Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2014

SUPPORTING INFORMATION TO THE MANUSRIPT

Effects of oligothiophene π-Bridge Length on Physical and Photovoltaic Properties of Star-Shaped Molecules for Bulk Heterojunction Solar Cells

Jie Min*[1], Yuriy N. Luponosov[2], Derya Baran[1], Sergei N. Chvalun[2,3], Maxim A. Shcherbina[2,4], Artem V. Bakirov[3], Petr V. Dmitryakov[3], Svetlana M. Peregudova[5], Nina Kausch-Busies[6], Sergei A. Ponomarenko[2,7], Tayebeh Ameri[1], Christoph J. Brabec[1,8]

[1]Institute of Materials for Electronics and Energy Technology (I-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstraße 7, 91058 Erlangen, Germany
[2]Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences, Profsoyuznaya st. 70, Moscow 117393, Russia
[3]Scientific and Research Centre Kurchatov Institute, 1 Kurchatov square, Moscow, 123182 Russia
[4]Moscow Institute of Physics and Technology, 4 Institutsky line, Dolgoprudny, Moscow region, 141700 Russia
[5]Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova St. 28, Moscow, 119991, Russia
[6]Heraeus Precious Metals GmbH & Co. KG, Conductive Polymers Division (Clevios), Chempark Leverkusen Build. B202, D-51368 Leverkusen, Germany
[7]Chemistry Department, Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russia
[8]Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstraße 2a, 91058 Erlangen, Germany

E-mail: Min.Jie@ww.uni-erlangen.de (J. Min)

CONTENTS

1. Materials synthesis 2

2. ^{1}H, ^{13}C NMR Spectra 8

3. GPC data 30
4. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data 31
5. Cyclovoltammetry analysis (CVA) data 35
6. X-ray diffraction (XRD) data 36
7. Atomic Force Microscopy (AFM) data 42
8. Hole mobility measurements. 46

1. Material synthesis

2-acetylthiophene (2a). A solution of 2-bromothiophene (38 g, 0.23 mol) in 370 mL of dry THF was added dropwise to a suspension of magnesium (5.71 g, 0.24 mol) in 10 mL of THF. The Grignard reagent was refluxed for 2 h, then cooled to room temperature and added dropwise to solution of acetyl chloride (18.3 g, 0.23 mol) and freshly prepared Li_2MnCl_4 (5.83 mmol) in 100 mL of THF at 0 °C. After addition of the Grignard reagent, the cooling bath was removed and stirring was continued for 1 hour. After completion of the reaction, it was poured into 400 mL of distilled water and extracted three times with freshly distilled diethyl ether. The solvent was evaporated in vacuum and the residue was dried at 1 Torr to give the crude product in 90% reaction yield (according to ^{1}H NMR). It was purified by distillation in vacuum (50 mBar, 122 °C) to give pure compound **2a** (24.1 g, 82 %) as a colourless liquid. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 2.56 (s, 3H), 7.12 (dd, 1H, $J_1 = 3.7$, $J_2 = 4.9$ Hz), 7.62 (dd, 1H, $J_1 = 1.2$, $J_2 = 4.9$ Hz), 7.68 (dd, 1H, $J_1 = 1.2$, $J_2 = 3.7$ Hz). Calcd (%) for C_6H_6OS: C, 57.12; H, 4.79; S, 25.41. Found: C, 57.16; H, 4.80; S, 25.31.

2,5,5-trimethyl-2-(2-thienyl)-1,3-dioxane (3a). Compound **2a** (4.5 g, 35.7 mmol) was dissolved in dry benzene (90 mL). After complete dissolution 2,2-dimethyl-1,3-

propanediole (16.6 g, 178 mmol) and p-TosH (1.36 g, 7.1 mmol) were added. Then the mixture was stirred at reflux for 18 hours using a Dean-Starck water separator. After that, the triethylamine (10 ml) was added and the mixture was extracted 3 times with toluene (300 mL). The combined organic phases were dried over sodium sulfate and filtered. The solvent was evaporated in vacuum and the residue was dried at 1 Torr. This crude product was purified by column chromatography on silica gel (eluent toluene : hexane (1:1)) to give pure product (5.38 g, 71%) as a colorless liquid. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 0.64 (s, 3H), 1.22 (s, 3H), 1.66 (s, 3H), 3.39 (d, 2H, J = 11 Hz), 3.65 (d, 2H, J = 11 Hz), 6.92–7.09 (overlapping peaks, 2H), 7.27 (dd, 1H, J_1 = 1.2, J_2 = 4.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* [ppm] 21.88, 22.65, 29.72, 32.42, 71.88, 98.77, 125.47, 125.50, 126.83, 145.57. Calcd (%) for $C_{11}H_{16}O_2S$: C, 62.23; H, 7.60; S, 15.10. Found: C, 62.32; H, 7.64; S, 15.00. MALDI MS: found *m/z* 212.090; calculated for $[M]^+$ 212.087.

2,5,5-trimethyl-2-[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thienyl]-1,3-dioxane (4a). 1.6 M solution of butyllithium (8.83 mL, 14.1 mmol) in hexane was added dropwise to a solution of compound **3a** (3.00 g, 14.1 mmol) in 80 mL of dry THF -78 ºC. Afterwards the reaction mixture was stirred for 60 min at -78 ºC and then IPTMDOB (2.88 mL, 14.1 mmol) was added in one portion. The reaction mixture was stirred for 1h at –78 ºC, then the cooling bath was removed, and the stirring was continued for 1h. After completion of the reaction, 150 mL of freshly distilled diethyl ether and 75 mL of distilled water and 14 mL of 1 M HCl were added to the reaction mixture. The organic phase was separated, washed with water, and dried over sodium sulfate and filtered. The solvent was evaporated to give 4.64 g (97%) of the pure product (purity was 100% according to ^{1}H NMR) as a brown solid. The product was used in the subsequent synthesis without further purification. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 0.61 (s, 3H), 1.21 (s, 3H), 1.32 (s, 12H), 1.64 (s, 3H), 3.36 (d, 2H, J = 11 Hz), 3.63 (d, 2H, J = 11 Hz), 7.05 (d, 1H, *J* = 3.7 Hz), 7.50 (d, 1H, *J* = 3.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* [ppm] 21.80, 22.63, 24.74, 29.71, 32.50, 72.00, 84.09, 98.91, 127.01, 137.14, 152.97. Calcd (%) for $C_{17}H_{27}BO_4S$: C, 60.36; H, 8.05; S, 9.48. Found: C, 60.45; H, 8.10; S, 9.33. MALDI MS: found *m/z* 339.148; calculated for

$[M+H]^+$ 339.180.

***tris*{4-[5'-(2-methyl-1,3-dioxolan-2-yl)-2,2'-bithien-5-yl]phenyl}amine (5a).** In an inert atmosphere, degassed solutions of *tris*(4-bromophenyl)amine (1.64 g, 3.40 mmol) and compound **4a** (4.11 g, 12.1 mmol) in toluene/ethanol mixture (80/8 mL) and 2M solution of aq. Na_2CO_3 (18 mL) were added to $Pd(PPh_3)_4$ (421 mg, 0.36 mmol). The reaction mixture was stirred under reflux for 22 h, and then it was cooled to room temperature and poured into 100 mL of water and 200 mL of toluene. The organic phase was separated, washed with water, dried over sodium sulfate and filtered. The solvent was evaporated in vacuum and the residue was dried at 1 Torr. The product was purified by column chromatography on silica gel (eluent toluene) to give pure compound **5** (2.53 g, 85%) as a yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 1.67 (s, 9H), 1.23 (s, 9H), 1.69 (s, 9H), 3.41 (d, 6H, J = 11 Hz), 3.71 (d, 6H, J = 11 Hz), 6.94 (d, 3H, *J* = 3.7 Hz), 7.06–7.17 (overlapping peaks, 9H), 7.47 (d, 6H, *J* = 8.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] 21.94, 22.70, 29.76, 32.27, 71.98, 98.71, 122.18, 124.41, 126.60, 127.44, 129.27, 144.03, 144.33, 146.49. Calcd (%) for $C_{51}H_{57}NO_6S_3$: C, 69.91; H, 6.56; N, 1.60; S, 10.98. Found: C, 69.68; H, 6.61; N, 1.45; S, 10.65. MALDI MS: found *m/z* 760.831; calculated for $[M]^+$ 761.149.

1,1',1''-[nitrilo*tris*(4,1-phenylenethiene-5,2-diyl)]triethanone (6a). 1M HCl (3.42 mL) was added to a solution of compound **5a** (1.00 g, 1.1 mmol) in THF (20 mL) and then the reaction mixture was stirred for 3 hours at reflux. During the reaction, the product was gradually formed as yellow precipitate. After completion of the reaction the organic phase was separated using diethyl ether, washed with water and filtered off to give pure compound **6a** (0.73 g, 95%) as yellow crystals. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 2.56 (9H, s), 7.14 (d, 6H, *J* = 8.5 Hz), 7.27 (3H, d, *J* = 3.7 Hz), 7.56 (d, 6H, *J* = 7.9 Hz), 7.64 (d, 3H, *J* = 4.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] 26.69, 123.53, 124.58, 124.76, 127.61, 128.79, 133.80, 142.83, 147.51, 152.41, 190.64. Calcd (%) for $C_{36}H_{27}NO_3S_3$: C, 69.99; H, 4.41; N, 2.27; S, 15.57. Found: C, 70.02; H, 4.58; N, 2.22; S, 15.33. MALDI MS: found *m/z* 616.878; calculated for $[M]^+$ 617.115.

2,2',2''-[nitrilo*tris*(4,1-phenylenethiene-5,2-diyleth-1-yl-1-

ylidene)]trimalononitrile N(Ph-1T-DCN-Me)$_3$. Compound **6a** (0.92 g, 1.4 mmol), malononitrile (0.54 g, 8.2 mmol) and dry pyridine (25 mL) were placed in a reaction vessel and stirred under argon atmosphere for 8 hours at 105 ºC using the microwave heating. After completeness of the reaction, the pyridine was evaporated in vacuum and the residue was dried at 1 Torr. This crude product was purified by column chromatography on silica gel (eluent dichloromethane). Further purification included precipitation of the product from its THF solution with toluene and hexane to give pure product as a black solid (0.86 g, 82%). ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 2.69 (9H, s), 7.16 (d, 6H, J = 8.5 Hz), 7.87 (d, 3H, J = 4.3 Hz), 7.59 (d, 6H, J = 8.5 Hz), 8.00 (d, 3H, J = 4.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] 23.15, 113.97, 114.50, 124.43, 124.77, 127.80, 135.46, 136.43, 147.67, 153.20, 161.47. Calcd (%) for $C_{45}H_{27}N_7S_3$: C, 70.94; H, 3.57; N, 12.87; S, 12.62. Found: C, 70.93; H, 3.49; N, 12.77; S, 12.63. MALDI MS: found *m/z* 760.831; calculated for $[M]^+$ 761.149.

1-(2,2':5',2''-terthien-5-yl)heptan-1-one (2d). Compound **2d** was obtained by the method described above for compound **2a** using 5-bromo-2,2':5',2''-terthiophene (7.87 g, 24.0 mmol), magnesium (0.59 g, 24.8 mmol), heptanoyl chloride (3.57 g, 24.0 mmol) and freshly prepared Li_2MnCl_4 (0.6 mmol) to give the crude product in 71% reaction yield (according to ^{1}H NMR). It was purified by a column chromatography on silica gel (eluent toluene) to give pure product (5.55 g, 64 %) as a yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 0.88 (t, 3H, J = 6.7 Hz), 1.20 – 1.44 (overlapping peaks, 6H), 1.73 (m, 2H, M = 5, J = 7.3 Hz), 2.85 (t, 2H, J = 7.3 Hz), 7.01 (dd, 1H, J_1 = 3.7, J_2 = 5.5 Hz), 7.09 (d, 1H, J = 3.7 Hz), 7.14 (d, 1H, J = 3.7 Hz), 7.17 – 7.23 (overlapping peaks, 2H), 7.24 (dd,1H, J_1 = 1.2, J_2 = 4.9 Hz), 7.58 (d, 1H, J = 3.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] 14.03, 22.49, 24.86, 29.01, 31.59, 39.03, 123.89, 124.24, 124.52, 125.11, 126.17, 127.99, 132.53, 134.92, 136.57, 138.32, 142.29, 144.89, 193.14. Calcd (%) for $C_{19}H_{20}OS_3$: C, 63.29; H, 5.59; S, 26.68. Found: C, 63.34; H, 5.61; S, 26.59.

2-hexyl-2-(2,2':5',2''-terthien-5-yl)-1,3-dioxolane (3d). Compound **10** (8.4 g, 23.3 mmol) was dissolved in dry benzene (350 mL). After complete dissolution, ethylene glycol (65 mL, 1.16 mol) and p-TosH (0.89 g, 4.7 mmol) were added. Then the mixture was stirred at reflux for 18 hours using a Dean-Starck water separator. After that, the equivalent amount of saturated aqueous sodium bicarbonate (4.7 mmol) water solution was added and the mixture was extracted 3 times with toluene (300 mL). The combined organic phases were dried over sodium sulfate and filtered. The solvent was evaporated in vacuum and the residue was dried at 1 Torr. This crude product was purified by column chromatography on silica gel (eluent toluene) to give pure product (8.22 g, 87%) as a yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 0.85 (t, 3H, $J = 6.7$ Hz), 1.18 – 1.49 (overlapping peaks, 8H), 1.99 (t, 2H, $J = 7.3$ Hz), 3.91–4.11 (overlapping peaks, 4H), 6.89 (dd,1H, $J_1 = 1.8$, $J_2 = 3.7$ Hz), 6.96 – 7.11 (overlapping peaks, 4H), 7.15 (dd, 1H, $J_1 = 1.0$, $J_2 = 3.7$ Hz), 7.20 ($J_1 = 1.0$, $J_2 = 5.5$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* [ppm] 14.06, 22.55, 23.67, 29.26, 31.72, 40.56, 65.00, 108.99, 123.31, 123.64, 124.08, 124.28, 124.43, 125.09, 127.85, 136.11, 136.18, 136.58, 137.10, 145.94. Calcd (%) for $C_{21}H_{24}O_2S_3$: C, 62.34; H, 5.98; S, 23.77. Found: C, 62.44; H, 6.04; S, 23.63. HRESIMS: found *m/z* 427.0828; calculated for $[M+Na]^+$ 427.0831.

2-[5''-(2-hexyl-1,3-dioxolan-2-yl)-2,2':5',2''-terthien-5-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d) was obtained by the method described above for compound **4a** using compound **3d** (8.08 g, 20.00 mmol), 1.6 M solution of n-butyllthium (12.50 mL, 20.00 mmol) in hexane, IPTMDOB (4.10 mL, 20.00 mmol) to give pure compound **4d** (10.4 g, 98%) as green crystals. The product was used in the subsequent synthesis without further purification. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 0.86 (t, 3H, $J = 6.7$ Hz), 1.25 – 1.44 (overlapping peaks with maximum at 1.34 ppm, 20H), 1.99 (t, 2H, $J = 7.3$ Hz), 3.95–4.07 (overlapping peaks, 4H), 6.89 (d, 1H, $J = 3.7$ Hz), 7.01 (d, 1H, $J = 3.1$ Hz), 7.02 (d, 1H, $J = 3.1$ Hz), 7.11 (d, 1H, $J = 3.7$ Hz), 7.21 (d, 1H, $J = 3.7$ Hz), 7.51 (d, 1H, $J = 3.7$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* [ppm] 14.05, 22.54, 23.66, 24.73, 29.24, 31.71, 40.55, 65.00, 84.18, 108.98, 123.48, 124.22, 124.79, 124.98, 125.11, 135.93, 136.47, 136.85, 137.95, 143.74, 146.14. Calcd (%) for $C_{27}H_{35}BO_4S_3$: C, 61.12; H, 6.65; S, 18.13. Found: C, 61.24; H, 6.70; S, 18.00.

***tris*{4-[5''-(2-hexyl-1,3-dioxolan-2-yl)-2,2':5',2''-terthien-5-**

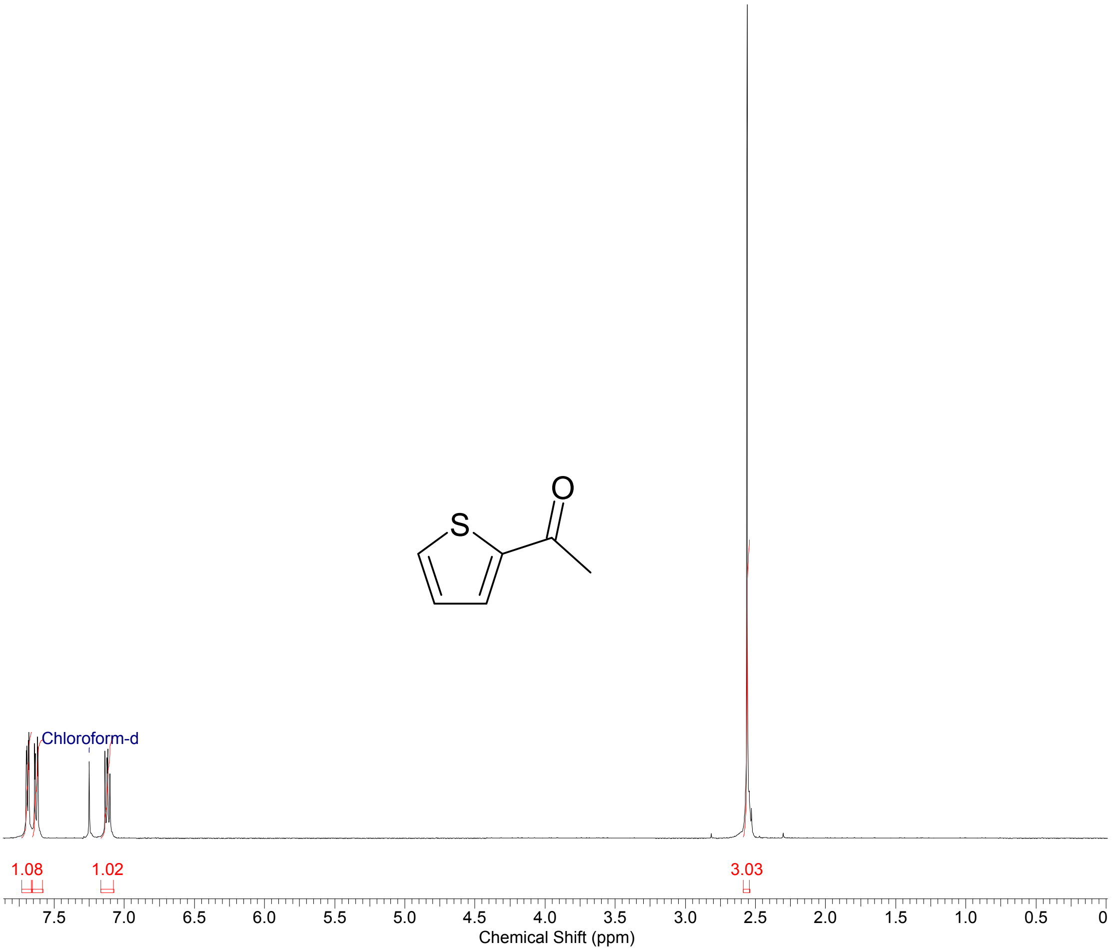
yl]phenyl}amine (**5d)** was obtained by the method described above for compound **5** using compound **4d** (4.99 g, 9.41 mmol), *tris*(4-bromophenyl)amine (1,26 g, 2.61 mmol), $Pd(PPh_3)_4$ (326 mg, 0.28 mmol) and aq. 2M Na_2CO_3 (14 ml) The crude product was purified by column chromatography on silica gel (eluent toluene) to give pure compound **5d** (3.13 g, 82%) as yellow solid.^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 0.85 (t, 9H, J = 6.7 Hz), 1.22-1.47 (overlapped peaks, 24H), 2.00 (t, 6H, J = 7.3 Hz), 3.92–4.09 (overlapped peaks, 12H), 6.89 (d, 3H, J = 3.7 Hz), 6.98–7.09 (overlapped peaks, 9H), 7.11–7.18 (overlapped peaks, 12H), 7.48 (d, 6H, J = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] 14.05, 22.56, 23.68, 29.27, 31.72, 40.57, 65.03, 109.02, 123.20, 123.33, 124.05, 124.18, 124.44, 124.58, 125.12, 126.55, 128.93, 135.82, 136.11, 136.21, 136.61, 142.84, 146.03, 146.45. Calcd (%) for $C_{81}H_{81}NO_6S_9$: C, 66.95; H, 5.62; N, 0.96; S, 19.86. Found: C, 70.06; H, 5.66; N, 0.91; S, 19.71. HRESIMS: found *m/z* 1452.3596; calculated for $[M+H]^+$ 1452.3623.

1,1',1''-[nitrilotris(4,1-phenylene-2,2':5',2''-terthiene-5'',5-diyl)]triheptan-1-one (**6d)** was obtained by the method described above for compound **6a** using compound **5d** (2.18 g, 1.5 mmol), 1M HCl (4.50 mL) and THF (70 ml). After the completeness of the reaction the organic phase was separated, washed with water and filtered off to give pure product (1.97 g, 99%) as orange crystals. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 0.88 (t, 9H, J = 6.7 Hz), 1.23-1.43 (overlapped peaks, 18H), 1.74 (m, 6H, M = 5, J = 7.3 Hz), 2.86 (t, 6H, J = 7.3 Hz) 7.10–7.20 (overlapped peaks, 18H), 7.22 (d, 3H, J = 4.3 Hz), 7.49 (d, 6H, J = 8.5 Hz), 7.58 (d, 3H, J = 4.3 Hz). Calcd (%) for $C_{75}H_{69}NO_3S_9$: C, 68.20; H, 5.27; N, 1.06; S, 21.85. Found: C, 68.25; H, 5.29; N, 0.89; S, 21.63.

2,2',2''-[nitrilotris(4,1-phenylene-2,2':5',2''-terthiene-5'',5-diylhept-1-yl-1-ylidene)]trimalononitrile (**N(Ph-3T-DCN-Hex)$_3$)** was obtained by the method described above for **N(Ph-1T-DCN-Me)$_3$** using compound **6d** (1.80 g, 1.4 mmol) and malononitrile (1.08 g, 16.4 mmol). The crude product was purified by column chromatography on silica gel (eluent toluene:THF, 10:1). Further purification included precipitation of the product from its THF solution with toluene and hexane to give pure product as a black solid (1.7 g, 84%). ^{1}H NMR (250 MHz, $CDCl_3$): δ

[ppm] 0.89 (t, 9H, J = 6.7 Hz), 1.29-1.37 (overlapped peaks, 12H), 1.46 (m, 6H, M = 5, J = 7.3 Hz), 1.68 (m, 6H, M = 5, J = 7.3 Hz), 2.89 (t, 6H, J = 7.3 Hz), 7.10 (d, 6H, J = 3.7 Hz), 7.12-7.18 (overlapped peaks, 9H), 7.21 (d, 3H, J = 4.2 Hz), 7.26 (d, 3H, J = 3.7 Hz), 7.47 (d, 6H, J = 8.6 Hz), 7.91 (d, 3H, J = 4.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] 13.98, 22.43, 29.21, 30.44, 31.26, 37.48, 113.84, 114.67, 123.41, 124.45, 124.81, 125.64, 126.63, 127.37, 128.66, 133.43, 134.87, 135.14, 135.18, 139.77, 144.01, 146.32, 146.55, 166.20. Calcd (%) for $C_{84}H_{69}N_7S_9$: C, 68.86; H, 4.75; N, 6.69; S, 19.70. Found: C, 68.06; H, 5.66; N, 0.91; S, 19.71. HRESIMS: found m/z 1452.3596; calculated for $[M+H]^+$ 1452.3623.

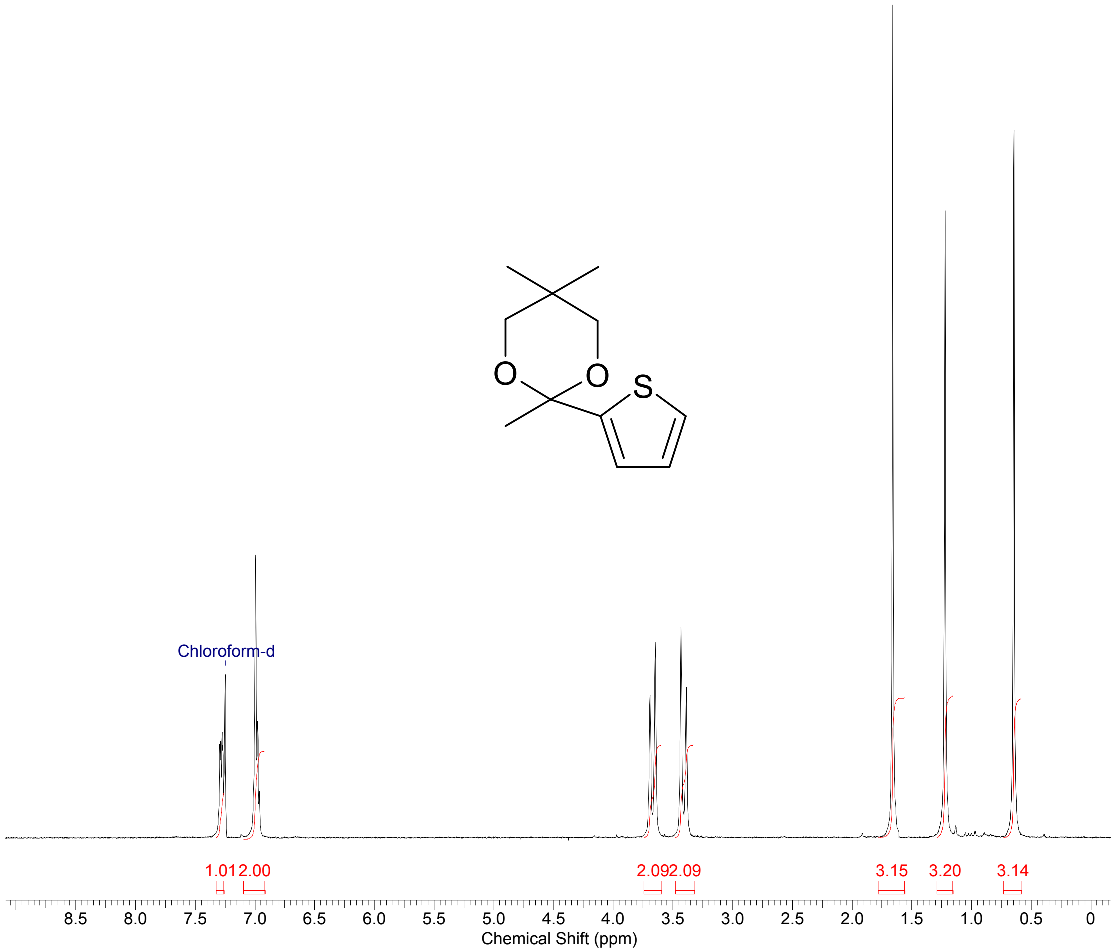
2. ^{1}H, ^{13}C NMR Spectra



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[2.54 .. 2.59]	3.030	6.88241e+6
2	[7.08 .. 7.17]	1.020	2.31650e+6
3	[7.58 .. 7.66]	1.000	2.27137e+6
4	[7.66 .. 7.73]	1.077	2.44575e+6

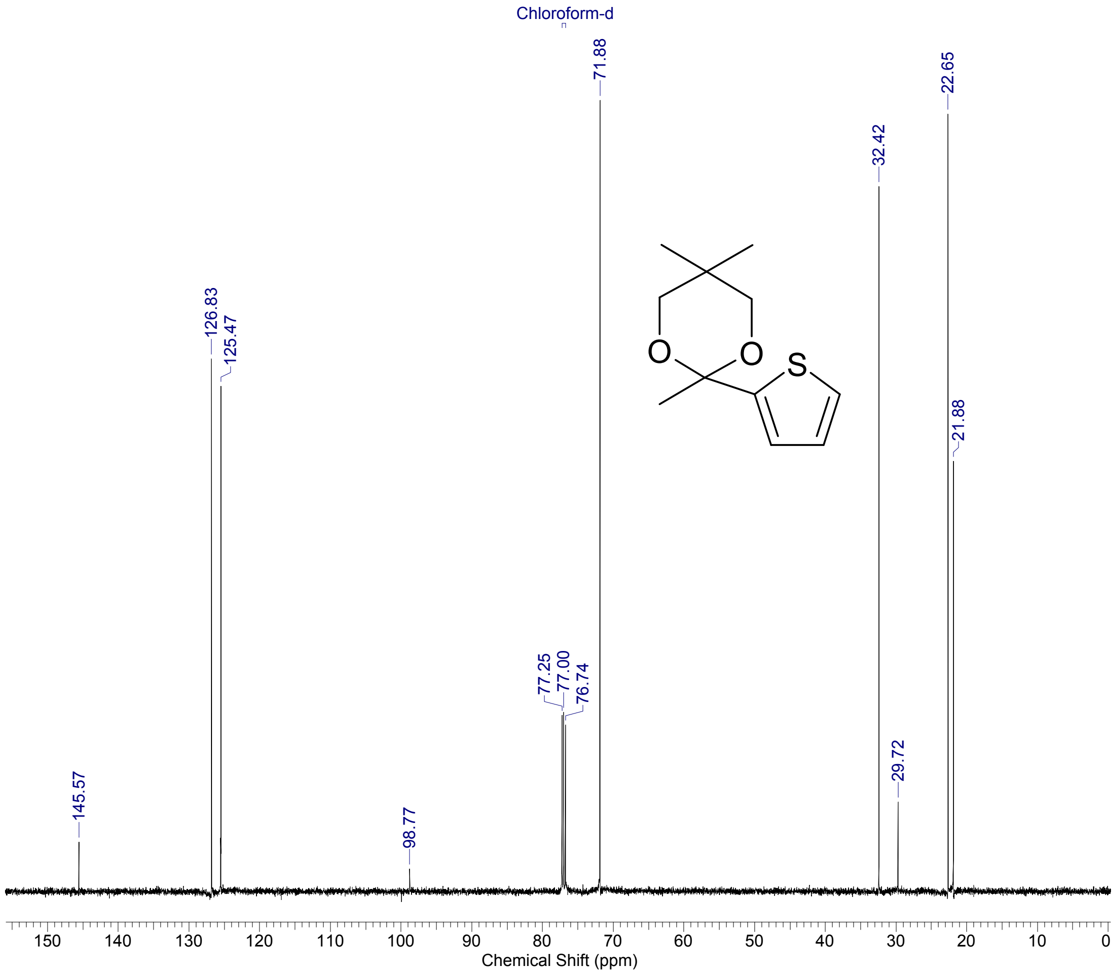
Figure S1. ^{1}H NMR spectrum of compound **2a** in CDCl$_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.59 .. 0.73]	3.137	1.33806e+7
2	[1.16 .. 1.29]	3.199	1.36429e+7
3	[1.56 .. 1.78]	3.153	1.34475e+7
4	[3.32 .. 3.48]	2.095	8.93311e+6
5	[3.60 .. 3.74]	2.089	8.90731e+6
6	[6.92 .. 7.09]	2.000	8.52982e+6
7	[7.26 .. 7.32]	1.006	4.28868e+6

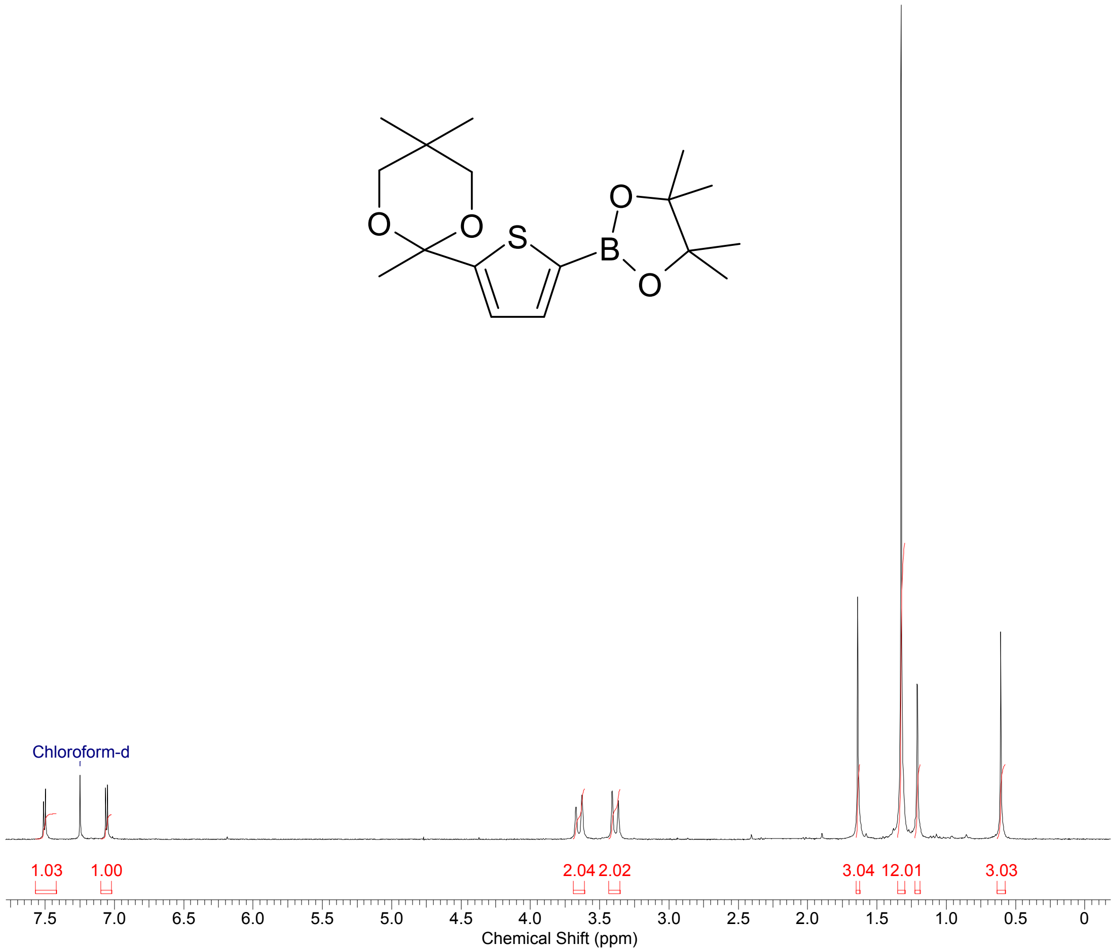
Figure S2. ^{1}H NMR spectrum of compound **3a** in CDCl$_3$



No.	(ppm)	(Hz)	Height
1	21.88	2751.9	0.5439
2	22.65	2849.1	0.9833
3	29.72	3738.1	0.1131
4	32.42	4077.2	0.8911
5	71.88	9040.9	1.0000
6	76.74	9651.3	0.2101
7	77.00	9684.3	0.2265
8	77.25	9715.5	0.2228
9	98.77	12422.8	0.0283
10	125.47	15780.9	0.6388
11	125.50	15784.5	0.5153
12	126.83	15951.3	0.6732
13	145.57	18308.6	0.0622

No.	Annotation	(ppm)
1	Chloroform-d	[76.74 .. 77.25]

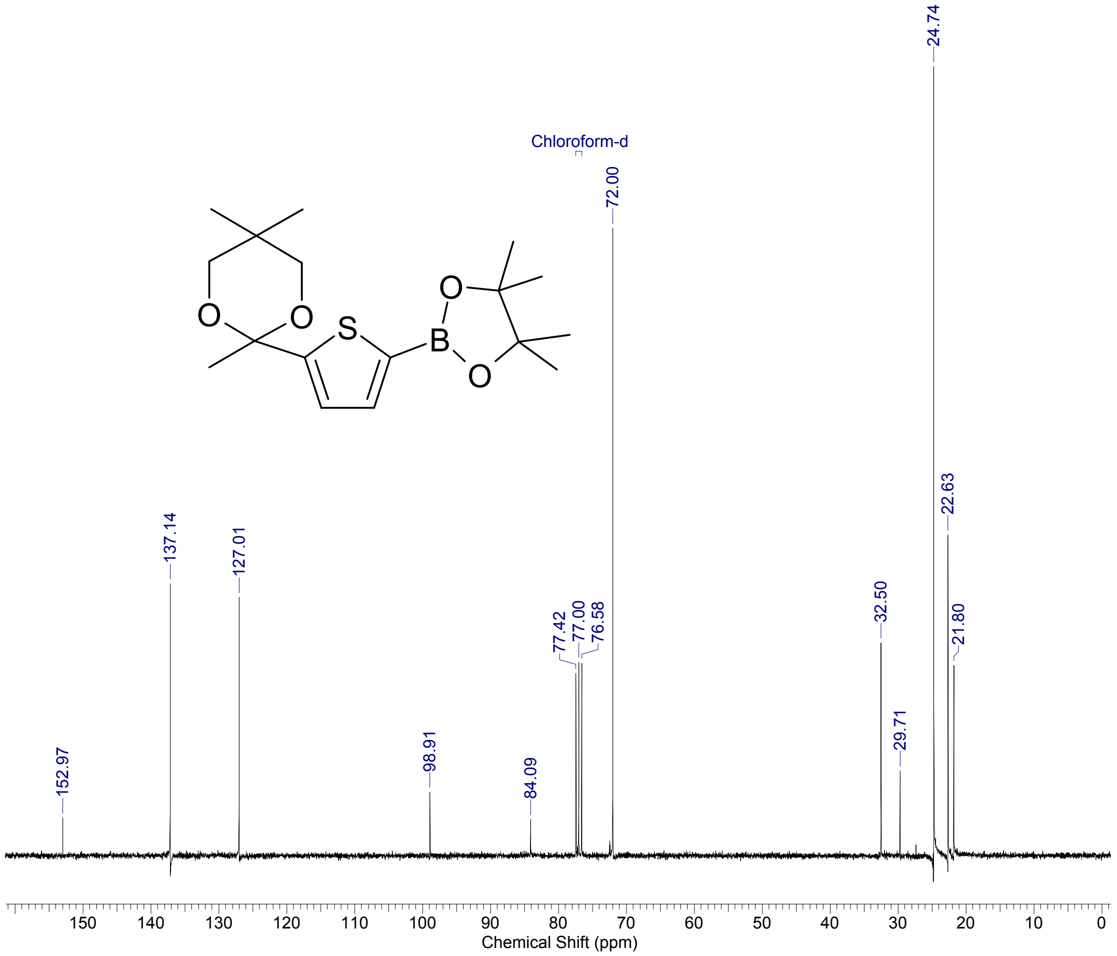
Figure S3. ^{13}C NMR spectrum of compound **3a** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.58 .. 0.63]	3.026	2.28664e+6
2	[1.19 .. 1.23]	3.031	2.29044e+6
3	[1.30 .. 1.35]	12.005	9.07297e+6
4	[1.62 .. 1.65]	3.035	2.29381e+6
5	[3.35 .. 3.43]	2.022	1.52824e+6
6	[3.61 .. 3.69]	2.041	1.54221e+6
7	[7.02 .. 7.10]	1.000	7.55749e+5
8	[7.42 .. 7.57]	1.030	7.78564e+5

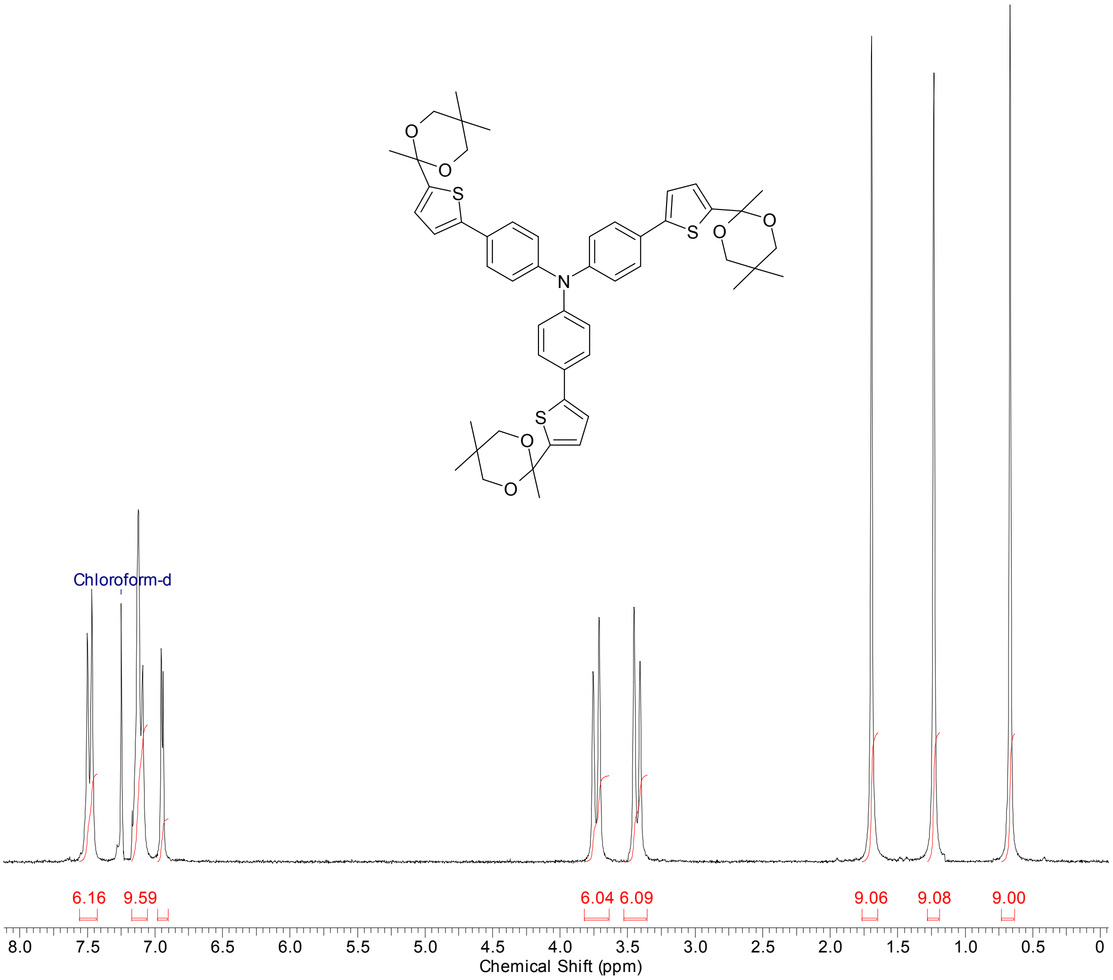
Figure S4. ^{1}H NMR spectrum of compound **4a** in $CDCl_3$



No.	(ppm)	(Hz)	Height
1	21.80	1645.6	0.2454
2	22.63	1708.1	0.3985
3	24.74	1867.6	1.0000
4	29.71	2242.2	0.1217
5	32.50	2453.0	0.2716
6	72.00	5434.2	0.7585
7	76.58	5779.6	0.2479
8	77.00	5811.5	0.2490
9	77.42	5843.4	0.2363
10	84.09	6347.0	0.0645
11	98.91	7465.1	0.0966
12	127.01	9586.2	0.3256
13	137.14	10350.6	0.3416
14	152.97	11545.0	0.0663

No.	Annotation	(ppm)
1	Chloroform-d	[76.58 .. 77.42]

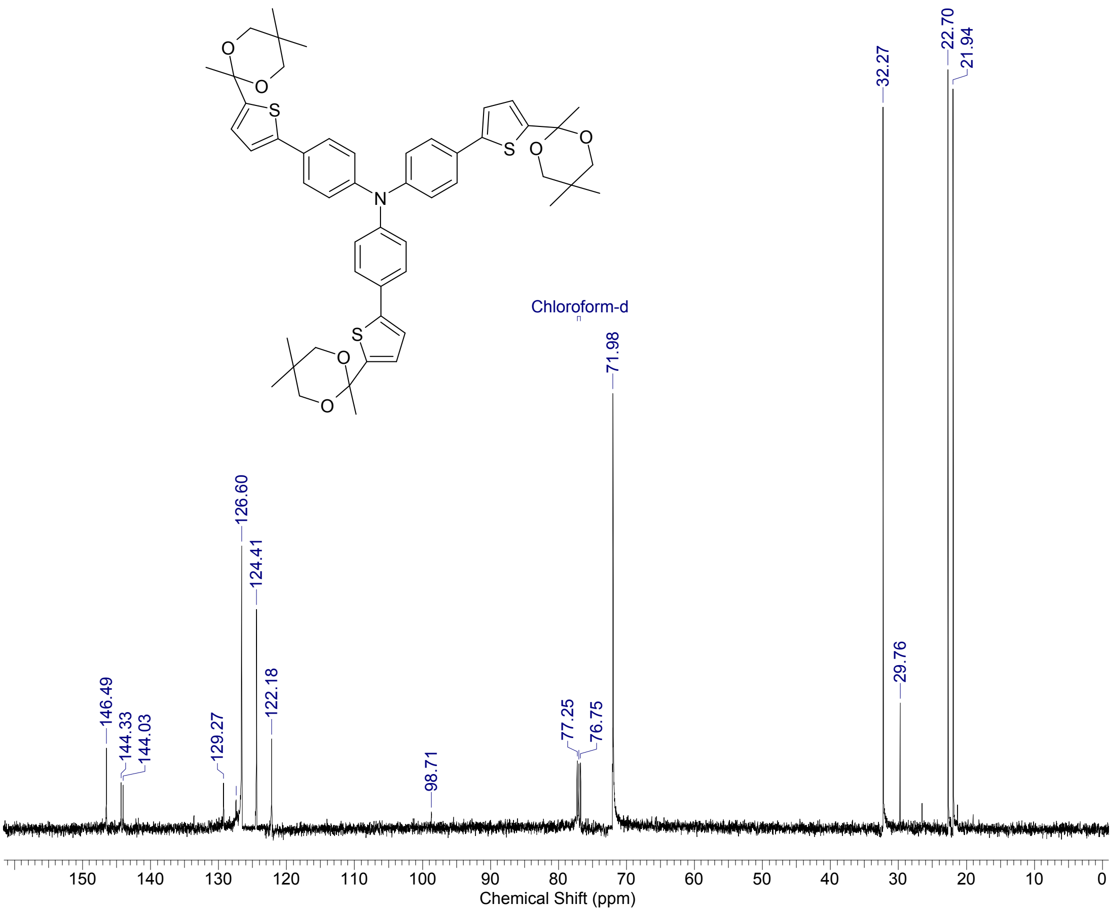
Figure S5. ^{13}C NMR spectrum of compound **4a** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.63 .. 0.73]	8.999	1.81593e+7
2	[1.19 .. 1.28]	9.079	1.83214e+7
3	[1.65 .. 1.76]	9.055	1.82723e+7
4	[3.36 .. 3.53]	6.091	1.22901e+7
5	[3.64 .. 3.82]	6.044	1.21957e+7
6	[6.90 .. 6.98]	3.000	6.05371e+6
7	[7.06 .. 7.17]	9.592	1.93550e+7
8	[7.43 .. 7.56]	6.162	1.24342e+7

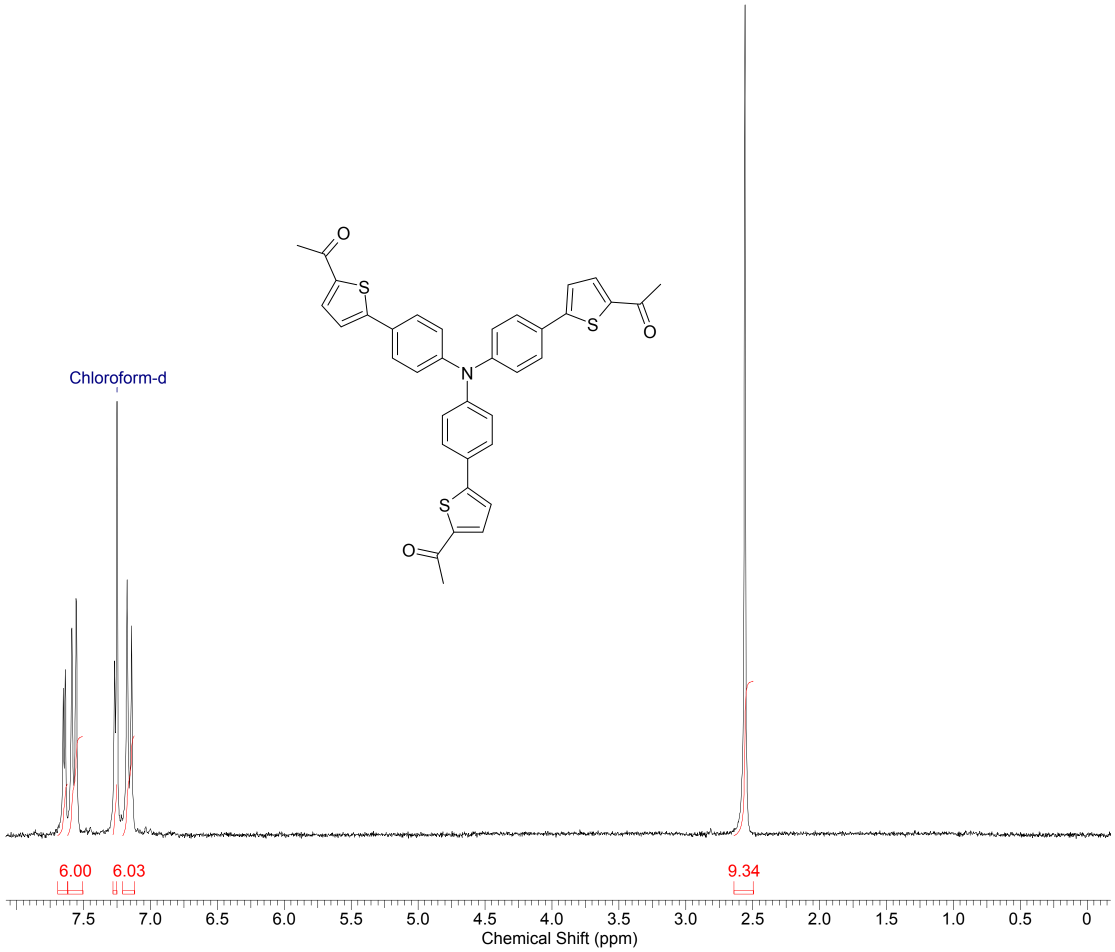
Figure S6. ^{1}H NMR spectrum of compound **5a** in $CDCl_3$



No.	(ppm)	(Hz)	Height
1	21.94	2759.6	0.9742
2	22.70	2855.1	1.0000
3	29.76	3743.3	0.1649
4	32.27	4058.2	0.9507
5	71.98	9052.8	0.5732
6	76.75	9652.6	0.0864
7	77.00	9684.4	0.0844
8	77.25	9716.3	0.0889
9	98.71	12414.4	0.0210
10	122.18	15367.2	0.1175
11	124.41	15646.8	0.2885
12	126.60	15922.8	0.3720
13	127.44	16028.9	0.0373
14	129.27	16258.9	0.0593
15	144.03	18114.9	0.0566
16	144.33	18152.0	0.0600
17	146.49	18424.5	0.1054

No.	Annotation	(ppm)
1	Chloroform-d	[76.75 .. 77.25]

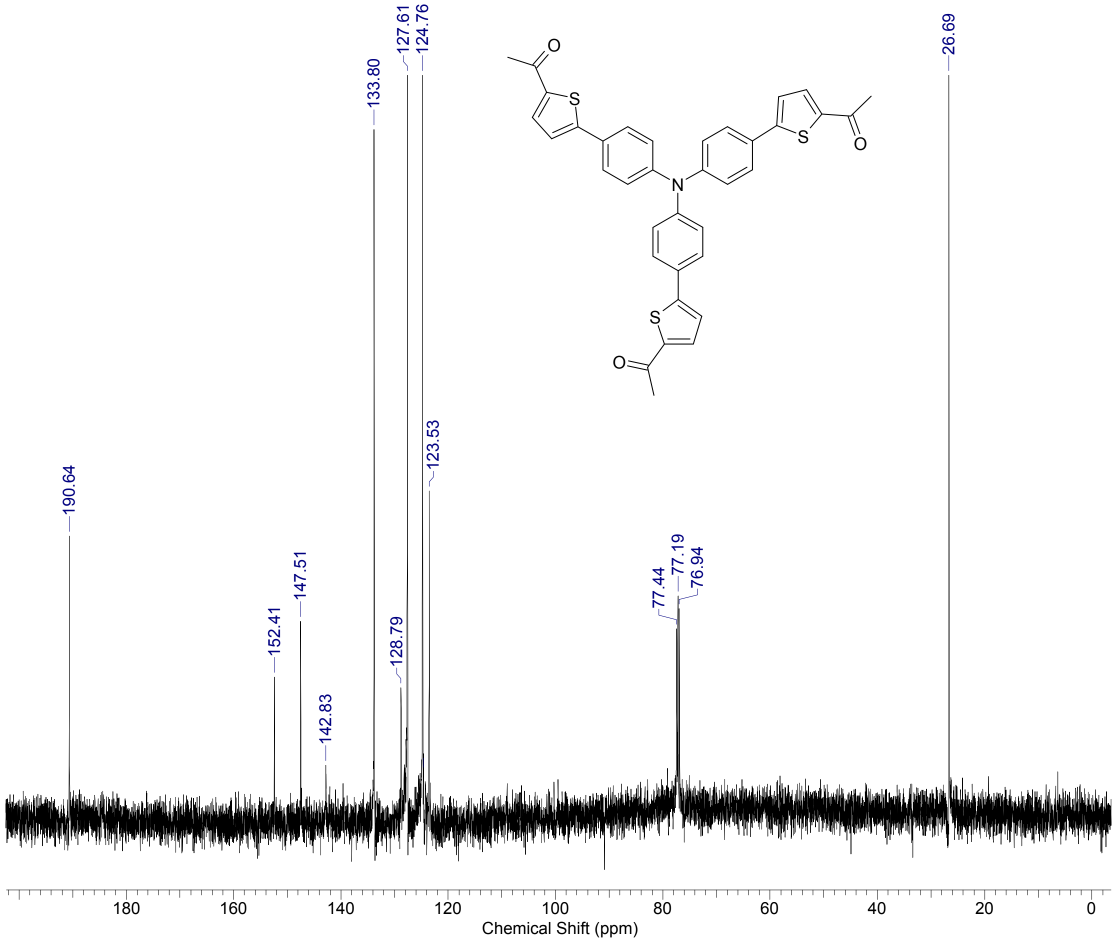
Figure S7. ^{13}C NMR spectrum of compound **5a** in CDCl$_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

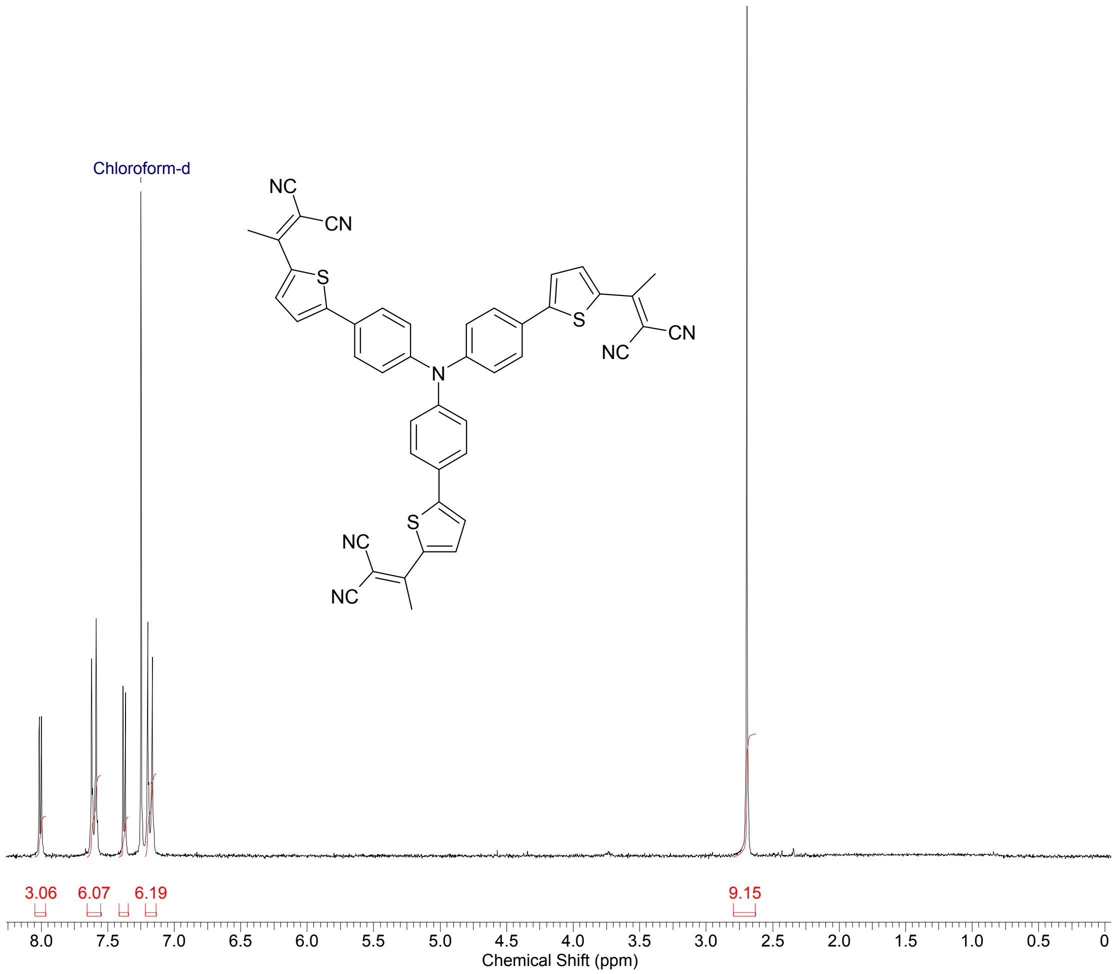
No.	(ppm)	Value	Absolute Value
1	[2.49 .. 2.64]	9.336	1.35817e+7
2	[7.12 .. 7.21]	6.034	8.77872e+6
3	[7.25 .. 7.28]	3.092	4.49820e+6
4	[7.51 .. 7.62]	6.000	8.72856e+6
5	[7.62 .. 7.69]	3.128	4.55003e+6

Figure S8. ^{1}H NMR spectrum of compound **6a** in $CDCl_3$



No.	(ppm)	(Hz)	Height
1	26.69	3356.7	1.0000
2	76.94	9676.4	0.1780
3	77.19	9708.3	0.1888
4	77.44	9740.1	0.1603
5	123.53	15536.1	0.2789
6	124.58	15668.8	0.0376
7	124.76	15691.8	0.7399
8	127.61	16049.2	0.8820
9	128.79	16197.8	0.1099
10	133.80	16827.7	0.5900
11	142.83	17963.5	0.0430
12	147.51	18552.7	0.1668
13	152.41	19168.4	0.1190
14	190.64	23977.2	0.2402

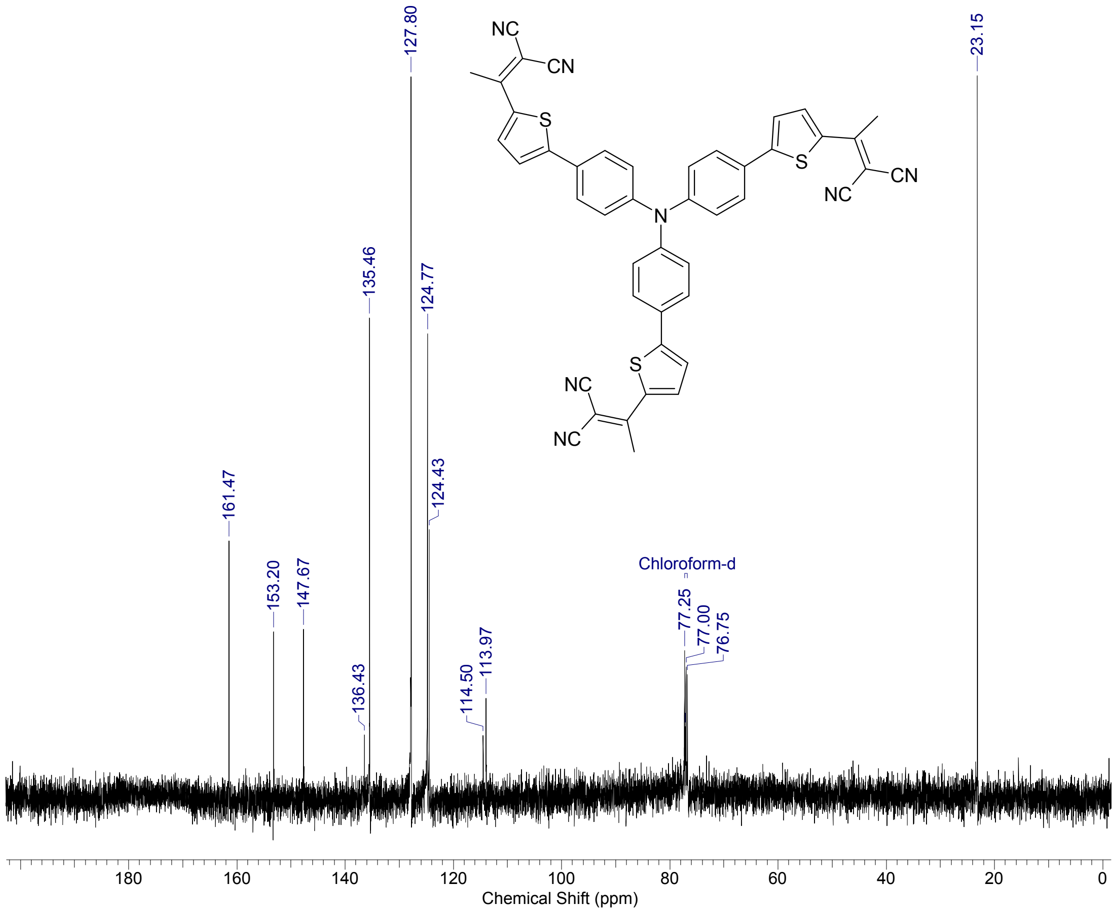
Figure S9. ^{13}C NMR spectrum of compound **6a** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[2.63 .. 2.80]	9.150	1.20673e+7
2	[7.14 .. 7.22]	6.186	8.15797e+6
3	[7.35 .. 7.41]	3.000	3.95642e+6
4	[7.55 .. 7.66]	6.073	8.00871e+6
5	[7.97 .. 8.05]	3.055	4.02912e+6

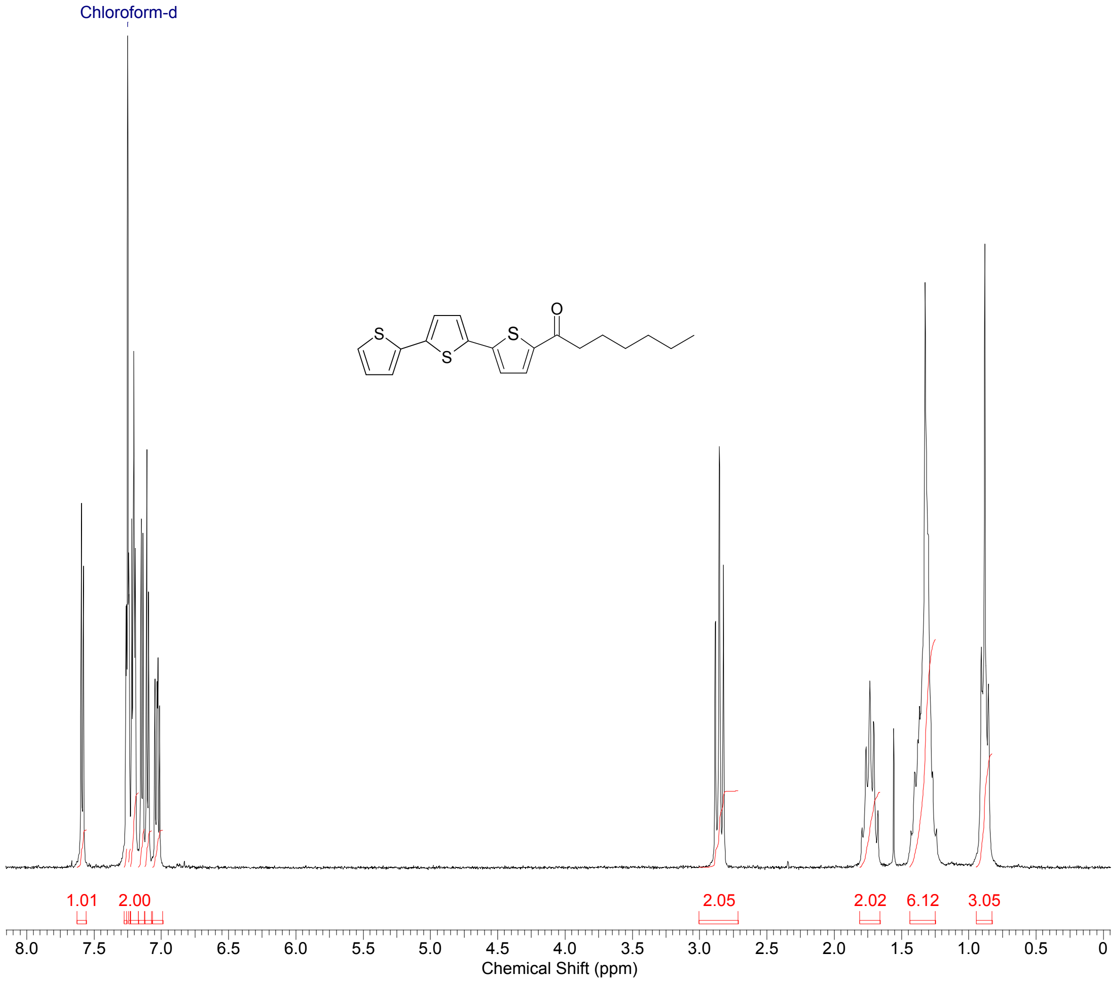
Figure S10. ^{1}H NMR spectrum of compound **N(Ph-1T-DCN-Me)$_3$** in CDCl$_3$



No.	(ppm)	(Hz)	Height
1	23.15	2911.7	1.0000
2	76.75	9652.6	0.1695
3	77.00	9684.4	0.1799
4	77.18	9707.4	0.0969
5	77.25	9716.3	0.2022
6	113.97	14334.0	0.1360
7	114.50	14401.2	0.0848
8	124.43	15650.3	0.3702
9	124.77	15692.8	0.6419
10	127.80	16073.1	0.9982
11	135.46	17037.4	0.6637
12	136.43	17159.5	0.0856
13	147.67	18573.1	0.2322
14	153.20	19268.4	0.2284
15	161.47	20308.7	0.3549

No.	Annotation	(ppm)
1	Chloroform-d	[76.75 .. 77.25]

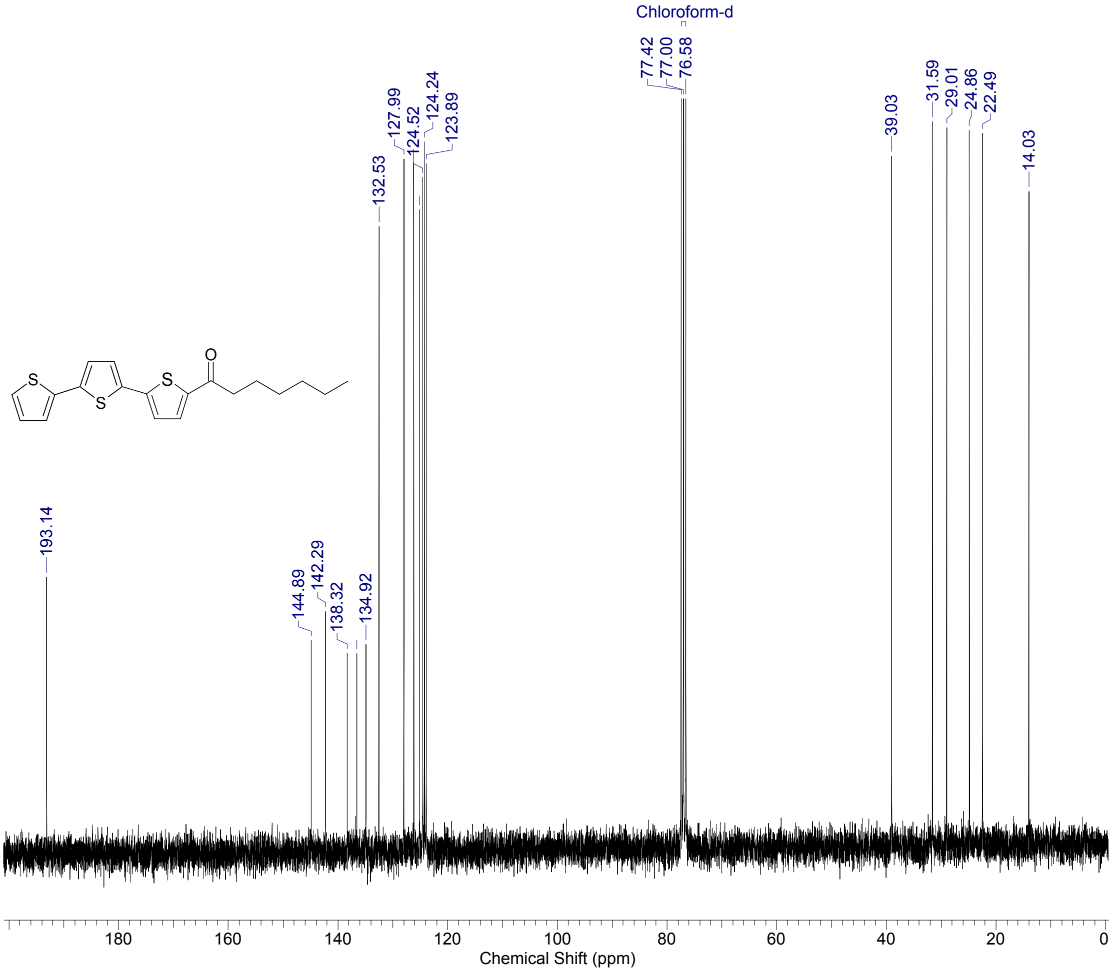
Figure S11. ^{13}C NMR spectrum of compound **N(Ph-1T-DCN-Me)$_3$** in CDCl$_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.83 .. 0.95]	3.048	2.60632e+7
2	[1.25 .. 1.44]	6.121	5.23441e+7
3	[1.66 .. 1.81]	2.019	1.72707e+7
4	[2.71 .. 3.01]	2.051	1.75386e+7
5	[6.99 .. 7.06]	1.000	8.55206e+6
6	[7.07 .. 7.12]	0.982	8.39712e+6
7	[7.13 .. 7.17]	1.020	8.72132e+6
8	[7.17 .. 7.23]	1.998	1.70887e+7
9	[7.23 .. 7.24]	0.498	4.25738e+6
10	[7.26 .. 7.28]	0.498	4.25719e+6
11	[7.56 .. 7.63]	1.005	8.59486e+6

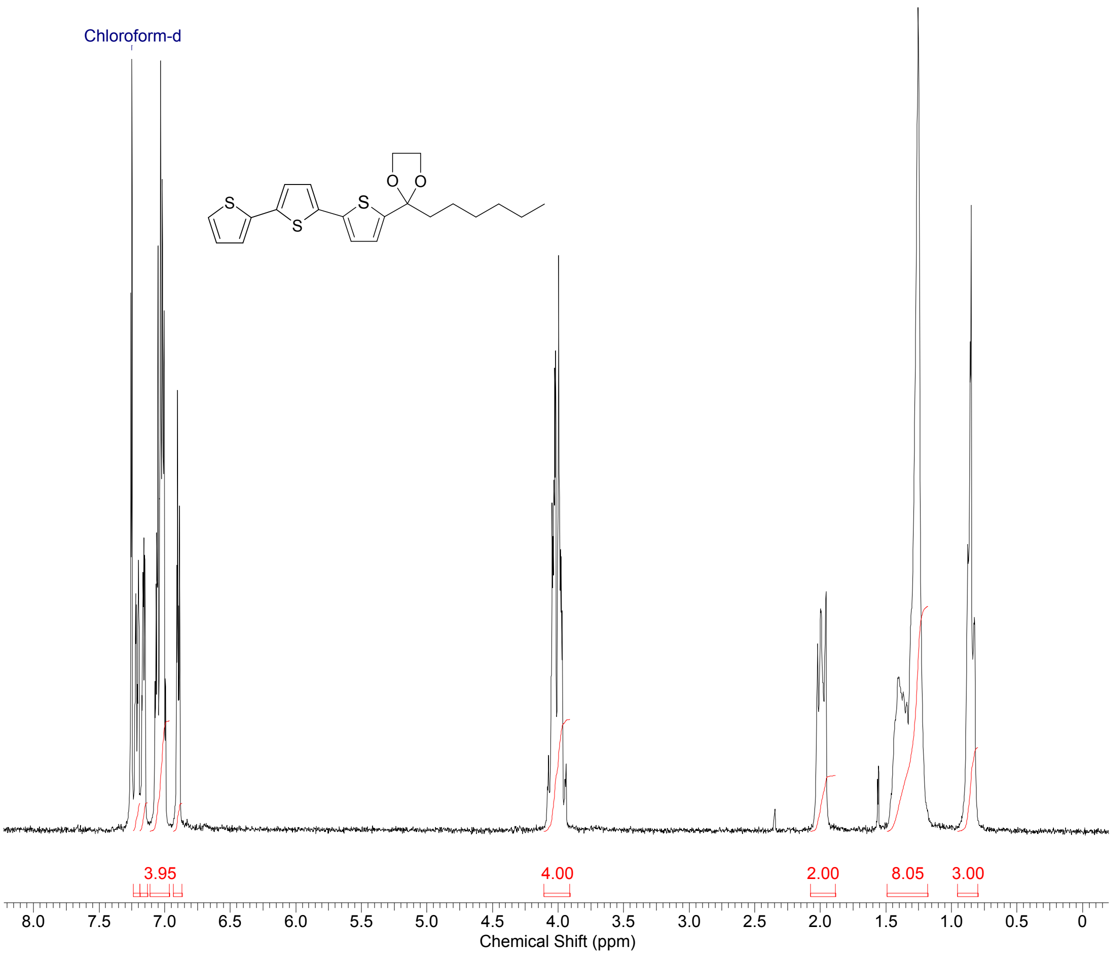
Figure S12. ^{1}H NMR spectrum of compound **2d** in $CDCl_3$



No.	(ppm)	(Hz)	Height
1	14.03	1059.1	0.5217
2	22.49	1697.6	0.5681
3	24.86	1876.7	0.5704
4	29.01	2189.3	0.5725
5	31.59	2384.5	0.5773
6	39.03	2946.2	0.5498
7	76.58	5779.8	0.9917
8	77.00	5811.8	1.0000
9	77.42	5843.8	0.9809
10	123.89	9350.9	0.5439
11	124.24	9377.1	0.5614
12	124.52	9398.7	0.5332
13	125.11	9442.7	0.5073
14	126.17	9523.2	0.5447
15	127.99	9660.0	0.5474
16	132.53	10002.9	0.4937
17	134.92	10183.2	0.1606
18	136.57	10307.8	0.1533
19	138.32	10440.2	0.1535
20	142.29	10739.8	0.1870
21	144.89	10936.0	0.1639
22	193.14	14577.7	0.2143

No.	Annotation	(ppm)
1	Chloroform-d	[76.58 .. 77.42]

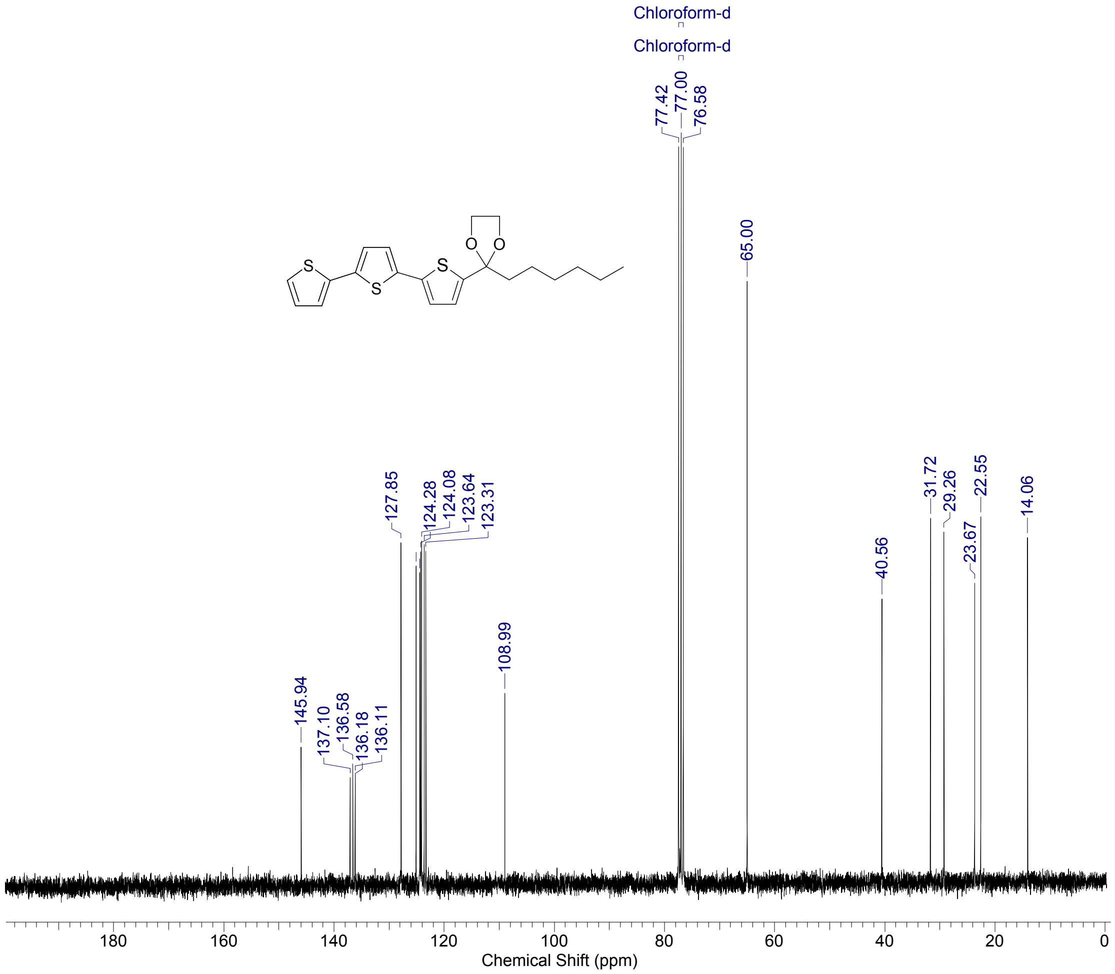
Figure S13. ^{13}C NMR spectrum of compound **2d** in CDCl$_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.80 .. 0.95]	2.996	3.52585e+7
2	[1.18 .. 1.49]	8.048	9.47216e+7
3	[1.89 .. 2.08]	1.996	2.34921e+7
4	[3.91 .. 4.11]	4.000	4.70785e+7
5	[6.87 .. 6.93]	1.000	1.17702e+7
6	[6.96 .. 7.11]	3.949	4.64766e+7
7	[7.13 .. 7.19]	1.025	1.20646e+7
8	[7.19 .. 7.24]	0.999	1.17627e+7

Figure S14. ^{1}H NMR spectrum of compound **3d** in CDCl$_3$

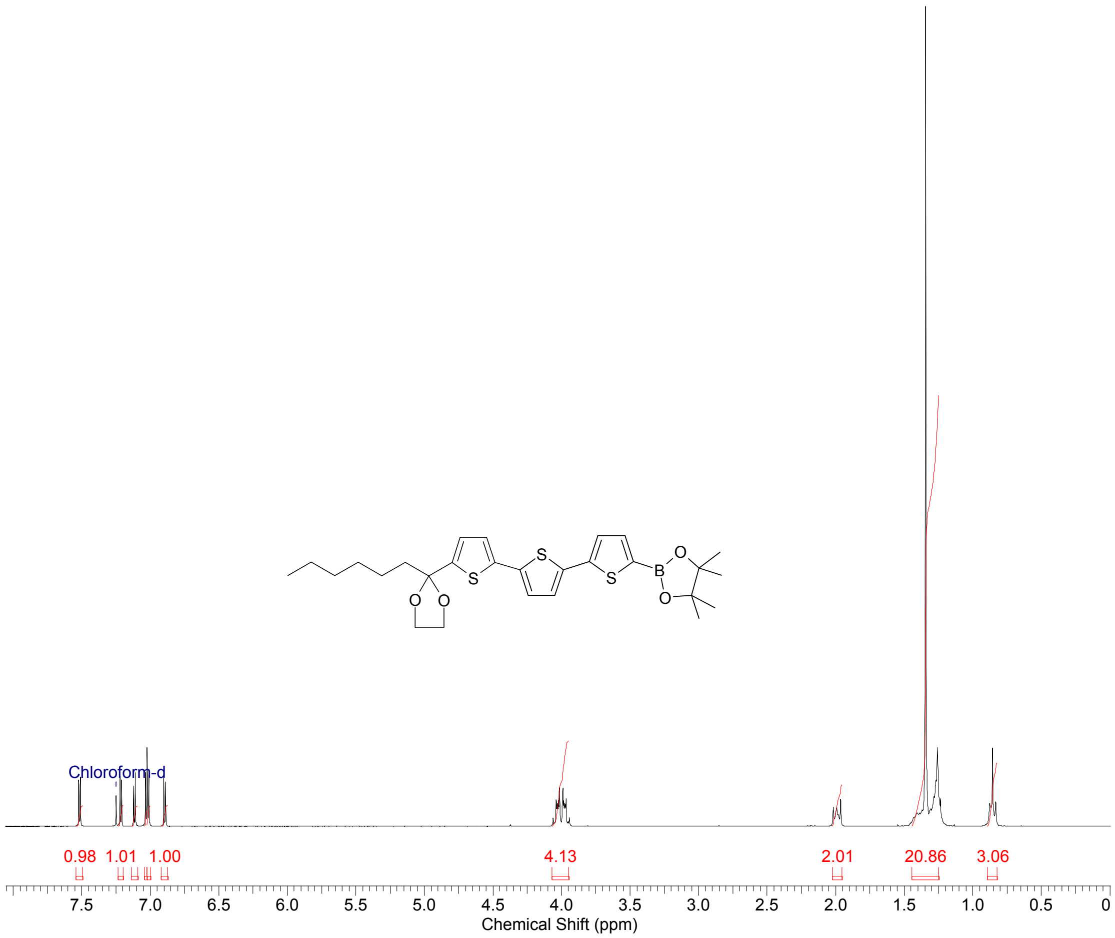


No.	(ppm)	(Hz)	Height
1	14.06	1061.0	0.4592
2	22.55	1702.2	0.4870
3	23.67	1786.9	0.3985
4	29.26	2208.2	0.4667
5	31.72	2394.0	0.4853
6	40.56	3061.0	0.3779
7	65.00	4906.4	0.8016
8	76.58	5779.7	0.9804
9	77.00	5811.8	1.0000
10	77.42	5843.6	0.9809
11	108.99	8226.2	0.2512
12	123.31	9306.9	0.4411

No.	(ppm)	(Hz)	Height
13	123.64	9331.8	0.4498
14	124.08	9365.5	0.4547
15	124.28	9380.3	0.4407
16	124.43	9391.8	0.4125
17	125.09	9441.9	0.4213
18	127.85	9649.8	0.4529
19	136.11	10273.4	0.1425
20	136.18	10278.7	0.1323
21	136.58	10309.0	0.1576
22	137.10	10348.0	0.1390
23	145.94	11015.5	0.1800

No.	Annotation	(ppm)
1	Chloroform-d	[76.58 .. 77.42]
2	Chloroform-d	[76.58 .. 77.42]

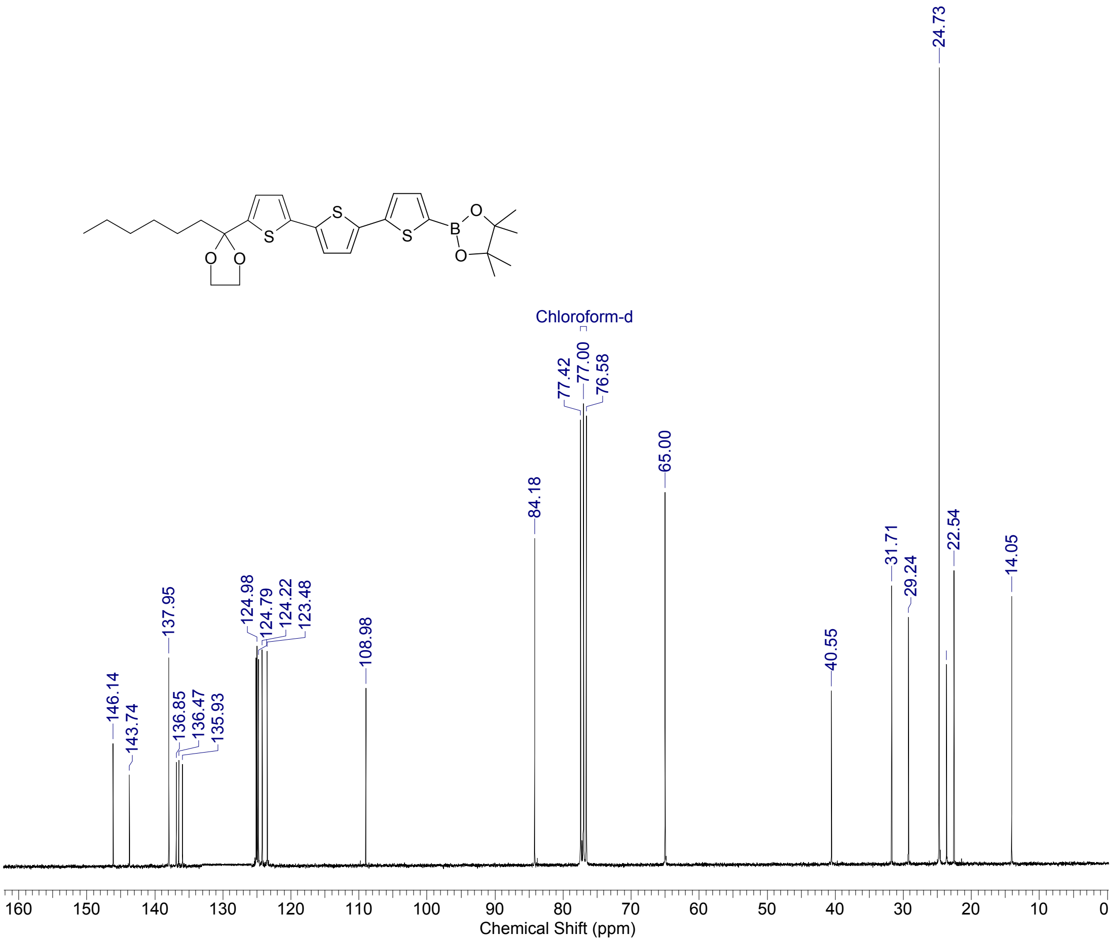
Figure S15. ^{13}C NMR spectrum of compound **3d** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.82 .. 0.89]	3.062	2.18472e+9
2	[1.25 .. 1.44]	20.865	1.48891e+10
3	[1.95 .. 2.03]	2.010	1.43426e+9
4	[3.95 .. 4.07]	4.132	2.94830e+9
5	[6.87 .. 6.92]	1.000	7.13596e+8
6	[7.00 .. 7.02]	0.988	7.05147e+8
7	[7.02 .. 7.04]	0.985	7.02767e+8
8	[7.09 .. 7.14]	0.976	6.96735e+8
9	[7.20 .. 7.23]	1.012	7.22231e+8
10	[7.49 .. 7.54]	0.984	7.01922e+8

Figure S16. ^{1}H NMR spectrum of compound **4d** in $CDCl_3$

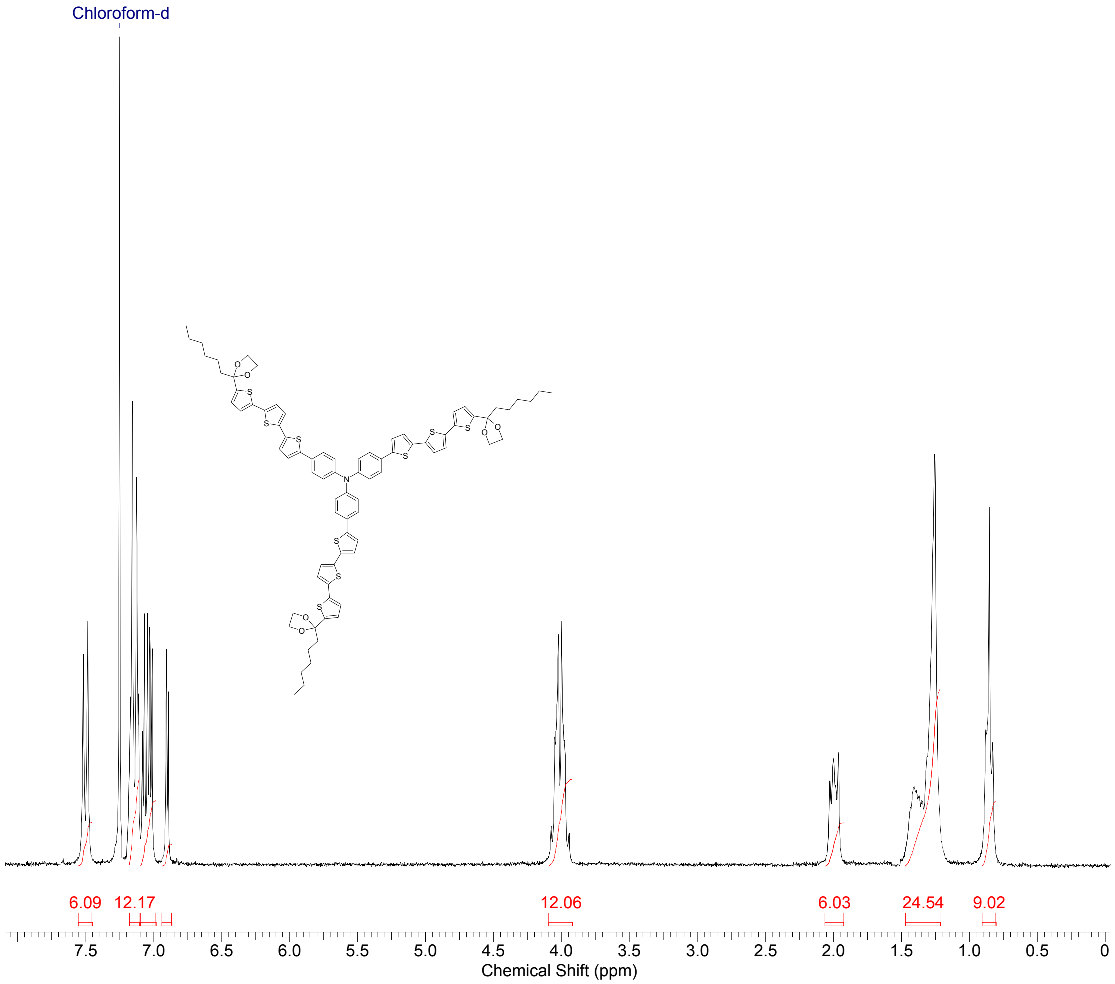


No.	(ppm)	(Hz)	Height
1	14.05	1060.6	0.3352
2	22.54	1701.5	0.3675
3	23.66	1785.8	0.2494
4	24.73	1866.5	1.0000
5	29.24	2207.3	0.3088
6	31.71	2393.3	0.3483
7	40.55	3060.3	0.2168
8	65.00	4906.2	0.4657
9	76.58	5780.0	0.5625
10	77.00	5811.8	0.5774
11	77.42	5843.9	0.5574
12	84.18	6353.8	0.4077

No.	(ppm)	(Hz)	Height
13	108.98	8225.5	0.2200
14	123.48	9320.1	0.2661
15	124.22	9375.7	0.2684
16	124.79	9418.8	0.2564
17	124.98	9433.1	0.2725
18	125.11	9443.3	0.2579
19	135.93	10259.6	0.1240
20	136.47	10300.4	0.1290
21	136.85	10329.5	0.1266
22	137.95	10411.9	0.2580
23	143.74	10848.9	0.1107
24	146.14	11030.7	0.1500

No.	Annotation	(ppm)
1	Chloroform-d	[76.58 .. 77.42]

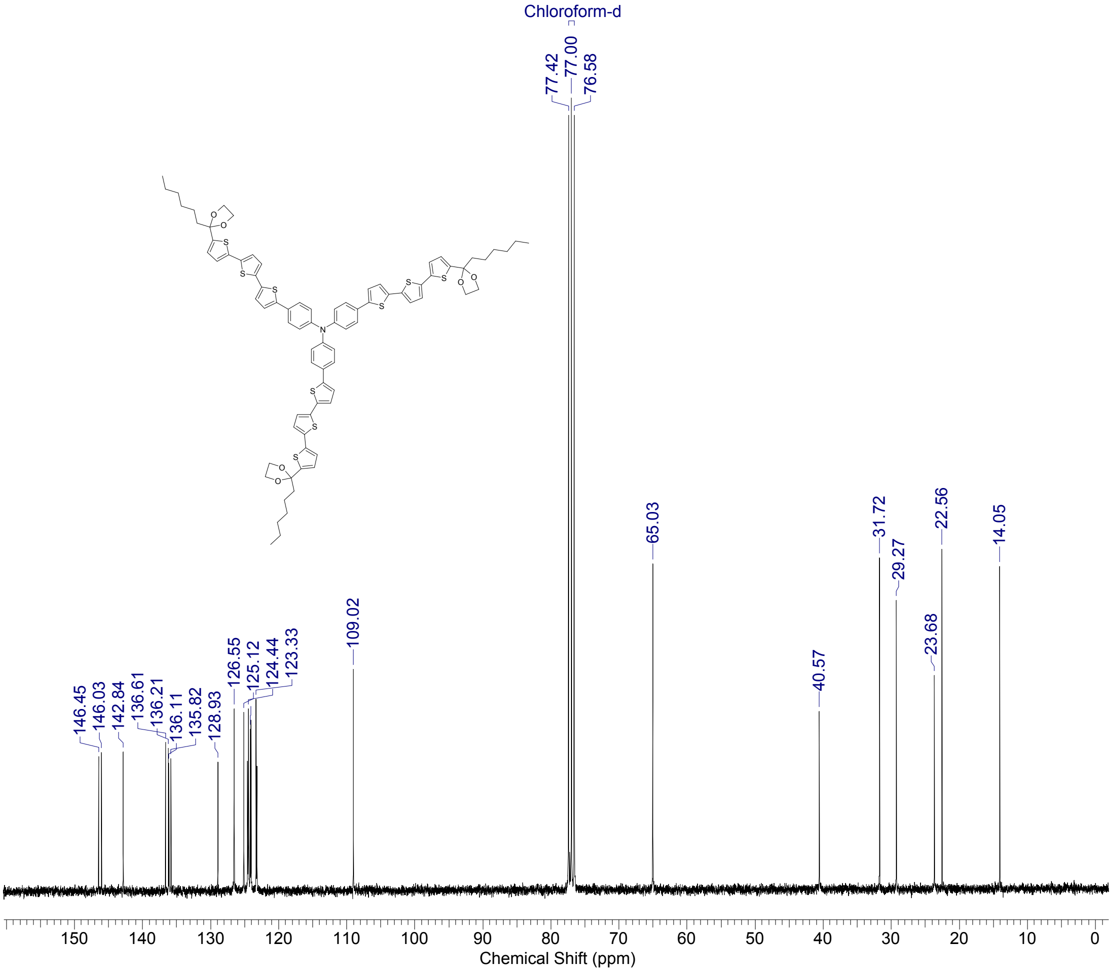
Figure S17. ^{13}C NMR spectrum of compound **4d** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.81 .. 0.91]	9.019	1.86898e+7
2	[1.22 .. 1.47]	24.536	5.08445e+7
3	[1.93 .. 2.06]	6.029	1.24939e+7
4	[3.92 .. 4.09]	12.056	2.49831e+7
5	[6.87 .. 6.94]	3.000	6.21666e+6
6	[6.98 .. 7.09]	9.054	1.87625e+7
7	[7.11 .. 7.18]	12.173	2.52245e+7
8	[7.45 .. 7.56]	6.092	1.26234e+7

Figure S18. ^{1}H NMR spectrum of compound **5d** in CDCl$_3$

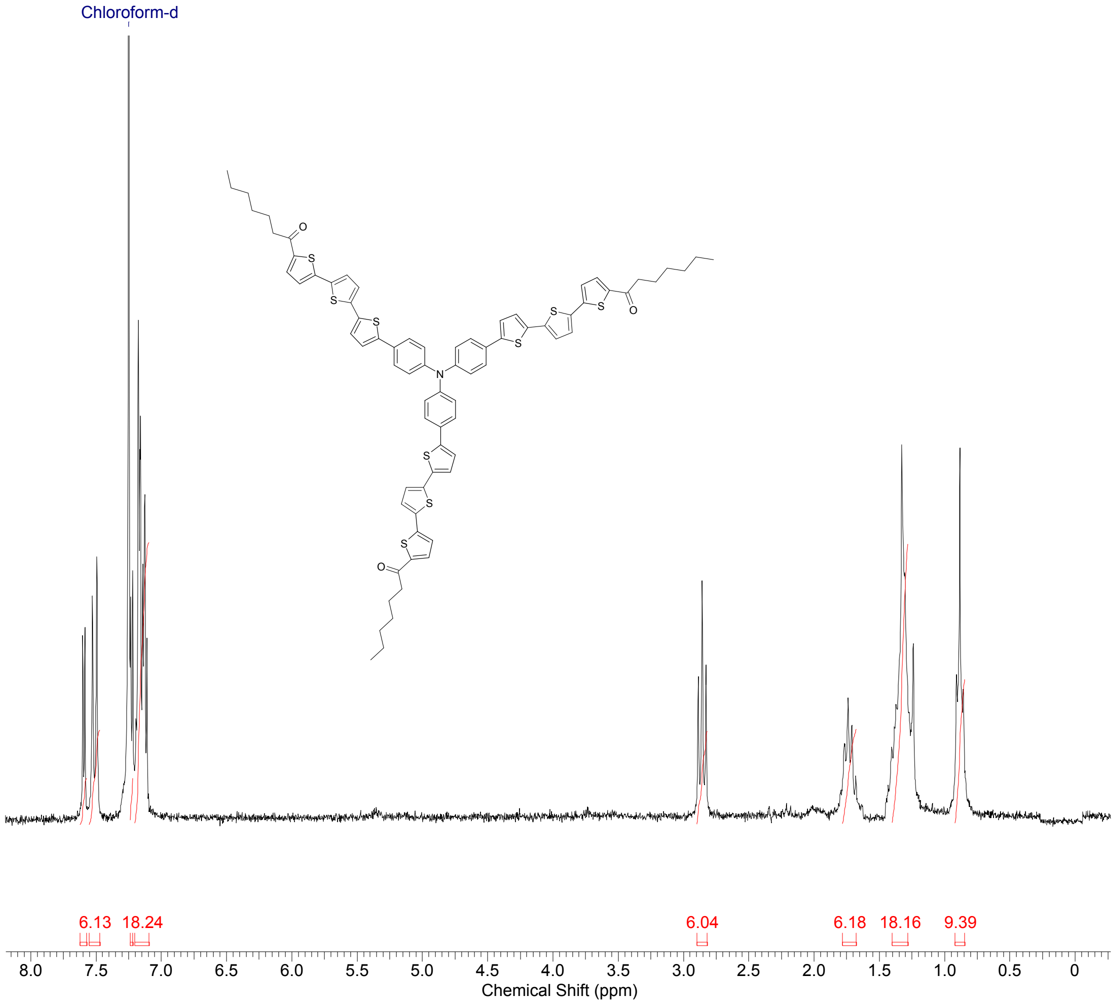


No.	(ppm)	(Hz)	Height
1	14.05	1060.3	0.4053
2	22.56	1702.4	0.4274
3	23.68	1787.2	0.2672
4	29.27	2208.9	0.3621
5	31.72	2394.5	0.4164
6	40.57	3062.3	0.2210
7	65.03	4908.1	0.4089
8	76.58	5779.9	0.9782
9	77.00	5811.8	1.0000
10	77.42	5843.7	0.9787
11	109.02	8228.4	0.2750
12	123.20	9298.6	0.1515
13	123.33	9308.3	0.2371
14	124.05	9363.2	0.2106

No.	(ppm)	(Hz)	Height
15	124.18	9373.2	0.1987
16	124.44	9392.3	0.2244
17	124.58	9402.8	0.1581
18	125.12	9444.1	0.2203
19	126.55	9551.9	0.2245
20	128.93	9731.7	0.1567
21	135.82	10251.6	0.1614
22	136.11	10273.4	0.1559
23	136.21	10280.7	0.1746
24	136.61	10311.3	0.1818
25	142.84	10781.3	0.1697
26	146.03	11021.8	0.1692
27	146.45	11053.8	0.1641

No.	Annotation	(ppm)
1	Chloroform-d	[76.58 .. 77.42]

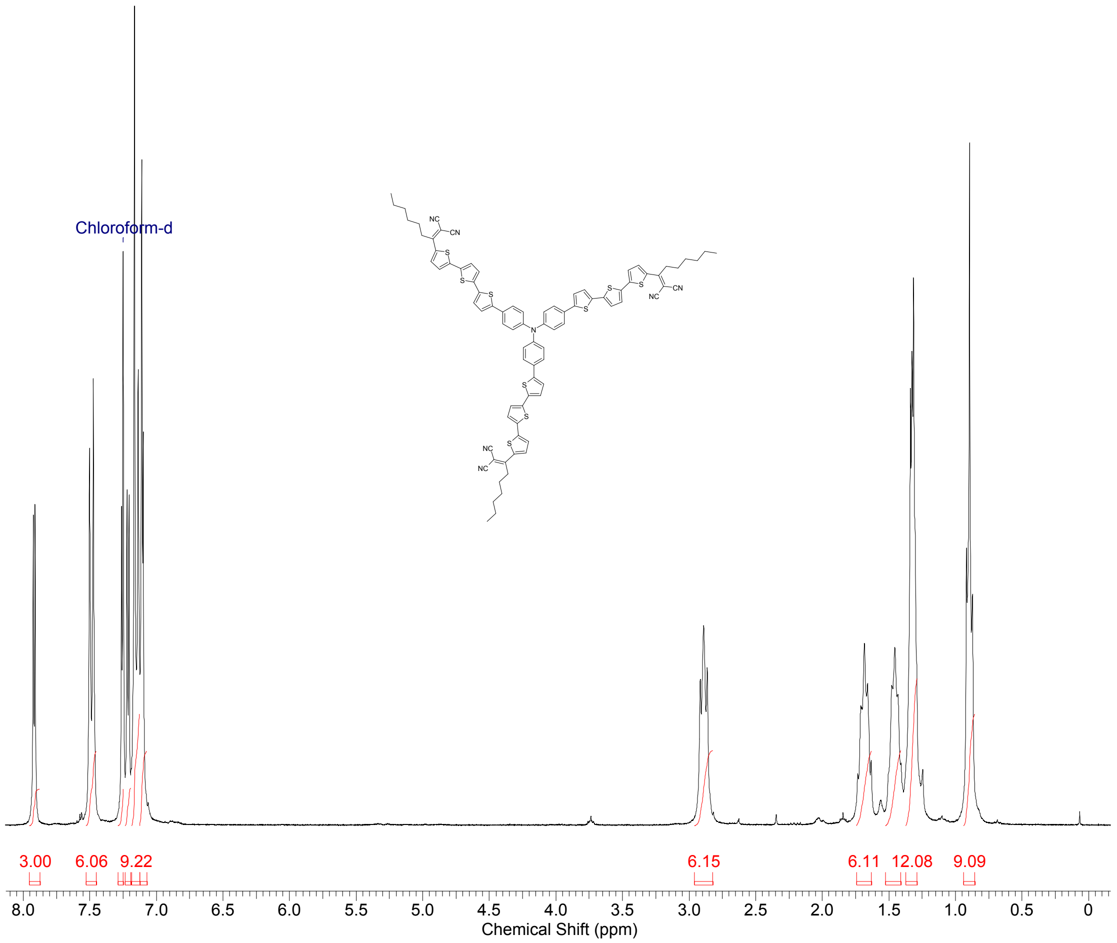
Figure S19. ^{13}C NMR spectrum of compound **5d** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.85 .. 0.92]	9.387	2.99249e+6
2	[1.28 .. 1.40]	18.156	5.78810e+6
3	[1.68 .. 1.78]	6.177	1.96931e+6
4	[2.82 .. 2.90]	6.041	1.92577e+6
5	[7.10 .. 7.20]	18.239	5.81464e+6
6	[7.22 .. 7.24]	3.013	9.60624e+5
7	[7.47 .. 7.55]	6.126	1.95290e+6
8	[7.57 .. 7.62]	3.000	9.56407e+5

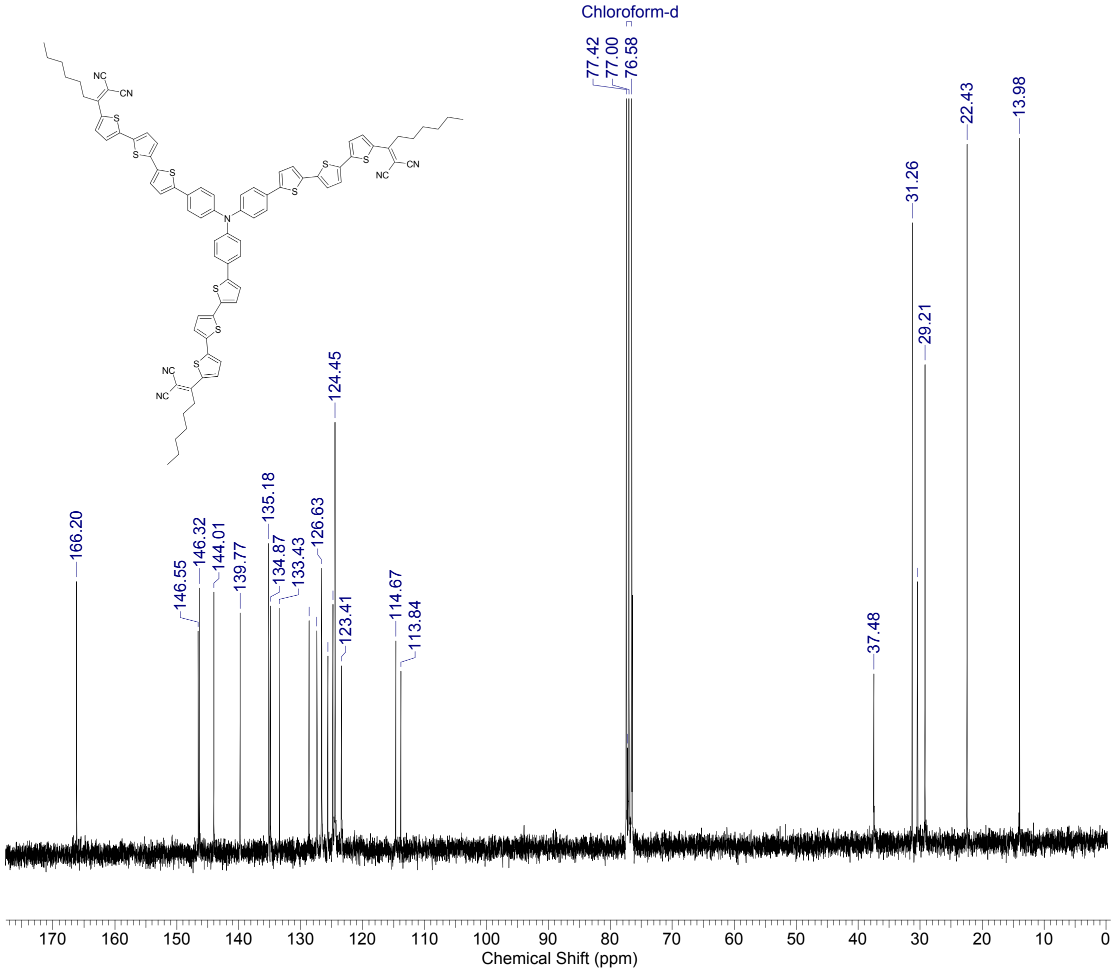
Figure S20. ^{1}H NMR spectrum of compound **6d** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.86 .. 0.94]	9.091	2.28489e+10
2	[1.29 .. 1.37]	12.079	3.03596e+10
3	[1.41 .. 1.52]	6.152	1.54627e+10
4	[1.63 .. 1.74]	6.115	1.53686e+10
5	[2.82 .. 2.96]	6.152	1.54630e+10
6	[7.07 .. 7.12]	6.090	1.53058e+10
7	[7.12 .. 7.18]	9.219	2.31710e+10
8	[7.19 .. 7.23]	3.120	7.84144e+9
9	[7.25 .. 7.29]	2.997	7.53344e+9
10	[7.45 .. 7.53]	6.061	1.52323e+10
11	[7.88 .. 7.95]	3.000	7.54002e+9

Figure S21. ^{1}H NMR spectrum of **N(Ph-3T-DCN-Hex)$_3$** in CDCl$_3$



No.	(ppm)	(Hz)	Height
1	13.98	1055.0	0.4090
2	22.43	1693.2	0.4055
3	29.21	2204.5	0.2773
4	30.44	2297.5	0.1510
5	31.26	2359.6	0.3599
6	37.48	2828.9	0.0971
7	76.46	5770.7	0.1429
8	76.58	5780.0	0.9918
9	77.00	5811.8	1.0000
10	77.20	5827.3	0.0542
11	77.42	5843.9	0.9786
12	113.84	8592.3	0.0988
13	114.67	8655.3	0.1165
14	123.41	9315.0	0.1020
15	124.45	9393.2	0.2437
16	124.81	9420.7	0.1378
17	125.64	9482.7	0.1075
18	126.63	9557.5	0.1586
19	127.37	9613.3	0.1222
20	128.66	9710.9	0.1281
21	133.43	10071.1	0.1352
22	134.87	10179.5	0.1368
23	135.14	10200.3	0.1379
24	135.18	10203.3	0.1730
25	139.77	10549.2	0.1327
26	144.01	10869.9	0.1447
27	146.32	11043.6	0.1471
28	146.55	11061.2	0.1220
29	166.20	12544.1	0.1508

No.	Annotation	(ppm)
1	Chloroform-d	[76.58 .. 77.42]

Figure S22. ^{13}C NMR spectrum of **N(Ph-3T-DCN-Hex)$_3$** in CDCl$_3$

3. GPC Data

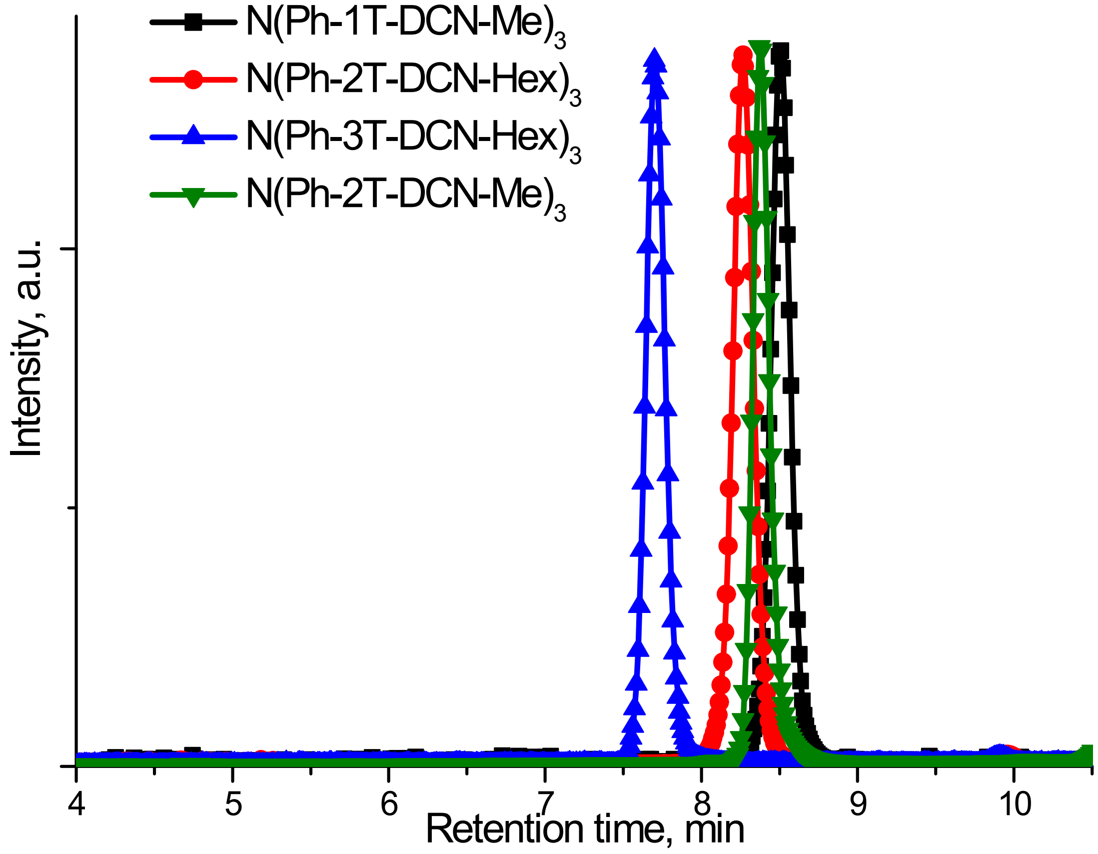


Figure S23. GPC-curves of pure N(Ph-1T-DCV-Me)$_3$, N(Ph-2T-DCV-Me)$_3$, N(Ph-2T-DCV-Hex)$_3$ and N(Ph-3T-DCV-Hex)$_3$, (column 500 Å, diode array detector).

4. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data

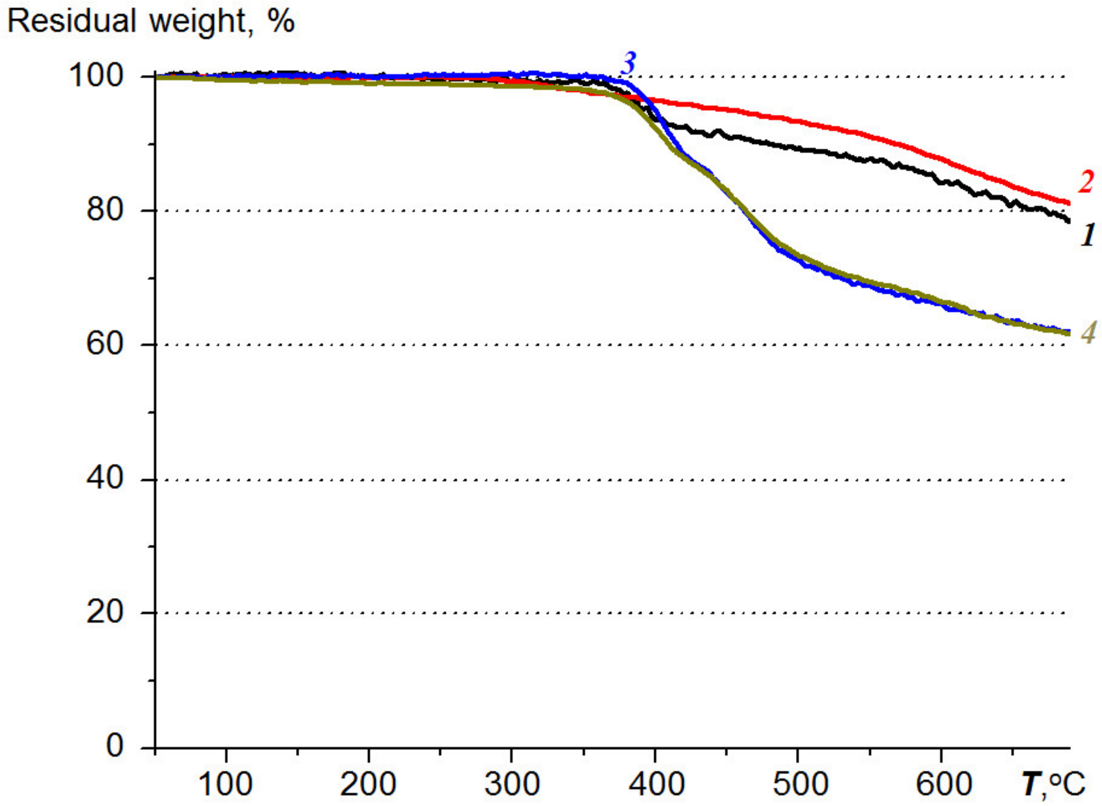


Figure S24. Thermogravimetric analysis of 1) **N(Ph-1T-DCN-Me)$_3$**; 2) **N(Ph-2T-DCN-Me)$_3$**; 3) **N(Ph-2T-DCN-Hex)$_3$**; 4) **N(Ph-3T-DCN-Hex)$_3$** in inert atmosphere (nitrogen flow).

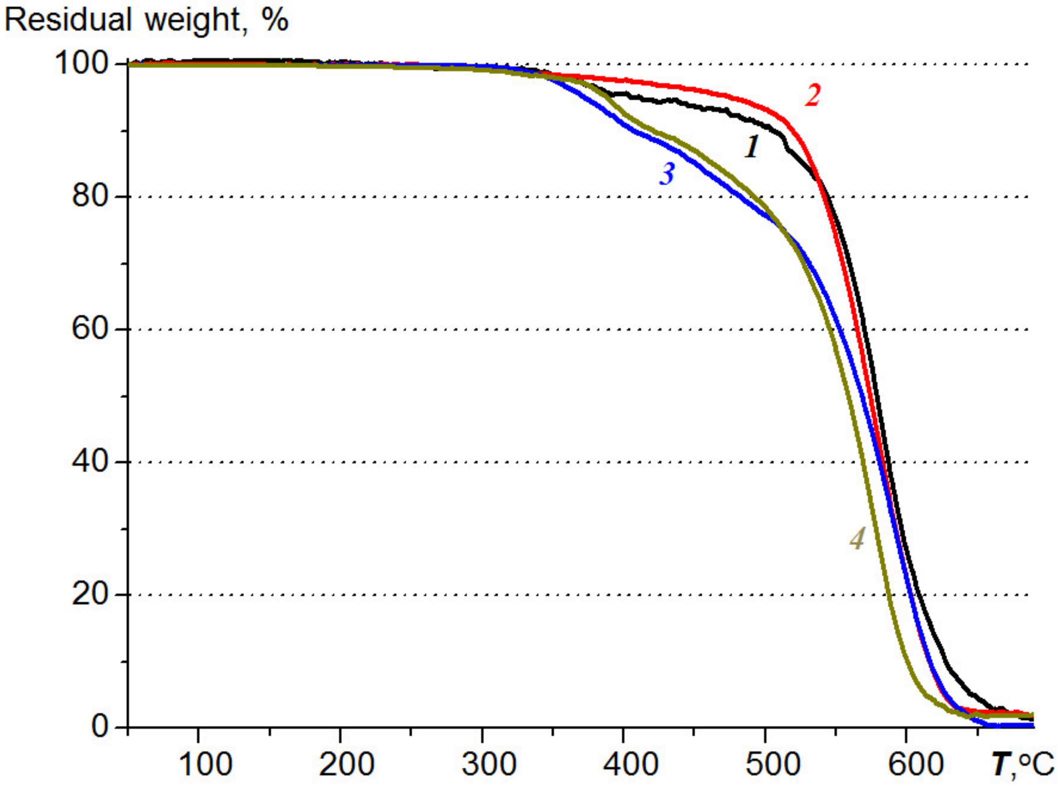


Figure S25. Thermogravimetric analysis of 1) **N(Ph-1T-DCN-Me)$_3$**; 2) **N(Ph-2T-DCN-Me)$_3$**; 3) **N(Ph-2T-DCN-Hex)$_3$**; 4) **N(Ph-3T-DCN-Hex)$_3$** in air flow.

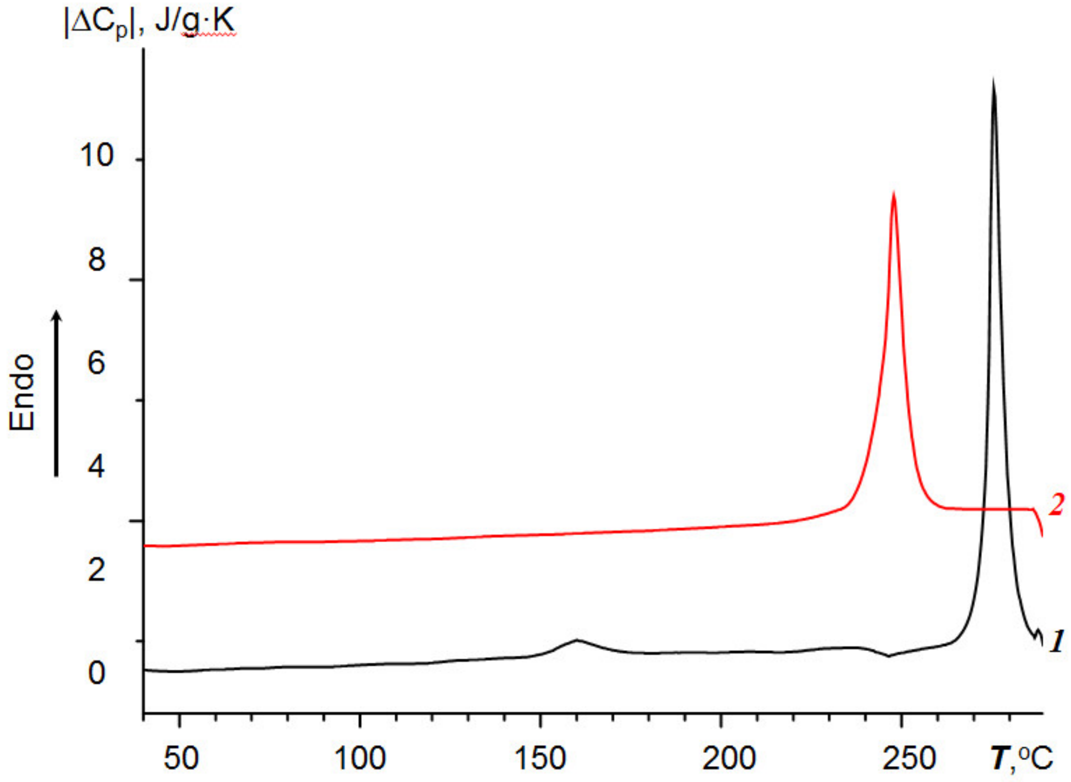


Figure S26.

DSC scans of the first heating of **N(Ph-1T-DCN-Me)$_3$** (1) and crystalline fraction of **N(Ph-2T-DCN-Me)$_3$** (2).

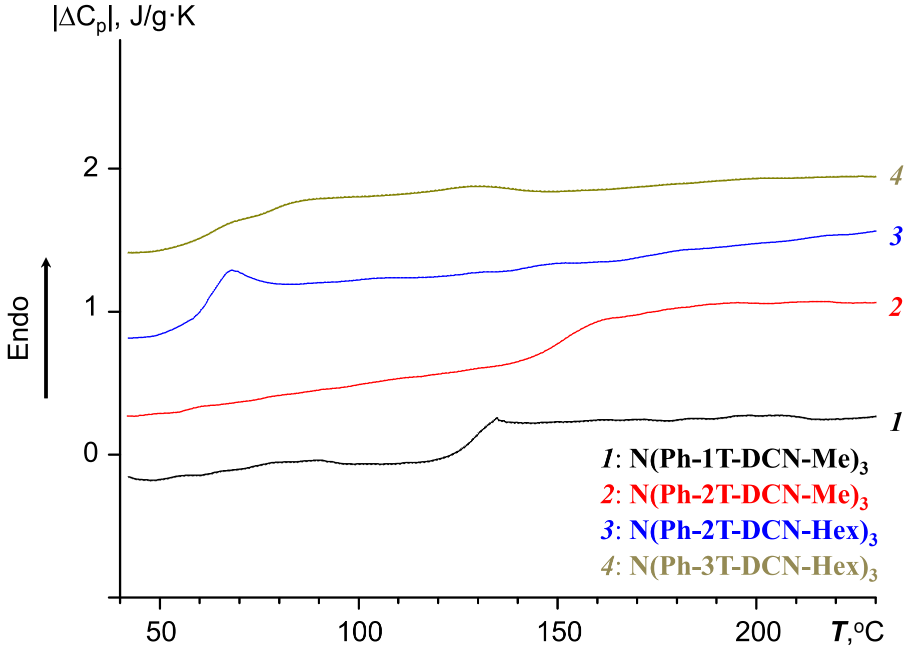


Figure S27. DSC scans of 1) **N(Ph-1T-DCN-Me)$_3$** (second heating scan); 2) **N(Ph-2T-DCN-Me)$_3$**; 3) **N(Ph-2T-DCN-Hex)$_3$**; 4) **N(Ph-3T-DCN-Hex)$_3$**. For the sake of simplicity, curves are shifted along heat flow axis.

5. Cyclovoltammetry analysis (CVA) data

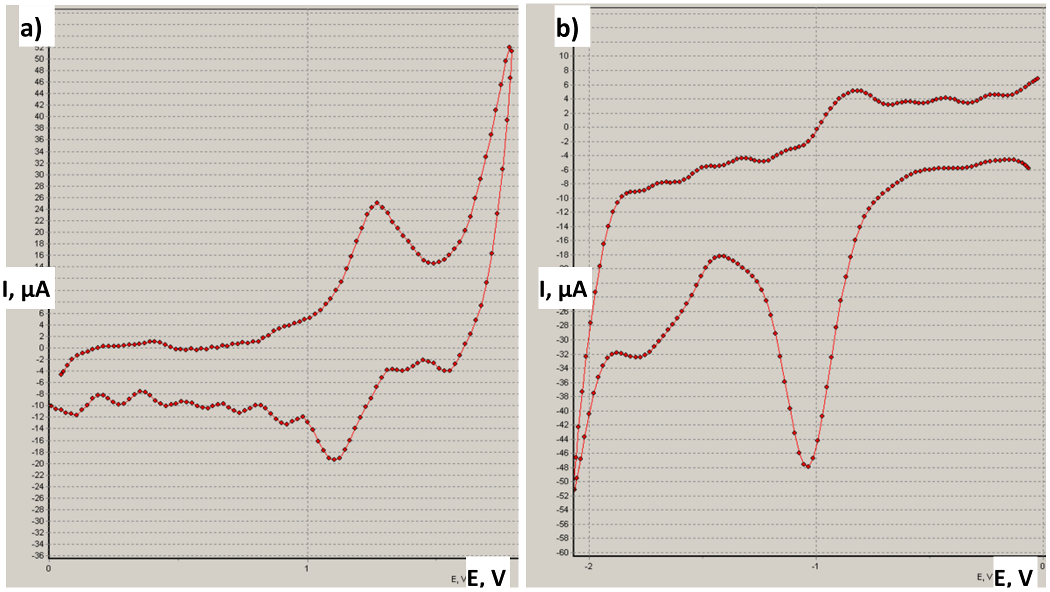


Figure S28. Electrochemical a) oxidation and b) reduction curves of **N(Ph-1T-DCN-Me)$_3$** in the 1,2-dichlorobenzene: acetonitrile (4:1) mixture of solvents using 0.1M Bu4NPF6 as supporting electrolyte.

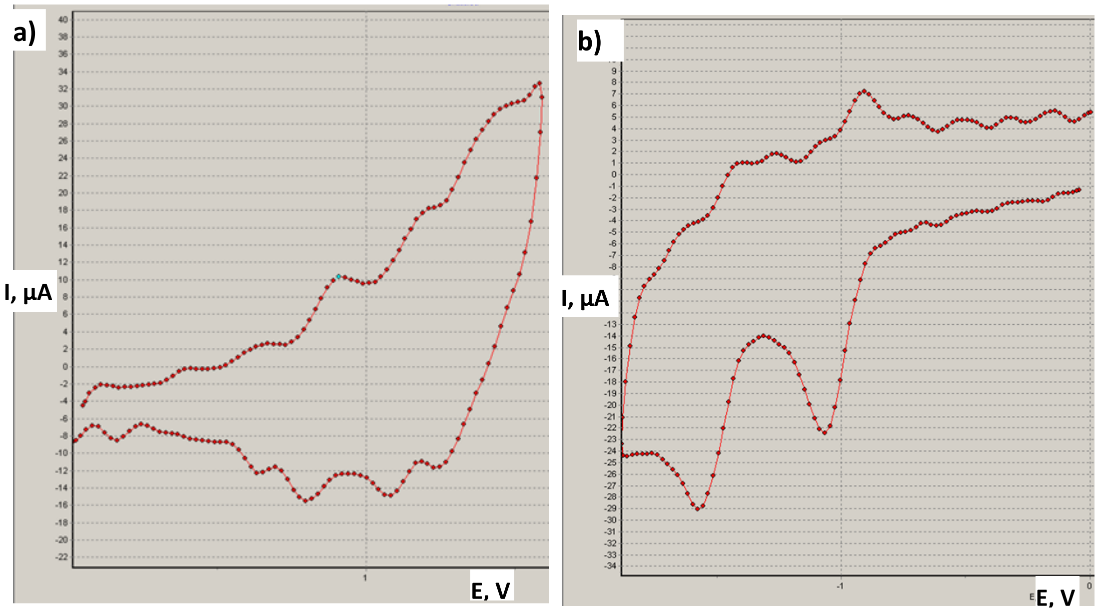


Figure S29. Electrochemical a) oxidation and b) reduction curves of **N(Ph-3T-DCN-Hex)$_3$** in the 1,2-dichlorobenzene: acetonitrile (4:1) mixture of solvents using 0.1M Bu4NPF6 as supporting electrolyte.

6. X-ray diffraction (XRD) data

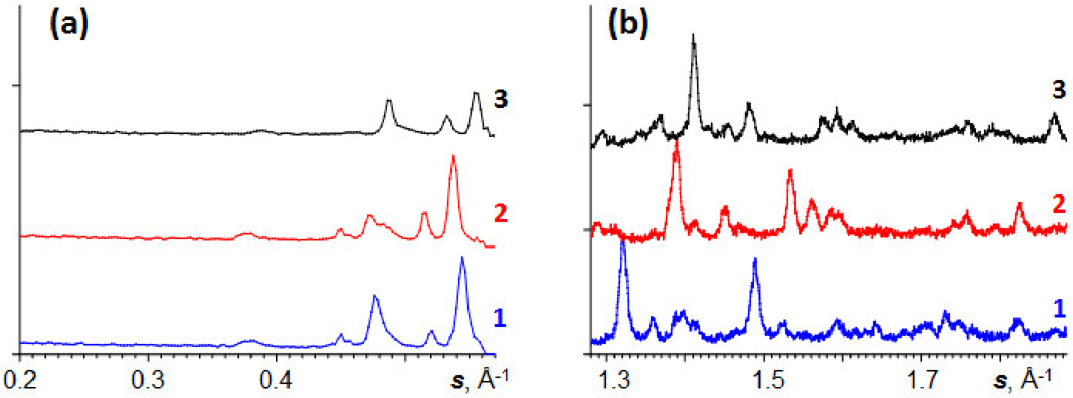


Figure S30. X-Ray scattering pattern of as-received sample of **N(Ph-1T-DCN-Me)$_3$** at room temperature. Insets show the temperature evolution of small-angle (a) and wide-angle (b) spectra: 140°C (1), 180°C (2), 30°C, cooled after melting at 260°C (3).

Table S1. Observed reflections for the stable crystalline modification of **N(Ph-1T-DCN-Me)$_3$** compound.

N	*hkl*	$d_{obs,}$ Å	$d_{calc,}$ Å	Δ$d_{,}$ Å
1	001	13.11	13.09	-0.02
2	010	12.43	12.46	0.03
3	011	11.91	11.91	< 0.005
4	$1\bar{1}1$	11.43	11.47	0.04
5	$1\bar{2}1$	8.51	8.53	0.02
6	102	8.13	8.15	0.02
7	012	7.18	7.19	0.01
8	$1\bar{2}2$	6.32	6.34	0.02
9	$\bar{1}21$	6.15	6.15	< 0.005
10	$1\bar{1}3$	5.67	5.67	< 0.005
11	$\bar{1}31$	5.34	5.34	< 0.005
12	$2\bar{1}2$	5.17	5.17	< 0.005
13	$2\bar{3}3$	4.59	4.59	< 0.005
14	$2\bar{2}4$	4.30	4.30	< 0.005
15	123	4.13	4.13	< 0.005
16	$\bar{2}10$	3.76	3.76	< 0.005
17	$\bar{1}\bar{1}1$	3.58	3.58	< 0.005
18	$0\bar{3}1$	3.55	3.55	< 0.005
19	$\bar{2}21$	3.48	3.48	< 0.005
20	212	3.33	3.33	< 0.005
21	125	3.21	3.20	-0.01
22	$\bar{2}32$	3.04	3.04	< 0.005
23	044	2.98	2.98	< 0.005
24	$1\bar{3}4$	2.92	2.92	< 0.005
25	$\bar{1}34$	2.82	2.82	< 0.005

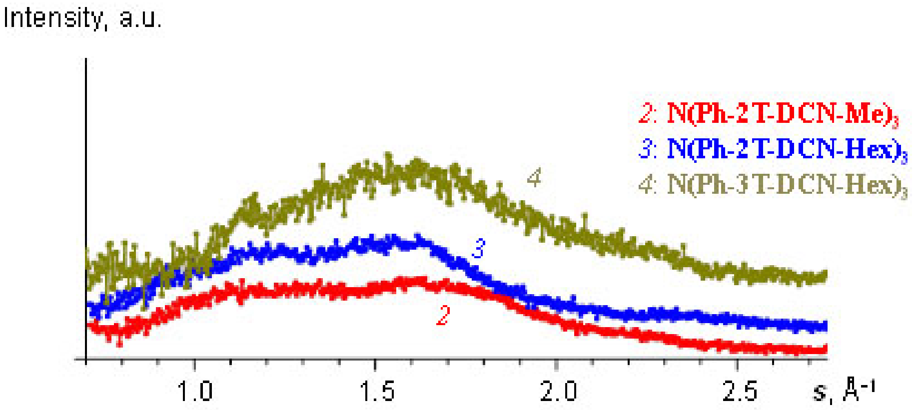


Figure S31. Wide-angle X-Ray scattering (WAXS) patterns of 2) **N(Ph-2T-DCN-Me)$_3$**; 3) **N(Ph-2T-DCN-Hex)$_3$**; 4) **N(Ph-3T-DCN-Hex)$_3$**. For the sake of simplicity, scans are shifted along Intensity axis.

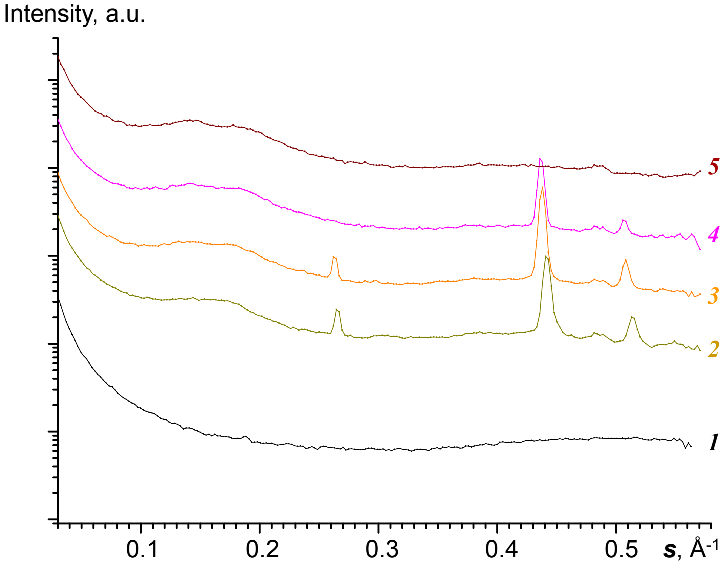


Figure S32. Small-angle X-Ray Scattering (SAXS) patterns of **N(Ph-2T-DCN-Me)$_3$** (1) and **N(Ph-3T-DCN-Hex)$_3$** (2-5) at room temperature (as-received samples, curves 1 and 2), 120°C (3), 140°C (4), 160°C (5). For the sake of simplicity, scans are shifted along Intensity axis.

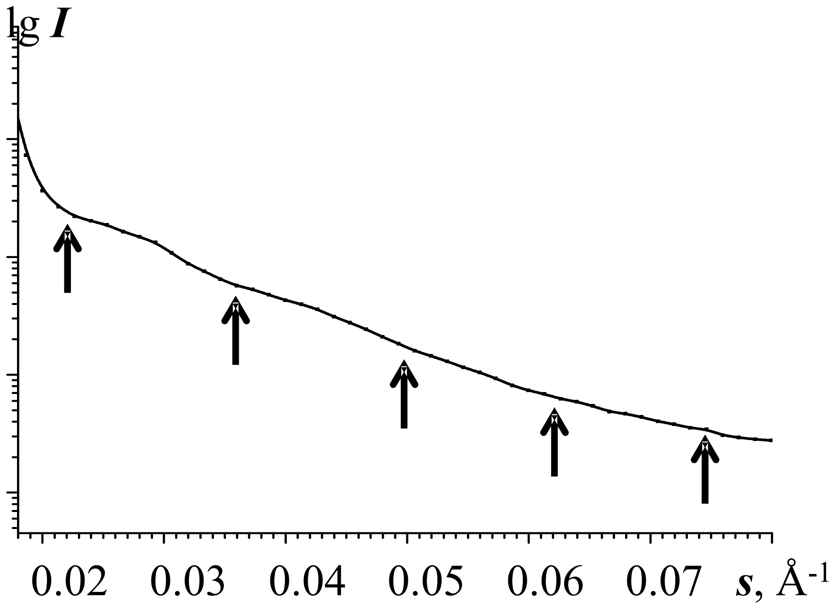


Figure S33. Typical X-Ray reflectivity curve for mixtures of star-shaped molecules (**N(Ph-2T-DCN-Me)$_3$**) with PC$_{71}$BM. Arrows show minima observed.

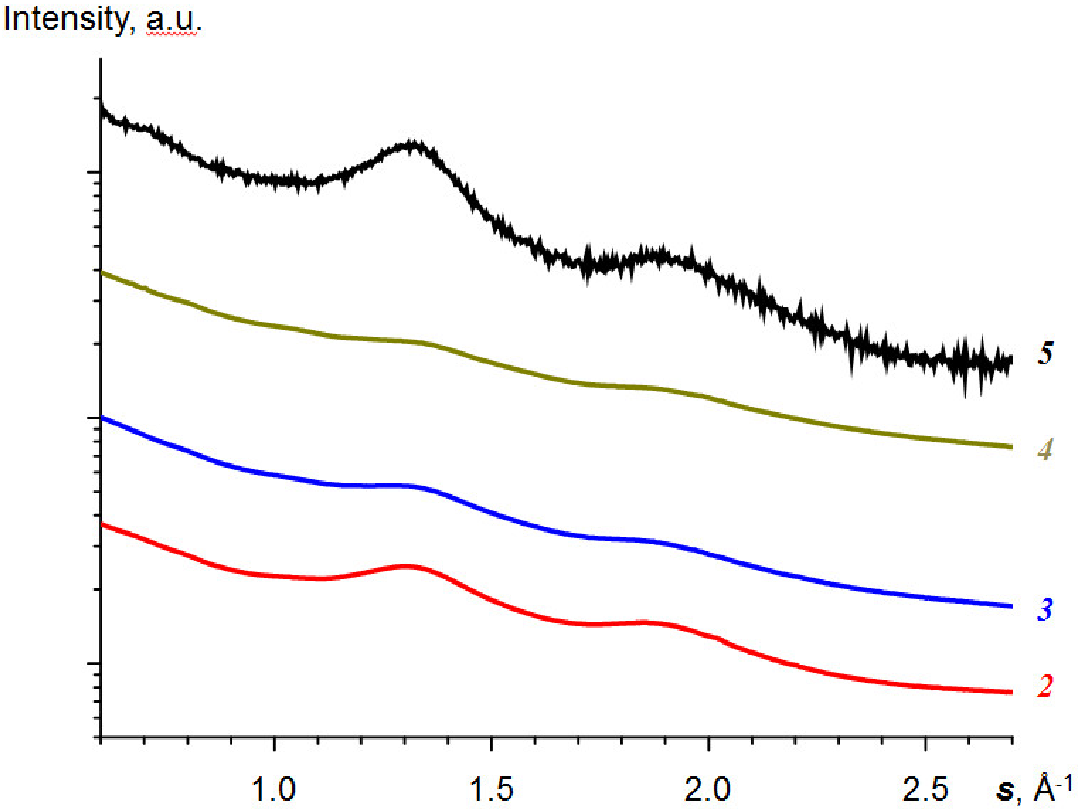


Figure S34. Grazing incidence X-Ray diffraction patterns of the mixtures of **N(Ph-2T-DCN-Me)$_3$** (2), **N(Ph-2T-DCN-Hex)$_3$** (3), **N(Ph-3T-DCN-Hex)$_3$** (4) with PC$_{71}$BM. Wide-angle X-Ray pattern of pure PC$_{71}$BM (5) is shown for comparison.

7. Atomic Force Microscopy (AFM) data

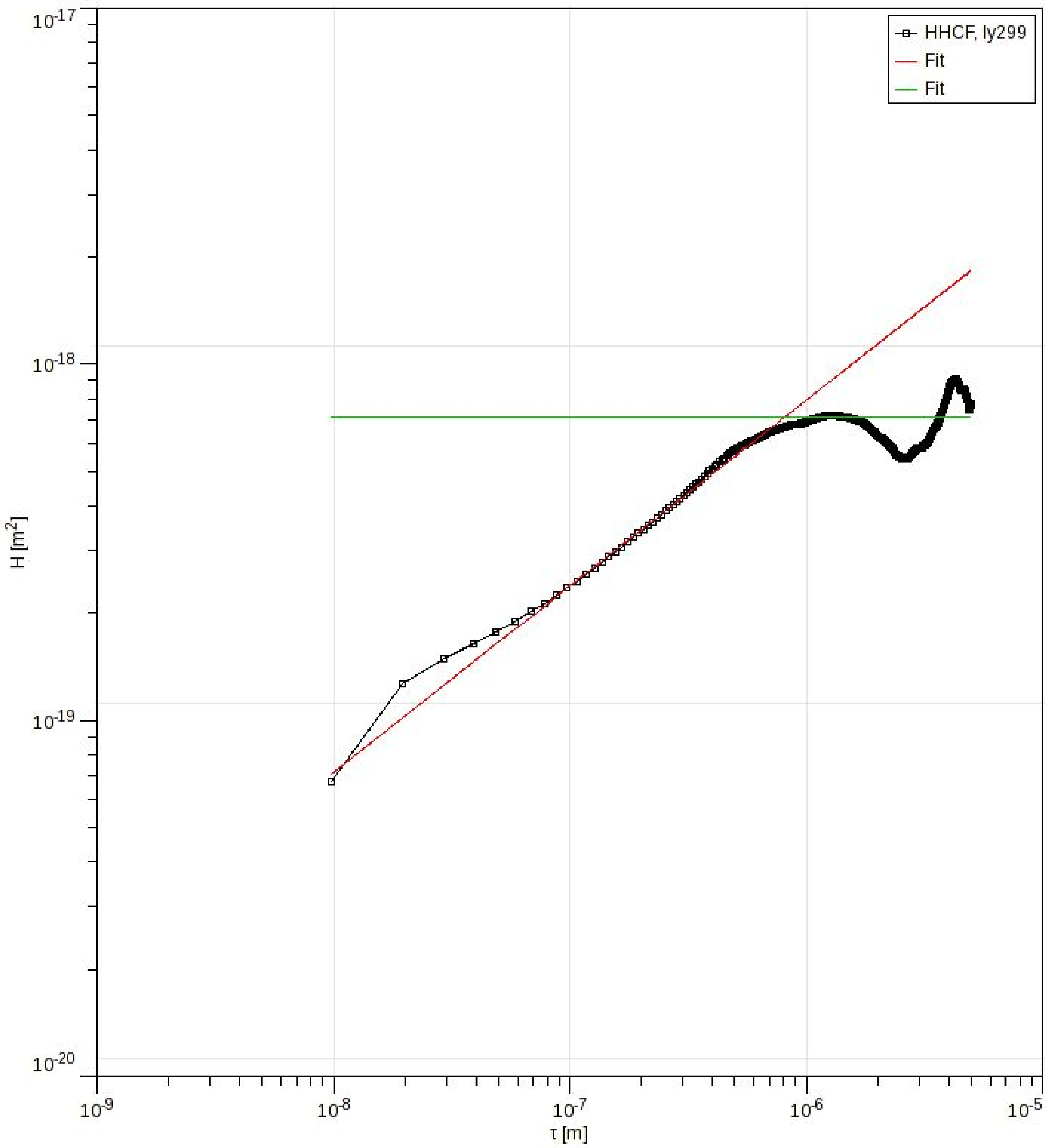


Figure S35. Height – height correlation function calculated from AFM image of **N(Ph-1T-DCN-Me)$_3$** : PC$_{71}$BM blend (**Figure 5a**).

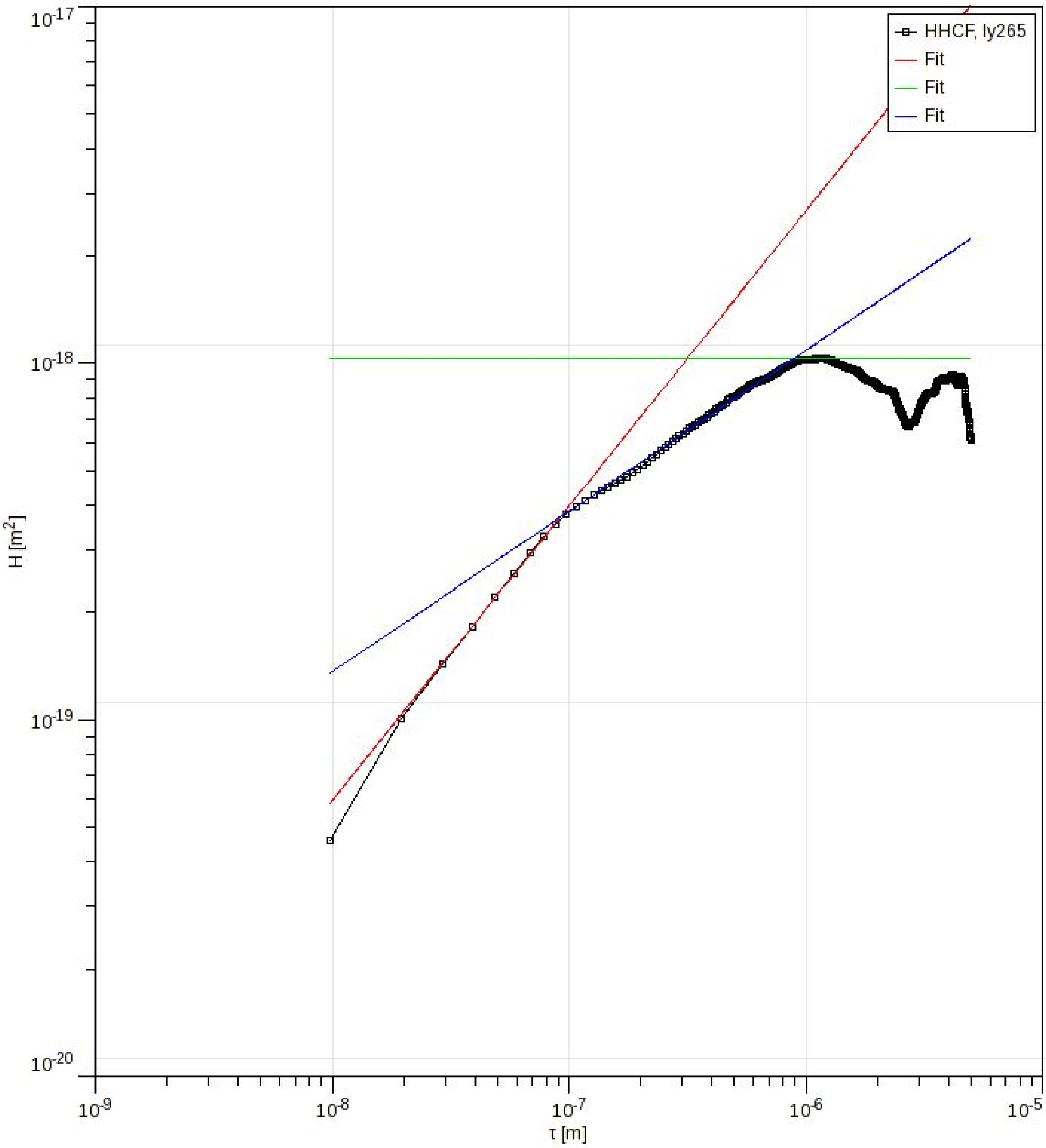


Figure S36. Height – height correlation function calculated from AFM image of **N(Ph-2T-DCN-Me)$_3$** : PC$_{71}$BM blend (**Figure 5b**).

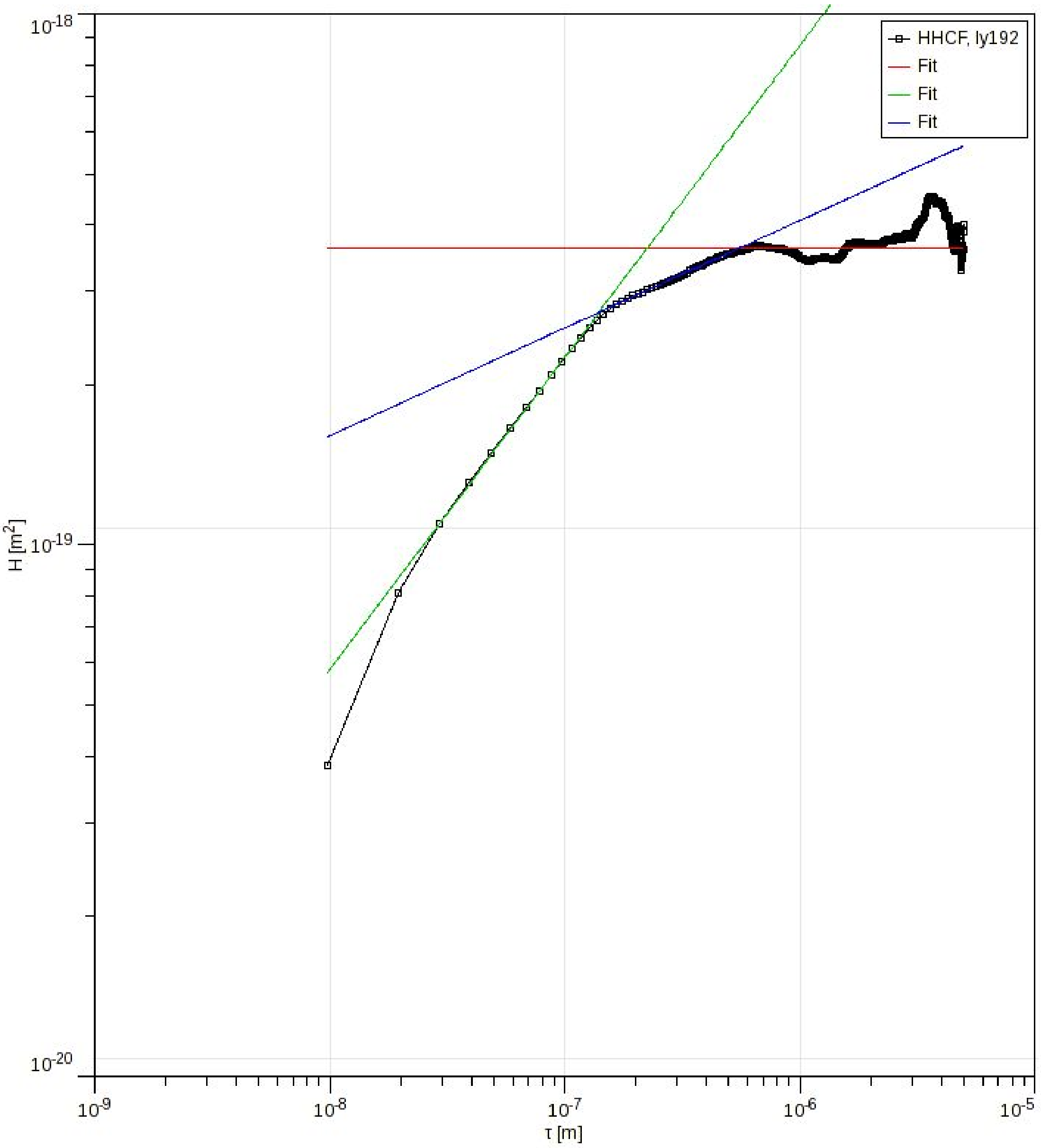


Figure S37. Height – height correlation function calculated from AFM image of **N(Ph-2T-DCN-Hex)$_3$** : PC$_{71}$BM blend (**Figure 5c**).

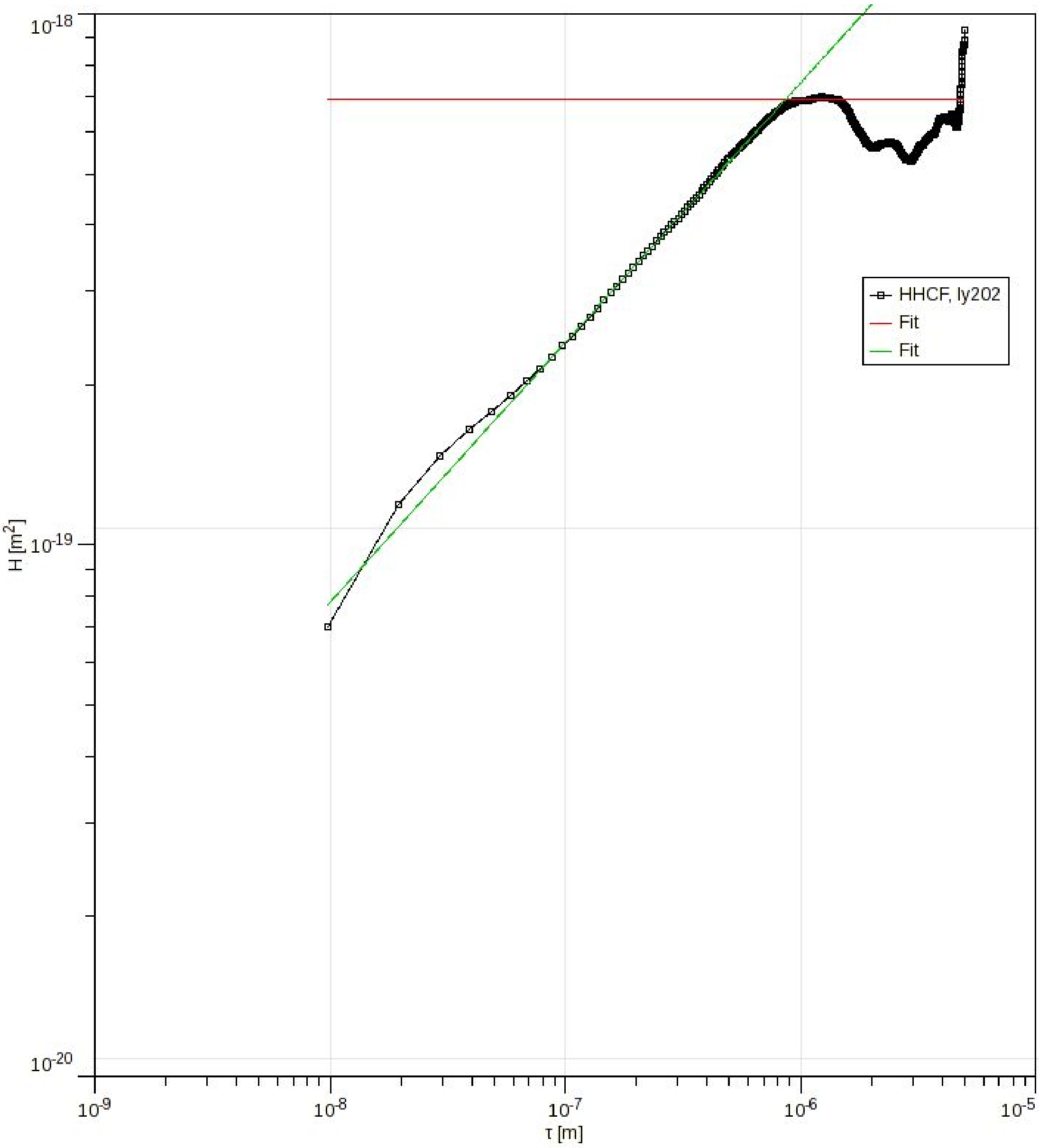


Figure S38. Height – height correlation function calculated from AFM image of **N(Ph-3T-DCN-Hex)$_3$** : PC$_{71}$BM blend (**Figure 5d**).

8. Hole mobility measurements

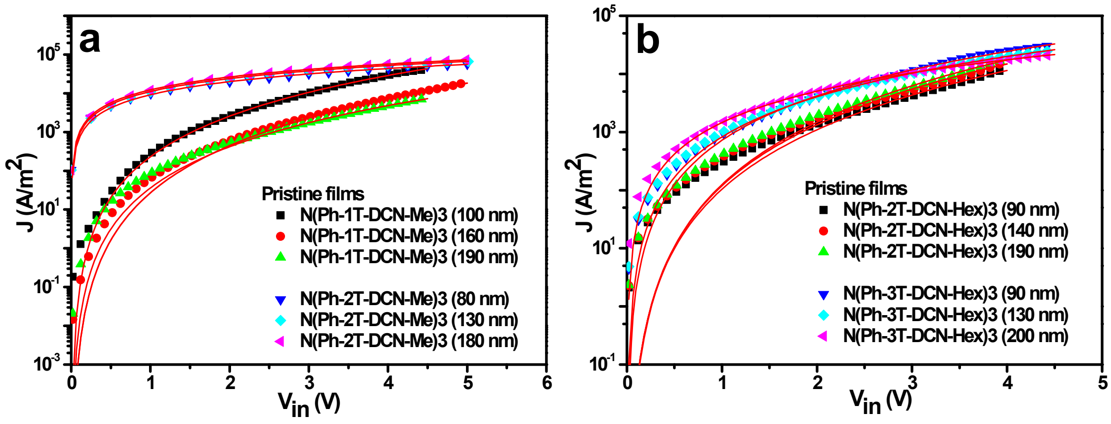


Figure S39. Hole only mobilities of pristine films of a) **N(Ph-1T-DCN-Me)$_3$** and **N(Ph-2T-DCN-Me)$_3$**; and b) **N(Ph-1T-DCN-Me)$_3$** and **N(Ph-2T-DCN-Me)$_3$**, which were determined by three different thicknesses.

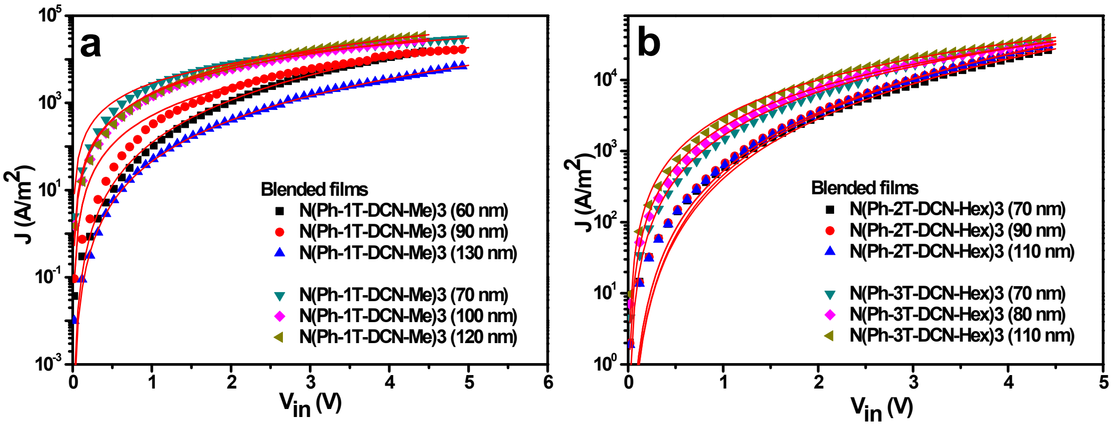


Figure S40. Hole only mobilities of blended films of a) **N(Ph-1T-DCN-Me)$_3$** and **N(Ph-2T-DCN-Me)$_3$**; and b) **N(Ph-1T-DCN-Me)$_3$** and **N(Ph-2T-DCN-Me)$_3$** with PC$_{71}$BM as acceptors, which were also determined by three different thicknesses.

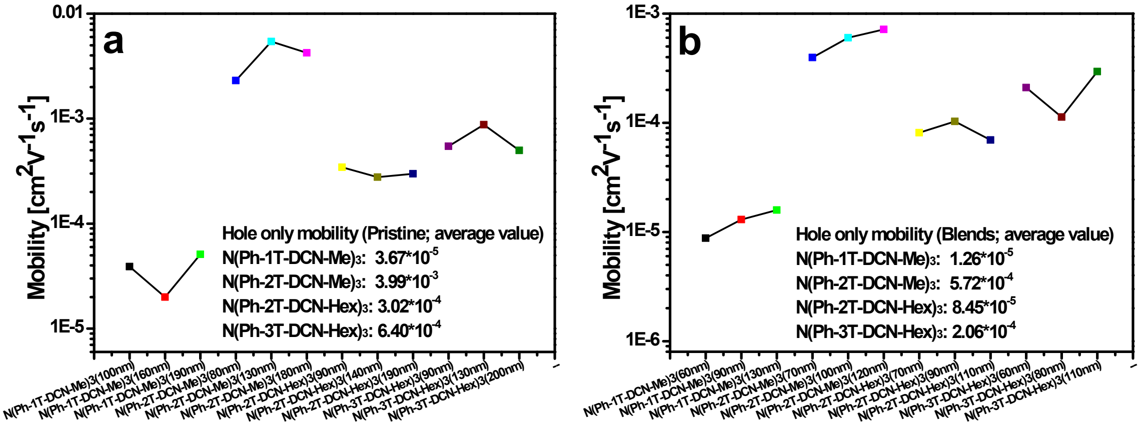


Figure S41. (a) Hole only mobilities of pristine (a) and blended (b) films with the four TPA-based molecules with $PC_{71}BM$ as acceptors, which were measured in a device geometry similar to solar cell devices for a range of thicknesses.