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Synthesis, characterization, electropolymerization, and theoretical study of 2,3-di-(2-thienyl)quinoxaline

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Summary

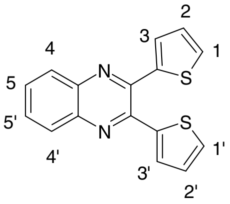
A new conjugated polymer combining in its structure thiophene rings and nitrogen containing heterocycles, poly[2,3-di(2-thienyl)quinoxaline], was synthesized by electrochemical methods using different experimental conditions. The monomer was electrochemically characterized. The morphology of the respective polymer was studied by SEM. The polymer shows low bandgap, dual p- and n-doping and good environmental stability. Theoretical calculations of global and local reactivity index such as frontier orbitals energy gap and Fukui functions present a good consistency with the experimental results.

Introduction

Conjugated polymers had useful materials in electronic devices because of their electrical, optical and mechanical properties [1]. Roncali [2,3] has shown the importance of the polythiophene family in various applications such as sensors, diodes, photovoltaic cells, and others. The use of polythiophenes in different applications depends on its doped state, which can be regulated by an external applied potential. Usually, these materials show only p- or n-type doping, nevertheless recently Reynolds et al. have electrosynthesized an alternating bi(ethylendioxythiophene) and pyridine polymer with dual p- and n-type doping. [4] Kokubo et al. have also obtained copolymers of thiophene and thiazole with dual doping. [5]

In other hand, the elaboration of electronic devices which requires n- and p-doping layers perfectly assembled is an important and difficult task. Systems with low band gap are good candidates to be used in this type of devices [6,7]. In this context many investigations are focused toward the synthesis of polymers with low bandgap, among these polymers those containing both thiophene rings or nitrogen containing heterocycles have been recently reported. [8,9] In particular, Kauffmann et al. [10] reported the synthesis of 2,3-di(2-thienyl)quinoxaline, with 49% yield, while Vegh et al. [11] reported 89% yield. In this work the monomer was obtained through a simple method of synthesis with 98% yield. The polymer, poly[2,3-di(2-thienyl)quinoxaline], which combine in its repeating unit (Scheme 1) thiophene with phenazine rings (not yet reported in the literature), was then obtained by electrochemical methods using different experimental conditions. The morphologies of the respective deposits were then characterized by SEM analysis.

Theoretical calculations were performed to help rationalize experimental data. With this purpose the electronic structure of the monomer, dimmer and trimmer species has been characterized through HF and DFT calculations to identify the reactive sites for polymerization, and determine the energy gap between the frontier molecular orbitals to explore the dependence of the energy gaps with the number of monomeric units. In this context a simple equation to predict the polymer bandgap as a function of the chain length is proposed.



Scheme 1. 2,3-di(2-thienyl)quinoxaline

Experimental

Measurements

^{1}H and ^{13}C NMR spectra were collected on a Bruker 200P spectrometer using chloroform-*d* as solvent and TMS as internal standard. FT-IR spectra were recorded on a Perkin-Elmer 1710 FT spectrophotometer using KBr pellets. Elemental analysis was performed on a Fison 1108 microanalyser. UV-VIS spectra were obtained on a UV-VIS NIR Shimadzu, UV 3101 PC using dimethylsulfoxide (DMSO) as solvent. The determination of melting point was carried out on a Stuart Scientific Melting Point Apparatus (SMP3). Potentiodynamic and potentiostatic measurements were acquired using a Voltalab PGZ100; electrochemical experiments were performed in a conventional three electrodes cell, using anhydrous acetonitrile or dichloromethane as solvent, and 0.1M tetraethylammonium tetrafluoroborate ($TEABF_4$, supplied by Aldrich) as support electrolyte. It was employed a Ag/AgCl electrode as reference in tetramethylammonium chloride with potential adjusted to that of SCE. [12] The working electrodes were platinum disc (0.1 cm^2 of geometrical area), platinum plate (2 cm^2 of geometrical area) or SnO_2 covered glass, (CG, 2 cm^2 of geometrical area). As counter electrode it was used a Pt gauze of large geometrical area, separated from the working electrode compartment by a fine frit glass. Prior to all the experiments, solutions were purged with high purity argon and it was maintained over the solution during the measurements. The morphology of the polymeric films was observed in a HR-SEM (JEOL 6400 F). The conductivity of the polymer was measured with a conductance meter Elchema, model CM-508, by the four probe method. All experiments were carried out at room temperature (20°C). Theoretical calculations were performed using the package Gaussian 98, Revision A.7. [13]

Synthesis of 2,3-di(2-thienil)quinoxaline

A mixture of 2,2'-thienil (200 mg; 0,9 mmol, supplied by Aldrich) and *o*-phenylenediamine (291 mg; 2,7 mmol) in ethanol was refluxed for 3h and cooled to room temperature. Yellow needles were obtained. This compound was filtrated and washed with diluted HCl and finally dried at 60 °C. 2,3-di(2-thienyl)quinoxaline was obtained in 98% yield. Elemental Analysis, found % (Calculated %): C, 65.39 (65.30); H, 3.31 (3.40); N, 9.54 (9.52); S, 19.18 (21.77). Melting Point: 147.7-148.1 °C. FTIR (cm^{-1}): 3093.8; 3054; 1520.6; 1422.0; 1298.8; 852.5; 844.9; 761.8; 711.5. ^{1}H-NMR ($CDCl_3$) 200MHz, ppm): 8.13-8.04 (m, 2H, 4,4'-H); 7.76-7.68 (m, 2H, 5,5'-H); 7.52-7.49 (m, 2H, 3,3'-H); 7.27-7.25 (m, 2H, 1,1'-H); 7.07-7.02 (m, 2H, 2,2'-H). ^{13}C-NMR ($CDCl_3$, 50MHz, ppm): 146.7; 141.5; 140.7; 130.2; 129.4; 128.9; 127.6. DEPT 135° ($CDCl_3$, 50MHz, ppm): 130.2; 129.4; 128.9; 127.6. UV-Vis: 260, 290, 380 (λ, nm).

Electropolymerization of 2,3-di(2-thienyl)quinoxaline

The monomer electropolymerization was carried out by either successive voltammetric scans or step potential perturbations. It was performed in the following conditions: $5.7\cdot10^{-3}$ M monomer, $2,2\cdot10^{-2}$ M supporting electrolyte ($TEABF_4$) in anhydrous dichloromethane or acetonitrile. The optimal potential range to polymerize by successive voltammetric scans was -0.60 to 2.10 V in dichloromethane, and from -0.50 to 1.80 V in acetonitrile. In the case of potential step experiments the optimal applied potential was 1.80 V in dichloromethane, and 1.56 V in acetonitrile.

Results and discussion

Synthesis and characterization of 2,3-di(2-thienyl)quinoxaline

The synthetic route of 2,3-di(2-thienyl)quinoxaline was performed from the procedure previously reported.[11] After 3h 2,2'-thienyl was quantitatively converted to product, without by-products. The purification process led to 98% yield, better than that already reported (89%). [11]

Electrochemical polymerization and characterization

Figure 1a shows the potentiodynamic j/E profiles during the first 20 voltammetric cycles on Pt of the monomer in dichloromethane. It can be observed that the oxidation potential of the electroactive species (near 1.6 V vs SCE) shifts continuously to smaller values when the number of cycles increases, while the corresponding reduction peak remain practically constant near 1.4 V vs SCE. This behavior is analogue to that observed during thiophene oxidation under the same experimental conditions. [14] Then, it could be inferred that the profile observed in this potential range can be assigned to the polymerization through the oxidation of thiophene rings in the molecule. The fact that potential gives less positive values during successive voltammetric scans is attributed to a high conjugation due to the increase of the chain length, as the oligomerization and polymerization processes take place. The oxidation charge is bigger than that of the corresponding reduction peak because in the first are included polymerization and p-doping charges while the reduction process involves only the p-undoping charge.

The other reduction peak initially shifts to less negative values until it reaches a practically constant value near -0.1 V vs SCE after 5 voltammetric cycles, when the electrode comes totally recovered by the polymeric film. This peak can be attributed to n-doping, which is normally observed in quinoxaline rings. [15]

With the aim to elucidate its response, the Pt electrode modified by the polymeric film was later immersed in another cell containing only the supporting electrolyte. Figure 1b shows the voltammetric profile obtained when the same electrolyte employed during electropolymerization was used. It can be clearly appreciated two redox pairs corresponding to a dual p- and n-type doping of polymer. To confirm this observation the response of the Pt modified electrode was now obtained using $LiBF_4$ as supporting electrolyte in the same solvent (Figure 1c). It can be observed that the redox pair attributed to p-doping process remain unchanged while the charge associated to the other redox process, attributed to the n-doping, increase significantly, which can be assigned to a high mobility of Li cations related to tetraehtylammonium, confirming that this process effectively corresponds to the incorporation and expulsion of positive ions during reversible partial polymer reduction (n-doping-undoping).

Considering that these peaks corresponds to p- or n-doping-undoping it is possible to calculate the polymer bandgap from the onset potentials of p- and n-doping processes, and using the empirical relationship proposed by Leeuw et al.[15] The calculated bandgap from this voltammogram (figure 1b) was estimated to be 1.00 eV, which is quite near the optimum bandgap (1.35 eV) for photovoltaic cells according to Janssen et al.[16] This bandgap is smaller than that of the respective monomer, which is in total agreement with the peaks displacement during p- and n-doping processes. The presence of both p- and n-doping make this novel conjugated polymer a good candidate to be used in the elaboration of photovoltaic cells since the loss of efficiency for recombination of the charges would be reduced.

On the other hand, it is worth to mention that this polymer is very stable in both aqueous medium as in normal laboratory environmental conditions for several months.

Figure 1d depict the j/t transients obtained on Pt working electrode during monomer oxidation by a potentiostatic step program. From these responses, the chosen electropolymerization potential was 1.8 V vs SCE. In this way, significant quantities of polymer can be produced in a short time. FTIR spectra shows the characteristic bands expected for the synthetized polymer, indicating that no overoxidation occurs in the potential range employed during electropolymerization. The conductivity of the polymer was $6\cdot10^{-8}$ $S\cdot cm^{-1}$. According to the EA results (Table 1), for each 5 monomer molecules there are 6 BF_4^- ions; since each monomer unit has two thiophene rings, then there is one BF_4^- per two thiophene rings.

Although the obtained polymer was insoluble in all common solvents, a thin film synthesized by only 5 voltammetric cycles was soluble in DMSO, which agrees with the fact that electropolymerization process begins by the deposition of short chain oligomers on the electrode surface. [14,17,18] The UV-Vis spectra of these short chain oligomers and that of the monomer in the same solvent (DMSO) are shown in Figure 2. A batochromic shift of the bands of the short chain oligomers with respect to those of the monomer, confirms the conjugation increase during polymerization. The bandgap of these oligomers calculated from the UV-Vis data is 2.21 eV. The difference from this value and those calculated from the electrochemical data (1.00 eV) is attributed to the conjugation increase when electropolymerization time increase. This agrees with the fact that a greater number of voltammetric cycles or electrolysis time leads to a polymer with higher conjugation, and therefore smaller bandgap. Besides, this difference might also be attributed to the measurement methodology already point out by others authors.

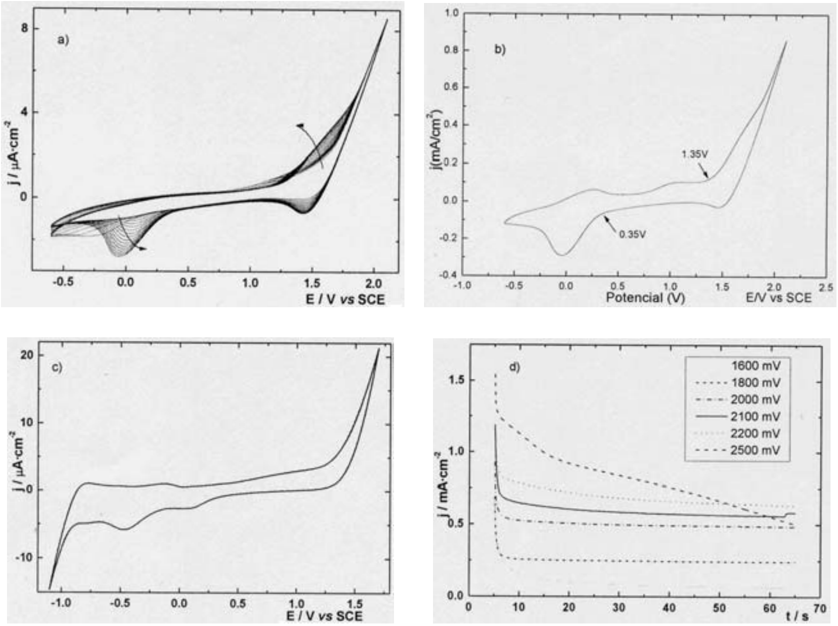


Figure 1. a) Potentiodynamic j/E profiles in CH_2Cl_2 of 2,3-di(2-thienyl)quinoxaline ($5.7\cdot10^{-3}$ M) using $TEABF_4$ as support electrolyte ($2.2\cdot10^{-2}$ M) on Pt disc electrode. Cycles 1 to 20, v = 100 $mV\cdot s^{-1}$. b) Polymer response (cycle n) in a solution containing only electrolyte ($TEABF_4$) $2.2\cdot10^{-2}$ M); v = 100 $mV\cdot s^{-1}$. c) ($LiBF_4$) $2.2\cdot10^{-2}$ M) in dichloromethane; v = 100 $mV\cdot s^{-1}$. d) j/t transients of 2,3-di(2-thienyl)quinoxaline ($5.7\cdot10^{-3}$ M) on Pt disc, using $TEABF_4$ ($2.2\cdot10^{-2}$ M) as support electrolyte in CH_2Cl_2.

Table 1. Elemental analysis results of BF_4^- doped poly(2,3-di(2-thienyl)quinoxaline obtained by potentiostatic method.

Element	% Theoretical *	% Experimental
C	50.66	48.71
H	2.11	1.77
N	7.39	6.83
S	16.89	15.97
B and F	22.95	26.72

*Referred to the % of each element considering the polymer doped with BF_4^- in a relation 1:1

The electropolymerization process was also carried out from an analogue electrolytic solution but using CG as working electrode. The j/t transients obtained in this case were very similar to those obtained on Pt. The optimal potential required on CG was 1.8 V vs SCE, and the deposit was a very uniform film, which showed good adherence in this electrode.

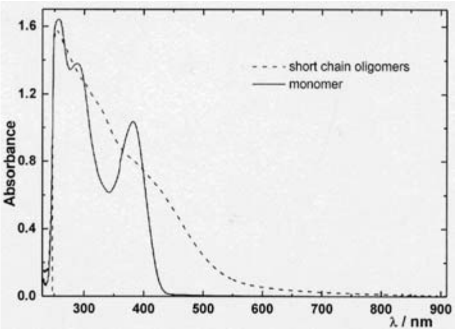


Figure 2. UV-Vis spectra of 2,3-di(2-thienyl)quinoxaline (—) and it polymer (oligomer) (----) in DMSO (5 voltammetric cycles).

The electrochemical behavior of the monomer on Pt in acetonitrile was very similar to that obtained in CH_2Cl_2, although the different potential range is obviously required. The p- and n-doping is observed as in CH_2Cl_2. To carried out potentiostatic experiments, a potential of 1.56 V was imposed in CH_3CN solution, which is smaller than in CH_2Cl_2. It can be explained by the low solubility of the oligomeric species in CH_3CN which produces a fast electrodeposition. This experiments was also carried out on CG as working electrode, and the same results as that on Pt were obtained.

SEM analysis

The polymeric films synthesized by potential step or successive voltammetric scans methods on CG, using CH_3CN as solvent were characterized by SEM analysis. Figure 3 shows the microphotographs of the polymer obtained by both methods. In Figure 3a it can be observed that the film obtained by potential step is homogeneous with respect to the nuclei size, which suggests that an instantaneous bidimensional growing mechanism might be operating. The film obtained by successive voltammetric scans, Figure 3b, is more compact and uniform and the particles are smaller than those obtained by the other method, although the same bidimensional growing mechanism is operating.

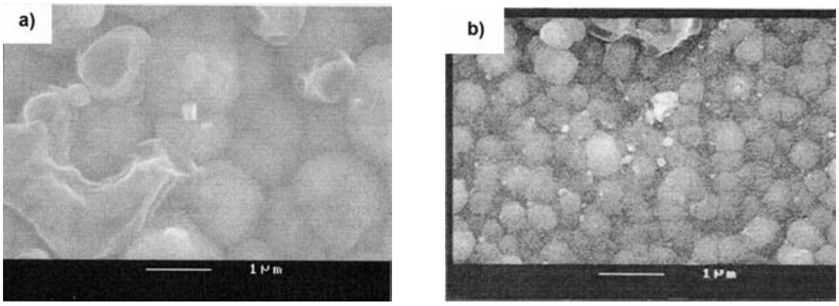


Figure 3. SEM analysis of poly(2,3-di(2-thienyl)quinoxaline) obtained. a) by potential step experiment and b) by successive voltammetric scans of the monomer in CH_3CN.

Theoretical calculations

Hints about the intrinsic reactivity of the system can be obtained from the analysis of the frontier molecular orbitals. The idea is to characterize the polymerization sites and to get insights on the polymerization mechanism. All calculations were carried out using the Gaussian 98 program with the standard 6-311G** basis set at the density functional (DFT) [19,20] level using the hybrid functional B3LYP made of Becke non local exchange functional with the correlation functional of Lee-Yang-Parr [21]. The molecular structure of 2,3-di(2-thienyl)quinoxaline was fully optimized. The analysis of densities of the frontier orbitals is expected to give insights to characterize the sites that are available for electrophilic or nucleophilic attacks.

Figures 4 shows the electron density associated to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). It can be noticed that the more reactive sites for an electrophilic attack (see the HOMO density) correspond to the carbons adjacent to the S atoms in the thiophene rings, therefore polymerization is expected on these sites.

Fukui functions have been quite useful in characterizing quantitatively the specific sites where chemical reaction may takes place, they were calculated using the finite difference approximation, that leads to: [22,23]

$$
\begin{aligned}
fK^{-} &= [q_K\,(N) - q_K\,(N\text{-}1)] \qquad (\mathbf{1})\\
fK^{+} &= [q_K\,(N+1) - q_K\,(N)]
\end{aligned}
$$

where f_k^- and f_k^+ are the electrophilic and nucleophilic indexes that indicate the susceptibility of atom k to react with electrophiles and nucleophiles, respectively. In the above equation, $q_k(N)$ is the atomic charge associated to atom k within the N-electron species. Fukui functions indicate that the preferred carbon atoms for an electrophilic attack are C_1 and C_1' in such a case the thiophene rings gets a positive charge and therefore the p doping takes place there Figure 5a. In contrast, the more reactive sites for a nucleophilic attack (see LUMO density) are more localized on the nitrogen containing heterocycle. In this case it gets negative charge and the n doping takes place on this site Figure 5b. This agrees with the electrochemical results.

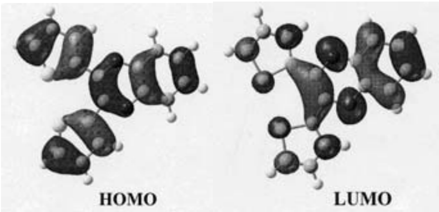


Figure 4. Representation of the HOMO and of the LUMO of 2,3-di(2-thienyl).

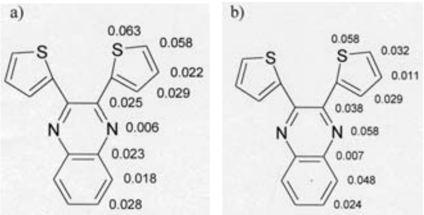


Figure 5. Fukui function values for an a) and b) nucleophilic attack.

Conclusions

A simple method of synthesis with best yield to obtain 2,3-di(2-thienyl)quinoxaline was carried out. A new conjugated polymer combining in its structure thiophene rings and nitrogen containing heterocycles, poly[2,3-di(2-thienyl)quinoxaline], has been synthesized and characterized by FTIR and SEM analysis. This polymer shows p- and n-doping and a low bandgap (1.00 eV), therefore it might be a promissory candidate to be use in electronic devices.

The values of the Fukui function on different atoms of the molecule allows to identify the sites that are able to the electrophilic or nucleophilic attack in agreement with that predicted by the electrochemical results. Theoretical calculations were also useful to characterize the bandgaps of the polymer material from the knowledge of monomer, dimmer and trimmer properties.

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