# Electrochemistry, Spectroscopy and Spectroelectrochemical Contrasting Properties of PEDOT and PEDTT Compounds

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**Abstract:** The conjugated copolymers 3,4-ethylenedioxythiophene (EDOT) and 3,4-ethylenedithiothiophene (EDTT) units have been investigated by cyclic voltammetry, electronic absorption spectroscopy and spectroelectrochemistry. The electrochemical properties of the monomer have given higher oxidation potential compared to their polymer. The optical and the electrochemical band gap of the PEDOT have shown a big difference compared to the PEDTT state. These polymers can be use as an electrochromic material.

Keywords: PEDOT, PEDTT, electro-polymerisation, low band-gap polymers, spectroelectrochemistry.

### 1. Introduction

Polythiophene derivatives have become attractive materials for use in device applications, because they possessed tunable band gaps, good redox stable properties and high conductivity in doped state.<sup>1,2</sup> 3,4-Ethylenedioxythiophene (EDOT) and 3,4-ethylenedithiothiophene (EDTT) are excellent examples for such a monomer design, where the fused 1,4-dioxane (dithiane) cycle decreases the steric effect and increases the donor ability.<sup>3,2</sup> The electropolymerisation of EDOT and EDTT compounds produces poly3,4ethylenedioxythiophene (PEDOT) and poly3,4ethylenedithiothiophene (PEDTT), (Figure 1) which have shown high conductivity and good stability.<sup>1, 3</sup>



Figure 1. The structures of **PEDOT** and **PEDTT** 

PEDOT is one of the best known conducting polymers due to its exceptional electronic and electrochemical properties such as high electronic conductivity and outstanding environmental stability in the oxidised (p-doped) state.<sup>2</sup> Furthermore, PEDOT exhibits a stark colour change between the neutral and doped states; it is dark blue in the neutral state and light blue (and highly transparent) when oxidised.<sup>1, 4</sup> Conjugated materials such as blue PEDOT, red poly(3-hexylthiophene) (P3HT) and green poly (aniline-N-butylsulfonate) (PANBS) absorb the three primary colours red, green and blue (RGB) for use in electrochromic devices.<sup>5</sup>

PEDOT is used in many fields such as Organic light emitting diodes, Organic field effect transistor, photovoltaic cells, batteries, display devices, smart windows and biosensors, particularly since it is also a good hole-injection material in some of these devices.<sup>1-4</sup> PEDOT is considered highly suitable for electrochromic applications due to its easy processability and high degree of electrochromic contrast in the visible region of the spectrum.<sup>6</sup> Excellent electrochromic behaviour has been observed in poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) due to its high conductivity, high stability and high contrast at low potential.<sup>7</sup> Several types of conducting polymers including polypyrrole, polyselenophene and their derivatives exhibit electrochromic behaviour and stability of their optical and electrical properties in both oxidised and neutral states. Such polymers have been used in many applications such as smart windows, electrochromic sunglasses and displays.<sup>8</sup>

## 2. Experimental

purchased 3,4-Ethylenedioxythiophene (EDOT) was commercially, and 3,4-ethylenedithiothiophene (EDTT) was prepared according to the literature procedures<sup>9</sup>. Cyclic voltammetry (CV) measurements and electropolymerisations were performed on a CH Instruments 660A electrochemical workstation with iR compensation using anhydrous dichloromethane or acetonitrile (MeCN) as the solvent. The electrodes were glassy carbon or ITO glass slide, platinum wire or gauze and silver wire as the working, counter and reference electrodes, respectively. All solutions through the reduction process were degassed (Ar) and contained monomer substrates in concentrations of ca. 10<sup>-4</sup> M, together with  $n-Bu_4NPF_6$  (0.1 M) as the supporting electrolyte. All measurements are referenced against the  $E_{1/2}$  of the Fc/Fc<sup>+</sup> redox couple. All electronic absorption spectra were recorded at room temperature on a UNICAM UV 300 spectrophotometer operating between 190 to 1100 nm and between 300 and 1100 nm for the monomer and polymer respectively. For solution spectra, a 1 cm<sup>3</sup> path length quartz cell was used and the baselines were measured before analysis by using the grown film on ITO slide.

#### 3. Result and Discussion

This paper describes the electrochemical and optical processes of EDOT and EDTT in monomer and polymer cases and studding the comparison their redox and optical properties of EDTT and EDOT. Both molecules were studied by cyclic voltammetry in dichloromethane solution.

#### **Electrochemistry of Monomers and Polymers**

The thiophene derivatives display two irreversible oxidation peaks at +1.12 and +1.49V for EDOT and at +0.99 and +1.59V for EDTT. The cyclic voltammograms of these compounds are shown in Figure 2.



**Figure 3:** Monomer Reduction of EDOT (left) and EDTT (right) of EDTT on a glassy carbon and gold respectively as working electrodes, Ag wire reference electrode and Pt counter electrode, substrate concentration 10<sup>-4</sup> M, tetrabutylammonium hexafluorophosphate as supporting electrolyte (0.1 M) and a scan rate of 0.1V s<sup>-1</sup>. The data is referenced to the Fc/Fc+ redox couple

The electrochemical HOMO-LUMO gap of the two monomers was determined from the difference in the onset of the first oxidation and reduction peaks (Figures 3). HOMO and LUMO levels are calculated by subtracting the onsets from the HOMO of ferrocene. All data are summarised in Table 1. By comparing the energy levels, the difference between the HOMO and LUMO values gave electrochemical HOMO-LUMO gaps for the monomers that are big different values. The monomer of EDTT has a higher oxidation potential than EDOT, but possesses a lower HOMO-LUMO gap.

 
 Table 1: Electrochemical Data for Energy levels of monomers EDOT and EDTT

Monomer	HOMO / eV	LUMO / eV	$E_g / eV$		
EDOT	-5.35	-2.83	2.52		
EDTT	-5.75	-3.66	2.09		

HOMO and LUMO values are calculated from the onset of the first peak of the corresponding redox wave and referenced to ferrocene, which has a HOMO of -4.8 eV.  $E_g$  is the HOMO-LUMO energy gap.

Figure 2: Cyclic voltammograms of EDOT and EDTT in

dichloromethane solution, using a glassy carbon and gold working electrodes, Ag/AgCl reference electrode, platinum

counter electrode, substrate concentration 10<sup>-4</sup> M,

tetrabutylammonium hexafluorophosphate as supporting electrolyte (0.1 M) and a scan rate of 0.1V s<sup>-1</sup>. The data is

Both **EDOT** and **EDTT** monomers were electropolymerised by repetitive cycling (300 segments) over the redox active peaks employing the same conditions and the same solvent, which were used for cyclic voltammetry. Growth of the polymers can be monitored through both the increase in current with each cycle and the development of a new peak at a lower potential than the monomer's oxidation wave. Good thin films of **PEDOT** and **PEDTT** were obtained on the working electrode surface. The growth traces for the poly **EDOT** and poly **EDTT** are presented in Figure 4. International Journal of Science and Research (IJSR) ISSN (Online): 2319-7064 Index Copernicus Value (2013): 6.14 | Impact Factor (2013): 4.438



**Figure 4:** Electrochemical growth of (a) PEDOT and (b) PEDTT, using glassy carbon and gold respectively as working electrodes Ag wire reference electrode and Pt counter electrode in monomer-free  $CH_2Cl_2$  (0.1 M TBAPF6 as supporting electrolyte). The data is referenced to the Fc/Fc+ redox couple, at a scan rate of  $100mVs^{-1}$ , over 300 segments.

Conversely, in the polymer case, PEDTT has shown a higher oxidation potential and wider band gap than PEDOT owing to an increase in the number of sulfur atoms in the PEDTT chain, which greatly affects the inter-ring conjugation.<sup>10,11</sup> This is a result of the extensive chalcogen---chalcogen steric interactions between the sulfur atoms (S…S interactions) leading to a twisted geometry, whilst the chalcogen---chalcogen interactions (O…S interactions) in PEDOT lead to a highly planar polymer, with a low band gap and oxidation potential. Therefore, the O…S contact provided the degree of rigidification and consequently increased effective conjugated length along the polymer chain.<sup>1, 3</sup> In addition, the stronger electron-withdrawing effect from the oxygen atoms in PEDOT will decrease the reduction potential.<sup>1</sup> The cyclic voltammetry of two polymers as films

on ITO glass as working electrode was investigated with silver and platinum wires as reference and counter electrodes respectively in a monomer-free acetonitrile solution. With the same concentration of supporting electrolyte as earlier; the cyclic voltammograms of both compounds are illustrated in Figure 4 and 5. The oxidation process (Figure 4) of both polymers features broad reversible peaks at +0.19 / +0.14 V for PEDOT and quasi reversible peak at +1.28 V for PEDTT. This indicates the oxidation of EDOT and EDTT units respectively in both polymers. The reduction process of deposited **PEDOT and PEDTT** films is shown in Figure 5, where the **PEDOT and PEDTT** exhibit once again an irreversible peak at -2.31 V for PEDOT and at -2.20V for PEDTT, which are almost the same value compared to their monomer case.



Figure 4: Cyclic voltammograms for polymer oxidation of PEDOT (left) and PEDTT (right) in monomer- free MeCN solution.



Figure 5: Cyclic voltammograms for polymer reduction of PEDOT (left) and PEDTT (right) in monomer- free MeCN solution.

The band gap of **PEDOT** and **PEDTT** was calculated by determining the onsets of both the oxidation and reduction for each to give the HOMO and LUMO energy levels, respectively, when subtracted from the known HOMO of ferrocene (-4.8 eV). All data are summarised in Table 2 and Figure 6. Significant difference between the band gaps of both polymers after electrode position was observed. However the small band gap of PEDOT compared to

PEDTT could be due to its increase of the conjugation chain in PEDOT.

Polymer	$E_{1ox}(V)$	HOMO	$E_{1red}(V)$	LUMO	HOMO-LUMO
		(eV)		(eV)	gap (eV)
PEDOT	+40	-4.0	-1.89	-2.70	1.30
PEDTT	+1.18	-4.90	-2.34	-2.75	2.15

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HOMO and LUMO values are calculated from the onset of the corresponding redox wave and referenced to ferrocene, which has a HOMO of 24.8 eV.

Current / IuA

**Figure 6:** Cyclic voltammograms of **PEDOT** and **PEDTT** as films on ITO glass slide. In monomer-free acetonitrile solution at scan rate of 0.1V s<sup>-1.1</sup>



Figure 7: Oxidative stability test of PEDOT (left) and PEDTT (right) in monomer free dichloromethane, at a scan rate of 100mVs<sup>-1</sup>, over 100 segments.

To determine if the electrochemical behaviour and the stability of both polymers were limited by diffusion, the oxidative stability was determined at increasing scan rate values (0.025, 0.050, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5 Vs<sup>-1</sup>) over the first oxidation peaks as depicted in Figure 8.



Figure 8: Cyclic voltammograms of PEDOT (left) and PEDTT (right) at varying scan rates in monomer free CH<sub>2</sub>Cl<sub>2</sub>

A linear relationship between scan rate and current peak maxima was observed for all three polymers (Figure 9), with correlation factor values of 0.9997 and 0.9492 for PEDOT

and PEDTT, respectively. This behaviour proves that the charge transport process is not diffusion limited.



Figure 9: Scan rate vs. peak current maxima of PEDOT (left) and PEDTT (right)

## UV-vis Electronic Absorption Spectra of PEDOT and PEDTT

The two polymers were prepared from a monomer solution with acetonitrile as solvent. During this experiment, the polymers were grown by repetitive cycling and then dedoped between -0.7 and -0.5 V for PEDOT and between -0.4 to -0.2 V for PEDTT. The absorption maxima are revealed at 579 nm for **PEDOT** and at 445 nm for **PEDTT**, which are in good agreement with the absorption maximum values reported in the literature (578 and 441 nm for **PEDOT** and **PEDTT** respectively)<sup>1</sup>. The absorption peak (445 nm) in PEDTT shows **a** hypsochromic shift compared to PEDOT, owing to the effect of steric hindrance from (S···S contact) of the neighbouring unit in PEDTT.

Therefore, this effect will decrease the degree of planarity throughout this polymer, whereas, distortion effect from  $(S \cdots S \text{ contact})$  disappeared in PEDOT,<sup>1</sup> which is exhibited broad absorption at 579 nm. The onsets of the longest wavelength absorption edge of three polymers exhibited optical band gaps of 1.68 eV for PEDOT and 2.22 eV for PEDTT. However there is a significant difference between these optical band gaps. All the electronic absorption spectra in acetonitrile solution for three polymeric species are shown in Figure 10.





Spectroelectrochemical properties of the polymers

UV-vis spectroelectrochemical measurements were performed on films grown on ITO glass and then de-doped. UV-vis spectroelectrochemistry was carried out for the polymers under oxidative conditions; the spectroelectrochemical plots for the oxidation of PEDOT PEDTT Figure and are shown in 11. Spectroelectrochemistry Oxidation of the PEDOT leads to a decrease in intensity of the  $\pi$ - $\pi$ \* transition at 500 nm and the simultaneous generation of a new band at longer wavelengths, this behaviour is attributed to the creation of polarons and bipolaron in the conjugated chain at 850-870 nm. The polaronic signature is difficult to pick out for PEDTT material, but is clearly observed in the spectra of PEDOT material. After +1.7 and +2 V there is a drop in absorbance in the two polymers that corresponds to the breakdown of the polymer into the solution.



Figure 11: Absorption spectroelectrochemical plots of oxidation of PEDOT (left) and PEDTT (right) Potentials are given vs. Ag wire reference electrode

## 4. Conclusions

The monomers and their subsequent polymers have been characterised by cyclic voltammetry, UV-vis absorption spectroscopy and UV-vis spectroelectrochemistry. The two monomers contain EDOT and EDTT units. All two monomers show differences in oxidation and reduction potentials. The HOMO-LUMO gap calculations show dissimilar values between the EDOT and EDTT, where the monomer of EDTT has given lower HOMO-LUMO gap and higher oxidation potential compared to the monomer of EDOT. The monomers were polymerised under oxidative conditions. After electro-polymerisation, PEDTT acquires a higher oxidation potential and larger band gap than PEDOT. This is due to, the effect of the intrachain (S $\cdots$ S contact) on the polymer backbone conjugation length; give a twisted geometry, steric hindrance and disruption along the conjugated length. In PEDOT chalcogen---chalcogen interactions (O····S interactions) provide a degree of rigidification and the conformation is planar and therefore the effective conjugated length is increased. PEDOT and PEDTT exhibited high stability toward repetitive oxidation cycles. The polymers showed potential for use as electrochromic films. PEDOT is very well known for its transparency in the doped state, and it is this feature which makes the polymer an ideal candidate as an electrochromic material. In contrast, PEDTT retains absorption

characteristics in the visible region; the peak at 441 nm is run down, but remains un-shifted throughout the oxidation process.

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