Synthesis and Mesomorphic Properties of Multiynylthiophenes: 2,3,4,5-Tetrakis(4-alkoxyphenylethynyl)thiophenes and 2,3,5-Tris(4-alkoxyphenylethynyl)thiophenes

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Received September 10, 2003. Revised Manuscript Received April 14, 2004

The synthesis and characterization of multiynylthiophenes, tetrakis(4-alkoxyphenylethynyl)thiophenes (**1**) and tris(4-alkoxyphenylethynyl)thiophenes (**2**), are reported, and their structure−mesomorphism relationship is discussed. The tetraynyl series **1** with a trapezoid core do not show any liquid-crystalline properties. With one less peripheral arm, series **2** compounds are of the Y-shape geometry with rigid linear spacers and nematic phases are observed for the octyloxyl, decyloxyl, and dodecyloxyl derivatives. Although the dipole−dipole interactions, desymmetrization, and disparity of the mesogenic cores can be accountable for their corresponding mesomorphic behaviors, the formation of the nematic phases of **2** may be most likely attributed to the shape disparity of these two series of compounds.

Introduction

Disclike molecules exhibiting a nematic mesophase have drawn much attention recently, especially for improving viewing angle characteristics of liquid-crystal displays[1] as well as for the application as polarizer materials.[2] There are fewer disclike molecules[3] reported to show the nematic phase compared to a mass number of calamitic nematogens.[4] Multiynyl derivatives[5,6] composed the largest part of discotic nematic mesogens. Different central units of benzene,[5] naphthalene,[5a,5d,6] and triphenylene[5a] have been reported for construction of multiynyl discogens. Among which, the multiynylbenzenes[5] have been the most investigated system. Surprisingly, thiophene has not been utilized as a central unit to build discotic nematogens, although there have been a couple examples introducing thiophene units to the sidearms of hexa-substituted benzene to give discogens.[7] More often, thiophene was incorporated into calamitic mesogens and lower transition temperatures were usually achieved.[8]

Recently, Swager et al. have reported bent-rod mesogens of diynylthiophenes in which the dipoles as well as the symmetry were utilized for the investigation of the liquid-crystal formation.[9] Building multiynyl molecules with a central thiophene unit by further attaching one or two more phenylethynyl arms to the bent-rod diynylthiophenes will impose shape anisotropy due to the sulfur atom in the central ring. The resulting polar noncalamitic cores may lead to better liquid crystallinity.[5a,5e] Different than the symmetric hexaynylbenzene system, a more opened structure, lower density of peripheral phenylethynyl arms, and nonidentical angles between adjacent peripheral arms can be achieved in the mutiynylthiophenes. The fewer number of phenylethynyl arms may reduce the possibility of intermolecular $\pi-\pi$ interactions and hence promote its liquid crystallinity. The irregularity of the angles between peripheral groups could also favor mesophase formation. Herein, we report the first examples of mesogenic multiynyl compounds with a central thiophene unit.

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10.1021/cm030612t CCC: $27.50

Experimental Section

All chemicals and solvents were reagent grades (Aldrich Chemical Co.) and used without further purification. Tetraiodothiophene was synthesized according to the literature.[10] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer. Chemical shifts are reported in ppm relative to residual $CHCl_3$ ($\delta = 7.26$, ^{1}H; 77.0, ^{13}C). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Absorption spectra were recorded with a Jasco V-550 spectrometer. Photoluminescence spectra were recorded with an Aminco Bowman Series 2 luminescence spectrometer. Differential scanning calorimetry (DSC) was measured on a Perkin-Elmer Pyris1 with heating and cooling rates of 5 and 10 °C min^{-1}. Polarized optical microscopy (POM) was carried out on a Nikon Eclipse E600 POL with a Mettler FP90/FP82HT hot stage system. Mass spectra were obtained on Finnigan MAT-95XL and elemental analyses were carried out on a Heraeus CHN-O-Rapid Analyzer at the NSC Regional Instrumental Center at National Chiao Tung University, Hsinchu, Taiwan, and at National Cheng Kung University, Tainan, Taiwan.

Synthesis of 2,3,4,5-Tetrakis(4-alkoxyphenylethynyl)thiophene (1). To a mixture of trans-dichlorobis(triphenylphosphine)palladium(II) (9 mg, 0.01 mmol), copper iodide (5 mg, 0.04 mmol), tetraiodothiophene (150 mg, 0.26 mmol), and diisopropylamine/toluene/THF (10/10/5 mL) was added to 1-alkoxy-4-ethynylbenzene (1.59 mmol) in THF (10 mL) dropwise under a nitrogen atmosphere at 60 °C. The mixture was stirred at 60 °C for 16 h. After cooling, the reaction mixture was washed with $NH_4Cl_{(aq)}$ (50 mL 3×) and H_2O (70 mL 3×) and dried over $MgSO_4$. After removal of the solvents, the residue was purified by column chromatography (SiO_2, *n*-hexane/dichloromethane 10:1) to yield **1** as a pale yellow powder.

1a: ($n = 4$) yield 61%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.51 (d, $J = 8.6$ Hz, 4H), 7.49 (d, $J = 8.7$ Hz, 4H), 6.88 (d, $J = 9.1$ Hz, 4H), 6.87 (d, $J = 8.8$ Hz, 4H), 3.99 (t, $J = 6.5$ Hz, 8H), 1.79 (m, 8H), 1.44−1.57 (m, 8H), 0.99 (t, $J = 7.4$ Hz, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.8, 159.5, 133.26, 133.16, 127.9, 124.5, 115.1, 114.7, 114.6, 114.4, 98.5, 95.9, 82.0, 80.8, 67.8, 31.2, 19.2, 13.8. HRMS (EI) *m/z* for $C_{52}H_{52}O_4S$ 772.3586, found 772.3586.

1b: ($n = 6$) yield 50%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.52 (d, $J = 9.0$ Hz, 4H), 7.50 (d, $J = 9.0$ Hz, 4H), 6.884 (d, $J = 9.0$ Hz, 4H), 6.876 (d, $J = 8.7$ Hz, 4H), 3.98 (t, $J = 6.5$ Hz, 8H), 1.780 (m, 8H), 1.52−1.26 (m, 24H), 0.92 (t, $J = 6.9$ Hz, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.8, 159.5, 133.24, 133.15, 127.8, 124.5, 115.0, 114.7, 114.6, 114.4, 98.5, 95.9, 82.1, 80.8, 68.1, 31.6, 29.2, 25.7, 22.6, 14.0. Anal. Calcd for $C_{60}H_{68}O_4S$ (885.2): C, 81.41; H, 7.74. Found: C, 81.48; H, 7.83.

1c: ($n = 8$) yield 54%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.51 (d, $J = 8.6$ Hz, 4H), 7.49 (d, $J = 8.6$ Hz, 4H), 6.88 (d, $J = 8.9$ Hz, 4H), 6.87 (d, $J = 8.8$ Hz, 4H), 3.98 (t, $J = 6.5$ Hz, 8H), 1.80 (m, 8H), 1.51−1.26 (m, 40H), 0.89 (t, $J = 6.8$ Hz, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.8, 159.5, 133.2, 133.1, 127.9, 124.5, 115.1, 114.7, 114.6, 114.4, 98.5, 95.9, 82.0, 80.8, 68.1, 31.8, 29.7, 29.4, 29.2, 26.0, 22.7, 14.1. Anal. Calcd for $C_{68}H_{84}O_4S$ (997.5): C, 81.88; H, 8.49. Found: C, 82.14; H, 8.73.

1d: ($n = 10$) yield 75%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.51 (d, $J = 8.6$ Hz, 4H), 7.49 (d, $J = 8.6$ Hz, 4H), 6.88 (d, $J = 8.9$ Hz, 4H), 6.87 (d, $J = 8.8$ Hz, 4H), 3.98 (t, $J = 6.6$ Hz, 8H), 1.79 (m, 8H), 1.47−1.28 (m, 56H), 0.89 (t, $J = 6.7$ Hz, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.8, 159.5, 133.25, 133.16, 127.8, 124.5, 115.1, 114.7, 114.6, 114.4, 98.5, 95.9, 82.0, 80.8, 68.2, 31.9, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1. Anal. Calcd for $C_{76}H_{100}O_4S$ (1109.7): C, 82.26; H, 9.08. Found: C, 81.55; H, 9.17.

1e: ($n = 12$) yield 65%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.52 (d, $J = 8.7$ Hz, 4H), 7.50 (d, $J = 8.7$ Hz, 4H), 6.882 (d, $J = 8.8$ Hz, 4H), 6.876 (d, $J = 8.8$ Hz, 4H), 3.98 (t, $J = 6.8$ Hz, 8H), 1.80 (m, 8H), 1.49−1.28 (m, 72H), 0.89 (t, $J = 6.8$ Hz, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.8, 159.5, 133.2, 133.1, 127.9, 124.5, 115.1, 114.7, 114.6, 114.4, 98.5, 95.9, 82.1, 80.8, 68.1, 31.9, 29.64, 29.59, 29.40, 29.35, 29.2, 26.0, 22.7, 14.1. Anal. Calcd for $C_{84}H_{116}O_4S$ (1221.9): C, 82.57; H, 9.57. Found: C, 82.69; H, 9.35.

Synthesis of 2,3,5-Tris(4-ethoxyphenylethynyl)-4-iodothiophene (2). To a mixture of trans-dichlorobis(triphenylphosphine)palladium(II) (30 mg, 0.04 mmol), copper iodide (16 mg, 0.08 mmol), and tetraiodothiophene (500 mg, 0.85 mmol) in diisopropylamine/toluene/THF (15/15/3 mL) was added 1-alkoxy-4-ethynylbenzene (2.98 mmol) dropwise at 60 °C under a nitrogen atmosphere. The mixture was stirred at 60 °C for 12 h. After cooling, the reaction mixture was washed with $NH_4Cl_{(aq)}$ (70 mL, 3×) and H_2O (100 mL, 3×), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, *n*-hexane/dichloromethane 8:1) to yield **2** as a pale yellow powder.

2a: ($n = 4$) yield 31%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.55−7.46 (m, 6H), 6.88 (d, $J = 8.7$ Hz, 6H), 3.99 (t, $J = 6.5$ Hz, 6H), 1.79 (m, 6H), 1.55−1.46 (m, 6H), 0.99 (t, $J = 7.4$ Hz, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.92, 159.88, 159.7, 133.28, 133.22, 133.18, 131.9, 125.5, 125.1, 114.7, 114.6, 114.2, 114.1, 99.3, 97.6, 96.1, 92.0, 83.7, 82.2, 80.6, 67.8, 31.2, 19.2, 13.8. HRMS (EI+) for $C_{40}H_{39}IO_3S$ *m/z* 726.1665, found 726.1672.

2b: ($n = 6$) yield 38%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.56−7.47 (m, 6H), 6.88 (pseudo d, $J = 7.5$ Hz, 6H), 3.98 (t, $J = 6.5$ Hz, 6H), 1.80 (m, 6H), 1.51−1.27 (m, 18H), 0.92 (t, $J = 6.8$ Hz, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.87, 159.84, 159.7, 133.25, 133.20, 133.15, 131.9, 125.5, 125.1, 114.7, 114.6, 114.2, 114.0, 99.3, 97.7, 96.2, 92.0, 83.7, 82.2, 80.6, 68.1, 31.6,, 29.2, 25.7, 22.6, 14.0. Anal. Calcd for $C_{46}H_{51}IO_3S$ (810.9): C, 68.14; H, 6.34. Found: C, 68.04; H, 6.37.

2c: ($n = 8$) yield 34%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.56−7.46 (m, 6H), 6.88 (d, $J = 8.7$ Hz, 6H), 3.98 (t, $J = 6.6$ Hz, 6H), 1.79 (m, 6H), 1.49−1.27 (m, 30H), 0.90 (t, $J = 6.9$ Hz, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.90, 159.87, 159.7, 133.3, 133.21, 133.17, 131.9, 125.5, 125.1, 114.7, 114.6, 114.2, 114.0, 99.3, 97.7, 96.2, 92.0, 83.7, 82.2, 80.6, 67.2, 31.8, 31.6, 29.3, 29.2, 29.0, 22.6, 14.1. Anal. Calcd for $C_{52}H_{63}IO_3S$ (859.0): C, 69.78; H, 7.09. Found: C, 69.81; H, 7.08.

2d: ($n = 10$) yield 34%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.55−7.46 (m, 6H), 6.88 (m, $J = 8.6$ Hz, 6H), 3.98 (t, $J = 6.5$ Hz, 6H), 1.80 (m, 6H), 1.54−1.28 (m, 42H), 0.89 (t, $J = 6.5$ Hz, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.9, 159.8, 159.6, 133.3, 133.2, 133.1, 131.9, 125.5, 125.1, 114.7, 114.6, 114.2, 114.0, 99.2, 97.6, 96.1, 91.9, 83.7, 82.2, 80.5, 68.1, 31.9, 29.5, 29.4, 29.3, 29.2, 26.0, 22.6, 14.07. Anal. Calcd for $C_{58}H_{75}IO_3S$ (979.2): C, 71.14; H, 7.72. Found: C, 70.80; H, 7.82.

2e: ($n = 12$) yield 31%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.55−7.46 (m, 6H), 6.88 (m, 6H), 3.98 (t, $J = 6.5$ Hz, 6H), 1.79 (m, 6H), 1.56−1.28 (m, 54H), 0.89 (t, $J = 6.7$ Hz, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.92, 159.87, 159.7, 133.3, 133.21, 133.17, 131.9, 125.5, 125.1, 114.7, 114.6, 114.2, 114.0, 99.3, 97.6, 96.2, 92.0, 83.7, 82.2, 80.6, 68.2, 53.4, 31.9, 29.63, 29.59, 29.37, 29.35, 29.2, 26.0, 22.7, 14.1. Anal. Calcd for $C_{64}H_{87}IO_3S$ (1063.3): C, 72.29; H, 8.25. Found: C, 72.19; H, 8.23.

Synthesis of 3-Cyano-2,4,5-tris(4-decyloxy-phenylethynyl)thiophene (3). Compound **2d** (201 mg, 0.206 mmol), copper iodide (82 mg, 0.43 mmol), and copper cyanide (110 mg, 1.23 mmol) were placed in a 100-mL Shlenk flask. Under nitrogen, dry *N*,*N*-dimethylformamide (50 mL) was introduced. With exclusion of light, the solution was heated to 130 °C for 24 h. After cooling, to the reaction mixture was added dichloromethane (100 mL). The mixture was washed with H_2O (200 mL, 2×) and the organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, *n*-hexane/dichloromethane 10:1) to yield **3** as a pale yellow powder (164 mg, 0.186 mmol, 91%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.51 (m, 6H), 6.88 (m, 6H), 3.99 (t, $J = 6.5$ Hz, 6H), 1.80 (m, 6H), 1.46−1.28 (m, 42H), 0.89 (t, $J = 6.7$ Hz, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 160.5, 160.1, 160.0, 133.6 (2C), 133.5 (2C), 133.2 (2C), 131.7, 127.0, 125.5, 115.1, 114.7 (4C), 114.6 (2C), 113.8, 113.6, 113.4, 112.9, 102.1, 100.0, 97.7, 79.6, 79.5, 78.4, 68.2 (2C), 68.1, 31.9 (3C), 29.5 (6C), 29.35 (3C), 29.28 (3C), 29.1 (3C), 26.0 (3C), 22.6 (3C),

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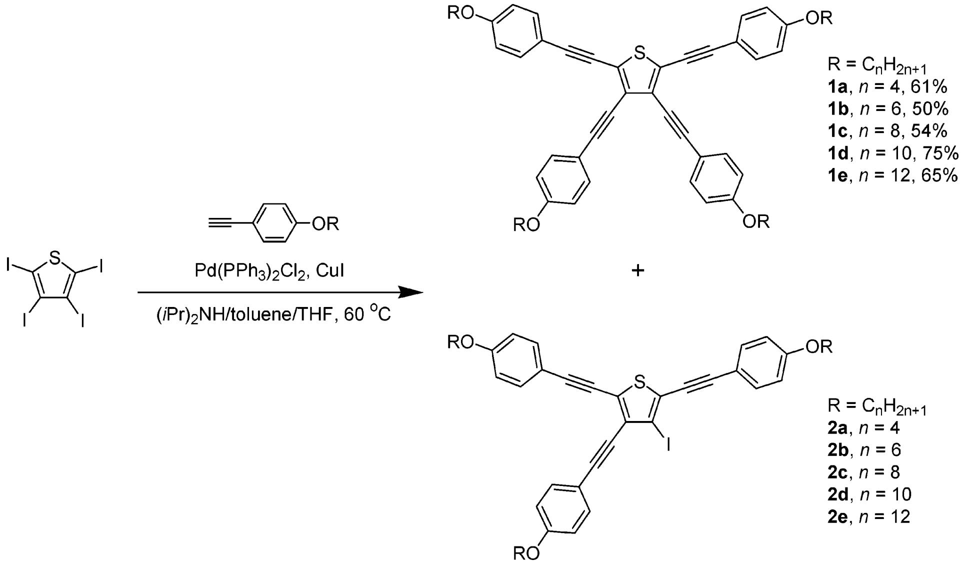
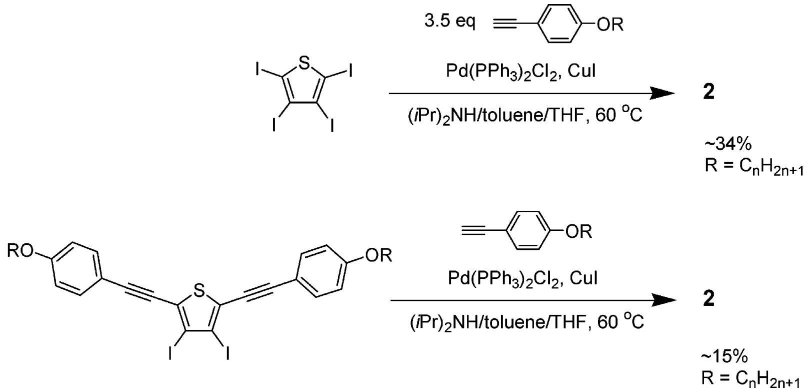
[10] Steinkopf, W.; Schmitt, H. F.; Fiedler, H. *Ann.* **1937**, *527*, 237.

Scheme 1. Synthesis of the Tetra(phenylynyl)thiophenes (1) and the Tri(phenylethynyl)thiophenes (2)



Scheme 2. Alternative Synthetic Routes of the Tri(phenylethynyl)thiophenes (2)



14.1 (3C). HRMS (FAB+) *m/z* for $C_{59}H_{75}NO_3S$ 877.5468, found 877.5465. Anal. Calcd for $C_{59}H_{75}NO_3S$ (878.3): C, 80.68; H, 8.61; N, 1.59. Found: C, 80.75; H, 8.57; N, 1.60.

Synthesis of 2′,4′,5′-Tris(4-decyloxy-phenylethynyl)-[2,3′]bithiophene (4). To a mixture of trans-dichlorobis-(triphenylphosphine)palladium(II) (12 mg, 0.02 mmol) and **2d** (201 mg, 0.21 mmol) in dry *N*,*N*-dimethylformamide (60 mL) was added 2-(tributylstannyl)thiophene (162 mg, 0.43 mmol) dropwise at 70 °C under a nitrogen atmosphere. The mixture was stirred at 70 °C for 23 h. After cooling, the reaction mixture was added to dichloromethane (50 mL) and washed with H_2O (200 mL, 2×). The organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, *n*-hexane/dichloromethane 10:1) to yield **4** (169 mg, 0.18 mmol) as a yellow powder in 88% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.04 (dd, $J = 3.7$, 1.2 Hz, 1 H), 7.49 (m, 6 H), 7.41 (dd, $J = 5.0$, 1.0 Hz, 1 H), 7.16 (dd, $J = 5.0$, 3.8 Hz, 1 H), 6.88 (d, $J = 8.7$ Hz, 6 H), 3.98 (t, $J = 6.5$ Hz, 6 H), 1.80 (m, 6 H), 1.49−1.29 (m, 42 H), 0.90 (t, 6.6 Hz, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.72, 159.69, 159.5, 136.7, 135.9, 133.1 (2C), 132.92 (2C), 132.89 (2C), 127.4, 126.5, 126.2, 125.7, 125.4, 118.0, 115.1, 114.7 (4C), 114.6 (2C), 114.5 (2C), 98.9, 98.2, 96.9, 83.4, 81.8, 81.1, 68.1 (3C), 31.9 (3C), 29.5 (6C), 29.4 (3C), 29.3 (3C), 29.2 (3C), 26.0 (3C), 22.6 (3C), 14.1 (3C). HRMS (FAB+) *m/z* for $C_{62}H_{78}O_3S_2$ 934.5392, found 934.5414. Anal. Calcd for $C_{62}H_{78}O_3S_2$ (935.4): C, 79.61; H, 8.40. Found: C, 79.70; H, 8.41.

Results and Discussion

Schemes 1 and 2 outline the synthesis of the tetraynylthiophenes, series **1** compounds, and triynylthiophenes, series **2** compounds. The tetraynylthiophenes **1a**−**1e** were synthesized by palladium-catalyzed Sonogashira cross-coupling[11] of tetraiodothiophene[10] with 6 equiv of 1-alkoxy-4-ethynyl-benzene (Scheme 1). Tetraiodothiophene instead of tetrabromothiophene was chosen for better reactivity with terminal alkynes. An excess of the acetylene reagents was used for minimizing the formation of mono-, di-, and trisubstituted products. In addition, the self-coupling reaction of the acetylene reagents also requires the excess addition of terminal alkynes. The triynyl derivatives **2a**−**2e** were also isolated in the reaction mixture in yields of ~3%. Alternatively, attaching an additional phenylethynyl group onto the 3-position of 3,4-diiodo-2,5-bis-(4-alkoxyphenylethynyl)-thiophene can also lead to the formation of **2** at somewhat higher yields of 15% (Scheme 2). The best yields of ~34% are obtained when 3.5 equiv of acetylene reagents are coupled with tetraiodothiophene.

The thermal and mesogenic data of series **1** and **2** compounds investigated by POM and DSC are summarized in Table 1. Surprisingly, no liquid-crystalline behavior can be detected for the tetraynylthiophenes of various chain lengths. The melting temperatures of series **1** compounds decrease with increasing chain length. Significant supercooling is observed for these

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[11] Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

Table 1. Phase Behavior of Compounds 1a–1d and 2a–2d[a]

Compound	Behavior
1a, *n* = 4	$\mathrm{K} \underset{62.4\ (-26.09)}{\overset{95.9\ (29.22)}{\rightleftharpoons}} \mathrm{I}$
1b, *n* = 6	$\mathrm{K} \underset{-12.8\ (-11.43)}{\overset{74.2\ (34.83)}{\rightleftharpoons}} \mathrm{I}$
1c, *n* = 8	$\mathrm{K} \underset{15.6\ (-30.53)}{\overset{73.8\ (50.20)}{\rightleftharpoons}} \mathrm{I}$
1d, *n* = 10	$\mathrm{K1} \xrightarrow{39.3\ (44.02)} \mathrm{K2} \xrightarrow{63.7\ (29.84)} \mathrm{I}$ $\mathrm{I} \xrightarrow{18.9\ (-37.60)} \mathrm{K1}$
1e, *n* =12	$\mathrm{K1} \xrightarrow{45.3\ (40.92)} \mathrm{K2} \xrightarrow{53.3\ (19.66)} \mathrm{I}$ $\mathrm{I} \xrightarrow{17.1\ (-37.11)} \mathrm{K1}$
2a, *n* = 4	$\mathrm{K} \underset{58.9\ (-2.58)}{\overset{110.9\ (32.21)}{\rightleftharpoons}} \mathrm{I}$
2b, *n* = 6	$\mathrm{K1} \xrightarrow{87.3\ (25.28)} \mathrm{K2} \xrightarrow{93.4\ (0.15)} \mathrm{I}$ $\mathrm{I} \xrightarrow{63.9\ (-25.48)} \mathrm{K1}$
2c, *n* = 8	$\mathrm{K} \xrightarrow{92.7\ (50.33)} \mathrm{I}$ $\mathrm{I} \xrightarrow{69.8\ (-0.37)} \mathrm{N} \xrightarrow{57.4\ (-42.99)} \mathrm{K}$
2d, *n* = 10	$\mathrm{K1} \xrightarrow{72.7\ (58.29)} \mathrm{K2} \xrightarrow{75.6^{*}} \mathrm{I}$ $\mathrm{I} \xrightarrow{72.00\ (-0.69)} \mathrm{N} \xrightarrow{32.8\ (-28.15)} \mathrm{K1}$
2e, *n* =12	$\mathrm{K1} \xrightarrow{86.5\ (95.25)} \mathrm{K2} \xrightarrow{91.9\ (13.18)} \mathrm{I}$ $\mathrm{I} \xrightarrow{69.1\ (-0.64)} \mathrm{N} \xrightarrow{57.39\ (-75.98)} \mathrm{K1}$

[a] The transition temperatures (°C) and enthalpies (in parentheses/kJ mol^{-1}) were determined by DSC at 10 °C /min. K, K1, and K2, crystalline phases; N, nematic mesophase; I, isotropic liquid. *n* denotes the length of the alkoxy chains. *As a shoulder of the previous peak at 72.7 °C.

tetraynyl compounds with the largest supercooling of 87 °C for the hexyloxy derivative **1b**. For the triynylthiophenes, series **2** compounds, no liquid crystalline behavior was observed upon heating. On cooling, the shorter chain analogues, **2a** and **2b**, still are not liquid crystalline. However, as shown in Figure 1, upon cooling the octyloxyl, decyloxyl, and dodecyloxyl derivatives, **2c**, **2d**, and **2e**, show Schlieren or marbled textures typical of nematic phases at 70, 72, and 69 °C, respectively, under polarized optical microscope. The widest range of mesophase stability which is 39 °C on cooling is found for the decyloxyl derivative **2d**.

It is interesting that the triynyl series **2** compounds with longer side chains show nematic phases and, on the other hand, the tetraynyl series **1** compounds are not liquid crystalline at all. For the well-known multiynylbenzenes, a mesophase range of 15 °C was found for the symmetrical hexakis[4-pentylphenyl]ethynyl]-benzene ($\mathrm{K} \rightarrow \mathrm{N_D}$, 170 °C; $\mathrm{N_D} \rightarrow \mathrm{I_{decomp}}$, 185 °C) and a wider range of 27 °C was reported for the polar 11-{pentakis[(4-pentylphenyl)ethynyl]phenoxy}undecan-1-ol ($\mathrm{K} \rightarrow \mathrm{N_D}$, 67 °C; $\mathrm{N_D} \rightarrow \mathrm{I}$, 94 °C).[5a,5e] The most pronounced difference between these two is the much lower transition temperatures of the pentaynyl derivative. These two mesogens do not differ much in their shapes and sizes but the shape anisotropy in the pentaynylbenzenes results in a polar core geometry. Therefore, the broader mesophase range and the considerably lower transition temperatures of the pentaynyl analogue are most likely resulting from the dipole–dipole interaction. On the other hand, series **1** and **2** differ considerably at their shapes, sizes, and dipole moments. With AM1 calculations[12] performed on model compounds of methoxy analogues of **1** and **2**, the optimized structures show approximately coplanar conformations for the cores and the methoxy groups are in plane with the attached phenyl ring. Various conformers with different relative orientations of the lone pairs of the oxygen atoms in methoxy groups are possible and the heats of formation for these conformers of tetraynyl analogue are similar, averaged 177.5 kcal mol^{-1}. The similarity is also found for the triynyl analogue with an averaged heat of formation of 155.3 kcal mol^{-1}. On the other hand, the calculations of dipoles are compli-

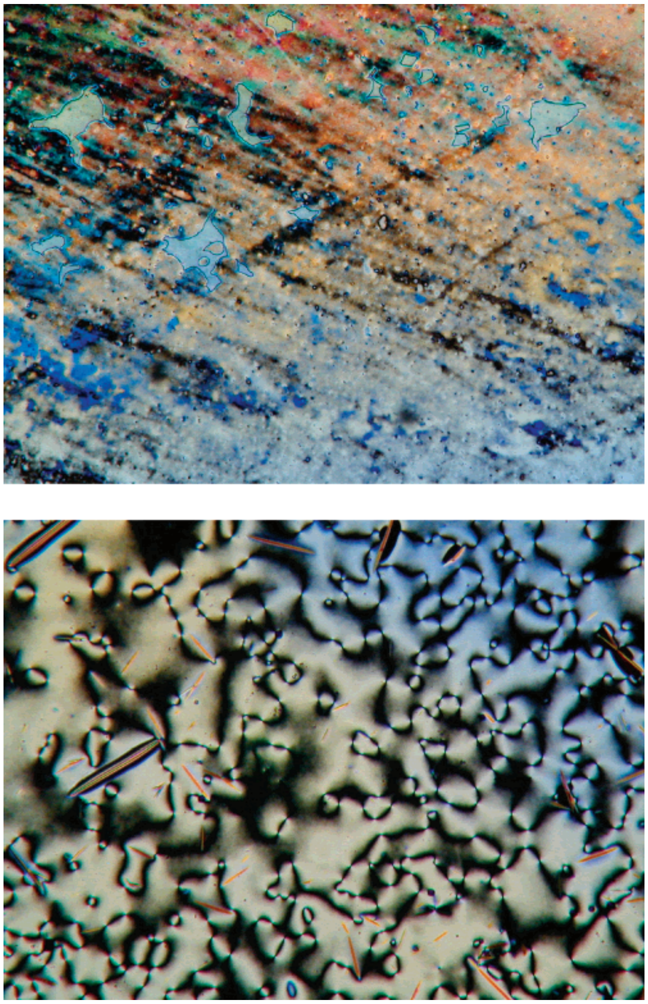

Figure 1. Micrographs of the marbled texture of **2d** at 68 °C (200x) (top) and the nematic Schlieren texture with coexistent needle crystals of **2e** at 66 °C (200×) (bottom) upon cooling from isotropic melts. Samples were sandwiched between glass slides and viewed through crossed polarizers.

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(12) The molecular geometries of **1** and **2** were optimized using the AM1 method by molecular software, PC Spartan Plus version 1.5.2 (Wavefunction, Inc.).

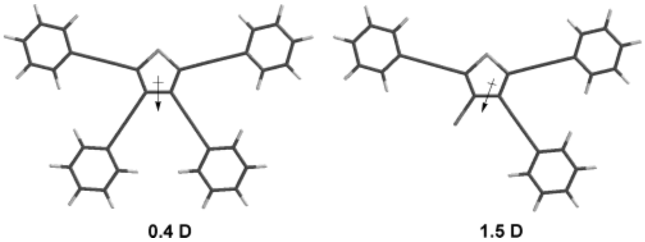

Figure 2. Optimized molecular structures and calculated dipole moments for **1′** and **2′**.

cated by the possible relative orientations of the lone pairs of the methoxy groups. The calculated dipole moments vary with a range from 1.0 to 3.7 D for the methoxy analogue of **1** and from 0.6 to 4.7 for the methoxy analogue of **2**. To simplify the dipole moment argument, the effect of replacing the phenylethynyl group with the iodo group can be realized by calculations on the alternative model compounds with no methoxy groups, **1′** for **1** and **2′** for **2**, and the results are shown in Figure 2. In both **1′** and **2′**, the outer phenyl rings are roughly coplanar with respect to the central thiophene ring and **1′** can be considered as a trapezoid while the core geometry of **2′** is optimized to be Y-shaped. The dipole moment of **1′** is calculated to be 0.4 D with a direction pointing away from the sulfur atom. For **2′**, a larger dipole moment of 1.5 D is obtained and the direction is now pointing to the iodide atom. The iodo group in **2** imposes not only a size change but also a directional change of the dipole moment. Similar to the multiynylbenzene pairs, the dipole−dipole interaction seems to have favored series **2** compounds to be more mesogenic than series **1** compounds. On the other hand, the shape disparity for the multiynylthiophene pair is much more pronounced than that for the multiynylbenzene pair. Hence, a more significant difference in mesogenic properties can be expected for the multiynylthiophene pair than for the multiynylbenzene pair. Also, the desymmetrization effect[9] may have promoted liquid crystallinity for **2**. Although the different mesomorphisms of **1** and **2** are attributed to their shape disparity, dipole moments, and desymmetrization, the shape disparity is believed to be of the main contribution and more detailed analysis upon the shape/mesomorphic properties of the multiynylthiophene pair will be discussed in the following paragraphs.

As for **1**, a close analogue of 1,2,4,5-tetrakis(4-tridecyloxy-phenylethynyl)benzene was reported to exhibit monotropic nematic phase.[13] On the basis of molecular modeling, it was proposed that the ortho alkyne arms may show the face-on $\pi-\pi$ interaction of the phenyl rings to give an effective rodlike shape.[13] However, the bending of the acetylenes may not be likely since the thereby caused strain will outweigh the small gain due to these intramolecular $\pi-\pi$ interactions. On the other hand, in the solid-state structure of hexakis(2-(4′-(hexyloxy)phenyl)ethynyl)benzene,[14] the peripheral phenyl rings are roughly coplanar with the central benzene ring and intramolecular $\pi-\pi$ interaction between peripheral phenyl rings is not likely to occur. Although the intramolecular interaction was not observed, the intermolecular $\pi-\pi$ interaction can be found by carefully examining its packing motif. For each molecule, one of the peripheral rings is found to show offset face-to-face intermolecular $\pi-\pi$ interaction with a phenyl ring of another molecule. In the case of **1**, the four arms are at angles of larger than 60° of the hexaynylbenzene analogue. Therefore, it is less likely for **1** to show intramolecular $\pi-\pi$ interaction to give an effective rodlike shape. This is also supported by the reported crystal structure of 3,4-bis(phenylethynyl)-2,5-bis(trimethylsilanylethynyl)thiophene in which the two phenyl rings are not in close proximity to show $\pi-\pi$ interaction.[15] Interestingly, one of the phenyl rings is also found to show offset face-to-face intermolecular $\pi-\pi$ interaction with a phenyl ring of another molecule. Therefore, for the comparison between the tetraynylthiophene and tetraynylbenzene compounds, the main difference is the additional dipole−dipole interaction in the thiophene analogue **1** and this dipolar interaction may have induced too strong intermolecular interaction for **1** to be liquid crystalline.

For **2**, the closest family of 2,5-diynylthiophene mesogens[9] reported by Swager et al. showed enantiotropic mesophases and increasing the lateral dipole gave a narrower stability of the enantiotropic nematic phase. In addition, lengthening of the terminal chains induced the formation of a lamellar phase. As seen for compounds **2a**−**2e**, attaching one more phenylethynyl moiety onto the diynylthiophene has reduced the stability of the nematic phase to be at best monotropic. Interestingly, the tilted lamellar phase observed for the diynylthiophenes with long alkoxy chains was not detected at all for the triynyl derivatives, even with dodecyloxy chains. The third rigid lateral arm has disturbed the motif of the nematic phase and has also prevented the smectic phase formation.

Laterally substituted mesogens are not unprecedented; however, the ones with rigid spacers have not been reported. Laterally substituted liquid crystals incorporating phenyl rings within the lateral segment have been reported,[16] and these molecules were best described to be Y-shaped. For the lateral segment, different spacers, the more rigid $-OOC-$,[16d] $-N{=}C-$,[16e] $-N{=}N-$,[16f] and the less rigid $-COO(CH_2)_nO-$,[16d] or no spacers[16g] have been investigated. The lengths of the spacers were believed to be an important factor for obtaining stable mesophases. Longer spacers allow the lateral segment to be in the orientation of the molecular axis and hence higher packing densities can be achieved for stabilization of the liquid-crystal phases. Two crystal structures of these mesogens have been reported and in both cases the molecules are Y-shaped and the peripheral rings are not all coplanar with the central

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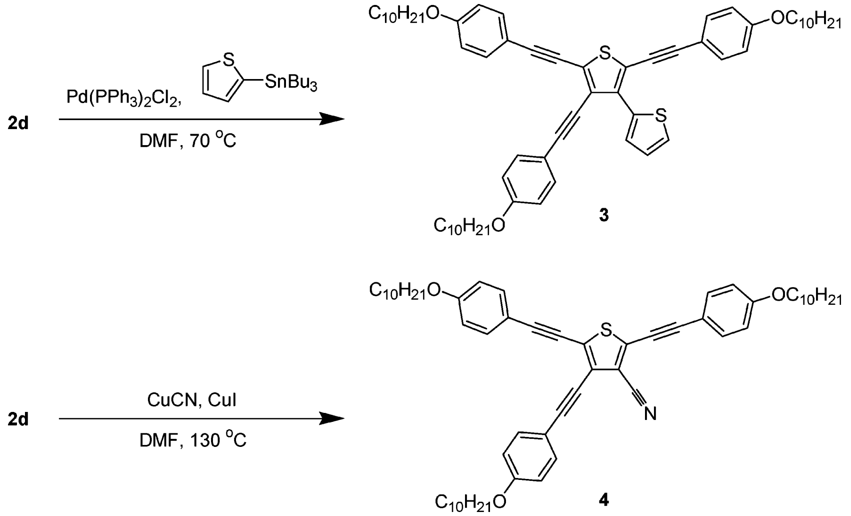
Scheme 3. Synthesis of 3 and 4: Derivatizing the Iodo Group of 2d



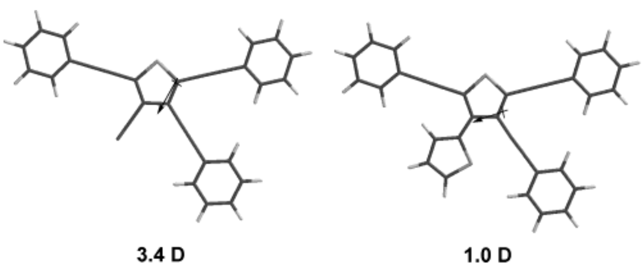


Figure 3. Optimized molecular structures and calculated dipole moments for the chainless derivatives of **3** (left) and **4** (right).

Table 2. Phase Behavior of Compounds 3 and 4[a]

Compound	Behavior
3 (CN)	K $\xrightarrow{63.6\ (59.35)}$ I; I $\xrightarrow{51.5\ (-1.31)}$ N $\xrightarrow{-1.2\ (-16.91)}$ K
4 (thienyl)	K $\xrightarrow{68.7\ (77.44)}$ I; I $\xrightarrow{55.9\ (-1.68)}$ N $\xrightarrow{8.6\ (-24.20)}$ K

[a] The transition temperatures (°C) and enthalpies (in parentheses/kJ mol^{-1}) were determined by DSC at 10 °C/min. K, crystalline phases; N, nematic mesophase; I, isotropic liquid.

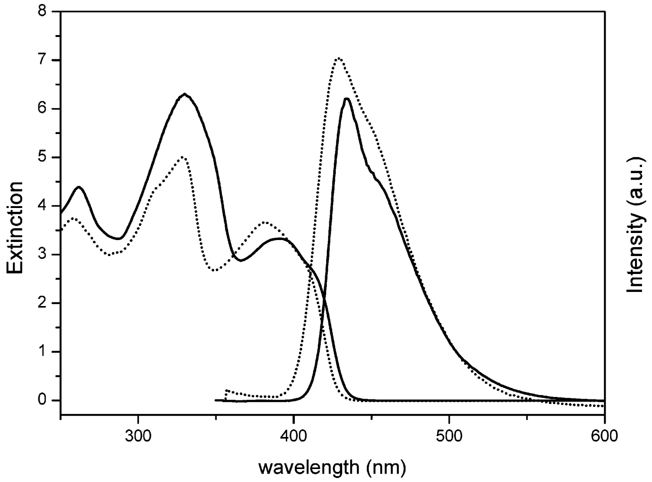


Figure 4. Absorption and emission spectra of **1c** (solid lines) and **2c** (dotted lines) in dichloromethane. Extinction unit: 10^4 dm^3 mol^{-1} cm^{-1}.

phenyl ring in the solid states.[16b,16c] On the contrary, the optimized structure of **2** shows high coplanarity of the rings and the rigid ethynyl linkers prevent the lateral moiety to line up with the molecular axis. The low stability of the nematic phase of series **2** compounds may be attributable to the rigid and open core structure that thwarts higher density packing. To the best of our knowledge, **2c**, **2d**, and **2e** represent the first examples of Y-shaped molecular geometry with rigid linear spacers to show liquid-crystalline behavior.

The reactivity of the iodo group in **2d** was verified by readily derivatizating into an electron-withdrawing cyano group (**3**, yield: 91%) and a bulky thienyl ring (**4**, yield: 88%) as shown in Scheme 3. As shown in Figure 3, different molecular dipoles are obtained for the chainless analogues of **3** and **4**. The introduction of a polar cyano group has increased the molecular dipole and the dipole moment of the model chainless compound is calculated to be 3.4 D. On the other hand, the attachment of a thienyl ring has lowered the molecular dipole and the dipole of the model compound without alkoxy chains is found to be 1.0 D for the most stable conformer. The mesogenic behaviors of these two are listed in Table 2. Both **3** and **4** exhibited a monotropic nematic phase as observed for **2d**. Compared with **2d**, both the more polar **3** and the less polar **4** exhibit wider mesophase ranges, 53 °C for **3** and 47 °C for **4**. The incorporation of a polar cyano group does widen the mesophase range as comparing the mesogenic behaviors of **2d** and **3**. On the other hand, although compound **4** has a smaller molecular dipole, it still showed a wider nematic range than **2d**. It should be noted that the orientation of the dipole of **4** is deviated from that of **2d**. In addition to the dipole orientation difference, the molecular shape of **4** is very different from that of **2d**. These results support our previous discussion about these rigid Y-shaped liquid crystals that molecular dipole imposes a significant impact on the mesophase stability while other factors, for example, molecular symmetry and shape, should also be considered.

The absorption and emission properties of these two series of compounds have been investigated by UV–vis and fluorescence spectroscopies. As shown in Figure 4, the absorption and photoluminescence spectra of **1c** and

2c do not show significant difference. Both the absorption and fluorescence spectra show a less than 9 nm blue shift for the triynyl series **2** compounds relative to the tetraynyl series **1** compounds. Apparently, the iodo group does not impose a noteworthy change on the HOMO−LUMO gap. However, the heavy iodo group has quenched the quantum yields[17] of these triynyl compounds significantly. The averaged quantum yield drops from 17% for the tetraynyl series **1** to 2% for the triynyl series **2**.

Conclusions

In summary, the multiynyl thiophene compounds of series **1** and **2** have been synthesized. The tetra(phenylethynyl)thiophenes, series **1**, are not liquid crystalline and modifications of the radiating arms may induce the formation of mesophases. The tri(phenylethynyl)thiophenes, series **2**, represent a new skeleton of laterally substituted materials with rigid linear spacers to show a nematic phase. Furthermore, the iodo group provides potential variations on the fourth position of the thiophene ring. Conversions of the iodo group into a cyano and a thienyl ring have yielded **3** and **4**. The mesomorphic properties of **2d**, **3**, and **4** indicate that molecular dipole and molecular shape are important factors but other factors, for example, molecular symmetry, should also be considered. Manipulations of the dipoles as well as the overall shapes with a variety of other substituents at the 4-position of **2** are necessary for better understanding of the structure−property correlations and are under investigation.

Acknowledgment. This work was supported by a grant from the National Science Council of Taiwan (NSC 92-2113-M-032-007).

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(17) Quantum yields were calculated using 9,10-diphenylanthracene as the reference.