

## PYRIDINE BASED POLYMERS. SYNTHESIS AND CHARACTERIZATION

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### ABSTRACT

Two new conjugated polymers, poly(2,3-di(thiophen-2-yl)pyrido[2,3-b]pyrazine) and poly(2,3-di(thiophen-2-yl)pyrido[3,4-b]pyrazine), based on thiophene and pyridine rings were chemically and electrochemically synthesized and characterized by IR, UV-Vis and elemental analysis. Monomers were chemically synthesized at high yield percentages and characterized by FTIR and NMR. Polymers showed *p*- and *n*-type doping as well as low *bandgap*, making them potential candidates for the development of electronic devices.

**Keywords:** 2,3-di(thiophen-2-yl)pyrido[2,3-b]pyrazine, 2,3-di(thiophen-2-yl)pyrido[3,4-b]pyrazine, poly(2,3-di(thiophen-2-yl)pyrido[2,3-b]pyrazine) and poly(2,3-di(thiophen-2-yl)pyrido[3,4-b]pyrazine).

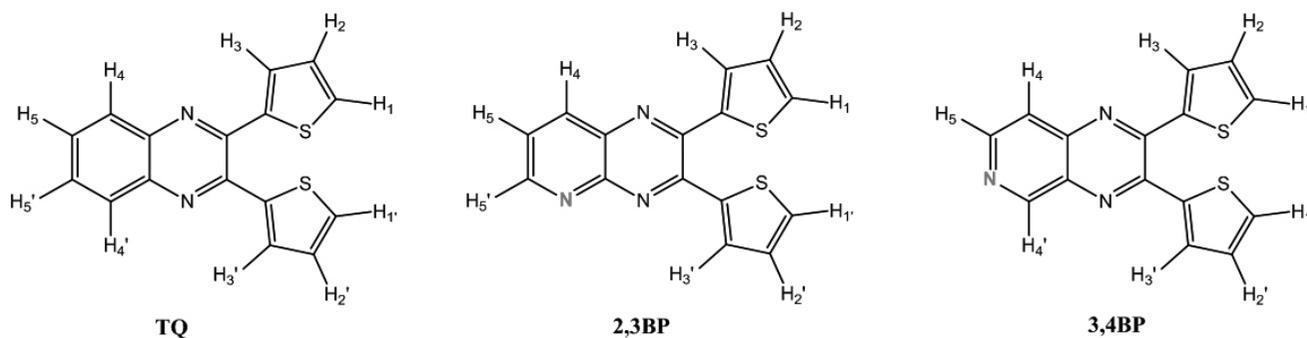
### INTRODUCTION

Thiophene based polymers have been widely investigated for the development of new technologic applications<sup>1,2</sup>. On the other hand, thanks to its structural diversity, nitrogen containing heterocycles have also attracted considerable interest in recent years due to their unique properties<sup>3-5</sup>. Thiophene and quinoxaline copolymers have been employed as electronic carriers in electroluminescent devices<sup>6</sup> and as material for organic light-emitting devices<sup>7</sup>, among others.

Likewise, thiophene combined with other hetero-aromatic rings such as pyrrole, pyridine, pyrazine, quinoxaline and aniline has been studied in order to obtain a stable compound that has low enough reduction potential to be used instead of fullerenes as *n*-type semiconductor in organic solar cells<sup>8,9</sup>.

In this context, our research group has developed different materials based on thiophene rings, and nitrogen containing rings in its structure to be employed for the development of photovoltaic devices<sup>10,11</sup>, e.g. the synthesis of 2,3-di(thiophen-2-yl)quinoxaline monomer was achieved using a simple method, with 98 % yield<sup>12</sup>. Other authors have found new synthetic route for the synthesis of this compound, using Grignard reagents with a 90% yield<sup>13</sup>. Moreover, it has also been reported the synthesis of pyrazine derivatives with antimicrobial activity, with yields close to 40%<sup>14</sup>.

This work is the continuation of our study concerning to conjugated pyrazine-like structures with the insertion of a new nitrogen atom into the monomer, from pyridine-based monomers synthesis, aimed to obtaining a better performance using 2,3-di(thiophen-2-yl)quinoxaline as reference, Fig. 1.



**Figure 1.** a) 2,3-di(thiophen-2-yl)quinoxaline (TQ), b) 2,3-di(thiophen-2-yl)pyrido[2,3-b]pyrazine, c) 2,3-di(thiophen-2-yl)pyrido[3,4-b]pyrazine.

### EXPERIMENTAL

#### Materials

All starting materials and reagents used were: acetonitrile (98 %, Merck); ethyl acetate for liquid chromatography (99.8%,Merck); chloroform (99.4%,Merck), anhydrous ferric chloride (Sigma); iodine for analysis (99.8%, Merck), ethanol (98 %, Merck), *o*-phenylenediamine (99 %, Aldrich Chemistry); silica gel 60 (Merck); 2,2'-thenil (98 %, Aldrich Chemistry); 2,3-diaminopyridine (Merck); 3,4-diaminopyridine (Merck); HCl concentrated (37 %, Merck). All reagents were used without further purification.

#### Measurements

<sup>1</sup>H NMR spectra were collected on a Bruker 400 spectrometer using chloroform-*d* as solvent and TMS as internal standard. FT-IR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets. Elemental analysis was performed on a Fison 1108 microanalyser. UV-VIS

spectra were obtained on a Analytik Jena Specord 40, using acetonitrile and chloroform 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 Voltammeter Analyzer CV-50W by BAS; electrochemical experiments were performed in a conventional three electrodes cell, using anhydrous acetonitrile as solvent, and 0.1 mol·L<sup>-1</sup> tetramethylammonium hexafluorophosphate (NH<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>PF<sub>6</sub>, supplied by Aldrich) as supporting electrolyte. It was employed a Ag/AgCl electrode as reference in tetramethylammonium chloride with potential adjusted to that of SCE. The working electrodes were platinum disc (0.1 cm<sup>2</sup> 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 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).

From UV-Vis spectra of the doped polymers the forbidden energy band was calculated, following the Born-Einstein energy relationship<sup>6</sup>. The frontier orbital energy HOMO ( $E_{\text{HOMO}}$ ) correlates linearly with the oxidation onset potential ( $E_{\text{on}}$ ) and it was calculated directly from the voltammograms<sup>10</sup>.

### Synthesis of monomers

#### Synthesis of 2,3-di(thiophen-2-yl)quinoxaline (TQ)

The synthetic route of 2,3-di(thiophen-2-yl)quinoxaline was performed from the procedure previously reported, with 93 % yield<sup>12</sup>. A mixture of 2,2'-thenil (200 mg; 0.9 mmol) and *o*-phenylenediamine (291 mg; 2.7 mmol) in ethanol was refluxed for 3 h and cooled to room temperature<sup>12</sup>. Elemental analysis, found % (calculated %): C, 65.23 (65.30); H, 3.54 (3.40); N, 9.58 (9.52); S, 21.65 (21.77). Melting point: 146.1-146.6 °C. FT-IR ( $\text{cm}^{-1}$ ): 3488.7, 3075.5, 1515.9, 1450.9, 1417.5, 836.9, 762.5. <sup>1</sup>H-NMR ( $\text{CDCl}_3$ , 400 MHz, ppm): 8.01-8.05 (m, 2H, 4,4'-H); 7.75-7.70 (m, 2H, 5,5'-H); 7.51-7.49 (m, 2H, 3,3'-H); 7.27-7.23 (m, 2H, 1,1'-H); 7.06-7.02 (m, 2H, 2,2'-H). UV-Vis (nm): 257, 274 and 382.

#### Synthesis of 2,3-di(thiophen-2-yl)pyrido[2,3-b]pyrazine (2,3BP)

A mixture of 2,2'-thenil (500 mg; 2.26 mmol) and 2,3-diaminepyridine (1.4 g, 0.128 mol) in ethanol was refluxed until a yellow solid was observed. The monomer was purified using a silica gel column and hexane : ethyl acetate mixture as eluent. Product was obtained in a 75 % yield. Elemental analysis, found % (calculated %): C, 60.85 (60.99); N, 14.29 (14.23); H, 2.54 (3.07); S, 18.98 (21.71). Melting point: 165.3-165.5 °C. FT-IR ( $\text{cm}^{-1}$ ) 3430.8, 3088.4, 1516.3, 1416.7, 845.8, 714.9. <sup>1</sup>H-NMR ( $\text{CDCl}_3$ , 400 MHz, ppm): 9.5 (s, 1H, 6); 8.79 (s, 1H, 4); 7.91-7.89 (d, 1H, 5); 7.60-7.57 (m, 2H, 1,1'); 7.38-7.37 (m, 2H, 3,3'); 7.10-7.06 (m, 2H, 2,2'). UV-Vis (nm): 253, 286 and 391.

#### Synthesis of 2,3-di(thiophen-2-yl)pyrido[3,4-b]pyrazine (3,4BP)

3,4BP was synthesized following the same procedure described above. The product was obtained in a 81 % of yield. Melting point: 163.9-164.8 °C. FT-IR ( $\text{cm}^{-1}$ ) 3447.8, 3101.7, 1596.8, 1520.1-1410.7, 829.7, 728.7. <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ) 400 MHz, ppm): 9.39 (s, 1H, 6); 8.68-8.67 (d, 1H, 4); 7.89-7.78 (d, 1H, 5); 7.49-7.47 (t, 2H, 1,1'); 7.28-7.27 (m, 2H, 3,3'); 7.0-6.96 (m, 2H, 2,2'). UV-Vis (nm): 253, 283 and 390.

### Chemical Polymerization

All of the polymers were synthesized in chloroform using methodology previously reported<sup>12</sup>. The corresponding polymers were named PTQ, P2,3BT and P3,4BT, respectively. Each monomer and  $\text{FeCl}_3$  were dissolved in chloroform to achieve a molar ratio of  $\text{FeCl}_3$  to monomer (4:1), while it was being stirred at room temperature under a  $\text{N}_2$  flow during 72 h. The resulting polymer was washed with water and ethanol, and the precipitated is dried in a vacuum oven. The resulting polymers were compacted into pellets and weighed. These pellets were then put into open weighing bottles, which were placed in a small desiccator protected from light and charged with ground iodine powder. Iodine uptake by the polymers was followed by mass differential.

Doped polymers were dissolved in DMSO to obtain UV-Vis absorption spectra. This enabled the forbidden energy band of each material to be worked out.

#### Synthesis of poly(2,3-di(2-thenil)quinoxaline) (PTQ)

PTQ was synthesized by following the same procedure explains above. After purification a brown-red solid was obtained with a yield of 34%. Elemental analysis, found % (calculated %): C, 54.71 (66.28); N, 14.29 (9.52); H, 1.82 (3.42); S, 17.15 (21.78). FT-IR ( $\text{cm}^{-1}$ ) 3441.1, 3093.9, 1423.2, 1418, 851.9, 763.4. UV-Vis (nm): 254, 291, 384.

#### Synthesis of poly(2,3-di(thiophen-2-yl)pyrido[2,3-b]pyrazine) (P2,3BP)

P2,3BP was synthesized following the same procedure explains for chemical polymerization. Additionally the solid was washed twice with ethyl acetate. After purification a brown-red solid was obtained with a yield of 31 %. Elemental analysis: found % (calculated %): C, 54.71 (60.99); N, 10.91 (14.23); H, 1.9 (3.07); S, 15.31 (21.71). FT-IR ( $\text{cm}^{-1}$ ): 3423.9, 3084.6, 1520, 852.3, 715.3. UV-Vis (nm): 260, 394.

#### Synthesis of poly(2,3-di(thiophen-2-yl)pyrido[3,4-b]pyrazine) (P3,4BP)

P3,4BP was synthesized by the same procedure explains for chemical polymerization, and the solid was washed with acetonitrile. After purification

a polymer as brown-red solid was obtained with a yield of 38 %. Elemental analysis: found % (calculated %): C, 49.27 (60.99); N, 10.91 (14.23); H, 1.9 (3.07); S, 15.31 (21.71). FT-IR ( $\text{cm}^{-1}$ ): 3430.1, 3100.4, 3074.6, 1598, 1520.4, 827.8, 729.8. UV-Vis (nm): 257, 290 and 395.

### Electrochemical polymerization

Electrochemical polymerizations were carried out following the procedure previously reported<sup>12</sup>.

#### Electropolymerization of 2,3-di(thiophen-2-yl)quinoxaline

The monomer electropolymerization was carried out by 20 successive voltammetric scans. It was performed in the following conditions:  $5.7 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$  monomer,  $2.2 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$  supporting electrolyte ( $\text{NH}_4(\text{CH}_3)_4\text{PF}_6$ ) in anhydrous acetonitrile. The optimal potential range to polymerize was -0.50 to 1.80 V.

#### Electropolymerization of 2,3-di(thiophen-2-yl)pyrido[2,3-b]pyrazine

P2,3BP electrosynthesis was carried out by 30 successive voltammetric scans. It was performed in the following conditions:  $5.7 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$  monomer,  $2.2 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$  supporting electrolyte ( $\text{NH}_4(\text{CH}_3)_4\text{PF}_6$ ) in anhydrous acetonitrile. The optimal potential range to polymerize was -1,0 to 1.5 V.

#### Electropolymerization of 2,3-di(thiophen-2-yl)pyrido[3,4-b]pyrazine

P3,4BP electrosynthesis was carried out by 30 successive voltammetric scans. It was performed in the following conditions:  $5.7 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$  monomer,  $2.2 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$  supporting electrolyte ( $\text{NH}_4(\text{CH}_3)_4\text{PF}_6$ ) in anhydrous acetonitrile. The optimal potential range to polymerize was -1.0 to 1.5 V.

## RESULTS AND DISCUSSION

### Synthesis and characterization of monomers

The synthetic route of all monomers was performed from the procedure previously reported<sup>12</sup>. After 3 h all compounds were quantitatively converted to product, without by-products.

### Chemical polymerization and characterization

All polymerizations afforded low reaction yields, *ca.* 30 %, considering just the insoluble fraction or higher molecular weight. Elemental analysis showed significant variation in the experimental and theoretical percentages, considering that the polymer in its oxidized state has  $\text{Fe}^{2+}$  ions trapped in its structure (2-3 atoms of Fe per monomer) which justifies the lower concentration of elements in the actual sample.

The solution UV-Vis absorption spectra for all polymers showed two or three distinct absorption bands: two or a single band around 250-300 nm can be assigned to the  $\pi-\pi^*$  transition while a long-wavelength absorption peaks, around 390 nm, can be attributed to intramolecular charge transfer between thiophene rings and acceptor moieties<sup>15,16</sup>. The polymers absorption spectra are red shifted compared to the corresponding monomers spectra (Figure 2), which can be attributed to an increase in the chain length<sup>17</sup>.

From UV-Vis spectrum of the doped polymers the forbidden energy band was calculated, following the Born-Einstein energy relationship<sup>6</sup>. Likewise, the conductivity of doped polymers was measured; an increase of up to 6 orders of magnitude compared to the neutral polymers was observed. Comparison of P2,3BP and P3,4BP with PTQ showed a conductivity increase of about 10 times, which is probably related to the insertion of the nitrogen atom into the aromatic ring that would confer higher planarity to the polymeric chain, generating thus improved charge transfer between parallel chains, Table 1.

**Table 1.** Conductivity of the synthesized species and  $E_g$  of the doped polymers.

polymer	conductivity ( $\text{S} \cdot \text{cm}^{-1}$ )		bandgap energy (eV)
	monomer	polymer	
PTQ	$2.0 \cdot 10^{-5}$	$2.4 \cdot 10^{-5}$	3.05
P2,3BP	$3.0 \cdot 10^{-10}$	$1.1 \cdot 10^{-4}$	3.82
P3,4BP	$3.0 \cdot 10^{-10}$	$0.7 \cdot 10^{-4}$	3.33

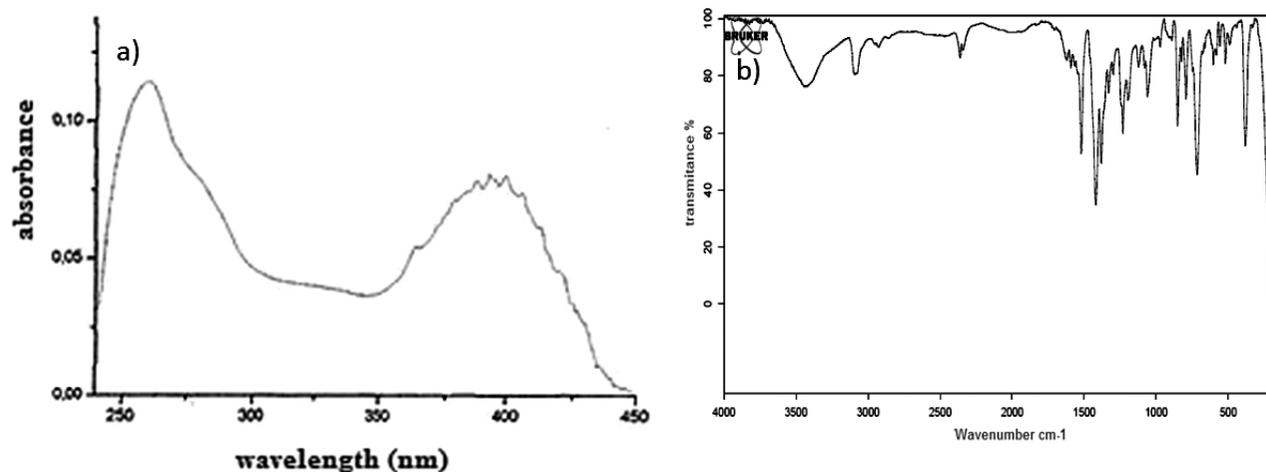


Figure 2. a) P2,3BP UV-Vis absorption spectrum; b) P2,3BP IR spectrum.

### Electrochemical polymerization and characterization

Figure 3 shows the potentiodynamic  $j/E$  profiles during the first 20 voltammetric cycles on Pt of each monomer in acetonitrile. Table 2 shows the oxidation potential of all monomers on Pt. In TQ potentiodynamic  $i/E$  profile it can be observed that the oxidation potential of the electroactive species (near 1.4 V vs SCE) shifts continuously to smaller values when the number of cycles increases, until it stabilized near 1.3 V while the corresponding reduction peak remain practically constant in 0.35 V. This behavior was previously reported under similar experimental conditions. 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<sup>12</sup>. It is well know that 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 monomers present the same behavior showing oxidation potentials near 1.1 and 1.2 for P2,3BP and P3,4BP, respectively (Table 2).

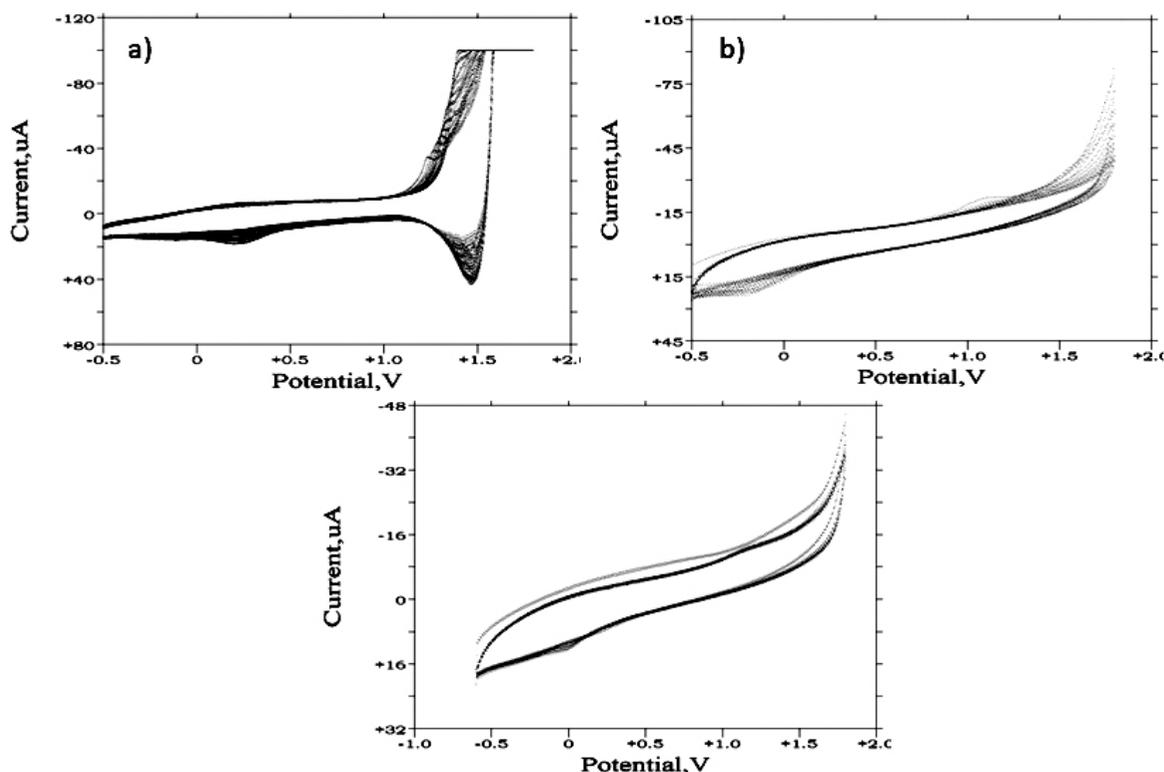


Figure 3. Potentiodynamic  $i/E$  profiles in acetonitrile: a) 2,3-di(2-thiophen)quinoxaline; b) 2,3-di(2-thiophenyl)pyrido[2,3-b]pyrazine; c) potentiodynamic 2,3-di(2-thiophenyl)pyrido[3,4-b]pyrazine.

**Table 2.** Electrical properties of the synthesized polymers.

polymer	reduction potential (eV)	oxidation potential (eV)	HOMO (eV)	LUMO (eV)
PTQ	0.35	1,35	-5.8	-2.75
P2,3BP	-0.2	1.10	-5.5	-1.68
P3,4BP	-0.9	1.20	-5.6	-2.27

### CONCLUSIONS

The synthesis of the proposed monomers was possible, following the same methodology previously implemented, with very good results. A new series of polymers was synthesized and characterized by FT-IR and NMR. Electrochemical characterization demonstrates that the polymers showed *p*- and *n*-doping and low *bandgap* (~ 1.00 eV), making those prospective candidates for the development of electronic devices.

### DEDICATION

This work is dedicated to Dr. Luis Núñez Vergara (RIP), to whom we express our sincere admiration and respect.

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