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1. General Information *Materials*

The chemicals used were employed directly from the respective companies without further purification.

4-Bromophenol (99%), n-BuLi (n/a), trimethyl borate (98%), sodium methanethiolate (≥90%), 4-bromo-2-fluoro-1-iodobenzene (95%), tetrakis(triphenylphosphine)palladium(0) (99%), tetra-n-butylammonium fluoride (97%), (diacetoxyiodo)benzene (98%), phenylboronic acid (95%) and the Karstedt-catalyst (n/a) were purchased from Sigma Aldrich. N,N'-Diisopropylcarbodiimide (99%) and copper(I) iodide (99.998%) were purchased from Alfa Aeser. Potassium carbonate (99%), magnesium (99%), triethylamine (99%), sodium bisulfite solution (40%), potassium iodide (99.5%) and potassium acetate (99%) were purchased from Grüssing GmbH. Sodium sulfate (99%) and iodine (99.5%) were purchased from ORG Laborchemie GmbH. Ethyl formiate (99%) and triphenylphosphine (n/a) were purchased from VWR. 4-Bromo-1-butene (99%) and 4-aminophthalonitrile (97%) were purchased from Apollo Scientific. Sodium chloride (99.5%) and ammonium acetate (99.5%) were purchased from Bernd Kraft GmbH. Bis(pinacolato)diboron (98%) and pentmathyldisiloxane (97%) were purchased from abcr GmbH. Toluene (n/a) was purchased from STAUB & CO. - SILBERMANN GmbH. Hydrochloric acid (37%) was purchased from Fischer Scientific. All chemicals employed were used as received, without further purification. Ethanol (99.8%), benzene (99.7%) and chloroform-d (99.8%) were purchased from Sigma Aldrich. Tetrahydrofuran (99.5%), dimethylformamide (99.5%) and chloroform (99.8%) were purchased from Fischer Scientific. Methanol (>98.5%) was purchased from VWR. Dichloromethane, cyclohexane (>99%), ethyl acetate, acetone and isopropyl alcohol were purchased from Jäkle. Ethanol, benzene, chloroform, cyclohexane, isopropyl alcohol, methanol and chloroform-d were used as received. All other solvents were distilled and, if necessary, dried via standard procedures before use. As inert gas, dry nitrogen was employed. For column chromatography, silica gel 60 from Macherey Nagel (70-230 mesh) was used. The reactions were controlled via thin film chromatography using silica gel (aluminium plates) from Merck with fluorescence indicator F254.

Instruments

A recycling GPC instrument (LC-20A) from Shimadzu was used, which was controlled using the LabSolutions software. The stationary phase used was PSS SDV 500 Å, 20-600 nm. A quartz immersion well reactor was used for photochemical reactions, which was equipped with a Hanovia 679A-36 immersion lamp (450 watts).

The NMR measurements were conducted on Bruker instruments (Avance-400, Bruker), with a frequency of 400.1 MHz for ¹H NMR and 100.0.0 MHz for ¹³C NMR. The obtained spectra were analyzed using the TopSpin 3.5 software. The chemical shifts of ¹H and ¹³C were reported relative to tetramethylsilane (SiMe₄). The residual protons and 13C shifts of the deuterated solvents were used as secondary standards, and their chemical shifts were taken from the literature (CDCl₃: δ = 7.26 ppm (¹H), δ = 77.16 ppm (¹³C); CD₂Cl₂: δ = 5.30 ppm (¹H), δ = 53.84 ppm (¹³C)).¹

Mass spectrometric measurements (MALDI-HRMS) were performed on a Bruker Daltonics ultrafleXtreme instrument. Polarising microscopy was carried out on a Nikon Eclipse LV100POL polarizing microscope equipped with a Linkam Scientific Instruments heating stage. X-ray diffraction patterns were obtained on a Bruker Nanostar (Detector Vantec2000, Microfocus Copper Anode, X-ray tube Incoatec) and analysed using the datasqueeze 3.0.17 software (Paul A. Heiney). The extruded samples transferred into Mark capillaries (Hilgenberg) were glued onto corresponding sample holders of the temperature unit of the instrument using a two-component adhesive (Henkel) and positioned in the X-ray beam.

2. Synthesis

Nona-1,8-dien-5-ol 7



Under nitrogen atmosphere, 20.7 g (850 mmol, 3.3 equiv.) of magnesium were layered with dry THF and some crumbs of iodine were added. After 30 min stirring at room temperature, 80.0 g (593 mmol, 2.3 equiv.) of 4-bromobut-1-ene **6** in 80 mL of dry THF were added dropwise over 45 min to the reaction solution. The mixture was then heated to reflux for one hour, and after cooling, 20.8 mL (19.1 g, 258 mmol, 1.0 equiv.) of ethyl formate were added dropwise. The reaction mixture was stirred overnight at room temperature, then treated with 100 mL of 1 M HCl and Et₂O, and the phases were separated. The aqueous phase was extracted three times with 75 mL of Et₂O each, and the combined organic phases were washed with distilled water until neutral. The organic phase was then dried over sodium sulfate, and the solvent was removed under reduced pressure.

Yield: 33.2 g (237 mmol, 92%) of a colourless oil.

¹**H NMR** (400.1 MHz, CDCl₃, 295 K): $\delta = 1.48 - 1.62$ (m, 4 H, -CH₂-), 2.08 - 2.27 (m, 4 H, -CH₂-), 3.63 - 3.69 (m, 1 H, CH), 4.98 (dddd, ²J = 10.2 Hz, ³J = 2.0 Hz, ⁴J = 1.4 Hz, ⁴J = 1.4 Hz, 2 H, =CH₂), 5.06 (dddd, ²J = 17.2 Hz, ³J = 3.6 Hz, ⁴J = 1.6 Hz, ⁴J = 1.6 Hz, 2 H, =CH₂), 5.84 (dddd, ³J = 16.9 Hz, ³J = 10.1 Hz, ³J = 6.7 Hz, ³J = 6.7 Hz, 2 H, CH) ppm.

The obtained data is in agreement with the literature.²



Under nitrogen atmosphere, 12.0 g (85.6 mmol, 1.2 equiv.) of **7** were dissolved in 150 mL of THF. Then, 12.3 g (71.3 mmol, 1.0 equiv.) of 4-bromophenol, 18.7 g (71.3 mmol, 1.0 equiv.) of PPh₃, and 9.97 mL (7.22 g, 71.3 mmol, 1.0 equiv.) of NEt₃ were added, and the reaction solution was cooled to 0°C. Afterwards, 14.4 g (71.3 mmol, 1.0 equiv.) of DIAD were added, and the reaction mixture was stirred at room temperature for six days. Subsequently, 100 mL of 2 M hydrochloric acid was added, and the resulting phases were separated. The aqueous phase was extracted three times with 30 mL of DCM each, and the combined organic phases were washed twice with 30 mL of saturated NaCl solution. The organic phase was then dried over sodium sulfate, and the solvent was removed under reduced pressure. Finally, the crude product was purified by column chromatography (silica gel, Cy:DCM = 4:1 (v/v)).

Yield: 17.1 g (57.8 mmol, 81%) of a colourless oil.

¹**H NMR** (400.1 MHz, CDCl₃, 295 K): $\delta = 1.65 - 1.82$ (m, 4 H, -CH₂-), 2.06 - 2.24 (m, 4 H, -CH₂-), 4.23 (quin., ³*J* = 5.9 Hz, 1 H, C*H*), 4.98 (dddd, ²*J* = 10.2 Hz, ³*J* = 2.0 Hz, ⁴*J* = 1.4 Hz, ⁴*J* = 1.4 Hz, 2 H, =CH₂), 5.06 (dddd, ²*J* = 17.2 Hz, ³*J* = 3.6 Hz, ⁴*J* = 1.6 Hz, ⁴*J* = 1.6 Hz, 2 H, =CH₂), 5.80 (dddd, ³*J* = 16.9 Hz, ³*J* = 10.1 Hz, ³*J* = 6.7 Hz, ³*J* = 6.7 Hz, 2 H, C*H*), 6.74 - 6.79 (AA'BB', 2 H, Ar-*H*), 7.32 - 7.37 (AA'BB', 2 H, Ar-*H*) ppm.

¹³**C NMR** (100.0 MHz, CDCl₃): δ = 29.6 (C_s), 33.1 (C_s), 76.9 (C_t), 112.7 (C_q), 115.3 (C_s), 117.8 (C_t), 132.4 (C_t), 138.1 (C_t), 157.8 (C_q) ppm.

[4-(Nona-1,8-dien-5-yloxy)phenyl]boronic acid 9



Under nitrogen atmosphere, 1.52 g (5.15 mmol, 1.0 equiv.) of **8** was dissolved in dry THF and the solution was then cooled to -78 °C. Subsequently, 4.20 mL (668 mg, 10.3 mmol, 2.50 M, 2.0 equiv.) of *n*-BuLi was added dropwise to the reaction solution at -78 °C, and the reaction solution was then allowed to thaw at -20 °C. Afterwards, the reaction solution was cooled again to -78 °C and 2.33 mL (2.17 g, 20.6 mmol, 4.0 equiv.) of trimethyl borate was added and stirred overnight at room temperature. Afterwards, 30 mL of saturated NH₄Cl solution was added, and the resulting phases were separated. The aqueous phase was extracted three times with 20 mL of DCM each, and the combined organic phases were washed twice with 20 mL of distilled water each, then dried over sodium sulfate and the solvent was removed under reduced pressure. The crude product was used directly without further purification.



Compound **11** was synthesised according to a literature procedure.³

Under nitrogen atmosphere, 6.50 g (21.6 mmol, 1.0 equiv.) of **10** were added to 50 mL of dry DMF (solution 1). Meanwhile, 1.97 g (28.1 mmol, 1.3 equiv.) of sodium methanethiolate were dissolved in 20 mL of dry DMF under a nitrogen atmosphere (solution 2). Solution 2 was then cooled to 0 °C and solution 1 was added while stirring. The reaction mixture was then warmed to room temperature and stirred overnight. Subsequently, the reaction mixture was diluted with distilled water, and the resulting precipitate was filtered off and washed three times with 20 mL of distilled water each.

Yield: 7.01 g (21.3 mmol, 99%) of colourless needles.

¹**H NMR** (400.1 MHz, CDCl₃, 295 K): δ = 2.45 (s, 3 H, CH₃), 6.97 (dd, ³J = 8.3 Hz, ⁴J = 2.2 Hz, 1 H, Ar-*H*), 7.15 (d, ⁴J = 2.2 Hz, 1 H, Ar-*H*), 7.61 (d, ³J = 8.3 Hz, 1 H, Ar-*H*) ppm.

The measured data is in agreement with previously reported data.³

{[4-Bromo-2-(methylthio)phenyl]ethynyl}triisopropylsilane 12



Under nitrogen atmosphere, 8.00 g (24.3 mmol, 1.0 equiv.) of **11** were dissolved in a mixture of 125 mL DCM and 125 mL NEt₃ and the solution was degassed for 30 min. Then, 139 mg (730 µmol, 0.03 equiv.) of copper(I) iodide and 534 mg (730 µmol, 0.03 equiv.) of $Pd(PPh_3)_4$ were added, and the reaction mixture was degassed for another 30 Next. 4.66 g (5.60 mL, 25.5 mmol. 1.05 equiv.) of min. ethynyltriisopropylsilane were slowly added dropwise to the cooled reaction solution at 0 °C, and the reaction mixture was stirred overnight at room temperature. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, Cy:DCM = 1:0 => 9:1 (v/v)).

Yield: 9.05 g (23.6 mmol, 97%) of a colourless oil.

¹**H-NMR** (400.1 MHz, CD₂Cl₂, 295 K): δ = 1.13 (s, 3 H, C*H*), 1.14(s, 18 H, C*H*₃), 2.47 (s, 3 H, C*H*₃), 7.20 (dd, 1 H, ³*J* = 8.1 Hz, ⁴*J* = 1.9 Hz, Ar-*H*), 7.24 (d, 1 H, ⁴*J* = 1.9 Hz, Ar-*H*), 7.28 (d, 1 H, ³*J* = 8.1 Hz, Ar-*H*) ppm.

¹³**C-NMR** (100.0 MHz, CD_2Cl_2 , 295 K): δ = 11.7 (C_t), 15.2 (C_p), 18.8 (C_p), 99.6 (C_q), 103.2 (C_q), 120.3 (C_q), 123.5 (C_q), 126.5 (C_t), 127.3 (C_t), 134.2 (C_t), 145.0 (C_q) ppm.

FT-IR (Film): *v* = 2941, 2920, 2889, 2863, 2150, 1878, 1538, 1457, 1377, 1257, 1213, 1068, 996, 881, 841, 809, 735, 716, 668, 657, 563, 518 cm⁻¹.

MALDI-HRMS, m/z (%): calculated: 382.0781 ([M⁺⁻], 100), found: 382.0774 ([M⁺⁻]).

Triisopropyl{[3-(methylthio)-4'-(nona-1,8-dien-5-yloxy)-[1,1'-biphenyl]-4-yl]ethynyl}silane **13**



Under nitrogen atmosphere, 1.75 g (4.56 mmol, 1.0 equiv.) of **12** was dissolved in 30 mL of THF and degassed for 30 minutes. Meanwhile, 2.21 g (16.0 mmol, 3.5 equiv.) of potassium carbonate was dissolved in 3 mL of distilled water and added to the reaction solution. The solution was degassed again for 30 minutes (solution 1). Meanwhile, 1.54 g (5.93 mmol, 1.3 equiv.) of **9** was dissolved in dry THF and degassed for 30 minutes (solution 2). 1 was then heated to boiling and 264 mg (228 µmol, 0.05 equiv.) of Pd(PPh₃)₄ was added to the boiling solution. Then, solution 2 was added dropwise to the boiling for 16 hours. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography (silica gel, Cy:EE = $1:0 \rightarrow 4:1 (v/v)$).

Yield: 2.01 g (4.56 mmol, 85%) of a yellow oil.

¹**H** NMR (400.1 MHz, CD₂Cl₂, 295 K): $\delta = 1.16$ (bs, 21 H, CH₃, CH), 1.70 – 1.86 (m, 4 H, -CH₂-), 2.11 – 2.27 (m, 4 H, -CH₂-), 2.53 (s, 3 H, CH₃), 4.34 (quin., 1 H, ³J = 5.9 Hz, CH), 4.98 (dddd, ³J = 10.2 Hz, ⁴J = 2.0 H, ⁴J = 1.4 Hz, ⁴J = 1.4 Hz, 2 H, =CH₂), 5.06 (dddd, ²J = 17.2 Hz, ³J = 3.6 Hz, ⁴J = 1.6 Hz, ⁴J = 1.6 Hz, 2 H, =CH₂), 5.83 (dddd, ³J = 16.9 Hz, ²J = 10.1 Hz, ³J = 6.7 Hz, ³J = 6.7 Hz, 2 H, CH), 6.96 (AA'BB', 2 H, Ar-H), 7.23 (dd, 1 H, ³J = 7.9 Hz, ⁴J = 1.8 Hz, Ar-H), 7.28 (d, 1 H, ⁴J = 1.8 Hz, Ar-H), 7.46 – 7.50 (m, 3 H, H-2, Ar-H) ppm.

¹³**C NMR** (100.0 MHz, CD_2Cl_2 , 295 K): δ = 12.8 (C_s), 16.2 (C_p), 19.9 (C_p), 30.9 (C_s), 34.4 (C_s), 78.0 (C_t), 99.4 (C_q), 105.4 (C_q), 116.1 (C_s), 117.6 (C_t), 120.8 (C_q), 123.3 (C_t), 123.7 (C_t), 129.5 (C_t), 133.9 (C_q), 134.6 (C_t), 139.6 (C_t), 142.7 (C_q), 143.9 (C_q), 160.0 (C_q) ppm.

FT-IR (Film): *v* = 2940, 2921, 2891, 2863, 2150, 1606, 1511, 1465, 1436, 1382, 1282, 1241, 1175, 1067, 993, 910, 881, 818, 747, 668, 619 cm⁻¹.

MALDI-HRMS, m/z (%): calculated: 518.3033 ([M⁺⁻], 100), found: 518.3025 ([M⁺⁻]).

[4-Ethynyl-4'-(nona-1,8-dien-5-yloxy)-[1,1'-biphenyl]-3-yl](methyl)sulfane 14



1.50 g (2.89 mmol, 1.0 equiv.) of compound **13** was dissolved in THF and 1.28 g (4.05 mmol, 1.4 equiv.) of TBAF • 3 H₂O was added. The resulting reaction solution was stirred at room temperature for 2 h and then the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, Cy:DCM = 1:1 (v/v)).

Yield: 973 mg (2.68 mmol, 93%) of a yellow oil.

¹**H NMR** (400.1 MHz, CDCl₃, 295 K): $\delta = 1.71 - 1.86$ (m, 4 H, -CH₂-), 2.11 - 2.27 (m, 4 H, -CH₂-), 2.55 (s, 3 H, CH₃), 3.54 (s, 1 H, CH), 4.36 (quin, 1 H, ³J = 5.9 Hz, CH), 4.98 (dddd, ²J = 10.2 Hz, ³J = 2.0 H, ⁴J = 1.4 Hz, ⁴J = 1.4 Hz, 2 H, =CH₂), 5.06 (dddd, ²J = 17.2 Hz, ³J = 3.6 Hz, ⁴J = 1.6 Hz, ⁴J = 1.6 Hz, 2 H, =CH₂), 5.85 (dddd, ³J = 16.9 Hz, ³J = 10.1 Hz, ³J = 6.7 Hz, ³J = 6.7 Hz, 2 H, CH), 6.95 - 6.99 (AA'BB', 2 H, Ar-H), 7.29 (dd, 1 H, ³J = 7.9 Hz, ⁴J = 1.7 Hz, Ar-H), 7.34 (d, 1 H, ⁴J = 1.7 Hz, Ar-H), 7.49 (d, 1 H, ³J = 7.9 Hz, Ar-H), 7.52 (AA'BB', 2 H, Ar-H) ppm.

¹³**C NMR** (100.0 MHz, CD_2Cl_2 , 295 K): δ = 15.3 (C_p), 29.9 (C_s), 33.4 (C_s), 77.0 (C_t), 81.4 (C_q), 84.0 (C_t), 115.1 (C_s), 116.6 (C_t), 118.4 (C_q), 122.6 (C_t), 123.0 (C_t), 128.6 (C_t), 132.6 (C_q), 133.8 (C_t), 138.6 (C_t), 142.3 (C_q), 142.8 (C_q), 159.1 (C_q) ppm.

FT-IR (Film): *v* = 2958, 2936, 2863, 1639, 1606, 1589, 1512, 1467, 1381, 1176, 1118, 994, 911, 882, 856, 821, 672, 541 cm⁻¹.

MALDI-HRMS, m/z (%): calculated: 362.1704 ([M⁺⁻], 100), found: 362.1699 ([M⁺⁻]).

(5-Bromo-2-{[3-(methylthio)-4'-(nona-1,8-dien-5-yloxy)-(1,1'-biphenyl)-4yl]ethynyl}phenyl)(methyl)sulfane **15**



Under nitrogen atmosphere, 950 mg (2.62 mmol, 1.0 equiv.) of **14** were dissolved in a mixture of 75 mL DCM and 75 mL NEt₃ and the solution was degassed for 30 min. Then, 15.8 mg (82.8 µmol, 0.03 equiv.) Cul and 151 mg (131 µmol, 0.05 equiv.) Pd(PPh₃)₄ were added and degassed for another 30 min (solution 1). Meanwhile, 1.09 g (3.31 mmol, 1.2 equiv.) of **11** were dissolved in 20 mL DCM under a nitrogen atmosphere and degassed for 30 min (solution 2). Solution 2 was then added dropwise to solution 1, which was cooled to 0 °C, and the reaction mixture was stirred overnight at room temperature. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, Cy:EE = 1:0 \rightarrow Cy:EE = 19:1, (v/v)).

Yield: 1.24 g (2.20 mmol, 80%) of an orange oil.

¹**H NMR** (400.1 MHz, CDCl₃, 295 K): $\delta = 1.71 - 1.88$ (m, 4 H, -CH₂-), 2.13 - 2.27 (m, 4 H, -CH₂-), 2.52 (s, 3 H, CH₃), 2.58 (s, 3 H, CH₃), 4.36 (quin., 1 H, ³J = 5.9 Hz, CH), 4.98 (dddd, ²J = 10.2 Hz, ³J = 2.0 H, ⁴J = 1.4 Hz, ⁴J = 1.4 Hz, 2 H, =CH₂), 5.06 (dddd, ²J = 17.2 Hz, ³J = 3.6 Hz, ⁴J = 1.6 Hz, ⁴J = 1.6 Hz, 2 H, =CH₂), 5.84 (dddd, ³J = 16.9 Hz, ³J = 10.1 Hz, ³J = 6.7 Hz, ³J = 6.7 Hz, 2 H, CH), 6.98 (AA'BB', 2 H, Ar-H), 7.25 (dd, 1 H, ³J = 8.1 Hz, ⁴J = 1.9 Hz, Ar-H) 7.27 (d, 1 H, ⁴J = 1.9 Hz, Ar-H), 7.30 (dd, 1 H, ³J = 8.0 Hz, ⁴J = 1.7 Hz, Ar-H), 7.35 (d, 1 H, ⁴J = 1.7 Hz, Ar-H), 7.39 (d, 1 H, ³J = 7.9 Hz, Ar-H), 7.52 (AA'BB', 2 H, Ar-H), 7.57 (d, 1 H, ³J = 8.0 Hz, Ar-H) ppm.

¹³**C NMR** (100.0 MHz, CDCl₃, 295 K): $\delta = 15.3$ (C_p), 15.4 (C_p), 29.6 (C_s), 33.2 (C_s), 76.6 (C_t), 92.6 (C_q), 94.6 (C_q), 115.2 (C_s), 116.3 (C_t), 119.3 (C_q), 120.1 (C_q), 122.5 (C_t), 123.0 (C_t), 126.5 (C_t), 127.3 (C_t), 128.3 (C_t), 132.7 (C_q), 133.1 (C_t), 133.6 (C_t), 138.1 (C_t), 141.8 (C_q), 142.0 (C_q), 144.1 (C_q), 158.7 (C_q) ppm.

FT-IR (Film): *v* = 3073, 3033, 2975, 2917, 2849, 2527, 2206, 1890, 1635, 1587, 1576, 1510, 1473, 1433, 1375, 1281, 1240, 1176, 1070, 909, 816, 750, 668 cm⁻¹.

MALDI-HRMS, m/z (%): calculated: 562.0994 ([M⁺⁻], 100), found: 562.0985 ([M⁺⁻]).

2-[4-Bromo-2-(methylthio)phenyl]-3-iodo-6-[4-(nona-1,8-dien-5yloxy)phenyl]benzo[b]thiophene **16** and 6-bromo-3-iodo-2-[3-(methylthio)-4'-(nona-1,8-dien-5-yloxy)-(1,1'-biphenyl)-4-yl]benzo[b]thiophene **17**



Compounds 16 and 17 were prepared analogously to the literature.⁴

900 mg (1.60 mmol, 1.0 equiv.) of **15** were dissolved in 10 mL of DCM and then 446 mg (1.76 mmol, 1.1 equiv.) of iodine and 566 mg (1.76 mmol, 1.1 equiv.) of PhI(OAc)₂ were added to the reaction solution, which was stirred for two hours at room temperature. Then, 50 mL of sodium bisulfite solution (40% (w/w))) was added, the phases were separated, and the aqueous phase was extracted three times with 30 mL of DCM. The combined organic phases were washed twice with 20 mL of distilled water, dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, Cy:EE = 19:1 (v/v)), and finally dissolved in DCM and precipitated with MeOH. The product mixture was used without isomer separation.

Yield: 787 mg (1.17 mmol, 73%) of a dark brown oil.

16: ¹**H NMR** (400.1 MHz, CDCl₃, 295 K): $\delta = 1.73 - 1.89$ (m, 4 H, -CH₂-), 2.13 - 2.29 (m, 4 H, -CH₂-), 2.58 (s, 3H, CH₃) 4.38 (quin., 1 H, ³J = 5.9 Hz, CH), 4.98 (dddd, ²J = 10.2 Hz, ³J = 2.0 H, ⁴J = 1.4 Hz, ⁴J = 1.4 Hz, 2 H, =CH₂), 5.06 (dddd, ²J = 17.2 Hz, ³J = 3.6 Hz, ⁴J = 1.6 Hz, ⁴J = 1.6 Hz, 2 H, =CH₂), 5.83 (dddd, ³J = 16.9 Hz, ³J = 10.1 Hz, ³J = 6.7 Hz, ³J = 6.7 Hz, 2 H, CH), 7.01 (AA'BB', 2 H, Ar-H), 7.43 (d, ³J = 8.0 Hz, 1 H, Ar-H), 7.60 (dd, ³J = 8.7 Hz, ⁴J = 1.7 Hz, 1 H, Ar-H), 7.67 (dd, 1 H, ³J = 8.7 Hz, ⁵J = 0.4 Hz, Ar-H), 7.68 (AA'BB', 2 H, Ar-H), 7.78 (dd, 1 H, ³J = 8.0 Hz,

⁴*J* = 1.9 Hz, Ar-*H*), 7.98 (dd, 1 H, ⁴*J* = 1.7 Hz, ⁵*J* = 0.4 Hz, Ar-*H*), 8.37 (d, ⁴*J* = 1.9 Hz, Ar-*H*) ppm.

17: ¹**H NMR** (400.1 MHz, CDCl₃, 295 K): $\delta = 1.73 - 1.89$ (m, 4 H, -C*H*₂-), 2.13 - 2.29 (m, 4 H, -C*H*₂-), 2.57 (s, 3H, C*H*₃) 4.38 (quin., 1 H, ³*J* = 5.9 Hz, C*H*), 4.98 (dddd, ²*J* = 10.2 Hz, ³*J* = 2.0 H, ⁴*J* = 1.4 Hz, ⁴*J* = 1.4 Hz, 2 H, =C*H*₂), 5.06 (dddd, ²*J* = 17.2 Hz, ³*J* = 3.6 Hz, ⁴*J* = 1.6 Hz, ⁴*J* = 1.6 Hz, 2 H, =C*H*₂), 5.83 (dddd, ³*J* = 16.9 Hz, ³*J* = 10.1 Hz, ³*J* = 6.7 Hz, ³*J* = 6.7 Hz, 2 H, C*H*), 7.01 (AA'BB', 2 H, Ar-*H*), 7.29 (d, 1 H, ³*J* = 8.1 Hz, H-15), 7.58 (AA'BB', 2 H, Ar-*H*), 7.70 (dd, 1 H, ³*J* = 8.4 Hz, ⁴*J* = 1.5 Hz, Ar-*H*), 7.73 (dd, 1 H, ³*J* = 8.1 Hz, ⁴*J* = 2.0 Hz, Ar-*H*), 7.82 (dd, 1 H, ³*J* = 8.4 Hz, ⁵*J* = 0.6 Hz, Ar-*H*), 7.97 (dd, ⁴*J* = 1.5 Hz, Ar-*H*), 7.97

16: ¹³**C NMR** (100.0 MHz, CDCl₃, 295 K): δ = 29.9 (C_s), 33.4 (C_s), 43.2 (C_p), 77.0 (C_t), 84.6 (C_q), 115.3 (C_t), 116.5 (C_t), 121.6 (C_t), 124.8 (C_t), 127.6 (C_t), 128.6 (C_t), 128.7 (C_t), 128.8 (C_q), 128.9 (C_q), 129.5 (C_t), 131.2 (C_q), 132.5 (C_t), 138.0(C_t) (C_t), 138.1(C_t) (C_q), 139.7(C_q), 140.0 (C_q), 143.7 (C_q), 146.5 (C_q), 158.7 (C_q) ppm.

17: ¹³**C NMR** (100.0 MHz, CDCl₃, 295 K): $\delta = 29.9$ (C_s), 33.4 (C_s), 43.1 (C_p), 77.0 (C_t), 85.0 (C_q), 115.3 (C_s), 116.5 (C_t), 119.9 (C_t), 120.4 (C_q), 125.4 (C_t), 125.6 (C_q), 126.6 (C_t), 127.2 (C_t), 128.6 (C_t), 128.7 (C_t), 130.6 (C_q), 133.6 (C_t), 134.3 (C_t), 138.1 (C_t), 139.6 (C_q), 140.3 (C_q), 140.8 (C_q), 148.4 (C_q), 159.2 (C_q) ppm.

FT-IR 16 + 17 (film): *v* = 3073, 2923, 2849, 2533, 1733, 1604, 1510, 1457, 1442, 1382, 1286, 1239, 1177, 1067, 1038, 910, 809, 735, 668, 517 cm⁻¹.

MALDI-HRMS, m/z (%): calculated: 674.0346 ([M⁺⁻], 100), found: 674.0337 ([M⁺⁻]).

2-Bromo-7-[4-(nona-1,8-dien-5-yloxy)phenyl]benzo[b]benzo[4,5]thieno[2,3d]thiophene **18**



Compound 18 was prepared analogously to the literature.⁴

Under nitrogen atmosphere, 600 mg (888 µmol, 1.0 equiv.) of the mixture of **16** and **17** were dissolved in 250 mL of DCM, and the solution was degassed and irradiated with a 450 W high-pressure mercury lamp for five hours in a Duran flask. Then, the solvent was removed under reduced pressure, and the crude product was precipitated with MeOH from DCM.

Yield: 450 mg (843 µmol, 95%) of a dark green highly viscous oil.

¹**H NMR** (400.1 MHz, CDCl₃, 295 K): $\delta = 1.71 - 1.89$ (m, 4 H, $-CH_2$ -), 2.13 - 2.30 (m, 4 H, $-CH_2$ -), 4.36 (quin., 1 H, ${}^{3}J = 5.9$ Hz, CH), 4.98 (dddd, ${}^{2}J = 10.2$ Hz, ${}^{3}J = 2.0$ H, ${}^{4}J = 1.4$ Hz, ${}^{4}J = 1.4$ Hz, 2 H, $=CH_2$), 5.06 (dddd, ${}^{2}J = 17.2$ Hz, ${}^{3}J = 3.6$ Hz, ${}^{4}J = 1.6$ Hz, ${}^{4}J = 1.6$ Hz, 2 H, $=CH_2$), 5.84 (dddd, ${}^{3}J = 16.9$ Hz, ${}^{3}J = 10.1$ Hz, ${}^{3}J = 6.7$ Hz, ${}^{3}J = 6.7$ Hz, 2 H, CH), 7.00 (AA'BB', 2 H, Ar-H), 7.57 (dd, 1 H, ${}^{3}J = 8.4$ Hz, ${}^{4}J = 1.7$ Hz, Ar-H), 7.60 (AA'BB', 2 H, Ar-H), 7.67 (dd, 1 H, ${}^{3}J = 8.3$ Hz, ${}^{4}J = 1.6$ Hz, Ar-H), 7.74 (dd, 1 H, ${}^{3}J = 8.4$ Hz, ${}^{5}J = 0.5$ Hz, Ar-H), 8.06 (dd, 1 H, ${}^{4}J = 1.7$ Hz, ${}^{5}J = 0.4$ Hz, Ar-H), 8.07 (dd, 1 H, ${}^{4}J = 1.6$ Hz, ${}^{5}J = 0.5$ Hz, Ar-H) ppm.

¹³**C NMR** (100.0 MHz, CDCl₃, 295 K): δ = 29.7 (C_s), 33.3 (C_s), 76.7 (C_p), 115.2 (C_t), 116.4 (C_t), 118.6 (C_q), 121.9 (C_t), 122.6 (C_t), 124.5 (C_t), 126.7 (C_t), 128.5 (C_t), 128.6

(C_t), 128.7 (C_q), 131.5 (C_t), 132.1 (C_q), 133.0 (C_q), 133.8 (C_q), 138.2 (C_t), 138.6 (C_q), 143.3 (C_q), 143.8 (C_q), 158.5 (C_q) ppm.

FT-IR (Film): *v* = 2921, 2851, 2232, 1639, 1595, 1511, 1458, 1243, 1177, 994, 912, 800, 670, 637, 614, 584, 552, 521 cm⁻¹.

MALDI-HRMS, m/z (%): calculated: 532.0530([M⁺⁻], 100), found: 532.0525 ([M⁺⁻]).



Compound **4** was prepared analogously to literature.⁵

10.1 g (70.6 mmol, 1.0 equiv.) of 4-aminophthalonitrile **3** were suspended in 150 mL of 2.5 M sulfuric acid and cooled to -10 °C. Then, 5.35 g (77.6 mmol, 1.1 equiv.) of sodium nitrite were added portion wise. The resulting orange suspension was stirred for an additional 30 min at 10 °C. Subsequently, the reaction mixture was filtered, and the filtrate was slowly added with stirring to a solution of 200 mL ice water and 12.9 g (77.6 mmol, 1.1 equiv.) of KI, which had been cooled to -10 °C. The reaction mixture was stirred overnight at room temperature. The reaction suspension was neutralized with 200 mL of 5 M sodium hydroxide and extracted three times with 150 mL of ethyl acetate. The combined organic phases were washed three times with 80 mL of saturated sodium bisulfite solution, then three times with 100 mL of a 1:1 mixture (v/v) of saturated NaCl solution and distilled water and dried over sodium sulfate. The solvent was then removed under reduced pressure. Yield: 14.0 g (55.0 mmol, 78%) of a brownish solid.

¹**H NMR** (400.1 MHz, CD₂Cl₂, 295 K): δ = 7.52 (d, 1 H, ³*J* = 7.8 Hz, Ar-*H*). 8.12 (dd, 1 H, ³*J* = 8.2 Hz, ⁵*J* = 1.6 Hz, Ar-*H*), 8.18 (d, 1 H, ⁴*J* = 1.6 Hz, Ar-*H*) ppm.

The obtained data is in agreement with the literature.⁵



Compound 5 was synthesised following a literature procedure.⁶

Under nitrogen atmosphere, 2.00 g (7.87 mmol, 1.0 equiv.) of **4** and 2.40 g (9.45 mmol, 1.2 equiv.) of B_2Pin_2 were dissolved in 30 mL of dry toluene and degassed for 30 minutes. Subsequently, 3.81 g (27.6 mmol, 3.5 equiv.) of KOAc was added and the reaction mixture was degassed for another 30 minutes. Then, 455 mg (394 µmol, 0.05 equiv.) of Pd(PPh₃)₄ was added, and the reaction mixture was heated to reflux for 16 hours. The solvent was removed under reduced pressure, the crude product was dissolved in 100 mL of diethyl ether and washed three times with 30 mL of distilled water and then three times with 30 mL of saturated NaCl solution. The organic phase was dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude product was used without further purification.

Yield: 1.70 g (6.68 mmol, 84%) of an orange oil.

¹**H NMR** (400.1 MHz, CDCl₃, 295 K): δ = 1.35 (s, 12 H, CH₃). 7.79 (dd, 1 H, ³J = 7.8 Hz, ⁵J = 0.6 Hz, Ar-*H*), 8.10 (dd, 1 H, ³J = 7.8 Hz, ⁴J = 1.1 Hz, Ar-*H*), 8.20 (dd, 1 H, ⁴J = 1.1 Hz, ⁵J = 0.6 Hz, Ar-*H*) ppm.

The obtained data is in agreement with the literature.⁶

4-{7-[4-(Nona-1,8-dien-5-yloxy)phenyl]benzo[b]benzo[4,5]thieno[2,3-d]thiophen-2yl}phthalonitrile **19**



Under nitrogen atmosphere, 927 mg (1.74 mmol, 1.0 equiv.) of **18** was dissolved in 50 mL of THF and degassed for 30 minutes. Then, 840 mg (6.08 mmol, 3.5 equiv.) of potassium carbonate was dissolved in 3 mL of distilled water and added to the reaction solution, and the solution was degassed for another 30 minutes (Solution 1). Meanwhile, 662 mg (2.61 mmol, 1.5 equiv.) of **5** was dissolved in dry THF and degassed for 30 minutes (Solution 2). Solution 1 was then heated to 77 °C, and Solution 2 was added dropwise over a period of 30 minutes. The reaction mixture was heated to reflux for 16 hours and then treated with saturated NaCl solution. The phases were separated, and the aqueous phase was extracted three times with 30 mL of DCM. The combined organic phases were washed twice with 20 mL of distilled water, dried over sodium sulfate, and then the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, DCM:Cy = 1:2 => DCM:Cy = 7:3 (v/v)) and by precipitation from DCM with MeOH.

Melting point: > 300 °C

Yield: 705 mg (1.21 mmol, 70%) of a yellow solid.

¹**H NMR** (400.1 MHz, CDCl₃, 295 K): $\delta = 1.72 - 1.90$ (m, 4 H, -CH₂-), 2.13 - 2.30 (m, 4 H, -CH₂-), 4.37 (quin., 1 H, ³J = 5.9 Hz, CH), 4.98 (dddd, ²J = 10.2 Hz, ³J = 2.0 H, ⁴J = 1.4 Hz, ⁴J = 1.4 Hz, 2 H, =CH₂), 5.06 (dddd, ²J = 17.2 Hz, ³J = 3.6 Hz, ⁴J = 1.6 Hz,

 ${}^{4}J$ = 1.6 Hz, 2 H, =CH₂), 5.84 (dddd, ${}^{3}J$ = 16.9 Hz, ${}^{3}J$ = 10.1 Hz, ${}^{3}J$ = 6.7 Hz, ${}^{3}J$ = 6.7 Hz, 2 H, CH), 7.00 (AA'BB', 2 H, Ar-*H*), 7.60 (AA'BB', 2 H, Ar-*H*), 7.64 (dd, 1 H, ${}^{3}J$ = 8.4 Hz, ${}^{4}J$ = 1.7 Hz, Ar-*H*), 7.68 (dd, 1 H, ${}^{3}J$ = 8.3 Hz, ${}^{4}J$ = 1.6 Hz, Ar-*H*), 7.86 (dd, 1 H, ${}^{3}J$ = 8.2 Hz, ${}^{4}J$ = 0.4 Hz, Ar-*H*), 7.92 (dd, 1 H, ${}^{3}J$ = 8.3 Hz, ${}^{5}J$ = 0.5 Hz, Ar-*H*), 7.97 (dd, 1 H, ${}^{3}J$ = 8.4 Hz, ${}^{5}J$ = 0.6 Hz, Ar-*H*), 7.99 (dd, 1 H, ${}^{3}J$ = 8.2 Hz, ${}^{4}J$ = 1.9 Hz, Ar-*H*), 8.08 (dd, 1 H, ${}^{4}J$ = 1.6 Hz, ${}^{5}J$ = 0.5 Hz, Ar-*H*), 8.09 (dd, 1 H, ${}^{4}J$ = 1.9 Hz, ${}^{5}J$ = 0.4 Hz, Ar-*H*), 8.10 (dd, 1 H, ${}^{4}J$ = 1.7 Hz, ${}^{5}J$ = 0.6 Hz, Ar-*H*) ppm.

¹³**C NMR** (100.0 MHz, CDCl₃, 295 K): $\delta = 29.7$ (C_s), 33.3 (C_s), 76.7 (C_p), 114.0 (C), 115.2 (C_t), 115.5 (C_q), 116.5 (C_t), 116.7 (C_q), 121.9 (C_t), 122.1 (C_t), 122.5 (C), 122.8 (C_t), 124.1 (C_t), 124.5 (C_t), 128.5 (C_t), 131.4 (C_q), 131.5 (C_t), 132.0 (C_t), 132.8 (C_q), 132.9 (C_q), 133.4 (C_q), 134.1 (C_t), 134.2 (C_q), 135.4 (C_q), 138.2 (C), 138.9 (C_q), 143.5 (C_q), 143.6 (C_q), 146.0 (C_q), 158.6 (C_q) ppm.

FT-IR 21 (Film): v = 2958, 2929, 2861, 2359, 2341, 1606, 1511, 1468, 1243, 1177, 822, 669, 566, 541, 519 cm⁻¹.

MALDI-HRMS, m/z (%): calculated: 580.1643 ([M⁺⁻], 100), found: 580.1638 ([M⁺⁻]).

4-[7-(4-{[1,9-Bis(1,1,3,3,3-Pentamethyldisiloxaneyl)nonan-5yl]oxy}phenyl)benzo[b]benzo[4,5]thieno[2,3-d]thiophen-2-yl]phthalonitrile **2**



Compound 2 was prepared analogously to the literature.⁷

Under nitrogen atmosphere, 80.0 mg (138 µmol, 1.0 equiv.) of **19** were dissolved in dry toluene, followed by the addition of 123 mg (827 µmol, 6.0 equiv.) 1,1,1,3,3-pentamethyldisiloxane and three droplets of Karstedt catalyst. The reaction mixture was heated at 80 °C for two hours. After completion of the reaction, the solvent was removed under reduced pressure, and the crude product was purified via column chromatography (silica gel, DCM:Cy = 7:3 (*v*/*v*)). The product was then dissolved in a small amount of DCM, precipitated from MeOH, and finally purified by GPC.

Yield: 80.6 mg (91.9 µmol, 67%) of a yellow solid.

Melting point: 177.7 °C

¹**H NMR** (400.1 MHz, CDCl₃, 295 K): $\delta = 0.04$ (s, 12 H, CH₃), 0.06 (s, 18 H, CH₃), 0.50 – 0.56 (m, 4 H, -CH₂-), 1.31 – 1.40 (m, 4 H, -CH₂-), 1.40 – 1.51 (m, 4 H, -CH₂-), 1.62 – 1.77 (m, 4 H, -CH₂-), 4.29 (quin., 1 H, ³J = 5.9 Hz, CH), 7.00 (AA'BB', 2 H, Ar-H), 7.60 (AA'BB', 2 H, Ar-H), 7.64 (dd, 1 H, ³J = 8.4 Hz, ⁴J = 1.7 Hz, Ar-H), 7.68 (dd, 1 H, ³J = 8.3 Hz, ⁴J = 1.6 Hz, Ar-H), 7.86 (dd, 1 H, ³J = 8.2 Hz, ⁴J = 0.4 Hz, Ar-H), 7.92 (dd, 1 H, ³J = 8.3 Hz, ⁵J = 0.5 Hz, Ar-H), 7.97 (dd, 1 H, ³J = 8.4 Hz, ⁵J = 0.6 Hz, Ar-H), 7.99

(dd, 1 H, ${}^{3}J$ = 8.2 Hz, ${}^{4}J$ = 1.9 Hz, Ar-*H*), 8.08 (dd, 1 H, ${}^{4}J$ = 1.6 Hz, ${}^{5}J$ = 0.5 Hz, Ar-*H*), 8.09 (dd, 1 H, ${}^{4}J$ = 1.9 Hz, ${}^{5}J$ = 0.4 Hz, Ar-*H*), 8.10 (dd, 1 H, ${}^{4}J$ = 1.7 Hz, ${}^{5}J$ = 0.6 Hz, Ar-*H*) ppm.

¹³**C** NMR (100.0 MHz, CDCl₃, 295 K): $\delta = 0.5$ (C_p), 2.1 (C_p), 18.6 (C_s), 23.6 (C_s), 29.3 (C_s), 33.9 (C_s), 78.2 (C_p), 114.0 (C), 115.5 (C_q), 116.5 (C_t), 116.7 (C_q), 121.9 (C_t), 122.1 (C_t), 122.5 (C_t), 122.8 (C_t), 124.1 (C_t), 124.5 (C_t), 128.5 (C_t), 131.4 (C_q), 131.5 (C_t), 132.0 (C_t), 132.8 (C_q), 132.9 (C_q), 133.4 (C_q), 134.1 (C_t), 134.2 (C_q), 135.4 (C_q), 138.9 (C_q), 143.5 (C_q), 143.6 (C_q), 146.0 (C_q), 158.6 (C_q) ppm.

MALDI-HRMS, m/z (%): calculated: 876.3122 ([M⁺⁻], 100), found: 876.3117 ([M⁺⁻]).

FT-IR (Film): *v* = 3043, 2953, 2927, 2854, 2797, 2233, 1592, 1512, 1457, 1409, 1387, 1344, 1294, 1250, 1177, 1044, 968, 836, 801, 752, 625, 582, 556, 526 cm⁻¹.

UV-Vis (CHCl₃): λ_{max} (ϵ / 10³) = 277 (40.3), 351 (36.7), 382 (32.7) nm.

Elemental analysis: calculated: C, 64.33; H, 6.89; N, 3.19; S, 7.31, found: C, 64.20; H 6.96; N, 3.16; S, 7.30.

2-[4-(Nona-1,8-dien-5-yloxy)phenyl]-7-phenylbenzo[b]benzo[4,5]thieno[2,3-d]thiophene **20**



Under nitrogen atmosphere, 800 mg (1.50 mmol, 1.0 equiv.) of **18** was dissolved in 50 mL of THF and degassed for 30 minutes. Then, 725 mg (5.25 mmol, 3.5 equiv.) of potassium carbonate was dissolved in 3 mL of distilled water and added to the reaction solution, and the solution was degassed for another 30 minutes (Solution 1). Meanwhile, 274 mg (2.25 mmol, 1.5 equiv.) of phenylboronic acid was dissolved in dry THF and degassed for 30 minutes (Solution 2). Solution 1 was then heated to 77 °C, and Solution 2 was added dropwise over a period of 30 minutes. The reaction mixture was heated to reflux for 16 hours and then treated with saturated NaCl solution. The phases were separated, and the aqueous phase was extracted three times with 30 mL of DCM. The combined organic phases were washed twice with 20 mL of distilled water, dried over sodium sulfate, and then the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, DCM:Cy = 1:2 => DCM:Cy = 7:3 (*v*/*v*)) and by precipitation from DCM with MeOH.

Yield: 212 mg (399 µmol, 27%) of a colourless solid.

Melting point: 285.6 °C

¹**H NMR** (400.1 MHz, CDCl₃, 295 K): 1.68 – 1.89 (m, 4 H, CH_2), 2.14 – 2.28 (m, 4 H, CH_2), 4.37 (quin., ${}^{3}J$ = 5.9 Hz, 1 H, CH), 5.00 (dddd, ${}^{2}J$ = 10.2 Hz, ${}^{3}J$ = 2.0 Hz, ${}^{4}J$ = 1.4 Hz, ${}^{4}J$ = 1.4 Hz, 2 H, = CH_2), 5.04 (dddd, ${}^{2}J$ = 10.2 Hz, ${}^{3}J$ = 2.0 Hz, ${}^{4}J$ = 1.4 Hz, 2 H, = CH_2), 5.05 (dddd, ${}^{3}J$ = 16.9 Hz, ${}^{3}J$ = 10.1 Hz, ${}^{3}J$ = 6.7 Hz,

 ${}^{3}J = 6.7$ Hz, 4 H, C*H*), 7.01 (AA'BB', 2 H, H-7, H-7', Ar-*H*), 7.39 (tt, ${}^{3}J = 7.3$ Hz, ${}^{4}J = 1.2$ Hz, 1 H, Ar-*H*), 7.48 – 7.51 (m, 2 H, Ar-*H*), 7.61 (AA'BB', 2 H, Ar-*H*), 7.66 (dd, ${}^{3}J = 8.3$ Hz, ${}^{4}J = 1.6$ Hz, 1 H, Ar-*H*), 7.70 (dd, ${}^{3}J = 8.3$ Hz, ${}^{4}J = 1.6$ Hz, 1 H, Ar-*H*), 7.70 (dd, ${}^{3}J = 8.3$ Hz, ${}^{4}J = 1.6$ Hz, 1 H, Ar-*H*), 7.70 (td, ${}^{3}J = 7.3$ Hz, ${}^{4}J = 1.2$ Hz, 2 H, Ar-*H*), 7.92 (dd, ${}^{3}J = 8.3$ Hz, ${}^{5}J = 0.5$ Hz, 1 H, Ar-*H*), 7.94 (dd, ${}^{3}J = 8.3$ Hz, ${}^{5}J = 0.5$ Hz, 1 H, Ar-*H*), 8.08 (dd, ${}^{4}J = 1.6$ Hz, ${}^{5}J = 0.5$ Hz, 1 H, Ar-*H*), 8.13 (dd, ${}^{4}J = 1.6$ Hz, ${}^{5}J = 0.5$ Hz, 1 H, Ar-*H*) ppm.

¹³C NMR (100 MHz, CDCl₃, 295 K): 29.7 (C_s), 33.3 (C_s), 76.7 (C_t), 115.2 (C_s), 116.4 (C_t), 121.9 (C_t), 121.9 (C_t), 121.9 (C_t), 122.5 (C_t), 124.3 (C_t), 124.7 (C_t), 127.5 (C_t), 127.6 (C_t, C-27), 128.5 (C_t), 129.1 (C_t), 131.8 (C_q), 132.4 (C_q), 133.2 (C_q), 133.3 (C_q), 133.7 (C_q), 138.2 (C_t), 138.3 (C_q), 138.4 (C_q), 140.8 (C_q), 143.2 (C_q), 143.3 (C_q), 158.5 (C_t) ppm.

MALDI-HRMS, m/z (%): calculated: 530.1733 ([M⁺⁻], 100), found: 530.1742 ([M⁺⁻]).

FT-IR (Film): *v* = 3060, 2922, 2852, 2360, 2341, 1638, 1509, 1456, 1237, 1177, 907, 812, 759, 690, 571, 537, 515 cm⁻¹.

3,3'-{5-[4-(7-Phenylbenzo[b]benzo[4,5]thieno[2,3-d]thiophen-2-yl)phenoxy]nonane-1,9-diyl}bis(1,1,1,3,3-pentamethyldisiloxane) **1**



Under nitrogen atmosphere, 143 mg (269 µmol, 1.0 Äq.) **20** and 399 mg (3.69 mmol, 10 Äq.) 1,1,1,3,3-pentamethyldisiloxane were dissolved in 5 mL dry toluene, five drops of Karstedt catalyst were added, and the solution was heated to 80 °C for 4 h. The solvent was then removed by distillation under reduced pressure and the crude product was purified by column chromatography (silica gel, Cy:DCM 4:1). The isomer formed in this reaction was finally separated by GPC.

Yield: 61.2 mg (74.0 µmol, 27 %) of a colourless solid.

Melting point: 140.5 °C

¹**H NMR** (400.1 MHz, CDCl₃, 295 K): 0.06 (s, 12 H, CH₃), 0.08 (s, 18 H, CH₃), 0.53 – 0.57 (m, 4 H, CH₂), 1.33 – 1.54 (m, 8 H, CH₂), 1.63 – 1.78 (m, 4 H, CH₂), 4.31 (quin., ${}^{3}J = 5.9$ Hz, 1 H, CH), 7.01 (AA'BB', 2 H, Ar-H), 7.39 (tt, ${}^{3}J = 7.3$ Hz, ${}^{4}J = 1.2$ Hz, 1 H, Ar-H), 7.48 – 7.51 (m, 2 H, Ar-H), 7.61 (AA'BB', 2 H, Ar-H), 7.66 (dd, ${}^{3}J = 8.3$ Hz, ${}^{4}J = 1.6$ Hz, 1 H, Ar-H), 7.70 (dd, ${}^{3}J = 8.3$ Hz, ${}^{4}J = 1.6$ Hz, 1 H, Ar-H), 7.70 (dd, ${}^{3}J = 8.3$ Hz, ${}^{4}J = 1.6$ Hz, 1 H, Ar-H), 7.70 (dd, ${}^{3}J = 8.3$ Hz, ${}^{5}J = 0.5$ Hz, 1 H, Ar-H), 7.93 (dd, ${}^{3}J = 8.3$ Hz, ${}^{5}J = 0.5$ Hz, 1 H, Ar-H), 7.93 (dd, ${}^{3}J = 8.3$ Hz, ${}^{5}J = 0.5$ Hz, 1 H, Ar-H), 7.93 (dd, ${}^{3}J = 8.3$ Hz, ${}^{5}J = 0.5$ Hz, 1 H, Ar-H), 8.08 (dd, ${}^{4}J = 1.6$ Hz, ${}^{5}J = 0.5$ Hz, 1 H, Ar-H), 8.10 (dd, ${}^{4}J = 1.6$ Hz, ${}^{5}J = 0.5$ Hz, 1 H, Ar-H) ppm.

¹³**C** NMR (100 MHz, CDCl₃, 295 K): 0.5 (C_p), 2.2 (C_p), 18.5 (C_s), 23.6 (C_s), 29.3 (C_s), 33.9 (C_s), 78.3 (C_t), 116.3 (C_t), 121.8 (C_t), 121.8 (C_t), 121.8 (C_t), 122.5 (C_t), 124.3 (C_t), 124.6 (C_t), 127.5 (C_t), 127.6 (C_t), 128.5 (C_t), 129.1 (C_t), 131.8 (C_q), 132.4 (C_q), 132.9 (C_q), 133.2 (C_q), 133.7 (C_q), 138.4 (C_q), 138.4 (C_q), 140.8 (C_q), 143.2 (C_q), 143.3 (C_q), 169.7 (C_q) ppm.

MALDI-HRMS, m/z (%): calculated: 826.3212 ([M⁺⁻], 100), found: 826.3218 ([M⁺⁻]).

FT-IR (Film): *v* = 2979, 2926, 2359, 2341, 1603, 1509, 1456, 1239, 1177, 950, 812, 758, 690, 570, 536, 516 cm⁻¹.

UV-Vis (CHCl₃): λ_{max} (ϵ / 10³) = 279 (25.8), 340 (51.9), 356 (45.4) nm.

Elemental analysis: calculated: C, 65.32; H, 7.55; S, 7.75, found: C, 64.92; H 7.47; S, 7.64.

3. NMR spectra



Figure S2: ¹³C NMR (100 MHz, CDCl₃, 295 K) of **8**.



Figure S3: ¹H NMR spectrum (400.1 MHz, CD_2CI_2 , 295 K) of **12**.















Figure S12: ¹³C NMR (100 MHz, CDCl₃, 295 K) of **16 + 17**.



Figure S13: ¹H NMR spectrum (400.1 MHz, CDCl₃, 295 K) of **18**.







Figure S17: ¹H NMR spectrum (400.1 MHz, CDCl₃, 295 K) of **2**.





Figure S19: ¹H NMR spectrum (400.1 MHz, CDCl₃, 295 K) of **20**.



Figure S20: ¹³C NMR (100 MHz, CDCl₃, 295 K) of **20**.



Figure S21: ¹H NMR spectrum (400.1 MHz, CDCI₃, 295 K) of $\mathbf{1}$.



4. IR Spectra



Figure S23: FT-IR spectrum of 2.



Figure S24: FT-IR spectrum of 1.

5. HRMS-MALDI spectra



Figure S25: HRMS spectrum of 1.



Figure S26: HRMS spectrum of 2.

6. Photophysical studies

The correction of the emission spectra was done by dividing the spectra by the concentration of the solutions and by the absorption coefficients of the molecules at the excitation wavelength. This could be done, because both measurements were performed on the same day with the same recording parameters. It was divided by the absorption coefficients to correct for the different absorption of the molecules at the excitation wavelength. With this method we were able to make qualitative statements about the fluorescence ability of **1** and **2** and compare them, highlighting the donor-acceptor structure of **2**.



Figure S27: Excitation measurements of **1** (A) and **2** (B). A: Measured in $CHCl_3$ at a concentration of 1.08 10⁻⁶ mol L⁻¹ at a fixed emission wavelength of 410 nm. B: Measured in $CHCl_3$ at a concentration of 1.13 10⁻⁶ mol L⁻¹ at a fixed emission wavelength of 530 nm.

Additionally, excitation spectra of both compounds were measured and are depicted in Figure S27. Both excitation spectra overlap perfectly with the absorption spectra and thus show that it does not matter which wavelength is used for irradiation and that fluorescence only occurs from the lowest S1 state. In addition, it proves the absence of other fluorescent species and therefore the purity of the materials.



Figure S28: Overlap of the different MOs of **1** (A and B) and **2** (C and D) when the mesogens are arranged antiparallel.

8. Calculation of transition dipole moments **1** and **2**

The absorption spectra of **1** and **2** were each fitted with the program *Origin* to obtain the individual signals. The *Gauss-amp* function was used to allow vertical stretching of the bell-shaped Gauss function, which represents the nature of the signals best. The determined areas of the signals are listed in table 1.

 $\begin{array}{c|c} \mbox{Table 1: Areas of the individual Peaks of the $S_0 \rightarrow S_1$ transition.} \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & &$

1	362.6 / 21.416	339.1 / 49.664	
2	384.4 / 38.265	346.3 / 27.343	327.3 / 9.7627

The areas of the absorption bands of **1** and **2** were added up and the results were subsequently squared giving the following values (Table 2)

Table 2: Square of sum of the absorption band areas of **1** and **2**:

	Square of the area [a.u.]					
1	5052.4					
2	5679.1					

The ratio of the squared absorption band areas of **2** and **1** (experimental ratio of the transition dipole moments) and the corresponding ratio of the theoretical obtained transition dipole moment were calculated. The obtained ratios were 1.12 for the experimental derivation and 1.09 for the calculated transition dipole moments.

9. Calculation of tilt-angle in SmC mesophase of **1**

It was assumed that in the double layer the aromatic building blocks that have a length L_{Ar} of 19.8 Å are intercalated completely, while the alkyl chains and siloxanes do not interfere, and have lengths L_{Alk} of 4.6 Å and L_{Si} of 6.4 Å.





Figure S29: Schematic illustration of a non-tilted double layer of **1** with the corresponding values.

In this assumption (Figure S29), the non-tilted (SmA) double layer has a theoretical overall height H_{SmA} of:

$$L_{Ar} + 2 \times L_{Alk} + 2 \times L_{Si} = H_{SmA}$$
⁽¹⁾

$$19.8 \text{ Å} + 2 \times 4.6 \text{ Å} + 2 \times 6.4 \text{ Å} = 41.8 \text{ Å}$$
(2)

This is for a non-tilted double layer, but the X-ray diffraction measurements showed that it is a tilted SmC mesophase and no SmA phase. With geometrical considerations (Figure S30), it is now possible to determine the theoretically expected tilt angle α .



Figure S30: Geometrically simplified representation of the tilted SmC mesophase of 1.

The tilted SmC mesophase can be described as a right triangle with the tilt angle α , the height of the tilted aromatic and alkyl parts H_{Tilt}, and the hypothenuse. H_{Tilt} can be calculated by subtracting the non-tilted siloxane moieties L_{Si} from the height of the SmC mesophase H_{SmC} that was derived from the SAXS measurements, while the hypothenuse is the length of the aromatic unit and the alkyl chains:

$$H_{\text{Tilt}} = H_{\text{SmC}} - 2 \times L_{\text{Si}} = 38.3 \text{ Å} - 2 \times 6.4 \text{ Å} = 25.5 \text{ Å}$$
(3)

$$H_{Ar-Alk} = L_{Ar} + 2 \times L_{Alk} = 19.8 \text{ Å} + 2 \times 4.6 \text{ Å} = 29.0 \text{ Å}$$
(4)

With this information, it is possible to calculate the tilt angle α by:

$$\alpha = \arccos \left(H_{\text{Tilt}} / H_{\text{Ar-Alk}} \right)$$
 (5)

$$\alpha = \arccos \left(25.5 \text{ Å} / 29.0 \text{ Å} \right) = 28.4^{\circ}$$
 (6)

Therefore, the theoretically expected tilt angle α is 28.4°. Only if a folding of the aliphatic area is assumed and the dimer length is further reduced by 2 x 0.75 Å a tilt of 22° is obtained.

10. Density Measurements by the Buoyancy Method

The density measurements of compounds **1** and **2** were carried out by the buoyancy method in mixtures of deionised water and methanol. The measurements were performed in accordance with the methods outlined in the literature.⁸ When the fibre floated in the water/methanol mixture the density of this mixture was then determined with a pycnometer. The resulting value is a minimum density for the material, since gas inclusions cannot be completely excluded.

11. Modelling

The SmA double layer of **1** was modelled based on the obtained X-ray data with the help of the computer programme *BIOVIA Materials Studio 2017 R2*. The double layer was simulated in the P1 unit cell, the geometry optimisation was employed with the module "Forcite Plus (2017R2)" with the force S 29 field "COMPASSII" and the atom based summation method. The Ewald summation method was then applied until the non-covalent interactions (electrostatic and van der Waals interactions) were large and negative and energy convergence was achieved.

12. X-ray data of compounds **1** and **2**

SmA, 126 °C (WAXS)		<i>c</i> = 38.3 Å			
h	k	I	d _{exp} [Å]	d _{calc} [Å]	Δ [Å]
0	0	1	38.3	38.3	0.01
0	0	2	19.2	19.2	0.02
Halo (siloxanes)			6.3	-	-
Halo (aliphatic)			4.9	-	-

Table 3: Experimental and calculated d-values of **1** at 126 °C:

Table 4: Experimental and calculated d-values of 1 at 102 °C:

SmA, 102	°C (WAXS)	<i>c</i> = 38.3 Å			
h	k	I	d _{exp} [Å]	d _{calc} [Å]	Δ [Å]

0	0	1	38.6	38.6	0.01
0	0	2	19.3	19.3	0.01
	Halo (siloxanes)		6.2	-	-
	Halo (aliphatic)		4.7	-	-

Table 5: Experimental and calculated d-values of 2 at 151 °C:

SmA, 151 °C (WAXS)		<i>c</i> = 38.3 Å			
h	k	I	d _{exp} [Å]	d _{calc} [Å]	Δ [Å]
0	0	1	52.7	52.7	0.01
	Halo		6.4	-	-

13. TOF measurements

Time-of-Flight (ToF) measurements:

The charge carrier transport of the asymmetric BTBT mesogens has been analysed using the time-of-flight (ToF) technique.⁹⁻¹¹ First, the samples were filled in 9.2 µm thick ITO cells (MUT, Poland) exhibiting planar alignment. Subsequently, the cells were sealed with NOA65 UV adhesive (Norland Products) to prevent any leakage of samples in the isotropic phase. The asymmetric BTBT mesogen-filled cells were exposed by a 355 nm pulsed Nd:YAG laser. A suitable positive (for holes) or negative (for electrons) bias voltage was applied using a KEITHLEY 6487 to observe the transient photocurrent curves for holes and electrons. The transient photocurrent curves for holes and electrons. The transient photocurrent estimating the transit time, the hole and electron mobilities were calculated using an equation:

$$\mu_{h,e}(T) = \frac{d^2}{V\tau} \tag{7}$$

Where, d is the thickness of cell, V is the applied positive or negative bias voltage and τ is the transit time for holes and electrons. During the measurements, the temperature was controlled with a precision of ±0.1 °C by using Linkam LTS 350 hot plate connected to a temperature controller Linkam TMS 94.

Data evaluation

General procedure:

The photocurrent was plotted versus the time double logarithmically (see Figures S31 – S34). The plateau and the decrease of the current in the graph were fitted linearly (blue line). The intersection of the two linear fits corresponds to the average transit time τ of the charge carriers and is used for the subsequent calculation of the charge carrier mobility μ according to equation (7).^[12]



Figure S31: Double logarithmic plot of the ToF measurement of **1** at 80 °C with an applied voltage of 35 V.



Figure S32: Double logarithmic plot of the electron ToF measurement of **1** at 100 $^{\circ}$ C with an applied voltage of 35 V.



Figure S33: Double logarithmic plot of the electron ToF measurement of $\mathbf{2}$ at 30 °C with an applied voltage of 190 V.



Figure S34: Double logarithmic plot of the electron ToF measurement of $\mathbf{2}$ at 150 °C with an applied voltage of 12 V.

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