A novel synthesis of 3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9-tosyl-9*H*-carbazole

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Abstract 3,6-bis(2,3-dihydrothieno [3,4-b][1,4]dioxin-5-yl)-9-tosyl-9*H*-carbazole (EDOTTsCz) was synthesized and electrochemically polymerized on glassy carbon electrode (GCE) in 0.1 M tetrabutyl ammonium tetrafluoroborate (NB_4BF_4)/acetonitrile (CH_3CN). Alternating copolymer was formed by CV method. Modified polymer electrode was characterized by Fourier transform Infrared Spectroscopy-Attenuated Transmission Reflectance (FTIR-ATR), Cyclic voltammetry (CV), Scanning electron microscopy-Energy dispersive X-ray analysis (SEM-EDX), Atomic force microscope (AFM) and Electrochemical impedance spectroscopy (EIS). Capacitive behaviors of the modified GCE were defined via Nyquist, Bode-magnitude, Bode-phase and Capacitance plots. A modified copolymer electrode provides enhanced capacitance evaluation, which may results in performance in energy storage devices.

Keywords: Copolymer, Capacitance, Scanning electron microscopy (SEM), Atomic force microscopy (AFM)

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1. Introduction

Conducting polymers (CPs) have been an ever developing area in polymer chemistry for four decade [1]. They include an interesting class of materials, which combine some of the mechanical features of plastics with electrical properties typical of metals. The ability to tailor the structure of conjugated polymers allow the rational synthesis of conducting polymers with a broad range of electronic properties since the nature of the repeating units and the functional groups alter the electronic character of polymers [2,3].

3,6-bis(2,3-dihydrothieno [3,4-b][1,4] dioxin-5-yl)-9-tosyl-9*H*-carbazole monomer was synthesized like in our previous synthesis procedure of 3,6-dibromo-9-tosyl-9*H*-carbazole [4]. A wide variety of π-conjugated polymers have been synthesized, and characterized in view of their physical and chemical properties. Simple monomers are polymerized with their π-conjugated backbone to form a network of highly delocalized electrons [5]. Electrochemical polymerization technique is more convenient method than chemical method, due to its catalyst-free, one-step conducting film formation, control of film thickness by controlling the deposition charge,

etc. [6-9]. Thus, the polymers were coated on the electrode surface and show good electroactivity [10-13].

The most widely studied electrochemically conducting polymers (CPs) can be divided four major classes: polypyrroles, polyanilines, polycarbazoles and polythiophenes [14-17]. They can be made into a wide variety of morphologies [18, 19] and used in a wide variety of applications, such as biosensor [20], solar cell [21], supercapacitor [22, 23], etc. In the class of conducting polymers with a π-conjugated backbone, polythiophenes are particularly interesting due to their good thermal and electrical properties, good stability and functionalization [24]. Chemical functionalization, in principle, allows for fine-tuning of polymers physical and electronic properties [25-27]. Poly(3,4-ethylenedioxythiophene) (PEDOT) is a thiophene derivative, exhibits many favorable properties, such as a low band gap (1.6 eV), a high lying HOMO, an easy conversion into the conducting state and a high stability in the conducting form. However, the poor solubility of PEDOT is a strong drawback for further applications in electrical and optical devices [28]. Compared to other unsubstituted polythiophene and its

derivatives, PEDOT exhibits a distinctly low oxidation potential and a small band gap in the oxidized state [29, 30]. Carbazole and its derivatives have been known for many years to exhibit excellent electro-active and photoactive properties due to their high hole-transporting mobility of the charge carriers [31-35], good environmental stability and photo-conductivities [36, 37].

Their electroluminescence is a result of the large enough band gap of the biphenyl unit. These properties are especially valuable for new polymeric materials, when these compounds are used as monomers in syntheses of polymer [38, 39].

Many potential applications of conducting polymers become limited because of their general insolubility in common organic solvents, poor mechanical properties and their insufficient environmental stability. To improve these properties, an electrochemical method was used to prepare copolymers with other monomers [40]. Electrochemical synthesis of copolymers is a good strategy in new electrically active materials that combine the properties of the constituent homopolymers [41-43]. Moreover, more and more new derivatives of the common CPs, novel CPs, or their copolymers with good fluorescence property, high electrical conductivity, satisfied thermal stability, or other properties, have been developed in literature [44].

Electrochemical impedance spectroscopy (EIS) allows the analysis of the properties of materials and systems by applying them alternate electric signals of different frequencies (voltage or current) and measuring the corresponding electric output signals (current or voltage) [45-52]. These signals can be applied in a broad frequency range, which makes it possible to cover a wide range of time constants. Moreover, EIS has been highlighted as a technique that is suitable to study the interfacial process [53, 54].

As a result, EDOTTsCz was electropolymerized on GCE and CFME. Polymer characterization was done by CV, FTIR-ATR, SEM-EDX, AFM and EIS analysis.

2. Experimental

2.1. Materials

All chemicals were used as received from Aldrich Chemical without further purification. Alumina polising suspension (Balkowski International Corporation, 0.05 CB micron Gamma Type, CR85S), Carbon fiber microelectrode (SGL SIGRAFIL C 320 B) and Carbon cement (LEIT-C-Plast) were used in the electropolymerization experiments.

2.2. Instrumentation

Cyclic voltammetry (CV) was performed using PARSTAT 2273 (software: powersuit and Faraday cage: BASI Cell Stand C3) in a three electrode configuration, which employing GCE (area: 0.07 cm^2) and CFME (area: 0.022 cm^2) as the working electrode, platinum wire as the counter electrode and Ag/AgCl as the reference electrode.

Modified electrodes were characterized by FTIR-ATR spectroscopy (Perkin Elmer, Spectrum One B, with an universal ATR attachment with a diamond and ZnSe crystal). Electrocoated copolymers were analyzed by Scanning electron microscopy (SEM) and Energy Dispersive X-ray analysis (EDX) using a Carl Zeiss Leo 1430 VP. Average values of the increase in thickness were obtained from SEM images taking into account the diameter of the uncoated CFME. The AFM images were obtained with Park System XE 100. In all AFM analysis, the non-contact mode was employed by using Al coated high resonance frequency silicon tips (265-400 kHz) with 4 μm thickness, 35 μm mean width, 125 μm length and 20-75 N/m force constant. High resolution images (1024x1024 pixels) and the raw data collected by the XEI image processing and analysis using left shadowing.

2.3. Electrochemical impedance spectroscopic measurements

The electrochemical impedance spectroscopic (EIS) measurements were taken in 0.1 M tetrabutyl ammonium tetrafluoroborate (NB_4BF_4) / acetonitrile (CH_3CN). EIS measurements were performed in monomer free electrolyte solution with a perturbation amplitude 10 mV over a frequency range of 10 mHz to 100 kHz with PARSTAT 2273.

3. Results and Discussions

3.1. Synthesis of EDOTTsCz monomer

2,3-dihydrothieno[3,4-b][1,4]dioxin substance (40.8 mmole) dissolves in 100 mL THF under nitrogen atmosphere and mixes by stirrer. Mixture condenses to -70 $^{\circ}$C with asetone-liquid nitrogen mixture. After mixing ~ 30 minutes, n-butyl lithium (39 mmole) was added by injection method via syringe. After 1 h, mixture temperature adjusted to 0 $^{\circ}$C, and $MgBr_2.Et_2O$ substance (42 mmole) was added to the mixture. 1 h later, 3,6-dibromo-9-tosyl-9*H*-carbazole (6.3 mmole) and $NiCl_2$ (0.92 mmole) dissolves in 30 ml THF and added to the mixture. Mixture was adjusted to the room temperature and mixes for 60 h at room temperature. Organic phase rinsed with 10 % NaOH and removes the organic phase from the mixture. Solvent removes from mixture by the help of rotary evaporator. Silica gel chromatography was evaluated with dichloromethane and crystallized with diethylether. The physical properties of substance are given as the following; Rf: 0.80 (n-hexan-dicholoromethane 1:1), melting point: 187 $^{\circ}$C (yield: 60 %).

FT-IR (KBr): 2960-2877 cm^{-1} (C-H aromatic), 1589 cm^{-1} (C=C, aromatic), 1171 cm^{-1} (S=O).

^{1}H-NMR (CDCl$_3$): δ 8.34-8.31 (dd, 2H, aromatic CH), 7.9 (dd, 2H, aromatic CH), 7.7 (dd, 2H, aromatic CH), 7.5 (m, 2H, aromatic CH), 7.4-7.3 (m, H, aromatic CH), 7.25 (s, H, aromatic CH), 7.1 (dd, 2H, aromatic CH), 3.5 (m, 2H, CH$_2$), 3.3 (m, 2H, CH$_2$), 2.31 (s, 3H, CH$_3$).

^{13}C-NMR (CDCl$_3$): δ 144 (CH), 138 (CH), 134 (CH), 129 (CH), 128 (CH), 127 (CH), 126 (CH), 126.37 (CH), 126.11 (CH), 123 (CH), 119 (C), 115 (C), 77.34 (CH$_2$), 77.22 (CH$_2$), 77.02 (CH$_2$), 76.70 (CH$_2$), 58.82 (CH), 24 (CH), 21.40 (CH), 21.20 (CH), 19.72 (CH), 13.67 (CH$_3$).

A novel synthesized monomer structure was given in **Fig.1**. EDOTTsCz was electropolymerized on CFME in 0.1 M NaClO$_4$ / CH$_3$CN by CV method. Polymerization was done at a scan rate of 100 mVs^{-1}, potential range: 0.5-1.6 V (**Fig. 2**). By increasing the initial monomer concentration ([EDOTTsCz]$_0$) from 1 mM (Q$_a$= 0.447 mC) to 10 mM (Q$_d$= 15.3 mC), total charges increases by electrogrowth process. New substrate surface occurs by electrogrowth process of every cycle on the surface. Thickness of electrode, chain

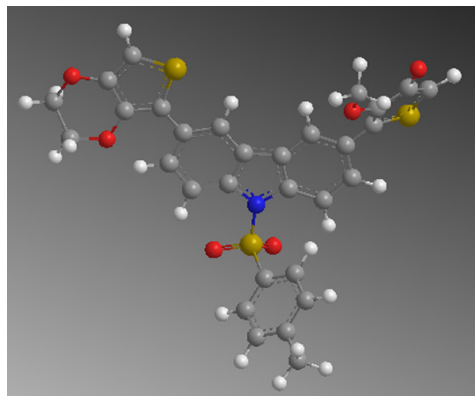length of copolymer and also current density increase by addition of monomer during electrogrowth process.

Fig. 1. 3 dimensional structure of 3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9-tosyl-9*H* carbazole.
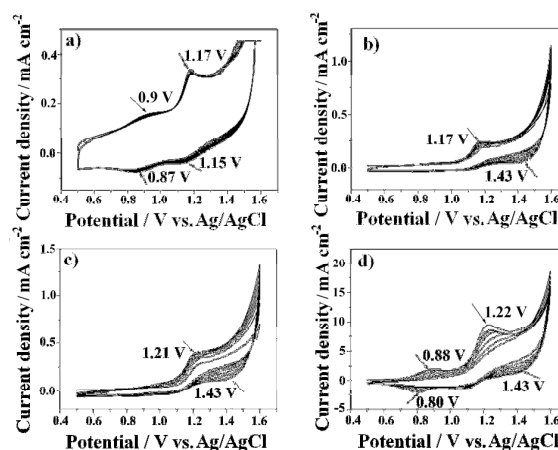

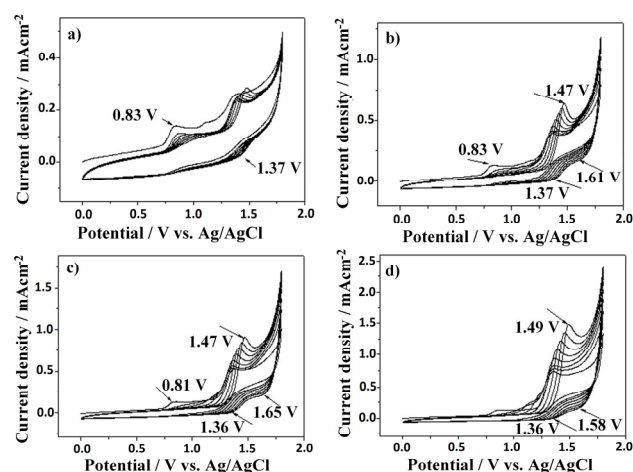**Fig. 2.** Electro-growth of 3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9-tosyl-9*H*-carbazole on CFME, **a)** [EDOTTsCz]$_0$=1 mM (Q$_a$= 0.447 mC); **b)** [EDOTTsCz]$_0$=3 mM (Q$_b$= 2.42 mC); **c)** [EDOTTsCz]$_0$=5 mM (Q$_c$= 9.064 mC); **d)** [EDOTTsCz]$_0$=10 mM (Q$_d$= 15.3 mC), 8th cycle, Scan rate: 100 mV s^{-1}, 0.1 M NaClO$_4$ / CH$_3$CN, Potantial range: 0.5 - 1.6 V.

Oxidation peak potentials of poly(EDOTTsCz) were obtained as 1.17 V, for [EDOTTsCz]$_0$= 1 mM and [EDOTTsCz]$_0$= 3 mM. By increasing of the initial monomer concentration from 5 mM to 10 mM, the oxidation peak potentials increase from

1.21V to 1.22 V. This is expected due to formation of more bulky structure.

3.1. Electropolymerization of EDOTTsCz on GCE in NBu₄BF₄ / CH₃CN

Fig. 3. Electrogrowth of 3,6-bis(2,3-dihydrothieno[3, 4-b][1,4]dioxin-5-yl)-9-tosyl-9*H*-carbazole on GCE, **a)** $[EDOTTsCz]_0$= 1 mM (Q_a= 1.217 mC); **b)** $[EDOTTsCz]_0$= 3 mM (Q_b= 2.127 mC); **c)** $[EDOTTsCz]_0$= 5 mM (Q_c= 2.931 mC); **d)** $[EDOTTsCz]_0$= 10 mM (Q_d= 4.054 mC), 8 cycle was taken for electrogrowth process. Scan rate: 100 mV s^{-1}, 0.1 M NB₄BF₄ / CH₃CN, Potential range: 0.0 - 1.8 V.

Peak potentials were obtained as ~0.83 V and ~1.37 V, respectively. There is no higher shift by addition of monomer concentration. However, current density increases higher amount from 0.1 mA cm^{-2} to 1.5 mA cm^{-2} by addition of $[EDOTTsCz]_0$ = 1 mM to $[EDOTTsCz]_0$ = 10 mM (**Fig.3**). In literature, poly(3,6-bis-(2-(3,4-ethylenedioxy) thienyl)-*N*-dodecylcarbazole) obtained by anodic coupling of 3,6-bis(2-(3,4-ethylenedioxy)-thienyl)-*N*-dodecylcarbazole in acetonitrile and the investigation of its in situ conductivity and in situ ESR behavior [55]. The polythiophene oxidation of literature is given by concern of paramagnetic polarons and diamagnetic bipolarons [56, 57]. These species are polymeric analogs cation radicals and dications. It has been proposed that oxidation leads first to polarons, and as the extent of oxidation increases along one chain, these polarons combine to form biopolarons.

3.2. Plot of anodic and cathodic peak current density vs. scan rate and square root of scan rate dependence of Poly(EDOTTsCz) / GCE in monomer-free electrolyte

When inspected the plot of Poly(EDOTTsCz) modified GCE anodic and cathodic peak current density vs. scan rate and square root of scan rate dependence in monomer free solution in 0.1 NB₄BF₄/CH₃CN, regression coefficient (R) for $[EDOTTsCz]_0$= 1 and 10 mM, respectively. The electrochemical process where diffusion controlled process applies for $[EDOTTsCz]_0$= 3 and 5 mM, respectively. It might also be an indication of thin film formation (**Table 1**).

Table 1. According to initial monomer concentration, scan rate and square root of scan rate change with regression coefficient.

Current density (i_p / mA cm^{-2}) can be calculated

Initial monomer concentration	Regression Coefficient (R)			
	Scan Rate-Current density		Square root of scan rate-Current density	
	Anodic	Cathodic	Anodic	Cathodic
1	0.9879	-0.9816	**0.9976**	**-0.9988**
3	**0.9963**	**-0.9905**	0.9929	-0.9427
5	**0.9982**	**-0.9961**	0.9892	-0.9607
10	0.9857	-0.9790	**0.9982**	**-0.9951**

for reversible system from Randless-Sevčik equation: i_p= $(2.69 \times 10^5) \times A \times D^{1/2} \times C_0 \times v^{1/2}$ (where v is the scan rate, A is electrode area, D is the diffusion coefficient of electro-active species in the solution). If peak current is proportional to v where thin film formation [58, 59]. If the peak current is proportional to $v^{1/2}$ in the range of scan rate, where diffusion control applies [60]. Diffusion coefficient (D) was obtained as 1.35×10^{-15} for $[EDOTTsCz]_0$= 1 mM, D= 6.14×10^{-16} for $[EDOTTsCz]_0$= 3 mM, D= 4.97×10^{-16} for $[EDOTTsCz]_0$= 5 mM and D= 1.14×10^{-17} for $[EDOTTsCz]_0$= 10 mM (**Fig.4**).
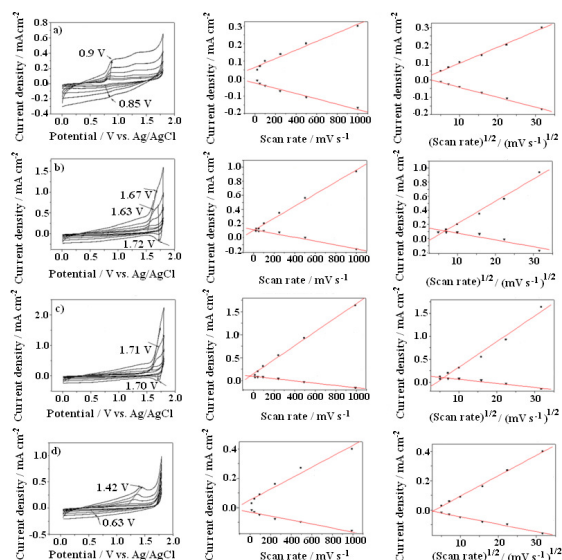
Fig. 4 Plot of anodic and cathodic peak current density vs. scan rate and square root of scan rate dependence of Poly(EDOTTsCz) / GCE in monomer free solution in 0.1 NB$_4$BF$_4$ / CH$_3$N, potential range: 0.5 V-1.6V scan rate: 25,50, 100, 250, 500, 1000 mVs^{-1} **a)** [EDOTTsCz]$_0$ = 1 mM, **b)** [EDOTTsCz]$_0$ = 3 mM **c)** [EDOTTsCz]$_0$ = 5 mM, **d)** [EDOTTsCz]$_0$ = 10 mM.

Electrochemical impedance spectroscopic results of Poly(EDOTTsCz) / GCE in NaClO$_4$ / CH$_3$CN

When inspected, Nyquist plot of Poly(EDOTTsCz)/GCE, low frequency capacitances (C$_{LF}$) were obtained as: C$_{LF}$= 2.1 mF cm^{-2} for [EDOTTsCz]$_0$= 1 mM, C$_{LF}$= 2.55 mF cm^{-2} for [EDOTTsCz]$_0$= 3 mM, C$_{LF}$= 2.62 mF cm^{-2} for [EDOTTsCz]$_0$=5 mM and C$_{LF}$= 2.41 mF cm^{-2} for [EDOTTsCz]$_0$=10 mM as given **Fig. 5.** The highest capacitance value, C$_{LF}$= 2.62 mF cm^{-2} was obtained for [EDOTTsCz]$_0$ = 5 mM.

Electrochemical impedance spectroscopy can be used to identify subtle changes on surface of polymer modified electrode [61]. Ac impedance spectroscopy is given as a result of specific power potential of electrochemical capacitor and combination of resistance [62].
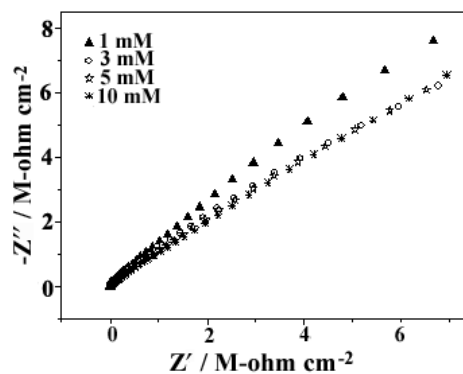

Fig. 5. Nyquist plot for Poly(EDOTTsCz) electrocoated on GCE, [EDOTTsCz]$_0$ = 1, 3, 5 and 10 mM in 0.1 M NaClO$_4$ / CH$_3$CN.

One important point in electrochemical impedance spectroscopy is the process of moving into electrode constitution with the resistances [63].

In our previous study, we have studied 9-tosyl-9*H*-carbazole for [EDOTTsCz]$_0$= 1, 3, 5 and 10 mM in 0.1 M NaClO$_4$ / CH$_3$CN. As a result of equivalent circuit models of R(CR)(QR)(CR), the highest C$_{LF}$ value was obtained at the frequency of 0.01 Hz in initial monomer concentration of 10 mM as 50 mF cm^{-2} [64].

A value of double layer capacitance (C$_{dl}$) can be calculated from a Bode-magnitude plot, by extrapolating the linear section to value ω (log ω= 0), the relationship IZI= 1/ C$_{dl}$, as shown in **Fig. 6**.

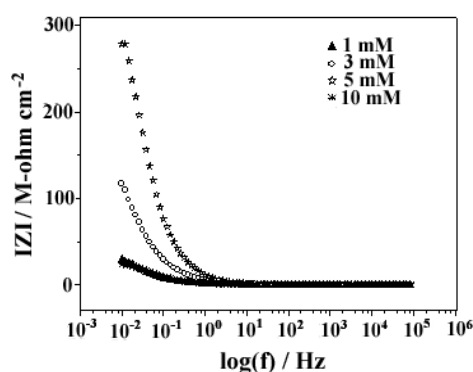**Fig. 6.** Bode-magnitude plot of Poly(EDOTTsCz) electrocoated on GCE, [EDOTTsCz]$_0$ = 1, 3, 5 and 10 mM in 0.1 M NaClO$_4$ / CH$_3$CN.

C_{dl} was obtained from Bode-magnitude plot as ~1.66 mF cm^{-2} for $[EDOTTsCz]_0$= 1, 3, 5 and 10 mM (**Fig. 6**).

Comparison of FTIR-ATR spectrum of EDOTTsCz and Poly(EDOTTsCz)

When examining FTIR-ATR spectrum of EDOTTsCz and polymer, some of peaks were shifted associated with polymer formation. For example, the peaks at 2960 and 2877 cm^{-1} correspond to C-H stretching,, at 1589 cm^{-1} attributed to C=C stretching, and at 1171 cm^{-1} belongs to S=O (**Fig. 7**).
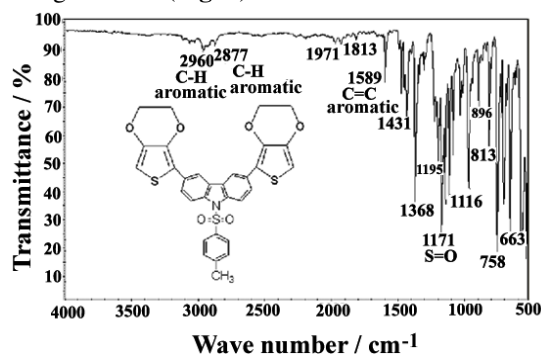

Fig. 7. FTIR-ATR spectrum of EDOTTsCz.

In FTIR-ATR spectrum of poly(EDOTTsCz) correspond to peak at 3585 cm^{-1} for C-H stretching, at 1624 cm^{-1} for C=C stretching, at 1431 cm^{-1} for CH$_3$, at 1369 cm^{-1} for C-O stretching, at 1096 cm^{-1} for dopant ion (ClO$_4^-$) and at 755 cm^{-1} for C-S stretching (**Fig. 8**).
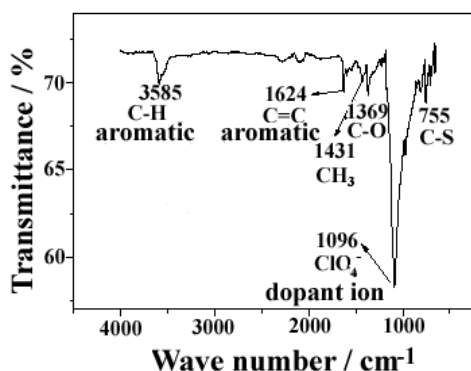

Fig. 8. FTIR-ATR spectrum of Poly(EDOTTsCz)/CFME, $[EDOTTsCz]_0$= 10 mM,

chronoamperometric method, 300 s, constant potential of 1.6 V in 0.1 M NaClO$_4$ / CH$_3$CN.

SEM-EDX Analysis

SEM image of Poly(EDOTTsCz) / CFME shows a homogeneous film (**Fig. 9**). EDX data was given in **Fig.10** and **Table 2.**
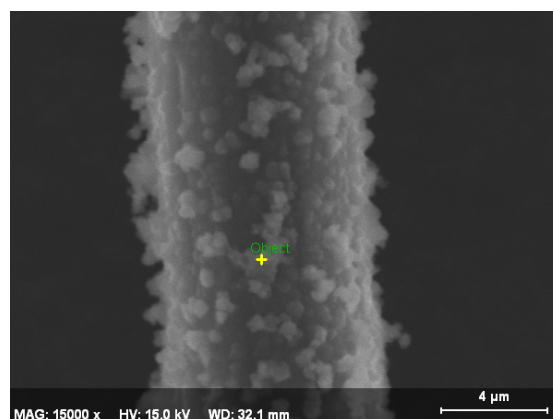

Fig. 9. SEM-EDX point analysis of Poly(EDOTTsCz), $[EDOTTsCz]_0$= 10 mM (Q_d= 15.3 mC). Electrograwth process was taken 8 cycle, scan rate: 100 mV s^{-1}, potential range: 0.5-1.6 in 0.1 M NaClO$_4$ / CH$_3$CN.

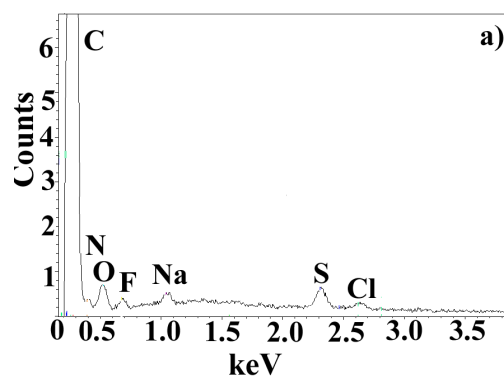**Fig.10.** EDX point analysis of Poly(EDOTTsCz) $[EDOTTsCz]_0$= 10 mM (Q_d= 15.3 mC). Electrogrowth process was taken 8 cycle, scan rate: 100 mV s^{-1}, potential range: 0.5-1.6 in 0.1 M NaClO$_4$ / CH$_3$CN.

Table 2. EDX point analysis of Poly(EDOTTsCz)

Elements	Point Analysis
	Weight / %
Carbon	56.80
Nitrogen	16.44
Oxygen	16.48
Fluorine	7.02
Sodium	2.27
Sulphur	0.68
Chlorine	0.31

AFM Analysis
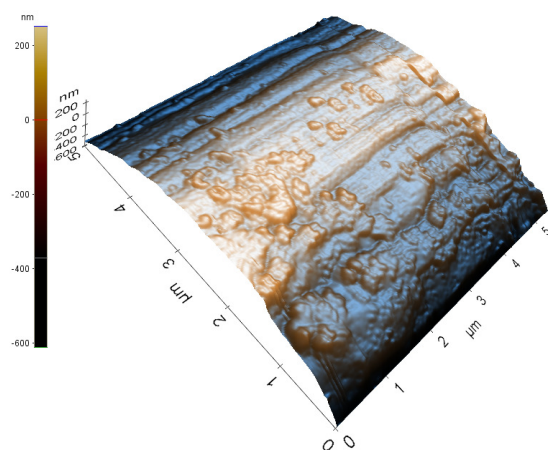
Fig. 11. AFM images of poly(EDOTTsCz) coated on CFME with scan size of 5µm x 5µm, scan rate: 1 Hz, [EDOTTsCz]$_0$= 10 mM (Q$_d$= 15.3 mC). Electropolymerization process was taken 8 cycle, scan rate: 100 mV s^{-1}, potential range: 0.5-1.6 in 0.1 M NaClO$_4$ / CH$_3$CN.

AFM images of poly(EDOTTsCz) shows the coating process by observing granules on CFME (**Fig.11**).

4. Conclusions

Conducting polymers have been used in energy storage devices due to their charge-discharge capability [65, 66]. Doping and de-doping process supplies the possibility of capacitor behavior (pseudocapacitance) for conducting polymers [67]. In this study, a new π conjugated substance was chemically synthesized and characterized by FTIR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. EDOTTsCz

monomer was electrochemically polymerized on GCE and CFME in 0.1 M NaClO$_4$ / CH$_3$CN and NB$_4$BF$_4$/CH$_3$CN, respectively. Modified copolymer was characterized by CV, FTIR-ATR, SEM-EDX, EIS, and AFM, respectively. In future, polymer may also be used as capacitor properties in energy storage devices. High power density and long stability may be supplied by using graphite anode electrode, carbon nanotube, and composite materials [68, 69].

5. Acknowledgments

6. References

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