DOI: 10.1002/masy.201000042

Synthesis and Characterization of Hexathiophenes with Methylthienyl Side Chains

*Geeta Saini, Josemon Jacob**

Summary: Two novel conjugated isomeric hexathiophenes **6T1** and **6T2** bearing 5-methyl-2-thienyl substituents have been synthesized by Suzuki coupling and oxidative dimerization method. These isomers were characterized by ^{1}H NMR, ^{13}C NMR, elemental and mass analysis. The two hexamers show good solubility in common solvents and show almost identical UV-vis absorption spectra in solution with a maximum cantered at 387 nm. These materials bearing thienyl substituents in the sidechain are anticipated to provide better charge transport in devices and hold promise for use in organic field effect transistors.

Keywords: conjugation; cross-coupling; Hexathiophenes; organic field effect transistors; UV-vis spectroscopy

Introduction

α-Conjugated oligo- and polythiophenes are the most promising candidates for applications in organic electronics.[1–3] Conjugated oligothiophenes constitute one of the most widely studied classes of organic semiconductors due to their potential applications in organic field effect transistors (OFETs).[4–9] It is well known that in the case of thiophene based materials, the electrical and optical properties are governed by the nature and type of substituents on the side chain. Several groups have investigated the synthesis and transistor characteristics of differently substituted oligothiophenes, particularly hexathiophenes.[5,10–14] These oligothiophenes besides serving as excellent candidate for transistors also act as model compounds for polymers to gain insight into the influence of substitution pattern on conjugation and packing.[15–18] Although both alkyl and aryl substituents have been investigated by different groups, the possibility of using thiophene based substituents to induce solubility has not been explored so far. Additionally, such molecules can provide additional charge transport pathways and thus lead to improved performance in transistor devices. Recently, we reported on the synthesis of tetrathiophenes bearing methylthiophene substituents with varying substitution pattern to understand the effect of such substitution on conjugation and band gap.[19] The present work deals with the synthesis and characterization of well defined isomeric methyl endcapped hexathiophenes bearing methylthienyl side chains with varying substitution pattern. The substitution pattern for the two isomers reported here are HT-TT-HT and TT-HH-TT (where H = head and T = tail).

The structures of the two substituted hexamers reported in this study along with the synthetic approach are shown in Scheme 1. These oligomers were synthesized either by a Pd catalyzed cross-coupling reaction or by oxidative coupling using a hypervalent iodine (III) reagent.[20] To synthesize **6T1** the boronate ester of **1** was Suzuki coupled with bromo compound **3** (for detailed synthesis of **1-3** see reference 19) in DME with 2 mol% catalyst to give **4** in 50% isolated yield. Oxidative dimerization of **4** using a combination of phenyl iodide

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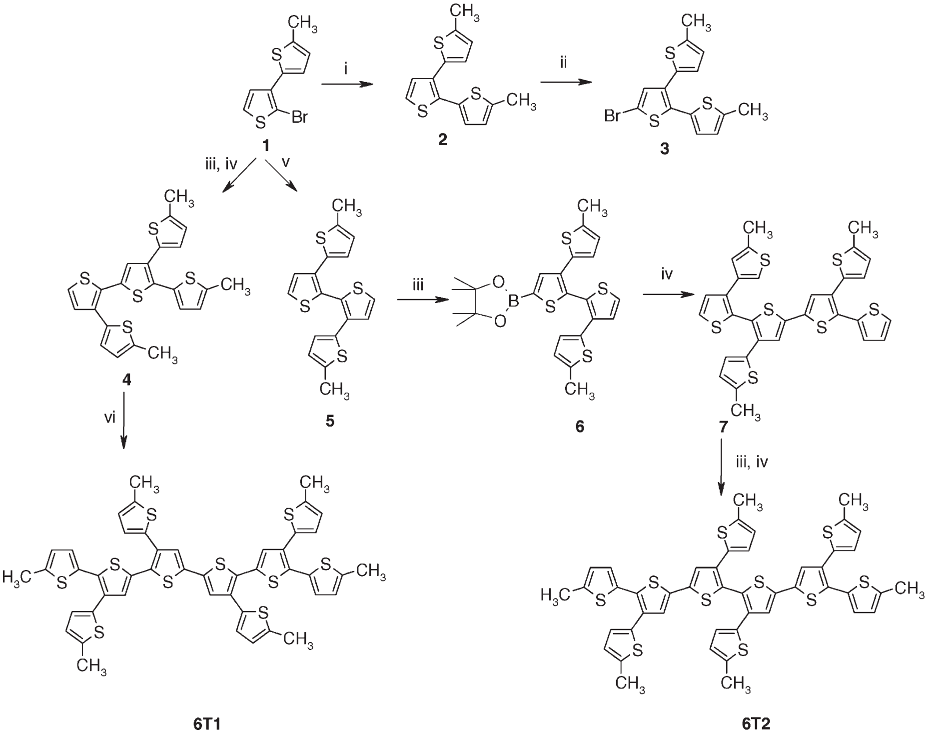
Centre for Polymer Science and Engineering, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India
Fax: 91 11 26591421;
E-mail: jacob@polymers.iitd.ac.in



Scheme 1.

Synthesis of hexamers. Reagents and conditions: i). 5-methyl-2-thiopheneboronic acid, $Pd(PPh_3)_4$, DME/2M Na_2CO_3; ii) NBS, $CHCl_3$ iii) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; iv) **3**, $Pd(PPh_3)_4$, DME/2M Na_2CO_3; v) Mg, $Ni(dppp)Cl_2$; THF; vi) PIFA, $BF_3.OEt_2$, DCM.

bis(trifluoroacetate) (PIFA) and boron trifluoride diethyl etherate ($BF_3.OEt_2$) gave **6T1** in 40% isolated yield.

To synthesize **6T2**, the dimer **5** was first synthesized from **1** by Kumada type cross coupling reaction in presence of $Ni(dppp)Cl_2$ in 52% yield.[21] **6** was prepared in 57% yield by lithiation of **5** using *n*-butyl lithium (*n*-BuLi) followed by reaction of the generated anion with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The boronate ester **6** was Suzuki coupled with bromo compound **3** to generate intermediate **7** in 66% yield. **7** was functionalized by reaction with *n*-BuLi followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to generate the corresponding boronate ester which was Suzuki coupled with **3** to give **6T2** in 42% yield. Both the hexathiophene isomers can also be recrystallized from THF and methanol. The hexathiophenes and the intermediates described above showed very good solubility in common organic solvents and were characterized by ^1H, ^{13}C NMR, elemental analysis, mass spectrometry, UV-vis absorption and emission spectroscopy.

Optical Properties

Figure 1 shows the absorption and emission spectra of hexathiophenes in dilute THF solution. The absorption maxima of **6T1** and **6T2** in solution appear at 385 and 387 nm, respectively. The observed absorption maxima values are less than the α-linked alkylsubstituted hexathiophenes reported previously[2,22] suggesting that there is less effective conjugation along the chain possibly arising from steric effects

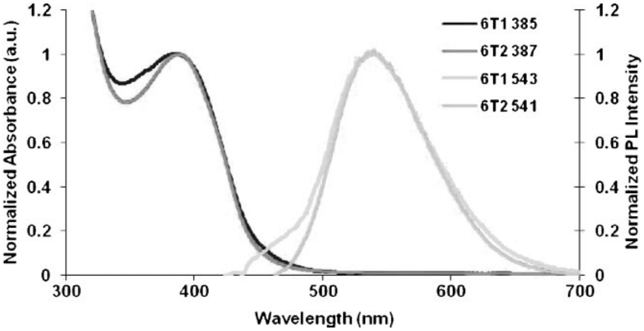


Figure 1.
UV-vis absorption and emission spectra of **6T1** and **6T2** in THF solution.

of the substitutents. Infact, the observed absorption maxima are very close to that of tetrathiophenes reported previously suggesting that the chromophore in both the molecules is restricted to four thiophene units. **6T1** and **6T2** have emission maxima at 541 and 543 nm, corresponding to a Stokes shift of 148 and 154 nm, respectively. The observed large Stokes shift for both the isomers can be attributed to their twisted structure in solution with a corresponding large change in conformation between ground and excited state.[23]

Experimental Part

All chemicals were used as supplied. Dry solvents stored in a glove box were used for all reactions expect for the Suzuki couplings. Reactions were performed in flame dried flasks under a nitrogen atmosphere. NMR experiments were measured on a Bruker 300 MHz spectrometer (^{1}H NMR at 300 MHz; ^{13}C NMR at 75 MHz) in $CDCl_3$ with TMS as internal standard, or Varian 400-MR spectrometer (^{1}H NMR at 400 MHz; ^{13}C NMR at 100 MHz) in $CDCl_3$ ($CHCl_3$ 7.26 ppm; $CDCl_3$ 77.16 ppm).

Synthesis

5,5‴-Dimethyl-3′-(methylthienyl)-[2,2′;5′,2″;3″,2‴] quaterthiophene (4)

n-Butyl lithium in hexane (4.34 mL, 1.6 M, 6.94 mmol) was added to a solution of **1** (1.5 g, 5.79 mmol) in dry THF (20 mL) in a Schlenk flask at −78 °C and the mixture was stirred for 20 min. 2-Isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (1.4 mL, 1.3 g, 6.94 mmol) was added, and the reaction was stirred overnight. The reaction was then quenched with saturated salt, and the product was extracted with diethyl ether, and the extract was washed with brine and dried over Na_2SO_4. After removal of solvent the crude product was used as such in the next step. The bromo compound **3** (325 mg, 0.915 mmol), the boronate ester (335 mg, 1.09 mmol) and Na_2CO_3 (193 mg, 1.83 mmol) were dissolved in a mixture of DME (9 mL) and water (1 mL) in a Schlenk flask, and the mixture was purged with nitrogen for 20 mintues. To this was added tetrakis(-triphenylphosphine)palladium (21 mg) and the mixture was heated at 95 °C for 15 h. The cooled mixture was extracted with $CHCl_3$ and the extract was washed with brine and dried over Na_2SO_4. The residue was chromatographed on silica with 0–2% ethyl acetate in hexane as eluent to give the title compound as a yellow viscous liquid. Yield = 170 mg (48%). δ_H (300 MHz; $CDCl_3$) 7.29 (s, 1H), 7.14 (d, 2H), 6.97 (d, 1H), 6.93 (d, 1H), 6.92 (d, 1H), 6.8(overlapping peaks 3H), 2.4 (overlapping peaks, 9H); δ_C (75 MHz; $CDCl_3$) 141.43, 140.28, 140.02, 134.89, 134.64, 133.31, 132.4, 132.29, 131.67, 130.14, 129.89, 127.84 (2peaks), 126.82, 126.51, 126.32, 125.43, 125.37, 125.23, 124.41, 15.21; Elemental analysis:

Calcd: C, 61.05; H, 4.03 Found: C, 61.36; H, 4.00%.

5,5‴″-Dimethyl-3′,3″,4‴,4″″-tetra(methylthienyl)-[2,2′;5′,2″;5″,2‴;5‴,2″″;5″″,2‴″]hexathiophene (6T1)

$BF_3.OEt_2$ (0.2 mL, 1.54 mmol) and PIFA (0.935 mmol, 397 mg) were added sequentially to a stirred solution of **4** (0.77 mmol, 350 mg) in CH_2Cl_2 (10 mL) at −40 °C under nitrogen atmosphere. The reaction mixture was stirred at same temperature for 6 h. After that the reaction was quenched by saturated solution of $NaHCO_3$ (20 mL) and was extracted with CH_2Cl_2 and the combined organic layers were washed with water, and dried over anhydrous Na_2SO_4. After the evaporation of the solvent the crude product was chromatographed on silica with 0–2% ethyl acetate in hexane as eluent to give the title compound as a yellow solid. Yield = 279 mg (40%). δ_H (400 MHz; $CDCl_3$) 7.38 (s, 2H), 7.20 (s, 2H), 6.98 (J = 2.7 Hz, d, 2H), 6.91 (J = 2.7 Hz, d, 2H), 6.89 (J = 2.4 Hz, d, 2H), 6.68-6.66 (overlapping peaks 4H), 6.58 (J = 3.6 Hz, d, 2H), 2.47 (s, 12H), 2.39 (s, 6H); δ_C (100 MHz; $CDCl_3$) 141.78, 140.66, 140.48, 138.28, 137.49, 135.03, 134.75, 134.47, 132.54, 132.41, 130.30, 127.99, 126.92 (2 peaks), 125.67, 125.51 (2 peaks), 125.49, 124.83, 123.73, 15.57 (3 peaks); MS: Calcd. for $C_{46}H_{34}S_{10}$, 906, Found: 905.99; Elemental analysis: Calcd: C, 60.89; H, 3.78; Found: C, 60.19; H, 3.96%.

5,5″-dimethyl-[2,3′:2′,2″:3″,2‴]quaterthiophene 5

To a solution of **1** (2.5 g, 9.65 mmol) in dry THF (10 mL) was added Mg (104 mg, 4.34 mmol) and catalytic amount of I_2. The reaction mixture was refluxed for 1 h. When all the magnesium dissolved, the reaction mixture was diluted by adding 10 mL of dry THF and Ni(dppp)Cl_2 (52 mg) was added. After stirring for 16 h at 75 °C, the reaction mixture was quenched by 2N HCl. The reaction mixture was extracted with $CHCl_3$ and the extract was washed with brine and dried over Na_2SO_4. After the evaporation of the solvent the crude product was chromatographed on silica with 0–2% ethyl acetate in hexane as eluent to give the title compound as a white solid. Yield = 1.72 g (78%). δ_H (300 MHz; $CDCl_3$) 7.44 (J = 5.1 Hz, d, 2H), 7.34 (J = 5.4 Hz, d, 2H), 6.83 (J = 3.6 Hz, d, 2H), 6.55 (J = 2.4 Hz, d, 2H), 2.35 (s, 6H),;δ_C (75 MHz; $CDCl_3$) 139.86, 136.39, 135.47, 127.31 (2 peaks), 126.26, 125.15, 124.48, 15.21; MS: Calcd. for $C_{18}H_{14}S_4$, 358.57, Found: 359.02; Elemental analysis: Calcd: C, 60.30; H, 3.94; Found: C, 60.63; H, 4.02%.

3,3′-Di(5″-methyl-2″-thienyl)2,2′-bithienyl-4,4,5,5-tetramethyl-[1,32,]dioxaborolane 6

n-Butyl lithium in hexane (2 mL, 1.6 M, 3.35 mmol) was added to a solution of **5** (1 g, 2.79 mmol) in dry THF (10 mL) in a Schlenk flask at −78 °C and the mixture was stirred for 20 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.68 mL, 624 mg, 3.35 mmol) was added and the reaction was stirred for 24 h after warming to room temperature. The reaction was then quenched with brine, and the product was extracted with diethyl ether. The extract was washed with brine and dried over Na_2SO_4. The crude product was chromatographed on silica with 0–5% ethyl acetate in hexane as eluent to give the title compound as a viscous brown liquid. Yield = 700 mg (52%). δ_H (300 MHz; $CDCl_3$) 7.75 (s, 1H), 7.37 (J = 5.4 Hz, d, 1H), 7.24 (J = 5.4 Hz, d, 1H), 6.75 (J = 3.3 Hz, d, 1H), 6.69 (J = 3.6 Hz, d, 1H), 6.45 (overlapping peaks, 2H), 2.2 (s, 6H), 1.3 (s, 12H); δ_C (75 MHz; $CDCl_3$) 139.81, 137.65, 136.94, 136.04, 135.32, 133.39, 127.57, 127.21, 125.18 (2peaks), 124.88, 84.34, 24.78, 15.21; MS: Calcd. for $C_{24}H_{25}BO_2S_2$, 484.53, Found: 485.12; Elemental analysis: Calcd: C, 59.49; H, 5.20; Found: C, 59.63; H, 5.26%.

5,5″″-Dimethyl-3′,4″-di(5-methyl-2-thienyl)-[2,2′;5′,2″;5″,2‴;3‴,2‴;3‴,2″″] quinquethiophene 7

The bromo compound **3** (600 mg, 1.69 mmol), the boronate ester **6** (0.979 mg, 0.2 mmol) and Na_2CO_3 (359 mg, 3.38 mmol) were dissolved in a mixture of DME (10 mL) and water (1.6 mL) in a Schlenk flask, and the mixture was purged with nitrogen for 20 min. To this was added tetrakis(triphenylphosphine)palladium (40 mg) and the mixture was heated at 95 °C for 15 h. The cooled mixture was extracted with CHCl$_3$ and the extract was washed with brine and dried over Na$_2$SO$_4$. The residue was chromatographed on silica with 0–5% ethyl acetate in hexane as eluent to give the title compound as a yellow solid. Yield = 700 mg (66%). δ_H (300 MHz; CDCl$_3$) 7.45 (d, 1H), 7.38 (s, 1H), 7.33 (d, 1H), 7.19 (s, 1H), 6.96 (d, 1H), 6.98-6.88 (overlapping peaks 2H), 6.83 (d, 1H) 6.6 (overlapping peaks, 2H), 6.56 (overlapping peaks, 2H), 2.2 (s, 6H),; δ_C (75 MHz; CDCl$_3$) 141.54, 140.18 (3 peaks), 137.82, 137.10, 136.62, 135.01, 134.59, 134.37, 132.31, (2peaks), 131, 127.80, 127.46 (2 peaks), 126.73 (2 peaks), 125.81, 125.47,125.22 (5 peaks), 125, 123.49. 24.78, 15.21; MS: Calcd. for $C_{32}H_{24}S_7$, 484.53, Found: 485.12; Elemental analysis: Calcd: C, 60.72; H, 3.82; Found: C, 60.06; H, 4.00%.

5,5′′′′′-Dimethyl-3′,4′′,3′′′,4′′′′-tetra(5-methyl-2-thienyl)-[2,2′;5′,2′′;5′′,2′′′;5′′′,2′′′′;5′′′′,2′′′′′] hexathiophene (6T2)

n-Butyl lithium in hexane (0.89 mL, 1.6 M, 1.42 mmol) was added to a solution of **7** (0.450 g, 0.712 mmol) in dry THF (10 mL) in a Schlenk flask at −78 °C and the mixture was stirred for 20 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (264 mg, 0.29 mL 1.42 mmol) was added and the reaction was stirred for 24 h after warming to room temperature. The reaction was then quenched with brine, and the product was extracted with diethyl ether and the extract was washed with brine and dried over Na$_2$SO$_4$. The crude product (0.270 g, 0.356 mmol), the bromo compound **3** (105 mg, 0.29 mmol), and Na$_2$CO$_3$ (62 mg, 0.58 mmol) were dissolved in a mixture of DME (5 mL) and water (0.3 mL) in a Schlenk flask, and the mixture was purged with nitrogen for 20 min. To this was added tetrakis(triphenylphosphine)palladium (7 mg) and the mixture was heated at 95 °C for 15 h. The cooled mixture was extracted with CHCl$_3$ and the extract was washed with brine and dried over Na$_2$SO$_4$. The residue was chromatographed on silica with 0–5% ethyl acetate in hexane as eluent to give the title compound as a yellow solid. Yield = 112 mg (42%). δ_H (400 MHz; CDCl$_3$) 7.38 (s, 2H), 7.20 (s, 2H), 6.98 (J = 2.7 Hz, d, 2H), 6.91 (J = 2.7 Hz, d, 2H), 6.89 (J = 2.4 Hz, d, 2H), 6.68-6.66 (overlapping peaks 4H), 6.58 (J = 3.6 Hz, d, 2H), 2.47 (s, 12H), 2.39 (s, 6H); δ_C (100 MHz; CDCl$_3$) 141.78, 140.66, 140.48, 138.28, 137.49, 135.03, 134.75, 134.47, 132.54, 132.41, 130.30, 127.99, 126.92 (2 peaks), 125.67, 125.51 (2 peaks), 125.49, 124.83, 123.73, 15.57 (3 peaks); MS: Calcd. for $C_{46}H_{34}S_{10}$, 906, Found: 905.99; Elemental analysis: Calcd: C, 60.89; H, 3.78; Found: C, 60.95; H, 3.95%.

Conclusion

Two isomeric hexathiophenes **6T1** and **6T2** bearing 5-methyl-2-thienyl solubilising side chains have been synthesized and characterized. The two isomers only differ from each other on the positions of the side arm substituents. UV-vis spectroscopic studies show almost identical absorption maxima for the two isomers suggesting that the two possess near identical chromophores. Introduction of thiophene substituents on the side arm is anticipated to provide better inter chain charge transport pathways in devices and the testing of these materials are currently underway.

Acknowledgements: The present work was supported by Department of Science and Technology, New Delhi, India. G.S. acknowledges a research fellowship from Council for Scientific and Industrial Research (CSIR), New Delhi, India.

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