Electronic Supplementary Information:

Chiral polymers based on thiophenes functionalized in the 3-position with a pendant containing a stereogenic sulfur atom. Synthetic and structural aspects

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Experimental Part

1. Materials and Methods

The commercially available reagents were used without further purification unless otherwise stated. The solvents: tetrahydrofuran, diethyl ether, dioxane were dried over sodium and distilled under argon. Dichloromethane was dried over calcium hydride and distilled under argon prior to use. Chloroform was purified and dried by distillation over P_2O_5.

The amines used in the reactions: (*i*Pr) $_2$EtN, pyridine, (*i*Pr) $_2$NH were dried over sodium hydroxide and distilled off under an argon atmosphere. The Et_3N was dried and distilled over sodium metal under an argon atmosphere. Reactions were preformed using standards laboratory techniques, in glass round bottom flasks or in Schlenk line evacuated and refilled with argon and were stirred with Teflon-coated magnetic stirring bars. Analytical TLC thin-layer chromatography was performed on silica gel 60 F_{254} precoated aluminum foil sheets (Merck supplier, DC Kieselgel 60 F254, layer thickness: 175 - 225 µm) and visualized by UV irradiation. The purifications by means of a column chromatography was achieved with silica gel Kieselgel 60 (70–230 mesh or 270-400 mesh).

NMR spectra were acquired at room temperature on a Bruker Avance 200 spectrometer (Bruker, Karlsruhe, Germany) operating at 200.16 MHz for ^{1}H, or on a Bruker Avance III 500 spectrometer operating at 500.13 MHz for ^{1}H, 150.33 MHz for ^{13}C experiments. The chemical shifts (δ) are reported in parts per million (ppm) in parts and are referenced with respect to TMS (δ = 0.0 ppm), as internal standard (^{1}H), in ^{31}P NMR referenced to 85% H_3PO_4 aqua solution as external standard, and the residual solvent peak of $CDCl_3$ (δ = 7.26 and 77.00 ppm in ^{1}H and ^{13}C NMR, respectively. Coupling constant (*J*) quoted in Hertz (Hz) to the nearest 0.1 Hz. The solid-state ^{13}C CP MAS experiments were performed on BRUKER Avance III 400 spectrometer (Bruker GMbH, Karlsruhe, Germany) operating at 400.13 for ^{1}H and 100.613 MHz for ^{13}C, equipped with a MAS probe head using 4 mm ZrO_2 rotors. A sample of native glycine was used for setting the Hartmann-Hahn condition and as external chemical shift reference ($\delta_{C=O}$ = 176.50 ppm). Spectra were recorded with MAS frequency of 8000 Hz and proton 90° pulse of 6.0 µs in length and a contact time of 4 ms.

UV-Vis spectra were recorded on an Analytik Jena SPECORD S600 spectrophotometer (Jena, Germany or a Nicolet Evolution 300 spectrophotometer in a quartz cuvette with 1.0 cm path length). Emission spectra were obtained using a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer (*Horiba Jobin Yvon*, Edison, New Jersey, USA). The light source was a 150 W xenon lamp. Mass spectrometry spectra were registered on spectrometer MAT95–Finnigan spectrometer. (Finnigan MAT, Bremen, Germany) using a chemical ionization (CI) or electron

ionization (EI) or FAB technique or using a Voyager ELITE MALDI-TOF mass spectrometer (MALDI-TOF). The specific rotations were measured on 241 MC–Perkin Elmer polarimeter (Perkin Elmer,Vienna, Austria) at room temperatures. The circular dichroism was recorded on CD6 Jobin Yvon spectrometer (Longjumeau, France). The enantiomeric excesses were determined by means of Varian ProStar 210 HPLC chromatography system with UV-VIS detector. The analytical chiral resolution was achieved with Chiralpak AS, Chiralcel OD (Daicel, Japan) chiral column packing.

Melting points (m.p.) were determined on Mel-Temp® apparatus or Betius (PHMK VEB Analytik, Dresden, Germany) and were uncorrected.

Synthetic procedures and spectral data:

1.1 Synthesis of monomeric thiophene derivatives functionalized with the substituent containing a stereogenic sulfur atom, as chiral precursors of polythiophenes

1.1.1 3-Methylthienyl Bromide (3)

To a solution of 3-thienylmethanol (1g; 8.75 mmol) in dry benzene (2 mL) at 0°C under argon atmosphere, a solution of PBr_3 (1.84g, 6.8 mmol) in benzene (1mL) was added dropwise. The reaction mixture was allowed to reach room temperature., and afterwards was refluxed for 2 h. After this time water (5mL) was added and the mixture was extracted in the separatory funnel. The separated in this way organic layer was washed with water (3x 5mL) and then dried over $MgSO_4$, filtered and concentrated in *vacuo*. The product was purified by distillation under reduced pressure (14mmHg/100°C) to give 1.09g of colorless liquid (70.5%).

^{1}H NMR (200 MHz, $CDCl_3$): δ 4.54 (s, 2H, CH_2); 7.13-7,16 (m, 1H); 7.31-7.35 (m, 2H). Spectral analysis matched with the data reported in[1].,.[2].

1.1.2 2-(3'-Thienyl)ethyl Bromide (4)

To a solution of 3-thienylethanol (7.4g; 57.7mmol) in dry benzene (10mL) at 0 ° C under argon atmosphere was slowly added a solution of PBr_3 (12.2g, 45.1mmol) in benzene (7mL). The reaction mixture was then allowed to warm to room temperature, and heated at the reflux for 4 h. At this time, water (35 mL) was added to the reaction mixture and extracted. The separated organic layer was washed three more times with 35 mL of water then dried over $MgSO_4$, filtered and concentrated in *vacuo*. The product was purified by distillation under reduced pressure (14mmHg / 100 ° C), yielding 8.69g of a colorless liquid (79%).

^{1}H NMR (200 MHz, $CDCl_3$): δ 3.21 (t, J=7.46 Hz, 2H,CH_2)*;* 3.57 (t, J=7.52 Hz, 2H, CH_2-Br); 6.98 (dd, J=4.98 Hz, J=0.78 Hz, 1H); 7.07 (m, 1H); 7.29 (m, 1H). Spectral analysis matched with the data reported in [3].

1.1.3 3-Thienylmethyl *p*-Tolyl Sulfide (5)

Metallic sodium (0.193 g, 8.37 mmol)) portionwise was added to methanol (10 mL) and the solution was stirred until the evolution of hydrogen gas ceased. Next, *p*-thiocresol (1.039 g, 8.37 mmol) was added to the obtained sodium methoxide, and the reaction solution was stirred for 15 minutes. The distilled 3-thienylmethyl bromide (1.487 g, 8.37 mmol) was slowly added dropwise to the sodium thiocresolate solution. After 2 hours, the methanol was evaporated to give 1.844 g of crude 3-thienylmethyl *p*-tolyl sulfide as a colorless liquid. The resulting product was purified via distillation (108°C/ 0,2mmHg) and 0.879 g (48% yield) of pure 3-thienylmethyl *p*-tolyl sulfide was obtained.

^{1}H NMR (200 MHz, $CDCl_3$): δ 2.32 (s, 3H, CH_3); 4.09 (s, 2H, CH_2); 7.01-7.10 (m, 4H, Ar); 7.20-7.28 (s, 3H, Ar).

^{13}C NMR (50MHz, $CDCl_3$) δ 20.96 ($\underline{C}H_3$); 34.21 ($\underline{C}H_2$); 122.44 ($\underline{C}_{2\text{-Thioph}}$); 125.72 ($\underline{C}_{5\text{-Thioph}}$); 128.02 (($\underline{C}_{4\text{-Thioph}}$); 129.56($C_{\text{ortho Ph}}$); 130.69 ($C_{\text{meta Ph}}$); 132.29 ($C_{\text{ipso-Ph}}$); 136.50 ($C_{\text{para-Ph}}$); 138.12 ($\underline{C}_{3\text{-Thioph}}$).

MS(CI) isobutane, m/z: 97[Thioph-3-CH_2]; 221 [M+1]; 317 [M+ Thioph-3-CH_2]; 343 [M+ *p*-Tol-S]

1.1.4 2-(3'-Thienyl)ethyl *p*-Tolyl Sulfide (6)

Metallic sodium (0.37 g, 16 mmol) portionwise was added to methanol (25 mL) and the solution was stirred until the evolution of hydrogen gas ceased. Next, p-thiocresol (2 g, 16 mmol) was added to the obtained sodium methoxide, and the reaction solution was stirred for 15 minutes. The distilled 2-(3'-thienyl)ethyl bromide (3.07 g, 16 mmol) was slowly added dropwise to the sodium thiocresolate solution. After 2 hours, the methanol was evaporated to give 3.65 g of crude 2-(3'-thienyl)ethyl *p*-tolyl sulfide as a colorless liquid. The resulting product was purified via distillation (100 ° C / 0.2mmHg) and 3.18 g (84.8% yield) of pure 2-(3'-thienyl)ethyl *p*-tolyl sulfide were obtained.

^{1}H NMR (200 MHz. $CDCl_3$): δ 2.38 (s, 3H, CH_3); 2.98 (t, J=7.99 Hz, 2H, CH_2-Thioph); 3.19 (t, J=7.87Hz; 2H, CH_2-S); 7.00-7.06 (m, 2H, Thioph); 7.18 (d, J=8.1 Hz, 2H, Ph-H_{meta}); 7.29-7.33 (m, 1H, Thiophf); 7.36 (d, J=8.08 Hz, 2H, Ph-H_{ortho})

^{13}C NMR (50MHz, $CDCl_3$) δ 20.95 (CH_3); 30.17 (CH_2-Thioph); 30.02 (CH_2-S); 120.93 ($C_{2\text{-Thioph}}$); 125.46 ($C_{5\text{-Thioph}}$); 127.94 (($C_{4\text{-Thioph}}$); 129.67($C_{\text{ortho Ph}}$); 130.16 ($C_{\text{meta Ph}}$); 132.42 ($C_{ipso\text{-Ph}}$); 137.32 ($C_{para\text{-Ph}}$); 140.51 ($C_{3\text{-Thioph}}$).

MS(CI) isobutane, m/z: 111 [Thioph-3-CH_2CH_2]; 235 [M+1]; 345 [M+ 111+1].

1.1.5 Oxidation of sulfides: General procedure:

To the solution of (thienyl)alkyl *p*-tolyl sulfide in methanol stirred at room temperature, a 30% solution of H_2O_2 was slowly added dropwise. After 24 h, water was added to the reaction mixture and all volume was transferred to a separatory funnel. The mixture was extracted several times with portions of dichloromethane. The combined organic layers were dried over $MgSO_4$, filtered and concentrated in *vacuo*. The resulting product was purified by column chromatography with an elution of Et_2O: hexane 1: 1.

Table 1 The conditions of the oxidation of sufides

Alkyl -(CH_2)**n**-	sulfide	H_2O_2	MeOH	Reaction conditions	Yield
n=1	0.4 g; 1.815 mmol	1.11 mL; (6 equiv)	10 mL	rt., 24h	66% (0.28g)
n=2	2.08g; 8.874 mmol	7 mL; (7.7 equiv)	70 mL	rt., 40h	93% (2.08g)

1.1.6 3-Thienylmethyl *p*-Tolyl Sulfoxide (7)

^{1}H NMR (200 MHz, $CDCl_3$): δ 2.40 (s, 3H, CH_3); 4.07 (d, J=3.98 Hz; 2H, CH_2); 6.77 (d, J= 4.96 Hz, 1H, Ar); 6.96 (d, J=2.48 Hz, 1H, Ar); 7.21-7.31 (m, 5H, Ar);

^{13}C NMR (50MHz, $CDCl_3$) δ 21.943 (CH_3); 57.92 (CH_2); 124.33 ($C_{\text{orto Ph}}$); 125.492 ($C_{\text{-Thioph}}$); 125.77 ($C_{\text{-Thioph}}$); 128.78 ($C_{\text{-Thioph}}$); 129.23 ($C_{ipso\text{-Ph}}$); 129.56 ($C_{\text{meta Ph}}$); 139.71 ($C_{para\text{-Ph}}$); 141.61 ($C_{3\text{-Thioph}}$).

MS(EI) isobutane, m/z: 97[Thioph-3-CH_2]; 236 [M+].

1.1.7 2-(3'-Thienyl)ethyl *p*-Tolyl Sulfoxide (8)–spectral data identical with those in 1.1.8.

1.1.8 (*R*)-(+)-2-(3'-Thienyl)ethyl *p*-Tolyl Sulfoxide (*R*)-8

A round-bottom flask equipped with a reflux condenser protected by a calcium chloride tube was charged with magnesium turnings (0.326 g, 0.0136 mol, 2 equiv), an iodine crystal, and filled with a portion of dry diethyl ether. While stirring, 2-(3'-thienyl)ethyl bromide (2.596g, 0.0136 mol, 2equiv) was added dropwise and was heated for 2h until the magnesium turnings disappeared. Upon the time the freshly prepared Grignard reagent solution was cooled down to 0°C and transferred dropwise to the solution of (-)-*O*-mentyl *p*-toluenesulfinate (2g, 0.0067mol, 1equiv), $[\alpha]_D$=-199.7 (acetone) in diethyl ether (10 mL). The mixture was kept stirring for 6h at 0°C and for 16h more at room temperature. Then it was hydrolyzed with 5% aqua solution of sulfuric acid. The mixture was extracted three times with dichloromethane (each time per 40 mL). The combined organic layers were washed with 5% potassium carbonate aqua solution, then water (50 mL), respectively, dried over $MgSO_4$, and concentrated via rotary evaporation. The product was purified by column chromatography on silica gel with diethyl ether/hexane (1:1, v/v) as an eluent to yield white crystals (1.468g, 86%).

$[\alpha]_D$= +115.96 (CH_2Cl_2)

m.p.=53-55°C

TLC: R_f=0.36 Et_2O

^{1}H NMR (200 MHz, $CDCl_3$): δ 2.42 (s, 3H, CH_3); 2.84-3.19 (m, 4H, CH_2CH_2); 6.92 (dd, J=1 Hz, J=4.9 Hz, 1H, Thioph); 7.00 (d, 1H, Thioph), 7.25 7.28 (m, 1H, Thioph); 7.32 (d, 2H$_{meta}$, J =8.01 Hz, Ar), 7.52 (d, 2H$_{ortho}$, J=8.16 Hz, Ar);

^{13}C NMR (50MHz, $CDCl_3$) δ 21.39 (s, 4-Ar-$\underline{C}H_3$), 22.77 (s, Thioph-$\underline{C}H_2CH_2$), 57. 53 (s, Thioph-$CH_2\underline{C}H_2$), 121.41 (s, 2-C_{Thioph}-H), 124.02 (s, 2 x *o*-$\underline{C}_{Ar}$-H), 126.07 (s, 5-$\underline{C}_{Thioph}$-H), 127.81(s, 4-$\underline{C}_{Thioph}$-H), 129.95 (s, 2 x *m*-$\underline{C}_{Ar}$-H), 138.83 (s, 3-$\underline{C}_{Thioph}$-CH_2), 140.28 (s, $\underline{C}_{Ar}$-S(O)), 141.51 (s, $\underline{C}_{Ar}$-CH_3);

MS(CI) isobutane, m/z: 111; 251 [M+1]; 501 [dimer+1]

HRMS(EI) m/z calculd.dla $C_{13}H_{14}OS_2$: 250.0476, found.:250.0486

IR (KBr) [cm^{-1}]: 3079; 3052; 2945; 2913, 1493; 1439; 1037 (S=O); 858; 810; 768.

1.1.9 2-(3'-Thienyl)ethyl *p*-Tolyl Sulfoxide (8) -racemic mixture

A round-bottom flask equipped with a reflux condenser protected by a calcium chloride tube was charged with magnesium turnings (0.72 g, 0.03 mol), an iodine crystal, and filled with a portion of dry diethyl ether. While stirring the contents of the flask, 2-(3'-thienyl)ethyl bromide (0.03 mol) was added dropwise until the magnesium turnings disappeared and the solution turned gray. To the freshly prepared Grignard reagent solution, *O*-ethyl *p*-toluenesulfinate (in situ generated from 3.49 g (0.02 mol) of *p*-toluenesulfinic chloride and ethanol), was added next. The reaction mixture was kept stirring at room temperature for 12 h. Then it was hydrolyzed with 5% aqua solution of sulfuric acid. The mixture was extracted three times with dichloromethane (each time per 40 mL). The combined organic layers were washed with 5% potassium carbonate aqua solution, then water (50 mL), respectively, dried over $MgSO_4$, and concentrated via rotary evaporation. The product (4.38g, 87%) was recrystallized from petroleum ether to give 1.57 g of the pure compound which was analyzed by spectroscopic methods.

m.p= 65-71°C

TLC: R_f=0.36 (SiO_2/Et_2O)

^{1}H NMR (200 MHz, $CDCl_3$): δ 2.41 (s, 3H, CH_3), 2.84-3.19 (m, 4H, CH_2CH_2), 6.91-7.00 (m, 2H, Ar$_{Thioph}$), 7.24-7.27 (m, 1H, Ar$_{Thioph}$), 7.32 (d, 2H$_{meta}$, J=8.14 Hz, Ar), 7.51 (d, 2H$_{ortho}$, J=8.14 Hz, Ar)

^{13}C NMR (50MHz, $CDCl_3$) δ 21.36 (s, 4-Ar-$\underline{C}H_3$), 22.79 (s, Thioph-$\underline{C}H_2CH_2$), 57. 56 (s, Thioph-$CH_2\underline{C}H_2$), 121.39 (s, 2-C_{Thioph}-H), 124.05 (s, 2 x *o*-$\underline{C}_{Ar}$-H), 126.04 (s, 5-$\underline{C}_{Thioph}$-H), 127.81(s, 4-$\underline{C}_{Thioph}$-H), 129.95 (s, 2 x *m*-$\underline{C}_{Ar}$-H), 138.88 (s, 3-$\underline{C}_{Thioph}$-CH_2), 140.42 (s, $\underline{C}_{Ar}$-S(O)), 141.49 (s, $\underline{C}_{Ar}$-CH_3)

MS(CI) isobutane, m/z 111; 251 [M+1]; 501 [dimer+1]

IR (KBr) [cm^{-1}]: 3079; 3052; 2957; 2920; 1493; 1444; 1086; 1037(S=O); 811; 777.

1.1.10 1-Hexadecanesulfinyl Chloride (10)

Hexadecanethiol, (20.68 g; 80mmol) placed in a three-necked flask equipped with a thermometer, a tube with calcium chloride encapped with gas outlet, and an adapter (gas inlet) connected with 3 gas washing bottles, was dissolved in 220ml of methylene chloride. The solution was cooled to -5 ° C and acetic anhydride (7.56ml, 80mmol) was added. The appearance of a white slurry was observed upon addition of the anhydride. Potassium permanganate was placed in a second flask connected to the gas washing bottles and equipped with a dropping funnel with venting. Concentrated HCl was added to the dropping funnel and chlorine evolution started. Chlorine was passed through the reaction mixture until a clear, pale yellow solution was obtained. The reaction flask was then connected through a trap cooled in an acetone-dry ice bath and a safety trap to a vacuum pump and excess chlorine and acetyl chloride were removed under reduced pressure. The product was obtained after evaporating the solvent under reduced pressure in 99.9% yield (24.7 g).

^{1}H NMR (200 MHz, $CDCl_3$): *δ* 0.89 (t, J=6.0 Hz, 3H, CH_3); 1.17-1.53 (m, 26H), 1.74-2.00 (m, 2H); 3.40 (t, J=7.60, 2H, CH_2-S)

^{13}C NMR (50MHz, $CDCl_3$) δ 12.84; 20.99; 21.40; 27.05; 27.86; 28.19; 28.38; 30.63; 63.23.

MS(CI) isobutane, m/z: 273 [$C_{16}H_{33}$-S(O)]; 309 [M+1]; 617 [2xM+1].

1.1.11 *O*-Methyl and Ethyl Hexadecanesulfinates (11; *O*-Methyl, 12; O-Ethyl)

To a solution of the alcohol in diethyl ether at 0 ° C under argon atmosphere triethylamine, followed by a solution of n-hexadecylsulfinyl chloride in diethyl ether were added. The reaction mixture was stirred at this temperature for 1 h. The progress of the reaction was monitored by TLC (Et_2O: petroleum ether 1: 1). An aqueous solution of 5% sulfuric acid was added to the reaction mixture, and the mixture was extracted. The separated organic layer was extracted with two more portions of 5% sulfuric acid, one portion of 5% aqueous $NaHCO_3$, and water. After phase separation, the organic layer was dried over magnesium sulfate, filtered and concentrated in vacuo. The products were obtained as a colorless oil.

Table 2 The preparation of *O*-Methyl and Ethyl Hexadecanesulfinates

R	Reagents			Conditions	Yield	
	$C_{16}H_{33}$-S(O)Cl	ROH	Amine			
Me	0.498g; 1.612mmol	0.258g; 8.06 mmol (5equiv)	Et_3N, 0.213g; 2.104mmol	Et_2O, 0°C., 1h	0.435g	89%[a]
Et	0.800 g; 2.590mmol	0.597g; 12.95 mmol (5equiv)	Et_3N, 0.340g; 3.367mmol	Et_2O, 0°C., 1h	0.746g	90%[b]

[a] Yield of the product without purification

[b] Yield of the product purified via column chromatography (SiO_2/ Et_2O: petroleum ether 1:1) R_f=0,71

***Rac O*-Methyl Hexadecanesulfinates (11)**

^{1}H NMR (200 MHz, $CDCl_3$): *δ* 0.84-0.92 (m, 3H, CH_3), 1.20-1.52 (m, 26H); 1.61-1.76 (m, 2H); 2.41-2.81 (m, 2H CH_2-S); 3.77 (s, 3H, OCH_3);

***Rac*- *O*-Ethyl Hexadecanesulfinate (12)**

^{1}H NMR (200 MHz, $CDCl_3$): *δ* 0.83-0.90 (m, 3H, CH_3), 1.20-1.51 (m, 26H); 1.34 (t, J=7.06Hz, 3H, $CH_{3(Et)}$); 1.60-1.71 (m, 2H); 2.63-2.80 (m, 2H); 4.00-4.18 (m, 2H).

^{13}C NMR (50MHz, $CDCl_3$) δ 14.09; 15.86; 21.29; 22.65; 28.72; 29.19; 29.30; 29.32; 29.49; 29.57; 29.61; 29.64; 31.88; 57.23; 64.63.

MS(CI) isobutane, m/z: 273 [$C_{16}H_{33}S(O)$]; 319 [M+1].

HRMS(FAB) m/z calcld.dla $C_{18}H_{39}O_2S$: 319.2659; found: 319.2671.

1.1.12 *Rac-n*-Hexadecyl 2-(3'-Thienyl)ethyl Sulfoxide(14)

A round-bottom flask equipped with a reflux condenser terminated with a calcium chloride tube, was charged with magnesium turnings, an iodine crystal, and dried over sodium and freshly distilled diethyl ether. To the stirred solution, 2-(3'-thienyl)ethyl bromide was slowly added dropwise and the mixture was heated for 2h. After this time, a Grignard solution was transferred into a solution of *O*-alkyl *n*-hexadecanesulfinate in diethyl ether at 0 ° C under argon. The mixture was stirred for a further 6 h at 0 ° C and then the ice bath was removed and the mixture was stirred for 16 h. The mixture was hydrolyzed with 5% sulfuric acid aqueous solution and was then extracted in a separating funnel with 3 portions of 40 mL of dichloromethane. The combined organic layers were washed with a 5% aqueous solution of potassium carbonate, water, dried over magnesium sulfate and the solvent was evaporated. The crude product was purified by chromatography with Et_2O: hexane (1: 1).

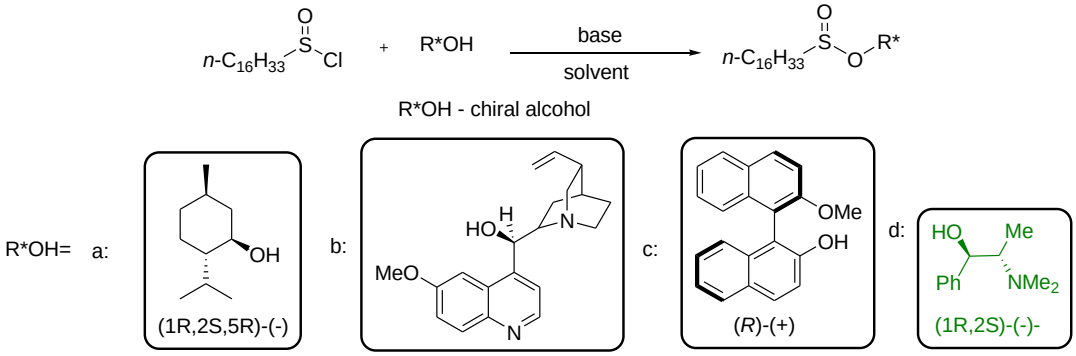
Table 3 The preparation of *rac-n*-hexadecyl 2-(3'-thienyl)ethyl sulfoxide(**14**)

R	Reagents			Conditions	Yield	
	$C_{16}H_{33}$-S(O)OR	2-(3'-thienyl)ethyl bromide	Mg			
Me	0.392g; 1.287mmol	0.750g; 3.925mmol (3.05equiv)	0.094g; 3.925mmol	Et_2O, 0°C., 24h	0.349g	70%[a]
Et	1.274 g; 4.0 mmol	1.535g; 8.0mmol (2equiv)	0.192g; 8.0mmol	Et_2O, 0°C., 24h	1.274g	83%[b]

m.p.=80-82°C, R_f (SiO_2/ Et_2O: petroleum ether 1:1) =0.064

^{1}H NMR (200 MHz, $CDCl_3$): *δ* 0.82-0.88 (m, 3H, CH_3); 1.23-1.49 (m, 26H); 1.66-1.77 (m, 2H); 2.51-2.77 (m, 2H, CH_2-S); 2.84-2.93 (m, 2H, CH_2-S); 3.08-3.15 (m, 2H, $C\underline{H_2}$); 6.95-6.97 (m, 1H, Thioph); 7.03-7.04 (m, 1H, Thioph); 7.24-7.29 (m, 1H, Thioph). ^{13}C NMR (150MHz, $CDCl_3$) δ 14.30; 22.66; 22.72; 23.41; 28.90; 29.23; 29.34; 29.57; 29.64; 29.69; 29.72; 31.96; 52.62; 53.01; 121.60; 126.22; 127.89; 139.07. MS(CI) isobutane, m/z: 111, 369 [$C_{16}H_{33}$-S-CH_2CH_2-Thioph]; 385 [M+1]. Elemental anal: calcld for $C_{22}H_{40}OS_2$ (%) : C, 68.69; H, 10.48; S, 16.67; found: C, 68.57; H, 10.62; S, 16.54. IR (KBr/ cm^{-1}) 3088; 2955; 2918; 2848; 1463; 1016 (S=O); 768; 720.

1.1.13 Synthesis of diastereomeric *n*-hexadecanesulfinic acid esters derived from optically active aliphatic and aromatic alcohols (R*OH)



General procedure:

To a stirred solution of the alcohol in an appropriate solvent under argon atmosphere, the base was added. A solution of *n*-hexadecylsulfinyl chloride dissolved in the same solvent was then added dropwise to the solution. The progress of the reaction was monitored by thin layer TLC. The crude product was isolated by extracting the reaction mixture with 5% K_2CO_3 aqueous solution, and water, in the case of sulfinates formed by condensation with quinine and *N*-methylephedrine. In the other cases, the reaction mixture was extracted with 5% H_2SO_4 solution, then 5% K_2CO_3 solution, and water. After the extractions, the organic layers were separated and dried over magnesium sulfate. The drying agent was filtered off and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography, on silica gel. The diastereomeric mixture of the *O*- *N*-methylephedrine sulfinate derivative was separated by flash chromatography on silica gel using ethyl acetate: hexane 8: 2 as an eluent.

Table 4 The condensations of *n*-hexadecylsulfinyl chloride with chiral alcohols

No	Reagents			Conditions	Yield **15a-d**	
	$C_{16}H_{33}$-S(O)Cl	R*OH	Base			
a	0.500g; 1.62mmol	(-)-Menthol, 0.253g; 1.62mmol	Et_3N, 0.246g; 2.43mmol	Et_2O, -30°C, 4h	0.371g	53%
b	1.000g; 3.233mmol	Quinine 1.049g; 3.233mmol	Et_3N, 0.654g; 6.466mmol	CH_2Cl_2, 0°C, 24h	1.025g	53%
c	0.123g; 0.399mmol (1.2 equiv)	(*R*)-(+)-2'-methoxy-2-hydroxy-1,1'-binaphthyl 0.100g, 0.333mmol	NaH (50%), 0.017g, 0.355mmol (1.05equiv)	NaH, Et_2O, 0°C, 1h	0.174g	92%
d	0.5g; 1.618mmol	*N*-methylephedrine 0.290g, 1.618mmol	NaH, 0.085g, 1.771mmol (1.1equiv)	NaH, Et_2O -30°C, 1h	0.716g	98%

1.1.13.1 *O*-(-)-Menthyl *n*-Hexadecanesulfinate (15a)

dr= 1:1; R_f (SiO_2/ Et_2O:hexane 1:2) =0.43

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.81-1.14 (m, 15H); 1.24-1.39 (m, 28H); 1.64-1.71 (m, 4H); 2.04-2.22 (m, 2H); 2.61-2.77 (m, 2H); 3.88-4.01 (dt, J=4.5Hz, 10.65, 1H). ^{13}C NMR (50MHz, $CDCl_3$): δ 14.07; 15.65; 20.76; 21.43; 21.87; 22.00' 22.65; 23.08; 23.24; 25.38; 25.55; 28.76; 29.21; 29.32; 29.51; 29.64; 31.57; 31.75; 31.89; 33.93; 34.05;

42.25; 43.60; 47.93; 58.30; 57.55; 57.76; 79.39; 82.53. MS(CI) isobutane, m/z: 139 [1-(2-*i*Pr-5-Me-Cyklohxsyl)]; 291 [$C_{16}H_{33}$-S(O)-O]; 429 [M+1]. Elem. Anal.: calcld for $C_{26}H_{52}O_2S$ (%) : C, 72.83; H, 12.22; S, 7.48; found: C, 72.76; H, 11.98; S, 7.52.

1.1.13.2 *O*-Quininyl *n*-Hexadecanesulfinate (15b)

dr =6:4

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.83-0.89 (m, 3H, $CH_{3(Hexadec)}$); 1.24 (m, 28H, $CH_{2(Hexadec)}$); 1.47-1.67 (m, 3H); 1.86 (bs, 2H); 2.25 (bs, 1H); 2.56-2.78 (m, 4H); 2.94-3.08 (m, 2H); 3.36-3.69 (m, 1H); 3.94 (s, 3H, OCH_3); 4.93-5.02 (m, 2H); 5.69-5.89 (m,2H); 7.30-7.49 (m, 3H, Ar); 8.03 (d, J=9.35 Hz, 1H, Ar); 8.74 (d, J=4.48 Hz, 1H, Ar). ^{13}C NMR (50MHz, $CDCl_3$): δ 14.16; 18.51; 21.02; 21.29; 22.72; 27.54; 27.60; 27.76; 28.68; 28.72; 29.25; 29.21; 29.29; 29.40; 29.53; 29.62; 29.68; 29.71; 31.95; 39.78; 42.65; 55.71; 56.67; 56.78; 57.62; 57.65; 60.11; 101.33; 114.43; 114.61; 119.96; 121.69; 121.96; 126.42; 132.03; 132.07; 141.64; 141.84; 143.67; 144.76; 147.41; 147.48; 157.98. MS(CI) isobutane, m/z: 136 ; 291; 309; 325; 597 [M+1]. Elem. Anal.: calcld for $C_{36}H_{56}N_2O_3S$ (%) : C, 72.44; H, 9.46; N, 4.69; S, 5.37; found: C, 72.49; H, 9.64; N, 4.65; S, 5.46.

1.1.13.3 (*R*)-[*O*-(2-Methoxy-1,1'-binaphthalen-2'-yl) Hexadecanesulfinate] (15c)

dr=6:4; R_f (SiO_2/ Et_2O:hexane 1:1) =0.45

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.85-0.91 (m, 3H, CH_3); 1.26-1.28 (m, 26H, CH_2); 1.67-1.77 (m, 2H); 2.26-2.30 (m, 2H); 3.75-3.79 (2xs, 3H, OCH_3); 7.02+7.12 (2xd, J=8.4 Hz, 1H); 7.19-7.51 (m, 6H); 7.58-7.68 (m, 1H); 7.83-8.02 (m, 4H). MS(CI) isobutane, m/z: 257; 483; 515; 557; 571.

1.1.13.4 ***O*- *N*- Methylephedrine *n*-Hexadecanesulfinate (15d)**

I diastereoisomer:(***R***$_S$) *de*=86%; R_f (SiO_2/ ethyl acetate) =0.25

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.83-0.89 (m, 3H, CH_3); 1.00 (d, J=6.69 Hz, 3H, CH_3); 1.24 (m, 26H); 1.60-1.75 (m, 2H); 2.28 (s, 6H, $N(CH_3)_2$); 2.69-2.85 (m, 3H,); 5.32 (d, J=4.62Hz, 1H, CH-O); 7.24-7.33 (m, 5H, Ph).

II diastereoisomer: (***S***$_S$) *de*=96.6%; R_f (SiO_2/ ethyl acetate) =0.125

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.84-0.91 (m, 3H, CH_3); 1.14 (d, J=6.57 Hz, 3H, CH_3); 1.25 (m, 26H); 1.57-1.68 (m, 2H); 2.29 (s, 6H, $N(CH_3)_2$); 2.74 (dt, J=7.12; 2.90 Hz, 2H, CH_2-S); 2.90-3.03 (m, 1H, CH); 5.19 (d, J=6.04Hz, 1H, CH-O); 7.24-7.37 (m, 5H, Ph). MS(CI) isobutane, m/z: 162, 452 [M+1]

1.1.14 (*S*)-(+)-*n*-Hexadecyl 2-(3'-Thienyl)ethyl Sulfoxide (14)

In a round bottom flask equipped with a reflux condenser protected with a calcium chloride tube, magnesium turnings (0.021 g, 0.8632 mmol) were placed, an iodine crystal was added, and then dried over sodium and freshly distilled diethyl ether (5 mL). 2-(3'-Thienyl)ethyl bromide (0.165g, 0.8632mmol, 2.5 equiv) was slowly added dropwise to the stirring solution and heated for 2h. After this time, a cooled to room temperature Grignard solution was added dropwise to a solution of *O*-*N*-methylephedrine (**S**)-(-)-*n*-hexadecanesulfinate (0.156 g, 0.3453 mmol) in diethyl ether (5 mL) at 0 ° C under argon atmosphere. The mixture was stirred for 6 h at 0 ° C and then the ice bath was removed and the mixture was stirred for 16 h. 5%-Sulfuric acid solution was added and methylene chloride was added to the hydrolyzed mixture. It was transferred to a separating funnel and extracted. The aqueous layer was washed with two more 20 mL portions of dichloromethane, then the combined organic layers were washed with a 5% aqueous solution of potassium carbonate, water, dried over magnesium sulfate, filtrated and the solvent was evaporated. The crude product was purified by chromatography with Et_2O: hexane (1: 1) to give pure sulfoxide in 77% yield.

m.p. = 77-80°C. $[\alpha]_D$= +8.35 (1.27; CH_2Cl_2). HPLC (Chiralpak AS; hexane:isopropanol 7:3), flow rate 0.67 ml/min. T_1= 20.73 min. Area=351305 (1.2%) T_2=23.78 min. Area =27809460 (98.8%).

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.85-0.91 (m, 3H, CH_3); 1.26 (m, 26H); 1.65-1.80 (m, 2H, CH_2); 2.55-2.83 (m, 2H, CH_2-S); 2.88-2.99 (m, 2H, CH_2-S); 3.12-3.19 (m, 2H, CH_2-Thioph); 6.99-7.00 (m, 1H, Thioph); 7.08 (m, 1H, Thioph); 7.28-7.32 (m, 2H, Thioph). MS(CI) isobutane, m/z: 111, 369 [$C_{16}H_{33}$-S-CH_2CH_2-Thioph]; 385 [M+1].

1.1.15 *Rac-p*-Chlorophenylsulfinyl Chloride (16)

4-Chlorothiophenol (14.46 g; 0.1 mol) placed in a three-necked flask equipped with a thermometer, a calcium chloride tube with a gas outlet, and an adapter (gas inlet) connected with 3 gas washing bottles in series (while a middle one contains conc. H_2SO_4) was dissolved in 100 mL of methylene chloride. The solution was cooled to -5 ° C and glacial acetic acid (3.65ml, 0.1mol) was added. Potassium permanganate was placed in a second flask connected to the gas washing bottles and equipped with a dropping funnel with venting. Concentrated HCl was added to the dropping funnel and chlorine evolution started. As chlorine was bubbled through the reaction mixture, the solution turned from light yellow to orange, and then the solution turned a pale-yellow color, indicating that the reaction was complete. The reaction flask was then connected through a trap cooled in an acetone-dry ice bath and a safety trap to a vacuum pump and excess chlorine and acetyl chloride were removed under reduced pressure. The product was obtained after evaporating the solvent in vacuo, as a light-yellow solid in 99% yield (19.4 g).

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.58 (d, 2H, J=8.35 Hz, 2H, Ar); 7.82 (d, J=8.40 Hz, 2H, Ar). ^{13}C NMR (50MHz, $CDCl_3$): δ 125.28 (C_{meta}(Ar)); 129.81 (C_{ortho}(Ar)); 140.14; 146.93. MS(CI) isobutane, m/z: 159 [Cl-C_6H_4S(O)] 205, 319 [Cl-C_6H_4S(O)x2 +1]. Elem. Anal.: calcld for $C_6H_4Cl_2OS$ (%) : C, 36.94; H, 2.07; S, 16.44; found: C, 37.32; H, 2.41; S, 16.02.

1.1.16 (*S*)-(-)- [*O*-(1*R*,2*S*,5*R*)-Menthyl *p*-Chlorobenzenesulfinate] (17)

To a solution of (-)-menthol (17.3 g, 88.66 mmol) in diethyl ether (50 ml) cooled to -78 ° C, triethylamine (10.76 g, 106.39 mmol) was added dropwise. A solution of *p*-chlorophenylsulfinyl chloride in diethyl ether (50ml) was then added dropwise to the solution. The reaction occurred under argon atmosphere and the progress of the reaction was monitored by TLC. The mixture was stirred for 24h with simultaneous warming to room temperature. After the reaction was complete it was hydrolyzed with 5% H_2SO_4 and extracted. The separated organic layer was further washed with 5% K_2CO_3 solution and water, dried over anhydrous magnesium sulfate. filtered and concentrated in vacuo. The product was obtained as an oil in 97%. yield. The crude product was a mixture of diastereoisomers (R_S: S_S) with *dr* = 3.8: 6.2 (determined by ^{1}H NMR analysis). The pure levorotatory diastereoisomer was isolated by crystallization from a solution of the crude product in acetone with the addition of few drops of concentrated HCl.

Physical and spectral are in accordance with the literature data[4, 5]

$[\alpha]_D$=-183.4 (1.65; acetone)

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.72 (d, J=6.94Hz, 3H);0.87 (d, J=7.09 Hz, 3H); 0.96 (d; J=6.4 Hz, 3H); 1.07-1.43 (m, 3H); 1.49 (m, 1H); 1.69 (d, J=11.21Hz, 2H); 2.03-2.17 (m, 1H); 2.27 (d, J=11.78Hz, 1H); 4.13 (dt; J=10.69; 4.44Hz, 1H); 7.50 (d, J=8.51Hz, 2H,Ar); 7.65 (d, J=8.51Hz, 2H, Ar). ^{13}C NMR (50MHz, $CDCl_3$): δ 15.47; 20.79; 22.03; 23.09; 25.23; 31.71; 33.90; 42.87; 47.81; 80.65; 126. 53 (C_{Ar}x2); 129.23 (C_{Ar}x2); 138.18; 144.50.

1.1.17 (*R*)-(+)-*p*-Chlorophenyl 2-(3'-Thienyl)ethyl-Sulfoxide (18)

A round bottom flask equipped with a reflux condenser protected with a calcium chloride tube, an iodine crystal was charged with magnesium turnings 0.191 g (7.94 mmol, 2.5equiv) followed by dried over sodium and freshly distilled diethyl ether (8 mL). 2-(3'-Thienyl)ethyl bromide (1.517g, 7.94mmol, 2.5equiv) was slowly added dropwise to the stirring solution and the reaction mixture was heated for 2h. -After this time, the Grignard reagent cooled to room temperature was added to a solution of *O*-menthyl (-) - *p*-chlorophenylsulfinate (1g, 3.176mmol, 1equiv) $[\alpha]_D$ = -183.4 (acetone) in diethyl ether (8mL) at 0 ° C. The mixture was stirred for 6 h at 0 °

C and then the ice bath was removed and the mixture was stirred for 16 h. It was hydrolyzed with 5% sulfuric acid solution, then was transferred to a separating funnel and extracted. The separated aqueous fraction was then extracted with 3 more 10 mL portions of dichloromethane, the combined organic layers were washed with a 5% aqueous solution of potassium carbonate, water, dried over magnesium sulfate filtrated and concentrated in vacuo. The residue was purified by chromatography eluting with Et_2O: hexane (1: 1) to give 0.809 g (94%) of the pure product.

$[\alpha]_D$= +109.9 (1,01; CH_2Cl_2). R_f (SiO_2/ Et_2O:hexane (1:1)) =0.125. m.p.= 53-55°C

^{1}H NMR (200 MHz, $CDCl_3$): δ 2.84-3.22 (m, 4H, CH_2CH_2); 6.91 (d, J=4.94 Hz, 1H, Thioph); 7.01 (m, 1H, Thioph); 7.26-7.30 (m, 1H, Thioph); 7.48-7.60 (m, 4H, Ph). ^{13}C NMR (50MHz, $CDCl_3$): δ 22.57 ($\underline{C}H_2$-Thioph); 57.46 ($\underline{C}H_2$-S); 121.55 ($C_{2\text{-Thioph}}$); 125.35 (C_{Ph}x2); 126.19 ($C_{5\text{-Thioph}}$); 127.67 ($C_{4\text{-Thioph}}$); 129.50 (C_{Ph}x2); 137.16; 138.38; 141.99. Elem. Anal.: calcld for $C_{12}H_{11}ClOS_2$ (%) : C, 53.22; H, 4.09; S, 23.68; found: C, 53.34; H, 4.02; S, 23.35.

1.1.18 (*R*)-(-)-*n*-Hexadecyl 2-(3'-Thienyl)ethyl-Sulfoxide (14)

A solution of hexadecylmagnesium bromide in THF (5mL) generated *in situ* from hexadecyl bromide (0.750g, 2.446mmol, 5equiv) and magnesium (0.059g; 2.446mmol, 5equiv) was added dropwise to the solution of (*R*)-(+)-*p*-chlorophenyl 2-(3'-thienyl)ethyl sulfoxide (0.133g, 0.491mmol) in diethyl ether (5 mL) cooled to 0 °C. The reaction mixture was stirred at this temperature for 6h and then warmed to room temperature. The progress of the reaction was monitored by thin-layer TLC. After 48 h, 5% H_2SO_4 and diethyl ether (20 mL) were added to the reaction mixture and the mixture was extracted. The separated organic layer was washed with 5% K_2CO_3 (20 mL) and water (10 mL), and then dried over magnesium sulfate, filtered, concentrated in vacuo. The crude product was purified by column chromatography (SiO_2 /Et_2O: hexane 1: 1) to give 0.140 g (74%) of product as a white solid.

$[\alpha]_D$= -8,5 (1,13; CH_2Cl_2). m.p= 81-83°C.; *ee*=98,6%. HPLC (Chiralpak AS; hexane:isopropanol 7:3), T_1= 21.41 min. Area=36679432 (99.3%) T_2=25.13min. Area =264293 (0.7%).

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.85-0.91 (m, 3H, CH_3); 1.25-1.43 (m, 26H); 1.69-1.76 (m, 2H); 2.56-2.79 (m, 2H, CH_2-S); 2.88-2.98 (m, 2H, CH_2-S); 3.12-3.19 (m, 2H, $C\underline{H}_2$); 6.98 (d, J=4.52 Hz, 1H, Thioph); 7.08 (m, 1H, Thioph); 7.28-7.32 (m, 1H, Thioph). MS(CI) izobutan, m/z: 111, 369 [$C_{16}H_{33}$-S-CH_2CH_2-Thioph]; 385 [M+1]. IR (KBr) vmax/cm^{-1} = 3091; 2954; 2917; 2847; 1464; 1017 (S=O); 779; 751; 723.

1.1.19 (*R*)- 2-(3'-Thienyl)ethyl *p*-Tolyl Sulfoximine, (*R*)-(-)-19,

Optically active 2-(3'-thienyl)ethyl-*p*-tolyl sulfoxide (1.78 g, 7.12 mmol) was dissolved in 6 mL of methylene chloride. A solution of *O*-mesitylenesulfonylhydroxylamine (2.295g, 10.66mmol) in methylene chloride (6 mL) was added dropwise to this solution at room temperature and stirred for 24h. Upon this time, the reaction mixture was poured into a cold 10% NaOH solution and stirred for 10 min. The solution was extracted in a separatory funnel and the layers were separated. The alkaline phase was extracted with 20 ml of methylene chloride (three times). The combined organic layers were extracted twice with 10% HCl solution (per 20 mL). The combined aqueous acidic fractions were neutralized with solid K_2CO_3. The suspension was then transferred to a separating funnel and extracted with methylene chloride (3x20 mL). The organic fractions were combined and dried over anhydrous MgSO4. After the desiccant was filtered off, the solvent was evaporated to give the residue as a white solid. The sulfoximine (1.5 g, 80%), $[\alpha]_D$ = -14.4 (1.2; CH_2Cl_2) was isolated after purification by column chromatography on silica gel using diethyl ether as an eluent.

m.p.= 84-87°C

^{1}H NMR (200 MHz, $CDCl_3$): δ 2.45 (s, 3H, CH_3); 2.69 (bs, 1H, NH); 3.00-3.11 (m, 2H, $C\underline{H}_2$-Thioph); 3.36-3.45 (m , 2H, $C\underline{H}_2$-S); 6.83-6.86 (m, 1H, Thioph); 6.93 (m, 1H, Thioph); 7.21-7.25(m, 1H, Thioph); 7.34 (d, J=8.11 Hz, 2H, Ph-H_{meta}); 7.86 (d, J=8.23 Hz, 2H, Ph-H_{orto})

^{13}C NMR (50MHz, $CDCl_3$) δ 21.49 ($\underline{C}H_3$); 24.00 ($\underline{C}H_2$-Thioph); 57.90 ($\underline{C}H_2$-S); 121.29 ($\underline{C}_{2\text{-Thioph}}$); 126.12 ($\underline{C}_{5\text{-Thioph}}$); 127.56 ($\underline{C}_{4\text{-Thioph}}$); 128.41 (2x$\underline{C}$ $_{\text{ortho Ph}}$); 129.84 (2x$\underline{C}$ $_{\text{meta Ph}}$); 137.78 ($C_{\text{ipso-Ph}}$); 138.77 ($C_{\text{para-Ph}}$); 144.03 ($\underline{C}_{3\text{-Thioph}}$).

MS(CI) isobutane, m/z: 110 [Thioph-3-CH_2CH_2]; 266 [M+1]; 376 [M+ 110+1].

HRMS(EI) m/z calcld.dla $C_{13}H_{15}NOS2$: 265.05935, found.:265.059509.

1.1.20 Tamura Reagent[6]

To a solution of *O*-(2-mesitylenesulfonyl)acethydroxamic acid ethyl ester (7.5 g, 0.026 mol) in 5 mL of dioxane cooled to 0 °C, 70% $HClO_4$ (3 ml, 0.035 mol) was slowly added dropwise. The reaction mixture was stirred at this temperature for 1 h. Then it was poured into 300 mL of ice water. The resulting white precipitate was filtered off and dissolved in diethyl ether (30mL). The solution was extracted with water several times, 25 mL each. The organic layer was dried over K_2CO_3 (only 0.5 min). The potassium carbonate was quickly filtered off under reduced pressure and the filtrate was poured into cold pentane (300 mL). -White needles formed were collected and dried for a few minutes in vacuo. MSH was isolated in 71%. CAUTION The substance may explode. Store only in plastic containers in the freezer (-18°C) and collect with plastic spatula.

^{1}H NMR (200 MHz, $CDCl_3$): δ_H=2.32 (s, 3H, CH_3Ar), 2.64 (s, 6H, s, 2xCH_3Ar), 7.00 (bs, 2H, NH_2), 7.00 (s, 2H, Ar-H). Spectral data matches with the data reported in [7].

1.1.21 *n*-Hexadecyl 2-(3'-Thienyl)ethyl-Sulfoximine (20)

To a solution of *O*-mesitylenesulfonylhydroxylamine (1.7 eguiv) in methylene chloride, n-hexadecyl 2-(3'-thienyl)ethyl sulfoxide in methylene chloride was added dropwise at room temperature and the mixture was stirred for 48h. After this time, the reaction mixture was poured into a cold 10% NaOH solution and stirred for 10 min. The solution was transferred into a separatory funnel, extracted and the separated aqueous phase was washed with methylene chloride (three times). The combined organic layers were extracted with two portions of 10% hydrochloric acid. The combined aqueous acidic phases were neutralized with solid K_2CO_3. The aqueous suspension was then transferred to a separating funnel and extracted with three portions of methylene chloride. The organic layers were combined, dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to give the product as a white solid. The product was purified by column chromatography on silica gel using chloroform and methanol (9: 1) as eluent.

Table 5 Imination of *n*-hexadecyl 2-(3'-thienyl)ethyl sulfoxide

***Rac*-*n*-hexadecyl 2-(3'-thienyl)ethyl sulfoximine (20)**					
No	Reagents R-S(O)-R^1 R=$C_{16}H_{33}$; R^1=3-Thioph-CH_2CH_2	MSH	Conditions	Yield	
1	0.440g; 1.44mmol	0.422g; 1.94mmol	CH_2Cl_2, rt., 48h	0.356g	78%
(*R*)-(-)- *n*-hexadecyl 2-(3'-thienyl)ethyl sulfoximine (*R*)-(20)					
2	0.2g; 0.52mmol	0.190g, 0.88mmol	CH_2Cl_2, rt., 48h	0.146g	71%

***Rac-n*-Hexadecyl 2-(3'-Thienyl)ethyl Sulfoximine (20)**

R_f =(SiO_2/$CHCl_3$:MeOH 9:1)=0.18. m.p.=68-69°C

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, J=6.75 Hz, 3H, CH_3); 1.24-1.30 (m, 24H); 1.34-1.38 (m, 2H); 1.76-1.82 (m, 2H); 2.45 (bs, 1H, NH); 2.90-2.94 (m, 2H, CH_2); 3.18-3.20 (m, 2H, CH_2); 3.26-3.30 (m, 2H, CH_2); 6.96 (dd, J=1.10; 4.95 Hz, 1H, Thioph); 7.06 (d, J=1.95 Hz, 1H, Thioph); 7.29-7.30 (m, 1H, Thioph). ^{13}C NMR (125MHz, $CDCl_3$): δ 14.07 ($\underline{C}H_3$); 22.40; 22.62; 23.32; 28.37; 29.02; 29.29; 29.43; 29.51; 29.58; 29.61; 31.85; 55.12; 55.16; 121.71; 126.44; 127.58; 137.86 (C_3-Thioph). MS (EI) m/z=110, [CH_2CH_2-3-Thioph-1]; 334; 399 [M]. Elem. Anal.: calcld for $C_{22}H_{41}NOS_2$ (%) : C, 66.11; H, 10.34; N, 3.50; S, 16.04; found: C, 65.97; H, 10.30; N, 3.51; S, 16.11. IR (KBr) vmax/cm^{-1} = 3302; 3072; 3052; 2953; 2915; 2847; 1470; 1198; 1122; 1099; 962; 783; 728.

(*R*)-(-)- Hexadecyl 2-(3'-Thienyl)ethyl Sulfoximine ((*R*)-20)

$[\alpha]_D$= -2.47 (0.89; CH_2Cl_2). R_f =(SiO_2/ethyl acetate: petroleum ether 2:1)=0.44. m.p.=71-73°C

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.87 (t, J=6.75 Hz, 3H, CH_3); 1.25 (m, 26H); 1.73-1.88 (m, 2H); 2.27 (bs, 1H, NH); 2.91-2.99 (m, 2H, CH_2); 3.16-3.24 (m, 2H, CH_2); 3.28-3.35 (m, 2H, CH_2); 6.98 (dd, J=1.10; 4.99 Hz, 1H, Thioph); 7.08 (m, 1H, Thioph); 7.29-7.34 (m, 1H, Thioph). ^{13}C NMR (50MHz, $CDCl_3$): δ 14.11 ($\underline{C}H_3$); 22.41; 22.67; 23.34; 28.42; 29.08; 29.26; 29.32; 29.48; 29.69; 31.89; 55.16; 121.78; 126.51; 127.62; 137.86 (C_3-Thioph). MS(CI) m/z=110, 400 [M+1]; 510 [M+1+110]. HRMS (EI) m/z calcld for $C_{22}H_{41}NOS_2$ obl.: 399.26138; found: 399.26296.

1.1.22 *N*-{[5-(5'-Hexyl-2,2'-bithienyl)]-*n*-hexadecyl-2-(3'-thienyl)ethyl} Sulfoximine (43)

n-Hexadecyl 2-(3'-thienyl)ethyl sulfoximine (0.144g, 0.359mmol), 5-bromo-5'-hexyl-2,2'-bitiophene (0.118g, 0.359mmol) were placed in a Schlenk flask under argon atmosphere. DMEDA (6.33 mg, 0.2 equiv), CuI (0.1 equiv), K_2CO_3 (0.198 g 4 equiv) and 4ml of freshly distilled dry toluene were added. The heterogeneous mixture was heated at 110 ° C for 18h. After this time, the solution was cooled to room temperature and 5mL of HCl (1M) was added. The mixture was extracted and the separated aqueous phase was washed 3x more with methylene chloride (10 ml each). The combined organic layers were dried ($MgSO_4$), filtered and concentrated in vacuo. The pure product, as an orange oil, was isolated by chromatography (SiO_2/ ethyl acetate: hexane 2: 8) in 18% yield (42 mg).

^{1}H NMR (600 MHz, $CDCl_3$): δ 0.87-0.89 (m, 6H 2xCH_3); 1.24-1.43 (m, 32H; 15xCH_2); 1.63-1.68 (m, 2H, CH_2); 1.74-1.81 (m, 2H, CH_2); 2.76 (t, J=7.56 Hz, 2H, CH_2); 2.98-3.10 (m, 2H, CH_2); 3.21 (t, J=7.86 Hz, 2H, CH_2); 3.40-3.45 (m, 1H; CH_2); 3.49-3.54 (m, 1H; CH_2); 6.37 (d, J=3.72 Hz, 1H; Thioph); 6.61 (d, J=3.36 Hz, 1H; Thioph); 6.78 (d, J=3.66 Hz, 1H; Thioph); 6.82 (d, J=3.48 Hz, 1H; Thioph); 6.97 (d, J=4.80 Hz, 1H; Thioph); 7.08 (m, 1H; Thioph); 7.31-7.32 (m, 1H; Thioph). ^{13}C NMR (150MHz, $CDCl_3$): δ 14.08; 14.12; 22.57; 22.68; 22.83; 23.91; 28.29; 28.73; 28.69; 29.23; 29.35; 29.46; 29.57; 29.64; 29.68; 30.14; 31.57; 31.91; 51.47; 52.05; 116.17; 121.64; 121.67; 122.07; 124.44; 126.66; 127.59; 128.71; 135.72; 137.49; 143.88; 147.01. MS(EI) m/z: 111; (CH2CH2-Thioph); 264 [C_6H_{13}-2,2'-bithiophen-N+1]; 647 [M-1]. HRMS (EI) m/z obl.dla $C_{35}H_{57}NOS_4$: 647.3320; zbadano: 647.3323.

1.1.23 *O*-2-(3'-Thienyl)ethyl Alkanesulfinates

General procedure:

Triethylamine was added dropwise to a solution of 3-thiopheneethanol in an appropriate solvent, followed by an equimolar amount of sulfinyl chloride. The reaction proceeded under argon at the given temperature and the progress of the reaction was monitored by TLC (Et_2O/petroleum ether 4: 6 or 1:1). Upon the reaction was complete, an aqueous solution of 5% sulfuric acid was added to the reaction mixture, and the organic phase (Et_2O or if THF, a portion of Et_2O should be added) was extracted with it. The separated organic layer was

extracted with two more portions of 5% sulfuric acid aqueous solution, one portion of 5% aqueous K_2CO_3, and water. After phase separation, the organic layer was dried over magnesium sulfate, the drying agent was filtered off and the solvent was evaporated. The crude product was purified by column chromatography on silica gel eluted with Et_2O/petroleum ether 4: 6 or 1:1.

Table 6 The preparation of sulfinates

R	Reagents			Conditions	Yield	
	R-S(O)Cl	3-thiopheneethanol	amine			
tert-Bu	1.41 g; 10mmol	1.28g; 10 mmol	Et_3N, 1.38mL; 10 mmol	Et_2O, rt., 3d	1.39 g	60%
3-Cl-Ad	3.95 g, 15.6mmol	2 g; 15.6 mmol	Et_3N, 2.16mL, 15.6 mmol	THF, rt., 5d	2.4 g	50%
n-$C_{16}H_{33}$	0,5g, 1,618mmol	0,207g, 1,618mmol	Et_3N, 0,213g, 2,103mmol	Et_2O, 0°C for 8h, 40h at rt a	0,568 g	87%

1.1.23.1 *rac*- *O*-2-(3'-Thienyl)ethyl *n*-Hexadecanesulfinate (25)

m.p= 39-41°C

R_f(SiO_2/ Et_2O: petroleum ether 1:1) = 0.25.

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.85-0.91 (m, 3H, CH_3); 1.22-1.52 (m, 25H), 1.57-1.72 (m, 3H); 2.66-2.76 (m, 2H, CH_2-Thioph); 3.05 (t, J=6.97 Hz, 2H, $CH_{2(Hexad)}$-S); 4.17-4.40 (m, 2H, CH_2-O-S); 6.97 (d, J=4.72 Hz, 1H, Thioph); 7.05 (m, 1H, Thioph); 7.27-7.30 (m, 1H, Thioph).

MS(FAB) m/z: 111 [CH_2CH_2-Thioph] 401 [M+1].

MS(CI) isobutane, m/z: 111 [CH_2CH_2-Thioph] 401 [M+1], 511 [M+111].

Elemental analysis: calcld for $C_{22}H_{40}O_2S_2$ (%) : C, 65.95; H, 10.06; S, 16.01; found: C, 65.85; H, 9.94; S, 15.81.

1.1.23.2 *rac*- *O*-2-(3'-Thienyl)ethyl 3-Chloroadamantanesulfinate (26)

$\eta^{20°C}$=1.5744

R_f (SiO_2/Et_2O:petroleum ether 4:6) =0.125

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.63-1.72 (m, 6H, 3x$C\underline{H}_2$(Ad)); 2.09-2.14 (m, 3x$C\underline{H}_2$(Ad)); 2.33 (bs, 2H, Ad); 3.05 (t, J=6.87 Hz, 2H, $C\underline{H}_2$-Thioph); 4.11-4.23 (m, 1H; $C\underline{H}_2$-O-S); 4.29-4.41(m, 1H; $C\underline{H}_2$-O-S); 6.96 (d, J=4.88 Hz, 1H, Thioph); 7.04 (d, J=1.30 Hz, 1H, Thioph); 7.28-7.30 (m, 1H, Thioph)

^{13}C NMR (50MHz, $CDCl_3$) δ 30.96; 31.08; 31.92; 32.45; 34.39; 43.17; 46.58; 61.96; 66.87; 69.49; 121.90; 125.74; 128.08; 137.23.

MS(CI) isobutane, m/z: 111; 311; 345 [M+1]; 455 [M+ 111].

Elemental analysis: calcld for $C_{16}H_{21}ClO_2S_2$ (%) : C, 55.71; H, 6.14; Cl, 10.28; found: C, 56.28; H, 6.29; Cl, 9.40.

1.1.23.3 *rac*- *O*-2-(3'-Thienyl)ethyl *tert*-Butanosulfinate (27)

$\eta^{20°C}$=1.5214

R_f (SiO_2/Et_2O:petroleum ether 4:6) =0.24

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.16 (s, 9H, $C(CH_3)_3$); 3.05 (t, J=6.88 Hz, $C\underline{H}_2$-Thioph); 4.11-4.23 (m, 1H; $C\underline{H}_2$-O-S); 4.28-4.40 (m, 1H; $C\underline{H}_2$-O-S); 6.98 (d, J=4.84 Hz, 1H, Thioph); 7.05 (d, J=2.23 Hz, 1H, Thioph); 7.25-7.29 (m, 1H, Thioph).

^{13}C NMR (50MHz, $CDCl_3$) δ 21.50 ($C(\underline{C}H_3)_3$); 31.01 ($\underline{C}H_2$-Thioph); 58.03 ($\underline{C}(CH_3)_3$); 69.24 ($\underline{C}H_2$-O-S); 121.75 ($C_{\text{-2Thioph}}$); 125.54 ($C_{\text{-5Thioph}}$); 128.12 ($C_{\text{-4Thioph}}$); 137.41 ($C_{\text{-3Thioph}}$);

MS(CI) izobutan, m/z: 111 [Thioph-3-CH_2CH_2]; 233 [M+1]; 343 [M+ 111].

HRMS(EI) m/z calcld .for $C_{10}H_{16}O_2S_2$: 232.0589, found.:232.0591.

IR (KBr) ν_{max}/cm^{-1} 3096; 3053; 2956; 2929; 2881; 1629; 1536; 1474; 1364; 1124; 1000; 878; 775.

1.2 Synthesis of polythiophene derivatives substituted with a side chain containing a stereogenic sulfur atom. Chemical oxidation with $FeCl_3$

General procedure: according to a procedure similar to that of Sugimoto et al. [8]

To a suspension of iron (III) chloride (4 equiv) in an appropriate solvent at room temperature under argon atmosphere, the monomer solution (1 equiv) was added dropwise over 20 minutes. A stream of argon was passed through the stirring reaction solution until evolved hydrogen chloride (4h) was removed and stirring was continued at room temperature. The reaction mixture was then diluted with chloroform or dichloromethane and a portion of 1M HCl or 5% H_2SO_4 (in the case of sulfoxides) was added. The mixture was transferred to a separating funnel and extracted. The organic layer was washed with an acid solution until the iron (III) ions were not detected in the inorganic phase (KSCN analysis). The separated organic fraction was dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by precipitation of the polymer in chloroform (dichloromethane) by methanol or hexane or was washed by Soxhlet extractions with methanol.

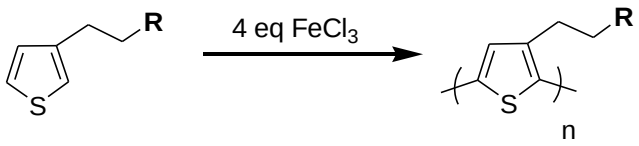
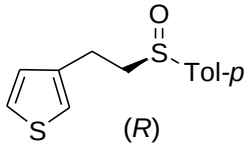
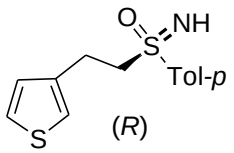
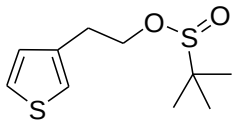
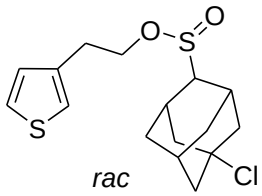
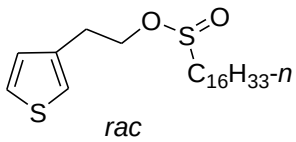
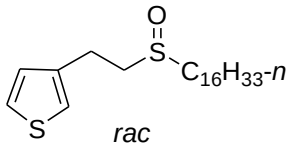
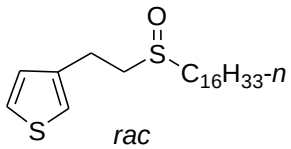
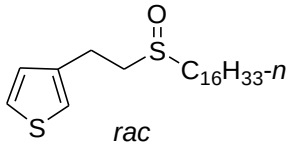
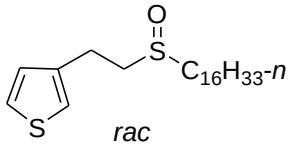
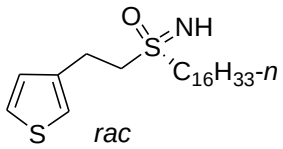
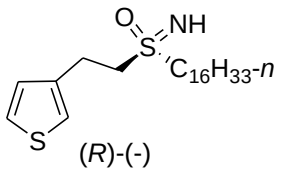


Table 7 The chemical polymerizations with $FeCl_3$

Reagents (g; mmol)				Conditions	Yield		Polymer
Monomer		**$FeCl_3$**	Solvent (mL)				
					Fraction soluble in $CHCl_3$	Insoluble in $CHCl_3$.	
 (*R*)	2.50g, 10 mmol	6.5g, 40mmol	CH_2Cl_2, 80mL	rt., 24h	0.5g (20%) (*Rac*) 2.5g	2g (80%)	*Rac*-**28**
 (*R*)	0.40g, 1.51 mmol	0.977g, 6.03mmol	$CHCl_3$, 16mL	rt., 24h	0.318g, (80%)	---	(*R*)-**31**
 *rac*	1.14g, 4.9 mmol	3.25g, 20mmol	$CHCl_3$, 40mL	rt., 24h	1.106g, (98%)	---	*Rac*-**33**
	0.50g, 1.61 mmol	1.05g, 6.44mmol	$CHCl_3$, 20mL	rt., 24h	0.07g (20%)	51%	*Rac*-**34**

 rac					0.356g, (71%)		
 rac	0.1g, 0.249 mmol	0.162g, 0.998mmol	$CHCl_3$, 5mL	rt., 24h	0.08g, (80%) unstable	------	--------
 rac	0.12g, 0.311 mmol	0.202g, 1.247mmol	$CHCl_3$, 5mL	rt., 4h	10% 0.12g (99%)	89%	*Rac*-**28**
 rac	0.1g, 0.260 mmol	0.168g, 1.039mmol	CH_3CN, 5mL	rt., 24h	No polymerization		*Rac*-**28**
 rac	0.078g 0.203 mmol	0.132g, 0.811mmol	CCl_4, 5mL	rt., 16h	0.046g (59%) (<99%)	0.031g (41%)	*Rac*-**28**
 rac	0.195g 0.507 mmol	0.329g, 2.028 mmol	$CHCl_3$/ CCl_4 (1:1), 5mL	rt., 16h	0.176g, (91%)	-----	*Rac*-**28**
 rac	0.1g, 0.250 mmol	0.162g, 1.00mmol	$CHCl_3$/ CCl_4 (1:1), 5mL	rt., 6h	0.057g, (58%)	-----	*Rac*-**32**
 (*R*)-(-)	0.1g, 0.250 mmol	0.162g, 1.00mmol	$CHCl_3$/ CCl_4 (1:1), 5mL	rt., 5h	0.058g, (59%)	-----	(*R*)-(-)-**32**

1.2.1 *rac*-(28) Polythiophene derivative obtained from (*R*)-(+)-2-(3'-Thienyl)ethyl *p*-Tolyl Sulfoxide

$[\alpha]_D$ =0 (CH_2Cl_2), soluble fraction (20%)

^{1}H NMR (200 MHz, $CDCl_3$): δ 2.43 (bs, 3H, CH_3); 3.05-3.08 (bm, 4H, 2xCH_2); 6.93-7.00 (2bm, 1H, 4-Thioph); 7.34 (bm, 2H$_{meta,}$ Ar); 7.52 (bm, 2H$_{ortho,}$ Ar). ^{13}C NMR (50MHz, $CDCl_3$) δ 21.39 (s, 4-Ar-$\underline{C}H_3$); 22.70 (bs, Thioph-$\underline{C}H_2CH_2$); 121.69 (bs, 2-C_{Thioph}-H), 124.42 (bs); 126.10 (s), 127.93 (bs); 129.51(bs); 138.95 (bs); 141.69 (bs).

1.2.2 *rac*-(29)Polythiophene derivative of *rac n*-Hexadecyl 2-(3'-Thienyl)ethyl Sulfoxide -

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.83-0.87 (bm, 3H, CH_3); 1.24 (bm, 26H); 1.76 (bm, 2H, CH_2); 2.72, 3.02, 3.32 (3xbm, 6H, 3xCH_2); 7.08, 7.12, 7.15, 7.20 (4xm, 1H, H-4-Thioph). ^{13}C NMR (125MHz, $CDCl_3$) δ 14.17; 21.29; 22.74; 28.78; 29.25; 29.36; 29.41; 29.58; 29.66; 29.70; 31.14; 31.96; 57.32; 57.72; 58.00; 121.74 i 122.08 (C-2Thioph); 125.67 i 125.85 (C-5Thioph); 127.88; 128.09; 128.34, 128.55 (C-4Thioph), 137.47(C-3Thioph). GPC (polystyrene) flow rate 0.8 ml/min. CH_2Cl_2, Paek T=6.24ml-15.63ml, Mn=2.24x10^5; Mw=7.5x10^6. Elem. Anal.: calcld for $C_{22}H_{38}OS_2$ (%) : C, 69.05; H, 10.01; S, 16.76; for: C, 67.08; H, 9.05; S, 13.21 (due to the presence of Cl ions).

1.2.3 -(31) Polythiophene derivative of (*R*)-(-)- 2-(3'-Thienyl)ethyl *p*-Tolyl Sulfoximine

$[\alpha]_D$= -55 (0.2; CH_2Cl_2);

^{1}H NMR (200 MHz, $CDCl_3$): δ 2.37 (bs, 3H, CH_3); 3.19 i 3.37 (ratio 34: 66) (2xbm, 4H, 2xCH_2); 6.84 i 6.96 (35:65) (2xbm, 1H, 4-Thioph); 7.30 (bm, 2H$_{meta,}$ Ar); 7.84 (bm, 2H$_{ortho,}$ Ar). MALDI TOF (DHB) m/z=1053 (4xM); 1157 (4xM+3Cl); 1350 (5xM+Cl). DHB- 3,5-dihydroxybenzoic acid (matrix).

1.2.4 *rac*-(32) Polythiophene derivative of *rac n*-Hexadecyl 2-(3'-Thienyl)ethyl Sulfoximine

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.87 (bm, 3H, CH_3); 1.25(bm, 26H); 1.84 (bm, 2H, CH_2); 3.88 & 3.37 ratio: 51:49 (2xbm, 6H, 3xCH_2); 7.05 (bm, 1H, H-4-Thioph);

1.2.5 (*R*)-(32) Polythiophene derivative of (*R*)-*n*-Hexadecyl 2-(3'-Thienyl)ethyl Sulfoximine

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (bm, 3H, CH_3); 1.25-1.41 (bm, 26H); 1.86 (bm, 2H, CH_2); 3.88 & 3.37 ratio: 53:47 (2xbm, 6H, 3xCH_2); 7.04, 7.07, 7.16, 7.20 (4xm, 1H, H-4Thioph). IR (KBr) [ν/cm^{-1}]: 3272 (stretching N-H); 2921; 2851(C-H stretching); 1635 (C=C r stretching); 1466 (CH_2 bending); 1201, 1108 (N=S=O stretching); 802 (bending out of plane.C$_\beta$-H Thioph.)

1.2.6 *rac*-(33) Polythiophene derivative of *rac*-*O*-2-(3'-Thienyl)ethyl *tert*-Butanosulfinate

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.18 (bm, 9H, C(CH_3)$_3$; 3.02 i 3.24 (ratio: 42:58) (2xbm, 2H $\underline{CH_2}$-Thioph); 4.29-4.39 (bm, 2H, $\underline{CH_2}$-O); 7.09 i 7.14 (ratio: 60:40) (2xbm, 1H, 4-Thioph). IR (KBr) [ν/cm^{-1}]: 3061; 2955; 2922; 1641; 1461; 1363; 1124 (-O-S=O); 1021; 978; 834; 732.

1.2.7 *rac*-(34) Polythiophene derivative of *rac*-*O*-2-(3'-Thienyl)ethyl 3-Chloroadamantanesulfinate

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.62-1.71(6H, 3x$\underline{CH_2}$(Ad)); 2.07-2.13 (m, 6H, 3x$\underline{CH_2}$(Ad)); 2.31(bm, 2H, Ad); 3.00 & 3.23 (ratio 45:55) (2xbm, 2H, $\underline{CH_2}$-Thioph); 3.84 & 4.28 (ratio 38:72) (2xbm, m, 2H; $\underline{CH_2}$-O-S); 7.08 & 7.15: ratio 62:38 (2xbm, 1H, 4-Thioph). ^{13}C NMR (50MHz, $CDCl_3$) δ 28.39; 29.85; 30.80; 31.42; 33.12; 35.12; 41.73; 45.35; 60.90; 65.79; 67.74; 128.10; 133.61.

1.2.8 Polythiophene derivative of *rac*-*O*-2-(3'-Thienyl)ethyl *n*-Hexadecanesulfinate

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.84-0.87 (bm, 3H, CH_3); 1.25 (bm, 26H); 1.67 (bm, 2H, CH_2); 2.74 (bm, 2H, $\underline{CH_2}$-S(O)); 3.05 i 3.25 ratio: 46:54 (2xbm, 2H, $\underline{CH_2}$-Thioph); 4.30 (bm, 2H, $\underline{CH_2}$-O-S); 7.10 (bm, 1H, H-4Thioph). Unstable.

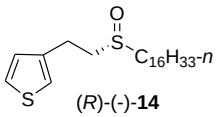
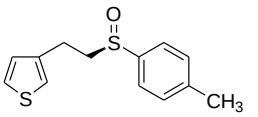
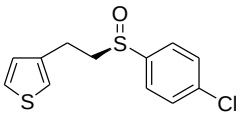
1.3 Synthesis of optically active polythiophene derivatives. Chemical oxidation with $Fe(ClO_4)_3$.

General procedure:

A solution of enantiomeric sulfoxide (1 equiv) in benzene was added dropwise to the stirred solution of 70% $HClO_4$ and $Fe(ClO_4)_3 \bullet 9H_2O$ (4 equiv). The reaction mixture was stirred for 24h at room temperature. The blue precipitate formed upon the reaction was filtered off and washed with hydrazine hydrate. The solid was then

dissolved in the appropriate amount of CH_2Cl_2 and extracted with a 5% H_2SO_4 solution. The extraction of the organic phase was continued until the iron ions was not detected in the inorganic layer (KSCN test). The organic layer was separated, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product isolated was purified by Soxhlet extraction with methanol. The polymerization product obtained in this manner was completely soluble in chloroform or methylene chloride.

Table 8 The chemical polymerizations with $Fe(ClO_4)_3 \bullet 9H_2O$

No	Reagents			Conditions	Yield
	monomer	$Fe(ClO_4)_3 \bullet 9H_2O$	70%$HClO_4$/ benzene		
(*R*)-(-)-32	 (*R*)-(-)-**14**	0.1g, 0.260mmol	0.537g, 1.04mmol	2ml/2ml	rt., 24h	94mg (95%) [a] 49mg (49%)[b]
(*R*)-(+)-28	 (*R*)-(+)-**8** $[a]_D$=+110,86(1,08; CH_2Cl_2)	0.1g, 0.399mmol	0.824g, 1.597mmol	2ml/2ml	rt., 24h	82mg (82%) [a] 54mg (55%)[b]
(*R*)-(+)-30	 (*R*)-(+)-**18** $[\alpha]_D$=+107,39 (1,38; CH_2Cl_2)	0.1g, 0.369mmol	0.762g, 1.477mmol	2ml/2ml	rt., 24h	46mg (47%)[b]

[a] Yield of the crude product

[b] Yield after a Soxhlet extraction

1.3.1 Polythiophene derivative of 2-(3'-Thienyl)ethyl *p*-Tolyl Sulfoxide (*R*)-(+)-28

$[\alpha]_D$ =+107.94 (0.158; CH_2Cl_2)

^{1}H NMR (200 MHz, $CDCl_3$): δ 2.35 (bs, 3H, CH_3); 3.07 (bm, 4H, 2xCH_2); 6.98 (bm, 1H, 4-Thioph); 7.35 (bm, 2H$_{meta,}$ Ar); 7.50 (bm, 2H$_{ortho,}$ Ar). Elem. Anal.: calcld for $C_{213}H_{312}OS_2$ (%) : C, 62.87; H, 4.87; S, 25.82; found: C, 61.01; H, 5.42; S, 24.05 (the presence of Cl dopants).

1.3.2 Polythiophene derivative of *n*-Hexadecyl-2-(3'-Thienyl)ethyl Sulfoxide (*R*)- (-)-29

$[\alpha]_D$= -62.60 (0.014; CH_2Cl_2)

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.87 (bm, 3H, CH_3); 1.25 (bm, 26H); 1.75 (bm, 2H, CH_2); 2.73. 3.02, 3.32 (3xbm, 6H, 3xCH_2); 7.08, 7.12, 7.15, 7.20 ratio: 32:16:24:28 (4xm, 1H, h-4-Thioph). Elem. Anal.: calcld for$C_{22}H_{38}OS_2$ (%) : C, 69.05; H, 10.01; S, 16.76; found: C, 61.36; H, 9.95; S, 11.67 (the presence of Cl ions).

1.3.3 Polythiophene derivative of *p*-Chlorophenyl-2-(3'-Thienyl)ethyl Sulfoxide (*R*)-(+)-30

$[\alpha]_D$=+104.16 (0.024; CH_2Cl_2)

^{1}H NMR (200 MHz, $CDCl_3$): δ 3.05 (bm, 4H, 2xCH_2); 7.03 (bm, 1H, 4-Thioph); 747 (bm, 4H, Ar).

2. Spectroscopic characterization of the isolated polythiophene derivatives

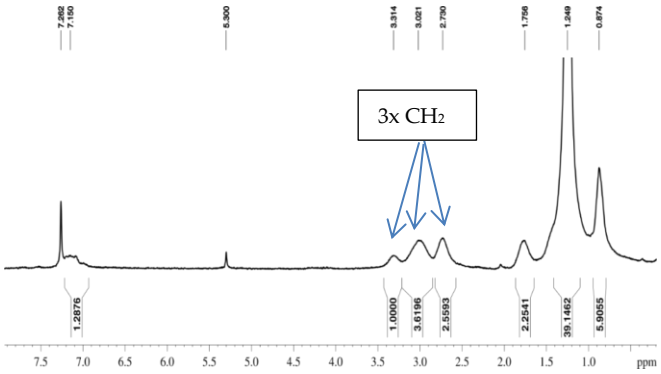
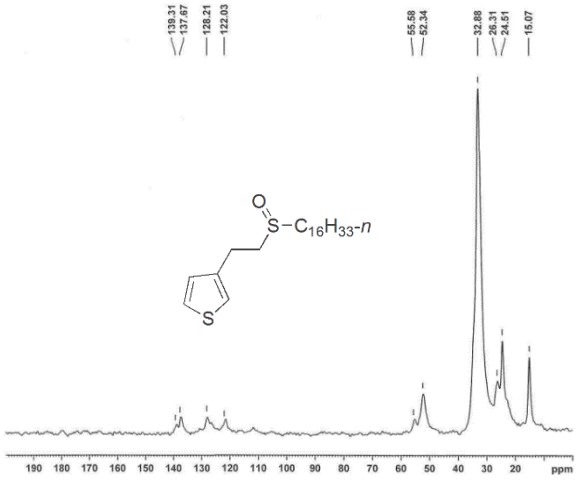


Fig. S1 ^{1}H NMR spectrum of the product **29**



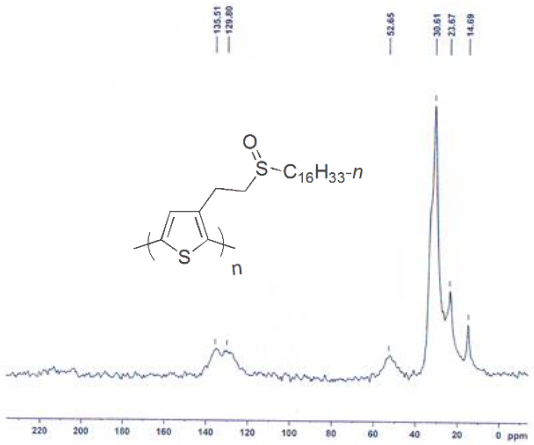


Fig. S2 ^{13} C CP MAS NMR spectra of *n*-hexadecyl 2-(3'-thienyl)ethyl sulfoxide and its polymeric analogue

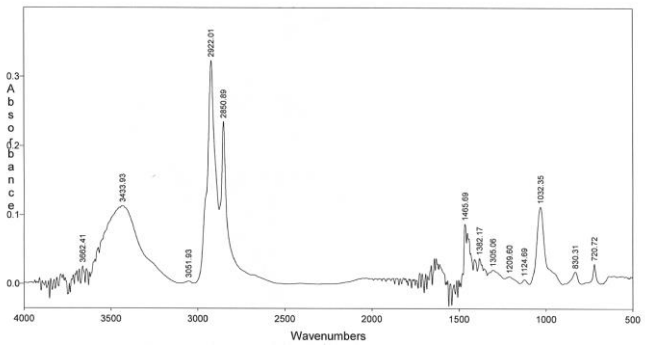


Fig.S3 IR spectrum from KBr pellet of r*ac*-**29**

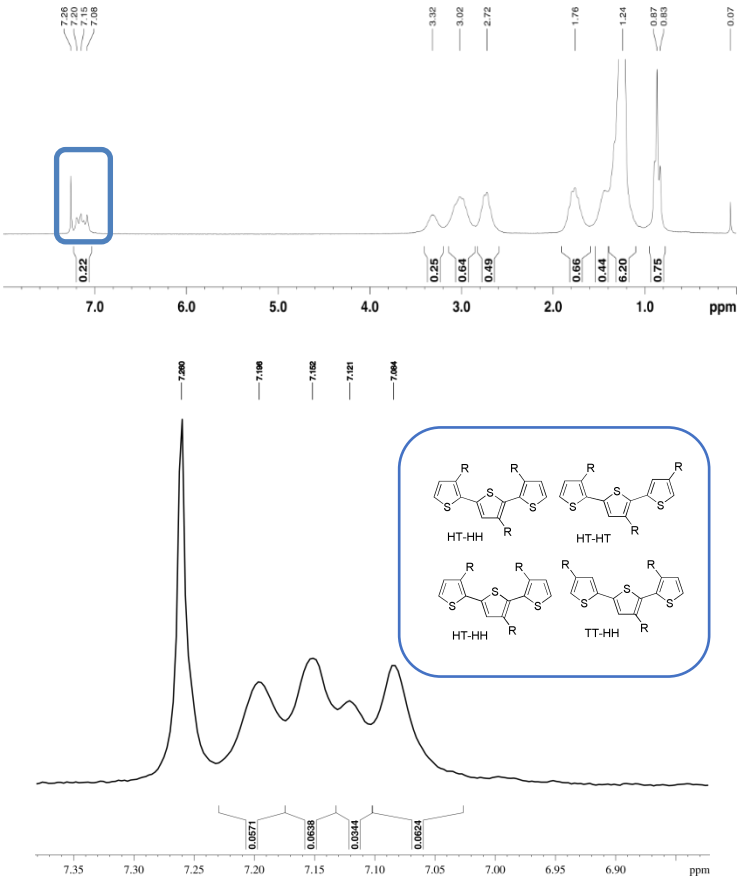


Fig. S4 ^{1}H NMR spectrum of the polymer **29** derived from *n*-hexadecyl 2-(3'-thienyl)ethyl sulfoxide (the polymer obtained from entry 3, Table 2)

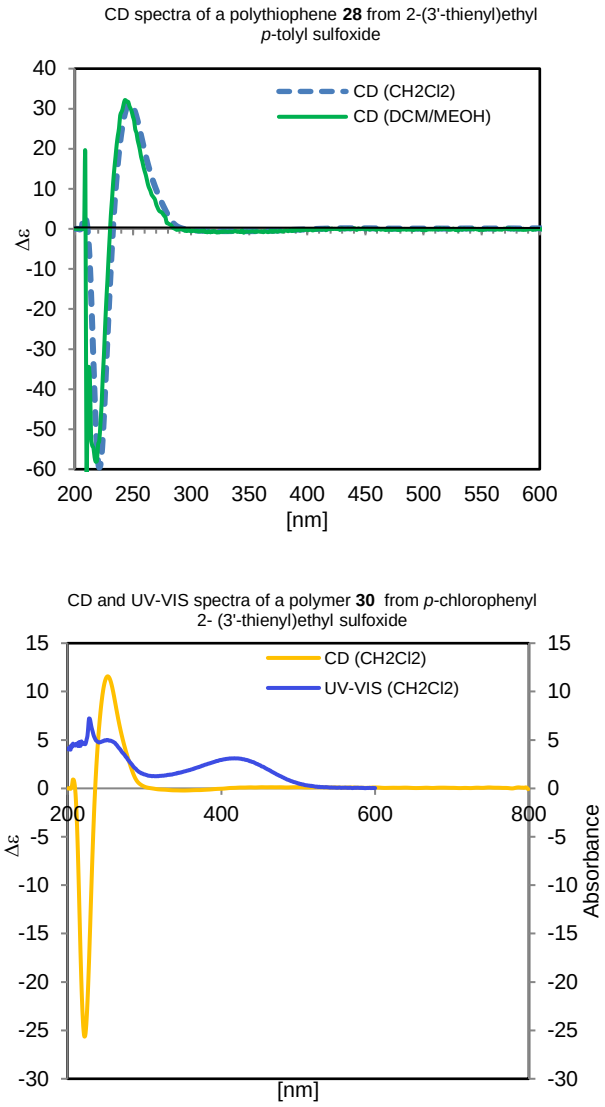


Fig. S5 Up: Circular dichroism spectra recorded for **28** polymer solutions in dichloromethane with a concentration of c = 1.06x10-3 M (dashed blue line), a polymer solution in the CH_2Cl_2-MeOH (4: 3) solvent system with a concentration of c = 1.207x10-3M (green solid line); Down: Circular dichroism spectrum of the polymer **30** solution in dichloromethane C = 2.68x10-3 M (orange line) and its UV-VIS spectrum in dichloromethane (blue line).

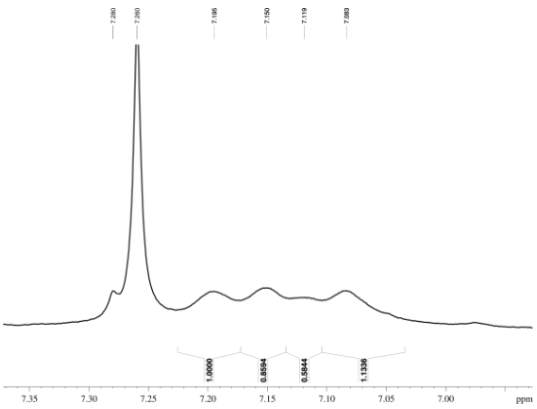


Fig. S6 The layout of resonance signals in the aromatic range of polymer **29**

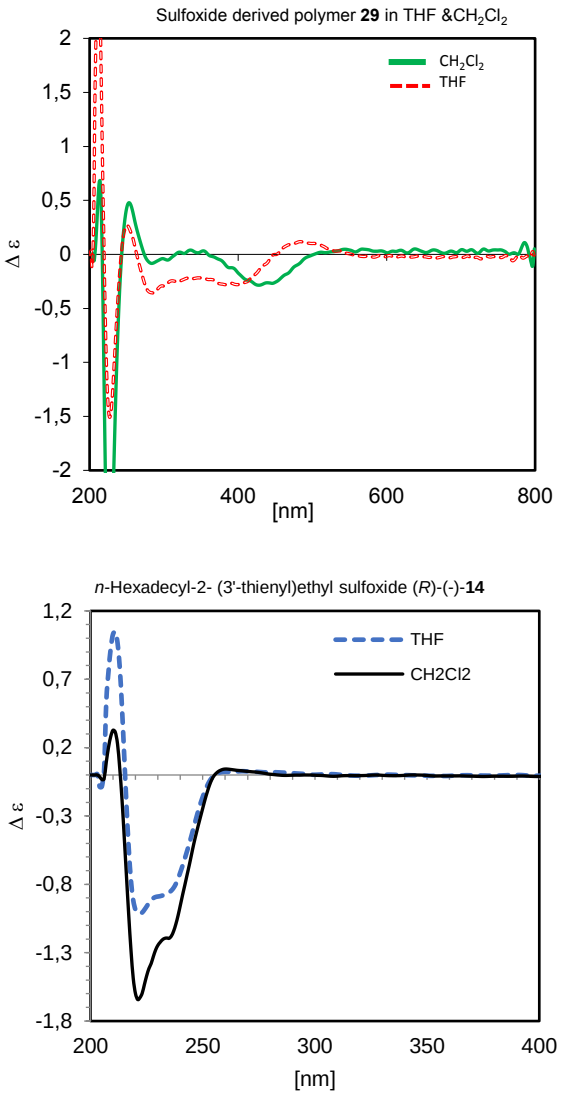


Fig. S7 Up: CD spectrum of the polymer of n-hexadecyl-2-(3'-thienyl)ethyl sulfoxide 29 in THF (C=3.659mM, red dashed line) and in CH2Cl2 (C=2.87mM, solid green line) Down: Circular dichroism spectrum of n-hexadecyl-2-(3'-thienyl)ethyl sulfoxide (R)(-)-14 recorded for a solution in tetrahydrofuran (C = 8.058mM, blue dotted line) and dichloromethane (C = 7.8mM, solid black line)

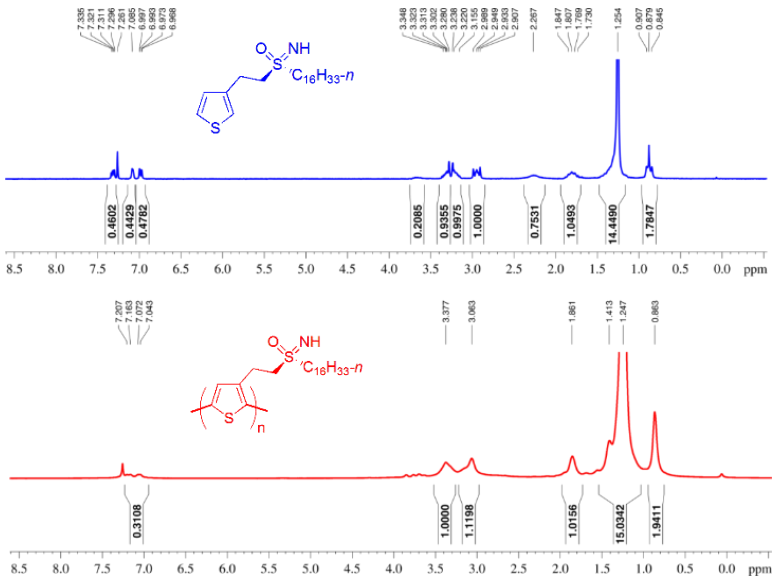


Fig. S8 The ^{1}H NMR spectra of **20** and **32**

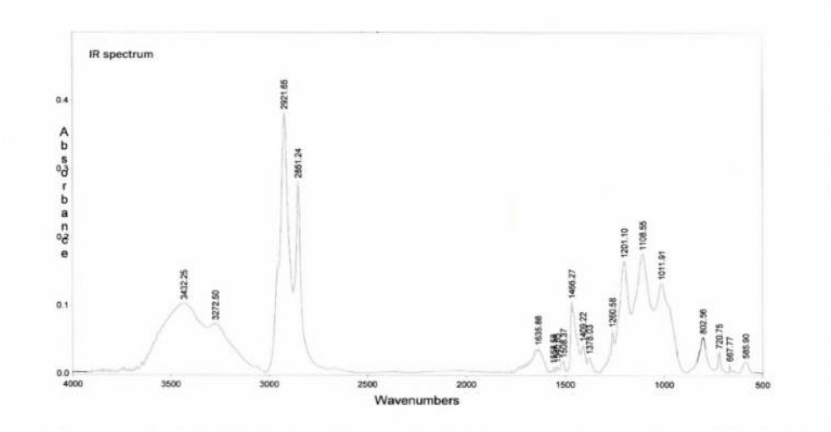


Fig. S9 IR spectrum of polymeric n-hexadecyl 2- (3'-thienyl)ethyl sulfoximine **32**

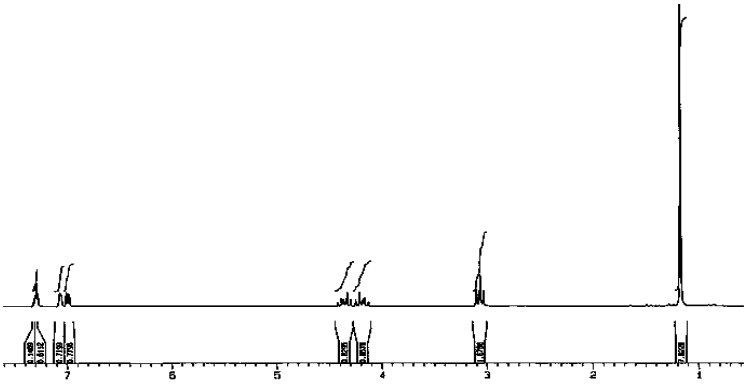


Fig. S10 ^{1}H NMR of monomer **24**

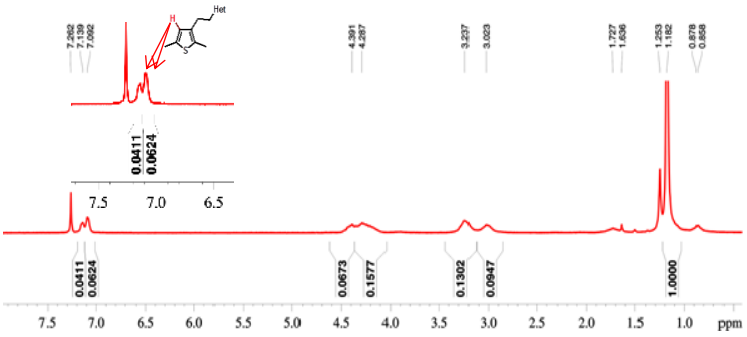


Fig. S11 ^{1}H NMR of polymeric sulfinate **33** (* signals assigned to hexane) Zooming in the aromatic area (here the determination of the percentage of the HT dyads wasn't possible due to signal overlapping)

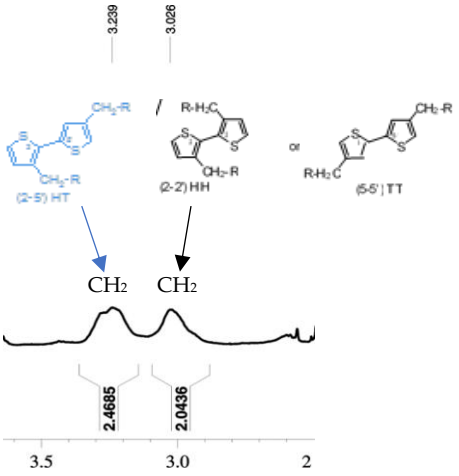


Fig. S12 ^{1}H NMR spectrum for the polythiophene **34** derivative in the aliphatic range showing two broadened resonance signals of the methylene group protons indicating the presence in the main chain of the regular HT-type dyad system and HH or TT couplings

2.1 UV-visible and emission spectra collected for the polythiophene derivatives samples

2.1.1 *(R)*-(-)-31

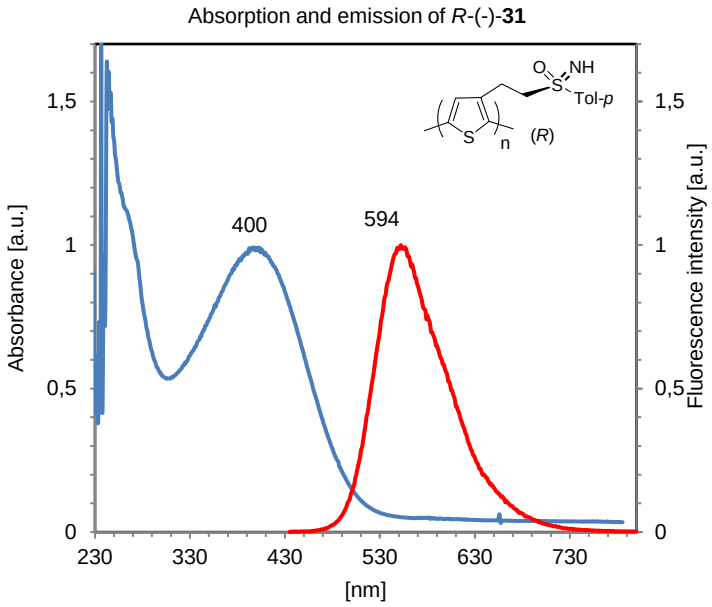


Fig. S13 The absorption spectrum recorded for the polymer of sulfoximine (*R*)-(-)- **31** in a chloroform solution C = 1.05 x10^{-3} M (blue line). Emission spectrum for the compound C = 4.56 x10^{-5} M ($CHCl_3$) (red line).

2.1.2 Rac-33

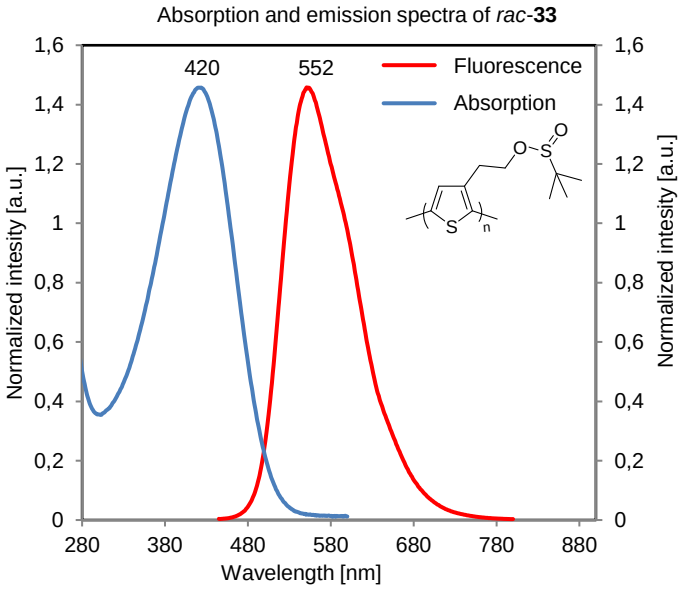


Fig. S14 Absorption and fluorescence spectrum at excitation wavelength 420 nm of a polymer sample C= 1.74x10^{-4} M ($CHCl_3$)

2.1.3 Rac-29

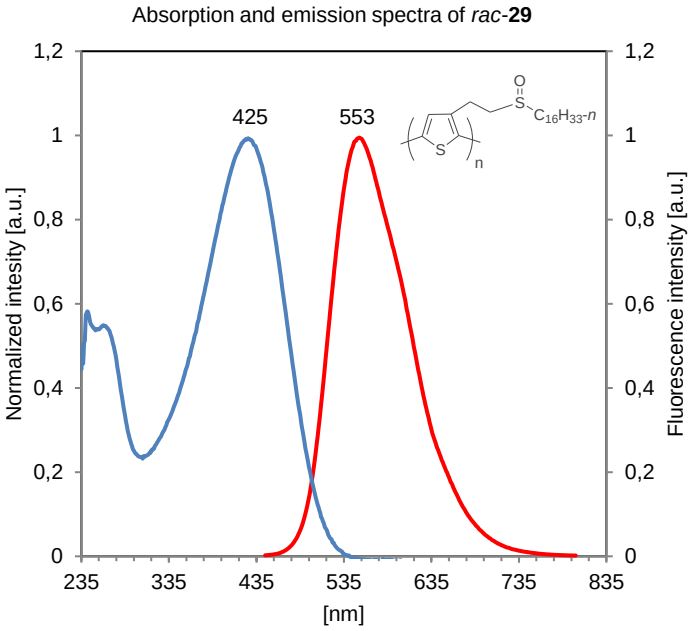


Fig. S15 Absorption and emission spectra of a solution of sulfoxide-based polythiophene in chloroform (C = 8.362×10^{-5} M). The racemic sulfoxide-based polythiophene *rac*-**29** was obtained by the Method 3. The absorption band has a maximum at 425 nm, the emission spectrum shows the peak with a maximum of 553 nm (λexc = 426nm).

2.1.4 (*R*)-(-)-29

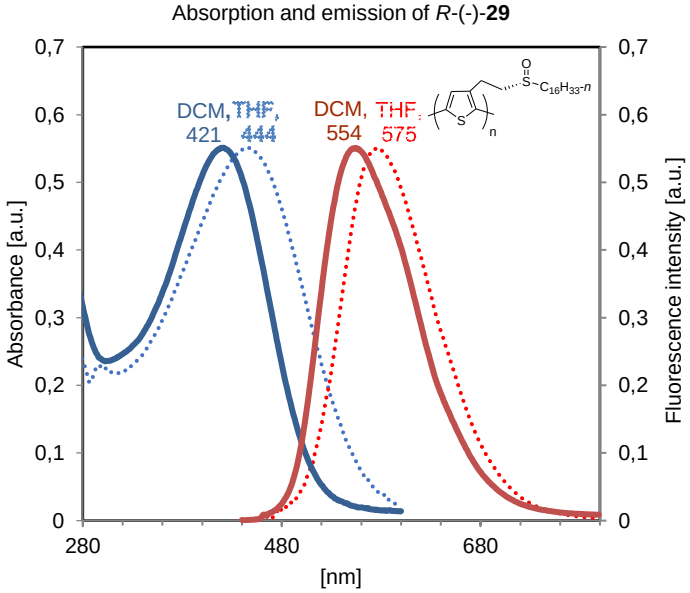


Fig. S16 Absorption and emission spectra for the polymerization product of *n*-hexadecyl 2-(3'-thienyl)ethyl sulfoxide in tetrahydrofuran and dichloromethane solutions

2.1.5 *Rac*-32

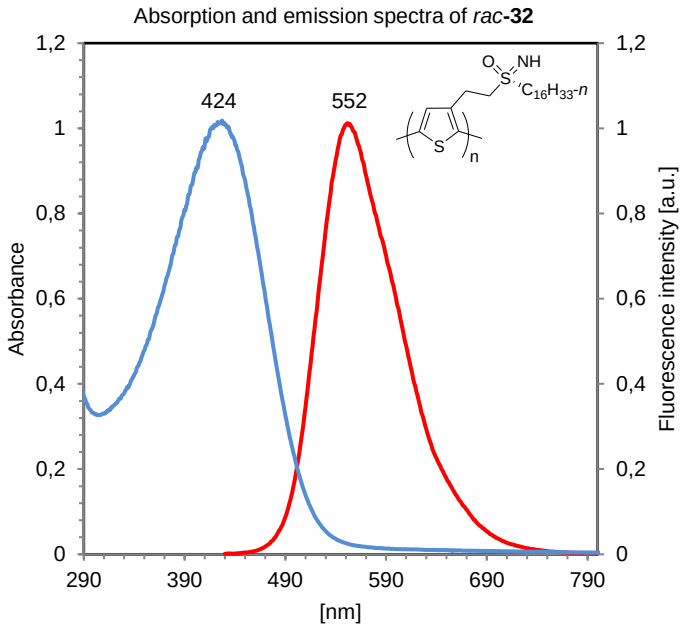


Fig. S17 UV-VIS spectrum of polymeric sulfoximine *rac* -**32** solution in chloroform at concentration C = 2.014x10^{-4} M (ε_{mol} = 5024.68 [dm^3 · mol^{-l} · cm^{-l}]) Fluorescence spectrum of polymer solution in chloroform at concentration C = 5.034x10 $^{-5}$ M.

2.1.6 (*R*)-(-)-32

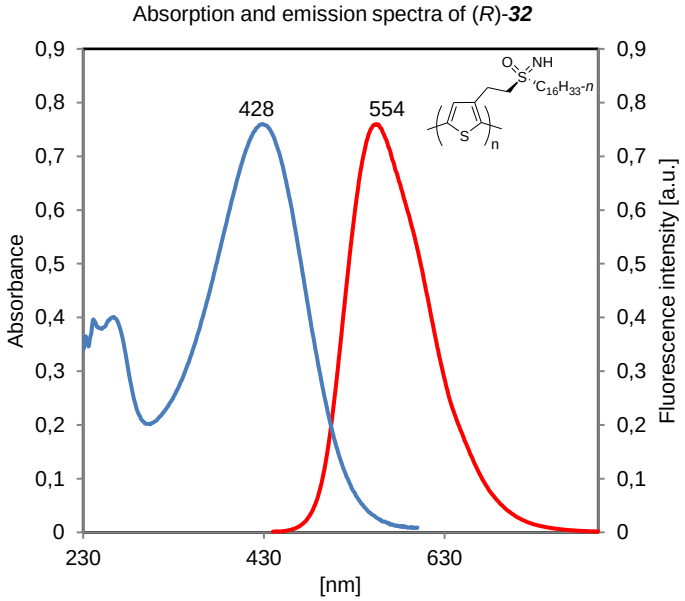


Fig. S18 Right: Fluorescence spectrum ($CHCl_3$, C = 1.309x10^{-4} M) -red line and UV-VIS- spectrum ($CHCl_3$, C = 1.309x10^{-4} M-blue line. The fluorescence intensity values have been normalized.

2.1.7 (R)-(+)-28
2.1.8 (R)-(+)-30

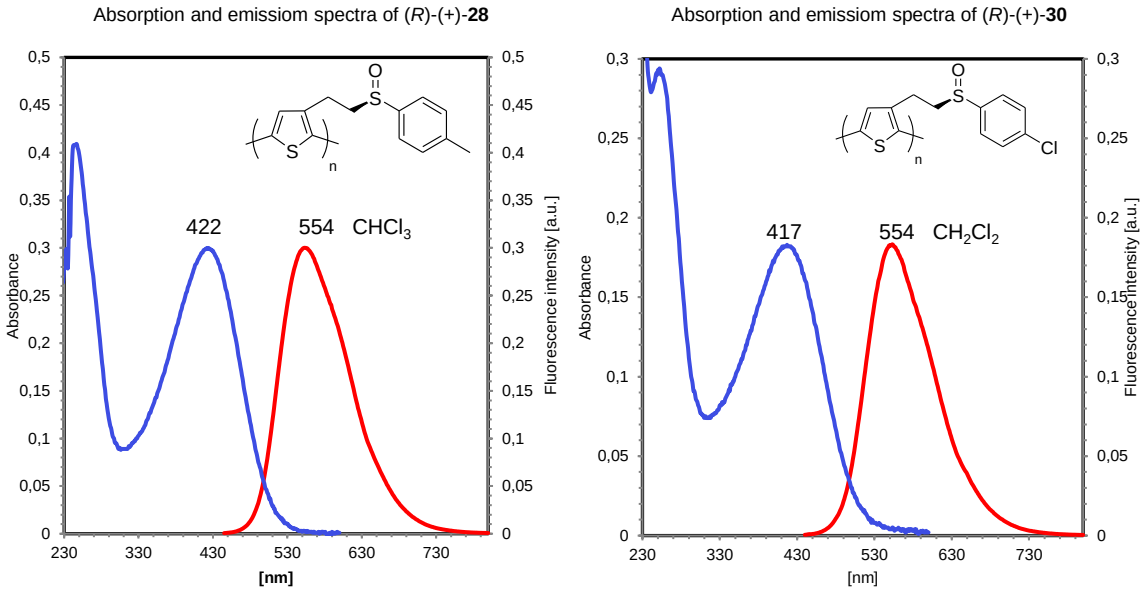


Fig. S19 Spectrum of absorption and emission of polymeric 2- (3'-thienyl) ethyl *p*-tolyl sulfoxide recorded in $CHCl_3$ (C = 2.684×10^{-5} M, (ε_{mol} = 11194dm^3 mol^{-1} cm^{-1}) and polymeric *p*- chlorophenyl 2-(3'-thienyl)ethyl sulfoxide at C=2.976×10^{-5} M in methylene chloride. The value of the fluorescence intensity units has been normalized.

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