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Study of Electrochemical and Electronic Effects of phenanthroline units into poly3,4-ethylenediselenathiophene (PEDST) chains

Saadeldin Elamin Taher[1*], Mohamed A. Elhag Ahmed[2,] Moftah A. Moustafa[1] and Nada Elzawi

[1]Tobruk University- Faculty of Sciences, Department of Chemistry Tubruk- Libya.

[2] Benghazi University- Faculty of Sciences, Chemistry Department Benghazi- Libya

Abstract: The representative of a new heterocyclic organic compound is reported. This compound, which is related to the 3-(2,3-dihydro-[1,4]diselenino[2,3-c]thiophen-5-yl)-8-(2,3-dihydro-[1,4]diselenino[2,3-c]thiophen-7-yl)-1,10-phenanthroline dmit2 (2-thioxo-1,3-dithiol-4,5-dithiolato) structure, has been prepared chemically and distinguished by using cyclic voltammetry experiments with iR compensation and electronic absorption spectra. This compound has polymerized successfully on the working electrode surface yielding polymer with reasonable band gap and practical stable to the anodic conditions, the scan rate test proves that the polymer is not diffusion limited.

Keywords: organic conjugated molecules, electropolymerisation, phenanthroline center core, electrochemival and electronic properties

1. INTRODUCTION

The organic conjugated materials are important class of semiconductor, which are used in numerous applications such as field effect transistors, electrochromics, photovoltaics, organic light emitting diodes, lasers, sensors and displays, by allowing flow of electrons through their π-orbital overlap in the polymer chain. Unique attention in the conjugated material poly (3,4-dioxyethylene)thiophene, PEDOT, as a material in organic semiconductor electronic devices has encouraged the study of many variants [1]. For instance, the EDOT unit has been used as a component in many molecular-based materials and copolymers. The structure of EDOT has also been manipulated to provide soluble analogues of PEDOT [1-8].Organic conjugated materials are able to display semiconducting manners as they have delocalized π-electrons occurrence from all the conjugated double bonds and this lets them to reveal electro activity along the main chain of the material. In the electropolymerisation the polythiophene will undergo deformation in the chain because of these bulky substituents and this in turn causes disruption of the conjugation chain and the decreasing of the conductivity [9, 10].

This trouble can be enhanced in two ways: cyclisation of the side groups can lower the steric hindrance, such as in 3,4-ethylenedioxythiophene (EDOT) and 3,4-ethylenedithiothiophene (EDTT) or growing the polymer through a terthiophene group where the sulfur groups will only be in the central thiophene. Cyclisation not only decreases the steric hindrance effect but also progress the donor ability and therefore inferiors the oxidation potential [11-13]. The poly (3,4-ethylenediselena) thiophene (PEDST) has been exposed high planarity degree in its conformation and upper stability compared to the poly 3,4-ethylenedithiothiophene (PEDTT).

PEDST shows strong interchain interaction between Se atoms which will a good factor be for describes the energy gap of its polymers [14]. The electronic and electrochemical band gap values reveal no significant difference between them, which are 1.79 and 1.55 eV respectively, where the electronic and electrochemical band gap values of the PDTT are 2.15 and 2.19 eV respectively, therefore the disagreement in energy gap between PEDST and PEDTT is possible to be ascribed to the weaker interchain interactions and higher distortion angles in PEDTT compared to PEDST structure The PEDST has been shown electrochemical and optical energy gap values closer to the poly3,4-ethylenedioxythiophene (EDOT), which are 1.35 and 1.63 eV respectively [13-15].

2. EXPERIMENTAL PROCEDURES

Cyclic voltammetry measurements were achieved by using bio analytical system voltametric analyzer CV-50W with iR compensation using dichloromethane as the monomer and monomer free solutions. The electrochemical cells consisted of three electrodes: a platinum working electrode, a platinum wire counter electrode and a silver wire as the reference electrode. All cyclic voltammetry experiments were referenced to the Fc/Fc$^+$ redox couple as an internal standard. All solutions were degassed (Ar) during a reduction experiment and contained monomer substrates at a concentration of ca. 10^{-4} M, together with n-Bu4NPF6 as the supporting electrolyte (0.1 M). Electronic absorption spectra were recorded at room temperature on a JENWAY 7310 UV/vis spectrophotometer.

3. RESULTS AND DISCUSSION

This paper discusses compound contains a heterocyclic organic compound (phenanthroline) as the core unit that has been attached to two EDST as e terminal units. The chemical structure of this compound is illustrated in Figure1.

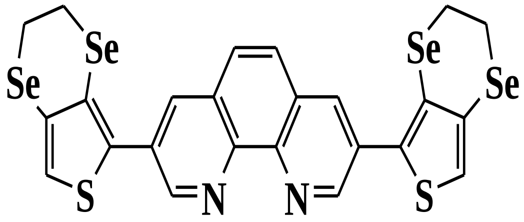

Figure **1.** Structures of 3-(2,3-dihydro-[1,4]diselenino[2,3-c]thiophen-5-yl)-8-(2,3-dihydro-[1,4]diselenino[2,3-c]thiophen-7-yl)-1,10-phenanthroline dmit2 (2-thioxo-1,3-dithiol-4,5-dithiolato) compound

3.1 Absorption Spectroscopy and Electrochemistry of Monomer

Absorption spectrum of monomer was performed in dichloromethane solution. The absorption spectra of monomer show peaks at 355 nm, being the π-π* transition from the conjugated portion of the compound. The electronic absorption spectrum of this compound in dichloromethane solution is shown in Figure 2.

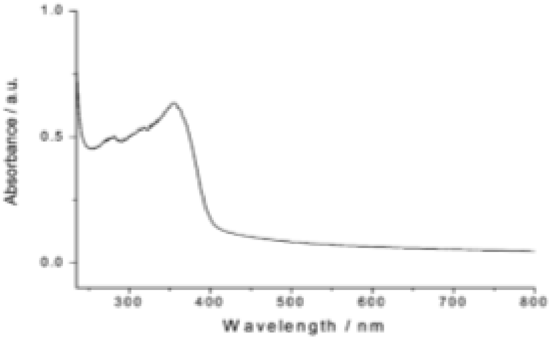

Figure 2. UV/vis spectroscopy of the monomer measured in dichloromethane solution.

Optical HOMO-LUMO gap of this compound was calculated from the onsets of the longest wavelength absorption peaks. The data for all the absorption maxima and the optical band gap value is summarized in Table 1.

Table 1. Absorption spectroscopy data of the monomer

UV-vis peaks (nm)	Optical E_g / eV
355	3.08

The cyclic voltammogram experiment of the monomer was performed in dichloromethane solution. The monomer oxidation gives one irreversible wave at +0.88 V, which is likely to be from the removal of two electrons from the EDST units.The monomer reveals irreversible reduction peaks at -1.78 V, which is likely to be from reduction of the central core unit. All monomer oxidation and reduction processes are depicted in Figure 3.

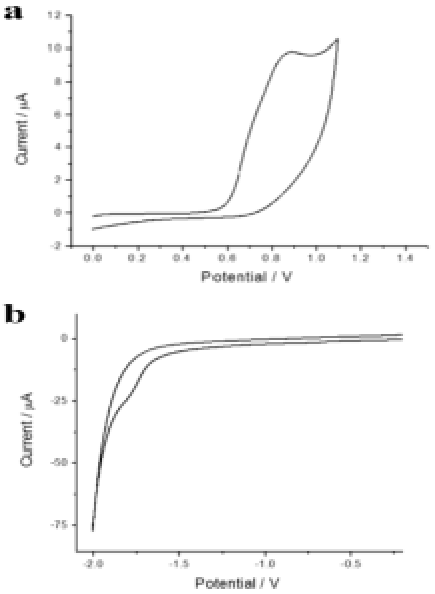

Figure 3. (a) Cyclic voltammograms of oxidation of monomer and reduction monomer and (b) in dichloromethane as solvent on a glassy carbon-working electrode.

The electrochemical HOMO-LUMO gap of the monomer 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 summarized in Table 2.

Table 2. Electrochemical Data for Energy levels of the monomer

Onset of oxidation /V	Onset of reduction /V	HOMO / eV	LUMO / eV	E_g / eV
+0.5	-1.88	-5.3	-2.92	2.38

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. By comparing the energy levels, the difference between the HOMO and LUMO values gave electrochemical HOMO-LUMO gaps for the monomer that is a different from the optical values possibly from the extended conjugation effect of the terminal units**.**

3.2 Electro-polymerization Properties

The monomer was subjected to electro polymerisation by repetitive cycling (300 segments) over the first oxidation wave. The polymer of monomer was grown using a high concentration solution (10^{-2} M). The growth trace of the corresponding polymer has shown in Figure 4.

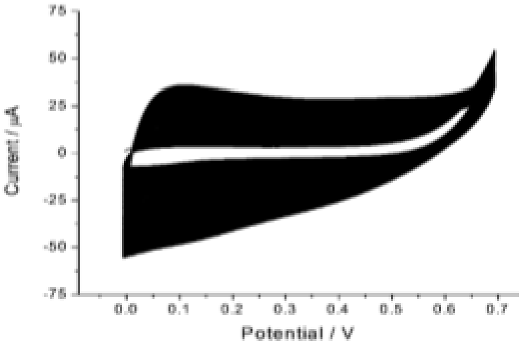

Figure 4. Electrochemical growth of the polymer in dichloromethane solution, using a glassy carbon working electrode, Ag wire reference electrode and Pt counter electrode, concentration of ca. 10^{-2} M, (0.1 M TBAPF$_6$ as supporting electrolyte). The data is referenced to the Fc/Fc+ redox couple, at a scan rate of 100mVs^{-1}, over 300 segments.

The oxidation and reduction analysis of the polymer have illustrated in Figure 5. The polymer revealed an irreversible peak at +0.6 V and reversible peak at ($E^{½}$ = 0.825V), the peak is likely due to the formation of a radical cation on the terminal units. The polymer reduction showed two irreversible peaks at -1.38 and -1.93 V, This peaks is likely to be the same peaks seen in the monomer.

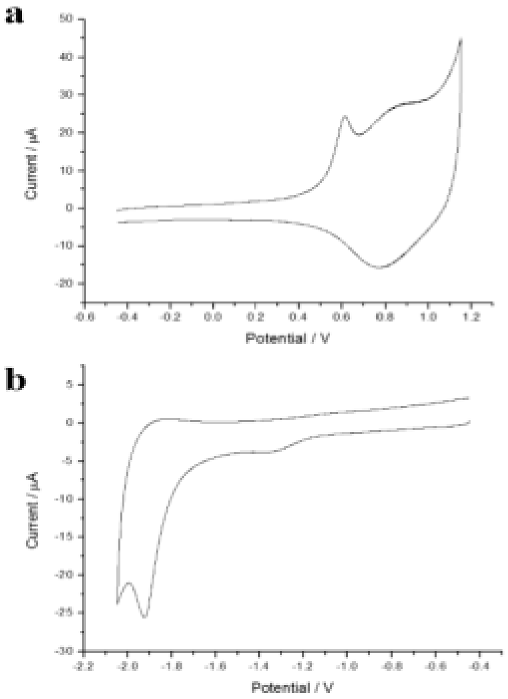

Figure 5. (a) Cyclic voltammograms of the polymer oxidation and the polymer reduction and (b) in CH_2Cl_2 as solvent as a thin film on a glassy carbon working electrode.

By the same procedure as before for energy level determination, the electrochemical band gap of the polymer was calculated from the difference in the onset of the first oxidation and reduction (Table**3**)

Table 3. Electrochemical Data for Energy levels of the polymer

Mon	Onset of oxidation /V	Onset of reduction /V	HOMO / eV	LUMO / eV	E_g / eV
-	+0.0.459	-1.609	-5.259	-3.191	2.1

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. Thus, the difference between the HOMO and LUMO values gave electrochemical band gap value of 2.1 eV. This value is lower than the calculated electrochemical HOMO-LUMO gap of their monomer, due to the extra conjugation length provided by the EDST and thiophene units.

3.3 Oxidation Stability and Scan Rate Properties of the Polymer

The stability of the polymer (Figure 6) to adhere to the glassy carbon electrode was evaluated by cycling over the redox-active peak for 100 segments, and measuring the percentage decrease in the current response. The polymer degrades amongst the number of cycles.

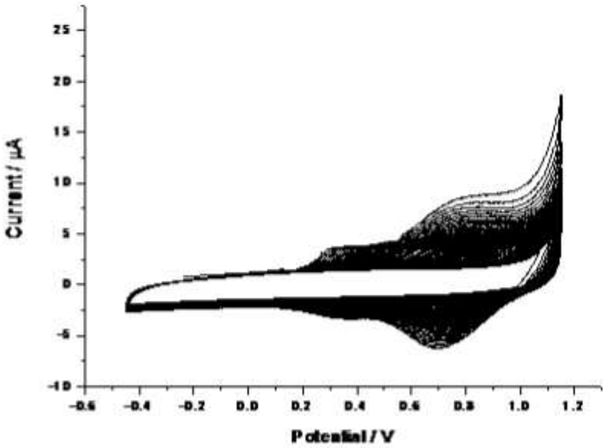

Figure 6. Oxidative stability test of the polymer in monomer-free CH_2Cl_2, at a scan rate 0.1 V^{-1}, over 100 segments, using glassy carbon working electrode

The linear regression shows that the process is not diffusion limited. When running the scan rate experiment (Figure 7a), it was noticed that the potential at where the peak max occurs shifts to a higher potential after each run. A graph was made of scan rate against peak max (voltage) to show this effect (Figure 7b).

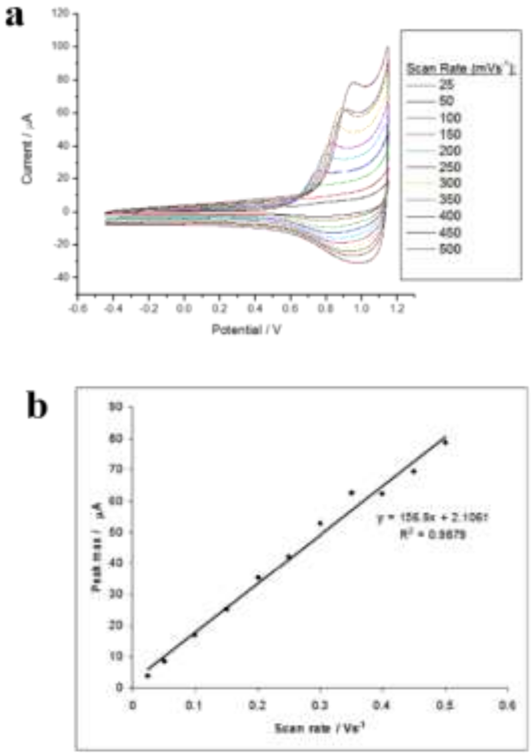

Figure 7. (a)Scan rate experiments of the polymer in monomer free dichloromethane at varying scan rates (left) and (b) scan rate vs. peak current maxima of the polymer(right).

4. CONCLUSION

The work aimed to analyse compounds using two techniques: cyclic voltammetry and UV-Vis spectroscopy and to calculate and determine properties such as the oxidation and reduction potentials of the monomers and polymers, band gap, diffusion limitation and changes in absorption spectra through p- and n-doping. The electro polymerisation of new monomer has been reported, where the polymer has been characterized by a variety of techniques. The electrochemical band gap of the polymer has lower values than that of its monomer, due to the extension of the conjugated chain length in the polymer. The polymer formed is not very stable over many cycles. A plot of scan rate versus peak current provides a straight-line graph with a high R^2 value in the polymer, indicating that the polymer is not diffusion-limited. The polymer formed is not very stable over many cycles.

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