

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

T. Ikeda*, H. Tamura, T. Sakurai, S. Seki

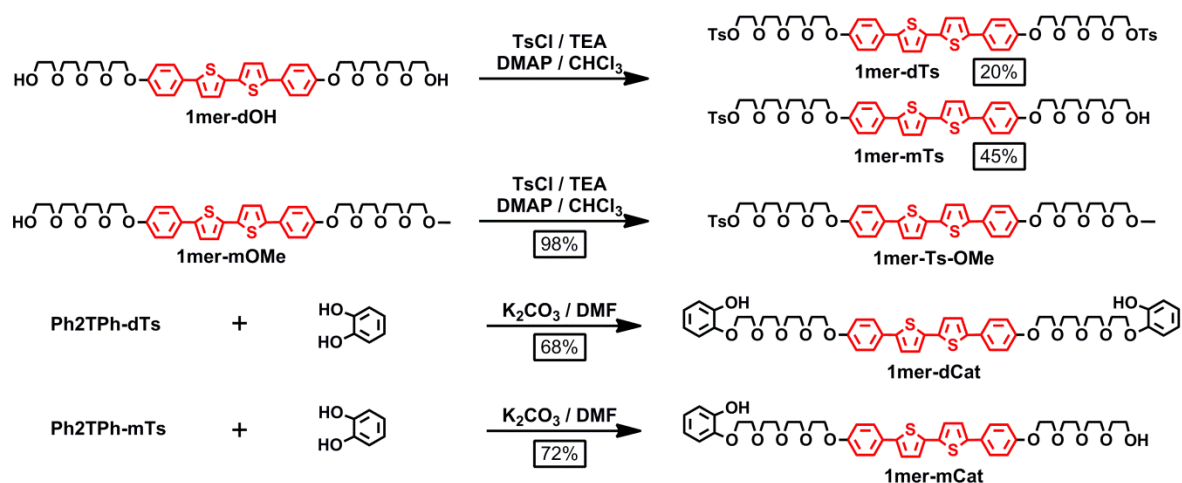
Supplementary Information

Table of contents

1. Synthesis of precursor oligomers	S2
2. ¹ H and ¹³ C NMR of the products	S11
3. MALDI-TOF MS of oligomers	S18
4. Fluorescence spectra of meta-linked oligomers	S19
5. AFM images of <i>o</i> -6mer and <i>m</i> -6mer	S19
6. FP-TRMC results of triazole-linked-8mer samples	S20

Correspondence Address
<p>Dr. Taichi Ikeda</p> <p>Research Center for Functional Materials National Institute for Materials Science Namiki 1-1, 305-0044 Tsukuba, JAPAN</p>

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 CHCl_3 (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 N_2 atmosphere. The solution was concentrated by evaporation. The concentrated solution was added dropwise to Et_2O (200 mL). The precipitate was recovered by filtration. The products were separated by column chromatography (SiO_2 , $\text{CHCl}_3 \rightarrow \text{CHCl}_3/\text{MeOH} = 94:6$). The products were obtained as yellow solids.

1mer-dTs: Yield: 1.2 g (20 %). ^1H NMR (400 MHz, CDCl_3): $\delta = 2.43$ (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); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 22.0, 67.9, 69.0, 69.6, 70.1, 70.9, 71.0, 71.1, 71.2, 115.4, 123.1, 124.6, 127.2, 127.4, 128.3, 130.2, 133.3, 136.2, 143.2, 145.1, 158.8$; MS (MALDI): found $m/z = 1009.63$; $\text{C}_{50}\text{H}_{58}\text{O}_{14}\text{S}_4$ requires 1010.27.

1mer-mTs: Yield: 2.3 g (45 %). ^1H NMR (400 MHz, CDCl_3): $\delta = 2.43$ (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); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 22.0, 62.1, 67.9, 69.0, 69.6, 70.1, 70.7, 70.8\text{--}71.3, 72.8, 123.1, 124.6, 127.2, 127.4, 128.3, 130.2, 133.3, 136.2, 143.2, 145.1, 158.8$; MS (MALDI): found $m/z = 855.64$; $\text{C}_{43}\text{H}_{52}\text{O}_{12}\text{S}_3$ requires 856.26.

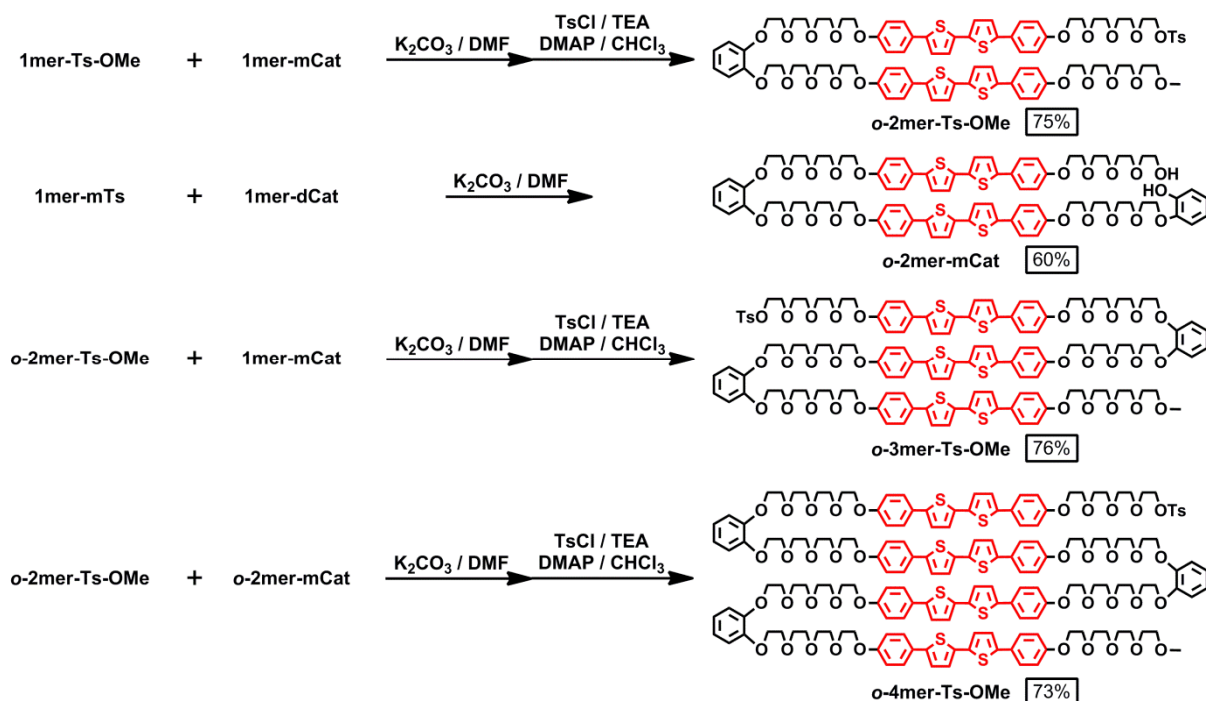
1mer-Ts-OMe: **1mer-mOMe** (2.1 g, 2.9 mmol), TEA (0.50 mL, 3.6 mmol) and DMAP (50 mg, 0.41 mmol) were dissolved in dry CHCl_3 (40 mL). After adding TsCl (0.70 g, 3.7 mmol), the reaction mixture was stirred at room temperature for 16 h under N_2 atmosphere. The

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 °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) 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 °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) 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, CDCl₃): δ = 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; C₄₂H₅₀O₁₁S₂ requires 794.28.



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

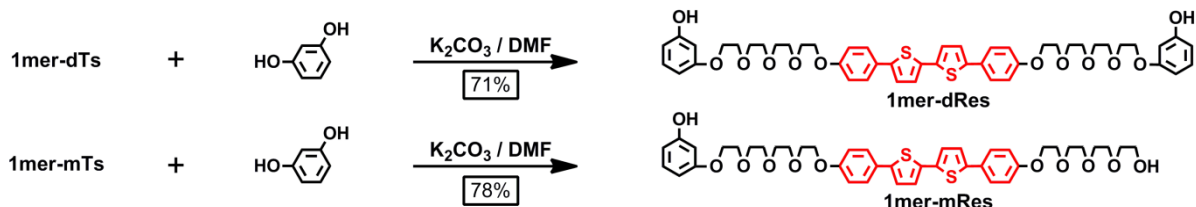
***o*-2mer-Ts-OMe:** 1mer-Ts-OMe (0.60 g, 0.69 mmol), 1mer-mCat (0.53 g, 0.67 mmol) and K₂CO₃ (0.10 g, 0.72 mmol) were mixed in dry DMF (5 mL). The reaction mixture was stirred at 80 °C for 16 h under N₂ atmosphere. The product was precipitated by adding Et₂O (80 mL). The precipitate was recovered by 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 the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, CHCl₃) to give the product as yellow solid. Yield: 0.82 g (75 %) ¹H NMR (400 MHz, CDCl₃): δ = 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); ¹³C NMR (100 MHz, CDCl₃): δ = 22.0, 59.4, 67.9, 69.0, 69.2, 69.6, 70.0, 70.1, 70.8–71.2, 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 %) 1H 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 %) 1H 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 K_2CO_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_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 (0.10 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_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: 0.34 g (73 %) 1H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3H), 3.37 (s, 3H), 3.54 (m, 2H), 3.59 (s, 4H), 3.62–3.76 (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); ^{13}C NMR (100 MHz, $CDCl_3$): 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; $C_{170}H_{198}O_{42}S_9$ requires 3201.09.

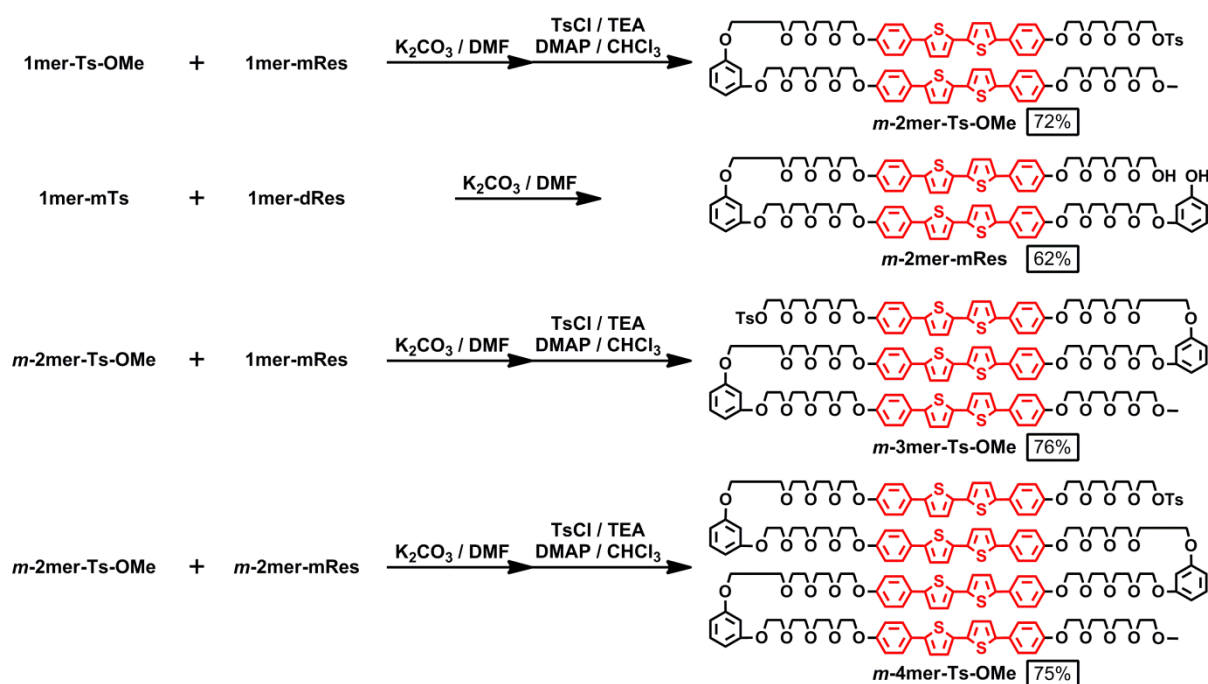


Scheme S3. Synthesis of functionalized monomers to build up *meta*-linked oligomers

1mer-dRes: **1mer-dTs** (1.5 g, 1.5 mmol), resorcinol (3.3 g, 30 mmol) and K_2CO_3 (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 N_2 atmosphere. After adding $CHCl_3$ (200 mL), the organic layer was washed with 1N NaCl aqueous solutions (200 mL \times 3). The solution was dried with $MgSO_4$, filtrated and concentrated by evaporation. The concentrated solution was added dropwise to Et_2O (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, $CHCl_3/MeOH$ = 97/3) to give the product as yellow solid. Yield: 0.93 g (71 %) 1H NMR (400 MHz, $CDCl_3/DMSO-d_6$ = 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); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 67.6, 67.8, 69.9, 70.0, 70.9, 71.1, 102.6, 106.3, 108.6, 115.3, 123.0, 124.5, 127.1, 127.3, 130.1, 136.1, 143.1, 158.4, 158.7, 160.2$; MS (MALDI): found $m/z = 885.85$; $\text{C}_{48}\text{H}_{54}\text{O}_{12}\text{S}_2$ requires 886.31.

1mer-mRes: 1mer-mTs (1.5 g, 1.7 mmol), resorcinol (1.9 g, 17 mmol) and K_2CO_3 (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 N_2 atmosphere. After adding CHCl_3 (200 mL), the organic layer was washed with 1N NaCl aqueous solutions (200 mL \times 3). The solution was dried with MgSO_4 , filtrated and concentrated by evaporation. The concentrated solution was added dropwise to Et_2O (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, $\text{CHCl}_3/\text{MeOH} = 97/3$) to give the product as yellow solid. Yield: 1.1 g (78 %) ^1H NMR (400 MHz, $\text{CDCl}_3/\text{DMSO}-d_6 = 40/1$): $\delta = 2.99$ (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); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 61.9, 67.6, 67.8, 69.9, 70.0, 70.5, 70.7\text{--}71.2, 72.9, 102.6, 106.3, 108.6, 115.3, 123.0, 124.5, 127.1, 127.4, 130.1, 136.1, 143.1, 158.4, 158.7, 160.3$; MS (MALDI): found $m/z = 793.88$; $\text{C}_{42}\text{H}_{50}\text{O}_{11}\text{S}_2$ 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 K_2CO_3 (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 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 (0.25 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_2O (80 mL). The precipitate was recovered by filtration. The products were roughly purified by column chromatography (SiO_2 , $CHCl_3 \rightarrow CHCl_3/MeOH = 95:5$). 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: 0.79 g (72 %). 1H NMR (400 MHz, $CDCl_3$): $\delta = 2.43$ (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); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 22.0, 59.4, 67.7, 67.9, 69.0, 69.6, 70.0, 70.8-71.3, 72.3, 102.1, 107.4, 115.4, 123.1, 124.6, 127.2, 127.4, 128.3, 130.2, 133.3, 136.2, 143.2, 145.1, 158.9, 160.3$; MS (MALDI): found $m/z = 1646.86$; $C_{86}H_{102}O_{22}S_5$ requires 1646.55.

***m*-2mer-mRes: 1mer-mTs** (0.24 g, 0.28 mmol), **1mer-dRes** (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 products were roughly purified by column chromatography (SiO_2 , $CHCl_3 \rightarrow CHCl_3/MeOH = 95:5$). 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: 0.27 g (62 %). 1H NMR (400 MHz, $CDCl_3$): $\delta = 2.65$ (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); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 62.1, 67.7, 67.9, 70.0, 70.7, 70.9-71.3, 72.9, 102.1, 102.9, 107.4, 108.5, 115.4, 123.1, 124.6, 127.2, 127.4, 130.2, 130.4, 136.2, 143.2, 158.8, 160.3$; MS (MALDI): found $m/z = 1570.09$; $C_{84}H_{98}O_{21}S_4$ requires 1570.55.

***m*-3mer-Ts-OMe**: ***m*-2mer-Ts-OMe** (0.26 g, 0.16 mmol), **1mer-mRes** (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 products were roughly purified by column chromatography (SiO_2 , $CHCl_3 \rightarrow CHCl_3/MeOH = 95:5$). 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 %). 1H NMR (400 MHz, $CDCl_3$): $\delta = 2.43$ (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, $CDCl_3$): $\delta = 22.0, 59.4, 67.7, 67.9, 69.0, 69.6, 70.0, 70.8-71.3, 72.3, 102.1, 107.4, 115.4, 123.1, 124.5, 127.2, 127.4, 128.3, 130.2, 133.3, 136.2, 143.2, 145.1, 158.8, 160.3$; MS (MALDI): found $m/z = 2423.16$; $C_{128}H_{150}O_{32}S_7$ requires 2423.82.

***m*-4mer-Ts-OMe**: ***m*-2mer-Ts-OMe** (0.24 g, 0.15 mmol), ***m*-2mer-mRes** (0.24 g, 0.15 mmol) and K_2CO_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_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 (0.10 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_2O (80 mL). The precipitate was recovered by filtration. The products were roughly purified by column chromatography (SiO_2 , $CHCl_3 \rightarrow CHCl_3/MeOH = 95:5$). 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 %). 1H NMR (400 MHz, $CDCl_3$): $\delta = 2.42$ (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): $\delta = 22.0, 59.4, 67.7, 67.9, 69.0, 69.6, 70.0, 70.7\text{--}71.3, 72.3, 102.1, 107.4, 115.4, 123.1, 124.5, 127.1, 127.4, 128.3, 130.1, 133.3, 136.2, 143.2, 145.1, 158.8, 160.3$; MS (MALDI): found $m/z = 3200.47$; $\text{C}_{170}\text{H}_{198}\text{O}_{42}\text{S}_9$ requires 3201.09.

2. ^1H and ^{13}C NMR of the products.

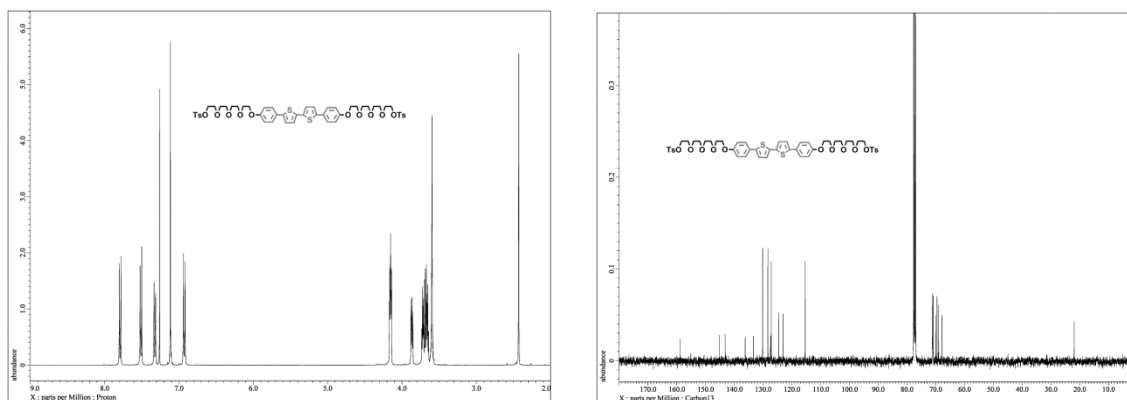


Figure S1 ^1H and ^{13}C NMR spectra of 1mer-dTs

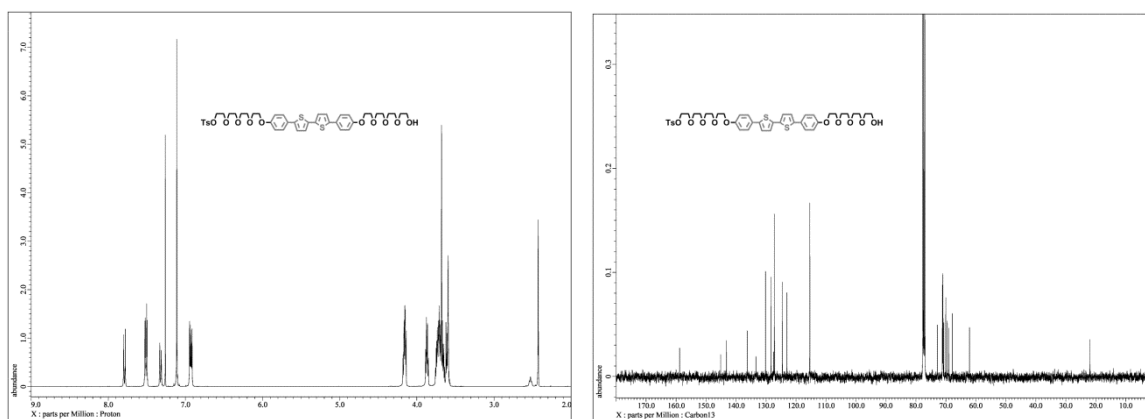


Figure S2 ^1H and ^{13}C NMR spectra of 1mer-mTs

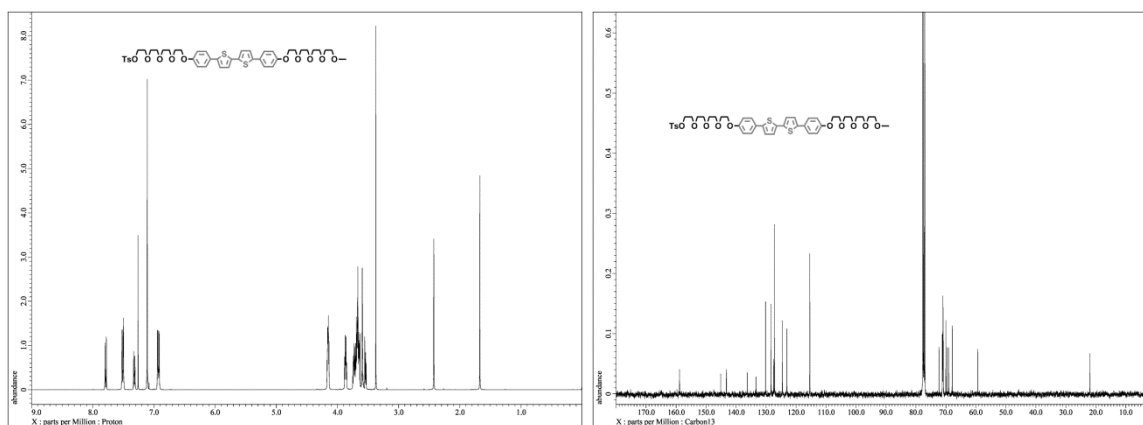


Figure S3 ^1H and ^{13}C NMR spectra of 1mer-Ts-Ome

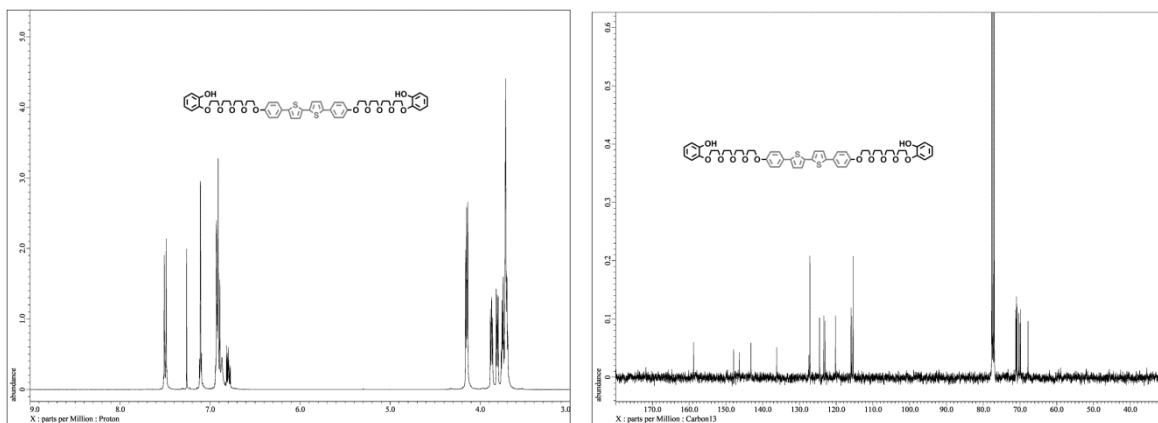


Figure S4 ^1H and ^{13}C NMR spectra of 1mer-dCat

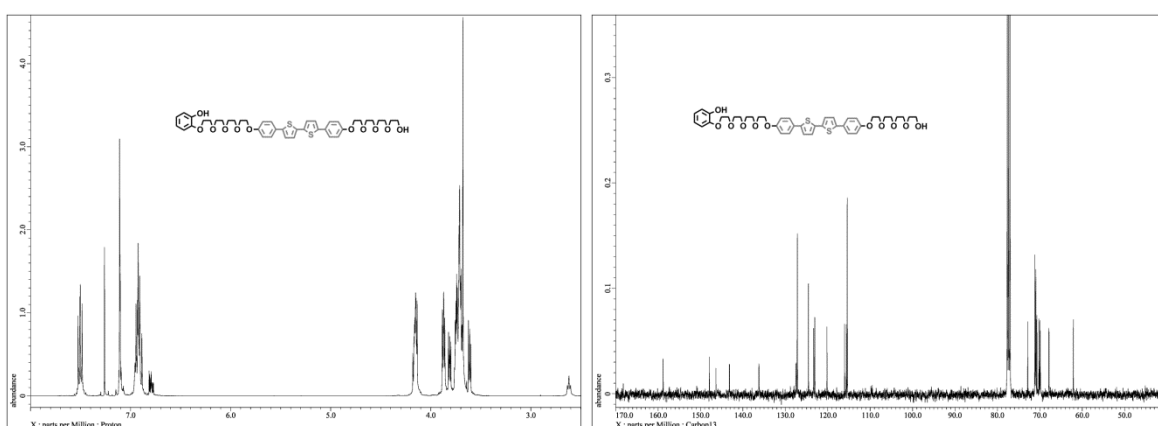


Figure S5 ^1H and ^{13}C NMR spectra of 1mer-mCat

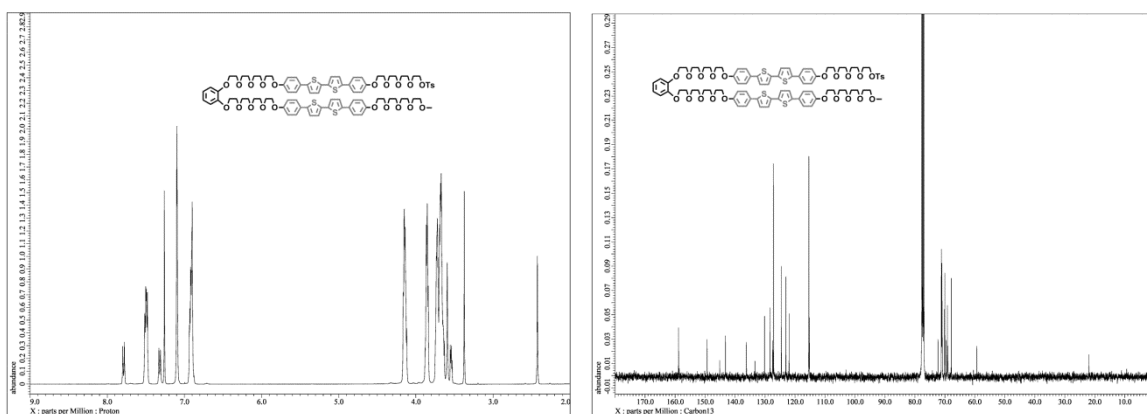


Figure S6 ^1H and ^{13}C NMR spectra of *o*-2mer-Ts-Ome

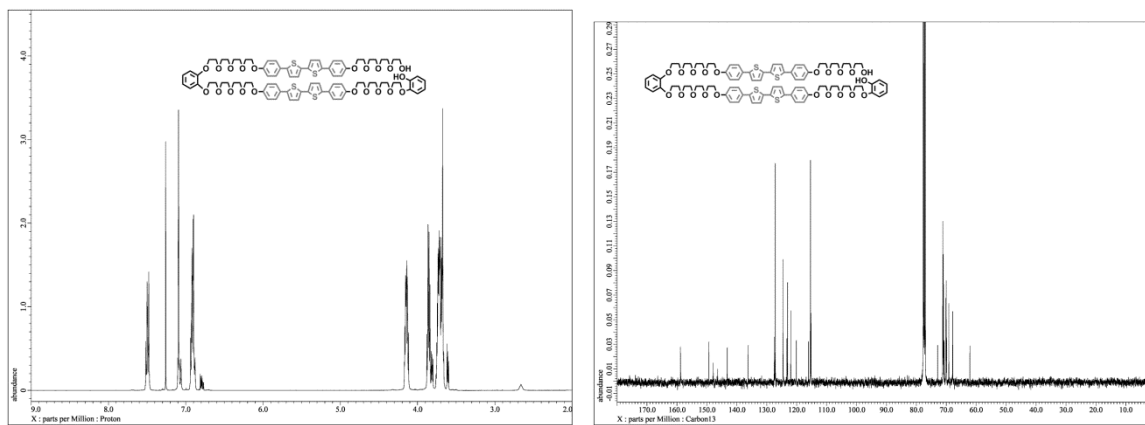


Figure S7 ^1H and ^{13}C NMR spectra of *o*-2mer-mCat

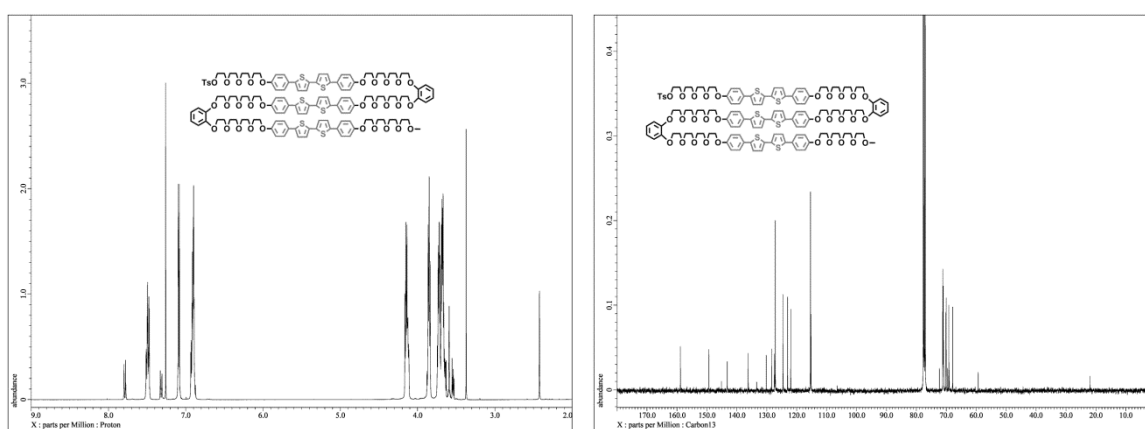


Figure S8 ^1H and ^{13}C NMR spectra of *o*-3mer-Ts-Ome

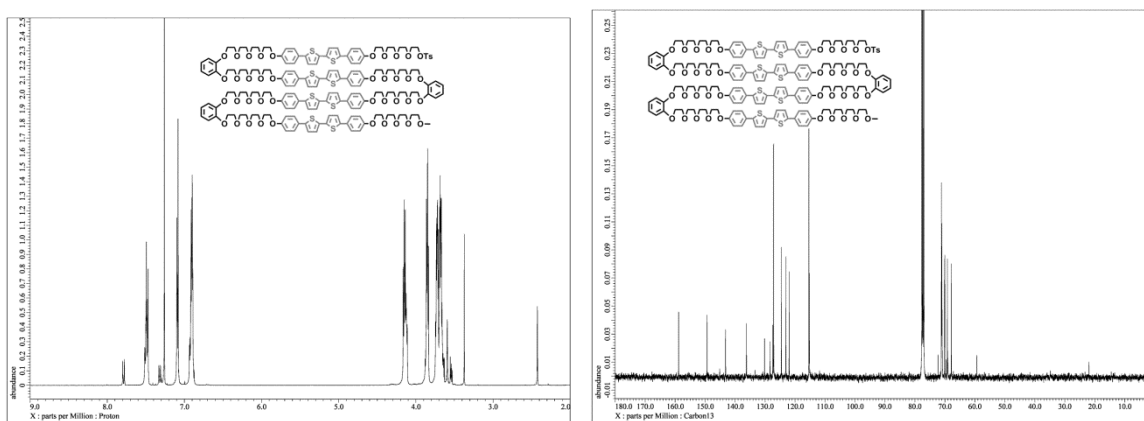


Figure S9 ^1H and ^{13}C NMR spectra of *o*-4mer-Ts-Ome

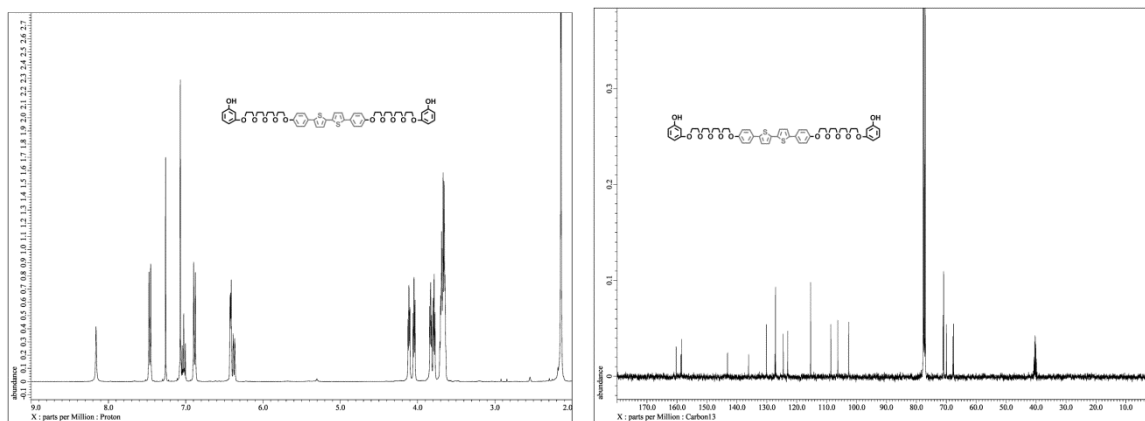


Figure S10 ^1H and ^{13}C NMR spectra of **1mer-dRes**

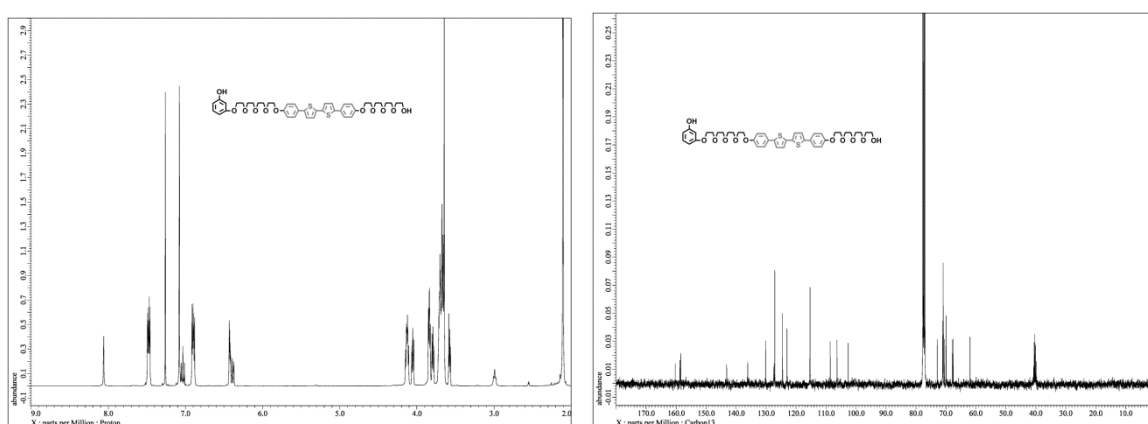


Figure S11 ^1H and ^{13}C NMR spectra of **1mer-mRes**

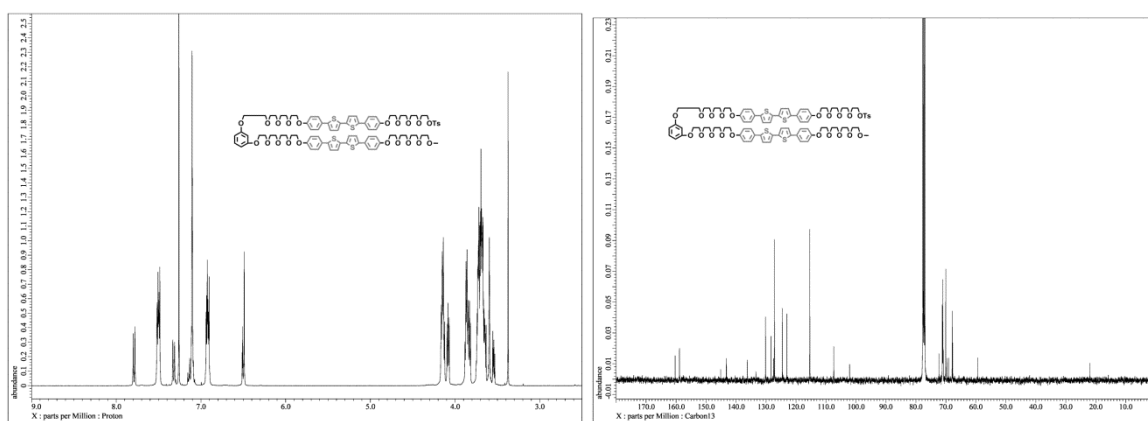


Figure S12 ^1H and ^{13}C NMR spectra of ***m*-2mer-Ts-OMe**

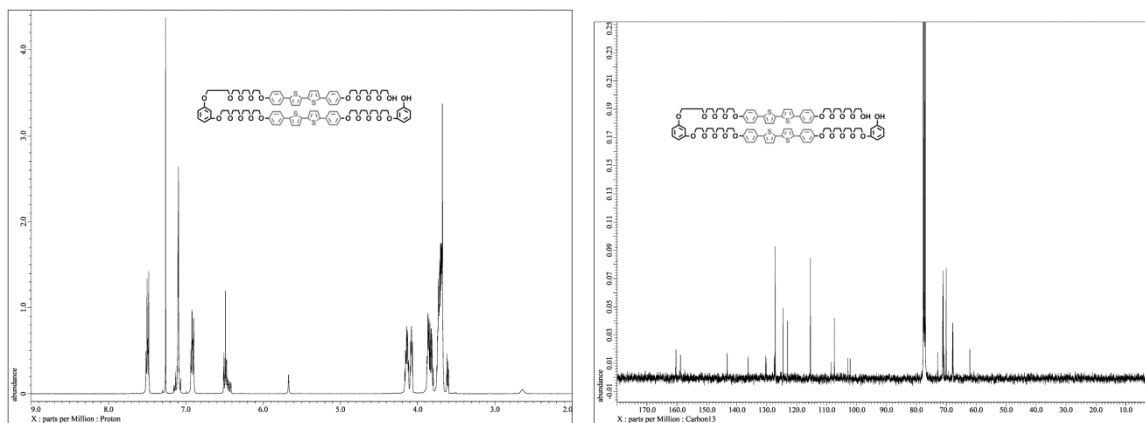


Figure S13 ^1H and ^{13}C NMR spectra of *m*-2mer-*m*Res

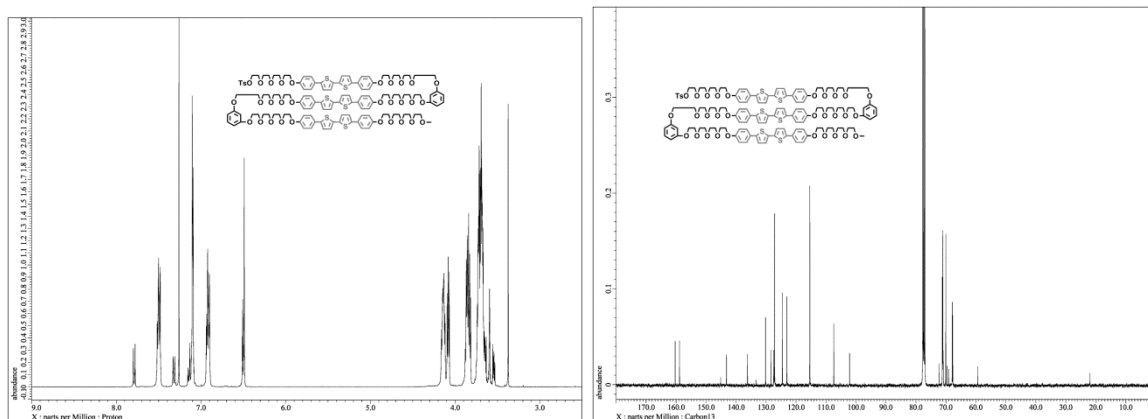


Figure S14 ^1H and ^{13}C NMR spectra of *m*-3mer-Ts-Ome

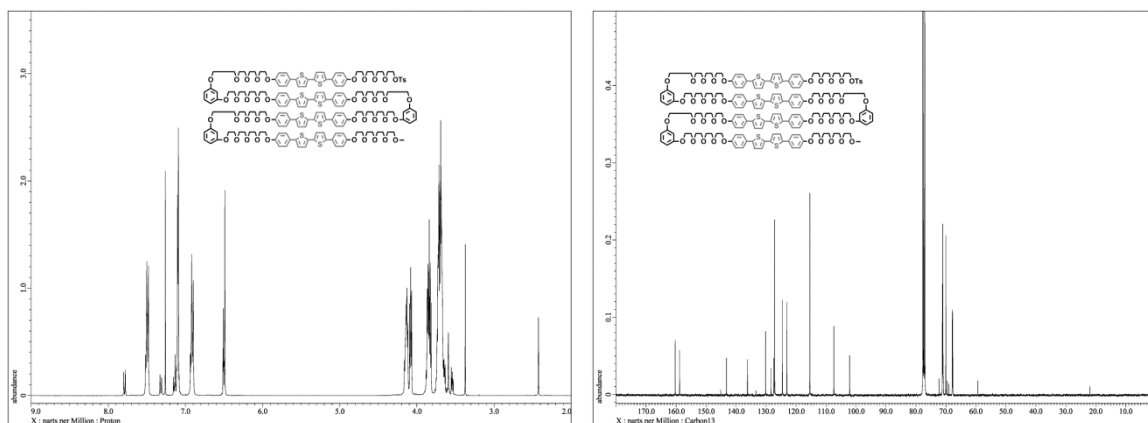


Figure S15 ^1H and ^{13}C NMR spectra of *m*-4mer-Ts-OMe

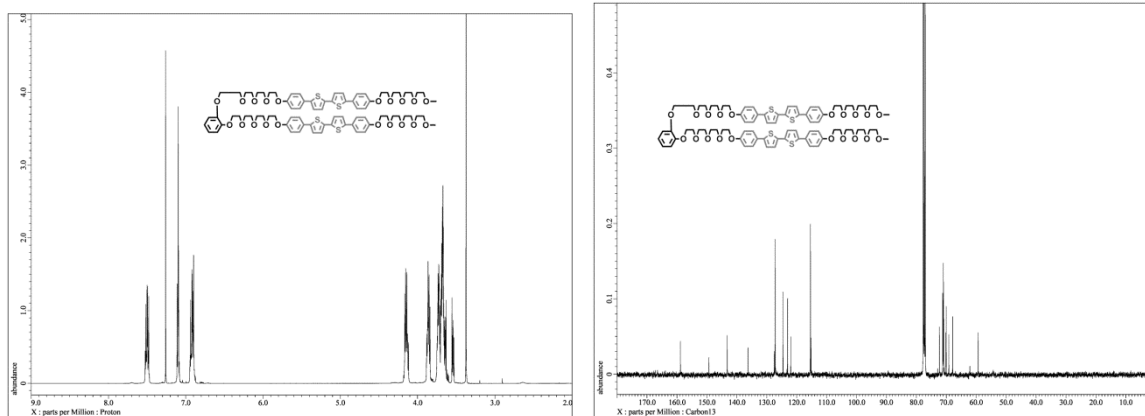


Figure S16 ^1H and ^{13}C NMR spectra of *o*-2mer

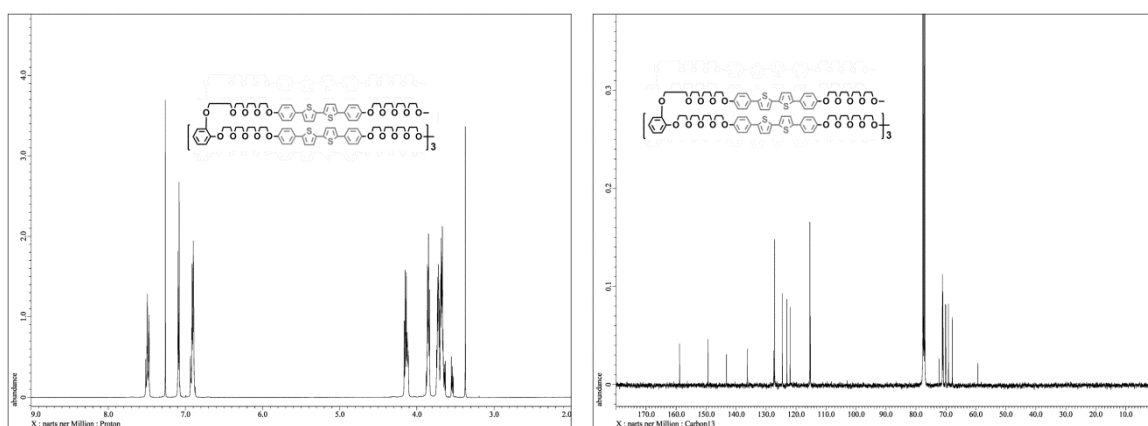


Figure S17 ^1H and ^{13}C NMR spectra of *o*-4mer

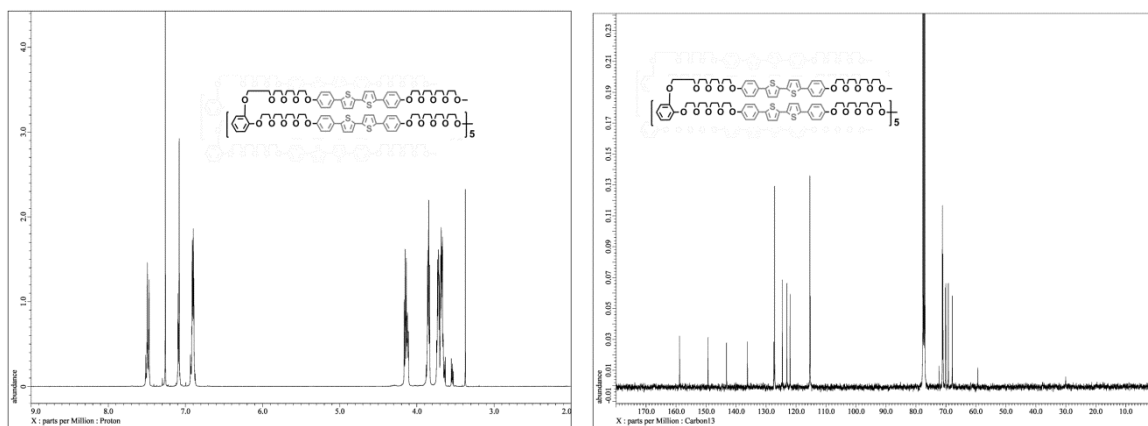


Figure S18 ^1H and ^{13}C NMR spectra of *o*-6mer

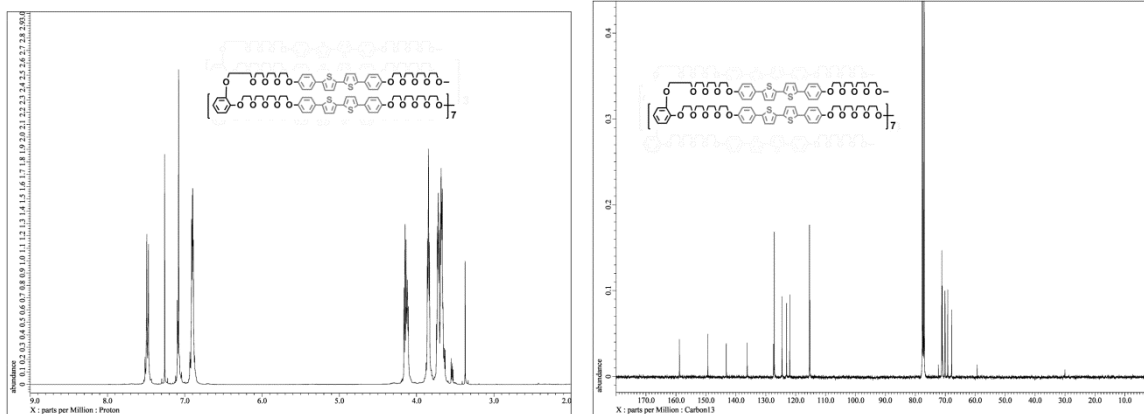


Figure S19 ^1H and ^{13}C NMR spectra of *o*-8mer

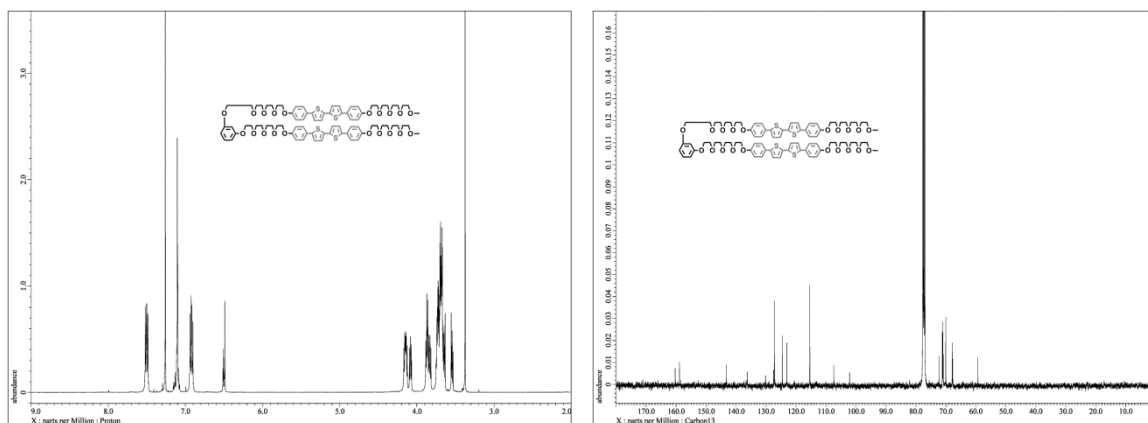


Figure S20 ^1H and ^{13}C NMR spectra of *m*-2mer

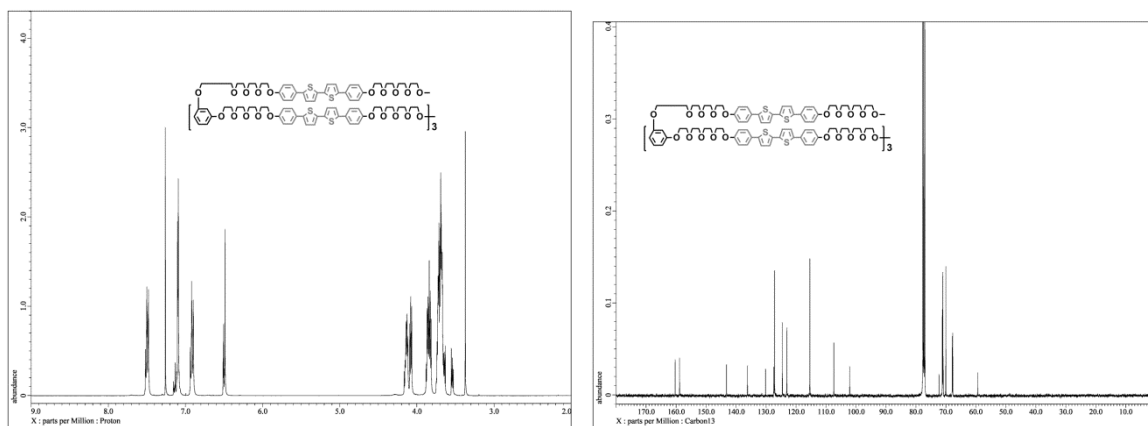


Figure S21 ^1H and ^{13}C NMR spectra of *m*-4mer

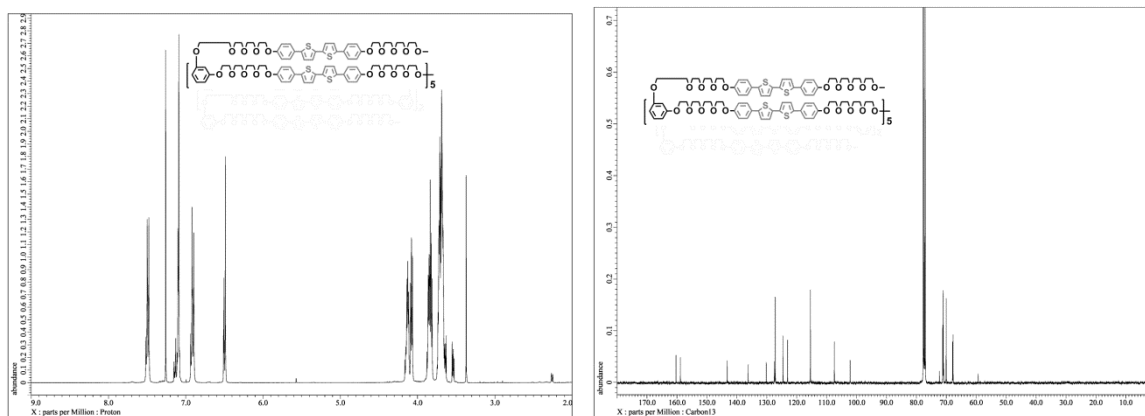


Figure S22 ^1H and ^{13}C NMR spectra of *m*-6mer

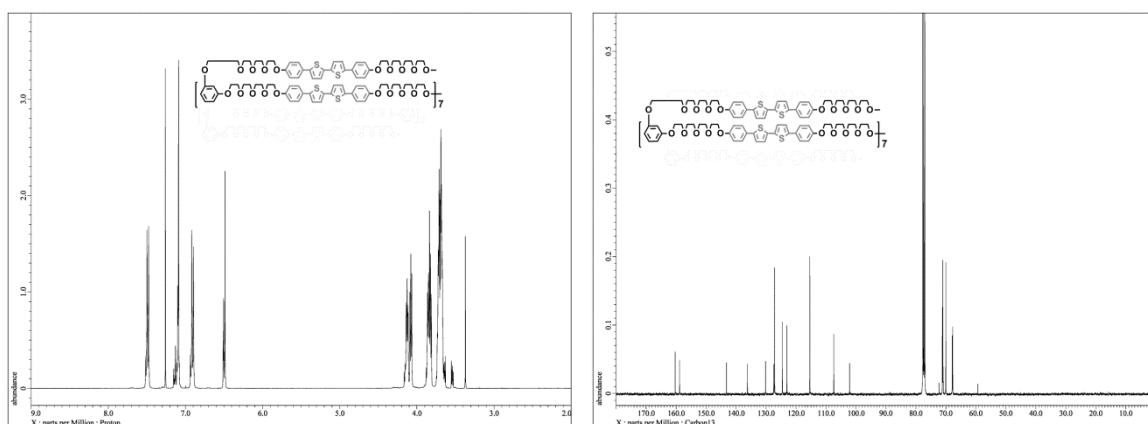


Figure S23 ^1H and ^{13}C NMR spectra of *m*-8mer

3. MALDI-TOF MS of oligomers

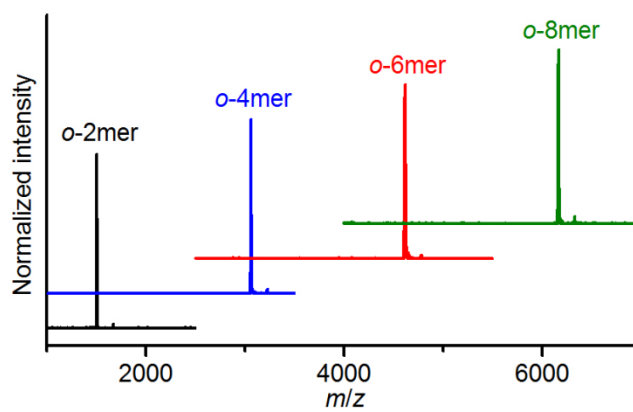


Figure S24 MALDI-TOF mass spectra of *ortho*-linked oligomers.

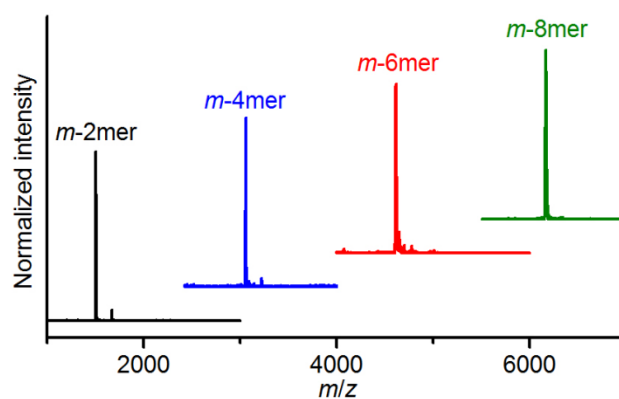


Figure S25 MALDI-TOF mass spectra of *meta*-linked oligomers.

4. Fluorescence spectra of *meta*-linked oligomers

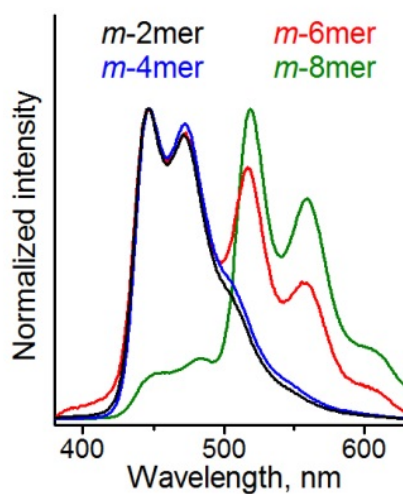


Figure S26 Fluorescence spectra of *meta*-linked oligomers. Excitation wavelength: 326 nm.

Solvent: *o*-Dichlorobenzene. Concentration of thiophene unit: 3.0×10^{-5} M.

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

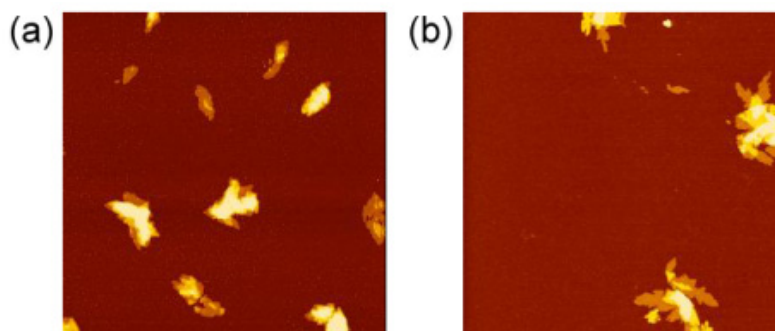


Figure S27 AFM images of the aggregates consisting of (a) *o*-6mer and (b) *m*-6mer.

Substrate: Silicon wafer, Scan area: $5 \mu\text{m} \times 5 \mu\text{m}$.

6. FP-TRMC results of triazole-linked-8mer samples

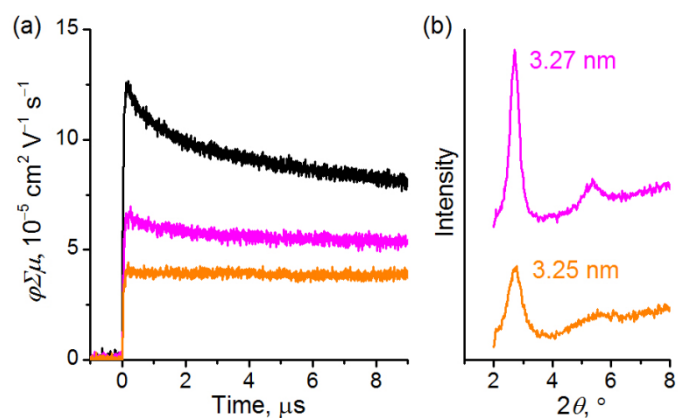


Figure S28 (a) Kinetic traces of conductivity transient upon 355 nm photoexcitation (5 mW) for *o*-8mer (black) and triazole-linked-8mer (magenta) nanosheets, and drop-cast films of triazole-linked-8mer (orange). (b) XRD patterns of triazole-linked-8mer nanosheets (magenta) and drop-cast films of triazole-linked-8mer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