# Preparation and characterization of novel polythiophenes bearing oligo(ethylene glycol) spacers and porphyrin units: Optical and electrochemical properties

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## ABSTRACT

Two thiophene monomers: 3-methyltetra(oxyethylene)oxy-4-methylthiophene (**MT**) and a monomer containing a meso-3,5-ditert-butyl-tetraphenylporphyrin unit linked via a tetra(ethylene glycol) spacer (**MTP**) were synthesized and characterized. Both monomers were copolymerized in different ratios **MT**:**MTP** (2:1 and 4:1), using $FeCl_3$ as oxidizing agent, to give the corresponding copolymers (**CTP-1** and **CTP-2**). **MTP** was also homopolymerized under the same reaction conditions to give the homopolymer (**PTP**). The obtained monomers and polymers were characterized by FTIR, $^1$H and $^{13}$C NMR spectroscopies. On the other hand, the optical properties of the polymers were studied by absorption and fluorescence spectroscopy in THF solution. All polymers exhibited the typical absorption bands of the porphyrin units: a Soret band at $\lambda = 422$ nm and four Q-bands between $\lambda = 500$ and 700 nm, as well as an additional band at $\lambda = 451$ nm, due to the polythiophene backbone. **PTP**, **CTP-1** and **CTP-2** showed fluorescence in the region between $\lambda = 500$ and 800 nm. Finally, the electrochemical properties of **MTP** and the obtained polymers were studied by cyclic voltammetry. Tetraphenylporphyrin (**TPP**) was used as model compound for comparative purposes. The obtained electrochemical data revealed the presence of the redox processes due to the porphyrin and the thiophene units. The reactivity of **MTP** toward electrochemical polymerization was studied.

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## 1. Introduction

Polythiophene (**PT**) is one of the most promising electro-conducting polymers due to its high stability, ease of structural modification and controllable electrochemical behavior. At the beginning, its applications were limited because of its insolubility in many organic solvents, due to its strong π-conjugated structure. Furthermore, alkyl chains have been introduced at the 3-position of the thiophene unit in order to obtain monomers able to give soluble polymers. This new kind of poly(3-alkylthiophene)s are processable conducting polymers, whose electronic properties can be modified, allowing their full characterization by chemical and physical methods [1]. The stability of poly(3-alkylthiophenes) in the doped state can be achieved by releasing the side alkyl chains crowding along the backbone or by introducing alkoxy groups. The incorporation of alkoxy groups into polythiophenes increase their conductivity significantly without reducing their solubility [2,3].

For many polythiophenes, interesting properties such as thermochromism [4–6], ionochromism [5–7], photochromism [8], piezochromism [9] and biochromism [10] have been reported in the literature. These color changes are due to transitions from a planar to a twisted conformation of the polymer backbone and vice versa, thereby modifying the effective conjugation length, which produces a shift of the absorption bands in their UV–visible spectra [11]. In polymers bearing alkoxy groups at 3-position of the thiophene rings, the lone pairs of the oxygen atom enter into conjugation with the polymer backbone, thereby inducing a planar conformation [12]. This causes an augment in the effective degree of conjugation, which improves significantly the electronic mobility and conductivity in these polymers.

The chromic properties of substituted polythiophenes make them excellent prospects for light emitting diodes [13], gas sensors [14–16], biomedical applications [17], metal ions sensors [18,19] and biosensors [20–23]. Besides, due to their potential medical and industrial applications in the elaboration of electrochemical ion sensors, porphyrin functionalized conducting polymers based on polythiophene have been prepared, in order to get a controlled electrochemical response to metal ions.

Porphyrins, which are highly delocalized π-systems, are a unique category of ionic scavengers, whose recognition properties arise from the heteroatoms present in their structure [24]. Due to their efficient light absorption, porphyrins have been the subject

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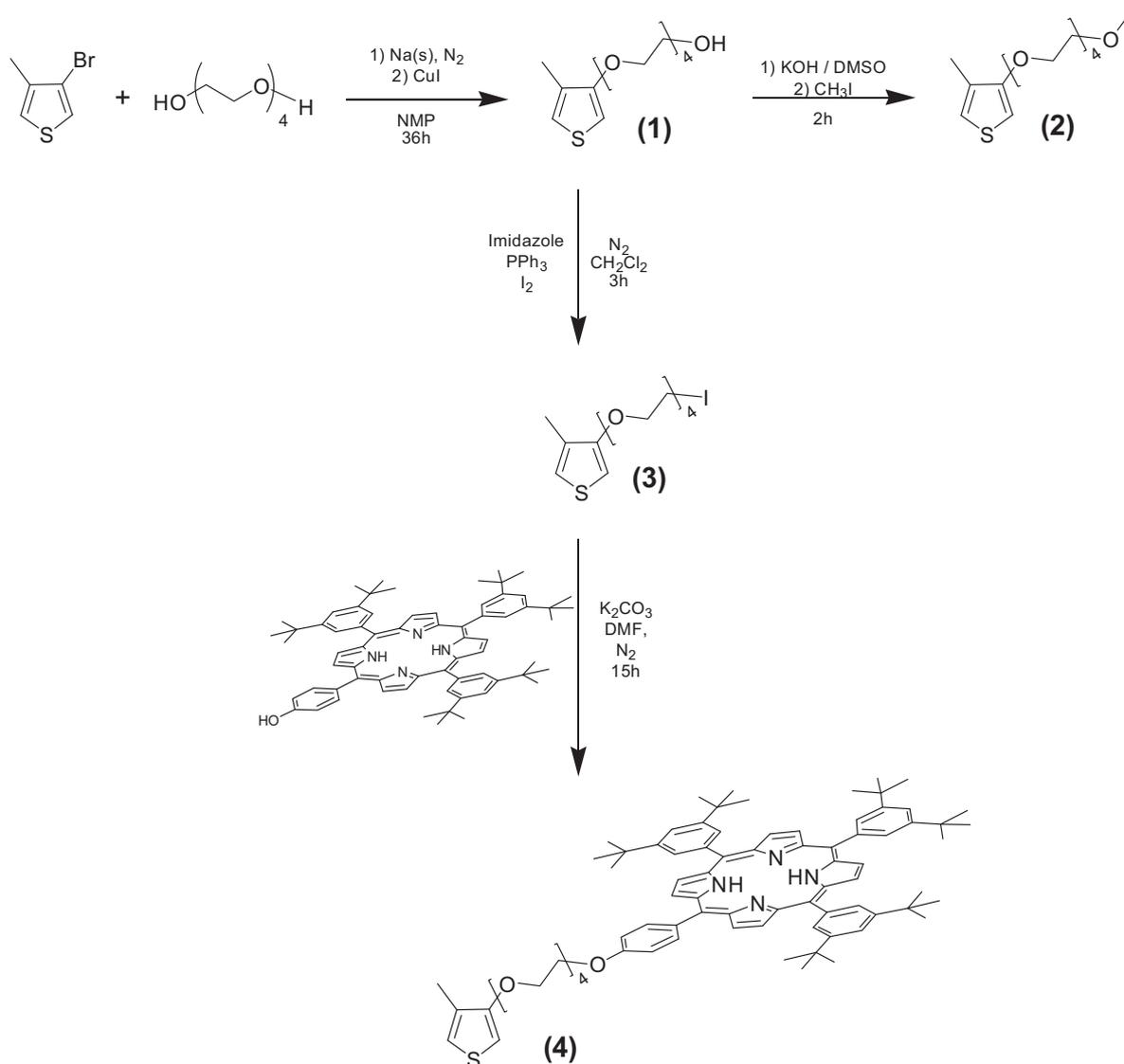
**Fig. 1.** Synthesis of the monomer **MTP**.

of intense research in solar energy transfer [25,26] and electron transfer systems [27,28]. Incorporation of porphyrins into polymers allows the easy handling, recycling and adaptation of this important set of complexant agents to continuous processes.

Herein, we report the synthesis and characterization of novel polythiophenes containing free-base meso-3,5-ditert-butyl-tetraphenylporphyrin units linked via well-defined oligo(ethylene glycol) spacers, for its future application in the development of solar cells. The obtained polymers were fully characterized by FTIR, ^{1}H and ^{13}C NMR spectroscopies. Moreover, their optical properties were investigated by absorption and fluorescence spectroscopy in THF solution, and their electrochemical behavior was studied by cyclic voltammetry in dichloromethane. Finally, the reactivity of **MTP** monomer toward electrochemical polymerization was also tested.

## 2. Experimental work

### 2.1. Apparatus

FTIR spectra of monomers and polymers were recorded on a Nicolet 510 P spectrometer in KBr pellets for solids and in film

for liquid compounds. ^{1}H NMR and ^{13}C NMR spectra of all compounds were carried out in CDCl$_3$ solution, using a Bruker Avance 400 spectrometer, operating at 400 and 100 MHz for ^{1}H and ^{13}C, respectively. Absorption spectra of the polymers in THF solution (concentration $3 \times 10^{-5}$ M) were scanned on a Varian Cary 1 Bio UV/vis spectrophotometer model 8452A. Molecular weights of the polymers, were determined by Gel Permeation Chromatography (GPC), using a Waters 2695 Instrument connected to a Differential Refractive Index Detector model Waters 2414. Measurements were performed using tetrahydrofurane (THF) as solvent against a polystyrene standard.

Steady state fluorescence spectra were recorded on a Photon Technology International LS-100 steady-state system with a pulsed xenon flash lamp as the light source. The slit widths on the excitation and emission monochromators equaled 2 and 1 nm, respectively. All spectra were obtained in solution (concentration $3 \times 10^{-6}$ M) with the usual right-angle configuration, exciting at $\lambda = 420$ nm.

Electrochemical measurements were performed with an Autolab PGSTAT100N in a small volume three-electrode cell. The electrolyte solution consisted of 0.10 M Bu$_4$NPF$_6$ (electrochemical grade from Fluka) in anhydrous CH$_2$Cl$_2$ (Aldrich 99.8%, <0.001%
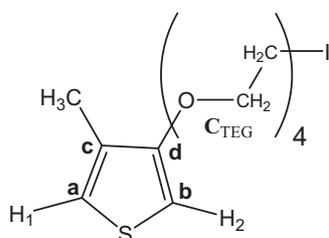
**Scheme 1.**

$H_2O$). $CH_2Cl_2$ was used as received and transferred via syringe under nitrogen. All the solutions were degassed with high purity nitrogen, which was pre-saturated with the solvent before entering the cell. The useful potential range for the electrolytic medium was from 1.4 V to −2.5 V. The working electrode was a 1.0 mm diameter glassy carbon electrode, a Pt wire served as auxiliary electrode, and an Ag wire was used as pseudo reference electrode. Ferrocene (Fc) was employed as an internal reference, and all potentials were referenced relative to the ferrocenium/ferrocene couple ($Fc^+/Fc$). The registered value of the $Fc^+/Fc$ couple in $CH_2Cl_2$ was 0.369 V. The highly polished glassy carbon electrode was repolished before use with 0.05 μm alumina paste (Buehler), rinsed with water, and sonicated for 5 min in distilled water. Then it was rinsed with acetone and dried with a tissue. All experiments were performed at room temperature (298 ± 2 K). Cyclic voltammograms were recorded at 0.1 V/s. For comparison purposes, cyclic voltammograms of tetraphenylporphyrin **TPP** were scanned under the same experimental conditions.

## 2.2. Chemicals

3-Bromo-4-methylthiophene, N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), methyl iodide and $FeCl_3$ employed in the synthesis were purchased from Aldrich and used as received. Prior to use, tetra(ethylene glycol) was dried under vacuum. Chloroform, used in the polymerizations was distilled over calcium hydride ($CaH_2$) in order to remove traces of water. The meso-3,5-ditert-butyl-tetraphenylporphyrin derivative employed in this work was prepared according to the method previously reported in the literature [29].

## 2.3. Synthesis of monomers and polymers

2-(2-(2-(2-(4-Methylthiophen-3-yloxy)ethoxy)ethoxy)ethoxy) ethanol (**1**) and 13-(4-methylthiophen-3-yloxy)-2,5,8,11-tetraoxatridecane (**MT**) (**2**) were synthesized according to the procedure previously reported by us [30,31].

3-(2-(2-(2-(2-Iodoethoxy)ethoxy)ethoxy)ethoxy)-4-methylthiophene (**3**) was obtained from **1** (Fig. 1) using a similar procedure to that previously described by us [30]. First, $CH_2Cl_2$ (5 mL), triphenylphosphine (0.393 g, 1.5 mmol), imidazole (0.102 g, 1.5 mmol) and iodine (0.381 g, 1.5 mmol) were mixed in a bottom round flask under inert atmosphere. Then, a solution of **1** (0.290 g, 1 mmol) in anhydrous dichloromethane (1 mL) was added. The solution was reacted for 3 h and the crude product was washed with water, in order to remove salts formed during the reaction. The organic phase was dried with anhydrous $MgSO_4$ and concentrated at reduced pressure. Finally, this compound was purified by flash column chromatography on silica gel, using a mixture of ethyl acetate:hexanes 80:20 as eluent. The pure product was obtained as light yellow oil (0.284 g, 0.72 mmol). Yield: 72%.

$^1$H NMR ($CDCl_3$, 400 MHz, ppm) (Scheme 1): 6.81 (s, 1H, $H^1$), 6.17 (s, 1H, $H^2$), 4.11 (t, $J_1$ = 4.89 Hz, $J_2$ = 4.73 Hz, 2H, tioph-O-$\underline{CH_2}$), 3.86 (t, $J_1$ = 4.86 Hz, $J_2$ = 4.72 Hz, 2H, tioph-O-$CH_2$-$\underline{CH_2}$), 3.76–3.73
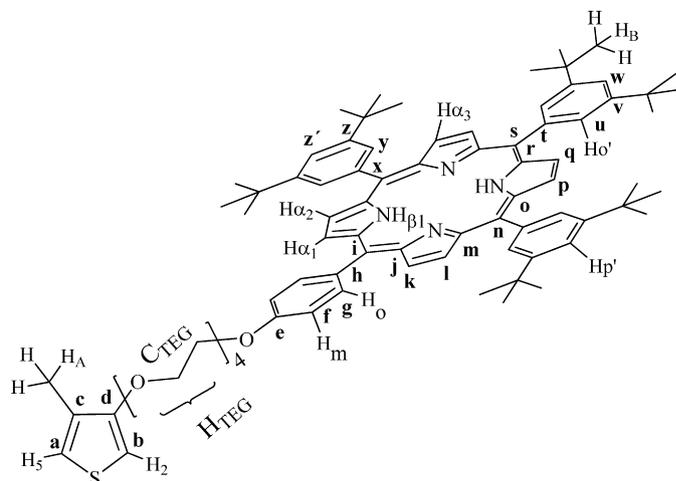


**Scheme 2.**

(m, 4H, $OCH_2$), 3.69–3.66 (m, 6H, all other $OCH_2$), 3.25 (t, $J_1$ = 6.92 Hz, $J_2$ = 6.73 Hz, 2H, $CH_2$-I), 2.10 (s, 3H, tioph-$CH_3$). $^{13}$C NMR ($CDCl_3$, 100 MHz, ppm) (Scheme 1): 156.0 (1C, $C_d$), 129.28 (1C, $C_c$), 120.07 (1C, $C_a$), 96.68 (1C, $C_b$), 72.11, 71.04, 70.88, 70.78, 70.36, 69.85, 69.77 (7C, $C_{TEG}$), 12.91 (1C, tioph-$CH_3$), 3.12 (1C, $CH_2$-I). HRMS ($C_{13}H_{21}O_4I$) $M^+$: $m/z$ = 368.19. Calculated: 368.20.

### 2.3.1. Monomer bearing a meso-3,5-ditert-butyl-tetraphenylporphyrin unit (**MTP**) (**4**)

**3** (0.043 g, 0.106 mmol) and the porphyrin derivative (0.104 g, 0.106 mmol) dissolved in DMF (15 mL) were reacted in the presence of $K_2CO_3$ (0.0294 g, 0.212 mmol), KI (0.0096 g, 0.0581 mmol) and a trace of 18-crown-6 ether. The reaction mixture was heated to reflux for 15 h; after this time, it was cooled to room temperature and concentrated at reduced pressure. The crude product was purified by flash column chromatography in silica gel, using hexanes:chloroform 7:3 as eluent, in order to remove the unreacted porphyrin derivative, and then with hexanes:ethyl acetate 7:3. The pure product (**4**) was obtained as a violet solid (0.050 g, 0.0423 mmol). Yield 17%.

$^1$H NMR (400 MHz, $CDCl_3$) (Scheme 2): $\delta$ = 8.91–8.94 (m, 8H), 8.11–8.18 (m, 8H), 7.83–7.834 (m, 3H), 7.28–7.33 (m, 3H), 6.83–6.84 (d, 1H), 6.18–6.19 (d, 1H), 4.44–4.46 (t, 2H), 4.15–4.17 (t, 2H), 4.07–4.1 (t, 2H), 3.89–3.94 (m, 4H), 3.80–3.85 (m, 6H), 2.14 (s, 3), 1.56 (s, 54H), −2.64 (s, 2H) ppm.

$^{13}$C NMR (100 MHz, $CDCl_3$) (Scheme 2): $\delta$ = 158.73 ($C_d$), 155.98 ($C_e$), 148.76 ($C_j$, $C_m$, $C_o$, $C_r$), 141.44 ($C_k$, $C_l$, $C_p$, $C_q$) 135.44 ($C_h$), 135.19 ($C_g$), 131.21, 129.72–129.22 ($C_y$, $C_{z'}$, $C_u$, $C_w$), 121.28 ($C_a$), 120.96, 119.90 ($C_n$, $C_s$), 119.45 ($C_i$), 112.98 ($C_f$), 96.84 ($C_b$), 71.10, 71.03, 70.87, 70.02, 69.82, 67.97 ($C_{TEG}$), 35.03, 31.73 (quaternary carbons of the tert-butyl groups), 12.58 ($CH_3$ of the tert-butyl groups) ppm.

### 2.3.2. Synthesis of the homopolymer (**PTP**)

Monomer **MTP** (**4**) (0.0332 g, 0.0281 mmol) was dissolved in dry $CH_2Cl_2$ (20 mL) and the solution was stirred for 10 min under inert atmosphere. A solution of $FeCl_3$ (0.0185 g, 0.114 mmol) in $CH_2Cl_2$ (10 mL) was added to the monomer solution until the mixture turned green; then it was stirred for 12 h. After this time, methanol (20 mL) was added to the reaction mixture, which became violet and was poured into water (60 mL) in order to precipitate the polymer. The crude product was separated by filtration, washed with methanol and treated with $NH_4OH$ 20% in order to reduce the polymer, since it was obtained in the oxidized form. Afterwards the polymer was purified by flash column chromatography in silica gel using hexanes:ethyl acetate 7:3 as eluent, increasing gradually the
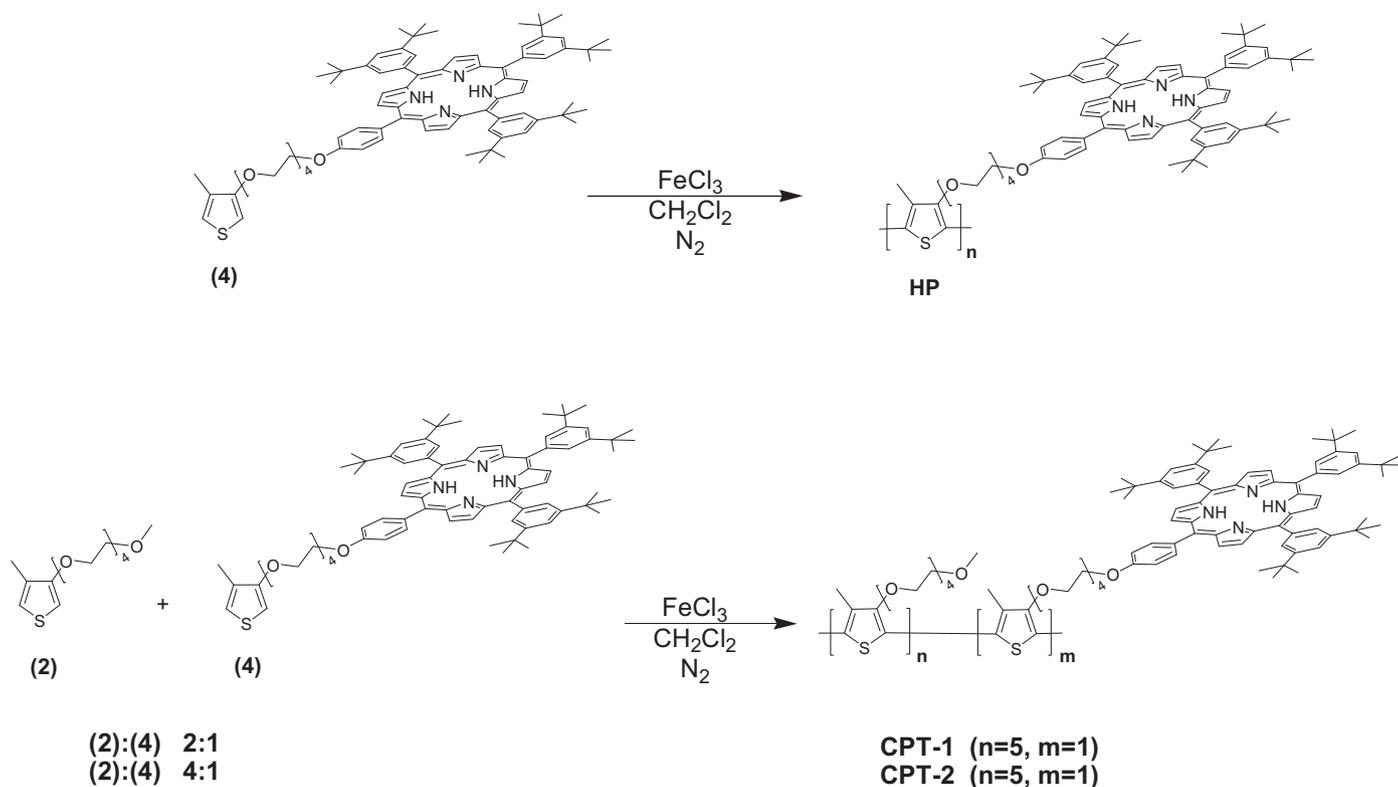
**Fig. 2.** Synthesis of the polymers **PTP**, **CTP-1** and **CTP-2**.

polarity until pure ethyl acetate. The pure polymer was obtained as a purple solid (0.015 g). Yield: 45%.

^{1}H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.88–8.91, 8.09–8.1, 7.8, 7.73–7.75, 7.54–7.56, 4.31–4.34, 3.66–3.79, 1.72–1.76, 1.54, −2.68 ppm.

### 2.3.3. Synthesis of copolymer (CTP-1)

**MTP** (**4**) (0.040 g, 0.0338 mmol) and **MT** (**2**) (0.0183 g, 0.0676 mmol) were dissolved in CH$_2$Cl$_2$ (4 mL); then FeCl$_3$ (0.0723 g, 0.0445 mmol) was added and the reaction mixture was stirred for 12 h. After this time, methanol (20 mL) and water (50 mL) were added in order to precipitate the polymer. The crude product was isolated by filtration and reduced with NH$_4$OH. Finally, the polymer was purified by soxhlet extraction, using a mixture of methanol:hexanes 8:2. After 12 h, the mixture was changed and the extraction was carried out with pure chloroform. The pure copolymer **CTP-1** was obtained as a dark purple solid (11.2 mg). Yield: 17%.

^{1}H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.88–8.90, 8.08–8.09, 7.79–7.8, 4.03, 3.78–3.79, 3.64–3.69, 3.54–3.56, 3.38, 2.05, 1.52, −2.69 ppm.

### 2.3.4. Synthesis of copolymer CTP-2

A solution of **MTP** (**4**) (0.0307 g, 0.0259 mmol) and **MT** (**2**) (0.0282 g, 0.1038 mmol) in CH$_2$Cl$_2$ (4 mL) was prepared; then FeCl$_3$ (82.5 mg) was added and the reaction mixture was stirred for 12 h. Afterwards, methanol (20 mL) and water (50 mL) were added in order to induce the precipitation of the polymer. The crude product was separated by filtration and reduced with NH$_4$OH. Furthermore, the polymer was purified by soxhlet extraction using a mixture of methanol:hexanes 8:2, and then chloroform 100%. The pure copolymer **CTP-2** was obtained as a dark purple solid (20.2 mg). Yield: 26%.

^{1}H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.89–8.90, 8.53–8.58, 8.45–8.48, 8.09, 7.79, 7.39, 4.03, 3.79, 3.63–3.69, 3.53–3.56, 3.37, 2.32, 2.03, 1.54, −2.69 ppm.

## 3. Results and discussion

In this work, we report the synthesis and characterization of a series of polythiophenes, one homopolymer (**PTP**) and two copolymers (**CTP-1** and **CTP-2**) bearing well defined oligo(ethylene glycol) spacers and meso-3,5-ditert-butyl-tetraphenylporphyrin units. The synthesis of the monomers and polymers are illustrated in Figs. 1 and 2, respectively.

The employed monomers were synthesized from 3-bromo-4-methyl-thiophene, which was reacted with the tetra(ethylene glycol) alkoxide (prepared in situ with sodium), using CuI as catalyst and NMP as solvent under inert atmosphere to give the corresponding 3-alkoxythiophene (**1**). This intermediate was treated in the presence of iodine, Ph$_3$P and imidazol in CH$_2$Cl$_2$ to generate an alkyl iodide (**3**). This compound was further reacted with the appropriate porphyrin derivative, in the presence of KI, using K$_2$CO$_3$ as base and DMF as solvent, to give the corresponding monomer **MTP** (**4**). On the other hand, (**1**) was reacted with CH$_3$I, using KOH as base and DMSO as solvent to produce the desired co-monomer **MT** (**2**).

**MTP** was polymerized, using FeCl$_3$ as oxidizing agent and CH$_2$Cl$_2$ as solvent, to give the corresponding homopolymer **PTP**. In addition, monomer **MTP** was also co-polymerized in the presence of monomer **MT**, using ratios **MT:MTP** (2:1 and 4:1) in order to obtain the corresponding copolymers **CTP-1** and **CTP-2**, respectively. The soluble part of these polymers was analyzed by ^{1}H NMR spectroscopy and Gel Permeation Chromatography (GPC).

### 3.1. Characterization of monomers and polymers

The structure of monomer **MTP** was confirmed by FTIR and NMR spectroscopies, whereas the characterization of **MT** has been previously reported by us [30]. The ^{1}H NMR spectra of **MTP** in CDCl$_3$ solution is shown in Fig. 3a. As we can observe, there is a multiplet
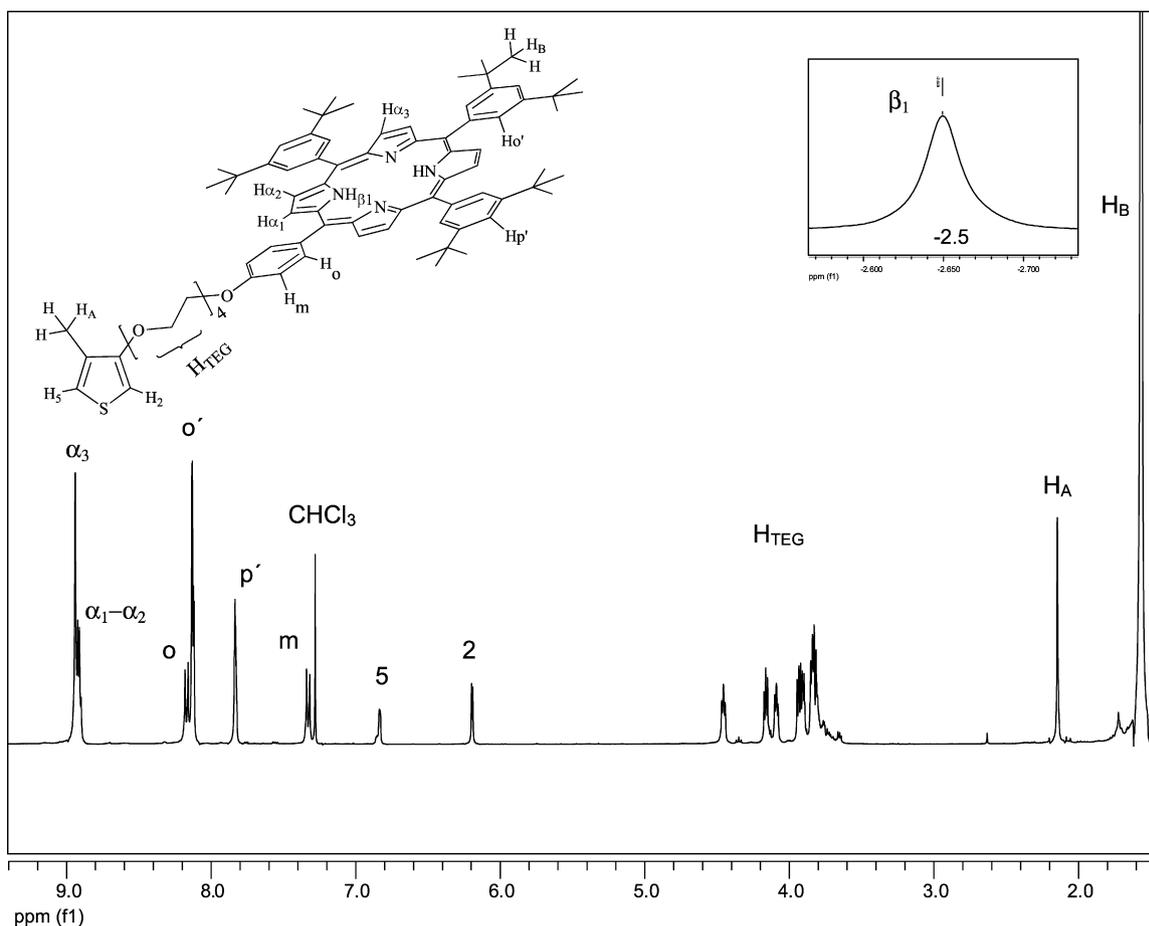
**Fig. 3.** $^1$H NMR spectrum of monomer **MTP** in CDCl$_3$ solution.

at 8.94–8.91 ppm, due to the protons H$_{\alpha1}$, H$_{\alpha2}$ and H$_{\alpha3}$ present in the meso-3,5-ditert-butyl-tetraphenylporphyrin unit followed by a signal at 8.18–8.16 ppm, assigned to the protons H$_o$. In addition, we can see a peak at 8.13 ppm, which is attributed to the protons H$_o$, present in the phenyl groups linked to the porphyrin core. A singlet at 7.83 ppm arising from the protons H$_p$, as well as a signal at 7.34–7.32 ppm, due to the protons H$_m$ also present in the phenyl rings, were also observed. The signals related to protons H$_2$ and H$_5$ of the thiophene ring appear at 6.19 and 6.83 ppm, respectively. In the aliphatic region of the spectrum, we can notice the signals of protons H$_{TEG}$ present in the tetra(ethylene glycol) segment between 4.47 and 3.81 ppm followed by two signals at 2.15 ppm and 1.56 ppm, due to the protons H$_A$ of the methyl group and the protons H$_B$ present in the tertbutyl groups, respectively. Finally, the signal attributed to the protons H$_{\beta1}$ present in the amino groups of the meso-3,5-ditert-butyl-tetraphenylporphyrin unit appear at −2.65 ppm [29].

In the $^{13}$C NMR spectrum of **MTP** (not shown), there are two signals at 158.73 and 155.99 ppm, due to carbons C$_d$ and C$_e$, respectively. Moreover, a signal at 148.76 ppm due to α pyrrolic carbons (C$_j$, C$_m$, C$_o$, C$_r$) as well as a peak at 141.44 ppm, which is attributed to the β pyrrolic carbons (C$_k$, C$_l$, C$_p$, C$_q$) were also observed, followed by two more signals at 135.44 and 135.19 ppm, due to carbons C$_h$ and C$_g$, respectively. The signals corresponding to carbons C$_y$, C$_{z'}$, C$_u$ and C$_w$ appeared in the range between 129.72 and 129.22 ppm (see Scheme 2).

The signal of C$_a$ appear at 121.28 ppm followed by the signal of carbons C$_s$ and C$_n$ at 119.90 ppm, and the signal of C$_i$ located at 119.45 ppm. In addition, a signal corresponding to carbons C$_f$ and

C$_b$ were seen at 112.98 ppm and 96.85 ppm, respectively. Regarding the aliphatic region of the spectrum, a series of signals due to the carbons present in the tetra(ethylene glycol) spacer (carbons C$_{TEG}$) were observed at 71.1–67.97 ppm, followed by two signals at 35.03 and 31.73 ppm, arising from the quaternary carbons and the CH$_3$ of the tertbutyl groups, respectively. At last, we can notice a signal at 12.6 ppm, due to the CH$_3$ group linked to the thiophene ring.

Concerning the polymers, in their $^1$H NMR spectra the absence of the signals due to protons in positions 2 and 5 of the thiophene ring confirmed that the polymerization and copolymerization of the **MTP** monomer took place successfully. However, the rest of the signals present in the $^1$H NMR spectrum of the **MTP** appear much broader in those of its corresponding polymers **PTP**, **CTP-1** and **CTP-2**.

In the $^1$H NMR spectrum of copolymer **CTP-1** (not shown), we can observe a low intensity signal at 3.38 ppm corresponding to the terminal methyl group present in the tetra(ethylene glycol) side chain, which is an indication that the copolymerization occurred effectively. We attempted to calculate the percentage of coupling taking into account the signal at 3.37 ppm, due to the terminal methyl group of the oligo(ethylene glycol) side chain of the **MT** units, and the signal at 1.52 ppm, due to the CH$_3$ group present in the tertbutyl groups of the **MTP** units. Nevertheless, the monomers ratios **MT**:**MTP** determined by NMR spectroscopy were not trustable because of the broadness of the signals so that it was calculated from the absorption spectra and resulted to be 1:1 for **CTP-1** and **CTP-2** (vide infra), even though different ratios **MT**:**MTP** were used (2:1 and 4:1) to prepare these copolymers. On the other
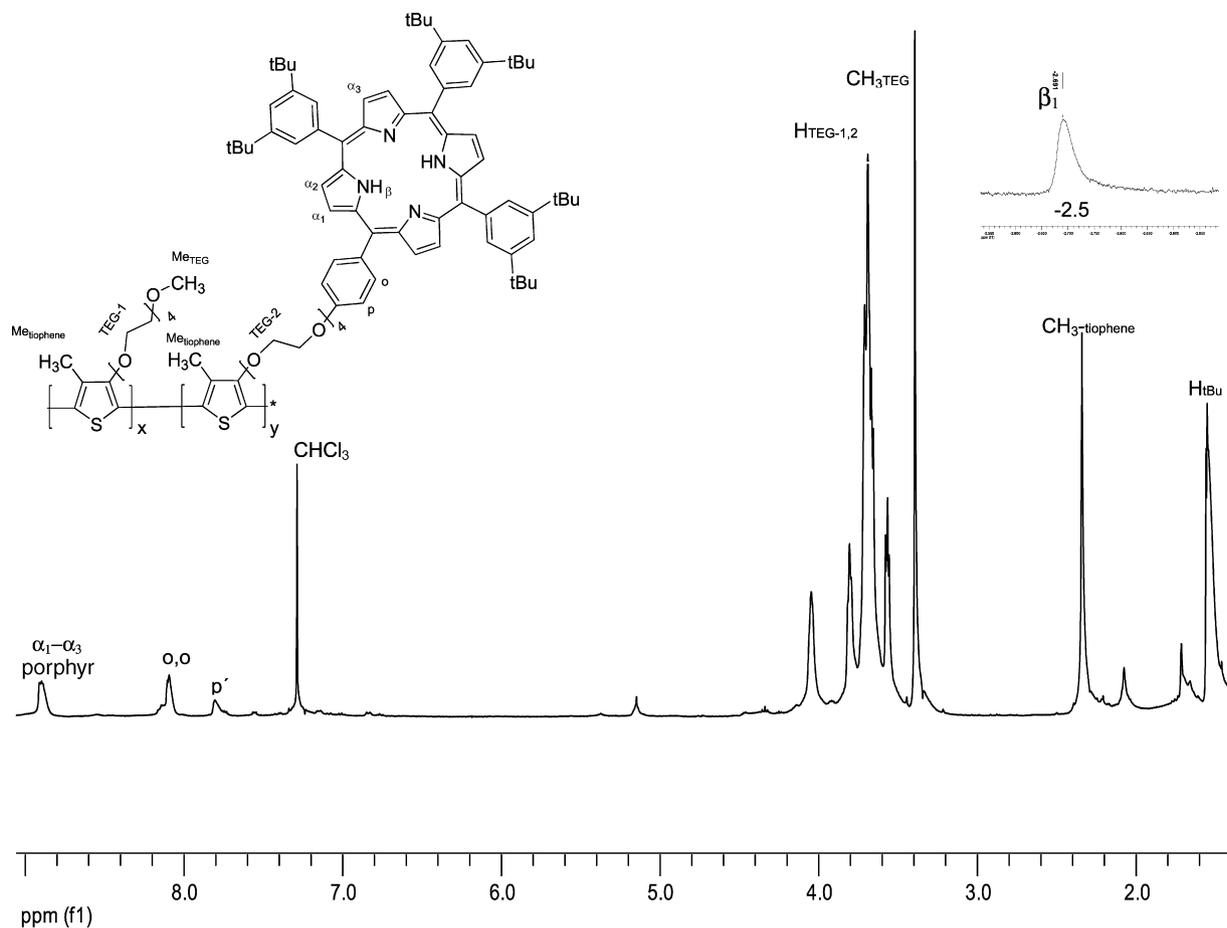
**Fig. 4.** $^1$H NMR spectrum of copolymer **CTP-2** in CDCl$_3$ solution.

hand, the $^1$H NMR spectrum **CTP-2** is shown in Fig. 4 and exhibited the same signals as its homologue **CTP-1**.

Molecular weights of the resulting polymers were determined by GPC in THF against a polystyrene standard and the results are summarized in Table 1. As we can see, all polymers exhibited from low to middle molecular weights.

Homopolymer **PTP** exhibited a weight-average molecular weight ($M_w$ = 24,168 g/mol) with a narrow polydispersity PD = 1.45, whereas its corresponding copolymer **CTP-1**, where a **MT**:**MTP** ratio 2:1 was used, showed a higher value ($M_w$ = 43,839 g/mol) and higher polydispersity PD = 2.79, since the copolymerization of **MTP** decreased significantly the steric hindrance during the polymerization reaction.

Although the obtained copolymers **CTP-1** and **CTP-2** exhibited the same **MT**:**MTP** content ratio (1:1), **CTP-2** has a lower molecular weight ($M_w$ = 11,458 g/mol) with lower polydispersity PD = 1.56. We believe that it is due to the fact that in **CTP-2**, where a **MT**:**MTP** 4:1 ratio was used, there was less pre-association of the **MTP** units prior to polymerization, which gave rise to lower molecular weight

polymers. Since both **CTP-1** and **CTP-2** contain about 50% of **MTP** units, we can affirm that the composition of the copolymers was mainly determined by the reactivity of the monomers rather than the stochiometry of the monomers.

### 3.2. Optical properties of the polymers

The optical properties of the polymers were studied by absorption and fluorescence spectroscopy; the results are summarized in Table 2. The UV–vis spectra of the **MTP** monomer and the obtained polymers **PTP**, **CTP-1** and **CTP-2** are shown in Fig. 5.

The **MTP** monomer and the obtained polymers containing meso-3,5-ditert-butyl-tetraphenylporphyrin units (**PTP**, **CTP-1** and **CTP-2**) show an intense Soret band due to the porphyrin at λ = 422 nm [29], followed by a second band situated at λ = 451 nm, due to the thiophene moieties. Besides, we can observe four Q bands, arising from the porphyrin unit at λ = 519, 555, 597 and 674 nm, which are visible for all compounds [29].

The intensity ratios $I_S/I_T$, where $I_S$ (Soret band) and $I_T$ (thiophene band), were calculated for **PTP**, **CTP-1** and **CTP-2**, giving values of 3.76, 1.95 and 1.80, respectively. In the case of the copolymers **CTP-1** and **CTP-2**, it is worth to point out that as the thiophene content (**MT**) increases with respect to the porphyrin units (**MTP**), the absorption band of the thiophene units augments in intensity with respect to the Soret band of the porphyrin group. Moreover a significant broadening is observed in both absorption bands. From these intensities ratios it was calculated that the composition in both copolymers is almost the same with a **MT**:**MTP** value of 1:1.

**Table 1**
Molecular weight of the obtained polymers.

| Polymer | $M_n$[a] (g/mol) | $M_w$[a] (g/mol) | PD[a] ($M_w/M_n$) |
|---------|---------|---------|---------|
| **PTP** | 16,609 | 24,168 | 1.45 |
| **CTP-1** | 15,670 | 43,839 | 2.79 |
| **CTP-2** | 7304 | 11,458 | 1.56 |

[a] Soluble part, obtained by GPC using THF as solvent, against a polystyrene standard.

**Table 2**
Optical properties of the **MTP** monomer and the polymers.

| Compound | Absorption, $\lambda$ (nm) | Cut off (nm) | Intensity ratio ($a$:$b$) | Emission, $\lambda$ (nm) | Cut off, $\lambda$ (nm) |
|---|---|---|---|---|---|
| **MTP** | 422,[a] 451,[b] 519, 555, 597, 674 | 712 | 1:6 | 654, 722 | 488 |
| **PTP** | 422,[a] 451,[b] 519, 555, 596, 674 | 703 | 1:3.76 | 654, 722 | 512 |
| **CTP-1** | 422,[a] 451,[b] 519, 555, 596, 674 | – | 1:1.95 | 541, 654, 722 | 817 |
| **CTP-2** | 423,[a] 451,[b] 517, 555, 596, 674 | – | 1:1.80 | 541, 601, 654, 722 | 814 |

[a] Absorption band of the porphyrin (Soret's band).
[b] Absorption band of the polythiophene backbone.

For **PTP** ($I_S/I_T = 3.76$) there is one porphyrin unit per thiophene unit as expected, whereas in **CTP-1** ($I_S/I_T = 1.95$) and **CTP-2** ($I_S/I_T = 1.80$) this intensities ratio is a half of the previous one, which indicates that there is one porphyrin unit per two thiophene units. This ratio can be found in copolymers where **MT**:**MTP** is 1:1, as it is the case in **CTP-1** and **CTP-2**.

According to the literature, polythiophenes bearing oligo(ethylene glycol) side chains usually show an absorption band at $\lambda_{max} = 425$ nm [30] when the backbone has a twisted conformation, however, when these polymers adopt a nearly planar conformation this band appears at ca $\lambda_{max} = 560$ nm [5,30]. Since the Soret band of the porphyrin ($\lambda_{max} = 422$ nm) is very intense overlaps and hides the band due to polythiophene in the twisted form ($\lambda_{max} = 425$ nm), so that only one absorption band can be seen. Very recently, a similar behavior was reported for some water soluble polythiophenes bearing porphyrin units [32]. Therefore, the polythiophene backbone exhibits two absorption bands one at 425 nm and another at 451 nm, which explain the broadening of these bands in the UV–vis spectra of copolymers **CTP-1** and **CTP-2**. This phenomenon was not observed in the absorption spectra of **PTP**. Since the absorption spectra of the model compound meso-3,5-ditert-butyl-tetraphenylporphyrin showed a narrow Soret band at 422 nm and the band at 451 nm was not observed, we can affirm that the latter exclusively arises from the polythiophene backbone.

According to the absorption bands, all polymers adopt a twisted conformation in THF solution. However, in the absorption spectra of **CTP-1** and **CTP-2** we can perceive a significant broadening of the bands at 425 and 451 nm due to the higher thiophene content with respect to that of porphyrin in these copolymers. From these results, we can affirm that the meso-3,5-ditert-butyl-tetraphenylporphyrin units present in the polymers provoke a twisting in the polythiophene backbone, mainly due to steric effects.

### 3.3. Fluorescence spectra of the polymers

In general, the emission spectra of free base porphyrins and Zn-metallated porphyrins have two emission regions: the first one situated between 400 and 500 nm and the second one located between 550 and 800 nm [29]. Herein, we can see that all the species showed the two bands at $\lambda = 654$ nm and 722 nm due to the porphyrin units (Fig. 6). In the particular case of copolymers **CTP-1** and **CTP-2**, we can notice the presence of an additional band at $\lambda = 541$ nm, which arises from the $S_1 \rightarrow S_0$ of the polythiophene backbone, which is not present in the emission spectra of **MTP**, **HTP** and the model porphyrin **TTP**. This can be due to the fact that in copolymers **CTP-1** and **CTP-2** the tiophene content is much higher with respect to that of porphyrin, which allows us to see the emission arising from the polythiophene backbone. In the case of **HTP** this band was not observed because the polythiophene content is equal to that of porphyrin so that the emission at $\lambda = 541$ nm can be quenched due to energy transfer phenomenon from the polythiophene backbone to the porphyrin units that exhibit a Q band at 555 nm [32].

### 3.4. Electrochemical properties of the polymers

#### 3.4.1. (a) Cyclic voltammetry of **MTP** and **TPP**

Fig. 7 shows a series of voltammograms that illustrate the qualitative electrochemical behavior of **MTP** in $CH_2Cl_2$ with 0.1 M $Bu_4NPF_6$ vs $Fc^+/Fc$ couple (curves b and d). For comparison, the cyclic voltammogram of the model compound, tetraphenylporphyrin **TPP**, is also shown (curves a and c). The initial positive-going
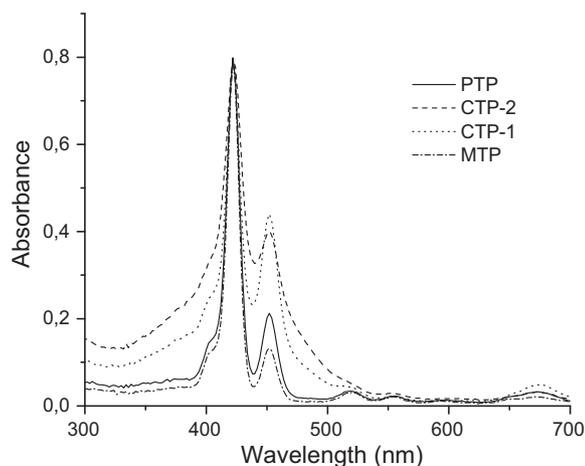


**Fig. 5.** Normalized absorption spectra of monomer **MTP** and the obtained polymers **PTP**, **CTP-1** and **CTP-2**.
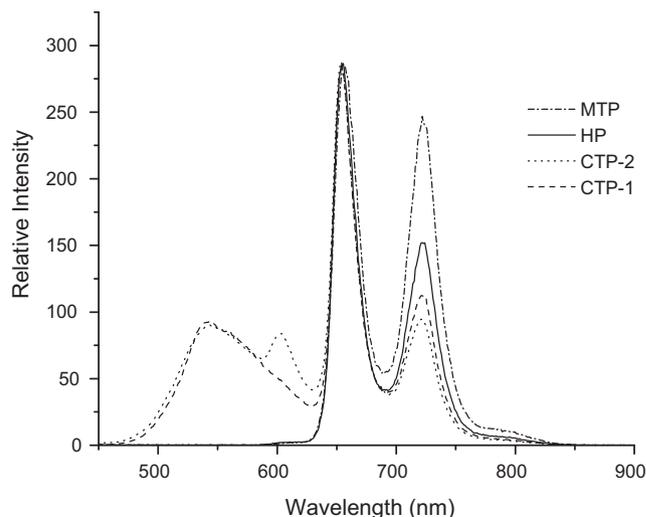


**Fig. 6.** Normalized fluorescence spectra of monomer **MTP** and the obtained polymers **PTP**, **CTP-1** and **CTP-2**.
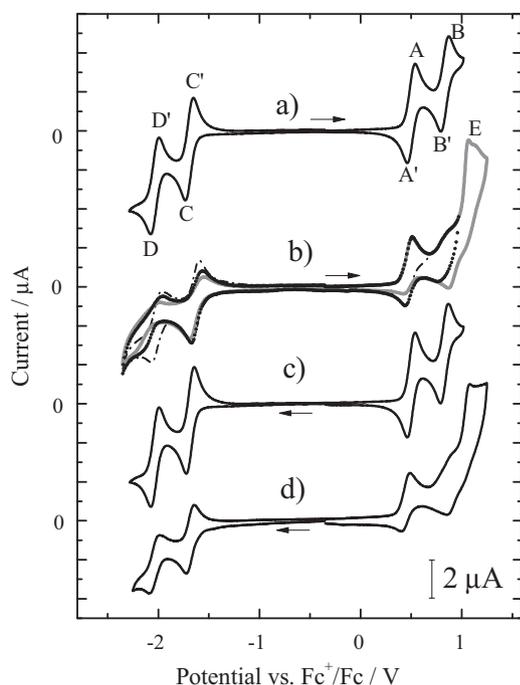
**Fig. 7.** Cyclic voltammograms of (a and c) 0.83 mM **TTP** and (b and d) 1.40 mM **MTP** in CH$_2$Cl$_2$ containing 0.1 M Bu$_4$NPF$_6$ at a glassy carbon working electrode. Scan rate: 0.1 V/s. (b) Positive-going sweep with switching potentials past first reduction peak (dash-dot curve) and past second reduction peak (dot curve).

**Table 3**
Electrochemical data of **TPP** and **MTP**.[a]

|  | TPP | MTP |
|---|---|---|
| System A/A′[b] |  |  |
| $E_{pa}$ (V) | 0.538 | 0.508 |
| $E_{pc}$ (V) | 0.459 | 0.443 |
| $\Delta E_p$ | 0.079 | 0.065 |
| System B/B′[b] |  |  |
| $E_{pa}$ (V) | 0.874 | 0.878 |
| $E_{pc}$ (V) | 0.795 | 0.763 |
| $\Delta E_p$ | 0.079 | 0.115 |
| System C/C′[c] |  |  |
| $E_{pc}$ (V) | −1.732 | −1.726 |
| $E_{pa}$ (V) | −1.653 | −1.648 |
| $\Delta E_p$ | 0.079 | 0.078 |
| System D/D′[c] |  |  |
| $E_{pc}$ (V) | −2.077 | −2.089 |
| $E_{pa}$ (V) | −1.993 | −1.991 |
| $\Delta E_p$ | 0.084 | 0.098 |
| Peak E[b] |  |  |
| $E_{pa}$ | – | 1.063 |

[a] All potentials were obtained during cyclic voltammetry of solutions in 0.1 M Bu$_4$NPF$_6$ in CH$_2$Cl$_2$. Glassy C working electrode diameter 1 mm, scan rate: 0.10 V/s. Potentials in V vs. Fc$^+$/Fc.
[b] Data obtained from the initial positive-going sweep.
[c] Data obtained from the initial negative-going sweep.

sweep for **TPP** (curve a) reveals two reversible redox reactions (systems A/A′ and B/B′), which have been assigned to monoelectronic transfers corresponding to the neutral/cation-radical and cation-radical/dication couples of the porphyrin ring, respectively [33,34]. As shown in curve b (dotted line), the initial positive going scan of **MTP** also shows the presence of the oxidation reactions of the porphyrin ring, systems A/A′ and B/B′. Solid line shows that when the scan is extended to 1.24 V, a third irreversible anodic peak (E), which is partially overlapped with the second oxidation of the porphyrin, is also observed. This peak E at 1.063 V is related to the oxidation of the thiophene unit [35,36]. Curve b also shows that the system B/B′ is less reversible than that in the **TPP** compound (curve a). This can be due to the proximity of the oxidation peak E with that of the cation-radical/dication couple of the porphyrin ring, and may be indicative of a possible coupled chemical reaction with the oxidation products formed in peak E. The peak potentials $E_p$ and $\Delta E_p$ values for **MTP** are reported in Table 3 and are compared with those of **TPP**. From these data, it is observed that the presence of the *t*-butyl substituents on the phenyl groups of the porphyrin unit and the 13-(4-methylthiophen-3-yloxy)-2,5,8,11-tetraoxatridecane moiety, does not change the oxidation potential values in **MTP** with respect to **TTP**.

When the cyclic voltammograms of **TPP** and **MTP** (Fig. 7, curves c and d, respectively) were recorded doing the sweep in negative direction, two redox reactions were observed in the potential range from −0.37 to −2.3 V vs Fc$^+$/Fc (systems C/C′ and D/D′). These two systems are characteristic of the neutral/anion-radical and anion-radical/dianion couples from the porphyrin ring, respectively [33,34]. In Fig. 7b, it is observed that the electrochemical behavior of the D/D′ redox couple, is modified when the potential is first swept in positive direction and then continued back to the negative direction. When the first positive scan is inverted either after the second electro-oxidation of the porphyrin ring (peak B) (dotted curve b) or after the oxidation of the thiophene unit (peak E) (solid curve b), the qualitative behavior of the system D/D′ dramatically changes. Both reduction and oxidation peaks become less

defined and the peak separation, $\Delta E_p = E_{pc} - E_{pa}$, increases from $\Delta E_p = 0.072$ V to $\Delta E_p$ about 0.250 V (Table 3). On the other hand, dash-dot curve b shows that when the potential is inverted after the first oxidation reaction (peak A), the qualitative behavior of system D/D′ is almost not modified with respect to the behavior observed when the initial sweep is started toward negative direction (curve d). These results may be indicative of the presence of some kind of interaction between the positive species generated during the positive sweep and the negative species formed during the negative scan.

All of our attempts to prepare polymers from **MTP** by successive sweeps over the potential range from −1.0 to 1.2 V were unsuccessful. It is well known that thiophene and many 3-substituted thiophenes have been successfully electropolymerized, leading to C–C couplings between the 2- and 5-positions of the thiophene ring. However, under our experimental conditions, with a glassy C electrode, using Bu$_4$NPF$_6$ in CH$_2$Cl$_2$ as the electrolytic medium, at 0.25 mV/s and applying an inversion potential after peak E, **MTP** could not be polymerized. An possible explanation is that the bulky tetra(oxyethylene)oxy-porphyrin substituent on the 3-position of the thiophene unit hinders the polymerization in those positions. On the other hand, it has also been reported that the anodic oxidation of tetraphenylporphyrins leads to polymers exhibiting significant low band gap values [37]. In those polymers, the coupling of the two monomers takes place in *para*-position of the phenyl ring, but in the case of **MTP**, since its *para*-position is highly hindered by the presence of the two adjacent bulky *t*-butyl substituents position, the polymerization does not occur.

### 3.4.2. (a) Cyclic voltammetry of the chemically obtained polymers **PTP, CTP-1** and **CTP-2**

Representative cyclic voltammograms of the homopolymer **PTP** (curve a) and the copolymers **CTP-1** and **CTP-2** (curves b and c) are shown in Fig. 8, for the initial positive-going sweep, and in Fig. 9 for the initial negative-going sweep. Comparing the cyclic voltammograms of **MTP** (Fig. 7b and d) with those of the polymers it can be noticed that ill-defined irreversible peaks are observed at about the same potentials where the oxidation and reduction of the porphyrin unit takes place. For the three polymers, an oxidation current is also seen at potentials close where the oxidation of the polythiophene backbone occurs. It is observed that as the
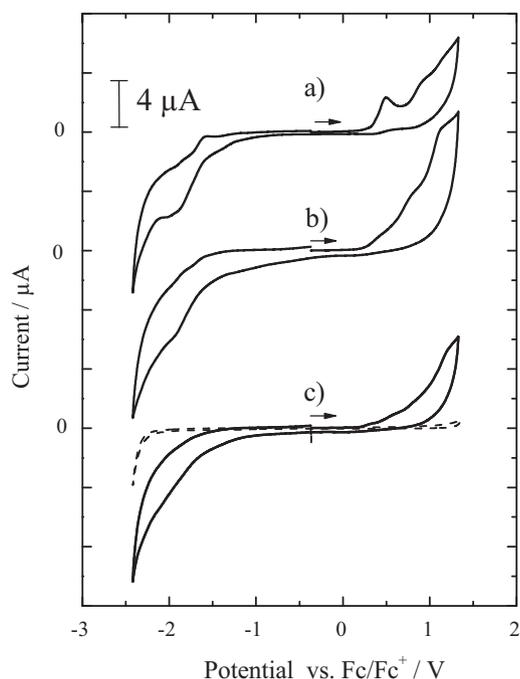
**Fig. 8.** Cyclic voltammograms of (a) **PTP**, (b) **CTP-1** and (c) **CTP-2** in CH$_2$Cl$_2$ containing 0.1 M Bu$_4$NPF$_6$ at a glassy carbon working electrode. Scan rate: 0.1 V/s. Dash curves: (b) switching potential past first reduction peak and (d) background voltammogram.

amount of monomer **MT** increases with respect to that of **MTP**, the oxidation and reduction peaks of copolymers **CTP-1** and **CTP-2** become gradually less defined. In fact, for the **CTP-2** copolymer, the peaks are not well defined (curve c), and only an increase in the current is observed in the regions where the meso-3,5-ditert-butyl-tetraphenylporphyrin units and polythiophene backbone are
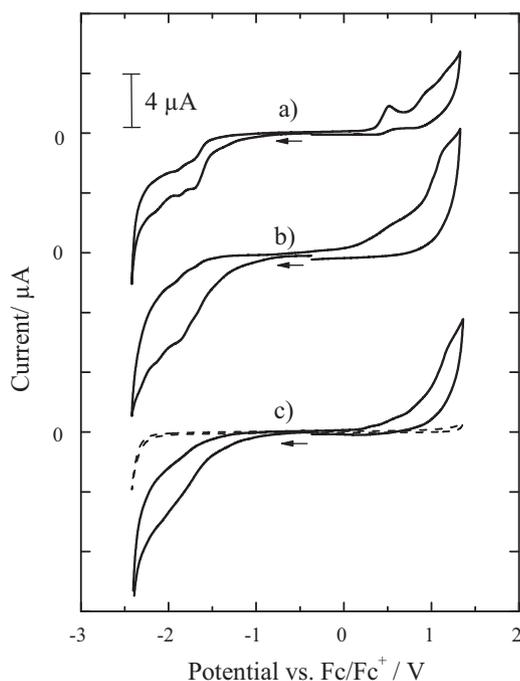


**Fig. 9.** Cyclic voltammograms of (a) **PTP**, (b) **CTP-1** and (c) **CTP-2** in CH$_2$Cl$_2$ containing 0.1 M Bu$_4$NPF$_6$ at a glassy carbon working electrode. Scan rate: 0.1 V/s. Dash curves: (b) switching potential past first reduction peak and (d) background voltammogram.

electroactive. It was confirmed that this increase in the current is not due to the electrolyte solution, when the cyclic voltammogram of the background is overlapped (dashed line) with the voltammogram of **CTP-2** (curve c).

## 4. Conclusion

A novel series of polythiophenes containing meso-3,5-ditert-butyl-tetraphenylporphyrin units and well defined oligo(ethylene glycol) spacers were synthesized and characterized. The homopolymer exhibited a middle molecular weight $M_w$, whereas the copolymers showed from middle to low $M_w$ values with an average **MT**:**MTP** ratio of 1:1, which reveals that the composition of the copolymers are dominated by the reactivity and steric hindrance of the monomers rather than by their stochiometry. All these polymers showed the expected characteristic absorption bands of the meso-3,5-ditert-butyl-tetraphenylporphyrin units and the absorption band related to the conjugated polythiophene backbone, which appeared at 451 nm. Moreover, the polymers exhibited emission bands at $\lambda = 654$ nm and 722 nm. Copolymers **CTP-1** and **CTP-2** exhibited also an additional emission band at $\lambda = 541$ nm, which is attributed to the polythiophene backbone. Concerning the electrochemical behavior, for all the polymers, an oxidation current is observed at potentials close where the oxidation of the thiophene system occurs. It was noticed that as the amount of monomer **MT** increases with respect to that of **MTP**, the oxidation and reduction peaks of copolymers **CTP-1** and **CTP-2** become gradually less defined, which may be due to the different distributions of the monomer units along the polymer structure.

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