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New photoactive oligo- and poly-alkylthiophenes

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ABSTRACT

A new type of ω-methoxy-functionalized oligo-(OCT) and poly-(PQ) hexylthiophene characterized by a tetrameric repeating unit was synthesized and characterized. The configurational regularity and the mean degree of functionalization per thiophenic ring, lower than in commonly synthesized PATs, permitted the obtainment of more ordered chain conformations especially in the solid (film) state. Solar cells based on OCT and PQ films (as *p*-donor polymeric layer) mixed with Single-walled Carbon Nanotubes (SWCNTs, used as electron-acceptor system) were prepared and investigated. A power conversion efficiency of 0.52% with a fill factor of 0.42, an open-circuit voltage of 0.48 V and a short-circuit current of 1.93 mA/cm^2 under 70 mW/cm^2 white light illumination is reported for the polymeric sample. The obtained performance is comparable with that of devices made with regioregular P3HT but the easiness of the monomer synthesis and polymer preparation, giving OCT and PQ with good yields, as well as the enhanced workability and filmability of the latters from diluted solutions of common organic solvents together with their low sensitivity to the environmental conditions (air oxygen, moisture, temperature) makes the synthesized materials very promising for the set-up of polymer photovoltaic cells.

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1. Introduction

Organic polymers have recently received great interest as semiconducting materials since they have band gaps that range from 1.5 to 3 eV, which make them very suitable for opto-electronic applications in the visible range. In this field, thiophene-based materials are a good example of compounds [1,2], with tuneable functional properties by suitable molecular engineering reactions. 3-substituted polythiophenes (PATs) have given relevant results in photovoltaic applications and electrooptical devices, where it is essential to reach high conductivities and high charge mobilities [3–5]. It is in fact well known that, to fabricate high-efficiency solar cells, the promising polymer should possess lower bandgap, in order to enlarge its absorption spectrum range, higher charge carrier mobility to reduce charge recombination and increase the photocurrent, and higher stability. The aim of this work is the synthesis and characterization of new thiophene derivatives bearing a ω-methoxy-functionalized hexamethylene side chain, able to enhance the solubility of the final polymer in common organic solvents [6,7]. This feature is particularly important for obtaining highly homogeneous thin films and must be carefully considered in the preparation of the polymer dealt with in this paper, having a low content of plastifying side chains and a high degree of regioregularity. In fact, the obtained poly(methoxyhexyl)thiophenes possess a degree of functionalization lower than conventional PATs (50 vs 100%), in order to improve their stability in the neutral state, preventing the oxidation exerted by the atmospheric oxygen [8]. Moreover, they are completely regioregular, in order to enhance the electronic properties deriving from the mean conjugation length of the polymeric backbone. On one hand, constitutional regularity is a fundamental prerequisite for long-range order and crystallization of the macromolecules to be achieved but, on the other hand, the presence of more packed main chains strongly lowers the solubility of the final polymer. Therefore an accurate control of the polymerization reactions has been ensured in order to enhance the polymeric soluble fraction content. An oligothiophenic derivative was also obtained, and its structural, optical and electrical properties were compared to those shown by the derivatives with higher molecular weight. Even if few works have been reported on thiophene oligomers, these π-conjugated systems are suitable for making light-based devices [9,10] and can be used directly to prepare the active layer of photovoltaic cells [11], or may constitute the repeating units of a polymeric material generally obtainable with easier synthetic procedures and showing better mechanical and thermal properties than those deriving from the polymerization of a monothiophenic monomer [12].

2. Experimental section

2.1. Materials and instrumentation

All the solvents and reagents used for the synthesis were purchased from Aldrich Chemical Company. NMR spectra were

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run on a Varian Inova 600 (600 MHz) or Varian Gemini 300 (300 MHz) FT-NMR spectrometer using TMS as reference. FT-IR spectra were carried out using a Perkin Elmer 1750 and a Perkin Elmer Spectrum One FT-IR spectrophotometer. Molecular weights were determined by size exclusion chromatography (SEC) relative to polystyrene standards on a HPLC Lab Flow 2000 apparatus equipped with a Phenogel mixed MXL column and a Linear Instrument UV–vis detector (model UVIS-200) working at 263 nm, with THF being used as an eluent at a flow rate of 1.0 ml/min. The UV–vis spectra were recorded with a Perkin Elmer Lambda 19 using spectroquality solvents. Thermal analysis was performed on a TA Instruments DSC 2920 at a heating rate of 10 °C/min. Microanalyses were carried out by Redox Laboratories (Monza, Italy).

2.2. Monomer synthesis

2.2.1. 3-(6-Methoxyhexyl)thiophene (M)

M was prepared by reacting 12.4 mmol of 3-(6-bromohexyl)-thiophene with 37.1 mmol of sodium methoxide 30% w/v in methanol, as reported in Ref. [5]. The crude M was purified by column chromatography (silica gel, *n*-heptane/diethyl ether 8:2) to give 1.96 g (9.88 mmol, 80% yield) of pure product.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21 (d, 1H); 6.95 (m, 2H); 3.26 (m, 5H); 2.62 (t, 2H); 1.59–1.37 (bm, 8H).

^{13}C NMR (300 MHz, $CDCl_3$): δ 143.8; 128.9; 125.7; 120.5; 73.5; 59.2; 31.1; 30.8; 30.2; 29.8; 26.6.

IR (KBr disk, cm^{-1}): 3102, 3050, 2977, 2931, 2857, 2826, 2807, 1537, 1478, 1459, 1409, 1387, 1199, 1119, 856, 833, 773, 684, 633.

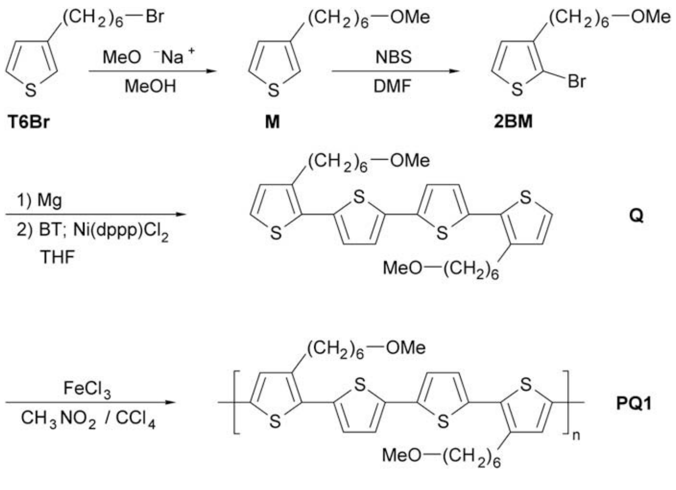
2.2.2. 2-Bromo-3-(6-methoxyhexyl)thiophene (2BM)

3.59 g (20.2 mmol) of *N*-bromosuccinimide (NBS) in 108 ml of *N*,*N*-dimethylformamide (DMF) were added to a solution of 4.00 g (20.2 mmol) of M in 108 ml of DMF. The mixture was reacted for 24 h at room temperature in the dark, after which it was poured into 200 ml of distilled water and extracted several times with *n*-pentane. After anhydrification and concentration of the collected organic phases 5.08 g (18.32 mmol) of pure 2BM (91% yield) were obtained.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18 (d, 1H); 6.78 (d, 1H); 3.38 (m, 5H); 2.59 (t, 2H); 1.59–1.37 (bm, 8H).

^{13}C NMR (300 MHz, $CDCl_3$): δ 142.5; 128.9; 125.8; 109.5; 73.5; 59.2; 30.3; 30.2; 29.9; 29.6; 26.6.

IR (KBr disk, cm^{-1}): 3106, 2977, 2931, 2857, 2826, 2807, 1539, 1479, 1461, 1409, 1119, 991, 829, 714, 635.



Scheme 1. Synthesis of PQ1.

Table 1
Yields and molecular weights of the synthesized polymers

Polymer sample	Reaction time (h)	Polymer yield[a] (%)	Octamer yield[b] (%)	M_n (Da)	M_w/M_n	DPn[c]
PQ1	1	46	40	3400	1.2	6
PQ2	3	61	15	6800	1.5	12

[a] After crude polymer fractionation (soluble fraction + octamer).
[b] In fractionated polymer.
[c] Relative to the tetrameric repeating units.

2.2.3. 5,5′-dibromo-2,2′-bithiophene (BT)

2.24 g (12.6 mmol) of NBS dissolved in 13.1 ml of DMF were added in 30′ to a solution of 1.00 g (6.0 mmol) of 2,2′-bithiophene in 25 ml of DMF. The mixture was reacted for 4 h at −20 °C and then poured in 400 ml of distilled water. 1.77 g (5.4 mmol) of pure BT (90% yield) were recovered by filtration on a glass frit. M.p. 151.4–152.0 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.95 (d, 2H); 6.84 (d, 2H).

^{13}C NMR (300 MHz, $CDCl_3$): δ 138.5; 131.4; 124.8; 112.2.

IR (KBr disk, cm^{-1}): 3091, 3068, 3038, 1504, 1416, 1058, 970, 867, 793, 787, 626, 456.

2.2.4. 3,3‴-di(6-methoxyhexyl)-2,2′:5′,2″:5″,2‴-quaterthiophene (Q)

0.557 g (22.91 mmol) of Mg and 4.4 ml of anhydrous THF were poured into a three-neck round-bottom flask and a solution of 4.29 (15.48 mmol) of 2BM was slowly added in 20′. After reacting for 120′ at room temperature and 20′ at 50 °C, the reaction mixture was transferred via cannula into a second flask containing 2.00 g (6.14 mmol) of BT, 84.76 mg (0.154 mmol) of Ni(dppp)Cl_2 and 35 ml of anhydrous THF. The mixture was refluxed for two days after which it was poured into a beaker containing 300 ml of 2% aqueous HCl. The product was recovered by extracting the aqueous phase several times with diethyl ether and after neutralization, anhydrification and evaporation of the solvent at reduced pressure, 4.70 g (8.41 mmol) of crude Q were obtained. The product was then purified by column chromatography (Al_2O_3/*n*-heptane:diethyl ether 8:2) giving 2.54 g (4.5 mmol) of pure Q (74% yield).

^{1}H NMR and ^{13}C NMR: see Table 3.

IR: see Table 2.

2.3. Synthesis of the polymers

2.3.1. 3,3‴,4⁗,3‴‴′-tetra(6-methoxyhexyl)-2,2′:5′,2″:5″,2‴:-5‴,2⁗:5⁗,2⁗′:5⁗′,2⁗″: 5⁗″,2‴‴′-octathiophene (OCT) and poly-[3,3‴-di(6-methoxyhexyl)-2,2′:5′,2″:5″,2‴-quaterthiophene] (PQ1)

0.59 g (3.65 mmol) of $FeCl_3$ dissolved in 3.6 ml of CH_3NO_2 were added dropwise, in 20′, to 0.50 g (0.89 mmol) of monomer Q in 10.5 ml of anhydrous CCl_4 under stirring and in inert atmosphere.

Table 2
IR absorption bands (cm^{-1}) and relative assignments for tetramer Q and polymer PQ1

Assignment	Q	PQ1
$\nu_{C–H\ \alpha\ thiophene}$	3088	–
$\nu_{C–H\ \beta\ thiophene}$	3074	3064
ν_{as} CH_3	2977	2969
ν_{as} CH_2	2930	2930
ν_{sym} CH_3	2894	–
ν_{sym} CH_2	2854	2857
ν_{as} CH_2–O	2827	2825
ν_{sym} CH_2–O	2806	2806
ν_{as} C=C	1501	1497
$\delta_{C–H}$ CH_3	1477	1477
ν_{sym} C=C	1459	1459
ν_{as} C–O–C	1115	1119
$\gamma_{C–H\ thioph.\ \alpha,\beta\ disubst.}$	699	–
$\gamma_{C–H\ \beta-thioph.\ trisubst.}$	–	834
$\gamma_{C–H\ thioph.\alpha,\alpha'\ disubst.}$	790	790

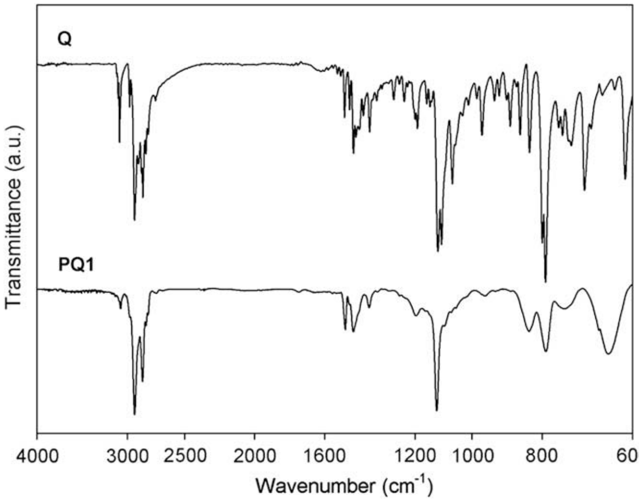


Fig. 1. IR spectra of tetramer Q and polymer PQ1.

After 40′ at room temperature the mixture was poured into 250 ml of MeOH/HCl 5% and filtered on a PTFE septum (0.40 μm pore size); the solid was washed several times with distilled water and methanol, dried and extracted at Soxhlet apparatus with further methanol to give 0.23 g (0.41 mmol) of PQ1 and, after evaporation of the extraction solvent at reduced pressure, 0.20 g (0.36 mmol) of octamer OCT.

2.3.1.1. OCT. ^{1}H NMR and ^{13}C NMR: see Table 4.

IR: 3060, 2973, 2930, 2894, 2857, 2827, 2806, 1497, 1478, 1459, 1119, 834, 790, 697.

Anal. calcd for ($C_{60}H_{74}O_4S_8$): C, 64.59; H, 6.68; O, 5.74; S, 22.99; Found: C, 64.53; H, 6.71; O, 5.79; S, 22.97.

2.3.1.2. PQ1. ^{1}H NMR (CDCl$_3$, ppm): δ 7.18 (d, 1H); 7.14 (m, 2H); 7.05 (m, 2H); 7.02 (d, 1H); 7.00 (s, 1H); 6.94 (d, 1H); 3.36 (t, 4H); 3.32 (s, 6H); 2.78 (t, 4H); 1.61 (m, 8H); 1.40 (m, 8H).

^{13}C NMR (CDCl$_3$, ppm): δ 141.1; 140.4; 137.4; 135.7; 130.7; 127.1; 124.7; 124.6; 73.5; 59.2; 33.2; 31.1; 30.1; 29.9; 26.7.

IR (Ge disk, cm^{-1}): see Table 2.

Anal. calcd for $[(C_{30}H_{36}O_2S_4)]_n$: C, 64.70; H, 6.52; O, 5.75; S, 23.03; Found: C, 64.58; H, 6.81; O, 5.81; S, 22.80.

2.3.2. Poly[3,3‴-di(6-methoxyhexyl)-2,2′:5′,2″:5″,2‴-quaterthiophene] (PQ2)

PQ2 was synthesized with the same procedure employed for PQ1, modifying only the reaction time; in particular, the solution of the oxidant was added in 1 h and the polymerization left to react for 2 h. 0.91 g (1.63 mmol) of PQ2 (61% yield) and 0.21 g (0.37 mmol) of OCT (15% yield) were obtained starting from 1.5 g (2.68 mmol) of Q. The results of the spectroscopic characterizations of PQ2 are the same as for PQ1.

Table 3
^{1}H and ^{13}C NMR signals and relative assignments for tetramer Q

Atom no.[a]	δ ^{1}H[b] (ppm)	δ ^{13}C (ppm)
1	3.32 (s)	58.8
2	3.36 (t)	73.1
3	1.57 (m)	29.8
4	1.40 (m)	26.2
5	1.40 (m)	29.6
6	1.66 (m)	30.8
7	2.78 (t)	29.4
8	–	139.9
9	6.93 (d)	130.3
10	7.17 (d)	124.1
11	–	130.6
12	–	135.5
13	7.01 (d)	126.8
14	7.12 (d)	124.1
15	–	137.0

[a] See Fig. 2.
[b] s = singlet; d = doublet; m = multiplet.

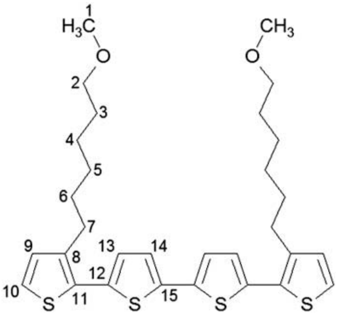


Fig. 2. Tetramer Q structure and numbering for NMR attribution.

3. Results and discussion

3.1. Synthesis and characterization

The preliminary purpose of this work was to develop a synthetic procedure for the obtainment of ω-functionalized polyalkylthiophenes (PATs) with high regioregularity starting from 3-(6-bromohexyl)thiophene (T6Br, Scheme 1), an intermediate product that can be easily obtained as reported in literature [13].

T6Br was transformed into 3-(6-methoxyhexyl)thiophene (M) using sodium methoxide in methanol, and the latter was selectively monobrominated with *N*-bromosuccinimide (NBS) in the 2-position by means of a suitably optimized procedure, leading to 2-bromo-3-(6-methoxyhexyl)thiophene (2BM) with high yield (91%). The latter was then reacted with Mg in anhydrous THF and added to a solution containing 5,5′-dibromo-2,2′-bithiophene (BT) and the cross-coupling catalyst in THF.

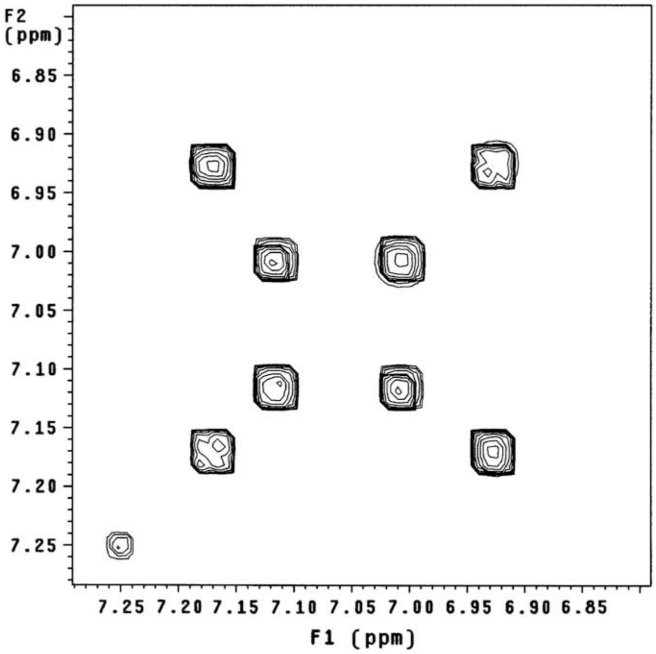


Fig. 3. COSY spectrum of tetramer Q.

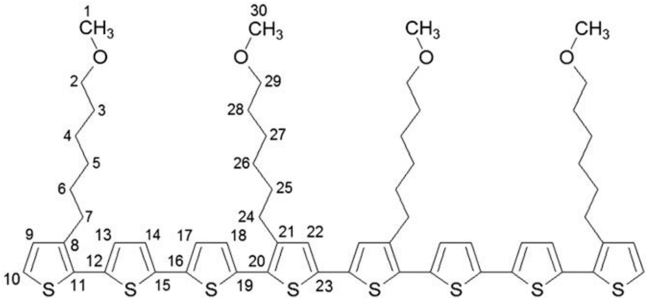


Fig. 4. Octamer OCT structure and numbering for NMR attribution.

From this reaction, 3,3‴-di-(6-methoxyhexyl)-2,2′:5′,2″:5″,2‴-quaterthiophene (Q, Scheme 1) was obtained in a satisfying yield (74%). Q was then subjected to an oxidative polymerization with iron trichloride using an accurately set-up procedure entailing the use of a CCl_4/CH_3NO_2 solvent mixture, capable of simultaneously fully solubilizing the tetramer and giving the oxidant in a highly active microcrystalline form, thus preventing the formation of insoluble polymeric fractions [14].

After purification from iron trichloride, the obtained fraction was composed of poly[3,3‴-di-(6-methoxyhexyl)-2,2′:5′,2″:5″,2‴-quaterthiophene] (PQ1) and of the octamer deriving from the coupling of two repeating units, 3,3‴,4⁗,3⁗‴-tetra(6-methoxyhexyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′,2⁗″:5⁗″,2⁗‴:5⁗‴-octathiophene (OCT) in a 6:4 molar ratio. The latter was easily separated from the polymer by prolonged extraction of the crude fraction using a Soxhlet apparatus and methanol as a solvent. From the obtained results (see Table 1) it can be inferred that the employment of a tetrathiophenic monomer strongly influences the course of the polymerization reaction. In fact, even if the oxidation potential of a tetramer is lower than that of the corresponding monothiophenic monomer, the reactivity of the former towards the oxidative polymerization is greatly lowered by the possibility to delocalize the radical cation involved in the growth process [15] over four aromatic rings. Moreover, the dimerization of Q leads to an octamer, OCT, even more stable (i.e. less reactive) than its precursor. These observations are in agreement with the obtainment of a final polymer, PQ1, with low molecular weights. A further polymerization reaction was attempted, lengthening the monomer dropping time (from 20′ to 1 h) and the subsequent reaction time (from 40′ to 2 h); these expedients lead to the obtainment a polymer (PQ2) with a higher molecular weight and also to an effective reduction of the octamer amount (see Table 1). In fact, since the oxidative polymerization via iron trichloride has a mechanism similar to a free-radical chain growth polymerization, the octamer amount could be controlled by the suitable choice of the polymerization conditions, mainly acting on the monomer concentration, on the monomer/oxidant ratio and on the transferring capability of the employed solvent. Another way could be the accurate control of the applied oxidation potential by the use of an electrochemical polymerization method.

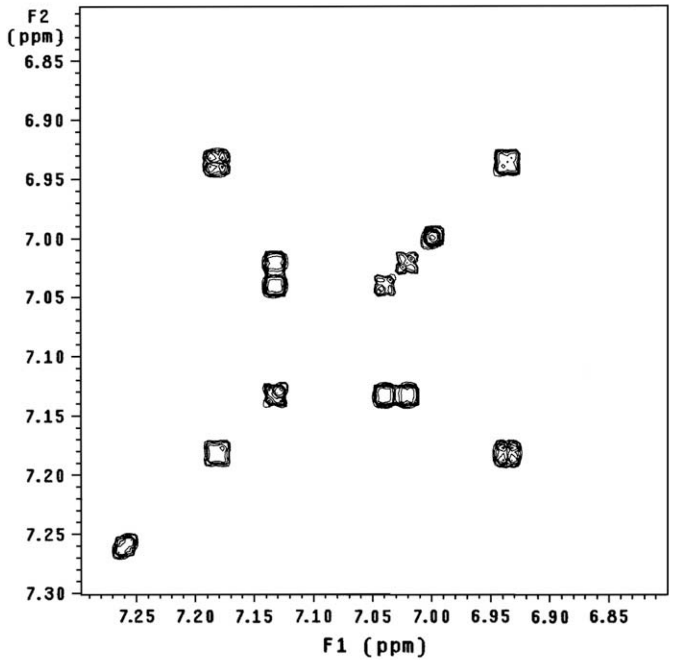


Fig. 5. COSY spectrum of octamer OCT.

Table 4
^1H and ^{13}C NMR signals and relative assignments for octamer OCT

Atom no.[a]	δ ^1H[b] (ppm)	δ ^{13}C (ppm)
1	3.32 (s)	58.8
2	3.36 (t)	73.1
3	1.58 (m)	29.8
4	1.41 (m)	26.2
5	1.41 (m)	29.6
6	1.68 (m)	30.8
7	2.78 (t)	29.4
8	–	140.0
9	6.94 (d)	130.3
10	7.18 (d)	124.2
11	–	130.6
12	–	135.6
13	7.02 (d)	126.8
14	7.13 (d)	124.2
15	–	137.0
16	–	137.1
17	7.13 (d)	124.2
18	7.04 (d)	126.6
19	–	135.1
20	–	129.8
21	–	140.6
22	7.00 (s)	126.8
23	–	135.1
24	2.76 (t)	29.6
25	1.68 (t)	30.6
26	1.41 (m)	29.6
27	1.41 (m)	26.2
28	1.58 (m)	29.8
29	3.37 (t)	73.1
30	3.32 (s)	58.8

[a] see Fig. 4.
[b] s = singlet; d = doublet; m = multiplet.

PQ1 and PQ2 were fully characterized by spectroscopic techniques owing to their very good solubility in common organic solvents.

3.2. FT-IR characterization

Frequencies and assignments of IR absorption bands of the monomer Q and polymer PQ1 are reported in Table 2. PQ2 signals are the same as recorded for PQ1.

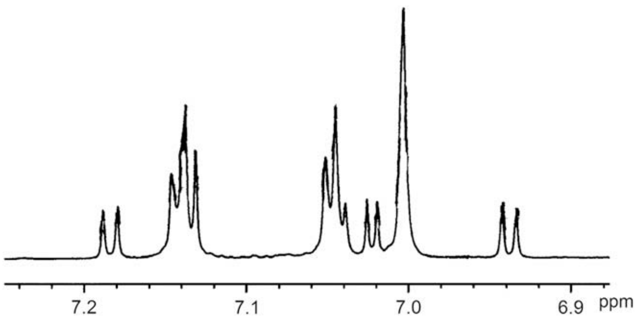


Fig. 6. Aromatic region (ppm) of ^1H NMR spectrum of PQ1.

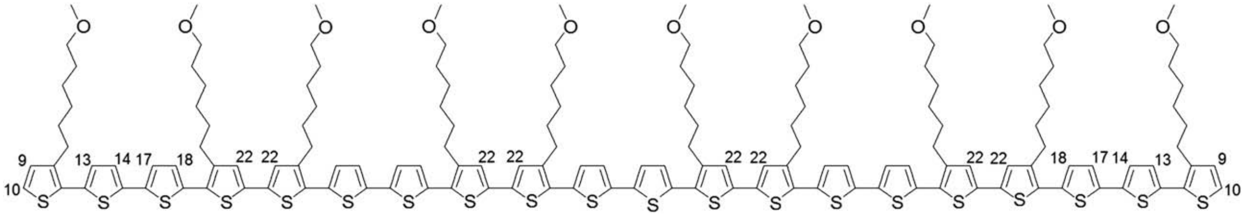


Fig. 7. Polymer PQ1 structure and numbering for NMR attribution.

The absence in PQ1 spectrum of the absorption due to α-thiophene C–H stretching (ν, 3088 cm^{-1}) and to the C–H bending out of plane (γ) in the 2,3-disubstituted thiophene ring (699 cm^{-1}) together with the presence of the γ C–H typical of both 2,5- and 2,3,5-substituted thiophenic rings (790 and 834 cm^{-1}, respectively) clearly confirms the 5,5‴ polymerization of the tetramer Q.

Qualitative information regarding the backbone conjugation can be gathered both from the frequency of the antisymmetric C=C ring stretching and from the intensity ratio between the symmetric and the antisymmetric C=C ring stretching I_{sym}/I_{asym}. Both these values were seen to decrease as the conjugation length increased, a finding which had already emerged from previous analyses conducted on PAT derivatives [16,17]. In the case of Q, the antisymmetric stretching is blue-shifted to 4 cm^{-1} if compared to that of PQ1 and its I_{sym}/I_{asym} ratio is significantly higher (2.3 vs 1.1) as clearly visible in Fig. 1.

This findings are in agreement with the results obtained by the UV–vis spectroscopy analysis of the two samples in film on quartz slides, revealing a λ_{max} of 420 nm for Q and 500 nm for PQ1, and indicating that the longer the polythiophenic chain is, the higher the probability of having longer conjugated segments will be. In fact, the same analysis conducted on OCT samples showed a ν_{as} C=C at 1499 cm^{-1}, a I_{sym}/I_{asym} ratio around 1.8 and a λ_{max} in film of 446 nm.

3.3. NMR analysis

A detailed ^{1}H and ^{13}C NMR analysis was performed on Q, OCT and PQ1 samples using bidimensional techniques to attribute all the H and C atoms of the obtained structures. First of all the tetramer Q was carefully examined and its ^{1}H and ^{13}C NMR data are collected in Table 3 together with the corresponding assignments obtained using pulsed techniques, i.e. COSY [18], HSQC [19], and HMBC [20]. The results of the COSY experiments are reported as an example.

The atoms are numbered as depicted in Fig. 2; only half of the structure is highlighted since the molecule is symmetric.

The signals of the aromatic protons 9 and 10, at 6.93 and 7.17 ppm, respectively, and those of protons 13 and 14 at 7.01 and 7.12 ppm were definitively assigned by means of the COSY experiment (Fig. 3).

The spectra of the octamer OCT are more complex since many peaks are found in the aromatic and aliphatic regions. Its structure is depicted in Fig. 4 and the result of the COSY experiment is depicted in Fig. 5.

The complete OCT assignment is reported in Table 4 showing that the peaks ascribable to the protons 9 and 10 are found in the same position as for the tetramer Q while the signal of proton 22 became a singlet centered at 7.00 ppm instead of a doublet at 6.93 ppm, as a result of the C–C bond involving carbon 23.

Fig. 6 shows the expansion of the aromatic region of the ^{1}H NMR spectrum of polymer PQ1, from which is possible to observe the doublet of the aromatic proton 10 at 7.18 ppm as well as the doublet ascribable to the aromatic proton 9 at 6.94 ppm. It is also possible to attribute the doublet at 7.02 to the aromatic proton 13.

All the aforementioned signals derive from the terminal repeating unit of PQ1. Other signals are found in the same region: the multiplet at 7.14 ppm, attributable to protons 14 and 17, the multiplet at 7.05 ppm ascribable to proton 18 and, finally, the singlet at 7.00 ppm stems from proton 22.

Considering the hypothesized structure of PQ1 depicted in Fig. 7, it is possible to observe that the ratio between the integrated intensity of the signals ascribable to proton 22 and those of terminal atoms 9 and 10 can give an indication of the polymeric chain length. The intensity of the peak at 7.00 ppm being four times the intensity of the signals at 7.18 and 6.94 ppm (Fig. 6), it can be assumed that PQ1 is composed of five tetrameric units linked together. The same result can be obtained considering the peak at 7.05 or that at 7.14 ppm. The GPC analysis indicates a slightly higher DPn (see Table 1) but this difference should not come as a surprise, since the chromatographic column was calibrated using polystyrenic standards, and not polythiophenic ones.

3.4. Thermal and morphological analyses

Two main transition temperatures ascribable to the main chain glass transition and melting temperatures (T_g and T_m, respectively) were recorded by DSC analysis of OCT, PQ1 and PQ2 (see Table 5).

The reported values were obtained in the second run, with a heating and cooling rates of 10 °C/min. PQ1 and PQ2 show broader and considerably weaker thermal transitions compared to those typical of conventional PATs [21,22]. Moreover, the double melting behavior characteristic of well-ordered completely functionalized PATs, generally ascribed to the two separate meltings of interdigitated side chains (lower temperature peak) and π-stacked main chains (higher temperature peak) [23,24], was not observed in our samples. All these observations are in agreement with the presence of an essentially amorphous structure.

OCT thermal behavior is instead quite different. The oligomer shows a very sharp melting peak until the first thermal cycle (88 °C) (see Fig. 8) and a very high value of melting enthalpy (75.7 J g^{-1}, 1st thermal cycle).

In the second run a second-order phase transition is found at −32 °C, a crystallization peak in the range 37–38 °C and a melting peak at 86 °C. The presence of sharp and very evident crystallization/melting peaks indicates the possibility for OCT to achieve a degree of long-range order higher than the Q derivatives at higher molecular weight PQ1 and PQ2. Its order in thin solid films is evident by observing the images obtained with an optical microscope operating with polarized light (ZEISS AXIO-IMAGER A1M) reported in Fig. 9.

Table 5
Thermal characteristics of the synthesized materials

Sample	T_g (°C)	T_m (°C)	ΔH_m (J/g)
OCT	−32	86	73.1
PQ1	−10	43–88	2.1
PQ2	−13	29–115	9.0

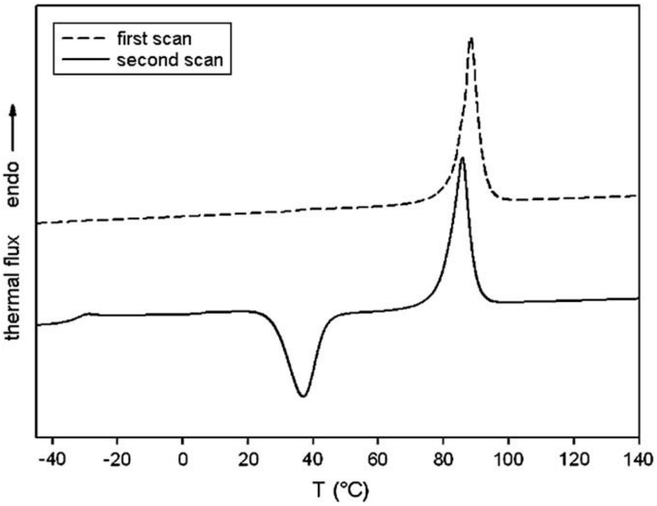


Fig. 8. DSC thermograms of OCT.

Films obtained by slow evaporation of $CHCl_3$ solutions of OCT on glass reveal its spherulitic structure while, at higher enlargements, the lamellar structure of a spherulite branch can also be observed.

3.5. Electrical measurements

Since oligo- and polythiophenes are of great interest as photoactive organic materials due to their tunable absorption spectrum, high film-forming capability, solubility [25], and small E_{gap} [26,27], the electrical and electrooptical characteristics of OCT and PQ1 have been carefully tested. Neutral sample conductivities were measured by means of an AI Alessi Industries four-probe system equipped with four Os cone-shaped tips, in air at room temperature on film cast on glass slides, using a Keithley 195A digital multimeter, a 610C electrometer and a 247 high voltage supply. The films' thickness was measured by means of a mechanical profilometer and was about 0.15 μm. The values of specific electrical conductivity of OCT and PQ1 are slightly higher if compared to other previously synthesized PATs [28,29] but they, however, fall within the values typical of insulating materials.

Octamer and polymer conductivities are indeed very similar (see Table 6); even if the former possesses a lower mean conjugation length in film than PQ1 (see above), it features a more ordered and crystalline structure that can help the electron mobility [30,31].

The measured photovoltaic devices were prepared as follows, according to the usually reported guidelines for the obtainment of bulk heterojunction solar cells [32]. Firstly, a pre-cleaned ITO glass supplied by China South Glass Holding Co. Ltd., Shenzhen, China (21 Ω per square) was covered by a 100 nm film of Poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS) 2.8 wt% dispersion in H_2O bought from Sigma–Aldrich Inc., using a BLE 3000 spincoater operating at 1200 rpm for 2 min. The film was then baked in air at 80 °C for 5 h. The synthesized oligomer and polymer, were firstly dissolved in $CHCl_3$ and added by a 3 wt% of Single-Walled Carbon Nanotubes (SWCNs), 12–15 Å diameter bought from Aldrich Chemical Co. and then kept in a warm ultrasonic bath for dispersion before fabrication. Their films were deposited on the substrate (ITO covered by PEDOT:PSS) using a BLE 3000 spincoater operating at 1000 rpm for 30 s. The final thickness of OCT and PQ1 films was around 100 nm, as determined by means of a Burleigh Vista AFM used as a profilometer. Finally, the counter electrode was deposited on a corner of the upper layer thermally under high vacuum (10^{-6} torr) using an Edwards 6306A coating system. The structure of the final device was then ITO/PEDOT:PSS/OCT (or PQ):SWCNT/Al. The active area of the cell was about 0.25 cm^2. *I–V* measurements were performed at room temperature using a HP 6611C 0–8 V/0–5 A DC power supply, a Keithley 195A digital multimeter and a Keithley 6485 picoammeter, operating in the range −2/+2 V and −0.5/0.5 mA. For photovoltaic characterization the cells were illuminated with 70 mW/cm^2 power intensity of white light from a tungsten–halogen lamp and the light intensity was estimated with a HP Radiant Flux Meter 8330A equipped with a Radiant Flux Detector 8334A. The calculation of the photoelectric conversion efficiency η was made using the equation:

$$\eta = \frac{V_{OC} I_{SC} FF}{P_I}$$

where V_{OC}, I_{SC}, FF and P_I are the open-circuit voltage (where $I=0$), the short-circuit current density (where $V=0$), the so-called fill factor and the power of the incident light, respectively. FF is defined as the ratio between the maximum power delivered by the cell and the potential power of the device and is a measure of the performance of the solar cell. It can be easily calculated knowing the load factor V_m/I_m to which the cell reaches its maximum power, being:

$$FF = \frac{I_m V_m}{I_{SC} V_{OC}}$$

The characteristics of the two prepared devices are reported in Table 6. From the reported data it is evident that the octamer has a short-circuit current and an open-circuit voltage lower than PQ1, but the fill factor (FF) and the photoelectric conversion efficiency η are essentially the same, and, however, in line with the results

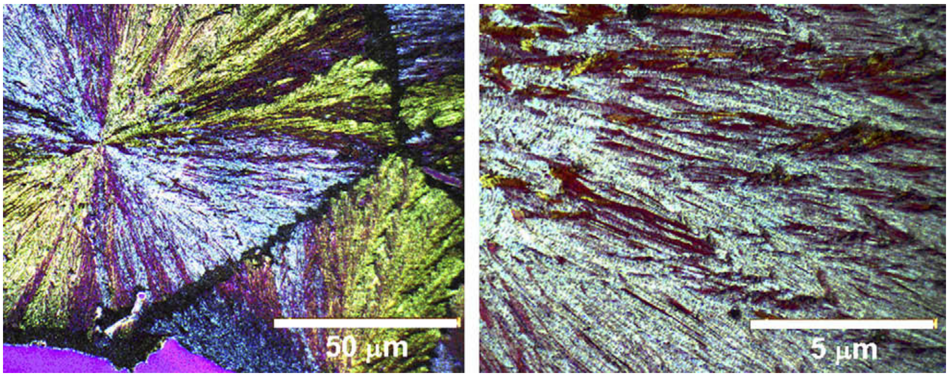


Fig. 9. Images of OCT in film on glass observed in polarized light (120°) at different enlargements.

Table 6
Electrical conductivity and photovoltaic performance of OCT and PQ1

Property	OCT	PQ1
σ (S cm^{-1})	5×10^{-7}	9×10^{-8}
V_{oc}[a] (V)	0.35	0.48
I_{sc}[a] (mA/cm^2)	1.61	1.93
V_m[a] (mW/cm^2)	0.26	0.39
FF	0.46	0.42
η (%)	0.35	0.52

[a] Under 70 mW/cm^2 white light illumination through the ITO electrode.

obtained with similar devices analyzed under the comparable experimental conditions [33–35].

4. Conclusion

A new polythiophenic derivative partially functionalized by a hexamethylenic side chain ω-ended by a methoxy group has been synthesized starting from a quaterthiophenic monomer. The molecular design of the latter has lead to the obtainment of a regioregular polymer using the simple and cost-effective oxidative polymerization with iron trichloride, avoiding the use of the polycondensation with organometallic derivatives, a more complex procedure and more sensitive to the reaction conditions. During the synthesis of the polymer, however, a non-negligible amount of the octathiophenic intermediate has been recovered, which showed some very interesting features, such as the tendency to spontaneously crystallize from its solutions, giving very clear spherulitic aggregates. The high crystallinity of the octamer probably compensates for its low molecular weight, since its thermal, electrical and photovoltaic characteristics are nearly the same as those of the longer corresponding polymer. From this standpoint, besides the polymeric sample, the octamer is particularly promising for the obtainment of organic bulk heterojunction solar cells, taking into account its very simple and straightforward method of synthesis and purification together with its excellent solubility and workability typical of low-molecular weight compounds.

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