Supplementary Information

Oriented quasi-domain structure of helical spin polymer prepared by electrochemical polymerization in cholesteric liquid crystal under magnetic field, showing helical stripes magnetic domain

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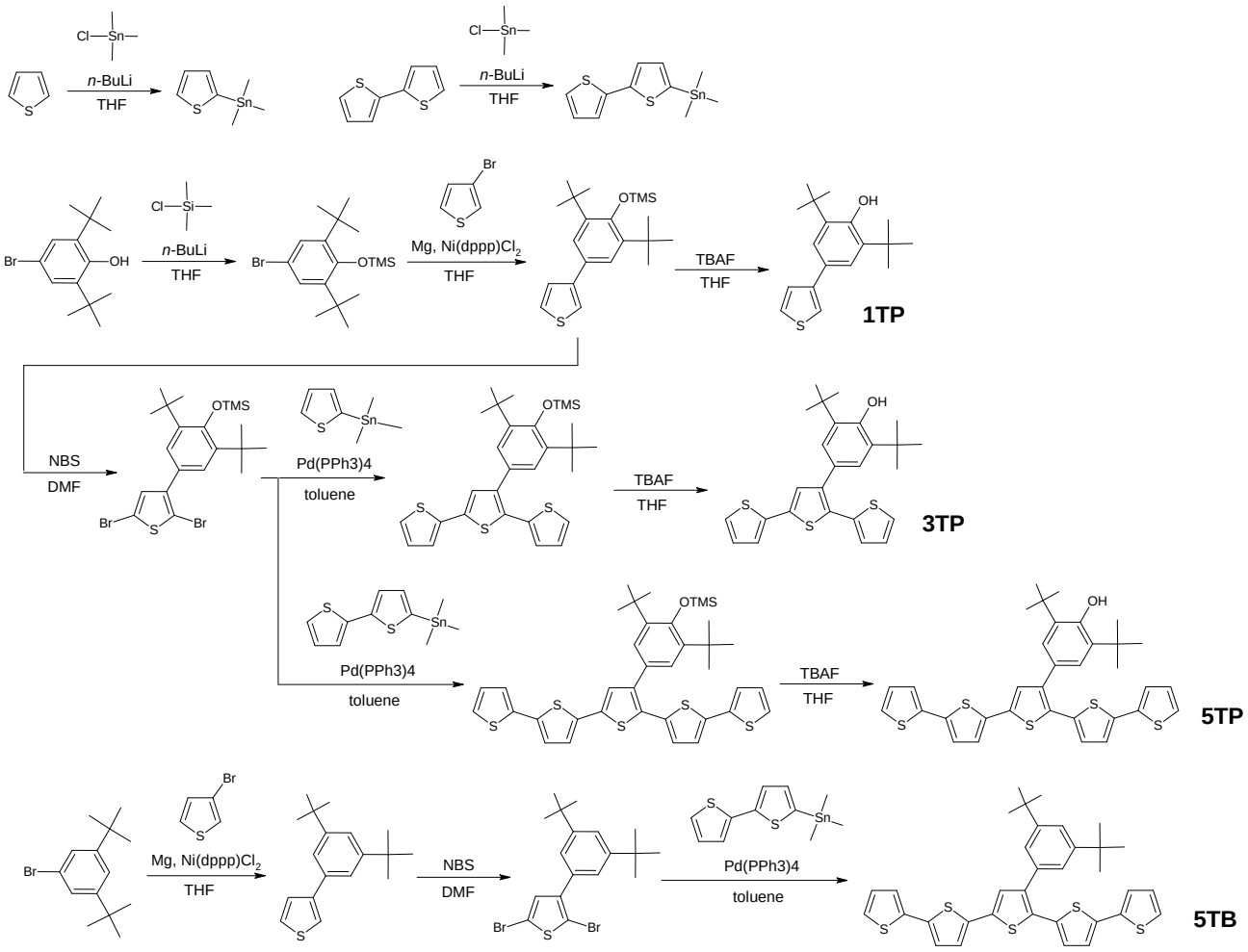

Scheme S1. Synthetic route of monomers. THF: tetrahydrofuran. *n*-BuLi: *n*-butyllithium. NBS: *N*-Bromosuccinimide. Ni(dppp)Cl_2: [1,3-Bis(diphenylphosphino)propane]nickel(II) dichloride. Pd(PPh_3)$_4$: tetrakis(triphenylphosphine)palladium(0). DMF: *N*,*N*-dimethylformamide.

Synthesis of 5-trimethyltin-thiophene:

This synthesis was carried out according to a previously reported method[1]. Quantities used: 2-Bromothiophene (3.0 g, 18.4 mmol), *n*-butyllithium (11.5 mL, 18.4 mmol), trimethyltin chloride (3.67 g, 18.4 mmol), THF (70 mL). The crude product (brown liquid) was used in the next step without purification.

Synthesis of 5-trimethyltin-2,2′-bithiophene:

This synthesis was carried out according to a previously reported method[2]. Quantities used: Bithiophene (4.5 g, 27.07 mmol), *n*-butyllithium (17 mL, 27.07 mmol), trimethyltin chloride (5.39 g, 27.07 mmol), THF (50 mL). The crude product (brown liquid) was used in the next step without purification.

Synthesis of (2,6-di-*tert*-butyl-4-bromophenoxy)trimethylsilane:

This synthesis was carried out according to a previously reported method[3]. Quantities used: 2,6-Di-*tert*-butyl-4-bromophenol (5.01 g, 17.6 mmol), *n*-butyllithium (16.5 mL, 26.3 mmol, 1.6 M in hexane), chlorotrimethylsilane (3.55 g, 32.7 mmol), THF (70 mL). Yield = 92% (5.77 g, 16.1 mmol, white solid). ^{1}H NMR (400 MHz; $CDCl_3$; TMS) δ 0.418 (s, 9H), 1.394 (s, 18H), 7.324 (s, 2H).

Synthesis of 3-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)thiophene:

This synthesis was carried out according to a previously reported method[4,5]. Quantities used: Mg (0.31 g, 12.8 mmol), (2,6-di-*tert*-butyl-4-bromophenoxy)trimethylsilane (3.50 g, 9.8 mmol), 3-bromothiophene (1.95 g, 11.9 mmol), [1,3-bis(diphenylphosphino)propane]nickel(II) chloride ($NiCl_2$(dppp), 0.044 g, 0.081 mmol), THF (30 mL). Yield = 45% (2.07 g, 5.75 mmol, white solid). ^{1}H NMR (400 MHz; $CDCl_3$; TMS) δ 0.453 (s, 9H), 1.47 (s, 18H), 7.36 (m, 3H), 7.493 (s, 2H).

Synthesis of 3-(3,5-di-*tert*-butyl-4-hydoxyphenyl)thiophene (1TP):

Under argon atmosphere, 3-(3,5-di-tert-butyl-4-trimethylsiloxyphenyl)thiophene (100 mg , 0.277 mmol) and tetrabutylammonium fluoride (1 M in THF, 0.55 mL, 0.55 mmol) in THF (6 mL) were added to an over-dried 50 mL round-bottom flask equipped with a stir-bar and stirred for 4 h at room temperature. After that, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$. The solvent was evaporated. The product was purified by column chromatography (silica gel, eluent: hexane) to afford the desired product (64.0 mg, 0.222 mmol, Yield: 80%, white solid). ^{1}H NMR (400 MHz; $CDCl_3$; TMS) δ 1.485 (s, 18H), 5.211 (s, 1H), 7.286–7.298 (q, 1H, *J* = 1.6 Hz), 7.307–7.325 (dd, 1H, *J* = 2.4 Hz), 7.337–7.358 (q, 1H, *J* = 2.8 Hz), 7.382 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 143.5, 136.3, 127.6, 126.7, 125.9, 123.6, 118.8, 34.5, 30.4. LC-MS (m/z): $[M + H]^+$ calcd. for $C_{18}H_{24}OS$, 288.45; found, 289.6.

Synthesis of 2,5-dibromo-3-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)thiophene:

This synthesis was carried out according to a previously reported method[4,5]. Quantities used: 3-(3,5-Di-tert-butyl-4-trimethylsiloxyphenyl)thiophene (2.73 g, 7.58 mmol), *n*-bromosuccinimide (NBS, 2.97 g, 16.68 mmol), DMF (50 mL). Yield = 38% (1.51 g, 2.91 mmol, white solid). ^{1}H NMR (400 MHz; $CDCl_3$; TMS) δ 0.511 (s, 9H), 1.511 (s, 18H), 7.099 (m, 1H), 7.49 (s, 2H).

Synthesis of 3′-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)-2,2′:5’,2′′-terthiophene:

Under argon atmosphere, 2,5-dibromo-3-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)thiophene (919 mg, 1.77 mmol) and 5-trimethyltin-thiophene (1314 mg, 5.33 mmol) in toluene (8 mL) were added to an over-dried 50 mL round-bottom flask equipped with a stir-bar and stirred for 0.5 h. Then, tetrakis(triphenylphosphine)palladium(0) (51.0 mg, 0.0443 mmol) was added to this solution and stirred under reflux at 100 °C for 48 h. After that, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$. The solvent was evaporated. The product was purified by column chromatography (silica gel, eluent: hexane) to afford the desired product (67.4 mg, 0.128 mmol, Yield: 7.3%, light yellow solid). ^{1}H NMR (400 MHz; $CDCl_3$; TMS) δ 0.451

(s, 9H), 1.389 (d, 18H, *J* = 11.6 Hz), 6.913–7.043 (m, 4H), 7.101 (quartet, 1H, *J* = 3.3 Hz), 7.175 (d, 2H, *J* = 4.8 Hz) , 7.301 (s, 2H).

Synthesis of 3′-(3,5-di-*tert*-butyl-4-phenoxy)-2,2′:5′,2′′-terthiophene (3TP):

Under argon atmosphere, 3′-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)-2,2′:5′,2′′-terthiophene (67.4 mg , 0.128 mmol) and tetrabutylammonium fluoride (1 M in THF, 0.25 mL, 0.25 mmol) in THF (3 mL) were added to an over-dried 50 mL round-bottom flask equipped with a stir-bar and stirred for 4 h at room temperature. After that, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$. The solvent was evaporated. The product was purified by column chromatography (silica gel, eluent: hexane) to afford the desired product (35 mg, 0.0773 mmol, Yield: 60%, light yellow solid). ^{1}H NMR (400 MHz; $CDCl_3$; TMS) δ 1.445 (d, 18H, *J* = 10.4 Hz), 5.308 (s, 1H), 6.952 (dd, 1H, *J* = 3.6 Hz), 6.989 (d, 1H, *J* = 2.9 Hz), 7.03 (d, 1H, *J* = 4 Hz), 7.057 (m, 1H), 7.113 (tri, 1H, *J* = 1.5 Hz), 7.154 (d, 2H, *J* =3.1 Hz), 7.191 (s, 2H), 7.239 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 140.6, 136.2, 134.6, 128.2, 127.8, 126.6 , 126.5, 124.6, 124.2, 123.6, 123.2, 34.5, 30.4. LC-MS (m/z): $[M + H]^+$ calcd. for $C_{26}H_{28}OS_3$, 452.69; found, 453.8.

Synthesis of 3′′-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethiophene:

Under argon atmosphere, 2,5-dibromo-3-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)thiophene (162 mg, 0.313 mmol) and 5-trimethyltin-2,2′-bithiophene (226 mg, 0.688 mmol) in toluene (3 mL) were added to an over-dried 50 mL round-bottom flask equipped with a stir-bar and stirred for 0.5 h. Then, tetrakis(triphenylphosphine)palladium(0) (7.23 mg, 0.00626 mmol) was added to this solution and stirred under reflux at 75 °C for 24 h. After that, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$. The solvent was evaporated. The product was purified by column chromatography (silica gel, eluent: hexane) to afford the desired product (22 mg, 0.0319 mmol, Yield: 10%, dark yellow solid). ^{1}H NMR (400 MHz; $CDCl_3$; TMS) δ 0.454 (s, 9H), 1.407 (s, 18H), 6.944 (d, 1H, *J* = 4.0 Hz), 6.973 (dd, 1H, *J* = 1.6 Hz), 6.996 (d, 1H, *J* = 4.0 Hz), 7.036 (m, 2H), 7.116 (dd, 2H, *J* = 3.33 Hz), 7.163 (s, 1H), 7.187 (m, 2H), 7.235 (dd, 1H, *J* = 1.87 Hz), 7.301 (s, 2H).

Synthesis of 3″-(3,5-di-*tert*-butyl-4-phenoxy)-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (5TP):

Under argon atmosphere, 3″-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (22 mg , 0.0319 mmol) and tetrabutylammonium fluoride (1 M in THF, 0.1 mL, 0.1 mmol) in THF (3 mL) were added to an over-dried 50 mL round-bottom flask equipped with a stir-bar and stirred for 4 h at room temperature. After that, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$. The solvent was evaporated. The product was purified by column chromatography (silica gel, eluent: hexane) to afford the desired product (15.7 mg, 0.0255 mmol, Yield: 80%, dark yellow solid). ^{1}H NMR (400 MHz; $CDCl_3$; TMS) δ 1.445 (s, 18H), 5.304 (s, 1H), 6.952 (d, 1H, *J* = 3.6 Hz), 6.989 (dd, 1H, *J* = 2.9 Hz), 7.006 (d, 1H, *J* = 4 Hz), 7.037 (dd, 1H, *J* = 2.9 Hz), 7.061 (dd, 1H, *J* = 1.5 Hz), 7.116 (dd, 2H, *J* =3.1 Hz), 7.144 (s, 1H), 7.192 (m, 2H), 7.236 (m, 1H), 7.242 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 140.8, 137.2, 136.0, 134.6, 128.0, 127.9, 127.2, 126.9, 126.5, 126.2, 124.7, 124.5, 124.4, 123.9, 123.5, 123.4, 34.5, 30.4. LC-MS (m/z): $[M + H]^+$ calcd. for $C_{34}H_{32}OS_5$, 616.94; found, 618.0.

Synthesis of 3-(3,5-di-*tert*-butyl-phenyl)thiophene:

Under argon atmosphere, Mg (0.542 g, 22.3 mmol) in THF (5 mL) was added to an over-dried 100 mL round-bottom flask equipped with a stir-bar. Then, this solution was slowly added dropwise to 1-bromo-3,5-di-*tert*-butyl-benzene (5.00 g, 18.6 mmol) in THF (5 mL) and stirred for 6 h at room temperature. After disappearance of Mg, this grignard suspension was added to a mixture of 3-bromothiophene (3.03 g, 18.6 mmol) and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride ($NiCl_2$(dppp), 0.065 g, 0.120 mmol) in THF (10 mL) and stirred under reflux for 12 h. When the reaction is completed, the reaction mixture poured into an aqueous sodium bicarbonate ($NaHCO_3$) and extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$. The solvent was evaporated. The product was purified by column chromatography (silica gel, eluent: hexane) to afford the desired product (3.54 g, 13.0 mmol, Yield: 70%, colorless liquid). ^{1}H NMR (400 MHz; $CDCl_3$; TMS) δ 1.409 (s, 18H), 7.394–7.433 (m, 3H, 2,4,5-*H*(thiophene)), 7.449–7.467 (m, 3H, 2,4,6-*H*(benzene)).

Synthesis of 2,5-dibromo-3-(3,5-di-*tert*-butyl-phenyl)thiophene

Under argon atmosphere, 3-(3,5-di-*tert*-butyl-phenyl)thiophene (3.50 g, 12.9 mmol) in DMF (15 mL) was added to an over-dried 100 mL round-bottom flask equipped with a stir-bar. After that, NBS (5.71 g, 32.1 mmol) was slowly added to the solution at 0 °C and stirred 24 h at room temperature. Then, the mixture was poured into an aqueous sodium bicarbonate ($NaHCO_3$) and extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$. The solvent was evaporated. The product was purified by column chromatography (silica gel, eluent: hexane) to afford the desired product (3.58 g, 8.32 mmol, Yield: 65%, white solid). ^{1}H NMR (400 MHz; $CDCl_3$; TMS) δ 1.375 (s, 18H), 7.055 (s, 1H), 7.344 (d, 2H, *J* = 1.6 Hz), 7.434 (t, 1H, *J* = 1.8 Hz).

Synthesis of 3″-(3,5-di-*tert*-butyl-phenyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗- quinquethiophene (5TB):

Under argon atmosphere, 2,5-dibromo-3-(3,5-di-*tert*-butyl-phenyl)thiophene (1.00 g, 2.32 mmol) and 5-trimethyltin-2,2′-bithiophene (1.68 g, 5.11 mmol) in toluene (10 mL) were added to an over-dried 100 mL round-bottom flask equipped with a stir-bar and stirred for 0.5 h. Then, tetrakis(triphenylphosphine)palladium(0) (53.0 mg, 0.0465 mmol) was added to this solution and stirred under reflux at 75 °C for 24 h. After that, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$. The solvent was evaporated. The product was purified by column chromatography (silica gel, eluent: hexane) to afford the desired product (145 mg, 0.241 mmol, Yield: 10%, dark yellow solid). ^{1}H NMR (400 MHz; $CDCl_3$; TMS) δ 1.334 (s, 18H), 6.917 (d, 1H, *J* =3.6 Hz), 6.982 (m, 2H), 7.041 (m, 2H), 7.122 (dd, 2H, *J* =3.7 Hz), 7.166 (s, 1H), 7.192 (m, 2H), 7.237 (dd, 1H, *J* = 2.1 Hz), 7.278 (d, 2H, *J* = 2 Hz), 7.422 (t, 1H, *J* = 1.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 140.9, 137.3, 134.8, 134.7, 128.0, 127.2, 127.0, 124.7, 124.6, 124.5, 124.4, 123.9, 123.8, 123.7, 123.6, 121.7, 35.0, 31.5. LC-MS (m/z): $[M + H]^+$ calcd. for $C_{34}H_{32}S_5$, 600.94; found, 602.0.

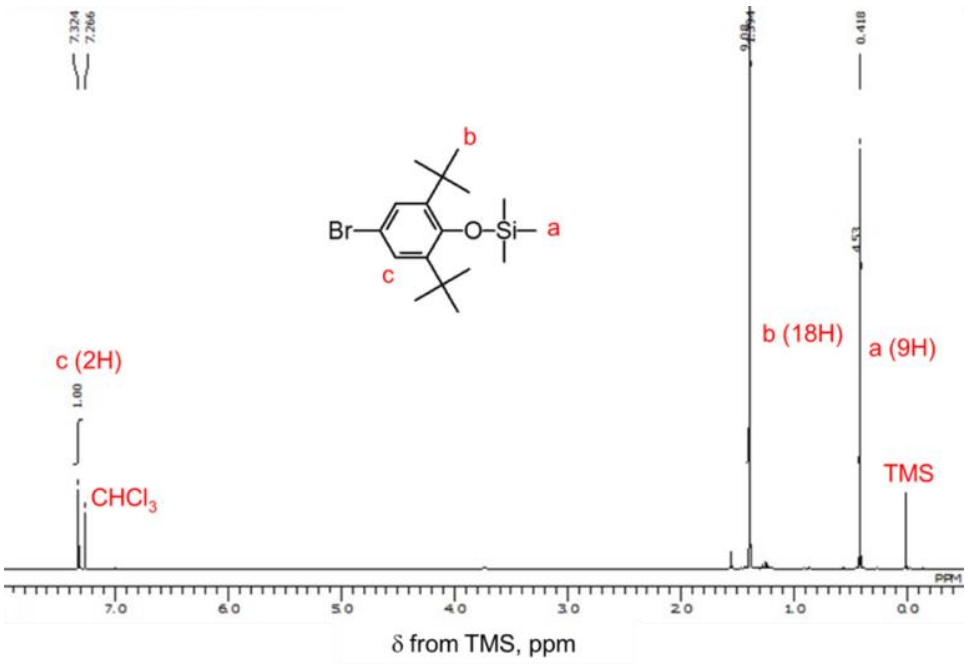

Figure S1. ^{1}H NMR data for (2,6-di-*tert*-butyl-4-bromophenoxy)trimethylsilane in $CDCl_3$, at 400 MHz.

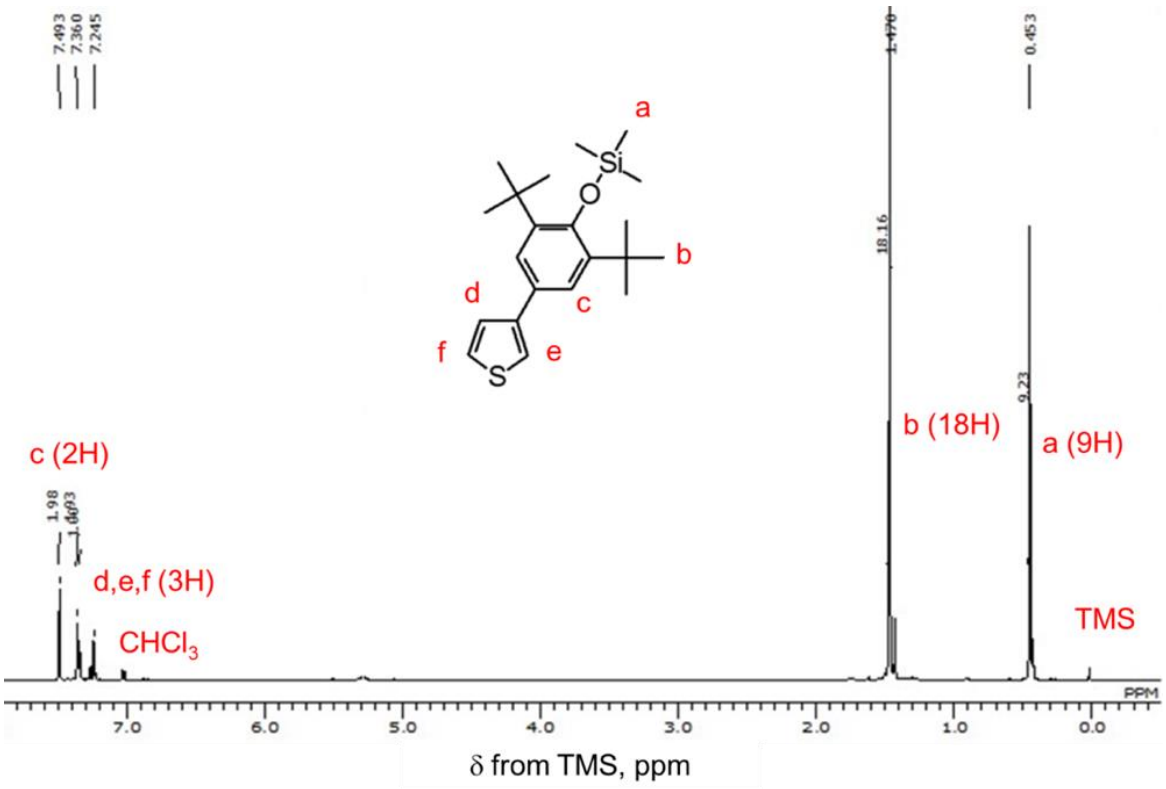

Figure S2. ^{1}H NMR data for 3-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)thiophene in $CDCl_3$, at 400 MHz.

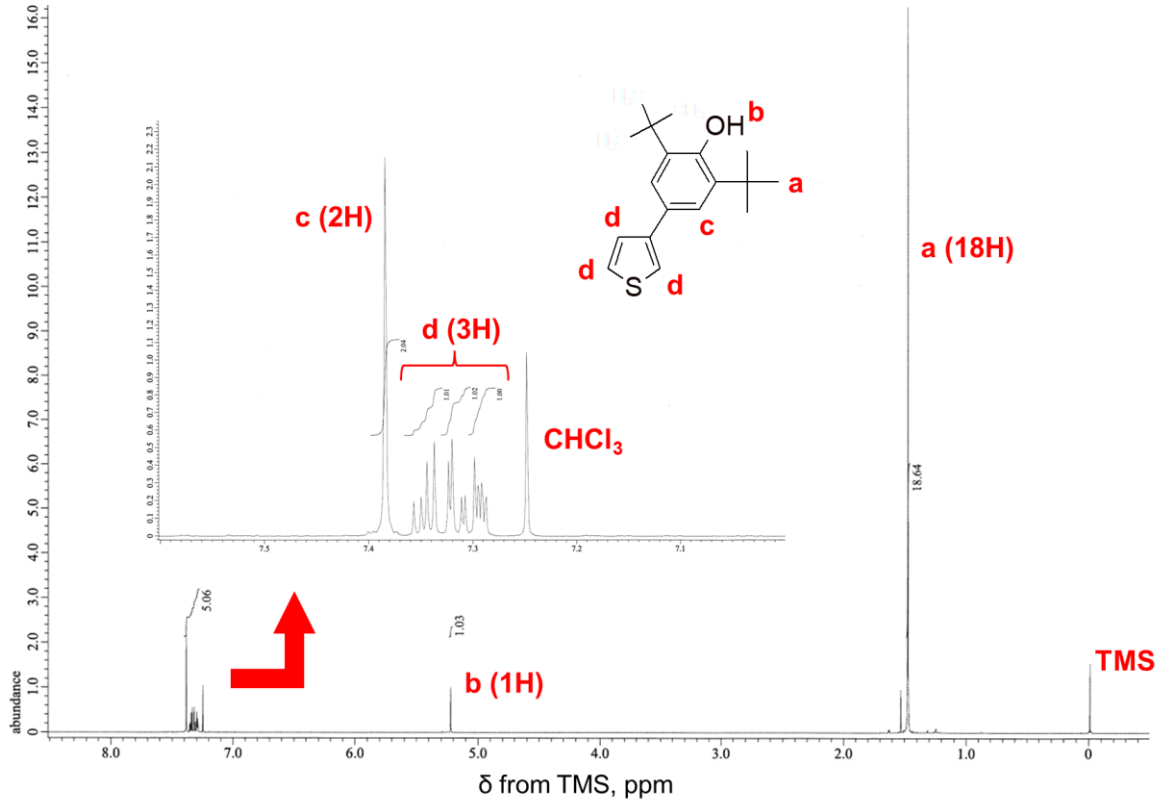

Figure S3. ^{1}H NMR data for 3-(3,5-di-*tert*-butyl-4-hydoxyphenyl)thiophene (1TP) in $CDCl_3$, at 400 MHz.

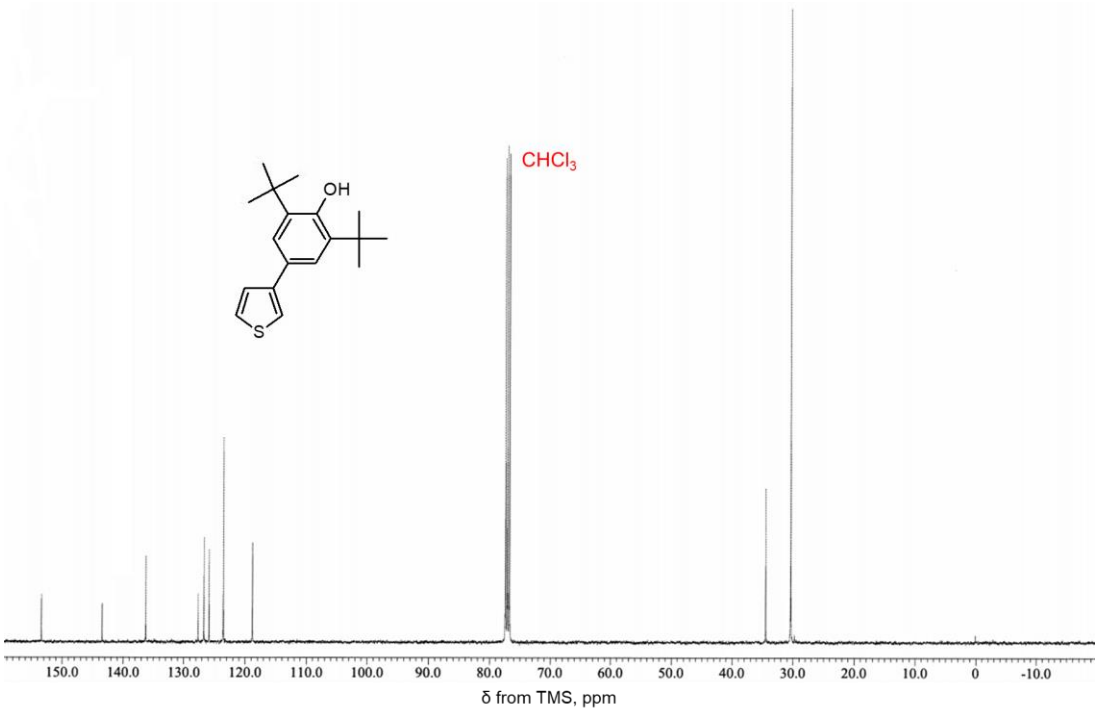

Figure S4. ^{13}C NMR data for 3-(3,5-di-*tert*-butyl-4-hydoxyphenyl)thiophene (1TP) in $CDCl_3$, at 100 MHz.

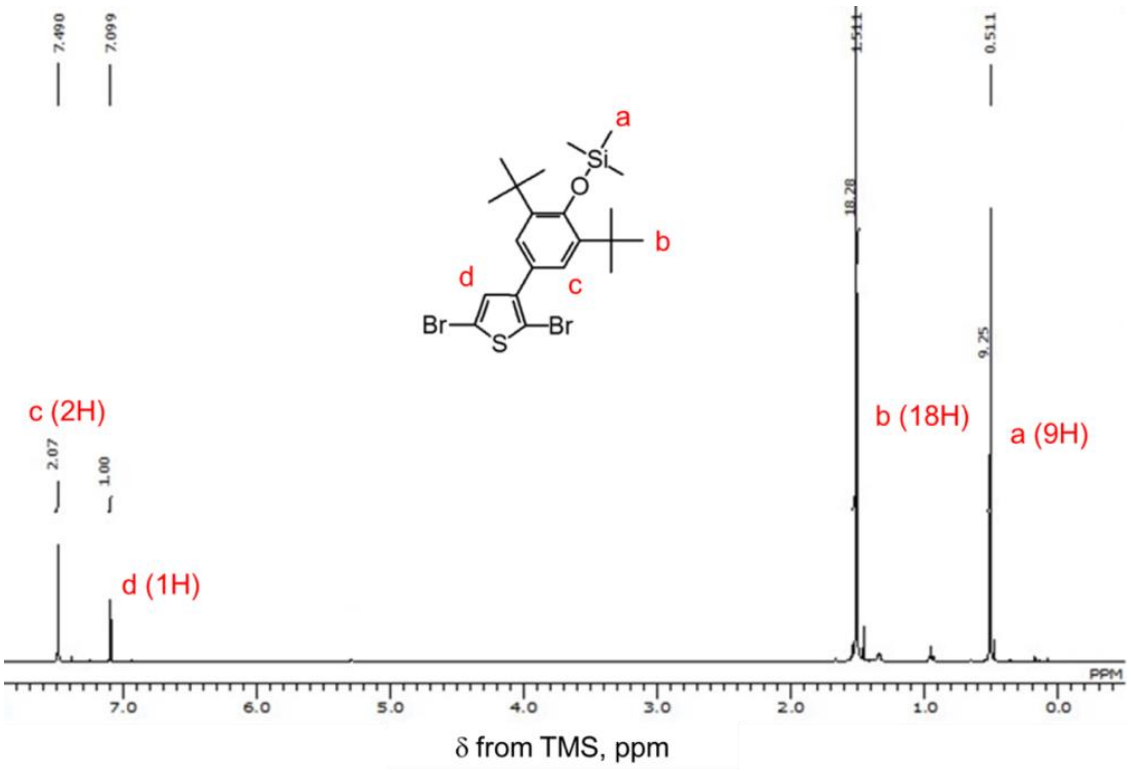

Figure S5. ^{1}H NMR data for 2,5-dibromo-3-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)thiophene in $CDCl_3$, at 400 MHz.

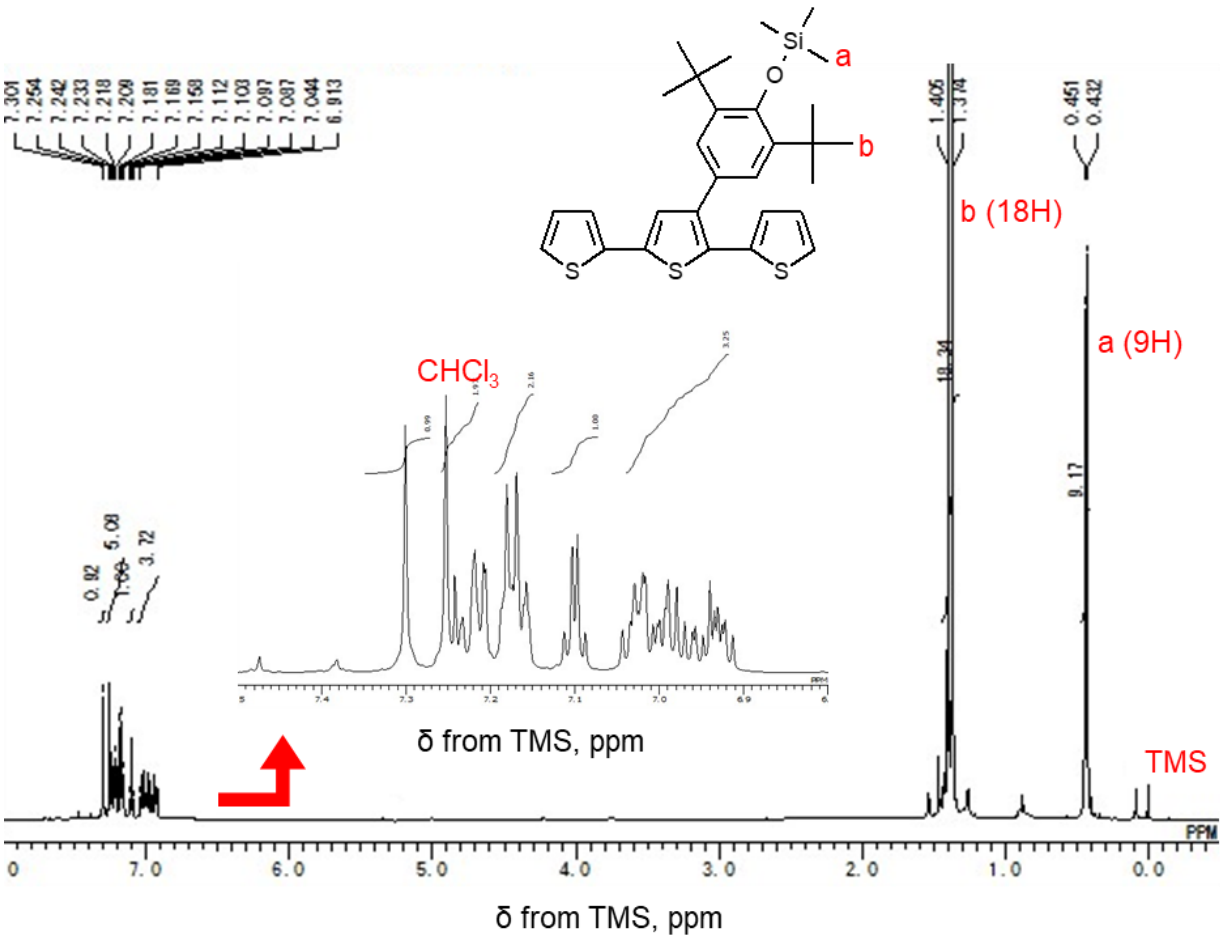

Figure S6. ^{1}H NMR data for 3′-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)-2,2′:5′,2″-terthiophene in $CDCl_3$, at 400 MHz.

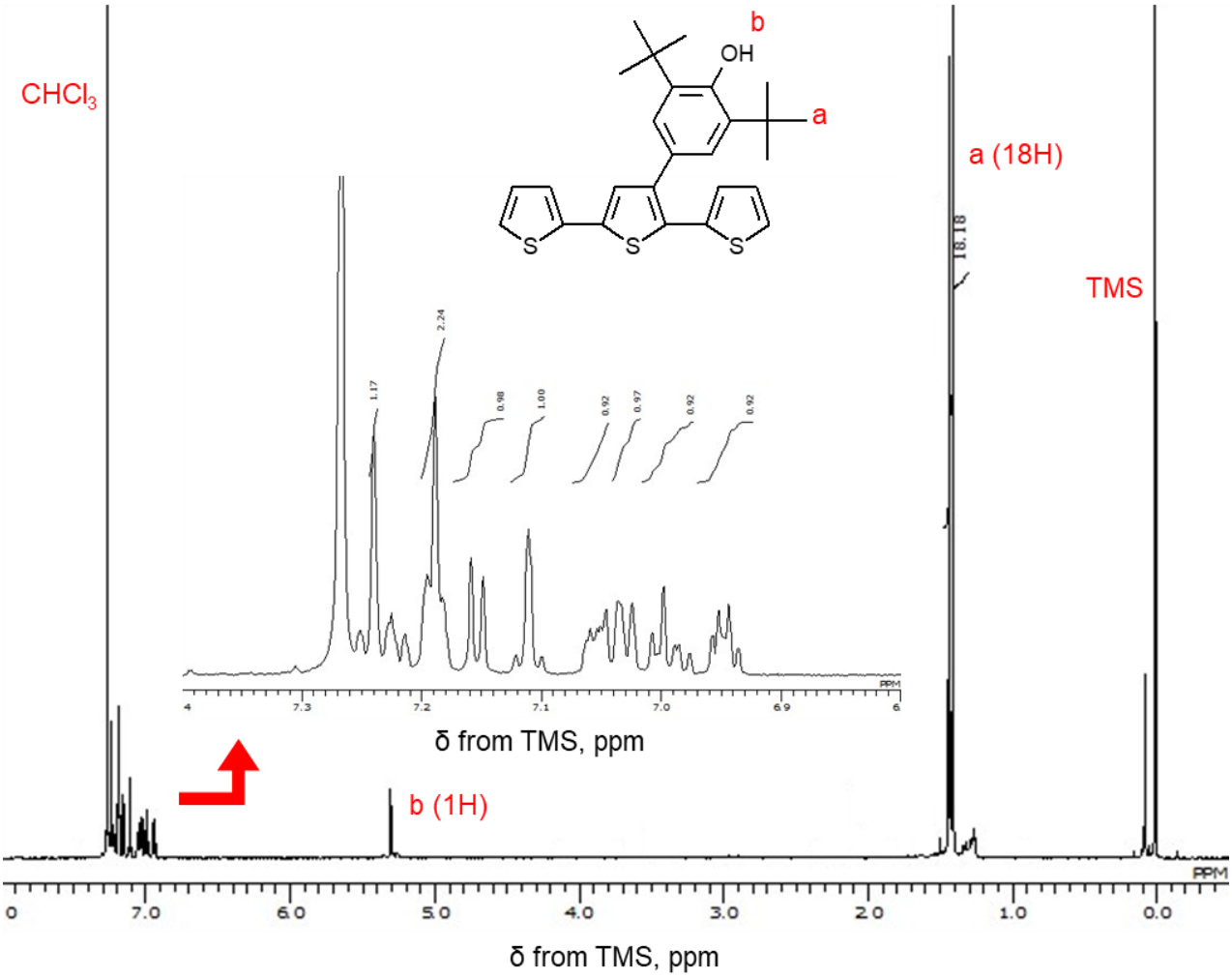

Figure S7. ^{1}H NMR data for 3′-(3,5-di-*tert*-butyl-4-phenoxy)-2,2′:5′,2″-terthiophene (3TP) in $CDCl_3$, at 400 MHz.

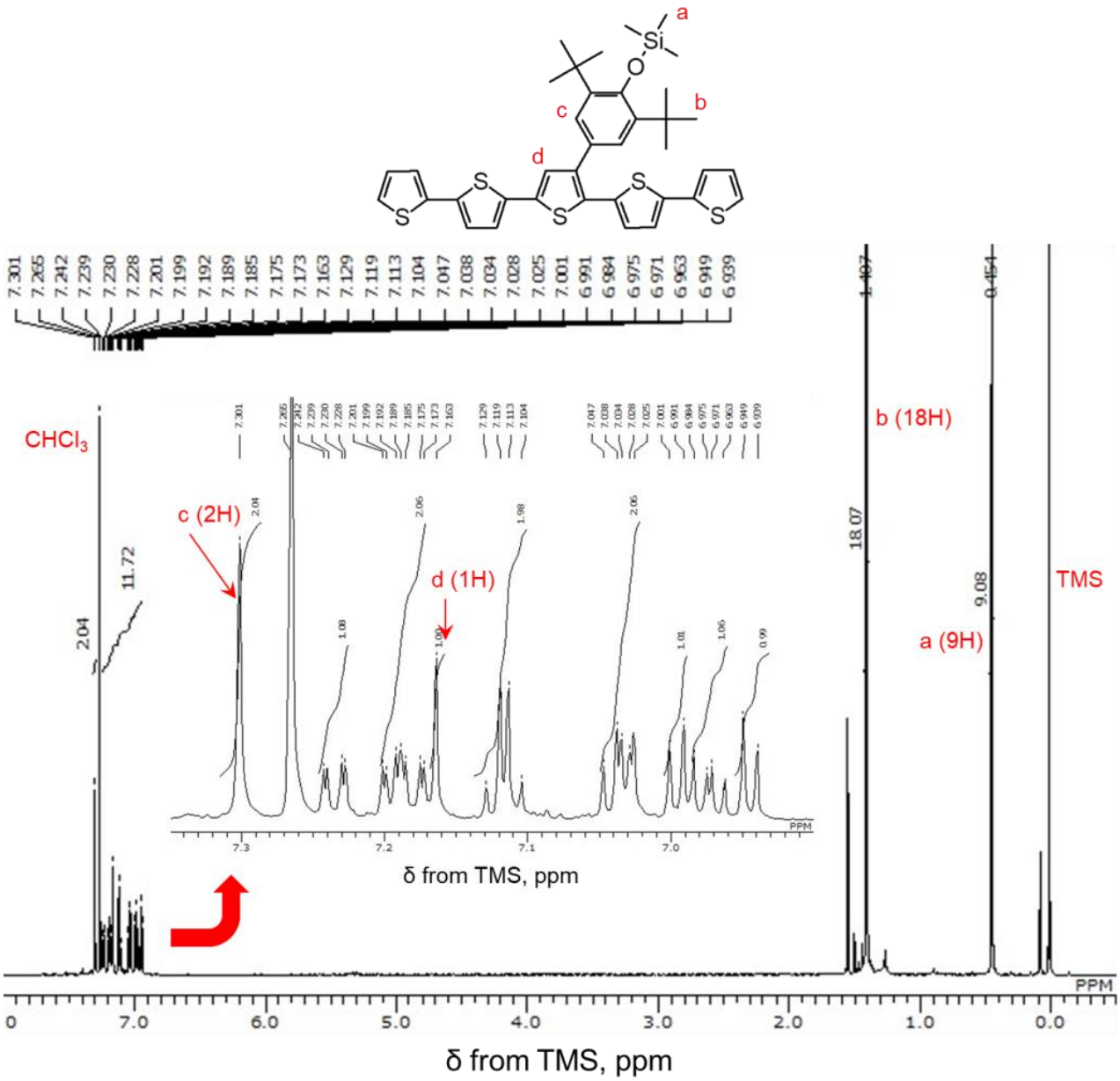

Figure S8. ^{1}H NMR data for 3″-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene in $CDCl_3$, at 400 MHz.

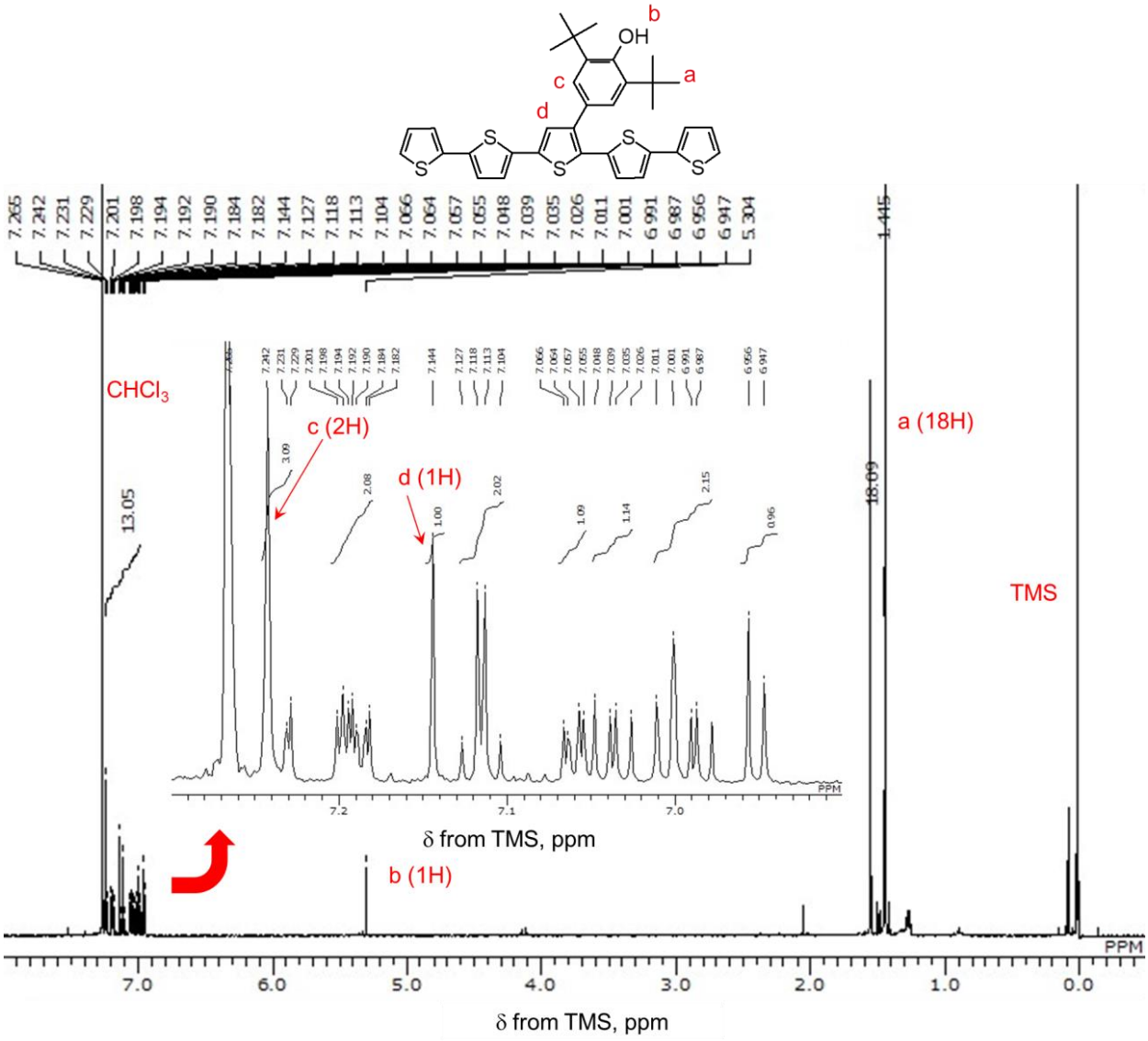

Figure S9. ^{1}H NMR data of 3″-(3,5-di-*tert*-butyl-4-phenoxy)-2,2′:5′,2″:5″,2‴:5‴,2⁗- quinquethiophene (5TP) in $CDCl_3$, at 400 MHz.

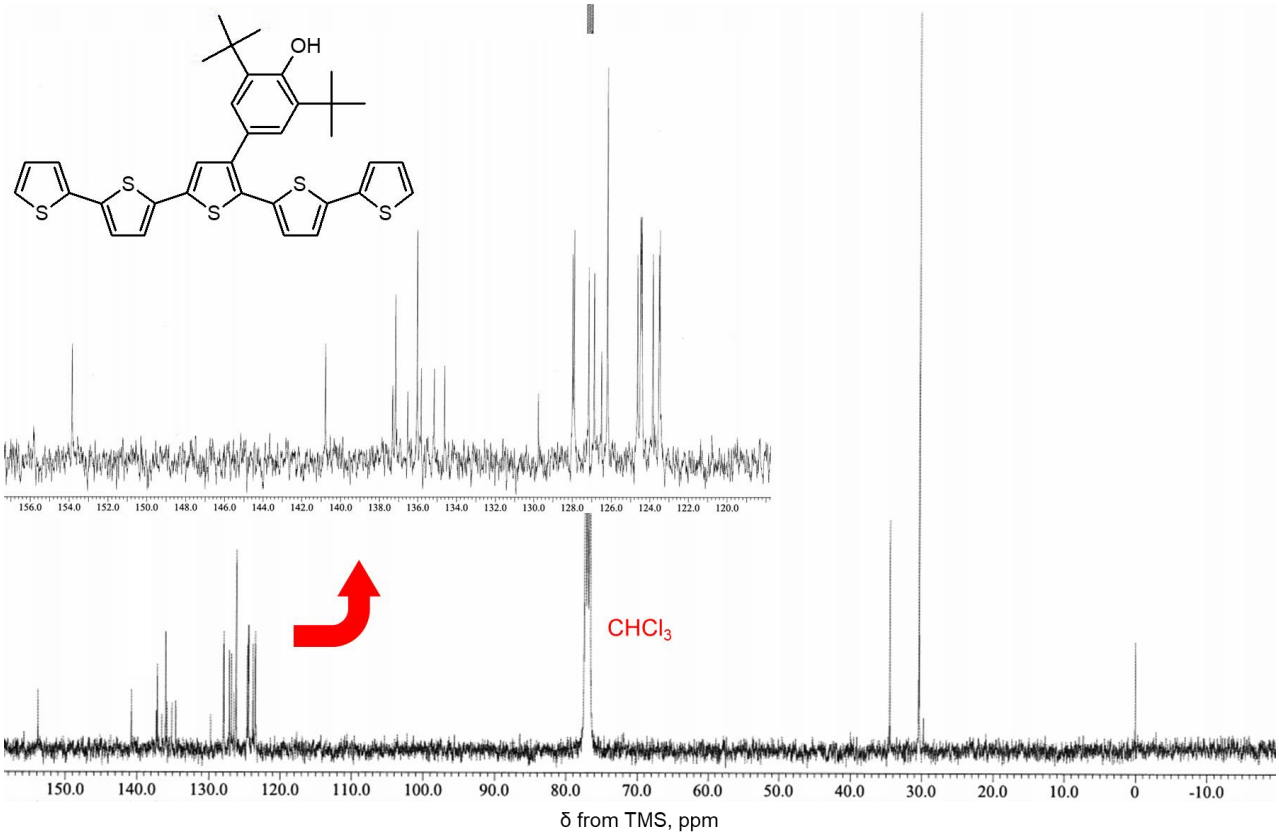

Figure S10. ^{13}C NMR data of 3″-(3,5-di-*tert*-butyl-4-phenoxy)-2,2′:5′,2″:5″,2‴:5‴,2⁗- quinquethiophene (5TP) in $CDCl_3$, at 100 MHz.

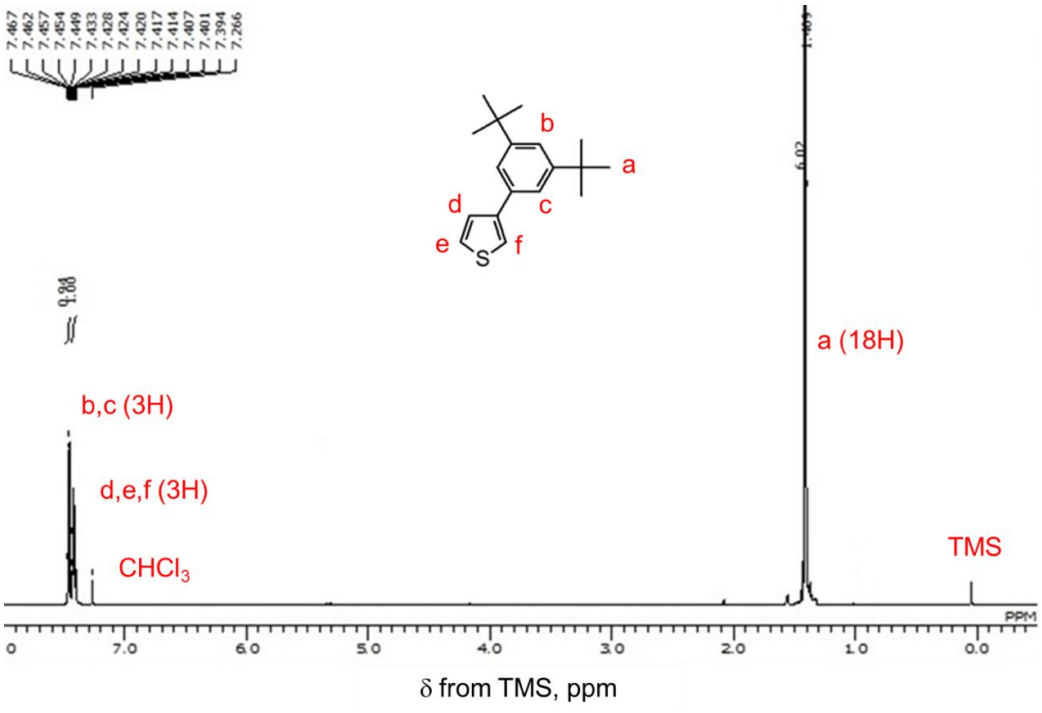

Figure S11. ^{1}H NMR data for 3-(3,5-di-*tert*-butyl-phenyl)thiophene in $CDCl_3$, at 400 MHz.

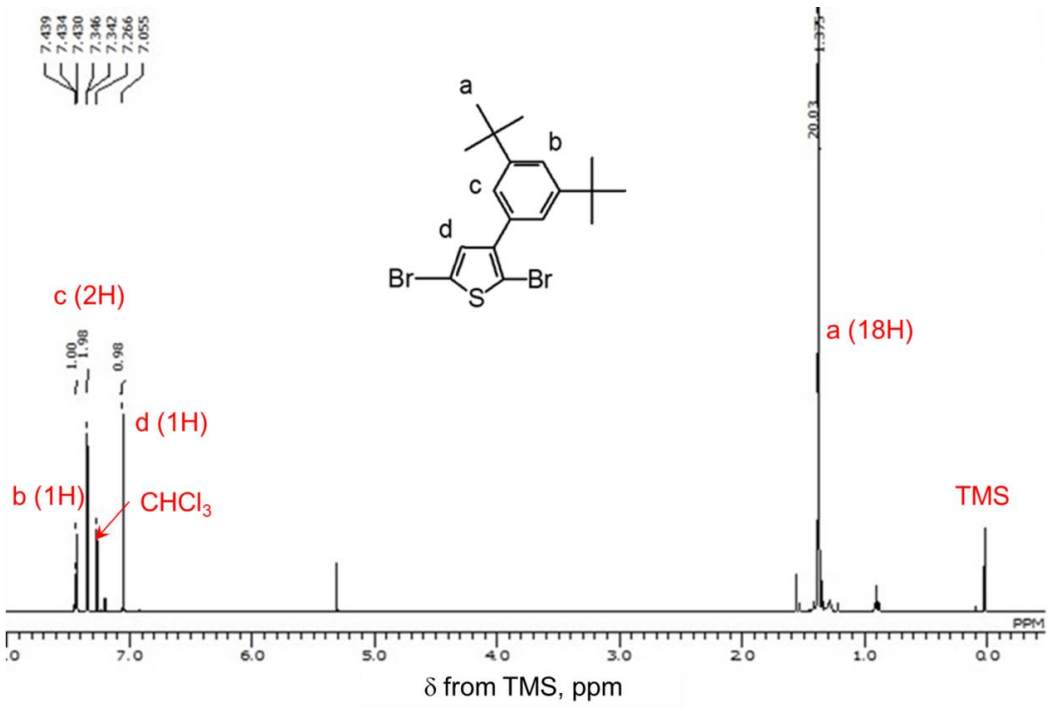

Figure S12. ^{1}H NMR data for 2,5-dibromo-3-(3,5-di-*tert*-butyl-phenyl)thiophene in $CDCl_3$, at 400 MHz.

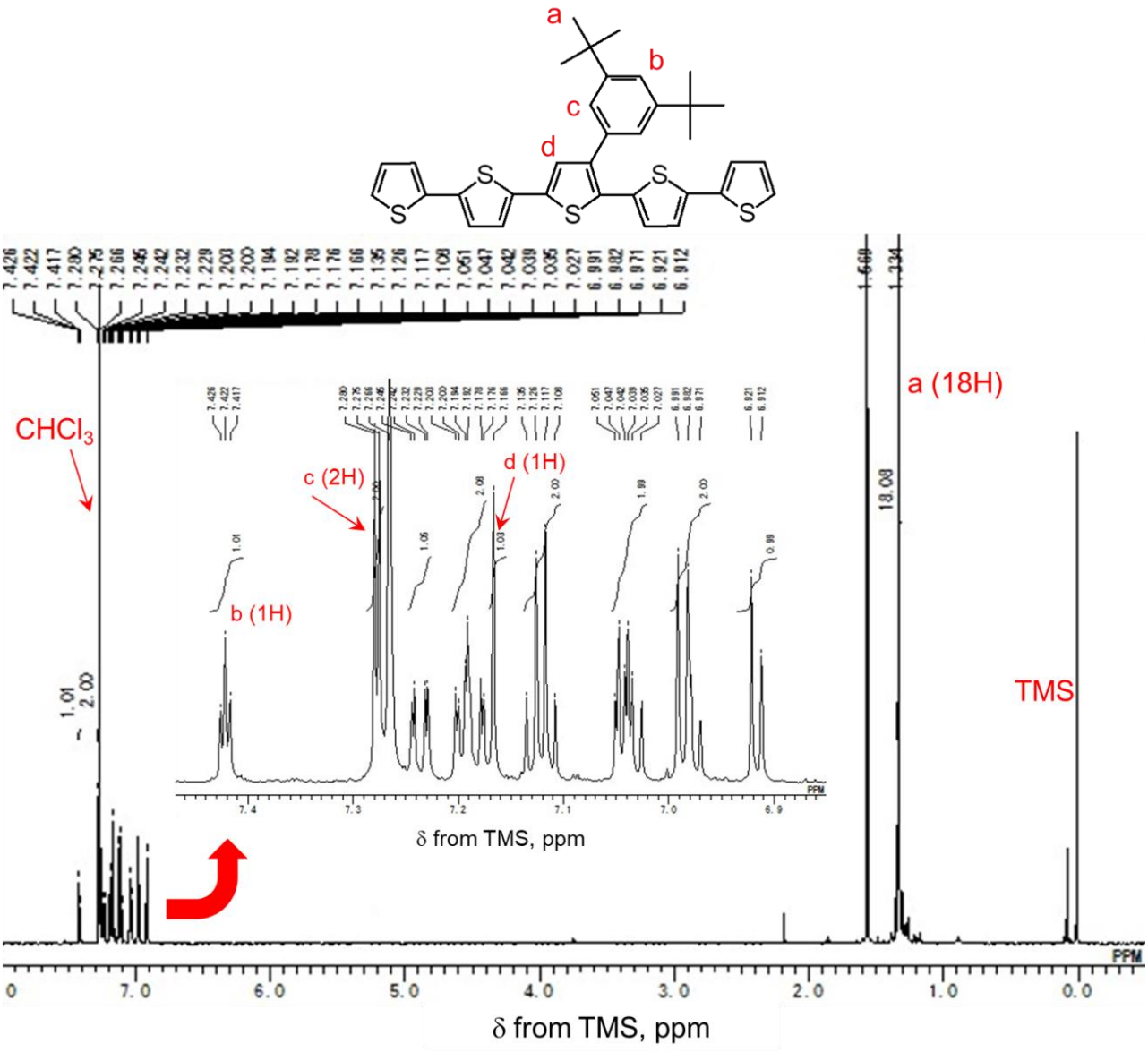

Figure S13. ^{1}H NMR data for 3″-(3,5-di-*tert*-butyl-phenyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (5TB) in $CDCl_3$, at 400 MHz.

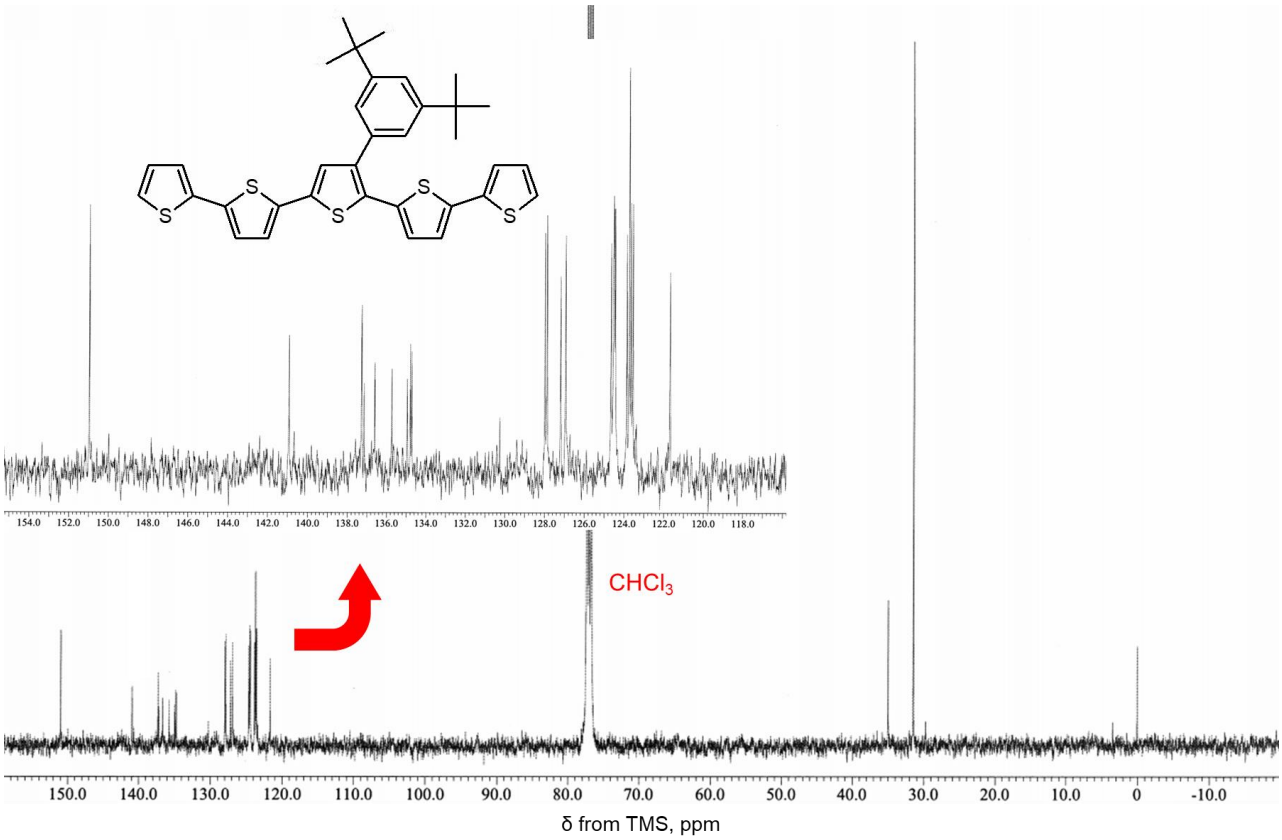

Figure S14. ^{13}C NMR data for 3″-(3,5-di-*tert*-butyl-phenyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (5TB) in $CDCl_3$, at 100 MHz.

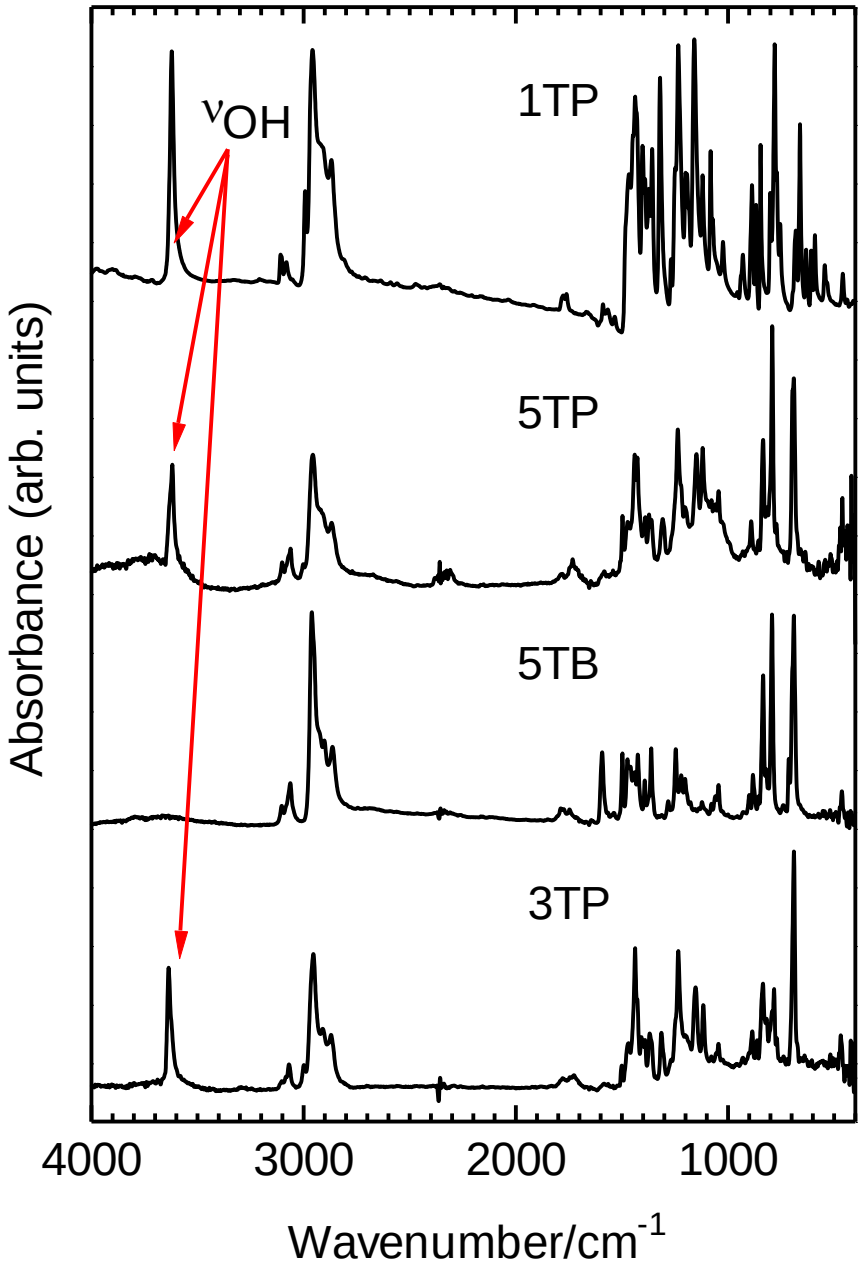

Figure S15. FT-IR spectra of 1TP, 5TP, 5TB and 3TP in KBr method.

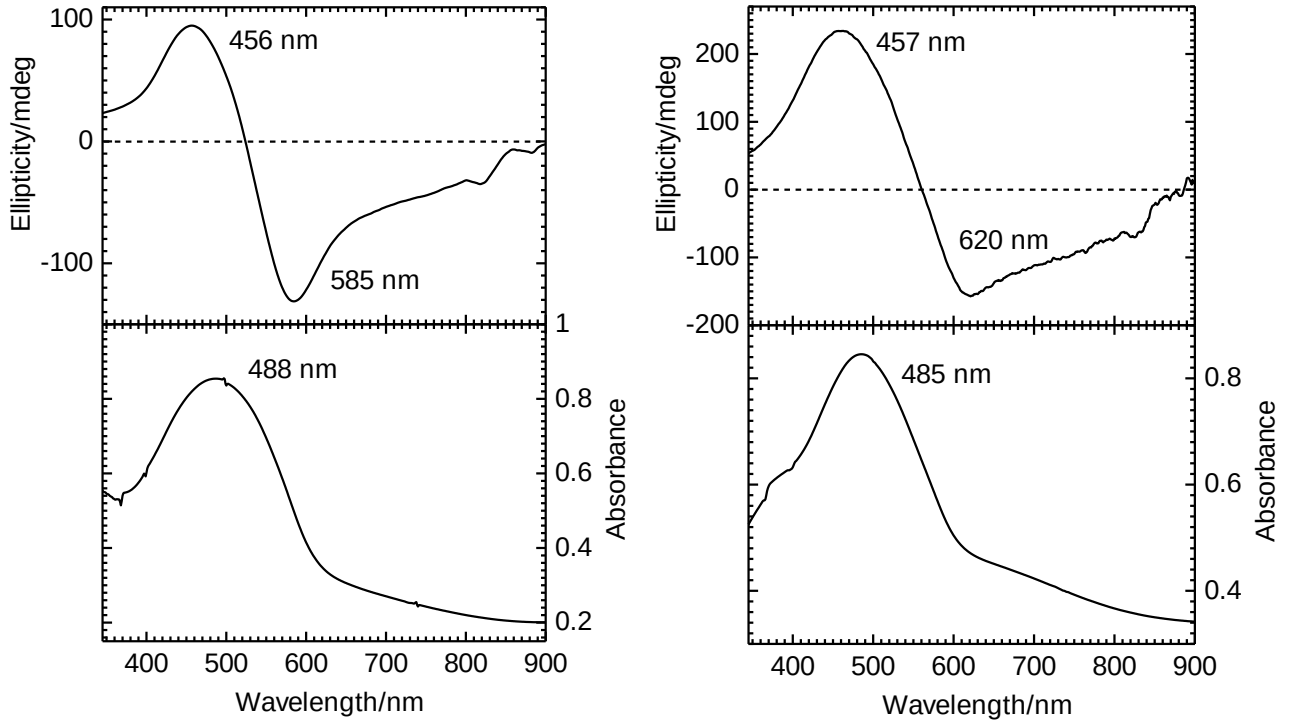

Figure S16. CD (top) and UV–vis optical absorption (bottom) spectra of (a) $p5TP_{(0T)}$, (b) $p5TB_{(0T)}$ reduced by hydrazine vapor.

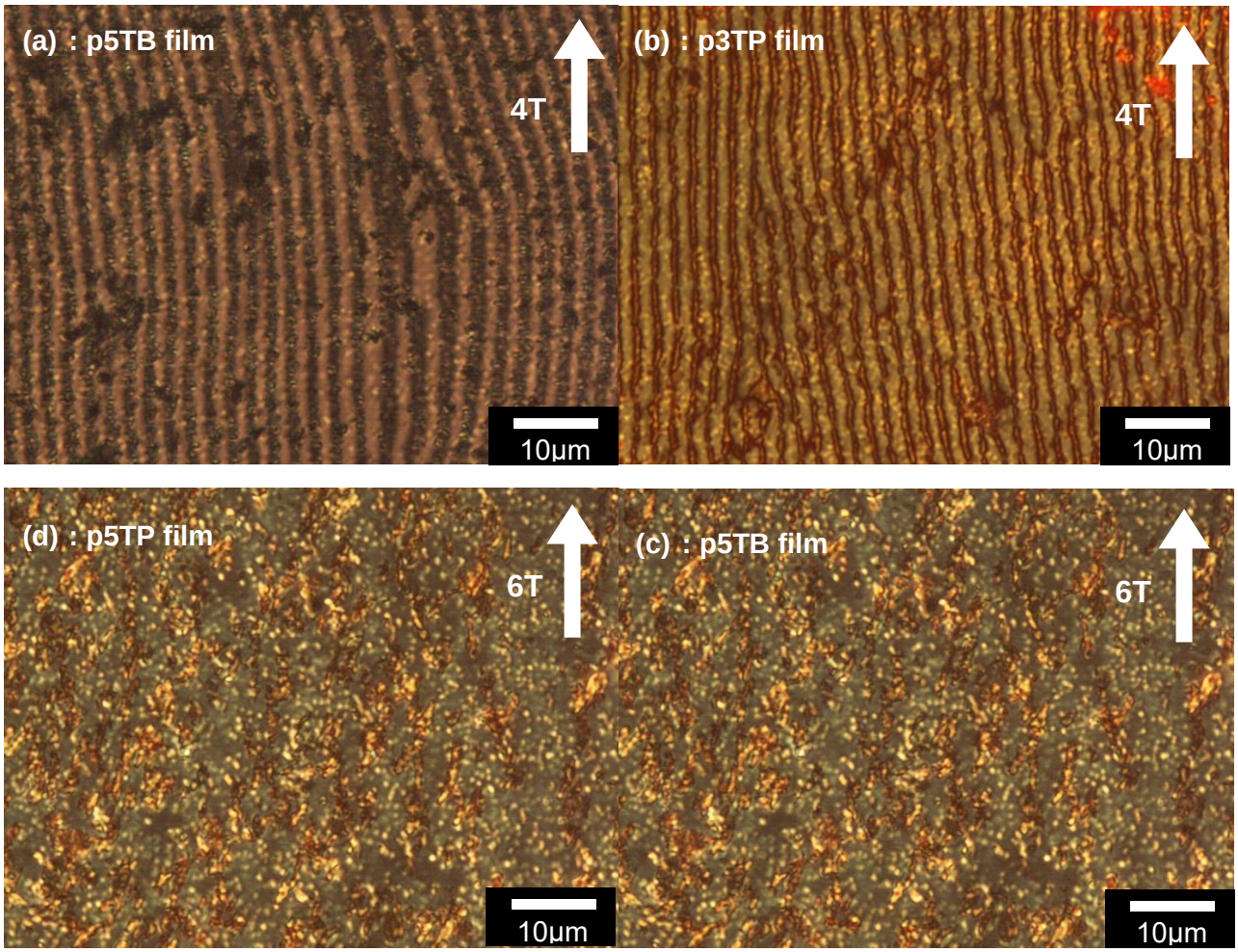

Figure S17. POM images of electrochemically prepared polymer films in CLC under magnetic field. p5TB prepared by electrochemical polymerization in CLC under magnetic field of (a) 4T ($p5TB_{(4T)}$) and (d) 6T ($p5TB_{(6T)}$). (b) p3TP prepared by electrochemical polymerization in CLC under magnetic field of 4T ($p3TP_{(4T)}$). (c) p5TP prepared by electrochemical polymerization in CLC under magnetic field of 6T ($p5TP_{(6T)}$).

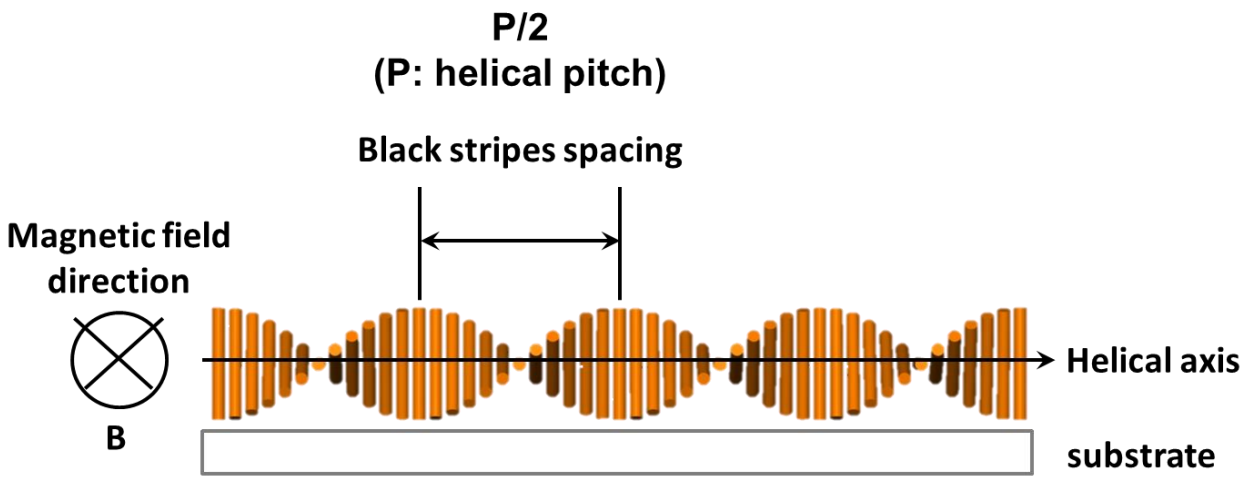

Figure S18. Conceptual image of the helical periodic structure of the CLC.

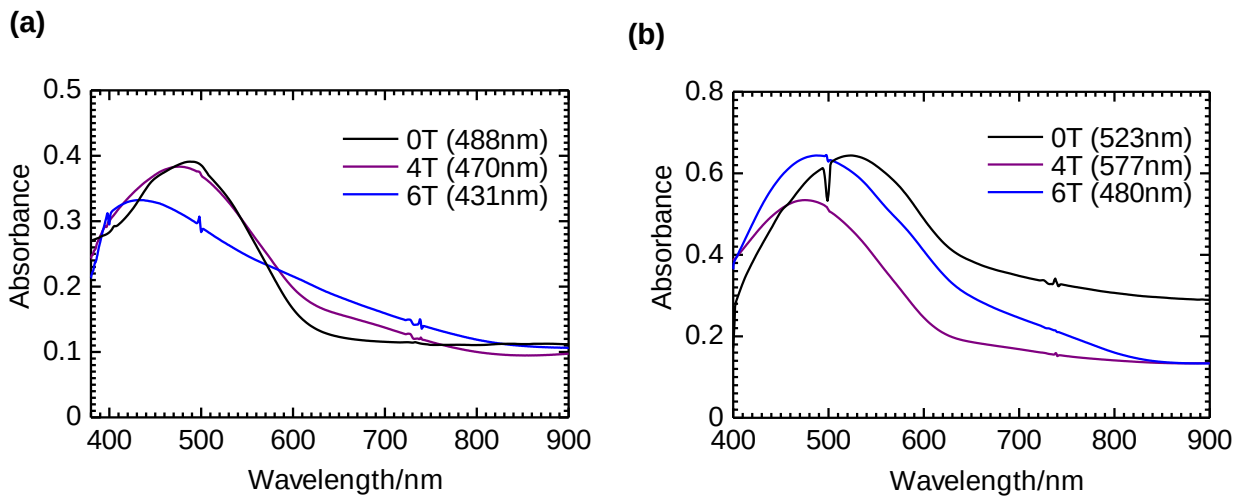

Figure S19. UV–vis spectra of (a) p5TP and (b) p3TP prepared in electrochemical polymerization in CLC under magnetic field (black line: 0T, purple line: 4T, blue line: 6T).

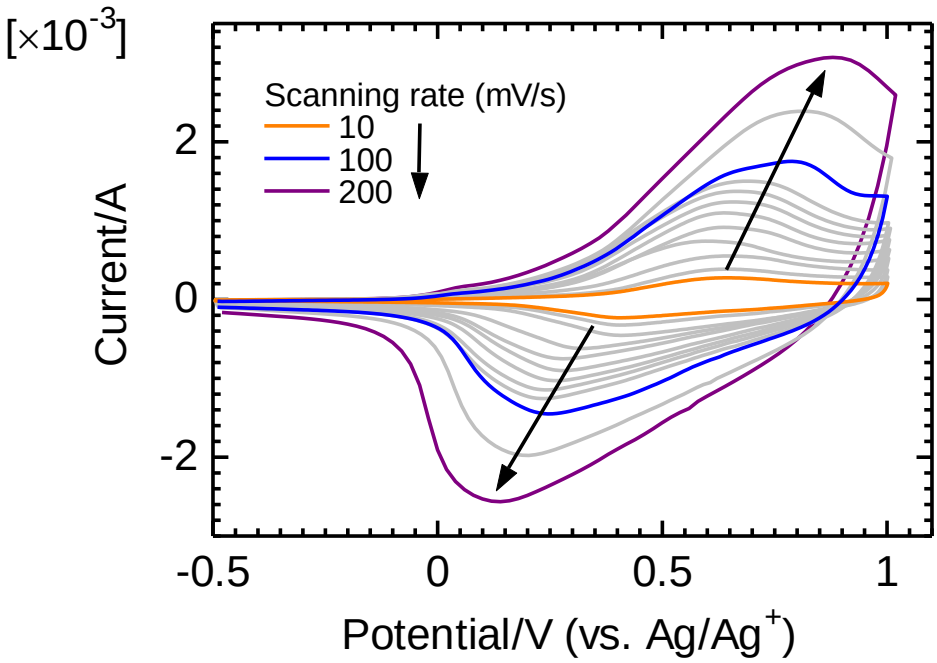

Figure S20. CV results for a $p3TP_{(0T)}$ film on ITO glass using 0.1M TBAP-acetonitrile solution at scan rates of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 and 200 mV/s.

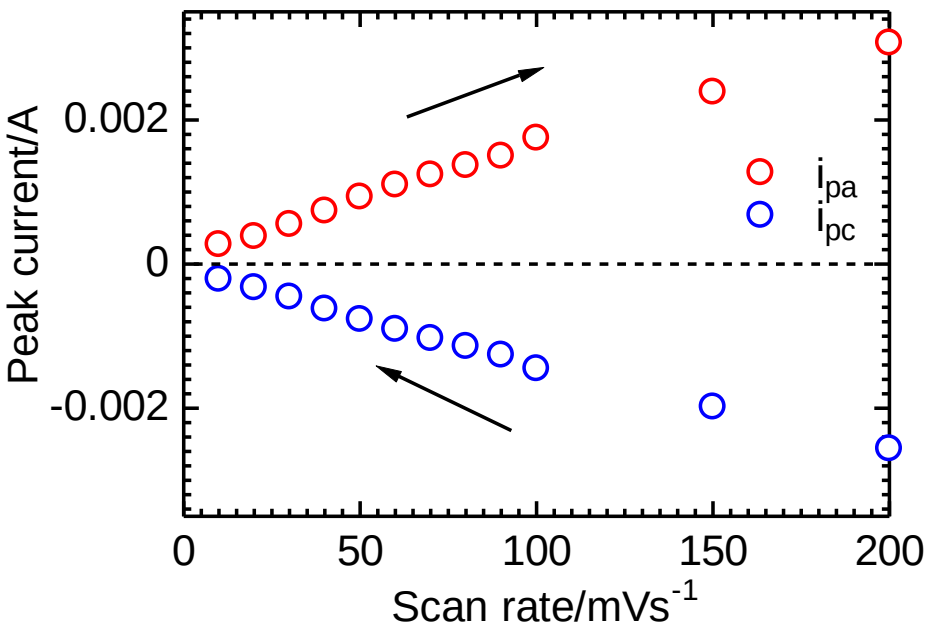

Figure S21. The redox property of p3TP$_{(0T)}$ films evaluated by plotting the intensity of the signal at each scan rate.

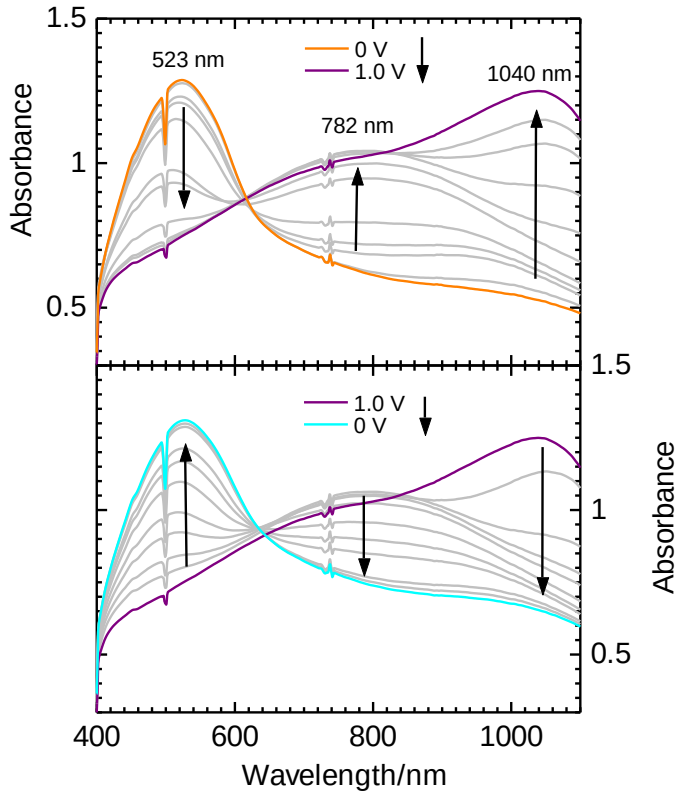

Figure S22. *In-situ* optical absorption spectra for a p3TP$_{(0T)}$ film in 0.1 M TBAP-acetonitrile solution at different voltages. UV–vis optical absorption spectra of a p3TP$_{(0T)}$ film during oxidation (upper) and reduction (bottom) between 1.0 V and 0 V at 0.1 V steps.

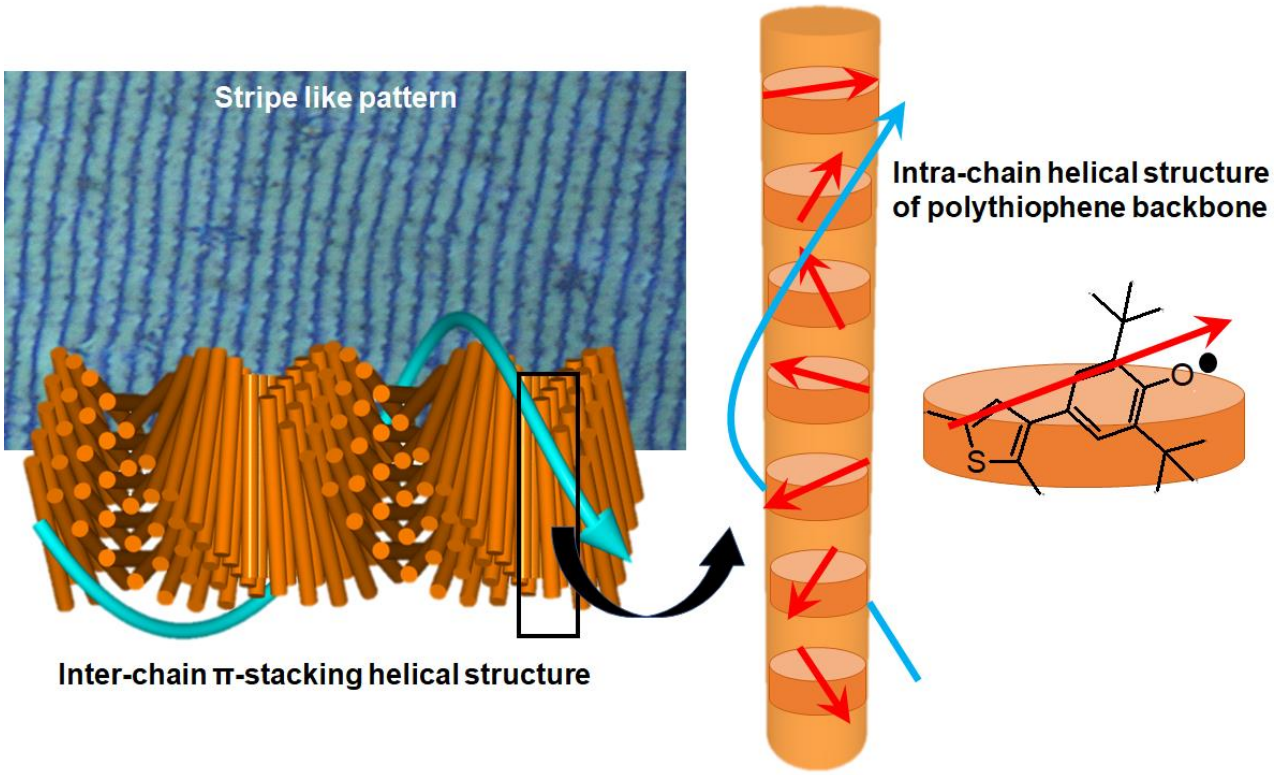

Figure S23. Plausible hierarchical helical structure of the polymer film. The polymer film synthesized in this study may have an interchain helical stacking structure and an intra-chain helical spin structure.

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