

Novel Thiophene Derivatives as Alternatives to Highly Electrochemical Conductivity Materials

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المخلص:

يتم التركيز في هذه الورقة العلمية على اشباه الموصلات العضوية التي بإمكانها أن تزيح اشباه الموصلات الغير عضوية في العديد من التطبيقات مثل الخلايا الشمسية و الصمامات الثنائية الباعثة للضوء و الترانزسترات و ذلك لان هذا النوع من المركبات العضوية يمتلك مرونة و استقرار عالي و كفاءة لونية عالية و طاقة فجوة صغيرة و تكلفة اقتصادية اقل مقارنة بنظيرتها الغير عضوية. المركب المستخدم في هذه الورقة هو احد المركبات المشتقة من الثيوفين أظهر خصائص الكترونية و ضوئية جيدة من خلال اختبارة بالطريقة الكهربية و الطريقة الضوئية (الاشعة فوق البنفسجية و الضوئية) حيث اعطى مركبا (البولمر) له سلسلة مترابطة طويلة و قمة امتصاص عند طول موجى عالي و طاقة فجوة صغيرة مقارنة بحالته في حال المونومير (قبل عملية البلمرة) و هذا يقلل من درجة الالتواء في المركب و يقلل المسافة بين باند التكافؤ و باند التوصيل (طاقة فجوة) مما يعطى إمكانية استخدام هذا النوع من المركبات في التطبيقات السابق ذكرها أعلاه.

ABSTRACT:

The research in this Paper is focused on creating organic materials that can match the inorganic semiconductors in terms of performance and stability. A new thiophene derivatives -2-(2,3-dihydro-7-(2,3-dihydro-[1,4]diselenino[2,3-c]thiophen-7-yl)-[1,4]diselenino[2,3-c] thiophene-5-carboxamido)-4-methylpentanoic acid have been characterized by absorption spectroscopy and cyclic voltammetry. The processes were made with H₂O and sodium phosphate (Na₃PO₄) as supporting electrolyte, at scan rate of 0.1 Vs⁻¹ on a glassy carbon working electrode Ag wire reference electrode and

Pt counter electrode. The absorption maximum for the monomer was appeared two peaks at 265 and 345 nm, which corresponds to a π - π^* transition from the conjugated material, the monomer was grown successfully on the electrode surface throughout repetitive cycling and shown polymer has (λ_{\max}) peak at 690nm indicative the extension of conjugated chain length in the polymer than the monomer.

Key-words: Thiophene derivatives, conjugated materials, electronic and electrochemical properties.

INTRODUCTION

An incorporation of extra oxidation and reduction active components into conjugated materials is an attractive purpose for several reasons. The treatment of the parent polymer's energy gap is one key advantage for device applications.¹ Polythiophene and its derivatives have been studied widely for their use in several applications, such as electroluminescence,^{2, 3} photovoltaics,^{4, 5} field effect transistors⁶, electrochromics^{7,8,9} and sensors^{10,11,12}. The electronic properties of thiophene derivatives depend on the effective conjugation length along the polymer chains. Organic conjugated compounds are able to exhibit semiconducting behavior as they have delocalised π -electrons take place at all the conjugated double bonds and this allows them to exhibit electro activity in the main chain of the polymer.^{13,14} Polyethylene-3,4-dioxythiophene (PEDOT) and poly3,4-ethylenedithiophene (PEDTT) are considered one of the most famous polythiophene derivatives used for device applications, owing to its outstanding hole injection properties, high oxidation stability and conductivity^{15,16}. PEDOT has exposed lower oxidation potential and tiny energy gap than PEDTT because of an increase in the number of sulfur atoms in the polymer chain of PEDTT, which can

be caused a distortion interrupting conjugation^{17,18}. An increase the degree of planarity and higher oxidation stability have been shown in Poly (3,4-ethylenediselena thiophene (PEDST) comparing to PEDTT owing to Stronger inter chain contacts between Se atoms. The electrochemical and optical properties of PEDST have revealed an agreement with PEDOT.¹⁹ The syntheses of the polythiophene can be achieved by electropolymerisation to produce polyaromatic conjugated materials. The material can be grown anodically through the oxidation of the monomer. The advantages of electropolymerisation include growth without a catalyst and the ability to control the film thickness. The formation of a polythiophene chain is achieved through the combination of thiophene cation radicals.^{13,20} This paper talk about compound contains bis EDST units attached with carboxamido)-4-methylpentanoic acid. The chemical structure of this compound is illustrated in Figure 1.

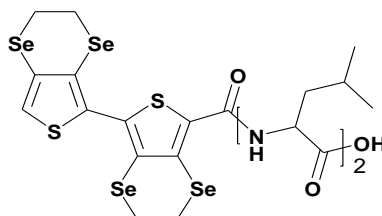


Figure1. Chemical structure of 2-(2,3-dihydro-7-(2,3-dihydro-[1,4]diselenino[2,3-c] thiophen-7-yl)-[1,4]diselenino[2,3-c]thiophene-5-carboxamido)-4-methylpentanoic acid

EXPERIMENTAL

1- Materials:

Ethylenediselena thiophene (EDST) was used as analyte (Monomer) at a concentration of *ca.* 10^{-4} M. Fc/Fc⁺ redox couple as an internal standard. H₂O and sodium phosphate (Na₃PO₄) as

supporting electrolyte). All solutions were degassed (Ar) during a reduction experiment.

2- Equipments and Cells

Cyclic Voltammetry (CV) is a technique commonly used to measure the redox properties of materials, the materials can be measured in solution or solid state. Cyclic voltammetry measurements were achieved by using bio analytical system voltametric analyzer CV-50W. The electrochemical cells consisted of three electrodes: a platinum working electrode, a platinum wire counter electrode and a silver wire as the reference electrode. Electronic absorption spectra were recorded at room temperature on a JENWAY 7310 UV/vis spectrophotometer.

RESULT AND DISCUSSIONS

The electronic absorption spectrum of monomer was recorded in H₂O and is shown in Figure 2.

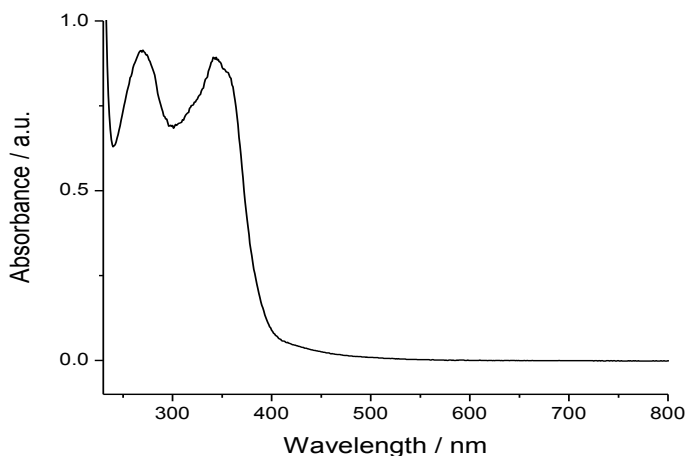


Figure 2. UV-V is spectra of the monomer measured

The spectrum of the monomer gives two main peaks at 265 and 345 nm. The first peak in this monomer is attributed to a π - π^* transition, while the peaks at 342 nm in this monomer is assigned to the conjugated system.

Electropolymerisation this compound was achieved through repetitive cycling over the first oxidation peak of the monomer, consequently the polymer was grown between 0 to +1.1 V referenced to Fc/Fc^+ . To determine the HOMO and LUMO energy levels and then the electrochemical HOMO-LUMO gap, by subtracting the onset of the first oxidation and reduction waves from the HOMO of ferrocene (-4.8 eV). The growth of the polymer was monitored through the increase in current with each cycle and the development of a new peak at lower potential as showed in Figure 3.

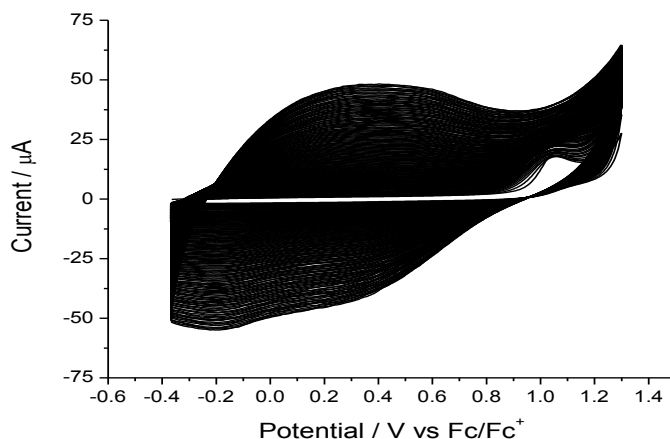


Figure 3. Polymer growth process using glassy carbon working electrode (Ag) wire reference electrode and (Pt) counter electrode

The electrochemical behavior of the polymer was analyzed by cyclic voltammetry. The polymer shows irreversible oxidation peaks at +0.36 V. The oxidation will be the removal of an electron from EDST group to forming a radical cation. The reduction of the polymer showed an irreversible peak at -2.29 V, which was attributed to the reduction of the attached unit. Both the oxidation and reduction cycles of the polymer are shown in Figures 4 and 5.

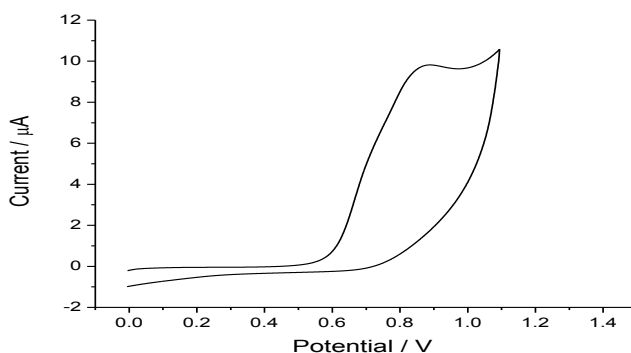


Figure 4. Oxidation Process of the polymer

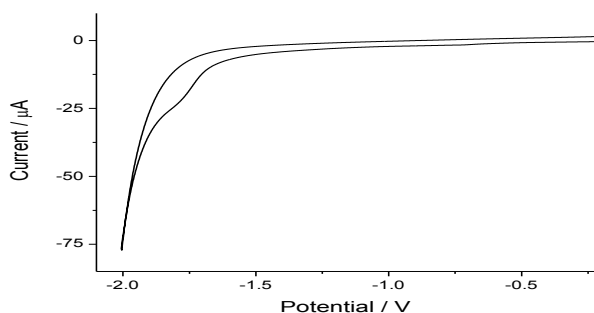


Figure 5. Reduction process of the polymer

The optical band gap of the polymer was determined by growing the polymer onto a piece of ITO-coated glass slide, the film of the polymer has shown higher stability on the slide rather than Pt working electrode surface. The polymer was grown by cycling between 0 and +0.79V vs. Fc/Fc⁺ (500 segments) then de-doped between -0.6 and -0.2 V. The spectrum shows an absorption maxima peak of 690 nm, which corresponds to red shift (bathochromic shift) for the π - π^* transition when compared to the monomer (342nm). The absorption spectrum for this polymer is shown in Figure.6.

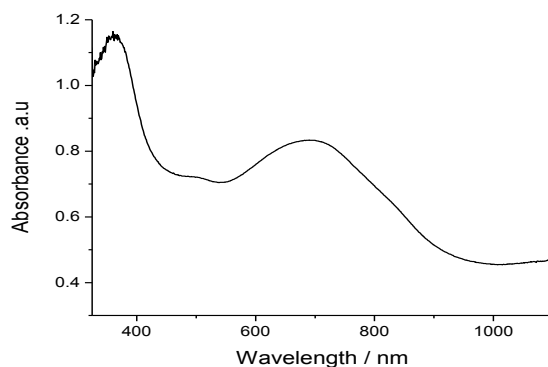


Figure 6. Solid state absorption spectrum of the polymer on ITO-coated glass

The optical band gaps of the polymer and monomer were calculated from the onsets of the longest wavelength absorption peaks. The data for all the absorption maxima and the optical band gap values are summarized in Table 1. The optical HOMO-LUMO gap of the monomer is 2.7 eV, while the optical band gap of the polymer is 1.47 eV. This also supports the assumption that the monomer of this compound has inferior conjugation chain compared to its polymer.

Table 1 Optical absorption data for monomer and the Polymer

	Main absorption peak / nm	Optical band gap / eV
Monomer	345	2.7
Polymer	690	1.47

CONCLUSION

The aim at this paper was to analyze compound using two techniques; cyclic voltammetry, and UV-V is spectroscopy to calculate and determine properties such as the oxidation and reduction potentials of the monomer and polymer and changes in absorption spectra through p- and n-doping. In conclusion the bis EDST units attached to carboxamido-4-methylpentanoic acid have been prepared and successfully electropolymerised when coated on to an Indium Tin Oxide (ITO) covered glass slide yielding a polymer with absorption maxima peak of (690 nm). The monomer of this compound has displayed a lower absorption maxima peak (345 nm) and higher optical HOMO-LUMO gap (2.7 eV) compared to its polymer (690 nm) (1.47 eV) respectively, due to the extension of conjugated length along the polymer chain.

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