Supplementary Materials:

Synthesis of Amorphous Conjugated Copolymers Based on Dithienosilole-Benzothiadiazole Dicarboxylic Imide withTuned Optical Band Gaps and High Thermal Stability

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Experimental Section

Monomers Synthesis

2,5-dibromothiophene **(1)** was synthesised according to a modified procedure of previously reported by Ponomarenko *et al.*[1]. 2,5-dibromo-3,4-dinitrothiophene (**2**) was prepared in accordance with the updated procedure as stated by Wen and Rasmussen[2]. 3,4-dinitro-2,2':5',2'-tertiophene (**3**) was synthesized in accordance with the updated procedure as reported by Rasmussen and Schwiderski[3]. 3',4'-diamino-2,2':5,2''-terthiophene **(4)** was synthesized in accordance with the updated procedure as described by Hailu and co-workers[4]. 4,6-bis(2-thienyl)-thieno[3,4-c][1,2,5]-thiadiazole**(5)** was prepared according to the modified established procedure as reported by Delgado *et al.*[5]. 4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-dimethyl ester **(6)** was prepared according to the modified procedure as documented by Wang *et al.*[6]. 4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-dicarboxylic acid **(7)** was prepared according to the modified established procedure as reported by Nielsen and co-workers[7]. 4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-dicarboxylic anhydride**(8)** was prepared according to the modified procedure as documented by Lan *et al.*[8]. 3,7-dimethyloctyl bromide **(9)** was prepared according to the modified procedure as indicated byMatsueda *et al.*[9]. *N*-(3,7-dimethyloctyl) phthalimide **(10)** was prepared according to the modified procedure as reported by Thomson and co-workers[10]. 3,7-dimethyl-1-octanamine **(11)** was prepared according to the modified procedure as documented by Yue *et al.*[11].4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-N-(3,7-dimethyloctyl)dicarboxylic imide

(12)and4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-*N*-octyl-dicarboxylic imide **(13)**weresynthesised according to the published procedure as reportedby Iraqi and co-workers[12-15].3,3',5,5'-tetrabromo-2,2'-bithiophene **(14)** was prepared according to the published procedureby Khor *et al*.[16]. 3,3'-dibromo-2,2'-bithiophene **(15)**was synthesised according to the modified procedure as indicated by Letizia and co-workers[17].4,4-dioctyldithieno[3,2-b:2',3'-d]silole **(16)**was prepared according to the published procedureby Beaujuge*et al*.[18].4,7-di(5-bromo-thien-2-yl)-2,1,3-benzothiadiazole-5,6-N-(3,7-dimethyloctyl)dicarboxylic imide **(M1)**and4,7-di(5-bromo-thien-2-yl)-2,1,3-benzothiadiazole-5,6-*N*-octyl-dicarboxylic imide **(M2)** were prepared according to the published procedure as reportedby Iraqi and co-workers[12-15]. Finally, 4,4-dioctyl-5,5'-bis(trimethylstannyl)dithieno[3,2-b:2',3'-d]silole**(M3)**was preparedaccording to the published procedure as reportedbyMedlej and co-workers[19].

2,5-dibromothiophene (1):

(25.0 g, 297.12 mmol)thiophenein 250 ml DMF was added to a flask and refrigerated to -15 °C. To this obtained solution, (110 g, 618.04 mmol)of NBS in 300 ml DMF was then added dropwise in the dark, and the reaction stirred overnightat room temperature. The reaction contents were placed into ice and dichloromethane and removed subsequently with dichloromethane.The organic phase is washed with a neutral pH of deionized H_2O. The organic layer gatheredand dried over anhydrous $MgSO_4$ and the solvent condensedto providethe product, which purified by vacuum distillation, and delivered**1** as a yellow oil (59.30 g, 245 mmol, 82% yield). ^{1}H NMR ($CDCl_3$, δ): 6.87 (s, 2H). ^{13}C NMR ($CDCl_3$, δ): 130.4, 111.6. FT-IR (cm^{-1}): 3096, 1726, 1516, 1410, 1200. EI-MS (m/z): 242 $[M]^+$. EA (%) calculated for $C_4H_2Br_2S$: C, 19.86; H, 0.83; Br, 66.06, S, 13.25. Found: C, 20.01; H, 0.85; Br, 65.02, S, 11.96.

2,5-dibromo-3,4-dinitrothiophene (2):

150 ml each of concentrated H_2SO_4andfuming H_2SO_4 (20% free SO_3) combined in a cooled flask at 0 °C. Into the flask, material**1** (26.00 g, 107.46 mmol) was added dropwise. 125 ml concentrated nitric acid was then added dropwise,whilethe reaction contents werekept below20 °C. A yellow precipitate formed rapidly duringthe addition of nitric acid. At 20 to 30 °C, the mixture was stirred for 3hours. The mixture was then poured into ice and a yellow precipitate filtrated upon melting of the ice.It thenwashed vigorouslywith deionized H_2O. The

product was recrystallized as yellow crystals from methanol to provide (32.50 g, 98 mmol, 91% yield) of **2**. ^{13}C NMR ($CDCl_3$, δ): 140.7, 113.4. FT-IR (cm^{-1}): 2886, 2851, 2813, 1535, 1497, 1345, 1081. EI-MS (m/z): 332 $[M]^+$. EA (%) calculated for $C_4Br_2N_2O_4S$: C, 14.47; N, 8.44; S, 9.66; Br, 48.15. Found: C, 14.51; N, 7.91; S, 9.19; Br, 46.57.

3′,4′-dinitro-2,2':5',2''-terthiophene (3):

(9.90 g, 29.82 mmol)of material **2**, (27.82 g, 74.54 mmol) of 2-(tributylstannyl)thiophene and (0.45 g, 0.64 mmol) of$PdCl_2(PPh_3)_2$ were added into a flask. The system was degassed withargon and 100 ml anhydrous toluene was added and heated at 115 °C for 24hours. The flask was then cooled to room temperature.The volatiles were extractedto attainedthe product, which is purified with gradient (petroleum ether, 0-50% DCM)by column chromatography to obtain an orange solid. The product was further purified from methanol by recrystallization to receive orange crystals**3** (9.10 g, 27 mmol, 90% yield). ^{1}H NMR ($CDCl_3$, δ): 7.62 (dd, 2H, J = 1.0 Hz, 5.0 Hz), 7.56 (dd, 2H, J = 1.0 Hz, 4.0 Hz), 7.19 (dd, 2H, J = 4.0 Hz, 5.0 Hz). ^{13}C NMR ($CDCl_3$, δ): 135.9, 133.9, 131.3, 131.2, 128.4, 128.0. FT-IR (cm^{-1}): 3076, 1821, 1528, 1379, 1348, 1299, 1223, 1066. EI-MS (m/z): 338 $[M]^+$. EA (%) calculated for $C_{12}H_6N_2O_4S_3$: C, 42.60; H, 1.79; N, 8.28; S, 28.42. Found: C, 42.49; H, 1.66; N, 8.13; S, 28.16.

3',4'-diamino-2,2':5,2''-terthiophene (4):

31 mL of ethanol and 62 mL of HCl (35%) were added to (3g, 8.86 mmol) of material **3** in a flask. To suchmixture, (31g, 163.50 mmol) of anhydrous tin(II) chloride 62mL in ethanol was added and stirred for 24hours at 30 °C. To room temperature, the mixture was then cooled and put into cold NaOH. To this mixture, toluene was applied, then vigorously stirred and filtered through celite. Toluene was used for extraction of the substance. The organic phases werewashed with NaCl and thendried over anhydrous $MgSO_4$. The solvent concentrated to obtain (2.4 g, 9 mmol, 97% yield)of material **4**as a brown solid. ^{1}H NMR ($CDCl_3$, δ): 7.30 (d, 2H, J = 2.0 Hz), 7.27 (s, 2H), 7.09-7.14 (m, 2H), 3.76 (bs, 4H). ^{13}C NMR ($CDCl_3$, δ): 136.0, 133.6, 127.8, 124.0, 124.0, 110.1. FT-IR (cm^{-1}): 3371, 3298, 3224, 3182, 3096, 1631, 1615, 1573, 1528, 1509, 1441, 1336, 1294, 1070. EI-MS (m/z): 278 $[M]^+$. EA (%) calculated for $C_{12}H_{10}N_2S_3$: C, 51.77; H, 3.62; N, 10.06; S, 34.55. Found: C, 51.69; H, 3.54; N, 9.97; S, 34.78.

4,6-bis(2-thienyl)-thieno[3,4-c][1,2,5]-thiadiazole (5):

(1.67 g, 5.99 mmol) of material **4** was dissolved in 30 ml dry pyridine in a flask and degassed byargon. To themixture, (1.60 g, 11.49 mmol)of*N*-thionylaniline was added dropwise.Then, (4.5 g, 41.42 mmol)of chlorotrimethylsilane was added dropwise to obtain a dark blue colour. At room temperature, the reaction contents werestirred for 3hours and then placedinto dichloromethane. Using deionized water,the solution waswashed with HCl and then extracted with dichloromethane. Over anhydrous $MgSO_4$, the organic phase was dried and thenfiltered. The solvent was evaporated to createthe product that is purified bychromatography with dichloromethaneto have (1.72g, 6 mmol, 93% yield) of material **5**as blue crystals. ^{1}H NMR ($CDCl_3$, δ): 7.59 (dd, 2H, J = 1.0 Hz, 3.5 Hz), 7.34 (dd, 2H, J = 1.0 Hz, 5.0 Hz), 7.12 (dd, 2H, J = 3.5 Hz, 5.0 Hz). ^{13}C NMR ($CDCl_3$, δ): 156.3, 135.0, 128.2, 125.4, 124.3, 112.4. FT-IR (cm^{-1}): 3102, 3073, 1797, 1525, 1483, 1365, 1223, 1137, 1047. EI-MS (m/z): 306 $[M]^+$. EA (%) calculated for $C_{12}H_6N_2S_4$: C, 47.04; H, 1.97; N, 9.14; S, 41.85. Found: C, 47.25; H, 2.18; N, 8.83; S, 39.16.

4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-dimethyl ester (6):

(1.86 g, 6.06 mmol) of material **5** and (1.73 g, 12.17 mmol) of dimethyl acetylenedicarboxylate were mixedin a flask. The system was evacuated and replenishedwith argon for three cycles prior toadding 40 mL anhydrous xylene. The reaction contents wererefluxed for 24hours. The flask was cooled to room temperature.The solvent was removed to createthe product that ispurified by column chromatography with gradient (petroleum ether, 0-50% DCM) to create(2.37 g, 6 mmol, 94% yield)yellow crystals of**6**. ^{1}H NMR ($CDCl_3$, δ): 7.62 (dd, 2H, J = 1.0 Hz, 5.0 Hz), 7.44 (dd, 2H, J = 1.0 Hz, 3.5 Hz), 7.22 (dd, 2H, J = 3.5 Hz, 5.0 Hz), 3.78 (s, 6H). ^{13}C NMR ($CDCl_3$, δ): 168.1, 153.6, 135.1, 132.0, 129.7, 129.0, 127.3, 126.2, 53.1. FT-IR (cm^{-1}): 3109, 2975, 2932, 2900, 2865, 2159, 2031, 1971, 1730, 1513, 1460, 1318, 1283, 1198. EI-MS (m/z): 416 $[M]^+$. EA (%) calculated for $C_{18}H_{12}N_2O_4S_3$: C, 51.91; H, 2.90; N, 6.73; S, 23.09. Found: C, 51.86; H, 2.94; N, 6.61; S, 22.97.

4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-dicarboxylic acid (7):

(4.00g, 100.00 mmol) ofSodium hydroxide was dissolved in 30 mL deionized water and added into a flask. To this solution, 200 ml ethanol and (2.27 g, 5.45 mmol) of material **6** wereadded, and the reaction contents wererefluxed for 24hours. Deionized H_2O was added to the flask, which is cooled to room temperature. Subsequently, themixture was cooled to 0 °C. To precipitate the product,the mixture was neutralised by HCl andfiltered.The precipitation

wasthen washed with deionized H_2O. Under high vacuum,the precipitationwas dried to create (1.80 g, 5 mmol,85% yield)yellow solid**7**. ^{1}H NMR (CD_3SOCD_3, δ): 7.86 (dd, 2H, J = 1.0 Hz, 5.0 Hz), 7.47 (dd, 2H, J = 1.0 Hz, 3.5 Hz), 7.25 (dd, 2H, J = 3.5 Hz, 5.0 Hz). ^{13}C NMR (CD_3SOCD_3, δ): 168.4, 152.5, 134.8, 133.0, 129.7, 129.3, 127.2, 123.8. FT-IR (cm^{-1}): 3106, broad (3300-2600), 2162, 2024, 1971, 1815, 1765, 1705, 1552, 1453, 1386, 1261, 1152, 1020. EI-MS (m/z): 387 $[M-H]^+$. EA (%) calculated for $C_{16}H_8N_2O_4S_3$: C, 49.48; H, 2.08; N, 7.21; S, 24.76. Found: C, 45.33; H, 2.70; N, 6.47; S, 21.35.

4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-dicarboxylic anhydride (8):

(1.15 g, 2.96 mmol) ofmaterial**7** and (10.00 g, 97.95 mmol) of anhydrous acetic anhydride were combined in a flask. The system was evacuated and replenished with argon for three cycle'sprior toadding 30 mL anhydrous xylene. For 6hours,the mixture was then heated at 130 °C. Subsequently, the mixture was cooled to room temperature.The solvent was evaporated to obtain (1.06 g, 3 mmol, 97% yield) red solid**8**. ^{1}H NMR ($CDCl_3$, δ): 8.11 (dd, 2H, J = 1.0 Hz, 4.0 Hz), 7.82 (dd, 2H, J = 1.0 Hz, 5.0 Hz), 7.33 (dd, 2H, J = 4.0 Hz, 5.0 Hz). ^{13}C NMR (CD_3SOCD_3, δ): 162.0, 156.0, 134.3, 132.6, 131.4, 127.8, 127.6, 125.5. FT-IR (cm^{-1}): 3131, 3109, 3081, 1808, 1765, 1552, 1453, 1393, 1247, 1152, 1088. EI-MS (m/z): 370 $[M]^+$. EA (%) calculated for $C_{16}H_6N_2O_3S_3$: C, 51.88; H, 1.63; N, 7.56; S, 25.97. Found: C, 52.11; H, 2.00; N, 7.20; S, 24.55.

3,7-dimethyloctyl bromide (9):

(21.10 g, 80.44 mmol) of triphenylphosphine was added to a mixture composed of (12.61 g, 79.69 mmol) of 3,7-dimethyloctyl alcohol and 250 ml dichloromethaneand stirred in a flask. (14.26 g, 80.14 mmol)of NBS was added portion-wise and stirred for 90 min at room temperature to this mixture. With $NaHCO_3$ solution,the mixture was then washed.Subsequently, it was dried over anhydrous $MgSO_4$, filtered and the solvent evaporated. For 1hour at room temperature,the substance was then stirred in petroleum ether, filtered and the filtrate evaporated. To yield (23.00 g, 59 mmol, 73% yield)colourless oil**9**, the obtained product was purified by chromatography with petroleum ether. ^{1}H NMR ($CDCl_3$, δ): 3.55-3.37 (m, 2H), 1.96-1.83 (m, 1H), 1.77-1.61 (m, 2H), 1.60-1.49 (m, 1H), 1.41-1.24 (m, 3H), 1.22-1.11 (m, 3H), 0.82-0.94 (m, 9H). ^{13}C NMR ($CDCl_3$, δ): 40.1, 39.2, 36.7, 32.3, 31.7, 28.0, 24.6, 22.7, 22.6, 19.0. FT-IR (cm^{-1}): 2953, 2925, 2868, 1464, 1382, 1261, 1173. EI-MS (m/z): 222.1 $[M]^+$. EA (%) calculated for $C_{10}H_{21}Br$: C, 54.30; H, 9.57; Br, 36.13. Found: C, 55.04; H, 9.53; Br, 34.23.

***N*-(3,7-dimethyloctyl)phthalimide (10):**

(4.07 g, 18.40 mmol) ofmaterial**9** and20 mLof anhydrous DMF were added into a flask. To this obtained mixture, (3.75 g, 20.27 mmol) potassium phthalimide was added and the reaction contents heated to 90 °C for 17hours. The mixture was cooled at room temperatureand placedin deionized H_2O. Then,the obtained product was extracted with dichloromethane. The organic extracts werecombined and washed with KOH and deionized water. Over anhydrous $MgSO_4$, the organic phase was dried. The solvent was then evaporated to obtain the product that purified via chromatography with dichloromethaneto afford(5.29 g, 18 mmol, 91% yield)as colourless oil**10**. ^{1}H NMR ($CDCl_3$, δ): 7.85 (dd, 2H, J = 3.0 Hz, 5.5 Hz), 7.72 (dd, 2H, J = 3.0 Hz, 5.5 Hz), 3.80-3.66 (m, 2H), 1.77-1.66 (m, 1H), 1.53-1.43 (m, 3H), 1.41-1.25 (m, 3H), 1.20-1.11 (m, 3H), 0.98 (d, 3H, J = 6.5 Hz), 0.87 (d, 6H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, δ): 168.4, 133.8, 132.2, 123.1, 39.2, 37.0, 36.3, 35.5, 30.7, 27.9, 24.5, 22.7, 22.6, 19.4. FT-IR (cm^{-1}): 2953, 2925, 2868, 1772, 1706, 1616, 1469, 1398, 1267, 1189, 1055. EI-MS (m/z): 288.2 $[MH]^+$. EA (%) calculated for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77; N, 4.87. Found: C, 72.17; H, 8.62; N, 4.43.

3,7-dimethyl-1-octanamine (11):

(6.03 g, 20.98 mmol) of material**10**,(4.0 mL, 65.0 mmol, 51%) of hydrazine hydrate and 100 ml of methanol weremixedin a flask. The reaction contents were refluxed beforedisappearing the starting material. Excess HCl was addedupon completion, and thenthe mixture was refluxed for 1h and cooled to room temperature. The precipitate was washed out with water and filtered. The methanol was condensedas well asthe residue was diluted with dichloromethane. The organic layer was washed with KOH, and thedichloromethanewas taken out from the product. With NaCl,the organic phase was washed and dried over anhydrous $MgSO_4$. The solvent was then concentrated to obtain (2.85 g, 18 mmol, 86%) compound **11**as a brown oil. ^{1}H NMR ($CDCl_3$, δ): 2.82-2.62 (m, 2H), 1.60-1.43 (m, 3H), 1.35-1.22 (m, 4H), 1.20-1.06 (m, 3H), 0.88 (dd, 9H, J = 2.0 Hz, 6.5 Hz). ^{13}C NMR ($CDCl_3$, δ): 41.1, 40.1, 39.3, 37.3, 30.5, 28.0, 24.7, 22.7, 22.6, 19.6. FT-IR (cm^{-1}): 3521, 3375, 3219, 3021, 2953, 2925, 2868, 2155, 2028, 1978, 1598, 1464, 1382, 1166, 1063. EI-MS (m/z): 157.2 $[M]^+$. EA (%) calculated for $C_{10}H_{23}N$: C, 76.36; H, 14.74; N, 8.90. Found: C, 71.74; H, 13.51; N, 7.71.

4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-*N*-(3,7-dimethyloctyl)dicarboxylic imide (12): (1.00 g, 2.69 mmol)of 4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-dicarboxylic

anhydride **(8)**, 50 mL of acetic acid (100%) and (0.88 g, 5.59 mmol)of3,7-dimethyl-1-octanamine **(11)**were combined in a flask. The system was evacuated and re-filled for three cycles with argon and heated at 110 °C overnight. The mixture was then cooled to room temperature.20 mLof acetic anhydride was added to the cooled mixture and then re-heated to110 °C for 6hours. Afterwards, the mixture was let at room temperature to be cooled and the solvent was concentrated to produce the product. It was then purified by chromatography with (60:10, petroleum ether: ethyl acetate) to yield (1.15 g, 2.3 mmol, 84% yield)of **12**as an orange solid. ^{1}H NMR ($CDCl_3$, δ): 7.91 (dd, 2H, J = 1.0 Hz, 3.5 Hz), 7.73 (dd, 2H, J = 1.0 Hz, 5.0 Hz), 7.30 (dd, 2H, J = 3.5 Hz, 5.0 Hz), 3.84-3.70 (m, 2H), 1.78-1.65 (m, 1H), 1.55-1.43 (m, 3H), 1.39-1.22 (m, 3H), 1.20-1.08 (m, 3H), 0.97 (d, 3H, J = 6.0 Hz), 0.86 (d, 6H, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$, δ): 165.7, 156.5, 133.1, 131.5, 130.2, 127.0, 126.9, 126.7, 39.2, 37.2, 37.0, 35.2, 31.0, 27.9, 24.6, 22.7, 22.6, 19.4. FT-IR (cm^{-1}): 3439, 3102, 3074, 2953, 2925, 2865, 1804, 1751, 1694, 1549, 1453, 1364, 1226, 1162, 1056. EI-MS (m/z): 510.1 $[MH]^+$. Elemental analysis (%) calculated for $C_{26}H_{27}N_3O_2S_3$: C, 61.27; H, 5.34; N, 8.24; S, 18.87. Found: C, 61.59; H, 5.56; N, 7.94; S, 16.79.

4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-*N*-octyl-dicarboxylic imide (13): The same synthesising procedure of**12** was adapt to prepare**13**except that (1.20 g, 9.28 mmol)of *N*-octylamine was used. (1.20 g, 2.5 mmol, 93% yield)of **13**was obtained as an orange solid. ^{1}H NMR ($CDCl_3$, δ): 7.91 (dd, 2H, J = 1.0 Hz, 3.5 Hz), 7.73 (dd, 2H, J = 1.0 Hz, 5.0 Hz), 7.30 (dd, 2H, J = 3.5 Hz, 5.0 Hz), 3.74 (t, 2H, J = 7.5 Hz), 1.65-1.76 (m, 2H), 1.23–1.41 (m, 10H), 0.88 (t, 3H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, δ): 165.8, 156.5, 133.1, 131.5, 130.2, 127.1, 126.9, 126.7, 39.0, 31.8, 29.1, 28.2, 27.0, 22.7, 14.0. FT-IR (cm^{-1}): 3443, 3102, 3070, 2918, 2854, 1808, 1754, 1694, 1556, 1457, 1364, 1226, 1169, 1098. EI-MS (m/z): 481.1 $[M]^+$. Elemental analysis (%) calculated for $C_{24}H_{23}N_3O_2S_3$: C, 59.85; H, 4.81; N, 8.72; S, 19.97. Found: C, 59.91; H, 4.93; N, 8.70; S, 20.72.

3,3',5,5'-tetrabromo-2,2'-bithiophene (14): (1.81 g, 10.88 mmol) of 2,2'-bithiophene was dissolved in 36 mL of glacial acetic acid and 27 mL of chloroform in a flask and cooled to 0 °C. To this mixture, (1.20 mL, 23.27 mmol) of bromine in 22 mL of chloroform were added dropwise during 1.5 hours. The second portion of bromine (1.20 mL, 23.27 mmol) in 22 mL of chloroform was added at room temperature through 1 hour. The mixture was stirred overnight and refluxed for 24 hours. The reaction contents were cooled to room temperature, and the solvent was removed to obtain the crude product which was purified via recrystallization from ethanol to afford (3.95 g, 8.19 mmol, 75.34%) of **14** as green crystal.

^{1}H NMR ($CDCl_3$, δ): 7.07 (s, 2H). ^{13}C NMR ($CDCl_3$, δ): 133.00, 129.56, 114.83, 112.13. FT-IR (cm^{-1}): 3088, 1481, 1446, 1389, 1290, 1130, 978, 800, 669. EI-MS (*m/z*): 481.6 $[M]^+$. Elemental analysis (%) calculated for $C_8H_2Br_4S_2$: C, 19.94; H, 0.42; S, 13.31; Br, 66.33. Found: C, 19.91; H, 0.53; S, 13.27; Br, 66.43.

3,3'-dibromo-2,2'-bithiophene (15): (3.75 g, 7.78 mmol) of **14** was added to the refluxing mixture of (1.96 g, 29.97 mmol) of zinc powder in 39 mL of ethanol, 3.9 mL of deionized water, 9.3 mL of glacial acetic acid, (0.8 mL, 3.0 M) of HCl in a flask over 30 minutes. The reaction contents were refluxed for 2 hours. Next, the flask was cooled to room temperature and filtered. Then, the excess of zinc was washed out with ethanol three times. The deionized water was then added to the filtrate and extracted using diethyl ether. The organic phase was washed with the deionized water, dried over anhydrous $MgSO_4$, and the solvent evaporated to afford the crude product. The crude product was purified through recrystallization from *n*-hexane to yield (1.73 g, 5.33 mmol, 68.62%) of **15** as white crystals. ^{1}H NMR ($CDCl_3$, δ): 7.43 (d, 2H, *J* = 5.5 Hz), 7.10 (d, 2H, *J* = 5.5 Hz). ^{13}C NMR ($CDCl_3$, δ): 130.84, 128.90, 127.55, 112.67. FT-IR (cm^{-1}): 3102, 3081, 1747, 1552, 1485, 1442, 1400, 1332, 1130, 1073, 924, 854, 701, 637. EI-MS (*m/z*): 323.8 $[M]^+$. Elemental analysis (%) calculated for $C_8H_4Br_2S_2$: C, 29.65; H, 1.24; S, 19.79; Br, 49.32. Found: C, 29.70; H, 1.34; S, 19.89; Br, 48.37.

4,4-dioctyldithieno[3,2-b:2',3'-d]silole (16): With three vacuum/argon cycles, a flask was purged. (9.76 mL, 24.4 mmol) of *n*-BuLi was added to 120 mL dry diethyl ether. The mixture was then cooled to –78 °C. To this solution, (3.97 g, 12.25 mmol) of **15** was dissolved in 40 mL dry THF, adding dropwise over 30 minutes with vigorous stirring for 3 hours at – 78 °C. To this mixture, (4.24 mL, 2.19 mmol) of di-*n*-octyldichlorosilane was dissolved in 80 mL dry THF, adding dropwise at – 78 °C and stirred for 5 hours. Subsequently, the reaction contents were stirred at room temperature overnight. NH_4Cl solution was added to the reaction mixture and extracted with diethyl ether. Subsequently, the organic phase was washed with deionized H_2O and NaCl solution. To obtain the product, the organic phase was dried over anhydrous $MgSO_4$, and evaporated. It was purified *via* chromatography with petroleum ether to yield (3.10 g, 7.40 mmol, 60.42%) of **16** as yellow oil. ^{1}H NMR ($CDCl_3$, δ): 7.21 (d, 2H, *J* = 4.5 Hz), 7.07 (d, 2H, *J* = 4.5 Hz), 1.47–1.35 (m, 4H), 1.34–1.17 (m, 20H), 0.98–0.84 (m, 10H). ^{13}C NMR ($CDCl_3$, δ): 149.19, 141.63, 129.62, 124.93, 33.15, 31.86, 29.17, 29.16, 24.19, 22.65, 14.09, 11.88. FT-IR (cm^{-1}): 3063, 2953, 2918, 2854, 1460, 1400, 1375, 1347,

1251, 1173, 1084, 995, 949, 875, 804, 694. EI-MS (*m/z*): 418.2 $[M]^+$. Elemental analysis (%) calculated for $C_{24}H_{38}S_2Si$: C, 68.84; H, 9.15; S, 15.31. Found: C, 69.08; H, 8.96; S, 14.11.

4,7-di(5-bromo-thien-2-yl)-2,1,3-benzothiadiazole-5,6-N-(3,7-dimethyloctyl)dicarboxylic imide (M1): (1.00 g, 1.96 mmol) of**12** and 100 mL of THF were combined in a flask. To this mixture, (1.74 g, 9.77 mmol) of *N*-bromosuccinimide (NBS) was added and stirred overnight at room temperature in the dark. The solvent was evaporated, then washed with cold CH_3OH, filtered and dried to achieve the product as a red solid. The product was then purified through chromatography with dichloromethane to afford (1.28 g,2 mmol, 98%)of**M1**as a red solid.^{1}H NMR ($CDCl_3$, δ): 7.80 (d, 2H, J = 4.0 Hz), 7.24 (d, 2H, J = 4.0 Hz), 3.70-3.84 (m, 2H), 1.78-1.66 (m, 1H), 1.54-1.44 (m, 3H), 1.41-1.22 (m, 3H), 1.20-1.11 (m, 3H), 0.98 (d, 3H, J = 6.0 Hz), 0.87 (d, 6H, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$, δ): 165.6, 155.9, 134.1, 133.0, 129.8, 126.4, 125.8, 118.7, 39.2, 37.3, 37.0, 35.2, 31.0, 27.9, 24.6, 22.7, 22.6, 19.4. FT-IR (cm^{-1}): 3429, 3120, 2957, 2918, 2865, 1747, 1691, 1563, 1460, 1364, 1283, 1073. EI-MS (m/z): 666.9 $[M]^+$. Elemental analysis (%) calculated for $C_{26}H_{25}Br_2N_3O_2S_3$: C, 46.78; H, 3.78; Br, 23.94; N, 6.30; S, 14.41. Found: C, 46.61; H, 3.61; Br, 23.95; N, 6.29; S, 14.64.

4,7-di(5-bromo-thien-2-yl)-2,1,3-benzothiadiazole-5,6-*N*-octyl-dicarboxylic imide (M2):The same synthesising procedure of **M1** was adapt to prepare **M2**, (1.00 g, 2.07 mmol) of compound **13** was used with 100 mL of THF and (1.84 g, 10.33 mmol) of NBS. (1.27 g, 2 mmol, 96% yield) of**M2**was obtained as a red solid. ^{1}H NMR ($CDCl_3$, δ): 7.80 (d, 2H, *J* = 4.0 Hz), 7.24 (d, 2H, *J* = 4.0 Hz), 3.75 (t, 2H, *J* = 7.0 Hz,), 1.66-1.75 (m, 2H), 1.23–1.40 (m, 10H), 0.88 (t, 3H, *J* = 6.5 Hz,). ^{13}C NMR ($CDCl_3$, δ): 165.7, 156.0, 134.1, 133.0, 129.8, 126.4, 125.9, 118.7, 39.0, 31.8, 29.1, 28.3, 27.0, 22.6, 14.1. FT-IR (cm^{-1}): 3421, 3120, 2953, 2911, 2850, 1744, 1687, 1556, 1446, 1375, 1244, 1176. EI-MS (*m/z*): 638.9 $[M]^+$. Elemental analysis (%) calculated for $C_{24}H_{21}Br_2N_3O_2S_3$: C, 45.08; H, 3.31; N, 6.57; S, 15.04; Br, 24.99. Found: C, 44.79; H, 3.41; N, 6.47; S, 15.74; Br, 28.80.

4,4-dioctyl-5,5'-bis(trimethylstannyl)dithieno[3,2-b:2',3'-d]silole (M3): In a flask, (0.25 g, 0.59 mmol) of **16** was added under argon the system was degassed. 7 mL of anhydrous *n*-hexane and (0.26 mL, 1.73 mmol) of tetramethylethylenediamine were added and cooled to –78 °C. To this solution, (0.59 mL, 1.49 mmol) of *n*-BuLi was added dropwise during 5 minutes and stirred for 3 hours. (0.31 g, 1.55 mmol) of trimethyltinchloride was quickly added. For 3 hours, the reaction was then stirred at room temperature overnight. Subsequently, the mixture was put into deionized H_2O and extracted with diethyl ether. With

brine solution, the combined organic phase was washed and dried over anhydrous $MgSO_4$, filtered and evaporated to obtain (0.36 g, 0.48 mmol, 81.35%) of **M3** as green sticky oil. ^1H NMR ($CDCl_3$, δ): 7.10 (s, 2H), 1.38–1.48 (m, 4H), 1.20–1.37 (m, 20H), 0.84–0.96 (m, 10H), 0.40 (s, 18H). ^{13}C NMR ($CDCl_3$, δ): 155.01, 143.12, 137.69, 124.95, 33.25, 31.90, 29.26, 29.18, 24.30, 22.69, 14.13, 12.00, -8.08. FT-IR (cm^{-1}): 2957, 2921, 2854, 1457, 1407, 1379, 1350, 1254, 1176, 1077, 964, 907, 768, 733, 697. EI-MS (*m/z*): 744.2 $[M]^+$. Elemental analysis (%) calculated for $C_{30}H_{54}S_2SiSn_2$: C, 48.41; H, 7.31; S, 8.61. Found: C, 52.44; H, 7.89; S, 9.70.

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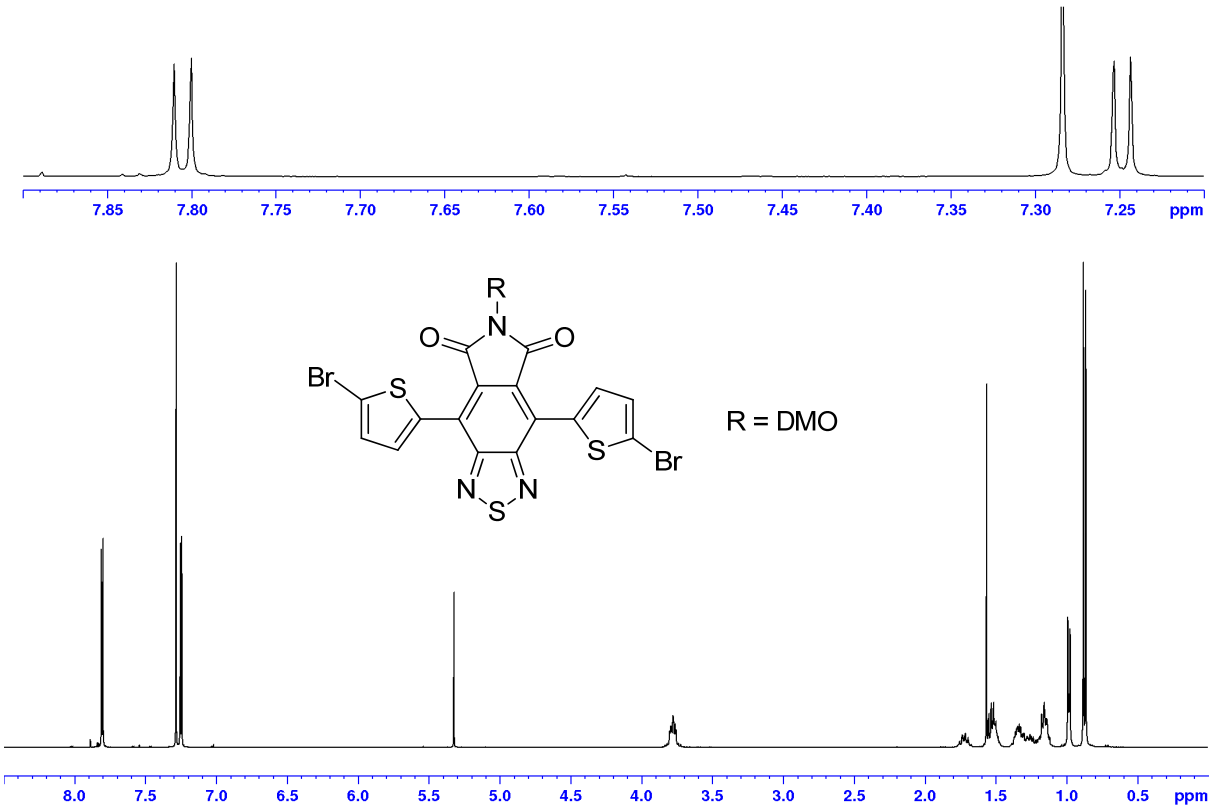

Figure S1.^{1}H NMR spectrum of **M1** in $CDCl_3$

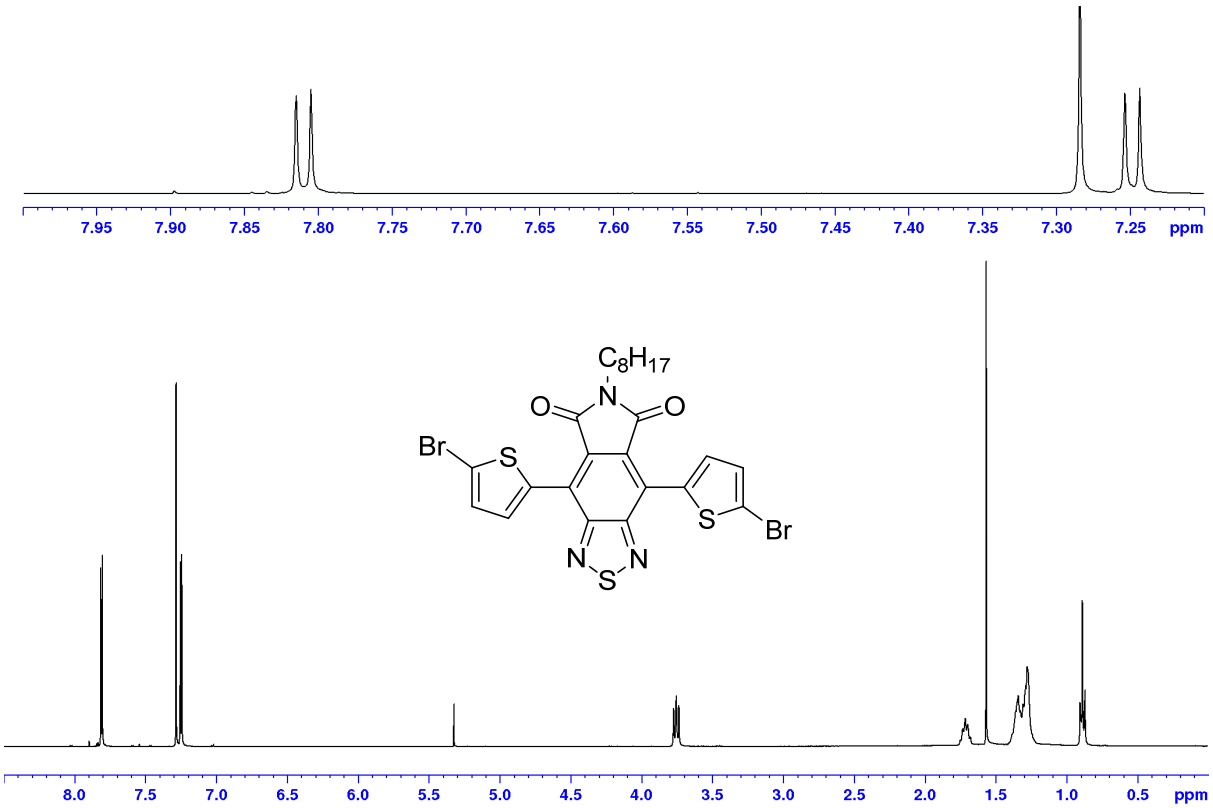

Figure S2.[1]H NMR spectrum of **M2** in $CDCl_3$

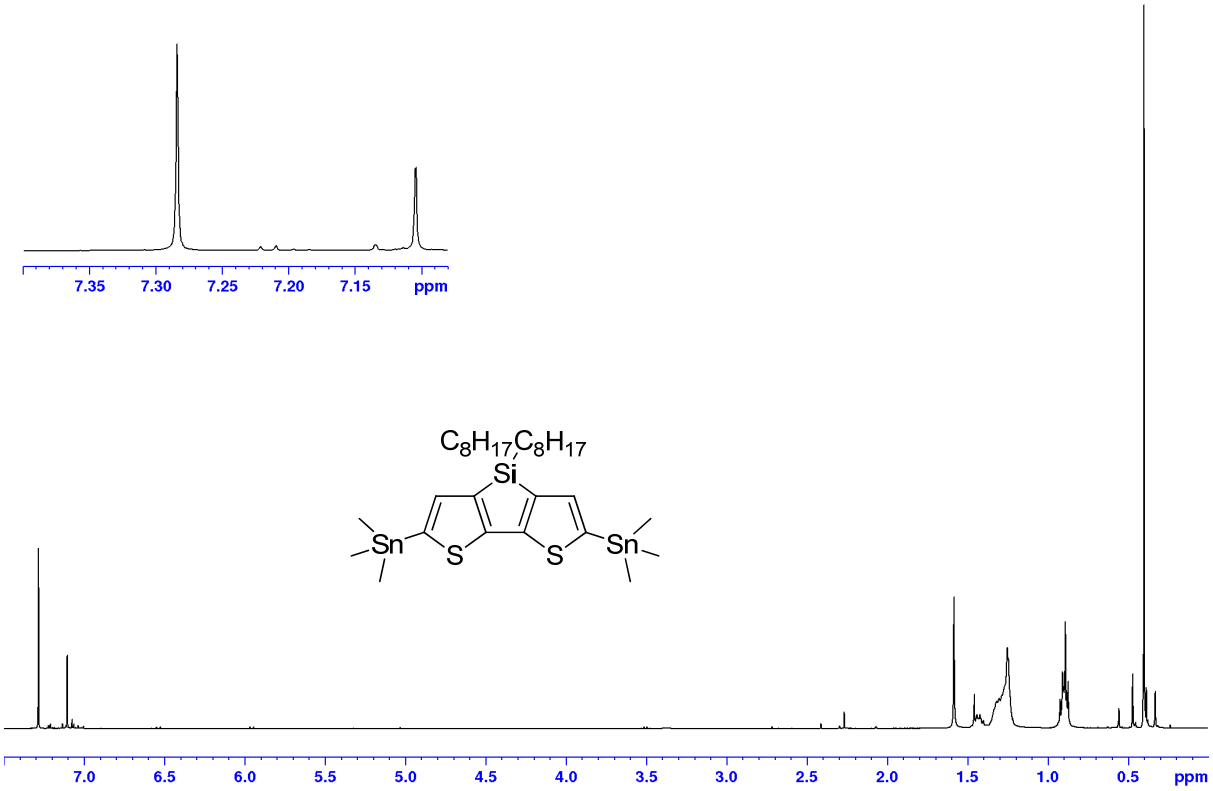

Figure S3. ^{1}H NMR spectrum of **M3** in $CDCl_3$

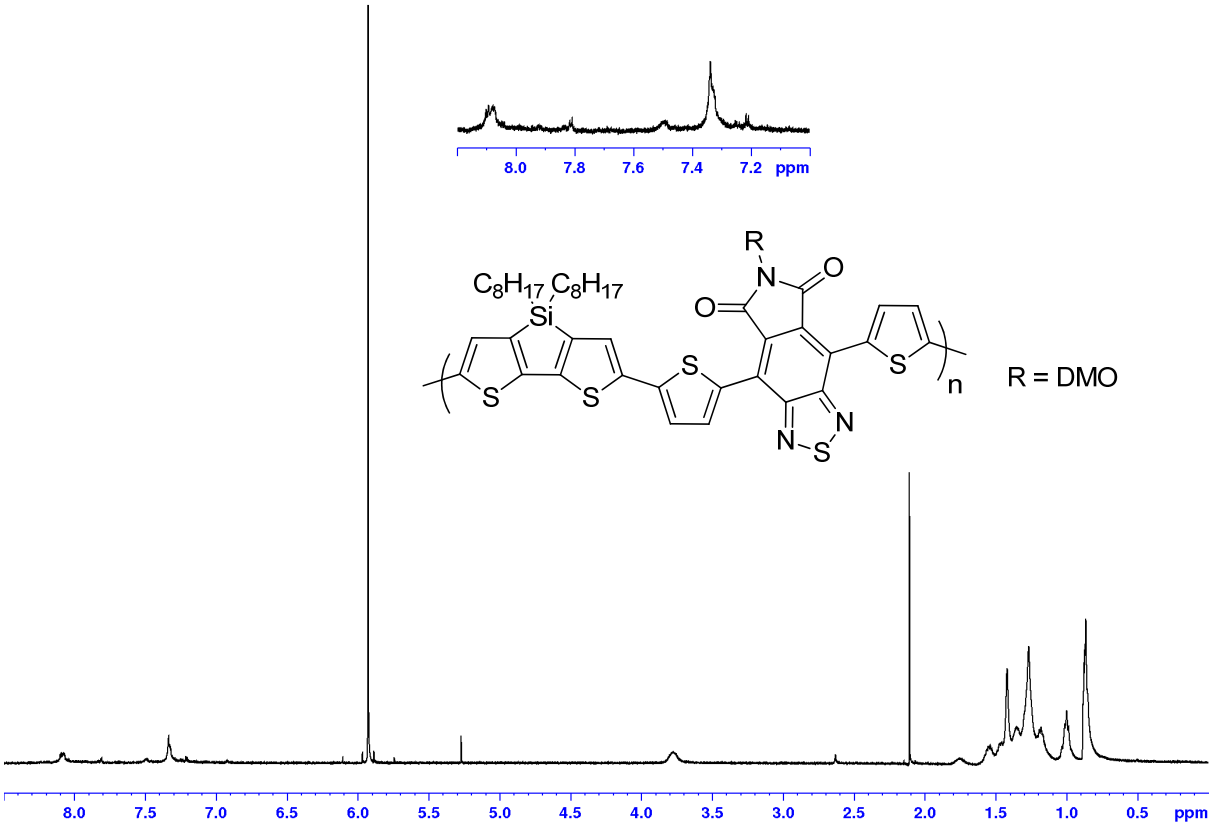

Figure S4. ^{1}H NMR spectrum of**PDTSDTBTDI-DMO**in $C_2D_2Cl_4$ at 100 °C

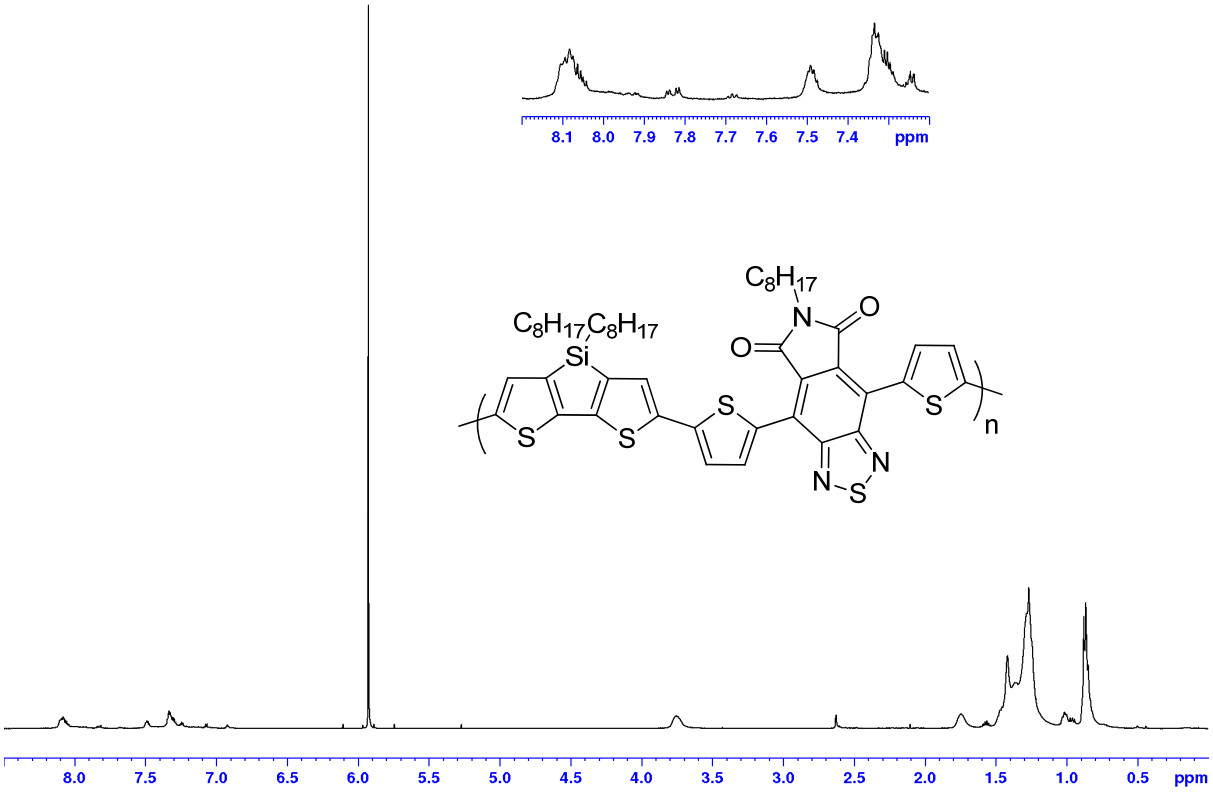

Figure S5. ^{1}H NMR spectrum of **PDTSDTBTDI-8** in $C_2D_2Cl_4$ at 100 °C