

# Synthesis and Characterization of Conducting Copolymer of *Trans*-1-(4-methyl-3'-thienyl)-2-(ferrocenyl)ethene with EDOT

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**ABSTRACT:** Ferrocene-substituted conducting polymer namely poly(*trans*-1-(4-methyl-3'-thienyl)-2-(ferrocenyl)ethene-*co*-3,4-ethylenedioxythiophene) [P(MTFE-*co*-EDOT)] was synthesized and its electrochromic properties were studied. Monomer, MTFE, was obtained using 2-(ferrocenyl)ethene and 3-methyl-4-bromothiophene. The structure of monomer was determined via Fourier transform infrared spectroscopy (FTIR), <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR techniques. The copolymer was synthesized using this monomer and EDOT. The resulting copolymer P(MTFE-*co*-EDOT) was characterized by cyclic voltammetry, FTIR, scanning

electron microscopy, atomic force microscopy, and UV-vis spectroscopy. The conductivity measurements of copolymer and PEDOT were accomplished by the four-probe technique. Although poly(*trans*-1-(4-methyl-3'-thienyl)-2-(ferrocenyl)ethene) [P(MTFE)] reveals no electrochromic activity, its copolymer with EDOT has two different colors (violet and gray). Band gap ( $E_g$ ) and  $\lambda_{\max}$  of P(MTFE-*co*-EDOT) were determined. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** ferrocene; EDOT; AFM; copolymerization

## INTRODUCTION

The design and synthesis of compounds for any type of applications in material science for use in sensor chemistry and/or electrochemistry are important areas of research. The synthesis of such structures is directly related to the availability of target molecules having useful physical or chemical properties, for example, sensitivity to light or heat, redox or pH activity, binding selectivity, and color reversibility with electrical charge.<sup>1,2</sup>

Polymers have been considered as organic materials that have characteristic properties such as hydrophobic surfaces, low thermal and electrical conductivities, chemical inertness, and low mechanical durability. However, a fundamental progress in the polymer science has absolutely changed this prospect. Synthesis of new types of polymeric materials with a remarkable electrical conductivity directly connected the polymer synthesis, applications, and electrochemistry.<sup>2–6</sup> The preparation of conjugated polymers containing additional functional groups

especially metal complexes and redox-active species are of concern by material scientists.<sup>7–10</sup>

Ferrocene (Fc) has widespread applications because of its remarkable electrochemical properties.<sup>11</sup> The stability, low cost, and reversible redox activity of Fc have attracted attention, and it is used in conducting polymers,<sup>12,13</sup> as a catalyst in organic synthesis,<sup>14–20</sup> in photo-induced electron-transfer systems,<sup>21</sup> and as electron transfer mediator.<sup>22</sup> Fc and its derivatives (amino acids, carbohydrates, DNA, and hormones) have also been investigated for applications in biological systems because of their stability in aqueous and aerobic media.<sup>11,23</sup>

Fc molecule was involved in redox-active polymers via ring opening of ferrocenophanes and in preparing of metal containing liquid crystals. The surface modification of electrodes in sensor designing and preparing the conducting polymer-modified electrodes is in scope of Fc research.<sup>24</sup>

Jonas and Schrader<sup>25</sup> synthesized 3,4-ethylenedioxythiophene (EDOT) by locking the 3- and 4-positions of thiophene with an ethylenedioxy group yielding a highly electron-rich fused heterocycle, which has low oxidation potential and is free from the possible  $\alpha$ ,  $\beta$  and  $\beta$ ,  $\beta$  linkages. Poly(3,4-ethylenedioxythiophene) (PEDOT) exhibits an optical band gap of 1.6 eV. Doped PEDOT is almost transparent in the visible region, and the neutral polymer is dark blue.

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Thus, this material is significant for its cathodically coloring electrochromic properties in device applications.<sup>26</sup>

This study deals with electrochemical properties of metal-containing conducting copolymer: poly (*trans*-1-(4-methyl-3'-thienyl)-2-(ferrocenyl)ethene-*co*-3,4-ethylenedioxythiophene) [P(MTFE-*co*-EDOT)]. MTFE was synthesized using 2-(ferrocenyl)ethene and 3-methyl-4-bromothiophene. The structure of monomer was identified via Fourier transform infrared spectroscopy (FTIR) and <sup>1</sup>H-NMR and <sup>13</sup>C-NMR techniques. The structure of the copolymer was characterized by cyclic voltammetry (CV), FTIR, scanning electron microscopy (SEM), atomic force microscopy (AFM), and UV-vis spectroscopy. Its band gap ( $E_g$ ) and  $\lambda_{max}$  were determined. Conductivity studies were achieved via the four-probe technique.

## EXPERIMENTAL

### Chemicals

3-Methylthiophene, bromine, chloroform, methyl(triphenylphosphine)bromide, zinc powder tetrahydrofuran, *n*-butyl lithium (*n*-BuLi), ferrocenecarboxaldehyde, ammonium chloride, diethyl ether, palladium-II-acetate, potassium carbonate, acetonitrile, EDOT, and tetrabutylammonium perchlorate (TBAP) were obtained from Aldrich (Steinheim, Germany). Potassium hydroxide, ethanol, acetic acid, sodium sulfate, magnesium sulfate, and silica gel were purchased from Merck (Darmstadt, Germany). All reagents and solvents were of analytical grade and used without further purification.

### Equipment

NMR spectra were recorded on a Bruker Instrument NMR Spectrometer DPX-400 in dimethylsulfoxide (DMSO). The FTIR spectra were obtained on Spectrum BXII (4000–400  $\text{cm}^{-1}$ ). CVs were carried out in TBAP (0.1M)/dichloromethane (DCM) electrolyte-solvent couple with a system consisting of an electrochemical analyzer (CH Instruments 600), a CV cell containing indium tin oxide (ITO)-coated glass or Pt plate as the working and counter electrodes, and a Ag wire pseudo-reference electrode. Measurements were taken at room temperature. The particle morphology of the copolymer films was examined by means of scanning electron microscopy (Carl-Zeiss EVO-40) operated at 20 kV. The three-dimensional AFM images of the copolymer film, which was synthesized on the Pt surface, were taken by means of AFM (Veeco). The UV-vis measurements were carried out on Shimadzu MultiSpec-1501 UV-vis spectrophotometer. Colorimetry measurements were taken on Minolta CS-100 spectrophotometer.

Electrical conductivities of the copolymer and PEDOT were measured using the four-probe technique by a standard conductometer. All experiments were carried out at room temperature.

### Synthesis of monomer

The synthesis of monomer (MTFE) was according to the procedure reported in previous studies.<sup>24,27</sup>

#### 3-Methyl-2,4,5-tribromothiophene

3-Methylthiophene (0.051 mol, 4.89 mL) and  $\text{CHCl}_3$  (12 mL) were placed in a round-bottomed flask, and  $\text{Br}_2$  (8.79 mL, 0.172 mol) was added dropwise into the vigorously stirred solution. The reaction mixture was kept at room temperature for 17 h and then refluxed for 2 h. After cooling to room temperature, a KOH solution (4.20 g) in ethanol (22.90 mL) was added. The mixture was refluxed for further 4 h, then poured into an ice/water mixture (60 mL), and extracted with  $\text{CHCl}_3$ . Colorless crystals of the desired product were obtained in 85% yield after recrystallization from a  $\text{CHCl}_3$ /EtOH mixture. The synthetic route of 3-methyl-2,4,5-tribromothiophene is shown in Figure 1.

#### 3-Methyl-4-bromothiophene

To acetic acid/water mixture (1 : 2, 27 mL), zinc powder (0.39 g, 6 mmol) and 3-methyl-2,4,5-tribromothiophene (0.62 g, 1.85 mmol) were added in small portions. The suspension was kept at room temperature for 1 h and then refluxed for 3 h. The mixture was then filtered off over a celite, and the product was extracted with diethyl ether from the filtrate. The solution was dried with  $\text{Na}_2\text{SO}_4$ , and the solvent was removed under low pressure, and then the residue was distilled under vacuum-reduced pressure. A yellow colored liquid was obtained in 80% yield as shown in Figure 1.

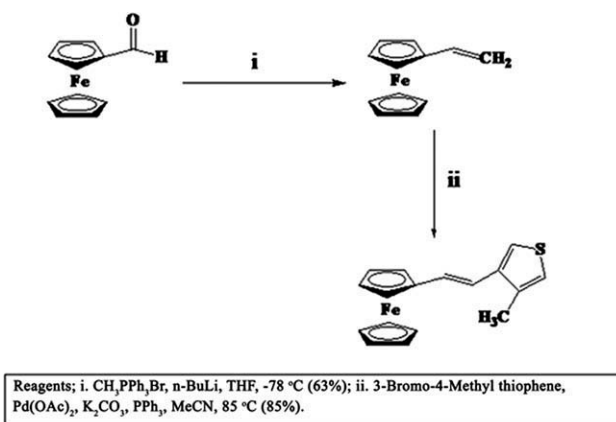
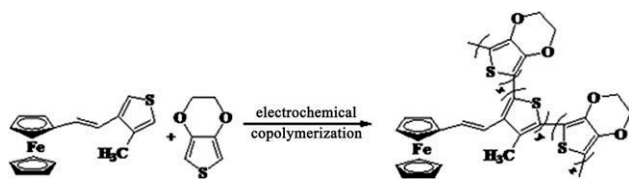


Figure 1 The synthetic route of monomer.



**Figure 2** Schematic representation of the electrochemical copolymerization.

### 2-(Ferrocenyl)ethene

Methyl(triphenylphosphine)bromide (1.193 g, 3.34 mmol) was dissolved in THF (30 mL) and cooled to  $-78^{\circ}\text{C}$ . *n*-BuLi (2.5M in hexane; 1.68 mL, 3.36 mmol) was added dropwise, and then the solution was allowed to warm to  $-10^{\circ}\text{C}$  and stirred for 2 h. The reaction mixture was then re-cooled to  $-78^{\circ}\text{C}$ , and a solution of ferrocenecarboxaldehyde (0.642 g, 3 mmol) in THF (15 mL) was added dropwise. The reaction mixture was stirred overnight at ambient temperature. After quenching with saturated aqueous ammonium chloride (40 mL), the reaction mixture was extracted with diethyl ether ( $3 \times 40$  mL), and then the combined organic layers were dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. The residue was purified by flash column chromatography to give the title compound as a red oil in 63% yield.

### Trans-1-(4-methyl-3'-thienyl)-2-(ferrocenyl)ethene

A mixture of palladium-II-acetate (18 mg, 5 mol %),  $\text{K}_2\text{CO}_3$  (0.3 g, 2 equiv),  $\text{PPh}_3$  (60 mg, 20 mol %), 2-(ferrocenyl)ethene (0.36 g, 1.69 mmol), and 3-methyl-4-bromothiophene (0.30 g, 1.69 mmol) in acetonitrile (30 mL) was heated in a sealed tube at  $85^{\circ}\text{C}$  for 3 days.<sup>28</sup> The cooled reaction mixture was then passed through a short column of silica gel eluting with diethyl ether. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography to afford the title compound as a red color powder in 85% yield. The synthesis of MTFE is accomplished as shown in Figure 1.

### Synthesis of conducting copolymer with EDOT

MTFE and EDOT were used for the synthesis of conductive copolymer, as shown in Figure 2. MTFE ( $1.3 \times 10^{-3}$  M) was dissolved in dichloromethane containing 0.1M of TBAP as electrolyte, and  $1.3 \times 10^{-3}$  M of EDOT was introduced into a single-compartment electrolysis cell. A three-electrode cell assembly was used, in which the working electrode was an ITO-coated glass. A Pt flake was used as the counter, and an Ag wire was used as the pseudo-reference electrodes. The copolymer was potentiodynamically deposited on ITO.

## RESULTS AND DISCUSSION

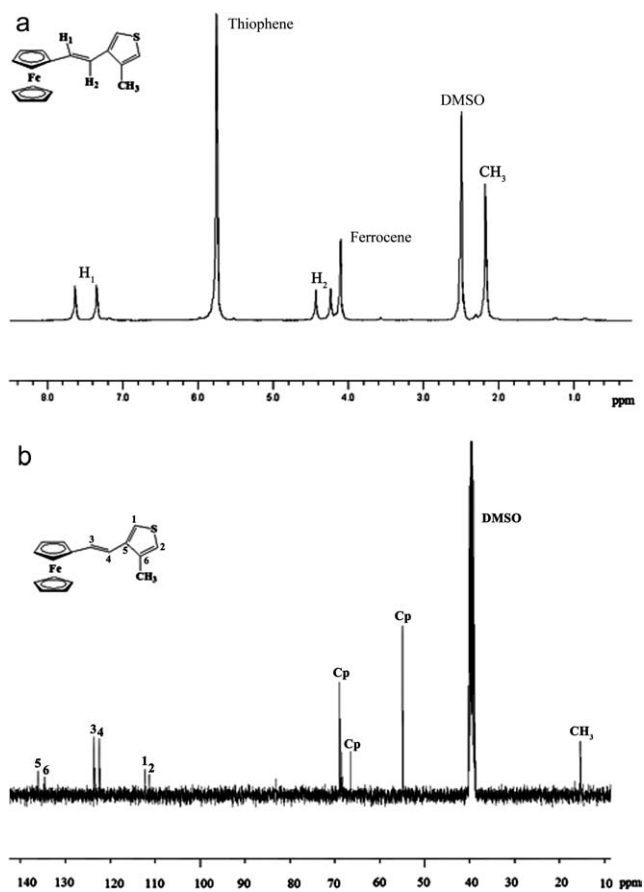
In this study, the synthesis of a new Fc-derivative monomer was achieved. The monomer MTFE and EDOT were polymerized via electrochemical method. The structures of monomer and copolymer were successfully characterized.

### NMR spectra

$^1\text{H-NMR}$  (400 MHz, DMSO): 7.5 (d, 1H,  $J_{1,2} = 16$  Hz,  $\text{H}_1$ ), 5.78 (s, 2H, thiophene), 4.30 (d, 1H,  $J_{1,2} = 16$  Hz,  $\text{H}_2$ ), 4.10 (s, Cp-Fc,  $5 \times 2$ ), 2.20 (s, 3H) [Fig. 3(a)].  $^{13}\text{C-NMR}$  (100 MHz, DMSO) [Fig. 3(b)]: 17.8 ( $\text{CH}_3$ ), 55.7 (Cp), 67.2 (Cp), 69.2 (Cp), 69.7 (Cp), 111.3 ( $\text{C}_1$ ), 113.2 ( $\text{C}_2$ ), 122.6 ( $\text{C}_4$ ), 125.2 ( $\text{C}_3$ ), 135.3 ( $\text{C}_6$ ), 137.8 ( $\text{C}_5$ ) (Cp: cyclopentadiene) [Fig. 3(b)]. These data are in accordance with the results obtained through FTIR study.

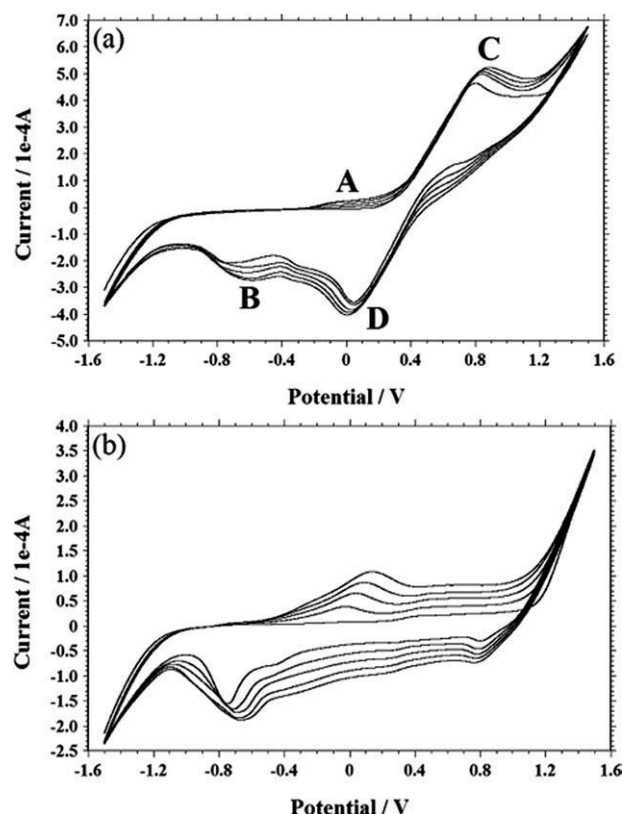
### FTIR spectra

The C—H stretching band of thiophene moiety is signified by the appearance of peak at  $3102\text{ cm}^{-1}$  of the monomer. Moreover, the aromatic C—H out-of-plane band appeared at  $875\text{ cm}^{-1}$ , whereas the



**Figure 3** (a)  $^1\text{H-NMR}$  spectrum of MTFE and (b)  $^{13}\text{C-NMR}$  spectrum of MTFE.





**Figure 4** Cyclic voltammograms of (a) P(MTFE-co-EDOT) and (b) PEDOT in 0.1M DCM/TBAP on an indium tin oxide (ITO)-coated glass plate-working electrode with 100  $\text{mV s}^{-1}$  scan rate.

aromatic C—H in-plane band emerged at  $1077 \text{ cm}^{-1}$  for the monomer. Differences in FTIR spectra between copolymer and monomer reveal the complete disappearance of C—H peaks between  $3102 \text{ cm}^{-1}$  and out-of-plane bending C—H peaks at  $875 \text{ cm}^{-1}$ . Disappearance of these peaks is the evidence of polymerization from 2- and 5-positions of the thiophene moiety of monomer.<sup>5</sup> The presence of a new peak at  $950 \text{ cm}^{-1}$  for copolymer is due to asymmetric C—O—C stretching of etheric units that stems from comonomer EDOT.<sup>5</sup> The peak at  $1141 \text{ cm}^{-1}$  belongs to perchlorate ions. This confirms that there is a doping process by perchlorate ions throughout the polymer chain. These data support the results obtained from  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  studies.

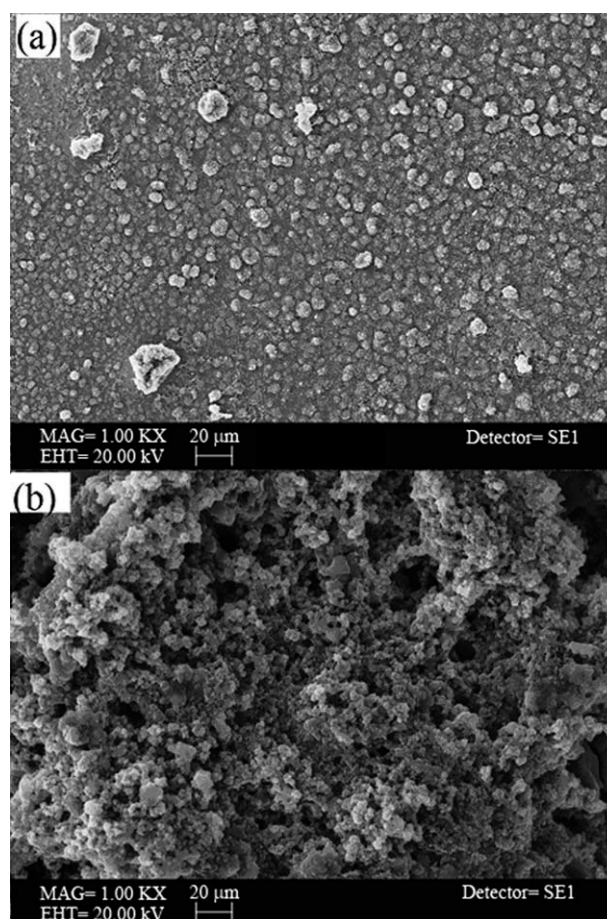
### Cyclic voltammetry

Oxidative electrocopolymerization of monomer in the presence of EDOT was carried out in 0.1M DCM/TBAP on an ITO-coated glass plate-working electrode with 100  $\text{mV s}^{-1}$  scan rate. Voltammograms of copolymer and PEDOT are given in Figure 4. Voltammograms of PEDOT and the copolymer are clearly different from each other. As expected, the CV for P(MTFE-co-EDOT) [Fig. 4(a)] shows two re-

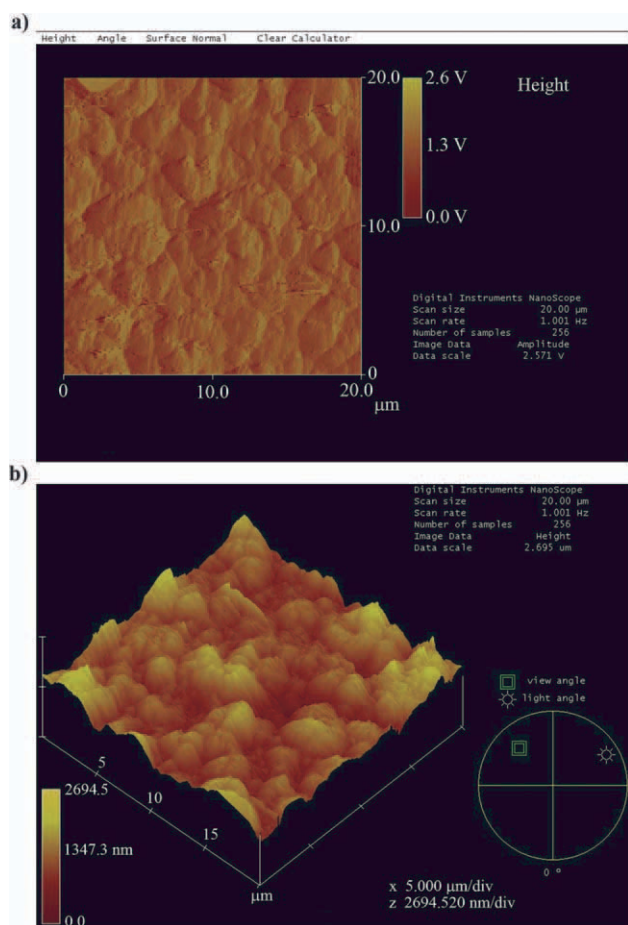
dox couples. When compared with the CV of PEDOT, the redox couple (A/B) is due to the copolymer backbone and the other redox couple (C/D) can be assigned to the Fc moiety. Characteristic oxidation and reduction peaks of Fc were observed at 0.78 and 0.17 V, respectively, versus Ag wire pseudo-reference electrode.<sup>29</sup> During potentiodynamic scan, the anodic peaks of P(MTFE-co-EDOT) appeared at 0.05 and 0.88 V, whereas the cathodic peak emerged at  $-0.60$  and  $0.02$  V. In the case of PEDOT, the anodic peak appeared at 0.14 V, whereas the cathodic peak emerged at  $-0.64$  V. As seen in Figure 4, redox potentials of copolymer are clearly different from PEDOT and Fc. Such results could be interpreted as an additional proof of copolymer formation.

### Surface morphology

To examine the surface morphology of the copolymer coated on the Pt surface, high-resolution SEM and AFM techniques were used. For this purpose, after the synthesis of the copolymer, the electrode was removed from the synthesis medium, washed



**Figure 5** SEM micrographs of (a) P(MTFE-co-EDOT) and (b) PEDOT (magnification,  $\times 1000$ ).



**Figure 6** The three-dimensional AFM images of the P(MTFE-*co*-EDOT) synthesized on the Pt surface in different magnification. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

with distilled water, and then dried. The SEM images of the copolymer and PEDOT are shown in Figure 5. Surface morphology micrographs of P(MTFE-*co*-EDOT) is clearly different than the PEDOT surface morphology. This is the evidence that copolymerization took place.

AFM provides a powerful technique to investigate the surface morphology at nanoscale to microscale and has become a new choice to study the surface structure of the polymer films. The three-dimensional AFM images of the polymer film, which was synthesized on the Pt surface, are shown in Figure 6(a,b) in two different magnifications.

### UV-vis spectroscopy

The UV-vis spectra of the copolymer P(MTFE-*co*-EDOT) film electrodeposited on ITO-coated glass were recorded (Fig. 7). In the oxidized state, the spectrum of P(MTFE-*co*-EDOT) film at 1.5 V reveals absorption bands at 450, 634, and 720 nm. Unfortunately, the copolymer film could not be neutralized

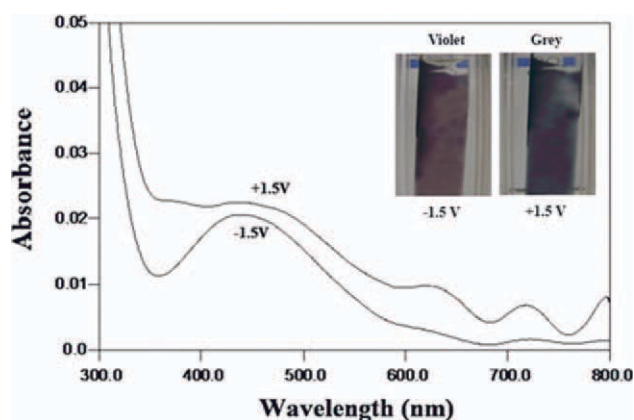
fully as the absorption bands attributed to charged P(MTFE-*co*-EDOT) species were not diminished even at high negative potentials. The optical band gap ( $E_g$ ) of P(MTFE-*co*-EDOT) was calculated as 1.95 eV (Table I). The optical band gap ( $E_g$ ) of copolymer was calculated from its absorption onset.<sup>30</sup>

### Colorimetry

The color of an electrochromic material was defined accurately by performing colorimetry measurements. The Commission Internationale de l'Éclairage system was used as the quantitative scale to define and compare colors. Measurements were performed in the same electrolyte using a Minolta CS-100 spectrophotometer. Three features of color, hue (*a*), saturation (*b*), and luminance (*L*), were measured and are recorded in Table I.





### Electrical conductivity of P(MTFE-*co*-EDOT)

Conductivity is related to both intermolecular and intramolecular charge transfers on the polymer backbone. Therefore, these results have shown that the dopant interacts with the double bond in the polymer backbone and forms a polaronic state (radical cation) as an electron was transferred from the double bond to the positive carrier at the double bond site. These holes or positive carriers are responsible for the electrical conduction in these materials.<sup>31</sup> Electrical conductivities of the P(MTFE-*co*-EDOT) and PEDOT materials were measured at room temperature by the four-probe technique. The samples were prepared by electrolysis with the sufficient thick films (ca. 50 μm) on ITO electrode. The conductivity of P(MTFE-*co*-EDOT) was found to be 0.26 S cm<sup>-1</sup>. This is much lower than the conductivity



**Figure 7** UV-vis spectra of the copolymer of MTFE with PEDOT grown galvanostatically on an ITO-coated glass plate-working electrode: (a) as grown in its oxidized state and (b) copolymer was reduced at -1.5 V. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

TABLE I  
Electrochemical and Optical Data for P(MTFE-co-EDOT) and PEDOT

Polymer	$E_{ox,1/2}$ (V) <sup>a</sup>	$\lambda$ (nm)	$E_g$ (eV)	$\sigma$ (S/cm)	Neutral state		Oxidized state	
P(MTFE-co-EDOT)	0.05	634	1.95	0.26		<i>L</i> 21 <i>a</i> 16 <i>b</i> -6		<i>L</i> 16 <i>a</i> -2 <i>b</i> -6
PEDOT	0.14	600	1.60	19		<i>L</i> 37 <i>a</i> 10 <i>b</i> -24		<i>L</i> 51 <i>a</i> -1 <i>b</i> -2

of PEDOT ( $19 \text{ S cm}^{-1}$ ) grown under similar conditions. The conductivity of copolymer is much lower than PEDOT because of electronic effect of Fc group and/or a combination of steric and electronic effects.<sup>24</sup>

#### Scan rate dependence of the peak currents

P(MTFE-co-EDOT) film was prepared via constant potential electrolysis. Its redox switching in monomer-free electrolyte revealed a single, well-defined redox process (Fig. 8). The current responses were directly proportional to the scan rate indicating that the copolymer film was electroactive and well adhered to the electrode.<sup>4,5,32</sup> The scan rates for the anodic and cathodic peak currents show a linear dependence as a function of the scan rate as illustrated in Figure 8(b).

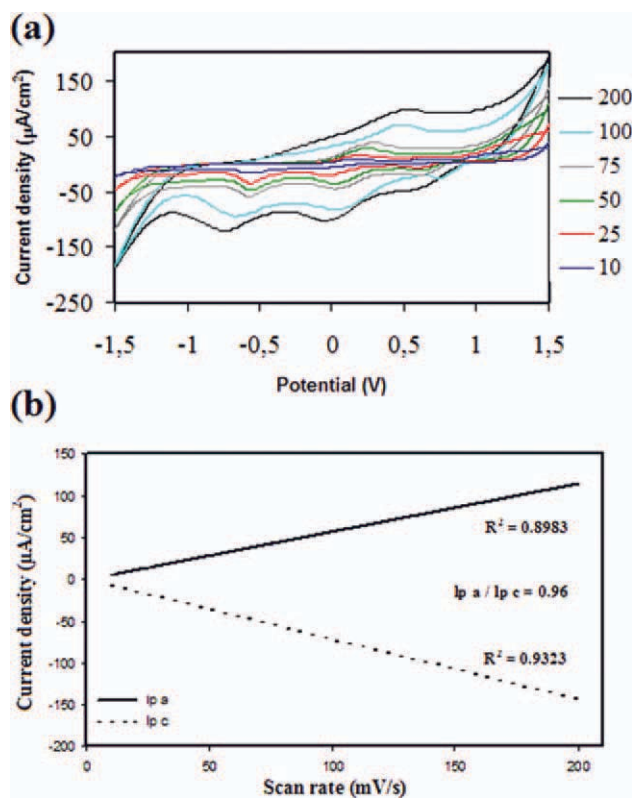


Figure 8 (a) Cyclic voltammogram of P(MTFE-co-EDOT) in monomer-free electrolyte at different scan rates and (b) anodic and cathodic peak currents as a function of the scan rate. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

#### CONCLUSIONS

A new Fc-derivative MTFE was successfully synthesized. The structure of the monomer was determined by NMR and FTIR techniques. Electrochemical polymerization of monomer and EDOT was achieved. The structure of P(MTFE-co-EDOT) was characterized using CV, FTIR, SEM, AFM, and UV-vis spectroscopy. The conductivity of copolymer and PEDOT was determined via four-probe technique. The results of CV, FTIR, AFM, and UV-vis spectroscopy studies showed that the formation of true copolymer was achieved. The conductivity and the band gap of P(MTFE-co-EDOT) were found to be  $0.26 \text{ S cm}^{-1}$  and  $1.95 \text{ eV}$ , respectively. The scan rate dependence of the peak current measurements revealed that the current responses were directly proportional to the scan rate. This indicates that the electrochemical processes at the electrode was not diffusion limited and were reversible even at very high scan rates. The copolymer is electroactive and well adhered to the electrode.



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