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# Supplementary Information

## Thiophene-Pyrrole Containing S,N-Heteroheptacenes: Synthesis, Optical, and Electrochemical Characterisation

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## Content

## Instrumentation

NMR spectra were recorded on a Bruker AMX 500 ($^1$H-NMR: 500 MHz, $^{13}$C-NMR: 125 MHz) or an Avance 400 spectrometer ($^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz). Chemical shift values ($\delta$) are expressed in parts per million using residual solvent protons ($^1$H-NMR: $\delta_H$ = 3.58 for [$D_8$]THF, 7.26 for $CDCl_3$, and 5.32 for [$D_2$]DCM; $^{13}$C-NMR: $\delta_C$ = 67.21 for [$D_8$]THF, 77.16 for $CDCl_3$, and 53.84 for [$D_2$]DCM) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). The assignments are Th-α-*H* (thiophene protons in α-position) and Th-β-*H* (thiophene protons in β.position). Elemental analyses were performed on an Elementar Vario EL or on an Elementar Vario MICRO cube. Melting points were determined using a Mettler Toledo DSC 823 or a Büchi Melting Point M-565. Thin layer chromatography was carried out on aluminum plates, pre-coated with silica gel, Merck Si60 $F_{254}$. Preparative column chromatography was performed on glass columns packed with silica gel, Merck Silica 60, particle size 40−63 µm, or aluminium oxide 90 active basic, Merck, particle size 40−200 µm. High resolution MALDI mass spectra (HRMS) experiments were recorded on a MS Bruker Reflex 2 (Bruker Daltonik GmbH, Bremen, Germany), MALDI-TOF mass spectra on a Bruker Daltonics Reflex III, using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. Chemical ionisation (CI) mass spectra were performed on a Finnigan MAT SSQ-7000. UV-Vis absorption spectra were recorded on a Perkin Elmer Lambda 19 spectrometer. Measurements of fluorescence quantum yields were performed in a Jasco-Spectrometer with an integrating sphere. Cyclic voltammetry experiments were performed with a computer-controlled Autolab PGSTAT30 potentiostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. All potentials were internally referenced to the ferrocene/ferricenium couple.

## Materials

Toluene (VWR), THF (Sigma-Aldrich), diethyl ether (VWR) and DMF (Merck) were dried and purified by a MB SPS-800 (MBraun). DCM, methanol, and petrol ether were purchased from VWR and distilled prior to use. Tris(4-bromophenyl)ammoniumyl hexachloroantimonate, sodium *tert*-butoxide, n-hexylamine, potassium thioacetate, acetone, triisopropyl chloride, N-bromosuccinimide, 1,2-dichloroethane, phosphoryl chloride, sodium bicarbonate, malonitrile, and ammonium acetate were purchased from Merck. $Pd(dba)_2$,

$Pd(dppf)Cl_2 \cdot CH_2Cl_2$, $Pd(PPh_3)_2Cl_2$ and $TBAF \cdot 3H_2O$ were purchased from Sigma Aldrich, 1,1'-bis(diphenylphosphino)ferrocene from Frontier Scientific, and potassium phosphate from ABCR.

Tetrabromothiophene,[1] 3-bromo-5-(triisopropylsilyl)-thieno[3,2-*b*]thiophene,[2] 2-bromo-6-(triisopropylsilyl)-dithieno[3,2-*b*:2′,3′-*d*]thiophene,[2] and *N*-Hexyl-dithieno[3,2-*b*:2′,3′-*d*]pyrrole[3] were prepared according to literature-known procedures.

## Synthesis

4-Hexyl-2-(trimethylstannyl)-dithieno[3,2-*b*:2',3'-*d*]pyrrole **2**

To a solution of 4-hexyl-dithieno[3,2-*b*:2',3'-*d*]pyrrole (2.00 g, 7.60 mmol) **1** in THF (35 mL) was slowly added *n*-BuLi (1.6 M in *n*-hexane, 4.80 mL, 7.60 mmol) at -78 °C. After stirring for 1 h at -78 °C, a solution of trimethyltin chloride (1.66 g, 8.33 mmol) in THF (8 mL) was added and the mixture was stirred for another 2 h at -78 °C. An aqueous $NaHCO_3$ solution (40 mL) was added and the mixture was extracted with *n*-hexane (3x40 mL). The combined organic phases were dried over $MgSO_4$. A brownish oil was obtained after removing the solvent in vacuum. $^1$H-NMR confirmed a conversion of **2** in about 94%. Stannyl **3** was used without further purification in the next step.

$^1$H-NMR (400 MHz, [D$_2$]DCM, 20 °C) $\delta$= 7.11 (d, $^3J$(H,H)= 5.3 Hz, 1H; Th-$\alpha$-*H*), 7.06 (s, 1H; Th-$\beta$-*H*), 7.03(d, $^3J$(H,H)= 5.3 Hz, 1H; Th-$\beta$-*H*), 4.20 (t, $^3J$(H,H)= 7.1 Hz, 2H; N-C$H_2$), 1.84–1.88 (m, 2H; N-CH$_2$-C$H_2$), 1.30-1.31 (m, 6H; N-(CH$_2$)$_2$-(C$H_2$)$_3$), 0.86 (t, $^3J$(H,H)= 7.0 Hz, 3H; N-(CH$_2$)$_5$-C$H_3$), 0.40 ppm (s, 9H; Sn-(CH$_3$)$_3$).

4-Hexyl-2-iodo-dithieno[3,2-*b*:2',3'-*d*]pyrrole **3**

To a solution of 4-hexyl-dithieno[3,2-*b*:2',3'-*d*]pyrrole **1** (2.00 g, 7.60 mmol) in THF (35 mL) was slowly added *n*-BuLi (1.6 M in *n*-hexane, 4.80 mL, 7.60 mmol) at -78 °C. After stirring for 1 h at -78 °C, the solution was cooled down to -90 °C. Iodine (2.03 g, 7.98 mmol) was added and the mixture was stirred for another 2 h at -78 °C. After purification by column chromatography ($Al_2O_3$, activity stage II; petroleum ether) a light brown oil was isolated. $^1$H-NMR confirmed a conversion to **3** of about 94%. Compound **3** was used without further purification in the next step.

$^1$H-NMR (400 MHz, [D$_2$]DCM, 20 °C) δ= 7.24 (s, 1H; Th-α-*H*), 7.14(d, $^3$*J*(H,H)= 5.3 Hz, 1H; Th-*β*-*H*), 7.02 (d, $^3$*J*(H,H)= 5.3 Hz, 1H; Th-*β*-*H*), 4.15 (t, $^3$*J*(H,H)= 7.2 Hz, 2H; N-C*H$_2$*), 1.79-1.85 (m, 2H; N-CH$_2$-C*H$_2$*), 1.27-1.31 (m, 6H; N-(CH$_2$)$_2$-(C*H$_2$*)$_3$), 0.83-0.89 ppm (m, 3H; N-(CH$_2$)$_5$-C*H$_3$*).

4,4'-Dihexyl-2,2'-bi[dithieno[3,2-*b*:2',3'-*d*]pyrrole] **4**

2-Iodo-*N*-(hexyl)-dithieno[3,2-*b*:2',3'-*d*]pyrrole **3** (1.66 g, 4.26 mmol), 2-trimethylstannyl-*N*-(hexyl)-dithieno[3,2-*b*:2',3'-*d*]pyrrole **2** (2.27 g, 5.33 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ (0.09 g, 0.13 mmol) were dissolved in DMF (11 mL). The mixture was degassed and stirred for 18 h at 80 °C. Water was added and the mixture was extracted several times with dichloromethane. The combined organic phases were dried over MgSO$_4$ and the solvents were removed in vacuum. The crude product was further purified by column chromatography (Al$_2$O$_3$, activity stage II, petroleum ether/dichloromethane: 4/1), and was recrystallized from isopropanol to give pure DTP dimer **4** (1.93 g, 3.68 mmol) as a yellow solid in 86% yield.

Mp. 118.0-119.5 °C; $^1$H-NMR (400 MHz, CDCl$_3$, 20 °C): δ= 7.13 (d, $^3$*J*(H,H)= 5.2 Hz, 2H; Th-*α*-*H*), 7.10 (s, 2H, Th-*β*-*H*), 6.99 (d, $^3$*J*(H,H)= 5.2 Hz, 2H; Th-*β*-*H*), 4.18 (t, $^3$*J*(H,H)= 7.1 Hz, 4H; N-C*H$_2$*), 1.85-1.92 (m, 4H; N-CH$_2$-C*H$_2$*), 1.28-1.38 (m, 12H; N-(CH$_2$)$_2$-(C*H$_2$*)$_3$), 0.88 ppm (t, $^3$*J*(H,H)= 5.2 Hz,6H; N-(CH$_2$)$_5$-C*H$_3$*)). $^{13}$C-NMR (400 MHz, CDCl$_3$, 20 °C): δ= 144.91, 144.83, 136.11, 123.21, 115.01, 113.41, 111.06, 106.90, 47.55, 31.58, 30.50, 26.82, 22.68, 14.19 ppm. HRMS (MALDI): *m/z*: calcd. for $C_{28}H_{32}N_2S_4$: 524.14428; found: 524.14499 [M$^+$] (δm/m= 1.35 ppm).

6,6’-Bis(triisopropylsilyl)-4,4'-dihexyl-2,2'-bi[dithieno[3,2-*b*:2',3'-*d*]pyrrole] **5**

Dimer **4** (0.80 g, 1.52 mmol) was dissolved in dry THF (10 mL) and cooled down to -78 °C. *N*-BuLi (2.40 mL, 3.81 mmol, 1.6 M in *n*-hexane) was added dropwise to the solution and the mixture was stirred for 1 h at -78 °C. Triisopropylsilyl chloride (0.70 mL, 1.26 mmol) was added slowly, the mixture was stirred for another 3 h at this temperature and then allowed to warm up to room temperature overnight. Brine (40 mL) was added to the mixture and the aqueous phase was extracted several times with dichloromethane (3x50 mL). The combined organic phases were dried over MgSO$_4$ and the solvents were removed in vacuum. The crude product was further purified by column chromatography (Al$_2$O$_3$, activity stage II, petroleum ether/ dichloromethane: 4/1), and was recrystallized from isopropanol to give pure TIPS-substituted dimer **5** (0.90 g, 1.06 mmol) as an orange solid in 70% yield.

Mp. 161.5-162.3 °C; $^1$H-NMR (400 MHz, [D$_8$]THF, 20 °C): δ= 7.15 (d, 2H; Th-*β*-*H*), 7.11 (s, 2H, Th-*β*-*H*), 4.19 (t, $^3$*J*(H,H)= 6.9 Hz, 4H; N-C*H$_2$*), 1.85-1.92 (m, 4H; N-CH$_2$-C*H$_2$*), 1.28-1.42 (m, 18H; N-(CH$_2$)$_2$-(C*H$_2$*)$_3$+Si-(C*H*)$_3$), 1.16 (d, $^3$*J*(H,H)= 7.4 Hz, 36H; Si-(CH)$_3$-(C*H$_3$*)$_6$), 0.87 (t, 6H, $^3$*J*(H,H)= 7.0 Hz; N-(CH$_2$)$_5$-C*H$_3$*)). $^{13}$C-NMR (100 MHz, [D$_8$]THF, 20 °C): δ= 148.16, 146.39, 137.08, 132.22, 120.90, 119.36, 113.60, 107.57, 47.48, 32.25, 31.19, 27.40, 23.31, 18.91, 14.18, 12.61 ppm. HRMS (MALDI): *m/z*: calcd. for $C_{46}H_{72}N_2S_4Si_2$: 836.41114; found: 836.41105 [M$^+$] (δm/m= 0.11 ppm). Elemental analysis: calculated (%) for $C_{46}H_{72}N_2S_4Si_2$: C 65.97, H 8.67, N 3.34, S 15.31; found: C 66.01, H 8.49, N 3.27, S 15.27.

### 6,6’-Bis(triisopropylsilyl)-3,3‘-dibromo-4,4'-dihexyl-2,2'-bi[dithieno[3,2-*b*:2',3'-*d*]pyrrole] **6**

Dimer **5** (795 mg, 0.95 mmol) was dissolved in dry THF (25 mL) and cooled down to 0 °C. A solution of NBS (372 mg, 2.09 mmol) in dry THF (4 mL) was added dropwise. The resulting solution was stirred for 4 days at room temperature in the absence of light. Brine (50 mL) was added and the solution was extracted several times with dichloromethane. The combined organic phases were dried over MgSO$_4$. Further purification by column chromatography (Al$_2$O$_3$, activity stage II, petroleum ether/dichloromethane: 8/2) gave pure dibromide **6** (887 mg, 0.89 mmol) as a yellow solid in 94%.

Mp. 186.6 – 187.7 °C; $^1$H-NMR (400 MHz, [D$_8$]THF, 20 °C): δ= 7.31 (s, 2H; Th-β-*H*), 4.61 (t, $^3$*J*(H,H)= 7.1 Hz, 4H; N-C*H$_2$*), 1.93 (m, 4H; N-CH$_2$-C*H$_2$*), 1.25-1.49 (m, 18H; N-CH$_2$-CH$_2$-(C*H$_2$*)$_3$+Si-(C*H*)$_3$), 1.16 (d, $^3$*J*(H,H)= 7.4 Hz, 36H; CH-(C*H$_3$*)$_2$), 0.87 ppm (t, $^3$*J*(H,H)= 7.0 Hz, 6H; N-(CH$_2$)$_5$-C*H$_3$*). $^{13}$C-NMR (100 MHz, [D$_8$]THF, 20 °C): δ= 149.55, 140.41, 135.08, 127.07, 120.21, 119.41, 117.22, 98.57, 46.43, 32.57, 32.33, 27.35, 23.33, 18.86, 14.14, 12.57 ppm. HRMS (MALDI): *m/z*: calcd. for $C_{46}H_{70}Br_2N_2S_4Si_2$: 992.23277; found: 992.23266 [M$^+$] (δm/m= 0.11 ppm). Elemental analysis: calculated (%) for $C_{46}H_{70}Br_2N_2S_4Si_2$: C 55.51 H 7.09, N 2.81, S 12.88; found C 55.69 H 7.21, N 2.75, S 12.83.

### 2,8-Bis(triisopropylsilyl)-4,5,6-trihexyl-thieno[3,2-*b*]thieno[2’’’’,3’’’’:4’’’,5’’’]pyrrolo-[2’’’,3’’’: 4’’,5’’]thieno[2’’,3’’:4’,5’]pyrrolo[2’,3’:4,5]thieno[2,3-*d*]pyrrole **7**

Dibromide **6** (400 mg, 0.40 mmol), sodium-*tert*-butoxide (386 mg, 4.02 mmol), Pd(dba)$_2$ (23 mg, 0.04 mmol) and dppf (89 mg, 0.16 mmol) were stirred in dry and degassed toluene (20 mL) at room temperature. After 20 min *n*-hexylamine (79 µL, 0.60 mmol) was added and the mixture was stirred at 110 °C for 18 h. Water (30 mL) and ether (30 mL) were added to the cooled reaction mixture and the resulting solid was filtered off. Further purification by column chromatography (flash-silica; dichloromethane) gave pure TIPS-substituted SN7 **7** as a yellow solid (244 mg, 0.26 mmol, 65%).

Mp. 227.8 °C (DSC); $^1$H-NMR (400 MHz, [D$_8$]THF, 20 °C): δ= 7.25 (s, 2H; Th-β-*H*), 4.61 (t, $^3J$(H,H)= 7.7 Hz, 2H; N-C*H$_2$*), 4.53 (t, $^3J$(H,H)= 7.1 Hz, 4H; N-C*H$_2$*), 1.96-2.02 (m, 4H; N-CH$_2$-C*H$_2$*), 1.83-1.84 (m, 2H; N-CH$_2$-C*H$_2$*), 1.40-1.44 (m, 6H; N-CH$_2$-CH$_2$-(C*H$_2$*)$_3$), 1.29-1.34 (m, 18H; N-CH$_2$-CH$_2$-(C*H$_2$*)$_3$+Si-(C*H*)$_3$), 1.19 (d, $^3J$(H,H)= 7.4 Hz, 36H; CH-(C*H$_3$*)$_2$), 0.85 ppm (t, $^3J$(H,H)= 7.0 Hz, 6H; C*H$_3$*), 0.79 ppm (t, $^3J$(H,H)= 7.0 Hz, 3H; C*H$_3$*). $^{13}$C-NMR: $^{13}$C-NMR could not be measured due to low solubility. HRMS (MALDI): *m/z*: calcd. for $C_{52}H_{83}N_3S_4Si_2$: 933.50029; found: 933.50087 [M$^+$] (δm/m= 0.62 ppm).

### 4,5,6-Trihexyl-thieno[3,2-*b*]thieno[2’’’’,3’’’’:4’’’,5’’’]pyrrolo[2’’’,3’’’:4’’,5’’]thieno[2’’,3’’:4’,5’]pyrrolo[2’,3’:4,5]thieno[2,3-*d*]pyrrole **SN7a**

To a solution of TIPS-SN7 **7** (143 mg, 0.15 mmol) in THF (30 mL) was added TBAF·3H$_2$O (580 mg, 1.84 mmol). The solution was stirred at room temperature under exclusion of light. After 20 h, water (50 mL) was added, the mixture was extracted with dichloromethane (3x50 mL), and dried over MgSO$_4$. After purification by column chromatography (Al$_2$O$_3$, activity stage II, petroleum ether/dichloromethane: 9/1), **SN7a** (89 mg, 0.15 mmol) was obtained as a colourless solid in 94% yield.

Mp. 209.0 °C (DSC); $^1$H-NMR (400 MHz, [D$_8$]THF, 20 °C): δ= 7.12 (s, 4H; Th-*α-H* ,Th-*β-H*), 4.60 (t, $^3J$(H,H)= 7.8 Hz, 2H; N-C*H$_2$*), 4.49 (t, $^3J$(H,H)= 7.4 Hz, 2H; N-C*H$_2$*), 1.94-1.98 (m, 4H; N-CH$_2$-C*H$_2$*), 1.81-1.88 (m, 2H; N-CH$_2$-C*H$_2$*), 1.22-1.36 (m, 18H; N-(CH$_2$)$_3$-(C*H$_2$*)$_3$), 0.86 (t, $^3J$(H,H)= 7.0 Hz, 6H; C*H$_3$*); 0.78 ppm (t, $^3J$(H,H)= 7.0 Hz, 3H; C*H$_3$*). $^{13}$C-NMR: $^{13}$C-NMR could not be measured due to low solubility. HRMS (MALDI): *m/z*: calcd. for $C_{34}H_{43}N_3S_4$: 621.23343; found: 621.23288 [M$^+$] (δm/m= 0.88 ppm).

### 2,8-Bis(triisopropylsilyl)-4,6-dihexyl-thieno[3,2-*b*]thieno[2’’’’,3’’’’:4’’’,5’’’]pyrrolo-[2''',3''':4'',5'']thieno[2'',3'':4',5']thieno[2',3':4,5]thieno[2,3-*d*]pyrrole **8**

Pd(dba)$_2$ (12 mg, 0.02 mmol) and dppf (49 mg, 0,081 mmol) were stirred in toluene (2 mL) at room temperature. After 10 min, dibromide **6** (380 mg, 0.38 mmol), potassium thioacetate (61 mg, 0.53 mmol), potassium phosphate (146 mg, 0.69 mmol), acetone (5 mL), and toluene

(20 mL) were added and the reaction mixture was heated up to 130 °C. After 3 d, the cooled reaction mixture was put into water (40 ml) and extracted with petroleum ether (30 mL) and dichloromethane (2x30 mL). After removing the solvent in vacuum, the crude product was further purified by column chromatography (flash silica, petroleum ether/dichloromethane: 20/1) to give the pure TIPS-substituted SN7c **8** (204 mg, 0.24 mmol, 62%) as a yellow solid.

Mp. 222.3 °C (DSC); $^1$H-NMR (400 MHz, [D$_8$]THF, 20 °C): $\delta$= 7.29 (s, 2H; Th-$\beta$-*H*), 4.42 (t, 4H, $^3J$ (H,H)= 6.9 Hz, 4H; N-C*H$_2$*), 1.95–2.02 (m, 4H; N-CH$_2$-C*H$_2$*), 1.27–1.47 (m, 18H; N-CH$_2$-CH$_2$-(C*H$_2$*)$_3$+Si-(C*H*)$_3$), 1.19 (d, $^3J$(H,H)= 7.4 Hz, 36H; CH-(C*H$_3$*)$_2$), 0.86 ppm (t, $^3J$(H,H)= 7.2 Hz, 6H; C*H$_3$*). $^{13}$C-NMR (100 MHz, [D$_8$]THF, 20 °C): $\delta$= 147.52, 137.57, 132.42, 131.94, 122.84, 122.17, 119.36, 115.65, 48.21, 32.23, 31.97, 27.37, 23.23, 18.90, 14.16, 12.61 ppm. HRMS (MALDI): *m/z*: calcd. for $C_{46}H_{70}N_2S_5Si_2$: 866.36756; found: 866.36535 [M$^+$] ($\delta$m/m= 2.55 ppm), 1782.67590 [2M$^+$].

### 4,6-Dihexyl-thieno[3,2-*b*]thieno[2’’’’,3’’’’:4’’’,5’’’]pyrrolo[2''',3''':4'',5'']thieno[2'',3'':4',5']thieno[2',3':4,5]thieno[2,3-*d*]pyrrole **SN7c**

To a solution of TIPS-SN7c **8** (150 mg, 0.17 mmol) in THF (11 mL) was added TBAF·3H$_2$O (1.09 g, 3.46 mmol). The solution was stirred at room temperature under exclusion of light. After 21 h, the solvent was removed and methanol (50 mL) was added and the resulting precipitate was filtered off. The pale yellow solid **SN7c** (85 mg, 0.15 mmol, 89%) was washed thoroughly with methanol (50 mL) and dried under vacuum.

Mp. 169.3 °C (DSC); $^1$H-NMR (400 MHz, [D$_8$]THF, 20 °C): $\delta$= 7.21 (d, $^3J$(H,H)= 5.3 Hz, 2H; Th-$\alpha$-*H*), 7.14 (d, $^3J$(H,H)= 5.3 Hz, 2H; Th-$\beta$-*H*), 4.39 (t, 4H, $^3J$ (H,H)= 7.0 Hz; N-C*H$_2$*), 1.93–2.01 (m, 4H; N-CH$_2$-C*H$_2$*), 1.27–1.45 (m, 12H; N-(CH$_2$)$_2$-(C*H$_2$*)$_3$), 0.87 ppm (t, $^3J$(H,H)= 7.1 Hz, 6H; C*H$_3$*). $^{13}$C-NMR (100 MHz, [D$_8$]THF, 20 °C): $\delta$= 145.11, 136.78, 131.47, 123.66, 122.75, 116.68, 115.60, 111.70, 48.25, 32.23, 31.80, 27.28, 23.19, 14.18 ppm. HRMS (MALDI): m/z: calcd. for $C_{28}H_{30}N_2S_5$: 554.10071; found: 554.09932 [M$^+$] ($\delta$m/m= 2.54 ppm).

### 2,3-Dibromo-5-(triisopropylsilyl)-thieno[3,2-*b*]thiophene **10**

3-Bromo-5-(triisopropylsilyl)-thieno[3,2-*b*]thiophene **9** (1.02 g, 2.72 mmol) was dissolved in 100 mL DMF at 0 °C. *N*-Bromosuccinimide (532 mg, 2.99 mmol) was added and the solution was allowed to slowly warm up to room temperature. After 17 h, diethyl ether (150 mL) and water (200 mL) were added. The aqueous phase was extracted with diethyl ether (2x150 mL). The combined organic phases were dried over $MgSO_4$. After removing the solvent in vacuo, the residue was further purified by column chromatography (flash-silica; petroleum ether) to afford 2,3-dibromo-5-(triisopropylsilyl)-thieno[3,2-*b*]thiophene **10** (1.14 g, 2.51 mmol, 92 %) as a white solid.

Mp. (DSC) 78.8 °C; $^1$H-NMR (400 MHz, [D2]DCM, 20 °C): δ= 7.36 (s, 1H; Th-β-*H*), 1.37 (m, 3H; Si-(C*H*)$_3$), 1.12 ppm (d, $^3J$(H,H)= 7.4 Hz, 18H; CH-(C*H$_3$*)$_2$). $^{13}$C-NMR (100 MHz, [D$_2$]DCM, 20 °C) δ= 144.20, 138.67, 138.40, 127.75, 113.19, 106.75, 18.66, 12.15 ppm. MS (EI): *m/z* (%): 454 (75) [*M*]$^+$, 411 (100) [M-$C_3H_7$]$^+$, 369 (25) [M-2$C_3H_7$]$^+$. Elemental analysis: calculated (%) for $C_{15}H_{22}Br_2S_2Si$: C 39.65, H 4.88, S 14.11; found: C 39.61, H 4.88, S 14.25.

2,5-Bis[3-bromo-5-(triisopropylsilyl)-thieno[3,2-*b*]thien-2-yl]-3,4-dibromothiophene **12**

To a stirred solution of 2,3-dibromo-5-(triisopropylsilyl)-thieno[3,2-*b*]thiophene **10** (454 mg, 1.00 mmol) in dry ether (3.7 mL) was added dropwise *n*-BuLi (0.69 mL, 1.10 mmol, 1.6 M in hexane) at -78 °C. After stirring for 1 h at this temperature, a solution of $ZnCl_2$ (147 mg, 1.08 mmol) in THF (7.4 mL) was added and the solution was stirred for 1 h at 0 °C. Then, 2,3,4,5-tetrabromothiophene (148 mg, 0.37 mmol) and Pd(dppf)$Cl_2 \cdot CH_2Cl_2$ (16 mg, 0.02 mmol) were added and the mixture was stirred for 26 h at 50 °C. After removing the solvent in vacuum, the crude product was further purified by column chromatography (flash silica, petroleum ether) to give pure tetrabromide **12** (212 mg, 0.21 mmol) as a white solid in 58% yield.

Mp. 227.2 – 231.1 °C; $^1$H-NMR (400 MHz, [D$_8$]THF, 20 °C): δ= 7.66 (s, 2H; Th-β-*H*), 1.39-1.50 (m, 6H; Si-(C*H*)$_3$), 1.18 ppm (d, $^3J$(H,H)= 7.3 Hz, 36H; CH-(C*H$_3$*)$_2$). $^{13}$C-NMR (100 MHz, [D$_8$]THF, 20 °C): δ= 146.52, 141.25, 140.62, 132.93, 130.40, 129.21, 117.60, 105.74, 18.73, 12.52 ppm. HRMS (MALDI): *m/z*: calcd. for $C_{34}H_{44}Br_4S_5Si_2$: 987.82736; found: 987.82616 [M$^+$] (δm/m= 1.21 ppm).

3,8-Bis(triisopropylsilyl)-5,6-dihexyl-thieno[2′,3′:4,5]thieno[3,2-*b*]thieno[2′′′,3′′′:4′′,5′′]thieno-[2′′,3′′:4′,5′]pyrrolo[2′,3′:4,5]thieno[2,3-*d*]pyrrole **13**

Tetrabromide **12** (200 mg, 0.20 mmol), Pd(dba)$_2$ (12 mg, 0.02 mmol), ddpf (49 mg, 0,081 mmol) and sodium *tert*-butoxide (311 mg, 3.24 mmol) were stirred in toluene (9 mL) at room temperature. After 20 min, 1-hexylamine was added and the reaction mixture was heated up to 110 °C. After 23 h, the cooled reaction mixture was put into water (40 ml) and extracted with petroleum ether (30 mL) and dichloromethane (30 mL). After removing the solvent in vacuum, the crude product was further purified by column chromatography (flash silica, petroleum ether/dichloromethane: 4/1) to give TIPS-substituted SN7b **13** (111 mg, 0.13 mmol, 64%) as a yellow solid.

Mp. 193.7 – 196.6 °C; $^1$H-NMR (400 MHz, [D$_8$]THF, 20 °C): δ= 7.53 (s, 2H; Th-β-*H*), 4.60 (t, $^3J$ (H,H)= 7.5 Hz, 4H; N-C*H$_2$*), 1.97–2.05 (m, 4H; N-CH$_2$-C*H$_2$*), 1.29–1.50 (m, 18H; N-CH$_2$-CH$_2$-(C*H$_2$*)$_3$+Si-(C*H*)$_3$), 1.19 (d, $^3J$(H,H)= 7.4 Hz, 36H; CH-(C*H$_3$*)$_2$), 0.85 ppm (t, $^3J$(H,H)= 7.1 Hz, 6H; C*H$_3$*). $^{13}$C-NMR (100 MHz, [D$_8$]THF, 20 °C): δ= 140.98, 135.67, 132.92, 130.06, 129.78, 129.63, 120.12, 118.05, 50.05, 32.46, 32.17, 27.08, 23.10, 18.86, 14.08, 12.65 ppm. HRMS (MALDI): *m/z*: calcd. for $C_{46}H_{70}N_2S_5Si_2$: 866.36756; found: 866.36735 [M$^+$] (δm/m= 0.24 ppm).

### 5,6-Dihexyl-thieno[2′,3′:4,5]thieno[3,2-*b*]thieno[2′′′,3′′′:4′′,5′′]thieno[2′′,3′′:4′,5′]pyrrolo-[2′,3′:4,5]thieno[2,3-*d*]pyrrole **SN7b**

To a solution of TIPS-substituted SN7b **13** (46 mg, 0.05 mmol) in THF (12 mL) was added TBAF· 3H$_2$O (348 mg, 1.10 mmol). The solution was stirred at room temperature under exclusion of light. After 26 h, methanol (70 mL) was added and the resulting precipitate was filtered off. The white solid of **SN7b** (29 mg, 0.052 mmol, 98%) was washed thoroughly with methanol (100 mL) and dried under vacuum.

Mp. 194.1 °C (DSC); $^1$H-NMR (400 MHz, [D$_8$]THF, 20 °C): δ= 7.37 (d, $^3J$(H,H)= 5.2 Hz, 2H; Th-α-*H*), 7.33 (d, $^3J$(H,H)= 5.2 Hz, 2H; Th-β-*H*), 4.52 (t, 4H, $^3J$ (H,H)= 7.5 Hz; N-C*H$_2$*), 1.94–2.02 (m, 4H; N-CH$_2$-C*H$_2$*), 1.44–1.52 (m, 4H; N-CH$_2$-CH$_2$-C*H$_2$*), 1.26–1.40 (m, 8H; N-(CH$_2$)$_3$-(C*H$_2$*)$_2$), 0.87 ppm (t, $^3J$(H,H)= 7.1 Hz, 6H; C*H$_3$*). $^{13}$C-NMR (100 MHz, [D$_8$]THF, 20 °C): δ= 138.92, 135.82, 129.52, 124.46, 124.00, 121.84, 119.21, 117.77, 50.12, 32.60, 32.26, 27.23, 23.20, 14.09 ppm. HRMS (MALDI): m/z: calcd. for $C_{28}H_{30}N_2S_5$: 554.10071; found: 554.10086 [M$^+$] (δm/m= 0.29 ppm).

### 6,6‘-Bis(triisopropylsilyl)-3,3'-dibromo-2,2'-bi[dithieno[3,2-*b*;2‘,3‘-*d*]thiophene] **15**

To a solution of diisopropylamine (0.35 mL, 2.49 mmol) in dry THF (25 mL) at 0 °C was added n-butyl lithium (1.6 M in hexane, 1.38 mL, 2.21 mmol) under Ar atmosphere. After stirring for 30 minutes at this temperature, the solution was cooled to -78 °C. A solution of (6-bromo-dithieno[3,2-*b*;2',3'-*d*]thien-2-yl)triisopropylsilane **14** (0.79 g, 1.84 mmol) in dry THF (5 mL) was added to the lithium diisopropylamide solution, and the reaction mixture was stirred for 1 hour at .78 °C, followed by the addition of CuCl$_2$ (335 mg, 2.49 mmol). The mixture was allowed to warm up slowly to room temperature and stirred overnight. After removing the solvent in vacuum, the crude product was further purified by column chromatography (petroleum ether) in order to get dibromide **15** (412 mg, 0.48 mmol) as a pale yellow solid in 52% yield.

Mp. 317.4 °C (DSC); $^1$H-NMR (400 MHz, [D$_8$]THF, 20 °C): δ= 7.67 (s, 2H; Th-β-*H*), 1.40-1.49 (m, 6H; Si-(C*H*)$_3$), 1.19 ppm (d, $^3$*J*(H,H)= 7.4 Hz, 36H; CH-(C*H*$_3$)$_2$). $^{13}$C-NMR (125 MHz, CDCl$_3$, 20 °C): δ= 143.85, 143.40, 139.41, 136.42, 130.83, 128.74, 128.44, 106.56, 18.80, 12.17 ppm. HRMS (MALDI): *m/z*: calcd. for $C_{34}H_{44}Br_2S_6Si_2$: 859.96474; found: 859.96399 [M$^+$] (δm/m= 0.87 ppm).

### 3,9-Bis(triisopropylsilyl)-6-hexyl-thieno[2’’,3’’:4’,5’]thieno[2’,3’:4,5]thieno[3,2-*b*]thieno[2’’,3’’:4’,5’]thieno[2’,3’:4,5]thieno[2,3-*d*]pyrrole **16**

Dibromide **15** (220 mg, 0.26 mmol), sodium-*tert*-butoxide (246 mg, 2.55 mmol), Pd(dba)$_2$ (15 mg, 0.03 mmol) and dppf (57 mg, 0.10 mmol) were stirred in dry and degassed toluene (11 mL) at room temperature. After 20 min *n*-hexylamine (51 µL, 0.38 mmol) was added and the mixture was stirred at 110 °C for 18 h. Water (30 mL) was added to the cooled reaction mixture and the aqueous phase was extracted with petroleum ether (30 mL) and dichloromethane (2x30 mL). The solvents were removed under reduced pressure. The crude product was purified by column chromatography under exclusion of light (flash-silica; petroleum ether/ dichloromethane 25:1). Pure TIPS-substituted SN7d **16** was obtained as a yellow solid (156 mg, 0.20 mmol, 74%).

Mp. 171.1 °C (DSC); $^1$H-NMR (400 MHz, [D$_8$]THF, 20 °C): δ= 7.57 (s, 2H; Th-β-*H*), 4.48 (t, 4H, $^3$*J* (H,H)= 6.9 Hz, 2H; N-C*H*$_2$), 1.99–2.07 (m, 2H; N-CH$_2$-C*H*$_2$), 1.42–1.48 (m, 6H; Si-(C*H*)$_3$) 1.26-1.36 (m, 6H; N-CH$_2$-CH$_2$-(C*H*$_2$)$_3$), 1.19 (d, $^3$*J*(H,H)= 7.4 Hz, 36H; CH-(C*H*$_3$)$_2$), 0.84 ppm (t, $^3$*J*(H,H)= 7.2 Hz, 3H; C*H*$_3$). $^{13}$C-NMR (100 MHz, [D$_8$]THF, 20 °C): δ= 141.93, 138.34, 136.46, 135.76, 129.86, 129.42, 126.30, 118.07, 49.14, 32.43, 32.24, 27.26, 23.08, 18.83, 14.15, 12.59 ppm. HRMS (MALDI): *m/z*: calcd. for $C_{40}H_{57}NS_6Si_2$: 799.23483; found: 799.23335 [M$^+$] (δm/m= 1.85 ppm).

### 6-Hexyl-thieno[2’’,3’’:4’,5’]thieno[2’,3’:4,5]thieno[3,2-*b*]thieno[2’’,3’’:4’,5’]thieno[2’,3’:4,5]-thieno[2,3-*d*]pyrrole **SN7d**

To a solution of TIPS-SN7d **16** (153 mg, 0.19 mmol) in THF (30 mL) was added TBAF·3$H_2O$ (1.20 g, 3.80 mmol). The solution was stirred at room temperature under exclusion of light. After 26 h, the solvent was removed and methanol (100 mL) was added and the resulting precipitate was filtered off. The pale yellow solid of **SN7d** (92 mg, 0.19 mmol, 99%) was washed with methanol (50 mL) and dried under vacuum.

Mp. 241.2 °C (DSC). $^1$H-NMR (500 MHz, [$D_8$]THF, 53 °C) δ= 7.43 (d, $^3J$(H,H)= 5.2 Hz, 2H; Th-*α*-*H*), 7.34 (d, $^3J$(H,H)= 5.2 Hz, 2H; Th-*β*-*H*), 4.42 (t, $^3J$(H,H)= 7.1 Hz, 2H; N-C*H₂*), 2.00-2.06 (m, 2H; N-$CH_2$-C$H_2$), 1.47–1.53 (m, 2H; N-$(CH_2)_2$-C$H_2$), 1.26–1.39 (m, 4H; N-$(CH_2)_3$-$(CH_2)_2$), 0.85 ppm (t, $^3J$(H,H)= 7.2 Hz, 3H; C$H_3$). $^{13}$C-NMR (125 MHz, [$D_8$]THF, 53 °C): δ= 140.02, 136.49, 133.30, 130.20, 126.11, 125.73, 121.28, 117.79, 49.18, 32.43, 32.15, 27.26, 23.04, 13.96 ppm. HRMS (MALDI): *m/z* calcd. for $C_{22}H_{17}NS_6$ 486.96798; found 486.96678 [$M^+$] (δm/m= 2.46 ppm).

## $^1$H-NMR and high resolution mass spectrum of SN7a

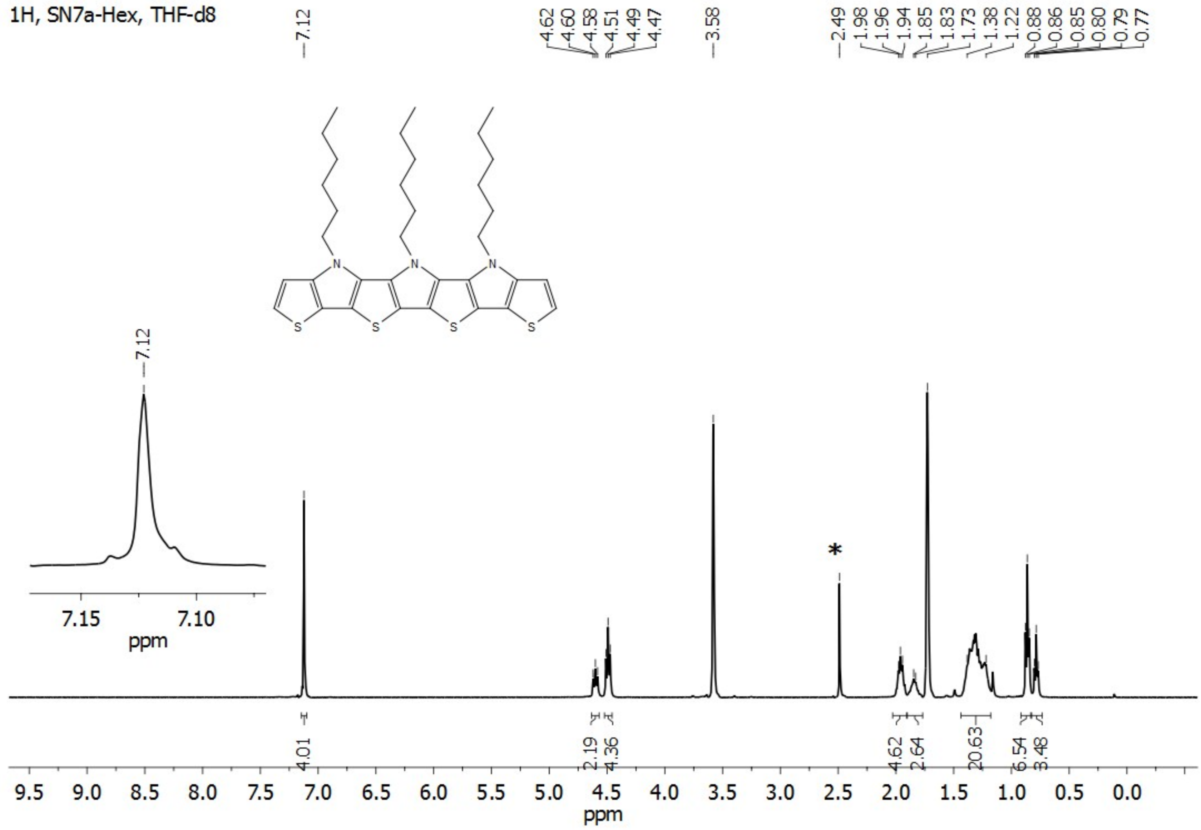

**Figure S1.** $^1$H-NMR spectrum of **SN7a** in [D$_8$]THF (400 MHz); *solvent impurities.

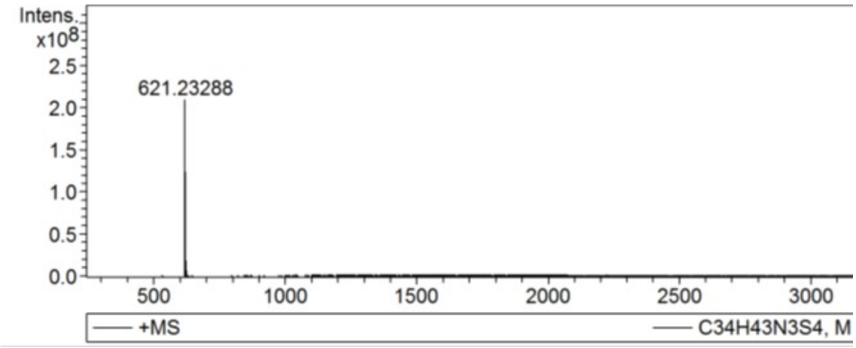

**Figure S2.** High resolution MALDI mass spectrum of **SN7a** (matrix: *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)).

## $^{1}$H-NMR, $^{13}$C-NMR and high resolution mass spectrum of SN7b

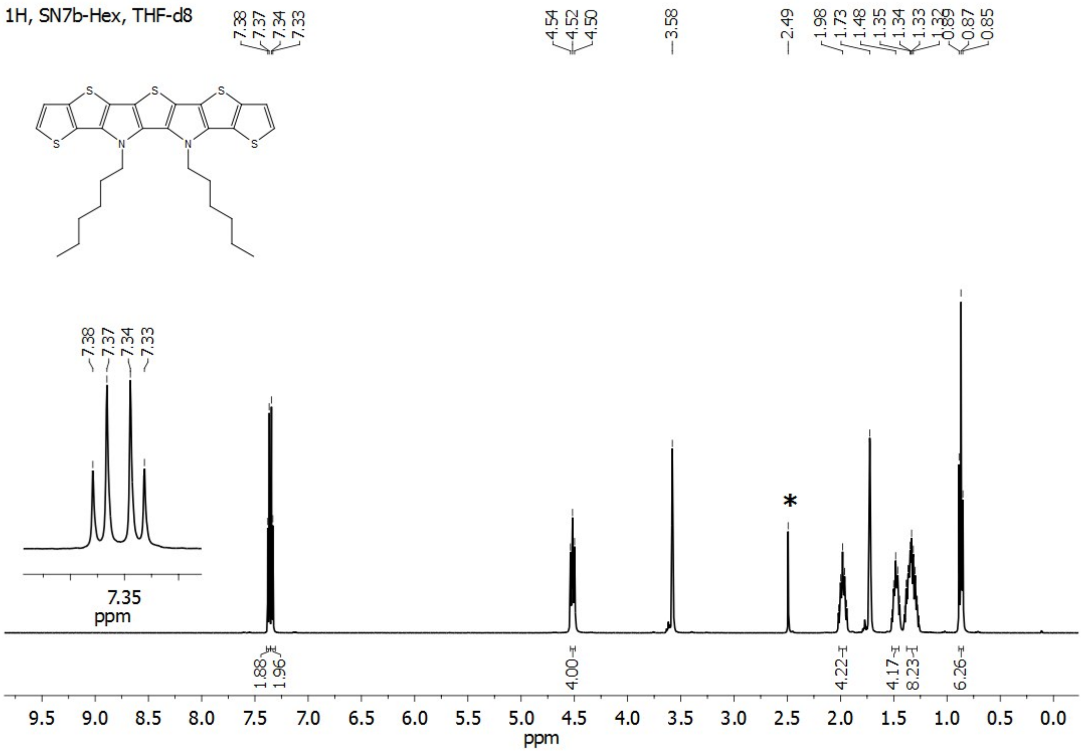

**Figure S3.** $^{1}$H-NMR spectrum of **SN7b** in [D$_8$]THF (400 MHz); *solvent impurities.

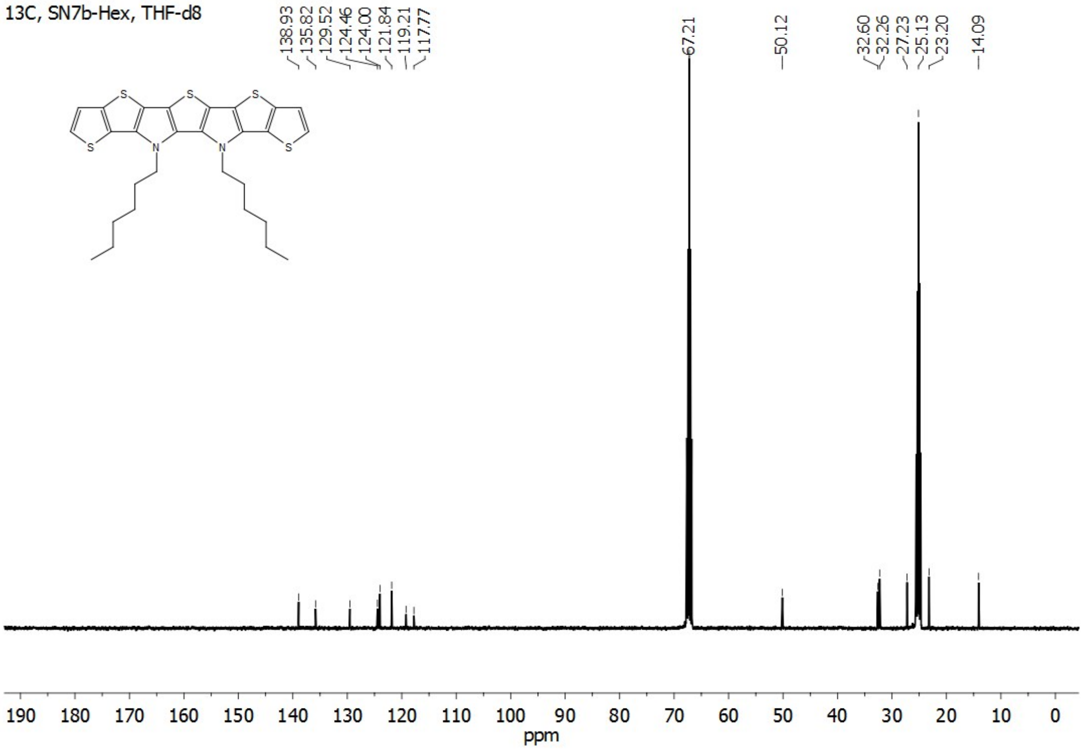

**Figure S4.** $^{13}$C-NMR spectrum of **SN7b** in [D$_8$]THF (100 MHz).

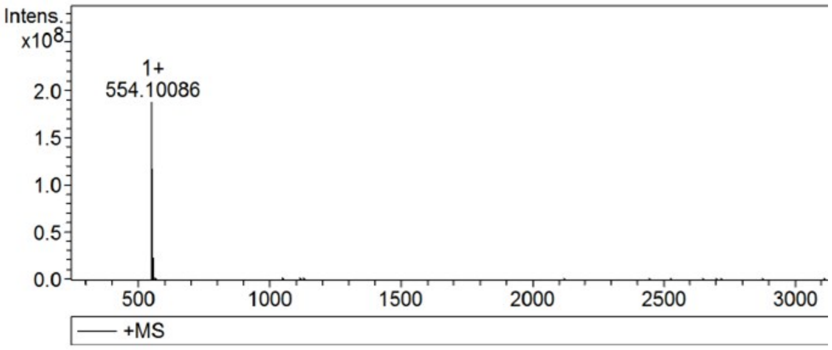

**Figure S5.** High resolution MALDI mass spectrum of **SN7b** (matrix: *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)).

## $^{1}$H-NMR, $^{13}$C-NMR, and high resolution mass spectrum of SN7c

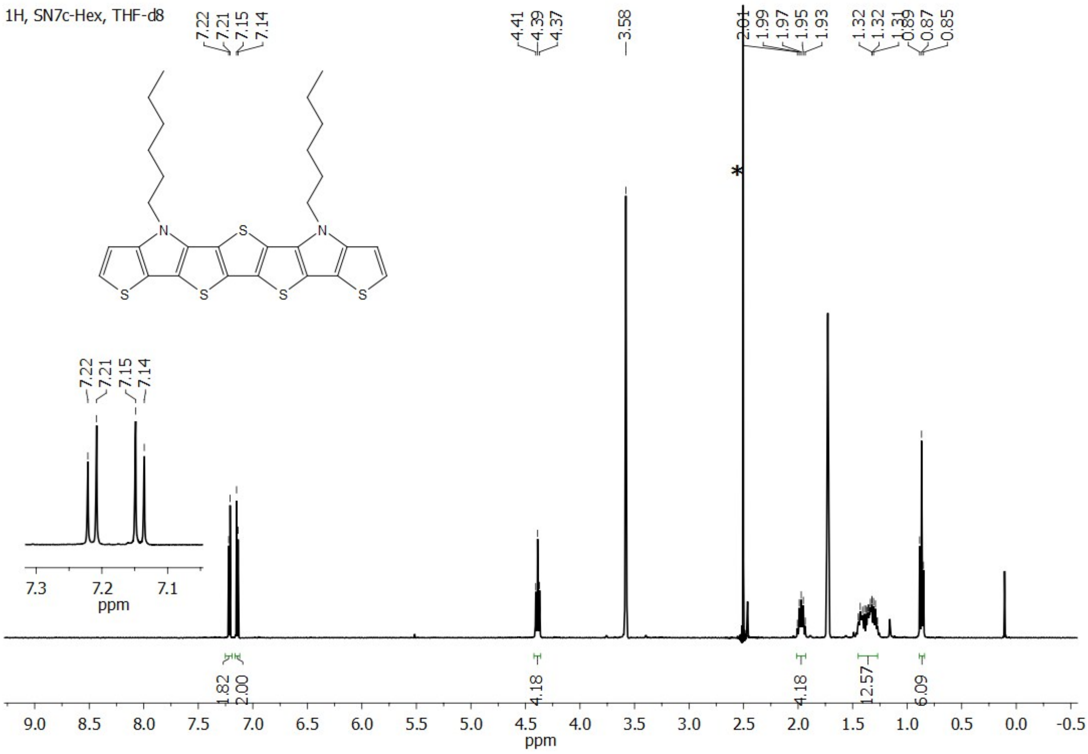

**Figure S6.** $^{1}$H-NMR spectrum of **SN7c** in [D$_8$]THF (400 MHz); *solvent impurities.

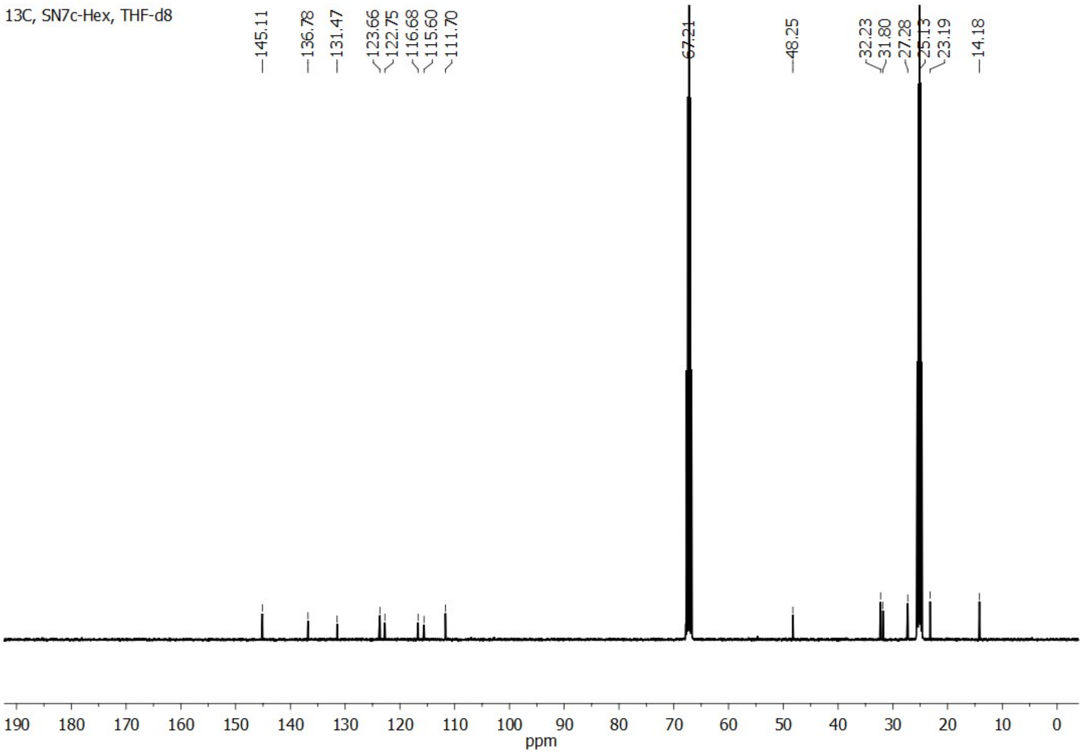

**Figure S7.** $^{13}$C-NMR spectrum of **SN7c** in [D$_8$]THF (100 MHz).

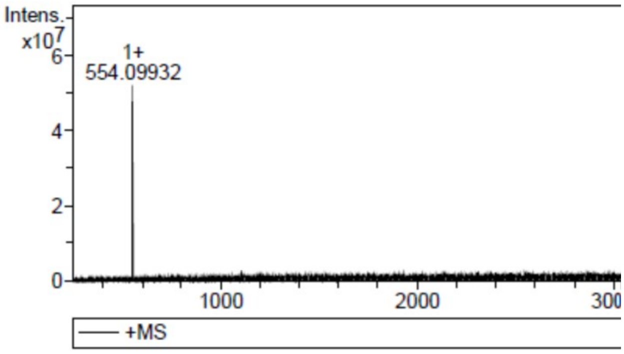

**Figure S8.** High resolution MALDI mass spectrum of **SN7c** (matrix: *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)).

## $^1$H-NMR, $^{13}$C-NMR, and high resolution mass spectrum of SN7d

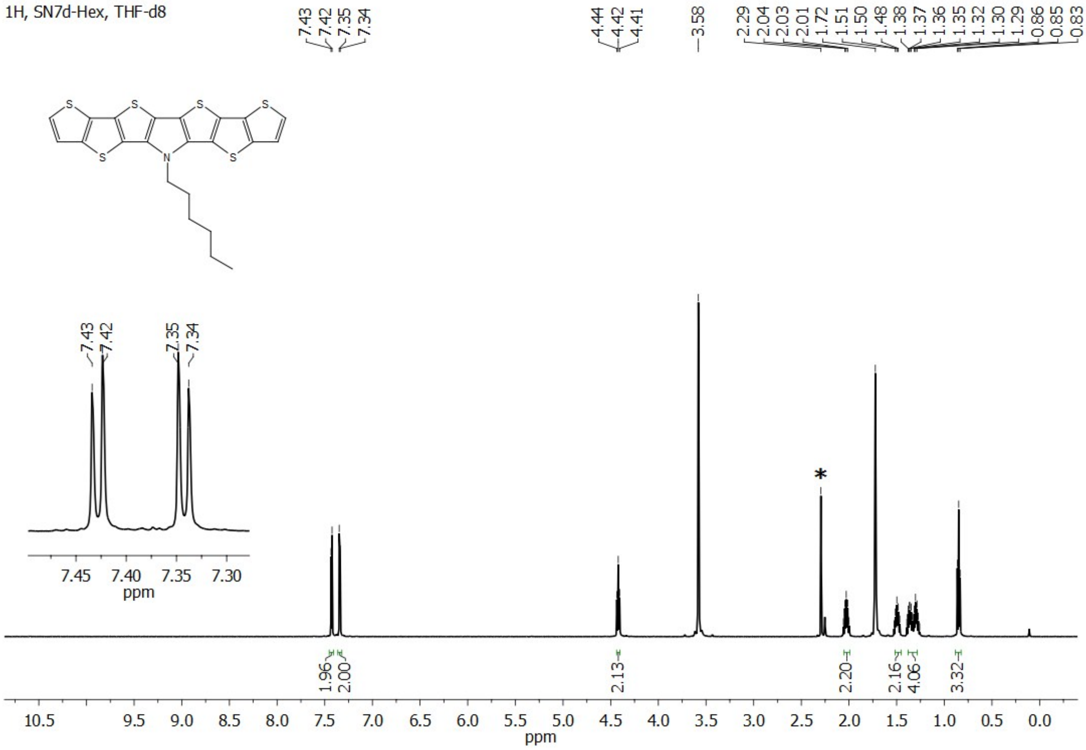

**Figure S9.** $^1$H-NMR spectrum of **SN7d** in [D$_8$]THF (500 MHz, 53 °C); *solvent impurities.

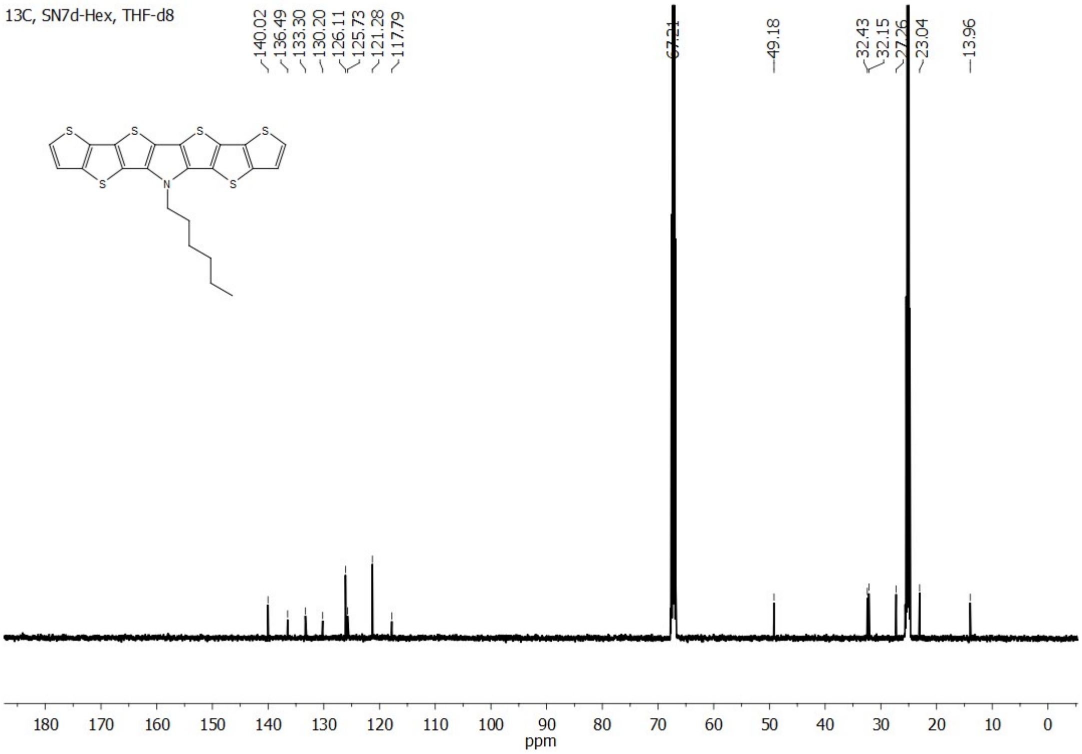

**Figure S10.** $^{13}$C-NMR spectrum of **SN7d** in [D$_8$]THF (125 MHz, 53 °C).

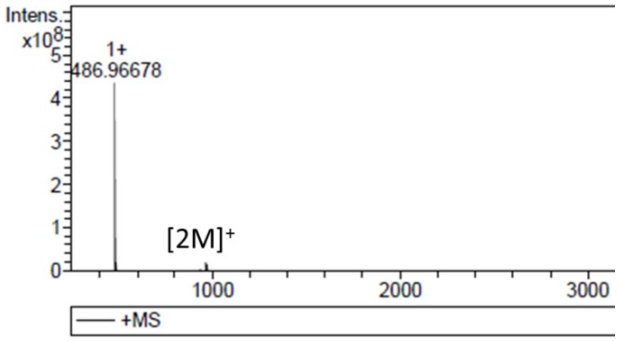

**Figure S11.** High resolution MALDI mass spectrum of **SN7d** (matrix: *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)).

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[2] X. Zhang, A. P. Côté, A. J. Matzger, *J. Am. Chem. Soc.* **2005**, *127*, 10502–10503.

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