Supporting Information for

On Surface Synthesis of an 11-Ring Sulfur-Doped Nonacene

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General Information

Reactions under argon atmosphere were carried out in oven-dried glassware, using solvents dried by passing through an activated alumina column on a PureSolvTM solvent purification system (Innovative Technologies, Inc., MA). Analytical thin layer chromatography was carried out using TLC-aluminum sheets with 0.2 mm of silica gel (Merck GF234) using UV light as the visualizing agent and an acidic solution of vanillin in ethanol as the developing agent. Chromatographic purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-63 μ m). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. All reagents were used as purchased, without further purification.

NMR spectra were recorded at 23 °C on a Bruker Avance 300, 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus. Chemical shifts (δ) are given as parts per million (ppm) downfield from tetramethylsilane, with calibration on the residual protio-solvent used (δ H = 7.26 ppm and δ C = 77.00 ppm for CDCl₃). Mass spectra were recorded on a Waters Micromass LCT Premier Spectrometer (APCI) or on an Autoflex Bruker Daltonics (MALDI). Melting points were determined using a Mettler Toledo MP70 apparatus.

Experimental Procedures and Characterization



Synthesis of the Double 1,7-Enyne 2



2,5-Bis(2-ethoxy-2-oxoethyl)terephthalic acid (S-2). Sodium (6 equiv, 2.13 g, 61.70 mmol) was added to abs. EtOH HPLC graded (120 mL, 0.13 M) under an Ar atmosphere at 0 °C. After warming up to 23 °C, the mixture was left to stir for 1 h. Ethyl acetoacetate (4 equiv, 7.80 mL, 61.7 mmol) was then added and the mixture was stirred at 23 °C for 10 min. Then, CuBr (2 equiv, 4.43 g, 30.9 mmol) and **S-1** (1 equiv, 5.00 g, 15.40 mmol) were added and the reaction mixture was refluxed for 16 h. After completion, the dark green reaction mixture was concentrated *in vacuo*, acidified with 1 M HCl (200 mL) and diluted with CH₂Cl₂ (200 mL). The title compound precipitated during extraction as a white solid placed between the two phases. Filtration of both phases and washing with water (300 mL) and CH₂Cl₂ (200 mL) provided **S-2** as a white solid (4.18 g, 12.3 mmol, 80% yield), which was taken on to the next step without further purification.

Melting point = 245-247 °C.

¹**H NMR (400 MHz, DMSO)** δ 10.36 (s, 1H), 8.97 (d, *J* = 9.1 Hz, 1H), 8.23 (ddd, *J* = 17.5, 14.0, 8.5 Hz, 6H), 8.06 (d, *J* = 7.3 Hz, 1H), 7.94 (dd, *J* = 16.4, 8.6 Hz, 2H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H).

¹³C NMR (101 MHz, DMSO) δ 170.8, 132.6, 130.6, 123.3, 69.2, 35.7.

HRMS (ESI-) m/z calc. for C₁₆H₁₇O₈ [M-H]⁻: 337.0929. Found: 337.0936.



6,9-Dihydropyrano[**3,4-***g*]**isochromene-3,8**(**1***H***,4***H*)**-dione** (**S-3**). To a stirred suspension of **S-2** (1.0 equiv, 7.40 g, 20.20 mmol) in anhydrous THF (0.33 M, 61.0 mL) was added BH₃·Me₂S (2.2 equiv, 4.20 mL, 44.4 mmol) at 0 °C. The mixture was then slowly heated to 55 °C and stirred at this temperature for 18 h. After cooling to 23 °C, 4.0 M HCl (200 mL) was added to the thus formed alcohol to quench the reaction and allow lactonization to take place. Then the compound was allowed to precipitate overnight from the acidic solution. Filtration and subsequent washing with water (200 mL) provided S-3 as a white solid (2.05 g, 9.40 mmol, 47% yield), which was taken on to the next step without further purification.

Melting point = 253-255 °C.

¹H NMR (400 MHz, DMSO) δ 7.29 (s, 1H), 5.34 (s, 2H), 3.80 (s, 2H).
¹³C NMR (101 MHz, DMSO) δ 170.7, 132.5, 130.5, 123.3, 69.1, 35.6.
HRMS (ESI+) m/z calc. for C₁₂H₁₀NaO₄ [M+Na]⁺ : 241.0471. Found: 241.0474.



2,2'-(2,5-Bis(bromomethyl)-1,4-phenylene)diacetic acid (S-4). An orange solution of **S-3** (1.0 equiv, 2.60 g, 11.9 mmol) in 33% HBr in acetic acid (30.0 mL, 0.40 M) was stirred under Ar at 23 °C for 2 h and then at 70 °C for 1 h. After cooling down to 23 °C, the mixture was poured into ice-water (150 mL). Filtration of the white precipitate afforded **S-4** as a pure white solid which was taken on to the next step without further purification (3.74 g, 9.84 mmol, 83% yield).

Melting point = 242-244 °C.

¹H NMR (300 MHz, DMSO) δ 7.34 (s, 1H), 4.69 (s, 2H), 3.70 (s, 2H).
¹³C NMR (101 MHz, DMSO) δ 170.8, 132.6, 130.6, 123.3, 69.2, 35.7.
HRMS (ESI-) m/z calc. for C₁₂H₁₁Br₂O₄ [M-H]⁻ : 376.9030. Found: 376.9032.



2,2'-(2,5-Bis(3-(trimethylsilyl)prop-2-yn-1-yl)-1,4-phenylene)diethanol (S-6). BH₃·SMe₂ (3.5 equiv, 1.95 mL, 20.6 mmol) was added dropwise to a solution of S-4 (1 equiv, 2.24 g, 5.88 mmol) in anhydrous THF (0.05 M, 118 mL) at 0 °C. Once the addition was completed, the ice bath was removed, and the resulting mixture was allowed to warm to 23 °C and then heated gradually to 80 °C. After refluxing at that temperature for 2 h, the mixture was cooled to 0 °C and quenched by slow addition of 1 M solution of HCl (80 mL). The product was extracted with AcOEt (3×100 mL) and the combined organic layers washed with brine (200 mL), dried (MgSO₄), filtered and concentrated under reduced pressure. The obtained diol S-5 was then taken on to the next step without further purification.

To a solution of ethynyltrimethylsilane (8 equiv, 5.50 mL, 38.6 mmol) in anhydrous THF (30 mL), was added *i*PrMgCl (8 equiv, 19.3 mL, 2 M in THF, 38.6 mmol) dropwise at 0 °C. After stirring for 30 min at 0 °C and 30 min at 23 °C, CuBr (1.2 equiv, 832 mg, 5.79 mmol) was added in one portion. The pale blue reaction mixture was stirred for 30 min at 23 °C before adding the crude **S-5** (1.0 equiv, 1.70 g, 4.83 mmol) as a suspension in anhydrous THF (60 mL). The pale grey mixture was then refluxed for 16 h. After being cooled to 23 °C, the bright yellow solution was poured into a saturated aqueous solution of NH₄Cl (100 mL). The aqueous layer was extracted with EtOAc (2×150 mL). The combined organic layers were washed with brine (100 mL), dried (MgSO₄), filtered and concentrated. The crude material was purified by column chromatography (cyclohexane/EtOAc 9:1 to 7:3) to afford **S-6** as a white solid (953 mg, 2.46 mmol, 42% yield over 2 steps).

Melting point = 92-94 °C.

¹**H NMR (400 MHz, CDCl₃)** δ 7.27 (s, 1H), 3.88 (t, *J* = 6.7 Hz, 2H), 3.61 (s, 2H), 2.90 (t, *J* = 6.7 Hz, 2H), 0.17 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 135.0, 133.9, 130.9, 104.6, 87.3, 63.0, 35.5, 24.0, 0.2. HRMS (ESI+) m/z calc. for C₂₂H₃₄O₂Si₂ [M+Na]⁺: 409.1990. Found: 409.1978.



2,2'-(2,5-Bis(3-(trimethylsilyl)prop-2-yn-1-yl)-1,4-phenylene)diacetaldehyde (S-7). To a solution of diol **S-6** (1 equiv, 920 mg, 2.380 mmol) in HPLC grade CH_2Cl_2 (0.1 M, 23.8 mL) were sequentially added DMP (2.4 equiv, 2.420 g, 5.710 mmol) and NaHCO₃ (4 equiv, 800 mg, 9.520 mmol). The resulting pale yellow mixture was stirred at 23 °C for 1 h and then a saturated aqueous solution of NaHCO₃ (20 mL) was added. The organic layer was separated and washed with sat. aq. Na₂S₂O₃ (40 mL) and brine (40 mL), dried (MgSO₄) and concentrated *in vacuo*. The yellow residue was purified through column chromatography (cyclohexane/EtOAc 95:5 to 9:1) to yield **S-7** as a white solid (402 mg, 1.050 mmol, 44% yield).

Melting point = 127-129 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 9.76 (t, *J* = 1.9 Hz, 1H), 7.24 (s, 1H), 3.79 (d, *J* = 1.9 Hz, 2H), 3.53 (s, 2H), 0.15 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 198.7, 135.0, 132.4, 130.5, 103.3, 88.1, 47.6, 24.5, 0.1.

HRMS (**APCI**+) m/z calc. for C₂₂H₃₁O₂Si₂ [M+H]⁺: 383.1857. Found: 383.1865.



((2,5-bis(3-methoxyallyl)-1,4-phenylene)bis(prop-1-yne-3,1-diyl))bis(trimethylsilane) (S-8). A suspension of (methoxylmethyl)triphenylphosphonium chloride (2.2 equiv, 158 mg, 460 μ mol) in anhydrous THF (3.1 mL) was cooled to -40 °C and then a solution of lithium bis(trimethylsilyl)amide (2.2 equiv, 77.0 mg, 460 μ mol) in dry THF (2.3 mL) was added dropwise. After stirring the mixture for 30 min at -40 °C, a solution of S-7 (1.0 equiv, 80.0 mg, 0.209 mmol) in dry THF (2.3 mL) was added dropwise. The reaction mixture was stirred for an additional 30 min at -40 °C, then slowly warmed to 23 °C and stirred overnight. A saturated aqueous solution of NH₄Cl (5 mL) was added and the mixture was extracted with EtOAc (3 × 15 mL). The organic layer was washed with brine, dried (MgSO₄) and concentrated *in vacuo*. The orange residue was purified through column chromatography on silica gel (cyclohexane to cyclohexane/EtOAc 99:1 to 97:3) to give S-8 as a pale yellow oil (2:1 *E/Z*, 57.0 mg, 130 μ mol, 62% yield).

¹**H NMR (400 MHz, CDCl**₃) δ 7.31 (d, *J* = 5.2 Hz, 1H), 7.27 (d, *J* = 4.7 Hz, 2H), 6.37 (d, *J* = 12.6 Hz, 2H), 5.99 (ddt, *J* = 6.1, 3.1, 1.5 Hz, 1H), 4.85 (dtd, *J* = 8.2, 7.1, 1.0 Hz, 2H), 4.48 (td, *J* = 7.4, 6.2 Hz, 1H), 3.64 (d, *J* = 1.9 Hz, 3H), 3.60 (t, *J* = 2.9 Hz, 6H), 3.52 (d, *J* = 2.3 Hz, 6H), 3.39 (dd, *J* = 7.4, 1.4 Hz, 2H), 3.27 (dd, *J* = 7.0, 0.9 Hz, 4H), 0.24 – 0.12 (m, 27H).

¹³C NMR (101 MHz, CDCl₃) δ 148.3, 148.2, 146.8, 146.7, 137.2, 137.2, 137.0, 136.9, 133.1, 133.0, 132.9, 132.8, 129.7, 129.5, 129.5, 129.2, 104.9, 104.8, 104.7, 104.5, 101.1, 101.0, 87.2, 87.1, 87.1, 87.0, 59.8, 59.8, 56.1, 56.0, 30.8, 30.8, 27.2, 23.7, 23.5, 0.3, 0.2.

HRMS (ESI+) m/z calc. for C₂₆H₃₈NaO₂Si₂ [M+Na]⁺: 461.2303. Found: 461.2299.



1,4-Bis(3-methoxyallyl)-2,5-di(prop-2-yn-1-yl)benzene (3). Protected alkyne **S-8** (1.0 equiv, 88.0 mg, 200 μ mol) was dissolved in abs. EtOH (0.11 M, 1.9 mL) and then, a solution of silver nitrate (6.0 equiv, 200 mg, 1.20 mmol) in deionized water (0.2 mL) was added, leading to the instant formation of a white precipitate. The mixture was stirred at 23 °C for 1.5 h and then the reaction was quenched by addition of aqueous Na₂S₂O₃ (3 mL) and diluted with 10 mL of EtOAc. The suspension was filtered and the remaining biphasic solution was extracted with EtOAc (3 × 10 mL), washed with more Na₂S₂O₃ (10 mL) and brine (10 mL), dried (MgSO₄) and concentrated under reduced pressure. Purification by column chromatography on silica gel (cyclohexane/EtOAc 95:5) afforded **3** as a white solid (23 mg, 78 μ mol, 39% yield).

Melting point = 76-78 °C.

¹**H** NMR (500 MHz, CDCl₃) δ 7.30 (s, 1H), 7.26 (s, 2H), 6.36 (d, *J* = 12.6 Hz, 2H), 5.98 (tt, *J* = 4.9, 1.5 Hz, 1H), 4.86 (dt, *J* = 12.8, 7.0 Hz, 2H), 4.46 (dt, *J* = 13.5, 6.8 Hz, 1H), 3.65 (d, *J* = 1.7 Hz, 3H), 3.56 (dt, *J* = 6.8, 3.5 Hz, 6H), 3.53 (d, *J* = 2.8 Hz, 6H), 3.40 (dd, *J* = 7.3, 1.3 Hz, 2H), 3.29 (d, *J* = 7.0 Hz, 4H), 2.19 – 2.14 (m, 2.3H).

¹³C NMR (126 MHz, CDCl₃) δ 148.4, 148.3, 146.8, 146.7, 137.4, 137.3, 137.2, 137.0, 133.1, 133.0, 133.0, 132.9, 129.9, 129.8, 129.7, 129.6, 104.8, 104.7, 101.1, 101.0, 82.5, 82.4, 82.2, 82.1, 70.7, 70.6, 70.6, 70.5, 59.8, 59.8, 56.1, 56.1, 30.9, 30.8, 27.4, 27.3, 22.2, 22.2, 22.0, 22.0.

HRMS (ESI+) m/z calc. for C₂₀H₂₂NaO₂ [M+Na]⁺: 317.1512. Found: 317.1520.

Synthesis of 8,10,20,22-Tetrahydrobenzo[d][1]benzothieno[3',2':11,12]heptaceno[2,3-b]thiophene (2)



2-Iododibenzo[*b,d*]**thiophene**. A solution of 2.5 M of *n*-BuLi in cyclohexane (1.3 equiv, 980 µL, 2.47 mmol) was added dropwise to a solution of 2-bromodibenzo[*b,d*]thiophene (1 equiv, 500 mg, 1.90 mmol) in dry THF (9 mL, 0.22 M) at -78 °C, under an Ar atmosphere, while maintaining a good stirring. After stirring for 1 h, a solution of iodine (1.3 equiv, 627 mg, 2.47 mmol) in THF (10 ml) was added dropwise. The reaction mixture was warmed to 23 °C and stirred at this temperature for 1 h. The reaction mixture was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layer was washed with NaHSO₃ (70 mL) and the solvent was removed under vacuum, without previously drying with MgSO₄ since some solid product was present. Trituration of the crude with cyclohexane (50 mL) afforded the title compound as a white solid (413 mg, 1.33 mmol, 70% NMR yield). 2-Iododibenzo[*b,d*]thiophene was obtained together with the product of dehalogenation (~18%), which can be observed on the ¹H and ¹³C NMR.

¹H NMR (300 MHz, CDCl₃) δ 8.48 (d, J = 1.3 Hz, 1H), 8.10 (dt, J = 6.5, 2.3 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.72 (dd, J = 8.4, 1.6 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.49 – 7.46 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 135.3, 130.8, 127.5, 124.8, 124.6, 123.0, 121.9.



2,2'-((2,5-Bis(3-methoxyallyl)-1,4-phenylene)bis(prop-1-yne-3,1-diyl))didibenzo[b,d]thiophene (4). PdCl₂(PPh₃)₂ (4.8 mg, 6.8 μ mol, 10 mol%) and CuI (2.6 mg, 14 μ mol, 20 mol%) were suspended in Et₃N (1.0 mL) and the mixture was bubbled with Ar for 10 min. A solution of 1,7-enyne **3** (1.0 equiv, 20 mg, 68

 μ mol) and 2-iododibenzo[*b*,*d*]thiophene (2.2 equiv, 46 mg, 150 μmol) in degassed THF (2.0 mL) was subsequently added and the reaction was stirred at 50 °C for 3 h. Then the mixture was diluted with EtOAc (10 mL), filtered through a short pad of silica gel compacted with EtOAc/NEt₃ 99:1 and concentrated under reduced pressure. Purification by column chromatography (cyclohexane/EtOAc 98:2) afforded **3** as a pale yellow solid (14 mg, 21 μmol, 31% yield).

Because of the low solubility of **3** organic solvents, a ¹³C NMR spectrum could not be recorded.

¹**H** NMR (300 MHz, CD₂Cl₂) δ 8.26 (d, *J* = 1.5 Hz, 2.8H), 8.20 – 8.11 (m, 2.8H), 7.90 – 7.83 (m, 2.8H), 7.81 (d, *J* = 8.3 Hz, 2.8H), 7.57 – 7.39 (m, 11H), 6.46 (d, *J* = 12.7 Hz, 2H), 6.05 (ddt, *J* = 5.7, 2.8, 1.5 Hz, 0.8H), 4.96 (dt, *J* = 12.8, 7.1 Hz, 2H), 4.57 (td, *J* = 7.5, 6.2 Hz, 0.8H), 3.86 (d, *J* = 3.6 Hz, 5.6H), 3.63 (d, *J* = 2.8 Hz, 2.4H), 3.52 (d, *J* = 7.3 Hz, 1.7H), 3.48 (d, *J* = 3.1 Hz, 6H), 3.42 (d, *J* = 7.1 Hz, 4H). HRMS (ESI+) m/z calc. for C₄₄H₃₅O₂S₂ [M+H]⁺: 659.2073. Found: 659.2081.



8,10,20,22-Tetrahydrobenzo[*d*][1]benzothieno[3',2':11,12]heptaceno[2,3-*b*]thiophene (2). To a MW vial containing a solution of **4** (1.0 equiv, 13 mg, 20 μ mol) in HPLC grade CH₂Cl₂ (0.02 M, 1 mL) was added cationic gold catalyst [JohnPhosAu(MeCN)]SbF₆ (1.5 mg, 10 mol%). The vial was sealed and the mixture was stirred at 50 °C for 1 hour under air. After cooling to 23 °C, NEt₃ (1 drop) was added and then the solvents were evaporated under reduced pressure. The remaining solid was dissolved in CH₂Cl₂ (1 mL) and MeOH (4 mL) was added to precipitate **2**, which was isolated by vacuum filtration under Ar and obtained as an off-white solid (6.9 mg, 11.6 µmol, 58% yield).

LDI-MS spectrum of hydroacene 1:



(MALDI+) m/z calc. for C₄₂H₂₆S₂ [M]+ : 594.1, found: 594.3.

NMR Spectra





6,9-Dihydropyrano[3,4-g]isochromene-3,8(1H,4H)-dione (S-3)







2,2'-(2,5-Bis(3-(trimethylsilyl)prop-2-yn-1-yl)-1,4-phenylene)diethanol (S-6)



2,2'-(2,5-Bis(3-(trimethylsilyl)prop-2-yn-1-yl)-1,4-phenylene)diacetaldehyde (S-7)

 $((2,5-bis(3-methoxyallyl)-1,4-phenylene) bis(prop-1-yne-3,1-diyl)) bis(trimethylsilane) \ (S-8)$

1,4-Bis(3-methoxyallyl)-2,5-di(prop-2-yn-1-yl)benzene (3)

2-Iododibenzo[*b*,*d*]thiophene

2,2'-((2,5-Bis(3-methoxyallyl)-1,4-phenylene)bis(prop-1-yne-3,1-diyl))didibenzo[b,d]thiophene (4)

Experimental details

The experiments were conducted in an ultra-high vacuum system with a 10^{-10} mbar range base pressure. The Au(111) sample was made atomically clean through cycles of Ar⁺ ion sputtering and thermal annealing at 700 K. The sublimation temperature of the precursors was set at 560K with a flux (0.1Hz/min) calibrated by a quartz microbalance. These precursors were then thermally evaporated onto the sample (held at room temperature) using water-cooled Knudsen-cell (Kentax GmbH). The sample was kept at 575K for 20 minutes to carry out dehydrogenation reactions. The thermal annealing process was conducted in a preparation chamber using a resistive heater. All *STM/STS* data were collected using low-temperature scanning tunneling microscopes (LT-Nanoprobe STM and LT-STM, ScientaOmicron) operating at a temperature of 4.5K. Bond resolved scanning tunneling microscopy (BR-STM) data were obtained in constant-height mode using a PtIr tip decorated with a CO molecule. The *dI/dV* measurements were performed using a lock-in amplifier (Zurich Instruments MFLI) set to a frequency of 630 Hz and an oscillation amplitude of 20 mV. Nc-AFM images have been acquired with the amplitude of 110 pm.

Additional STM data

Figure S1a shows overview of isomers of **1** obtained through on-surface dehydrogenation. Differently shaped molecules are marked by dashed color rectangles. Figure S1b shows typical high resolution STM image of **1**, whereas Figures S1c-e presents the BR-STM images of most often observed isomers, marked by dashed rectangles in panel (a). On the right corresponding structural schemes are visualized.

Figure S1. (a) Overview filled state STM image of the Au(111) surface after thermal dehydrogenation of molecular precursors, (b) high resolution STM image of **1**, (c-e) bond-resolved STM images acquired with a CO decorated tip showing isomers **1**, **1a** and **1b**, corresponding structural schemes are shows on the right, tunneling current: 25 pA (a), 100 pA (b), bias voltage: -1.0 V (a, b), 5 mV (c, d, e). scale bar: 0.3 nm

Calculation details

The calculations of atomic structure and charge density of heptaceno[2,3-b:11,12-b']bis[1]benzothiophenes (**1**, HpBDT) on Au(111) were performed using density functional theory (DFT) with the projector augumented waves $(PAW)^1$ and van der Waals corrected exchange-correlation functional $(vdW-DF)^2$ available in VASP (Vienna ab-initio simulation package).³ The optPBE-vdW implementation of the vdW-DF method was used in the calculations.⁴ In electronic structure calculations the HSE06 hybrid functional has been utilized.⁵

A kinetic energy cutoff for the plane wave expansion of single particle wave functions was set to 700 eV. The Brillouin zone was sampled by a $1 \times 2 \times 1$ Monkhorst-Pack k-point grid including the

 Γ point.⁶ The convergence criterion for the total energy in the self-consistency cycle was chosen as 10^{-6} eV.

The Au(111) substrate has been modeled by a slab of 4 atomic layers. Periodic replicas of the slab were separated by a vacuum gap of 12 Å in order to avoid the interaction between surfaces of the slab. All the atomic positions were fully relaxed by a conjugate gradient method, except the bottom layer, until the maximum force in any direction was less than 0.01 eV/Å. During the geometry optimization the Au atoms in the bottom layer were fixed in their bulk positions. The calculations have been performed in the rectangular 12×6 surface unit cell with bulk Au lattice constant $a_{bulk} = 4.182$ Å.

The local density of states maps have been calculated according to the Tersoff-Hamann approach in the constant-current mode.⁷ The charge transfer analysis has been performed based on the Bader charges.⁸

Electron density

To shed more light on the problem of molecule-surface interaction we have computed the electron density distribution. Figure S2 shows the electron density within a plane perpendicular to the Au(111) surface and passing through both S atoms of the HpBDT molecule. It is evident that electron density is concentrated around the molecule and the Au atoms of the substrate. There is no trace of real chemical bonds, which are expected to be most visible in the case of S and Au atoms. Thus this is an additional argument supporting the scenario of the weak HpBDT-Au(111) interaction (physisorption).

Figure S2. Electron density distribution in a plane perpendicular to the Au(111) surface and passing through both S atoms of the HpBDT molecule. Only the molecule and the top Au layer are visible. High density values are shown in red, yellow and light blue.

Electronic structure comparison

In order to analyse the influence of the sulfur doping we have computed the projected density of states (PDOS) for a range of molecules including: heptacene (Hp), nonacene (Nn), dibenzo[a,t]nonacene (Nn-benzene) and heptaceno[2,3-b:11,12-b']dithiophene (Hp-S). Structural schemes of these molecules are displayed in Figure S3.

 $heptaceno \cite[2,3-b:11,12-b'] bis \cite[1] benzothiphene$

Figure S3. Structural schemes of heptaceno[2,3-b:11,12-b']bis[1]benzothiophene (**1**, HpBDT), heptacene (Hp), nonacene (Nn), dibenzo[a,t]nonacene (Nn-benzene) and heptaceno[2,3-b:11,12-b']dithiophene (Hp-S).

Figure S4 shows the PDOS calculated for the molecules (gas phase) visualized schematically in S3. The data shows clearly that the calculated gap of the hydrocarbon isoelectronic counterparts of acenothienes is slightly (by approximately 0.1-0.2 eV) reduced. Here, we compare the nonacene (green) with heptaceno[2,3-b:11,12-b']dithiophene (Hp-S, blue) and dibenzo[a,t]nonacene (Nn-benzene, yellow) with heptaceno[2,3-b:11,12-b']bis[1]benzothiophene (**1**, HpBDT, black). The

attachment of peripheral benzene ring to the nonacene or heptaceno[2,3-b:11,12-b']dithiophene core leads to slight increase of the gap (HpBDT vs. Hp-S; Nn-benzene vs. Nn). In all cases the calculated gap is smaller compared to the shorter member of the acene family, namely the heptacene (red). Taking into account the above analysis we shall expect the gap of heptaceno[2,3-b:11,12-b']bis[1]benzothiophene (**1**, HpBDT) to be smaller compared to nonacene and larger than for heptacene. This is in agreement with the STS measurements for heptacene (~1.61 eV), nonacene (~1.23 eV) and **1** (~1.37 eV) on Au(111).^{9,10}

Figure S4. PDOS calculated for the gas-phase structures of heptaceno[2,3-b:11,12-b']bis[1]benzothiophene (**1**, HpBDT, black) heptacene (Hp, red), nonacene (Nn, green), dibenzo[a,t]nonacene (Nn-benzene, yellow) and heptaceno[2,3-b:11,12-b']dithiophene (Hp-S, blue).

In the STS measurement we observe stabilization of HOMO after sulfur substitution (HOMO of **1** recorded at ~-0.47 V, HOMO of heptacene⁹ at ~-0.45 V, HOMO of nonacene¹⁰ at ~ -0.35 V).

Influence of Au(111) on heptaceno[2,3-b:11,12-b']bis[1]benzothiophene electronic structure

Figure S5 shows the PDOS calculated for **1** (HpBDT) in the gas-phase conformation (blue) and for the optimized geometry (red) on Au(111). It is clear that shapes and positions of the peaks corresponding to the molecule states are only weakly affected by the presence of the substrate. In particular there are no new states suggesting strong electron hybridization. Only small shift of

electron states towards higher energies is visible, which suggests some charge transfer from HpBDT to the Au surface. Indeed, the calculated Bader charge difference yields 0.83 electrons, coming mainly from S and H atoms.

Therefore we could conclude that the molecule 1 is weakly adsorbed on the Au(111).

Figure S5. PDOS calculated for the gas-phase structures of **1** (HpBDT, blue) and **1** (HpBDT, red) optimized on Au(111).

- 1. P.E. Blöchl, Phys. Rev. B, 1994, **50**, 17953
- 2. M. Dion, H. Rydberg, E. Schöder, D.C. Langreth, B.I. Lundqvist, Phys. Rev. Lett., 2004, 92, 246401
- G. Kresse, J. Furthmüller, Phys. Rev. B, 1996, 54, 11169; G. Kresse, D. Joubert, Phys. Rev. B, 1999, 59, 1758
- G. Roman-Perez, J.M. Soler, Phys. Rev. Lett., 2009, **103**, 096102; J. Klimes, D.R. Bowler, A. Michaelides, J. Phys.: Condens. Matter, 2010, **22**, 022201; J. Klimes, D.R. Bowler, A. Michaelides, Phys. Rev. B, 2011, **83**, 195131
- 5. A.V. Krukau, O.A. Vydrov, A.F. Izmaylov, G.E. Scuseria, J. Chem. Phys., 2006, 125, 224106
- 6. H.J. Monkhorst, J.D. Pack, Phys. Rev. B, 1976, 13, 5188
- 7. J. Tersoff, D.R. Hamann, Phys. Rev. Lett., 1983, 50, 1998
- 8. Bader, R. F. W. Atoms in Molecules: A Quantum Theory; Oxford University Press: New York, 1990.

- 9. R. Zuzak, R. Dorel, M. Kolmer, M. Szymonski, S. Godlewski, A.M. Echavarren, Angew. Chem. Int. Ed., 2018, **57**, 10500-10505
- R. Zuzak, R. Dorel, M. Krawiec, B. Such, M. Kolmer, M. Szymonski, A.M. Echavarren, S. Godlewski, ACS Nano, 2017, 11, 9321-9329