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Synthesis, Characterization and Study of electrical properties of novel Azo polymer and Azo poly chelates

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Abstract

4,6 Dinitroresorcinol undergo reduction with alcoholic alkali to form a new Azo polymer Poly[Azo(1-napthol)] These Co-ordination polymers Poly azo chelates were prepared with Cu^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2} and Zn^{+2} Metal ions. The newly polymer synthesised at scheme-1 shown in Figure-1 were characterized by various spectral techniques. The polychelates reported in this study were coloured solids and practically insoluble in water and in regular organic solvents. We have characterized with elemental analysis, molar magnetic susceptibilities, spectroscopic (IR & Reflactance) data and Thermogravimetric analysis. Nonaqueous conductometric titrations were used to determine the number average molecular weight $\overline{Mn}$ of the compound. Room temperature conductivity data for ligand and its polychelates indicated that the electrical conductivity of these compounds lie in the semi-conducting range ($1.33x10^{-8}$ to $8.20x10^{-11}cm^{-1}$). The $\log\sigma$ vs 1/T plots were found to be linear, which also indicated the semiconducting behavior of the ligand and the polychelates in the temperature range studied. The general conduction behaviour of the electrical conductivity (σ) can be described by $\sigma = \sigma_0 \exp(-Ea/kT)$, where σ_0 is a constant, Ea the activation energy of the conduction process. The magnitude depends on T the absolute temperature and where K is the Boltzman constant. Activation energy (Ea) Az-ligand (Polymer) The Azo polymer (Az),poly[azo(1-napthol)] and poly chelates is derived from the slope of plots with values from 0.60 – 1.78 eV and they are shown to follow this order Az-Cu^{+2}>Az-Mn^{+2}>Az-lig>Az-Co^{+2}>Az-Zn^{+2}>Az-Ni^{+2}.

Keywords: Azo polymer, poly chelates, electrical conductivity, Thermal activation Energy, Spectroscopic Characterization.

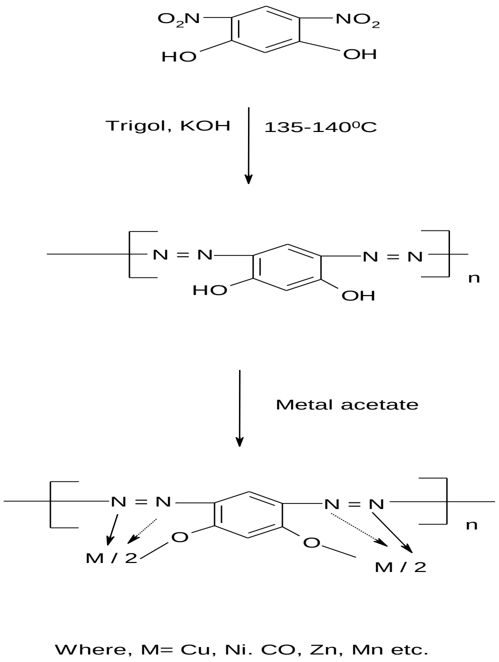
Introduction

Aromatic azo polymers are azo-group containing polymers, which can be prepared by oxidative polymerization of aromatic diamines in the presence of catalysts[1-3]. Ravve and fitko[4] have prepared AzoPolymers by coupling of different bisdiazonium salts to various poly phenols or phenol formaldehyde condensates. The azo polynmers have been synthesized on the basis of amalgamation of numerous suitable azo structures known from the prior references by the breakdown of bisdiazonium salt[5], or by their antecedents[6] by hydrogen liberation from aromatic diamines through free radical[7], by poly conensation of azo benzene derivatives or by homo polymerization of dyes having[8-13] olefinic groups[14-16]. However, due to their azo structure the azo polymers (poly (azo arylenes) and azo poly chelates) cannot be dyed and pigmented in traditional ways and are infusible and insoluble. May change the properities up to great extent for these polymer chain. -OH groups, Due to the rapid development of the study of electrical properties of organic polymers in recent years Many Polymers doped or by metal atom held together classified us as organic semi conductors[17-19] well Known polymers having poly acetylene, poly phenylene, polyaniline etc.[20-25] most of the conducting polymers are of conjugated chain systems. Few dopents improves the conductivity of the polymers[26-30], one such are where the poly (azoarylenes) having conjugated system has been reported[31], but the conducting properties not studied Hence so all the polymers and poly azo chelates are synthesised for their electrical conducting properties and externally a considerable interest in hunting of photoactive materials which aim to convert solar to electrical energy efficiently. Therefore, it is important to synthesize and study new semiconducting materials for sustainable energy. Since azo arylene polymers based on dinitro arylene have been prepared and reported[52], it was considered worthwhile, to investigate the polymers obtained by its reduction with alcoholic alkaline of 4, 6 dinitro Resorcinol. The work reported in the present communication is storage of poly [azo (1-naphthol)] (Az) and its chelation with metal ion adjacent to the polymeric chain, as very few studies deal with this issue.

Recently, few applications of single crystal of co-ordination polymer ligating with transition metal ions have been found and been proved helpful[32-43], in addition multidentate organic ligands with transition metal compounds are being investigated at a large scale leading to the synthesis of new coordination supramolecules and polymers during last few years[44-48].

Polymer Metal complexes have strong research area now because of its semiconducting and catalytic properties[49]. The literature survey indicates that a great deal of work are done on the bivalent transition metal complexes of tri-tetra-hexavalent transition and inner transition metal ions with parent ligand polymer with an azo group[50]. Therefore, we have prepared a some new polyazochelates, parent ligand being Poly[azo(1-napthol)] (Az) with Az-Cu^{+2}, Az-Ni^{+2}, Az-Co^{+2}, Az-Mn^{+2} and Az-Zn^{+2}. These complexes have been characterized by elemental analysis, magnetic susceptibilities, spectroscopic (reflectance and IR) data and TG analysis, the number average molecular weight, was determined by non-aqueous conductometric titration[51], measurement of electrical volume conductivity using 2 probe D.C. Technique as per ASTM method.

The present paper deals with synthesis, characterization and electrical properties of azo polymer and its azo poly chelates are shown in Figure-1.



Poly(azo(1-napthol)-M^{+2}] polymer. Where M: Cu^{+2}, Co^{+2}, Ni^{+2}, Mn^{+2}, Zn^{+2}

Figure-1: The Synthetic route B-1 for the Formation of ligand and Co-ordination Polymers.

Materials and Methods

All chemicals were of either analytical grade or laboratory grade. The synthesis of poly[azo (1-Napthol)] was carried out in two steps. The preparation of poly [azo(1-Napthol)] ($_{Az}$) was according to a literature method[52].

Preparation of poly [azo (1-napthol)] as the azo ligand (Az): Iso nitrile (azo) ligand (Alcohilc alkaline reduction solution of 4,6 dintro resorcinol in trigol + KOH) self polymerization method reported for polymerization (dinitro ary lenes)[52]. A mixture of 4,6 dinitro resorcinol (17.0 gms, 0.1 mole) in tri ethylene glycol (Trigol) 150 ml was dissolved by adding solid KOH (44.8 gm, 0.8 mole) slowly (over about 10 m at room temperature) was stirred well till KOH was dissolved. After that the reaction was maintained at 100^0C for 3 hr and then the temperature was increased to 135-140^0C for 5 hr. The reaction was quenched by drop wise addition of a mixture of ethanol-HCl (50:50 V/V) and pH of the mixture was neutralized then it was frozen in an ice bath then desired solid was separated by filtration and washed with water and then solid was dried in oven. It was finally purified by dissolving in DMF and re precipitating by the addition of water. 90% Black Powder from yield.

Preparation of Co-ordination polymers (Azo poly chelates): In to a solution of metal with (0.005 mole) water (100 ml) was added drop wise Solution of ligand 0.01 mole(H) Azo polymer (Az) in water with rapid stirring. Thus, the pH for the the various azo ligands lies between 4.5 to 6 pH. The green blue solid was separated and purified as previously described. The polymer was filtered, suspended, then digested in a boiling water bath for 2 h. Finally, the solid greenish blue product was filtered and washed with a 1:1 mixture of water, ethanol and acetone died. The polymer [Az-M^{+2}] was dried in air. The Az-Cu^{+2}, Az-Ni^{+2}, Az-Co^{+2}, Az-Mn^{+2}, Az-Zn^{+2} polymers were very modest yield nearly full scale.

Electrical conductivity measurements: Polymers films of 2.88 cm diameter and about 0.23cm thickness were prepared from the pure polymers under $1x10^4$lbs/$inch^2$. Electrical volume conductivity measurements were carried using the standard most accurate 2-probe D.C. technique according to ASTM method[53]. The resistance of the materials was measured by using 'Hewlett Packard 4329A high resistance meter'. The well powdered compounds were pelletalise disotactically in a steel die under a pressure of $1x10^4$lbs/$inch^2$ using hydraulic press. A thin aluminium foil was placed to have good electrical contact. The pellet was kept in between two spring-loaded brass electrodes of a specially designed sample holder. A suitable electric furnace was used for electrical conductivity measurements at various temperatures, and the sample holder was introduced in the centre of the furnace.

The value of band gap can be obtained by using the Tauc relation ah υ = A (hυ -E_g)n

Measurements: The Az-ligand and its family of coordination polymers were thoroughly investigated using several analytical techniques. Elemental analysis of the ligand and polymer samples was performed using a Perkin Elmer C, H, N elemental analyzer from Italy. Infrared spectroscopy was employed to obtain IR spectra of the ligand and polymers in KBr using a Nicolet 760 D Spectrophotometer. Solid state diffuse reflectance spectra of all the coordination polymer complexes were recorded on a Backman DK-2A Spectrophotometer equipped with a solid reflectance attachment using MgO as the reference compound. The Number average molecular weights of the polymers were determined according to a previously reported method[54] Magnetic susceptibility measurements of the complexes were carried out using the Gouy method to determine their magnetic properties. Molar susceptibility values were diamagnetism corrected using Pascal's constants for diamagnetism of cation atoms. Thermogravimetric analysis of the polymer samples was performed on a PERKIN ELMER PYRIS 1 TGA in a slow streaming air environment to obtain their thermal degradation profiles.

Solid state electronic absorption spectra of the solid polymeric complexes were collected on a Beckman DK-2A spectrophotometer utilizing a solid reflectance accessory with MgO as the reference. Metal ion content of the coordination polymers was analyzed by decomposing a weighed amount of each chelate in mineral acids followed by quantitative determination according to a literature method[52].

Into a 100 mg chelate sample 1 ml of HCl, H_2SO_4 and $HClO_4$ each and 1 gm of $NaClO_4$ was added. Dried the sample with evaporating till it was converted into a solid salt then dissolved the salt in double distilled water with making up the volume. This solution was titrated with standard EDTA solution for determination of metal content.

Electrical Conductivity Measurements: Effect of chemical structure: Table-6 shows Volume Electrical Conductivity of pure prepared polymers under different electrical fields the electrical conductivity increased as the applied voltage increased as shown in the results. The applied voltage modified the polarization of azo moieties, enhanced their dipole moment and facilitated the charge transfer. The results confirmed that the influence of the investigated polymers chemical structures on the measured conductivity was apparent, since The Electrical conductivity polymeric chelates significantly influenced by the type of metal atom. Type of Polymeric ligands, size and shape of macromolecules. Since sometimes it is happening that the polymeric chelates has been formed, in that polymeric chelates it was thought that there might be cross-linking metal bridges between polymer chain. The formation of chelate polymer is consistent with the fact that all the polychelates also produced coloured solid products, which are insoluble in water or common organic solvents.

Temperature effect: Table-5 represents Electrical Conductivity of the prepared polymers at different temperature the electrical conductivity as a function of temperature increases systematically with temperature. Data show in Table-5 from the Linier plot of log electrical conductivity (σ) vs inverse absolute temperature, the corresponding calculated activation energy was reported in Table-5 for the first hypothesis the increasing in the conductivity with temperature elevation is belong to increasing the band distribution levels of conduction electrons from HOMO to LUMO by increasing temperature, this stand for an activation energy lay in 0.1 – 0.15 eV [55]. The second hypothesis is slightly changing the level of the thermal segmental mobility by increasing the temperature above the Tg. This need higher activation Energy than the First One[56] the result in Table-5 demonstrated that the second hypothesis is over way.

Results and Discussion

The synthesis of poly[azo(1-napthol)] was performed by reductive polymerisation of 4,6 dinitro resorcinol in triethylene glycol (Trigol) and KOH. The resulting Az-ligand was a black colour powder. The ligand is charactarized by elemental analysis & IR spectroscolic techniques as given below.

Elemental Analysis: The metal and C, H, N contents of ligand and metal complexes are shown Table-1 and are also consistent with the predicted structure.

IR Analysis: Table-2 showing tentative assignments of the important infrared spectral bands and the principal stretching frequencies for the synthesized azo ligand (Az) and its Co-ordination polymers KBr disks on Nicolet FTIR-760 spectrophotometer Azo-moiety has an excellent Intensity Bands are shown on IR spectra, Which are essentially the bands are because of phenolic hydroxyl (-OH) Functional group. This broad band between 3800-2700cm^{-1} in ligand and all the complexes is because of (-OH) group. The inflections in this band are seen at 2780 and 2820 cm^{-1} assigned to asymmetric and symmetric of $-CH_2$ group of CMO. The Bands at 3200–3650 $cm^{-1}$for $–CH_3$ and for the aromatic structures IR Frequencies bands at 3050, 1600, 1010 cm^{-1}. The bands correspond to OH stretching (3360-3400cm^{-1}), bending (1420 cm^{-1}), rocking (1280 cm^{-1}) and wagging (1090 cm^{-1}) vibrations due to the coordinated water molecules in their coordination polymers[57].

The Co-ordination polymers of Az-ligand were insoluble in usual organic solvents. Individually also one can decide that how this polymer falls in Poly dispersiity index but that will only give an overall picture, not based on molecular weight and thus it the Co-ordination polymers cannot be characterized in terms of molecular mass by conventional methods like osmometry, viscometry etc. No melting observed for these Co-ordination polymers upto 300°C this was followed by the Non-aqueous conductometric titrations were used to estimate Number Average Molecular weight $\overline{Mn}$ of Azo Polymer (Az).

Titration of required samples (without water) was done in Pyridine with the help of standardized sodium methoxide solution (in pyridine) prepared as titrating base using conductance measurements on conductance bridge METROHM KNODUCTOSKOP E 365.

Several other changes seemed likely, noting the widening of a band in the 3360-3450 cm^{-1} region was an obvious sign. Band due to and another band due to in plane deformation of –OH at 1420 cm^{-1} in the IR spectrum of Azo ligand (Az) shift to 1408 cm^{-1} in the IR spectrum of Complex due to deprotonation on the oxygen of the –OH group of the ligand and forms a coordination bond with metal ions whereas the same band at 1406 cm^{-1} in the IR spectrum of azo ligand (Az) was shifted to 1420 cm^{-1} in the IR spectrum of Azo liqand (Az) due to the absorption behaviour of the ligand, this was hereby analysed on the spectra of the complexes[58]. It was corroborated by a very weak band at 1090 & 1280 cm^{-1} assigned to the C-O Streching and -OH bending vibration of C-OH group of azo moieties, respectively.

Table-1: Analysis of Az-ligand and its Co-ordination polymers.

Compound Empirical Formula	Formula weight Mol Cal g/mol	Yield %	Elemental Analysis			
			% C	% H	% N	% M
			Calc/Found	Calc/Found	Calc/Found	Calc/Found
$C_{20}H_{08}N_8O_2$	392	90	43.90/43.8	2.43/2.40	31.14/34.1	-
$C_{20}H_{10}N_8O_2$. Cu^{+2}.$2H_2O$	493.5	74	48.63/48.60	2.43/2.40	22.69/22.65	12.86/12.80
$C_{20}H_{10}N_8O_2$. Nl^{+2}.$2H_2O$	489	72	49.07/49.00	2.45/2.45	22.90/22.90	12.06/12.00
$C_{20}H_{10}N_8O_2$. Co^{+2}.$2H_2O$	489	70	49.07/49.00	2.45/2.45	22.90/22.90	12.09/12.00
$C_{20}H_{10}N_8O_2$. Mn^{+2}.$2H_2O$	485	76	49.48/49.45	2.47/2.45	23.09/23.00	11.34/11.30
$C_{20}H_{10}N_8O_2$. Zn^{+2}.$2H_2O$	489	68	48.48/48.45	2.42/2.40	22.62/22.60	13.13/13.10

Table-2: Spectral Features and magnetic moment of metal chelates.

Co-ordination polymers (Metal Chelates)	μ_{eff} BM	Electronic Spectraldata cm^{-1}	Transition	IR spectral features common for all cm^{-1}
Az – Cu^{+2} ($C_{20}H_{10}N_8O_2$. Cu^{+2}.$2H_2O$)	5.88	23370 15650	Change Transfer $^2B_{1g} \rightarrow {}^2A_{1g}$	3800 – 2700 1420 – OH Azo moiety
Az – Ni^{+2} ($C_{20}H_{10}N_8O_2$. Nl^{+2}.$2H_2O$)	3.1	22500 15290	$^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (F) $^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (F)	2780 – CH_2 2820
Az – Co^{+2} ($C_{20}H_{10}N_8O_2$. Co^{+2}.$2H_2O$)	5.15	24660 19990 8792	$^4T_{1g}$ (F) $\rightarrow {}^6T_{2g}$ (V^1) $^4T_{2g}$ (F) $\rightarrow {}^4A_{2g}$ (V^2) $^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$ (P)	3200 – 3650 - CH_3 3050 1600 Aromatic 1010
Az – Mn^{+2} ($C_{20}H_{10}N_8O_2$. Mn^{+2}.$2H_2O$)	3.35	24040 18650 16225	$^6A_{1g} \rightarrow {}^4T_{2g}$ (^4G) $^6A_{1g} \rightarrow {}^6A_{1g}$ (^4E_g) $^6A_{1g} \rightarrow {}^4A_{1g}$ (^4G)	1406 ± 14 –N = N– 1110 C-O-M 1280 & O-M 1090 Bands
Az – Zn^{+2} ($C_{20}H_{10}N_8O_2$. Zn^{+2}.$2H_2O$)	D*	-	-	-

Table-3: Number Average Mol. Wt ($\overline{Mn}$) of poly[azo(1-napthol)] estimated by non-aqueous conductometric Titrations.

Azo Polymer (Azo-ligand)	Milliequivalents of base required for neutralization of one OH Group (First Break(Y)	Milliequivalents of base required for Complete neutralization (X)	Degree of polymerization D_p=X/Y	Number average molecular weight ($\overline{Mn}$)
Az-ligand	80	835	10.5	1250

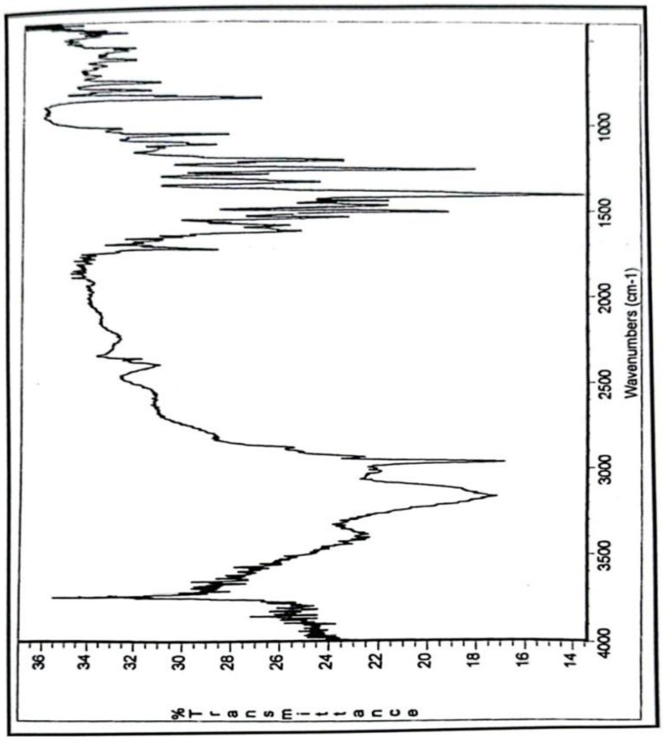


Figure-2: IR Spectrum of $C_{20}H_{08}N_8O_2$ poly [azo (1-Napthol)] / [Azo-ligand].

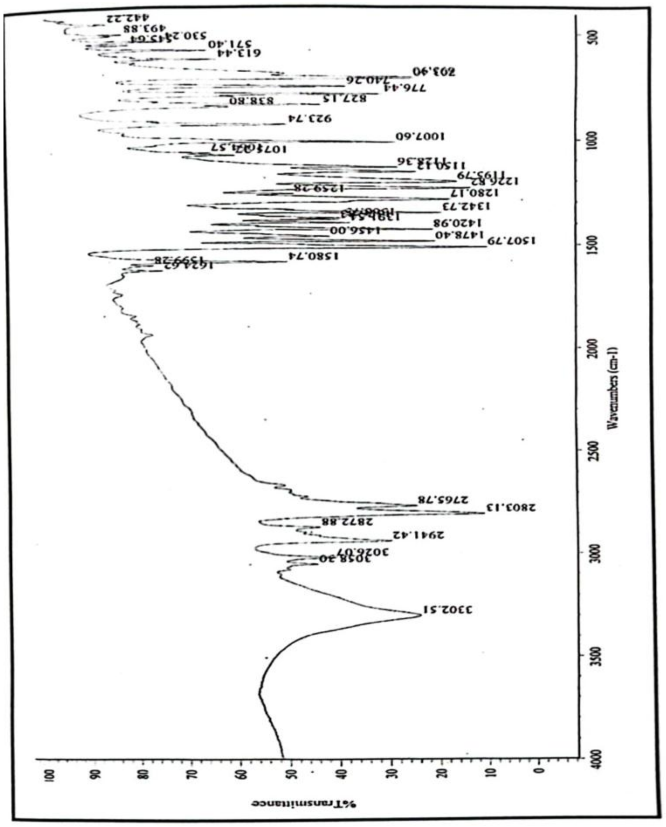


Figure-3: IR Spectrum of $C_{20}H_{10}N_8O_2$. $Cu^{+2}.2H_2O$, Co-ordination Polymer / Polyazo chelate.

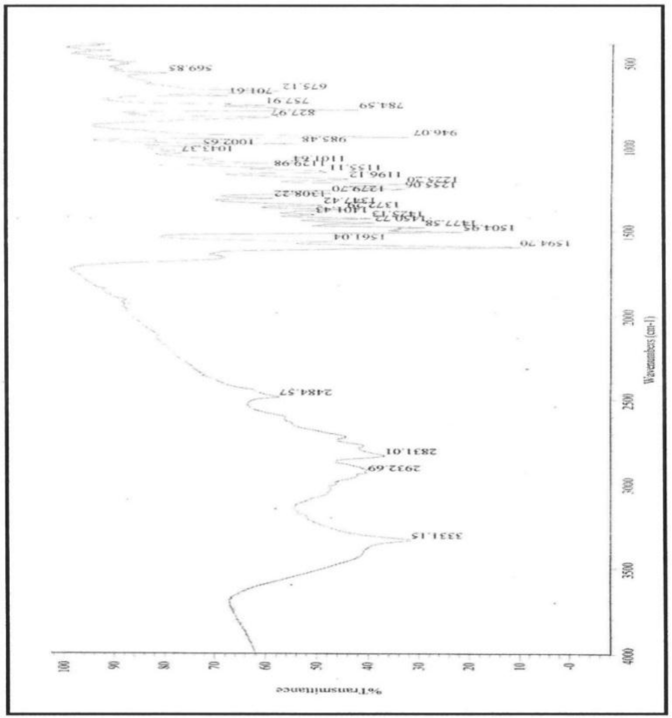


Figure-4: IR Spectrum of $C_{20}H_{10}N_8O_2$. $Nl^{+2}.2H_2O$ Co-ordination Polymer / Polyazo chelate.

Magnetic Measurements: Magnetic moments of metal complexes are listed in Table-2. The diffuse electronic spectrum of the copper (+2) complex shows two exceptionally broad bands at around 15,650 and 23,370 cm^{-1}. The first band might arise from a $^2B_{1g} \rightarrow {}^2A_{1g}$ transition, while the second is tentatively assigned to a charge transfer process. The primary band exhibits fine structures indicating a slightly distorted octahedral geometry for the copper (+2) metal complex, as noted previously[59,60]. Meanwhile, the spectrum of the nickel (+2) complex elucidates two clear bands at around 22,500 and 15,290 cm^{-1} assigned to $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ transitions respectively, suggesting the nickel (+2) ion resides in an octahedral environment. The measured µeff value in the range of 3.0-3.20 BM is consistent with this proposed structural motif. Two absorption bands at 24660, 19990 & 8792 cm^{-1} due to the $^4T_{1g}(F)\rightarrow{}^6T_{2g}(V1)$, $^4T_g(F)\rightarrow{}^4A_{2g}(V2)$ and $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ transitions respectively were assigned to Co^{+2} metal complex. These absorption bands and µeff value are the fingerprints for the octahedral configuration of Co^{+2} metal complex[61,62] observed µ in the range of 4.4 – 5.2 BM.

In the Mn^{+2} polymer complex the spectrum contained two bands situated at: 18650 cm^{-1}, and 24040 cm^{-1}. These bands can be attributed to $^6A_{1g}\rightarrow{}^4T_{2g}$ (4G) and $^6A_{1g}\rightarrow{}^6A_{1g}$ (4Eg) and $^6A_{1g}\rightarrow{}^4A_{1g}$ (4G) transitions respectively. The absorption bands of these compounds are found to occur around 18650 cm^{-1} attributed to $^6A_{1g}\rightarrow{}^4T_{1g}$ (^4G) and second around 24040 cm^{-1} due to $^6A_{1g}\rightarrow{}^4T_{2g}$ (^4G) transition. The study of these data reveals that Mn^{+2} compound has an octahedral structure.

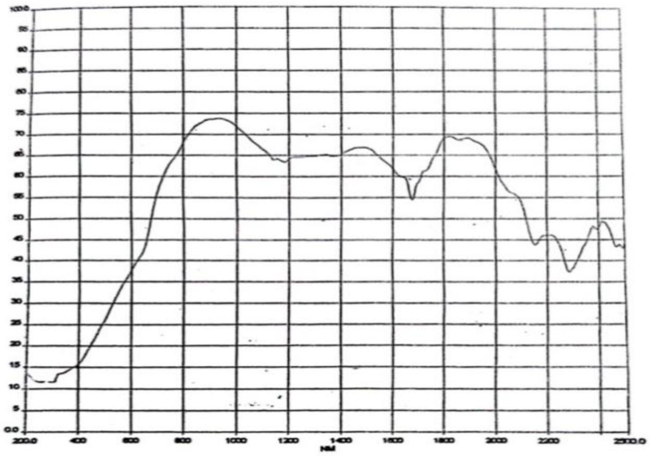


Figure-5: Reflectance spectrum of $C_{20}H_{10}N_8O_2$. Cu^{+2}.$2H_2O$ Co-ordination Polymer.

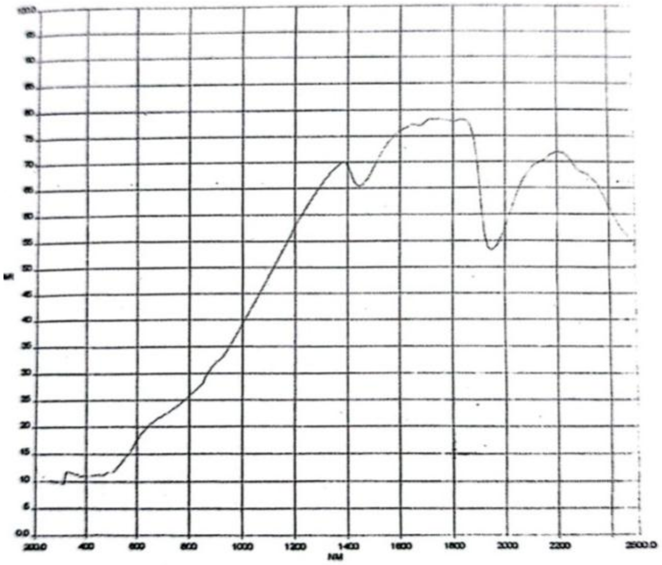


Figure-6: Reflectance spectrum of $C_{20}H_{10}N_8O_2$. Co^{+2}.$2H_2O$ Co-ordination Polymer.

Thermal Studies: For TGA data (Table-4) of Co-ordination polymers sample from room temperature to 600^0C the Degradation of Co-ordination polymers is visible above 300^0C. The degradation rate of Ni-Cu alloy frozen at a temperature between 350 and 400^0C is a maximum. This could be because of the catalyst of metal oxides that they make in situ. When heated to 450^0C, 80% of its weight of each polymer disappeared. Standard Inspection Print of the thermograms of all polymer samples showed that they had significant weight loss in the range of 200 to 350^0C. It is quite possibly due to the presence of a coordinated water molecule. This is further assisted by Nikolaev et al.[63].

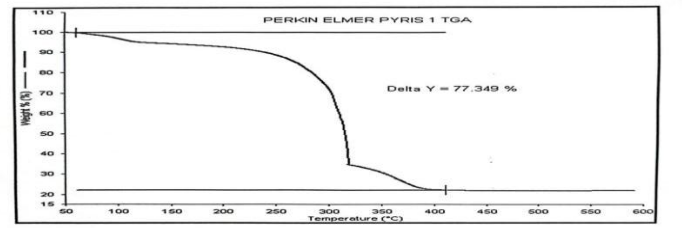


Figure-7: TGA Thermogram of Azopolychelate – ($C_{20}H_{10}N_8O_2$. Cu^{+2}.$2H_2O$) (Co-ordination Polymer).

Table-4: TGA data for Az-ligand containg Co-ordination Polymers.

Co-ordination Polymers (Metal Chelates)	% Wt loss at temperature			
	250	300	350	400
Az – Cu^{+2} ($C_{20}H_{10}N_8O_2$. Cu^{+2}.$2H_2O$)	6.2	7.8	16	70
Az – Ni^{+2} ($C_{20}H_{10}N_8O_2$. Nl^{+2}.$2H_2O$)	7.5	24.8	66	70
Az – Co^{+2} ($C_{20}H_{10}N_8O_2$. Co^{+2}.$2H_2O$)	2.8	5.3	24	67
Az – Mn^{+2} ($C_{20}H_{10}N_8O_2$. Mn^{+2}.$2H_2O$)	6.6	14.8	24	68
Az – Zn^{+2} ($C_{20}H_{10}N_8O_2$. Zn^{+2}.$2H_2O$)	7.0	20.0	60	75

Table-5: Electrical data of Azo ligand (Az) and its Polychelates.

Ligand/Poly Chelates	Activation Energy (Ea)(eV)	Electrical Conductivity (σ)($\Omega^{-1}cm^{-1}$)	Band Gap	The Break Temperature (K)
Az-ligand	1.12	1.52×10^{-11}	2.24	410-460
Az-Cu^{+2} ($C_{20}H_{10}N_8O_2$. Cu^{+2}.$2H_2O$)	1.78	8.20×10^{-11}	3.56	470-510
Az-Ni^{+2} ($C_{20}H_{10}N_8O_2$. Nl^{+2}.$2H_2O$)	0.60	1.33×10^{-8}	1.2	480-510
Az-Co^{+2} ($C_{20}H_{10}N_8O_2$. Co^{+2}.$2H_2O$)	0.98	1.15×10^{-10}	1.96	460-510
Az-Mn^{+2} ($C_{20}H_{10}N_8O_2$. Mn^{+2}.$2H_2O$)	1.40	8.00×10^{-11}	2.8	470-520
Az-Zn^{+2} ($C_{20}H_{10}N_8O_2$. Zn^{+2}.$2H_2O$)	0.90	1.44×10^{-8}	1.8	460-510

Table-6: Electrical Conductivity of the Azo-Polymer (Az-ligand) & its azo polychelates under different Temperatures.

Temp/(C^o)	Az-ligand	(Az-Cu^{+2})	(Az-Ni^{+2})	(Az-Co^{+2})	(Az-Mn^{+2})	(Az-Zn^{+2})
35	1.78 x 10^{-11}	1.50 x 10^{-11}	1.33 x 10^{-8}	1.56 x 10^{-10}	8.20 x 10^{-11}	5.87 x 10^{-11}
50	4.77 x 10^{-11}	1.36 x 10^{-11}	2.88 x 10^{-9}	3.00 x 10^{-10}	1.02 x 10^{-10}	1.09 x 10^{-9}
110	1.00 x 10^{-11}	1.36 x 10^{-11}	3.75 x 10^{-10}	6.80 x 10^{-11}	4.09 x 10^{-11}	2.12 x 10^{-9}
124	7.13 x 10^{-12}	1.40 x 10^{-11}	6.00 x 10^{-10}	4.05 x 10^{-11}	3.50 x 10^{-11}	0.60 x 10^{-9}
128	5.35 x 10^{-12}	1.43 x 10^{-11}	6.70 x 10^{-10}	3.08 x 10^{-11}	3.40 x 10^{-11}	0.50 x 10^{-9}
150	5.70 x 10^{-12}	1.61 x 10^{-11}	6.94 x 10^{-10}	3.11 x 10^{-11}	3.30 x 10^{-11}	0.23 x 10^{-9}
170	9.70 x 10^{-12}	2.75 x 10^{-11}	4.15 x 10^{-10}	2.81 x 10^{-11}	3.30 x 10^{-11}	0.17 x 10^{-9}
190	1.60 x 10^{-11}	6.24 x 10^{-11}	1.87 x 10^{-11}	3.09 x 10^{-11}	3.30 x 10^{-11}	0.18 x 10^{-9}
200	2.80 x 10^{-11}	9.82 x 10^{-11}	2.03 x 10^{-11}	3.25 x 10^{-11}	3.30 x 10^{-11}	0.17 x 10^{-9}
205	2.84 x 10^{-11}	1.48 x 10^{-11}	2.03 x 10^{-11}	3.40 x 10^{-11}	3.30 x 10^{-11}	0.20 x 10^{-10}
225	5.85 x 10^{-11}	2.15 x 10^{-11}	2.05 x 10^{-11}	3.54 x 10^{-11}	3.62 x 10^{-11}	0.23 x 10^{-10}
230	6.80 x 10^{-11}	3.75 x 10^{-11}	1.68 x 10^{-11}	3.40 x 10^{-11}	4.02 x 10^{-11}	0.25 x 10^{-10}
245	1.80 x 10^{-10}	7.00 x 10^{-11}	1.85 x 10^{-11}	6.20 x 10^{-11}	6.61 x 10^{-11}	0.33 x 10^{-10}
250	3.40 x 10^{-10}	1.34 x 10^{-11}	2.20 x 10^{-11}	7.88 x 10^{-11}	9.90 x 10^{-11}	0.53 x 10^{-10}
260	6.80 x 10^{-10}	3.04 x 10^{-11}	2.50 x 10^{-11}	11.1 x 10^{-11}	1.57 x 10^{-10}	0.87 x 10^{-10}
270	1.37 x 10^{-9}	7.22 x 10^{-11}	3.40 x 10^{-11}	14.4 x 10^{-11}	3.40 x 10^{-10}	1.11 x 10^{-11}
Ea$_{(eV)}$	1.12	1.78	0.60	0.98	1.40	0.90
log σ_0	+1.54	-0.61	-5.40	+1.60	-1.61	-2.00

Electrical Conductivity: Electrical Conductivity was recorded at 308K, at various Temperatures as summarized in Table-6. The ligand and polychelates show semiconducting nature with electrical conductivity (σ) running from 1.33x10^{-8} to 8.20x10^{-11} ohm^{-1}cm^{-1} at room temperature. The general behaviour of the electrical conductivity (σ) obeys the relation (σ) = σ_0 exp (-Ea/KT), where σ_0 is the constant, Ea is the activation energy of the conduction process. T the absolute temperature and K the Boltzman constant. Figure-8 to Figure-10 Represent Temperature Dependence of the Electrical Conductivity of ligand and Polychelates. Linear figures of log (σ) vs 1/T are showing that the samples are semiconductor over the studied temperature range. The conductivity plots clearly indicates that there is a normal semiconductor behavior (n-type)[64] wherein the conductivity increases with temperature as opposed to the positive temperature coefficient of conductivity for semi conductors[65].

The electrical conductivities of azo polymers and azo polymeric chelates are in the region of 10^{-11} to 10^{-8} cm^{-1} at room temp (308 K). However the conductivities of azo polymers and all chelates is generally very small at room temp but can be enhanced with temperature except initial increase is very slow up to/after a point between 410-510 (depends on the specific azo polymers/polymeric chelates etc.). While the logarithmic plots (σ) of inverse temperature for all specimens exhibited linearity at elevated temperatures, signifying the break Temperature where this transition occurred. Below this critical point, the rate of change in log 1/T was more gradual than the accelerated alteration seen above the break point in the higher heat range. It is from examining the divergence in gradient above versus below this break temperature within the high temperature regime that the activation energy E can be derived. Meanwhile, the temperature at which the specimens began demonstrating simple Arrhenius behavior served to define the transition temperature between the two observed reaction rates.

Activation energy provides a direct gauge of semiconductor band gaps. Therefore, lower activation energy correlates to narrower band gaps[66]. Among the studied polychelates, electrical conductivity at 308 K varied dramatically in magnitude. This differentiation may be attributed to dissimilarities in their conjugation, resonance, and the ionic radii of diverse metal ions. The activation energies for electrical conduction of the Az-ligand and their polychelates were determined from the slopes of these plots within the higher temperature region, ranging from 0.60 to 1.78 eV. The ordering from lowest to highest activation energy was Az-Cu^{+2}> Az-Mn^{+2}>Az-ligand>Az-Co^{+2}>Az-Zn^{+2}> Az-Ni^{+2}. The outcomes indicate that electrical conductivity and activation energy of polychelates fluctuate with the metal ion, which may suggest that incorporating different metal ions into the chelates augments their ionization propensity[67-70].

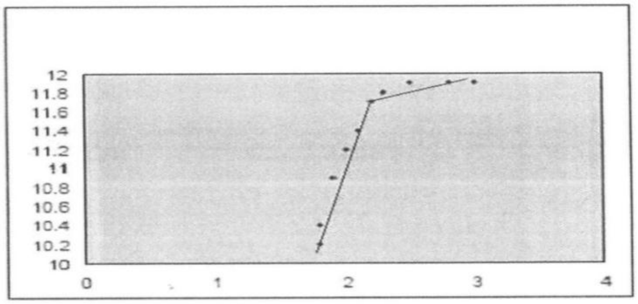


Figure-8: Electrical Conductivity of Az-Cu+2 Polychelate (where, X-Axis = 1/T x 10^3 (°K)^1 and Y-Axis = -log σ).

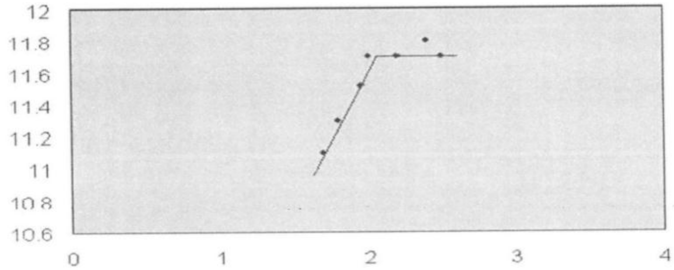


Figure-9: Electrical Conductivity of Az-Co*2 Polycate (Where, X-Axis = 1/T x 10^3 (°K)^1 and Y-Axis = -log σ).

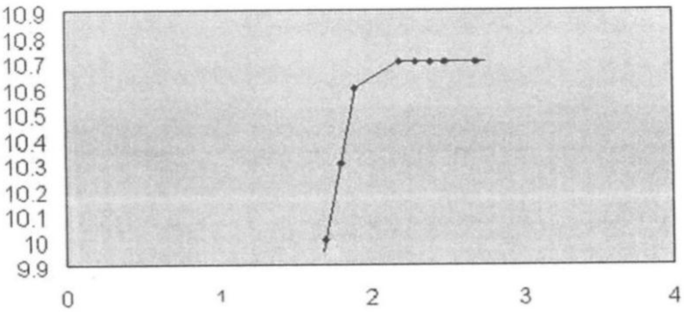


Figure-10: Electrical Conductivity of Az-Mn+2 Polychelate (Where, X-Axis = 1/T x 10^3 (°K)^1 and Y-Axis = -log a.

Conclusion

The crystalline structure of poly[azo(1-napthol)] is supported through elemental analysis, infrared spectroscopy, thermogravimetric analysis, and reflectance spectroscopy. Azochromophoric complexes display octahedral geometry according to reflectance spectral and conductometric studies. Further experimentation on various azo polymers formulated as Az-M^{+2} revealed that the degree of polymerization increases along with longer reaction durations. Both ligands and corresponding metal complexes exhibit decent thermal stability. Electrical conductivity analyses of the entire series of polymeric chelates classify them as semiconducting materials with high resistivity. Interestingly, copper (+2) and manganese (+2) polychelates presented enhanced conduction properties potentially caused by partial planarity within certain polymer segments. This work may facilitate the development of novel complexes with useful electrical conducting characteristics for promising electronic applications.

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References

1. Bach, H.C. (1966). Polymerproperties. Polymer Preprints, 7, 576.
2. Bach, H.C. (1969). Polymer characteristics. *Journal of Polymer Science*, 22, 799.
3. Kotyarevskii, E.K. (1964). Polymer studies. *Izvestiya Akademii Nauk SSSR*, 10, 1954.
4. Asquith, R.S. (1977). Dyeing properties of polymers. *Journal of the Society of Dyers and Colourists*, 93(4), 114-120.
5. Ravve, A., & Fitko, C. (1964). Polymer synthesis. *Journal of Polymer Science*, 2, 1925.
6. Berlin, A. A., & Parini, V. P. (1959). Polymer research. *Izvestiya Akademii Nauk SSSR*, 1674.
7. Berlin, A.A. (1964). Polymer advancements. *Izvestiya Akademii Nauk SSSR*, 705.
8. Sosin, S.L. (1964). Polymer studies. *Izvestiya Akademii Nauk SSSR*, 354.
9. Blako, N. (1961). Polymer compositions. U.S. Patent No. 2, 994, 693.
10. Mircea, I. (1975). Polymer chemistry. Makromolekul are Chemie, 174, 883. https://doi.org/10.1002/macp.1975. 021740501
11. Ryo, O. (1986). Polymer applications. Chemical Abstracts,

105, 61189b.

12. Jerca, F. A., Jerca, V.V., & Hoogenboom, R. (2022). Advances and opportunities in the exciting world of azobenzenes. *Nature Reviews Chemistry*, 6, 51-59. https://doi.org/10.1038/s41570-021-00334-4

13. Dembitsky, V.M., Gloriozova, T.A., & Poroikov, V.V. (2017). Pharmacological and predicted activities of naturalazo compounds. *Natural Products and Bioprospecting*, 7, 151-169. https://doi.org/10.1007/s13659-017-0118-5

14. Tanabe Seiyaku Co. Ltd. (1966). Polymer compositions. French Patent No.1,436, 140.

15. Asquith, R.S. (1977). Dyeing properties of polymers. *Journal of the Society of Dyersand Colourists*, 93(4), 114-120.

16. Inukai, Y. (1984). Polymer science advancements. *Contemporary Topics in Polymer Science*, 4, 183.

17. Berlin, A.A., & Matviejeva, N.G. (1960). Polymer chemistry. Uspekhi Khimii, 29,277.

18. Mark, J.E. (Ed.). (2003). Encyclopedia of polymer science and technology (3rded.). Wiley Inter science.

19. Bhandari, M., Kaur, D.P., & Alam, S. (2023). Electrically conducting smart biodegradable polymers and their applications. In Advances in biodegradable polymers (pp. 391-413). Springer. https://doi.org/10.1007/978-3-031-18328-7_17

20. Bredas, J. L., & Chance, R. R. (1990). Conjugated polymeric materials: Opportunities in electronics. optoelectronics, and molecular electronics. Springer.

21. Aldissi, M. (1993). Intrinsically conducting polymers: An emerging technology. Kluwer Academic Publishers.

22. McBride, J. W., & Lam, L. (2007). Polymeric materials in power engineering. In International Conference of Polymeric Materials in Power Engineering (ICPMPE), Bangalore, India, 4-6 October (pp. 9).

23. Shea, J. J. (2002). Conducting polymers, fundamentals and applications (Book Review). IEEE Electrical Insulation Magazine, 18(3), 60-61. https://doi.org/10.1109/MEI.2002.1014969

24. Shea, J. J. (2004). Conductive electro active polymers, intelligent materials systems. 2nd ed. (Book Review). IEEE Electrical Insulation Magazine, 20(2), 52. https://doi.org/10.1109/MEI.2004.1287471

25. Hannel, S., Fouvry, S., Kapsa, P., & Vincent, L. (2001). The fretting liding transition as a criterion for electrical contact performance. *Wear*, 249(9), 761-770.

26. Hjelm, J., Handel, R. W., Hagfeldt, A., Constable, E. C., House croft, C. E., & Forster, R. J. (2005). Conducting metallopolymers: The roles of molecular architecture and redox matching. *Inorganic Chemistry*, 44(4),

27. Apitz, D., Bertram, R. P., Benter, N., Sommer-Larsen, P., Johansen, P. M., & Buse, K. (2006). Investigation of holographic storage in conjugated polymers. *Chem Phys Chem*, 7(2), 468-476.

28. Nalwa, H. S. (1997). Handbook of organic conductive molecules and polymers (Vols. 1-4). John Wiley & Sons.

29. Chandrasekhar, P. (1999). Conducting polymers, fundamentals and applications. Kluwer Academic Publishers.

30. Obadhun, J., Oparah, E. N., Agho, O. B., & Okheh, Q. (2020). Synthesis, characterization and antimicrobial properties of polyaniline encapsulated azo dye. *International Journal of Scientific Research and Engineering Development*, 7(7), 229-236.

31. Kaynak, A. (1998). Electromagnetic shielding and conductivity of polypyrrole composites. *Materials Research Bulletin*, 33(8), 1309-1320. https://doi.org/10.1016/S0025-5408(98)00107-5

32. Batten, S. R., & Robson, R. (1998). Interpenetrating metal-organic frameworks. Angewandte Chemie International Edition, 37(11), 1460-1494.

33. Yaghi, O. M., O'Keeffe, M., Ockwig, N. W., Chae, H.K., Eddaoudi, M., & Kim, J. (2003). Reticular synthesis and the design of new materials. *Nature*, 423(6941), 705-714.

34. Kitagawa, S., Kitaura, R., & Noro, S. I. (2004). Functional porous coordination polymers. Angewandte Chemie International Edition. 43(18), 2334-2375. https://doi.org/10.1002/anie.200300610

35. Kitagawa, S., & Uemura, K. (2005). Dynamicporous coordination polymers. *Chemical Society Reviews*, 34(2), 109-119. https://doi.org/10.1039/B313997C

36. Roesky, H.W., & Andruh, M. (2003). Coordination polymers with nitrogen-donorligands. *Coordination Chemistry Reviews*, 236(1-2), 91-119. https://doi.org/10.1016/S0010-8545(02) 00210-8

37. Janiak, C. (2003). Engineering coordination polymers towards applications. *Dalton Transactions*, (14), 2781-2804. https://doi.org/10.1039/B305705B

38. Patel, N.H., Patel, K.N., & Patel, M.N. (2002). Synthesis and characterization of coordination polymers. *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, 32(10), 1879-1894. https://doi.org/10.1081/SIM-120016470

39. Selvaraj, V. (2021). An overview on recently developed techniques, mechanisms and intermediates involved in the advanced azodyedegradation for industrial applications. *Journal of Molecular Structure*, 1224, 129195. https://doi.org/10.1016/j.molstruc.2020.129195

40. Kumar, A. (2023). Role of conducting polymersin corrosion protection. *World Journal of Advanced Research* *and Reviews*, 17(2), 045-047. https://doi.org/ 10.30574/ wjarr. 2023.17.2. 0245

41. Dam, S. (2024). Engineering gas sensors with conducting polymers. Sensors and Actuators B: Chemical, 401, 134987. https://doi.org/10.1016/j.snb.2023.134987

42. Ahmed, H. (2023). Conducting polymers-based sensors: An overview. *Journal of Materials Science: Materials in Electronics*, 34(12), 987. https://doi.org/10.1007/s10854-023-10234-5

43. Ali, Y. (2018). Biomedical applications of aromatic azo compounds. *Mini-Reviews in Medicinal Chemistry*, 18(18), 1548-1558. https://doi.org/10.2174/138955751866 6180604083017

44. Moulton, B., & Zaworotko, M. J. (2001). From molecules to crystal engineering: Supramolecular isomerism and polymorphism in net works olids. *Chemical Reviews*, 101(6), 1629-1658. https://doi.org/10.1021/cr9900432

45. Zhang, G. Q., Yang, G. Q., & Ma, J. S. (2006). Two-dimensional coordination polymers. *Crystal Growth & Design*, 6(2), 357-360. https://doi.org/10.1021/cg0503246

46. Ghosh, A. K., Ghoshal, D., Ribas, J., Mostafa, G., & Chaudhuri, N. R. (2006). Coordination polymers with varying dimensionality. *Crystal Growth & Design*, 6(1), 36-39. https://doi.org/10.1021/cg0502080

47. Zang, S. Q., Su, Y., Li, Y. Z., Zhu, H. Z., & Meng, Q. J. (2006). Novel coordination polymers with luminescent properties. *Inorganic Chemistry*, 45(7), 2972-2978. https://doi.org/ 10.1021/ic0517067

48. Xu, Y., Yuan, D., Wu, B., Han, L., Wu, M., Jiang, F., & Hong, M. (2006). Coordination polymers with mixed ligands. *Crystal Growth & Design*, 6(5), 1168-1174. https://doi.org/ 10.1021/cg050624y

49. Kaliyappan T. & Kannan P. (2000). Co-ordination polymers. *Progress in Polymer Science*, 25(3), 343-370. https://doi.org /10.1016/S0079-6700(00)00008-6

50. Kitagawa S., Kitaura R., & Noro S.I. (2004). Functional porous coordination polymers. *Angewandte Chemie International Edition*, 43(18), 2334-2375. https://doi.org/10.1002/anie.200300610

51. Mitra R. P., & Chatterjee, S. K. (1963). Polymer studies. *Indian Journal of Chemistry*, 1, 62.

52. Desousa, G. A. (1978). Polymer chemistry. *Journal of Polymer Science: Polymer Chemistry Edition*, 16(10), 2671-2686. https://doi.org/10.1002/pol.1978.170161013

53. ASTM (1981). Annual book of standards, D.C. resistance or conductivity of insulating materials D527, part 39. American Society for Testing and Materials.

54. Apitz, D., Bertram, R.P., Benter, N., Sommer-Larsen, P., Johansen, P.M., & Buse, K. (2007). Holographic storage in conjugated polymers. *Chem Phys Chem*, 9(5), 768-775. https://doi.org/10.1002/cphc.200600672

55. Knudson, E., Helf, E., Quan, X., & Smith, S.D. (1993). Polymer properties. Macromolecules. 26(10), 2698-2703. https://doi.org/10.1021/ma00062a026

56. Khattab, A. F., Mahamood, S. F., & Shahab, Y. A. N. (2008). Optical properties of polymers. *Journal of Optoelectronics and Advanced Materials*, 10(6), 1463-1467.

57. Parekh, H. M., Panchal, P. K., & Patel, M. N. (2006). Thermal studies of coordination polymers. *Journal of Thermal Analysis and Calorimetry*, 86(3), 803-807. https://doi.org/10.1007/s10973-006-7631-7

58. Charles, R. G., Freiser, H., Friedel, R., Hilliard, L. E., & Johnston, R. D. (1958). Infrared absorption spectra of metal chelates derived from 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline, and 4-methyl-8-hydroxyquinoline. *Spectrochimica Acta*, 8(1), 1-9. https://doi.org/ 10.1016/ 0371-1951(58)80001-7

59. Hathway, B. J., & Tomlinson, A. A. G. (1970). Coordination chemistry of metal complexes. *Coordination Chemistry Reviews*, 5(1), 1-34. https://doi.org/10.1016/S0010-8545(00)80099-2

60. Pancholi, H. B., & Patel, M. M. (1996). Polymeric Schiff base complexes. *Journal of Polymer Materials*, 13, 261-267.

61. Papplardo, R. (1960). Spectroscopic studies of polymers. *The Journal of Chemical Physics*, 33(2), 613-614. https://doi.org/10.1063/1.1731193

62. Lewis, J., & Wilkins, R. S. (1960). Modern coordination chemistry. NewYork: Inter science Publishers.

63. Nikolav, A. V., Logvinenko, V. A., & Mychina, L. T. (1969). Thermal analysis of polymers. In Thermal Analysis (Vol. 2, pp. 779). Academic Press.

64. El-Manakhly, K. A. (1998). Electrical and magnetic properties of some anthraquinone omicron-carboxylicphenyl hydrazone metal complexes. *Journal of the Indian Chemical Society*, 75, 315.

65. Aswar, A. S., & Munshi, K .N. (1995). Studies on electrical properties of semiconducting chelate polymers. Journal of the Indian Chemical Society, 72, 883.

66. Katon, J.E. (1968). Organicsemiconductingpolymers. MarcelDekker,Inc.

67. Patel, M. N., Patel, P. P., & Upadhyaya, H. D. (1991). Electrical, thermal, magnetic, and spectral properties of polymeric Schiff base complexes derived from bis (salycyladehyde) sulphone and benzidine. *Indian Journal of Chemistry*, 30A, 813.

68. Bhadra, S., & Khastgir, D. (2007). Degradation and stability of polyaniline. Polymer Degradation and Stability. 92(10), 1824-1832. https://doi.org/10.1016/

j.polymdegradstab.2007.07.002

69. Massi, M., Al bonetti, C., Facchini, M., Cavallini, M., & Biscarini, F. (2006). Toward molecular electronics: Organic thin films. *Advanced Materials*, 18(20), 2739-2742. https://doi.org/10.1002/adma.200600614

70. Marques A. T., Silva J. A., Silva M. R., Beja A. M., Justino, L. L. G., & Sobral, A. J. F. N. (2008). Structural studies of coordination polymers. *Journal of Chemical Crystallography*, 38(4), 295-299. https://doi.org/10.1007/s10870-007-9308-9