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POLY (ESTER-AMIDE) HAVING PENDENT 8-QUINOLINOL MOIETY AS A NOVEL POLYMERIC LIGAND

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ABSTRACT

The Poly(ester-amide) (PEA) was prepared by polycondensation of 1,4-phenylenebisphthalamic acid and commercial epoxy resin i.e. diglycidyl ether of bis phenol- A. The PEA was then treated with 5-chloromethyl-8-quinolinol hydrochloride. The resultant polymeric ligand designated as PEA-8-quinolinol (PEAQ) was characterised by elemental analysis, IR spectral studies and thermogravimetry. The polymeric metal chelates of PEAQ with Cu^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+} and Co^{2+} metal ions were prepared and characterised by metal:ligand ratio, IR and reflectance studies, magnetic properties, thermogravimetry and microbicidal activity.

Key words: Polyester amide, Epoxy resin, Spectral studies, Magnetic properties, Thermogravimetry, Microbicidal activity, Polymeric metal chelates.

INTRODUCTION

Literature survey reveals that polymer bearing 8-quinolinol moiety have many potential application in areas such as waste water treatment to recover metals, protective coatings, water disinfectants, antifouling paints, antimicrobial, surgical materials , gels and ointment for medical uses[1-7]. Several scientists[8-11] published a series of papers on polymers and copolymers of 8-quinolinol either present as end group or as pendent group with a view to study their complexing ability and biological activity. The study of 8-quinolinol containing polyester has also been reported[12]. On the basis of this the present authors have made an attempt to synthesize poly (ester-amide) containing 8-quinolinol as pendent group. Thus synthesis, Characterization and chelating properties of novel ligand namely (5-methyleneoxy8-quinolinolyl) poly (ester-amide) PEAQ have been presented in this communication. The whole research work is scanned in Scheme-1.

EXPERIMENTAL

Materials

All the chemicals were of LR grade. Commercial epoxy resin. (DGEBA i.e. diglycidyl ether of bispenol-A) was purchased from local market. The epoxy equivalent of this DGBEA was found to be ≈ 170. Bisamicacid namely 1,4-phenylenebisphthalamic acid was prepared by reported method[13].

Synthesis of polymeric ligands

The ligand PEAQ was prepared as follow:

(1) Synthesis of poly (ester-amide) (PEA):

The synthesis of PEA was prepared by method reported for the synthesis of PEA based on unsaturated bisamic acid and diamine[14]. In a stirred glass round bottom flask with condenser, DGBEA (0.1mole) and 1,4-phenylenebisphthalamic acid (0.12 mole) in 50 ml acetone were mixed, followed by the addition of 1 ml pyridine as catalyst. The reaction mixture was refluxed until the reaction mixture gave the negative test for epoxy group[15]. After completion of the reaction receiving constant acid value i.e 50mg KOH/gm the reaction product was washed several times with large amount of acetone to remove unreacted reactants. The poly(ester-amide) resin thus obtained was in form of semisolid mass. Yield was 90%.

Analysis: $(C_{43}H_{40}N_2O_8)_n$ $(712)_n$

	C %	H %	N %
Calcd	72.47	5.61	3.93
Found	72.3	5.6	3.9

M_n (VPO) (DMF): 4400

(2) Preparation of 5 – Chloromethyl – 8 – Quinolinol Hydrochloride:
According to the reported method[16] a mixture of 8-quinolinol (7.3 gm 0.05 mole) concd HCl (8ml) and 37% formalin solution (8ml 0.05 mole) was treated with dry gaseous hydrochloric acid for 1.5 hrs. The resulting yellow solid was filtered. Washed and dried. The yield was 77% and m.p. 280 °C[16].

(3) Preparation of polymeric ligand PEAQ.
It was prepared by employing the method reported for 5-alkoxymethyl 8-quinolinol[16]. According to this method sodium bicarbonate (0.1 mole) was added to a suspension of 5- choloromethyl8-quinolinol hydrochloride (0.1 mole) and PEA (0.05 mole) in THF. The reaction mixture was refluxed for 2 hr with frequent shaking. The resulting mixture was made alkaline with dilute ammonia solution and the solid separated was filtered off. The solid PEAQ was collected, washed with alcohol and air dried. The yield was 65%. It was green in colour.

Synthesis of polymeric chelates:
The polymeric metal chelates of PEAQ were synthesized by reaction of PEAQ with corresponding metal acetates. The detail procedure is as follows.
A dried PEAQ polymer (0.01 mole) was dissolved in 200 ml aqueous solution of 20% formic acid and warmed on a water bath for 10 minutes. To this solution a warm solution of metal acetate (0.01 mole) in 50% aqueous formic acid solution was added drop wise with constant stirring. The reaction mixture as made alkaline with dilute ammonia solution in order to precipitate out polymeric chelates. The resultant contents were further digested on water bath for an hour. Finally the solid polymer chelates were filtered off. Washed with hot water followed by acetone, DMF and dried in air. Thus the polymer chelates of PEAQ with Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} transition metal ions have been prepared.

Measurements
Elemental analyses for C,H and N content were carried out on TF 1101 elemental analyzer (Italy). IR spectra of polymer ligand and their metal chelates were scanned on a NICOLET 760 DR FTIR spectrophotometer in KBr phase. The metal content of polychelates were performed by decomposing a weighed amount of each polymer chelate followed by EDTA titration as reported in literature[17]. Magnetic susceptibility measurements of all the polychelates were carried out at room temperature by the Gouy method using Mercury tetrathiocyanato cobaltate (II) Hg [Co (NCS)4] as a calibrant. The diffuse reflectance spectra of all the solid polychelates were recorded on a Backman DK-2A spectrophotometer with solid reflectance attachments. MgO was employed as the reference attachments. MgO was employed as the reference compound. Thermal behaviour of these metal chelates were studied by TGA performed on thermogravimetric analyzer.

RESULTS AND DISCUSSION

Characterization of polymeric Ligand PEAQ:
The PEA sample was in form of pasty mass. The C,H,N contents and are consistent with the predicted sample. The number average molecular weight by end group COOH analysis and by VPO method is 4400. It was directly used for further reaction product i.e. PEAQ.
PEAQ ligand was light green powder insoluble in solvents such as water, acetone, dioxane, DMSO and DMF. Results of elemental analyses of PEAQ for C,H and N reported in Table-1 are found to be

consistent with the predicted structure as shown in scheme 1.Examination of IR spectrum of PEAQ reveals that a broad band in the range of 3370-3400 cm^{-1} is assigned to stretching vibration of O-H bonded with ring containing nitrogen[18]. The absorption bands at 1465, 1430, 1512 and 1606 cm^{-1} in the IR spectrum of PEAQ are characteristics for 8-quinolinol moiety[17]. The weak bands at 2726 and 2820 cm^{-1} attributes to aliphatic chain. The band at 1165 cm^{-1} is due to C-O stretching of aliphatic ether group. An intense and clear band of an ester and amide carbonyl of polyester amide has been indicated by the strong absorption frequency around 1735cm^{-1}. In addition to these evidences of PEAQ ligands, the IR spectrum of parent ligands has many characteristic bands occurring in 5,5'methylene bis(8-quinolinol) [18].Further conforming the predicted structure as shown in Scheme-1.

The thermal behaviour of PEAQ was studied by thermogravimetric analysis. The TGA data are presented in Table II and its thermogram is shown in Fingure-1.Examination of these data reveals that the ligand degrade in a single step and decompose in the temperature range of 300-450ºC. Almost 90% weight loss is reached at 500-600 ºC temperature.

Characterization of Polymeric Chelates:

The polymeric chelates of PEAQ with different metal ions such as Cu^{2+}, Ni^{2+}, Co^{2+}, $Mn^{2+}$and Zn^{2+} vary in color from dark green to brown. The IR spectra of all of the polymeric chelate of PEAQ are similar to each other in their general shape, but the comparison of the IR spectrum of the parent ligand PEAQ with those of its polymeric chelate has revealed certain characteristic difference.

One of the significant differences to be expressed between the IR spectrum of the parent ligand and that of its metal coordinated polymers is the presence of much broader bands in the region of 3000-3600 cm^{-1} for the polymeric chelate, as the oxygen of the O-H group of the ligand forms a coordination bond with the metal ions. This is explained by the fact that water molecules could have strongly absorbed to the polymer sample during its formation. Another noticeable difference is that the band due to C=N stretching vibration of 8-hydroxyquinoline at 1600 cm^{-1} in the IR spectrum of PEAQ is shifted lower frequency, whereas the band at 1420 cm^{-1} in the IR spectrum of PEAQ assigned to in-plane –OH deformation[19] is shifted towards higher frequency in the spectra of the coordination polymers. This may be due to chelation of metal with 8-hydroxyquinoline. This features has been further confirmed by a weak band at 1100 cm^{-1} corresponding to C-O-M stretching[19] and the band around 780 and 640 cm^{-1} corresponding to the M-N vibration in coordination polymers. Thus, all of these characteristic feature of the IR studies suggest the structure of the polymeric chelate shown in Scheme 1.

Examination of data about metal content in each polymeric chelates (Table- I and II) has revealed a 1:1 metal:ligand stoichiometry in all the polymeric chelates. Magnetic moment (μ_{eff}) data of polymer chelates given in Table I has reveals that all metal chelates like Cu^{2+}, Ni^{2+} and Co^{2+}, Mn^{2+} are paramagnetic, while that of Zn^{2+} is diamagnetic in nature. The electronic spectral data assignment are shown in Table-3. The diffuse electronic spectrum of PEAQ with Cu^{+2} ions show two broad bands at 14950 and 23529 cm^{-1} due to $^2B_{1g}\rightarrow{}^2A_1g$ transition and charge transfer spectra respectively suggesting a distorted octahedral structure for PEAQ polymer chelates. The PEAQ with Ni^{2+} and Co^{+2} ion polychelates give two absorption bands respectively at 14925, 24096 and 9025 cm^{-1} corresponding to $^3A_{1g}\rightarrow 3T_1g(F)$,$^3A_{2g}\rightarrow{}^3T_2g(F)$, and $^3A_{2g}\rightarrow{}^3T_1g(P)$ and 14925, 22471 and 9550 cm^{-1} corresponding to $^4T_{1g}(F) \rightarrow 4A_{2g}$, $^4T_{1g}\rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F)\rightarrow{}^4T_2g(F)$ respectively[20-22]. Thus, absorption band of diffuse reflectance spectral and the values of magnetic moment (μ_{eff}) have indicated an octahedral configuration for the Ni^{2+}, and Co^{2+} polychelates. The spectra of polychelates of Mn^{2+} ion show two weak bands at 18349 cm^{-1} and 23869 cm^{-1} and 16828 assigned to the transition $^6A_{1g}\rightarrow{}^4T_{2g}$ (G) , $^6A_{1g}\rightarrow{}^4T_{1g}$(G) and $6A_{1g}\rightarrow{}^4T_1g(G)$ respectively and assigned an octahedral structure for PEAQ chelates. As the spectrum of the Zn^{2+} chelates is not well resolved it is not interpreted but its μeff value reveals its diamagnetic nature as expected. The TGA data (typical in figure-1) of all polymeric chelates are shown in Table-2. Inspection of TGA data and thermograms of reveals that the rate of decomposition of all polymeric chelates is initially low up to 200ºC temperature and rapidly increases to maximum in the range 400-500 ºC. This might be due to accelerated catalytically by `*insitu*` formation of metal oxide. The thermal stability of all these polymeric chelates is quite similar.

CONCLUSIONS

The investigation described in the present paper reveals the following conclusions:

1. The reaction epoxy based poly (ester-amide) with 5-chloromethyl-8-quinolino hydrochloride afford a 5-methyleneoxy-8-quinolinoyl poly(ester-amide) (PEAQ) polymeric ligands containing 8-quinolinol as a pendent groups.
2. The applicability of PEAQ polymeric ligand was explored by preparing polymer chelates using different divalent metal ions. It indicates that the prepared polymer ligands have good chelating property and high thermal stability.
3. The metal chelates are thermally less stable than the corresponding polymeric ligand. Further the polymer chelates of Cu^{2+}, Ni^{2+}, and Co^{2+} are paramagnetic, while that of Zn^{+2} is diamagnetic nature.
4. Further work in the connection with other polymeric ligands and ion-exchanging properties are under progress.

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Table-1:Elemental analyses of polymeric metal Chelates of PEAQ and their metal chelates.

Sample designation	Elemental Analysis								Magnetic moment μ_{eff}
	C%		H%		N%		M%		
	Cald	Found	Cald	Found	Cald	Found	Cald	Found	B.M
PEAQ	71.45	71.4	5.10	4.9	5.29	5.2	-----	----	------
PEAQ (Cu^{2+})	67.52	67.5	4.64	4.6	5.00	4.9	5.67	5.6	1.78
PEAQ (Ni^{2+})	67.82	67.8	4.66	4.6	5.02	5.0	5.26	5.24	3.00
PEAQ (Co^{2+})	67.80	67.7	4.66	4.5	5.02	4.9	5.28	5.27	4.03
PEAQ (Mn^{2+})	68.05	68.0	4.68	4.6	5.04	4.8	4.94	4.90	5.39
PEAQ (Zn^{2+})	67.41	67.3	4.63	4.6	4.99	4.8	5.83	5.82	D

D= Diamagnetic

Table-2:Thermogravimetric analysis of PEAQ and its metal chelates

Sample	% Weight loss at different temperature (°C)					
	100	200	300	400	500	600
PEAQ	4	9	30	48	63	70
PEAQ (Cu^{2+})	2	4	20	50	70	90
PEAQ (Ni^{2+})	1.5	3	18	48	73	90
PEAQ (Co^{2+})	1.5	3	18	50	75	94
PEAQ (Zn^{2+})	2	4	19	51	74	93
PEAQ (Mn^{2+})	2	4	45	70	90	95

Table-3: Spectral Features and Magnetic Moment of PEAQ Metal Chelates

Metal Chelates	Electronic spectral data (cm^{-1})	Transition	IR spectral features common for all (cm^{-1})	
PEAQ-Cu^{2+}	23529	Charge transfer	1650	QuinolineMoiety

	14950	$^2B_{1g}\rightarrow{}^2A_{1g}$	1565 1500 1460	
PEAQ-Ni^{2+}	24096 14925 9025	$^3A_{2g}\rightarrow{}^3T_{2g}(F)$ $^3A_{1g}\rightarrow{}^3T_{1g}(F)$ $^3A_{2g}\rightarrow{}^3T_{1g}(P)$	2920 2850 1450	CH_2
PEAQ-Co^{2+}	22471 14925 9550	$^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ $^4T_{1g}(F)\rightarrow{}^4A_{2g}$ $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$	1100 500	C-O-M & O-M Bands
PEAQ-Mn^{2+}	23869 18349 16826	$^6A_{1g}\rightarrow{}^6A_{2g}$ (G) $^6A_{1g}\rightarrow{}^4T_{2g}$ (G) $^6A_{1g}\rightarrow{}^4T_{1g}$(G)	710 750	Ar-Cl
PEAQ-Zn^{2+}		---------	------	------

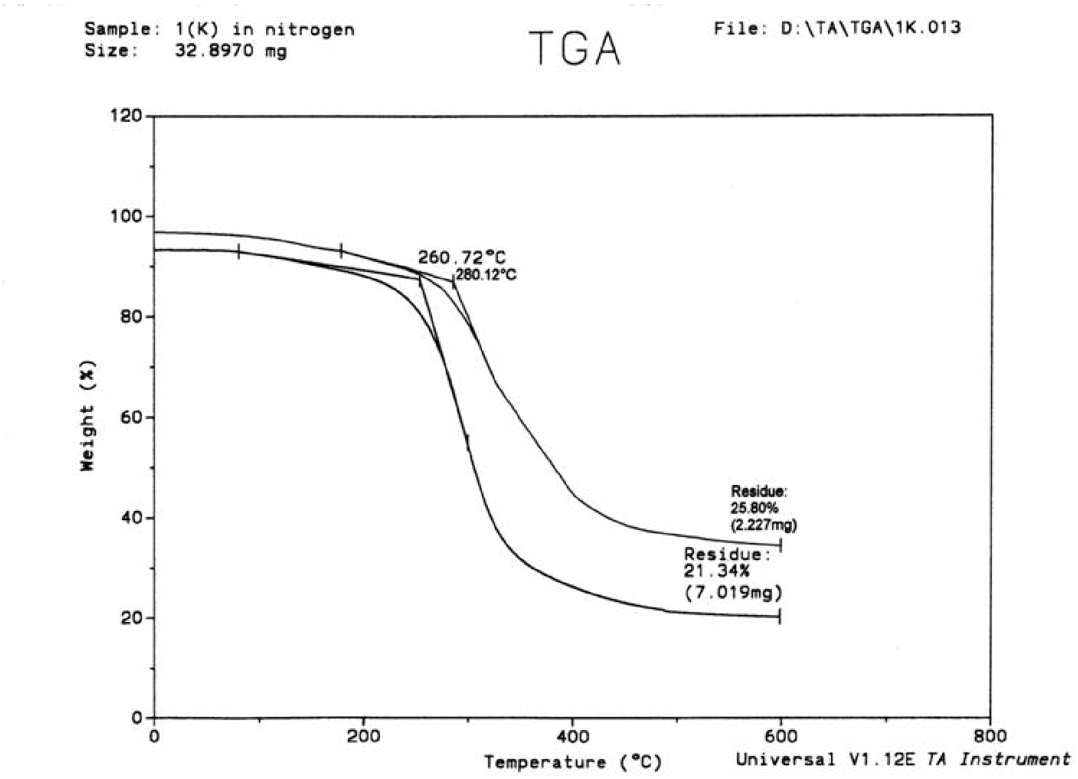
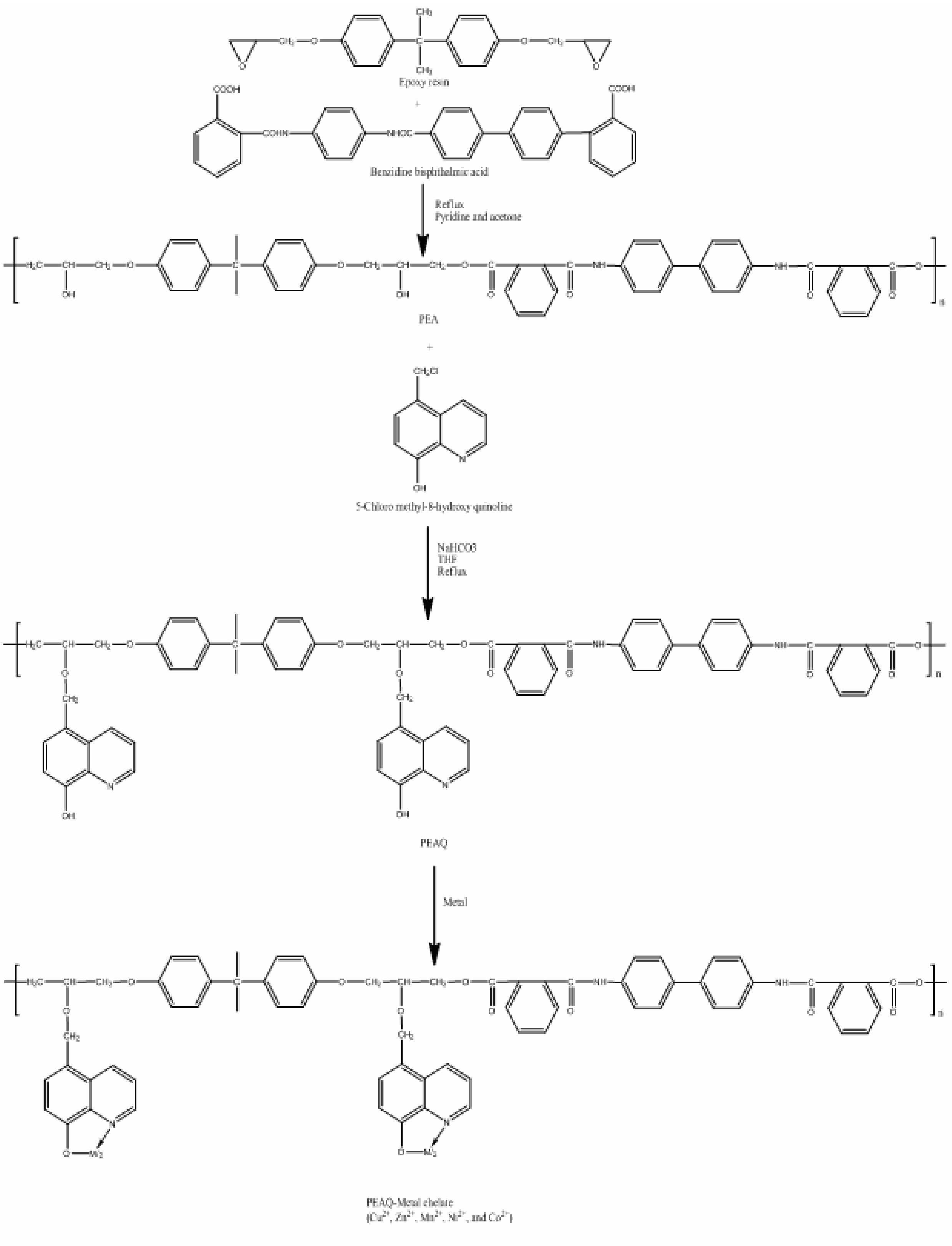


Fig.-1: TGA Thermogram of (1) PEAQ ligand (upper) and (2) PEAQ-Mn^{+2} polychelate (lower)


Epoxy resin
+
Benzidine bisphthalmic acid
Reflux
Pyridine and acetone
PEA
+
5-Chloro methyl-8-hydroxy quinoline
NaHCO3
THF
Reflux
PEAQ
Metal
PEAQ-Metal chelate
(Cu^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, and Co^{2+})

Scheme-1

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