Synthesis and and Characterisation of Novel Regioregular Polythiophenes − Tuning the Redox Properties

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The synthesis and full characterisation of three novel regioregular polythiophenes **8**, **9**, and **15** is presented. By varying the nature of the substituents on the polythiophene backbone in these materials it is possible to increase their first oxidation potential by almost 0.5 V. Because the first reduction potential follows the same trend, the electrochemical band gap of these polymers is essentially constant. The constant band gap inferred from the electrochemical data is confirmed by the onset of the optical absorption spectrum of the polythiophenes, which shows only small changes.

Introduction

The current interest in conjugated polymers is motivated by their role as functional materials in applications like light-emitting diodes, field-effect transistors, photovoltaic cells and lasers. To optimise the performance of such devices, a thorough understanding of the relationships between molecular structure and macroscopic properties is important. Tremendous knowledge on the interplay between chemical structure, mesoscopic structure and physical properties of conjugated polymers has been unravelled over the past decades.[1]

Substituted regioregular polythiophenes[2] stand out as some of the most promising members of the conjugated polymer family, because they are stable and processable, they show very high charge-carrier mobilities[3] and they become highly conducting upon doping.[4] The very high charge-carrier mobilities recently measured for regioregular poly(3-alkylthiophenes) makes them potential candidates for the active layer in field-effect transistors and other electronic devices. The long-term stability of conjugated polymers under ambient conditions, and hence the operational lifetime of the electronic devices, is strongly influenced by the presence of oxygen, moisture and light. Currently, it is of paramount importance to improve operational lifetimes of all-polymer electronic devices, and hence an increase in the long-term stability of conjugated polymers under ambient conditions is desirable. One of the important parameters to control and tune in this regard is the electrochemistry of the polymer. By tuning the redox properties of the polymer, degradation by, for example, oxidation might be suppressed. Hence, by increasing the first oxidation potential, an improved stability towards oxidation of the polymer by air and moisture can be expected.

Our approach towards this goal was to introduce different substituents with a variation in electronic structure onto the conjugated polythiophene backbone. As a reference in terms of electro-optical properties we use regioregular poly(3-dodecylthiophene) **1**. We introduced the substituent on every second thiophene segment while keeping a solubilising dodecyl chain on the other thiophene segment (Figure 1).

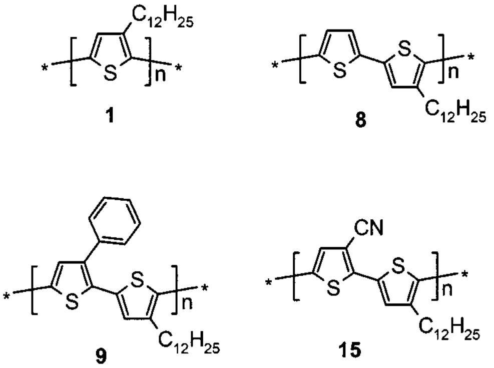

Figure 1. Investigated polythiophenes

The fixed alternation of alkyl chain and substituent was achieved by synthesising the appropriate head-to-tail bithiophenes, which were subsequently polymerised in a regioregular fashion using the McCullough method[4] or by a variation using $ZnCl_2$ instead of $MgBr_2$. We have prepared three novel regioregular polythiophenes **8**, **9** and **15** (Figure 1) and here we report the synthesis, characterisation, and electrochemical and optical properties of these new conjugated materials.

Results and Discussion

Synthesis and Characterisation

The synthesis of polythiophenes **8** and **9** is outlined in Scheme 1. When LDA is used as the lithiating reagent at low temperature, a selectivity of 97% between the two α-

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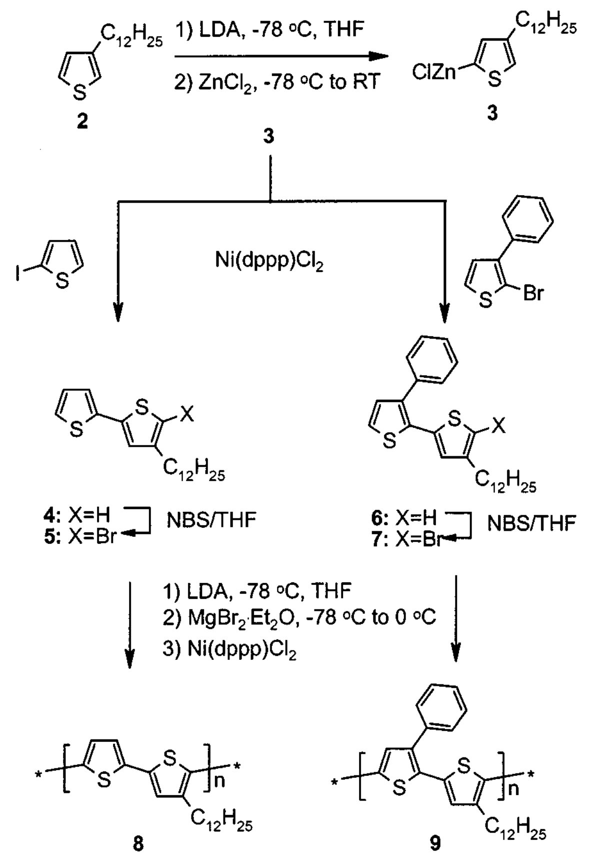


Scheme 1. Synthesis of polymers **8** and **9**

protons in 3-dodecylthiophene **2** is obtained. The 4-dodecyl-2-thienylzincio derivative **3** is generated by subsequent transmetallation with $ZnCl_2$. This derivative is an important building block in our synthesis. By coupling with 2-iodothiophene using $[NiCl_2(dppp)]$ as catalyst, bithiophene **4** is formed in 68% yield. Coupling **3** with 2-bromo-3-phenylthiophene, again using $[NiCl_2(dppp)]$ as catalyst, gives bithiophene **6** in 73% yield. Bithiophenes **4** and **6** are then selectively α-brominated with NBS in THF due to the activating effect of the dodecyl chain, to give the brominated bithiophenes **5** and **7** in 56% and 52% yield, respectively.

The bithiophenes **5** and **7** were then polymerised by the McCullough method.[4] Lithiation with LDA gives selective abstraction of the α-protons. The corresponding Grignard derivatives are generated by subsequent transmetallation with $MgBr_2$, which gives the crude polymers upon addition of the cross-coupling catalyst $[NiCl_2(dppp)]$. Purification was performed by subsequent Soxhlet extractions with methanol, hexane, dichloromethane, and finally chloroform. From Size Exclusion Chromatography (SEC) relative to polystyrene standards an average molecular weight of 22600 g/mol was obtained for **9** with a Poly Dispersity Index (PDI) of 1.3. Due to strong aggregation of **8** in common organic solvents at room temperature a reproducible molecular weight could not be obtained from SEC. The amount of head-to-tail couplings of all polymers was deduced from ^1H NMR spectroscopy to be >95%. The aromatic parts of the spectra showed negligible or very small amounts of irregular couplings. Estimation of the amount of head-to-tail couplings from this part of the spectra is difficult due to the somewhat broad thiophene β-proton resonances. An alternative quantification of the head-to-tail ratio is available from analysis of the benzylic CH_2 resonances. As an example the full ^1H spectrum of polymer **9** is

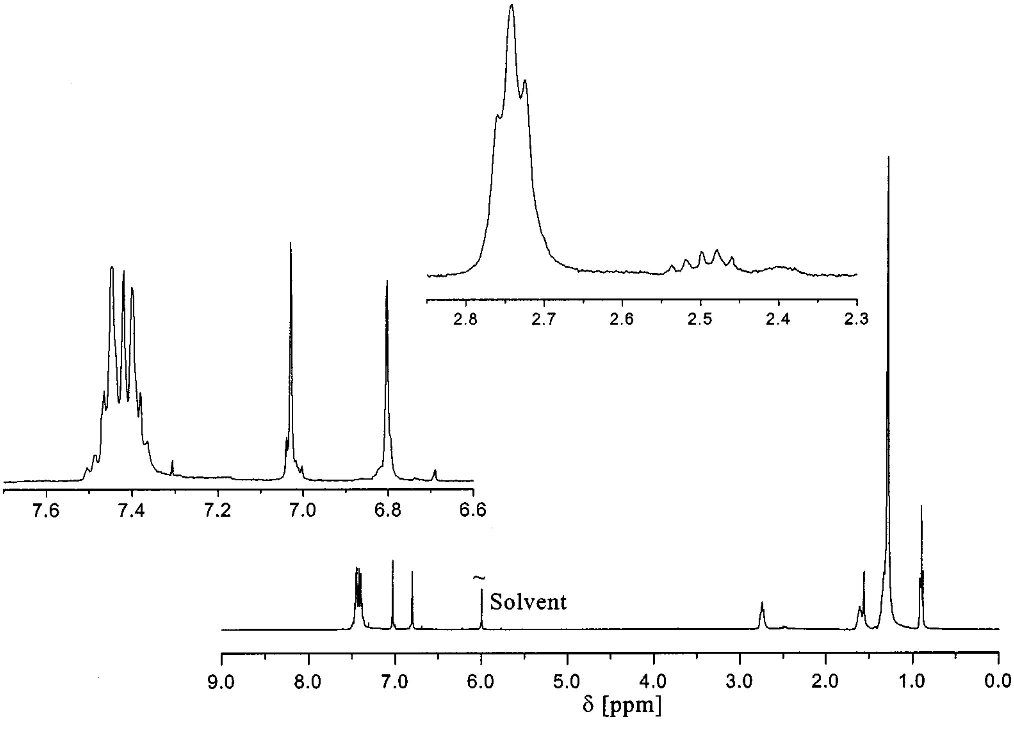
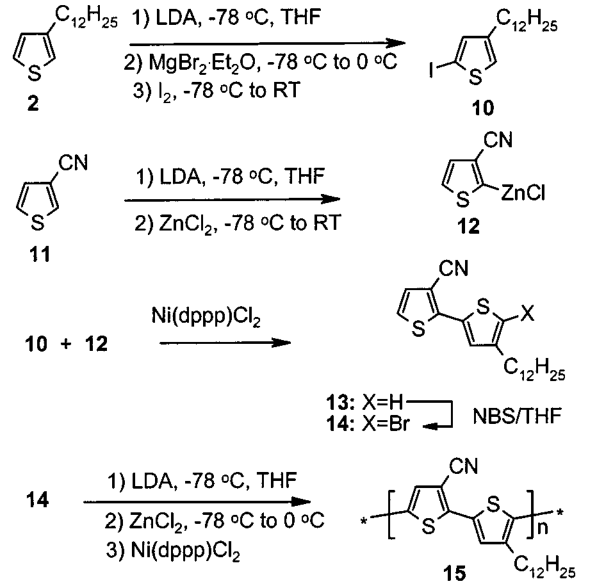


Figure 2. ^1H NMR spectrum of **9** in 1,1,2,2-[D_2]tetrachloroethane

shown in Figure 2, along with enlargements of the aromatic and benzylic regions.

The aromatic region shows a broad multiplet between $\delta = 7.36$ and 7.52 for the phenyl protons and then two singlets for the two thiophene β protons at $\delta = 7.03$ and 6.80. In the benzylic part between $\delta = 2.70$ and 2.80, the CH_2 protons from head-to-tail coupled bithiophenes give rise to a broad triplet. Between $\delta = 2.44$ and 2.55 a very broad, low-intensity signal is observed. This signal is interpreted as arising from benzylic CH_2 groups on terminal thiophenes of the polymer chain and from benzylic CH_2 groups on irregularly coupled bithiophene fragments in the chain. This interpretation is based on the work of Barbarella et al.,[5] who assigned the positions of the ^1H resonances in a systematic series of regiochemically well-defined alkyl-substituted oligothiophenes. The signal from the benzylic CH_2 groups between $\delta = 2.44$ and 2.55 integrates to $\approx$ 5%, which includes both end-groups and irregular couplings. Hence, we estimate the regioregularity of **9** to be >95%. A regioregularity of >95% for **8** was estimated from a similar analysis of the ^1H NMR spectra.

The synthetic approach to polymer **15** is outlined in Scheme 2. 4-Dodecyl-2-iodothiophene **10** was synthesised in 87% yield by selective lithiation of **2** with LDA as described above, followed by transmetallation with $MgBr_2{\cdot}Et_2O$. This step was taken to prevent the possible reaction of 4-dodecyl-2-iodothiophene with the still present 2-lithio-4-dodecylthiophene to give 3-dodecyl-5-iodo-2-lithiothiophene and 3-dodecylthiophene.



Scheme 2. Synthesis of polymer **15**

Selective 2-lithiation of 3-cyanothiophene **11** with LDA[6] is followed by transmetallation with $ZnCl_2$ to give **12**, which is then coupled with **10** using $[NiCl_2(dppp)]$ as catalyst to give **13** in 33% yield. Selective α-bromination with NBS in THF gives **14** in 73% yield. Due to the incompatibility of the cyano group with Grignard reagents at room temperature we chose to use $ZnCl_2$ instead of $MgBr_2$ in the polymerisation step, along with $[NiCl_2(dppp)]$ as the catalyst. The polymer was obtained as violet films after Soxhlet extractions with methanol, hexane, dichloromethane and finally chloroform. A regioregularity of >95% for **15** was estimated from the ^1H NMR spectrum as described above for **9**. From SEC analysis an average molecular weight of 4600 g/mol was obtained.

UV/Vis Spectroscopy

The UV/Vis spectra of **1**, **9** and **15** in chloroform solution (Figure 3, dotted lines) at room temperature all possess λ_{max} values around 450 nm, characteristic of individually dissolved polythiophene backbones. When solutions of these polymers are spin-cast on glass substrates red shifts of 105 nm for **1** and **9** and 90 nm for **15** are observed (Figure 3, full lines). Furthermore, some unresolved vibrational fine structure is observed in the UV/Vis spectra of the thin films. In chloroform at room temperature polymer **8** (Figure 3, dashed line), however, shows a UV/Vis spectrum that strongly resembles that of the thin spin-cast film (Figure 3, full line). The red shift of the UV/Vis spectrum towards that of the thin film indicates strong aggregation of **8** in chloroform solution at room temperature, probably accompanied by a significant planarisation of the backbone.

Variable-temperature UV/Vis spectroscopy on polymer **8** in chloroform solution (Figure 4) shows that, upon heating to above 42 °C, λ_{max} shifts from 540 nm to 450 nm. This suggests a transition from an aggregated state to a state where individually dissolved polythiophene chains dominate.

When a UV/Vis spectrum of **9** is recorded immediately after spin coating (Figure 3, dashed line) λ_{max} is found to be around 520 nm and no vibrational fine structure is observed. Annealing the film by heating in vacuum for only a few minutes leads to a red shift of λ_{max} and the occurrence of vibrational fine structure. This can be explained by the steric demand of the phenyl groups, which causes a twisted thiophene backbone. By annealing the film a planarisation of the thiophene backbone occurs, as shown by the observed red shift. Similar annealing effects have been observed for other phenyl-substituted polythiophenes.[7]

Figure 3 and the data collected in Table 1 show that changing the nature of the substituent on every second thiophene ring in polymers **1**, **8**, **9**, and **15** gives rise to relatively small changes in the optical band gap of the polymer, and the onset of absorption of these polymers is found between 1.84 and 1.94 eV.

Electrochemistry

The cyclic voltammograms of drop-cast films of **1**, **8**, **9** and **15** (Figure 5) on a Pt electrode recorded in acetonitrile (containing 0.1 M TBA-PF_6) show a continuous increase of the position of the anodic peak potential of the first oxidation wave (E_{pa}^{ox}). By removing every second alkyl chain in a

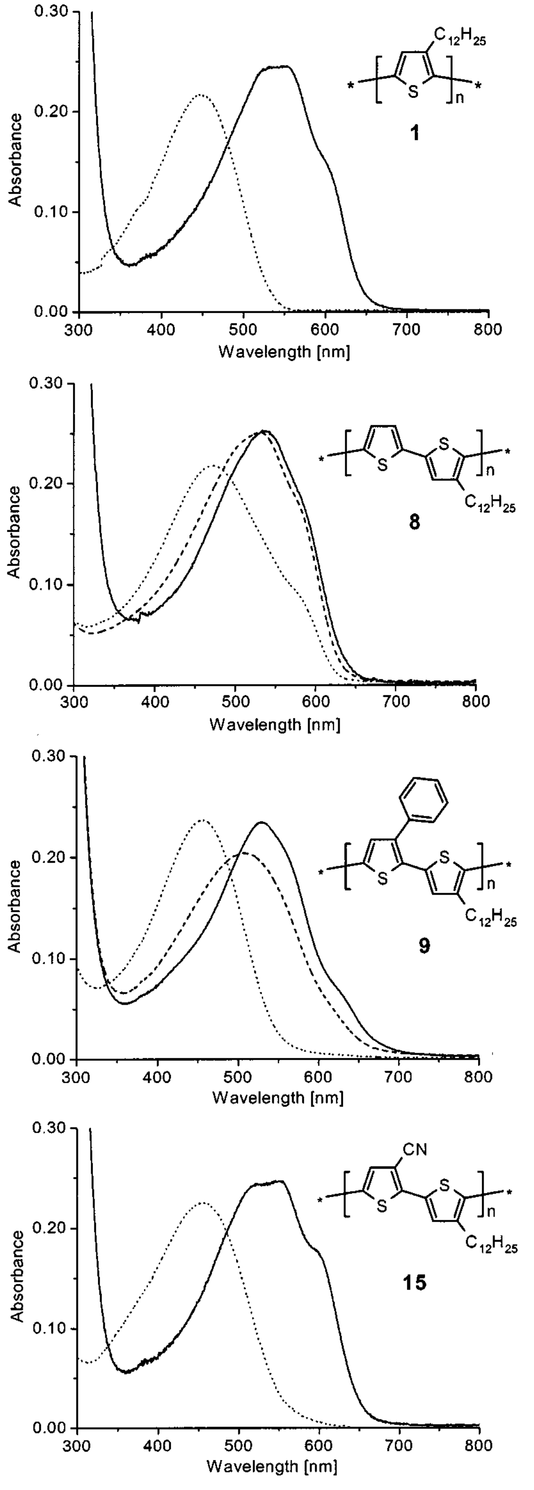


Figure 3. UV/Vis spectra of **1**, **8**, **9** and **15** in CHCl$_3$ solution (dotted lines) and as thin spin cast films on glass substrates (full lines)

regular fashion along the backbone, going from **1** to **8**, the first oxidation wave is increased by 0.10 V. When a phenyl group is introduced as the alternating substituent in **9**, an increase in E_{pa}^{ox} of 0.30 V relative to **1** is observed. As expected, the strongest effect on E_{pa}^{ox} is observed when the electron-withdrawing cyano group is introduced, as in **15**. Here E_{pa}^{ox} increases to 1.25 V and is hence shifted by 0.49 V relative to **1**. The anodic peak potentials of the first reduction wave (E_{pa}^{red}) of the polymers shift in the same direction. Although the reduction of **1** occurs below −1.95 V, i.e. outside the electrochemical window of acetonitrile, and could not be determined, the anodic peak potentials of **8**, **9**, and **15**, are observed at −1.83, −1.75, and −1.44 V, respectively. The electrochemical band gap ($E_g = E_{pa}^{ox} - E_{pa}^{red}$) remains essentially constant at $E_g = 2.74 \pm 0.05$ V as a result of the shifts of both the first oxidation and first reduction potentials. The almost constant value of the electrochemical band gap corroborates with the small changes in the optical band gaps (Table 1)

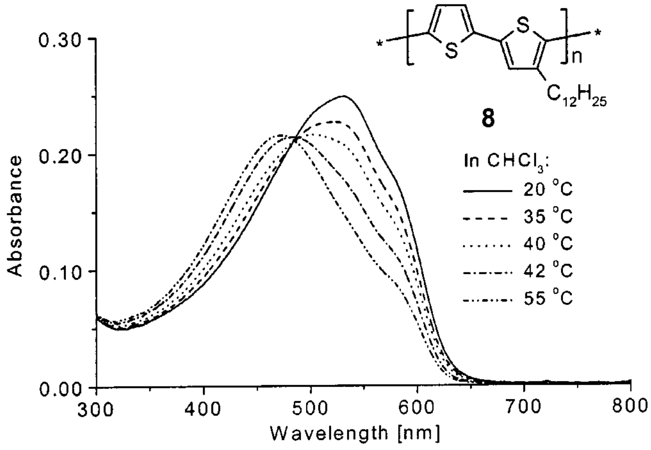


Figure 4. Variable temperature UV/Vis spectra of **8** in CHCl$_3$

Conclusion

In conclusion we have presented the synthesis and characterisation of three novel polythiophenes. The properties of these along with **1** are summarised in Table 1.

By varying the nature of the substituent on the backbone of polythiophenes the first oxidation potential can be increased by almost 0.50 V. A simple substitution of every second dodecyl chain with hydrogen (compare **1** and **8**) already results in an increase of E_{pa}^{ox} by 0.10 V, while the introduction of a cyano group as in **15**, shifts E_{pa}^{ox} by 0.49 V relative to **1**. While the differences in oxidation potential are significant, the electrochemical band gap remains more or less constant because the reduction potential increases along with the oxidation potential. The optical band gap is less than the electrochemical band gaps, but remains essentially constant for the four polymers described in this study. As a result we have obtained a series of materials in which the band gap remains constant while the electronic levels of the highest occupied molecular orbitals and lowest unoccupied molecular orbitals can be varied over 0.5 eV.

Table 1. Summary of properties of polymers **1**, **8**, **9** and **15**

Polymer	M_w [a] [g/mol]	PDI	DP[b]	$CHCl_3$ λ [nm]	Peak maximum film λ [nm]	E_g [c] [eV]	Peak onset film λ [nm]	E_g [d] [eV]	E_{pa}^{ox} [e] [V]	E_{pa}^{red} [e] [V]	E_g [f] [eV]
1	29,600	1.4	85	450	553	2.24	648	1.91	0.76	<−1.95	>2.71
8	[g]	[g]	[g]	450[h]	537	2.31	640	1.94	0.86	−1.83	2.69
9	22,600	1.3	86	450	530	2.34	675	1.84	1.06	−1.73	2.79
15	4,600	1.6	16	450	552	2.25	653	1.90	1.25	−1.44	2.69

[a] SEC relative to polystyrene standard. – [b] Number average degree of polymerisation calculated as number of thiophene units. – [c] Optical band gap E_g from absorption maximum. – [d] Optical band gap E_g from absorption onset. – [e] Anodic peak potential in the cyclic voltammogram of a thin spin-cast film on a Pt electrode vs. SCE in a 0.1 M TBA-PF$_6$ acetonitrile electrolyte. – [f] Electrochemical band gap $E_g = E_{pa}^{ox} - E_{pa}^{red}$. – [g] Strong aggregation excluded analysis with SEC. – [h] At 55 °C.

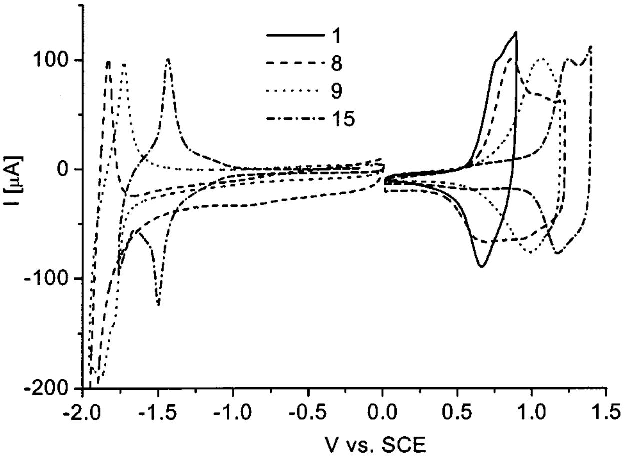


Figure 5. Cyclic voltammograms of **1**, **8**, **9** and **15** as thin films on a Pt electrode vs. SCE immersed in acetonitrile containing 0.1 M TBA-PF$_6$

Experimental Section

General: All solvents used were of AR grade, except for THF, which was distilled from Na-K alloy prior to use. All reactions involving organometallic reagents were conducted in oven-dried glassware under an Ar atmosphere. Regioregular poly(3-dodecylthiophene) (**1**) was synthesised according to the metathesis method described by McCullough[8] and was 98% regioregular as inferred from ^1H NMR spectroscopy. 3-Dodecylthiophene (**2**), 2-iodothiophene, 3-cyanothiophene (**10**) and all other reagents were obtained from commercial sources, except for 2-bromo-3-phenylthiophene, which was prepared according to a literature procedure.[9] ^1H and ^{13}C NMR spectra were recorded on either a Varian Gemini 300 or a Varian Mercury 400 instrument with $CDCl_3$, [D$_8$]toluene or 1,1,2,2-[D$_2$]tetrachloroethane as solvents and tetramethylsilane as internal standard (δ = 0). Absorption spectra were obtained using a Perkin–Elmer Lambda 40 UV/Vis spectrometer. Mass spectrometry (MS) analyses were performed on a Shimadzu GCMS-QP5000 instrument. Cyclic voltammograms were measured on drop-cast films of the polymers on the working electrode in CH_3CN with 0.1 M tetrabutylammonium hexafluorophosphate (TBA-PF$_6$) as supporting electrolyte using a Potentioscan Wenking POS73 potentiostat. The working electrode was a platinum disc (0.2 cm^2), the counter electrode was a platinum plate (0.5 cm^2) and a saturated calomel electrode was used as the reference. Size exclusion chromatography (SEC) was performed using a Plgel 5μ 500Å column, calibrated against polystyrene standards, in chloroform with UV detection at 254 nm.

4-Dodecyl-[2,2′]-bithiophene (4): Diisopropylamine (2.53 g, 25 mmol) was added dropwise to a solution of BuLi (13.8 mL, 22 mmol) in THF (50 mL) cooled to −40 °C. After stirring for 30 min. 3-dodecylthiophene (5.0 g, 20 mmol) in THF (5 mL) was added dropwise. The suspension was stirred at −78 °C for 1 h and then $ZnCl_2$ (3.2 g, 25 mmol) in THF (50 mL) was added dropwise. The mixture was allowed to reach room temperature and then transferred to a solution of 2-iodothiophene (4.62 g, 22 mmol) and [NiCl$_2$(dppp)] (100 mg, 1 mol %) in THF (25 mL). After stirring overnight at room temperature the reaction mixture was poured into water (150 mL) and extracted with hexane (3 × 100 mL). The combined organic phases were washed with water (100 mL), and brine and dried over Na_2SO_4. After filtration and evaporation of the solvent in vacuum Kugelrohr distillation (210 °C/0.015 mbar) gave **4** (4.55 g, 68%). – ^1H NMR (400.2 MHz, $CDCl_3$): δ = 7.18 (dd, J_1 = 5.13 Hz, J_2 = 1.10 Hz, 1 H, Th), 7.14 (dd, J_1 = 3.66 Hz, J_2 = 1.10 Hz, 1 H, Th), 7.01 (d, J = 1.47 Hz, 1 H, Th) 6.99 (dd, J_1 = 5.13 Hz, J_2 = 3.66 Hz, 1 H, Th), 6.79 (m, 1 H, Th), 2.57 (t, J = 7.69 Hz, 2 H, Th-C*H*$_2$-CH$_2$-), 1.65–1.58 (m, 2 H, Th-CH$_2$C*H*$_2$-), 1.40–1.20 (m, 18 H, -(C*H*$_2$)$_9$-), 0.88 (t, J = 6.59 Hz, 3 H, -CH$_2$C*H*$_3$). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 144.3, 138.1, 137.2, 127.9, 125.4, 124.3, 123.6, 119.2 (Th-Th), 32.2 (Th-*C*H$_2$-), 30.5, 30.6, 29.9, 29.9, 29.9, 29.8, 29.7, 29.6, 29.5 [signals from -(*C*H$_2$)$_9$-], 22.9 (*C*H$_2$CH$_3$), 14.4 (CH$_2$*C*H$_3$). – MS: *m*/*z* (%) = 334 (12), 193 (17), 180 (100). – $C_{20}H_{30}S_2$ (334.59): calcd. C 71.79, H 9.04; found C 71.98, H 9.17.

5-Bromo-4-dodecyl-[2,2′]-bithiophene (5): *N*-Bromosuccinimide (1.45 g, 8.70 mmol) was added in small portions to **4** (2.90 g, 8.67 mmol) in THF (10 mL) and the reaction mixture was left stirring overnight. After removal of the solvent in vacuum the residue was treated with hexane (50 mL) and filtered. The succinimide was washed with hexane (2 × 20 mL) and the hexane fractions were combined. Removal of the solvent in vacuum gave a yellow oil which was purified by column chromatography (silica/hexane) to give **5** (2.01 g, 56%). – ^1H NMR (300.1 MHz, $CDCl_3$): δ = 7.21 (dd, J_1 = 4.95 Hz, J_2 = 1.10 Hz, 1 H, Th), 7.10 (dd, J_1 = 3.57 Hz, J_2 = 1.10 Hz, 1 H, Th), 7.00 (dd, J_1 = 4.97 Hz, J_2 = 3.58 Hz, 1 H, Th), 6.88 (s, 1 H, Th), 2.56 (t, J = 7.42 Hz, 2 H, Th-C*H*$_2$-), 1.65–1.60 (m, 2 H, Th-CH$_2$C*H*$_2$-), 1.45–1.25 [m, 18 H, -(C*H*$_2$)$_9$-], 0.93 (t, J = 6.32 Hz, 3 H, -CH$_2$C*H*$_3$). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 142.9, 136.9, 127.9, 124.6, 124.6, 123.8, 107.7 (Th-Th), 32.1 (Th-*C*H$_2$-), 29.8–29.4 [multiple signals from -(*C*H$_2$)$_9$-], 22.9 (*C*H$_2$CH$_3$), 14.3 (CH$_2$*C*H$_3$). – MS: *m*/*z* (%) = 414 (9), 333 (12)

179 (100). − $C_{20}H_{29}BrS_2$ (413.49): calcd. C 58.10, H 7.07; found C 58.02, H 7.01.

4′-Dodecyl-3-phenyl-[2,2′]-bithiophene (6): Diisopropylamine (2.53 g, 25 mmol) was added dropwise to a solution of BuLi (13.8 mL, 22 mmol) in THF (50 mL) cooled to −40 °C. After stirring for 30 min. 3-dodecylthiophene (5.0 g, 20 mmol) in THF (5 mL) was added dropwise. The suspension was stirred at −78 °C for 1 h and then $ZnCl_2$ (3.2 g, 25 mmol) in THF (50 mL) was added dropwise. The mixture was allowed to reach room temperature and then transferred to a solution of 2-bromo-3-phenylthiophene (4.78 g, 22 mmol) and [$NiCl_2$(dppp)] (100 mg, 1 mol %) in THF (25 mL). After stirring overnight at 60 °C the reaction mixture was poured into water (150 mL) and extracted with hexane (3 × 100 mL). The combined organic phases were washed with water (100 mL), and brine and dried over Na_2SO_4. After filtration and concentration the solution was filtered through a short column of silica gel. The solvent was removed in vacuum and the oil was purified by column chromatography (silica/hexane) to give **6** (6.0 g, 73%). − ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 7.40−7.30 (m, 5 H, Ar), 7.19 (d, *J* = 5.22 Hz, 1 H, Th), 7.03 (d, *J* = 5.22 Hz, 1 H, Th), 6.78 (d, *J* = 1.38 Hz, 1 H, Th), 6.73 (m, 1 H, Th), 2.47 (t, *J* = 7.42 Hz, 2 H, Th-CH_2CH$_2$-), 1.58−1.46 (m, 2 H, Th-CH$_2$CH_2-), 1.38−1.25 (m, 18 H, -(CH_2)$_9$-), 0.88 (t, *J* = 6.32 Hz, 3 H, -CH$_2$CH_3). − MS: *m*/*z* (%) = 410 (29), 269 (15), 256 (100). − $C_{26}H_{34}S_2$ (410.69): calcd. C 76.04, H 8.34; found C 76.37, H 8.42.

5′-Bromo-4′-dodecyl-3-phenyl-[2,2′]-bithiophene (7): *N*-Bromosuccinimide (1.75 g, 9.75 mmol) was added in small portions to **6** (4.0 g, 9.74 mmol) in THF (20 mL) and the reaction mixture was left stirring overnight. After removal of the solvent in vacuum the residue was treated with hexane (100 mL) and filtered. The succinimide was washed with hexane (2 × 50 mL) and the hexane fractions were combined. Removal of the solvent in vacuum gave a yellow oil which were purified by column chromatography (silica/hexane) to give **7** (2.5 g, 52%). − ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 7.42−7.36 (m, 5 H, Ar), 7.28 (d, *J* = 5.22 Hz, 1 H, Th), 7.10 (d, *J* = 5.22 Hz, 1 H, Th), 6.70 (s, 1 H, Th), 2.49 (t, *J* = 7.42 Hz, 2 H, Th-CH_2-), 1.56−1.53 (m, 2 H, Th-CH$_2$CH_2-), 1.40−1.22 [m, 18 H, -(CH_2)$_9$-], 0.89 (t, *J* = 6.32 Hz, 3 H, -CH$_2$CH_3). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 142.4, 139.4, 136.2, 135.7, 131.4, 130.8, 129.5, 128.7, 127.8, 127.7, 127.6, 124.4, 109.3 (Th-Th-Ar), 32.2 (Th-*C*H$_2$-), 29.9−29.4 [multiple signals from -(*C*H$_2$)$_9$-], 22.9 (*C*H$_2$CH$_3$), 14.4 (CH$_2$*C*H$_3$). − MS: *m*/*z* (%) = 490 (26), 295 (8), 255 (100). − $C_{26}H_{33}BrS_2$ (489.58): calcd. C 63.79, H 6.79; found C 64.10, H 6.93.

Poly(4-dodecyl-[2,2′]-bithiophene) (8): Diisopropylamine (0.50 mL, 3.50 mmol) was added dropwise to a solution of BuLi (2.10 mL, 3.36 mmol) in THF (30 mL) cooled to −40 °C. After stirring for 30 min. at −40 °C the solution was cooled to −78 °C followed by dropwise addition of **5** (1.33 g, 3.22 mmol) in THF (5 mL) while maintaining the temperature below −70 °C. The mixture was then stirred at −78 °C for 1 h. $MgBr_2{\cdot}Et_2O$ (0.86 g, 3.30 mmol) was added and the resulting white slurry was stirred at −60 °C for 30 min. followed by stirring for 30 min. at −40 °C. The mixture was allowed to warm to 0 °C at which point [$NiCl_2$(dppp)] (8.7 mg, 0.5 mol %) was added. After stirring for 16 h at room temperature another portion of [$NiCl_2$(dppp)] (8.7 mg, 0.5 mol %) was added, followed by stirring at room temperature for 8 h. The deep-magenta coloured solution was poured into MeOH (300 mL), filtered and washed with MeOH (3 × 100 mL), water (3 × 100 mL) and then again with MeOH (3 × 100 mL). The polymer was purified by Soxhlet extractions (MeOH, hexane, CH_2Cl_2, $CHCl_3$). The chloroform fraction was concentrated and dried in vacuum, followed by addition of MeOH. The polymer **8** was isolated as violet flakes (260 mg, 25%). − ^{1}H NMR (300.1 MHz, [D$_8$]toluene, 80 °C): δ = 6.84 (broad s, 1 H, Th), 6.74 (broad m, 2 H, Th), 2.53 (broad m, 2 H, Th-CH_2-), 1.50−0.90 [broad m, 20 H, -(CH_2)$_{10}$-], 0.80−0.60 (broad m, 3 H, -CH$_3$).

Poly(4′-dodecyl-3-phenyl-[2,2′]-bithiophene) (9): Diisopropylamine (0.66 mL, 4.72 mmol) was added dropwise to a solution of BuLi (2.8 mL, 4.50 mmol) in THF (30 mL) cooled to −40 °C. After stirring for 30 min. at −40 °C the solution was cooled to −78 °C followed by dropwise addition of **7** (2.10 g, 4.30 mmol) in THF (10 mL) while maintaining the temperature below −70 °C. The mixture was then stirred at −78 °C for 1 h. Then $MgBr_2{\cdot}Et_2O$ (1.16 g, 4.5 mmol) was added and the resulting white slurry stirred at −60 °C for 30 min. followed by stirring for 30 min. at −40 °C. The mixture was allowed to warm to 0 °C at which point [$NiCl_2$(dppp)] (12.0 mg, 0.5 mol %) was added. After stirring for 16 h at room temperature another portion of [$NiCl_2$(dppp)] (12.0 mg, 0.5 mol %) was added, followed by stirring at room temperature for 10 h. The deep red coloured solution was poured into MeOH (300 mL), filtered and washed with MeOH (3 × 100 mL), water (3 × 100 mL) and then again with MeOH (3 × 100 mL). The polymer was purified by Soxhlet extractions (MeOH, hexane, CH_2Cl_2, $CHCl_3$). The chloroform fraction was concentrated and dried in vacuum followed by addition of MeOH. The polymer **9** was isolated as violet flakes (400 mg, 22%). − ^{1}H NMR (400.2 MHz, 1,1,2,2-[D$_2$]tetrachloroethane, 50 °C): δ = 7.52−7.36 (m, 5 H, Ar), 7.03 (s, 1 H, Th), 6.80 (s, 1 H, Th), 2.74 (t, *J* = 6.59 Hz, 2 H, Th-CH_2CH$_2$-), 1.68−1.55 (m, 2 H, Th-CH$_2$CH_2-), 1.45−1.25 [m, 18 H, -(CH_2)$_9$-], 0.90 (t, *J* = 6.96 Hz, 3 H, -CH$_2$CH_3). − ^{13}C NMR (100.6 MHz, 1,1,2,2-[D$_2$]tetrachloroethane, 50 °C): δ = 141.6, 140.6, 137.2, 135.5, 134.9, 132.3, 131.7, 130.9, 130.7, 130.4, 130.1, 129.6 (Th-Th-Ar), 33.4 (Th-*C*H$_2$-), 31.7−30.0 [multiple signals from -(*C*H$_2$)$_9$-], 24.2 (*C*H$_2$CH$_3$), 15.7 (CH$_2$*C*H$_3$). − SEC: M_w = 22600 g/mol with PDI = 1.3.

4-Dodecyl-2-iodothiophene (10): Diisopropylamine (2.53 g, 25 mmol) was added dropwise to a solution of BuLi (15.6 mL, 25 mmol) in THF (50 mL) cooled to −40 °C. After stirring for 30 min. at −40 °C the solution was cooled to −78 °C followed by dropwise addition of **2** (5.0 g, 20 mmol) in THF (5 mL) while maintaining the temperature below −70 °C. The mixture was then stirred at −78 °C for 1 h. Then $MgBr_2{\cdot}Et_2O$ (6.45 g, 25 mmol) was added and the resulting white slurry was allowed to warm to 0 °C and stirred at this temperature for a few minutes. After recooling to −78 °C, I_2 (6.35 g, 25 mmol) in THF (30 mL) was added dropwise, the mixture was allowed to reach room temperature and stirred for 1 h. After quenching with water (150 mL) and standard workup, purification was done by a simple filtration through a short column (silica/hexane) to give **10** (6.61 g, 87%). The pale yellow oil obtained consisted of 97% of the desired 2,4-isomer **10** and 3% of the 2,3-isomer as inferred from GC-MS and ^{1}H NMR spectroscopy. − ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 1.65 Hz, 1 H, Th), 6.96 (m, 1 H, Th), 2.62 (t, *J* = 7.7 Hz, 2 H, Th-CH_2-), 1.65−1.60 (m, 2 H, Th-CH$_2$-CH_2-), 1.35−1.25 [m, 18 H, -(CH_2)$_9$-], 0.94 (t, *J* = 6.3 Hz, 3 H, -CH$_2$CH_3). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 145.3, 138.1, 126.1 (Th), 72.9 (*C*-I), 32.1 (Th-*C*H$_2$-), 30.5−29.4 [multiple signals from -(*C*H$_2$)$_9$-], 22.9 (*C*H$_2$CH$_3$), 14.3 (CH$_2$*C*H$_3$). − MS: *m*/*z* (%) = 378 (6), 237 (6), 251 (5), 224 (100). − $C_{16}H_{27}IS$ (378.36): calcd. C 50.79, H 7.19; found C 50.60, H 7.24.

3-Cyano-4′-dodecyl-[2,2′]-bithiophene (13): Diisopropylamine (2.23 g, 22 mmol) was added dropwise to a solution of BuLi (13.0 mL, 21 mmol) in THF (30 mL) cooled to −40 °C. After stirring for 30 min. at −40 °C the solution was cooled to −78 °C followed by dropwise addition of **11** (2.18 g, 20 mmol) while maintaining the temperature below −70 °C. The mixture was then stirred at −78 °C for 1 h. Then $ZnCl_2$ (3.0 g, 22 mmol) was added and, after stirring for 30 min. at −78 °C, the mixture was allowed to warm slowly to room temperature where it was stirred for 30 min. The clear yellow solution was then added dropwise to a mixture of **10** (6.5 g, 17.2 mmol) and [$NiCl_2$(dppp)] (108 mg, 1 mol %) in THF (30 mL). After refluxing for 6 h the mixture was cooled to room temperature, poured into water (200 mL) and extracted with Et_2O (3 × 100 mL). The combined organic phases were washed with water (100 mL), brine (100 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvent in vacuum purification was performed by column chromatography (silica, hexane/CH_2Cl_2 1:1) to give **13** (2.0 g, 33%). − ^{1}H NMR (400.2 MHz, $CDCl_3$): δ = 7.43 (m, 1 H, Th), 7.17 (m, 2 H, Th), 6.99 (m, 1 H, Th), 2.61 (t, J = 7.69 Hz, 2 H, Th-CH_2-), 1.65−1.61 (m, 2 H, Th-CH_2CH_2-),1.32−1.26 [m, 18 H, -(CH_2)$_9$-], 0.88 (t, J = 6.59 Hz, 3 H, -CH_2CH_3). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 147.5, 144.9, 132.9, 130.2, 128.7, 124.5, 122.6, 115.9, 105.1 (Th-Th-*C*N), 32.2 (Th-*C*H_2-), 30.6−29.5 [multiple signals from -(*C*H_2)$_9$-], 22.9 (*C*$H_2$$CH_3$), 14.4 ($CH_2$*C*$H_3$). − MS: m/z (%) = 359 (10), 218 (13), 205 (100).

5′-Bromo-3-cyano-4′-dodecyl-[2,2′]-bithiophene (14): *N*-Bromosuccinimide (0.90 g, 5.2 mmol) was added in portions to **13** (1.80 g, 5.0 mmol) in THF (10 mL) and the reaction mixture was left stirring overnight. After removal of the solvent in vacuum the residue was treated with hexane (30 mL) and filtered. The succinimide was washed with hexane (3 × 15 mL) and the hexane fractions combined. Removal of the solvent in vacuum gave a yellow solid which was purified by column chromatography (silica, hexane/CH_2Cl_2 1:3) to give **14** (1.6 g, 73%). − ^{1}H NMR (400.2 MHz, $CDCl_3$): δ = 7.27 (s, 1 H, Th), 7.22 (d, J = 5.49 Hz, 1 H, Th), 7.19 (d, J = 5.49 Hz, 1 H, Th), 2.57 (t, J = 7.69 Hz, 2 H, Th-CH_2-), 1.62−1.55 (m, 2 H, Th-CH_2CH_2-), 1.32−1.26 [m, 18 H, -(CH_2)$_9$-], 0.88 (t, J = 6.60 Hz, 3 H, -CH_2CH_3). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 146.3, 143.8, 132.7, 130.3, 128.2, 124.9, 115.7, 112.0, 105.4 (Th-Th-*C*N), 32.1 (Th-*C*H_2-), 29.9−29.4 [multiple signals from -(*C*H_2)$_9$-], 22.9 (*C*$H_2$$CH_3$), 14.3 ($CH_2$*C*$H_3$). − MS: m/z (%) = 438 (7), 204 (100). − $C_{21}H_{28}BrNS_2$ (438.50): calcd. C 57.52, H 6.44; found C 57.64, H 6.38.

Poly(3-cyano-4′-dodecyl-[2,2′]-bithiophene) (15): Diisopropylamine (0.22 g, 2.1 mmol) was added dropwise to a solution of BuLi (1.2 mL, 1.9 mmol) in THF (20 mL) cooled to −40 °C. After stirring for 30 min. at −40 °C the solution was cooled to −78 °C followed by dropwise addition of **14** (0.77 g, 1.75 mmol) in THF (10 mL) while maintaining the temperature below −70 °C. The mixture was then stirred at −78 °C for 1 h. Then $ZnCl_2$ (0.29 g, 2.1 mmol) was added and the resulting mixture stirred at −60 °C for 30 min. followed by stirring for 30 min. at −40 °C. The mixture was allowed to warm to 0 °C at which point [$NiCl_2$(dppp)] (4.7 mg, 0.5 mol %) was added. After stirring for 20 h at room temperature another portion of [$NiCl_2$(dppp)] (4.7 mg, 0.5 mol %) was added, followed by stirring at room temperature for 8 h. The deep-red coloured solution was poured into MeOH (200 mL), filtered and washed with MeOH (3 × 50 mL), water (3 × 50 mL) and then again with MeOH (3 × 50 mL). The polymer was purified by Soxhlet extractions (MeOH, hexane, CH_2Cl_2, $CHCl_3$). The chloroform fraction was concentrated and dried in vacuum followed by addition of MeOH. Polymer **15** was isolated as a violet film (170 mg, 27%). − ^{1}H NMR (300.1 MHz, 1,1,2,2-[D_2]tetrachloroethane, 60 °C): δ = 7.54 (s, 1 H, Th), 7.33 (s, 1 H, Th), 2.85−2.80 (m, 2 H, Th-CH_2-), 1.84−1.64 (m, 2 H, Th-CH_2CH_2-), 1.58−1.22 [m, 18 H, -(CH_2)$_9$-], 1.00−0.86 (m, 3 H, -CH_2CH_3). − SEC: M_w = 4600 g/mol with PDI = 1.6.

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