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## ARTICLE

## Effects of different dopants on the band gap and electrical conductivity of poly(phenylene-thiazolo[5,4-*d*]thiazole) copolymer

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Poly(phenylene-thiazolo[5,4-*d*]thiazole) (p-PhTT) is an alternating copolymer having semiconductivity and low band gap energy. In this study, p-PhTT polymer was synthesized by the reaction of terephthalaldehyde and rubeanic acid (dithiooxamide). The synthesized p-PhTT was doped with different chemical agents such as HCl, Cu(II), Fe(III), H<sub>3</sub>BO<sub>3</sub> and I<sub>2</sub>. The doped p-PhTT polymer samples were examined by using UV-*vis.*, FT-IR, cyclic voltammetry (CV) and electrical conductivity. The optical ( $E_g^{opt}$ ) and electrochemical ( $E_g^{CV}$ ) band gap energies of doped and undoped p-PhTT were calculated as 2.56 and 2.50 eV from the UV-*vis.* and CV measurements, respectively. The Fe(III) doping decreased the  $E_g^{CV}$  energy of p-PhTT polymer from 2.50 to 2.35 eV according to the CV data. The other dopants increased the band gap energy of the polymer above 2.50 eV. The electrical conductivities of p-PhTT polymers were also measured. It was found that the Fe(III) doping of p-PhTT increased the electrical conductivity from 0.35 to 12  $\mu$ S/cm.

### 1. Introduction

In recent years, conductive polymers are receiving increasing attention due to their potential usages in the areas of optic, electronic and solar energy technologies.<sup>1-4</sup> The doping of polyaniline, polyacetylene, polypyrrole, polythiophene and poly(*p*-phenylene) have been studied extensively. Commonly, the electrical conductivity, HOMO and LUMO energy levels, and the band gap energies of these polymers have been investigated after the doping process.<sup>5-11</sup> The electro-optical properties of conductive polymers can be manipulated by doping with various chemical compounds. The concept of doping is based on the use of different chemical agents that directly interact with the polymer chains. The chemical doping process can be performed by using the protonic acids, Lewis acids and redox agents. The doping may result in protonation, complexation or oxidation/reduction of polymers.<sup>10</sup>

As a solar energy materials, thiazolo[5,4-*d*]thiazole polymers are semiconductors with relatively low band gap energies. Also, they have an interesting ring structure including N and S hetero atoms. Some thiazolo[5,4-*d*]thiazole polymers have been synthesized for different potential applications and their electrochemical, optical, charge transport and photovoltaic properties have been examined. For instance, thiophene-thiazolo[5,4-*d*]thiazole,<sup>11,13</sup> thiophene-thiazolo[5,4-*d*]thiazole-naphthalene,<sup>14</sup> bithiophene-co-thiazolo[5,4-*d*]thiazole,<sup>15</sup> benzodithiophenethiazolo[5,4-*d*]thiazole, dithienosilole-thiazolo[5,4-*d*]thiazole,<sup>16</sup> benzodithiophene with thiazolo[5,4-

*d*]thiazole<sup>17</sup> and di(2-furyl)thiazolo[5,4-*d*]thiazole<sup>18</sup> copolymers have been reported.

In this study, poly(phenylene-thiazolo[5,4-*d*]thiazole (p-PhTT) was synthesized by the reaction of terephthalaldehyde and rubeanic acid.<sup>4,9</sup> The synthesized p-PhTT was doped with HCl, I<sub>2</sub>, Cu(II), Fe(III) and H<sub>3</sub>BO<sub>3</sub> chemical agents. The doped and undoped forms of p-PhTT polymer were examined by using UV-*vis.*, FTIR, cyclic voltammetry (CV) and electrical conductivity. The HOMO and LUMO levels and band gap energies of were calculated.

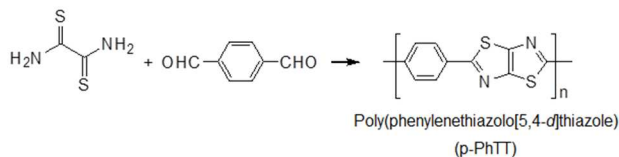
### 2. Results and discussion

#### 2.1. Synthesis and doping of p-PhTT polymer

Poly(phenylene-thiazolo[5,4-*d*]thiazole) (p-PhTT) alternating copolymer was synthesized by using terephthalaldehyde (1,4-benzenedicarboxaldehyde) and rubeanic acid (dithiooxamide). (Scheme.1).<sup>4,19-21</sup> p-PhTT copolymer has a conjugated chain system with alternating phenylene and thiazolo[5,4-*d*]thiazole groups. The phenylene group includes aromatic  $\pi$ -ring electrons and the thiazolo[5,4-*d*]thiazole includes  $n$  electrons of N and S hetero atoms.<sup>4,22</sup> The doping of p-PhTT polymer with different dopants (protonating, redox or chelating agents) may result in the interaction of dopants with the  $\pi$ -electrons of the aromatic rings and the  $n$  electrons of N and S atoms. Conjugated polymers can be either partially oxidized (*p*-type doping) or reduced (*n*-type doping) by electron donor or acceptor redox agents. Charge defects may be

introduced during the redox doping process, which may improve the electrical conductivity of the polymer. For example, the doping of *trans*-polyacetylene with I<sub>2</sub> can produce positive charge defects on the conjugated  $\pi$ - bonds.<sup>5</sup>

In our previous study,<sup>4</sup> we had synthesized and characterized p-PhTT polymer. The synthesis reaction is given in Scheme 1. The polymer is stable up to 200 °C. The UV-vis. absorption spectrum of the polymer shows two maximum absorbances at 264 and 485 nm. The polymer exhibits fluorescence emissions at 467 nm with an excitation at 380 nm, and at 497 nm with an excitation at 420 nm in DMSO solution. The HOMO, LUMO and the band gap energies are -5.19, -2.63 and 2.56 eV, respectively.<sup>4</sup>



Scheme 1. Synthesis reaction of p-PhTT copolymer.

In this study, the doping of p-PhTT polymer has been investigated by using HCl, Cu(II), Fe(III), H<sub>3</sub>BO<sub>3</sub> and I<sub>2</sub> chemical agents. HCl is a strong acid and it can protonate effectively the nitrogen atoms of p-PhTT backbone. H<sub>3</sub>BO<sub>3</sub> is a very weak protonating acid and it is also a Lewis acid due to electron acceptor boron ((N:→B(OH)<sub>3</sub>). Boric acid doping may result in the protonation of the polymer and the complexation via N:→B bonding. Fe(III) ions may show a redox doping behavior and a complexation doping behavior. Cu(II) ion is a complex forming Lewis acid. I<sub>2</sub> is a redox dopant as an electron donor and it is also a complex forming agent with N, O and S atoms of the polymer chains.<sup>23</sup> Here, p-PhTT polymer was doped with the different chemical materials. The spectroscopic and electronic behaviors of the doped polymer samples have been examined.

## 2.2. UV-vis. spectroscopy of doped p-PhTT

The spectroscopic effects of the doping process were studied by using the various types of dopants. The UV-vis. spectral changes were examined in detail after the doping. The UV-vis. measurements were performed in p-PhTT solutions in DMSO. At first, the UV-vis. spectra of HCl and H<sub>3</sub>BO<sub>3</sub> doped p-PhTT polymers were compared with the spectrum of undoped polymer as shown in Fig. 1. The HCl and H<sub>3</sub>BO<sub>3</sub> doped p-PhTT samples exhibited blue shifted UV-vis. spectra compared to the spectrum of the undoped polymer. In addition, the maximum absorption band at 485 nm disappeared after HCl and H<sub>3</sub>BO<sub>3</sub> doping. The H<sub>3</sub>BO<sub>3</sub> and HCl doped polymers showed similar optical absorption behaviors.

The UV-vis. absorptions of Cu(II), Fe(III) and I<sub>2</sub> doped p-PhTT samples were also studied. The obtained UV-vis. absorption spectra of the doped polymers were compared with the spectrum of the undoped polymer in Fig. 2. It was noted that the spectrum of Cu(II) doped polymer showed similar absorption behavior to the spectra of the HCl and H<sub>3</sub>BO<sub>3</sub> doped samples (Figs. 1 and 2). Cu(II) is a Lewis acid and it is coordinated with the N atoms of p-PhTT

polymer. Unlike the undoped p-PhTT, the spectra of Fe(III) and I<sub>2</sub> doped polymer samples showed absorbances between 270 and 385 nm wavelengths. Both Fe(III) and I<sub>2</sub> are redox type doping materials and they have exhibited the maximum absorption bands at 372 and 385 nm, respectively. These electronic absorptions due to the Fe(III) and I<sub>2</sub> dopants can be attributed to the  $\pi$ - $\pi^*$  transitions. The maximums and onsets of the absorption bands were both used in the calculations of the optical band gap energies ( $E_g^{\text{Opt, Max}}$  and  $E_g^{\text{Opt, Onset}}$ ) of the p-PhTT samples.

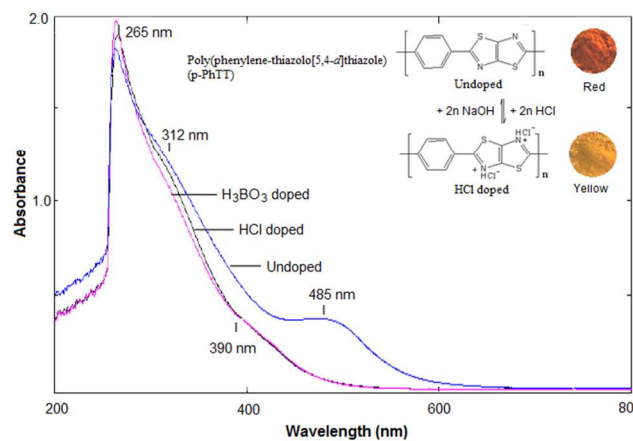


Fig. 1. UV-visible spectra of undoped, H<sub>3</sub>BO<sub>3</sub> and HCl doped p-PhTT polymers in DMSO.

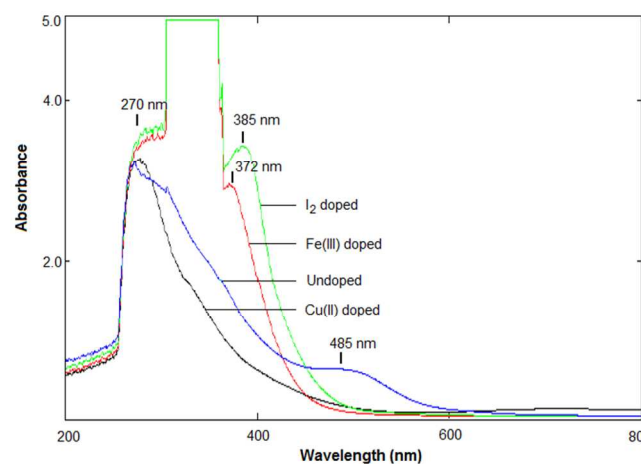


Fig. 2. UV-visible spectra of Cu(II), Fe(III) and I<sub>2</sub> doped p-PhTT polymers in DMSO.

## 2.3. FT-IR spectroscopy of doped p-PhTT

The doping of the p-PhTT copolymer with HCl, Cu(II), Fe(III), H<sub>3</sub>BO<sub>3</sub> and I<sub>2</sub> was also investigated by FT-IR analysis. The obtained FT-IR spectra of the doped samples are given in Fig. 3. According to the FTIR results, HCl doping of p-PhTT copolymer shifted the C=N vibration peak from 1678 cm<sup>-1</sup> to 1690 cm<sup>-1</sup> due to the protonation. Unlike the HCl doping, the other dopants shifted the C=N vibration peak to the lower frequencies. No significant change was observed for the aromatic C=C vibration peaks after the doping. The increase of the intensity of the peak at 1385 cm<sup>-1</sup> may possibly indicate the

formation of a new B-N bond after doping with  $\text{H}_3\text{BO}_3$ . In the spectrum of  $\text{H}_3\text{BO}_3$  doped sample, the peak at  $1194\text{ cm}^{-1}$  was assigned to the B-O vibration.

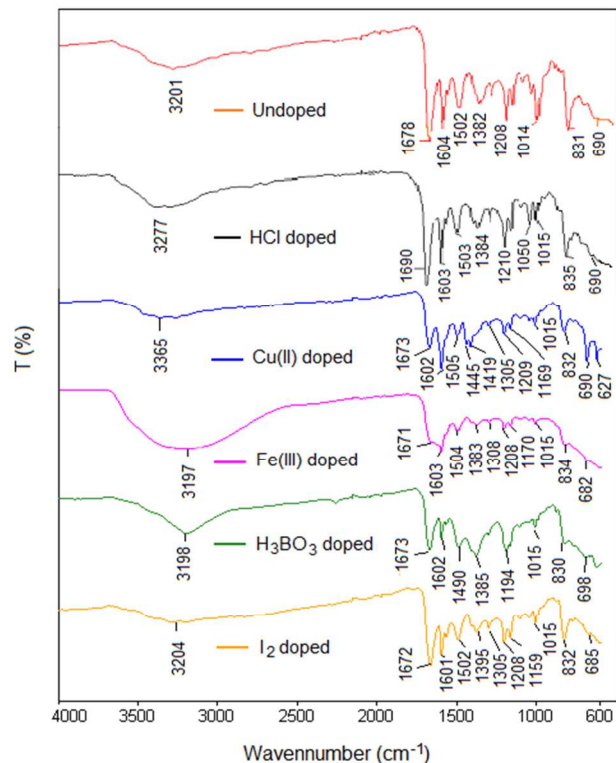


Fig. 3. FTIR spectra of the doped p-PhTT polymer samples.

#### 2.4. CV of doped p-PhTT

The electrochemical properties of the doped p-PhTT polymers were analyzed by the cyclic voltammetry (CV). The obtained results were used to determine the energy levels of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and the band gap energies ( $E_g^{\text{CV}}$ ). Figure 4 shows the cyclic voltammograms of the p-PhTT samples in acetonitrile together with  $\text{LiClO}_4$  electrolyte. The oxidation ( $E_{1/2}^{\text{Ox}}$ ) and reduction ( $E_{1/2}^{\text{Red}}$ ) potentials of the doped and undoped p-PhTT polymer samples were determined from Fig. 4, and they are given in Table 1. The determined oxidation and reduction potentials were used in the calculations of the HOMO and LUMO energy levels of the doped p-PhTT polymers (Table 1).

#### 2.5. HOMO, LUMO and band gap energies of doped p-PhTT

In our work, the optical and electronic properties of HCl, Cu(II), Fe(III),  $\text{H}_3\text{BO}_3$  and  $\text{I}_2$  doped p-PhTT copolymers were also investigated by using the UV-vis absorption spectroscopy and the cyclic voltammetry. The optical band gap energies ( $E_g^{\text{Opt, Max}}$  and  $E_g^{\text{Opt, Onset}}$ ) were calculated according to the UV-vis. absorption data by using  $E_g^{\text{Opt}} = 1240/\lambda$ .<sup>24</sup> In addition, the electrochemical band gap energies ( $E_g^{\text{CV}}$ ) of the doped polymer samples were calculated from their CV data. At first, the HOMO and LUMO energy levels were

calculated from the oxidation and reduction potential values, respectively (Eqs. 1 and 2).<sup>25,26</sup> Then, the  $E_g^{\text{CV}}$  energies were obtained from the differences of the HOMO and LUMO energy levels by using Eq. 3.<sup>25</sup> The obtained  $E_g^{\text{Opt}}$  and  $E_g^{\text{CV}}$  energies together with HOMO, LUMO,  $E_{1/2}^{\text{Ox}}$  and  $E_{1/2}^{\text{Red}}$  values are both given in Table 1.

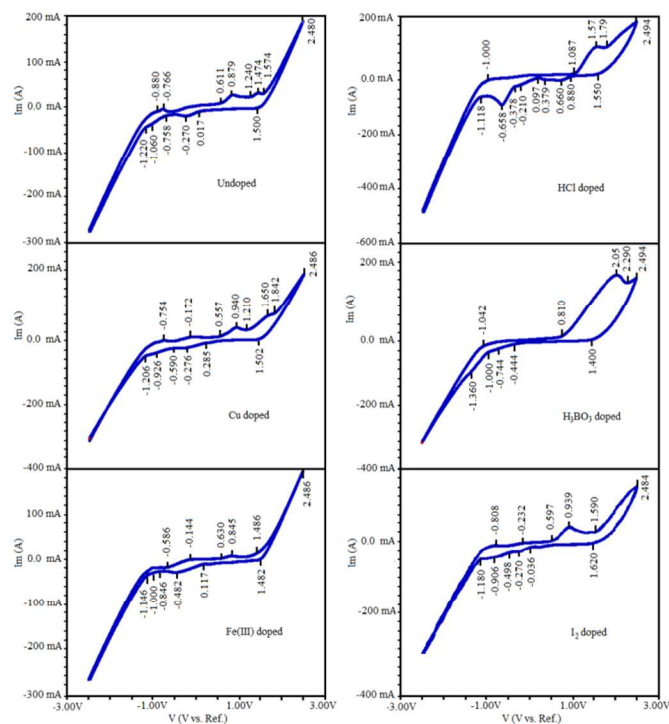


Fig. 4. Cyclic voltammograms of the doped p-PhTT polymer samples.

$$E_{\text{HOMO}} = -(E_{1/2}^{\text{Ox}} + 4.34) \text{ eV} \quad (1)$$

$$E_{\text{LUMO}} = -(E_{1/2}^{\text{Red}} + 4.34) \text{ eV} \quad (2)$$

$$E_g^{\text{CV}} = -(E_{\text{HOMO}} - E_{\text{LUMO}}) \text{ eV} \quad (3)$$

The comparisons of the HOMO, LUMO and  $E_g^{\text{CV}}$  energies of each doped polymer samples with the undoped polymer are also given as an energy diagram in Fig. 5. Looking at the energy levels of the doped p-PhTT polymers, it can be seen that the all dopants changed the band gap energies of the p-PhTT polymer. The lowest HOMO, LUMO and  $E_g^{\text{CV}}$  energies were observed in the case of Fe(III) doped polymer. Previously, the band gap energies of the polymers including thiazolo[5,4-*d*]thiazole unit have been studied by different researchers. The thiazolo[5,4-*d*]thiazole solar energy polymers have low band gap energies in the range of 1.70-2.50 eV. Some examples of the band gap energies of the thiazolo[5,4-*d*]thiazole polymers from the literature are given in Table 2.

#### 2.6. Electrical conductivity of doped p-PhTT

The electrical conductivities of the doped and undoped p-PhTT polymer samples were measured by using a four-point method. The obtained results are given in Fig. 6. It was found that the undoped p-

PhTT polymer has an electrical conductivity of 0.35  $\mu\text{S}/\text{cm}$ . After doping, the all dopants increased the conductivity of p-PhTT

**Table 1.** Optical and electrochemical band gap energies of the doped p-PhTT polymers.

Sample	UV-vis. absorption				CV		
	$\lambda_{\text{Onset}}$ (nm)	$E_{\text{g}}^{\text{Opt, Onset}}$ (eV)	$\lambda_{\text{Max}}$ (nm)	$E_{\text{g}}^{\text{Opt, Max}}$ (eV)	HOMO (eV) ( $E_{1/2}^{\text{Ox}}$ (V))	LUMO (eV) ( $E_{1/2}^{\text{Red}}$ (V))	$E_{\text{g}}^{\text{CV}}$ (eV)
Undoped	610	2.03	485	2.56	-5.27 (0.926)	-2.76 (-1.579)	2.50
HCl doped	520	2.38	312	3.97	-5.67 (1.328)	-2.95 (-1.389)	2.72
Cu(II) doped	515	2.41	330	3.76	-5.87 (1.526)	-2.85 (-1.495)	3.02
H <sub>3</sub> BO <sub>3</sub> doped	520	2.38	312	3.97	-5.77 (1.430)	-2.92 (-1.422)	2.85
Fe(III) doped	510	2.43	372	3.33	-6.33 (1.986)	-3.98 (-0.365)	2.35
I <sub>2</sub> doped	520	2.38	385	3.22	-5.88 (1.538)	-3.12 (-1.218)	2.76

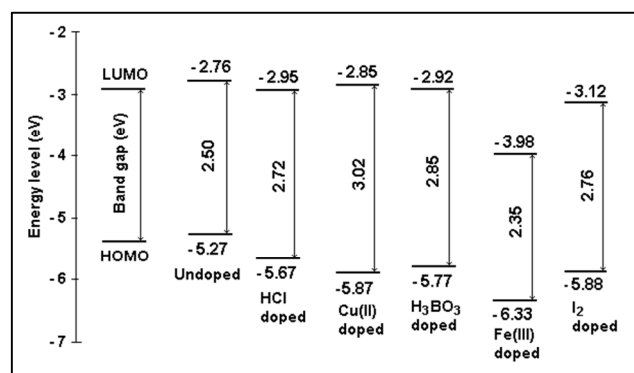
**Table 2.** Band gap energies of some thiazolo[5,4-d]thiazole polymers.

Polymer	Band gap (eV)
Poly(di(2-furyl)thiazolo[5,4-d]thiazole).....	2.00 <sup>18</sup>
Poly(thiophene-thiazolo[5,4-d]thiazole)	1.80 <sup>12,13</sup>
Poly{(2,5-bis(3-decylthiophen-2-yl)thiazolo[5,4-d]thiazole-5,5'-diyl)-alt-(2,6-[(1,5-didecyloxy)naphthalene])}	2.21 <sup>14</sup>
Poly(2,5-dithienylthiazolo[5,4-d]thiazole)	1.79 <sup>27</sup>
P1: Poly(bithiazole-thiazolothiazole)	
P2: Poly(benzodithiophene-thiazolothiazole)	1.82-1.99 <sup>17</sup>
P1: Poly[9,9-didecylfluorene-2,7-diyl-alt-2,5-bis-(3-hexylthiophene-2-yl)thiazolo[5,4-d]thiazole]	
P2: Poly[9,9-dioctyldibenzosilole-2,7-diyl-alt-2,5-bis-(3-hexylthiophene-2-yl)thiazolo[5,4-d]thiazole]	
P3: Poly[4,4'-bis(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole-alt-2,5-bis-(3-hexylthiophene-2-yl)thiazolo[5,4-d]thiazole]	1.80-2.14 <sup>28</sup>
Thieno[3,2-b]thiophene and thiazolo[5,4-d]thiazole copolymers	1.82-1.85 <sup>29</sup>
Poly(2,5-bis(3-hexylthiophen-2-yl)-thiazolo[5,4-d]thiazole)	1.91 <sup>30</sup>
P1: poly[2-(5-(2-decyl-2H-benzo[d][1,2,3]triazol-4-yl)thiophen-2-yl)-5-(thiophen-2-yl)thiazolo[5,4-d]thiazole]	
P2: Poly[2-(5-(2-decyl-2H-benzo[d][1,2,3]triazol-4-yl)furan-2-yl)-5-(furan-2-yl)thiazolo[5,4-d]thiazole]	1.7-1.9 <sup>31</sup>
Dithienylthiazolo[5,4-d]thiazole polymers	1.78-1.86 <sup>32,33</sup>
Poly(phenylene-thiazolo[5,4-d]thiazole) (In this study)	2.50-2.56

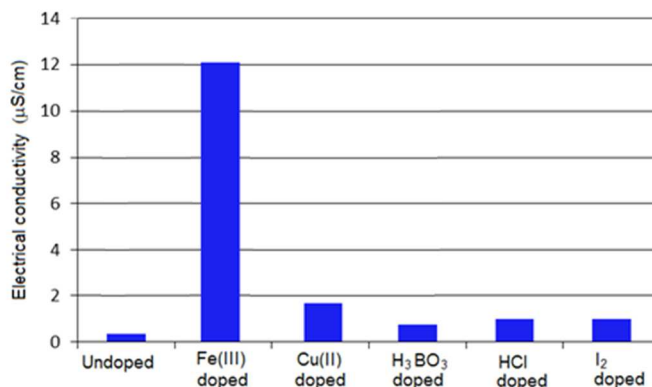
copolymer. These results clearly showed that the p-PhTT copolymer is a semiconductive material and its electrical conductivity can be increased by protonic acids (HCl, H<sub>3</sub>BO<sub>3</sub>), Lewis acids (Cu(II), Fe(III), H<sub>3</sub>BO<sub>3</sub>) and redox materials (I<sub>2</sub>, Fe(III)). The maximum increase in the electrical conductivity was noted in the case of Fe(III) doping.

Examining the UV-vis. spectrum of the Fe(III) doped polymer in Fig. 2, it can be seen that the absorbance due to the  $\pi$ - $\pi^*$  transitions increased dramatically. This increase indicates that the Fe(III) doping delocalizes the  $\pi$  electrons of the aromatic units. Interestingly, the HOMO, LUMO and band gap energies of the Fe(III) doped polymer was found as the lowest values among the doped polymer samples. The increase in the electrical conductivity of the p-PhTT can be attributed to the low HOMO,

LUMO and  $E_{\text{g}}^{\text{CV}}$  energies. Furthermore, the delocalization of the  $\pi$  electrons in the polymer after the Fe(III) doping has significant effect (Fig. 5).<sup>33-37</sup> Some researchers have also studied the effect of Fe(III) doping on the electrical conductivity of polymers. For example, the doping of polystyrene<sup>38</sup> and some coordination polymers<sup>39</sup> were studied. It was found that the Fe(III) doping was effective for the enhancement of the electrical conductivity.



**Fig. 5.** HOMO and LUMO energy levels of the doped and undoped p-PhTT.



**Fig. 6.** Electrical conductivities of the doped and undoped p-PhTT polymers.

## 2.7. XRD analysis

The XRD patterns of undoped PhTT, HCl and Fe(III) doped PhTT polymer samples were also taken and the obtained results are given in Fig. 7. The XRD patterns showed that the undoped and Fe(III) doped PhTT samples have amorphous structures. However, the HCl doped sample has a new crystalline peak at  $32.76^\circ$  ( $d=2.73 \text{ \AA}$ ). The intermolecular hydrogen bonds and the ionic interactions between the doped polymer chains increased the crystallinity of the PhTT polymer.

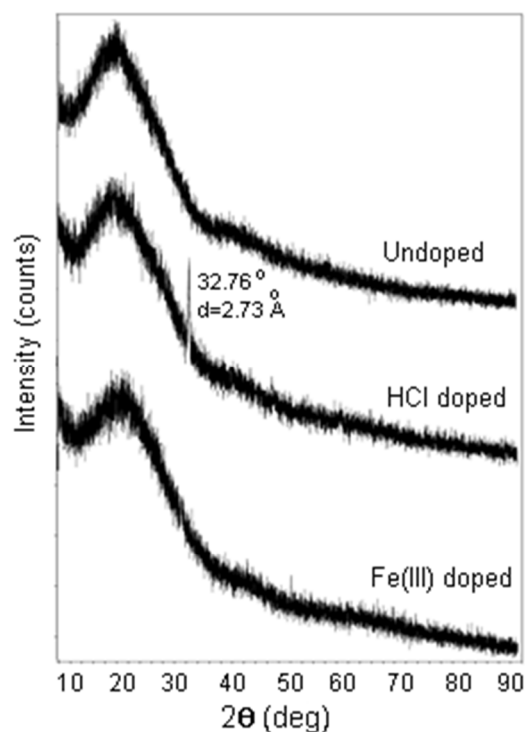


Fig. 7. XRD patterns of undoped, HCl and Fe(III) doped PhTT.

## 2.8. SEM microscopy analysis

To examine the morphology of doped and undoped polymer samples, the electron microscopy analysis was performed. The SEM images of undoped PhTT, HCl and Fe(III) doped PhTT polymer samples are demonstrated in Fig. 8. According to the SEM results, the undoped PhTT sample has about 1-5  $\mu\text{m}$  spherical particles. After HCl doping, the particle sizes of the PhTT decreased drastically to the submicron range with some large particles. Also the morphology of the PhTT particles changed due to the HCl doping. This morphological change in the HCl doped polymer is supported by the increased crystallinity in the XRD results (Fig. 7). The Fe(III) doped polymer sample exhibited micron size spherical particles with more aggregation.

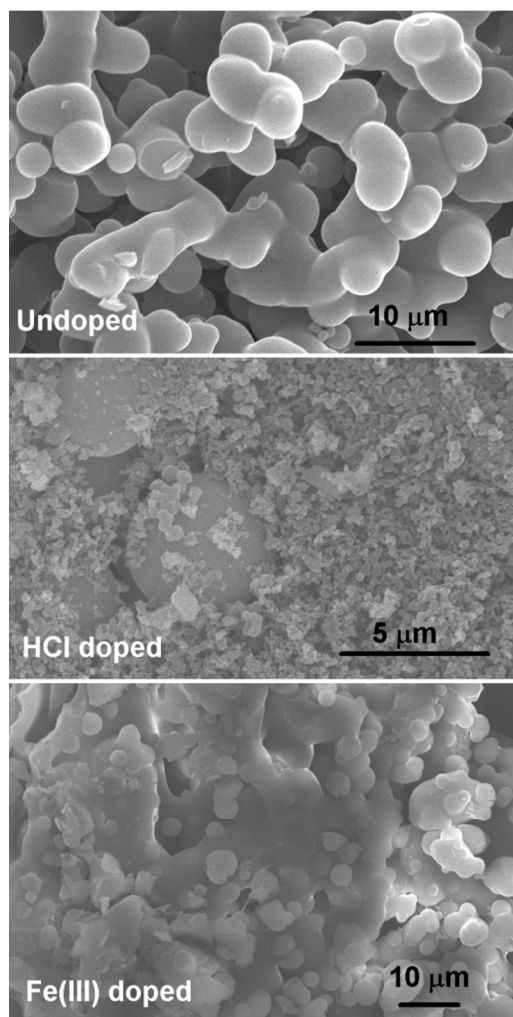


Fig. 8. SEM images of undoped, HCl and Fe(III) doped PhTT.

## 3. Experimental

### 3.1. Materials

Terephthalaldehyde (1,4-benzenedicarboxaldehyde) was obtained from Alfa Aesar GmbH & Co KG (Karlsruhe, Germany). Rubenic acid (dithioamide) was purchased from Fluka (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany). Poly(phenylene-thiazolo[5,4-*d*]thiazole) (p-PhTT) copolymer was prepared from the reaction of terephthalaldehyde and rubenic acid. Dimethylsulfoxide (DMSO) and acetonitrile ( $\text{CH}_3\text{CN}$ ) were from Merck (Darmstadt, Germany). Lithium perchlorate ( $\text{LiClO}_4$ ) was received from Fluka (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany). HCl solution (37%),  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{H}_3\text{BO}_3$  and  $\text{I}_2$  were purchased from Merck (Darmstadt, Germany).

### 3.2. Synthesis of poly(phenylenethiazolo[5,4-d]thiazole)

Poly(phenylene-thiazolo[5,4-*d*]thiazole) (p-PhTT) alternating copolymer was synthesized by using terephthalaldehyde (1,4-benzenedicarboxaldehyde) and rubenic acid (dithiooxamide) (Scheme.1).<sup>4,19-21</sup> For the synthesis of p-PhTT polymer, 2.68 g (20 mmol) terephthalaldehyde and 2.40 g (20 mmol) rubenic acid were mixed in 50 mL ethanol. Then, 5 mL of 1 M NaOH solution was added into the solution. A brown product precipitated after heating for 5 h at 80 °C. The obtained precipitate was filtered, washed and dried at 105 °C for 2 hours.<sup>4</sup> The yield of the reaction was calculated as 35%.

### 3.3. Doping of p-PhTT with different chemical agents

The p-PhTT polymer was doped with HCl, Cu(II), Fe(III), H<sub>3</sub>BO<sub>3</sub> and I<sub>2</sub> chemical agents. The doping of the p-PhTT polymer has been examined by using UV-vis. absorption, FT-IR, cyclic voltammetry (CV) and electrical conductivity. The UV-vis. and electrochemical CV measurements were performed with the polymer solutions in DMSO and CH<sub>3</sub>CN. For the FT-IR and electrical conductivity measurements, the doping processes were carried out by mixing and grinding in the solid phase. 15 mg quantities of solid Cu(CH<sub>3</sub>COO).H<sub>2</sub>O, FeCl<sub>3</sub>.6H<sub>2</sub>O, H<sub>3</sub>BO<sub>3</sub> and I<sub>2</sub> were added into the each 50 mg of p-PhTT.

### 3.4. UV-Vis, FT-IR, CV and conductivity measurements

For the UV-vis. measurements, seven different polymer solutions having the concentration of 0.065 g/L p-PhTT were prepared in DMSO. These polymer solutions were doped by using 0.1 M HCl, 0.001 M Cu(II), 0.001 M Fe(III), 0.0003 M I<sub>2</sub> and 0.004 M H<sub>3</sub>BO<sub>3</sub> solutions. The UV-vis. spectra of the doped and undoped polymer solutions were recorded on a Shimadzu UV-vis. 2401 PC model double beam spectrophotometer between 200 and 800 nm. The FT-IR spectra of the doped polymer powders were recorded on a Perkin Elmer Spectrum Two model spectrophotometer.

The doped and undoped p-PhTT samples were also examined by using the electrochemical cyclic voltammetry (CV) using 0.0625 g/L p-PhTT solutions in CH<sub>3</sub>CN. During the preparation of the solutions, LiClO<sub>4</sub> was added as an electrolyte to provide a concentration of 0.05 M. Cu(CH<sub>3</sub>COO)<sub>2</sub>.H<sub>2</sub>O, FeCl<sub>3</sub>.6H<sub>2</sub>O, I<sub>2</sub> and H<sub>3</sub>BO<sub>3</sub> dopant chemicals were added into the prepared p-PhTT solutions. The CV measurements of the solutions were performed at 100 mV/s on Gamry 750 EQCM model potentiostat between -2.5 and 2.5 volt. The measurements were carried out using Ag/AgCl reference electrode (E= +0.197 V) and two platinum electrodes as the working and the counter electrodes. The electrical conductivity changes have been studied after doping of p-PhTT polymer with different agents. The prepared samples were pressed into the discs after mixing of undoped polymer powders and the dopant chemicals. The electrical conductivities of the samples were measured by using a four-point system (Lucas Pro4).

## 4. Conclusions

In this work, poly(phenylene-thiazolo[5,4-*d*]thiazole) (p-PhTT) copolymer was synthesized and it was used for the doping experiments. The doping of p-PhTT with HCl, Cu(II), Fe(III), H<sub>3</sub>BO<sub>3</sub> and I<sub>2</sub> was examined by UV-vis., FI-TR, CV and electrical conductivity measurements. It was observed that the all dopants increased the electrical conductivity of p-PhTT polymer. The maximum increase in the electrical conductivity was obtained in the case of Fe(III) doping. It was found that the semiconductive p-PhTT polymer has an electrical conductivity of 0.35 μS/cm and band gap energy of 2.50 eV. The use of different dopants has changed the electro-optic properties and the HOMO, LUMO energy levels of the polymer. As a solar energy material, poly(phenylenethiazolo[5,4-*d*]thiazole) copolymer may have various potential uses in the fields of light emitting diodes (LEDs), photovoltaics (PVs) and nonlinear optics (NLOs). In potential energy applications of poly(phenylenethiazolo[5,4-*d*]thiazole) copolymer, the doping effect should be taken into account.

## Notes

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