

Electrochemical Behaviour of Thienyl-Fluorinated- β -Diketone Substrates and Their Conductivity in Solution

Zaid A. Al-Anber[†], Mohammed A. Al-Anber* and Samir Al-Taweel

Department of Chemical Science, Faculty of Science, Mu'tah University

P.O.Box 7, Al-Karak 61710, Jordan

Fax: (962)(6)4654061; Tel: (962)(7)77272677; E-Mail: masachem@yahoo.com

The cyclic voltammetric investigations of π -conjugated thienyl fluorinated β -diketone (donor-acceptor moieties) substrates in the acetonitrile solution have been reported. We have performed cyclic voltammetry to show the influence of the fluorinated β -diketone substituent on the redox potential of thienyl unit. The cyclic voltammetry curves present one irreversible oxidation potential wave around + 1.88 V. This wave has reported for the thienyl unit. In addition, the curves have one-reversibly redox potential wave ($E_{1/2}$), which is related for the fluorinated- β -diketone moiety. This redox wave is found between -1.10 to -1.53 V. Based on the geometrical structures substrates, these waves are discussed. The expected oligomers or dimer has been deposited as solid film. The electrical conduction of thienyl substrates has been evaluated in solution using conductivity. The influence of the substituents on the energy level and energy gap has been calculated using electronic spectra.

Key Words: Cyclic voltammetry, Fluorinated- β -diketones, Thienyl unit, Coordination compounds, Conductivity, Electronic spectra.

INTRODUCTION

Polyheterocycles have attracted much interest because of their promising properties such as electrical and optical properties¹⁻⁷. The most studies have been devoted on thiophene and their α -oligomers, which are used as repeating units for constructing electro-conductive polythiophenes⁸⁻¹¹. These polythiophenes have a potential use in the rechargeable batteries, electrochromic display devices and supercapacitors¹². The electroconductive properties are enhanced *via* the substituents on their repeating thiophene

[†]Department of Chemical Engineering, Faculty of Engineering Technology, Al Balqa University, Amman, Jordan.

monomers. These substituents must be chosen basing on their ability to decrease band gaps, increase polarizability and optimize luminance efficiencies. For example, upon substitution of the bithiophene with CH_3^- , OH^- , NH_2^- , CN^- and CCH^- influence the energy level and energy gaps¹³. Alkyl substituents are often increasing the solubility and possess band gaps smaller than the polythiophene itself^{14,15}. The polar and bulky substituents also increase the hydrophilicity of polythiophenes^{16,17}.

The position of substituents also influence the electronic structure of oligothiophene. Quite a high number of β -functionalized thiophenes and oligothiophenes have been recently synthesised by varying the formulation of the starting monomer in order to modulate the physical and chemical properties of the relevant polymers¹⁰. In particular, the substitution at the β -position can increase both conjugation and conductivity¹⁷.

Once of modification, the thienyl β -diketones ligands are synthesized, where β -diketone substituent on the thiophene, bithiophene and terthiophene backbone are in use^{18,19}. Furthermore, large branches of β -diketone are known as fluorinated compounds where they enhance the thermal stability of coordination compounds²⁰. The enol-ketone equilibrium chemistry of β -diketone is favored by strong inductive withdrawing group such as fluorine atom. This equilibrium influences the redox potential in voltammetric experiments as well as the electro-conductive oligomerization mechanism¹⁴. The electrochemical studies of the thienyl substrate containing fluorinated β -diketones compounds are not widely known.

Beyond this fundamental aspect, these molecules have attracted attention for various applications of ligands in coordination and organometallic chemistry as well as building blocks for the generation of supramolecular structures^{21,22}.

In this paper, we consider new thienyl fluorinated β -diketones substrates of donor-acceptor moieties as well as selected kind of substituents are in use. We have performed cyclicvoltammetry only to show the influence of substituents on the redox potential and to predict a proposed oligomerization mechanism. For the evaluation of conducting capability of thienyl substrates, the conductivity is measured. Electronic transition spectra is measured to show the influence of the energy gaps. Furthermore, the minor interest of this study is the electro-deposition of thinly fluorinated β -diketone as expected oligomers on the platinum plate.

EXPERIMENTAL

Compound **1** was obtained from Aldrich/Sigma-Aldrich; compounds **2-6** were synthesized according to literature procedures²⁵.

Cyclic voltammetry (CV) was performed with a one-compartment glass cell with a platinum disc (and for solid film deposition using platinum

plate) (1 mm² apparent surface area, 99 %, Schiefer, Hamburg) or a glassy carbon disc (HTW, Thierhaupten) embedded into a PTFE cylinder as working electrode. A platinum wire counter electrode and a silver reference electrode (Ag/Ag⁺, 0.01 M AgNO₃ in a solution of 0.1 M tetra-*n*-butyl ammonium hexafluorophosphate, TBFP (Fluka, dried in an oil pump vacuum at 120 °C) in acetonitrile) were used. For ease of comparison, all electrode potentials were converted using the ferrocene/ferrocenium redox couple as a reference point ($E_{\text{FeC}} = 0 \text{ mV}$)²⁶. All CVs were run at a scan rate of $dE/dt = 200 \text{ mV s}^{-1}$ using an electrolyte solution of 0.1 M of tetra-*n*-butyl ammonium hexafluorophosphate in acetonitrile with a concentration of the compounds of 5 mM. CVs were recorded using a Volta-lab 3.1 potentiostat (Radiometer) equipped with a digital electrochemical analyzer DEA 101 and an electrochemical interface IMT 102. All experiments were run at room temperature (25 °C) under argon purified with a CuO catalyst for dioxygen removal.

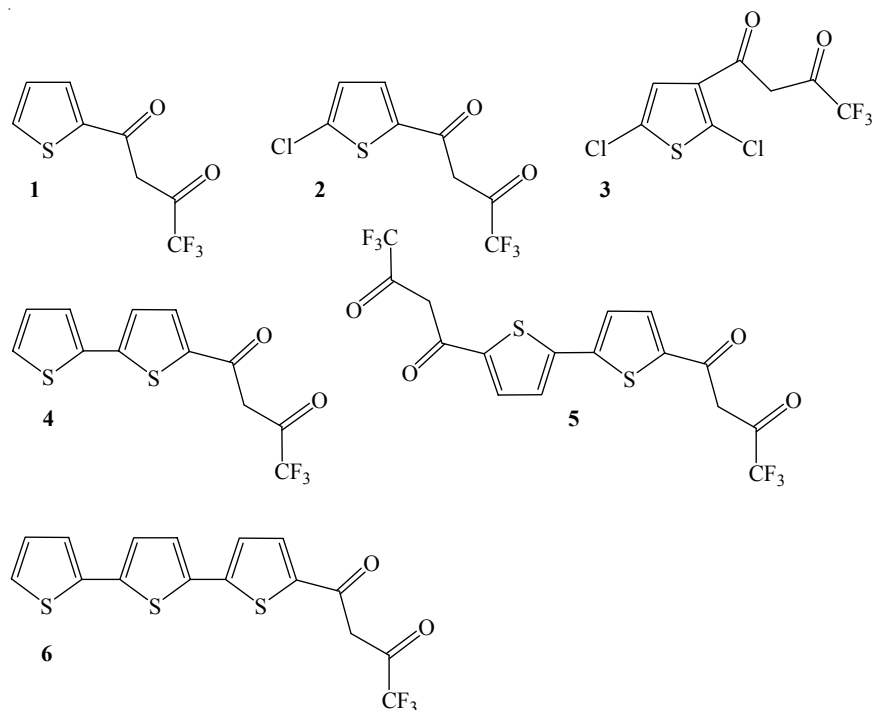
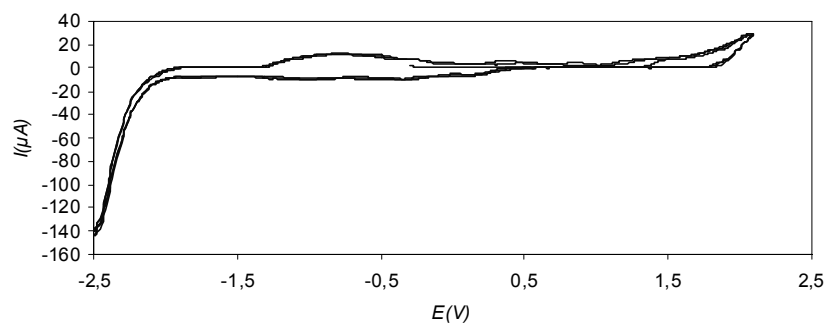
The electronic spectra of all molecules are recorded in acetonitrile solution. The electronic spectra have been measured for the same solution under inert argon gas using a Perkin-Elmer Lambda 650 UV-Vis spectrophotometer, working in the wavelength range 900-190 nm. The conductivity and pH were performed using hand held conductivity and pH meters, respectively, which are combined electrode conductivity and pH meters. The models of Cond. 315i/SET and pH 315i/SET are equipped with temperature probe. The samples are poured into two separate clean beakers. Then, the electrodes of the conductivity and pH indicators are submerged into the beakers containing the samples of 0.1 M acetonitrile solution. The experiments were conducted three times and the mean values were considered.

RESULTS AND DISCUSSION

Electrochemical behaviour of thienyl-fluorinated- β -diketones

The redox behaviour of selected thienyl-fluorinated- β -diketone substrates (**1-6**) is carried out using cyclic voltammetry in acetonitrile solution (Fig. 1). Due to the fast polymerization and deposition of solid film on the working electrode, the scan rate was used at 200 mV/s. The electrochemical behaviour of the acetonitrile solution background is represented in Fig. 2. The electrochemical data of respective molecules are listed in Table-1.

The voltammetric response of the respective substrates shows a cathodic-anodic system as demonstrated in equation 1. Particularly, the cyclic voltammogram for 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione substrate (**1**) shows initially large irreversible anodic wave at + 1.88 V (Fig. 3). In analogy to the reported electrochemical data of thiophene and oligothiophenes²³, this oxidation potential wave relates to the thienyl unit. When the scanning is

Fig. 1. Thienyl fluorinated β -diketone substratesFig. 2. Cyclic voltammogram of acetonitrile solution background in the presence of $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ ($c = 0.1 \text{ M}$) at 25°C under argon at a scan rate of 200 mV s^{-1}

going toward the negative potential, the cyclic voltammogram exhibits one cathodic reversible redox wave at $E_{1/2} = -1.10 \text{ V}$ ($\Delta E = 300\text{-}570 \text{ mV}$) vs. $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}$. This Redox wave is corresponded to the reduction wave for the fluorinated β -diketone unit (eqn. 1) Where, T = thienyl unit; K = fluorinated β -diketone moiety; n = number of thienyl units in the substrate molecule.

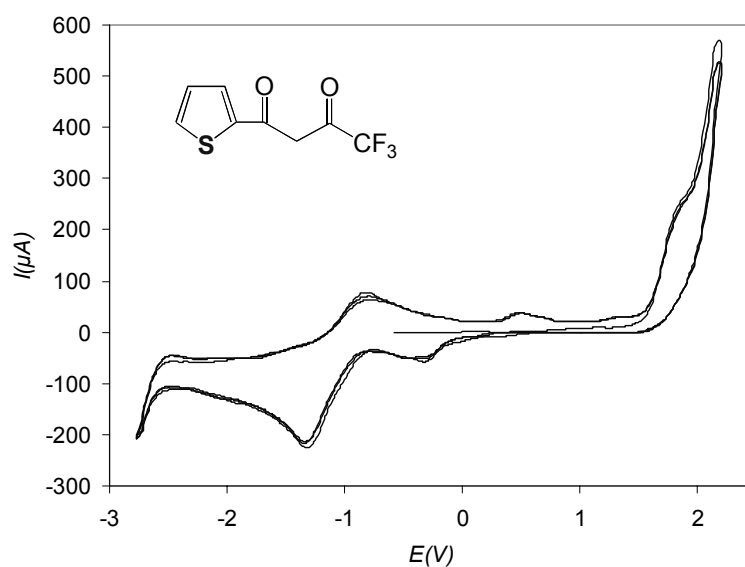
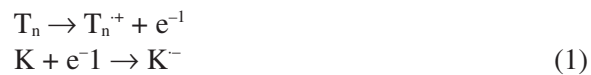


Fig. 3 Cyclic voltammogram of 2-thienyl trifluoroacetone (**1**) in acetonitrile solution in the presence of $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ ($c = 0.1 \text{ M}$) at 25°C under argon at a scan rate of 200 mV s^{-1} ; potentials are referenced to FcH/FcH^+ as internal standard ($E_{1/2} = 0.00 \text{ V}$, CH_3CN)

TABLE-1
ELECTROCHEMICAL DATA OF COMPOUNDS 1-6,
ALL POTENTIALS vs. FcC

Compd.	Fluorinated β -diketone moiety				Thienyl unit
	E_{red} (V)	E_{oxid} (V)	$E_{1/2}$ (V)	ΔE (mV)	E_{oxid} (V)
1	-1.38	-0.81	-1.10	570	+1.88
2	-1.30	-0.90	-1.10	400	+1.70
3	-1.55	–	–	–	–
3*	-1.55	–	–	–	+0.60
4	-1.68	-1.30	-1.49	380	+1.19 +1.49
5	-1.46	-1.04	-1.25	10	–
6	-1.68	-1.38	-1.53	300	+1.03 +1.47

*Electrochemical data for the second and third cycle.

In order to clarify the redox potential wave of the diketone moiety for each substrate, the cyclic voltammetry for the acetylacetone, hexafluoroacetylacetone and hexafluoroacetylacetone-ferrocene molecules are investigated. Their CV's show: firstly, the electrochemical behavior of the hexafluoroacetylacetone-ferrocene has very well developed reduction wave ($E_{1/2} = -1.33$ V). This wave is in agreement with the measured value for all substrates (**1-6**). Secondly, the related measurements for the acetylacetone and hexafluoroacetylacetone show no waves at all, but only a steadily growing cathodic current. The suggestion in fact the π -conjugation in the thienyl or cyclopentadienyl units may participate as main reason for reducing the *keto*-function. One support for this proposed explanation can be gleaned from the observations of the fluorinated- β -diketone redox potentials for **1**, **4** and **6**. They basically shift to the more negative values by decreasing of their π -conjugation. In addition, the oxidation potential of thienyl unit shifts to the lower positive value by increasing the number of thienyl units. This might be return to the simple π -conjugation consideration by increasing in the charge density. These results are matching those found by Khodaei²⁴.

The cyclic voltammogram for 1-(5-chloro-thiophen-2-yl)butane-1,3-dione (**2**), where one of the thienyl protons is replaced by one chlorine atom, the related shape of cyclic voltammogram was found similar for **1**. One different feature could be detected, where the oxidation potential of thienyl unit shifts to the lower value (+ 1.70 V) (Fig. 4). This Figure clearly indicates the effect of enol-ketone equilibrium for the β -diketone unit. This equilibrium influences the redox potential through the voltammetric experiments²¹, which is favoured by the strong inductive electron withdrawing substituent. The explanation in fact this substituent enhances the *enol* contents by one chlorine atom (compound **2** vs. **1**) and then the π -conjugations are increasing. The modification of π -conjugations enhance the electronic occupied levels that are available at higher energies. For this reason, the oxidation potential of such substrates is decreasing.

One more feature can be detected from the cyclic voltammogram of **2**, the redox potential of fluorinated- β -diketone moiety is partially quasi-reversible process ($i_{pc} < i_{pa}$).

Fig. 5a represents the cyclic voltammogram for the 3-(2,5-dichloro-thienyl)-4,4,4-trifluoro-1,3-butanedione (**3**). It shows only one partially quasi-reversible reduction wave at - 1.55 V, which is corresponding to the fluorinated- β -diketone moiety. The reduction wave shifts to the more negative potential by 0.17 and 0.25 V (compound **3** vs. **1** and **2**, respectively). These new features are due to the structural and electronic properties. The position of the fluorinated- β -diketone unit and the presence of two chlorine atoms are participating to enhance *enol*-formation and increasing the delocalization of π -system. Wherefore; the oxidation of thienyl molecule and the formation of solid film oligomers are completely inhibited in the first scan as discussed later of this paper.

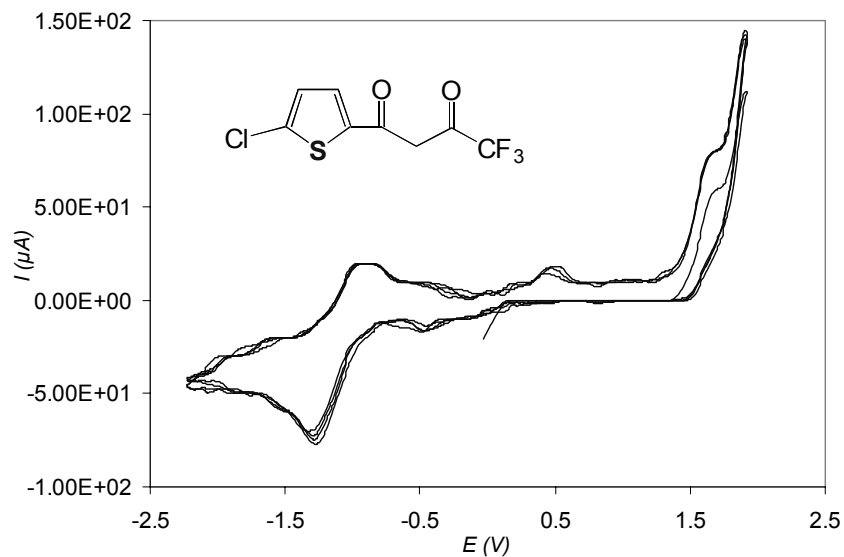
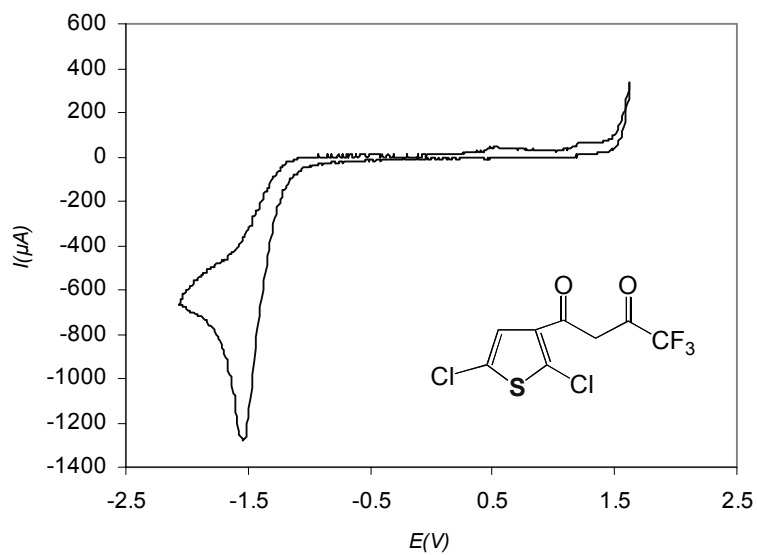


Fig. 4 Cyclic voltammogram of 1-(5-chloro-thiophen-2-yl)butane-1,3-dione (**2**) in acetonitrile solution in the presence of $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ ($c = 0.1 \text{ M}$) at 25°C under argon at a scan rate of 200 mV s^{-1} ; potentials are referenced to FcH/FcH^+ as internal standard ($E_{1/2} = 0.00 \text{ V, CH}_3\text{CN}$)



(a)

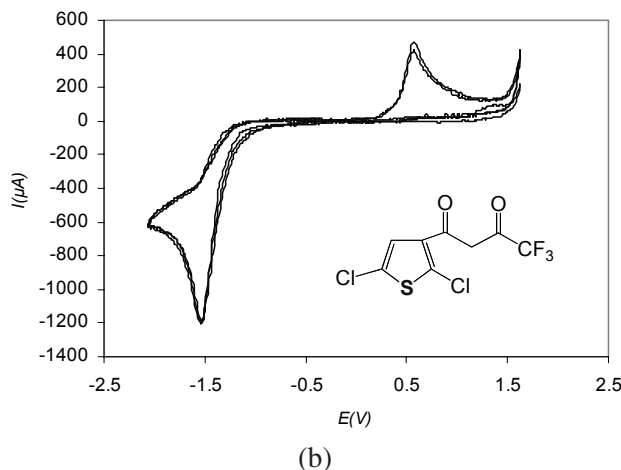


Fig. 5. Cyclic voltammogram of 3-(2,5-dichloro-thienyl)-4,4,4-trifluoro-1,3-butanedione (**3**) in acetonitrile solution in the presence of $[n\text{-Bu}_4\text{N}][\text{PF}_4]$ ($c = 0.1 \text{ M}$) at 25°C under argon at a scan rate of 200 mV s^{-1} ; potentials are reference to FcH/FcH^+ as internal standard ($E_{1/2} = 0.00 \text{ V}$, CH_3CN), (a) first cycle, (b) first, second and third cycles

Furthermore, when the potential scan is just reversed after the first reduction wave, the second and third waves in Fig. 5b have been appeared as new irreversible wave at $+0.60 \text{ V}$. This electrochemical behaviour is due to the chemical changes on the respective substrate during the recording of the first cycle. This suggestion may participate to appear such wave at lower positive voltage.

The electrochemical behaviour of the 1-(5- α -bithienyl)-4,4,4-trifluoro-1,3-butanedione (**4**) and 1-(5- α -trithienyl)-4,4,4-trifluoro-1,3-butanedione (**6**) are shown in Figs. 6 and 7, respectively. The cyclic voltammograms of **4** and **6** have two anodic irreversible waves at $+1.19$ (as a major wave): $+1.49 \text{ V}$ and $+1.03$ (as a major wave): $+1.47 \text{ V}$, respectively. These anodic potentials are related to the oxidation of thienyl unit. The major oxidation potential shifts to the lower potential (compound **6** vs. **4**). The main reason for such shift is return to both number of thienyl units and the extending of the p-systems in the substrate backbone. In addition, the electrochemical reduction corresponds to the fluorinated- β -diketone moieties (in the compounds **4** and **6**) that appear at -1.68 V .

The CV of 1,1'-(2,2'-bithiophene-5,5'-diyl)bis(4,4,4-trifluorobutane-1,3-dione) (**5**) does not show any clearly anodic waves (Fig. 8). The two fluorinated- β -diketone moieties on the thiophene backbone participate for such hiding anodic wave. The slightly quasi-reversible redox couple waves of β -diketone units slightly shift to the lower negative values that appear at -1.25 V .

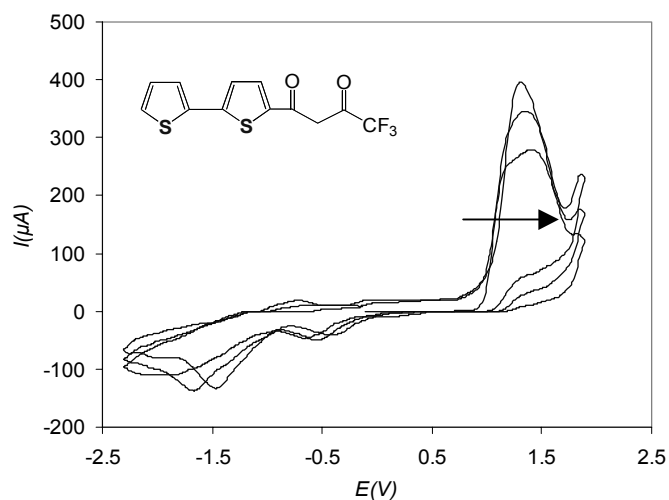


Fig. 6. Cyclic voltammogram of 1-(5- α -bithienyl)-4,4,4-trifluoro-1,3-butanedione (**4**) in acetonitrile solution in the presence of $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ ($c = 0.1 \text{ M}$) at 25°C under argon at a scan rate of 200 mV s^{-1} ; potentials are reference to FcH/FcH^+ as internal standard ($E_{1/2} = 0.00 \text{ V}$, CH_3CN)

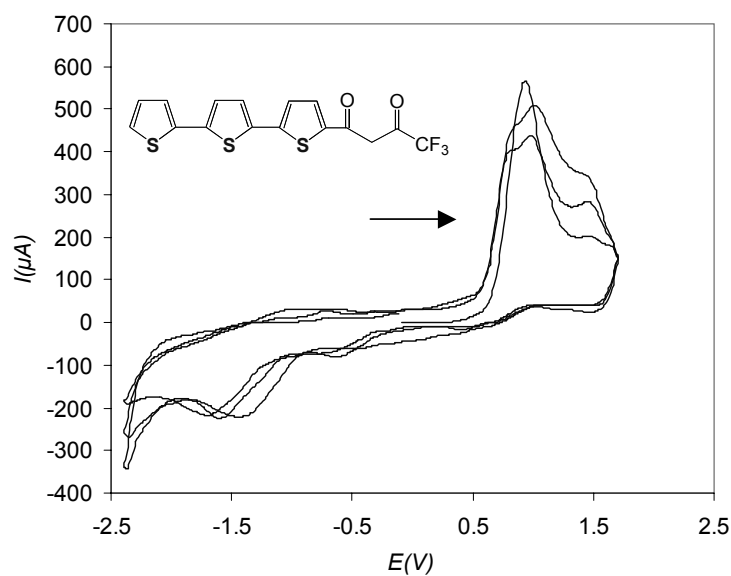


Fig. 7. Cyclic voltammogram of 1-(5- α -trithienyl)-4,4,4-trifluoro-1,3-butanedione (**6**) in acetonitrile solution in the presence of $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ ($c = 0.1 \text{ M}$) at 25°C under argon at a scan rate of 200 mV s^{-1} ; potentials are reference to FcH/FcH^+ as internal standard ($E_{1/2} = 0.00 \text{ V}$, CH_3CN)

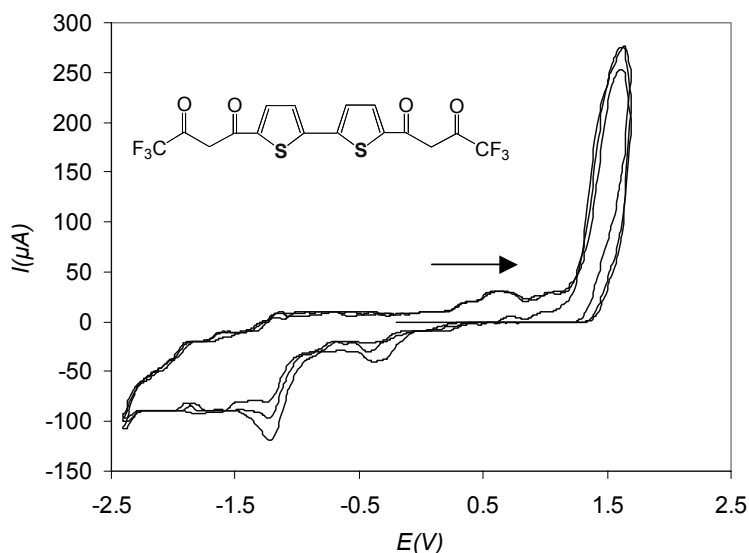


Fig. 8. Cyclic voltammogram of 1,1'-(2,2'-bithiophene-5,5'-diyl)bis(4,4,4-trifluorobutane-1,3-dione) (**5**) in acetonitrile solution in the presence of $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ ($c = 0.1 \text{ M}$) at 25°C under argon at a scan rate of 200 mV s^{-1} ; potentials are reference to FcH/FcH^+ as internal standard ($E_{1/2} = 0.00 \text{ V}$, CH_3CN)

Electrodeposition of oligothiophene solid film on Pt-plate

The depositing of the solid-film for the expected oligomers on the Pt-plate is formed; this is after the electrochemical oxidation of thienyl unit²⁵. The polymer chain consists of linked aromatic units, which in case of thiophene molecules are primarily 2,5-coupled. The coupling occurs at the carbon atoms, which are known to be the most reactive toward addition and substitution reaction²⁵⁻²⁷. The polymerization reaction is a very complicated story, where the general reaction steps are shown in the proposed **Scheme-I**, which is based on cyclic voltammetry measurements.

From the obtained CVs, the current intensities increase during the recording where the multi oxidation potential waves of thin units grow at $+1.70 \text{ V}$ (SCE on the forward scan). In addition, during the electrochemical oxidation, the deep brown solid film agglutinates on the surface of Pt-plate (working electrode) under the argon environment. It is likely the solid oligomers forms²³. These observations could be ascribed to the formation of a solid film of expected dimer or oligomers, which is in agreement for the reported films in the literature, and they are already evident^{28,29} for our proposed suggestion in **Scheme-I**.

These oligomerization is a result of the oxidation thienyl ring, where the fluorinated- β -diketone and chlorine units could participate for enhancing and controlling the oligomerization. By analogy with the conjugated polymers models, the chemical or electrochemical changing of thienyl oligomers in solution is generally described by a successive formation of radical cation and dications according the following reactions²³ as appear in eqn. 2.

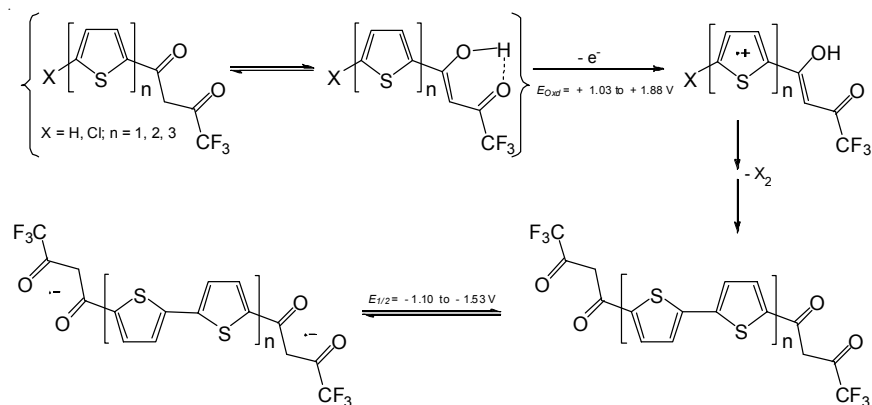


Therefore, we can reasonably expect and propose that the first observed oxidation potential wave in **4** and **6** is corresponded for the formation of radical cation, while the second wave for the dications. This leads to the formation of π -dimer or π -oligomers. The polymerization pathway for the heterocyclic seems general³⁰: a) oxidation of thiophene moiety to a radical cation, b) dimerization of the radical cation, c) proton loss to yield neutral dimer, d) oxidation of dimer to its radical cation, e) reaction of dimer radical cation with another radical cation, f) oxidized conducting polymer.

The substrate geometry explains the different oxidation potentials through their substituent positions. When the α -positions are free, the cation radical undergoes a fast coupling reaction in solution and then forming either a dimer or a polymer, which involves the coupling between two cation radicals. For the same cation of the radical-cation, the radical coupling reaction is involved when the β -terminal positions are substituted by the chloride or fluorinated- β -diketone. We propose this reaction involves the hindrance of the α, α' -coupling and then the protonated dimer are followed by the nucleophilic attacking and hind not the coupling by one β -positions³¹.

The oxidation potentials of thienyl in **1** shift to the more positive potential and appear at + 1.88 V (**1** vs. thiophene monomer). This indicates that one radical cation is formed, while the dications are produced in case of thiophene monomer ($E_{\text{oxd}} = +0.33$ and + 0.69 V). The potential is then repeatedly scanned within the limits of -0.30 - + 2.0 V, the continuous cycling shows a rising the new anodic system. This is an indicative for forming the polymeric film on Pt-plate, which shows a good adhesion and stability of polymer on the surface of the electrode.

Furthermore, the oxidation values of thienyl unit are shifted to the lower positive potential by 0.18 V (compounds **2** vs. **1**). The chlorine atom and the increasing of π -conjugation are both participated to form the solid film oligomers on Pt-plate.

**Scheme-I**

The oligomerization in **3** is slightly inhibited. This is due to the geometrical structure for this substrate, where is blocked by two chlorine atoms and one fluorinated-β-diketone unit. Therefore, no any possible oxidation wave is appeared in the CV through the electrochemical scan for such substrate. However, after the reduction of fluorinated-β-diketone unit, the thienyl ring is oxidized at +0.60 V. This oxidation wave is slightly appeared near the oxidation wave value for thiophene monomer ($E_{\text{oxd}} = +0.33$ & $+0.69$ V). The suggestion is directed toward the electro degradation of substrate. The obtained polymer is depositing on the working electrode, which is slightly similar to that producing polymer from thiophene monomer. To support that, the scan is just going from zero potential toward the negative scan (-2.5 V) then return to the more positive potential up to $+2.0$ V. The new CV shows an identical oxidation wave at $+0.60$ V.

In addition, two oxidation waves are detected at $+0.92$: $+1.60$ V and $+0.75$: $+1.48$ V, which are related to the oxidation of thienyl ring in both bithiophene and terthiophene, respectively. While the oxidation waves of the same ring are detected at $+1.19$: $+1.49$ V and $+1.03$: $+1.47$ V (in the case of **4** and **6**, respectively). The results are comparing the bithiophene *vs.* **4** and then terthiophene *vs.* **6**. The thienyl oxidation waves are shifted to the more positive potential. This is due to the substituent on the substrate backbone, where the electro-polymerization is slightly preferred. This could be explained by extending π -system delocalization.

In general, the results show the oxidation potential is shifted to the lower value according the trend of **6** < **4** < **1**. This is due to the π -electrons

along the π -conjugated backbone. In addition, π -dimer is easily formed as the numbers of thiophene unit decreases in the substrates as well as the π -conjugated precursors are especially hard to polymerize²⁰. Furthermore, the first anodic wave is completely irreversible³¹.

The oxidation of **5** does not show any observed polymer whatever the conditions. This is due to the presence of two fluorinated- β -diketone units, which is blocking the α -positions. Also, the cation radicals can not undergo either coupling or nucleophilic attack. This is due to the steric hindrance by the substituents, which is clearly appeared in molecule **5**. These observations are in agreement with the similar reported work²⁹.

Spectroscopic and conductivity behaviour

Electrochemical potential and band gap are among the most important physical properties to be taken into account in order to envision applications of the material as well as electro-conductive polymerization. Therefore, the electronic transition band in UV-Vis spectra and transition energies are calculated. Table-2 shows the results for the selected substrates of **1**, **4**, **6** and **5**. From the UV-Vis spectra, the absorption bands near 383 and 421 nm have assigned to ($\pi_{(\text{HOMO})} \rightarrow \pi^*_{(\text{LUMO})}$) transitions. The generally increasing wavelengths (*i.e.*, lower transition energy gap) are observed in trend of **1** < **4** < **6**. This trend is due to the number of thienyl units. Wherein the energy gap decreases as the thienyl unit increases, this is because the delocalization of *p*-electrons along the conjugated backbone. The π -conjugation makes more occupied levels available at higher energies and this is the reason for the lower of band gap ($E_{\text{HOMO}}-E_{\text{LUMO}}$), which shifts the oxidation potentials to the lower value.

As comparison, the results show that the energy gap of **5** has lower value than in case of **4**. The suggestion may return to the extended of the π -electrons delocalization between the conjugated backbone and the pair of fluorinated- β -diketone substituents. In addition, the fluorinated- β -diketone unit extends the *p*-delocalization through enol content of the equilibrium causing low-band gap with donor-acceptor moieties. The correlation between the experimental oxidation potentials (from CV) and the observed electronic transition energies expressed as maximum wavelength (λ_{max}) shows in Fig. 9 a closed and convening correlation.

Conductivity data

In order to measure the conducting capability of selected thienyl substrates in solution, Electrical conductivity is evaluated. Electrical conductivity measure the ability of thiophenes to conduct an electrical current⁷. When an electrical potential difference is placed across a conductor, it is movable

charges flow, giving rise to an electric current. π -Conjugated oligomers and polymer are flowing easily the current using π -system. The obtained results in Table-2 show that the molecule **5** has the best conductive properties, while molecule **2** has the lowest value. The extended of the π -system delocalization through: firstly, increasing the number of thienyl unit in the substrate backbone lead to increase the conductivity in trend of **6** > **4** > **1**. Secondly, π -system is more delocalized and extended by the pair of fluorinated β -diketone moieties, *e.g.*, compound **5**. The conductivity of this compound increases up to 12.4 $\mu\text{s}/\text{cm}$. Finally, one inductive withdrawing group enhance the *enol-ketone* equilibrium (for example is shown in **2**), this leads to increase the π -system delocalization as well as the conductivity (4.40 $\mu\text{s}/\text{cm}$).

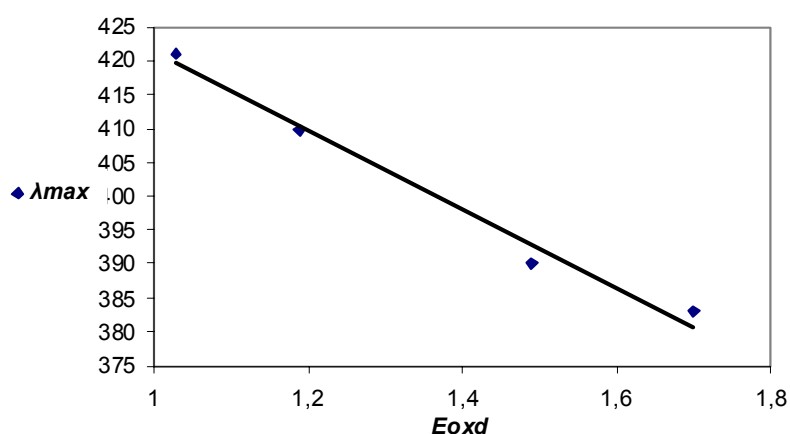


Fig. 9. Correlation between the experimental oxidation potentials (from CV) and the observed electronic transition energies expressed as maximum wavelength (λ_{max})

TABLE-2
CONDUCTIVITY, pH AND ELECTRONIC λ_{max} DATA OF
 π -CONJUGATED THIENYL FLUORINATED β -DIKETONES
LIGANDS (**2, 4, 5, 6**) IN ACETONITRILE SOLUTION

Compd.	pH	λ_{max} (nm)	Cond. ($\mu\text{s}/\text{cm}$)
1	6.39	363	5.16
2	7.34	383	4.40
4	5.88	390	5.50
5	4.10	410	12.4
6	5.27	421	5.8

Conclusion

Fluorinated- β -diketone substituent can be used for modifying the synthesis and conductivity of the electro-conductive polythiophene, where more occupied level are available at higher energies. This modification are satisfied by low band gap, rich and extended π -system delocalization on the thiophene substrate, substituted by inductive withdrawing group, and the suitable β -position in the substrate. Therefore, compound **2** is the easiest electro-polymerized. The molecules of **5** and **6** are highly conductive in solution. This is due to the extended and increases the π -system delocalization. The expected oligomers are adherent as a solid film on the Pt-plate.

ACKNOWLEDGEMENTS

The authors are thankful to Prof. H. Lang for providing the cyclic voltammetry facilities (TU-Chemnitz, Germany). Thanks are also due to for the Chemist Arwa Hutaibat for the experimental UV/Vis and conductivity measurements [Dead Sea Laboratory, Prince Faisal Center for Dead Sea, Environmental and Energy Research (PFC-DSEER)], Mutah University, Karak, Jordan.

REFERENCES

1. W.D. Gill, T.C. Clarke and G.B. Street, *Appl. Phys. Commun.*, **2**, 211 (1982).
2. D. Baeriswyl, G. Harbeke, H. Keiss and W. Meyer, in eds.: J. Mort and C.P. Fisher, *Electronic Properties of Polymers*, Wiley, New York (1982).
3. G.B. Street and T.C. Clarke, *IBM J. Res. Dev.*, **25**, 51 (1982).
4. K.G. Wynne and G.B. Street, *IEC Prod. Res. Dev.*, **21**, 23 (1982).
5. C.B. Dunke and H.W. Gibson, *Encycl. Chem. Technol.*, **18**, 755 (1982).
6. F. Garnier and G. Tourillon, *J. Electroanal. Chem.*, **148**, 299 (1983).
7. U. Salzner, J.B. Lagowski, P.G. Pickup and A. Poirier, *Synth. Met.*, **96**, 177 (1998).
8. a) J. Hamblin, L.J. Childs, N.W. Alcock and M.J. Hannon, *J. Chem. Soc. Dalton Trans.*, 164, (2002). b) H.K. Liu and X. Tong, *Chem. Commun.*, 1316 (2002). c) V.F. Razumov, S.B. Brichkin, O.M. Pilugia, T.P. Karpova, S.Z. Vatsadze, D.A. Lemenovskii, M. der Schro", N.R. Chapness and M.V. Alfi-mov, *Russ. Chem. Bull. Inter. Ed.*, **51**, 476 (2002). d) M. Albrecht, *Chem. Rev.*, **101**, 3457 (2001), (refs. cited therein).
9. Ch. Zanardi, R. Scanu, L. Pigani, M.I. Pilo, G. Sanna, R. Seeber, N. Spano, F. Terzi and A. Zucca, *Electrochim. Acta*, **51**, 4859 (2006).
10. a) J. Roncali, *Chem. Rev.*, **92**, 711 (1992). b) G. Schopf and G. Kobmehl, *Advances in Polymer Science, Polythiophene-Electrically Conductive Polymer*, Springer, Vol. 129, pp. 1-166 (1997). c) G. Barbarella, M. Melucci and G. Sotgiu, *Adv. Mater.*, **17**, 1581 (2005). d) S. Kirchmeyer and K. Reuter, *J. Mater. Chem.*, **15**, 2077 (2005). e) N.H. Singh, *Handbook of Organic Conductive Molecules and Polymers*, Wiley-VCH, New York (1997). f) D. Fichou, *Handbook of Oligo- and Polythiophenes*, Wiley-VCH, New York (1998).

11. a) P.W. Reynolds, *J. Heterocycl. Chem.*, **21**, 1231 (1984). b) E. Schulz, K. Fahmi and M. Lemaire, *Acro. Organics Acta*, **1**, 10 (1995); b) G. Horowitz, *Adv. Mater.*, **10**, 365 (1990); c) A. Dodabalapur, L. Torsi and H.E. Katz, *Science*, **268**, 270 (1995). d) A. Dodabalapur, L. Torsi, H.E. Katz and R.C. Haddon, *Science*, **269**, 1560 (1995). e) A. Kraft, A.C. Grimsdale and A.B. Holmes, *Angew. Chem. Int. Ed.*, **37**, 402 (1998). f) T. Noda, H. Ogawa and Y. Shirota, *Adv. Mater.*, **11**, 283 (1999). g) T. Noda and Y. Shirota, *J. Am. Chem. Soc.*, **120**, 9714 (1998). h) N. Noma, T. Tsuzuki and Y. Shirota, *Adv. Mater.*, **7**, 647 (1995). i) D.T. McQuade, A.E. Pullen and T.M. Swager, *Chem. Rev.*, **100**, 2537 (2000). j) J. Roncali, *J. Mater. Chem.*, **9**, 1875 (1999).
12. a) M. Mastragostino, C. Arbizzani, A. Bongini, G. Barbarella and M. Zambianchi, *Electrochim. Acta*, **38**, 135 (1993); b) K.S.V. Santhanam and N. Gupta, *TRIP*, **1**, 284 (1993); c) S. Paero, S. Passerini and B. Scrosati, *Mol. Cryst. Liq. Cryst.*, **229**, 97 (1993); d) S.C. Huang, S.M. Huang, H. Ng and R. B. Kaner, *Synth. Met.*, **55-57**, 4047 (1993).
13. U. Salzner and T. Kiziltpe, *J. Org. Chem.*, **64**, 764 (1999).
14. B.M. Salim and S.M. Khalil, *Z. Naturforsch.*, **60a**, 47 (2005).
15. T.-A. Chen and R.D. Rieke, *Synth. Met.*, **60**, 175 (1993).
16. M. Kozaki, S. Tanaka and Y. Yamashita, *J. Chem. Soc. Chem. Commun.*, 1137 (1992).
17. J. Roncali, *Chem. Rev.*, **92**, 711 (1992).
18. a) S. Al-Tarawneh, MSc. Thesis, Mu'tah University, 2003. b) S. Al-Tarawneh, MSc. Thesis, Jordan University, 2001. c) S. Al-Taweel, F. Khalili, Y. Yousef and S. Al-Tarawneh, *Jordan J. Chem.*, (2007) (in press).
19. G. Gritzner and J. Kuta, *Pure Appl. Chem.*, **56**, 4 (1984).
20. J.C. Reid and M. Calvin, *J. Am. Chem. Soc.*, **72**, 2948 (1950).
21. F. Henry, J.R. Holtzclaw and P. James, *J. Inorg. Nucl. Chem.*, **29**, 1931 (1957).
22. a) B.M. Foxman and H. Mazurek, *Inorg. Chem.*, **18**, 113 (1979). b) E. Bouwman, J.C. Huffman, E.B. Lobkovsky, G. Christou, H.L. Tsai and D.N. Hendrickson, *Inorg. Chem.*, **31**, 4436 (1992). c) R. Schneider, Th. Weyhermueller, K. Wieghardt and B. Nuber, *Inorg. Chem.*, **32**, 4925 (1993).
23. B. Nessakh, G. Horowitz, F. Garnier, F. Deloffre, P. Srivastava and A. Yassar, *J. Electroanal. Chem.*, **399**, 97 (1995).
24. M.M. Khodaei, A.R. Khosropour and J. Abassi, *J. Iran. Chem. Soc.*, **2**, 289 (2005).
25. a) J. Roncali, *Chem. Rev.*, **92**, 711 (1992). b) T. Yamamoto, K. Sanechika and A. Yamamoto, *J. Polym. Sci. Polym. Lett. Ed.*, **18**, 9 (1980).
26. a) J.F. Ambrose and R.F. Nelson, *J. Electrochem. Soc.*, **92**, 1161 (1968). b) C.Z. Hotz, P. Kovacic and I.A. Khoury, *J. Polym. Sci. Polym. Chem.*, **21**, 2617 (1983).
27. a) R.N. Adams, *Acc. Chem. Res.*, **2**, 175 (1996). b) G. Tourillon and F. Garnier, *J. Electroanal. Chem.*, **135**, 173 (1982).
28. A.F. Diaz, J.I. Castillo, J.A. Logan and W.Y. Lee, *J. Electroanal. Chem.*, **129**, 115 (1981).
29. F. Cherioux, L. Guyard and P. Audebert, *Chem. Commun.*, 2225 (1998)
30. E.M. Genies, G. Bidan and A.F. Diaz, *J. Electroanal. Chem.*, **149**, 101 (1983).
31. P. Audebert, J.-M. Catel, G. Le Coustumer, V. Duchenet and P. Hapiot, *J. Phys. Chem. B*, **102**, 8661 (1998)