

The Synthesis and Electrochemical Characterization of an Electron Donor-Acceptor Co-Monomer

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Abstract

This article presents the synthesis, characterization and electrochemical polymerization conditions of 4, 5-dithiophene imidazole (Th2-Im) co-monomer with donor-acceptor character carrying thiophene and imidazole monomer synthesized using Still Cross Coupling reaction. The obtained synthesis product (Th2-Im) was characterized by FT-IR, XPS and SEM images. In the synthesis structure, the presence of S atom belonging to the Th ring was observed in the 175 eV region, and the presence of N atom belonging to the Im ring was observed in the 411 eV region. In addition, B atom, which would indicate the presence of dopant anion, was observed in the 202 eV region. It was determined by SEM images that Poly (Th2-Im) had a more distinct and regular geometric texture than Poly (Th) morphologically. It was determined that Th2-Im was oxidized at 0.6 V from electrochemical polymerization. From monomer free CV, it was determined that Poly (Th2-Im) showed 3 oxidation peaks as 0.25V, 0.75V and 1.2V and 3 reduction peaks as 0.7V, 0.4V and 0.1 V. It was determined that the synthesis polymer obtained from these data could be polymerized more easily than Th and Im and the donor-acceptor character could be clearly observed in CV graphs.

Keywords: Thiophene, imidazole, electron donor-acceptor, electropolymerization

1. Introduction

Conductive polymers are known as synthetic metals (MacDiarmid et al. 2001). It is a research area that attracts a lot of attention from researchers. Conductive polymers are important because they have practical and effective use in applications such as electrochromic devices (Invernale et al., 2010), photovoltaics (Baran et al., 2010), light emitting diodes (Beaupr'e et al., 2010) and super capacitors (Mahimai et al., 2024). Monomers such as pyrrole (Py) (Zhou et al., 2002), thiophene (Th) (Zhang et al., 2022), carbazole (Cz) (Dmitrieva et al., 2022), aniline (An) (Pournaghi-Azar et al., 2007) are frequently used monomers to obtain conductive polymers due to their superior properties. Th from these monomers is preferred for various areas of use due to its good conductivity properties, but it has a high oxidation potential. For this reason, the solution used during electropolymerization must be resistant to high oxidation. In order to overcome such negativities, Th is combined with other monomers or groups that will provide a donor-acceptor relationship, thus reducing the high oxidation potential. Imidazole monomer is a monomer used as an electron donor. In our previous study (Dolas et al., 2016), Th₃-Im monomer was synthesized with Imidazole (Im) as donor and Th monomer as the acceptor. Thus, electropolymerization of Th monomer was achieved under easier conditions. Polymerization of this monomer on different substrates and comparison of impedance data were performed. However, electrochemical examination of another synthesis product, Th₂-Im co- monomer, and comparison with Th and Im were not performed in detail. For this reason, in this study, 2 Th ring-bound imidazole monomer (Th₂-Im) was synthesized by Still Cross Coupling reaction and isolated by column chromatography using 4:1 petroleum ether: ethyl acetate solvent mixture and its electrochemical properties were investigated and compared with Th and Im. Electropolymerization was carried out in ACN-BFEE electrolyte (5 ml) using 0.01 M

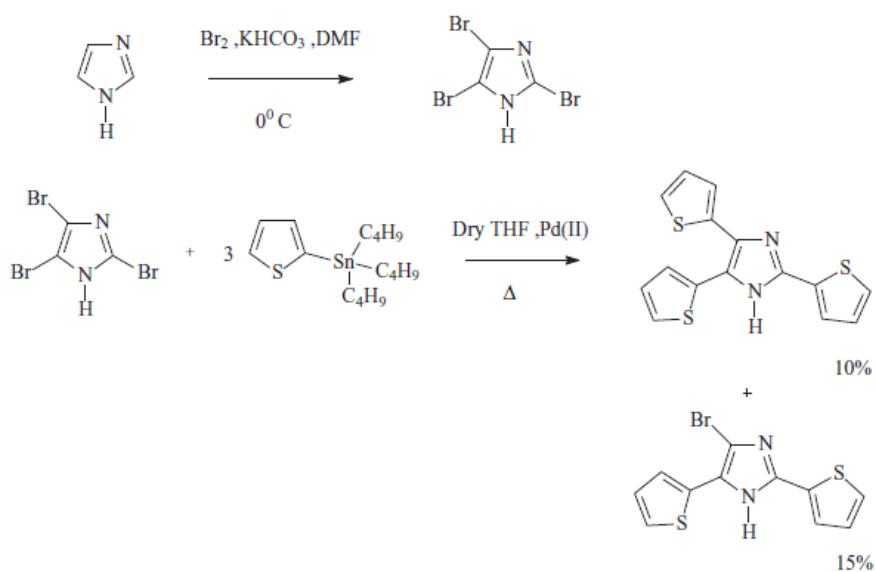
monomer in the potential range of 0-1.8 V with a scanning speed of 100 mV/s. Electropolymerization of the co-monomer synthesized under the same conditions was compared with the electropolymerization of Th monomer and Im monomer.

2. Material and Methods

Th, Im, Acetonitrile (ACN) (E Chromasolv for HPLC for far UV) were purchased from Sigma-Aldrich. Boron trifluoride diethyletherate (BFEE) were purchased from FLUKA. 4,5-dithiophene imidazole (Th₂-Im) co-monomer was synthesized as described in our previous study. Briefly; Thiophene and Imidazole rings were first prepared to be combined as described below. First, imidazole was brominated (2, 3, 4-tribromoimidazole) by Bahnous method (Bahnous et al. 2006). Then, brominated Im and Th were combined by Still Cross Coupling reaction with dry THF in the presence of Pd catalyst. As shown in Scheme 1, one of the obtained products, Th₂-Im was isolated by column chromatography and dried.

2.1. Instruments

Electrochemical polymerization was performed with a Princeton Applied Research Potentiostat model 2263 Potentiostat/Galvanostat interfaced to a PC computer and controlled PowerSuit software package in one-compartment cell by a three-electrode setup. Pt wires was used as counter and working electrodes, Ag wire was used as reference electrode. Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) spectrometer (Perkin-Elmer, Spectrum One, having a universal ATR attachment with a diamond and ZnSe crystal C70951). A Perkin-Elmer spectrum software was used to carry out the FTIR-ATR measurements between 650 and 4000 cm⁻¹. UV-Visible data were obtained by using Perkin-Elmer Lambda 35 UV-Visible Spectrophotometer device. QUANTA 400F Field Emission SEM was performed to view the polymer surface images and PHI 5000 VersaProbe was used to obtain the X-ray photoelectron spectroscopy (XPS) data.



3. Result and Discussion

The characterization of the obtained product (Th₂-Im) is given comparatively in Figure 1. Accordingly, FT-IR spectrum (Figure 1a) was obtained for the

characterization of structural bonds, XPS graph (Figure 1b) for the characterization of atomic content, and SEM image (Figure 1c) for the image of the obtained polymers. FT-IR peaks were collected in Table 1.

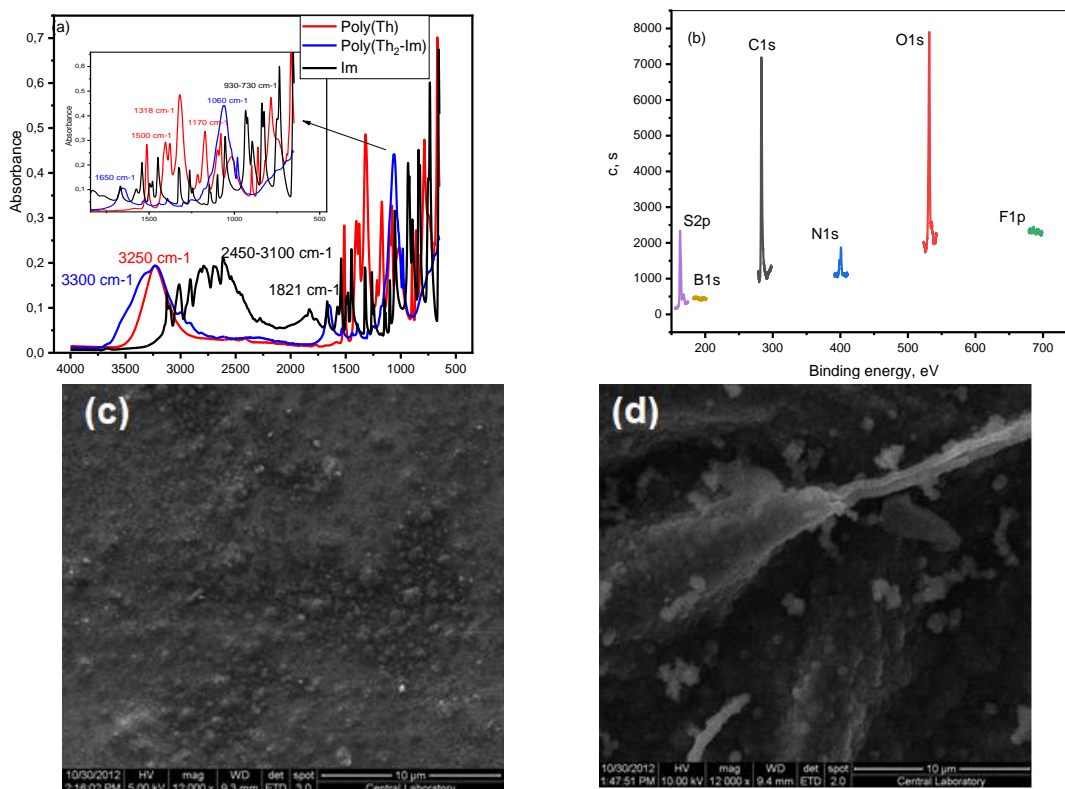


Figure 1. a) The FT-IR spectrum of Poly(Th), Im and Poly(Th₂-Im); b) XPS graph of Th₂-Im; SEM images of c) Poly(Th) and d) Poly(Th₂-Im)

As seen in the FT-IR spectrum, quite multiple sharp peaks were observed in the region (700-900 cm^{-1}) expressing aromatic ring CH bending I for Poly (Th) and Im, while broad peaks were observed in the same region in the Poly (Th2-Im) sample. In addition, C-S stretching peaks specific to the Th ring were

observed at 1170 cm^{-1} for Poly (Th), while they shifted to 1175 cm^{-1} for Poly (Th2-Im). For Poly (Th2-Im), C=C stretching peaks were observed at 1450 cm^{-1} , conjugation at 1650 cm^{-1} , aromatic =CH at 2900 cm^{-1} , and hydrogen bond stretching peaks belonging to NH were observed at 3300 cm^{-1} .

Table 1. The assignments peaks of the Im, Poly (Th) and Poly (Th2-Im)

Observed peak, cm^{-1}			
Im	Poly (Th)	Poly (Th2-Im)	Peak Assignments
400-750	400-750	730	Aromatic ring -CH bending (Socretis, 1980)
-	1170	1175	-CS stretching (Tanaka et al. 1986)
1100	1065	1060	Dopant anion (Dolas et al. 2016)
1318	1418	1450	Symmetric ring -C=C stretching (Furukawa et al. 1987)
1650, 1500	1500	1650	Conjugation
2750	-	2900	Aromatic ring =CH stretching (Sönmez and Sarac, 2002)
3100-2450	3250	3300	-NH stretching (Furukawa et al. 1987)

When the XPS graph was examined, the presence of the S atom belonging to the Th ring in the synthesis structure was observed in the 175 eV region, and the presence of the N atom belonging to the Im ring was observed in the 411 eV region. In addition, the B atom, which would indicate the presence of a small amount of dopant anion, was observed in the 202 eV region. In addition, the different texture of the SEM image of the obtained Poly(Th2-Im) from Poly(Th) was considered as evidence of a new co-monomer. It was observed that

Poly(Th2-Im) had a more distinct and regular geometric texture morphologically.

3.1. Electrochemical Polymerization:

To compare co-monomer Th2-Im with Th and Im monomer, each monomer and co-monomer were electrochemically polymerized using 100 mV s^{-1} scan rate in the potential range of 0-1.8 V. The applied conditions were: the amount of substance used was 0.01 M; BFEE:ACN (1:5 by volume) as electrolyte and 4 cycles. The obtained polymer growth (cyclic voltammetry-CV) graphs are given in Figure 2.

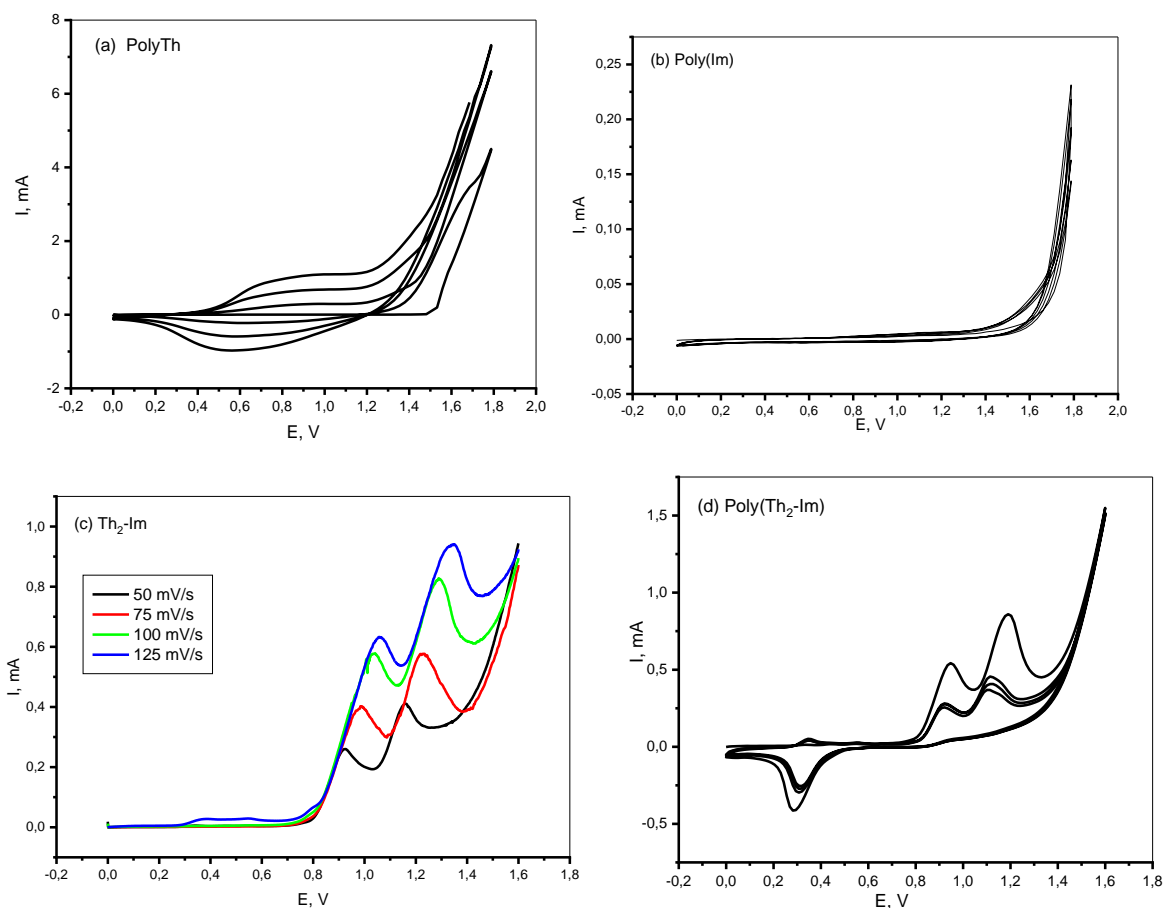


Figure 2. The CV of a) Poly (Th), b) Poly(Im), c) The LSV graph of Th₂-Im, d) The CV graph of Poly(Th₂-Im). (concentration: 0.01M; electrolyte: BFEE:ACN (1:5 as volume) Potential Range: 0-1.8V; scan rate: 100 mV s⁻¹, cycle number: 4.)

In order to perform the electropolymerization of Th and Im monomers, the potential range was selected high. In this range, Th was oxidized at 1.5 V, while Im was oxidized at 1.7 V. Th₂-Im was determined to be oxidized at 0.6 V in this range by taking linear sweep voltammetry (LSV) (Figure 2 c) at different scanning speeds.

Accordingly, it was polymerized very well on the electrode surface. In order to see the oxidation of the obtained polymers, the current changes at different scanning speeds in a monomer-free environment were examined. The data obtained in this investigation are given in Figure 3.

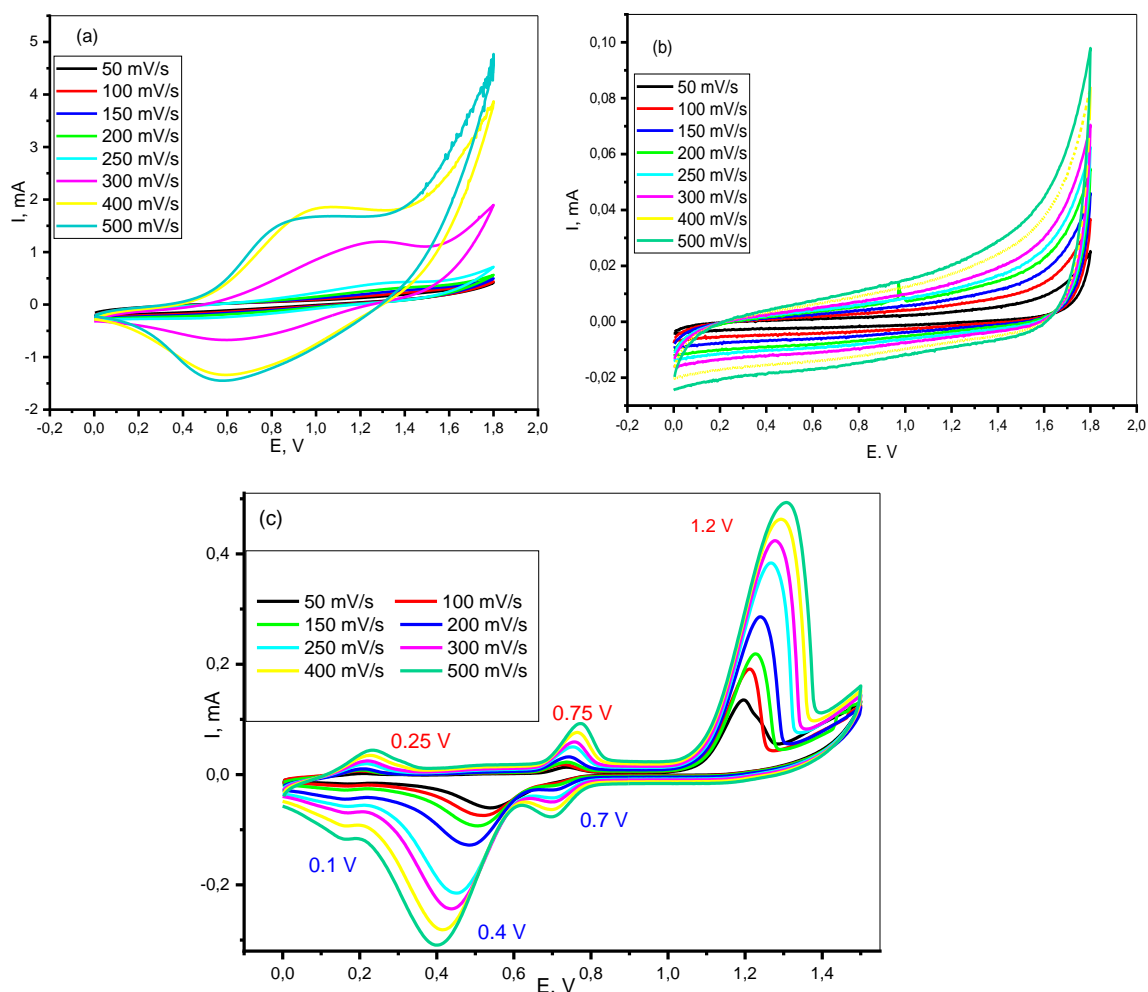


Figure 3. Monomer free graphs of a) Poly (Th), b) Poly(Im) and c) Poly(Th2-Im). (1:5 BFEE: ACN electrolyte; 0-1.5V potential range; Pt electrode)

When the obtained graphs were examined, it was seen that the polymer deposited on the electrode surface in the applied conditions of Poly (Th) (Figure 3a) was oxidized at 0.9 V, while Poly (Im) was oxidized at approximately 1.75 V. When the monomer-free environment graphs were examined at the same scanning speeds for Poly (Th2-Im), 3 oxidation peaks were clearly observed as 0.25 V, 0.75 V and 1.2 V and 3 reduction peaks as 0.7 V, 0.4 V and 0.1 V. It was determined from these data that the synthesis polymer obtained could be

polymerized more easily compared to Th and Im and that the donor-acceptor character could be clearly observed in the CV graphs. When the Th2-Im Comonomer transitioned into the polymer state, it was observed that the polymer state formed around the electrode and remained in the form of oligomer in the solution was dark green. The polymer state was also characterized by the visible region spectrum. The UV spectrum is given in Figure 4.

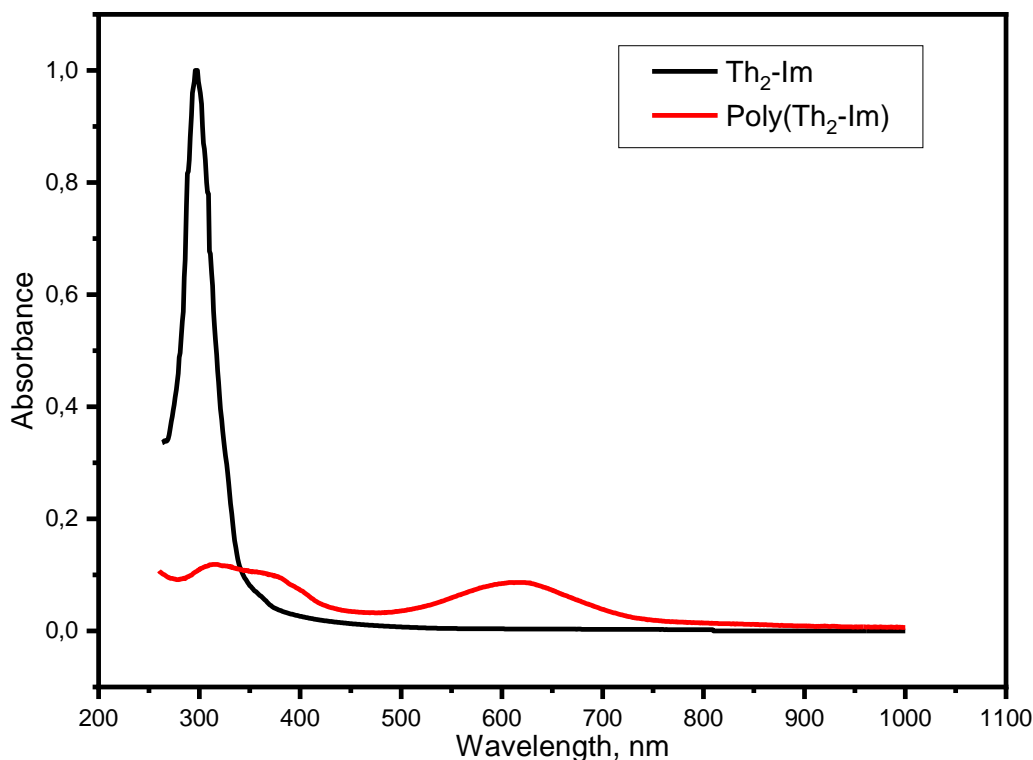


Figure 4. The UV spectrum of Th₂-Im and Poly(Th₂-Im), comparatively.

The UV spectrum of the solution prepared from the co-monomer obtained at the end of the synthesis gave a peak in the range of 260-300 nm; when the solution containing this co-monomer was electropolymerized, both the polymer accumulated around the electrode and the oligomer structure formed in the solution as long chains appeared dark green. It was thought that this situation was proven by the broad peak that poly(Th₂-Im) gave at 600 nm, unlike the co-monomer state. The broad peak in this region could not be observed in Th₂-Im.

4. Conclusion

In this study, by using Im and Th monomers, which are difficult to electropolymerize, electron donor-acceptor co-monomer carrying two Th rings (Th₂-Im) was obtained by Still Cross Coupling reaction. It was aimed to perform electropolymerization of Th and Im at lower potential and determine electron exchanges. FT-IR, XPS and SEM images of the obtained synthesis product were obtained and the difference between Im and Th was revealed. Accordingly, C-S stretching peaks specific to Th ring were observed at

1170 cm⁻¹ for Poly(Th) while it shifted to 1175 cm⁻¹ for Poly(Th₂-Im). C=C stretching peaks were observed at 1450 cm⁻¹ for Poly(Th₂-Im), conjugation at 1650 cm⁻¹, aromatic =CH at 2900 cm⁻¹, hydrogen bond stretching peaks belonging to -NH at 3300 cm⁻¹. In the synthesis structure, the presence of the S atom belonging to the Th ring was observed in the 175 eV region, and the presence of the N atom belonging to the Im ring was observed in the 411 eV region. In addition, the B atom, which indicates the presence of a small amount of dopant anion, was observed in the 202 eV region. It was determined by SEM images that Poly(Th₂-Im) had a more distinct and regular geometric texture than Poly(Th). It was determined that Th₂-Im was oxidized at 0.6 V from electrochemical polymerization. From monomer free CV, it was determined that Poly(Th₂-Im) showed 3 oxidation peaks as 0.25 V, 0.75 V and 1.2 V and 3 reduction peaks as 0.7 V, 0.4 V and 0.1 V. It was determined from these data that the synthesis polymer obtained could be polymerized more easily compared to Th and Im and that the donor-

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