Control of optical and electrical properties of nanosheets by chemical structure of turning point in foldable polymer

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Supplementary Information

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S1
1. Synthesis of precursor oligomers

**Scheme S1.** Synthesis of functionalized monomers to build up *ortho*-linked oligomers

1mer-dTs and 1mer-mTs: 1mer-dOH (4.2 g, 6.0 mmol), triethylamine (TEA, 1.0 mL, 7.2 mmol) and *N,N*-dimethyl-4-aminopyridine (DMAP, 0.1 g, 0.82 mmol) were dissolved in dry CHCl3 (80 mL). After adding *p*-toluenesulfonyl chloride (TsCl, 1.2 g, 6.3 mmol), the reaction mixture was stirred at 40 °C for 16 h under N2 atmosphere. The solution was concentrated by evaporation. The concentrated solution was added dropwise to Et2O (200 mL). The precipitate was recovered by filtration. The products were separated by column chromatography (SiO2; CHCl3 → CHCl3/MeOH = 94:6). The products were obtained as yellow solids.

**1mer-dTs:** Yield: 1.2 g (20%). 1H NMR (400 MHz, CDCl3): δ = 2.43 (s, 6H), 3.60 (s, 8H), 3.63–3.75 (m, 12H), 3.87 (t, J = 4.8 Hz, 4H), 4.15 (m, 8H), 6.92 (d, J = 8.8 Hz, 4H), 7.11 (s, 4H), 7.32 (d, J = 7.6 Hz, 4H), 7.51 (d, J = 8.8 Hz, 4H), 7.79 (d, J = 7.6 Hz, 4H); 13C NMR (100 MHz, CDCl3): δ = 22.0, 67.9, 69.0, 69.6, 70.1, 70.9, 71.0, 71.1, 71.2, 115.4, 123.1, 124.6, 127.2, 127.4, 128.3, 130.2, 133.3, 136.2, 143.2, 145.1, 158.8; MS (MALDI): found m/z = 1009.63; C30H38O18S4 requires 1010.27.

**1mer-mTs:** Yield: 2.3 g (45%). 1H NMR (400 MHz, CDCl3): δ = 2.43 (s, 3H), 2.53(br, 1H), 3.57–3.76 (m, 22H), 3.87 (m, 4H), 4.16 (m, 6H), 6.93 (m, 4H), 7.11 (s, 4H), 7.32 (d, J = 8.0 Hz, 2H), 7.51 (m, 4H), 7.79 (d, J = 8.0 Hz, 2H); 13C NMR (100 MHz, CDCl3): δ = 22.0, 62.1, 67.9, 69.0, 69.6, 70.1, 70.7, 70.8–71.3, 72.8, 123.1, 124.6, 127.2, 127.4, 128.3, 130.2, 133.3, 136.2, 143.2, 145.1, 158.8; MS (MALDI): found m/z = 855.64; C43H52O12S3 requires 856.26.

**1mer-Ts-OMe:** 1mer-mOMe (2.1 g, 2.9 mmol), TEA (0.50 mL, 3.6 mmol) and DMAP (50 mg, 0.41 mmol) were dissolved in dry CHCl3 (40 mL). After adding TsCl (0.70 g, 3.7 mmol), the reaction mixture was stirred at room temperature for 16 h under N2 atmosphere. The
solution was concentrated by evaporation. The concentrated solution was added dropwise to Et₂O (200 mL). The precipitate was recovered by filtration. The product was purified by column chromatography (SiO₂, CHCl₃ → CHCl₃/MeOH = 95:5). The product was obtained as yellow solid. Yield: 2.5 g (98 %) ¹H NMR (400 MHz, CDCl₃): δ = 2.43 (s, 3H), 3.37 (s, 3H), 3.54 (m, 2H), 3.59 (s, 4H), 3.62–3.76 (m, 16H), 3.87 (m, 4H), 4.15 (m, 6H), 6.93 (d, J = 8.8 Hz, 4H), 7.11 (s, 4H), 7.32 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.8 Hz, 4H), 7.78 (d, J = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 22.0, 59.4, 67.9, 69.0, 69.6, 70.0, 70.9–71.2, 72.3, 115.4, 123.1, 124.5, 127.2, 127.4, 128.3, 130.2, 133.3, 136.2, 143.2, 145.1, 158.8; MS (MALDI): found m/z = 870.13; C₄₄H₅₄O₁₂S₃ requires 870.28.

1mer-dCat: 1mer-dTs (1.5 g, 1.5 mmol), catechol (3.3 g, 30 mmol) and K₂CO₃ (0.5 g, 3.6 mmol) were mixed in dry DMF (15 mL). The reaction mixture was stirred at 80 ºC for 16 h under N₂ atmosphere. After adding CHCl₃ (200 mL), the organic layer was washed with 1N NaCl aqueous solutions (200 mL × 3). The solution was dried with MgSO₄, filtrated and concentrated by evaporation. The concentrated solution was added dropwise to Et₂O (200 mL). The precipitate was recovered by filtration. The product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, CHCl₃) to give the product as yellow solid. Yield: 0.89 g (68 %) ¹H NMR (400 MHz, CDCl₃): δ = 3.66–3.77 (m, 16H), 3.81 (m, 4H), 3.87 (t, J = 4.8 Hz, 4H), 4.15 (m, 8H), 6.77–6.84 (m, 2H), 6.84–6.94 (m, 11H), 7.11 (s, 4H), 7.49 (d, J = 8.8 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 67.8, 69.8, 70.0, 70.4, 70.8, 71.0, 71.2, 115.4, 115.8, 116.0, 120.2, 123.0, 123.4, 124.5, 127.1, 127.4, 136.2, 143.2, 146.3, 147.9, 158.8; MS (MALDI): found m/z = 885.85; C₄₈H₅₄O₁₂S₂ requires 886.31.

1mer-mCat: 1mer-mTs (1.5 g, 1.7 mmol), catechol (1.9 g, 17 mmol) and K₂CO₃ (0.5 g, 3.6 mmol) were mixed in dry DMF (15 mL). The reaction mixture was stirred at 80 ºC for 16 h under N₂ atmosphere. After adding CHCl₃ (200 mL), the organic layer was washed with 1N NaCl aqueous solutions (200 mL × 3). The solution was dried with MgSO₄, filtrated and concentrated by evaporation. The concentrated solution was added dropwise to Et₂O (200 mL). The precipitate was recovered by filtration. The product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, CHCl₃) to give the product as yellow solid. Yield: 1.0 g (72 %) ¹H NMR (400 MHz, CDCl₃): δ = 2.62 (t, J = 6.0 Hz, 1H), 3.61 (t, J = 5.2 Hz, 2H), 3.64–3.77 (m, 18H), 3.81 (m, 2H), 3.87 (t, J = 4.8 Hz, 4H), 4.15 (m, 6H), 6.76–6.82 (m, 1H), 6.87–6.97 (m, 8H), 7.11 (s, 4H), 7.50 (m, 4H); ¹³C NMR
(100 MHz, CDCl$_3$): $\delta = 62.1$, 67.8, 67.9, 69.9, 70.0, 70.1, 70.2, 70.7, 70.8, 71.0, 71.2, 72.9, 115.4, 115.6, 116.0, 120.2, 123.0, 123.3, 124.5, 127.2, 127.4, 127.5, 136.2, 143.2, 146.3, 147.9, 158.8; MS (MALDI): found $m/z = 793.97$; C$_{42}$H$_{50}$O$_{11}$S$_2$ requires 794.28.

Scheme S2. Synthesis of functionalized precursors to build up ortho-linked oligomers

**o-2mer-Ts-OMe:** 1mer-Ts-OMe (0.60 g, 0.69 mmol), 1mer-mCat (0.53 g, 0.67 mmol) and K$_2$CO$_3$ (0.10 g, 0.72 mmol) were mixed in dry DMF (5 mL). The reaction mixture was stirred at 80 ºC for 16 h under N$_2$ atmosphere. The product was precipitated by adding Et$_2$O (80 mL). The precipitate was recovered by filtration. The product was dissolved in CHCl$_3$ then insoluble materials were removed by filtration. The solvent was removed by evaporation. The yellow solid was dissolved in CHCl$_3$ (5.0 mL) with TEA (0.25 mL, 1.8 mmol) and DMAP (0.05 g, 0.41 mmol). After adding TsCl (0.30 g, 1.6 mmol), the reaction mixture was stirred at room temperature for 16 h under N$_2$ atmosphere. The product was precipitated by adding Et$_2$O (80 mL). The precipitate was recovered by filtration. The product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, CHCl$_3$) to give the product as yellow solid. Yield: 0.82 g (75 %) $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.43$ (s, 3H), 3.37 (s, 3H), 3.54 (t, $J = 4.8$ Hz, 2H), 3.59 (s, 4H), 3.62–3.76 (m, 32H), 3.85 (m, 12H), 4.15 (m, 14H), 6.87–6.95 (m, 12H), 7.10 (s, 8H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.49 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 22.0$, 59.4, 67.9, 69.0, 69.2, 69.6, 70.0, 70.1, 70.8–71.2, 72.3,
115.2, 115.4, 122.0, 123.1, 124.5, 127.2, 127.4, 128.3, 130.2, 133.3, 136.2, 143.2, 145.1, 149.3, 158.8; MS (MALDI): found $m/z = 1646.15$; $C_{86}H_{102}O_{22}S_{5}$ requires 1646.55.

**o-2mer-mCat**: **1mer-mTs** (0.24 g, 0.28 mmol), **1mer-dCat** (0.50 g, 0.56 mmol) and $K_2CO_3$ (0.10 g, 0.72 mmol) were mixed in dry DMF (4 mL). The reaction mixture was stirred at 80 °C for 16 h under $N_2$ atmosphere. The product was precipitated by adding $Et_2O$ (80 mL). The precipitate was recovered by filtration. The product was dissolved in mixed solvent of CHCl$_3$/MeOH (19/1), then insoluble materials were removed by filtration. The solution was concentrated by evaporation. The product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, CHCl$_3$) to give the product as yellow solid. **Yield**: 0.26 g (60 %) $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.66$ (br, 1H), 3.61 (t, $J = 4.8$ Hz, 2H), 3.65–3.77 (m, 34H), 3.81 (m, 2H), 3.85 (m, 12H), 4.14 (m, 14H), 6.79 (m, 1H), 6.87–6.95 (m, 15H), 7.05–7.12 (m, 9H), 7.49 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 62.1$, 67.8, 69.2, 69.9, 70.0, 70.1, 70.7, 70.8, 70.9, 71.0, 71.2, 115.2, 115.4, 116.1, 120.1, 122.0, 123.1, 123.3, 124.5, 127.2, 127.4, 136.2, 143.2, 146.4, 147.9, 149.3, 158.8; MS (MALDI): found $m/z = 1569.62$; $C_{84}H_{98}O_{21}S_{4}$ requires 1570.55.

**o-3mer-Ts-OMe**: **o-2mer-Ts-OMe** (0.26 g, 0.16 mmol), **1mer-mCat** (0.13 g, 0.16 mmol) and $K_2CO_3$ (0.05 g, 0.36 mmol) were mixed in dry DMF (2 mL). The reaction mixture was stirred at 80 °C for 16 h under $N_2$ atmosphere. The product was precipitated by adding $Et_2O$ (80 mL). The precipitate was recovered by filtration. The product was dissolved in CHCl$_3$ then insoluble materials were removed by filtration. The solvent was removed by evaporation. The yellow solid was dissolved in CHCl$_3$ (5.0 mL) with TEA (0.15 mL, 1.1 mmol) and DMAP (0.03 g, 0.25 mmol). After adding TsCl (0.15 g, 0.78 mmol), the reaction mixture was stirred at room temperature for 16 h under $N_2$ atmosphere. The product was precipitated by adding $Et_2O$ (80 mL). The precipitate was recovered by filtration. The product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, CHCl$_3$) to give the product as yellow solid. **Yield**: 0.29 g (76 %) $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.42$ (s, 3H), 3.37 (s, 3H), 3.54 (m, 2H), 3.59 (s, 4H), 3.62–3.76 (m, 48H), 3.85 (m, 20H), 4.14 (m, 22H), 6.87–6.94 (m, 20H), 7.09 (s, 12H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.49 (m, 12H), 7.78 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 22.0$, 59.4, 67.9, 69.0, 69.2, 69.6, 70.0, 70.1, 70.8–71.2, 72.3, 115.2, 115.4, 122.0, 123.1, 124.5, 127.2, 127.4, 128.3, 130.2, 133.3, 136.2, 143.2, 145.1, 149.3, 158.8; MS (MALDI): found $m/z = 2423.07$; $C_{128}H_{150}O_{32}S_{7}$ requires 2423.82.
**o-4mer-Ts-OMe: o-2mer-Ts-OMe** (0.24 g, 0.15 mmol), **o-2mer-mCat** (0.24 g, 0.15 mmol) and K₂CO₃ (0.10 g, 0.72 mmol) were mixed in dry DMF (3 mL). The reaction mixture was stirred at 80 °C for 16 h under N₂ atmosphere. The product was precipitated by adding Et₂O (80 mL). The precipitate was recovered by filtration. The product was dissolved in CHCl₃ then insoluble materials were removed by filtration. The solvent was removed by evaporation. The yellow solid was dissolved in CHCl₃ (5.0 mL) with TEA (0.10 mL, 0.72 mmol) and DMAP (0.02 g, 0.16 mmol). After adding TsCl (0.10 g, 0.52 mmol), the reaction mixture was stirred at room temperature for 16 h under N₂ atmosphere. The product was precipitated by adding Et₂O (80 mL). The precipitate was recovered by filtration. The product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, CHCl₃) to give the product as yellow solid. Yield: 0.34 g (73 %) ¹H NMR (400 MHz, CDCl₃): δ = 2.43 (s, 3H), 3.37 (s, 3H), 3.54 (m, 2H), 3.59 (s, 4H), 3.62−3.76 (m, 66H), 3.85 (m, 28H), 4.14 (m, 28H), 6.86−6.96 (m, 28H), 7.09 (m, 16H), 7.32 (d, J = 8.4 Hz, 2H), 7.49 (m, 16H), 7.79 (d, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 22.0, 59.4, 67.9, 69.0, 69.2, 69.6, 70.0, 70.1, 70.8−71.4, 72.3, 115.2, 115.4, 122.0, 123.1, 124.5, 127.1, 127.4, 128.3, 130.2, 133.3, 136.2, 143.1, 145.1, 149.3, 158.8; MS (MALDI): found m/z = 3201.79; C₁₇₀H₁₉₈O₄₂S₉ requires 3201.09.

**Scheme S3.** Synthesis of functionalized monomers to build up meta-linked oligomers

**1mer-dRes:** 1mer-dTs (1.5 g, 1.5 mmol), resorcinol (3.3 g, 30 mmol) and K₂CO₃ (0.5 g, 3.6 mmol) were mixed in dry DMF (15 mL). The reaction mixture was stirred at 80 °C for 16 h under N₂ atmosphere. After adding CHCl₃ (200 mL), the organic layer was washed with 1N NaCl aqueous solutions (200 mL × 3). The solution was dried with MgSO₄, filtrated and concentrated by evaporation. The concentrated solution was added dropwise to Et₂O (200 mL). The precipitate was recovered by filtration. The product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, CHCl₃/MeOH = 97/3) to give the product as yellow solid. Yield: 0.93 g (71 %) ¹H NMR (400 MHz, CDCl₃/DMSO-d₆ = 40/1): δ = 3.62−3.72 (m, 16H), 3.76−3.85 (m, 8H), 4.05 (m, 4H), 4.11 (m, 4H), 6.37 (d, J
= 8.0 Hz, 2H), 6.42 (m, 4H), 6.88 (d, J = 8.8 Hz, 4H), 7.03 (t, J = 8.0 Hz, 2H), 7.07 (s, 4H), 7.46 (d, J = 8.8 Hz, 4H), 8.16 (br, 2H); 13C NMR (100 MHz, CDCl3): δ = 67.6, 67.8, 69.9, 70.0, 70.9, 71.1, 102.6, 106.3, 108.6, 115.3, 123.0, 124.5, 127.1, 127.3, 130.1, 136.1, 143.1, 158.4, 158.7, 160.2; MS (MALDI): found m/z = 885.85; C48H54O12S2 requires 886.31.

1mer-mRes: 1mer-mTs (1.5 g, 1.7 mmol), resorcinol (1.9 g, 17 mmol) and K2CO3 (0.5 g, 3.6 mmol) were mixed in dry DMF (15 mL). The reaction mixture was stirred at 80 °C for 16 h under N2 atmosphere. After adding CHCl3 (200 mL), the organic layer was washed with 1N NaCl aqueous solutions (200 mL × 3). The solution was dried with MgSO4, filtrated and concentrated by evaporation. The concentrated solution was added dropwise to Et2O (200 mL). The precipitate was recovered by filtration. The product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, CHCl3/MeOH = 97/3) to give the product as yellow solid. Yield: 1.1 g (78 %) 1H NMR (400 MHz, CDCl3/DMSO-d6 = 40/1): δ = 2.99 (br, 1H), 3.58 (m, 2H), 3.63–3.73 (m, 18H), 3.79 (t, J = 4.8 Hz, 2H), 3.84 (m, 4H), 4.05 (t, J = 4.8 Hz, 2H), 4.13 (m, 4H), 6.36–6.45 (m, 3H), 6.90 (m, 4H), 7.03 (t, J = 8.0 Hz, 1H), 7.08 (s, 4H), 7.47 (m, 4H), 8.06 (s, 1H); 13C NMR (100 MHz, CDCl3): δ = 61.9, 67.6, 67.8, 69.9, 70.0, 70.5, 70.7–71.2, 72.9, 102.6, 106.3, 108.6, 115.3, 123.0, 124.5, 127.1, 127.4, 130.1, 136.1, 143.1, 158.4, 158.7, 160.3; MS (MALDI): found m/z = 793.88; C42H50O11S2 requires 794.28.

Scheme S4. Synthesis of functionalized precursors to build up meta-linked oligomers
**m-2mer-Ts-OMe:** 1mer-Ts-OMe (0.60 g, 0.69 mmol), 1mer-mRes (0.53 g, 0.67 mmol) and K₂CO₃ (0.10 g, 0.72 mmol) were mixed in dry DMF (5 mL). The reaction mixture was stirred at 80 °C for 16 h under N₂ atmosphere. The product was precipitated by adding Et₂O (80 mL). The precipitate was recovered by filtration. The product was dissolved in CHCl₃ then insoluble materials were removed by filtration. The solvent was removed by evaporation. The yellow solid was dissolved in CHCl₃ (5.0 mL) with TEA (0.25 mL, 1.8 mmol) and DMAP (0.05 g, 0.41 mmol). After adding TsCl (0.30 g, 1.6 mmol), the reaction mixture was stirred at room temperature for 16 h under N₂ atmosphere. The product was precipitated by adding Et₂O (80 mL). The precipitate was recovered by filtration. The product was purified by column chromatography (SiO₂, CHCl₃ → CHCl₃/MeOH = 95:5). The product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, CHCl₃) to give the product as yellow solid. Yield: 0.79 g (72 %). ¹H NMR (400 MHz, CDCl₃): δ = 2.43 (s, 3H), 3.37 (s, 3H), 3.54 (m, 2H), 3.60 (s, 4H), 3.63−3.76 (m, 32H), 3.81−3.89 (m, 12H), 4.08 (m, 4H), 4.15 (m, 10H), 6.48−6.52 (m, 3H), 6.92 (m, 8H), 7.08−7.16 (m, 9H), 7.32 (d, J = 7.6 Hz, 2H), 7.50 (m, 8H), 7.79 (d, J = 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 22.0, 59.4, 67.7, 67.9, 69.0, 69.6, 70.0, 70.8−71.3, 72.3, 102.1, 107.4, 115.4, 123.1, 124.6, 127.2, 127.4, 128.3, 130.2, 133.3, 136.2, 143.2, 145.1, 158.9, 160.3; MS (MALDI): found m/z =1646.86; C₈₆H₁₀₂O₂₂S₅ requires 1646.55.

**m-2mer-mRes:** 1mer-mTs (0.24 g, 0.28 mmol), 1mer-dRes (0.50 g, 0.56 mmol) and K₂CO₃ (0.10 g, 0.72 mmol) were mixed in dry DMF (4 mL). The reaction mixture was stirred at 80 °C for 16 h under N₂ atmosphere. The product was precipitated by adding Et₂O (80 mL). The precipitate was recovered by filtration. The product was dissolved in mixed solvent of CHCl₃/MeOH (19/1), then insoluble materials were removed by filtration. The solution was concentrated by evaporation. The products were purified by column chromatography (SiO₂, CHCl₃ → CHCl₃/MeOH = 95:5). The product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, CHCl₃) to give the product as yellow solid. Yield: 0.27 g (62 %). ¹H NMR (400 MHz, CDCl₃): δ = 2.65 (br, 1H), 3.61 (t, J = 4.6 Hz, 2H), 3.65−3.76 (m, 34H), 3.79−3.89 (m, 14H), 4.08 (m, 6H), 4.14 (m, 8H), 5.67 (s, 1H), 6.41−6.52 (m, 6H), 6.92 (m, 8H), 7.06−7.16 (m, 10H), 7.50 (m, 8H); ¹³C NMR (100 MHz, CDCl₃): δ = 22.1, 67.7, 67.9, 70.0, 70.7, 70.9−71.3, 72.9, 102.1, 102.9, 107.4, 108.5, 115.4, 123.1, 124.6, 127.2, 127.4, 130.2, 130.4, 136.2, 143.2, 158.8, 160.3; MS (MALDI): found m/z =1570.09; C₈₄H₉₈O₂₁S₄ requires 1570.55.
\textbf{m-3\text{mer}-Ts-OMe}: \textbf{m-2\text{mer}-Ts-OMe} (0.26 g, 0.16 mmol), \textbf{1\text{mer}-mRes} (0.13 g, 0.16 mmol) and K$_2$CO$_3$ (0.05 g, 0.36 mmol) were mixed in dry DMF (2 mL). The reaction mixture was stirred at 80 °C for 16 h under N$_2$ atmosphere. The product was precipitated by adding Et$_2$O (80 mL). The precipitate was recovered by filtration. The product was dissolved in CHCl$_3$ then insoluble materials were removed by filtration. The solvent was removed by evaporation. The yellow solid was dissolved in CHCl$_3$ (5.0 mL) with TEA (0.15 mL, 1.1 mmol) and DMAP (0.03 g, 0.25 mmol). After adding TsCl (0.15 g, 0.78 mmol), the reaction mixture was stirred at room temperature for 16 h under N$_2$ atmosphere. The product was precipitated by adding Et$_2$O (80 mL). The precipitate was recovered by filtration. The products were roughly purified by column chromatography (SiO$_2$, CHCl$_3$ → CHCl$_3$/MeOH = 95:5). The product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, CHCl$_3$) to give the product as yellow solid. Yield: 0.29 g (76 %). $^1$H NMR (400 MHz, CDCl$_3$): δ = 2.43 (s, 3H), 3.37 (s, 3H), 3.54 (m, 2H), 3.59 (s, 4H), 3.62–3.78 (m, 48H), 3.80–3.90 (m, 20H), 4.08 (m, 8H), 4.14 (m, 14H), 6.48–6.52 (m, 6H), 6.92 (m, 12H), 7.08–7.16 (m, 14H), 7.32 (d, J = 8.0 Hz, 2H), 7.50 (m, 12H), 7.79 (d, J = 8.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 22.0, 59.4, 67.7, 67.9, 69.0, 69.6, 70.0, 70.8–71.3, 72.3, 102.1, 107.4, 115.4, 123.1, 124.5, 127.2, 127.4, 128.3, 130.2, 133.3, 136.2, 143.2, 145.1, 158.8, 160.3; MS (MALDI): found m/z = 2423.16; C$_{128}$H$_{150}$O$_{32}$S$_7$ requires 2423.82.

\textbf{m-4\text{mer}-Ts-OMe}: \textbf{m-2\text{mer}-Ts-OMe} (0.24 g, 0.15 mmol), \textbf{m-2\text{mer}-mRes} (0.24 g, 0.15 mmol) and K$_2$CO$_3$ (0.10 g, 0.72 mmol) were mixed in dry DMF (3 mL). The reaction mixture was stirred at 80 °C for 16 h under N$_2$ atmosphere. The product was precipitated by adding Et$_2$O (80 mL). The precipitate was recovered by filtration. The product was dissolved in CHCl$_3$ then insoluble materials were removed by filtration. The solvent was removed by evaporation. The yellow solid was dissolved in CHCl$_3$ (5.0 mL) with TEA (0.10 mL, 0.72 mmol) and DMAP (0.02 g, 0.16 mmol). After adding TsCl (0.10 g, 0.52 mmol), the reaction mixture was stirred at room temperature for 16 h under N$_2$ atmosphere. The product was precipitated by adding Et$_2$O (80 mL). The precipitate was recovered by filtration. The products were roughly purified by column chromatography (SiO$_2$, CHCl$_3$ → CHCl$_3$/MeOH = 95:5). The product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, CHCl$_3$) to give the product as yellow solid. Yield: 0.35 g (75 %). $^1$H NMR (400 MHz, CDCl$_3$): δ = 2.42 (s, 3H), 3.37 (s, 3H), 3.54 (t, J = 4.8 Hz, 2H), 3.59 (s, 4H), 3.63–3.77 (m, 64H), 3.80–3.89 (m, 28H), 4.08 (m, 12H), 4.14 (m, 18H),
6.47–6.52 (m, 9H), 6.91 (m, 16H), 7.07–7.16 (m, 19H), 7.31 (d, \( J = 8.0 \) Hz, 2H), 7.50 (m, 16H), 7.79 (d, \( J = 8.0 \) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 22.0, 59.4, 67.7, 67.9, 69.0, 69.6, 70.0, 70.7–71.3, 72.3, 102.1, 107.4, 115.4, 123.1, 124.5, 127.1, 127.4, 128.3, 130.1, 133.3, 136.2, 143.2, 145.1, 158.8, 160.3; \) MS (MALDI): found \( m/z = 3200.47 \); \( \text{C}_{170}\text{H}_{198}\text{O}_{42}\text{S}_{9} \) requires 3201.09.
2. $^1$H and $^{13}$C NMR of the products.

Figure S1 $^1$H and $^{13}$C NMR spectra of 1mer-dTs

Figure S2 $^1$H and $^{13}$C NMR spectra of 1mer-mTs

Figure S3 $^1$H and $^{13}$C NMR spectra of 1mer-Ts-Ome
Figure S4 $^1$H and $^{13}$C NMR spectra of 1mer-dCat

Figure S5 $^1$H and $^{13}$C NMR spectra of 1mer-mCat

Figure S6 $^1$H and $^{13}$C NMR spectra of o-2mer-Ts-Ome
Figure S7 $^1$H and $^{13}$C NMR spectra of o-2mer-mCat

Figure S8 $^1$H and $^{13}$C NMR spectra of o-3mer-Ts-Ome

Figure S9 $^1$H and $^{13}$C NMR spectra of o-4mer-Ts-Ome
Figure S10 $^1$H and $^{13}$C NMR spectra of 1mer-dRes

Figure S11 $^1$H and $^{13}$C NMR spectra of 1mer-mRes

Figure S12 $^1$H and $^{13}$C NMR spectra of $m$-2mer-Ts-OMe
Figure S13 $^1$H and $^{13}$C NMR spectra of m-2mer-mRes

Figure S14 $^1$H and $^{13}$C NMR spectra of m-3mer-Ts-Ome

Figure S15 $^1$H and $^{13}$C NMR spectra of m-4mer-Ts-OMe
Figure S16 $^1$H and $^{13}$C NMR spectra of o-2mer

Figure S17 $^1$H and $^{13}$C NMR spectra of o-4mer

Figure S18 $^1$H and $^{13}$C NMR spectra of o-6mer
Figure S19 $^1$H and $^{13}$C NMR spectra of $o$-8mer

Figure S20 $^1$H and $^{13}$C NMR spectra of $m$-2mer

Figure S21 $^1$H and $^{13}$C NMR spectra of $m$-4mer
3. MALDI-TOF MS of oligomers

Figure S24 MALDI-TOF mass spectra of ortho-linked oligomers.
4. Fluorescence spectra of meta-linked oligomers

Figure S26 Fluorescence spectra of meta-linked oligomers. Excitation wavelength: 326 nm.
Solvent: o-Dichlorobenzene. Concentration of thiophene unit: $3.0 \times 10^{-5}$ M.

5. AFM images of o-6mer and m-6mer

Figure S27 AFM images of the aggregates consisting of (a) o-6mer and (b) m-6mer.
Substrate: Silicon wafer, Scan area: 5 μm × 5 μm.
6. FP-TRMC results of triazole-linked-8mer samples

Figure S28 (a) Kinetic traces of conductivity transient upon 355 nm photoexcitation (5 mW) for o-8mer (black) and triazole-linked-8mer (magenta) nanosheets, and drop-cast films of triazole-linked-8mer (orange). (b) XRD patterns of triazole-linked-8mer nanosheets (magenta) and drop-cast films of triazole-linked-8mer (orange) used in the FP-TRMC analysis. Corresponding \( d \) spacing values in nm are given at the right side of each peak.