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Effect of regioregularity and role of heteroatom on the chiral behavior of oligo(heteroalkyl thiophene)s

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Abstract

Novel optically active oligothiophenes bearing electron-donating chiral side chains have been prepared by synthetic methods suitable to achieve regioregular head-to-tail and head-to-head/tail-to-tail derivatives. In particular, the chiral (*S*)-(2-methyl)butyl moiety was linked at position 3 of the thiophene ring through heteroatoms, such as S or O, to evaluate its effect on the macro molecular aggregation and, consequently, on the chiroptical properties of the material in the solid state. The materials have been fully characterized and investigated by optical and chiroptical methods upon aggregation both from the solution and as cast films. Compared with the related head-to-tail and head-to-head/tail-to-tail poly(3-alkyl)thiophene derivatives, with the same optically active moiety directly linked to the ring and possessing a higher polymerization degree, the chiroptical properties of the newly synthesized oligomers were significant, or even better, and provided insight into the role of intrachain–interchain interactions between the heteroatom and the thienyl sulfur atom.

KEYWORDS

chiral heteroalkyl thiophene, circular dichroism, regioregular oligothiophenes, solvatochromism

1 | INTRODUCTION

Chiral conjugated polymers, owing to the combination of chirality with electrical conductivity, are potentially useful in many areas such as polarization-sensitive electrooptical devices, polarized photoluminescence (PL) and electroluminescence, or chiral enantioselective sensors,[1,2] and therefore, they have long been the object of intense research work.

Chiral polythiophenes, in particular, were initially prepared by chemical or electrochemical oxidation of monomers with a chiral substituent covalently attached to the 3-position of the thiophene ring.[2] The first chiral poly(3-alkyl)thiophene (P3AT) bearing the optically active moiety in the side chain, obtained by electrochemical polymerization, was investigated in 1988 by Lemaire et al.[3] In early investigations, however, the optically active derivatives were frequently mixtures of regioisomers involving steric interactions, as in the case of head-to-head (HH) couplings, determining a decrease of conjugation length as well as lower chiroptical properties. A decisive breakthrough in the research was represented by the possibility to prepare regioregular derivatives starting from monomeric 3-alkylthiophene through the development of regiospecific polymerization routes, such as those of McCullough et al.[4] and Chen and Rieke,[5] which allowed to achieve the desired regioregular head-to-tail (HT) couplings, giving access to a wide range of chiral P3ATs with markedly enhanced chiroptical properties. Circular dichroism (CD) studies allowed to demonstrate that in HT P3ATs, the aggregation involves essentially planar polymer chains that have a helical interchain order, rather than an intramolecular helical conformation. In particular, HT poly{3-[(*S*)-(2-methylbutyl)]thiophene} (PMBT) was deeply investigated and was found to display chiral anisotropy factor *g* values as high as $1.0 \cdot 10^{-2}$ at 612 nm[22] and a high degree of crystallinity (65%)[6,7] upon aggregation from the solution by gradual addition of a weak solvent. During the ordering process, a kind of sergeants-and-soldiers principle acts, in which the longest chains determine the chirality of the aggregated form, that is, the aggregation of π-conjugated polymers is a multichain event even in the case of very dilute solutions.[8] Indeed, HT PMBT in the solid state consists mainly of stacks of nearly coplanar extended chains,[9] and reasonable values for the distances of interacting thiophene units have been found by applying the exciton coupling scheme.[10]

More recently, we reported the synthesis of the regioregular HH/tail-to-tail (TT) isomeric homologue of PMBT, obtained by polymerization of the bithiophenic monomer 3,3′-bis[(*S*)-(2-methylbutyl)]thiophene.[11] As evidenced by CD, the polymer displays both in solution and in the solid state chain sections having helical structure, as a consequence of steric interactions between side chain alkyl groups, that disfavor coplanarity of thiophene rings, and therefore, the obtainment of supramolecular chiral aggregates upon aggregation from the solution. For this reason, the introduction of a heteroatom, such as sulfur or oxygen, between the thiophene ring and the chiral alkyl group should provide a reduction of the steric hindrance and promote conformations suitable to produce improved rings coplanarity with a longer extent of conjugation in the main chain, even in HH/TT regioregular polymeric derivatives. In addition, it is widely reported[12–19] that the presence of intramolecular interactions between the thienyl sulfur atom and the pendant sulfur or oxygen atom located in the adjacent moiety appears to provide a strong contribution to planarity of the backbone.

However, if compared with chiral P3ATs, less research concerning optically active 3-sulfanyl or 3-alkoxy thiophene polymeric derivatives can be found in the literature.[2] In particular, the presence of more than one single phase upon aggregation was reported for 4,4′-bis[(*S*)-2-methylbutylsulfanyl]-2,2′-bithiophene polymerized in the presence of ferric chloride, providing the corresponding TT/HH regioregular polythiophene. This resulted optically active when the random and optically inactive monomolecular phase present in good solvents was first converted into a chiral monomolecular (or loosely aggregated) phase and then into one or more associate phases upon treatment with poor solvent or obtained as cast film.[20]

Chiral HT and HH/TT poly(3-alkoxythiophene)s bearing the optically active 3,7-dimethyloctyloxy moiety in the side chain, as spin-coated films or upon aggregation from the solution, exhibited CD spectra characterized by large bisignate Cotton effects and high *g* factors values as originated by the formation of coplanar strands stacked in a chiral way.[15,16] Similar results were also obtained with diblock copolymers constituted by 3-alkyl and 3-alkoxy polythiophene blocks bearing the (*S*) and/or (*R*)-3,7-dimethyloctyl moiety linked directly to the ring and/or through the oxygen atom, upon addition of poor solvent to the chloroform solution, giving rise to aggregation as helical supramolecular structures again characterized by high *g* values.[21]

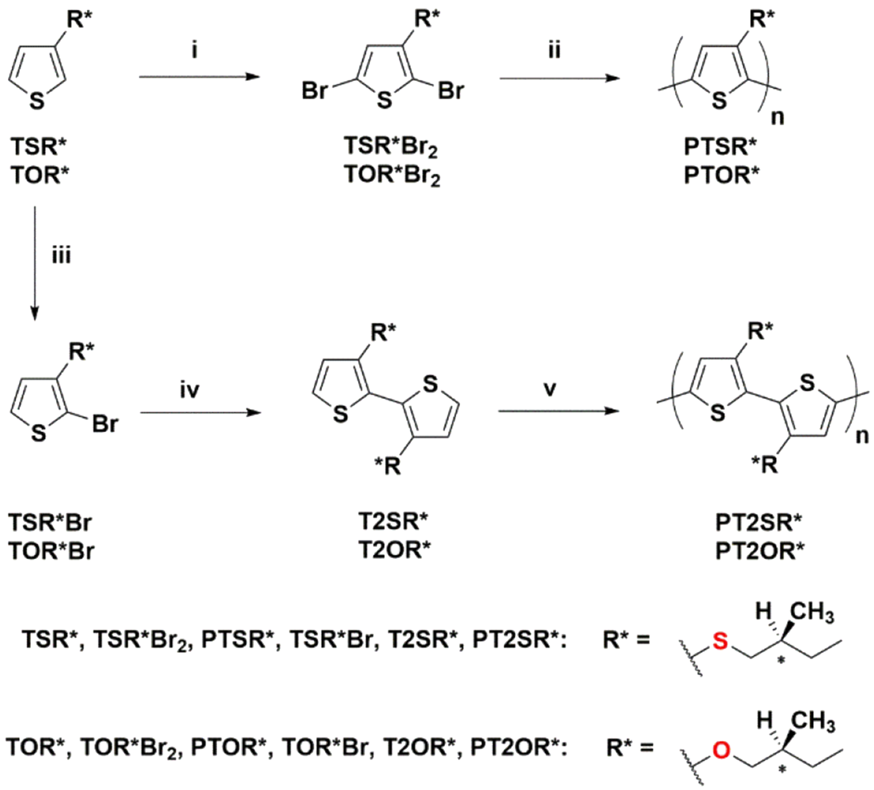
In this context, we have considered of interest the preparation of optically active oligomeric polythiophene derivatives bearing a chiral 3-sulfanyl or 3-alkoxy moiety in the side chain and possessing known regioregularity in order to investigate and assess by chiroptical methods their behavior upon aggregation from the solution and in the solid state as cast films. The same (*S*)-(2-methyl)butyl moiety was used as the chiral component, with the aim to obtain results comparable with those reported for the above-mentioned optically active P3ATs[11,22] and better elucidate the effect of the sulfur and oxygen spacers on aggregation process and functional properties. The synthetic routes to monomers **TSR*Br$_2$**, **TOR*Br$_2$**, **T2SR***, and **T2OR*** as precursors to the derivatives **PTSR***, **PTOR***, **PT2SR***, and **PT2OR***, respectively, are reported in Scheme 1.

2 | MATERIALS AND METHODS

2.1 | Materials

All commercial reagents and solvents were purchased from Sigma-Aldrich and used as received unless otherwise stated. *N*-Bromosuccinimide (NBS) was recrystallized from hot water, and pyridine (Fluka) was freshly distilled before use. Anhydrous solvents were prepared following literature procedures[23] and stored over molecular sieves. All manipulations involving air- or moisture-sensitive reagents were performed under nitrogen in dried glassware.

SCHEME 1 Synthetic route to optically active heteroalkyl thiophene monomers and oligomers. Reagents and conditions: (i) 2 equiv of NBS, CH_2Cl_2, reflux; (ii) 1 equiv of hexylmagnesiumbromide in Et_2O, Ni(dppp)Cl_2, 2-MeTHF, reflux; (iii) 1 equiv of NBS, DMF, 0°C; (iv) 0.5 equiv of bis(pinacolato) diboron, Pd(dppf)Cl_2, $NaHCO_3$, THF/H_2O 2/1, MW, 90°C for **T2SR***; *n*-butyllithium in hexane, Fe(acac)$_3$, THF for **T2OR***; (v) 4 equiv of $FeCl_3$, $CHCl_3$ room temp



2.2 | Methods and characterization

Microwave (MW) irradiation was performed in a Milestone MicroSYNTH Labstation operating at 2,450 MHz and equipped with pressure and temperature sensors.

The ^{1}H-NMR spectra were recorded with a Varian Mercury 400 (400 MHz) spectrometer at room temperature in $CDCl_3$ solutions, using tetramethylsilane as an internal reference. Chemical shifts are given in ppm.

Molecular mass and dispersity index of the oligomers were determined at room temperature by gel permeation chromatography (GPC) in tetrahydrofuran (THF) solution on a high-performance liquid chromatography (HPLC) Lab Flow 2000 apparatus equipped with a Rheodyne 7725i injector, a Phenomenex Phenogel mixed bed 5μ MXL type column and an RI K-2301 KNAUER detector. Calibration curves were obtained by using monodisperse polystyrene standards. Before being measured, the materials were dissolved in THF (ca. 1 mg/ml) and filtered over a 0.2-μm pore size filter.

The decomposition temperature (T_d) of the oligomers was determined in the 20–800°C temperature range on a thermogravimetric analysis (TGA) TA Instruments Q600 apparatus operating at a heating rate of 20°C/min under nitrogen atmosphere. A differential scanning calorimetry (DSC) TA Instruments Q2000 operating under nitrogen in the −50°C to 200°C temperature range at a heating rate of 10°C/min was used to determine the glass transition temperature (T_g) of the oligomers.

Ultraviolet–visible (UV–Vis) and PL spectra were carried out on a PerkinElmer Lambda 20 and PerkinElmer LS50B spectrophotometer, respectively, at 25°C on 10^{-3}/10^{-4} M $CHCl_3$ solutions in 1 cm quartz cells. Thin film measurements were made on samples cast from chlorobenzene solutions on quartz slides by drop-casting.

Infrared (IR) spectra were carried out on Ge disks using a PerkinElmer 1750 or a Spectrum One spectrophotometer.

High-resolution mass spectroscopy (HRMS) (electrospray ionization [ESI]) spectra were recorded on a Waters XEVO Q-TOF instrument.

Optical activities were measured on $CHCl_3$ solutions with a PerkinElmer 341 digital polarimeter, equipped with a Toshiba sodium bulb, using a cell path length of 0.1 cm. Specific rotation values at the sodium D line are expressed as degree dm^{-1} g^{-1} dl.

The CD spectra were recorded at the same solute molar concentration as the UV–Vis spectra in 1cm quartz cells, at room temperature, on $CHCl_3$ or $CHCl_3/CH_3CN$ solutions, by a Jasco 810 dichrograph; $\Delta\varepsilon$ values, expressed as L mol^{-1} cm^{-1}, were calculated by the following equation: $\Delta\varepsilon = [\Theta]/3{,}300$, where the molar ellipticity Θ is in degree cm^2 dmol^{-1}. The chiral anisotropy ratio g ($\Delta\varepsilon/\varepsilon$) was calculated by the ratio between the maximum $\Delta\varepsilon$ (in absolute value) and the ε value at the same wavelength. The molar concentration in terms of one substituted thiophene repeating unit was equal for each sample both in pure $CHCl_3$ and in all the $CHCl_3/CH_3CN$ mixtures and assumed to remain constant within the range of solvent composition tested. The molar concentrations of the samples were $1.6\cdot10^{-4}$, $1.7\cdot10^{-4}$, $1.6\cdot10^{-4}$, and $1.8\cdot10^{-4}$ M for **PTSR***, **PTOR***, **PT2SR***, and **PT2OR***, respectively.

2.3 | Synthetic methods

2.3.1 | (+)-2,5-Dibromo-3-[(*S*)-(2-methylbutyl)sulfanyl]thiophene (TSR*Br$_2$)

To a two-necked flask containing a solution of **TSR*** (0.246 g, 1.3 mmol) in 7.0 ml of CH_2Cl_2, NBS (0.518 g, 2.9 mmol) was added portionwise under stirring and protection from light. The mixture was heated at 45°C and maintained at this temperature for 24 h. After the organic layer was cooled and washed with water, the crude product was purified by column chromatography on silica gel with cyclohexane to obtain **TSR*Br$_2$** (0.419 g, 92% yield) as a colorless oil: $[\alpha]_D^{25}$ = +14.1 (c = 0.5 in $CHCl_3$); ^{1}H-NMR (400 MHz, $CHCl_3$, δ): 6.90 (s, 1H, Ar 4-H), 2.83 (dd, 1H, $CH_\alpha S$), 2.67 (dd, 1H, $CH_\beta S$), 1.62–1.46 (m, 2H, $CHCH_3$ and $CH_\alpha CH_3$), 1.31–1.19 (m, 1H, $CH_\beta CH_3$), 1.01 (d, 3H, $CHCH_3$), and 0.89 (t, 3H, CH_2CH_3); HRMS (ESI$^+$, m/z): $[M + H]^+$ calcd for $C_9H_{13}Br_2S_2^+$, 342.8825; found: 342.8823.

2.3.2 | 2-Bromo-3-[(*S*)-(2-methylbutyl)sulfanyl]thiophene (TSR*Br)

A solution of NBS (0.497 g, 2.8 mmol) in 4.0 ml of dimethylformamide (DMF) was added dropwise at 0°C in 1 h, under stirring and in the dark, to a solution of **TSR*** (0.520 g, 2.8 mmol) in 4.0 ml of DMF. The reaction mixture was stirred for 24 h protected from the light, then diluted with water, and finally extracted with Et_2O. After being dried over Na_2SO_4 and solvent evaporation at reduced pressure, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate 19:1 v/v as eluent to give **TSR*Br** (0.723 g, 98% yield) as a colorless liquid: ^{1}H-NMR (400 MHz, $CHCl_3$, δ): 7.24 (d, J = 5.6 Hz, 1H, Ar 5-H), 6.92 (d, J = 5.6 Hz, 1H, Ar 4-H), 2.87 (dd, 1H, $CH_\alpha S$), 2.68 (dd, 1H, $CH_\beta S$), 1.60–1.42 (m, 2H, $CHCH_3$ and $CH_\alpha CH_3$), 1.32–1.20 (m, 1H, $CH_\beta CH_3$), 1.00 (d, 3H, $CHCH_3$), and 0.89 (t, 3H, CH_2CH_3).

2.3.3 | (+)-3,3′-Bis[(*S*)-(2-methylbutyl)sulfanyl]-2,2′-bithiophene (T2SR*)

A mixture of **TSR*Br** (0.342 g, 1.3 mmol), bis(pinacolato)diboron (0.197 g, 0.8 mmol), Pd(dppf)Cl_2 (0.053 g, 5% mol), and $NaHCO_3$ (0.325 g, 3.9 mmol) in THF/water 2:1 (3.0 ml) was irradiated by MW at 90°C for 40 min. The reaction mixture was then cooled to room temperature, diluted with dichloromethane, and washed with water; the solvent was evaporated under reduced pressure, and the product purified by flash chromatography with cyclohexane as eluent to afford **T2SR*** (0.433 g, 90% yield) as a yellowish oil: $[\alpha]_D^{25}$ = +17.3 (c = 0.3 in $CHCl_3$); ^{1}H-NMR (400 MHz, $CHCl_3$, δ): 7.36 (d, J = 5.3 Hz, 2H, Ar 5-H), 7.08 (d, J = 5.3 Hz, 2H, Ar 4-H), 2.80 (dd, 2H, $CH_\alpha S$), 2.62 (dd, 2H, $CH_\beta S$), 1.60–1.38 (m, 4H, $CHCH_3$ and $CH_\alpha CH_3$), 1.24–1.10 (m, 2H, $CH_\beta CH_3$), 0.92 (d, 6H, $CHCH_3$), 0.83 (t, 6H, CH_2CH_3); HRMS (ESI$^+$, m/z): $[M + H]^+$ calcd for $C_{18}H_{27}S_4^+$, 371.0995; found: 371.0993.

2.3.4 | (+)-3-[(*S*)-(2-Methylbutoxy)]thiophene (TOR*)

To a solution of 3-methoxythiophene (Alfa Aesar) (0.760 g, 6.7 mmol) in 8.4 ml of toluene, (*S*)-(−)-2-methyl-1-butanol (1.4 ml, 13.3 mmol) and *p*-toluenesulfonic acid monohydrate (0.189 g, 1.0 mmol) were sequentially added under stirring and inert atmosphere. After 24 h at reflux, the mixture was cooled to room temperature, poured into 100 ml of water, and then extracted with CH_2Cl_2. The organic phase was washed with water, dried over Na_2SO_4, and concentrated by evaporation under reduced pressure. The crude product was purified by column chromatography on silica gel with cyclohexane/CH_2Cl_2 80:20 v/v as eluent to afford **TOR*** (0.764 g, 67% yield) as a yellow liquid: $[\alpha]_D^{25}$ = +8.7 (c = 0.4 in $CHCl_3$); ^{1}H-NMR (400 MHz, $CHCl_3$, δ): 7.15 (dd, J = 5.5 Hz, J = 3.2 Hz, 1H, Ar 5-H), 6.76 (dd, J = 5.5 Hz, J = 1.6 Hz, 1H, Ar 4-H), 6.22 (dd, J = 3.3 Hz, J = 1.6 Hz, 1H, Ar 2-H), 3.81 (dd, 1H, $CH_\alpha O$), 3.73 (dd, 1H, $CH_\beta O$), 1.94–1.88 (m, 1H, $CHCH_3$), 1.62–1.50 (m, 1H, $CH_\alpha CH_3$), 1.36–1.20 (m, 1H, $CH_\beta CH_3$), 1.01 (d, 3H, $CHCH_3$), and 0.94 (t, 3H, CH_2CH_3); HRMS (ESI$^+$, m/z): $[M + H]^+$ calcd for $C_9H_{15}OS^+$, 171.0843; found: 171.0842.

2.3.5 | (+)-2,5-Dibromo-3-[(*S*)-2-methylbutoxy]thiophene (TOR*Br$_2$)

The same procedure described for **TSR*Br$_2$** was followed starting from **TOR*** (0.199 g, 1.2 mmol) and NBS (0.464 g, 2.6 mmol) in CH_2Cl_2 to give **TOR*Br$_2$** (0.328 g, 54% yield) as a colorless oil: $[\alpha]_D^{25} = +4.0$ ($c = 0.6$ in $CHCl_3$); ^{1}H-NMR (400 MHz, $CHCl_3$, δ): 6.76 (s, 1H, Ar 4-H), 3.85 (dd, 1H, $CH_\alpha O$), 3.77 (dd, 1H, $CH_\beta O$), 1.90–1.76 (m, 1H, $CHCH_3$), 1.60–1.48 (m, 1H, $CH_\alpha CH_3$), 1.32–1.18 (m, 1H, $CH_\beta CH_3$), 1.01 (d, 3H, CH_3CH), and 0.94 (t, 3H, CH_3CH_2); HRMS (ESI$^+$, m/z): $[M + H]^+$ calcd for $C_9H_{13}Br_2OS^+$, 326.9053; found: 326.9052.

2.3.6 | 2-Bromo-3-[(*S*)-2-methylbutoxy] thiophene (TOR*Br)

The same procedure described for **TSR*Br** was followed starting from **TOR*** (0.565 g, 3.3 mmol) and NBS (0.591 g, 3.3 mmol) in DMF obtaining **TOR*Br** (0.740 g, 90% yield) as a light brown oil: ^{1}H-NMR (400 MHz, $CHCl_3$, δ): 7.18 (d, J = 5.9 Hz, 1H, Ar 5-H), 6.73 (d, J = 5.9 Hz, 1H, Ar 4-H), 3.89 (dd, 1H, $CH_\alpha O$), 3.81 (dd, 1H, $CH_\beta O$), 1.88–1.78 (m, 1H, $CHCH_3$), 1.62–1.50 (m, 1H, $CH_\alpha CH_3$), 1.32–1.20 (m, 1H, $CH_\beta CH_3$), 1.01 (d, 3H, CH_3CH), and 0.95 (t, 3H, CH_3CH_2); HRMS (ESI$^+$, m/z): $[M + H]^+$ calcd for $C_9H_{14}BrOS^+$, 248.9948; found: 248.9947.

2.3.7 | (+)-3,3′-Bis[(*S*)-(2-methylbutoxy)]-2,2′-bithiophene (T2OR*)

A solution of *n*-butyl lithium in hexane 2.5 M (0.4 ml, 1.0 mmol) was added dropwise under inert atmosphere at −70°C to a solution of **TOR*Br** (0.215 g, 0.9 mmol) in dry THF (3 ml). After 30 min, $Fe(acac)_3$ (Alfa Aesar) (0.494 g, 1.4 mmol) was added to the reaction mixture, and the mixture allowed to reach room temperature under stirring overnight before quenching with water. The aqueous phase was extracted with Et_2O, and the combined organic phases were washed with brine. After being dried over Na_2SO_4 and removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica with hexane as eluent to afford **T2OR*** (0.050 g, 16% yield) as a dark green oil constituted by a 60:40 mixture of HH and HT regioisomers: $[\alpha]_D^{25} = +42.7$ ($c = 0.4$ in $CHCl_3$); ^{1}H-NMR (400 MHz, $CHCl_3$, δ): 7.07 (d, J = 5.7 Hz, 2H, Ar 5-H and 5′-H, **HH**), 7.02 (d, J = 5.7 Hz, 1H, Ar 5-H, **HT**), 6.88 (d, J = 1.8 Hz, 1H, Ar 3′-H, **HT**), 6.83 (d, J = 5.7 Hz, 2H, Ar 4-H and 4′-H, **HH**), 6.81 (d, J = 5.7 Hz, 1H, Ar 4-H, **HT**), 6.10 (d, J = 1.8 Hz, 1H, Ar 5′-H, **HT**), 4.01 and 3.94 (m, 4H, 3- and 3′-OCH_α and 3-OCH_β, **HH**), 4.01 and 3.94 (m, 2H, 3-OCH_α and 3-OCH_β, **HT**), 3.81 and 3.73 (m, 2H, 4′-OCH_α and 4′-OCH_β, **HT**), 2.00–1.80 (m, 4H, $CHCH_3$), 1.70–1.50 (m, 4H, $CH_\alpha CH_3$), 1.44–1.18 (m, 4H, $CH_\beta CH_3$), 1.12–1.06 (m, 12H, $CHCH_3$), 1.02–0.90 (m, 12H, CH_2CH_3); HRMS (ESI$^+$, m/z): $[M + H]^+$ calcd for $C_{18}H_{26}NaO_2S_2{}^+$, 361.1271; found: 361.1270.

2.3.8 | Oligo{3-[(*S*)-(2-methylbutyl) sulfanyl]thiophene} (PTSR*)

To a three-necked flask containing **TSR*Br₂** (0.313 g, 0.9 mmol), dried 2-methyltetrahydrofuran (5 ml) and 2 M of hexylmagnesium bromide in Et_2O (0.5 ml, 1.0 mmol) were sequentially added under stirring and nitrogen atmosphere. The solution was heated to reflux in the dark for 1 h. Then, $Ni(dppp)Cl_2$ (0.024 g, 5 mol%) was added, and the mixture left under stirring and reflux overnight. After being dried, chloroform was added, and the mixture was washed with water, followed by drying over Na_2SO_4. The organic phase was concentrated to small volume and finally treated with hot MeOH to afford **PTSR*** (0.121 g, 73% yield) as a dark red solid; ^{1}H-NMR (400 MHz, $CHCl_3$, δ): 7.38 (s, 1H, backbone Ar 4-H), 3.00–2.60 (m, 2H, CH_2S), 1.80–1.15 (m, 3H, CH_3CH and CH_3CH_2), 1.10–0.95 (m, 3H, CH_3CH), and 0.95–0.78 (t, 3H, CH_3CH_2).

2.3.9 | Oligo{3-[(*S*)-(2-methylbutoxy)] thiophene} (PTOR*)

To a three-necked flask containing **TOR*Br₂** (0.296 g, 0.9 mmol), dry THF (5 ml) and 2 M of hexylmagnesium bromide in Et_2O (0.5 ml, 1.0 mmol) were sequentially added under stirring and nitrogen atmosphere. The solution was heated to reflux in the dark for 1 h. Then, $Ni(dppp)Cl_2$ (0.024 g, 5 mol%) was added, and the mixture was left under stirring and reflux for 1 h. After being dried, chloroform was added, and the mixture was washed with water, followed by drying over Na_2SO_4. The organic phase was concentrated to small volume and finally treated with hot MeOH to afford **PTOR*** (0.079 g, 53% yield) as a dark blue powder: ^{1}H-NMR (400 MHz, $CHCl_3$, δ): 7.02–6.80 (bm, 1H, backbone Ar 4-H), 4.10–3.90 (m, 2H, CH_2O), 2.08–1.90 (m, 1H, CH_3CH), and 1.78–0.86 (m, 8H, CH_3CH, CH_3CH_2 and CH_3CH_2).

2.3.10 | Oligo{3,3′-bis[(*S*)-(2-methylbutyl) sulfanyl]-2,2′-bithiophene} (PT2SR*)

To a solution of **T2SR*** (0.075 g, 0.2 mmol) in anhydrous $CHCl_3$ (8.1 ml), $FeCl_3$ (0.131 g, 0.8 mmol) was added under a weak stream of nitrogen at room temperature. The suspension was left under stirring for 24 h, turning from greenish to dark blue color. Then, 50 ml of THF and 100 ml of $CHCl_3$ were added; the mixture was washed several times with 2% v/v aqueous HCl up to complete elimination of the iron(III) ion (negative essay with NH_4SCN) and finally with water to neutrality. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure, and finally treated with MeOH to afford **PT2SR*** (0.071 g, 97% yield) as a brownish waxy solid: ^{1}H-NMR (400 MHz, $CHCl_3$, δ): 7.38 (d, 1H, terminal Ar 5-H), 7.22–7.12 (ms, 2H, backbone Ar 4-H and 4′-H), 7.08 (d, 1H, terminal Ar 4-H), 2.96–2.82 (m, 2H, $CH_\alpha S$), 2.76–2.62 (m, 2H, $CH_\beta S$), 1.70–1.40 (m, 2H, CH_3CH), 1.34–1.10 (m, 2H, $CH_\alpha CH_3$), 1.04–0.98 (m, 2H, $CH_\beta CH_3$), 0.98–0.92 (m, 6H, CH_3CH), 0.92–0.78 (m, 6H, CH_2CH_3).

2.3.11 | Oligo{3,3′-bis[(*S*)-(2-methylbutoxy)]-2,2′-bithiophene} (PT2OR*)

The same procedure described for **PT2SR*** was followed starting from the HH and HT mixtures of regioisomers labeled as **T2OR*** (0.050 g, 0.1 mmol) and $FeCl_3$ (0.065 g, 0.4 mmol) in $CHCl_3$ to obtain **PT2OR*** (0.032 g, 95% yield) as a black solid: ^{1}H-NMR (400 MHz, $CHCl_3$, δ): 7.18–7.08 (m, 2H, backbone Ar 4-H and 3′-H, **HH**), 7.08–6.92 and 6.92–6.68 (m, 2H, backbone Ar 4-H and 3′-H, **HH** and backbone Ar 4-H and 4′-H, **HT**), 4.2–3.6 (m, 4H, OCH_2), 2.0–1.8 (m, 2H, $CHCH_3$), 1.7–1.5 (m, 2H, $CH_\alpha CH_3$), 1.4–1.2 (m, 2H, $CH_\beta CH_3$), 1.1–1.0 (m, 6H, $CHCH_3$), and 1.0–0.9 (m, 6H, CH_2CH_3).

3 | RESULTS AND DISCUSSION

3.1 | Synthesis

The monothiophene and bithiophene monomers **TSR*Br₂**, **TOR*Br₂**, **T2SR***, and **T2OR*** (Scheme 1) used for the preparation of the corresponding oligomeric derivatives were obtained respectively from the starting materials **TSR*** and **TOR***.

The synthesis of (+)-3-[(*S*)-(2-methylbutyl)sulfanyl] thiophene (**TSR***)[24] was carried out following the method reported for the related 3-*S*-hexyl thiophene[12] by nucleophilic reaction of 3-mercaptothiophene[12] with (+)-(*S*)-1-bromo-2-methylbutane, prepared in turn by reaction with LiBr[25] of the *p*-toluensulfonate ester of enantiomerically pure (−)-(*S*)-2-methyl-1-butanol, obtained through a modified literature procedure[26] (see Supporting Information for details).

(+)-3-[(*S*)-(2-Methylbutoxy)]thiophene (**TOR***) was obtained by transetherification of commercial 3-methoxythiophene with (−)-(*S*)-2-methyl-1-butanol, according to the procedure reported by Xu for the related 3-*O*-hexyl thiophene derivative.[27]

Treatment of **TSR*** and **TOR*** with NBS according to established procedures[28,29] allowed to obtain the related 2,5-dibromo derivatives **TSR*Br₂** (*dextrorotatory* enantiomeric isomer of the previously reported compound)[30] and **TOR*Br₂**, as well as the 2-bromo derivatives **TSR*Br**[24] and **TOR*Br**, subsequently used for the preparation of the HH bithiophene monomers **T2SR*** and **T2OR***.

In particular, (+)-3,3′-bis[(*S*)-(2-methylbutyl) sulfanyl]-2,2′-bithiophene **T2SR*** was obtained in high yield following the synthetic protocol based on MW-assisted Suzuki–Miyaura reaction recently adopted for similar, optically inactive, derivatives.[31] By contrast, the preparation of the related oxyalkyl disubstituted bithiophene monomer **T2OR*** through this route was unsatisfactory. Moreover, despite the expected higher reactivity due to the presence of oxygen directly connected to the thiophene ring, the synthesis by oxidative coupling with BuLi/$CuCl_2$[31] was also inconclusive. However, (+)-3,3′-bis[(*S*)-(2-methylbutoxy)]-2,2′-bithiophene **T2OR*** could be obtained from **TOR*Br** with BuLi in the presence of $Fe(acac)_3$ according to the method adopted for similar derivatives,[32] although mixed with 40% of the HT regioisomer, as established by ^{1}H-NMR spectroscopy (see Section 2 and Figure S2B).

The optically active monothiophene and bithiophene monomers were then polymerized, respectively, by regiospecific organometallic coupling to the corresponding HT derivatives and by simple oxidative coupling with $FeCl_3$, leading to HH/TT derivatives in consequence of the chemical equivalence of the bithiophenic reactive sites.

The GRIM (Grignard Metathesis) procedure,[33,34] involving a magnesium/bromine exchange after the initial treatment with a Grignard reagent, was adopted for the polymerization of **TSR*Br₂** and **TOR*Br₂**, in order to obtain highly regioregular HT derivatives, owing to the selectivity of the sterically hindered catalyst Ni(dppp)Cl_2 that does not promote HH or TT couplings. However, similar to what was obtained by Goldoni et al.[29] in the polymerization of 3-(butylthio)thiophene, in our case, the polymerization of **TSR*Br₂**, carried out under the same reaction conditions, gave a low molecular mass product probably due to unfavorable interactions between the catalyst and the thioethereal moiety. Consequently, the polymerization of **TOR*Br₂** was performed with the aim to obtain a macromolecular derivative with a comparable polymerization degree.

The polymerization of (+)-3,3′-bis[(*S*)-(2-methylbutyl) sulfanyl]-2,2′-bithiophene (**T2SR***) and (+)-3,3′-bis[(*S*)-

(2-methylbutoxy)]-2,2′-bithiophene (**T2OR***) to the corresponding **PT2SR*** and **PT2OR*** oligomeric derivatives was carried out following the simple and well-established oxidative coupling with iron(III) trichloride. The symmetrical structure and chemical equivalence of the coupling positions in the HH bithiophenic monomer allow to obtain a completely regioregular derivative that displays only HH/TT junctions between the thiophene rings, despite the use of a nonregiospecific method. **T2OR***, actually a mixture of the HH and HT regioisomers (60:40 molar ratio), was anyhow submitted to oxidative coupling with $FeCl_3$, in order to obtain a product (**PT2OR***) at least partially comparable with the related sulfanyl derivative **PT2SR***.

All the macromolecular samples were characterized for molecular mass, thermal, and spectral properties. As reported in Table 1, the average polymerization degrees of **PTSR*** and **PTOR*** were of comparable magnitude. The average molecular mass of **PT2SR*** appears significantly lower with respect to the HT derivative, being substantially constituted by bithiophenic tetramers, as confirmed also by the ^{1}H-NMR spectrum (see below). The related polymeric derivative with TT/HH regioregularity, obtained under the same conditions as **PT2SR*** by polymerization of the TT monomer (+)-4,4′-bis[(*S*)-(2-methylbutyl) sulfanyl]-2,2′-bithiophene,[20] displayed a M_n value of 17,000 g/mol reasonably in consequence of deeper fractionation of the crude polymeric product with respect to **PT2SR***, as inferred by the 59% reaction yield (vs. our 97%) reported in the above paper. By contrast, **PT2OR***, obtained with yield similar to **PT2SR***, displayed higher DP value, which is to be related to a positive role towards polymerization played by the alkoxy group, although the presence of a fraction with lower molecular weight, that is, approximately bithiophenic dimers, was also detected by GPC.

3.2 | IR and ^{1}H-NMR characterizations

The IR spectrum of **PTSR*** displays the expected absorptions characteristic of 2,5-coupled 3-substituted polythiophenes: aromatic C—H stretching at 3,071 cm^{-1} and one out-of-plane deformation of aromatic C—H at 803 cm^{-1} due to the trisubstituted ring. The alkyl chain gives stretching vibrations in the region 2,963–2,854 cm^{-1} and deformation modes below 1,475 cm^{-1}.

In **PT2SR***, the alkylsulfanyl chain gives rise to C—H stretching vibrations in the region 2,963–2,846 cm^{-1} and to deformation modes around 1,478, 1,458, 1,434 (S—CH_2), and 1,378 cm^{-1}. The aromatic C—H stretching and out-of-plane deformation are found at 3,079 and 814 cm^{-1}, respectively.

The alkoxy pendants of **PTOR*** give C—H stretching at 2,959–2,850 cm^{-1} (CH_2 and CH_3). Ring vibrational modes are seen at 1,523, 1,446, and 1,350 cm^{-1}. The band at 1,068 cm^{-1} is assigned to C (ring)—O—C stretch. The vibrational band at 802 cm^{-1} is attributable to C—H_β out-of-plane deformation mode of thiophene rings. Similarly, **PT2OR*** gives the corresponding absorptions at 2,966–2,850, 1,523, 1,398, and 1,353 cm^{-1}. The C (ring)—O—C stretch appears at 1,064 cm^{-1} and the C—H_β out-of-plane deformation mode of thiophene rings at 802 cm^{-1}.

The chemical structure and regioregularity degree of **PTSR*** and **PTOR*** were evaluated by ^{1}H-NMR spectroscopy in $CDCl_3$. The spectrum of **PTSR*** (Figure S3A) displays a major singlet at 7.38 ppm that is assigned to 4-H of the backbone, in accordance to the chem. shift value reported for HT poly(3-butylsulfanylthiophene) obtained by similar regiospecific Kobayashi procedure,[29] along with other low intensity resonances, attributed to the terminal protons of oligomeric chains, and to minor HH/TT connections at around 7.2 ppm, lowering the HT regioregularity degree to about the 90%, as measured by ^{1}H-NMR. By contrast, the spectrum of **PTOR*** displays a

TABLE 1 Yields and characterization data of macromolecular derivatives

Sample	Yield (%)[a]	M_n (g/mol)[b]	Đ[c]	DP[d]	T_g (°C)[e]	T_d (°C)[f]
PTSR*	73	2,600	1.8	14	0	288
PTOR*	53	3,600	2.0	21	5	263
PT2SR*	97	1,500	1.2	8	−26	139
PT2OR*	95	700	1.1	4	−16	114
		3,400	1.3	20		

[a] Weight of product/weight monomer × 100.

[b] Number average molar mass determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF).

[c] Dispersity.

[d] Average polymerization degree expressed as monothiophenic repeating units.

[e] Glass transition temperature determined by differential scanning calorimetry (DSC) (second heating cycle).

[f] Decomposition temperature determined by thermogravimetric analysis (TGA).

broad resonance of the backbone 4-H proton at 7.02–6.80 ppm (Figure S3B), upfielded with respect to the corresponding proton of **PTSR***, as a consequence of increased electron density induced by the oxygen atom directly linked to thiophene ring. No accurate evaluation of the regioregularity degree can be made for **PTOR***, as the resonances of the 4-H proton related to the four possible triad sequences (HT/HT, TT/HT, HT/HH, and TT/HH), reported as ranging in the intervals 7.04–6.84 ppm[35] or 6.95–6.83 ppm[36] for various poly(3-alkoxythiophene)s obtained under nonregiospecific conditions, are clearly overlapped. However, as the maximum intensity of the 4-H resonance of **PTOR*** is centered at 6.90 ppm, very close to the 6.91-ppm value reported for highly regioregular HT linkage in poly(3-decyloxythiophene) obtained by the same GRIM method,[37] we can conclude that **PTOR*** is characterized by highly predominant HT regioregularity.

The expected structure for **PT2SR*** is confirmed by the ^{1}H-NMR spectrum (Figure S4A) that displays at 7.2 ppm the resonance of the 4-H proton of the backbone, as well as the presence of intense signals related to terminal groups, as evidenced by the GPC measurements indicating a low molecular mass of this sample. As expected, the spectrum of **PT2SR*** appears identical to that reported for the above-mentioned poly{4,4′-bis[(*S*)-(2-methylbutyl)sulfanyl]-2,2′-bithiophene} possessing TT/HH regioregularity.[20] On the other hand, the clear presence of signals related to the 4-H and 5-H hydrogens of terminal thiophene rings, in addition to the low-molecular-weight value determined by GPC (Table 1), confirms that the polymerization of **T2SR*** actually occurred to a limited extent, yielding a tetrameric derivative constituted by bithiophenic counits.

The ^{1}H-NMR spectrum of **PT2OR*** (Figure S4B) confirms the obtainment of a material having a substantially regiorandom structure, with the presence of three broad signals centered at 7.13, 6.97 (main), and 6.83 ppm, related, respectively, to the presence of prevalently HH/TT oligomers and to HH/TT/HT and HT/HT junctions.[35,36,38]

3.3 | Thermal properties

As shown in Table 1, both **PTSR*** and **PTOR*** display a similar thermal behavior, with a slightly higher value of the glass transition temperature and a lower decomposition temperature for **PTOR*** with respect to **PTSR***. The values for the glass transition temperature of the bithiophene derivatives **PT2SR*** and **PT2OR*** appear lower with respect to their counterparts **PTSR*** and **PTOR***, attributable to their lower molecular mass and reduced planarity of the backbone caused by the presence of HH junctions. The alkoxy derivatives **PTOR*** and **PT2OR*** exhibit a slightly higher rigidity than **PTSR*** and **PT2SR***, respectively, ascribable to larger conjugation extent in the backbone induced by the electron donor alkoxy group that increases the polarity of the aromatic system, favoring a more compact arrangement of the macromolecules in the solid state.

Both **PT2SR*** and **PT2OR*** show remarkably lower thermal stability with respect to the related HT regioregular samples (Figure S5) to be again attributed to higher flexibility of the main chain, with the oxygen-containing derivatives **PTOR*** and **PT2OR*** becoming more unstable upon heating with respect to **PTSR*** and **PT2SR***.

The absence of endothermic peaks related to melting, and the presence of glass transitions only in the DSC thermograms (Figure S6), suggests an overall amorphous character in the solid state of all the oligomeric derivatives.

3.4 | Optical properties

The UV–Vis spectra of the monomers (Table 2 and Figure 1A) display, as expected, a remarkable red shift of the absorption maxima of the alkoxy derivatives with respect to the related sulfanyl compounds, with this effect being more evident in the bithiophene compounds (52 vs. 35 nm) and is attributed to higher coplanarity between the thiophene rings induced by the O atom as compared with S. Accordingly, the aromatic conjugation originated by connecting two thiophene rings in the bithiophenic monomers is higher in the alkoxy derivatives (28 nm when passing from **TOR*** to **T2OR***) with respect to the sulfanyl derivatives (11 nm when passing from **TSR*** to **T2SR***). However, it has to be noted that a significant electron-donating ability is also displayed by the sulfanyl monomers compared with the related 3-alkylthiophene and 3,3′-dialkyl bithiophene derivatives, exhibiting maximum absorptions at lower wavelengths, 241[39] and 248 nm,[11] respectively.

The UV–Vis spectra of the macromolecular derivatives in solution (Table 2 and Figure 1B) show absorption maxima related to the π–π* electronic transition of the backbone aromatic system. The HT regioregular derivatives confirm the electron-releasing mesomeric effect of oxygen directly linked to the thiophene ring, displaying a stronger red shift of the maximum wavelength passing from **TOR*** to **PTOR*** (274 nm) with respect to the shift shown passing from **TSR*** to **PTSR*** (218 nm). In addition to its lower polymerization degree, it is possible that steric effects of the bulky thioalkyl moiety distorting the

TABLE 2 Maximum absorption (λ_{max}) of monomers and absorption/emission (λ_{em}) wavelengths (nm) of oligomers in $CHCl_3$ solution and as films obtained from chlorobenzene solution

Solution						Film
Monomer	**λ_{max} (nm)**	**Oligomer**	**λ_{max} (nm)**	**λ_{em} (nm)**	**Stokes shifts**	**λ_{max} (nm)**
TSR*	265	**PTSR***	483	601	118[a] 4,579[b]	509
TOR*	300	**PTOR***	574	665	91[a] 2,250[b]	580
T2SR*	276	**PT2SR***	416	582	166[a] 7,333[b]	469
T2OR*	328	**PT2OR***	522	612	90[a] 2,834[b]	529

[a] In nm.
[b] In cm^{-1}.

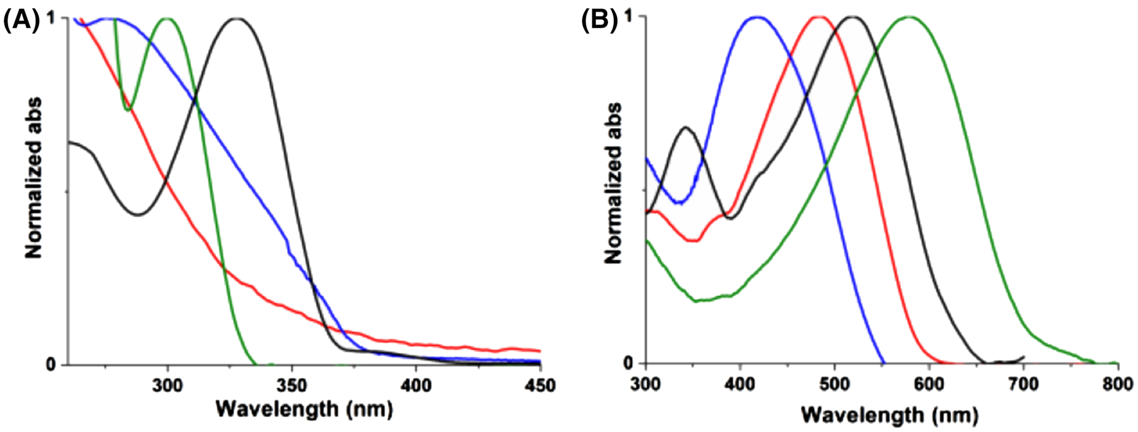


FIGURE 1 Normalized absorption spectra in $CHCl_3$ of monomers (A) and oligomers (B) (red line, **TSR*** and **PTSR***; green line, **TOR*** and **PTOR***; blue line, **T2SR*** and **PT2SR***; black line, **T2OR*** and **PT2OR***)

main chain are also contributing to reduce the bathochromic shift in **PTSR*** with respect to **PTOR***.[40] The maximum absorption wavelengths of **PTOR*** (574 nm in solution, 580 nm as film) appear blue shifted compared with those observed for the optically active HT poly(3-alkoxythiophene) containing the 3,7-dimethyloctyloxy moiety and characterized by a much higher PD value of 57 (602 nm in solution, 635 nm as film).[15] However, the absorption maxima in $CHCl_3$ solution of HT poly(3-hexyloxythiophene) (580 nm)[40] and HT poly(3-decyloxythiophene) (565 nm)[37] having also high PD (71 and 45, respectively) are of similar magnitude to that of **PTOR***, thus suggesting high regioregularity and sufficiently extended aromatic conjugation in **PTOR*** despite its oligomeric structure. The same consideration also holds for **PTSR***, absorbing in $CHCl_3$ at a wavelength (483 nm) not much different from the absorption maximum of HT poly[(3-butylthio)thiophene] (502 nm)[30] and at similar wavelength as HT poly[(3-hexylthio)thiophene] (485 nm),[40] despite its much lower polymerization degree (14 vs. 22 and 76, respectively).

Both the λ_{max} values of the bithiophene derivatives **PT2SR*** and **PT2OR*** in $CHCl_3$ solution are blue shifted compared with **PTSR*** and **PTOR*** as a consequence of their lower polymerization degree and backbone configuration, which is expected to disfavor coplanar arrangements of the conjugated aromatic rings. As expected, the λ_{max} value of **PT2SR*** appears lower than the value (469 nm) reported[20] for the polymeric TT/HH derivative poly{4,4′-bis[(*S*)-(2-methylbutyl)sulfanyl]-2,2′-bithiophene} but not much dissimilar from the chemically pure oligomer HH/TT octithiophene bearing the side chain thiohexyl moiety (434 nm in CH_2Cl_2).[12]

In addition to a weak absorption at 345 nm, ascribable to the presence of a shorter oligomeric fraction, as suggested by GPC, it is noteworthy that the λ_{max} (522 nm) of **PT2OR*** is strongly red shifted compared with both the derivatives **PTSR*** and **PT2SR***. Indeed, despite that **PT2OR*** is actually a mixture of oligomers with an overall regiorandom structure, as suggested by its lower maximum absorption wavelength with respect to regioregular HH/TT poly(3,3′-dibutoxy-2,2′-bithiophene) and TT/HH poly(4,4′-dibutoxy-2,2′-bithiophene) with similar polymerization degrees (545 and 574 nm, respectively),[38] as well as to the optically active HH/TT poly[3,3′-bis(3,7-dimethyloctyloxy)-2,2′-bithiophene] (583 nm)[16] and other regioregular mono-alkoxy substituted polythiophenes (583–588 nm),[36] it is confirmed that the oxygen atom promotes a remarkable electron delocalization, even in the absence of prevalent regioregularity and high polymerization degree. It is again to be noted that the maximum absorption values in solution of all the sulfanyl and alkoxy oligomeric derivatives are in any case red shifted with respect to the related maxima of HT (431 nm)[22] and TT/HH P3ATs (392 nm)[11] materials bearing the same chiral moiety in the side chain.

PL spectra carried out on the macromolecular derivatives (Table 2 and Figure S7B) allowed to assess lower Stokes shift values of the alkoxy derivatives with respect to the sulfanyl derivatives, indicative of reduced energy level difference of the excited states of the formers. As deduced by the UV–Vis absorption spectra, and in agreement with the results obtained with the above-mentioned optically active regioregular poly(3-alkoxythiophene)s,[16] this confirms the increased extent of aromatic resonance and hence coplanarity of the thiophenic rings in **PTOR*** and **PT2OR***. Interestingly, as Stokes shift values ranging around 2,000 cm^{-1} are considered typical of rigid conjugated polymers in solution,[41,42] it appears that **PTOR*** and **PT2OR*** are characterized by significantly higher stiffness with respect to their sulfanyl counterparts.

Solvatochromism experiments were carried out on the chloroform solutions of the oligomers upon gradual addition of a poor solvent, such as acetonitrile, in order to promote a transition from the disordered random coil conformation to self-assembling and microaggregation of the macromolecules.

The addition of acetonitrile to the chloroform solutions of HT **PTSR*** and **PTOR*** (Figure 2A,C) produces a gradual decrease of light absorption with a broadening of the band related to the electronic π–π* transition, as well as a slight red shift of the maximum

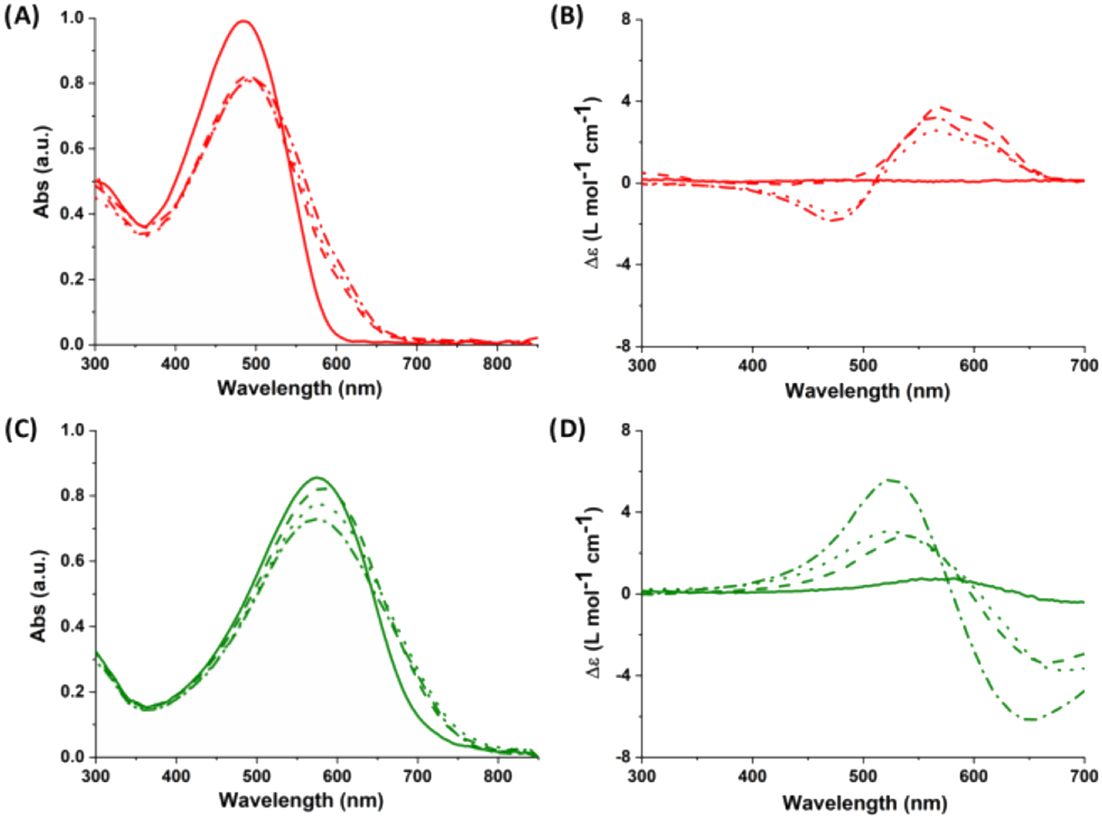


FIGURE 2 Absorption (A) and circular dichroism (CD) (B) spectra of **PTSR*** in $CHCl_3$ (red solid line), $CHCl_3/CH_3CN$ 40:60 (red dashed line), $CHCl_3/CH_3CN$ 30:70 (red dotted line) and $CHCl_3/CH_3CN$ 20:80 (red dashed-dotted line); absorption (C) and CD (D) spectra of **PTOR*** in $CHCl_3$ (green solid line), $CHCl_3/CH_3CN$ 60:40 (green dashed line), $CHCl_3/CH_3CN$ 40:60 (green dotted line) and $CHCl_3/CH_3CN$ 20:80 (green dashed-dotted line)

wavelength (~10 nm) without particularly evident vibronic features. Upon a similar treatment, **PT2OR*** (Figure 3C) behaves similarly to **PTSR*** and **PTOR*** as far as the main absorption is concerned, with the absorption at 345 nm, related to a shorter, more soluble, oligomeric fraction insensitive to the change of solvent. By contrast, HH/TT **PT2SR*** (Figure 3A) exhibits the appearance of a new band close to 470 nm at a $CHCl_3/CH_3CN$ composition of 10/90 v/v, suggesting the presence of structures possessing more extended electronic conjugation upon aggregation, regardless of the presence of unfavorable HH junctions.

The UV–Vis spectra of thin films of **PTSR***, **PTOR***, **PT2SR***, and **PT2OR***, obtained by drop-casting from chlorobenzene solution, are reported in Figure 4 and the related data in Table 2. In addition to a sequence of absorption maxima similar to the solution in chloroform, all samples exhibit broader bands and appear furtherly red shifted with respect to those of the aggregated structures obtained from solvatochromism experiments, with **PT2SR*** confirming the presence in the solid state of multiple aggregated structures.

3.5 | CD spectroscopy

The CD spectrum of **PTSR*** in pure chloroform (Figure 2B) does not display any optical activity in the spectral region related to the π–π* electronic transition of polythiophene, as expected, owing to the random coil conformation of the macromolecules. By contrast, a weak CD signal is present in the spectrum of **PTOR*** (Figure 2D) at around 580 nm, in correspondence to the UV–Vis absorption, suggesting an intrinsically chiral structure of short main chain sections, even in dilute solution, to be reasonably ascribed to the increased rigidity of the backbone induced by the mesomeric effect of the side chain alkoxy group. The gradual addition of the poor solvent acetonitrile produces in both **PTSR*** and **PTOR*** the appearance of bisignate dichroic signals of opposite sign, with crossover points related to the UV–Vis maxima (at around 520 nm for **PTSR*** and 580 nm for **PTOR***) (Table 3).

A bisignated CD signal is characteristic of exciton coupling between transition dipole moments of chromophores on adjacent polymer chains in the aggregate state, whereas for individual polymer chains with a helical

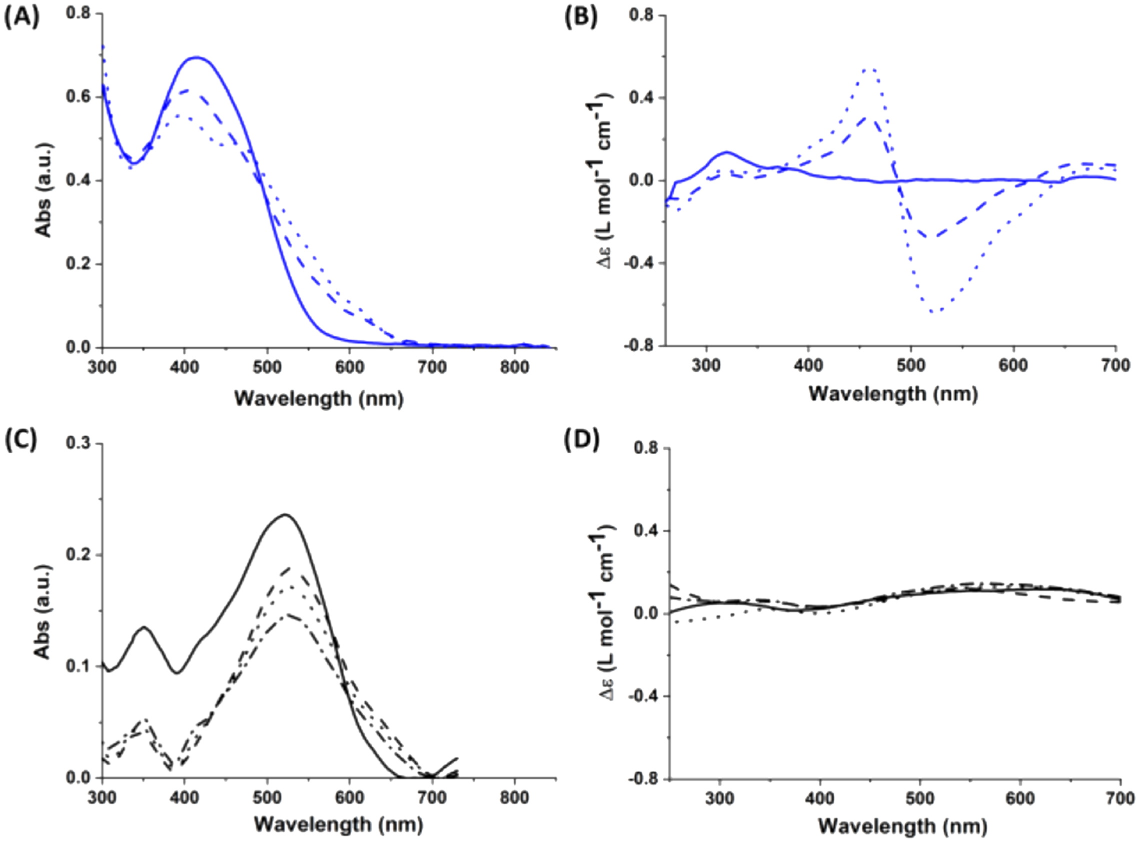


FIGURE 3 Absorption (A) and circular dichroism (CD) (B) spectra of **PT2SR*** in $CHCl_3$ (blue solid line), $CHCl_3/CH_3CN$ 30:70 (blue dotted line), and $CHCl_3/CH_3CN$ 10:90 (blue dashed line); absorption (C) and CD (D) spectra of **PT2OR*** in $CHCl_3$ (black solid line), $CHCl_3/CH_3CN$ 60:40 (black dashed line), $CHCl_3/CH_3CN$ 40:60 (black dotted line), and $CHCl_3/CH_3CN$ 20:80 (black dashed-dotted line)

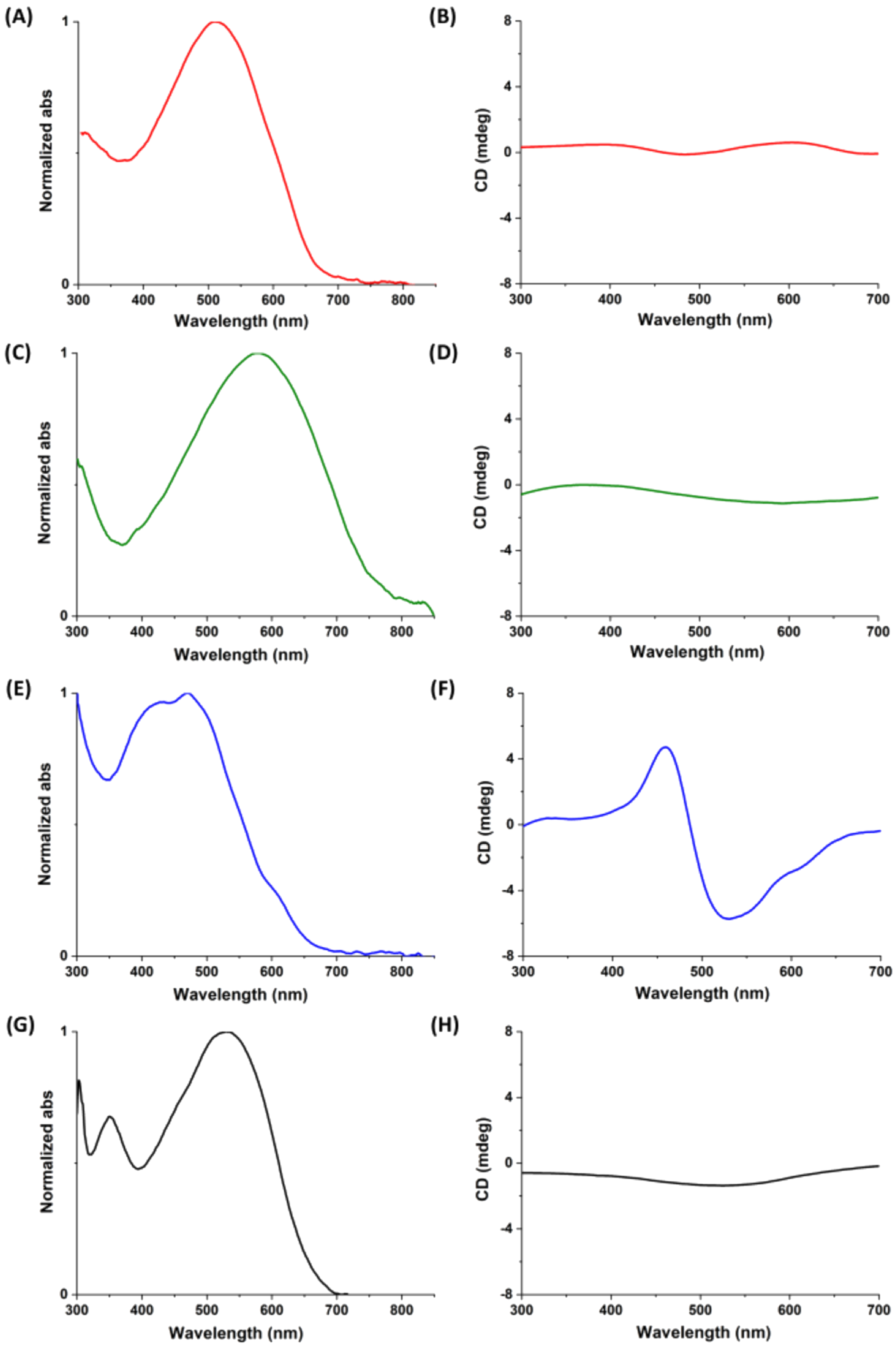


FIGURE 4 Absorption and circular dichroism (CD) spectra of **PTSR*** (A, B), **PTOR*** (C, D), **PT2SR*** (E, F), and **PT2OR*** (G, H) as films cast from chlorobenzene

TABLE 3 Circular dichroism (CD) spectra at 25°C of oligomers in the microaggregated state

Sample	Solvent $CHCl_3$:CH_3CN (v/v)	$\Delta\varepsilon_1$[a]	λ_1[b]	λ_0[c]	$\Delta\varepsilon_2$[a]	λ_2[b]
PTSR*	20:80	+3.21	563	512	−1.80	474
PTOR*	20:80	−6.09	650	579	+5.59	523
PT2SR*	10:90	−0.63	523	486	+0.55	458
PT2OR*	20:80	+0.15	561	-	-	-

[a] $\Delta\varepsilon$ expressed in L mol^{-1} cm^{-1}.
[b] Wavelength (in nm) of the maximum dichroic absorption.
[c] Wavelength (in nm) of the crossover point of dichroic bands.

conformation, the CD effect is not expected to be bisignated.[22,43] Thus, the bisignated CD spectra observed in π-conjugated oligomers with optically active pendant side chains such as **PTSR*** and **PTOR*** are due to a chiral supramolecular structure of predominantly planar macromolecules.[44]

In particular, the alkoxy derivative **PTOR*** displays higher optical activity, as well as higher chiral anisotropy factor g ($\Delta\varepsilon/\varepsilon$) ($2 \cdot 10^{-3}$ at 651 nm) with respect to **PTSR*** ($1 \cdot 10^{-3}$ at 562 nm), which exhibits, in addition to the bisignate band, a positive CD signal as a shoulder around 630 nm. The *g* value of **PTOR*** is close to the reported value of $3 \cdot 10^{-3}$ at 568 nm found for the optically active HT poly(3-alkoxythiophene) bearing the3,7-dimethyloctyloxy moiety in the side chain.[16] These findings can be interpreted as due to aggregation of macromolecules giving rise to supramolecular arrangements of opposite helicity both in **PTOR*** (*levo* helix sense) and, to a less extent, in **PTSR*** (*dextro* helix sense), where aggregates possessing intrinsic chiral structure are also present. Even at a very low polymerization degree, the oligomer HT **PTOR*** is able to give chiral supramolecular aggregates characterized by a significant g value, similarly to the related HT poly{3-[(*S*)-(2-methylbutyl)]thiophene} possessing remarkably higher molecular mass.[6,22]

The CD spectrum (Figure 3B) of HH/TT sulfanyl derivative **PT2SR*** in dilute $CHCl_3$ solution shows a weak signal in the spectral region 300–400 nm, indicative of the presence of a small amount of chain sections possessing one-handed helical sense. By gradual addition of acetonitrile, a moderate but clear bisignate dichroic signal related to exciton coupling between the thiophene rings in the backbone appears in consequence of chiral supramolecular aggregation, similar and with opposite helicity, with respect to **PTSR***. Indeed, the crossover point of CD spectrum is centered at 486 nm, corresponding to the wavelength of the shoulder displayed in the corresponding UV–Vis spectrum and related to aggregates of **PT2SR*** (Figure 3A). However, the maximum optical activity (*g* $3{\cdot}10^{-4}$ at 522 nm) results to be lower than in **PTSR*** mainly in consequence of its lower polymerization degree, disfavoring the formation of large chiral macromolecular aggregates. In addition, a shoulder around 600 nm is present in the CD spectrum, similarly to **PTSR***, to be attributed to an optically active phase constituted by oligomeric strands of one prevailing helicity. Similar UV–Vis and CD spectra were also observed upon aggregation of the above-mentioned polymeric TT/HH derivative poly{4,4′-bis[(*S*)-(2-methylbutyl) sulfanyl]-2,2′-bithiophene} by addition of methanol or *n*-hexane to its chloroform solution, or by evaporation from a good solvent, and attributed to the formation of more than one single aggregate phase, depending on the experimental conditions.[20]

It therefore appears that the possibility of coplanar arrangement of thiophene rings exists also in the case of disfavoring HH connections originated by the presence of 3,3′-disubstituted 2,2′-bithiophene counits. The extra sulfur atom linked to each thiophene ring may in fact induce self-aggregation via S···S interactions and weak CH···S hydrogen bonding.[12–14] The directionality of the above interactions, as well as the large polarizability of sulfur in thioether fragments, would favor the formation of highly anisotropic supramolecular systems characterized by antiplanar conformations involving reduced steric hindrance between the side chain substituents[31] even in the case of oligomeric constitution of the material.

By contrast, the CD spectrum in chloroform (Figure 3D) of the alkoxy oligomer **PT2OR***, possessing actually a regiorandom configuration, shows weak CD positive signals (*g* $2{\cdot}10^{-4}$ at 555 nm) with maxima related to the UV–Vis main chain absorptions, indicative of intrinsic chirality of the backbone limited to short sections, insensitive to the addition of poor solvent. Thus, the absence of exciton coupling in the CD spectrum of **PT2OR***, in contrast to what observed for **PTOR***, can be attributed to the absence of regioregular sections capable to promote sufficiently extended coplanarity of the thiophene rings, so as to favor the development of chiral supramolecular structures upon aggregation of the macromolecules.

It is worth noting that both side chain heteroatom and regioisomerism appear to affect the CD sign of the aggregates obtained by addition of poor solvent to the chloroform solution of the oligomeric samples: indeed, the CD sign is inverted upon heteroatom change in the samples possessing the same kind of regioregularity, the same occurring when the HT oligomers are compared with the corresponding HH/TT samples possessing equal heteroatom. We may tentatively attribute this behavior to the presence of slightly different conformations leading to aggregates of opposite helicity. In the case of the thioalkyl derivatives, where the presence of the above-mentioned S···S interactions favors coplanarity of the thiophene rings both in the HT and HH/TT compounds, the different regioisomerism may give rise to the difference in the helical sense of the π-stacking structures, although the chiral substituent has identical configuration. In the case of oxyalkyl derivatives, it is the mesomeric effect of oxygen that favors coplanarity and **PTOR*** behaves similarly to the related HT PMBT bearing the same chiral alkyl group in the side chain, but displays opposite CD sign with respect to **PTSR***. Accordingly, **PT2OR***, although not producing any exciton couplet, due to its low degree of HH/TT regioregularity, however, displays a positive CD signal of opposite sign with respect to both **PTOR*** and **PT2SR***. An inversion of the CD sign in HT and HH/TT poly(3-alkoxythiophene)s bearing the optically active 3,7-dimethyloctyloxy moiety in the side chain was also observed.[16]

It appears, however, that experimental procedure of aggregation and molecular structure of the material significantly affect the chiral behavior of the samples. In fact, when thin films of **PTSR*** and **PTOR*** are produced by slow evaporation of dilute chlorobenzene solutions, the resulting CD spectra differ from those obtained from solvatochromism experiments.

In particular, **PTSR*** (Figure 4B), **PTOR*** (Figure 4D), and **PT2OR*** (Figure 4G) actually display low optical activity with respect to that given by addition of acetonitrile to the chloroform solution. By contrast, the CD spectrum of a thin film of **PT2SR*** resulting from slow evaporation of dilute chlorobenzene solutions (Figure 4F) is similar to that given by the microaggregates formed upon acetonitrile addition to the chloroform solution, likely in consequence of its more homogeneous molecular composition (Table 1) with respect to the other derivatives. Thus, low dispersity value and regioregularity degree appear as relevant factors affecting the ordering process of the macromolecules from the solution to the solid state.

In conclusion, both the HT oligomeric derivatives **PTSR*** and **PTOR*** are able to display a behavior similar to HT poly{3-[(*S*)-(2-methylbutyl)]thiophene}, with formation of chiral supramolecular aggregates upon aggregation from the solution, although with lower optical activity originated by their low polymerization degree. Indeed, it is confirmed that the S or O heteroatom interposed between the chiral residue and the thiophene ring favors coplanarity of aromatic rings in the backbone, owing to interactions between the thienyl sulfur and the S or the O atom connecting the side chain.

Notwithstanding its unfavorable regioregularity, even the behavior of the HH/TT sulfanyl derivative **PT2SR*** appears substantially analogous to that of **PTSR*** and displays in the microaggregated state a relevant amount of chains with supramolecular chirality with respect to macromolecular strands possessing a prevailing one-handed helical sense. In comparison with the previously investigated optically active HH/TT P3AT bearing the same (*S*)-(2-methyl)butyl chiral residue directly linked to the thiophene ring, which is characterized by the presence of helical intrachain conformations disfavoring the formation of chiral supramolecular structures,[11] **PT2SR*** appears more prone to produce helical interchain order even at a much lower polymerization degree (8 vs. 172 in terms of one thiophenic repeating unit). This can be attributed to the presence of the thioalkyl sulfur atom that promotes a more coplanar arrangement of thiophene rings with respect to the HH/TT optically active P3AT derivative.

4 | CONCLUSION

HT and HH/TT optically active oligothiophenes bearing the (*S*)-(2-methyl)butyl residue linked at position 3 of the thiophene ring through sulfur or oxygen atom have been prepared with the aim to compare their chiroptical properties with those of the related HT and HH/TT P3AT derivatives possessing the same chiral moiety. Compared with the polymers, both the sulfanyl and alkoxy oligomers display red-shifted absorption maxima indicative of enhanced aromatic conjugation in the backbone due to the electron-releasing properties of the heteroatom. Upon aggregation from the solution by means of poor solvent addition, both the HT oligomers, and particularly the HT 3-alkoxy derivative, exhibit chiroptical properties, in consequence of the formation of supramolecular chiral aggregates, similarly to the related HT P3AT derivative possessing higher molecular mass. In addition, the HT 3-sulfanyl derivative displays the presence of individual chains possessing helical conformation. The HH/TT 3-sulfanyl derivative behaves similarly to its HT counterpart, although with lower chiral anisotropy, showing however a greater tendency to give chiral supramolecular aggregates than the related optically active HH/TT P3AT polymeric derivative. By contrast, the HH/TT 3-alkoxy oligomer, actually constituted by macromolecules with a mixture of HH/TT and HT connections, appears unable to produce relevant chiroptical properties upon aggregation and exhibits only the presence of short sections possessing chiral conformation in the aggregated state. It is also to be noted that these materials do not display relevant chiroptical properties as cast films obtained by direct evaporation from the solution, thus suggesting, as previously observed, that the aggregation of these π-conjugated materials is a stepwise event which requires to start from very dilute solutions and gradually add a weak solvent so that the process may take place with significant formation of chiral aggregates. To this respect, high regioregularity degree and low dispersity values appear to be favorable parameters positively affecting the film formation from the solution. In addition to favoring the extent of conjugation in the main chain, of interest for application to polarization-sensitive devices in photovoltaic cells and organic light-emitting diodes (OLEDs), the presence of oxygen or sulfur as connecting atom between the thiophene ring and the chiral alkyl side chain allows to achieve supramolecular chiral aggregations, of interest for CPL applications, not dissimilar, or better, with respect to those obtained with the related chiral P3ATs even in the case of a low polymerization degree.

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DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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SUPPORTING INFORMATION

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