Synthesis and Spectral Properties of a Highly Soluble Push-Pull Type of Quinoidal Thiophenes

Toshiaki Takahashi, Kazuo Takimiya, Tetsuo Otsubo,* and Yoshio Aso

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Iodo-substituted mono- and bi-thiophene derivatives 8a,b. A typical experimental procedure is as follows. Into a solution of 3,4-[2,2-bis(butoxymethyl)trimethylene-1,3-diyl]thiophene (**7a**) (630 mg, 2.21 mmol) in dry THF (20 mL) cooled at $-78\text{ }^{\circ}\text{C}$ was slowly added a solution of 1.56 *M* butyllithium (1.5 mL, 2.34 mmol) in hexane, and the mixture was allowed to warm to rt and stir for 1 h. A solution of iodine (550 mg, 2.16 mmol) in THF (15 mL) was added over a period of 30 min, and the mixture was stirred at rt for 4 h. After aq. sat. sodium hydrogen sulfite (10 mL) was added, the mixture was stirred at rt for 10 min and extracted with ether (50 mL $\times$ 3). The extracts were combined, washed with brine, and dried (MgSO_4). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, 1:1 hexane-dichloromethane) to give a pale yellow oil of **8a** (831 mg, 89% yield): ^1H NMR (400 MHz, CDCl_3) δ 0.91 (t, $J = 7.4$ Hz, 6H), 1.36 (m, 4H), 1.53 (m, 4H), 2.46 (s, 2H), 2.68 (d, $J = 1.4$ Hz, 2H), 3.358 (d, $J = 10.8$ Hz, 2H), 3.361 (d, $J = 10.8$ Hz, 2H), 3.41 (t, $J = 6.5$ Hz, 4H), 6.81 (t, $J = 1.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9 ($\times$ 2), 19.3 ($\times$ 2), 31.7 ($\times$ 2), 34.4, 35.1, 54.7, 64.4, 71.1 ($\times$ 2), 73.6 ($\times$ 2), 120.9, 147.0, 153.7; MS (DI) m/z 422 (M^+); Anal. Calcd for $\text{C}_{17}\text{H}_{27}\text{IO}_2\text{S}$: C, 48.34; H, 6.44%. Found: C, 48.21; H, 6.46%.

8b: 69% yield from **7b**; a yellow solid; mp $43\text{--}44\text{ }^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 0.91 (t, $J = 7.5$ Hz, 12H), 1.36 (m, 8H), 1.54 (m, 8H), 2.47 (s, 2H), 2.59 (s, 2H), 2.67 (s, 2H), 2.79 (s, 2H), 3.38 (m, 8H), 3.413 (t, $J = 6.6$ Hz, 4H), 3.420 (t, $J = 6.6$ Hz, 4H), 6.65 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9 ($\times$ 4), 19.3 ($\times$ 4), 31.7 ($\times$ 4), 33.3, 34.4, 35.3, 35.6, 54.7, 55.5, 62.8, 71.1 ($\times$ 4), 73.7 ($\times$ 4), 113.6, 126.5, 133.4, 141.9, 143.2, 147.5, 154.1; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene) m/z 718.6 (M^+); Anal. Calcd for $\text{C}_{34}\text{H}_{53}\text{IO}_4\text{S}_2$: C, 56.97; H, 7.45%. Found: C, 56.80; H, 7.47%.

Dicyanomethyl-substituted mono- and bi-thiophene derivatives 9a,b. A typical procedure: into a solution of sodium hydride (60% in oil, 156 mg, 3.9 mmol) was added malononitrile (127 mg, 1.93 mmol) under a nitrogen atmosphere, and the mixture was stirred at rt for 1.5 h. After tetrakis(triphenylphosphine)palladium (236 mg, 0.20 mmol) was added, a solution of **8a** (725 mg, 1.72 mmol) in dry THF (15 mL) was slowly added over a period of 45 min, and then the mixture was refluxed for 6.5 h. Ice-water (30 mL) was added, and most of the THF solvent was evaporated. The residue was acidified with dil. hydrochloric acid to pH 2 and extracted with dichloromethane (100 mL). The extract was washed with brine and dried (MgSO_4). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, dichloromethane) followed by gel-permeation liquid chromatography (JAIGEL 1H/2H, chloroform) to give a purple oil of **9a** (328 mg, 53% yield): ^1H NMR (400 MHz, CDCl_3) δ 0.91 (t, $J = 7.4$ Hz, 6H), 1.34 (m, 4H), 1.53 (m, 4H), 2.57 (m, 2H), 2.73 (m, 2H), 3.37 (d, $J = 9.0$

Hz, 2H), 3.33 (d, $J = 9.0$ Hz, 2H), 3.42 (t, $J = 6.6$ Hz, 4H), 4.02 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.2 ($\times 2$), 19.6 ($\times 2$), 31.8 ($\times 2$), 34.8, 37.9, 39.6, 54.9, 66.0, 71.6 ($\times 2$), 74.6 ($\times 2$), 113.3, 114.6, 145.2, 170.7, 179.7; MS (DI) m/z 360 (M^+); IR (neat) 2218 cm^{-1} ; Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{N}_2\text{O}_2\text{S}$: C, 66.63; H, 7.83; N, 7.77%. Found: C, 66.68; H, 7.88; N, 7.81%.

9b: 80% yield from **8b**; vermilion oil; ^1H NMR (400 MHz, CDCl_3) δ 0.908 (t, $J = 7.5$ Hz, 6H), 0.911 (t, $J = 7.5$ Hz, 6H), 1.36 (m, 8H), 1.54 (m, 8H), 2.62 (d, $J = 1.0$ Hz, 2H), 2.69 (s, 2H), 2.71 (s, 2H), 2.74 (s, 2H), 3.39–3.42 (m, 8H), 3.42 (t, $J = 6.6$ Hz, 8H), 5.07 (s, 1H), 6.75 (t, $J = 1.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0 ($\times 4$), 19.4 ($\times 4$), 22.3, 31.7 ($\times 4$), 32.6, 33.4, 34.5, 34.7, 55.7, 55.9, 71.2 ($\times 4$), 73.8 ($\times 4$), 110.8 ($\times 2$), 111.5, 115.0, 125.7, 130.2, 143.2, 144.3, 147.8, 149.2; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z 653.6 (M^+); IR (neat) 2211 cm^{-1} ; Anal. Calcd for $\text{C}_{37}\text{H}_{54}\text{N}_2\text{O}_4\text{S}_2$: C, 67.85; H, 8.31; N, 4.28%. Found: C, 67.74; H, 8.30; N, 4.10%.

Quinoidal mono- and bi-thiophenes 5a,b and 6a,b. A typical procedure is described as follows. In a nitrogen atmosphere, a mixture of 1,3-dithiole-2-thione (25 mg, 0.19 mmol), dimethyl sulfate (25 mg, 0.20 mmol), and acetic acid (5 mL) was refluxed for 1 h. A solution of **9a** (60 mg, 0.17 mmol) in acetic acid (10 mL) and then triethylamine (0.1 mL, 0.72 mmol) were successively added. The mixture was refluxed for further 1 h, and, after cooled to rt, treated with dichloromethane (50 mL). The dichloromethane solution was successively washed with water (50 mL $\times 2$) and with aq. sat. sodium hydrogen carbonate (30 mL), and then dried (MgSO_4). After evaporation of the solvent, the residue was purified by column chromatography (silica gel/dichloromethane), preparative gel-permeation liquid chromatography (JAIGEL 1H/2H, chloroform), and finally recrystallization from acetone to give golden needles of **5a** (61 mg, 80% yield): mp 180–181 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 0.92 (t, $J = 7.4$ Hz, 6H), 1.35 (m, 4H), 1.54 (m, 4H), 2.74 (s, 2H), 2.78 (s, 2H), 3.36 (d, $J = 9.0$ Hz, 2H), 3.41 (d, $J = 9.0$ Hz, 4H), 3.43 (t, $J = 6.6$ Hz, 4H), 6.83 (d, $J = 6.4$ Hz, 1H), 6.87 (d, $J = 6.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9 ($\times 2$), 19.2 ($\times 2$), 31.5 ($\times 2$), 34.3, 36.1, 54.8, 56.3, 71.2 ($\times 2$), 74.1 ($\times 2$), 115.6, 116.5, 116.6, 121.9, 123.3, 141.6, 149.5, 159.8, 163.9; MS (DI) m/z 460 (M^+); IR (KBr) 2203 cm^{-1} ; Anal. Calcd for $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_2\text{S}_3$: C, 59.97; H, 6.13; N, 6.08%. Found: C, 59.96; H, 6.14; N, 6.00%.

5b: 55% yield from **9b** and 1,3-dithiole-2-thione; golden needles from acetone–acetonitrile; dp 241 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 0.92 (t, $J = 7.4$ Hz, 12H), 1.36 (m, 8H), 1.55 (m, 8H), 2.67 (s, 2H), 2.76 (s, 2H), 2.77 (s, 2H), 2.83 (s, 2H), 3.36–3.48 (m, 16H), 6.72 (d, $J = 6.6$ Hz, 1H), 6.76 (d, $J = 6.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9 ($\times 4$), 19.4 ($\times 4$), 31.6 ($\times 4$), 34.2, 35.6, 36.1 ($\times 2$), 52.7, 54.8, 55.2, 71.3 ($\times 4$), 74.1 ($\times 2$), 74.2 ($\times 2$), 117.2, 118.2, 118.4, 119.9, 121.2, 122.8, 140.9, 142.1, 142.6, 144.3, 156.0, 159.3, 162.6; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z 753.4 (M^+); IR (KBr) 2195 cm^{-1} ; Anal. Calcd for

C₄₀H₅₄N₂O₄S₄: C, 63.62; H, 7.21; N, 3.71%. Found: C, 63.61; H, 7.21; N, 3.68%.

6a: 75% yield from **9a** and benzo[d]-1,3-dithiole-2-thione; golden needles from acetonitrile; mp 174–175 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, *J* = 7.4 Hz, 6H), 1.35 (m, 4H), 1.54 (m, 4H), 2.79 (s, 2H), 2.83 (s, 2H), 3.37 (d, *J* = 9.0 Hz, 2H), 3.42 (d, *J* = 9.0 Hz, 2H), 3.45 (t, *J* = 6.4 Hz, 4H), 7.32–7.52 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9 (× 2), 19.4 (× 2), 31.6 (× 2), 34.4, 36.4, 54.9, 58.5, 71.4 (× 2), 74.2 (× 2), 115.3, 116.3, 117.8, 122.8, 123.0, 127.8, 127.9, 135.3, 136.7, 142.8, 144.5, 160.0, 164.9; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 509.1 (M⁺); IR (KBr) 2207 cm⁻¹; Anal. Calcd for C₂₇H₃₀N₂O₂S₃: C, 63.49; H, 5.92; N, 5.48%. Found: C, 63.49; H, 5.94; N, 5.44%.

6b: 64% from **9b** and benzo[d]-1,3-dithiole-2-thione; golden powder from acetone-acetonitrile; mp 285–286 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, *J* = 7.4 Hz, 12H), 1.36 (m, 8H), 1.55 (m, 8H), 2.66 (s, 2H), 2.80 (s, 2H), 2.82 (s, 2H), 2.86 (s, 2H), 3.37–3.50 (m, 16H), 7.24–7.42 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 14.3 (× 4), 19.7 (× 4), 31.8 (× 4), 34.4, 35.8, 36.4, 36.6, 54.3, 55.1, 55.5, 71.1 (× 4), 74.0 (× 2), 74.2 (× 2), 117.1, 118.0, 119.3, 121.1, 122.3, 122.6, 127.5 (× 2), 135.5, 136.0, 137.0, 142.2, 143.3, 145.4, 156.0, 159.7, 163.3; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 802.1 (M⁺); IR (KBr) 2197 cm⁻¹; Anal. Calcd for C₄₄H₅₆N₂O₄S₄: C, 65.63; H, 7.01; N, 3.48%. Found: C, 65.66; H, 7.03; N, 3.46%.

Formyl-substituted terthiophene derivative 11. Into a solution of the terthiophene derivative **10** (447 mg, 0.51 mmol) and DMF (40 μL, 0.51 mmol) in 1,2-dichloroethane (20 mL) cooled at 0 °C was added phosphorus oxychloride (0.10 mL, 1.09 mmol) under a nitrogen atmosphere, and the mixture was refluxed for 8 h. After cooled to rt, 1.5 M aq. sodium hydroxide (10 mL) was added. The mixture was stirred for 30 min, and then extracted with chloroform (50 mL × 3). The extracts were combined, washed with brine, and dried (MgSO₄). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, chloroform) to give a yellow oil of **11** (434 mg, 95% yield): ¹H NMR (400 MHz, CDCl₃) δ 0.89–0.93 (m, 18H), 1.32–1.42 (m, 12H), 1.51–1.58 (m, 12H), 2.63 (s, 2H), 2.75 (s, 2H), 2.76 (s, 2H), 2.78 (s, 2H), 2.79 (s, 2H), 2.94 (s, 2H), 3.42–3.45 (m, 24H), 6.74 (s, 1H), 9.77 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9 (× 6), 19.4 (× 6), 31.7 (× 6), 33.3, 33.4, 34.2, 34.5, 34.7, 35.4, 55.5 (× 3), 71.2 (× 6), 73.9 (× 6), 114.5, 124.5, 126.8, 129.6, 129.8, 138.3, 143.0, 143.6, 143.7, 147.4, 147.8, 158.1, 181.3; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 911.1 (M⁺); Anal. C₅₂H₈₀O₇S₃: C, 68.38; H, 8.83%. Found: C, 68.35; H, 8.80%.

Bromo- and formyl-substituted terthiophene derivative 12. Into an ice-cooled solution of **11** (434 mg, 0.48 mmol) in a mixed solvent of DMF (20 mL) and chloroform (5 mL) was added NBS (118 mg, 0.66 mmol), and the mixture was stirred at rt for 2.5 h. After aq. sat. sodium

hydrogen carbonate (10 mL) was added, the mixture was extracted with chloroform (50 mL $\times$ 3). The extracts were combined, washed with brine, and dried (MgSO₄). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, chloroform) to give an orange solid of **12** (368 mg, 78% yield): mp 57–58 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.89–0.93 (m, 18H), 1.32–1.42 (m, 12H), 1.51–1.58 (m, 12H), 2.54 (s, 2H), 2.71 (s, 2H), 2.76 (s, 2H), 2.79 (s, 2H), 2.80 (s, 2H), 2.93 (s, 2H), 3.40–3.45 (m, 24H), 9.77 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9 ($\times$ 6), 19.3 ($\times$ 6), 31.6 ($\times$ 6), 33.2, 33.6, 34.1, 34.5, 35.3, 35.4, 55.1, 55.5, 55.6, 71.2 ($\times$ 6), 73.8 ($\times$ 6), 102.0, 124.9, 128.0, 128.3, 129.9, 137.9, 142.7, 143.2, 144.0, 147.3, 148.1, 157.9, 181.3; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z 989.9 (M⁺); Anal. Calcd for C₅₂H₇₉BrO₇S₃: C, 62.94; H, 8.02%. Found: C, 63.07; H, 7.95%.

Bromo- and benzo-1,3-dithiol-2-yl-substituted terthiophene derivative 13. A mixture of *p*-toluenesulfonic acid monohydrate (29 mg, 0.16 mmol) and 1,2-benzenedithiol (51.5 mg, 0.36 mmol) in benzene (80 mL) was refluxed for 3.5 h, while water in the reaction system was removed by azeotropic distillation. A solution of **12** (184 mg, 0.19 mmol) in benzene (40 mL) was added, and the mixture was again refluxed for 2 h, while water was removed by azeotropic distillation. After aq. sat. sodium hydrogen carbonate (40 mL) was added, the mixture was stirred for 30 min and extracted with chloroform (50 mL $\times$ 3). The extracts were combined, washed with brine, and dried (MgSO₄). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, 2:1 hexane–dichloromethane) to give a yellowish green oil of **13** (148 mg, 71% yield): ¹H NMR (400 MHz, CHCl₃) δ 0.89–0.93 (m, 18H), 1.32–1.42 (m, 12H), 1.51–1.58 (m, 12H), 2.56 (s, 2H), 2.59 (s, 2H), 2.66 (s, 2H), 2.67 (s, 2H), 2.68 (s, 2H), 2.72 (s, 2H), 3.38–3.44 (m, 24H), 6.43 (s, 1H), 7.03–7.07 (AA'BB' m, 2H), 7.17–7.21 (AA'BB' m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9 ($\times$ 6), 19.4 ($\times$ 6), 31.6 ($\times$ 6), 33.0, 33.5, 34.5 ($\times$ 2), 34.7, 35.4, 51.6, 55.0, 55.2, 55.4, 71.4 ($\times$ 6), 73.8 ($\times$ 3), 73.9 ($\times$ 3), 100.9, 121.9 ($\times$ 2), 125.5, 125.8 ($\times$ 2), 125.9, 127.4, 128.5, 129.1, 137.5 ($\times$ 2), 141.7, 142.3, 142.5, 143.7, 146.5, 147.9; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z 1114.2 (M⁺); Anal. Calcd for C₅₈H₈₃BrO₆S₅: C, 62.39; H, 7.49%. Found: C, 62.10; H, 7.20%.

Quinoidal terthiophene 6c. In a nitrogen atmosphere, a mixture of sodium hydride (60% in oil, 34 mg, 0.84 mmol) and malononitrile (30 mg, 0.46 mmol) in dry THF (5 mL) was stirred for 1 h at rt. Under dark, tetrakis(triphenylphosphine)palladium(0) (17 mg) and dppf (16 mg) were added, and a solution of **13** (82 mg, 0.073 mmol) in dry THF (15 mL) was added over a period of 30 min. The mixture was refluxed for 5 h and then treated with 2 *N* hydrochloric acid (15 mL). After stirred for 10 min at rt, the mixture was extracted with chloroform (50 mL $\times$ 3). The extracts were combined, washed with brine, and dried (MgSO₄). After evaporation of the

solvent, the residue was purified by column chromatography (silica gel, chloroform) followed by recrystallization from acetone to give a black powder of **7c** (14.1 mg, 17%): mp 217–218 °C; ^1H NMR (400 MHz, CHCl_3) δ 0.89–0.93 (m, 18H), 1.32–1.42 (m, 12H), 1.51–1.58 (m, 12H), 2.70 (s, 2H), 2.74 (br s, 4H), 2.84 (br s, 4H), 2.88 (s, 2H), 3.37–3.53 (m, 24H), 7.22–7.28 (m, 2H), 7.34–7.36 (m, 2H); MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z 1097.9 (M^+); IR (KBr) 2178 cm^{-1} ; Anal. Calcd for $\text{C}_{61}\text{H}_{82}\text{N}_2\text{O}_6\text{S}_3$: C, 66.63; H, 7.52; N, 2.55%. Found: C, 66.40; H, 7.54; N, 2.54%.

X-ray crystallographic analysis of 5b. Single crystals were grown by recrystallization from chloroform. The X-ray crystal structure analysis was made on a Rigaku AFC7R four-circle diffractometer ($\text{MoK}\alpha$ radiation, $\lambda = 0.71069\text{ \AA}$, graphite monochromator, $T = 296\text{ K}$, φ scan, $2\theta_{\text{max}} = 55.0^\circ$). The structure was solved by the direct methods. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the crystallographic software package teXsan (Molecular Structure Corporation, 2000). Crystal data for **5b**: $\text{C}_{40}\text{H}_{54}\text{N}_2\text{O}_4\text{S}_4$, $M = 755.12$, black needles, $0.50 \times 0.08 \times 0.03\text{ mm}^3$, *triclinic*, space group *P*–*1* (no. 2), $a = 12.77(1)$, $b = 17.90(2)$, $c = 9.388(5)\text{ \AA}$, $\alpha = 97.01(6)$, $\beta = 98.04(5)$, $\gamma = 98.57(7)^\circ$, $V = 2078(2)\text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.06\text{ g cm}^{-3}$, $R_I = 0.062$ for 4793 observed reflections ($I > 1.0\sigma(I)$) and 452 variable parameters, $R_w = 0.140$ for all data.

Figure S1. Solvent dependency of the absorption bands in wavenumber units of **5a,b** and **6a–c** with π^* scales.