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Synthesis, characterization and optical properties of novel oligothiophenes bearing pyrene units attached via well defined oligo (ethylene glycol) spacers

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ABSTRACT

Two new thiophene monomers bearing pyrene units attached via di(ethylene glycol) and tetra(ethylene glycol) spacers were synthesized, 3-methyl-4-(diethoxy) thiophene (**M2**) and 3-methyl-4-(tetraethoxy) thiophene (**M4**). These monomers were linked to thiophene and bithiophene via a Suzuki coupling reaction to give the corresponding terthiophenes and quaterthiophenes: [3,3-(di (diethoxypyrene)), 4,4‴dimethyl–2,2: 5′2″-terthiophene (**TT2**)], [3,3-(di(tetraethoxypyrene)), 4,4‴dimethyl–2,2:5′2″-terthiophene (**TT4**)], [3,3‴-di(diethoxypyrene), 4,4‴methyl-2,2′:5′: 2″:5″,2‴-quaterthiophene (**QT2**)], and [3,3‴-di(tetraethoxypyrene), 4,4‴methyl -2,2′:5′:2″:5″,2‴-quaterthiophene (**QT4**)]. The obtained oligothiophenes were characterized by ^{1}H, ^{13}C NMR spectroscopies and MALDI-TOF mass spectrometry. The optical properties of these compounds were studied by absorption and fluorescence spectroscopy. The absorption spectra of these compounds exhibited a broad absorption band at λ_{max} = 350 nm arising from the $S_0 \rightarrow S_2$ transition of the pyrene group. This broadening is an indication of the presence of pyrene–pyrene interactions in the ground state. A discrete band at ca λ = 385 due to the $S_0 \rightarrow S_1$ transition (n–π^*) of the oligothiophene backbone was also observed. The emission spectra of oligomers **TT2**, **TT4**, **QT2** and **QT4** showed a "monomer emission" band at λ_M = 379–450 nm followed by an intense excimer emission band at λ_E = 570 nm due to intramolecular pyrene–pyrene interactions. The effect of the flexible spacer length as well as that of the oligomer backbone influences significantly the formation of pyrene–pyrene complexes.

1. Introduction

Polythiophenes have been widely studied in the last 25 years because they show reasonably good stability, ease of structural modification, controllable optical properties and electrochemical behaviour [1–3]. Nevertheless its applications were limited because of its insolubility in many organic solvents, due to its extended π-conjugated structure [4]. Oligothiophenes are very promising for the development of novel organic electronic materials. For instance, the conducting properties of tetramers and hexamers have allowed the development of organic semiconductors and light-emitting diodes [5,6]. Oligothiophenes also show chromic effects similar to those found for their corresponding polymers [7,8]. Later, alkyl chains have been incorporated into the thiophene units in order to get monomers able to give soluble polymers. The incorporation of alkoxy groups into polythiophenes increases significantly their conductivity without diminishing their solubility in organic solvents [9,10].

It is very well known that π-conjugated oligomers are considered as promising materials since their optical and electrical properties make them excellent prospects for the elaboration of optoelectronic devices such as OFETs [11], OLEDs [12], electro-optic modulators and photovoltaic cells [13]. In oligothiophenes, the high conjugation degree causes a red-shift of the absorption and emission transition bands to the visible range, a significant reduction of the oxidation potentials as well as a high stabilization of the resulting radical-cation species, which is helpful for the elaboration of electronic materials [14].

On the other hand, pyrene is a fluorescent probe that has been widely used for polymer labeling because it easily forms excimers. Moreover, pyrene has a longer singlet lifetime than other chromophores, which facilitates the excimer formation. The main

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photophysical properties of pyrene excimers have been studied in detail by Winnik [15]. An excimer emission band appears if an excited-state molecule associates with a ground-state molecule after which the photon is delocalized over the conjugate to show a net change in the fluorescence spectral profile. The resulting photophysical properties give us useful information about the conjugated geometry, internal stacking and long distance pyrene–pyrene interactions.

In a previous work Aso et al. [16] improved the emission properties of oligothiophenes modified it with pyrene units at the 2- or 3-positions (Fig 1a). The insertion of pyrenes has the advantage of not only enhancing the fluorescence but also the thermal stability and charge-transport capability of the oligothiophene films.

Moggia et al. [17] prepared pyrene-substituted oligothiophene derivatives (Fig 1b) in order to study the influence of the pyrene groups on the opto-electronic properties. Spectroscopic studies in solution show that the introduction of the pyrene moieties induces a significant extension of electronic conjugation and, consequently, a reduction of the gap value.

In our research group, we have synthesized and characterized different series of π-conjugated polymers and oligomers bearing pyrene units in their structure [18]. We studied the effect of the internal stacking in the optical and photophysical properties [19–22]. Very recently, we carried out the incorporation of pyrene units into dendritic molecules bearing porphyrin and fullerene moieties in order to study the fluorescence energy transfer phenomenon (FRET) as a function of the distance between the donor (pyrene) and the acceptor group (porphyrin or fullerene) [23–25]. We reported also a series of polythiophenes containing pyrene groups attached via alkyl chains. These polymers exhibited good thermal stability and showed the presence of non parallel intramolecular pyrene–pyrene interactions [26].

Oligothiophene systems exhibit outstanding opto-electronic properties arising from their well defined conjugated backbone and the chromophores attached to it [27]. Indeed, the molecular architecture of the oligomers can be modified by changing the conjugated backbone length or by the incorporation of photoactive chromophores such as pyrene. This strategy is very useful to modulate their optical and photophysical properties in order to develop luminescent materials [28–30].

Here, we describe the synthesis, characterization and optical properties of a series of oligothiophenes [terthiophenes (**TT2, TT4**) and quaterthiophenes (**QT2, QT4**)], where TT means Terthiophene, QT means Quaterthiophene, 2 and 4 indicate the presence of di (ethylene glycol) and tetra(ethylene glycol) chains, respectively. These oligothiophenes bearing pyrene units attached via di (ethylene glycol) and tetra(ethylene glycol) spacers (Fig 2) were prepared in order to study the influence of the geometry of the molecules on the optical properties and the formation of excimers. Monomers and oligomers were characterized by ^{1}H and ^{13}C NMR spectroscopies and MALDI-TOF mass spectrometry. Finally their optical properties of were studied by absorption and fluorescence spectroscopy.

2. Experimental work

2.1. Apparatus

^{1}H NMR and ^{13}C NMR spectra of all the compounds were carried out in $CDCl_3$ solution, using a Bruker Avance 400 spectrometer, operating at 400 MHz and 100 MHz for ^{1}H and ^{13}C, respectively. MALDI-TOF mass spectra of the oligomers were recorded using dithranol as matriz, on a Bruker Daltonics flexAnalysis

Absorption spectra of the oligomers in $CHCl_3$ solution (spectrometric grade, concentration 1×10^{-5} M) were scanned on a Varian Cary 1 Bio UV/vis spectrophotometer model 8452A using quartz cells with a width of 1 cm. Steady state fluorescence spectra were recorded on a Photon Technology International LS-100 steady-state system with a pulsed Xenon flash lamp as the

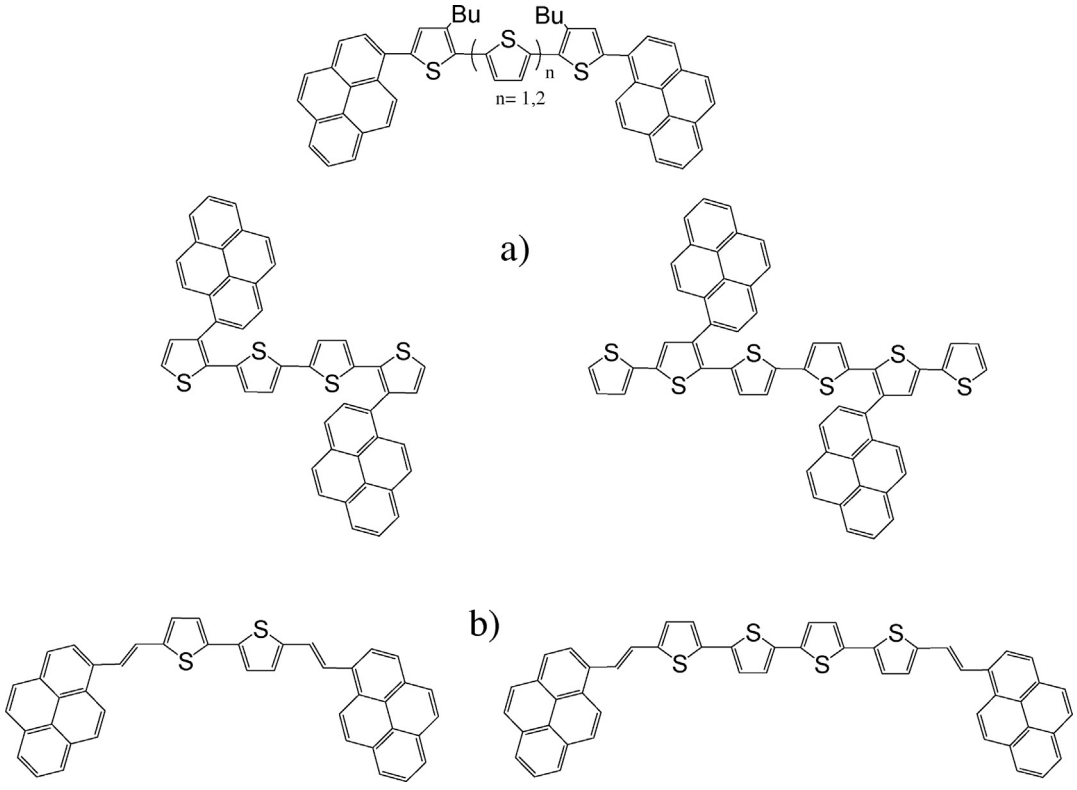

Fig. 1. (a) Chemical structure of pyrene-modified oligothiophenes, (b) pyrene-modified oligothiophenes Moggia.

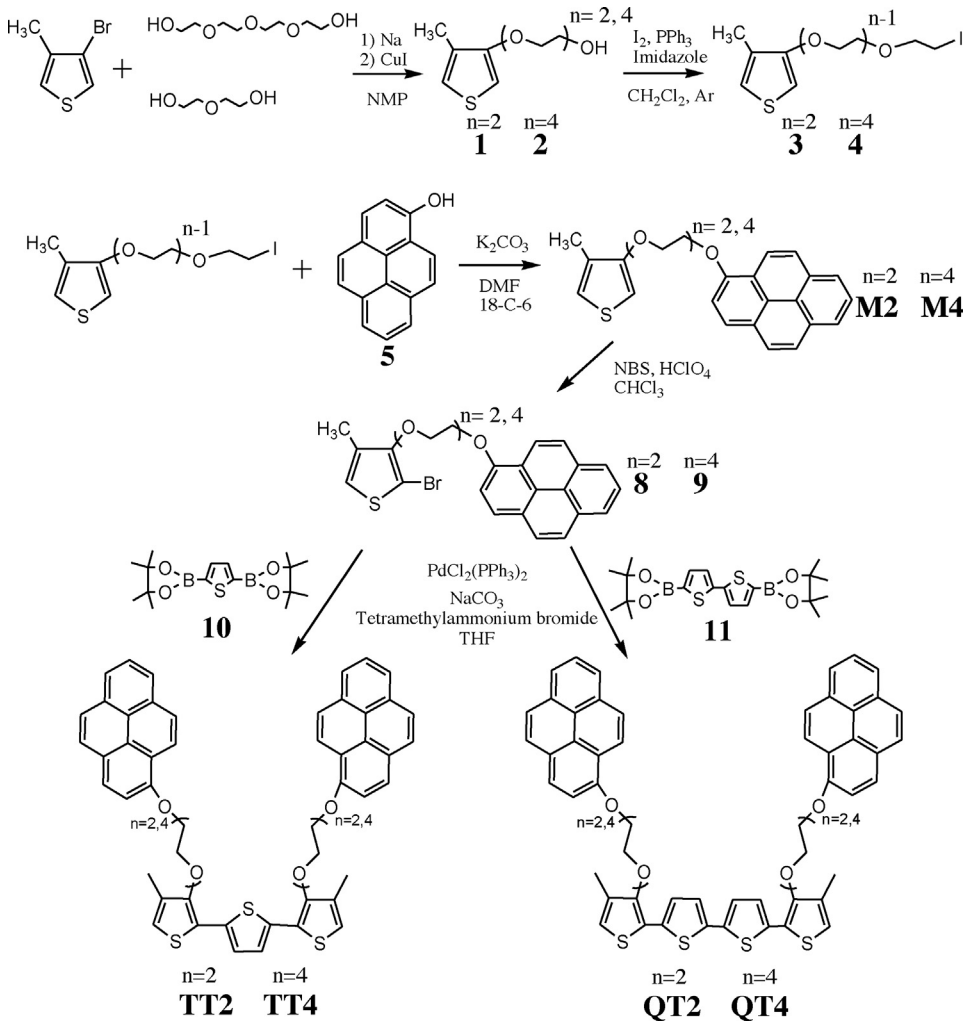

Fig. 2. Synthesis of oligothiophenes **TT2**,**TT4**, **QT2**, **QT4**.

light source. The slit widths on the excitation and emission monochromators equaled 1 and 1 nm, respectively. All spectra were obtained in $CHCl_3$ solution (spectrometric grade, concentration 1×10^{-6} M for all compounds), with the usual right-angle configuration, exciting at $\lambda = 345$ nm.

2.2. Chemicals

All the reagents involved in the synthesis were purchased from Aldrich and used as received. The solvents used in the reactions were dried and purified by simple distillation.

2.3. Synthesis of monomers and oligomers (terthiophenes and quaterthiophenes)

3-Methyl-4-(diethoxy) thiophene **(1)** was synthesized using a similar procedure reported by our research group [31,32]. Di (ethylene glycol) (7.49 g, 70.6 mmol) and Na (1.68 g, 73.3 mmol) were reacted at 80 °C for 4 h under nitrogen atmosphere to give the corresponding alkoxide. Afterwards, a mixture of 3-bromo-4-methylthiophene (5.0 g, 28.2 mmol), CuI (5.9 g, 31 mmol) in NMP (60 mL) was added and the reaction mixture, which was heated at 110 °C for 48 h. Then, it was cooled to room temperature, filtered, and the filtrates were extracted with diethyl ether (3×50 mL). The solution was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. Finally, the product was purified by column chromatography in silica gel, using hexane:ethyl acetate (60:40) as eluent to give **1** as a light yellow oil (2.68 g, 13.4 mmol). Yield: 47%.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) (Fig. 3): 6.81–6.78 (m, 1H, H^5), 6.15 (d, 1H, $J = 2.9$ Hz, H^2), 4.09 (t, 2H, Thioph—O—$\underline{CH_2}$, $J = 0.3$ Hz), 3.83 (t, 2H, Thioph—O—CH_2—$\underline{CH_2}$, $J = 0.3$ Hz), 3.71 (t, 2H, HO—$\underline{CH_2}$—CH_2-, $J = 0.3$ Hz), 3.65 (t, 2H, HO—CH_2—$\underline{CH_2}$—, $J = 0.9$ Hz), 2.08 (s, 3H, $\underline{CH_3}$—Thioph).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 155.8 (1C, Thioph—O), 129.17 (1C, Thioph—CH_3), 120.1 (1C, C5-Thioph), 96.75 (1C, C2-Thioph), 72.74 (1C, $\underline{CH_2}$—CH_2—OH), 69.69 (1C, Thioph—O—$\underline{CH_2}$), 69.65 (1C, Thioph—O—CH_2—$\underline{CH_2}$), 61.78 (1C, CH_2—OH), 12.82 (1C, CH_3).

3-Methyl-4-(tetraethoxy) thiophene **(2)** was synthesized using a similar procedure as that described for the previous compound [33]. Tetra(ethylene glycol) (13.74 g, 70.75 mmol) and Na (1.71 g, 27.8 mmol) were reacted at 80 °C for 4 h under nitrogen atmosphere to give the corresponding alkoxide. Afterwards, a mixture of 3-bromo-4-methylthiophene (5.0 g, 28.2 mmol), CuI (5.71 g, 29.9 mmol) in NMP (10 mL) was added and the reaction mixture, which was heated at 110 °C for 48 h. Then, it was cooled to room temperature, filtered, and the filtrates were extracted with diethyl ether (3×50 mL). The solution was dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. Finally, the crude product was purified by column chromatography in silica gel, using hexane:ethyl acetate (1:1) as eluent to give **2** as a light yellow oil (3.96 g, 13.5 mmol). Yield: 48%.

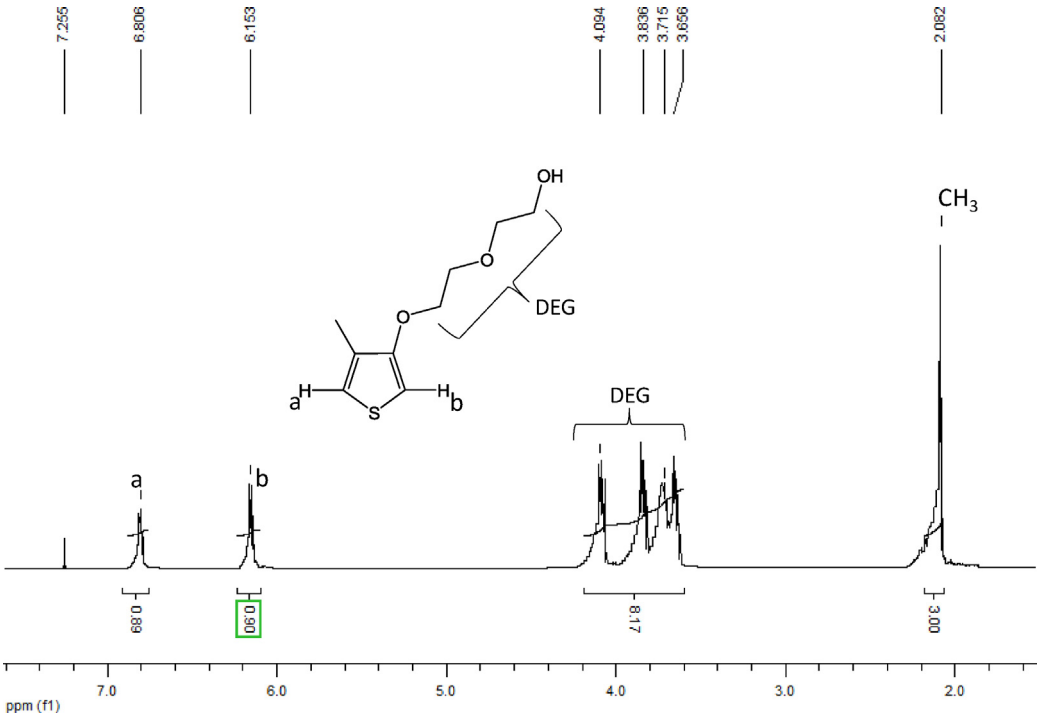

Fig. 3. ^{1}H NMR spectrum of 3-methyl-4-(diethoxy) thiophene (**1**) in $CDCl_3$ solution.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 6.79–6.81 (m, 1H, H^5), 6.15 (d, 1H, J = 3.0 Hz, H^2), 4.08–4.11 (m, 2H, Thioph—O—$\underline{CH_2}$), 3.82–3.86 (m, 2H, Thioph—O—CH_2—$\underline{CH_2}$), 3.64–3.74 (m, 10H, all the other OCH_2), 3.57–3.60 (m, 2H, $\underline{CH_2}$—OH), 2.08 (s, 3H, $\underline{CH_3}$—Thioph). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 155.96 (1C, Thioph—O), 129.29 (1C, Thioph—CH_3), 120.10 (1C, C5-Thioph), 96.74 (1C, C2-Thioph), 72.71 (1C, $\underline{CH_2}$—CH_2—OH), 70.99 (Thioph—O—$\underline{CH_2}$), 70.79 (1C, Thioph—O—CH_2—$\underline{CH_2}$), 70.74, 70.44, 69.85, 69.75 (4C, O—CH_2), 61.85 (1C, CH_2—OH), 12.89 (1C, CH_3).

3-Methyl-4-(4-(iodo) diethoxy) thiophene **(3)** was obtained from **1** using a similar procedure to that previously described by Almeida et al. [31]. First, CH_2Cl_2 (50 mL), triphenylphosphine (0.78 g, 3 mmol), imidazole (0.2 g, 3 mmol) and iodine (0.76 g, 3 mmol) were mixed in a bottom round flask under inert atmosphere. Then, a solution of **1** (0.59 g, 2 mmol) in anhydrous dichloromethane (20 mL) was added. The mixture 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, the crude product was purified by flash column chromatography on silica gel, using a mixture of ethyl acetate: hexanes (40:60) as eluent. The pure product was obtained as a light yellow solid (0.87 g, 1.8 mmol). Yield: 98 %. Because of its instability, this compound was immediately used in the next reaction.

3-Methyl-4-(4-(iodo) tetraetoxy) thiophene **(4)** was synthesized from **2** using a similar procedure as that described for the previous compound. First, CH_2Cl_2 (100 mL), triphenylphosphine (2.09 g, 8 mmol), imidazole (0.54 g, 8 mmol) and iodine (2.04 g, 8 mmol) were mixed in a bottom round flask under inert atmosphere. Then, a solution of **2** (1.56 g, 5 mmol) in anhydrous dichloromethane (50 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 (1:1) as eluent. The pure product was obtained as a light yellow solid (2.0 g, 4.7 mmol). Yield: 91%. Because of its instability this compound was immediately used in the next reaction.

1-Hydroxypyrene **(5)** [34]. Pyrene carboxaldehyde (10.0, 43.4 mmol) and *m*-chloroperbenzoic acid (11.31 g, 65.5 mmol) were dissolved in dry methylene chloride and refluxed with stirring under argon atmosphere for 24 h. The solution was concentrated at reduced pressure to give a red–brown residue. A solution of 10% $NaHCO_3$ (120 mL) was added to this residue with vigorous stirring, resulting in effervescence. Once the effervescence ceased, the remaining methylene chloride was removed at reduced pressure to give a dark purple solution and a powder. The precipitate was collected by filtration, washed with water, and allowed to dry, giving a brown solid. This solid was dissolved in a mixture of methanol (50 mL) and THF (50 mL), then 12 mL of 25% aqueous KOH solution was added to this mixture, which was then stirred under argon for 4 h. The mixture was concentrated under reduced pressure, diluted with 150 mL of a 2% aqueous KOH solution, and extracted two times with a mixture benzene/diethyl ether (1:1) (200 mL each) to remove the unreacted aldehyde and other organic impurities. The aqueous layer was collected and cooled in an ice bath and then acidified to pH 2 with concentrated HCl, resulting in the formation of a precipitate. This precipitate was collected by filtration and washed with water and then with 10% $NaHCO_3$, giving a black solid, which was dried under vacuum. The product was purified by flash chromatography using hexanes/ethyl acetate (75:25) as eluent. Removal of the solvent under reduced pressure gave a yellow solid (5.5 g). Yield: 58 %. Mp 176–178 °C (lit. 178–180 °C).

3-Methyl-4-(4-(pyren-1-yl) diethoxy) thiophene **(M2)**. 1-Hydroxypyrene **(5)** (1.35 g, 6.2 mmol) and 3-methyl-4-(4-(iodo) dietoxy) thiophene **(3)** (2.5 g, 6.2 mmol) dissolved in DMF (150 mL) were reacted in the presence of K_2CO_3 (5.99 g, 43 mmol), and a trace of 18-crown-6 ether. The reaction mixture was heated to reflux for 48 h; after this time, it was cooled to room temperature

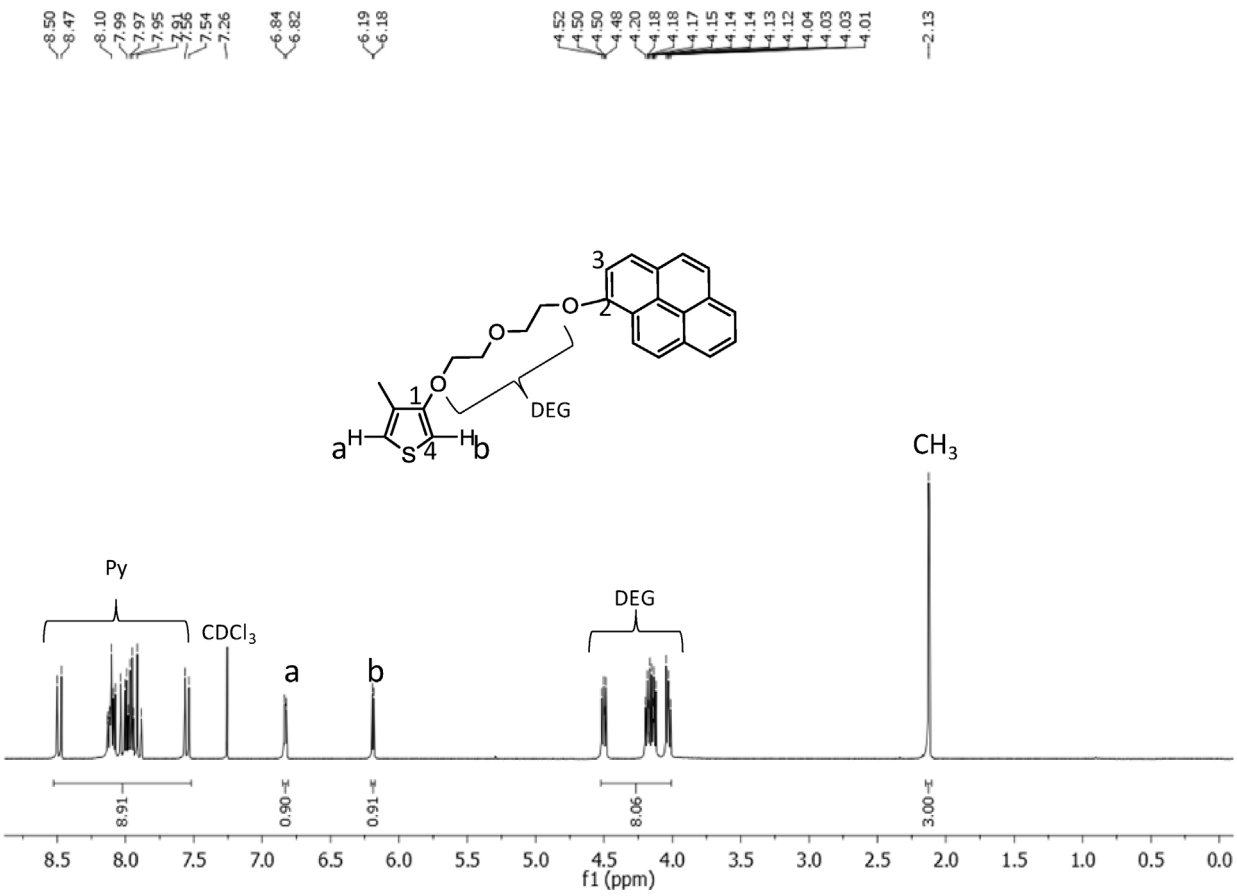

Fig. 4. ^{1}H NMR spectrum of monomer **M2** in $CDCl_3$ solution.

and concentrated at reduced pressure. The crude product was purified by flash column chromatography in silica gel, using hexanes:chloroform 1:1 as eluent, in order to remove the unreacted 1-hydroxypyrene, and then with hexanes:ethyl acetate 6:4. The pure product **(6)** was obtained as light greenish yellow oil (1.25 g, 4 mmol). Yield: 65 %.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) (Fig. 4): 8.54–7.48 (m, 9H, Py), 6.86 (m, 1H, H^a), 6.19 (d, 1H, H^b, J = 4 Hz), 4.43 (t, 2H, Py—O—$\underline{CH_2}$, J = 0.4 Hz), 4.15 (t, 2H, Thioph—O—$\underline{CH_2}$, J = 1.2 Hz), 4.07 (t, 2H, Py—O—CH_2—$\underline{CH_2}$, J = 0.4 Hz), 3.98 (t, 2H, Thioph—O—CH_2—$\underline{CH_2}$, J = 1.2 Hz), 2.13 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 156.05 (C^1, Thioph), 152.98 (C^2, Py); 131.87, 131.84, 129.35, 127.41, 126.58, 126.28, 125.97, 125.65, 125.61, 125.28, 125.07 124.48, 124,39, 121.52, 120.78, 120.18($C_{Py\text{-}thioph}$); 109.71(C^4, Thioph), 96.81 (C^3, Py), 70.27, 70.14, 69.87, 68.88 (C_{O-CH_2}), 12.96 (CH_3–Thioph).

3-Methyl-4-(4-(pyren-1-yl) tetraethoxy) thiophene **(M4)**. 1-Hydroxypyrene **(5)** (1.02 g, 4.7 mmol) and 3-methyl-4-(4-(iodo) dietoxy) thiophene **(4)** (2.0 g, 4.7 mmol) dissolved in DMF (150 mL) were reacted in the presence of K_2CO_3 (4.62 g, 33.5 mmol), and a trace of 18-crown-6 ether. The reaction mixture was heated to reflux for 48 h; then 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 1:1 as eluent, in order to remove the unreacted 1-hydroxypyrene, and then with hexanes:ethyl acetate 1:1. The pure product **(M4)** was obtained as a light greenish yellow oil, more oily than **(M2)** (1.37 g, 2.8 mmol). Yield: 60%.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) (Fig. 5): 8.52–7.49 (m, 9H, Py), 6.81 (m, 1H, H^a), 6.10 (d, 1H, H^b, J = 4.4 Hz), 4.44 (t, 2H, Py—O—$\underline{CH_2}$, J = 0.4 Hz), 4.03 (t, 2H, Thioph—O—$\underline{CH_2}$, J = 2.4 Hz), 3.85–3.70 (m, 12H, all O—$\underline{CH_2}$), 2.11 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 156.01 (C^1, Thioph), 153.00 (C^2, Py); 131.85, 131.81, 129.26, 127.37, 126.5, 126.27, 125.94, 125.62, 125.57, 125.23, 125.04, 124.45, 124.34, 121.52, 120.69, 120.07 ($C_{Py\text{-}thioph}$); 109.63(C^4, Thioph), 96.68 (C^3, Py); 71.16, 70.98, 70.88, 70.85, 70.06, 69.78, 69.70, 68.80 (C_{O-CH_2}), 12.91 (CH_3—Thioph).

2-Bromo-4-methyl-3-(3-(pyren-1-yl) dietoxy) thiophene **(8)** was synthesized from **M2** using a similar procedure described by Goldberg and Alper [35]. To a suspension of *N*-bromosuccinimide NBS (0.026 g, 0.15 mmol) in $CHCl_3$ (5 mL), 3-methyl-4-(4-(pyren-1-yl) dietoxy) thiophene **(M2)** (0.061 g, 0.15 mmol) and 70% $HClO_4$, (1 mol %) were added. The reaction mixture was stirred for 1.5 h at room temperature; afterwards K_2CO_3 (ca. 20 mg) was added. The solids were filtered, the solvent was evaporated at room temperature, and the residue was distilled under vacuum to give **8** as clear greenish yellow crystals (0.045 g). Yield: 65%.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) (Fig. 6): 8.56–7.49 (m, 9H, Py), 6.79 (m, 1H, H^a), 4.46 (t, 2H, Py—O—$\underline{CH_2}$, J = 0.4 Hz), 4.27 (t, 2H, Thioph—O—$\underline{CH_2}$, J = 2.4 Hz), 4.08 (t, 2H, Py—O—CH_2—$\underline{CH_2}$, J = 0.4 Hz), 3.94 (t, 2H, Thioph—O—CH_2—$\underline{CH_2}$, J = 1.2 Hz), 2.14 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 155.95 (C^1, Thioph), 152.68 (C^2, Py); 131.77, 131.74, 129.15, 127.21, 126.38, 126.08, 125.67, 125.35, 125.41, 125.18, 124.87 124.18, 124.29, 121.42, 120.68, 120.08($C_{Py\text{-}thioph}$); 109.41(C^4-Br), 96.71 (C^3, Py), 70.07, 69.96, 69.77, 68.68 (C_{O-CH_2}), 12.76 (CH_3–Thioph).

2-Bromo-4-methyl-3-(3-(pyren-1-yl) tetraetoxy) thiophene **(9)** was synthesized from **M4** using a similar procedure as described for the previous compound. To a suspension of *N*-

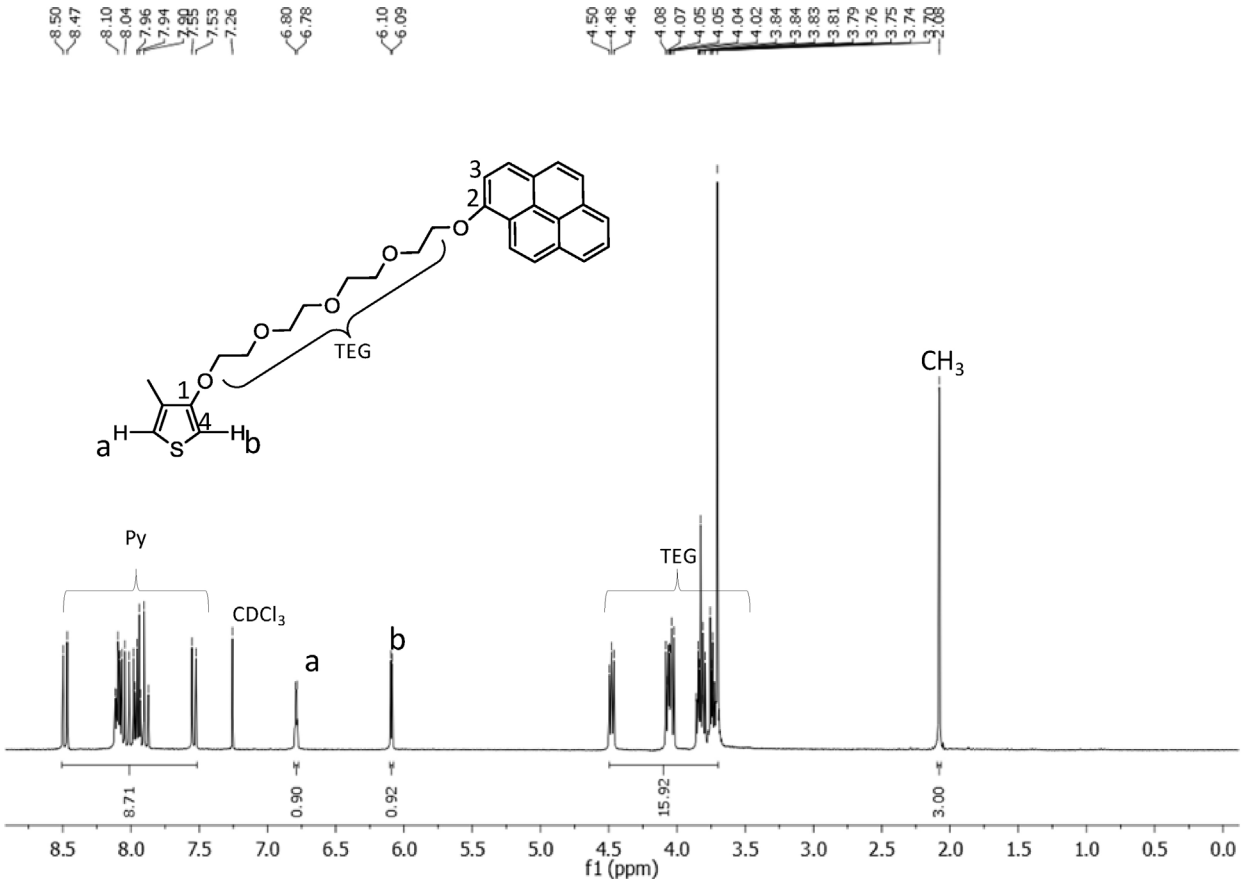

Fig. 5. ^{1}H NMR spectrum of monomer **M4** in $CDCl_3$ solution.

bromosuccinimide NBS (0.31 g, 1.7 mmol) in $CHCl_3$ 5 mL, 3-methyl-4-(4-(pyren-1-yl) tetraetoxy) thiophene **(M4)** (0.861 g, 1.7 mmol) and 70% $HClO_4$, (1 mol %) were added. The reaction mixture was stirred for 1.5 h at room temperature. Afterwards K_2CO_3 (ca. 20 mg) was added, the solids were filtered, the solvent was evaporated at room temperature, and the residue was distilled under vacuum to give **9** as clear greenish yellow crystals (0.69 g). Yield: 70%.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) (Fig. 7): 8.49–7.53 (m, 9H, Py), 6.76 (m, 1H, H^a),

4.49 (t, 2H, Py—O—$\underline{CH_2}$, J = 0.1 Hz), 4.13 (t, 2H, Thioph—O—$\underline{CH_2}$, J = 1.2 Hz), 4.07 (t, 2H, Py—O—CH_2—$\underline{CH_2}$, J = 2.8 Hz), 3.83 (t, 2H, Thioph—O—CH_2—$\underline{CH_2}$, J = 4 Hz), 3.74 (m, 8H, the rest of O—$\underline{CH_2}$), 2.10 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 155.8 (C^1, Thioph), 152.91 (C^2, Py); 131.55, 131.61, 129.16, 127.27, 126.32, 126.07, 125.64, 125.52, 125.47, 125.13, 124.87, 124.25, 124.14, 121.32, 120.49, 119.93 ($C_{Py-thioph}$); 109.33(C^4-Br), 96.48 (C^3, Py); 71.06, 70.68, 70.67, 70.67, 69.89, 69.66, 69.54, 68.34 (C_{O-CH_2}), 12.72 (CH_3–Thioph).

2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) thiophene **(10)**. First 2,5-dibromothiophene was synthesized, using a bromination procedure similar to that described for the previous compound. To a suspension of *N*-bromosuccinimide NBS (8.88 g, 49 mmol) in hexanes 100 mL, thiophene (2 g, 23 mmol) and 70% HClO, (1 mol %) were added, and the reaction mixture was stirred for 30 min at room temperature. Later, K_2CO_3 (ca. 20 mg) was added, the solids were filtered, the solvent was evaporated at room temperature, and the residue was distilled under vacuum to give 2,5-dibromothiophene (5.03 g). Yield: 87.5%.

The corresponding oxoborolane **(10)** was obtained using a procedure previously reported by Wu et al. [36]. A solution of *n*-butyllithium (2 ml, 21 mmol, 2.5 M in hexanes) was added dropwise to a solution of 2,5-dibromothiophene (2.5 g, 10.3 mmol) in 50 mL of anhydrous THF under nitrogen at −78 °C. Then, it was stirred at −78 °C for 2 h, and 2-isopropoxy-4, 4,5,5-tetramethyl-1,3,2-dioxaborolane (4.42 ml, 21.7 mmol) was added. After 24 h the mixture was poured into water and extracted with chloroform three times. The organic phase was washed with water and brine, and dried over $MgSO_4$. After the removal of the organic solvents, the crude product was purified by flash chromatography using hexanes/chloroform 80:20 as eluent. The product was obtained a white solid (2.9 g). Yield: 65 %. Mp: 226.5–228 °C (lit. 227–231 °C).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.66 (d, 2H, Thioph), 1.32 (s, 24H, —CH_3)

^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 137.76 (4C, Thioph), 84.21 (4C, C—O), 24.85 (8C, CH_3).

5,5′-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene **(11)**. First 5,5′-dibromo-2,2′-bithiophene was synthesized, using a bromination procedure similar to that described for the previous compound. To a suspension of *N*-bromosuccinimide NBS (2.82 g, 15.86 mmol) in hexanes 50 mL, 2,2-bithiophene (7.55 g, 1.25 mmol) and 70% HClO, (1 mol %) were added, and the reaction mixture was stirred for 30 min at room temperature. Afterwards K_2CO_3 (ca. 20 mg) was added, the solids were filtered, the solvent was evaporated at room temperature, and the residue was distilled under vacuum to give 2.21 g of 5,5′-dibromo-2,2′-bithiophene (90.5 %). The oxoborolane **(11)** was obtained using a procedure previously reported by Wu et al. [36]. A solution of *n*-butyllithium (0.57 ml, 6.2 mmol, 2.5 M in hexanes) was added dropwise to a solution of 5,5′-dibromo-2,2′-bithiophene (0.96 g, 2.9 mmol) in anhydrous THF under nitrogen at −78 °C. Then, it was

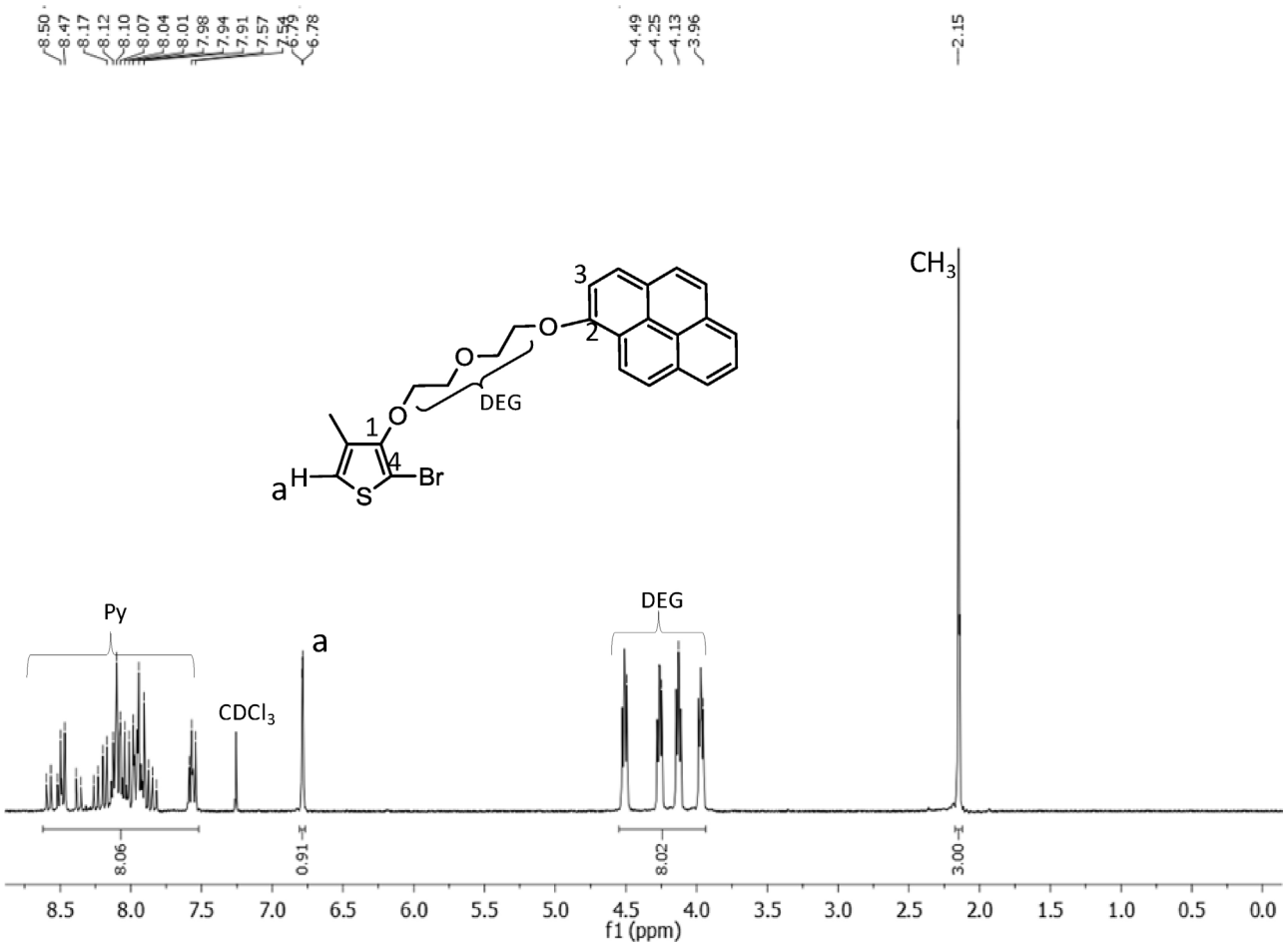

Fig. 6. ^{1}H NMR spectrum of the brominated monomer (**8**) in $CDCl_3$ solution.

stirred at −78 °C for 2 h; then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.27 mL, 6.2 mmol) was added. After overnight the mixture was poured into water and extracted with chloroform three times. The organic phase was washed with water and brine, and dried over $MgSO_4$. After the removal of the solvents, the crude product was purified by flash chromatography using a mixture hexanes/chloroform 80:20 as eluent. The pure product was obtained as a brown solid (0.86 g). Yield: 69.5 %. Mp: 226.5–228 °C (lit. 227–231 °C).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.52–7.51 (d, 2H, Thioph, J = 4.8 Hz), 7.29–7.28 (d, 2H, Thioph, J = –4.8 Hz), 1.34 (s, 24H, —CH_3)

^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 143.96 (2C, C_2 Thioph–Thioph), 138.09 (4C, $C_{3,4}$ Thioph), 125.9 (2C, C_5 Thioph-B), 84.3 (4C, C—CH_3) 24.84 (8C, CH_3).

2.3.1. Synthesis of terthiophene (*TT2*)

This trimer was obtained using a procedure similar to that described by Anant et al. [37]. The compounds 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) thiophene **(10)** (0.336 mg, 1 mmol), 2-bromo-4-methyl-3-(3-(pyren-1-yl) dietoxy) thiophene **(8)** (0.595 g, 2.1 mmol), tetramethylammonium bromide (ca.), and Na_2CO_3 (2 M, 2 mL) were dissolved in 30 mL of anhydrous THF. The solution was purged with nitrogen for 20 min. Then, bis(triphenylphosphine) palladium(II) dichloride (57 mg, 0.05 mmol) was added and the reaction mixture was heated with stirring at 80 °C. The reaction progress was followed by TLC and after 24 h it was worked up. The cooled mixture was extracted with dichloromethane, and the extracts were washed with saturated brine and dried over Na_2SO_4. The crude product was purified by column chromatography in silica gel, using a mixture chloroform: hexanes (80:20) as eluent to obtain (**TT2**) (620 mg). Yield: 54%.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) (Fig. 8): 8.52–7.50 (m, 18H, Py), 6.85 (d, 2H, H^a, J = 4.6 Hz), 6.79 (d, 2H, H^b, J = 4.2 Hz), 4.47 (t, 4H, Py—O—$\underline{CH_2}$, J = 0.41 Hz), 4.25 (t, 4H, Thioph—O—$\underline{CH_2}$, J = 1.1 Hz), 4.10 (t, 4H, Py—O—CH_2—$\underline{CH_2}$, J = 0.2 Hz), 4.0 (t, 4H, Thioph—O—CH_2—$\underline{CH_2}$, J = 1.1 Hz), 2.16 (s, 6H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 153.63 (C^1, Thioph), 153.41 (C^2, Py); 132.30, 132.17, 131.69, 131.65, 130.32, 130.26, 130.19, 128.91, 128.72, 127.60, 126.18, 126.10, 125.18, 123.66, 123.04, 121.73, 120.13, 118.95 ($C_{Py-thioph}$), 110.07 (C^4, Thioph), 96.73 (C^3, Py), 72.73, 70.79, 70.18, 68.92 (C_{O-CH_2}), 13.78 (CH_3–Thioph).

2.3.2. Synthesis of terthiophene (*TT4*)

This trimer obtained using a procedure similar to that described for the previous compound. 2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) thiophene **(10)** (0.13 g, 0.4 mmol), 2-Bromo-4-methyl-3-(3-(pyren-1-yl) tetraetoxy) thiophene **(9)** (0.466 g, 0.8 mmol), tetramethylammonium bromide (ca.), and Na_2CO_3 (2 M, 1.5 mL) were dissolved in 30 mL of anhydrous THF. The solution was purged with nitrogen for 20 min; then bis(triphenylphosphine) palladium(II) dichloride (20 mg, 0.002 mmol) was added and the reaction mixture was heated with stirring at 80 °C. The reaction progress was followed by TLC and after 24 h was worked up. The cooled mixture was extracted with dichloromethane, and the extracts were washed with saturated brine and dried over Na_2SO_4. The crude product was purified by column

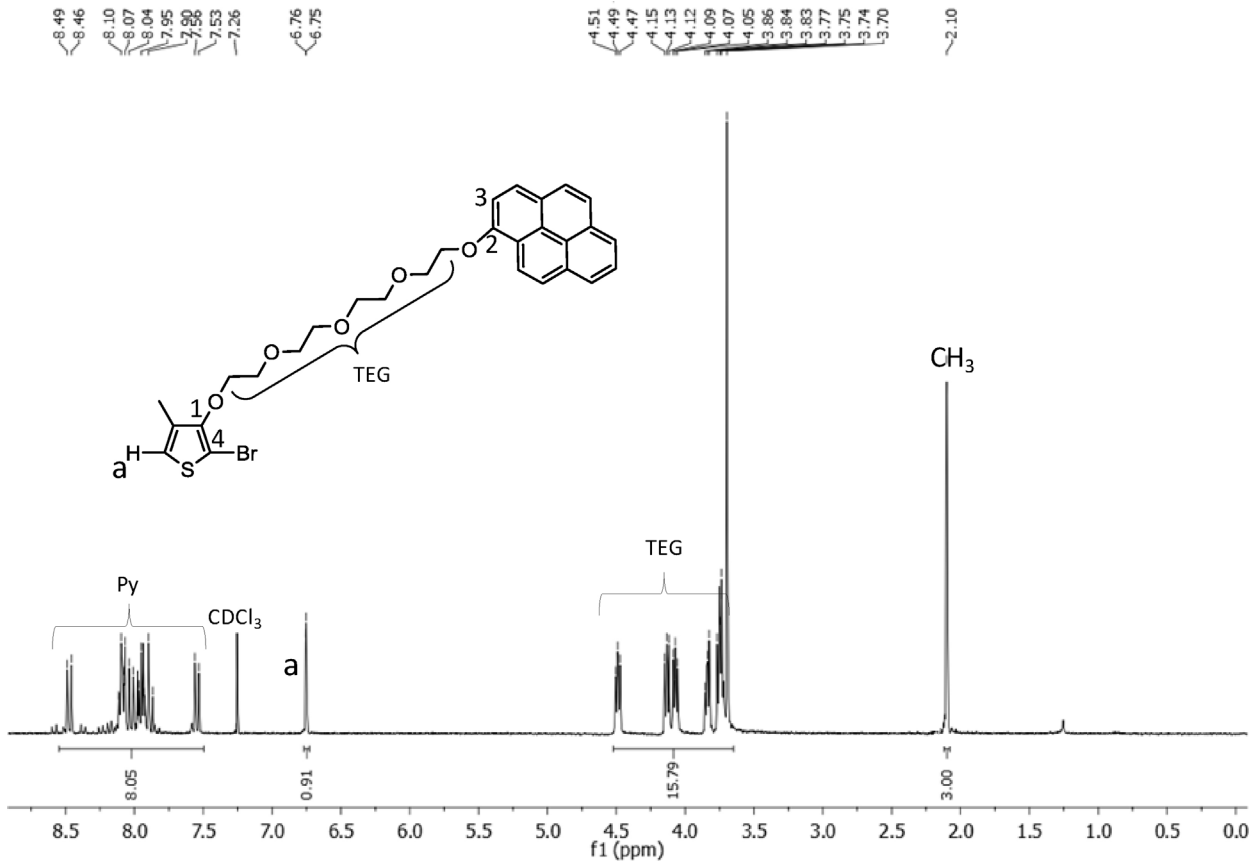

Fig. 7. ^{1}H NMR spectrum of brominated monomer (**9**) in $CDCl_3$ solution.

chromatography in silica gel, employing chloroform: hexanes (90:10) as eluent to obtain **TT4** (519 mg). Yield: 58%.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) (Fig. 9): 8.5–7.52 (m, 18H, Py), 6.78 (d, 2H, H^a, J = 4.3 Hz), 6.67 (d, 2H, H^b, J = 4.1 Hz), 4.47 (t, 4H, Py—O—$\underline{CH_2}$, J = 0.35 Hz), 4.06 (t, 4H, Thioph—O—$\underline{CH_2}$, J = 2.1 Hz), 3.86–3.70 (m, 24H, all O—$\underline{CH_2}$), 2.08 (s, 6H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 155.95 (C^1, Thioph), 152.95 (C^2, Py); 131.79, 131.75, 129.24, 127.32, 126.48, 126.21, 125.84, 125.67, 125.55, 125.20, 125.09, 124.44, 124.30, 121.43, 120.09, 119.99 ($C_{Py–thioph}$); 109.62(C^4, Thioph), 96.59 (C^3, Py); 71.17, 70.97, 70.88, 70.84, 70.33, 70.09, 69.77, 69.66 (C_{O-CH_2}), 12.84 (CH_3–Thioph).

2.3.3. Synthesis of quaterthiophene (*QT2*)

This quatertiophene was obtained using a similar procedure to that described for the previous compound. 5,5′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene **(11)** (0.5 g, 1.2 mmol), 2-bromo-4-methyl-3-(3-(pyren-1-yl) dietoxy) thiophene **(8)** (0.69 g, 2.4 mmol), tetramethylammonium bromide (ca.), and Na_2CO_3 (2 M, 3 mL) were dissolved in 30 mL of anhydrous THF. The solution was purged with nitrogen for 20 min, then bis (triphenylphosphine) palladium(II) dichloride (69 mg, 0.06 mmol) was added and the reaction mixture was heated with stirring at 80 °C. The reaction progress was followed by TLC and after 24 h the reaction mixture was worked up. The cooled mixture was extracted with dichloromethane, and the extracts were washed with saturated brine and dried over Na_2SO_4. The crude product was purified by column chromatography with silica gel, using chloroform: hexane (80:20) as eluent to give (**QT2**) (718 mg). Yield: 61%.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) (Fig. 10): 8.51–7.53 (m, 18H, Py), 6.84 (d, 2H, H^a, J = 4.0 Hz), 6.79 (d, 2H, H^b, J = 4.1 Hz), 6.48 (d, 2H, H^c, J = 4.4 Hz), 4.49 (t, 4H, Py—O—$\underline{CH_2}$, J = 0.40 Hz), 4.26 (t, 4H, Thioph—O—$\underline{CH_2}$, J = 1.2 Hz), 4.11 (t, 4H, Py—O—CH_2—$\underline{CH_2}$, J = 0.2 Hz), 3.96 (t, 4H, Thioph—O—CH_2—$\underline{CH_2}$, J = 1.1 Hz), 2.16 (s, 6H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 153.62 (C^1, Thioph), 153.42 (C^2, Py); 132.17, 131.27, 131.17, 130.32, 130.27, 130.14, 128.91, 127.61, 126.39, 126.19, 126,10, 125.45, 124,92, 124.89, 124.82, 123.67, 123.04, 121.70, 119.88 ($C_{Py–thioph}$); 110.07 (C^4, Thioph), 96.72 (C^3, Py), 72.72, 70.79, 70.18, 68.93, 68.80 (C_{O-CH_2}), 13.77 (CH_3–Thioph).

2.3.4. Synthesis of quaterthiophene (*QT4*)

This quatertiophene was obtained employing a similar procedure to that described for the previous compound. 5,5′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene **(11)** (0.171 g, 0.4 mmol), 2-bromo-4-methyl-3-(3-(pyren-1-yl) tetraetoxy) thiophene **(9)** (0.471 g, 0.8 mmol), tetramethylammonium bromide (ca.), and Na_2CO_3 (2 M, 3 mL) were dissolved in 30 mL of anhydrous THF. The solution was purged with nitrogen for 20 min, then bis(triphenylphosphine) palladium(II) dichloride (23 mg, 0.02 mmol) was added and the reaction mixture was heated with stirring at 80 °C. The reaction progress was followed by TLC and after 24 h it was worked up. The cooled mixture was extracted with dichloromethane, and the extracts were washed with saturated brine and dried over Na_2SO_4. The crude product was purified by column chromatography in silica, using a mixture chloroform: hexanes (80:20) as eluent to obtain **QT4** (620 mg). Yield: 54%.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) (Fig. 11): 8.49–7.56 (m, 9H, Py), 6.78 (d, 2H, H^a, J = 4.1 Hz), 6.73 (d, 2H, H^b, J = 4.0 Hz), 6.39 (d, 2H, H^c, J = 4.3 Hz), 4.48 (t, 2H, Py—O—$\underline{CH_2}$, J = 0.4 Hz), 4.07 (t, 2H, Thioph—O—$\underline{CH_2}$, J = 2.1 Hz), 3.82-3.70 (m, 12H, all O—$\underline{CH_2}$), 2.07 (s, 3H, CH_3).

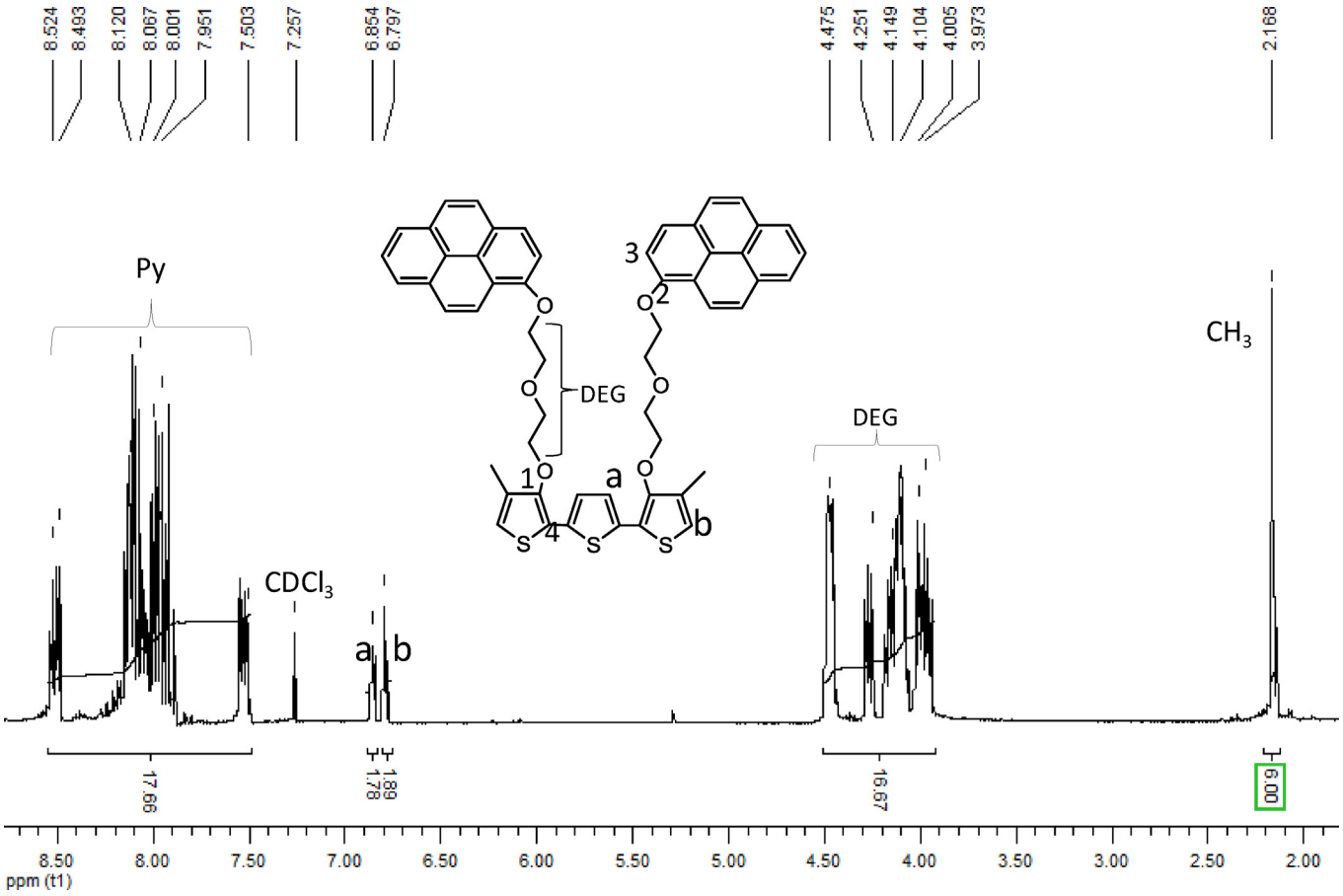

Fig. 8. ^{1}H NMR spectrum of terthiophene (**TT2**) in $CDCl_3$ solution.

^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 155.95 (C^1, Thioph), 153.48 (C^2, Py); 131.79, 131.75, 129.25, 127.33, 126.48, 126.22, 125.90, 125.56, 125.20, 124.99, 124.56, 124.40, 124.30, 121.44, 120.66, 120.00, 119.77, 109.60, ($C_{Py-thioph}$); 109.60(C^4, Thioph), 96.60 (C^3, Py); 72.57, 71.16, 70.97, 70.84, 70.33, 70.88, 69.66, 68.81 (C_{O-CH_2}), 12.86 (CH_3–Thioph).

3. Results and discussion

We carried out the synthesis and characterization of two monomers and a new series of oligothiophenes: terthiophenes (**TT2, TT4**) and quaterthiophenes (**QT2, QT4**). The synthesis of the monomers and the oligomers is illustrated in Fig. 2. The new monomers were prepared from 3-bromo-4-methyl-thiophene. This compound was reacted with di(ethylene glycol) and tetra (ethylene glycol) alkoxides (prepared in situ with sodium), using CuI as catalyst and NMP as solvent under inert atmosphere to give the corresponding 3-alkoxythiophenes (**1, 2**). These intermediates were reacted with I_2, using triphenyl phosphine, imidazole and CH_2Cl_2 as solvent to obtain the iodinated intermediates (**3, 4**). Such compounds were reacted with 1-hydroxypyrene (**5**) using K_2CO_3 as base, 18-Crown-6 as catalyst and DMF as solvent to yield the desired monomers (**M2, M4**). Bromination of the monomers was performed in position 2 of the thiophene ring with NBS in acidic medium ($HClO_4$).

On the other hand, we achieved the synthesis of the oxoborolanes [2,5-bisoxoborolanethiophene (**10**) and 5,5′-bisoxoborolane-2,2′-bithiophene (**11**)]. First, we prepared the brominated compounds 2,5-dibromothiophene and 5,5′-dibromo-2,2′-bithiophene, using NBS as a source of bromine. The oxoborolanes were obtained using *n*-butyllithium, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and anhydrous THF as solvent under nitrogen at −78 °C.

C–C couplings were performed via Suzuki reaction between the monomers, brominated in position 2 of the thiophene ring, and the oxoborolanes, using Na_2CO_3 and $PdCl_2(PPh_3)_2$ to yield the desired terthiophenes (**TT2, TT4**) and quaterthiophenes (**QT2, QT4**).

3.1. Characterization of monomers and oligomers

The structure of monomers was confirmed by NMR spectroscopy. The ^{1}H NMR spectrum of monomer (M**2**) in $CDCl_3$ solution is shown in Fig. 4. As we can see, there is a multiplet at 8.54–7.48 ppm due to the protons of the pyrene unit, followed by a multiplet at 6.86 assigned to proton H^a of thiophene ring and a doublet at 6.19 ppm due to proton H^b with $J = 4$ Hz. A triplet at 4.43 ppm due to the protons Py—O—$\underline{CH_2}$, with $J = 0.4$ Hz and triplet at 4.15 ppm attributed to proton of Thioph—O—$\underline{CH_2}$ with $J = 1.2$ Hz can be also observed. In addition, a triplet at 4.07 ppm due to the protons Py—O—CH_2—$\underline{CH_2}$ with $J = 0.4$ Hz, followed by a triplet 3.98 ppm corresponding to protons Thioph—O—CH_2—$\underline{CH_2}$ with $J = 1.2$ Hz and a singlet at 2.13 due to the CH_3 protons are also seen.

The ^{1}H NMR spectrum of monomer (M**4**) in $CDCl_3$ solution is shown in Fig. 5. As we can notice, there is a multiplet at 8.52–7.49 ppm due to the protons of the pyrene unit, followed by a multiplet at 6.81 assigned to proton H^a of thiophene ring and a doublet at 6.10 ppm, due to proton H^b with $J = 4.4$ Hz. A triplet at 4.44 ppm due to the protons Py—O—$\underline{CH_2}$, with $J = 0.4$ Hz followed

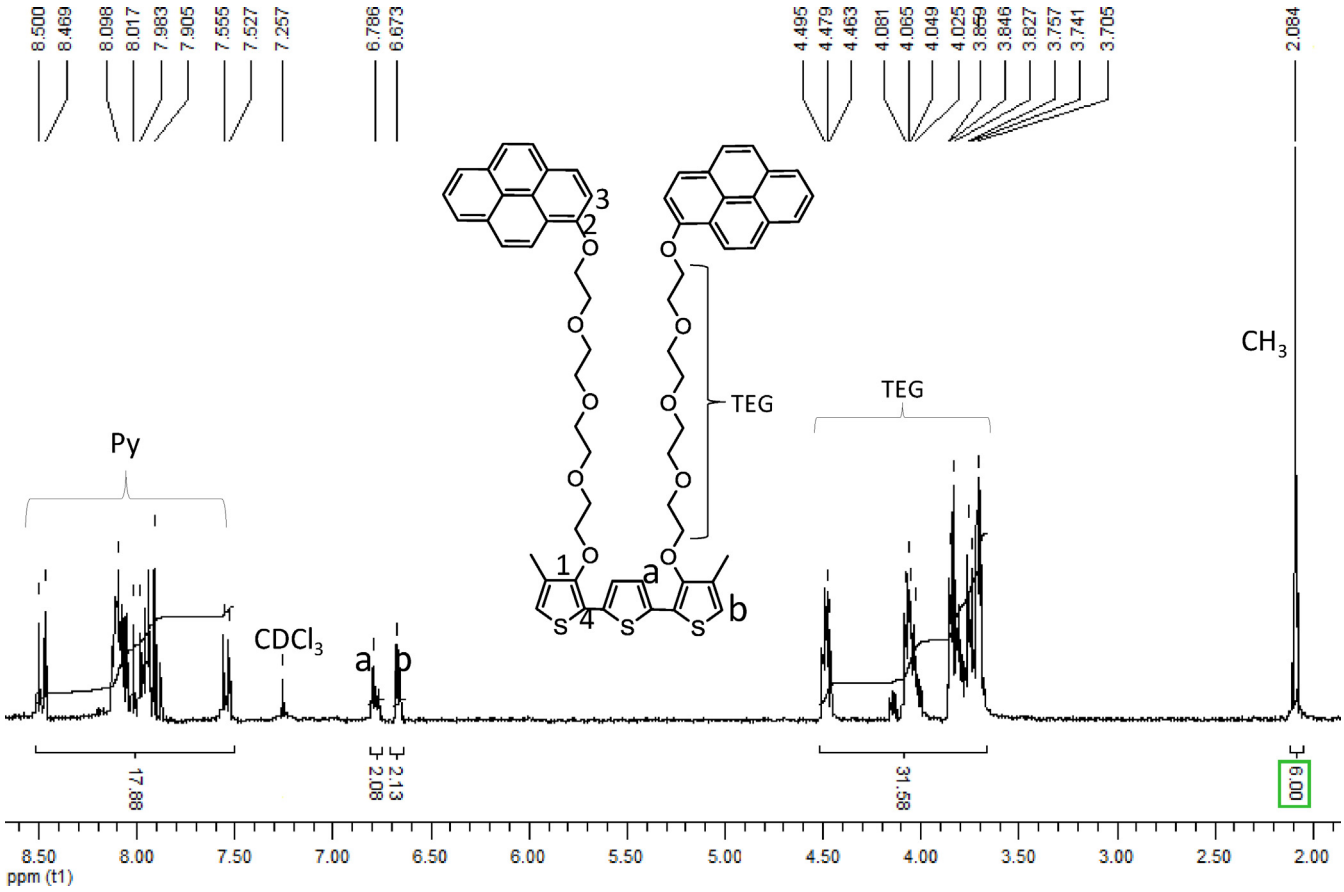

Fig. 9. ^{1}H NMR spectrum of terthiophene (**TT4**) in $CDCl_3$ solution.

by a second triplet at 4.03 ppm attributed to proton of Thioph—O—$\underline{CH_2}$ with J = 2.4 Hz are also observed. Finally, a multiplet at 3.85–3.70 ppm due to the remaining protons O—$\underline{CH_2}$, and a singlet at 2.11 due to the CH_3 protons appear in the aliphatic region of the spectrum.

The structures of oligomers were confirmed by MALDI-TOF mass spectrometry using dithranol as matrix, the calculated mass of each oligomer corresponds to the molecular ion in each case. The MALDITOF spectra of these compounds are shown in Fig. 12.

3.1.1. Optical properties

The optical properties of the monomers and oligomers, were studied by absorption spectroscopy and steady state fluorescence spectroscopy in the UV–vis range; the results are summarized in Table 1. The absorption spectra of the compounds bearing di (ethylene glycol) spacers (**M2**, **TT2** and **QT2**) and those of the compounds bearing tetra(ethylene glycol) spacers (**M4**, **TT4** and **QT4**) are shown in Fig. 13a and b, respectively. As we can see, all the compounds show a well structured band at λ = 280 nm due to the $S_0 \rightarrow S_3$ transition of the pyrene moiety, followed by a broad absorption band at λ_{max} = 350 nm arising from the $S_0 \rightarrow S_2$ transition of the pyrene group. This band considerably overlaps with the $S_0 \rightarrow S_1$ band (n–π^*) of the oligothiophene backbone, which appears at ca. λ = 385 nm. Similar absorption values were found for a series of oligothiophenes bearing alkyl and alkoxy substituents, previously reported in the literature [27]. The $S_0 \rightarrow S_1$ band usually appears at 370 nm, however, it is forbidden by symmetry and very low in intensity so that it can be seen only in high concentration solutions [15].

Thiophene monomers usually show an absorption band at ca. 280 nm that in this case overlaps with that of the $S_0 \rightarrow S_3$ transition of the pyrene moiety [38]. The large broadening of the band at λ = 350 nm reveals the presence of intramolecular pyrene–tiophene interactions in all compounds, since this broadening appears even in the spectra of the monomers (**M2** and **M4**), where there is only one pyrene unit. Pyrene–pyrene intramolecular interactions take place in the oligomers (**TT2**, **TT4**, **QT2** and **QT4**) but its presence was further confirmed by the formation of excimers, which can be observed in the fluorescence spectra of these compounds.

The fluorescence spectra of the monomers **M2** and M**4** are shown in Fig. 14. As we can notice, in the emission spectra of both monomers, there is a well structured emission band at λ_M = 385–450 nm, due to the "monomer emission", which arises from the $S_1 \rightarrow S_0$ transition of pyrene in the non-associated state [8] As expected, for **M2** and **M4** no excimer emission was observed because no pyrene–pyrene interactions are possible in these compounds. In this case the emission practically arises from the pyrene moieties.

The emission spectra of oligomers **TT2**, **TT4**, **QT2** and **QT4** are shown in Fig. 15. Here, we observe a discrete "monomer emission" band at λ_M = 379–450 nm due to the $S_1 \rightarrow S_0$ transition of the pyrene units in the non-associated state. Furthermore, we can perceive a low intensity broad emission band at λ_M = 470 nm, which can be attributed to the oliothiophene backbone. Similar fluorescence wavelength values were reported in a previous work, for a series of oligothiophenes bearing alkyl and alkoxy substituents [27]. Finally a very intense broad excimer emission band was seen at λ_E = 570 nm, which is undoubtedly due to the presence of intramolecular pyrene–pyrene interactions. In these oligomers, the pyrene units interact in a non parallel way, which causes a significant red-shift of the emission band. A similar behaviour was

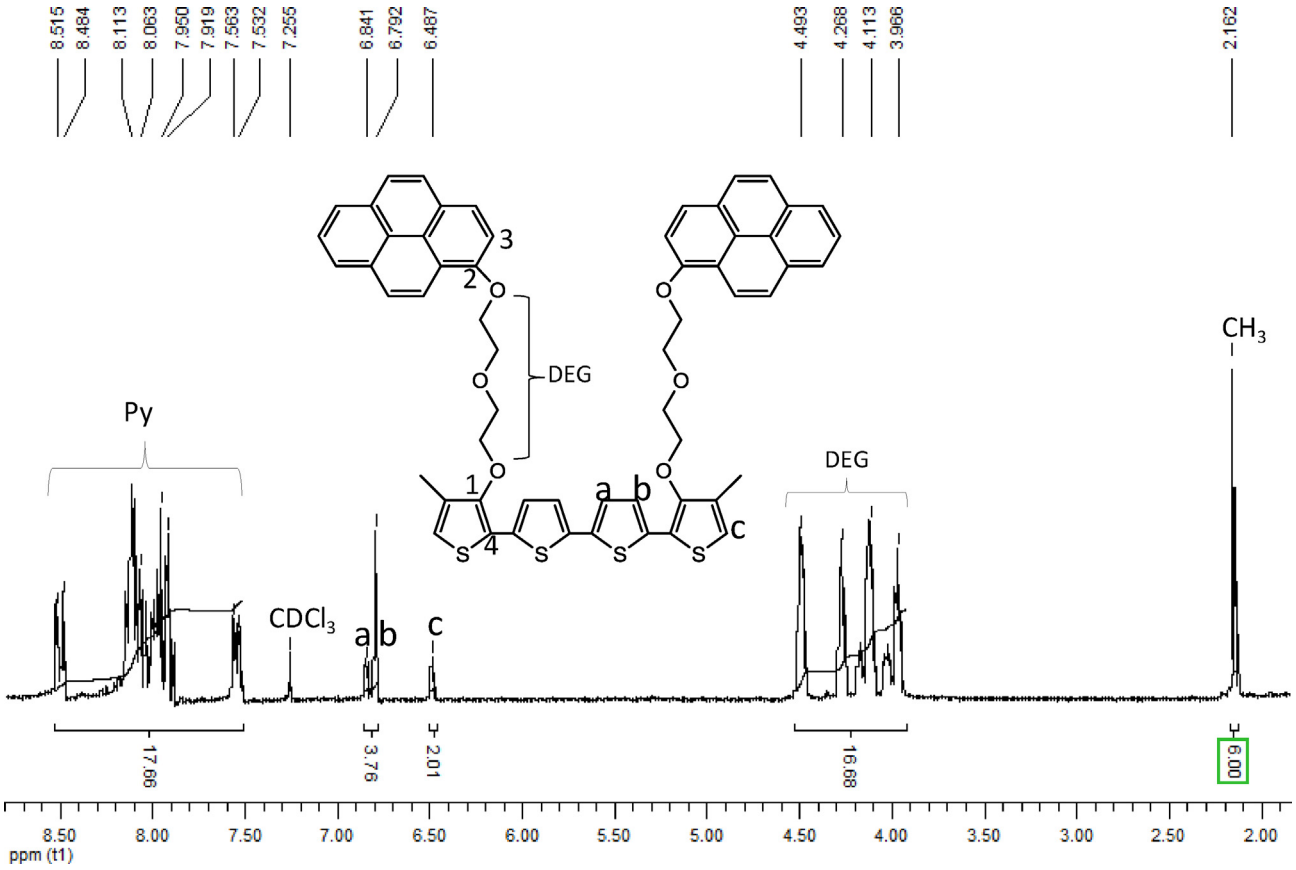

Fig. 10. ^{1}H NMR spectrum of quaterthiophene **QT2** in $CDCl_3$ solution.

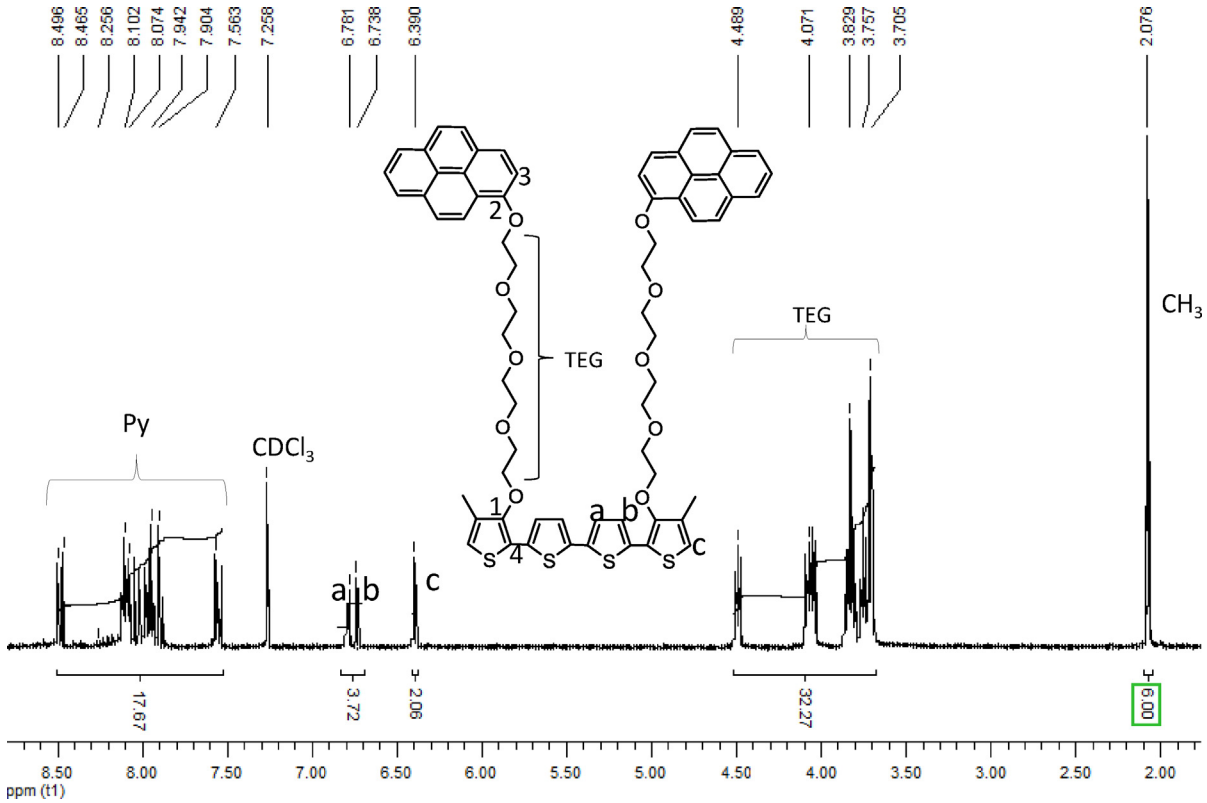

Fig. 11. ^{1}H NMR spectrum of quaterthiophene (**QT4**) in $CDCl_3$ solution.

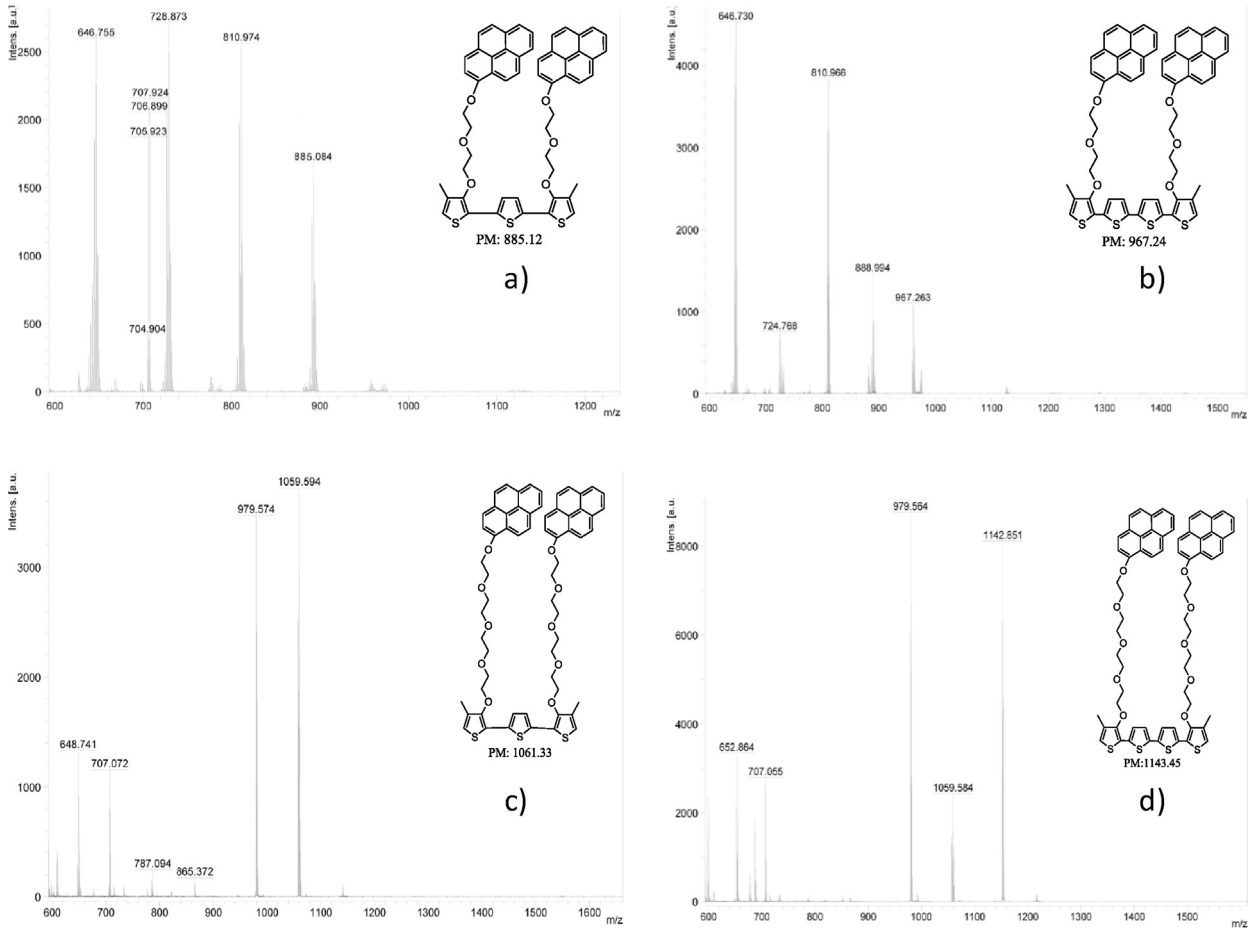

Fig. 12. Mass spectra of terthiophenes [(a)**TT2** (c)**TT4**] and quaterthiophenes [(b) **QT2**, (d) **QT4**].

observed in other pyrene containing polymers such *cis*-poly(1-ethynyl-pyrene), which shows an excimer emission at $\lambda_E = 550$ nm. [21] Despite the presence of the flexible oligo(ethylene glycol) segments, it seems that the rigidity of oligomer backbone does not allow the pyrene moieties encountering in a face to face way.

We calculated the ratio I_E/I_M for the different oligomers, where I_E is the intensity of the excimer emission band and I_M the intensity of the monomer emission band. The results are summarized in Table 1. As we can see, **TT2** and **TT4** show I_E/I_M values of 4.14 and 4.97, respectively; it is evident that the longer the oligo(ethylene glycol) segment is the more intense is the excimer emission band. If we compare **QT2** ($I_E/I_M = 4.68$) with **QT4** ($I_E/I_M = 7.64$) we can observe a similar behaviour. Longer flexible spacers diminish the geometry restrictions and allow the pyrene units to encounter and interact to form excimers. However, if we compared **TT2** ($I_E/I_M = 4.14$) with **QT2** ($I_E/I_M = 4.68$) we can notice that the longer the oligo(ethylene glycol) backbone is the easier is for the pyrene units to encounter by diffusion to form an excimer. The same pattern can be observed for the oligomers **TT4** ($I_E/I_M = 4.97$) and **QT4** ($I_E/I_M = 7.64$), but in this case the difference in excimer intensity between the trimer and the tetramer is considerably higher. The effect of the flexible spacer length jointly with that of the oligomer backbone considerably influences the presence of intramolecular pyrene–pyrene interactions in these compounds. In all these oligomers there is a natural tendency of the pyrene units to interact in the ground state via π–π interactions, which can be

Table 1
Optical properties of the monomers **M2**, **M4** and of the oligomers **TT2, TT4, QT2, QT4**.

Compound	Absorption λ (nm)	ε ($M^{-1}\,cm^{-1}$) at λ = 345 nm	Cut off (nm)	Emission λ (nm)	Cut off λ (nm)	I_E/I_M
M2	345[a]	28,669	395	385–450[b]	500	–
TT2	350[a]	29,829[d]	395	425[b], 570[c]	670	4.14
QT2	345[a]	40,164	395	425[b], 570[c]	670	4.68
M4	345[a]	21,143	395	385–450[b]	500	–
TT4	345[a]	44,924	395	425[b], 570[c]	670	4.97
QT4	345[a]	45,886	395	425[b], 576[c]	670	7.64

[a] Absorption band of the pyrene unit, the band of thiophene is overlapping with the band of pyrene.
[b] Monomer emission.
[c] Excimer emission.
[d] ε at 350 nm.

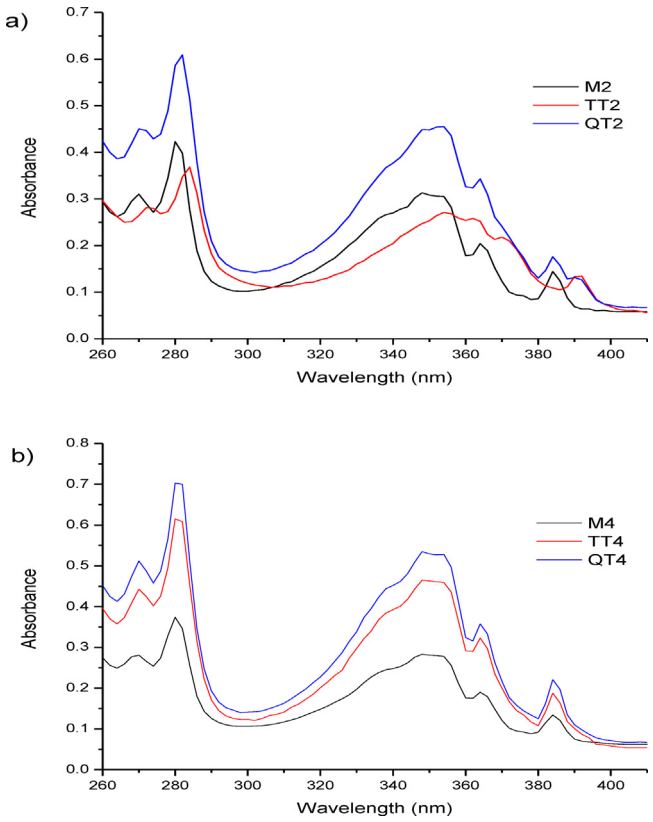

Fig. 13. (a) absorption spectra of **M2,TT2**, **QT2** and (b) absorption spectra of **M4,TT4**, **QT4** in $CHCl_3$ solution (spectrometric grade, concentration 1×10^{-5} M).

seen in the absorption spectra. On the other hand the oligothiophene backbone exhibits a slightly twisted conformation ($\lambda = 385$ nm) [27].

The quantum yields of the monomers and oligomers were determined by standard methods [39] using pyrene ($\Phi = 0.32$) in cyclohexane as reference [15]. The fluorescence quantum yields relative were calculated using the equation described by Fery-Forgues and Lavabre [40]. The results are shown in Table 2

An increase in the fluorescence quantum yield of the oligomers with respect to their monomers matches with the number of the pyrene units in the molecule.

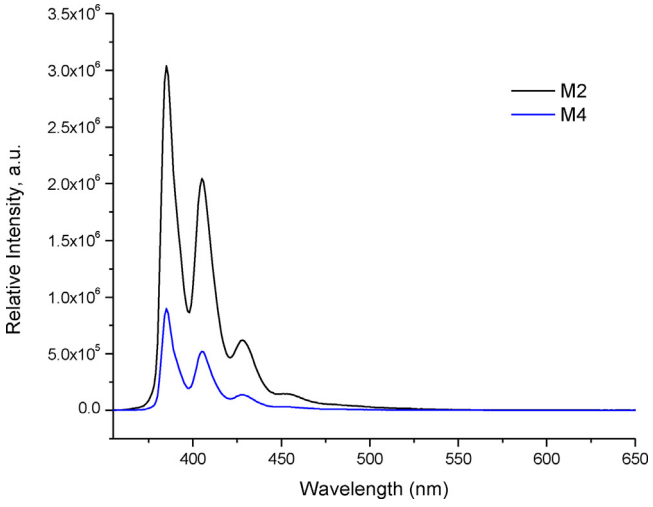

Fig. 14. Emission spectrum of the monomers **M2, M4** in $CHCl_3$ solution.

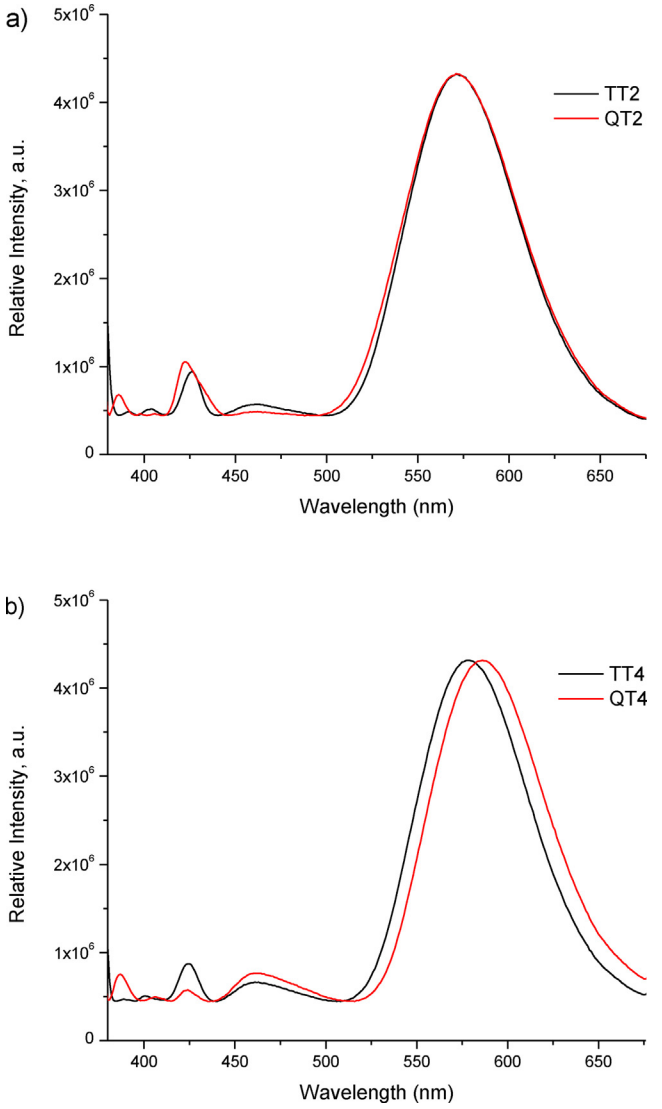

Fig. 15. Emission spectrum of the oligomers: (a) **TT2, QT2** and (b) **TT4, QT4** in $CHCl_3$ solution.

Table 2
Fluorescence quantum yields relative of the monomers **M2, M4** and of the oligomers **TT2, TT4, QT2, QT4**.

	Pyrene	**M2**	**TT2**	**QT2**	**M4**	**TT4**	**QT4**
$\Phi_{(F)}$	0.32	0.49	0.68	0.74	0.35	0.69	0.68

4. Conclusions

A new series of oligothiophenes bearing pyrene units attached via well defined oligo(ethylene glycol) spacers were synthesized and characterized. The absorption spectra of monomers and oligomers exhibited two absorption bands at 280 and 350 nm due to the $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_2$ transitions of the pyrene units. The absorption band of the oligothiophene backbone can be also observed at $\lambda = 385$ nm. The fluorescence spectra of monomers (**M2** and **M4**) exhibited a monomer emission band at 350–450 nm whereas the oligomers (**TT2, TT4, QT2** and **QT4**) exhibited the same emission band followed by an intense excimer emission at 570 nm, which reveals the presence of intramolecular pyrene–pyrene interactions in these oligomers. Such interactions take place in the ground state which can be confirmed by the absorption spectra.

The longer the flexible spacer and oligomer backbone length are, the stronger the intramolecular pyrene–pyrene interactions will be. This phenomenon can be observed in the fluorescence spectra by the formation of excimers.

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