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Synthesis and characterization of oligo(2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-*b*]thiophene)s: effect of chain length and end-group on their optical and charge transport properties

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8. References

General methods. All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. 5,5′-Bistannyl-thieno[3,2-*b*]thiophene[1] and 2-bromo-3-dodecylthiophene[2] were synthesized according to literature. Microwave-assisted reaction was carried out on a CEM Discover SP microwave reactor in sealed vessels. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300-MHz spectrometer or 400-MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. Elemental analysis was carried out on an Eager 300 elemental analyzer. Cyclic voltammetry (CV) was performed on a CHI660a electrochemical analyzer with a three-electrode cell in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) CH_2Cl_2 solution at a scan rate of 100 mV/s. A Pt disk (2-mm diameter) was used as working electrode with a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The redox potential was calibrated by the ferrocene/ferrocenium (Fc/Fc+). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the equations: HOMO = - (4.40+E^{ox}_{onset}) eV, LUMO = - (4.40+E^{re}_{onset}) eV.[3] Absorption spectra were obtained on a PerkinElmer Lambda35 UV/Vis Spectrometer. Molecular mass was measured by means of LDI-1700 MALDI-TOF mass spectroscopy (Linear Scientific Inc.) with DIT as the substrate. Out-of-plane X-ray diffraction (XRD) was recorded on Bruker D8 Discover thin-film diffractometer with Cu Kα radiation (λ = 1.54056 Å) operated at 40 kV and 40 mA. In-plane XRD of the thin films were measured with a Rigaku Smart Lab with Cu Kα source (λ = 1.54056 Å) in the air. Atomic force microscopy (AFM) measurements were performed in tapping mode on a SPA400HV instrument with a SPI 3800 controller (Seiko Instruments Inc., Japan). Two dimensional grazing incidence X-ray diffraction

(GIXD) was measured at the Bejing Synchrotron Radiation Facility (SSRF) on the beamline BL14B1 with λ = 1.24 Å.

2,5-Bis(3-dodecylthiophen-2-yl)thieno[3,2-*b*]thiophene (**T4**). 2-Bromo-3-dodecylthiophene (10.4 g, 31.2 mmol), 5,5′-bistannyl-thieno[3,2-*b*] thiophene (11.2 g, 15.6 mmol) were added into a 500 ml Schlenk flask. The system was evacuated and back-filled with argon for three times. Then $Pd(PPh_3)_4$ (185 mg, 0.16 mmol) was added to the flask in a glove box. After the addition of solvent (Tol : DMF = 120 mL:30 mL), the mixture was heated at 85 ^oC in the absence of light for 12 hours. The brown solution was allowed to cool to room temperature, quenched with aqueous KF, and extracted with dichloromethane. The organic layer was collected and dried with $MgSO_4$. After removing of the solvent via rotary evaporation, the crude product was purified by column chromatography on silica gel and recrystallized from dichloromethane-ethanol to give the bright-yellow needle-like solid with a yield of 70% (7.0 g). ^1H NMR (300 MHz, $CDCl_3$): 7.23(s, 1H), 7.21(d, *J* = 6Hz, 2H), 6.96 (d, *J* = 6 Hz, 2H), 2.79(t, 4H), 1.25(m, 40H), 0.85~0.89(m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 140.27, 139.17, 137.65, 130.76, 130.06, 124.33, 118.04, 31.95, 30.83, 29.71, 29.68, 29.63, 29.58, 29.51, 29.38, 29.26, 22.72, 14.14. Anal. calcd for $C_{38}H_{56}S_4$: C, 71.19; H, 8.80. Found: C, 71.22; H, 8.78. MALDI-TOF-MS m/z: 640.3, calcd for $C_{38}H_{56}S_4$= 640.33.

2-(5-Bromo-3-dodecylthiophen-2-yl)-5-(3-dodecylthiophen-2-yl)thieno[3,2-*b*]thiophene (**1a**). A solution of **T4** (1.28 g, 2 mmol) in 40 mL dry chloroform was cooled to 0 ^oC for 20 minutes. NBS (356 mg, 2 mmol) in DMF (40 mL) was added dropwise. Then the mixture was allowed to warm to the room temperature for 12 hours. The mixture was then poured into water, extracted with chloroform and then dried with $MgSO_4$. Upon evaporation off the solvent, the residue was purified by chromatography (petroleum ether) on silica gel to give a pale yellow solid (650 mg, 50%). ^1H

NMR (300 MHz, $CDCl_3$): 7.23(s, 1H), 7.21(d, 1H), 7.19(s, 1H), 6.96(d, 1H), 6.92(s, 1H), 2.70~2.78(m, 4H), 1.59~1.62(m, 4H), 1.25(m, 36H), 0.87(t, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) : 140.48, 140.37, 139.41, 138.16, 136.03, 132.66, 132.20, 130.60, 130.07, 124.43, 118.46, 117.91, 111.05, 31.93, 30.79, 30.66, 29.65, 29.60, 29.56, 29.48, 29.43, 29.36, 29.24, 29.17, 22.70, 14.12. MALDI-TOF-MS m/z: 718.2, calcd for $C_{38}H_{55}BrS_4$ = 718.24.

2,5-Bis(5-bromo-3-dodecylthiophen-2-yl)thieno[3,2-*b*]thiophene (**1b**). Procedure for the preparation of **1a** was followed but 2.2 equiv. NBS was used. Yield: 90% (1.43 g, yellow solid). ^{1}H NMR (300 MHz, $CDCl_3$): 7.18(s, 2H), 6.92(s, 2H), 2.71(t, 4H), 1.54(m, 4H), 1.25(m, 36H), 0.88(t, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) : 141.01, 139.32, 136.58, 132.70, 132.06, 118.38, 111.22, 31.94, 30.66, 29.67, 29.57, 29.43, 29.38, 29.18, 22.71, 14.14. MALDI-TOF-MS m/z: 796.2, calcd for $C_{38}H_{54}Br_2S_4$=796.15.

2,5-Bis(3-dodecyl-5-stannylthiophen-2-yl)thieno[3,2-*b*]thiophene (**2**). A solution of **T4** (2.0 g, 3.1 mmol) in 20 mL THF was cooled to 0 ^{o}C for 20 minutes, to which 2.6 mL *n*-BuLi (6.5 mmol, 2.5 M in hexane) was added dropwise. The mixture was kept at 0 ^{o}C for 20 minutes and then allowed to warm to room temperature for another 1 hour. Then trimethyltin chloride (1.3 g, 6.5 mmol) was added in one portion. After 10 hours at room temperature, water was added to quench the reaction. Extracted with CH_2Cl_2 and washed with water, the organic layer was collected and dried with $MgSO_4$. Recrystallization from EtOH gave a brown solid in 98% yield (2.94 g). ^{1}H NMR (300 MHz, $CDCl_3$): 7.21(s, 1H), 7.02(s, 1H), 2.74~2.82(m, 4H), 1.57(m, 4H), 1.25(m, 36H), 0.86(t, 6H), 0.39(s, 18H).

T8. A mixture of **1a** (440 mg, 0.61 mmol), bis(pinacolato) diboron (78 mg, 0.3 mmol) , $Pd_2(dba)_3$ (12 mg, 0.012 mmol), $HPCy_3{\cdot}BF_4$ (14 mg, 0.036 mmol) and CsF (650 mg, 4.2 mmol) in dry dioxane

(20 mL) was reflux for 18 hours at 80 °C. After cooling to room temperature the mixture was poured into water and stirred for 1 hour. Extracted with dichloromethane, washed with water for three times, the organic extracts were dried with $MgSO_4$. After the solvent was removed, the residue was purified by chromatography (silica gel, petroleum ether : chloroform = 1:2) to give a red solid of **T8** (350 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) : 7.24(s, 2H), 7.21 (d, 2H), 7.03(s, 2H), 6.96(d, 2H), 2.76~2.80(m, 8H), 1.64~1.71(m, 8H), 1.26~1.37(m, 72H), 0.85~0.89(m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) : 140.96, 140.31, 139.27, 137.26, 135.34, 130.73, 130.08, 126.66, 124.37, 117.97, 31.94, 30.80, 30.62, 29.70, 29.67, 29.61, 29.59, 29.57, 29.49, 29.38, 29.25, 22.71, 14.12. Anal. calcd for $C_{76}H_{110}S_8$: C, 71.3; H, 8.66. Found: C, 71.22; H, 8.68. MALDI-TOF-MS m/z: 1278.6, calcd for $C_{76}H_{110}S_8$=1278.64.

Compound **3**. A similar procedure was followed as the preparation of **1a**. The product was got as a red solid in 50% yield (340 mg). ^{1}H NMR (300 MHz, $CDCl_3$) : 7.25(s, 1H), 7.24(s, 1H), 7.22(d, 1H), 7.19(s, 1H), 7.03(s, 2H), 6.96(d, 1H), 6.92(s, 1H), 2.71~2.82(m, 8H), 1.54(m, 8H), 1.26(m, 72H), 0.88(m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) : 141.08, 140.96, 140.93, 140.31, 139.55, 139.28, 139.15, 139.03, 137.94, 137.80, 137.24, 136.30, 135.48, 135.27, 132.71, 132.19, 130.73, 130.09, 130.02, 129.78, 126.66, 124.37, 118.43, 117.98, 117.81, 117.68, 111.11, 31.94, 30.61, 30.66, 29.67, 29.62, 29.56, 29.48, 29.43, 29.38, 22.71, 14.13. MALDI-TOF-MS m/z: 1356.6, calcd for $C_{76}H_{109}BrS_8$=1356.55.

T12. Compound **1a** (720 mg, 1 mmol) and compound **2** (483 mg, 0.5 mmol) were added in a 100 mL Schlenck tube. After charged and back-filled with argon for three times, 20 mg $Pd(PPh_3)_4$ was added to the tube in a glove box. A mixture of dry toluene(20 mL) and DMF (5 mL) were added and the reaction was carried out at 85 °C for 24 hours and then poured into water and stirred for 1

hour. The mixture was extracted with dichloromethane. The organic extracts were washed with water and dried with $MgSO_4$. After the solvent was removed, the residue was purified by chromatography(silica gel, petroleum ether : chloroform = 1:2) to give a dark red solid (729 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) : 7.27(s, 2H), 7.24(s, 2H), 7.21 (d, 2H), 7.04(s, 4H), 6.96 (d, 2H), 2.78(m, 12H), 1.70(m, 12H), 1.27~1.41(m, 108H), 0.88(m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) : 140.98, 140.32, 139.28, 139.15, 137.92, 137.54, 137.25, 135.32, 130.72, 130.09, 129.93, 126.69, 124.38, 117.99, 117.81, 117.74, 31.94, 30.80, 30.62, 29.68, 29.62, 29.56, 29.49, 29.38, 29.26, 22.70, 14.13. Anal. calcd for $C_{114}H_{164}S_{12}$: C, 71.34; H, 8.61. Found: C, 71.32; H, 8.58. MALDI-TOF-MS m/z: 1918.0, calcd for $C_{114}H_{164}S_{12}$=1917.95.

T20. In a glove box, **3** (136 mg, 0.1 mmol) and **2** (50 mg, 0.05 mmol) were added in a 10 mL microwave tube. Then 0.75 mL toluene, 0.75 mL DMF and 5.8 mg $Pd(PPh_3)_4$ were added. The microwave-assisted reaction was conducted at 180 ^{o}C for 2 hours then the mixture was cooled to room temperature. The crude product was collected by filtration and washed with acetone. Chromatography (silica gel, petroleum ether : chloroform = 1:2) was used to further purify the product. **T20** was afforded as red powder in a yield of 75% (118 mg). ^{1}H NMR (300 MHz, $CDCl_3$) : 7.27(s, 8H), 7.25(s, 2H), 7.22(d, 2H), 7.04(s, 8H), 6.96 (d, 2H), 2.78(m, 20H), 1.78(m, 20H), 1.27~1.41(m, 180H), 0.88(m, 30H). ^{13}C NMR was failed to collect due to the limit solubility of the product. Anal. calcd for $C_{190}H_{272}S_{20}$: C, 71.37; H, 8.57. Found: C, 71.34; H, 8.62. MALDI-TOF-MS m/z: 3197.5, calcd for $C_{190}H_{272}S_{20}$=3197.49.

2-(3-Dodecylthiophen-2-yl)-5-(3-dodecyl-5-formylthiophen-2-yl)thieno[3,2-*b*]thiophene (**4a**). **T4** (1.28 g, 2.00 mmol) was dissolved in 40 mL 1,2-dichloroethane at 0 ^{o}C under argon, to which 2.4 mL fresh distilled DMF was added in one potion. The mixture was kept reacting for 20 minutes

before 0.2 mL $POCl_3$ (2.2 mmol) was added dropwise. Then the reaction mixture was warmed up to 60 °C and stirred for 12 hours, poured into ice water, neutralized with Na_2CO_3, and then extracted with CH_2Cl_2. The organic extracts were washed with water and then dried over $MgSO_4$. The residue was purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1) to afford the product as a yellow solid (1.06 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): 9.84(s, 1H), 7.62(s, 1H), 7.41(s, 1H), 7.24(d, J = 6Hz, 1H), 6.97(d, J = 6 Hz, 1H), 2.77~2.86(m, 4H), 1.63~1.67(m, 4H), 1.25(m, 36H), 0.85~0.89(m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 182.46, 141.35, 140.77, 140.72, 140.65, 140.52, 139.52, 139.30, 138.90, 135.97, 130.41, 130.19, 124.70, 119.49, 117.78, 31.94, 30.40, 29.69, 29.66, 29.58, 29.56, 29.49, 29.44, 29.41, 29.37, 29.29, 22.70, 14.13. MALDI-TOF-MS m/z: 668.3, calcd for $C_{39}H_{56}OS_4$= 668.32.

2,5-Bis(3-dodecyl-5-formylthiophen-2-yl)thieno[3,2-*b*]thiophene (**4b**). A procedure similar to the preparation of **4a** was followed but 2.5 equiv. $POCl_3$ was added. A red brown solid was obtained (906 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): 9.85(s, 2H), 7.63(s, 2H), 7.43(s, 2H), 2.85(t, 4H), 1.64~1.70(m, 4H), 1.25~1.38(m, 36H), 0.87(t, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) : 182.51, 141.23, 141.12, 140.72, 140.56, 138.84, 137.66, 119.34, 31.91, 30.39, 29.66, 29.64, 29.55, 29.46, 29.41, 29.35, 22.68, 14.11. MALDI-TOF-MS m/z: 696.3, calcd for $C_{40}H_{56}O_2S_4$= 696.32.

2-(3-Dodecyl-5-bromothiophen-2-yl)-5-(3-dodecyl-5-formylthiophen-2-yl)thieno[3,2-*b*]thiophene (**5**). In a 250 mL round bottom flask, **4a** (0.69 g, 1.0 mmol) was dissolved in a mixture of DMF (15 mL) and chloroform (15 mL). After cooling at 0 °C for 20 minutes, NBS (0.40 g, 2.2 mmol) was added in five portions. The mixture was stirred and kept in the dark for 4 hours before it was poured into water and extracted with CH_2Cl_2. The organic extracts were dried with $MgSO_4$, and the crude product was purified by column chromatography on silica gel with petroleum ether:

dichloromethane (1:1) as eluent to give a yellow powder in a yield of 95% (710 mg). ^{1}H NMR (300 MHz, $CDCl_3$): 9.85(s, 1H), 7.62(s, 1H), 7.40(s, 1H), 7.21(s, 1H), 6.93(s, 1H), 2.70~2.86(m, 4H), 1.62~1.70(m, 4H), 1.25(m, 36H), 0.87(m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) : 182.48, 141.27, 141.11, 140.91, 140.39, 139.54, 138.87, 137.87, 136.47, 132.80, 131.83, 119.40, 118.23, 111.53, 31.93, 30.63, 30.39, 29.68, 29.65, 29.57, 29.48, 29.40, 29.36, 29.22, 22.70, 14.12. MALDI-TOF-MS m/z: 746.2, calcd for $C_{39}H_{55}BrOS_4$= 746.23.

Compound **6**. A procedure similar to **T8** was followed. The crude product was purified by column chromatography (silica gel, petroleum ether : chloroform = 1:2) to give a dark red solid with a yield of 84% (280 mg). ^{1}H NMR (300 MHz, $CDCl_3$): 9.85(s, 2H), 7.62(s, 2H), 7.42(s, 2H), 7.29(s, 2H), 7.05 (s, 2H), 2.78~2.86(m, 8H), 1.40~1.42(m, 8H), 1.34(m, 8H), 1.26(m, 64H), 0.87(m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) : 182.43, 141.34, 141.27, 140.81, 140.75, 140.70, 139.25, 139.07, 138.92, 136.28, 135.53, 129.74, 126.82, 119.38, 117.45, 84.26, 31.94, 30.57, 30.37, 29.72, 29.70, 29.67, 29.63, 29.59, 29.51, 29.46, 29.38, 24.77, 22.71, 14.13. MALDI-TOF-MS m/z: 1334.5, calcd for $C_{78}H_{110}O_2S_8$=1334.63.

2-(3-Dodecyl-5-bromothiophen-2-yl)-5-(3-dodecyl-5-cyano-thiophen-2-yl)thieno[3,2-*b*]thiophene (**7**). Compound **5** (1.5 g, 2.0 mmol) was added to a solution of hydroxylamine hydrochloride (0.28 g, 4.0 mmol) in DMSO (30 mL), and the resulting solution was stirred at 100 ^{o}C for 3 hours. Then 0.3 mL concentrated HCl (12 M) was added and the mixture was stirred for another 1 hour. After cooling to room temperature, water (20 mL) was added to the reaction mixture, which was then extracted with CH_2Cl_2. The organic extracts were washed with water and dried with $MgSO_4$. After purification by column chromatography (silica gel, petroleum ether : chloroform = 2:1), compund **7** was obtained with a total yield of 80% (1.19 g). ^{1}H NMR (300 MHz, $CDCl_3$): 7.46(s, 1H), 7.33(s,

1H), 7.21(s, 1H), 6.93(s, 1H), 2.70~2.81(m, 4H), 1.59~1.62(m, 4H), 1.18(m, 36H), 0.89(m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) : 141.25, 140.30, 139.84, 139.38, 138.26, 138.01, 134.88, 132.82, 131.79, 119.64, 118.10, 114.13, 111.61, 107.53, 31.97, 30.65, 30.45, 29.66, 29.60, 29.57, 29.46, 29.41, 29.16, 29.11, 22.74, 14.17. MALDI-TOF-MS m/z: 743.2, calcd for $C_{39}H_{54}BrNS_4$=743.23.

Compound **8**. A mixture of **4a** (680 mg, 1 mmol), *p*-toluenesulfonic acid monohydrate (17.2 mg, 0.1 mmol) and ethylene glycol (621 mg, 10 mmol) in toluene (30 mL) was refluxed for 24 hours. The resulting water was azeotropically removed by a Dean-Stark type water separator. After Na_2CO_3 (525 mg in 20 mL water) was added at room temperature, the mixture was extracted with toluene. The organic extracts were dried over Na_2SO_4. After the solvent was removed, a brown solid (620 mg) was obtained in the yield of 87% and used directly without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): 7.21~7.23(m, 3H), 7.03(s, 1H), 6.96(d, J = 6Hz, 1H), 6.05(s, 1H), 4.04~4.17(m, 4H), 2.71~2.81(m, 4H), 1.53~1.65(m, 4H), 1.25(m, 36H), 0.85~0.87(m, 6H).

Compound **9.** Compound **8** (600 mg, 0.85 mmol) was dissolved in anhydrous THF (20 ml) and cooled to -78 ^{o}C with a dry-ice/acetone bath. Then 0.36 ml *n*-BuLi (2.5 M in hexane, 0.9 mmol) was added to the mixture dropwise. The mixture was kept reaction at -78 ^{o}C for 40 minutes before Bu_3SnCl (0.30 ml, 1.0 mmol) was added in one portion. The mixture was allowed to warm to room temperature and reacted overnight. Water (20 ml) was added to quench the reaction and extracted with CH_2Cl_2. The organic extracts were washed with dilute KF solution to remove any tributyltin chloride residual and dried with $MgSO_4$. After evaporation of the solvent, the product was got as a brown solid in 95% yield (807 mg) and used directly without further purification.^{1}H NMR (300 MHz, $CDCl_3$) : 7.22(d, 2H), 7.02(s, 1H), 6.98(s, 1H), 6.06(s, 1H)4.01~4.17(m, 4H), 2.71~2.81(m, 4H), 1.57~1.64 (m, 12H), 1.09~1.35 (m, 46H), 0.85~0.94 (m, 15H).

Compound **10**. A mixture of **9** (1.75 mmol), **1b** (1.47 g, 1.84 mmol), and $Pd(PPh_3)_4$ (101 mg, 0.09 mmol) in toluene (40 mL) and DMF (10 mL) was stirred at 85 °C for 24 hours. Then the reaction was cooled to 50 °C, hydrochloric acid (10 mL, 2M in water) was added, the mixture was stirred at that temperature for 1 hour and allowed to cool down to room temperature overnight. After extracted with dichloromethane, washed with water for three times, $MgSO_4$ was added to dry the organic layer. Evaporation off the solvent, the residue was purified by chromatography (silica gel, petroleum ether : chloroform = 4:1) to give a bright red solid of **10** (920 mg) in the yield of 40%. ^{1}H NMR (300 MHz, $CDCl_3$) : 9.85(s, 1H), 7.62(s, 1H), 7.42(s, 1H), 7.28(s, 1H), 7.19(s, 1H), 7.04 (s, 2H), 6.92(s, 1H), 2.70~2.81(m, 8H), 1.70(m, 8H), 1.26(m, 72H), 0.87(m, 12H). ^{13}C NMR(75 MHz, $CDCl_3$) : 182.48, 140.66, 139.06, 136.37, 135.71, 132.16, 129.98, 124.71, 118.41, 117.53, 111.13, 31.93, 30.77, 30.65, 30.60, 30.39, 29.66, 29.60, 29.57, 29.48, 29.43, 29.40, 29.36, 29.28, 29.19, 22.70, 14.12. MALDI-TOF-MS m/z: 1384.5, calcd for $C_{77}H_{109}BrOS_8$=1384.54.

Compound **11**. A similar procedure was followed as the preparation of **7**. The purification by column chromatography (silica gel, petroleum ether : chloroform = 2:1) gave a red solid (135 mg) in the yield of 90%. ^{1}H NMR (300 MHz, $CDCl_3$) : 7.47(s, 1H), 7.35(s, 1H), 7.28(s, 1H), 7.25(s, 1H), 7.20 (s, 1H), 7.04 (s, 2H), 6.93 (s, 1H), 2.73~2.78(m, 8H), 1.66(m, 8H), 1.26(m, 90H) (H_2O included), 0.87(m, 12H). ^{13}C NMR was failed to collect due to the limit solubility of the product. MALDI-TOF-MS m/z: 1381.5, calcd for $C_{77}H_{109}BrOS_8$=1381.54.

T4-2CN. **4b** (300 mg, 0.43 mmol) was added to a solution of hydroxylamine hydrochloride (105 mg, 1.51 mmol) in DMSO (30 mL), and the resulting solution was stirred at 100 °C for 3 hours. Then 0.15 mL concentrated HCl (12 M) was added and the mixture was stirred for another 1 hour. After cooling to room temperature, water (20 mL) was added to quench the reaction mixture, which

was then extracted with CH_2Cl_2. The organic extracts were washed with water and dried with $MgSO_4$. Purification by column chromatography (silica gel, petroleum ether : CH_2Cl_2 =1:1) afforded **T4-2CN** as a yellow solid with a yield of 90% (270 mg). ^{1}H NMR (600 MHz, $CDCl_3$): 7.47(s, 2H), 7.36(s, 2H), 2.78~2.80(m, 4H), 1.62~1.66(m, 4H), 1.26(m, 36H), 0.87~0.89(t, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) : 140.74, 140.34, 139.88, 137.82, 136.12, 119.64, 114.04, 107.95, 31.91, 30.44, 29.62, 29.52, 29.35, 29.07, 22.69, 14.11. Anal. calcd for $C_{40}H_{54}N_2S_4$: C, 69.51; H, 7.88. Found: C, 69.53; H, 7.89. MALDI-TOF-MS m/z: 690.2, calcd for $C_{40}H_{54}N_2S_4$= 690.32.

T8-2CN. The same procedure was followed as the preparation of **T4-2CN**. Purification by column chromatography (silica gel, petroleum ether : chloroform = 1:1) afforded the product as a red solid with a yield of 50% (176 mg). ^{1}H NMR (600 MHz, $CDCl_3$): 7.46 (s, 2H), 7.35 (s, 2H), 7.28 (s, 2H), 7.05 (s, 2H), 2.71~2.86 (m, 8H), 1.64~1.70 (m, 8H), 1.26~1.39 (m, 72H), 0.86~0.89 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): 141.46, 140.54, 140.28, 139.89, 139.15, 138.37, 135.61, 126.86, 119.75, 117.57, 114.21, 107.44, 31.91, 30.58, 30.44, 29.67, 29.47, 29.37, 29.08, 22.70, 14.12. Anal. calcd for $C_{78}H_{108}N_2S_8$: C, 70.43; H, 8.18. Found: C, 70.17; H, 8.22. MALDI-TOF-MS m/z: 1328.6, calcd for $C_{78}H_{108}N_2S_8$= 1328.63.

T12-2CN. A 100 mL Schlenk tube containing a mixture of **7** (570 mg, 0.77 mmol) and **2** (370 mg, 0.38 mmol) was charged in vacuum and back-filled with argon for three times. Then $Pd(PPh_3)_4$ (45 mg, 0.04 mmol), toluene (20 mL) and DMF (5 mL) were added. The mixture was stirred at 85 ^{o}C for 24 hours. The mixture was cooled to room temperature and poured into 200 mL water and was extracted with dichloromethane. The extracts were washed with water for three times and dired with $MgSO_4$. After the solvent was removed, the residue was purified by column chromatography (silica gel, petroleum ether : chloroform = 1:1) to give a dark red solid (400 mg) in the yield of 65%. ^{1}H

NMR (600 MHz, $CDCl_3$) : 7.46 (s, 2H), 7.34 (s, 2H), 7.28 (s, 2H), 7.27 (s, 2H), 7.04 (s, 4H), 2.77~2.81 (m, 12H), 1.64~1.70 (m, 12H), 1.26~1.39 (m, 108H), 0.86~0.89 (m, 18H). ^{13}C NMR was failed to collect due to the limit solubility of the product. Anal. calcd for $C_{116}H_{162}N_2S_{12}$: C, 70.75; H, 8.29. Found: C, 70.67; H, 8.14. MALDI-TOF-MS m/z: 1967.9, calcd for $C_{116}H_{162}N_2S_{12}$= 1967.94.

T20-2CN. A similar procedure was followed as the syntheses of **T12-2CN**. Dark red solid with a yield of 50% (70 mg) was obtained after purification by column chromatography (silica gel, petroleum ether : chloroform = 1:1). ^1H NMR (600 MHz, $CDCl_3$) : 7.46 (s, 2H), 7.34 (s, 2H), 7.27 (s, 2H), 7.04 (m, 8H), 2.79 (m, 20H), 1.68~1.70 (m, 20H), 1.26~1.42 (m, 180H), 0.86~0.89 (m, 30H). ^{13}C NMR was failed to collect due to the limit solubility of the product. Anal. calcd for $C_{192}H_{270}N_2S_{20}$: C, 70.07; H, 8.38. Found: C, 70.09; H, 8.41. MALDI-TOF-MS m/z: 3244.5, calcd for $C_{192}H_{270}N_2S_{20}$= 3244.56.

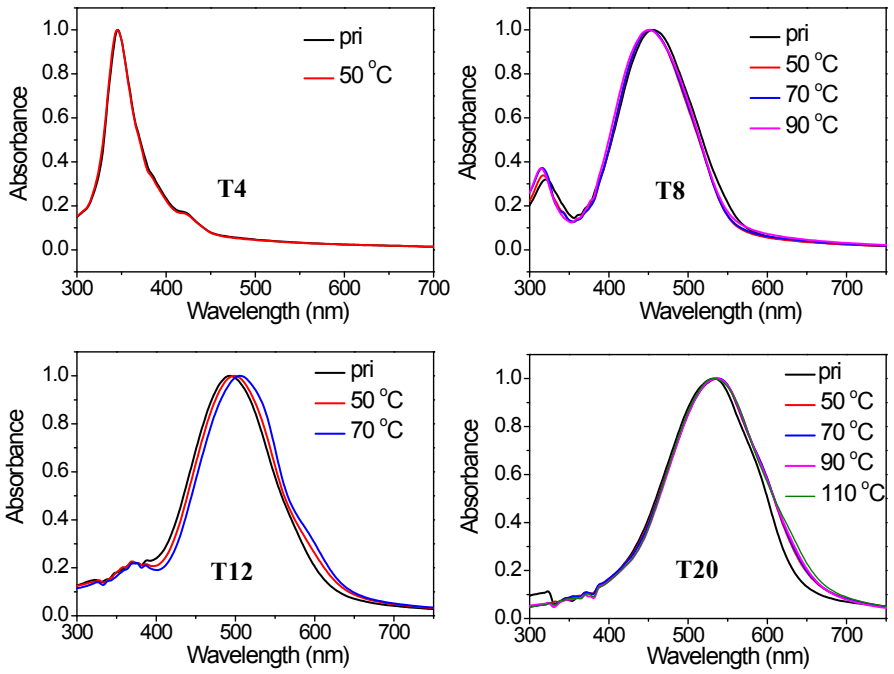

Figure S1. Film Uv-vis absorption spectra of **Tn** after thermal annealing for 20 minutes.

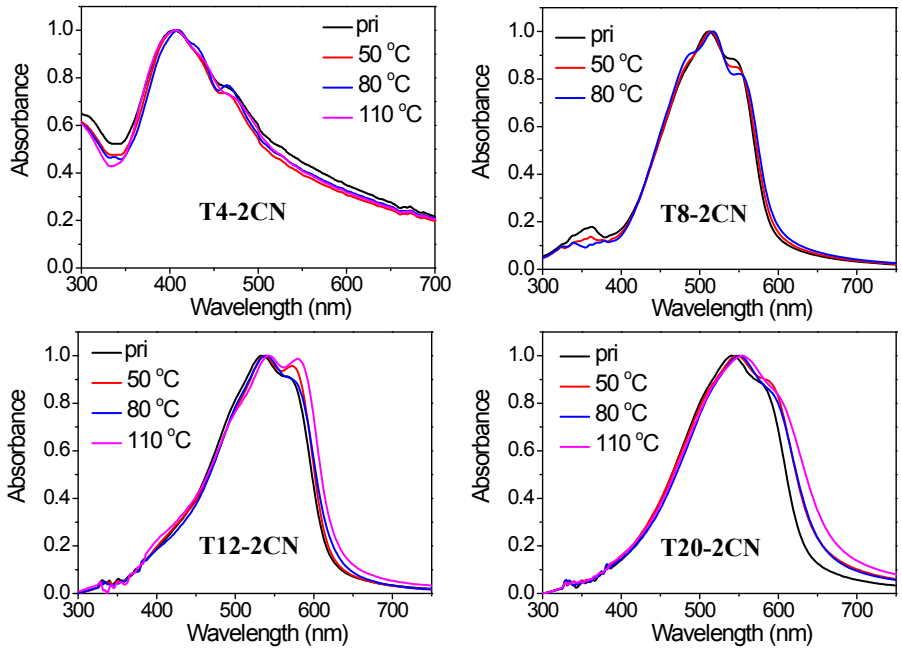

Figure S2. Film Uv-vis absorption spectra of **Tn-2CN** after thermal annealing for 20 minutes.

Table S1. Thermal Properties of **Tn** and **Tn-2CN**

oligomer	T_m (°C)	T_L* (°C)	ΔH (J/g)
T4	69.60, 71.03	306	96.05
T8	101.20	375	78.63
T12	99.87	384	51.14
T20	117.03, 126.03	410	0.76, 28.25
T4-2CN	91.27, 101.20, 128.37	365	44.39, 73.89
T8-2CN	111.03, 120.03	372	34.95, 23.29
T12-2CN	106.38, 120.03	398	20.67
T20-2CN	157.03	380	31.86

* The temperature with 5% mass loss (T_L) was determined by TGA with a heating rate of 10 °C min^{-1} under nitrogen

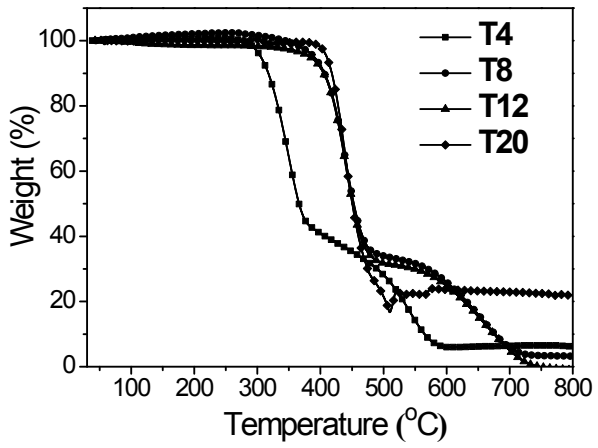

Figure S3. TGA curves of **Tn** with a heating rate of 10 °C/min under nitrogen atmosphere.

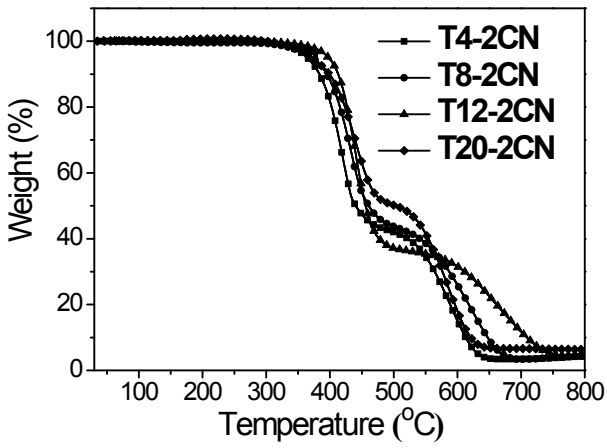

Figure S4. TGA curves of **Tn-2CN** with a heating rate of 10 °C/min under nitrogen atmosphere.

Table S2. Crystallographic data and structure refinement parameters of **T4-C6**

	T4-C6[a]
Empirical formula	$C_{26}H_{32}S_4$
Formula weight	472.76
Temperature (K)	185 (2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a, b, c (Å)	11.7143(10), 7.8255 (7), 13.5651 (12)
α, β, γ (°)	90.00, 98.445(2), 90.00
Volume (Å^3)	1230.03(19)
Z	2
Density (Calculated) (Mg/m^3)	1.276
Crystal size	0.19 × 0.15 × 0.10 mm
θ range for data collection	2.49 to 25.98 °
Limiting indices	$-12 \leq h \leq 14$, $-9 \leq k \leq 9$, $-16 \leq l \leq 16$
Reflns collected	6387
Independent reflns	2434
Reflns observed	2096
R(int)	0.0243
Goodness-of-fit on F^2	1.096
Final R indices [I>2σ(I)]	R1 = 0.0407, wR2 = 0.1129
R indices	R1 =0.0478, wR2 = 0.1204
Largest diff. peak and hole	0.483 and -0.245 e Å^{-3}

[a]CCDC number: 1020843.

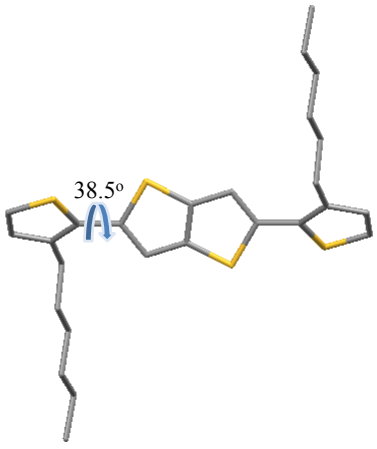

Figure S5. Molecular conformation of **T4-C6**. The torsion angle between thiophene and thieno[3,2-*b*]thiophene is 38.5°.

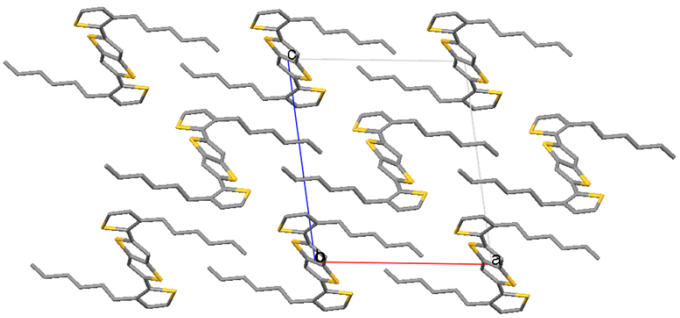

Figure S6. Packing diagram of **T4-C6** projected along *b*-axis. Layer-by-layer structure can be found along *c*-axis.

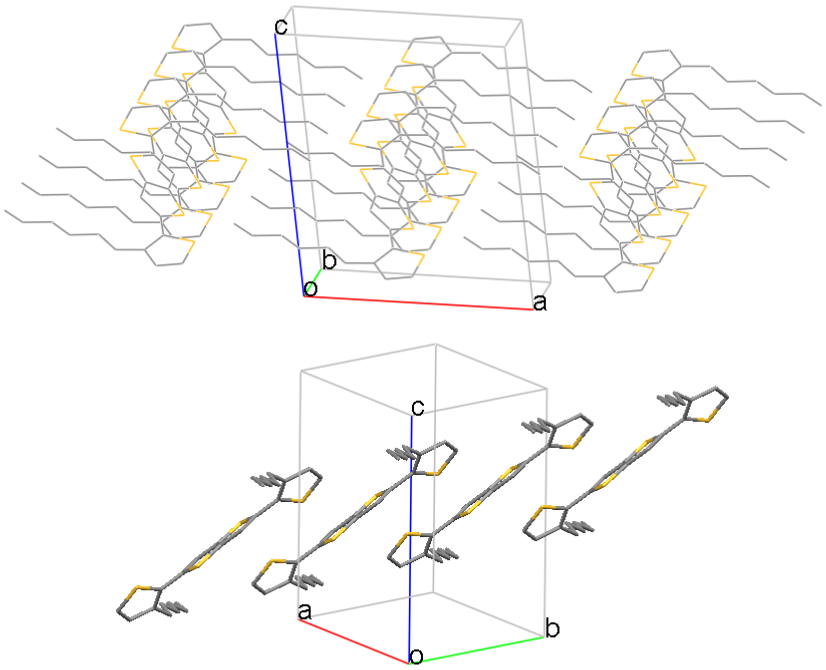

Figure S7. 2D-lamellar packing diagram of **T4-C6** in the ab plane (top) and along the b-axis, the interaction exist between thiophene and thieno[3,2-*b*]thiophene (down).

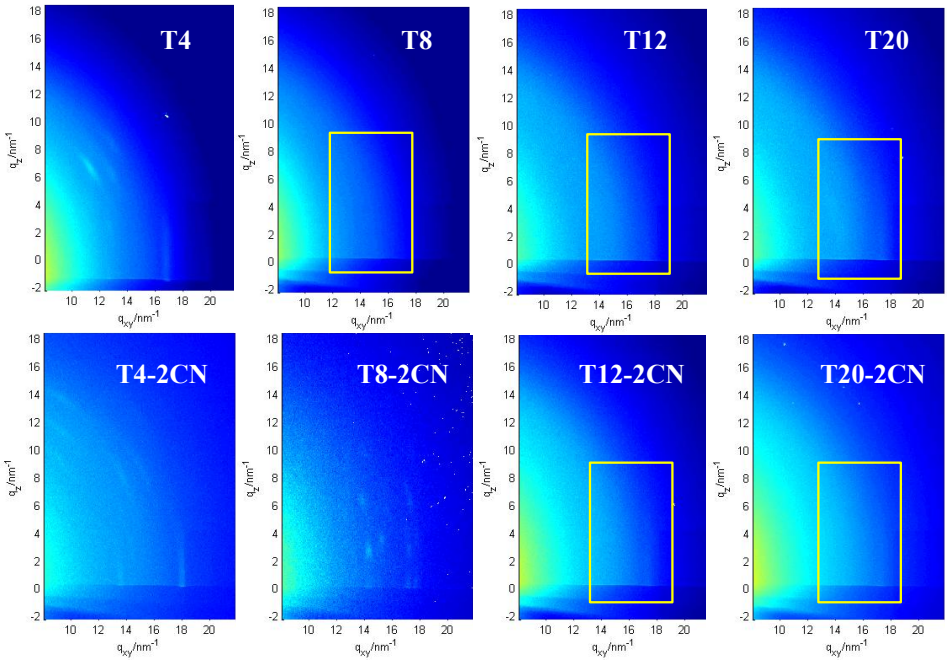

Figure S8. Zoomed 2D-GIXD images of **Tn** and **Tn-2CN** films showing the diffraction peaks between q_{xy} = 8 nm^{-1} - 22 nm^{-1}.

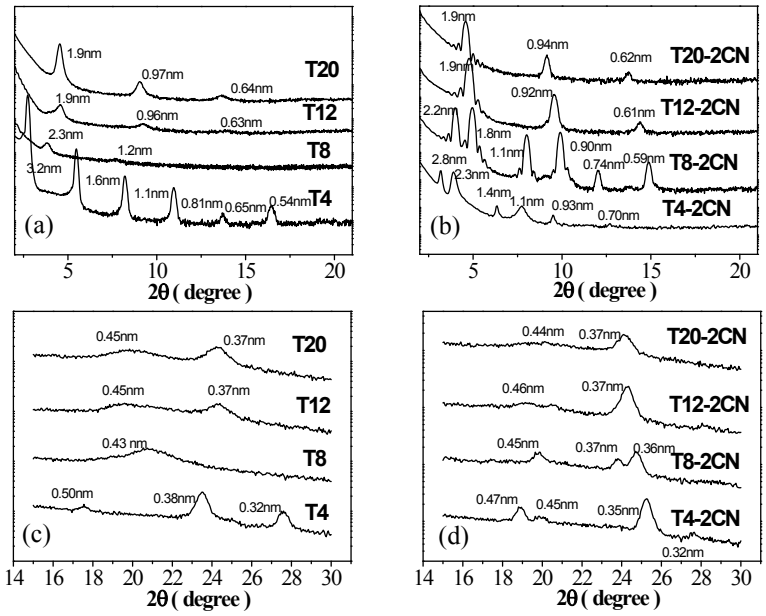

Figure S9. Out-of-plane (a,b) and in-plane (c,d) XRD patterns of **Tn** and **Tn-2CN** films. The corresponding *d*-spacings are given on the diffraction peaks.

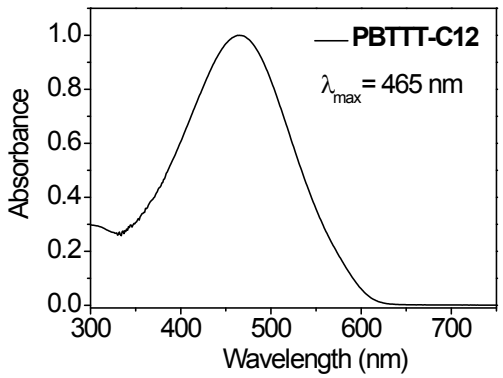

Figure S10. Uv-vis absorption spectrum of **PBTTT-C12** in chloroform with a concentration of 10^{-5} M (repeating unit). The polymer **PBTTT-C12** with M_w = 40000-80000 was bought from Aldrich (L753963).

References

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