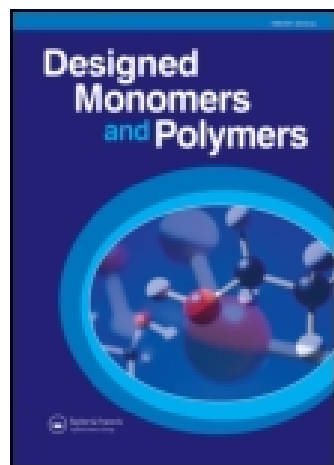


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### Luminescent polythiophenes-containing porphyrin units: synthesis, characterization, and optical properties

Aldo Vázquez-Arce<sup>a</sup>, Gerardo Zaragoza-Galán<sup>a</sup>, Edgar Aguilar-Ortíz<sup>a</sup>, Eric G. Morales-Espinoza<sup>a</sup>, Efraín Rodríguez-Alba<sup>a</sup> & Ernesto Rivera<sup>a</sup>

<sup>a</sup> Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México Ciudad Universitaria, C.P. 04510, D.F., Mexico.

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## Luminescent polythiophenes-containing porphyrin units: synthesis, characterization, and optical properties

Aldo Vázquez-Arce, Gerardo Zaragoza-Galán, Edgar Aguilar-Ortíz, Eric G. Morales-Espinoza, Efraín Rodríguez-Alba and Ernesto Rivera\*

*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México Ciudad Universitaria, C.P. 04510, D.F., Mexico*

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A novel thiophene monomer containing a meso-tetraphenylporphyrin (MTPP) unit linked via an alkyl spacer was synthesized and characterized. This monomer was copolymerized in the presence of 3-dodecylthiophene (MDT) in different ratios MTPP: MDT (1:2, 1:4, and 1:6), using  $\text{FeCl}_3$  as oxidizing agent, to give the corresponding copolymers (CP12, CP14, and CP16). In addition, MTPP and MDT were also homopolymerized under the same reaction conditions to give homopolymers PTPP and PDT, respectively. The obtained compounds were characterized by FTIR and  $^1\text{H}$  NMR spectroscopy. 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: a Soret band at  $\lambda=422$  nm and four Q-bands between  $\lambda=500$ –700 nm. Moreover, an additional band was observed at  $\lambda=328$  nm, due to the polythiophene backbone. CP14 and CP16 showed intense emission in the region between  $\lambda=550$ –800 nm.

**Keywords:** polythiophene; porphyrin; optical properties; fluorescence

### 1. Introduction

Polythiophene (PT) has been considered one of the most promising electro-conducting polymers due to its high stability, ease of structural modification, controllable optical and electrochemical properties. At the beginning, its applications were limited because of its insolubility in many organic solvents, due to its strong  $\pi$ -conjugated structure. Furthermore, alkyl chains have been introduced at the third position of thiophene in order to obtain monomers able to give soluble polymers. This new family of poly(3-alkylthiophene)s are processable conducting polymers, whose electronic properties can be modified, allowing their full characterization by different spectroscopic techniques.[1] The stability of poly(3-alkylthiophenes) in the doped state can be reached by incorporating alkyl side chains along the backbone or by introducing alkoxy groups. The incorporation of alkoxy groups into PT increases significantly their conductivity without reducing their solubility in organic media.[2,3]

For many PT, interesting properties, such as thermochromism,[4–6] ionochromism,[5–7] photochromism,[8] piezochromism,[9] and biochromism,[10] have been studied. These color changes are mainly due to transitions from planar to twisted conformation of the polymer backbone and vice versa, which modifies the effective

conjugation length, thereby producing a shift of the absorption bands in their UV–visible spectra.[11] In PT-bearing alkoxy groups at 3-position of the thiophene rings, the lone pairs of the oxygen atoms enter into conjugation with the polymer backbone, inducing a planar conformation.[12,13] 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 PT make them excellent prospects for the elaboration of light emitting diodes,[14] gas sensors,[15–17] biomedical applications,[18] metal ion sensors,[19,20] and biosensors.[21–24]

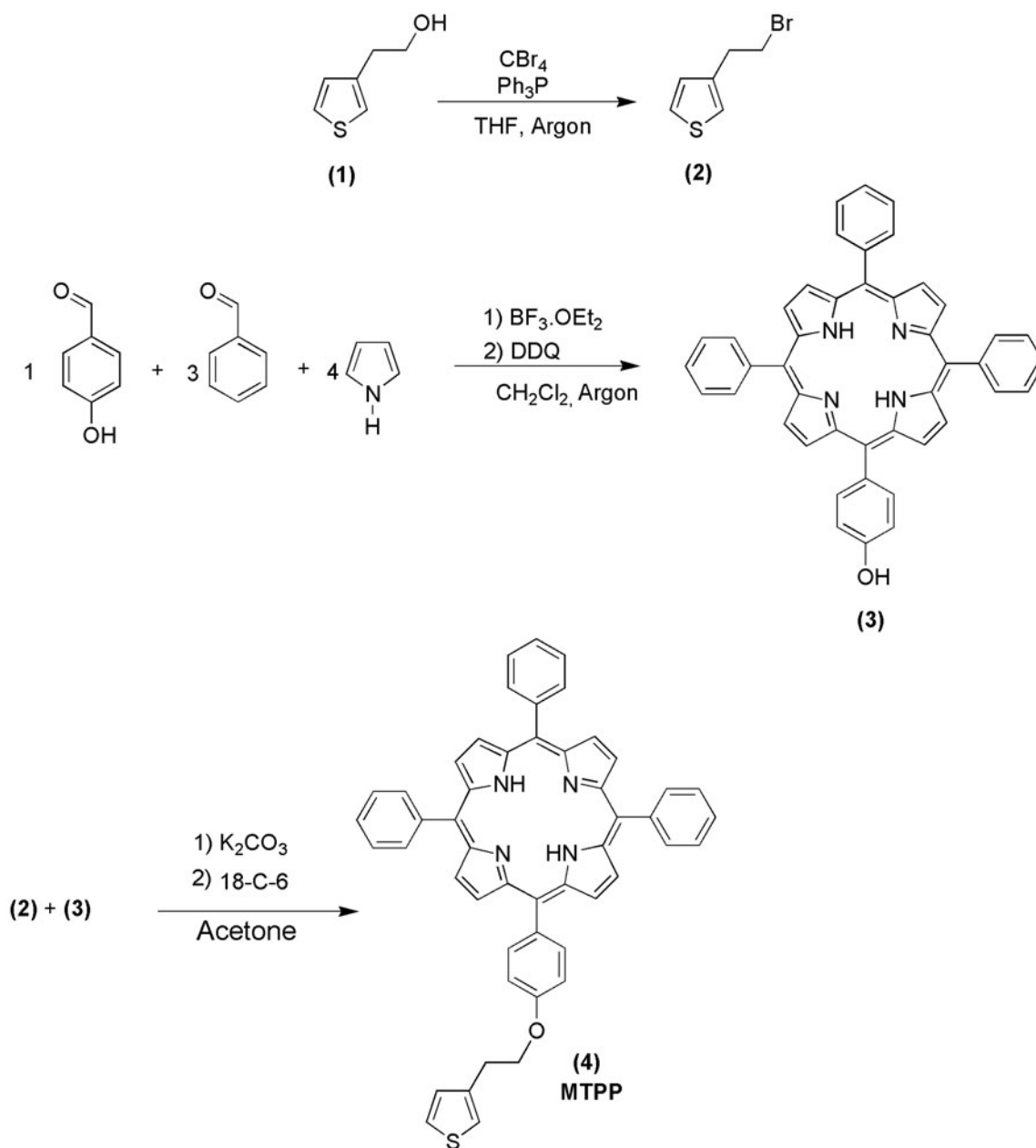
On the other hand, porphyrins are highly delocalized  $\pi$ -conjugated systems that are considered as a unique category of ionic scavengers, whose recognition properties arise from the heteroatoms present in their structure.[25] Due to their efficient light absorption, porphyrins have been the subject of deep research in solar energy transfer [26–28] and electron transfer systems.[29–31] Incorporation of porphyrins into polymers allows the easy handling, recycling, and adaptation of this important set of complexant agents into continuous processes.

Previously, we published the synthesis and characterization of different PT-containing photoactive groups and

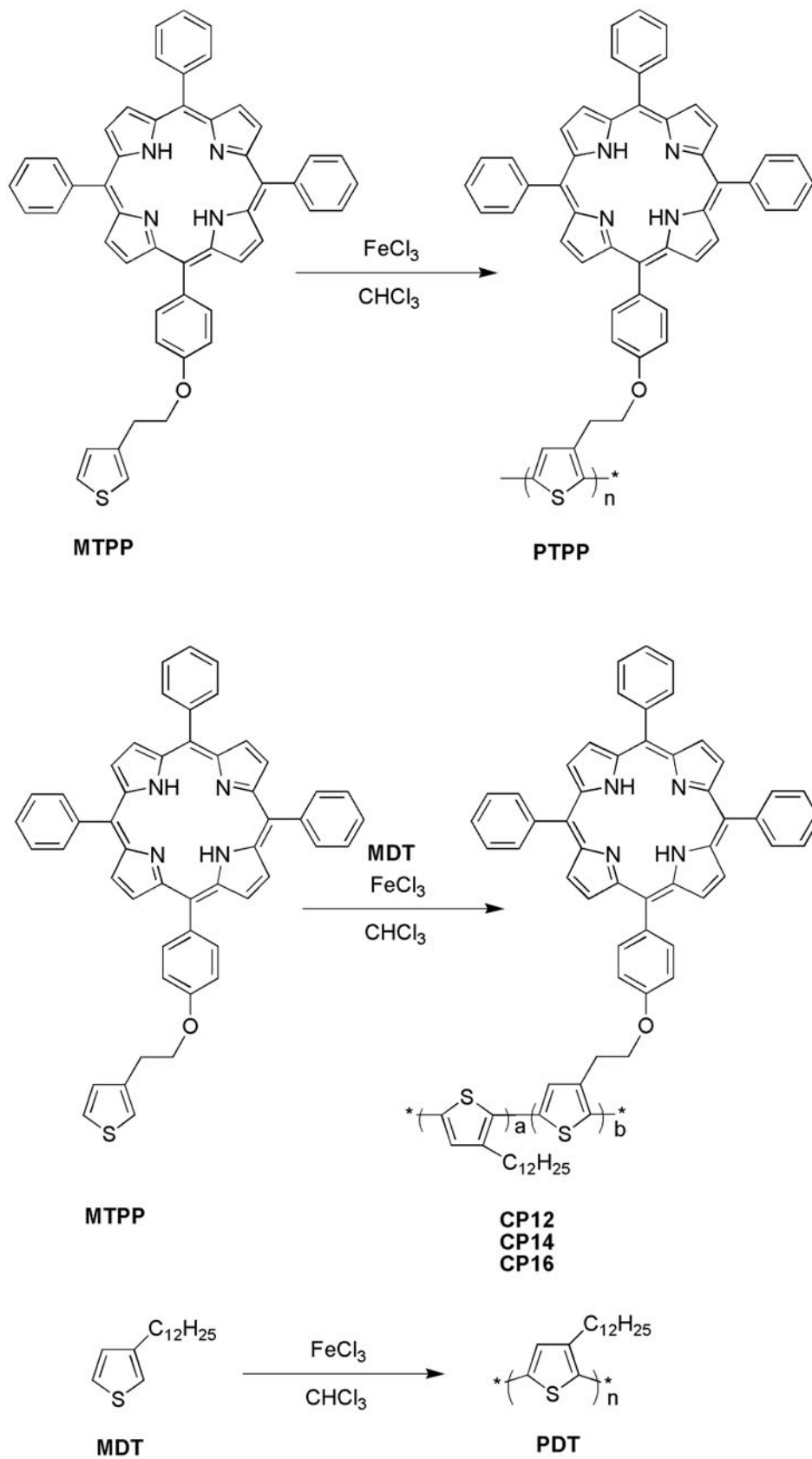
\*Corresponding author. Email: [riverage@unam.mx](mailto:rивerage@unam.mx)

complexant agents.[32–34] Very recently, we reported a novel series of PT containing freebase meso-3,5-ditert-butyl-tetraphenylporphyrin units linked to the polymer backbone via well-defined oligo(ethylene glycol) spacers. [35] These polymers showed the expected characteristic absorption bands of the porphyrin units as well as an additional absorption band at 451 nm due to the conjugated PT backbone. Moreover, these polymers exhibited intense emission bands at  $\lambda=654$  nm and 722 nm, whereas some related copolymers exhibited also an additional emission band at  $\lambda=541$  nm, which is attributed to the PT backbone.

Herein, we report the synthesis of a new series of PT bearing less sterically hindered meso-tetraphenylporphyrin (MTPP) units and alkyl side chains in their structure (Schemes 1 and 2). The obtained polymers were fully characterized by FTIR and  $^1\text{H}$  NMR spectroscopy, and their optical properties were studied by absorption and fluorescence spectroscopy. The obtained results were analyzed and compared with those observed for a series of PT-bearing meso-3,5-ditert-butyl-tetraphenyl porphyrin units and oligo(ethylene glycol) spacers, previously reported by us [35].



Scheme 1. Synthesis of monomer MTPP.



Scheme 2. Synthesis of the polymers PTPP, PDT, and copolymers CP12, CP14 and CP16.

## 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.  $^1\text{H}$  NMR spectra of all compounds were carried out in  $\text{CDCl}_3$  solution, using a Bruker Avance 400 spectrometer, operating at 400 MHz. 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 tetrahydrofuran (THF) as solvent against a polystyrene standard.

Fluorescence spectra corrected for emission detection were recorded on a Fluorolog-3 spectrophotometer with an FL3-11 special configuration, which is designed to record simultaneously two emission scans (T-shape). All spectra were obtained in THF solution (concentration  $3 \times 10^{-6}$  M) with the usual right-angle configuration, exciting the samples at  $\lambda = 420$  nm.

### 2.2. Chemicals

2-(thiophen-3-yl)ethanol, 4-hydroxy benzaldehyde, benzaldehyde, pyrrole, and  $\text{FeCl}_3$  employed in the synthesis were purchased from Aldrich and used as received. Chloroform, used in the polymerizations, was distilled over calcium hydride ( $\text{CaH}_2$ ) in order to remove traces of water.

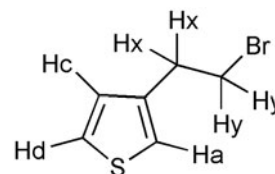
### 2.3. Synthesis of monomers and polymers

#### 2.3.1. Synthesis of 3-(2-bromoethyl)thiophene (2)

2-(Thiophen-3-yl)ethanol (**1**) (0.5 g, 0.39 mmol), triphenylphosphine (1.329 g, 5.07 mmol) were dissolved in anhydrous THF (10 mL). In a separated flask,  $\text{CBr}_4$  (1.681 g, 5.06 mmol) was dissolved in THF (5 mL), and this solution was added to the previous one. The resulting mixture was stirred for 24 h at room temperature. Then, it was filtered, and the organic solution was dried with  $\text{MgSO}_4$  and concentrated at reduced pressure. The crude product was purified by flash column chromatography in silica gel, using hexanes and then a mixture of hexanes:ethyl acetate 7:3 as eluent. The desired product (**2**) was obtained as a yellow oil (0.506 g, 2.647 mmol). Yield: 90%.

FTIR (film):  $\nu = 3012$  (C–H of thiophene), 2923 ( $\text{CH}_2$ ), 1614 (C=C), 1321 (C–Br), 958, 802 (out of plane, H–C=), 724 (C–S)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) (Scheme 3)  $\delta = 7.30$ –7.28 (dd,  $J = 5$  Hz, 1H,  $\text{H}^d$ ), 7.07 (m, 1H,  $\text{H}^a$ ), 6.98 (m, 1H,  $\text{H}^c$ ), 3.35 (t,  $J = 7.4$  Hz, 2H,  $\text{H}^x$ ), 3.236 (t,  $J = 7.5$  Hz, 2H,  $\text{H}^y$ ).



Scheme 3. Assignment of the signals for 3-(2-bromoethyl)thiophene (**2**).

#### 2.3.2. Synthesis of 5-(4-hydroxyphenyl) 10, 15, 20-trisphenylporphyrin (3)

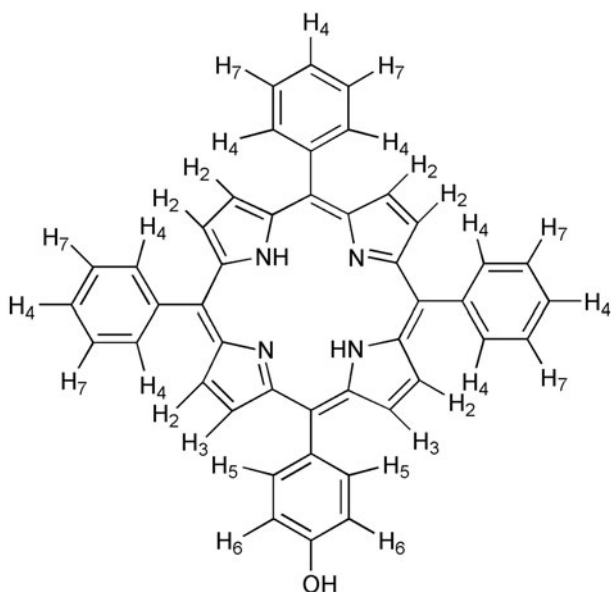
In a 2 L three neck round bottom flask, pyrrole (0.842 g, 12.55 mmol) was dissolved in anhydrous  $\text{CH}_2\text{Cl}_2$  (100 mL) previously filtrated in alumina. Afterwards, 4-hydroxybenzaldehyde (0.383 g, 3.13 mmol) and benzaldehyde (1 g, 9.42 mmol) were added. Then, an additional amount of  $\text{CH}_2\text{Cl}_2$  was added reaching a total volume of 1.25 L. After stirred for 10 min,  $\text{BF}_3 \cdot \text{OEt}_2$  (0.588 g, 4.14 mmol) dissolved in EtOH (3 mL) was added, under argon atmosphere and the reaction mixture was stirred for 1.5 h. After that, DDQ (2.139 g, 9.42 mmol) was added and the reaction continued for 6 more hours until it was quenched with a few drops of triethylamine. Then, the solution was filtrated and concentrated at reduced pressure. The crude product was purified by column chromatography in alumina, using a mixture of hexanes/chloroform 2:8 as eluent. The desired porphyrin (**3**) was obtained as a purple powder (0.345 g, 0.546 mmol). Yield: 15.52%.

FTIR (KBr):  $\nu = 3450$  (O–H), 3019 (C–H aromatic), 1690 (N–H), 1623 (C=C), 1461, 1377, 1243 (C–N), 1182 (C–O), 980 (out of plane, H–C=)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) (Scheme 4)  $\delta = 8.92$ –8.91 (d,  $J = 5.2$  Hz, 2H,  $\text{H}^3$ ), 8.86 (s, 6H,  $\text{H}^2$ ), 8.23 (m, 6H,  $\text{H}^7$ ), 8.08–8.06 (d,  $J = 8.4$  Hz, 2H,  $\text{H}^5$ ), 7.783 (m, 9H,  $\text{H}^4$ ), 7.30–7.29 (d,  $J = 8.0$  Hz, 2H,  $\text{H}^6$ ),  $-2.73$  (s, 2H, NH).

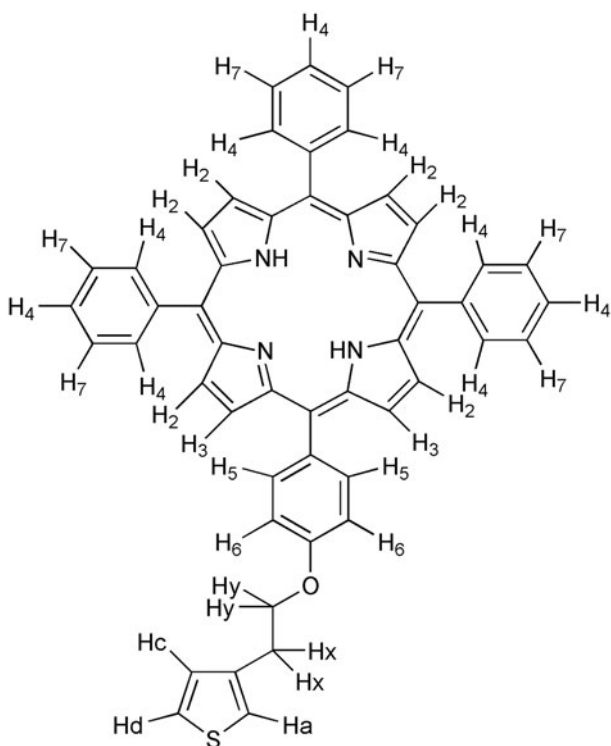
#### 2.3.3. Synthesis of monomer MTPP (4)

3-(2-Bromoethyl)thiophene (**2**) (0.086 g, 0.45 mmol), 5-(4-hydroxyphenyl) 10, 15, 20-trisphenylporphyrin (**3**) (0.3 g, 0.41 mmol) were dissolved in anhydrous acetone (10 mL). Then,  $\text{K}_2\text{CO}_3$  (0.152 g, 1.099 mmol) and 18-crown-6 (0.119 g, 0.45 mmol) were added. The reaction mixture was heated to reflux for 48 h with vigorous stirring; the solution was filtrated and concentrated at reduced pressure. The crude product was purified by column chromatography in silica gel, employing a mixture of hexanes:chloroform 9:1 and then hexanes/ethyl acetate 7:3 as eluent. The desired monomer was obtained as a purple solid (0.050 g, 0.066 mmol). Yield: 17%.



Scheme 4. Assignment of the signals for 5-(4-hydroxyphenyl)10,15,20-trisphenylporphyrin (3).

FTIR (film):  $\nu=3310$  (N–H), 3010 (C–H of thiophene), 2921, 2895 ( $\text{CH}_2$ ), 1731, 1610 (C=C), 1461, 1377, 1240 (C–N), 1178, 1001 (C–O), 958, 802 (out of plane, H–C=), 726 (C–S)  $\text{cm}^{-1}$ .



Scheme 5. Assignment of the signals for monomer MTPP (4).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) (Scheme 5)  $\delta=8.91\text{--}8.89$  (*d*,  $J=5.2$  Hz, 2H,  $\text{H}^3$ ), 8.87 (s, 6H,  $\text{H}^2$ ), 8.82 (m, 6H,  $\text{H}^7$ ), 8.13–8.11 (*d*,  $J=8.4$  Hz, 2H,  $\text{H}^5$ ), 7.78 (m, 9H,  $\text{H}^4$ ), 7.38–7.37 (*d*,  $J=5$  Hz, 1H,  $\text{H}^d$ ), 7.28–7.28 (*d*,  $J=8.0$  Hz, 2H,  $\text{H}^6$ ), 7.24 (m, 1H,  $\text{H}^a$ ), 7.18 (m, 1H,  $\text{H}^c$ ), 4.44 (*t*,  $J=7.5$  Hz, 2H,  $\text{H}^y$ ), 3.33 (*t*,  $J=7.4$  Hz, 2H,  $\text{H}^x$ ),  $-2.73$  (s, 2H, NH) ppm.

### 2.3.4. Synthesis of the poly(3-dodecyl thiophene) (PDT)

3-Dodecyl thiophene (0.070 g, 0.27 mmol) was dissolved in dry  $\text{CHCl}_3$  (10 mL), then  $\text{FeCl}_3$  (0.180 g, 0.66 mmol) dissolved in  $\text{CHCl}_3$  (10 mL) was added to the solution. The reaction mixture was stirred for 12 h at room temperature under inert atmosphere. Afterwards, the resulting solution was poured into a mixture of methanol/water 1:3 (80 mL) in order to precipitate the product. Furthermore it was filtrated, washed with methanol and treated with 10 mL of  $\text{NH}_4\text{OH}$  20% in order to reduce the polymer. Finally, the crude product was purified by column chromatography in silica gel using a mixture of hexanes: ethyl acetate 7:3 and then with pure ethyl acetate as eluent. Polymer PDT was obtained as a dark yellow powder. Yield: 45%. The spectroscopic data correspond to those previously reported in the literature.[36]

### 2.3.5. Synthesis of the homopolymer PTPP

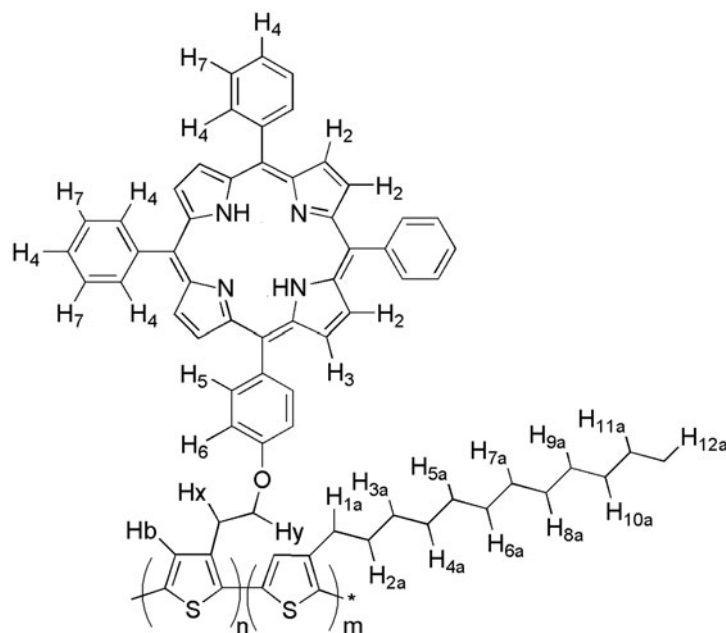
PTPP was synthesized using the same method employed for the preparation of PDT, but this polymer resulted to be insoluble and precipitated from the reaction mixture. The crude product was filtrated, washed with methanol and treated with 10 mL of  $\text{NH}_4\text{OH}$  20% in order to reduce the polymer. PTPP was obtained as a dark purple powder. Relative yield: 60%

FTIR (KBr,  $\text{cm}^{-1}$ ): 3110 (C–H of the thiophene), 2932, 2853 ( $\text{CH}_2$ ), 1718, 1691 (C=C), 1463, 1365, 1276 (C–N), 1174, 1062 (C–O), 918, 830 (out of plane, H–C=), 712 (C–S).

## 2.4. Synthesis of the copolymers CP12, CP14, and CP16

### 2.4.1. General procedure (described for CP41)

5-(4-(2-Thiophenyl)-oxyethylphenyl)10,15,20-trisphenyl porphyrin (MTPP) (0.03 mmol) and 3-dodecyl thiophene (MDT) (0.13 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (4 mL). Then,  $\text{FeCl}_3$  (72.3 mg, 0.26 mmol) was added, and the reaction mixture was stirred at room temperature for 12 h. After that, it was poured into a mixture of methanol (20 mL) – water (50 mL) in order to precipitate the polymer. The obtained solid was filtrated, washed with methanol and treated with a  $\text{NH}_4\text{OH}$  20% solution. The crude product was purified by Soxhlet extraction with chloroform for



Scheme 6. Assignment of the signals for CP41.

24 h. Pure copolymer CP41 was obtained as a dark purple powder. Yield: 20%.

FTIR (KBr):  $\nu = 3100$  (C–H of the thiophene), 2931, 2855 ( $\text{CH}_2$ ), 1717, 1690 (C=C), 1465, 1367, 1276 (C–N), 1174, 1064 (C–O), 917, 831 (out of plane, H–C=), 711 (C–S)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) (Scheme 6)  $\delta = 8.85$  ( $\text{H}^2\text{--H}^3$ ), 8.13 ( $\text{H}^7$ ), 8.10 ( $\text{H}^5$ ), 7.74 ( $\text{H}^4$ ), 7.26 ( $\text{H}^6$ ), 4.47 ( $\text{H}^y$ ), 3.33 ( $\text{H}^x$ ), 2.62 ( $\text{H}^{1a}$ ), 1.56 ( $\text{H}^{2a}\text{--H}^{4a}$ ), 1.47 ( $\text{H}^{5a}\text{--H}^{11a}$ ), 0.88 ( $\text{H}^{12a}$ ),  $-2.76$  (NH) ppm.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of the monomer and polymers

Monomer MTPP was synthesized according to the synthetic sequence shown in Scheme 1. First, 2-(thiophen-3-yl)ethanol (**1**) was treated in the presence  $\text{CBr}_4$  and  $\text{Ph}_3\text{P}$  in THF under argon atmosphere to give 3-(2-bromoethyl)thiophene (**2**). Separately, 4-hydroxy benzaldehyde (1 eq), benzaldehyde (3 eq), and pyrrole (4 eq) were reacted in the presence of  $\text{BF}_3 \cdot \text{OEt}_2$  in THF under inert atmosphere. The resulting intermediate was further oxidized with DDQ to give the 5-(4-hydroxyphenyl) 10, 15, 20-trisphenylporphyrin (**3**). Finally, compounds **2** and **3** were reacted using  $\text{K}_2\text{CO}_3$  as base and acetone as solvent with a catalytic amount of 18-crown-6 to give the desired monomer 5-(4-(2-thiophenyl)-oxyethylphenyl) 10,15,20-trisphenyl porphyrin (**4**), named here MTPP.

The preparation of the polymers and copolymers is illustrated in Scheme 2. Monomer MTPP was homopolymerized in the presence of  $\text{FeCl}_3$ , using chloroform as solvent under argon atmosphere. The obtained product was further reduced with  $\text{NH}_4\text{OH}$  to give the desired polymer PTPP. Unfortunately, this compound resulted to be totally insoluble in common organic solvents, and it was only characterized by FTIR spectroscopy.

Similarly, comonomer 3-dodecylthiophene (MDT) commercially available from Aldrich was homopolymerized under the above-mentioned reaction conditions to give the corresponding polymer PDT. This polymer is very soluble in organic solvents. The spectroscopic characterization of this polymer has been already reported in the literature.[36]

Finally, both monomers MTPP and MDT were copolymerized using  $\text{FeCl}_3$  as oxidizing agent and chloroform as solvent under argon atmosphere. For that, different ratios of MTPP: MDT were employed in order to obtain a series of copolymers: 1:2 (CP12), 1:4 (CP14) and 1:6 (CP16). Only the last two copolymers resulted to be fairly soluble in chloroform and THF so that they could be fully characterized.

#### 3.2. Characterization of the monomer and polymers

The obtained monomer and polymers were identified by FTIR and  $^1\text{H}$  NMR spectroscopy, and the related data

with the assignment of the signals for each compound are given in the experimental section.

Molecular weights of the obtained polymers were determined by GPC against a polystyrene standard, and the results are summarized in Table 1. As we can see, homopolymer PDT prepared as reference shows the highest molecular weight ( $M_w = 26,746$  g/mol), whereas homopolymer PTPP resulted to be totally insoluble. Concerning the copolymers, CP12 resulted to be insoluble in common organic solvents, whereas CP14 and CP16 showed molecular weights about ( $M_w = 11,675 - 12,406$  g/mol). The insolubility of PTPP and CP12 can be due to the high porphyrin content in these polymers, which allows the formation of intramolecular H-aggregates along the polymer backbone.

### 3.3. Optical properties of the polymers

The optical properties of monomer MTPP and soluble copolymers CP14 and CP16 were studied by absorption and fluorescence spectroscopy in the UV-vis region; the results are summarized in Table 2.

#### 3.3.1. Absorption spectra of the polymers

The absorption spectra of the porphyrins usually show a series of bands that are very characteristic of this family of aromatic compounds. For instance, the absorption spectrum of free-base tetraphenylporphyrin exhibits a very intense band at ca  $\lambda = 420$  nm (Soret band), followed by a series of less intense bands (Q bands) located between  $\lambda = 500 - 700$  nm, which are responsible of the purple color of these compounds. Free-base porphyrins possess a 2D symmetry that gives rise to four Q bands, whereas in metallated porphyrins, only two Q bands are observed.

The absorption spectra of monomer MTPP (Figure 1(A)) show a series of well-defined bands. The first band appears at  $\lambda = 282$  nm and arises from the thiophene ring of the monomer. Besides we can observe the Soret band of the porphyrin unit at  $\lambda = 422$  nm as well as four Q bands situated at  $\lambda = 519, 555, 597,$  and  $674$  nm, respectively.

Table 1. Molecular weights of the obtained polymers.

Polymer	$M_n^a$ (g/mol)	$M_w^a$ (g/mol)	PD <sup>a</sup> ( $M_w/M_n$ )
PTPP <sup>b</sup>	—	—	—
PDT	17,312	26,746	1.54
CP12 <sup>b</sup>	—	—	—
CP14	7514	11,675	1.56
CP16	8313	12,406	1.49

<sup>a</sup>Soluble part, obtained by GPC using THF as solvent, against a polystyrene standard.

<sup>b</sup>Not determined because of the insolubility of the polymer.

Regarding the obtained copolymers, the absorption spectrum of CP14 is shown in Figure 1(B). The UV-vis spectra of copolymers CP14- and CP16-containing tetraphenylporphyrin units are very similar and exhibited a  $\pi-\pi^*$  band at  $\lambda = 328$  nm arising from the PT backbone, followed by an intense Soret band centred at  $\lambda = 422$  nm and four Q bands at  $\lambda = 519, 555, 597,$  and  $674$  nm. It is worth to point out that in these copolymers increasing the content of MDT units with respect to that of MTPP (porphyrin-containing thiophene) causes a significant broadening of the PT band ( $\lambda = 328$  nm), so that it partially overlaps the Soret band in the absorption spectrum. This can be attributed to the higher polydispersity of these copolymers, where the thiophene content is much higher than that of porphyrin.

#### 3.3.2. Fluorescence spectra of the polymers

Fluorescence spectra of free-base and metallated porphyrins usually show two emission regions. The first one located between  $\lambda = 400 - 500$  nm, due to the  $S_2 \rightarrow S_0$  transition whereas the second one, which is more intense appears between  $\lambda = 550 - 800$  nm and arises from the  $S_1 \rightarrow S_0$  transition. The emission spectra of monomer MTPP and copolymer CP14, exciting at  $\lambda = 422$  nm, are shown in Figure 2.

The emission spectrum of monomer MTPP shows a set of bands at  $\lambda = 654$  nm and  $\lambda = 720$  nm coming from the porphyrin unit, due to the  $S_1 \rightarrow S_0$  transition. In the fluorescence spectrum of copolymer CP14, beside these bands, we can observe an additional band at 605 nm, which is not present in the emission spectrum of the monomer. It is evident that this band arises from the PT backbone that adopts a twisted conformation.

### 3.4. Comparison with other porphyrin-containing PT

To get a deeper insight into the influence of the spacers on the optical properties of the porphyrin-containing PT, we made a comparison between the absorption and fluorescence spectra of one of the copolymers reported here (CP14), which contains alkyl side chains, with a copolymer having oligo(ethylene glycol) spacers (alkoxy groups) (CTP-1), previously reported by us. Figure 3 shows the structures and the absorption spectra of CP41 and CTP-1, respectively.

As we can notice, both copolymers exhibit a Soret band at ca  $\lambda = 422$  nm as well as four Q bands at  $\lambda = 519, 555, 594,$  and  $674$ , so that the spectroscopic features due to the porphyrin unit are practically identical. However, the PT with oligo(ethylene glycol) chains (CTP-1) exhibits an additional absorption band at 451 nm due to the PT backbone, which has a slightly twisted conformation because of the steric hindrance of the porphyrin units. In contrast, the PT-bearing alkyl



Table 2. Optical properties of the MTPP monomer and the obtained polymers.

Compound	Absorption $\lambda$ (nm)	Cut off (nm)	Emission $\lambda$ (nm)	Cut off $\lambda$ (nm)
MTPP	282 <sup>a</sup> , 422 <sup>b</sup> , 519 <sup>c</sup> , 555 <sup>c</sup> , 597 <sup>c</sup> , 674 <sup>c</sup>	712	654 <sup>e</sup> , 720 <sup>e</sup>	810
PTPP <sup>f</sup>	—	—	—	—
CP12 <sup>f</sup>	—	—	—	—
CP14	328 <sup>a</sup> , 422 <sup>b</sup> , 519 <sup>c</sup> , 555 <sup>c</sup> , 594 <sup>c</sup> , 674 <sup>c</sup>	—	605 <sup>d</sup> , 654 <sup>e</sup> , 720 <sup>e</sup>	800
CP16	328 <sup>a</sup> , 422 <sup>b</sup> , 519 <sup>c</sup> , 555 <sup>c</sup> , 594 <sup>c</sup> , 674 <sup>c</sup>	—	605 <sup>d</sup> , 654 <sup>e</sup> , 720 <sup>e</sup>	800

<sup>a</sup>Absorption band of the PT backbone.

<sup>b</sup>Absorption band of the porphyrin (Soret's band).

<sup>c</sup>Absorption band of the porphyrin (Q bands).

<sup>d</sup>Emission band of the PT backbone.

<sup>e</sup>Emission band of the porphyrin.

<sup>f</sup>Not determined because of the insolubility of the polymer.

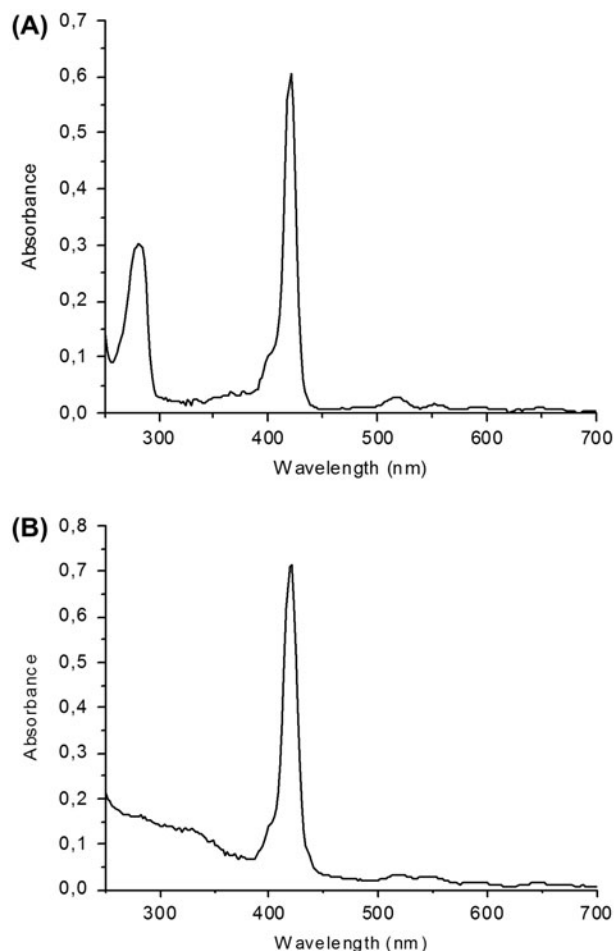


Figure 1. Absorption spectra of: (A) monomer MTPP and (B) copolymer CP14.

chains (CP14) does not show this band, instead, a broad absorption band, due to the PT backbone, can be seen at 328 nm. Consequently, CP14 adopts a more twisted conformation than that observed for CTP-1. Alkoxy substituted PT bearing a planar conformation usually exhibit a maximum absorption band at ca. 560 nm, whereas those having a twisted conformation do it at ca  $\lambda = 425$  nm

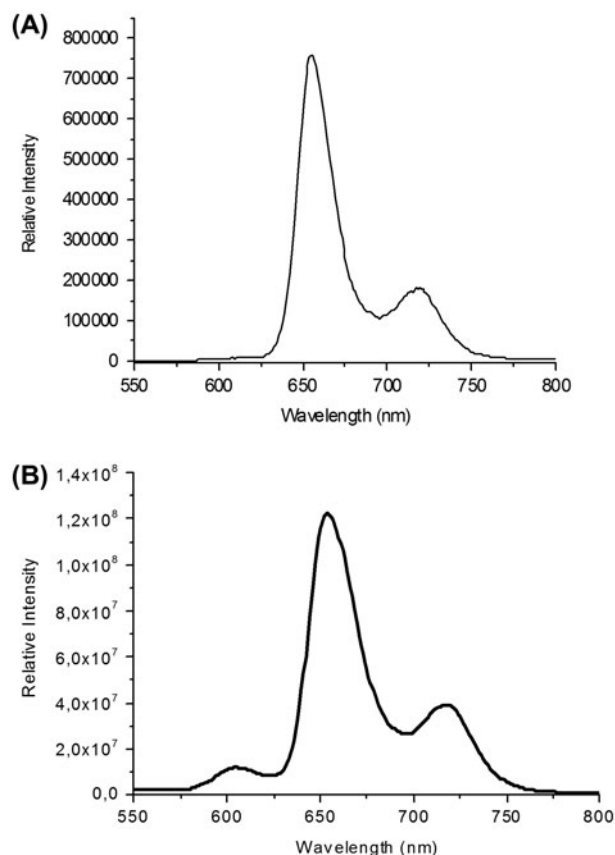


Figure 2. Fluorescence spectra of: (A) monomer MTPP and (B) copolymer CP14.

[37]. As it could be expected CTP-1 shows higher degree of conjugation than CP14 because the oxygen atoms of the oligo(ethylene glycol) chain enter into conjugation with the PT backbone, thereby inducing planarity, whereas the alkyl chains of CP14 cause a torsion of the polymer backbone.

On the other hand, the normalized emission spectra of CP41 and CTP-1 are shown in Figure 4. Both polymers exhibit the characteristic emission bands of the porphyrin moiety at 654 and 720 nm. Moreover, they

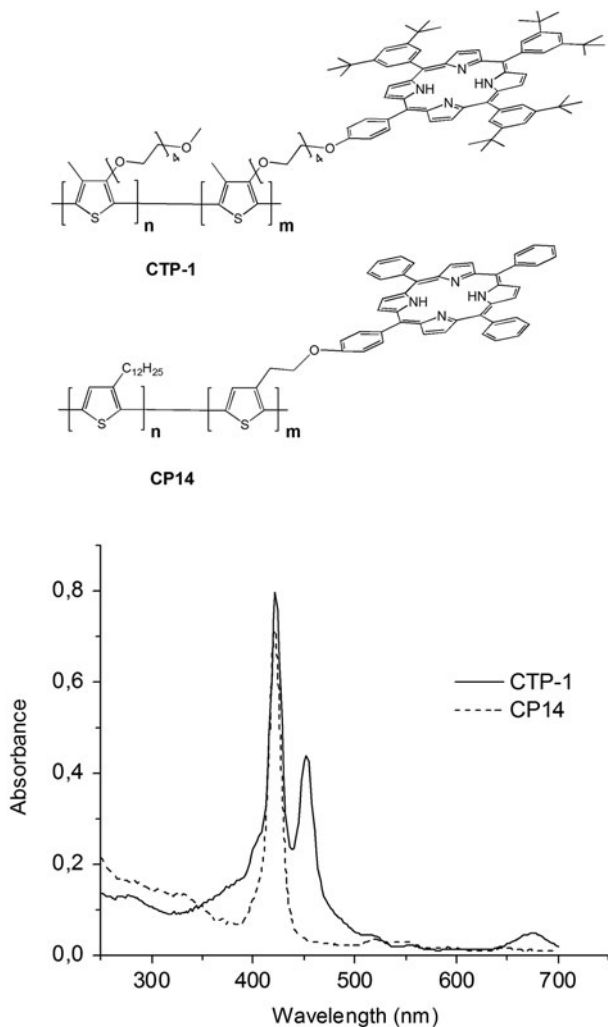


Figure 3. Comparison of the absorption spectra of polymer bearing alkyl chains CP14 and polymer bearing oligo(ethylene glycol) chains CTP-1.

show also a blue-shifted band centered at 605 and 541 for CP41 and CTP-1, respectively, which reveals that these polymers have different conjugation lengths. Although Figure 4 shows normalized fluorescence spectra of CP41 and CTP-1, it is worth to point out that the emission of CP41 is  $4.25 \times 10^5$  times more intense than that of CTP-1. This can be attributed to an energy transfer process from the porphyrin unit to the conjugated PT backbone in CTP-1, which shows significant absorption beyond 430 nm.

The band gap ( $E_g$ ) was calculated from absorption spectra for both polymers giving values of 3.78 eV and 2.75 eV for CP14 and CTP-1, respectively. These values were obtained taking into account the absorption band of the PT backbone. As we can see, the polymer with alkoxy chains CTP-1 resulted to be more conductor than its analogue CP14. Unfortunately, it was not possible to carry out cyclic voltammetry experiments with CP14 to

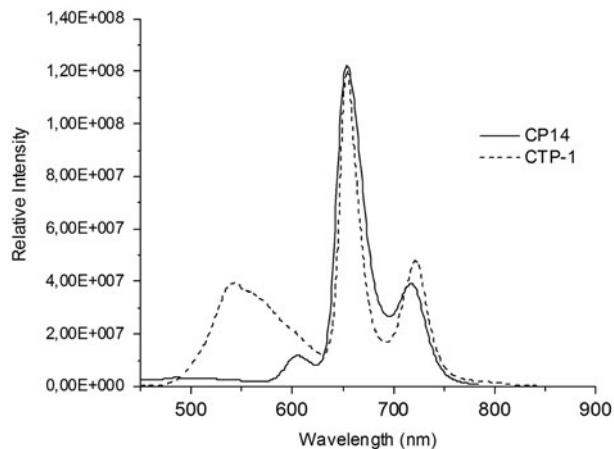


Figure 4. Comparison of the normalized emission spectra of polymer bearing alkyl chains CP14 and polymer bearing oligo(ethylene glycol) chains CTP-1. In order to normalize both spectra, the fluorescence spectrum of CTP-1 was multiplied by a factor of  $4.5 \times 10^5$ .

corroborate these values, because this polymer was very insoluble in acetonitrile.

#### 4. Conclusion

A novel series of PT containing meso-tetraphenylporphyrin units were synthesized and characterized. The homopolymer PTPP and copolymer CP12 were only characterized by FTIR spectroscopy because of their insolubility. However, copolymers CP14 and CP16 were also characterized by  $^1\text{H}$  NMR spectroscopy and showed molecular weights about ( $M_w = 11,675 - 12,406$  g/mol). All these polymers showed the expected characteristic absorption bands of the meso-tetraphenylporphyrin units and the absorption band related to the PT backbone, which appeared at  $\lambda = 328$  nm. According to this value, we can conclude that the obtained polymers exhibit low conjugation degree and twisted conformation. Moreover, the polymers showed two emission bands at  $\lambda = 654$  nm and 720 nm. Copolymers CP14 and CP16 exhibited also an additional emission band at  $\lambda = 605$  nm, arising from the PT backbone. The results were compared with those previously observed for another series of PT-bearing sterically hindered meso-3,5-ditert-butyl-tetraphenylporphyrin units. It was found that porphyrin-containing polymers having alkyl chains are less conjugated and significantly more emissive than those bearing oligo(ethylene glycol) segments.

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