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Supporting Information

Pd-Free Synthesis of Dithienothiophene-Based Oligoaryls for Effective Hole-Transporting Materials by Optimized Cu-Catalyzed Annulation and Direct C-H Arylation

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Part I: Experimental Section

Part II:

1. General information:

Unless otherwise noted, all reactions were carried out with magnetic stirring and in flame-dried glassware under nitrogen. Required chemicals including various copper catalysts, ligands and bases are commercially available. Anhydrous or reagent-grade solvents such as dichloromethane, chloroform, dimethylsulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylpropyleneurea (DMPU), 1,2-dichlorobenzene, xylenes and mesitylene were purchased from Sigma-Aldrich, Acros or Alfa Aesar and used directly without further purifications. Syringes used to transfer reagents and solvents were purged with nitrogen prior to use. Reactions were monitored by thin layer chromatography (TLC, aluminum plates coated with silica gel, Merck 60, F-254). The spots were visualized by UV light. Flash column chromatography was performed using silica gel (spherical, 63-210 μm or 40-75 μm). Melting points were measured on a Fargo MP-2D apparatus. NMR spectra were recorded on a Bruker Magnet System 300 or 500 MHz instrument. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.0 ppm for ^{13}C NMR). For the characterization of the observed signal multiplicities, the following abbreviations were applied: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), quint (quintet), m (multiplet), comp (complex), app (apparent), and br (broad). The mass spectra recorded by fast atom bombardment (FAB) techniques were recorded in a 3-nitrobenzyl alcohol- or glycerine-matrix, or by Matrix-Assisted Laser Desorption/Ionization (MALDI) techniques were operated with a Bruker autoflex speed. Absorption spectra (UV-Vis) were measured on a Hitachi U-4100 UV-Vis spectrophotometer. Photoluminescence spectra (PL) were measured on a Hitachi F-7000 fluorescence spectrophotometer. The optical band gap (E_g^{opt}) of the synthesized hole-transporting materials was calculated from the intersection of absorption and PL spectra. The experiments of cyclic voltammetry were carried out with an Autolab electrochemical analyzer using a Pt working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. The measurements were conducted in dry CH_2Cl_2 solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte under a scan rate of 100 mVs^{-1}. The half-wave potential, $E_{1/2}$, was calculated by $(E_{pa}+E_{pc})/2$, where E_{pa} and E_{pc} are the potential energy of anodic and cathodic peaks, respectively. The HOMO energy level, E_{HOMO}, was calculated by $E_{HOMO} = -[E_{1/2(\text{vs. Ag/AgClsat'd})} + 0.197_{(\text{vs. NHE})} + 4.500_{(\text{vs. vacuum})}]$ eV; $E_{LUMO} = E_{HOMO} + E_g^{opt}$. Thermogravimetric analysis (TGA) was run on a TA Instrument Q500. Differential scanning calorimetry (DSC) was run on a Netzsch Instrument LT-DSC (Netzsch 204 F1).

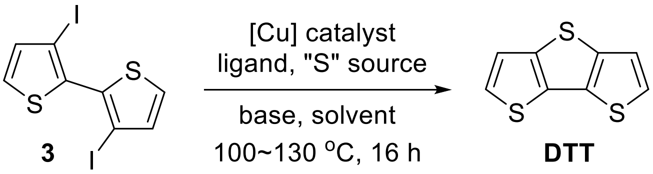
2. Device fabrication of the perovskite solar cells (PSCs):

A TiO_2 compact layer (~30 nm in thickness) was deposited onto the FTO substrate surface by spin-coating a solution of titanium diisopropoxide bis(acetylacetonate) (75 wt.% of $Ti(acac)_2O\textit{i}Pr_2$ in isopropanol). A 150 nm-thick mesoporous TiO_2 film (TiO_2 particle size: ~20 nm, crystalline phase: anatase) was spin-coated onto the compact-TiO_2/FTO substrate surface using home-made pastes and heated to 500 °C for 30 min. After sintering the TiO_2 layer, the films were cooled to room temperature and immersed in $TiCl_4$ solution (0.04 M in water) at 70 °C for 30 min. The films were then rinsed by deionized water and then annealed at 500 °C for 30 min again. After cooling to room temperature, the substrate/films were transferred to a nitrogen-filled glove box. A solution consisting of PbI_2 (1.80 M) and CH_3NH_3I (1.80 M) in γ-butyrolactone (GBL) and DMSO (5/5, v/v) was coated onto the TiO_2 substrate by a two-step spin-coating process at 1000 and 5000 rpm for 10 and 20 sec, respectively. At the second spin-coating step, the substrate/films were treated with 50 μL toluene by drop-casting. The substrate/films were then left on standing for over 60 mins before dried on a hot plate at 100 ^oC for 10 min. **TTh101**, **CHC05**, **CHC06**, **CHC07** and **spiro-OMeTAD** (as reference cell) was each dissolved in chlorobenzene (50 mg/mL). Each solution was stirred while heating to 80~90 ^oC for 20 min. Next, 17.5 μL of a solution of lithium bis(trifluoromethane)sulfonimide (Li-TFSI, 520 mg) in acetonitrile (1 mL) and 28.5 μL 4-*tert*-butylpyridine (TBP) were added directly to the corresponding hole-transporting material (HTM) solutions prepared from previous step. This as-prepared HTM solution was spin-coated onto the substrate/films at 2000 rpm for 30 sec. Finally, the Ag cathode layer was deposited by thermal evaporation (~100 nm). The active area of each cell was fixed at 0.16 cm^2 by a metal mask.

3. PCE evaluation of the perovskite solar cells (PSCs):

An IPCE spectrometer (EQE-R-3011, ENLI Technology Co. Ltd., Taiwan) calibrated with a single-crystal silicon reference cell was used for the incident monochromatic photon-to-current conversion efficiency (IPCE) measurements. An AM 1.5G solar simulator (Yamashita Denso Corporation, YSS-50A) was used as the irradiation light source for the characteristic current density-voltage (J-V) measurements. The intensity of the simulated sunlight was calibrated to 100 mW/cm^2. The J-V characteristics of the cell under an illumination of AM 1.5G simulated sunlight were obtained by applying the external potential bias to the cell and measuring the photocurrent output with a Keithley model 2400 digital source meter (Keithley, USA).

General Procedure A for the synthesis of dithienothiophenes (DTT):



To a solution of $CuCl_2$ (10~20 mol%), 1,10-phenanthroline (10~20 mol%), potassium thioacetate (1.50 mmol) and K_3PO_4 (1.50 mmol) in *p*-xylene (2.0 mL) in a flame-dried Schlenk tube was added 3,3'-diiodo-2,2'-bithiophene (**3**) (1.00 mmol) and under N_2. The reaction mixture was then heated at 130 °C under N_2 for 16 hours. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with ethyl acetate (2 × 30 mL), and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by flash chromatography (hexanes) afforded the desired product **DTT**[1] in 85~92 % isolated yields (entry 22 and 31 of Table 1 in main text).

Table S1. E-factor values for the DTT synthesis based on conventional routes (Approaches A, B) and our new method (Approach C) (**Scheme 1** in main text).

Approach A	Amount (g)	Waste (g)
dibromobithiophene	1.97	0
bis(phenylsulfonyl) sulfide	1.94	0
1.6 M *n*-BuLi in *n*-hexane	5.78	5.78
dry diethyl ether	49.91	0
water	50	0
Na_2SO_4	3	3
silica gel	150	150
petroleum ether	300	0
CH_2Cl_2	60	0
Total	**622.6**	**158.78**
Product	**0.8**	**-**

Total waste = 158.79 g; Product = 0.80 g

E-factor = 198

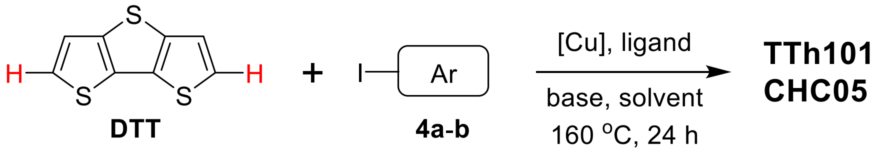
Approach B	Amount (g)	Waste (g)
3,3'-**d**ibromo-2,2'-bibenzo[b]thiophene	0.21	0
potassium thioacetate	0.06	0
bis(dibenzylidenacetone)palladium(0)	0.03	0.03
dppf	0.04	0.04
potassium phosphate	0.19	0.19
dry toluene	4.34	0
degassed acetone	0.39	0
diethyl ether	1.43	0
water/methanol (1:1)	100	0
methanol	100	0
celite	50	50
toluene	100	0
Total	**356.69**	**50.26**
Product	**0.09**	-

Total waste = 50.26 g; Product = 0.09 g
E-factor = 558

Approach C	Amount (g)	Waste (g)
3,3'-**d**iiodo-2,2'-bithiophene	1.26	0
potassium thioacetate	0.51	0
$CuCl_2$	0.09	0.09
1,10-**p**henanthroline	0.12	0.12
K_3PO_4	0.96	0.96
p-**x**ylene	1.72	0
water	50	0
ethyl acetate	54.12	0
brine	10	0
Na_2SO_4	3	3
silica gel	36	36
hexanes	300	0
Total	**457.78**	**40.17**
Product	**0.54**	-

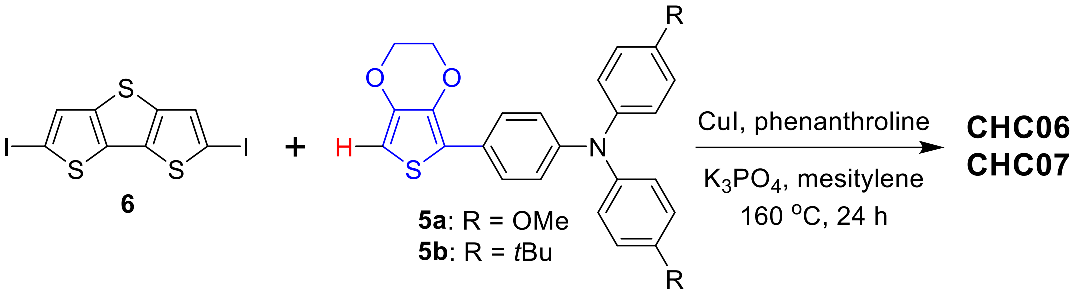
Total waste = 40.17 g; Product = 0.54 g
E-factor = 74

General Procedure B for the synthesis of DTT-based HTMs (TTh101&CHC05):

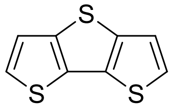


To a solution of CuI (30 mol%), 1,10-phenanthroline (30 mol%) and K_3PO_4 (3.00 equiv.) in DMPU (1.0 mL) in a sealed tube were added dithienothiophene (**DTT**) (0.50 mmol) and the corresponding end-group (**4a** or **4b**) (1.10 mmol) under N_2. The reaction mixture was then heated at 160 °C under N_2 for 24 hours. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with dichloromethane (2 × 20 mL), and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by flash chromatography yielded the desired **TTh101**[2] (78 %: entry 15 of Table 2 in main text) or **CHC05** (61 %) respectively.

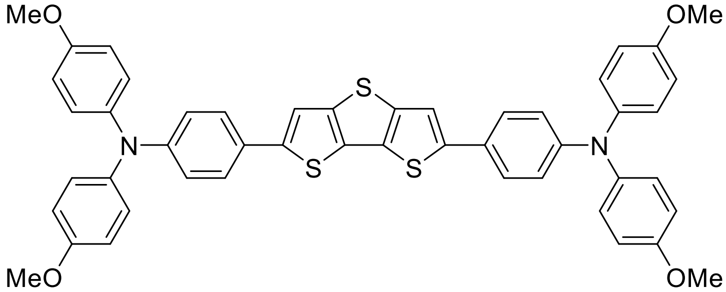
General Procedure C for the synthesis of DTT-based HTMs (CHC06&CHC07):



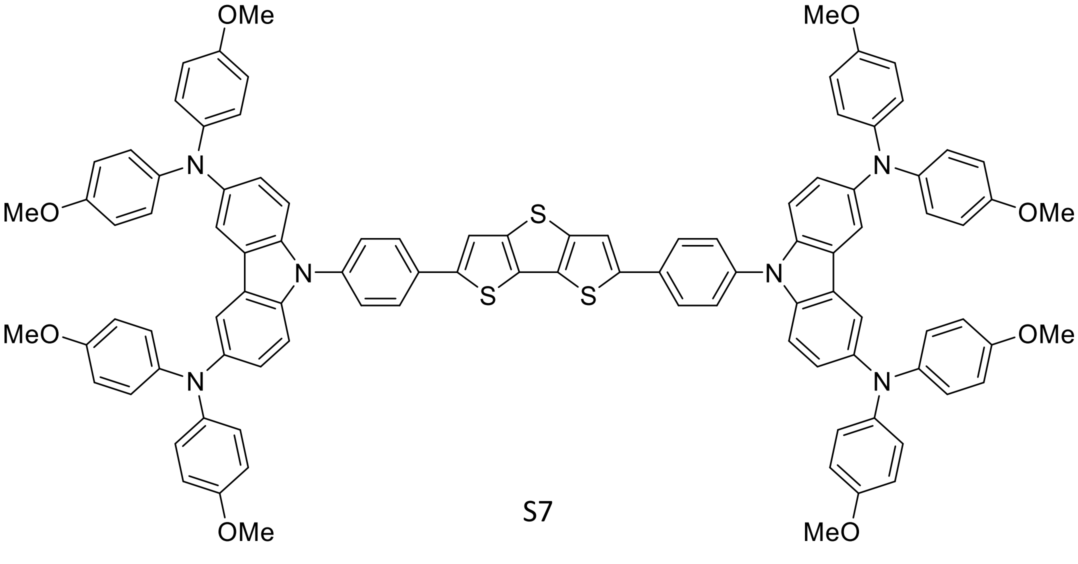
To a solution of CuI (30 mol%), 1,10-phenanthroline (30 mol%) and K_3PO_4 (3.00 equiv.) in mesitylene (1.0 mL) in a sealed tube were added the diiodo-**DTT**[3] (**6**) (0.50 mmol) and the corresponding end-group[4] **5a** or **5b** (1.10 mmol) under N_2. The reaction mixture was then heated at 160 °C under N_2 for 24 hours. After the reaction mixture had cooled to room temperature, water (15 mL) was added. The mixture was extracted with dichloromethane (2 × 20 mL), and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by flash chromatography followed by recrystallization (dichloromethane and hexanes) afforded the desired products **CHC06** (25 %) or **CHC07** (22 %) respectively.



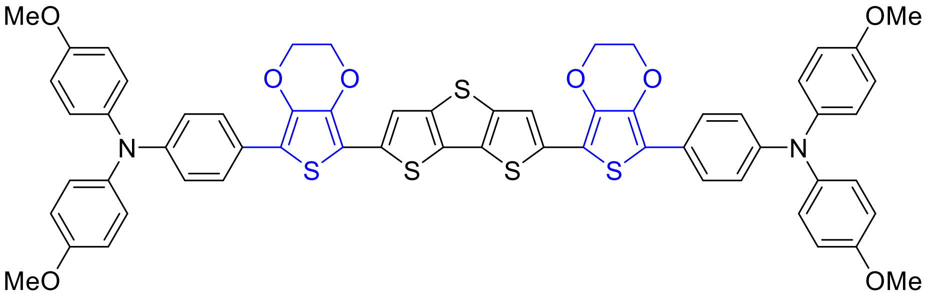
Dithienothiophene (**DTT**)[1] was prepared from 3,3'-diiodo-2,2'-bithiophene (**3**) (418 mg, 1.00 mmol) in the presence of $CuCl_2$ (28 mg, 0.20 mmol), 1,10-phenanthroline (36 mg, 0.20 mmol), K_3PO_4 (318 mg, 1.50 mmol) and potassium thioacetate (171 mg, 1.50 mmol) in *p*-xylene (2.0 mL) according to **General Procedure A**. Pale brown solid (180 mg, 92 %); m.p.: 65.8-67.8 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.36 (d, J = 5.2 Hz, 2 H), 7.29 (d, J = 5.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 141.7, 131.0, 125.9, 120.9.



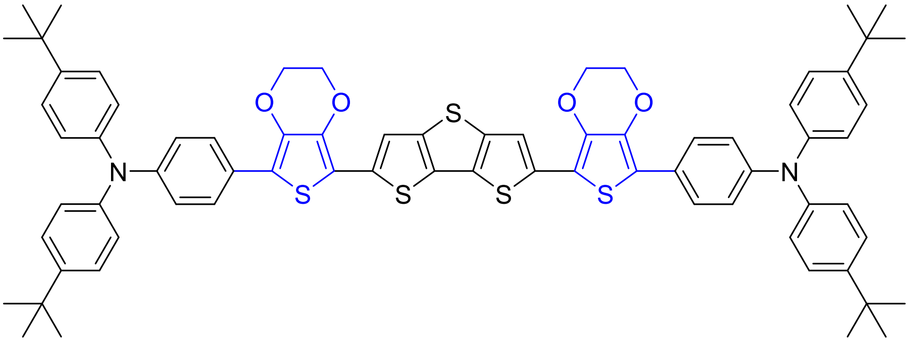
(**TTh101**)[2] was prepared from dithienothiophene (**DTT**) (98 mg, 0.50 mmol) and **4a** (474 mg, 1.10 mmol) in the presence of CuI (29 mg, 0.15 mmol), 1,10-phenanthroline (27 mg, 0.15 mmol) and K_3PO_4 (319 mg, 1.50 mmol) in DMPU (1.0 mL) according to **General Procedure B** and giving after column chromatography (dichloromethane : tetrahydrofuran : hexanes = 2 : 25 : 73) the pure product **TTh101** (313 mg, 78 %). Yellow solid; m.p.: 108-110 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.42 (d, J = 8.6 Hz, 4 H), 7.32 (s, 2 H), 7.10 (d, J = 8.8 Hz, 8 H), 6.95 (d, J = 8.6 Hz, 4 H), 6.87 (d, J = 8.8 Hz, 8 H), 3.81 (s, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 156.0, 148.4, 145.0, 141.2, 140.4, 129.2, 126.7, 126.4, 126.2, 120.3, 114.8, 114.7, 55.4.



(**CHC05**) was prepared from dithienothiophene (**DTT**) (98 mg, 0.50 mmol) and **4b**[5] (906 mg, 1.10 mmol) in the presence of CuI (29 mg, 0.15 mmol), 1,10-phenanthroline (27 mg, 0.15 mmol) and K_3PO_4 (319 mg, 1.50 mmol) in DMPU (1.0 mL) according to **General Procedure B** and giving after column chromatography (tetrahydrofuran : hexanes = 40 : 60) the pure product **CHC05** (484 mg, 61 %). Yellow solid; m.p.: 194-195 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.81 (d, J = 8.2 Hz, 4 H), 7.67 (s, 4 H), 7.59 (d, J = 8.2 Hz, 4 H), 7.56 (s, 2 H), 7.33 (d, J = 8.7 Hz, 4 H) , 7.15 (d, J = 8.7 Hz, 4 H), 7.00 (d, J = 8.4 Hz, 16 H) , 6.78 (d, J = 8.4 Hz, 16 H), 3.78 (s, 24 H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 154.7, 144.2, 142.5, 142.1, 141.9, 137.33, 137.31, 133.1, 130.4, 127.1, 126.9, 124.4, 124.3, 124.1, 116.9, 116.4, 114.5, 110.6, 55.5; HRMS (MALDI): calcd. for $C_{100}H_{78}N_6O_8S_3$: 1586.5038, found: 1586.5022 (M^+).



(**CHC06**) was prepared from the diiodo-**DTT** (**6**) (224 mg, 0.50 mmol) and the end-group (**5a**) (490 mg, 1.10 mmol) in the presence of CuI (29 mg, 0.15 mmol), 1,10-phenanthroline (27 mg, 0.15 mmol) and K_3PO_4 (319 mg, 1.50 mmol) in mesitylene (1.0 mL) according to **General Procedure C**. Purification by flash chromatography (tetrahydrofuran : hexanes = 45 : 55) followed by recrystallization (dichloromethane : hexanes = 1 : 3) gave the pure product **CHC06** (135 mg, 25 %). Dark red solid; m.p.: 200-201 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.52 (d, J = 8.7 Hz, 4 H), 7.36 (s, 2 H), 7.07 (d, J = 8.9 Hz, 8 H), 6.92 (d, J = 8.7 Hz, 4 H), 6.83 (d, J = 8.9 Hz, 8 H), 4.37 (app s, 4 H), 4.32 (app s, 4 H), 3.80 (s, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 155.8, 147.3, 141.1, 140.6, 138.3, 137.1, 135.4, 129.1, 126.7, 126.5, 124.7, 120.4, 115.6, 115.4, 114.6, 109.0, 64.9, 64.6, 55.4; MS (FAB): 1083 (M^+, 0.7 %), 107 (86 %), 77 (100 %); HRMS (FAB): calcd. for $C_{60}H_{46}N_2O_8S_5$: 1082.1858, found: 1082.1870.



(**CHC07**) was prepared from the diiodo-**DTT** (**6**) (224 mg, 0.50 mmol) and the end-group (**5b**) (547 mg, 1.10 mmol) in the presence of CuI (29 mg, 0.15 mmol), 1,10-phenanthroline (27 mg, 0.15 mmol) and K_3PO_4 (319 mg, 1.50 mmol) in mesitylene (1.0 mL) according to **General Procedure C**. Purification by flash chromatography (tetrahydrofuran : hexanes = 25 : 75) followed by recrystallization (dichloromethane : hexanes = 1 : 3) gave the pure product **CHC07** (130 mg, 22 %). Dark red solid; m.p.: 279-280 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.57 (d, J = 8.6 Hz, 4 H), 7.37 (s, 2 H), 7.28 (d, J = 8.6 Hz, 8 H), 6.97-7.14 (comp, 12 H), 4.38 (app s, 4 H), 4.33 (app s, 4 H), 1.34 (s, 36 H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 146.8, 145.8, 144.7, 141.2, 138.3, 137.4, 135.4, 129.2, 126.7, 126.0, 125.9, 124.1, 123.9, 122.7, 115.5, 109.3, 64.9, 64.6, 34.3, 31.4; HRMS (MALDI): calcd. for $C_{72}H_{70}N_2O_4S_5$: 1186.3934, found: 1186.3977 (M^+).

References:

[1] Park, K.-H.; Park, J.-B.; Zong, K. *Synthesis* **2016**, *48*, 4126–4130.

[2] Liu, X.; Kong, F.; Guo, F.; Cheng, T.; Chen, W.; Yu, T.; Chen, J.; Tan, Z. a.; Dai, S. *Dyes and Pigments* **2017**, *139*, 129-135.

[3] Marder, S. R.; Brédas, J.-L. *et al. J. Phys. Chem. B* **2010**, *114*, 749–755.

[4] Chang, Y.-C.; Lee, K.-M.; Lai, C.-H.; Liu, C.-Y. *Chem. Asian J.* **2018**, *13*, 1510–1515.

[5] Shi, Y.; Hou, K.; Wang, Y.; Wang, K.; Ren, H. C.; Pang, M. Y.; Chen, F.; Zhang, S. *J. Mater. Chem. A* **2016**, *4*, 5415-5422.

Figure S1. The UV-Vis absorption and photoluminescence spectra of **TTh101**, **CHC05**, **CHC06** and **CHC07** in CH_2Cl_2 solution.

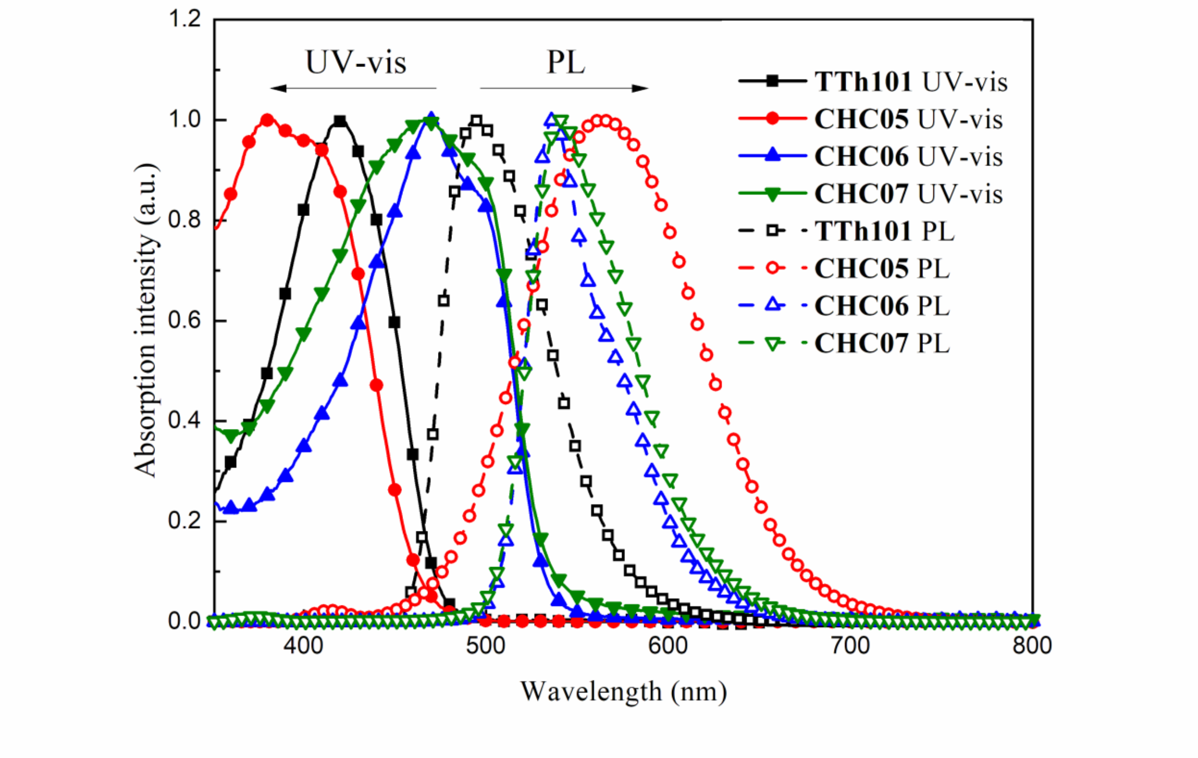


Figure S2. Cyclic voltammetry spectra of **TTh101**, **CHC05**, **CHC06** and **CHC07** in CH_2Cl_2 solution.

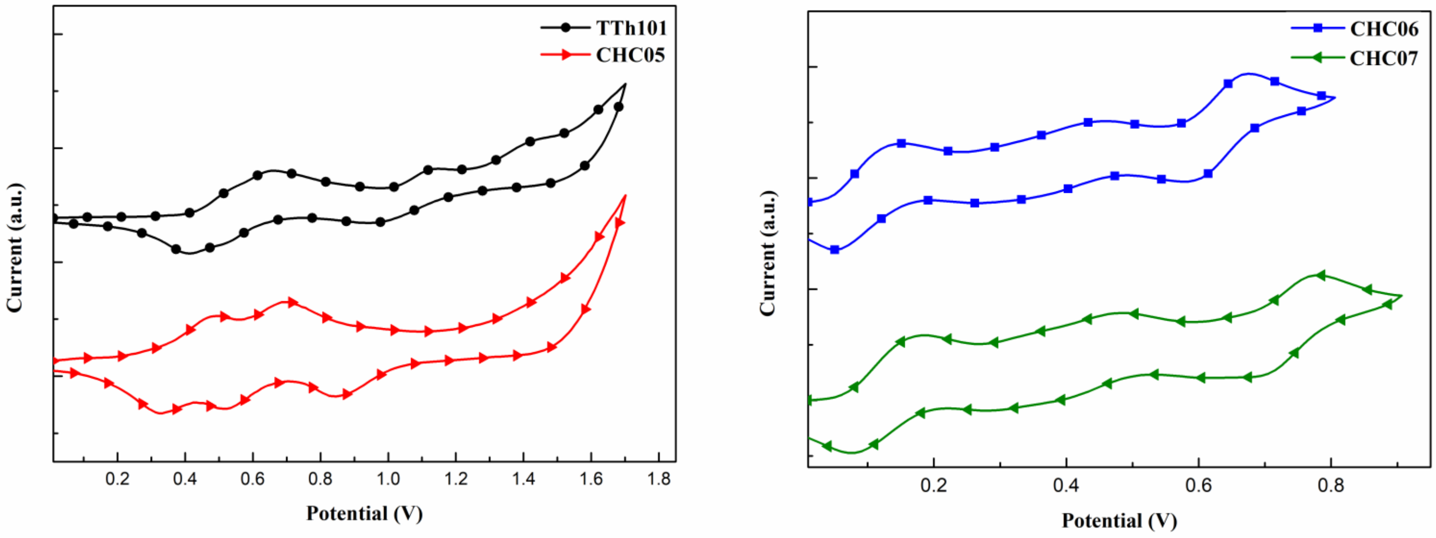


Figure S3. Thermogravimetric analysis curves of **TTh101**, **CHC05**, **CHC06** and **CHC07**.

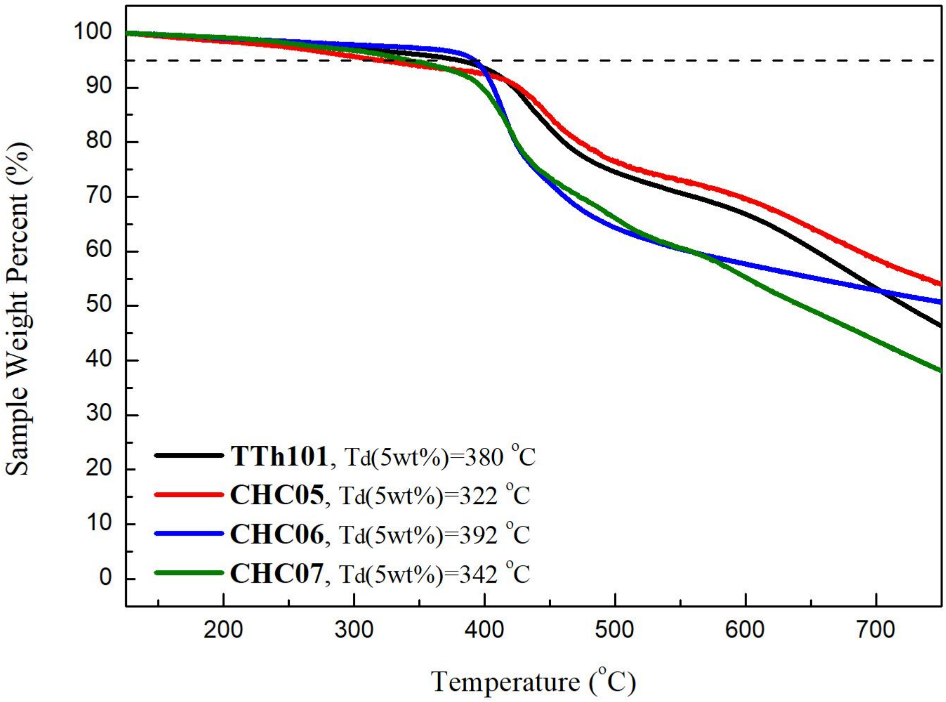


Figure S4. Differential scanning calorimetry curves of **TTh101**, **CHC05**, **CHC06** and **CHC07**.

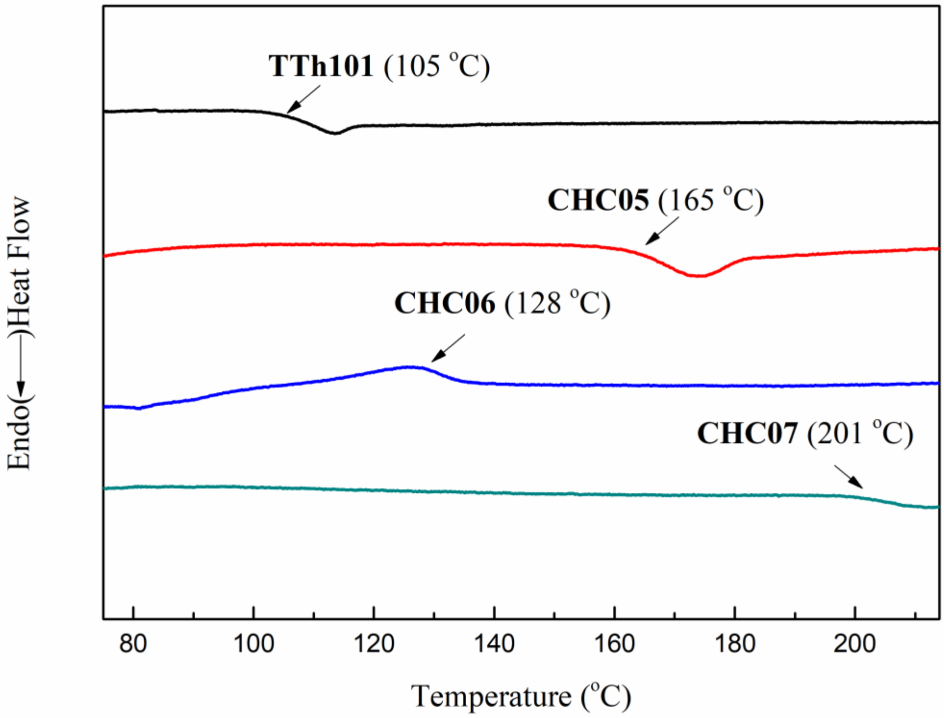
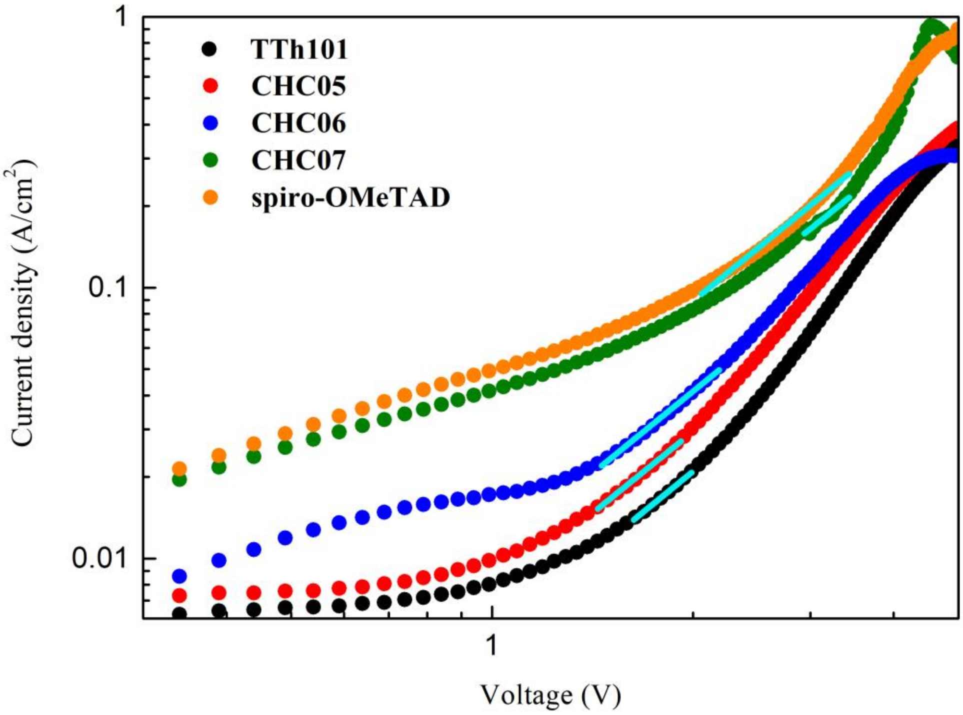
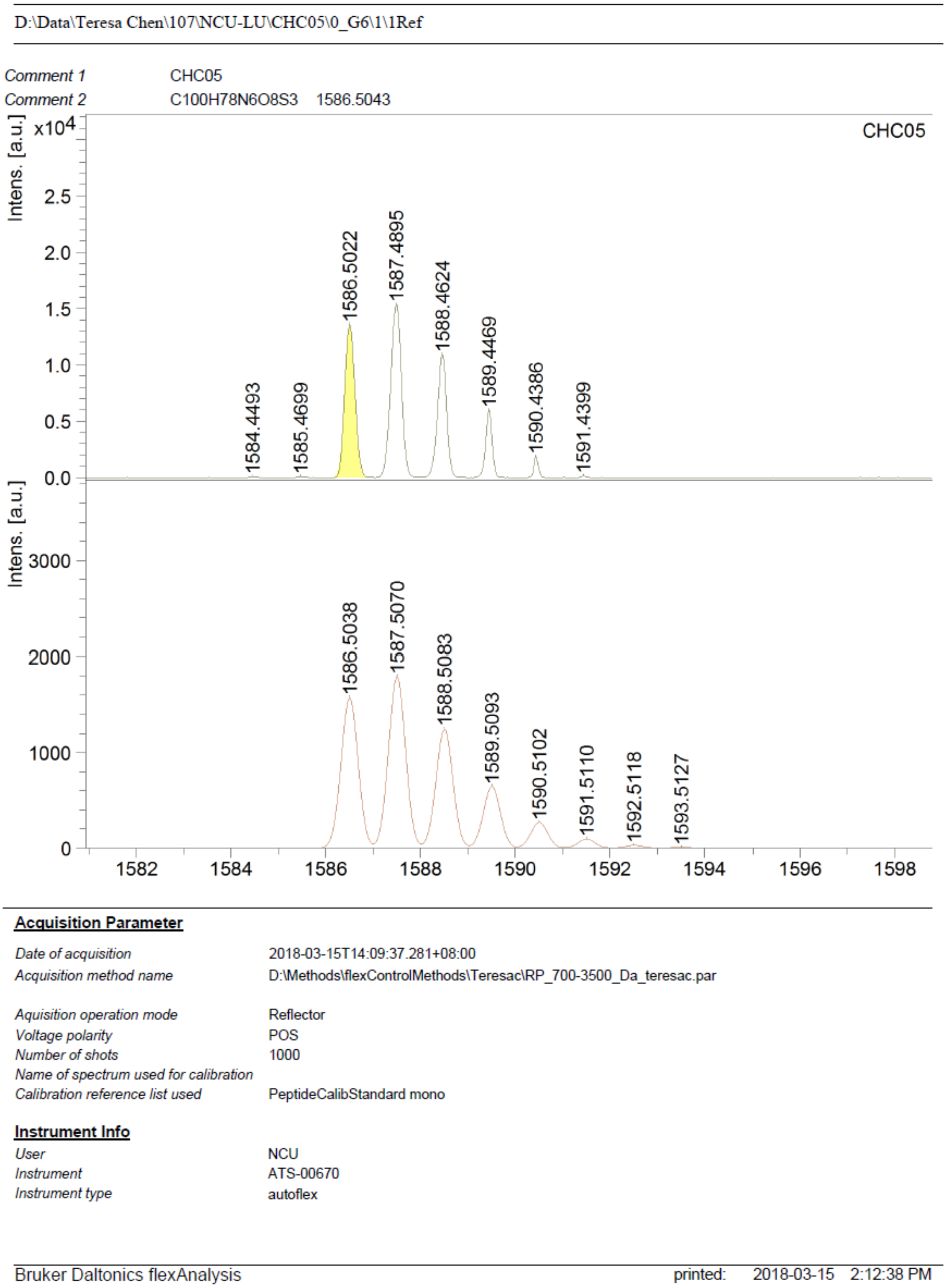


Figure S5. J-V curves for the determination of the hole mobility of HTMs in the space-charge limited current (SCLC) region.



HTMs	hole mobility, μ (cm^{2}V^{-1}s^{-1})
TTh101	2.46×10^{-5}
CHC05	2.89×10^{-5}
CHC06	3.44×10^{-5}
CHC07	6.21×10^{-5}
spiro-OMeTAD	1.28×10^{-4}

Figure S6. Mass Spectrum of **CHC05** (MALDI).



D:\Data\Teresa Chen\107\NCU-LU\CHC05\0_G6\1\1Ref

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Comment 2	C100H78N6O8S3 1586.5043

Acquisition Parameter

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Aquisition operation mode	Reflector
Voltage polarity	POS
Number of shots	1000
Name of spectrum used for calibration	
Calibration reference list used	PeptideCalibStandard mono

Instrument Info

User	NCU
Instrument	ATS-00670
Instrument type	autoflex

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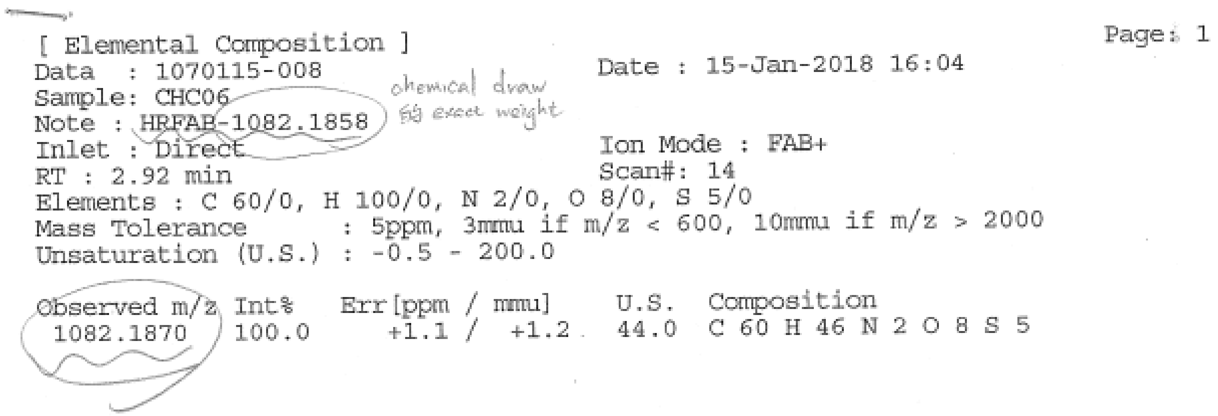
Figure S7. Mass Data of **CHC06** (FAB).



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Sample: CHC06
Note : HRFAB-1082.1858
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RT : 2.92 min                           Scan#: 14
Elements : C 60/0, H 100/0, N 2/0, O 8/0, S 5/0
Mass Tolerance      : 5ppm, 3mmu if m/z < 600, 10mmu if m/z > 2000
Unsaturation (U.S.) : -0.5 - 200.0

Observed m/z  Int%    Err[ppm / mmu]    U.S.  Composition
  1082.1870   100.0      +1.1 /  +1.2   44.0  C 60 H 46 N 2 O 8 S 5
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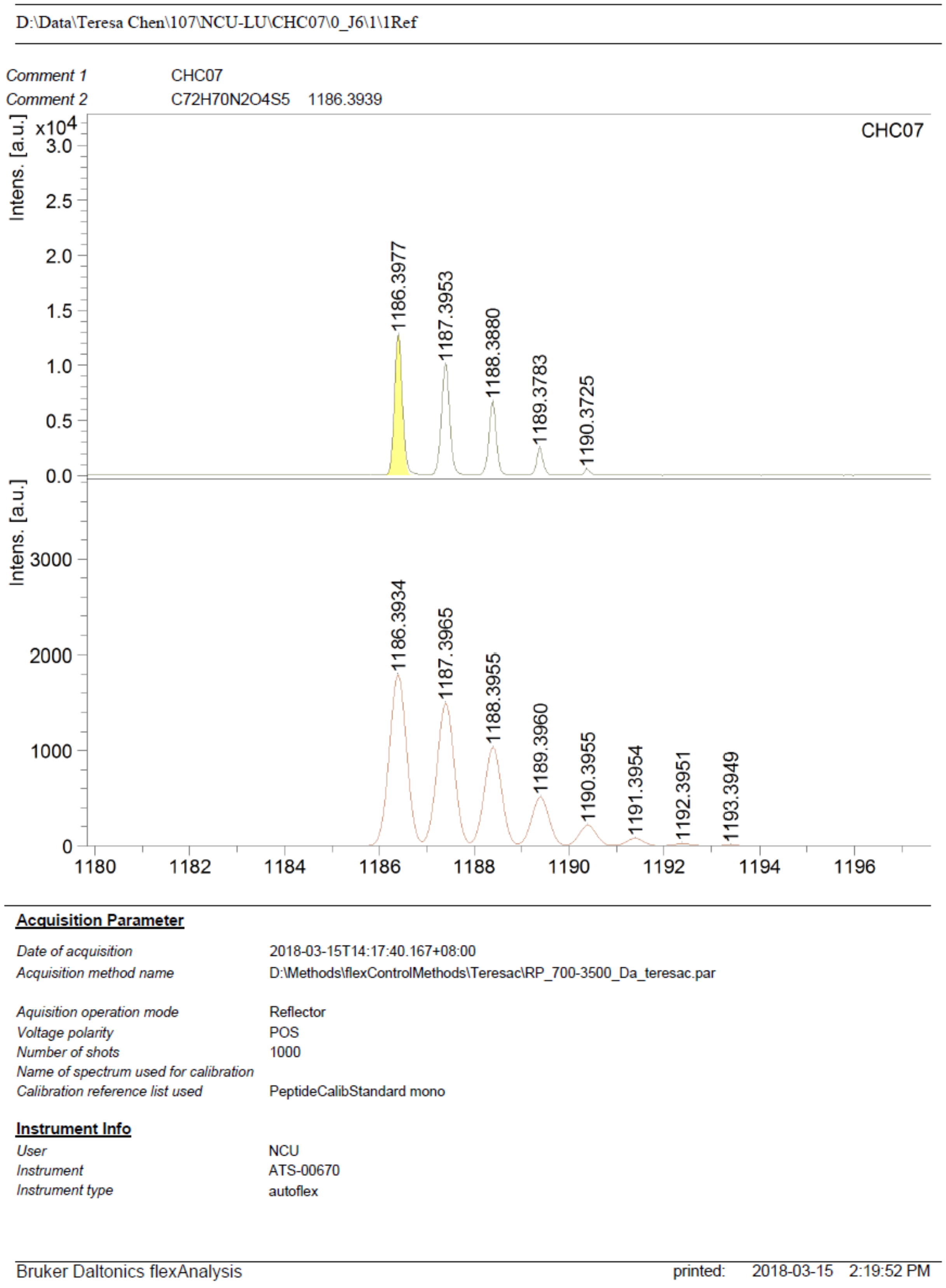
chemical draw
的 exact weight

Figure S8. Mass Spectrum of **CHC07** (MALDI).



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Instrument Info

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Figure S9. ^{1}H NMR Spectrum of **DTT** (500 MHz, $CDCl_3$)

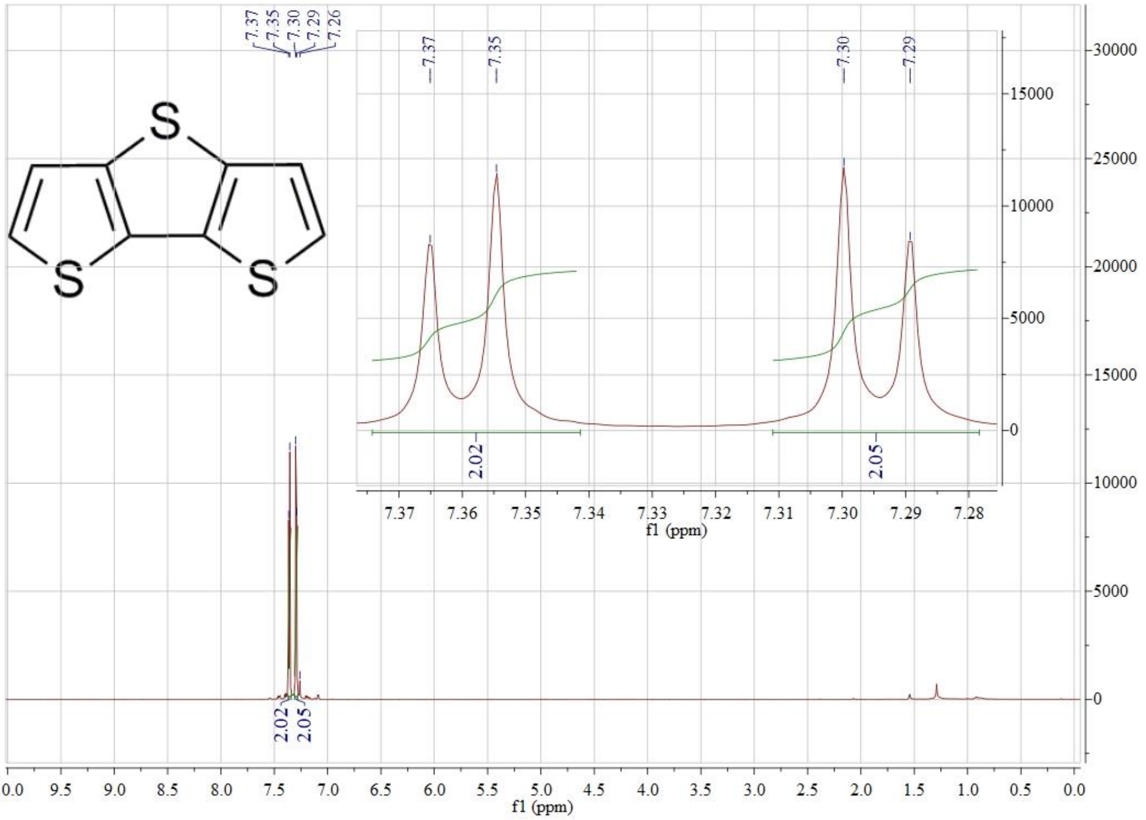

Figure S10. ^{13}C NMR Spectrum of **DTT** (125 MHz, $CDCl_3$)

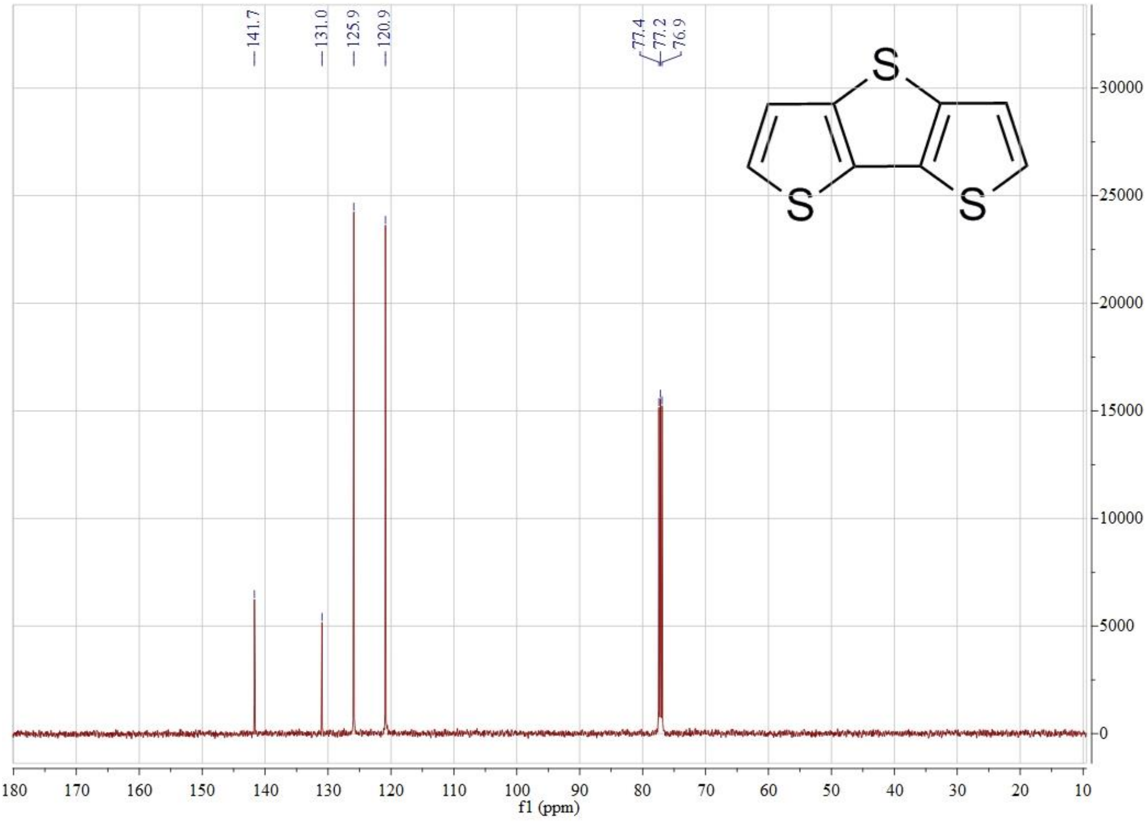

Figure S11. ^{1}H NMR Spectrum of **TTh101** (300 MHz, $CDCl_3$)

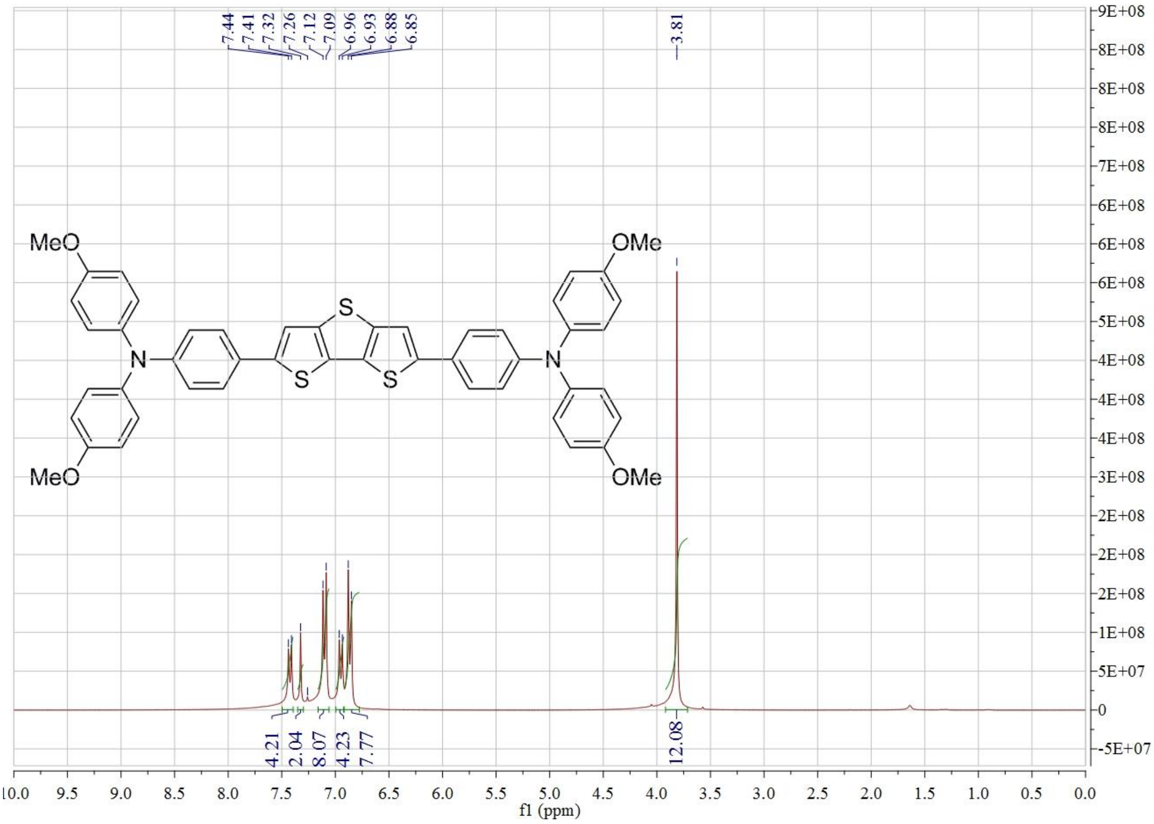

Figure S12. ^{13}C NMR Spectrum of **TTh101** (75 MHz, $CDCl_3$)

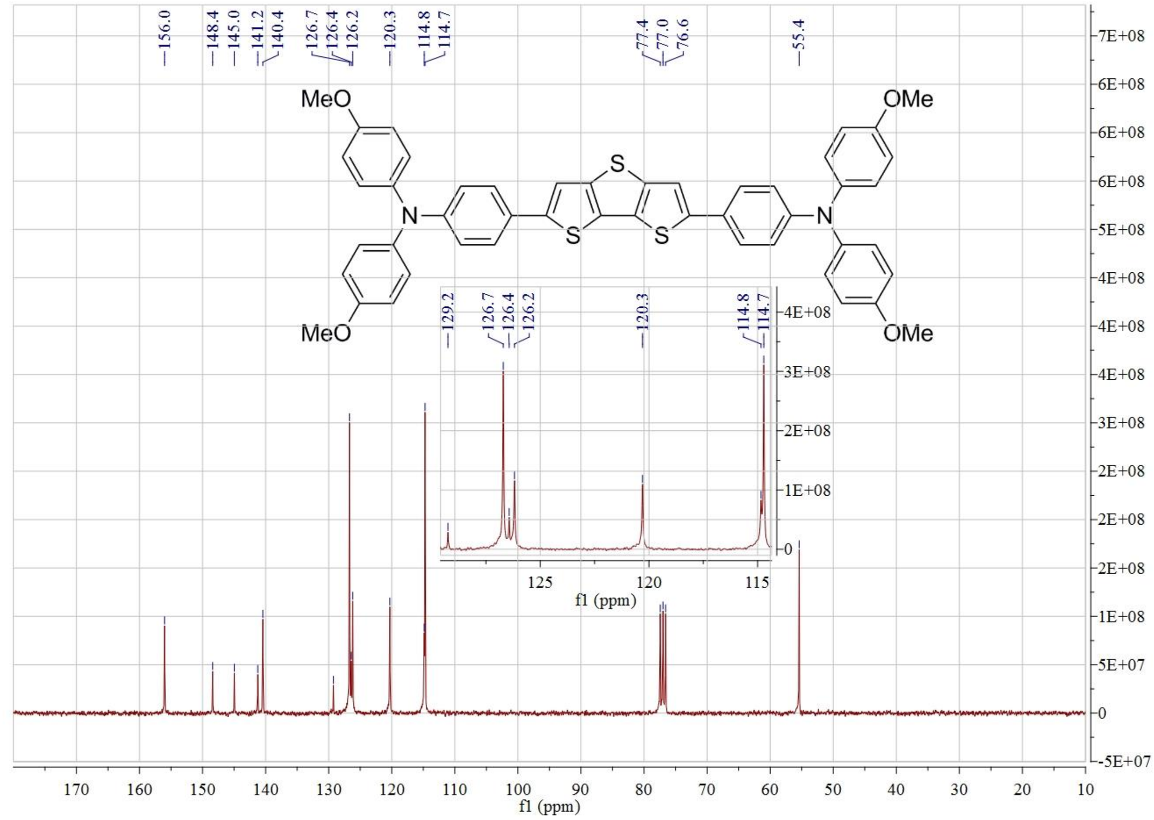

Figure S13. ^{1}H NMR Spectrum of **CHC05** (500 MHz, $CDCl_3$)

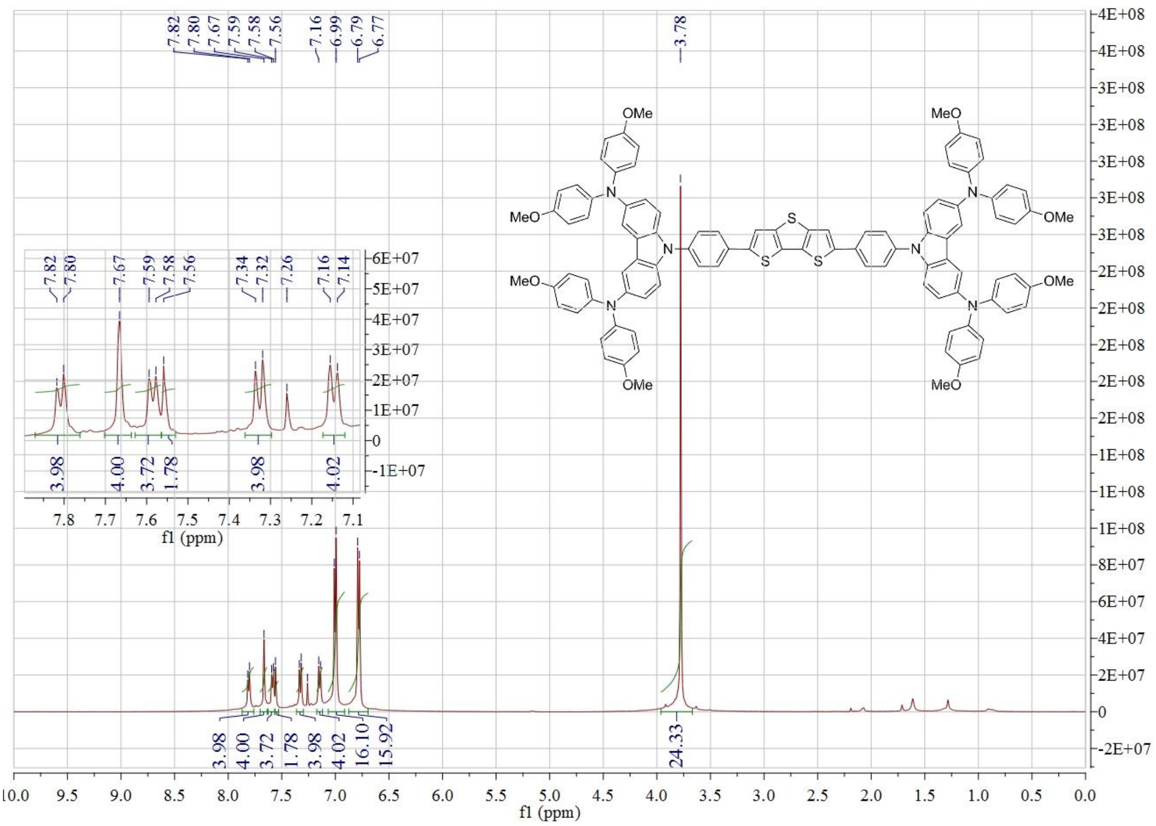

Figure S14. ^{13}C NMR Spectrum of **CHC05** (125 MHz, $CDCl_3$)

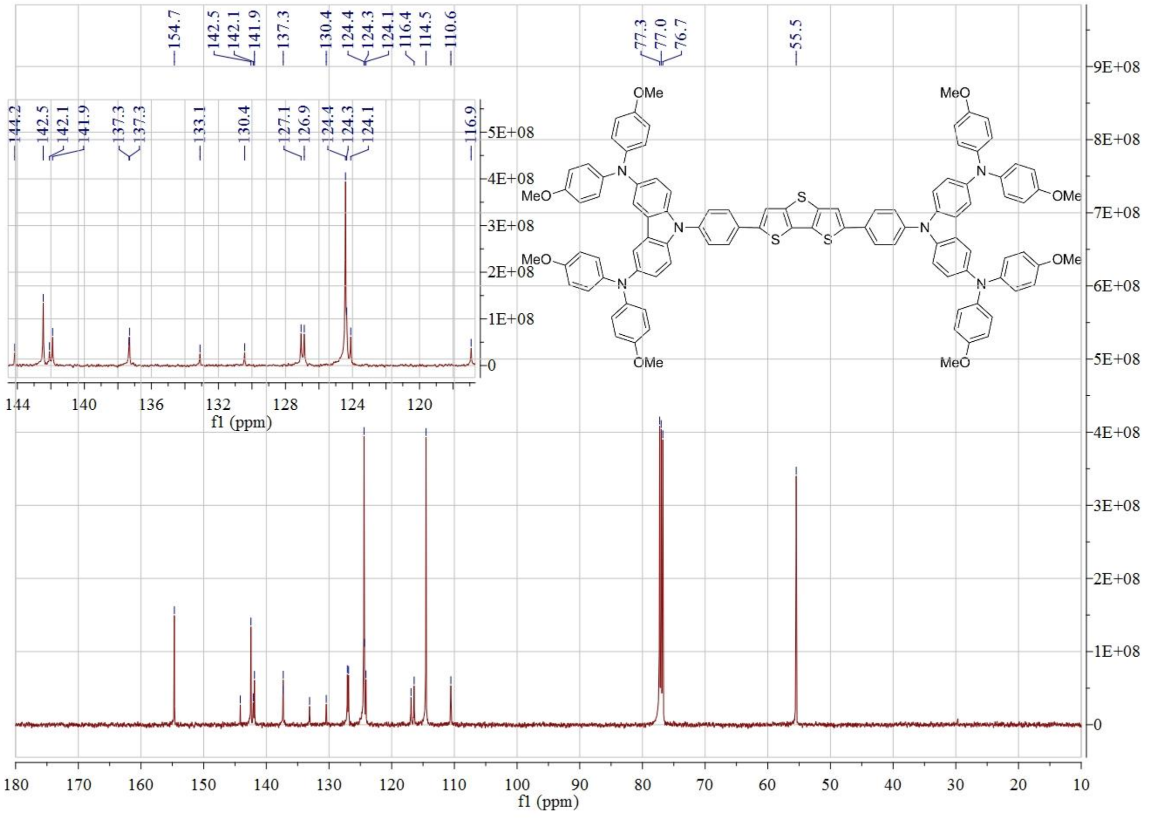

Figure S15. ^{1}H NMR Spectrum of **CHC06** (300 MHz, $CDCl_3$)

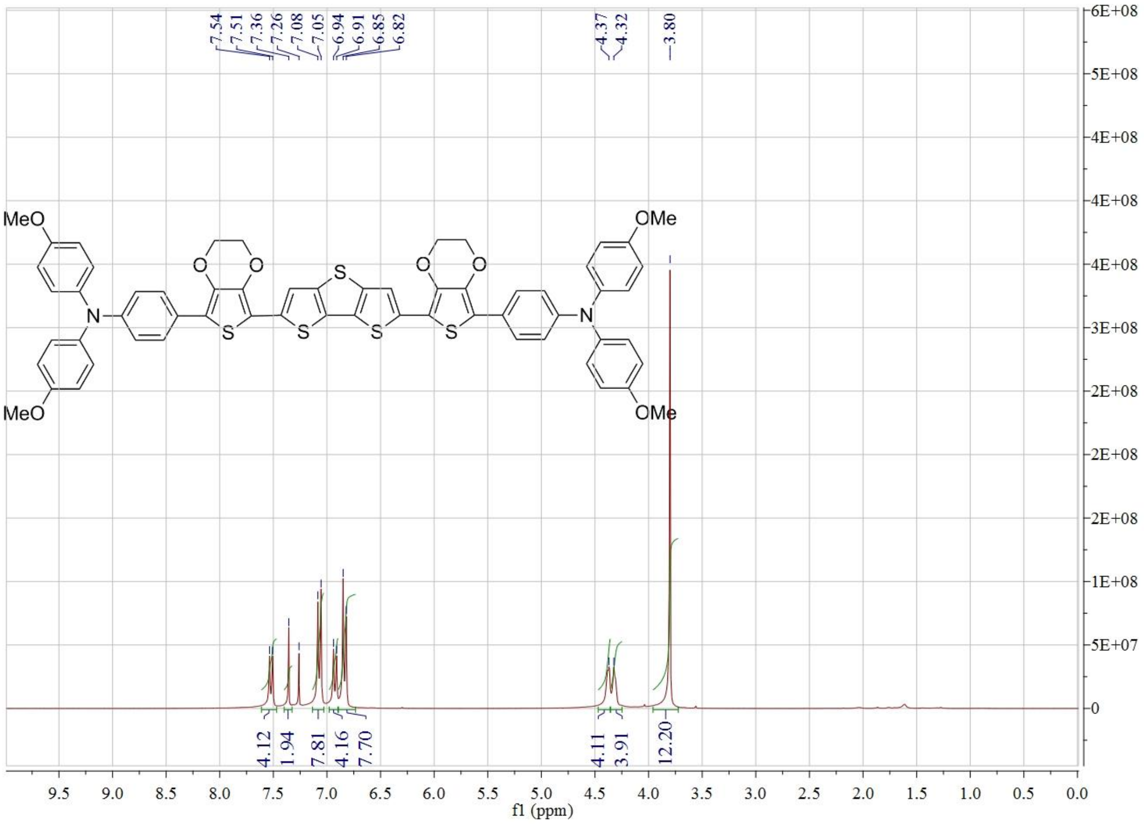

Figure S16. ^{13}C NMR Spectrum of **CHC06** (75 MHz, $CDCl_3$)

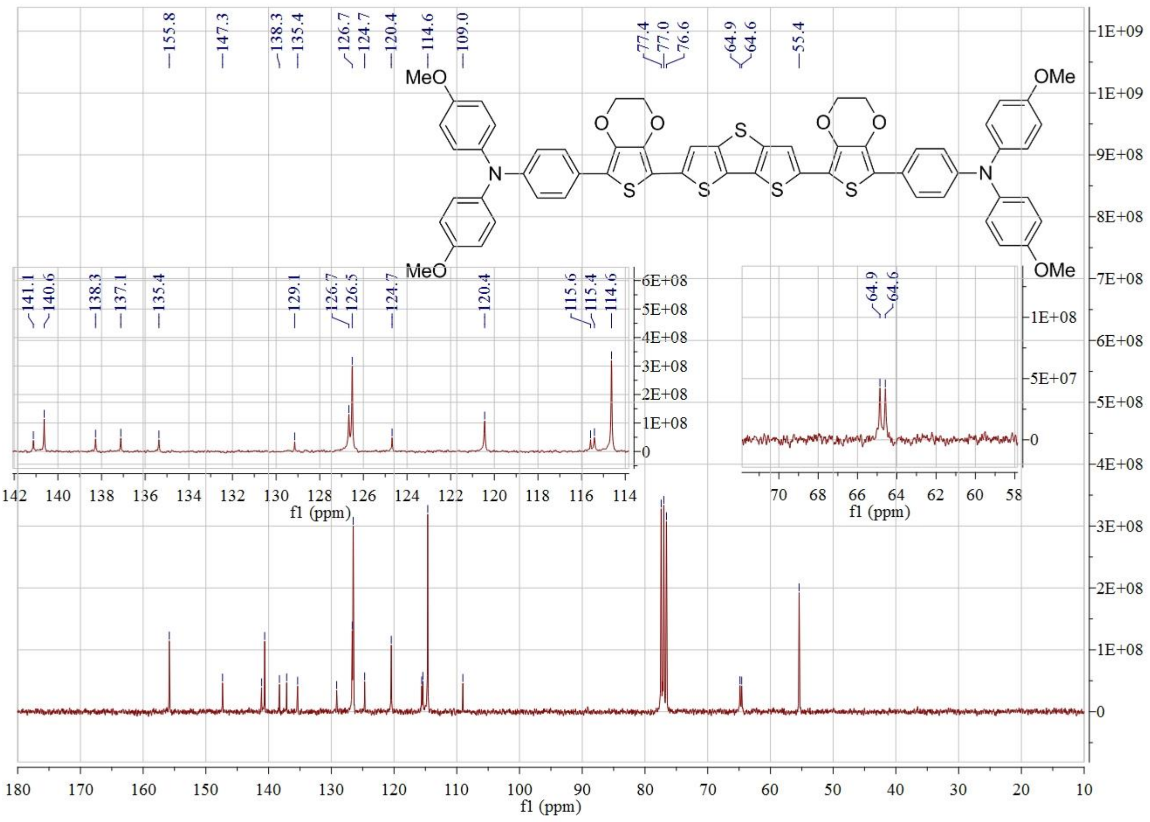

Figure S17. ^{1}H NMR Spectrum of **CHC07** (500 MHz, $CDCl_3$)

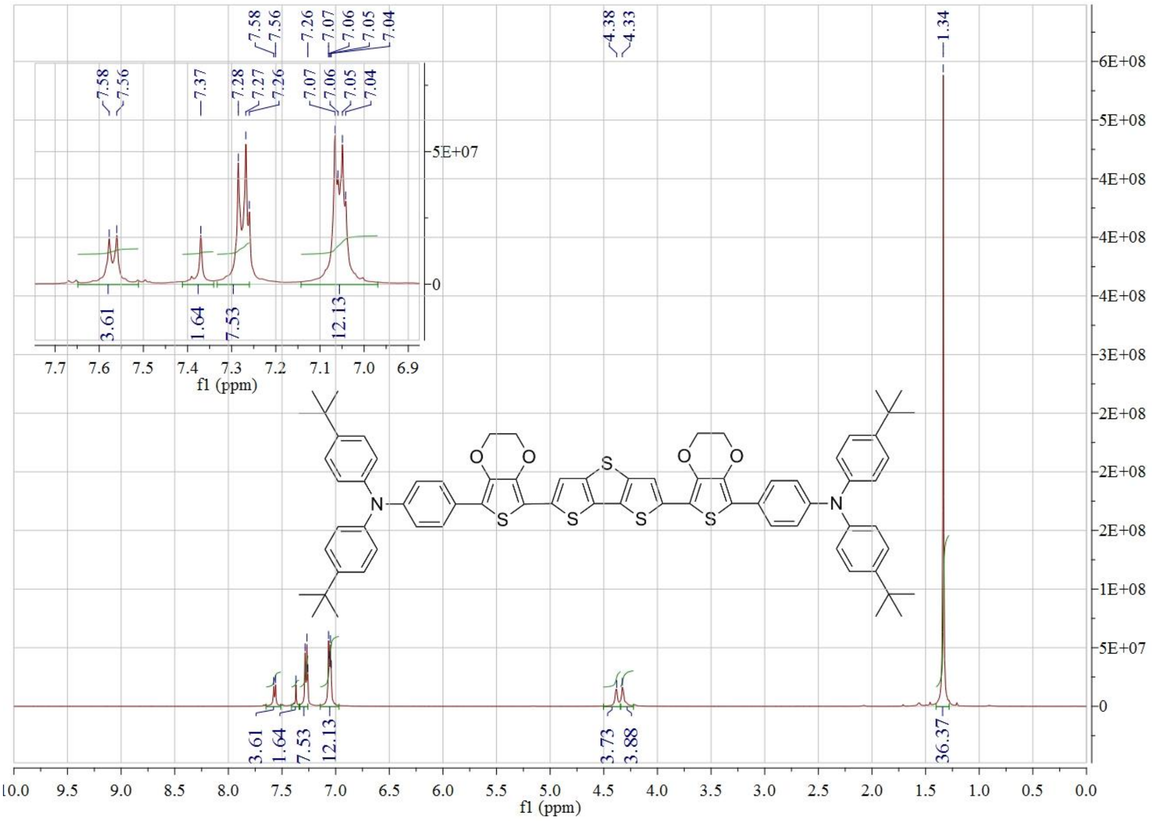

Figure S18. ^{13}C NMR Spectrum of **CHC07** (125 MHz, $CDCl_3$)