



# Thermal Stability, Conductivity, and Band Gaps of Oligo-2-[(phenylimino) methyl] Phenol and Oligomer-metal Complexes

İsmat Kaya\* and Sermet Koyuncu

Department of Chemistry, Faculty of Sciences and Arts, Çanakkale Onsekiz Mart University, TR-17020, Çanakkale, Turkey

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## ABSTRACT

Schiff base oligomer of 2-[(phenylimino) methyl] phenol (2-PIMP) was synthesized via oxidative polycondensation reaction in an alkaline medium by using air ( $O_2$ ) as oxidant. Oligomer-metal complex compounds were synthesized from the reactions of oligo-2-[(phenylimino) methyl] phenol (O-2-PIMP) with  $Co^{+2}$ ,  $Ni^{+2}$ ,  $Cu^{+2}$ ,  $Cr^{+3}$ ,  $Pb^{+2}$ , and  $Zn^{+2}$  ions. While synthesized Schiff base oligomer was soluble in most common organic solvents, its metal complexes were only soluble in dimethylsulphoxide. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and electrochemical energy gaps ( $E_g$ ) of monomer, oligomer, and oligomer-metal complexes were calculated from oxidation and reduction onset values. Also, optical band gaps ( $E_g$ ) of monomer, oligomer, and oligomer-metal complexes were calculated from their absorption edges. Conductivity measurements of doped and undoped Schiff base oligomer and oligomer-metal complexes were carried out by electrometer at the room temperature and atmospheric pressure and were calculated by four-point probe technique. When iodine was used as doping agent, conductivity of oligomer and oligomer-metal complexes were observed to be increased. The weight losses of 2-PIMP, O-2-PIMP, O-2-PIMP-Co, O-2-PIMP-Ni, O-2-PIMP-Cu, O-2-PIMP-Cr, O-2-PIMP-Pb, and O-2-PIMP-Zn were found to be 100.00%, 79.09%, 68.28%, 65.97%, 51.33%, 70.14%, 54.13% and 66.77%, respectively, at 1000°C by using TG analyses.

## Key Words:

oligo-2-[(phenylimino) methyl] phenol;  
oligomer-metal complexes;  
band gap;  
conductivity;  
thermal analysis.

## INTRODUCTION

Conjugated Schiff base polymers and oligomers have been widely studied for the last two decades due to their excellent thermal, mechanical, electronic, optical, optoelectronic, and fibre-forming properties [1-5]. CH=N group is isoelectronic with the CH=CH group in these oligomers and the incorporation of nitrogen atom into the conjugated

system is another approach to form classes of materials with equally interesting electronic and optical properties [6]. Because of these properties of Schiff base oligomers they have become an increasingly interesting subject in the field of semiconductor and optical materials because these materials possess great potential for device applica-

(\*) To whom correspondence to be addressed:  
E-mail: [kayaismet@hotmail.com](mailto:kayaismet@hotmail.com)

tions such as light emitting diodes, thin film transistors, and photovoltaic cells [7,8]. Optical and electrical properties of the metal complexes have also become increasingly another interesting matter in the field of semiconductor and optical materials. Since, these materials possess great potential for device applications such as Schottky diode, solid state devices, and optical sensor [9].

Optical and electrochemical band gaps of low band gap polymers were calculated by Vanderzande et al. [10]. Conductivity and band gap of some Schiff base polymers including halogen atoms such as fluorine and chlorine were investigated by Kaya et al. [11,12]. The thermal and conductivity properties of Zn (II), Ni (II), Th (II), Cd (II), Mg (II) complex compounds of poly(8-acryloxyquinoline) were studied by Kaliyappan et al. [13]. The thermal and anti-microbial properties of oligophenols with a Schiff base substitute and their oligomer metal complex compounds were investigated by Kaya et al. [14]. The thermal stability of poly(acryloyl benzoic hydrazide) and its complexes with some transition metals was examined by Gad et al. [15]. The thermal decomposition behaviour of poly(acrylic acid) and its metal complexes were studied by Sebastian et al. [16]. Kaya et al. have studied thermal degradation of oligo-2-[(4-fluorophenyl) imino methylene] phenol and some of its oligomer-metal complexes [17]. The conducting properties of poly(2-hydroxy-4-acryloxyacetophenone-phenylimine), poly(2-hydroxy-4-acryloxyacetophenone-*N*-phenylimine-*co*-methacrylate) and their metal complexes were studied by Thamizharasi et al. [18].

In this work, we have synthesized Schiff base oligomer oligo-2-[(phenylimino) methyl] phenol (O-2-PIMP) and its metal complexes and investigated their thermal, electrochemical, optical, and electrical properties. Thermal behaviours and electrochemical properties of Schiff base oligomer and oligomer-metal complexes were determined by TGA-DTA and cyclic voltammetry techniques, respectively. Electrical properties of doped and undoped oligomer and oligomer-metal complexes were determined by four-point probe technique at a room temperature and atmospheric pressure. Also, O-2-PIMP-Co, O-2-PIMP-Ni, O-2-PIMP-Cu, O-2-PIMP-Cr, O-2-PIMP-Pb and O-2-PIMP-Zn were characterized by using FTIR, elemental analysis, and TG techniques.

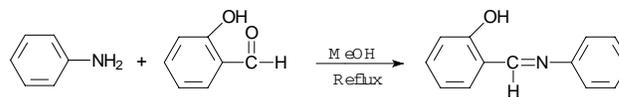
## EXPERIMENTAL

### Materials

Aniline, salicylaldehyde, tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) and ferrocene were supplied from Fluka. Acetonitrile, Co (AcO)<sub>2</sub> 4H<sub>2</sub>O, Ni (AcO)<sub>2</sub> 4H<sub>2</sub>O, Cu (AcO)<sub>2</sub> 4H<sub>2</sub>O, Pb (AcO)<sub>2</sub> 3H<sub>2</sub>O, Zn (AcO)<sub>2</sub> 2H<sub>2</sub>O, CrCl<sub>2</sub> 6H<sub>2</sub>O, and tetrahydrofuran (THF), dimethylformamide (DMF), dimethylsulphoxide (DMSO), methanol, and CHCl<sub>3</sub> which were used as solvent were supplied from Merck (Germany) and they were used as received. Hydrochloric acid (37%, HCl) and KOH were supplied from Merck, also.

### Synthesis of 2-[(phenylimino) methyl] Phenol

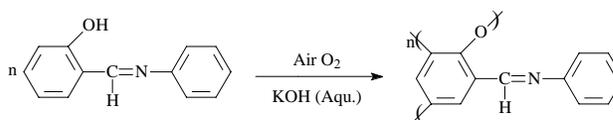
2-[(phenylimino) methyl] (2-PIMP) phenol was prepared by the condensation of salicylaldehyde (0.025 mol) and aniline (0.025 mol) in methanol (15 mL) achieved by boiling the mixture under reflux for 3 h (Scheme I). The precipitated 2-[(phenylimino) methyl] phenol was filtered and recrystallized from methanol and dried in vacuum desiccators.



Scheme I

### Synthesis of Oligo-2-[(phenylimino) methyl] Phenol (O-2-PIMP)

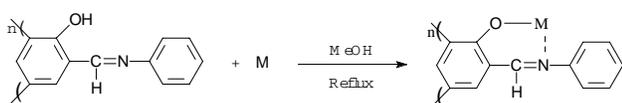
2-[(phenylimino) methyl] phenol (0.025 mol) was dissolved in an aqueous solution of KOH (10%) (0.025 mol). The reaction mixture was stirred at 70°C for 10 h. The air oxygen was passed into the mixture at rate 8.5 L h<sup>-1</sup> during the course of the reaction. The compound was obtained according to the published procedure (Scheme II) [19]. It was cooled to room temperature and then 0.025 mol of HCl (37%) was added to the reaction mixture. The mixture was filtered and washed with hot water (3 x 50 mL) for separating the mineral salts. Unreacted monomer was separated by washing the product of methanol and the product dried in the oven at 110°C.



Scheme II

### Synthesis of Oligo-2-[(phenylimino) methyl] Phenol-metal Complexes

A solution of  $M(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$  (0.250 mol) [(M: Ni, Co, Cu),  $\text{Pb}(\text{AcO})_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ , and/or  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ] in methanol (10 mL) was added to a suspension of oligo-2-[(phenylimino) methyl] phenol (O-2-PIMP) (0.250 mol/unit) in THF (20 mL) (Scheme III) [6]. The mixture was stirred and heated at 70°C for 5 h. The precipitated complexes were filtered and washed with cold methanol/THF, then dried in the oven. Metal sorption capacities and colours of oligomer-metal complexes are as follows: O-2-PIMP-Cr: 8.95%, dark green; O-2-PIMP-Co: 10.81%, dark brown; O-2-PIMP-Ni: 13.12%, brown; O-2-PIMP-Cu: 27.76%, brown; O-2-PIMP-Zn: 12.32%, dark brown; O-2-PIMP-Pb: 24.96%, dark brown.



Scheme III

### Electrical Properties

Conductivity was measured on a Keithley 2400 Electrometer. The pellets were pressed on hydraulic press developing up to 1687.2 kg/cm<sup>2</sup>. Iodine doping was carried out by exposure of the pellets to iodine vapour at atmospheric pressure and room temperature in a desiccator [3].

### Electrochemical Properties

Electrochemical properties of oligomer and oligomer-metal complexes were determined by CH instruments 660B cyclic voltammetry. The electrochemical cell consists of an Ag wire pseudo-reference electrode (RE), Pt wire as counter electrode (CE) and glassy carbon as working electrode (WE) immersed in 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) as supporting electrolyte. The voltammetric measurements of oligomer and its metal complexes were carried out in acetonitrile and DMSO, respectively and scan rate was 250 mVs<sup>-1</sup> [10]. The potentials were calibrated to the ferrocene redox couple  $E^\circ(\text{Fc}/\text{Fc}^+) = +0.41$  V vs. Ag/Ag<sup>+</sup>. The HOMO and LUMO energy levels and electrochemical energy gaps ( $E'_g$ ) were calculated from oxidation and reduction onset values.

### Optical Properties

The optical band gaps ( $E_g$ ) of monomer, oligomer, and oligomer-metal complex compounds were calculated from their absorption edges and are given in Table 2. Ultraviolet-visible (UV-vis) spectra were measured by Perkin Elmer Lambda 25. The absorption spectra of monomer, oligomer, and oligomer-metal complexes were recorded by using methanol and DMSO at 25°C [10].

### Characterization Techniques

The infrared spectra were measured by a Perkin Elmer FTIR spectrometer. The FTIR spectra were recorded using universal ATR sampling accessory (4000-550 cm<sup>-1</sup>). Elemental analysis was carried out with a LECO CHNS 932. The UV-vis spectra of monomer, oligomer, and oligomer-metal complex compounds were recorded by using methanol and DMSO, respectively. Thermal data were obtained by using Perkin Elmer Diamond Thermal Analysis. The TG-DTA measurements were made between 20-1000°C (in N<sub>2</sub>, rate 10°C/min). SEC analyses were performed at 30°C by using DMF/MeOH:4/1 v/v as eluent at a flow rate of 0.4 mL/min and a refractive index detector. The instrument (Shimadzu 10AVp series HPLC-SEC system) was calibrated with a mixture of polystyrene standards (Polymer Laboratories; the peak molecular weights,  $M_p$ , between 162 and 19880) using GPC software for the determination of the number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ) and polydispersity index (PDI) of the oligomer sample. For SEC investigations, a Macherey-Nagel GmbH was used (100 Å and 7.7 nm diameter loading material) 3.3 mm i.d. × 300 mm column.

## RESULTS AND DISCUSSION

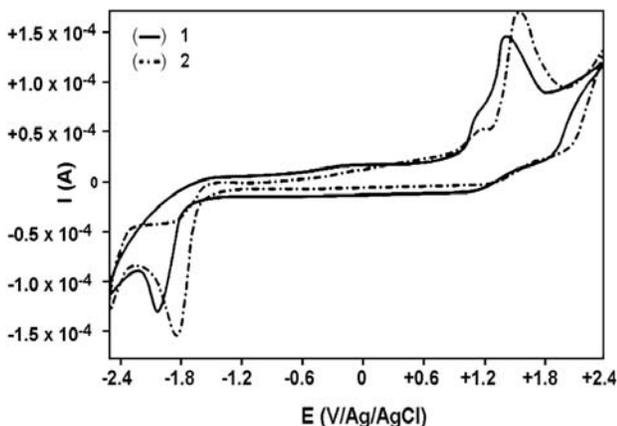
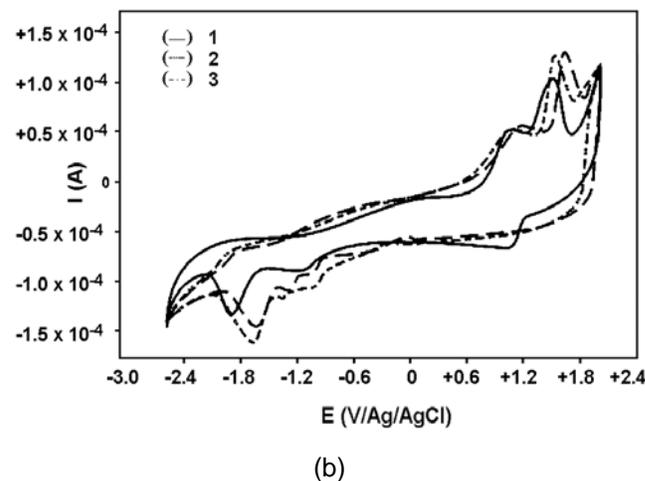
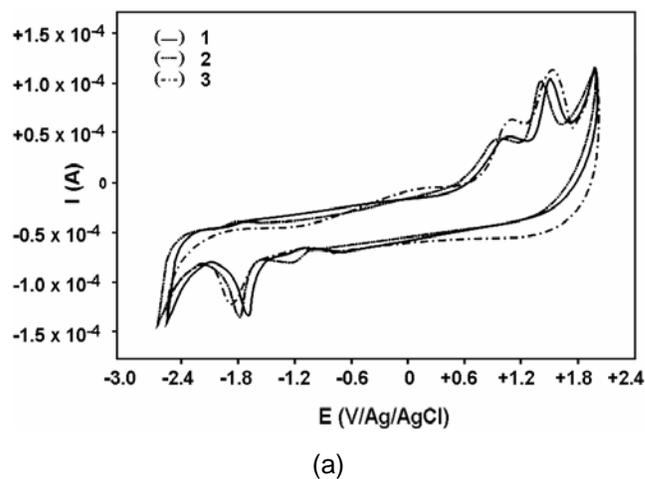
The voltammetric measurements of 2-PIMP, O-2-PIMP, O-2-PIMP-Co, O-2-PIMP-Ni, O-2-PIMP-Cu, O-2-PIMP-Cr, O-2-PIMP-Pb, and O-2-PIMP-Zn were carried out in acetonitrile and DMSO, respectively. The HOMO and LUMO energy levels and electrochemical energy gaps ( $E'_g$ ) were calculated from oxidation and reduction onset values and are given in Table 1 and shown in Figures 1, 2a, and 2b.

**Table 1.** HOMO-LUMO positions of 2-PIMP, O-2-PIMP, O-2-PIMP-Cu, O-2-PIMP-Ni, O-2-PIMP-Co, O-2-PIMP-Cr, O-2-PIMP-Pb, and O-2-PIMP-Zn.

Products	$E_{red}$ (V)	$E_{ox}$ (V)	LUMO (eV)	HOMO (eV)	$E'_g$ (eV)
2-PIMP	-2.02	+1.41	-2.46	-5.77	3.31
O-2-PIMP	-1.81	+1.56	-2.65	-5.80	3.15
O-2-PIMP-Cu	-1.64	+1.51	-2.84	-5.76	2.92
O-2-PIMP-Ni	-1.73	+1.43	-2.79	-5.78	2.99
O-2-PIMP-Co	-1.81	+1.58	-2.68	-5.74	3.06
O-2-PIMP-Cr	-1.84	+1.51	-2.72	-5.76	3.04
O-2-PIMP-Pb	-1.65	+1.53	-2.82	-5.84	3.02
O-2-PIMP-Zn	-1.59	+1.64	-2.86	-5.98	3.12

Electrochemical energy gaps ( $E'_g$ ) of 2-PIMP, O-2-PIMP, O-2-PIMP-Co, O-2-PIMP-Ni, O-2-PIMP-Cu, O-2-PIMP-Cr, O-2-PIMP-Pb, and O-2-PIMP-Zn were found to be 3.79, 3.29, 2.02, 2.42 and 2.56 eV, respectively. The absorption spectra of 2-PIMP, O-2-PIMP, O-2-PIMP-Co, O-2-PIMP-Ni, O-2-PIMP-Cu, O-2-PIMP-Cr, O-2-PIMP-Pb, and O-2-PIMP-Zn were recorded by using methanol and DMSO at 25°C, respectively and are given in Table 2 and shown in Figures 3 and 4.

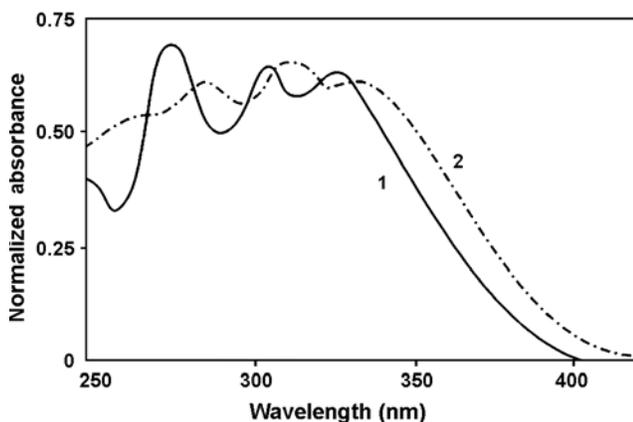
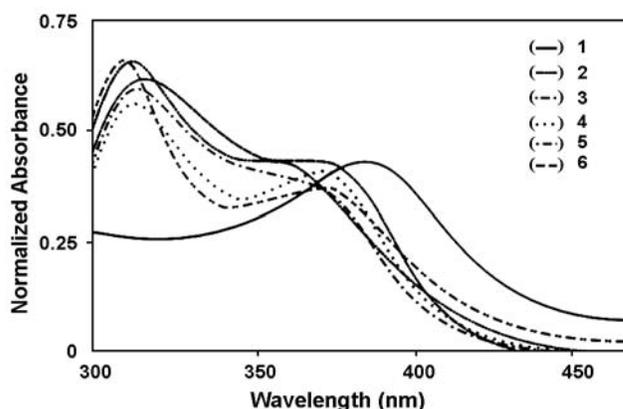
While HOMO-LUMO energy level values of 2-PIMP and O-2-PIMP were determined from the low energy absorption edge of electronic absorption spectra, ( $E'_g$ ) could also be determined from solution oxi-

**Figure 1.** Cyclic voltammograms of 1 mM (1) 2-PIMP and (2) O-2-PIMP in acetonitrile at a sweep rate of 250 mV s<sup>-1</sup>.**Figure 2.** Cyclic voltammograms of 1 mM oligomer metal complexes of: (a) 1= Cu<sup>+2</sup>; 2= Ni<sup>+2</sup>; 3=Co<sup>+2</sup> and (b) 1= Cr<sup>+3</sup>; 2= Pb<sup>+2</sup>; 3=Zn<sup>+2</sup> in DMSO at a sweep rate of 250 mV s<sup>-1</sup>.

**Table 2.** Optical band gaps and  $\lambda_{\max}$  (nm) values of monomer, oligomer, and oligomer-metal complexes.

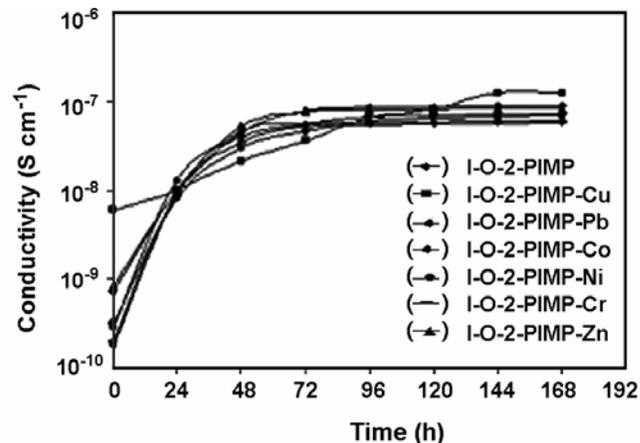
Products	$\lambda_{\max}$ (nm)	$E_g'$ (eV)
2-PIMP	332	3.17
O-2-PIMP	341	3.05
O-2-PIMP-Cu	384	2.81
O-2-PIMP-Ni	354	2.95
O-2-PIMP-Co	358	3.06
O-2-PIMP-Cr	372	3.01
O-2-PIMP-Pb	377	2.86
O-2-PIMP-Zn	373	3.08

dation ( $E_{\text{ox}}$ ) and reduction ( $E_{\text{red}}$ ) potentials. Due to nonlinear poly-conjugation of O-2-PIMP, electrochemical band gap values ( $E_g'$ ) of 2-PIMP have higher values than oligomer as a result of an increase of oxidation ( $E_{\text{ox}}$ ) and reduction potentials ( $E_{\text{red}}$ ). As a consequence of this change, band gap decreased approximately 0.5 eV. Since, polydispersity index value of O-2-PIMP was found to be 1.90; its CV curve obtained was different from that of monomer. Band gap values of oligomer metal complexes (O-2-PIMP-Co, O-2-PIMP-Ni, O-2-PIMP-Cu, O-2-PIMP-Cr, O-2-PIMP-Pb, and O-2-PIMP-Zn) can also be determined from electronic absorption spectra and cyclic voltammetry measurements. Low energy absorption edge of O-2-PIMP-Cu was observed higher than 2-

**Figure 3.** Absorption spectra of: (1) 2-PIMP and (2) O-2-PIMP.**Figure 4.** Absorption spectra of oligomer-metal complexes (1= Cu<sup>2+</sup>, 2= Ni<sup>2+</sup>, 3= Co<sup>2+</sup>, 4= Cr<sup>3+</sup>, 5= Pb<sup>2+</sup> and 6=Zn<sup>2+</sup>).

PIMP, O-2-PIMP, O-2-PIMP-Co, O-2-PIMP-Ni, O-2-PIMP-Cr, O-2-PIMP-Pb and O-2-PIMP-Zn. While oxidation potential of O-2-PIMP-Cu was observed to be 0.84 eV, the reduction potential of O-2-PIMP-Cu was observed to be -1.18 eV. Thus, electrochemical band gap of O-2-PIMP-Cu was found to be 2.02 eV. As a result, O-2-PIMP-Cu demonstrated higher conductivity than the other oligomer-metal complexes.

O-2-PIMP and oligomer-metal complex compounds have conductivities of 10<sup>-10</sup>-10<sup>-9</sup> S/cm. When doped with iodine, their conductivities could be increased by about two orders of magnitude (up to 10<sup>-8</sup> - 10<sup>-7</sup> S/cm). Figure 5 and Table 3 present the doping results of I-O-2-PIMP, I-O-2-PIMP-Co, I-O-2-PIMP-Ni, I-O-2-PIMP-Cu, I-O-2-PIMP-Cr, I-O-2-PIMP-Pb, and I-O-2-PIMP-Zn complexes with iodine in the various time lengths at 25°C. Although the

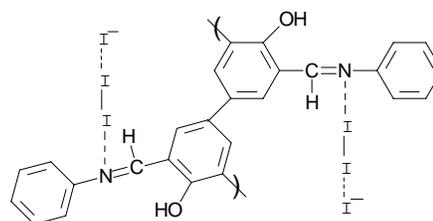
**Figure 5.** Electrical conductivity of I<sub>2</sub>-doped O-2-PIMP and its metal complexes vs. doping time at 25°C.

**Table 3.** Time changes of the conductivity values of O-2-PIMP, O-2-PIMP-Co, O-2-PIMP-Ni, O-2-PIMP-Cu, O-2-PIMP-Cr, O-2-PIMP-Pb and O-2-PIMP-Zn compounds.

Time (h)	Conductivity ( $\times 10^{-12}$ S $\text{cm}^{-1}$ )						
	O-2-PIMP	O-2-PIMP-Cu	O-2-PIMP-Ni	O-2-PIMP-Co	O-2-PIMP-Cr	O-2-PIMP-Pb	O-2-PIMP-Zn
0	183	5832	821	718	284	321	198
24	8763	10124	9456	9644	12934	8145	9168
48	46421	21312	44757	51516	38912	29338	34328
72	54821	35414	75624	78534	55416	45417	52517
96	56914	64418	79443	84314	66518	61124	54472
120	57311	83516	81321	86132	69684	64385	55428
144	58112	124121	82114	87252	71456	67758	56225
168	58718	124414	82832	87948	72187	68321	56937

structures of O-2-PIMP, O-2-PIMP-Co, O-2-PIMP-Ni, O-2-PIMP-Cu, O-2-PIMP-Cr, O-2-PIMP-Pb, and O-2-PIMP-Zn differ from each other, there was not observed any significant difference in their conductivities. This effect may possibly be due to this fact that actually all of these oligomer and oligomer-metal complexes belong to the same class. In the doping of O-2-PIMP with iodine, it was found that the conductivity of I-O-2-PIMP at first increased greatly with doping time, but then tended to level-off. The maximum (or saturated) conductivity was  $5.8 \times 10^{-8}$  S/cm (as shown in Figure 5). The increase in conductivity indicates that a charge-transfer complex is formed between O-2-PIMP and the dopant iodine. Consequently, Figure 5 not only shows the conductivity/doping time relationship but it also indicates how quickly the doping reaction can take place. The experiments showed that a longer doping time is needed to obtain the maximal conductivity. As a result, the conductivity/doping time curve varies with doping conditions. In order to exclude the influence of doping conditions, the conductivities of doped I-O-2-PIMP, I-O-2-PIMP-Co, I-O-2-PIMP-Ni, I-O-2-PIMP-Cu, I-O-2-PIMP-Cr, I-O-2-PIMP-Pb, and I-O-2-PIMP-Zn have been related to the doping level and their values are corrected to  $5.8 \times 10^{-8}$ ,  $8.7 \times 10^{-8}$ ,  $8.2 \times 10^{-8}$ ,  $1.3 \times 10^{-8}$ ,  $7.2 \times 10^{-8}$ ,  $6.8 \times 10^{-8}$  and  $5.6 \times 10^{-8}$  S/cm (as shown in Figure 5). Because of bathochromic effect of O-2-

PIMP-Cu, this metal complex has the highest conductivity value among the oligomer-metal complexes. Diaz et al. have suggested the conductivity mechanisms of Schiff base polymers doped with iodine [3]. Nitrogen is a very electronegative element and capable of coordinating an iodine molecule. The nitrogen atom coordination with iodine has been suggested in the literature as depicted in Scheme IV [20-22].

**Scheme IV.** Coordination of iodine during O-2-PIMP doping.

The infrared spectra of monomer, oligomer, and oligomer-metal complex compounds were measured by Perkin-Elmer FTIR. The FTIR spectral data of 2-PIMP, O-2-PIMP, and oligomer metal complexes are given in Table 4 in which, the bands of OH and  $-\text{CH}=\text{N}$  groups are observed at 3220 and 1610  $\text{cm}^{-1}$ , and 3295 and 1615  $\text{cm}^{-1}$ , respectively.

The number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ) and polydispersity index (PDI) values of O-2-PIMP were found to be 1770, 2225  $\text{gmol}^{-1}$  and 1.257, respectively. The

**Table 4.** FTIR Spectral data of 2-PIMP, O-2-PIMP, and oligomer-metal complexes.

Compounds	Wavenumber (cm <sup>-1</sup> )					
	-OH	-CH=N	-C=C-	-C-O-	Metal-O	Metal-N
2-PIMP	3220	1613	1588, 1570, 1482	1274	-	-
O-2-PIMP	3295	1615	1570, 1483, 1455	1275	-	-
O-2-PIMP-Cu	3421	1611	1589, 1534, 1483	1319	615	695
O-2-PIMP-Ni	3400	1615	1589, 1545, 1415	1272	615	694
O-2-PIMP-Co	3343	1618	1493, 1444, 1415	1271	570	614
O-2-PIMP-Pb	3354	1610	1498	1260	520	658
O-2-PIMP-Zn	3428	1624	1587, 1489	1270	582	693
O-2-PIMP-Cr	3406	1606	1572, 1530, 1484	1277	537	690

elemental analysis data of monomer, oligomer, and oligomer-metal complexes are given in Table 5.

The oxyphenylenes are involved in the formation of free radicals leading to polymer or oligomer formation and it is appeared that they are involved in bond formation. Thus the phenyl rings in the polymer or oligomer appear to be linked primarily at *ortho* position and oxyphenylene. The <sup>1</sup>HNMR and <sup>13</sup>CNMR results showed that the polymerization of 2-methoxy-6-[(4-methylphenyl) imino] methylphenol is proceed-

ed by C-C and C-O-C coupling from *ortho* position according to -OH group and oxyphenylene, respectively [23].

### Thermal Studies

Thermal data of monomer, oligomer, and oligomer-metal complexes were obtained by using a Perkin-Elmer Diamond Thermal Analysis system. The TGA-DTA measurements were made between 15-1000°C (in N<sub>2</sub>, rate 10°C/min) and they are given in Table 6

**Table 5.** Elemental analyses data and yields of 2-PIMP, O-2-PIMP, and oligomer-metal complexes.

Compounds	Calculated (Found) (%)				Yield (%)
	C	H	N	Metal	
2-PIMP	79.19 (78.95)	5.58 (5.45)	7.11 (7.00)	-	95
O-2-PIMP	80.00 (79.62)	4.62 (4.83)	7.18 (7.55)	-	90
O-2-PIMP-Cu	60.34 (59.76)	3.48 (2.90)	5.42 (4.98)	24.58 (24.00)	78
O-2-PIMP-Ni	61.49 (63.75)	3.55 (3.01)	5.52 (4.27)	23.14 (22.78)	54
O-2-PIMP-Co	61.43 (63.25)	3.54 (3.00)	5.51 (4.21)	23.21 (22.86)	38
O-2-PIMP-Pb	38.79 (43.26)	2.24 (2.03)	3.48 (2.85)	51.52 (50.65)	67
O-2-PIMP-Cr	63.16 (54.42)	3.64 (2.30)	5.67 (3.66)	21.05 (20.50)	32
O-2-PIMP-Zn	59.91 (62.40)	3.46 (3.20)	5.38 (4.15)	25.11 (24.72)	69

**Table 6.** Thermal decomposition values of 2-PIMP, O-2-PIMP, and oligomer-metal complexes.

Compounds	$T_{on}^a$	$W_{max}T^b$	20% weight Losses	% Carbine Residue (at 1000°C)
2-PIMP	165	206	175	0.00
O-2-PIMP	180	216	196	20.91
O-2-PIMP-Cu	185	214, 298, 374	291	48.67
O-2-PIMP-Ni	308	382, 560	381	34.03
O-2-PIMP-Co	215	338, 499	247	31.72
O-2-PIMP-Pb	187	271, 389	350	45.87
O-2-PIMP-Zn	290	362, 840	403	33.23
O-2-PIMP-Cr	165	205, 479, 582, 695	197	29.86

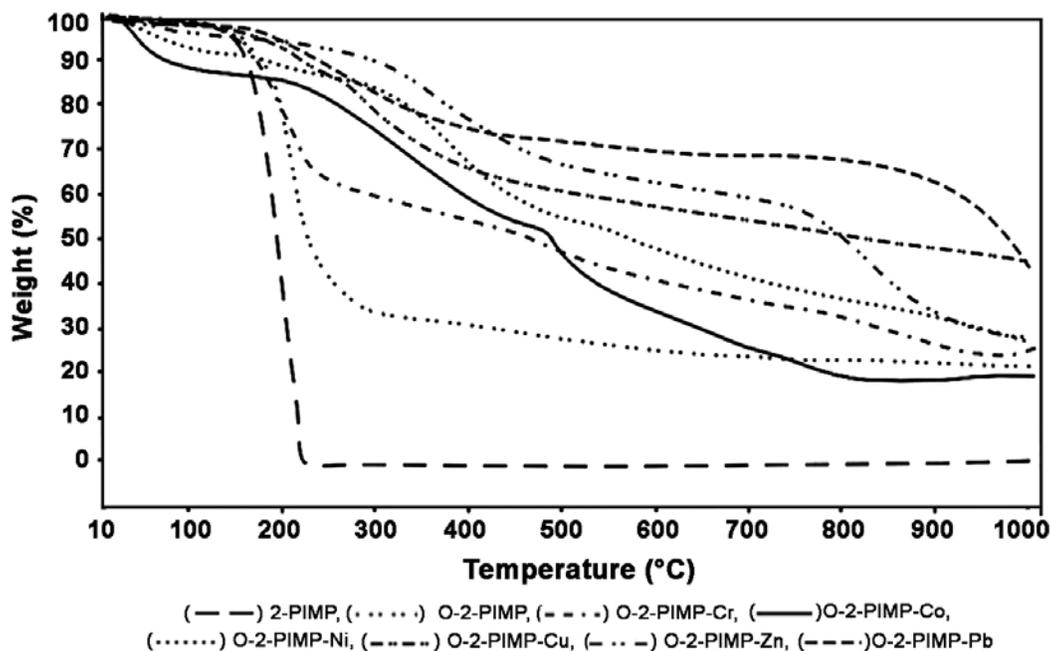
(a) The onset temperature. (b) Maximum Weight Temperature

and Figure 6.

A modification of the thermal stability by polycondensation which it depends on the metal cation electronegativity is foreseeable [24]. Oligomer and all of oligomer-metal complexes show onset temperature values in the range 165-308°C.

The water presence is also seen in TG curves of oligomer-metal complexes (Figure 6) which appears up to 4%-12% weight losses in the range 50-150°C

and resembles both crystallization (50-150°C) and coordination water (150-200°C) removal [24]. This can also explain the differences, which appear between the experimental and calculated elemental analysis values. O-2-PIMP-Cr demonstrated lower thermal stability than the other oligomer-metal complexes. According to metal sorption capacities of oligomer-metal complexes,  $Cu^{+2}$  ion was absorbed more efficiently by the O-2-PIMP.

**Figure 6.** TGA Curves of 2-PIMP, O-2-PIMP, and O-2-PIMP-metal complexes.

## CONCLUSION

In this work, we determined the properties of oligomer and oligomer-metal complex compounds with potential low-band gap characteristics. The conductivity values of O-2-PIMP-Cu complex compound were higher than O-2-PIMP, O-2-PIMP-Co, O-2-PIMP-Ni, O-2-PIMP-Cr, O-2-PIMP-Pb, and O-2-PIMP-Zn complexes. The band gap values of monomer and oligomer were higher than those of oligomer-metal complexes due to the electron-donating property of the azomethane group. It increases the HOMO more than the LUMO and therefore lowers the band gap. The observed band gaps are sufficiently low which make these oligomer and oligomer-metal complexes highly promising for photovoltaic applications. According to our thermal analysis results, the highest onset temperature was observed for O-2-PIMP-Ni complex.

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