
	2c	40	6	4	50	290	98



Scheme-III: Benzyl alcohol oxidation reaction

TABLE-5
OXIDATION OF BENZYL ALCOHOL WITH PQCoPc AND PQFePc BY VARIOUS OXIDANTS

Oxidant	Catalyst	Aldehyde (Bzald)	Quinine (BzQn)	Acid (BzAc)	Total conv. (%)	TON (mole of product/ mole of catalyst)	TOF (h^{-1}) (mole of product/ mole of catalyst × time)
TBHP	1c	82	8	8	98	588	200
	2c	79	9	8	96	570	194
H_2O_2	1c	56	12	-	68	396	136
	2c	55	9	-	64	380	130
m-CPBA	1c	36	10	6	52	300	104
	2c	27	8	7	42	236	84

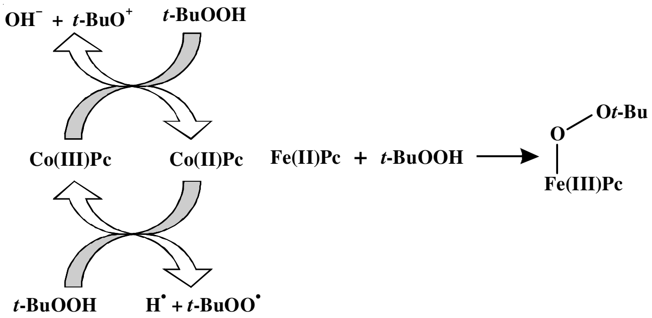
TABLE-6
COMPARISON STUDY OF VARIOUS CATALYSTS WITH PQCoPc AND PQFePc CATALYSTS

Catalyst	Reaction time	Reaction temperature (°C)	Oxidant	Conversion (%)	Ref.
CuPc^A	0.5 h	70	TBAOX	25.0	[34]
CoPc^B	5.5 h	70	TBHP	26.6	[35]
PdPc^B	24 h	50	*m*-CPBA	31.3	
MnTEPyP^C	4 h	60	TBHP	47.0	[36]
CuTPP^D	40 min	60	O_2	40 (in toluene) 35 (in benzene)	[37]
PQFePc	3 h	50	TBHP	98	Present work
PQCoPc	3 h	50	TBHP	96	

^{A}Pc = Un-substituted phthalocyanine; ^{B}Pc = perfluoroalkylphthalocyanine; ^{C}TEPyP = water soluble metalporphyrins; ^{D}TPP= copper meso-tetraphenylporphyrin

transition metals present in the phthalocyanine ring [22]. Thus, it is concluded that PQCoPc catalyst exhibits more oxidation reaction compared with PQFePc catalyst (PQCoPc > PQFePc).

Comparison study of various catalysts with PQCoPc and PQFePc Catalysts for oxidation of benzyl alcohol: In present work, the reaction mechanism of PQCoPc and PQFePc with TBHP gives an active species. When phthalocyanine was compared to a porphyrin molecule with the same oxidation state of the central metal atom, phthalocyanine shows good stability and exhibits a strong oxidizing ability. When oxidant as TBHP, in the first step formation of PcCo(III)-OO*t*-Bu or PcFe(III)-OO*t*-Bu. Normally, peroxides react with porphyrin Fe complex *via* homolytic cleavage of the O-O bond to form porphyrin $Fe^{IV=O}$ or porphyrin $Fe^{V=O}$ species. It indicates that porphyrin Fe would be reacting with *t*-BuOOH, similarly, the $PQFe_{IV=O}$ or $PQFe^{V=O}$ reaction takes place in **Scheme-III** [38,39]. The catalytic oxidation of benzyl alcohol using different catalyst and their comparative data are presented in Table-6.



Scheme-IV: Red-ox reactions involving as *t*-BuOOH

Conclusion

In present work, the synthesis, characterization and the catalytic properties of two novel peripherally tetrasubstituted phthalocyanine compounds in association with primaquine functionalized groups *i.e.* Fe(II) phthalocyanine (PQFePc) and Co(II) phthalocyanine (PQCoPc) were conducted. All the synthesized compounds were characterized by FTIR, UV-visible, mass, XRD, elemental analysis and thermogravimetric studies. The PQFePc and PQCoPc complexes show good aggregation behaviour in DMF and DMSO solvents. The catalytic activities of PQCoPc and PQFePc were executed for the oxidation of benzyl alcohol with various oxidants by varying the temperature, oxidant/catalytic ratio and substrate/catalyst ratio affect. The oxidation reactions were carried out to determine the optimum conditions of catalysts. Both PQCoPc and PQFePc complexes showed good catalytic activity for the oxidation of benzyl alcohol with high benzaldehyde selectivity by using *tert*.-butyl hydroperoxide (TBHP) as an oxidant. In conclusion, these catalytic works are expedient, time saving and determined to be the best oxidation conditions with high turnover number (TON) and turnover frequency (TOF) values.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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