Synthesis, Electronic, and Morphological Properties of Tetrahedral Oligothiophenes with n-Hexyl Terminal Groups


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1. Synthetic procedures of the starting materials and H-TnTM (n=2, 3).

2-Hexylthiophene\[^{[S1]}\]
A solution of \(n\)-BuLi (1.43M hexane solution, 51.7 mL, 74 mmol) was added to a solution of thiophene (5.6 mL, 70 mmol) in anhydrous THF (40 mL) over 30 min below -60 °C under nitrogen. After the stirring at 0 °C for an hour 1-bromohexane (10.3 mL, 74 mmol) was added slowly below -60 °C. The reaction mixture was allowed to warm up to room temperature and stirred overnight. Water (100 mL) was added carefully with ice-water. The aqueous layer was extracted with ether (50 mL x 4). The combined organic layers was washed with water (100 mL x 2) and brine (100 mL), dried over anhydrous sodium sulfate. After the filtration and concentration the residue was purified by distillation under reduced pressure (90–95 °C, 10 mmHg) to give 2-hexylthiophene (7.27 g, 62%) as colorless liquid. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta=7.08\) (dd, \(J=5.0, 1.0\) Hz, 1H), 6.89 (dd, \(J=5.0, 3.5\) Hz, 1H), 6.76 (dq, \(J=3.5, 1.0\) Hz, 1H), 2.81 (td, \(J=7.5, 1.0\) Hz, 2H), 1.67 (quintet, \(J=7.5\) Hz, 2H), 1.39–1.26 (m, 6H), 0.89 ppm (t, \(J=7.0\) Hz, 3H).

2-Bromo-5-hexylthiophene\[^{[S2]}\]
N-Bromosuccinimide (7.56 g, 42.5 mmol) was added slowly to a solution of 2-hexylthiophene (7.15 g, 42.5 mmol) in DMF (25 mL) at room temperature under dark. Water (50 mL) was added after the reaction mixture was stirred overnight at room temperature. The reaction mixture was extracted with hexane/ethyl acetate (1:1 v/v, 100 mL) and the organic layer was washed with water (100 mL x 2) and brine (100 mL). The organic layer was dried over anhydrous sodium sulfate. After the filtration and concentration the residue was purified by column chromatography on silica gel eluted with hexane to give 2-bromo-5-hexylthiophene (10.45 g, 93%) as colorless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta=6.82\) (d, \(J=4.0\) Hz, 1H), 6.51 (d, \(J=4.0\) Hz, 1H), 2.72 (t, \(J=3.4\) Hz, 2H), 1.62 (quintet, \(J=3.4\) Hz, 2H), 1.36–1.26 (m, 6H), 0.88 ppm (t, \(J=7.0\) Hz, 3H).

5-Hexyl-2,2′-bithiophene\[^{[S3]}\]
A solution of 2-bromothiophene (5.25 g, 32.2 mmol) in anhydrous ether (30 mL) was added to a suspension of magnesium (817 mg, 32.2 mmol) with anhydrous ether (10 mL) over 20 min under nitrogen. The reaction mixture was heated to reflux for 4 hours to prepare the solution of 2-thienylmagnesium bromide. This freshly prepared ethereal solution of Grignard reagent was added dropwise to the suspension of 2-bromo-5-hexylthiophene (6.62 g, 26.8 mmol) and Ni(dppp)Cl\(_2\) (291 mg, 0.54 mmol) in anhydrous ether (50 mL) at room temperature under nitrogen. The reaction mixture was heated to reflux for 2 days. 1M HCl aq (40 mL) was added slowly at 0 °C and the aqueous layer was extracted with ether (250 mL x 2). The combined organic layers were washed with saturated sodium bicarbonate (100 mL x 2), water (100 mL x 3), and brine (100 mL), and then dried over anhydrous
sodium sulfate. After the filtration and concentration the residue was purified by column chromatography on silica gel eluted with hexane to give 5-hexyl-2,2'-bithiophene (5.5 g, 79%) as colorless solid. 1H NMR (500 MHz, CDCl₃): δ=7.14 (dd, J=5.0, 1.0 Hz, 1H), 7.08 (dd, J=3.5, 1.0 Hz, 1H), 6.97 (dd, J=5.0, 3.5 Hz, 1H), 6.96 (d, J=3.5 Hz, 1H), 2.77 (t, J=7.5 Hz, 2H), 1.67 (quintet, J=7.5 Hz, 2H), 1.40−1.29 (m, 6H), 0.88 ppm (t, J=7.0 Hz, 3H).

5-Bromo-2'-hexyl-2,2'-bithiophene[^54]  
N-Bromosuccinimide (1.92 g, 10.8 mmol) was added to a solution of 5-hexyl-2,2'-bithiophene (2.69 g, 10.8 mmol) in DMF (30 mL) at room temperature under dark. After the reaction mixture was stirred overnight at room temperature, water (50 mL) was added slowly. The reaction mixture was extracted with ethyl acetate (150 mL). The organic layer was washed with water (100 mL × 4) and brine (100 mL), and dried over anhydrous sodium sulfate. After the filtration and concentration the residue was purified by column chromatography on silica gel eluted with hexane to give 5-bromo-2'-hexyl-2,2'-bithiophene (3.42 g, 97%) as colorless solid. 1H NMR (500 MHz, CDCl₃): δ=6.93 (d, J=3.5 Hz, 1H), 6.90 (d, J=3.5 Hz, 1H), 6.82 (d, J=3.5 Hz, 1H), 6.66 (d, J=3.5 Hz, 1H), 2.77 (t, J=7.5 Hz, 2H), 1.66 (quintet, J=7.5 Hz, 2H), 1.40−1.27 (m, 6H), 0.89 ppm (t, J=7.0 Hz, 3H).

5-(Tributylstannyl)-2,2'-bithiophene[^55]  
A solution of n-BuLi (1.43M hexane solution, 18.5 mL, 26.4 mmol) was added to a solution of 2,2'-bithiophene (4.39 g, 26.4 mmol) in anhydrous THF (90 mL) over 10 min at −70 °C under nitrogen. The reaction mixture was stirred at −70 °C for 90 min and −20 °C at 30 min, tributyltin chloride (8.95 mL, 33 mmol) was added over 5 min at −70 °C. The reaction mixture was stirred at ambient temperature overnight. Water (100 mL) was added carefully at 0 °C, and the organic layer was extracted with hexane/ethyl acetate (1:1 v/v, 100 mL×3). The combined organic layers were washed with water (100 mL×2) and brine (100 mL), then dried over anhydrous sodium sulfate. After the filtration and concentration the residue was purified by column chromatography on alumina (basic, activity II–III) eluted with hexane to give a mixture of 2,2'-bithiophene, 5-(tributylstannyl)-2,2'-bithiophene, and 5,5'-(tributylstannyl)-2,2'-bithiophene (molar ratio; 8.78:14) as colorless liquid. This mixture was used in the next step without further purification. 1H NMR (400 MHz, CDCl₃): δ=7.28 (dd, J=3.6, 1.2 Hz, 1H), 7.16 (dd, J=4.8, 1.2 Hz, 1H), 7.16 (d, J=3.6 Hz, 1H), 7.05 (d, J=3.6 Hz, 1H), 6.99 (dd, J=4.8, 3.6 Hz, 1H), 1.61−1.54 (m, 6H), 1.39−1.30 (m, 6H), 1.14−1.09 (m, 6H), 0.90 ppm (t, J=7.2 Hz, 9H).

5-Hexyl-2,2':5',2''-terthiophene[^56]  
A mixture of 2-bromo-5-hexylthiophene (2.37 g, 9.6 mmol), 5-(tributylstannyl)-2,2'-bithiophene
(2.19 g, 4.8 mmol), and [Pd(PPh₃)₄] (440 mg, 0.36 mmol) in toluene (40 mL) was heated reflux overnight under nitrogen. After cooling water (50 mL) was added slowly and the aqueous layer was extracted with hexane/ethyl acetate (1:1 v/v, 50 mL x3). The combined organic layers were washed with water (100 mL x2) and brine (100 mL) and dried over anhydrous sodium sulfate. After the filtration and concentration the residue was purified by column chromatography on silica gel eluted with hexane/methylene chloride (90:10 v/v) to give 5-hexyl-2,2′:5′,2″-terthiophene (1.33 g, 83%) as yellow crystals. ¹H NMR (400 MHz, CDCl₃): δ= 7.19 (dd, J=5.2, 1.2 Hz, 1H), 7.15 (dd, J=3.6, 1.2 Hz, 1H), 7.05 (d, J=3.6 Hz, 1H), 7.00 (dd, J=5.2, 3.6 Hz, 1H), 6.98 (d, J=3.6 Hz, 1H), 6.97 (d, J=3.6 Hz, 1H), 6.67 (d, J=3.6 Hz, 1H), 2.79 (t, J=7.4 Hz, 2H), 1.68 (quintet, J=7.4 Hz, 2H), 1.40–1.29 (m, 6H), 0.90 ppm (t, J=7.2 Hz, 3H).

5-Bromo-5′-hexyl-2,2′:5′,2″-terthiophene

N-Bromosuccinimide (70 mg, 3.9 mmol) was added to a solution of 5-hexyl-2,2′:5′,2″-terthiophene (1.3 g, 3.9 mmol) in DMF (60 mL) at room temperature under dark. After the reaction mixture was stirred overnight at room temperature, water (50 mL) was added slowly. The reaction mixture was extracted with methylene chloride (100 mL x2). The combined organic layers were washed with 1M HCl (100 mL x2) and water (100 mL x2), and dried over anhydrous sodium sulfate. After the filtration and concentration the residue was purified by column chromatography on silica gel eluted with hexane/methylene chloride (97:3 v/v) to give 5-bromo-5′-hexyl-2,2′:5′,2″-terthiophene (1.37 g, 86%) as green solid. ¹H NMR (400 MHz, CDCl₃): δ= 6.97–6.95 (m, 4H), 6.88 (d, J=4.0 Hz, 1H), 6.67 (d, J=3.6 Hz, 1H), 2.79 (t, J=7.6 Hz, 2H), 1.68 (quintet, J=7.6 Hz, 2H), 1.42–1.29 (m, 6H), 0.89 ppm (t, J=6.8 Hz, 3H).

Tetrakis(5-(2-thienyl)-2-thienyl)methane (H-T2TM)

A mixture of 2-bromothiophene (3.91 g, 24 mmol), Bu₃Sn-T1TM (4.50 g, 3.0 mmol), and [Pd(PPh₃)₄] (1.39 g, 1.20 mmol) in toluene (90 mL) was heated reflux overnight under nitrogen. After cooling 1M HCl (50 mL) was added slowly at room temperature. The aqueous layer was extracted with methylene chloride (100 mL x5) and the combined organic layers were washed with 1M HCl (100 mL) and water (100 mL x2), and dried over anhydrous sodium sulfate. After the filtration and concentration the residue was purified by column chromatography on silica gel eluted with hexane/toluene (67:33 v/v) to give H-T2TM (1.25 g, 62%) as pale yellow crystals. ¹H NMR (300 MHz, CDCl₃) δ= 7.19 (dd, J=4.8, 1.2 Hz, 4H), 7.14 (dd, J=3.6, 1.2 Hz, 4H), 7.09 (d, J=3.9 Hz, 4H), 7.09 (d, J=3.6 Hz, 4H), 7.06 (d, J=3.9 Hz, 4H), 7.06 (d, J=3.9 Hz, 4H), 6.98 (dd, J=4.8, 3.6 Hz, 4H).

Tetrakis(5-(2-thienyl)-2-thienyl)methane (H-T3TM)

A mixture of 5-bromo-2,2′-bithiophene (4.54 g, 18.5 mmol), Bu₃Sn-T1TM (3.47 g, 2.3 mmol), and
[Pd(PPh₃)₄] (1.07 g, 0.92 mmol) in toluene (70 mL) was heated reflux overnight under nitrogen. After cooling 1M HCl (50 mL) was added slowly at room temperature. The aqueous layer was extracted with methylene chloride (100 mL×5) and the combined organic layers were washed with 1M HCl (100 mL) and water (100 mL×2), and dried over anhydrous sodium sulfate. After the filtration and concentration the residue was purified by column chromatography on silica gel at 60–70 °C eluted with hexane/toluene (70:30 v/v) to give H-T3TM (800 mg, 35%) as yellow crystals. ¹H NMR (400 MHz, CDCl₃) δ=7.20 (dd, J=5.2, 1.2 Hz, 4H), 7.15 (dd, J=3.6, 1.2 Hz, 4H), 7.09 (d, J=4.0 Hz, 4H), 7.07 (d, J=4.0 Hz, 4H), 7.05 (s, 8H), 7.01 (dd, J=5.2, 3.6 Hz, 4H).

2. Purification of Bu₃Sn-T1TM.

Table 1. Relation between C–Sn bond cleavage in Bu₃Sn-T1TM and the activity of alumina.¹

<table>
<thead>
<tr>
<th>Type of alumina</th>
<th>Activity of alumina²</th>
<th>C–Sn bond cleavage³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>I</td>
<td>Observed</td>
</tr>
<tr>
<td>Neutral</td>
<td>III</td>
<td>None</td>
</tr>
<tr>
<td>Neutral</td>
<td>V</td>
<td>None</td>
</tr>
<tr>
<td>Basic</td>
<td>II–III</td>
<td>Observed</td>
</tr>
<tr>
<td>Basic</td>
<td>IV–V</td>
<td>None</td>
</tr>
</tbody>
</table>

[a] 150 mesh of alumina were used. [b] Activity of Al₂O₃ is estimated in terms of the ratio of water (wt%) in alumina;¹⁷ activity I: 0%, activity II: 3 wt% of water, activity III: 8 wt% of water, activity IV: 10 wt% of water, and activity V: 15 wt% of water. [c] C–Sn bond cleavage was confirmed by ¹H NMR spectroscopy.

It was found that not the basicity but the activity of alumina was important for prevention of C–Sn bond cleavage in Bu₃Sn-T1TM (Table 1). Namely, C–Sn bond cleavage was not observed by using the alumina whose activity is less than II. So we chose the neutral alumina with activity III for the purification of Bu₃Sn-T1TM. The impurities, which could not be separated by alumina, were successfully removed by GPC (Figure S1).
Figure S1. Purification of Bu$_3$Sn-T1TM. Judging from the $^1$H NMR spectra in aliphatic region, impurities were effectively removed by chromatography on alumina and GPC.
3. Absorption and fluorescence spectra of Hex-TnTM (n=2–4).

Figure S2. Absorption (solid lines) and fluorescence (dashed lines) spectra of (a) Hex-T2TM (red lines) and Hex-2T-Hex (blue lines), (b) Hex-T3TM (red lines) and Hex-3T-Hex (blue lines), and (c) Hex-T4TM (red lines) and Hex-4T-Hex (blue lines).
4. Cyclic voltammograms of **Hex-TnTM** (n=1–4).

![Cyclic voltammograms of Hex-TnTM](image)

**Figure S3.** Cyclic voltammograms of **Hex-TnTM** (n=1–4).
5. Cyclic voltammograms of Hex-$n$-Hex ($n$=1–4).

Figure S4. Cyclic voltammograms of Hex-$n$-Hex ($n$=1–4).
6. DSC measurements of \textbf{H-T3TM}.

![DSC traces of H-T3TM](image)

Figure S5. DSC traces of \textbf{H-T3TM}. Scan rate is 10 °C min⁻¹.

7. References