Supporting Information

Syntheses, Structures, Spectroscopic Properties, and π-Dimeric Interactions of [n.n]Quinquethiophenophanes

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α,ω-Bis(5'-bromo-3'-octyl-2,2'-bithien-5-yl)alkanes (6a,b). A typical synthetic procedure is as follows. *N*-Bromosuccinimide (300 mg, 1.68 mmol) was added to a solution of 1,2-bis(3'-octyl-2,2'-bithien-5-yl)ethane **5a**[17] (480 mg, 0.82 mmol) in DMF (40 mL) at 0 °C, and then the mixture was stirred at rt for 11 h. After cooling to 0 °C, water (30 mL) was added. The mixture was filtered through a celite pad, and extracted with hexane (30 mL x 3). The extracts were combined, washed with brine, and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography on silica gel with hexane to give yellow fine crystals of **6a** (540 mg, 89%): mp 39–40 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.7 Hz, 6H), 1.26–1.42 (m, 20H), 1.56 (quin, *J* = 7.8 Hz, 4H), 2.64 (t, *J* = 7.8 Hz, 4H), 3.18 (s, 4H), 6.74 (d, *J* = 3.6 Hz, 2H), 6.85 (d, *J* = 3.6 Hz, 2H), 6.86 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 29.2, 29.4 (2 carbons), 29.5, 30.7, 32.0, 32.2, 110.1, 125.3, 126.2, 132.4, 132.6, 133.1, 140.1, 144.2; MS (EI) *m/z* 738, 740, 742 (M^+); Anal. Calcd for $C_{34}H_{44}Br_2S_4$: C, 55.13; H, 5.99%. Found: C, 55.28; H, 5.89%.

6b: 93% yield from 1,3-bis(3'-octyl-2,2'-bithien-5-yl)propane **5b**[17]; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 6H), 1.26–1.42 (m, 20H), 1.57 (quin, *J* = 7.8 Hz, 4H), 2.10 (quin, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.8 Hz, 4H), 2.89 (t, *J* = 7.6 Hz, 4H), 6.74 (d, *J* = 3.4 Hz, 2H), 6.86 (d, *J* = 3.4 Hz, 2H), 6.86 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 29.1, 29.3, 29.5 (2 carbons), 30.7, 32.0, 33.2, 110.0, 124.9, 126.2, 132.6, 132.8, 139.9, 145.3; MS (EI) *m/z* 752, 754, 756 (M^+); Anal. Calcd for $C_{35}H_{46}Br_2S_4$: C, 55.69; H, 6.14%. Found: C, 55.65; H, 6.12%.

α,ω-Bis(3'-octyl-5'-trimethylsilylethynyl-2,2'-bithien-5-yl)alkanes (7a,b). A typical synthetic procedure is as follows. A mixture of **6a** (509 mg, 0.68 mmol), (trimethylsilyl)acetylene (430 mg, 4.1 mmol), $Pd(PPh_3)_4$ (65 mg), and copper(I) iodide (10 mg) in triethylamine (10 mL) was heated to 70 °C for 12 h, and then poured into 1 *N* hydrochloric acid (15 mL) with ice-cooling. After the insoluble materials were removed by filtration through a celite pad, the filtrate was extracted with dichloromethane (20 mL x 3). The extracts were combined, successively washed with aq. sat. sodium bicarbonate (100 mL) and brine (100 mL), and dried ($MgSO_4$). After evaporation of the

solvent, column chromatography of the residue (silica gel, 5:1 hexane–dichloromethane) gave a yellow oil of **7a** (515 mg, 97%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 18H), 0.87 (t, *J* = 7.0 Hz, 6H), 1.26–1.42 (m, 20H), 1.56 (quin, *J* = 7.8 Hz, 4H), 2.65 (t, *J* = 7.8 Hz, 4H), 3.19 (s, 4H), 6.75 (d, *J* = 3.5 Hz, 2H), 6.92 (d, *J* = 3.5 Hz, 2H), 7.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –0.13, 14.1, 22.6, 29.0, 29.2, 29.4 (2 carbons), 30.4, 31.8, 32.1, 97.6, 99.3, 120.4, 125.2, 126.0, 132.8, 133.4, 135.5, 138.8, 144.1; MS (EI) *m/z* 774 (M^+); Anal. Calcd for $C_{44}H_{62}S_4Si_2$: C, 68.15; H, 8.06%. Found: C, 68.40; H, 8.25%.

7b: 97% yield from **6b**; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 18H), 0.87 (t, *J* = 7.0 Hz, 6H), 1.26–1.42 (m, 20H), 1.56 (quin, *J* = 7.8 Hz, 4H), 2.09 (quin, *J* = 7.4 Hz, 2H), 2.66 (t, *J* = 7.8 Hz, 4H), 2.90 (t, *J* = 7.4 Hz, 4H), 6.75 (d, *J* = 3.5 Hz, 2H), 6.93 (d, *J* = 3.5 Hz, 2H), 7.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.0, 14.1, 22.7, 29.1, 29.3, 29.5, 30.5, 31.9, 33.1, 97.8, 99.3, 120.4, 125.0, 126.1, 133.0, 133.2, 135.6, 138.8, 145.3; MS (EI) *m/z* 788 (M^+); Anal. Calcd for $C_{45}H_{64}S_4Si_2$: C, 68.47; H, 8.17%. Found: C, 68.54; H, 8.25%.

α,ω-Bis(5'-ethynyl-3'-octyl-2,2'-bithien-5-yl)alkanes (8a,b). A typical synthetic procedure is as follows. A mixture of **7a** (264 mg, 0.32 mmol) and KOH (95 mg) in benzene (4 mL) and methanol (12 mL) was stirred at rt for 5 h. After the solvent was evaporated, the residue was extracted with dichloromethane (30 mL x 3). The extracts were combined, and washed successively with aq. sat. sodium bicarbonate (100 mL), brine (100 mL), and water (100 mL). After dryness ($MgSO_4$) and evaporation of the solvent, the residue was purified by column chromatography (silica gel, 5:2 hexane–dichloromethane) followed by recrystallization from hexane to give yellow fine crystals of **8a** (186 mg, 93%): mp 57–58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 6H), 1.26–1.42 (m, 20H), 1.56 (quin, *J* = 7.8 Hz, 4H), 2.66 (t, *J* = 7.8 Hz, 4H), 3.18 (s, 4H), 3.34 (s, 2H), 6.74 (d, *J* = 3.7 Hz, 2H), 6.92 (d, *J* = 3.7 Hz, 2H), 7.07 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 29.0, 29.2, 29.3, 29.4, 30.4, 31.8, 32.0, 77.1, 81.6, 119.2, 125.2, 126.1,

133.0, 133.2, 135.8, 138.8, 144.1; MS (EI) *m/z* 630 (M^+); Anal. Calcd for $C_{38}H_{46}S_4$: C, 72.33; H, 7.35%. Found: 72.35; H, 7.37%.

8b: quantitative yield from **7b**; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 6H), 1.26–1.42 (m, 20H), 1.59 (quin, *J* = 7.8 Hz, 4H), 2.10 (quin, *J* = 7.4 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 4H), 2.90 (t, *J* = 7.4 Hz, 4H), 3.35 (s, 2H), 6.75 (d, *J* = 3.6 Hz, 2H), 6.94 (d, *J* = 3.6 Hz, 2H), 7.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 29.0, 29.2 (2 carbons), 29.3, 29.4, 30.4, 31.8, 33.0, 77.1, 81.6, 119.1, 124.9, 126.2, 132.9, 133.2, 135.9, 138.7, 145.3; MS (EI) *m/z* 644 (M^+); Anal. Calcd for $C_{39}H_{48}S_4$: C, 72.62; H, 7.50%. Found: 72.47; H, 7.52%.

Eglinton coupling of 8a,b to cyclic dimers (9a,b). A typical synthetic procedure is as follows. A solution of **8a** (156 mg, 0.25 mmol) in pyridine (50 mL) was slowly added into a mixture of pyridine (150 mL), copper(II) acetate anhydride (1.2 g) at 45 °C over a period of 20 h, and then the mixture was stirred at the same temperature for 3 h, cooled to rt, and then poured into 5 *N* hydrochloric acid (100 mL) and chloroform (100 mL) with ice-cooling. The chloroform layer was separated, and the aqueous layer was extracted with chloroform (40 mL x 3). The combined extract was washed successively with 1 *N* hydrochloric acid (150 mL x 4), aq. sat. sodium bicarbonate (150 mL), brine (150 mL), and water (150 mL). After dryness ($MgSO_4$) and evaporation of the solvent, the residue was purified by column chromatography (alumina, dichloromethane) followed by preparative GPLC (JAIGEL-1H/2H, chloroform) to give a yellow semisolid of **9a** (34 mg, 22%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 12H), 1.25–1.42 (m, 40H), 1.59 (m, 8H), 2.63 (t, *J* = 7.8 Hz, 8H), 3.17 (s, 8H), 6.73 (d, *J* = 3.6 Hz, 4H), 6.92 (d, *J* = 3.6 Hz, 4H), 7.11 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 29.0, 29.2, 29.3, 29.4, 30.3, 31.8, 31.9, 77.5, 78.7, 119.4, 125.8, 126.2, 133.7, 134.8, 136.6, 138.9, 143.8; MS (MALDI-TOF) *m/z* 1256 (M^+); Anal. Calcd for $C_{76}H_{88}S_8$: C, 72.56; H, 7.05%. Found: 72.45; H, 7.15%.

9b: 9% yield from **8b**; yellow fine crystals from hexane; mp 154–156 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 12H), 1.26–1.42 (m, 40H), 1.54–1.60 (m, 8H), 2.09 (quin, *J* = 7.3 Hz, 4H), 2.64

(t, *J* = 7.9 Hz, 8H), 2.89 (t, *J* = 7.3 Hz, 8H), 6.74 (d, *J* = 3.6 Hz, 4H), 6.89 (d, *J* = 3.6 Hz, 4H), 7.11 (s, 4H); MS (MALDI-TOF) *m/z* 1285 (M^+); Anal. Calcd for $C_{78}H_{92}S_8$: C, 72.84; H, 7.21%. Found: 73.08; H, 7.03%.

[2.2]- and [3.3]Quinquethiophenophanes (4a,b). A typical synthetic procedure is as follows. A mixture of **9a** (53 mg, 0.042 mmol), $Na_2S•9H_2O$ (86 mg, 0.36 mmol), and KOH (4 mg) in dioxane (16 mL) was refluxed for 22 h. After water (50 mL) was added, the mixture was extracted with chloroform (10 mL x 4). The extracts were combined and successively washed with sat. aq. ammonium chloride (50 mL), brine (50 mL), and water (50 mL). After dryness ($MgSO_4$) and evaporation of the solvent, the residue was purified by column chromatography (silica gel, carbon disulfide) followed by recrystallization from chloroform–methanol to give yellow fine crystals of **4a** (23 mg, 41%): mp 175–177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 12H), 1.24–1.40 (m, 40H), 1.60 (quin, *J* = 7.8 Hz, 8H), 2.64 (t, *J* = 7.8 Hz, 8H), 3.13 (s, 8H), 6.76 (d, *J* = 3.5 Hz, 4H), 6.88 (s, 4H), 6.92 (d, *J* = 3.5 Hz, 4H), 6.94 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 29.1, 29.2, 29.4, 29.5, 29.7, 30.5, 31.9, 32.1, 124.2, 125.6, 125.9 (2 carbons), 130.2, 134.5, 135.1, 135.8, 139.7, 143.1; MS (FAB) *m/z* 1324 (M^+); Anal. Calcd for $C_{76}H_{92}S_{10}$: C, 68.83; H, 6.99%. Found: C, 68.92; H, 7.16%.

4b: 17% yield from **9b**; yellow fine crystals from chloroform–methanol; mp 158–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 12H), 1.24–1.40 (m, 40H), 1.60 (quin, *J* = 7.8 Hz, 8H), 2.15 (quin, *J* = 6.5 Hz, 4H), 2.64 (t, *J* = 7.8 Hz, 8H), 2.93 (t, *J* = 6.5 Hz, 8H), 6.62 (d, *J* = 3.5 Hz, 4H), 6.79 (d, *J* = 3.5 Hz, 4H), 6.89 (s, 4H), 6.93 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 29.3, 29.4, 29.6, 29.8, 30.5, 31.9, 32.8, 123.9, 125.0, 125.4, 126.0, 130.4, 134.2, 134.6, 135.9, 139.6, 145.4; MS (MALDI-TOF) *m/z* 1352.5 (M^+); Anal. Calcd for $C_{78}H_{96}S_{10}$: C, 69.18; H, 7.15%. Found: C, 69.10; H, 7.10%.

Monobromo derivatives of α,ω-bis(3'-octyl-2,2'-bithien-5-yl)alkanes (10c–e). The monobromination of **5c–e** to **10c–e** was carried out using one equivalent of NBS in a similar manner

as above-described for the dibromination of **5a,b** to **6a,b**.

10c: 61% yield from **5c**; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85–0.89 (m, 6H), 1.26–1.42 (m, 20H), 1.53–1.61 (m, 4H), 1.86–1.90 (m, 4H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.82–2.88 (m, 4H), 6.71 (d, *J* = 3.4 Hz, 1H), 6.72(d, *J* = 3.4 Hz, 1H), 6.84 (d, *J* = 3.6 Hz, 1H), 6.86 (s, 1H), 6.89 (d, *J* = 3.6 Hz, 1H), 6.90 (d, *J* = 5.3 Hz, 1H), 7.12 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.6, 29.0, 29.1, 29.2 (2 carbons), 29.3, 29.5, 29.7, 30.5, 30.7, 30.8, 31.8, 109.8, 123.1, 124.4, 124.5, 125.5, 126.0, 129.7, 130.9, 132.3, 132.5, 133.8, 138.9, 139.6, 145.1, 145.8; MS (MALDI-TOF) *m/z* 687.0 (M^+); Anal. Calcd for $C_{36}H_{49}BrS_4$: C, 62.67; H, 7.16%. Found: C, 62.67; H, 7.21%.

10d: 60% yield from **5d**; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 6H), 1.26–1.42 (m, 20H), 1.48 (quin, *J* = 7.5 Hz, 2H), 1.55–1.65 (m, 4H), 1.74 (quin, *J* = 7.0 Hz, 2H), 1.75 (quin, *J* = 7.0 Hz, 2H), 2.64 (t, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 6.71 (d, *J* = 3.4 Hz, 1H), 6.72 (d, *J* = 3.4 Hz, 1H), 6.84 (d, *J* = 3.6 Hz, 1H), 6.86 (s, 1H), 6.89 (d, *J* = 3.6 Hz, 1H), 6.90 (d, *J* = 5.3 Hz, 1H), 7.12 (d, *J* = 5.3 Hz, 1H); MS (MALDI-TOF) *m/z* 701.3 (M^+); Anal. Calcd for $C_{37}H_{51}BrS_4$: C, 63.13; H, 7.30%. Found: C, 63.08; H, 7.31%.

10e: 56% yield from **5e**; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 6H), 1.26–1.42 (m, 20H), 1.40–1.48 (m, 4H), 1.54–1.63 (m, 4H), 1.62–1.75 (m, 4H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.76–2.84 (m, 4H), 6.71 (d, *J* = 3.4 Hz, 1H), 6.72 (d, *J* = 3.4 Hz, 1H), 6.84 (d, *J* = 3.6 Hz, 1H), 6.86 (s, 1H), 6.89 (d, *J* = 3.6 Hz, 1H), 6.90 (d, *J* = 5.3 Hz, 1H), 7.12 (d, *J* = 5.3 Hz, 1H); MS (MALDI-TOF) *m/z* 713.7 (M^+); Anal. Calcd for $C_{38}H_{53}BrS_4$: C, 63.57; H, 7.44%. Found: C, 63.51; H, 7.44%.

Mono(trimethylsilylethynyl) derivatives of α,ω-bis(3'-octyl-2,2'-bithien-5-yl)alkanes (11c–e). The trimethylsilylethynylation of **10c–e** to **11c–e** was carried out in a similar manner as above-described for the conversion of **6a,b** to **7a,b**.

11c: 99% yield from **10c**; yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 9H), 0.85–0.89 (m, 6H), 1.26–1.42 (m, 20H), 1.53–1.61 (m, 4H), 1.86–1.90 (m, 4H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.82–2.88 (m, 4H), 6.71 (d, *J* = 3.6 Hz, 2H), 6.89 (d, *J* = 3.6 Hz, 1H), 6.89 (d, *J* = 5.1 Hz, 1H), 6.91(d, *J* = 3.6 Hz, 1H), 7.03 (s, 1H), 7.10 (d, *J* = 5.1 Hz, 1H); MS (MALDI-TOF) *m/z* 704.9 (M^+); Anal. Calcd for $C_{41}H_{58}S_4Si$: C, 69.63; H, 8.27%. Found: C, 69.61; H, 8.10%.

11d: 95% yield from **10d**; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 9H), 0.88 (t, *J* = 7.0 Hz, 6H), 1.26–1.42 (m, 20H), 1.49 (quin, *J* = 7.5 Hz, 2H), 1.55–1.65 (m, 4H), 1.74 (quin, *J* = 7.0 Hz, 4H), 2.66 (t, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 4H), 6.71 (d, *J* = 3.6 Hz, 2H), 6.89 (d, *J* = 3.6 Hz, 1H), 6.89 (d, *J* = 5.1 Hz, 1H), 6.91 (d, *J* = 3.6 Hz, 1H), 7.03 (s, 1H), 7.12 (d, *J* = 5.1 Hz, 1H); MS (MALDI-TOF) *m/z* 718.5 (M^+); Anal. Calcd for $C_{42}H_{60}S_4Si$: C, 69.94; H 8.38%. Found: C, 69.92; H, 8.33%.

11e: 88% yield from **10e**; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 9H), 0.88 (t, *J* = 7.0 Hz, 6H), 1.26–1.42 (m, 20H), 1.40–1.48 (m, 4H), 1.55–1.66 (m, 4H), 1.66–1.75 (m, 4H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.81 (t, *J* = 7.0 Hz, 4H), 6.71 (d, *J* = 3.6 Hz, 2H), 6.90 (d, *J* = 3.6 Hz, 1H), 6.91 (d, *J* = 5.1 Hz, 1H), 6.91 (d, *J* = 3.6 Hz, 1H), 7.05 (s, 1H), 7.12 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ –0.1, 14.1, 22.7, 28.8, 29.1 (2 carbons), 29.2 (2 carbons), 29.4, 29.5, 30.0, 30.4, 30.7, 31.4, 31.9, 97.8, 99.2, 120.2, 123.2, 124.3, 124.5, 125.6, 126.0, 129.8, 131.1, 132.8, 133.2, 133.7, 135.5, 138.6, 139.0, 145.8, 146.5; MS (MALDI-TOF) *m/z* 732.7 (M^+); Anal. Calcd for $C_{43}H_{62}S_4Si$: C, 70.24; H, 8.50%. Found: C, 70.26; H, 8.53%.

Mono(ethynyl) derivatives of α,ω-bis(3'-octyl-2,2'-bithien-5-yl)alkanes (12c–e). The detrimethylsilylation of **11c–e** to **12c–e** was carried out in a similar manner as above-described for the conversion of **7a,b** to **8a,b**.

12c: quantitative yield from **11c**; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85–0.89 (m, 6H), 1.26–1.42 (m, 20H), 1.53–1.61(m, 4H), 1.86–1.90 (m, 4H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.82–2.88 (m, 4H), 3.33 (s, 1H), 6.71 (d, *J* = 3.6 Hz, 2H), 6.89 (d, *J* = 3.6 Hz, 1H), 6.89 (d,

J = 5.1 Hz, 1H), 6.91 (d, *J* = 3.6 Hz, 1H), 7.07 (s, 1H), 7.11 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.6, 26.5, 29.1, 29.2, 29.3 (2 carbons), 29.4 (2 carbons), 29.5, 29.8 (2 carbons), 30.4, 30.7, 30.9 (2 carbons), 31.9, 77.2, 123.2, 124.5, 124.9, 125.6, 127.0, 129.8, 130.9, 132.8, 133.8, 135.1, 139.1, 139.7, 140.3, 140.4, 145.2, 147.2; MS (MALDI-TOF) *m/z* 633.2 (M^+); Anal. Calcd for $C_{38}H_{50}S_4$: C, 71.87; H, 7.94%. Found: C, 71.57; H, 7.84%

12d: quantitative yield from **11d**; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 6H), 1.26–1.42 (m, 20H), 1.49 (quin, *J* = 7.5 Hz, 2H), 1.55–1.65 (m, 4H), 1.74 (quin, *J* = 7.0 Hz, 4H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 4H), 3.35 (s, 1H), 6.71 (d, *J* = 3.6 Hz, 2H), 6.89 (d, *J* = 3.6 Hz, 1H), 6.89 (d, *J* = 5.1 Hz, 1H), 6.91 (d, *J* = 3.6 Hz, 1H), 7.08 (s, 1H), 7.12 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.6, 26.5, 28.5, 29.1, 29.2, 29.3, 29.4, 29.5, 29.8, 30.0, 30.4, 30.7, 31.3, 31.9, 77.3, 77.6, 123.2, 124.4, 124.9, 125.6, 126.9, 129.8, 131.0, 132.7, 133.7, 133.8, 135.1, 139.1, 139.6, 140.3, 145.6, 147.6; MS (MALDI-TOF) *m/z* 646.9 (M^+); Anal. Calcd for $C_{39}H_{52}S_4$: C, 72.16; H, 8.07%. Found: C, 72.05; H, 8.25%.

12e: 97% yield from **11e**; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 6H), 1.26–1.42 (m, 20H), 1.40–1.48 (m, 4H), 1.54–1.63(m, 4H), 1.62–1.75 (m, 4H), 2.67(t, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.81 (t, *J* = 7.5 Hz, 4H), 3.35 (s, 1H), 6.71 (d, *J* = 3.6 Hz, 2H), 6.89 (d, *J* = 3.6 Hz, 1H), 6.89 (d, *J* = 5.1 Hz, 1H), 6.91 (d, *J* = 3.6 Hz, 1H), 7.08 (s, 1H), 7.12 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.6, 26.5, 29.1, 29.2, 29.3 (2 carbons), 29.4, 29.5, 29.7, 29.8, 30.4, 30.7, 30.9, 31.8, 77.1, 123.2, 124.5, 124.9, 125.6, 126.9, 129.8, 130.9, 132.7, 133.8, 135.1, 139.1, 139.6, 140.3 (2 carbons), 145.1, 147.2; MS (MALDI-TOF) *m/z* 661.1 (M^+); Anal. Calcd for $C_{40}H_{54}S_4$: C, 72.45; H, 8.21%. Found: C, 72.67; H, 8.15%.

Acyclic dimers (13c–e). The Eglinton couplings of monoacetylenes **12c–e** to the acyclic dimers **13c–e** were carried out in a similar manner as above-described for the conversion of **8a,b** to **9a,b**.

13c: 98% yield from **12c**; orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85–0.89 (m, 12H), 1.26–1.42 (m, 40H), 1.53–1.61 (m, 8H), 1.86–1.90 (m, 8H), 2.69 (t, *J* = 8.0 Hz, 4H), 2.72 (t, *J* = 8.0

Hz, 4H), 2.82–2.88 (m, 8H), 6.73 (d, *J* = 3.6 Hz, 2H), 6.74 (d, *J* = 3.6 Hz, 2H), 6.90 (d, *J* = 3.6 Hz, 2H), 6.91 (d, *J* = 5.1 Hz, 2H), 6.95 (d, *J* = 3.6 Hz, 2H), 7.12 (d, *J* = 5.1 Hz, 2H), 7.14 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.7, 29.1, 29.2, 29.4 (2 carbons), 29.5, 29.8, 30.4, 30.7, 30.9, 31.9, 78.6, 118.9, 123.2, 124.5, 124.7, 125.6, 126.4, 129.8, 131.0, 132.6, 133.8, 134.9, 137.2, 138.9, 139.1, 145.2, 146.4; MS (MALDI-TOF) *m/z* 1265.2 (M^+); Anal. Calcd for $C_{76}H_{98}S_8$: C, 71.98; H, 7.79%. Found: C, 71.71; H, 7.83%.

13d: 97% from **12d**; orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 12H), 1.26–1.42 (m, 40H), 1.49 (quin, *J* = 7.5 Hz, 4H), 1.55–1.65 (m, 8H), 1.74 (quin, *J* = 7.0 Hz, 8H), 2.67 (t, *J* = 8.0 Hz, 4H), 2.72 (t, *J* = 8.0 Hz, 4H), 2.82 (t, *J* = 7.5 Hz, 8H), 6.70 (d, *J* = 3.6 Hz, 2H), 6.71 (d, *J* = 3.6 Hz, 2H), 6.89 (d, *J* = 3.6 Hz, 2H), 6.89 (d, *J* = 5.1 Hz, 2H), 6.93 (d, *J* = 3.6 Hz, 2H), 7.10 (d, *J* = 5.1 Hz, 2H), 7.12 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.6, 28.5, 29.1, 29.2, 29.4, 29.5, 29.9, 30.3, 30.7, 31.2, 31.8, 77.5, 78.7, 118.8, 123.1, 124.3, 124.6, 125.5, 126.3, 129.7, 131.0, 132.5, 133.7, 134.9, 137.1, 138.8, 138.9, 145.4, 146.6; MS (MALDI-TOF) *m/z* 1292.4 (M^+); Anal. Calcd for $C_{78}H_{102}S_8$: C, 72.28; H, 7.93%. Found: C, 72.22; H, 7.91%.

13e: 84% yield from **12e**; orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 12H), 1.26–1.42 (m, 40H), 1.38–1.44 (m, 8H), 1.54–1.62 (m, 8H), 1.63–1.73 (m, 8H), 2.66 (t, *J* = 8.0 Hz, 4H), 2.71 (t, *J* = 8.0 Hz, 4H), 2.77 (t, *J* = 7.5 Hz, 8H), 6.67 (d, *J* = 3.6 Hz, 4H), 6.86 (d, *J* = 3.6 Hz, 2H), 6.87 (d, *J* = 5.1 Hz, 2H), 6.91 (d, *J* = 3.6 Hz, 2H), 7.06 (d, *J* = 5.1 Hz, 2H), 7.09 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.7, 28.8, 29.1, 29.2, 29.4 (2 carbons), 29.5, 30.0, 30.4, 30.7, 31.4, 31.9, 77.5, 78.6, 118.8, 122.6, 124.3, 124.6, 125.6, 126.3, 129.8, 131.1, 132.5, 133.7, 135.0, 137.2, 138.9, 139.0, 145.7, 146.9; MS (MALDI-TOF) *m/z* 1322.5 (M^+); Anal. Calcd for $C_{80}H_{106}S_8$: C, 72.56; H, 8.07%. Found: C, 72.60; H, 8.01%.

Bis(bithienylalkyl)quinquethiophenes (14c–e). The thiacyclization of the diacetylenes **13c–e** with sodium sulfide to the quinquethiophenes **14c–e** was carried out in a similar manner as above-described for the conversion of **9a,b** to **4a,b**.

14c: 60% yield from **13c**; orange semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85–0.89 (m, 12H), 1.26–1.42 (m, 40H), 1.53–1.61 (m, 8H), 1.86–1.90 (m, 8H), 2.71 (t, *J* = 8.0 Hz, 4H), 2.73 (t, *J* = 8.0 Hz, 4H), 2.82–2.88 (m, 8H), 6.72 (d, *J* = 3.6 Hz, 2H), 6.73 (d, *J* = 3.6 Hz, 2H), 6.90 (d, *J* = 5.3 Hz, 2H), 6.90 (d, *J* = 3.6 Hz, 2H), 6.93 (d, *J* = 3.6 Hz, 2H), 6.98 (s, 2H), 7.03 (s, 2H) 7.12 (d, *J* = 5.3 Hz, 2H); MS (MALDI-TOF) *m/z* 1302.9 (M^+); Anal. Calcd for $C_{76}H_{100}S_9$: C, 70.10; H, 7.74%. Found: C, 70.05; H, 7.56%.

14d: 57% yield from **13d**; orange semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 6H), 0.88 (t, *J* = 7.0 Hz, 6H), 1.26–1.42 (m, 40H), 1.48 (quin, *J* = 7.5 Hz, 4H), 1.58–1.68 (m, 8H), 1.74 (quin, *J* = 7.0 Hz, 8H), 2.70 (t, *J* = 8.0 Hz, 4H), 2.72 (t, *J* = 8.0 Hz, 4H), 2.81 (t, *J* = 7.5 Hz, 8H), 6.69 (m, 4H), 6.87 (d, *J* = 5.3 Hz, 2H), 6.88 (d, *J* = 3.6 Hz, 2H), 6.91 (d, *J* = 3.6 Hz, 2H), 6.96 (s, 2H), 7.00 (s, 2H), 7.10 (d, *J* = 5.3 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.7, 28.6, 29.1, 29.2, 29.3, 29.4, 29.5, 30.0, 30.5, 30.7, 31.3, 31.9, 123.2, 124.0, 124.4, 124.5, 125.6 (2 carbons), 126.4, 129.8, 130.3, 131.1, 133.4, 133.7, 134.3, 135.9, 139.1, 139.8, 145.6, 145.9; MS (MALDI-TOF) *m/z* 1328.4 (M^+); Anal. Calcd for $C_{78}H_{104}S_9$: C, 70.43; H, 7.88%. Found: C, 70.36; H, 7.79%.

14e: 69% yield from **13e**; orange semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91–0.96 (m, 12H), 1.26–1.42 (m, 40H), 1.42–1.49 (m, 8H),1.63–1.72 (m, 8H), 1.72–1.78 (m, 8H), 2.76 (t, *J* = 8.0 Hz, 4H), 2.78 (t, *J* = 8.0 Hz, 4H), 2.85 (t, *J* = 7.5 Hz, 8H), 6.75 (m, 4H), 6.94 (d, *J* = 5.3 Hz, 2H), 6.95 (d, *J* = 3.6 Hz, 2H), 6.97 (d, *J* = 3.6 Hz, 2H), 7.02 (s, 2H), 7.04 (s, 2H) 7.14 (d, *J* = 5.3 Hz, 2H); MS (MALDI-TOF) *m/z* 1353.4 (M^+); Anal. Calcd for $C_{80}H_{108}S_9$: C, 70.74; H, 8.01%. Found: C, 70.77; H 8.01%.

Diformyl derivatives (15c–e). A typical synthetic procedure is as follows. Phosphorus oxychloride (1.0 mL) was added to a mixture of **14c** (447 mg, 0.34 mmol) and DMF (50 mg, 0.69mmol), and 1,2-dichloroethane (10 mL). The mixture was refluxed for 13 h and cooled to rt. After 1 *N* aq NaOH solution (50 mL) was added, the mixture was stirred at room temperature for 3 h, and extracted with chloroform (30 mL x 3). The extracts were combined, successively washed with

1 *N* hydrochloric acid (30 mL) and water (30 mL), and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography on silica gel with chloroform to give an orange semisolid of **15c** (283 mg, 61%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85–0.89 (m, 12H), 1.26–1.42 (m, 40H), 1.53–1.61 (m, 8H), 1.86–1.90 (m, 8H), 2.71 (t, *J* = 8.0 Hz, 4H), 2.77 (t, *J* = 8.0 Hz, 4H), 2.82–2.88 (m, 8H), 6.74 (d, *J* = 3.6 Hz, 2H), 6.79 (d, *J* = 3.6 Hz, 2H), 6.93 (d, *J* = 3.6 Hz, 2H), 6.98 (s, 2H), 7.02 (s, 2H), 7.11 (d, *J* = 3.6 Hz, 2H), 7.56 (s, 2H), 9.80 (s, 2H); MS (MALDI-TOF) *m/z* 1354.4 (M^+); Anal. Calcd for $C_{78}H_{100}O_2S_9$: C, 68.98; H, 7.42%. Found: C, 68.91; H, 7.36%.

15d: 68% yield from **14d**; orange semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 12H), 1.26–1.42 (m, 40H), 1.49 (quin, *J* = 7.5 Hz, 4H), 1.55–1.65 (m, 8H), 1.75 (quin, *J* = 7.0 Hz, 8H), 2.70 (t, *J* = 8.0 Hz, 4H), 2.75 (t, *J* = 8.0 Hz, 4H), 2.82 (t, *J* = 7.5 Hz, 4H), 2.84 (t, *J* = 7.5 Hz, 4H), 6.72 (d, *J* = 3.6 Hz, 2H), 6.76 (d, *J* = 3.6 Hz, 2H), 6.92 (d, *J* = 3.6 Hz, 2H), 6.97 (s, 2H), 7.01 (s, 2H), 7.09 (d, *J* = 3.6 Hz, 2H), 7.55 (s, 2H), 9.78 (s, 2H); MS (MALDI-TOF) *m/z* 1383.4 (M^+); Anal. Calcd for $C_{80}H_{104}O_2S_9$: C, 69.31; H, 7.56%. Found: C, 69.25; H, 7.57%.

15e: 55% yield from **14e**; orange semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 12H), 1.26–1.42 (m, 40H), 1.42–1.49 (m, 8H), 1.60–1.68 (m, 8H), 1.68–1.78 (m, 8H), 2.70 (t, *J* = 8.0 Hz, 4H), 2.76 (t, *J* = 8.0 Hz, 4H), 2.80 (t, *J* = 7.5 Hz, 4H), 2.82 (t, *J* = 7.5 Hz, 4H), 6.71 (d, *J* = 3.6 Hz, 2H), 6.75 (d, *J* = 3.6 Hz, 2H), 6.91 (d, *J* = 3.6 Hz, 2H), 6.96 (s, 2H), 7.00 (s, 2H), 7.08 (d, *J* = 3.6 Hz, 2H), 7.54 (s, 2H), 9.78 (s, 2H); MS (MALDI-TOF) *m/z* 1412.4 (M^+); Anal. Calcd for $C_{82}H_{108}O_2S_9$: C, 69.64; H, 7.70%. Found: C, 69.56; H, 7.64%.

Bis(dibromoethenyl) derivatives (16c–e). A typical synthetic procedure is as follows. A solution of **15c** (205mg, 0.15mmol) in 1.2-dichloroethane (15 mL) was added to a mixture of tetrabromomethane (200 mg, 0.60 mmol) and triphenylphosphine (317 mg, 1.21 mmol) in 1,2-dichloroethane (3 mL) at 0 °C. The mixture was stirred at rt for 2 h, and then filtered through a celite pad. After evaporation of the solvent, the residue was purified by column chromatography on

silica gel with chloroform–hexane (v/v = 1:1) to give an orange semisolid of **16c** (244 mg, 97% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85–0.89 (m, 12H), 1.26–1.42 (m, 40H), 1.53–1.61 (m, 8H), 1.86–1.90 (m, 8H), 2.70 (t, *J* = 8.0 Hz, 8H), 2.82–2.88 (m, 8H), 6.73 (d, *J* = 3.6 Hz, 4H), 6.92 (d, *J* = 3.6 Hz, 2H), 6.97 (d, *J* = 3.6 Hz, 2H), 6.97 (s, 2H), 7.01 (s, 2H), 7.02 (s, 2H), 7.52 (s, 2H); MS (MALDI-TOF) *m/z* 1664.8 (M^+); Anal. Calcd for $C_{80}H_{100}Br_4S_9$: C, 57.54; H, 6.04%. Found: C, 57.68; H, 5.99%.

16d: 90% yield from **15d**; orange semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 12H), 1.26–1.42 (m, 40H), 1.47 (quin, *J* = 7.5 Hz, 4H), 1.57 (quin, *J* = 7.0 Hz, 4H), 1.63 (quin, *J* = 7.0 Hz, 4H), 1.72 (quin, *J* = 7.0 Hz, 8H), 2.67 (t, *J* = 8.0 Hz, 4H), 2.69 (t, *J* = 8.0 Hz, 4H), 2.79 (t, *J* = 7.5 Hz, 8H), 6.68 (d, *J* = 3.6 Hz, 2H), 6.69 (d, *J* = 3.6 Hz, 2H), 6.90 (d, *J* = 3.6 Hz, 2H), 6.94 (d, *J* = 3.6 Hz, 2H), 6.95 (s, 2H), 6.97 (s, 2H), 6.98 (s, 2H), 7.48 (s, 2H); MS (MALDI-TOF) *m/z* 1696.0 (M^+); Anal. Calcd for $C_{82}H_{104}Br_4S_9$: C, 58.01; H, 6.17%. Found: C, 58.02; H, 6.23%.

16e: 45% yield from **15e**; orange semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 12H), 1.26–1.42 (m, 40H), 1.42–1.49 (m, 8H), 1.54–1.68 (m, 8H), 1.68–1.74 (m, 8H), 2.68 (t, *J* = 8.0 Hz, 4H), 2.70 (t, *J* = 8.0 Hz, 4H), 2.79 (t, *J* = 7.5 Hz, 8H), 6.68–6.71 (m, 4H), 6.90 (d, *J* = 3.6 Hz, 2H), 6.94 (d, *J* = 3.6 Hz, 2H), 6.95 (s, 2H), 6.98 (s, 2H), 7.00 (s, 2H), 7.49 (s, 2H); MS (MALDI-TOF) *m/z* 1724.3 (M^+); Anal. Calcd for $C_{84}H_{108}Br_4S_9$: C, 58.45; H, 6.31%. Found: C, 58.64; H, 6.37%.

Diethynyl derivatives (17c–e). A typical synthetic procedure is as follows. LDA (1.0 mL. 0.5 mmol, 0.5 *M* hexane) was added to a solution of **16c** (132 mg, 0.08 mmol) in THF (20 mL) at –60 °C. After water (10 mL) was added to the reaction mixture, it was extracted with chloroform (30 mL x 3). The extracts were combined, washed with water (30 mL x 2), and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography on silica gel with chloroform–hexane (v/v = 1:2) to give an orange semisolid of **17c** (78 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85–0.89 (m, 12H), 1.26–1.42 (m, 40H), 1.53–1.61 (m, 8H), 1.86–1.90

(m, 8H), 2.70 (t, *J* = 8.0 Hz, 8H), 2.82–2.88 (m, 8H), 3.35 (s, 2H), 6.73 (d, *J* = 3.6 Hz, 4H), 6.92 (d, *J* = 3.6 Hz, 4H), 6.98 (s, 2H), 7.02 (s, 2H), 7.08 (s, 2H); MS (MALDI-TOF) *m/z* 1349.3 (M^+); Anal. Calcd for $C_{80}H_{100}S_9$: C, 71.16; H, 7.46%. Found: C, 71.07; H, 7.39%.

17d: 83% yield from **16d**; orange semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 12H), 1.26–1.42 (m, 40H), 1.49 (quin, *J* = 7.5 Hz, 4H), 1.59 (quin, *J* = 7.0 Hz, 4H), 1.62 (quin, *J* = 7.0 Hz, 4H), 1.75 (quin, *J* = 7.0 Hz, 8H), 2.67 (t, *J* = 8.0 Hz, 4H), 2.71 (t, *J* = 8.0 Hz, 4H), 2.83 (t, *J* = 7.5 Hz, 8H), 3.35 (s, 2H), 6.70–6.74 (m, 4H), 6.92 (d, *J* = 3.6 Hz, 4H), 6.98 (s, 2H), 7.02 (s, 2H), 7.08 (s, 2H); MS (MALDI-TOF) *m/z* 1379.4 (M^+); Anal. Calcd for $C_{82}H_{104}S_9$: C, 71.46; H, 7.61%. Found: C, 71.41; H, 7.68%.

17e: 81% yield from **16e**; orange semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 6H), 0.88 (t, *J* = 7.0 Hz, 6H), 1.26–1.42 (m, 40H), 1.42–1.46 (m, 8H), 1.54–1.68 (m, 8H), 1.68–1.74 (m, 8H), 2.67 (t, *J* = 8.0 Hz, 4H), 2.70 (t, *J* = 8.0 Hz, 4H), 2.80 (t, *J* = 7.5 Hz, 8H), 3.34 (s, 2H), 6.70–6.74 (m, 4H), 6.92 (d, *J* = 3.6 Hz, 4H), 6.97 (s, 2H), 7.02 (s, 2H), 7.08 (s, 2H); MS (FAB) *m/z* 1405 (M^+); Anal. Calcd for $C_{84}H_{108}S_9$: C, 71.74; H, 7.74%. Found: C, 71.63; H, 7.64%.

Cyclic monomers (**18c–e)**. The intramolecular Eglinton coupling of **17c–d** to **18c–d** was carried out in a similar manner as above-described for the conversion of **8a,b** to **9a,b**.

18c: 76% yield from **17c**; orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85–0.89 (m, 12H), 1.26–1.42 (m, 40H), 1.53–1.61 (m, 8H), 1.86–1.90 (m, 8H), 2.70 (t, *J* = 8.0 Hz, 8H), 2.82–2.88 (m, 8H), 6.67 (d, *J* = 3.6 Hz, 2H), 6.69 (d, *J* = 3.6 Hz, 2H), 6.89 (d, *J* = 3.6 Hz, 2H), 6.90 (d, *J* = 3.6 Hz, 2H), 6.97 (s, 2H), 7.04 (s, 2H), 7.10 (s, 2H); MS (MALDI-TOF) *m/z* 1347.5 (M^+); Anal. Calcd for $C_{80}H_{98}S_9$: C, 71.27; H, 7.33%. Found: C, 71.38; H, 7.27%.

18d: 86% yield from **17d**; orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86–0.91 (m, 12H), 1.26–1.42 (m, 44H), 1.49–1.65 (m, 8H), 1.60–1.76 (m, 8H), 2.58–2.70 (m, 8H), 2.78–2.91 (m, 8H), 6.58 (d, *J* = 3.6 Hz, 2H), 6.63 (d, *J* = 3.6 Hz, 2H), 6.82 (d, *J* = 3.6 Hz, 2H), 6.89 (d, *J* = 3.6 Hz, 2H), 6.95 (s, 2H), 7.07 (s, 2H), 7.08 (s, 2H); MS (MALDI-TOF) *m/z* 1373.5 (M^+); Anal. Calcd for

$C_{82}H_{102}S_9$: C, 71.56; H, 7.47%. Found: C, 71.38; H, 7.44%.

18e: 78% yield from **17e**; orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 12H), 1.26–1.42 (m, 48H), 1.54–1.70 (m, 16H), 2.65 (t, *J* = 8.0 Hz, 4H), 2.68 (t, *J* = 8.0 Hz, 4H), 2.79 (t, *J* = 7.5 Hz, 8H), 6.66 (d, *J* = 3.6 Hz, 2H), 6.67 (d, *J* = 3.6 Hz, 2H), 6.88 (d, *J* = 3.6 Hz, 2H), 6.89 (d, *J* = 3.6 Hz, 2H), 6.96 (s, 2H), 7.02 (s, 2H), 7.11 (s, 2H); MS (FAB) *m/z* 1403 (M^+); Anal. Calcd for $C_{84}H_{106}S_9$: C, 71.84; H, 7.61%. Found: C, 71.68; H, 7.68%.

[4.4]-, [5.5]-, and [6.6]Quinquethiophenophanes (4c–e). The thiacyclization of the diacetylenes **18c–e** with sodium sulfide to the quinquethiophenes **4c–e** was carried out in a similar manner as above-described for the conversion of **9a,b** to **4a,b**.

4c: 50% yield from **18c**; orange cotton-like crystals from hexane–benzene; mp 156–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 8.0 Hz, 12H), 1.26–1.42 (m, 40H), 1.57 (quin, *J* = 8.0 Hz, 8H), 1.86–1.90 (m, 8H), 2.65 (t, *J* = 8.0 Hz, 8H), 2.82–2.88 (m, 8H), 6.68 (d, *J* = 3.6 Hz, 4H), 6.89 (d, *J* = 3.6 Hz, 4H), 6.89 (s, 4H), 6.92 (s, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.7, 29.3 (2 carbons), 29.4, 29.6, 29.8, 30.4, 31.9, 124.0, 124.9, 125.3, 126.2, 130.3, 134.1, 134.4, 135.8, 139.6, 145.4; MS (MALDI-TOF) *m/z* 1378.7 (M^+); Anal. Calcd for $C_{80}H_{100}S_{10}$: C, 69.51; H, 7.29%. Found: C, 69.33; H, 7.50%.

4d: 46% yield from **18d**; orange cotton-like crystals from hexane; mp 140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 12H), 1.26–1.46 (m, 44H), 1.59 (quin, *J* = 7.5 Hz, 8H), 1.67 (quin, *J* = 7.0 Hz, 8H), 2.61 (t, *J* = 8.0 Hz, 8H), 2.82 (t, *J* = 7.5 Hz, 8H), 6.59 (d, *J* = 3.6 Hz, 4H), 6.77 (s, 4H), 6.84 (d, *J* = 3.6 Hz, 4H), 6.85 (s, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.7, 25.6, 29.2, 29.3, 29.4 (2 carbons), 29.6, 29.8, 30.4, 31.9, 123.9, 125.1, 125.3, 126.0, 130.3, 133.7, 134.2, 135.7, 139.3, 144.9; MS (MALDI-TOF) *m/z* 1410.8 (M^+); Anal. Calcd for $C_{82}H_{104}S_{10}$: C, 69.83; H, 7.43%. Found: C, 69.65; H, 7.47%.

4e: 52% yield from **18e**; orange cotton-like crystals from hexane; mp 142–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 12H), 1.26–1.42 (m, 48H), 1.62 (quin, *J* = 7.5 Hz, 8H), 1.62 (quin, *J* = 7.0 Hz, 8H), 2.67 (t, *J* = 7.0 Hz, 8H), 2.80 (t, *J* = 7.5 Hz, 8H), 6.67 (d, *J* = 3.6 Hz, 4H), 6.87 (d, *J* = 3.6 Hz, 4H), 6.94 (s, 4H), 6.95 (s, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.7, 27.8, 29.3 (2 carbons), 29.4, 29.6, 29.8, 30.4, 30.9, 31.9, 124.1, 124.9, 125.2, 126.2, 130.3, 133.6, 134.4, 135.8, 139.6, 145.9; MS (MALDI-TOF) *m/z* 1437.1 (M^+); Anal. Calcd for $C_{84}H_{108}S_{10}$: C, 70.14; H, 7.57%. Found: C, 70.22; H, 7.60%.

5,5””-Dimethyl-3’,4”’-dioctyl-2,2’:5’,2”:5”,2”’:5”’,2””-quinquethiophene (3). Compound **3** was prepared in a high yield according to the conventional protocol, with Sonogashira reaction of 5-bromo-5’-methyl-3-octyl-2,2’-bithiophene[17] to 5’-methyl-3-octyl-5-trimethylsilylethynyl-2,2’-bithiophene, desilylation to 5-ethynyl-5’-methyl-3-octyl-2,2’-bithiophene, Eglinton coupling to 1,4-bis(5’-methyl-3-octyl-2,2’-bithien-5-yl)-1,3-butadiyne, and finally thiophene ring formation to **3**.

5’-Methyl-3-octyl-5-trimethylsilylethynyl-2,2’-bithiophene: 97% yield from 5-bromo-5’-methyl-3-octyl-2,2’-bithiophene; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.23 (s, 9H), 0.87 (t, *J* = 7.0 Hz, 3H), 1.24–1.35 (m, 10H), 1.58 (quin, *J* = 7.8 Hz, 2H), 2.49 (d, *J* = 1.0 Hz, 3H), 2.65 (t, *J* = 7.8 Hz, 2H), 6.69 (dq, *J* = 3.4 Hz, *J* = 1.0 Hz, 1H), 6.88 (d, *J* = 3.4 Hz, 1H), 6.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.12, 14.1, 15.2, 22.6, 29.0, 29.2, 29.3 (2 carbons), 30.4, 31.8, 97.6, 99.1, 120.1, 125.6, 126.2, 132.9, 133.0, 135.5, 138.6, 140.5; MS (EI) *m/z* 388 (M^+); Anal. Calcd for $C_{22}H_{32}S_2Si$: C, 67.98; H, 8.30%. Found: C, 68.00; H, 8.35%.

5-Ethynyl-5’-methyl-3-octyl-2,2’-bithiophene: 97% yield from 5’-methyl-3-octyl-5-trimethylsilylethynyl-2,2’-bithiophene; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.25 (m, 10H), 1.58 (quin, *J* = 7.8 Hz, 2H), 2.48 (d, *J* = 1.0 Hz, 3H), 2.66 (t, *J* = 7.8 Hz, 2H), 3.33 (s, 1H), 6.68 (dq, *J* = 3.4 Hz, *J* = 1.0 Hz, 1H), 6.90 (d, *J* = 3.4 Hz, 1H), 7.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 15.2, 22.6, 29.0, 29.2, 29.3, 29.4, 30.4, 31.8,

77.1, 81.5, 119.0, 125.6, 126.3, 132.7, 133.2, 135.8, 138.6, 140.6; MS (EI) *m/z* 316 (M^+); Anal. Calcd for $C_{19}H_{24}S_2$: C, 72.10; H, 7.64%. Found: C,72.15; H, 7.80%.

1,4-Bis(5'-methyl-3-octyl-2,2'-bithien-5-yl)-1,3-butadiyne: 97% yield from 5-ethynyl-5'-methyl-3-octyl-2,2'-bithiophene; yellow fine crystals from hexane; mp 84–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 6H), 1.24–1.38 (m, 20H), 1.59 (quin, *J* = 7.8 Hz, 4H), 2.49 (d, *J* = 1.0 Hz, 6H), 2.67 (t, *J* = 7.8 Hz, 4H), 6.70 (dq, *J* = 3.4 Hz, *J* = 1.0 Hz, 2H), 6.93 (d, *J* = 3.4 Hz, 2H), 7.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 15.3, 22.6, 29.0, 29.2, 29.3, 29.4, 30.4, 31.8, 77.4, 78.5, 118.8, 125.7, 126.6, 132.6, 134.8, 137.1, 138.9, 140.9; MS (EI) *m/z* 630 (M^+); Anal. Calcd for $C_{38}H_{46}S_4$: C, 72.33; H, 7.35%. Found: C, 72.04; H, 7.38%.

3: 70% yield from 1,4-bis(5'-methyl-3-octyl-2,2'-bithien-5-yl)-1,3-butadiyne; yellow cotton-like crystals from hexane; mp 86–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 6H), 1.24–1.38 (m, 20H), 1.66 (quin, *J* = 7.8 Hz, 4H), 2.51 (d, *J* = 1.0 Hz, 6H), 2.70 (t, *J* = 7.8 Hz, 4H), 6.71 (dq, *J* = 3.4 Hz, *J* = 1.0 Hz, 2H), 6.91 (d, *J* = 3.4 Hz, 2H), 6.98 (s, 2H), 7.03 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 15.3, 22.6, 29.2, 29.3, 29.4, 29.5, 30.5, 31.8, 123.9, 125.6, 125.8, 126.3, 130.2, 133.5, 134.3, 135.9, 139.7, 140.1; MS (EI) *m/z* 664 (M^+); Anal. Calcd for $C_{38}H_{48}S_5$: C, 68.62; H, 7.27%. Found: C, 68.91; H, 7.16%.

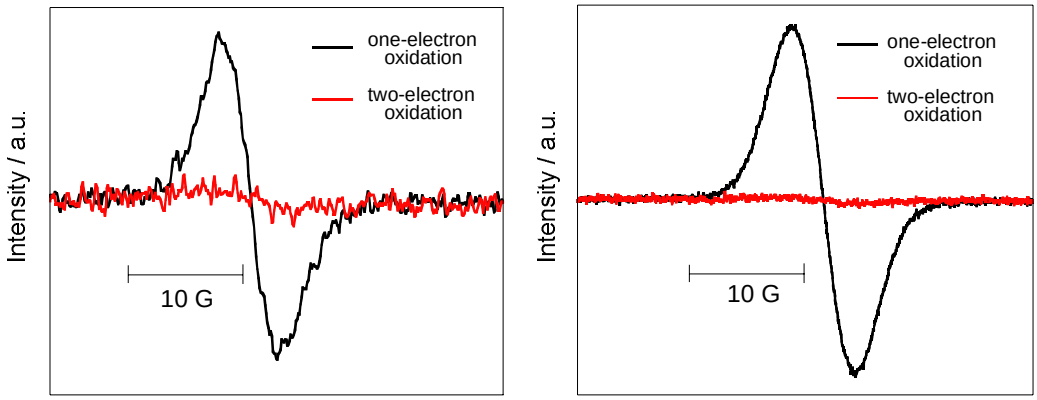

Figure S1. ESR spectra of **4a** (left, g = 2.0022) and **4b** (right, g = 2.0022) in dichloromethane under controlled oxidation with $FeCl_3$.

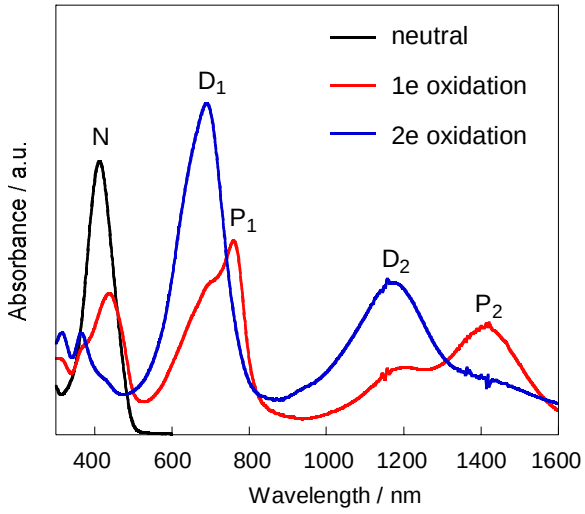

Figure S2. Electronic absorption spectra of **4d** in dichloromethane under controlled oxidation at rt with $FeCl_3$. N, P, and D denote neutral, polaronic, and π-dimeric bands, respectively.

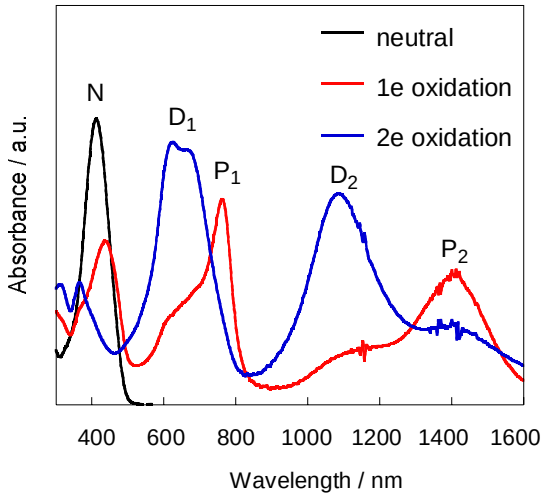

Figure S3. Electronic absorption spectra of **4e** in dichloromethane under controlled oxidation at rt with $FeCl_3$. N, P, and D denote neutral, polaronic, and π-dimeric bands, respectively.

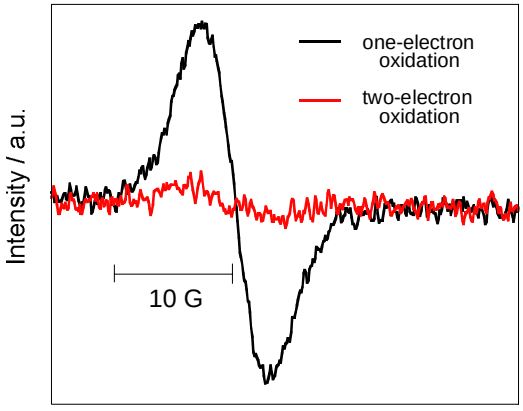

Figure S4. ESR spectra of **4c** (g = 2.0023) in dichloromethane under controlled oxidation with $FeCl_3$.