

Supporting information

Synthesis and Structural Analysis of Thiophene-pyrrole-based S,N-heteroacenes

Christoph Wetzel, Amaresh Mishra, Elena Mena-Osteritz, Andreas Liess, Matthias Stolte, Frank Würthner and Peter Bäuerle*

Institut für Organische Chemie II und Neue Materialien, Universität Ulm, Albert-Einstein-Allee 11 89081 Ulm, Germany, and Institut für Organische Chemie & Center for Nanosystems Chemistry, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

peter.baeuerle@uni-ulm.de

Physical measurements and instrumentation

NMR spectra were recorded on a Bruker AMX 500 (^1H NMR: 500 MHz, ^{13}C NMR: 125 MHz) or an Avance 400 spectrometer (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz) at 25 °C unless otherwise noted. Chemical shift values (δ) are expressed in parts per million using residual solvent protons (^1H NMR, $\delta_{\text{H}} = 7.26$ for CDCl_3 , $\delta_{\text{H}} = 3.58$ for THF- d_8 , $\delta_{\text{H}} = 5.93$ for $\text{C}_2\text{D}_2\text{Cl}_4$; ^{13}C NMR, $\delta_{\text{C}} = 67.21$ for THF- d_8) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). The assignments are -CHO (aldehyde protons), DCV-H (dicyanovinyl protons). Coupling constants (J) relate to proton-proton couplings unless otherwise noted. Melting points were determined using Mettler Toledo DSC 823° and Büchi Melting Point B-545. Elemental analyses were performed on an Elementar Vario EL. Thin layer chromatography was carried out on aluminum plates, pre-coated with silica gel, Merck Si₆₀ F₂₅₄. Preparative column chromatography was performed on glass columns packed with silica gel, Silica 60, particle size 0.04-0.063 mm (Macherey-Nagel). High resolution MALDI-TOF mass spectra were recorded on a Bruker solariX.

Optical measurements in solution were carried out in 1 cm cuvettes with Merck Uvasol grade dichloromethane. Absorption spectra were recorded on a Perkin Elmer Lambda 19 spectrometer and corrected fluorescence spectra were recorded on a Perkin Elmer LS 55 fluorescence spectrometer. Cyclic voltammetry and differential pulse 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 an Ag/AgCl reference electrode. All potentials were internally referenced to the ferrocene/ferrocenium couple.

X-ray diffraction data of a light-brown single crystal of SN6 **4** were collected in a stream of nitrogen at 100 K on a Bruker APEXII CCD area detector diffractometer using graphite-monochromated Mo K α radiation. The diffraction data of an orange crystal of SN6-dialdehyde **5** were collected in a stream of nitrogen at 180 K on a Agilent SuperNova, Cu at zero, Atlas CCD using graphite-monochromated Cu K α radiation. Data collection strategy was performed with the APEX2 software, data reduction and cell refinement with SAINT.¹ An absorption correction based on the semi-empirical ‘multi-scan’ approach was performed with the SADABS algorithm.¹ The structure was solved by direct methods with SHELXS-97,² revealing all atoms of the S,N-heterohexacene backbone in **4** and **5** and parts of the alkyl side chains. All remaining atoms, including the H atoms, were discernible from difference Fourier maps during refinement on F² with SHELXL-97.² For the final model, all non-H atoms were refined anisotropically. H atoms were finally placed in calculated positions, riding the parent C atom with C-H distance constraints of 0.93 Å for aromatic H atoms, 0.98 Å for methyl H atoms and 0.99 Å for methylene H atoms, and with U_{iso}(H) = 1.2U_{eq}(C) for aromatic and 1.5U_{eq}(C) for aliphatic H atoms.

Thin films of SN6 **6** (30 nm) were deposited on heated Si/SiO₂ as well as OTES-modified substrates in a BOC Edwards Auto 306 evaporator. The pressure was 10⁻⁶ mbar, the substrate temperature was adjusted to 160 °C, and the sublimation temperature was set as needed to achieve deposition rates of 0.2-0.7 nm/min. Afterwards, 30 nm gold were evaporated through steel shadow masks, yielding the source and drain contacts. The channel length and width were 100 and 200 μm, respectively. The sublimation of gold was done at a pressure of 3×10⁻⁶ mbar and a deposition rate of about 2.0 nm/min. Current voltage characteristics of the OTFTs were measured at ambient conditions with an Agilent 4155C semiconductor parametric analyzer (Agilent Technologies, Inc., Santa Clara, CA). All devices were electrically isolated beforehand by scratching the organic film around the device with a needle of the used Micromanipulator 4060. The recorded p-channel transfer characteristics were measured in the saturation regime at a drain-source voltage of V_{DS} = -50 V and a gate voltage from V_{GS} = 10 V to -50 V. The mobility was then determined from the slope of the plot of the square root of the drain current I_{DS} vs. V_{GS}.

AFM measurements were carried out with a Bruker AXS MultiMode™ Nanoscope IV System in tapping mode under ambient conditions. The used silicon cantilevers (OMCL-AC 160TS, Olympus) had a resonance frequency of ~300 kHz and a spring constant of ~42 N m⁻¹.

DFT-calculations have been performed with the exchange correlation functional M06-2x/6-31G+(d,p).³

Materials

Chemicals

Toluene (VWR) was dried under reflux over CaH₂ (Merck). THF (Sigma Aldrich), DMF (Merck) and diethylether (Merck) were dried and purified by a MB SPS-800 (MBraun). DCM, *n*-hexane and acetone were purchased from VWR and distilled prior to use. Sodium-*tert*-butoxide, *n*-hexylamine, 1,2-dichloroethane, phosphoryl chloride, sodium bicarbonate, malonodinitrile and ammonium acetate were purchased from Merck. Pd(dppf)Cl₂·CH₂Cl₂ and Pd(dba)₂ were purchased from Sigma Aldrich, *n*-BuLi (1.6 N in hexane) from Acros Organics and 1,1'-Bis(diphenylphosphino)ferrocene from Frontier Scientific. ZnCl₂ (VWR) was dried in high vacuum at high temperature.

Substrates for OTFT measurements

Highly doped n-type Si (100) wafers (SiMat) with 100 nm SiO₂ were used as substrates (capacitance per unit area $C_1 = 34 \text{ nF cm}^{-2}$). Additionally, the Si/SiO₂ wafers were treated with *n*-octadecyltriethoxysilane (OTES) to yield OTES-modified substrates.⁴ The Si/SiO₂ wafers were immersed in Piranha solution (H₂SO₄:H₂O₂, 7:3) for 30 min and afterwards rinsed with deionized water. Afterwards, the wafers were rinsed with toluene, acetone and isopropanol in an APT Spin 150 Spin Coater for 30 s at 3000 rpm and treated in an UVO-Cleaner[®]-Ozone Cleaning Device 42A-220 (Jelight Company) for another 5 min. The wafers were then covered with a solution of OTES in trichloroethylene ($c = 3.6 \text{ mmol}$) for 10 s. The residual solution was removed in the spin coater at 3000 rpm for 30 s and the coated wafers were left overnight in a desiccator under NH₃ atmosphere. Then, the wafers were cleaned with toluene in an ultrasonic bath. Prior to deposition of the organic film, all wafers were rinsed with toluene, acetone and isopropanol for 30 s at 3000 rpm in the spin coater. The bare Si/SiO₂ substrates were additionally treated in the UVO-Cleaner for 5 min.

Synthesis

3,6-Dibromo-2,5-bis(3-bromothiophen-2-yl)thieno[3,2-b]thiophene (3)

The synthesis of tetrabromo derivative **3** was earlier reported by McCulloch and co-workers by a selective Negishi coupling between 3,6-dibromo-2,5-diiodothieno[3,2-b]thiophene and zincated 2,3-dibromothiophene.⁵ In this work, we have shown that building block **3** can also

be obtained in a reasonable yield of 73% by Pd-catalyzed cross-coupling of zincated 2,3-dibromothiophene and 2,3,5,6-tetrabromo[3,2-*b*]thienothiophene. Most importantly, in our procedure using 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene we could save two reaction steps in the sequence.

In a dried Schlenk-tube *n*-butyl lithium (1.6 M in hexane, 3.50 mL, 5.61 mmol) was added dropwise to a stirred solution of 2,3-dibromothiophene (1.23 g, 5.10 mmol) in dry ethyl ether (5 mL) at -78 °C. The resulting solution was stirred at -78 °C for 1 h. Then a solution of ZnCl₂ (0.70 g, 5.15 mmol) in dry THF (7 mL) was added. After stirring 1 h at 0 °C 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene (0.78 g, 1.71 mmol) and Pd(dppf)Cl₂·CH₂Cl₂ (0.083 g, 0.102 mmol) were added. The mixture was heated to 50 °C. After 18 h water (10 mL) was added. The resulting solid was filtered off and washed with water, acetone and ether and tetrabromo derivative **3** was obtained as a yellow microcrystalline material (0.78 g, 1.26 mmol, 73%). Mp. 223.1-225.8 °C. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.13 (d, 2 H, ³*J* = 5.3 Hz), 7.48 (d, 2 H, ³*J* = 5.3 Hz). ¹³C NMR could not be recorded due to the low solubility of compound **3**. HRMS: *m/z* calcd. for C₁₄H₄Br₄S₄ 615.59238 (M⁺), found 615.59220. The data matches with the literature values.⁵

*4,9-Dihexyl-thieno[3,2-*b*]thieno[2''',3''':4'',5'']pyrrolo[2'',3'':4',5']thieno[2',3':4,5]-thieno[2,3-*d*]pyrrole (4)*

3,6-Dibromo-2,5-bis(3-bromothien-2-yl)thieno[3,2-*b*]thiophene (293 mg, 0.47 mmol), sodium-*tert*-butoxide (726 mg, 7.56 mmol), Pd(dba)₂ (27 mg, 0.047 mmol) and dppf (105 mg, 0.19 mmol) were stirred in dry and degassed toluene (20 mL) at room temperature. After 20 min *n*-hexylamine (0.15 mL, 1.13 mmol) was added and the mixture was stirred at 110 °C for 18 h. Water was added to the cooled reaction mixture and the aqueous phase was extracted with ethyl ether (15 mL) and dichloromethane (2 x 15 mL). The solvents were removed under reduced pressure. The crude product was purified by column chromatography under exclusion of light (flash-silica; *n*-hexane/dichloromethane 4:1). Pure SN6 **4** was obtained as a pale yellow solid (127 mg, 0.25 mmol, 54%). Mp. 163 °C. ¹H-NMR (400 MHz, THF-*d*₈): δ [ppm] = 0.87 (t, 6 H, ³*J* = 7.1 Hz, CH₃), 1.28 – 1.46 (m, 12 H, CH₂), 1.96 (quintet, 4 H, CH₂), 4.37 (t, 4 H, ³*J* = 7.1 Hz, N-CH₂), 7.14 (d, 4 H, ³*J* = 5.3 Hz, CH), 7.17 (d, 4 H, ³*J* = 5.3 Hz, CH). ¹³C-NMR (100 MHz, THF-*d*₈): δ [ppm] = 14.15, 23.22, 27.32, 31.93, 32.25, 48.38, 111.71, 114.85, 116.54, 122.20, 123.07, 137.66, 144.85. Elemental analysis: calcd. (%) for C₂₆H₃₀N₂S₄: C 62.61, H 6.06, N 5.62, S 25.71; found C 62.83, H 5.88, N 5.51, S 25.92. HRMS (MALDI-TOF): *m/z* calcd. for C₂₆H₃₀N₂S₄ (M⁺) 498.12863 found 498.12882.

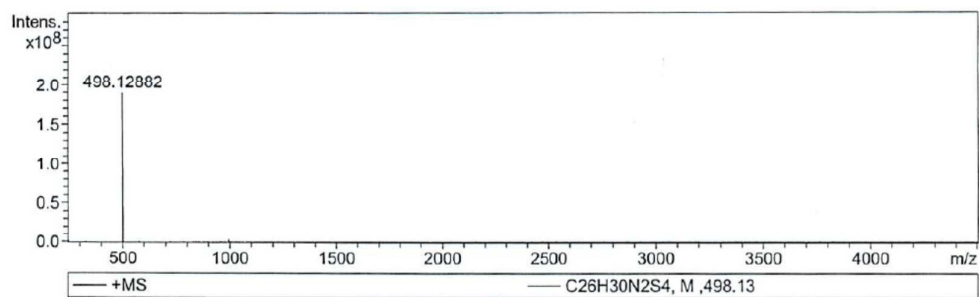
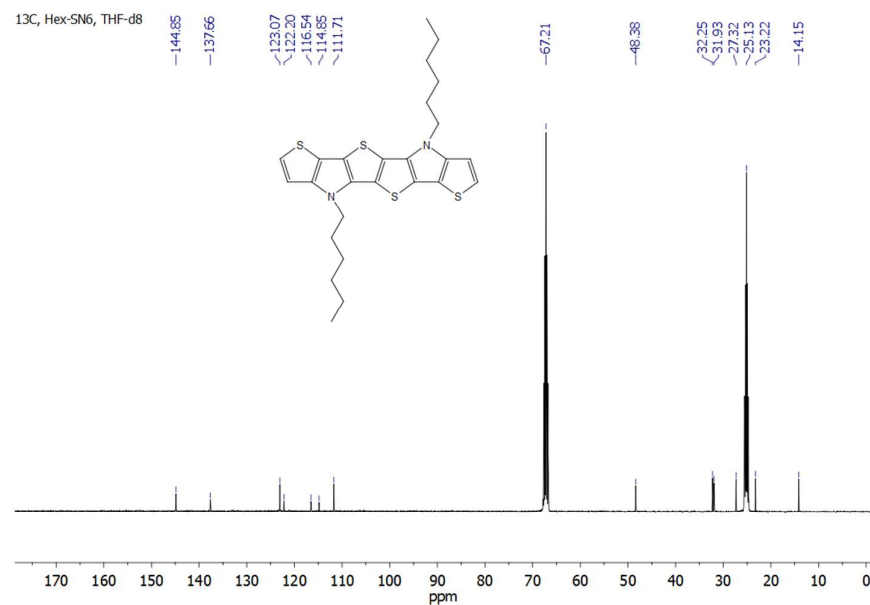
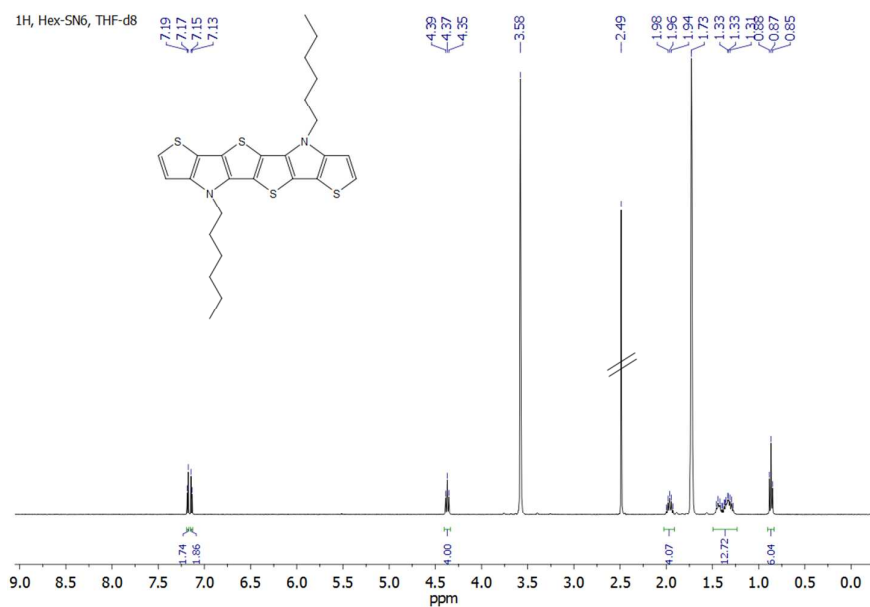
[4,9-Dihexyl-thieno[3,2-b]thieno[2''',3''':4'',5'']pyrrolo[2'',3'':4',5']thieno-[2',3':4,5]thieno-[2,3-d]pyrrol]-2,7-dicarbaldehyde (5)

A solution of *N,N*-dimethylformamide (0.29 mL, 3.79 mmol) in 1,2-dichloroethane (6 mL) was cooled down to 0 °C. Phosphoryl chloride (0.35 mL, 3.79 mmol) was added and the solution was stirred for 2 h at room temperature. Then a solution of SN6 **4** (63 mg, 0.13 mmol) in 1,2-dichloroethane (30 mL) was added dropwise. The solution was stirred at 75 °C. After 19 h the suspension was diluted with dichloromethane (400 mL). Then the solution was given to a saturated NaHCO₃ solution (700 mL). The mixture was stirred for 3 h at room temperature. The aqueous phase was extracted with dichloromethane (2 x 200 mL). After removing the solvent and purification by column chromatography (flash-silica; dichloromethane) dialdehyde **5** was obtained as an orange solid (56 mg, 0.10 mmol, 80%). Mp. 319 °C. ¹H-NMR (400 MHz, TCE-d₂): δ [ppm] = 0.81 (t, 6 H, 3J = 6.9 Hz, CH₃), 1.23 – 1.35 (m, 12 H, CH₂), 1.88 (quintet, 4 H, CH₂), 4.24 (t, 4 H, 3J = 7.1 Hz, N-CH₂), 7.56 (s, 2 H, CH), 9.76 (s, 2 H, CHO). ¹³C-NMR (125 MHz, 357 K, TCE-d₂): δ [ppm] = 13.96, 22.56, 26.81, 31.18, 31.49, 48.61, 116.85, 118.82, 124.44, 124.73, 141.18, 141.45, 144.28, 182.46. Elemental analysis: calcd. (%) für C₂₈H₃₀N₂O₂S₄: C 60.62, H 5.45, N 5.05, S 23.12; found: C 60.43, H 5.48, N 4.94, S 23.09. HRMS (MALDI-TOF): *m/z* calcd. for C₂₈H₃₀N₂O₂S₄ (M⁺) 554.11846; found 554.11814.

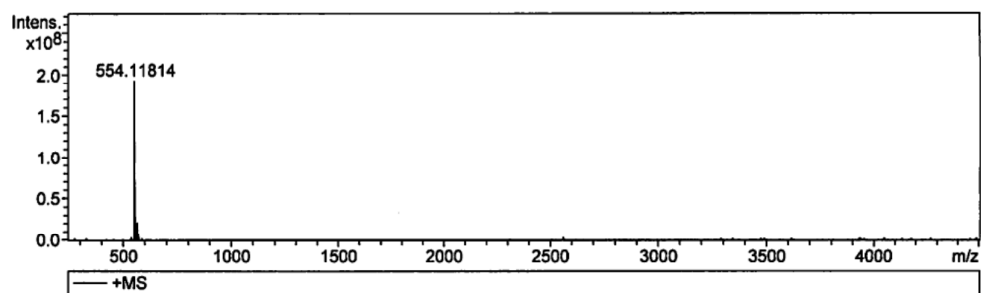
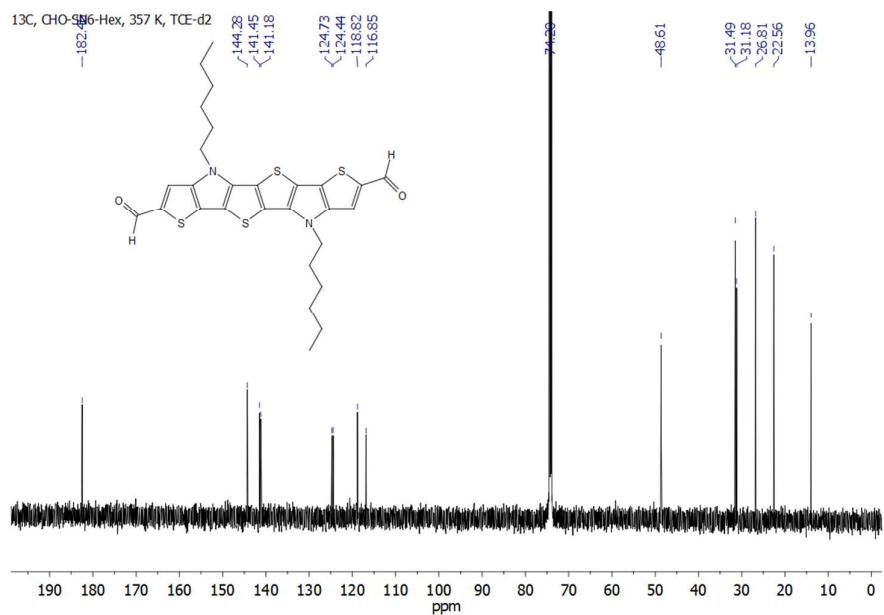
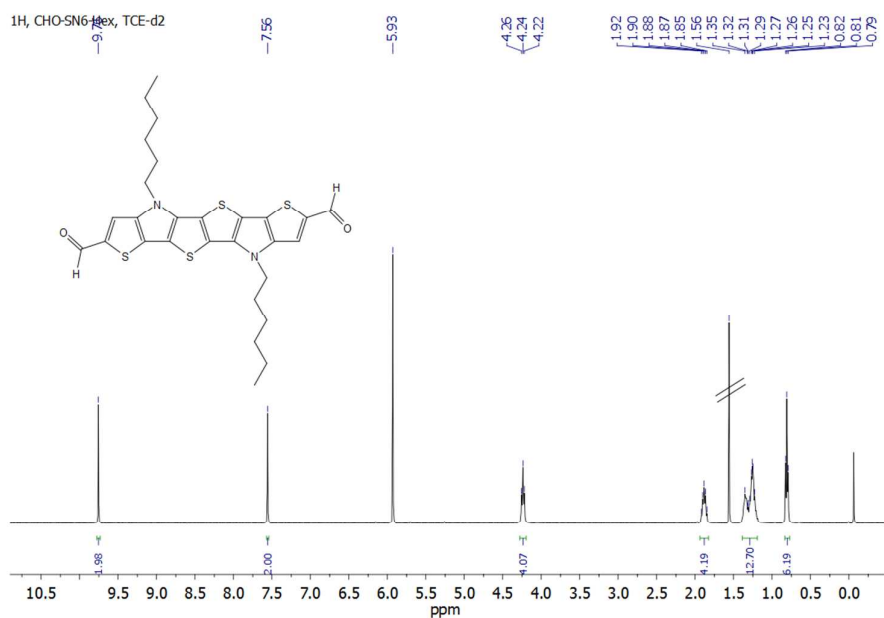
[4,9-Dihexyl-thieno[3,2-b]thieno-[2''',3''':4'',5'']pyrrolo[2'',3'':4',5']thieno-[2',3':4,5]thieno-[2,3-d]pyrrol]-2,8-bis[methan-1-yl-1-yliden]dimalonodinitrile (6)

Dialdehyde **5** (39 mg, 0.07 mmol), malonodinitrile (93 mg, 1.41 mmol), and ammonium acetate (54 mg, 0.70 mmol) were dissolved in 1,2-dichloroethane (50 mL) and the reaction mixture was heated at 80 °C. After 48 h another portion of malonodinitrile (93 mg, 1.40 mmol) and a large excess of ammonium acetate were added and the reaction was continued until completion of the reaction which was checked by TLC. After 7 days the mixture was allowed to cool down to room temperature. After removing the solvent the crude product was purified by column chromatography (flash-silica; dichloromethane). The oligomer **6** was obtained as a blue solid (38 mg, 0.06 mmol, 83%). Mp. 366 °C. ¹H-NMR (500 MHz, 360 K, TCE-d₂): δ [ppm] = 0.88 (t, 6 H, 3J = 7.1 Hz, CH₃), 1.32 – 1.47 (m, 12 H, CH₂), 1.99 (quintet, 4 H, CH₂), 4.31 (t, 4 H, 3J = 7.1 Hz, N-CH₂) 7.65 (s, 2 H, CH), 7.70 (s, 2 H, DCV-H). ¹³C-NMR could not be measured due to low solubility. HRMS (LDI-TOF): *m/z* calc. for C₃₄H₃₀N₆S₄ (M⁺) 650.14093; found 650.14102.

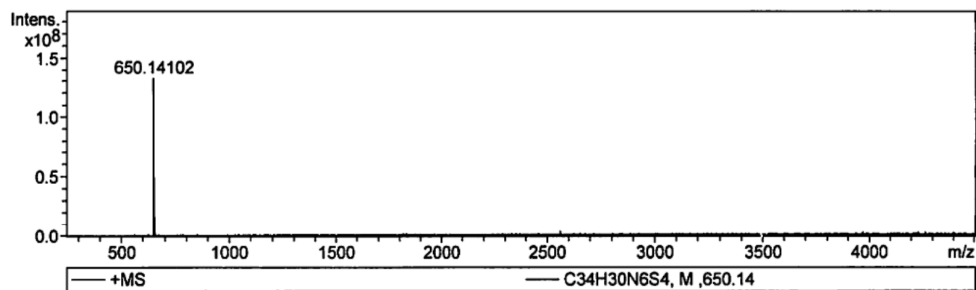
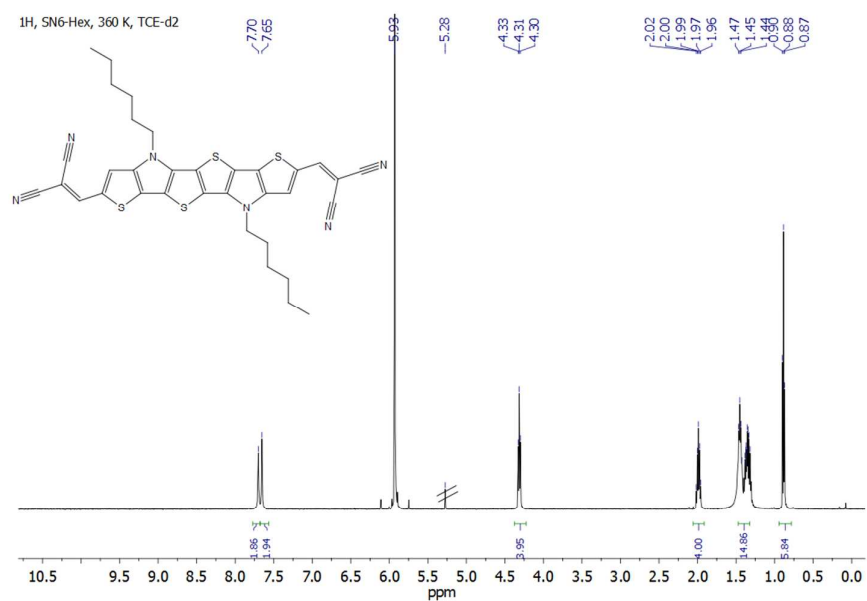
NMR and HR-MS of SN6 4



NMR and HR-MS of dialdehyde SN6 5



NMR and HR-MS of SN6 6



X-Ray Crystal Structure Analysis

S,N-heteroacene **4** (CCDC number: 954178)

Bond precision: C-C=0.0017 Å Wavelength=0.71073

Cell: a=5.0953(9) b=26.540(5) c=8.7806(16)
alpha=90 beta=95.669(4) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	1181.6(4)	1181.6(4)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C ₂₆ H ₃₀ N ₂ S ₄	C ₂₆ H ₃₀ N ₂ S ₄
Sum formula	C ₂₆ H ₃₀ N ₂ S ₄	C ₂₆ H ₃₀ N ₂ S ₄
Mr	498.80	498.76
D _x , g cm ⁻³	1.402	1.402
Z	2	2
Mu (mm ⁻¹)	0.421	0.421
F ₀₀₀	528.0	528.0
F ₀₀₀ '	529.13	
h,k,lmax	8,42,14	5,42,14
Nref	5121	4206
Tmin,Tmax	0.965,0.975	0.658,0.747
Tmin'	0.900	

Correction method= MULTI-SCAN

Data completeness= 0.821

R(reflections)= 0.0342(3638)

S = 1.069

Theta(max)= 34.800

wR2(reflections)= 0.0814(4206)

Npar= 146

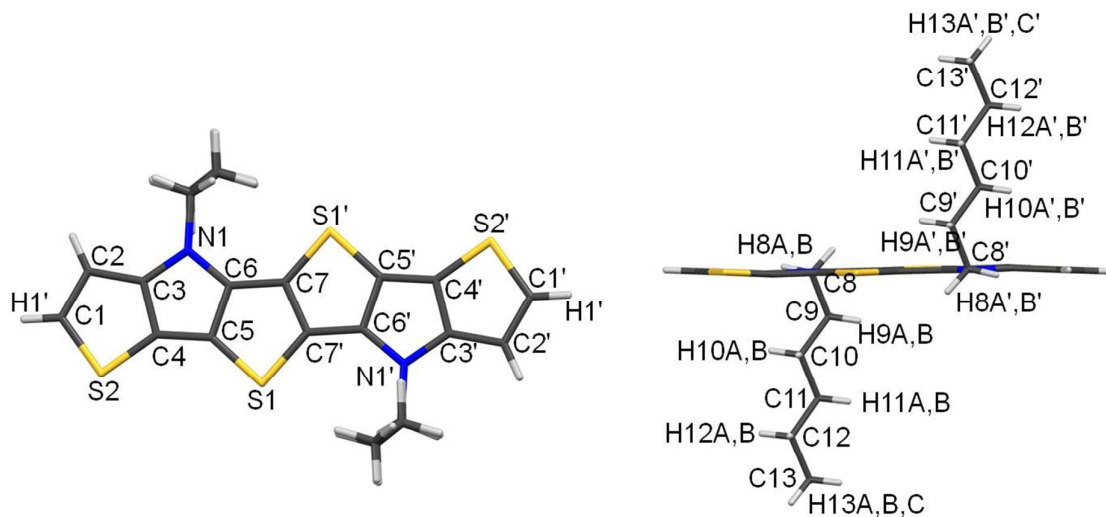


Figure S1: Single crystal X-ray structure analysis of hexyl-substituted SN6 **4** showing the labeled individual molecule on the (8 48 -2) plane, left and perpendicular to the (8 48 -2) plane, right.

Table S1: Bond lengths, angles and torsion angles of S,N-heteroacene **4**

Atom 1	Atom 2	Bond length (Å)	Atom 1	Atom 2	Atom 3	Angle (°)
C1	C2	1.366(2)	S2	C1	C2	113.8(1)
C2	C3	1.421(2)	C1	C2	C3	110.3(1)
C3	C4	1.399(2)	C2	C3	C4	114.1(1)
C1	S2	1.737(1)	C3	C4	S2	110.81(8)
S2	C4	1.718(1)	C4	S2	C1	91.06(6)
C4	C5	1.414(1)	C5	C4	C3	106.89(9)
C5	C6	1.401(2)	C4	C3	N1	109.74(9)
C3	N1	1.384(1)	C3	N1	C6	106.79(9)
N1	C6	1.379(1)	N1	C6	C5	110.10(9)
C6	C7	1.419(1)	C6	C5	C4	106.48(9)
C7	C7'	1.398(2)	C3	N1	C8	126.7(1)
C5	S1	1.738(1)	C6	C5	S1	112.68(8)
S1	C7'	1.743(1)	C5	S1	C7	90.02(5)
N1	C8	1.458(2)	S1	C7'	C7	113.55(8)
C8	C9	1.530(2)	C7'	C7	C6	111.09(9)
C9	C10	1.524(2)	C7	C6	C5	112.66(9)
C10	C11	1.528(2)	N1	C8	C9	112.7(1)
C11	C12	1.525(2)	C8	C9	C10	113.6(1)
C12	C13	1.525(2)	C9	C10	C11	113.3(1)
	Atom 1	Atom 2	Atom 3	Atom 4	Torsion angle (°)	
	S2	C4	C5	S1	8.8(2)	
	C1	C2	C3	N1	-174.3(1)	
	N1	C6	C7	C7'	-179.4(1)	
	S1	C7'	C7	S1'	180.00(5)	
	N1	C3	C4	S2	175.42(7)	
	N1	C6	C5	S1	179.39(7)	
	C2	C3	N1	C8	-8.7(2)	
	C3	N1	C8	C9	-105.0(1)	
	N1	C8	C9	C10	55.1(1)	
	C8	C9	C10	C11	-179.1(1)	
	C9	C10	C11	C12	177.3(1)	
	C10	C11	C12	C13	-178.4(1)	

Table S2: Intermolecular short contacts (below the Van der Waals radii) in the X-Ray structure analysis of heteroacene **4**.

Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length (nm)
S1	H8B	x,y,z	2-x,2-y,1-z	0,2974
C3	S1	x,y,z	1+x,y,z	0,3417
H8B	S1	x,y,z	2-x,2-y,1-z	0,2974
S1	C3	1-x,2-y,1-z	2-x,2-y,1-z	0,3417
S1	S2	x,y,z	2-x,2-y,2-z	0,3555
S2	S1	x,y,z	2-x,2-y,2-z	0,3555
S2	S2	x,y,z	2-x,2-y,2-z	0,355

Table S3: Intramolecular short contacts (below the Van der Waals radii) in the X-Ray structure analysis of heteroacene **4**.

Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length (nm)
S1	H9A	x,y,z	1-x,2-y,1-z	0,2947
N1	H10A	x,y,z	x,y,z	0,2644
H9A	S1	x,y,z	1-x,2-y,1-z	0,2947
N1	H10A	1-x,2-y,1-z	1-x,2-y,1-z	0,2644

S,N-heteroacene dialdehyde **5** (CCDC number 954178)

Bond precision:	C-C = 0.0018 Å	Wavelength=1.54184
Cell:	a=4.84737(17) b=16.2215(6) c=16.7511(5)	
	alpha=86.998(3) beta=81.961(3) gamma=84.851(3)	
Temperature: 180 K	Calculated	Reported
Volume	1297.90(8)	1297.90(8)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C ₂₈ H ₃₀ N ₂ O ₂ S ₄	C ₂₈ H ₃₀ N ₂ O ₂ S ₄
Sum formula	C ₂₈ H ₃₀ N ₂ O ₂ S ₄	C ₂₈ H ₃₀ N ₂ O ₂ S ₄
Mr	554.82	554.78
D _x , g cm ⁻³	1.420	1.420
Z	2	2
Mu (mm ⁻¹)	3.601	3.602
F ₀₀₀	584.0	584.0
F ₀₀₀ '	587.95	
h,k,lmax	6,20,21	6,20,20
Nref	5430	5339
T _{min} ,T _{max}	0.673,0.863	0.737,1.000
T _{min} '	0.371	

Correction method= MULTI-SCAN

Data completeness= 0.983

R(reflections)= 0.0264(5115)

S = 1.043

Theta(max)= 76.290

wR₂(reflections)= 0.0733(5339)

Npar= 327

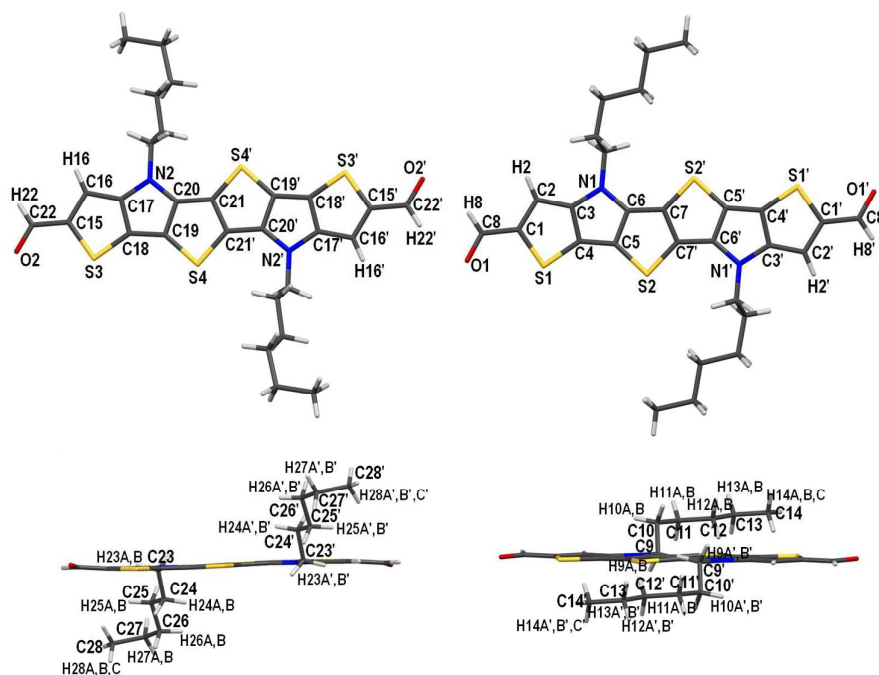


Figure S2: Single crystal X-ray structure analysis of hexyl-substituted dialdehyde-SN6 **5** showing the two distinct molecules in the unit cell in a front view, top and side view, bottom. In the images, the atomic labels are included.

Table S4: Bond lengths, angles and torsion angles of S,N-heteroacene dialdehyde **5**

	Atom 1	Atom 2	Bond length (Å)		Atom 1	Atom 2	Atom 3	Angle (°)			
Molecule 1	C22	O2	1.219(2)	Molecule 1	O2	C22	C15	125.3(1)			
	C22	C15	1.438(2)		C22	C15	S3	120.6(1)			
	C15	C16	1.378(2)		S3	C15	C16	113.8(1)			
	C16	C17	1.402(2)		C15	C16	C17	110.3(1)			
	C17	C18	1.408(2)		C16	C17	C18	114.4(1)			
	C18	C19	1.409(2)		C17	C18	S3	111.18(9)			
	C19	C20	1.406(2)		C18	C17	N2	110.1(1)			
	C20	C21	1.415(2)		C17	N2	C20	106.7(1)			
	C21	C21'	1.398(1)		N2	C20	C19	110.4(1)			
	S4	C21'	1.741(1)		C20	C19	C18	106.4(1)			
	S4	C19	1.739(1)		C20	C19	S4	112.69(9)			
	C20	N2	1.371(2)		C19	S4	C21'	89.84(6)			
	N2	C17	1.377(2)		S4	C21'	C21	113.82(8)			
	C18	S3	1.723(1)		C21'	C21	C20	111.1(1)			
	S3	C15	1.752(1)		C17	N2	C23	125.7(1)			
	N2	C23	1.464(2)		Molecule 2	O1	C8	C1	124.2(1)		
	C23	C24	1.519(2)			C8	C1	S1	119.0(1)		
	C24	C25	1.525(2)			S1	C1	C2	113.70(9)		
	C25	C26	1.520(2)			C1	C2	C3	110.3(1)		
	C26	C27	1.536(2)			C2	C3	C4	113.9(1)		
	C27	C28	1.518(2)			C3	C4	S1	111.62(8)		
	Molecule 2	O1	C8			1.223(2)	C4	S1	C1	90.52(6)	
		C8	C1			1.442(2)	C4	C3	N1	109.63(9)	
		C1	C2			1.386(2)	C3	N1	C6	106.61(9)	
		C2	C3			1.408(1)	N1	C6	C5	110.4(1)	
		C3	C4			1.407(2)	C6	C5	C4	106.6(1)	
		C4	C5			1.407(1)	C6	C5	S2	112.60(8)	
C5		C6	1.403(2)	C5		S2	C7'	90.02(5)			
C6		C7	1.415(1)	S2		C7'	C7	113.50(8)			
C7		C7'	1.391(2)	C7'		C7	C6	111.5(1)			
C7'		S2	1.740(1)	C7		C6	C5	112.4(1)			
S2		C5	1.735(1)	C3		N1	C9	127.06(9)			
C6		N1	1.374(1)								
N1		C3	1.388(2)	Molecule 1		Atom 1	Atom 2	Atom 3	Atom 4	Torsion Angle (°)	
C4		S1	1.715(1)			O2	C22	C15	S3	2.7(2)	
S1		C1	1.744(1)			S3	C18	C19	S4	-1.7(3)	
N1		C9	1.460(2)			S4	C21'	C21	S4'	180.00(6)	
C9		C10	1.522(2)			S4'	C21	C20	N2	-2.5(2)	
C10		C11	1.530(2)			C21	C20	N2	C23	8.5(2)	
C11		C12	1.527(2)			Molecule 2	O1	C8	C1	S1	3.4(2)
C12		C13	1.525(2)				S1	C4	C5	S2	-2.1(2)
C13		C14	1.524(2)				S2	C7'	C7	S2'	180.00(6)
					S2'		C7	C6	N1	-1.2(2)	
					C7		C6	N1	C9	-2.9(2)	

Table S5: Intermolecular short contacts (below the Van der Waals radii) in the X-Ray structure analysis of S,N-heteroacene dialdehyde **5**.

Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length (nm)
O2	H2	x,y,z	-x,l-y,l-z	0,2639
O2	H8	x,y,z	-x,l-y,l-z	0,2589
H16	O1'	x,y,z	l+x,y,z	0,2326
H16	C8'	x,y,z	l+x,y,z	0,2846
H23A	O1'	x,y,z	l+x,y,z	0,2628
C22	H22'	x,y,z	l-x,l-y,l-z	0,2846
H22	C22'	x,y,z	l-x,l-y,l-z	0,2846
O2'	H2'	x,y,z	x,y,-l+z	0,2639
O2'	H8'	x,y,z	x,y,-l+z	0,2589
H16'	O1	x,y,z	-l-x,l-y,-z	0,2326
H16'	C8	x,y,z	-l-x,l-y,-z	0,2846
H23A'	O1	x,y,z	-l-x,l-y,-z	0,2628
C22'	H22	x,y,z	l-x,l-y,l-z	0,2846
H22'	C22	x,y,z	l-x,l-y,l-z	0,2846
C16	C8 ^c	x,y,z	-x,l-y,l-z	0,3269
C16 ^c	C8	x,y,z	-x,l-y,l-z	0,3269

Table S6: Intramolecular short contacts (below the Van der Waals radii) in the X-Ray structure analysis of S,N-heteroacene dialdehyde **5**.

Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length (nm)
S2	H9B'	-x,1-y,-z	-x,1-y,-z	0,2926
H9B	C12	-x,1-y,-z	-x,1-y,-z	0,2856
H9B	H12B	-x,1-y,-z	-x,1-y,-z	0,231
H9B	S2'	-x,1-y,-z	-x,1-y,-z	0,2926
H9B	C12	-x,1-y,-z	-x,1-y,-z	0,2856
H9B	H12B	-x,1-y,-z	-x,1-y,-z	0,231
C16	H23A	x,y,z	x,y,z	0,2896
C25	H28A	x,y,z	x,y,z	0,2865
H25B	C28	x,y,z	x,y,z	0,2825
H25B	H28A	x,y,z	x,y,z	0,2264
C16'	H23A'	x,y,z	x,y,z	0,2896
C25'	H28A'	x,y,z	x,y,z	0,2865
H25B'	C28'	x,y,z	x,y,z	0,2825
H25B'	H28A'	x,y,z	x,y,z	0,2264

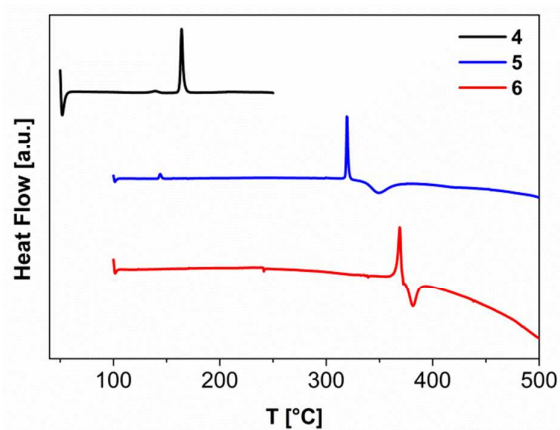


Figure S3: DSC trace of SN6-derivatives **4-6** measured under Ar flow at heating rate of 10 ° C/min.

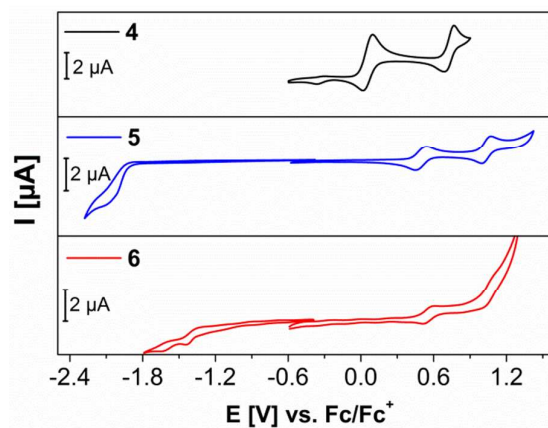


Figure S4: Cyclic voltammograms of SN6 derivatives **4-6**

Table S7: Electrical properties of OTFTs of SN6 6 prepared by vacuum deposition on different substrates at a substrate temperature of 160 °C measured in air.

Substrate	$\mu_{p,max}$ (cm ² V ⁻¹ s ⁻¹)	μ_p^a (cm ² V ⁻¹ s ⁻¹)	I_{on}/I_{off}^a (a.u.)	V_{th}^a (V)
Si/SiO ₂	3.5×10^{-4}	2.9×10^{-4}	9×10^2	1
Si/SiO ₂ /OTES	2.1×10^{-2}	2.0×10^{-2}	10^5	4

^a Average value of at least three devices.

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