Selective Even-Numbered Bromination of Triptycene Tris(thiadiazoles)

-Supporting Information-

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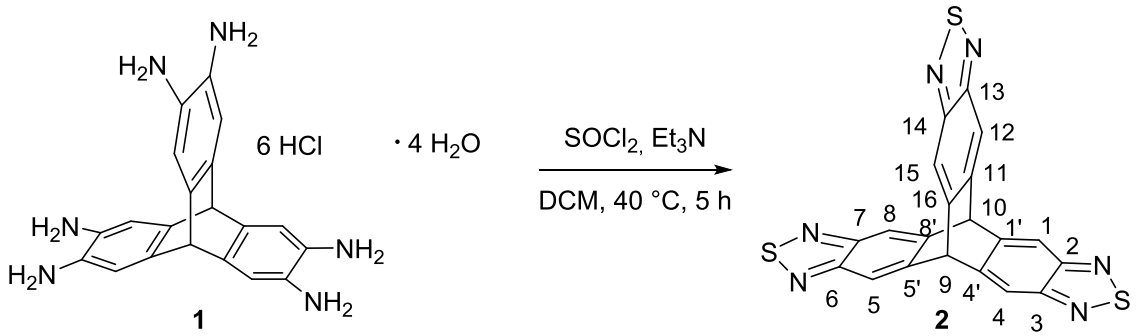
1. General Remarks

All reagents and solvents were obtained from Fisher Scientific, Alfa Aesar, Sigma-Aldrich or VWR and were used without further purification unless otherwise noted. For thin layer chromatography Silica gel 60 F_{254} plates from Merck were used and examined under UV-light irradiation (254 nm and 365 nm). Flash column chromatography was performed on silica gel from Sigma-Aldrich (particle size: 0.04-0.063 mm) using petroleum ether, dichloromethane and/or ethyl acetate. Ultra-Performance Liquid Chromatography (UPLC) was performed on a Waters UPLC-SQD2 machine connected to a single quadrupole mass spectrometer with an APCI (Atmospheric Pressure Chemical Ionization) source. A BEH-C8, 2.1/50 mm column with a gradient of 30/70 – 10/90 H_2O/MeCN and a flow of 0.6 mL/min was used. High-Performance Liquid Chromatography (HPLC) was performed on an Agilent Technologies 1200 machine with a Macherey-Nagel VP 250/21 Nucleodur C8 Gravity, 5 µm or a Macherey-Nagel VP 250/21 Nucleosil column. Melting points (not corrected) were measured

with a Büchi Melting Point B-545. IR-Spectra were recorded on a Ge ATR crystal with a Bruker Lumos spectrometer. NMR spectra were taken on a Bruker DRX 400 (400 MHz), Bruker DRX 500 (500 MHz), Bruker Avance 300 (300 MHz) and Bruker Avance 500 (500 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of $CHCl_3$ in the corresponding deuterated solvent. HRMS experiments were carried out on a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer solariX (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7.0 T superconducting magnet and interfaced to an Apollo II Dual ESI/MALDI source with DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), CCA (α-cyano-4-hydroxycinnamic acid) or dithranol as matrix. DART experiments were performed on a FT-ICR Apex-Qe mass spectrometer. Absorption spectra were recorded on a Jasco UV-VIS V-660 or Jasco UV-VIS V-670. Emission spectra were recorded on a Jasco FP-6500. Electrochemical data were obtained in THF containing 1 mM experimental compound and 0.1 M Bu_4PF_6, as indicated. 1 mM ferrocene was used as an internal standard. Cyclic voltammagrams were obtained at a scan rate of 0.2 mV/s using a Pt working electrode, a Pt/Ti counter electrode, and a Ag reference electrode. Elemental analysis was performed by the Microanalytical Laboratory of the University of Heidelberg using an Elementar Vario EL machine. Crystal structure analysis was accomplished on Bruker APEX II Quazar or on a Bruker APEX I diffractometer with a molybdenum source ($\lambda(MoK_\alpha)$ = 0.71073 Å). All crystallographic information files (CCDC1022905-CCDC1022908) have been deposited in the Cambridge Crystallographic Data Centre and can be downloaded free of charge via www.ccdc.camac.uk/data_request/cif.

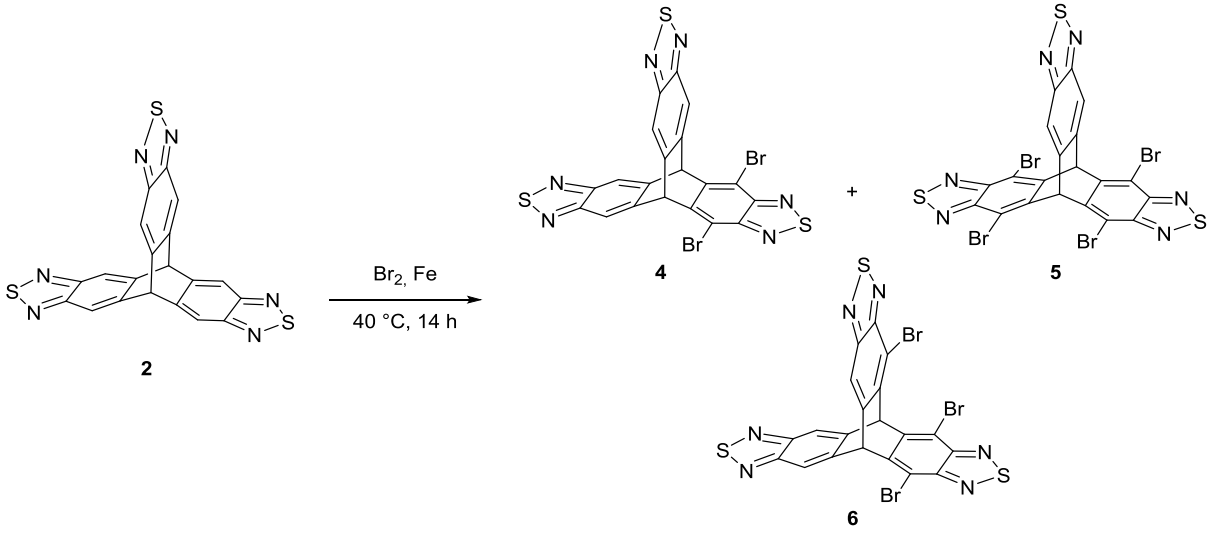
2. Synthesis and Characterization

Triptycene[2,3-*c*:6,7-*c*':13,14-*c*'']tris([1,2,5]thiadiazole) (**2**).



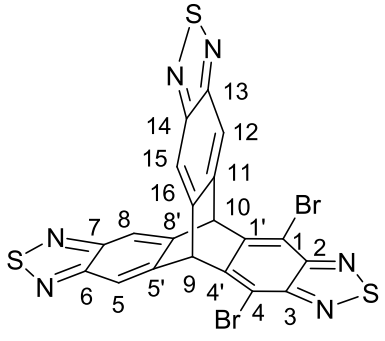
2,3,6,7,14,15-Hexaammoniumtriptycene hexachloride tetrahydrate[S1] **1** (500 mg, 0.790 mmol) was suspended in DCM (abs.) (20 mL) under Ar atmosphere and treated with $SOCl_2$ (0.4 mL, 5.5 mmol). Et_3N (3.0 mL, 22 mmol) was added slowly within 45 min at 0 °C. The suspension was further stirred for 5.5 h at 40 °C. After cooling to room temperature the suspension was poured into H_2O (200 mL) and extracted with DCM (2 x 100 mL). The organic phase was washed with conc. HCl (50 mL), dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography (SiO_2, petroleum ether:ethyl acetate = 9:1, R_f = 0.21) to give 280 mg (83%) of triptycene tristhiadiazole **2** as pale yellow solid with a high degree of purity. By sublimation (300 °C, 1.2 mbar) of **2** (170 mg) 110 mg of crystalline material was obtained with m.p. 363 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09 ppm (s, 6H, Ar-*H*), 5.85 (s, 2H, bridgehead-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.3 ppm (Ar-*C*=N), 142.9 (Ar-*C*), 116.5 (Ar-*C*-H), 53.4 (*C*-9,10). FT-IR (ATR): $\tilde{\nu}$ = 3072 (w) cm^{-1}, 3055 (w), 2979 (w), 2965 (w), 1735 (w), 1639 (w), 1553 (w), 1522 (m), 1472 (w), 1434 (m), 1362 (w), 1274 (w), 1261 (m), 1228 (w), 1200 (m), 1190 (m), 1132 (w), 952 (w), 910 (m), 837 (s), 824 (s), 771 (s), 694 (w), 666 (w), 623 (w). UV/Vis ($CHCl_3$): λ_{max} = 408 nm, 386, 314. UV/Vis ($CHCl_3$): λ_{max} = 335 nm, 322. Fluorescence ($CHCl_3$): λ_{em} (λ_{ex}) = 373 nm (325). CV (THF, NBu_4PF_6): $E_{1/2}^{red1}$ = -1.93 V (Fc). MS (DART): *m/z* = 446.01 $[M+NH_4]^+$, 429.00 $[M+H]^+$. Anal. calcd. for $C_{20}H_8N_6S_3$: C: 56.06, H: 1.88, N: 19.61, found: C: 56.10 , H: 2.05, N: 19.79.

Bromination of 2 with 150 equivalents of Br_2 and 12 equivalents of Fe-powder: 1,4-Dibromotriptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]thiadiazole) (4), 1,4,5-tribromo-triptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]-thiadiazole) (6) 1,4,5,8-tetrabromo-triptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]-thiadiazole) (5).



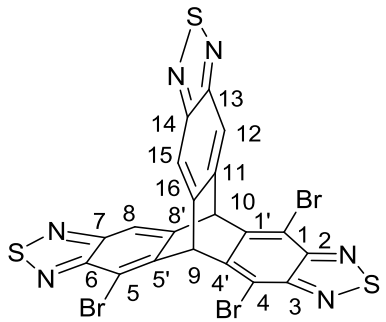
2 4 5 6

A suspension of triptycenetristhiadiazole **2** (50 mg, 0.12 mmol) and Fe powder (78 mg, 1.4 mmol) in Br_2 (0.9 mL, 18 mmol) was heated for 14 h at 40 °C. DCM (100 mL) was added to the reaction mixture and washed with sat. $NaHSO_3$ (aq.) solution (2 x 100 mL). The organic phase was dried over Na_2SO_4 and the solvent evaporated. A first separation by column chromatography (SiO_2, petroleum ether:ethyl acetate = 16:1, (**5**, petroleum ether:DCM = 1:1, R_f = 0.12), (**4**, petroleum ether:DCM = 1:1, R_f = 0.08) was followed by reversed phase HPLC with a gradient of MeCN/H_2O from 75/25 (v/v) to 100/0 (v/v) in 30 min. Traces of hexabromotriptycenetristhiadiazole **3**, pentabromotriptycenetristhiadiazole **7** and monobromo-triptycenetristhiadiazole have not been isolated. Tetrabromotriptycenetristhiadiazole (**5**) (14 mg, 0.018 mmol, 15%), tribromotriptycenetristhiadiazole (**6**) (0.3 mg, 0.4 µmol, 0.3%), dibromotriptycenetristhiadiazole (**4**) (22 mg, 0.037 mmol, 31%) and starting material (**2**) (17 mg, 0.039 mmol, 34%) were obtained as white solids.



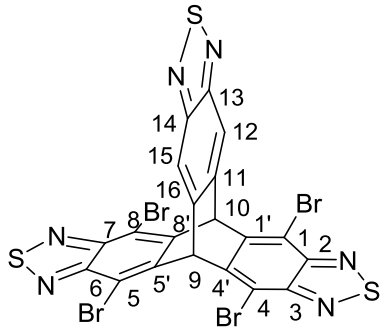
4

The 5th HPLC fraction gave **4** with m.p. 250 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.16 ppm (s, 4H, Ar-*H*), 6.38 (s, 2H, bridgehead-*H*). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.2 ppm (*C*-6,7,13,14), 152.1 (*C*-2,3), 143.1 (*C*-1',4'), 141.5 (*C*-5',8',11,16), 117.2 (Ar-*C*-H), 110.3 (Ar-*C*-Br), 52.8 (*C*-9,10). FT-IR (ATR): $\tilde{\nu}$ = 3063 (w) cm^{-1}, 2923 (w), 2851 (w), 2247 (w), 1736 (w), 1613 (w), 1525 (m), 1493 (m), 1477 (m), 1437 (m), 1265 (s), 1231 (m), 1190 (m), 1101 (w), 906 (m), 853 (s), 827 (s), 805 (m), 778 (m), 729 (s), 665 (w), 648 (w), 630 (w), 615 (w). UV/Vis ($CHCl_3$): λ_{max} = 334 nm. Fluorescence ($CHCl_3$): λ_{em} (λ_{ex}) = 415 nm (324). CV (THF, NBu_4PF_6): $E_{1/2}^{red1}$ = -1.67 V (Fc). MS (EI$^+$): *m/z* = 585.82 (100) [M]$^+$, 586.82 (26) [M+H]$^+$. Anal. calcd. for $C_{20}H_6Br_2N_6S_3 \cdot \frac{5}{6} CH_2Cl_2$: C: 37.00, H: 1.23, N: 12.21, found: C: 37.01 , H: 1.28, N: 12.07.



6

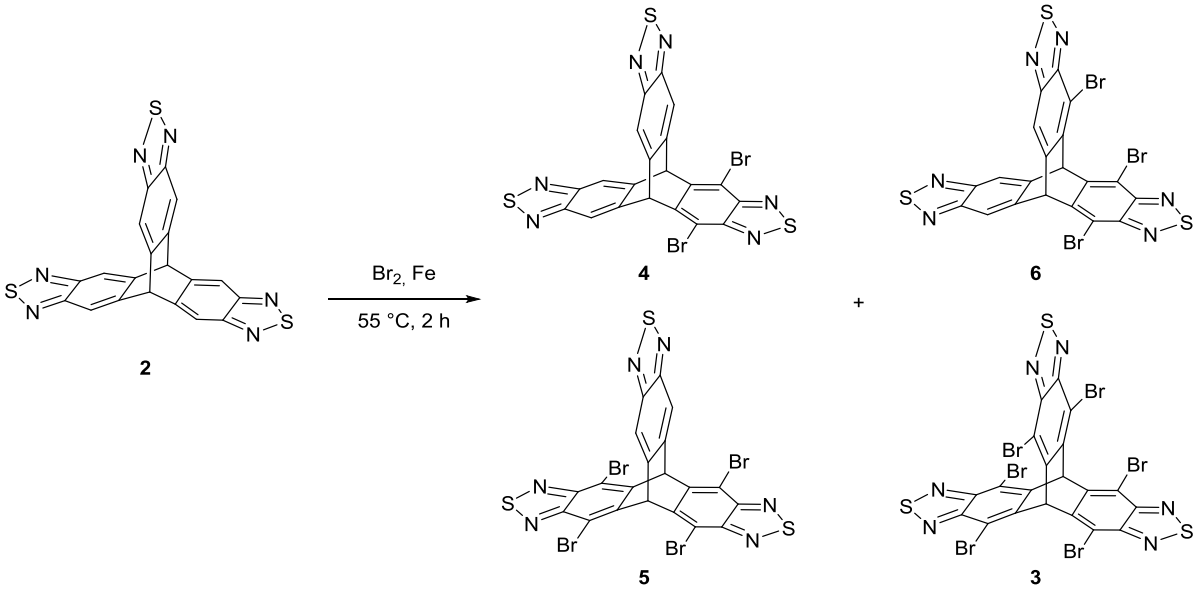
The 4th HPLC fraction gave **6** with ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.26 ppm (s, 1H, Ar-*H*), 8.20 (s, 1H, Ar-*H*), 8.12 (s, 1H, Ar-*H*), 6.96 (s, 1H, bridgehead-*H*), 6.39 (s, 1H, bridgehead-*H*). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 154.3 (*C*-13) ppm, 154.3 (*C*-14), 153.6 (*C*-7), 153.0 (*C*-6), 152.2 (*C*-2), 152.2 (*C*-3), 143.0 (*C*-4'), 142.9 (*C*-1'), 142.5 (*C*-5'), 141.3 (*C*-8'), 141.2 (*C*-16), 140.4 (*C*-11), 117.8 (*C*-12), 117.3 (*C*-15), 116.2 (*C*-8), 111.7 (*C*-4), 110.9 (*C*-1), 110.3 (*C*-5), 53.2 (*C*-10), 52.2 (*C*-9). HRMS (MALDI, DCTB): *m/z* = 834.95925 [2M+DCTB]$^+$, 665.72701 [M]$^+$, 583.80255 [M-Br]$^+$, 499.28792 [M-2Br]$^+$. (calc. for $C_{20}H_5Br_3N_6S_3$: 665.72470).



5

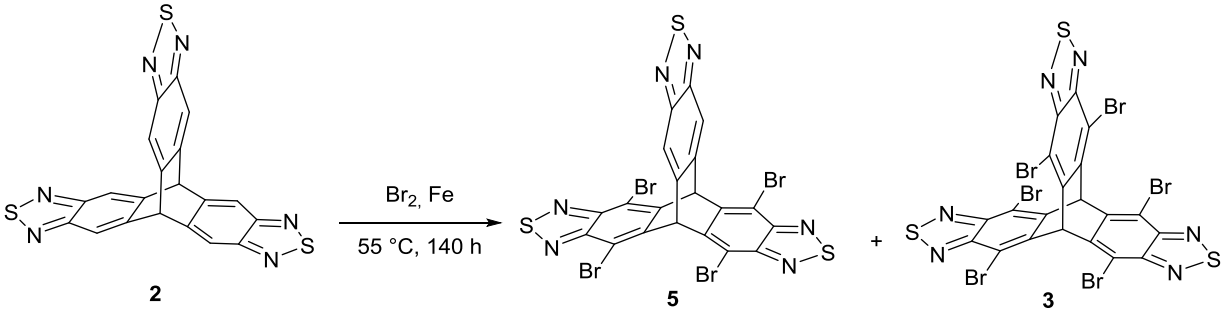
The 3rd HPLC fraction gave **5** with m.p. 284 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.27 ppm (s, 2H, Ar-*H*), 6.99 (s, 2H, bridgehead-*H*). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.2 ppm (*C*-13,14), 152.2 (*C*-2,3,6,7), 142.2 (*C*-1',4',5',8'), 140.1 (*C*-11,16), 117.8 (Ar-*C*-H), 110.8 (Ar-*C*-Br), 52.5 (*C*-9,10). FT-IR (ATR): $\tilde{\nu}$ = 2920 (m) cm^{-1}, 2850 (w), 2247 (w), 1736 (w), 1609 (w), 1528 (w), 1493 (m), 1372 (m), 1299 (w), 1267 (s), 1233 (m), 1190 (w), 1104 (w), 935 (m), 907 (m), 862 (s), 837 (m), 787 (w), 723 (s), 665 (w), 648 (w), 622 (w), 610 (w). UV/Vis ($CHCl_3$): λ_{max} = 333 nm. Fluorescence ($CHCl_3$): λ_{em} (λ_{ex}) = 412 nm (323). CV (THF, NBu_4PF_6): $E_{1/2}^{red1}$ = -1.61 V (Fc). MS (MALDI): *m/z* = 738.41 (100), 743.64 (96) $[M]^-$, 745.63 (65) $[M]^-$, 741.64 (60) $[M]^-$, 663.71 (60) $[M\text{-}Br]^-$, 552.28 (58), 661.71 (58) $[M\text{-}Br]^-$, 739.42 (52), 488.27 (49), 365.13 (35), 665.71 (20). Anal. calcd. for $C_{20}H_4Br_4N_6S_3 \cdot \frac{1}{3}$MeCN: C: 32.76, H: 0.67, N: 11.71, found: C: 33.25 , H: 0.97, N: 11.30.

Bromination of 2 with 34 equivalents of Br_2 and 6 equivalents of Fe-powder: 1,4-Dibromotriptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]thiadiazole) (**4**), **1,4,5-tribromo-triptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]-thiadiazole)** (**6**), **1,4,5,8-tetrabromo-triptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]-thiadiazole)** (**5**), **1,4,5,8,12,15-hexabromo-triptycene[2,3-*c*:6,7-*c*':13,14-*c*"]tris([1,2,5]thiadiazole)** (**3**).

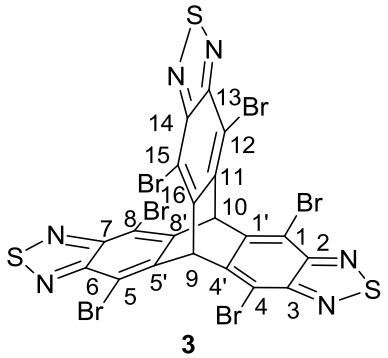


Into a screw capped vial Fe powder (320 mg, 5.6 mmol) and Br_2 (1.6 mL, 32 mmol) was added and stirred for 30 min at room temperature. Triptycenetristhiadiazole **2** (400 mg, 0.94 mmol) was added in one portion and the brown suspension was heated to 55 °C. After 2 h the reaction was cooled to room temperature and poured into sat. $NaHSO_3$ (aq.) solution (200 mL). The aqueous phase was extracted with DCM (2 x 150 mL). The combined organic phase was dried over Na_2SO_4 and the solvent evaporated. Separation by column chromatography (SiO_2, petroleum ether:ethyl acetate = 25:1, (**5**, petroleum ether:DCM = 1:1, R_f = 0.12), (**4**, petroleum ether:DCM = 1:1, R_f = 0.08) was followed by normal phase HPLC ($CHCl_3$/*n*-hexane 40/60 (v/v) for the dibromotriptycenetristhiadiazole (**4**) and $CHCl_3$/*n*-hexane 20/80 (v/v) for the tetrabromotriptycenetristhiadiazole (**5**). Traces of pentabromotriptycene-tristhiadiazole **7** and monobromotriptycenetristhiadiazole have not been isolated. Hexabromo-triptycenetristhiadiazole (**3**) (52 mg, 0.058 mmol, 6%), tetrabromotriptycenetristhiadiazole (**5**) (130 mg, 0.175 mmol, 18%), tribromotriptycenetristhiadiazole (**6**) (18 mg, 0.027 mmol, 2%), dibromotriptycenetristhiadiazole (**4**) (181 mg, 0.309 mmol, 32%) and starting material (**2**) (75 mg, 0.175 mmol, 18%) were obtained as white solids. The analytical data are in accordance to the data described above.

Bromination of 2 with 600 equivalents of Br_2 and 12 equivalents of Fe-powder: 1,4,5,8-tetrabromo-triptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]-thiadiazole) (**5**) and **1,4,5,8,12,15-Hexabromotriptycene[2,3-*c*:6,7-*c*':13,14-*c*"]tris([1,2,5]thiadiazole) (3)**.



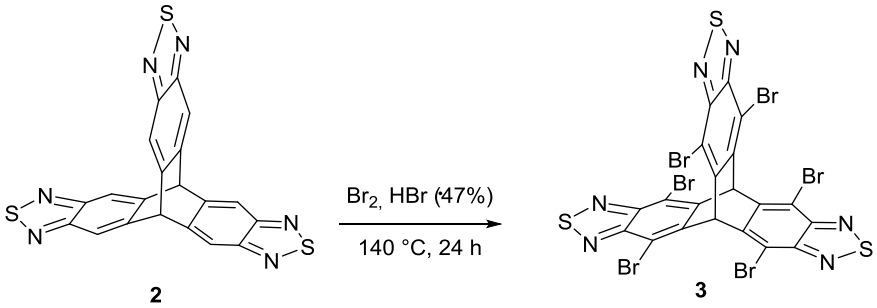
A suspension of triptycenetristhiadiazole (**2**) (100 mg, 0.233 mmol) and Fe powder (160 mg, 2.80 mmol, 12 eq.) in Br_2 (7.0 mL, 140 mmol, 600 eq.) was heated at 55 °C for 140 h. After cooling down to room temperature, DCM (200 mL) was added and the reaction mixture washed with sat. $NaHSO_3$ (aq.) solution (5 x 200 mL). The organic phase was dried over Na_2SO_4 and the solvent evaporated. The crude product was purified by column chromatography (SiO_2, 1st petroleum ether:ethyl acetate = 16:1, 2nd petroleum ether:DCM = 1:1, 3rd petroleum ether:DCM = 1:1) to give 140 mg (67%) of hexabromotriptycenethiadiazole (**3**, petroleum ether:DCM = 1:1, R_f = 0.20) and 15 mg (9%) of tetrabromotriptycenetristhiadiazole (**5**, petroleum ether:DCM = 1:1, R_f = 0.12) as white solid. Traces of tribromotriptycenetristhiadiazole (**6**) and dibromotriptycenetristhiadiazole (**4**) have not been isolated.



M.p. 298 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 ppm (s, 2H, bridgehead-*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 152.4 ppm (Ar-*C*-Br), 141.8 (Ar-*C*=N), 111.4 (Ar-*C*), 52.5 (*C*-9, 10). FT-IR (ATR): $\tilde{\nu}$ = 3017 cm^{-1} (w), 2921 (m), 2851 (w), 2247 (w), 1725 (w), 1616 (w), 1495 (m), 1376 (w), 1299 (w), 1271 (s), 1191 (m), 1108 (m), 974 (m), 946 (m), 974 (m), 946 (m), 906 (m), 867 (s), 839 (m), 725 (m), 648 (w), 628 (w). UV/Vis ($CHCl_3$): λ_{max} = 332 nm. Fluorescence ($CHCl_3$): λ_{em} (λ_{ex}) = 419 nm (322). CV (THF, NBu_4PF_6): $E_{1/2}^{red1}$ = -1.58 V (Fc).

MS (MALDI): *m/z* (%) = 901.45 (100) $[M]^-$, 903.45 (78) $[M]^-$, 899.46 (69), 905.45 (32), 897.46 (24). Anal. calcd. for $C_{20}H_2N_6S_3Br_6$: C: 26.63, H: 0.22, N: 9.32, found: C: 26.61 , H: 0.50, N: 9.12.

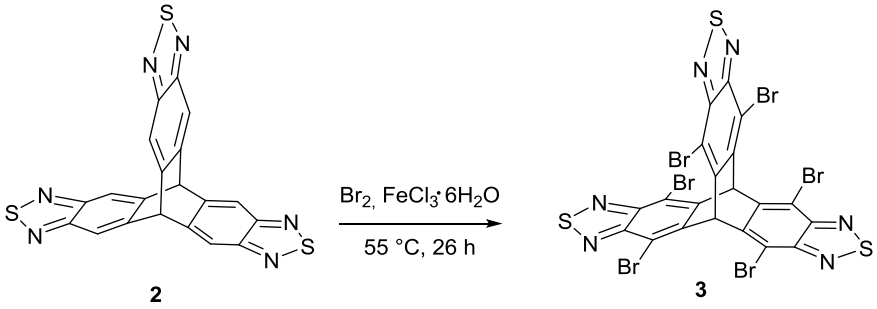
Bromination of 2 with 50 equivalents of Br_2 and HBr: 1,4,5,8,12,15-Hexabromotriptycene[2,3-*c*:6,7-*c*':13,14-*c*"]tris([1,2,5]thiadiazole) (3).



2 3

In a screw capped vial triptycenetristhiadiazole (**2**) (20 mg, 0.047 mmol) was suspended in HBr (47%, 0.12 mL) and Br_2 (0.12 mL, 4.7 mmol, 50 eq.) was added. The brown suspension was heated at 140 °C for 24 h. After cooling to room temperature, DCM (30 mL) was added and the reaction mixture washed with sat. $NaHSO_3$ (aq.) solution (2 x 100 mL). The combined organic phase was dried over Na_2SO_4 and the solvent evaporated. The crude product was filtered with DCM through a small pad of silica to give after removal of solvents 40 mg (94%) of hexabromotriptycenethiadiazole (**3**). The analytical data are in accordance to the data described above.

Bromination of 2 with 50 equivalents of Br_2 and $FeCl_3 \cdot 6H_2O$: 1,4,5,8,12,15-Hexabromotriptycene[2,3-*c*:6,7-*c*':13,14-*c*"]tris([1,2,5]thiadiazole) (3).

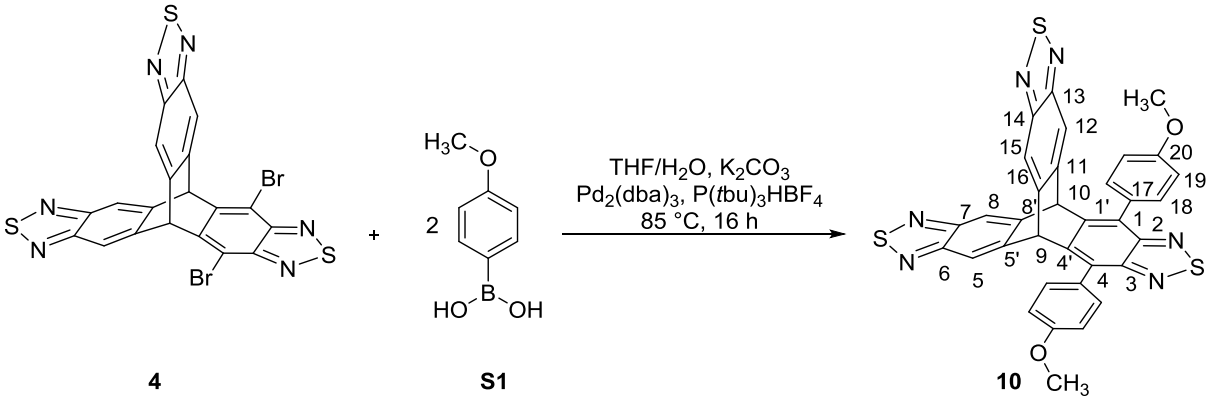


2 3

A suspension of triptycenetristhiadiazole (**2**) (300 mg, 0.70 mmol) and $FeCl_3 \cdot 6H_2O$ powder (1.13 g, 4.20 mmol, 6 eq.) in Br_2 (1.8 mL, 35 mmol, 50 eq.) was heated in a screw capped vial at 55 °C for 26 h. After cooling to room temperature, the brown solution was poured into sat. $NaHSO_3$ (aq.) solution (200 mL) and extracted with DCM (2 x 100 mL). The organic phase was dried over Na_2SO_4 and the solvent evaporated. The crude product was filtered as a solution of DCM through a small pad of silica to give after removal of solvents 615 mg (97%)

of hexabromotriptycenethiadiazole (**3**) as white powder. The analytical data are in accordance to the data described above.

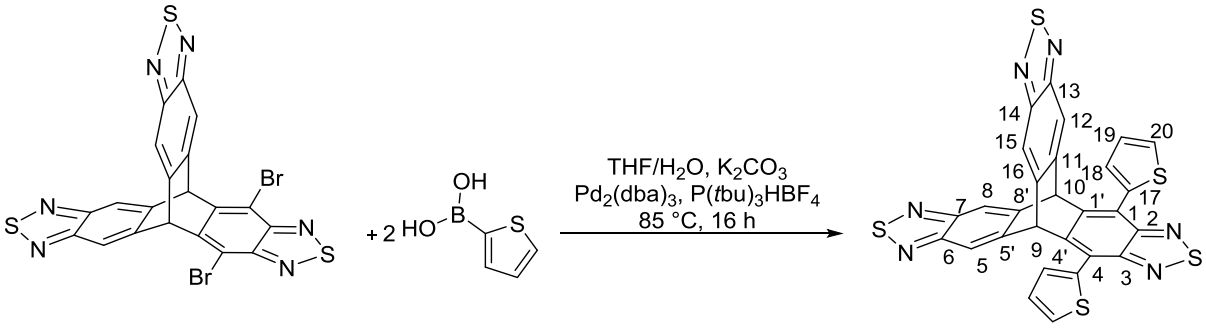
1,4-Di(*p*-methoxyphenyl)-triptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]thiadiazole) (10).



4 **S1** **10**

Dibromotriptycenetristhiadiazole **4** (16 mg, 0.030 mmol) and the boronic acid **S1** (46 mg, 0.307 mmol) were packed under argon and a degassed mixture of THF (0.5 mL) and aqueous K_2CO_3 solution (1 M, 0.5 mL) was added. The solution was degassed again for 2 min and tris(dibenzylidenacetone)dipalladium(0) (2 mg, 0.0021 mmol 7 mol%) and tri-*tert*-butylphosphonium tetrafluoroborate (2 mg, 0.007 mmol, 23 mol%) were added. After heating under argon for 15 h at 85 °C the solution was cooled to room temperature and DCM (10 mL) was added. The aqueous phase was separated and extracted with DCM (10 mL). The combined organic phase was washed with H_2O (3 x 20 mL), dried over Na_2SO_4 and the solvent was removed in vacuo. The residue was purified by flash column chromatography (SiO_2, petroleum ether:ethyl acetate = 4:1, R_f = 0.28) to obtain 18 mg (93%) of bisanisyl triptycene **10** as bright yellow solid with m.p. 356 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.99 ppm (s, 4H, 5,8,12,15-*H*), 7.57 (d, ^3J = 8.7 Hz, 4H, 19-*H*), 7.26 (d, ^3J = 8.7 Hz, 4H, 18-*H*), 6.06 (s, 2H, bridgehead-*H*), 4.01 (s, 6H, -C*H*$_3$). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 160.2 ppm (*C*-20), 154.4 (*C*-6,7,13,14), 154.1 (*C*-2,3), 143.6 (*C*-5',8',11,16), 139.7 (*C*-1',4'), 131.7 (*C*-19), 129.3 (*C*-1,4), 127.4 (*C*-17), 116.4 (*C*- 5,8,12,15), 114.6 (*C*-18), 55.6 (O-*C*H$_3$), 50.4 (*C*-9,10). IR (ATR): $\tilde{\nu}$ = 2956 cm^{-1} (s), 2924 (s), 2853 (s), 1738 (w), 1607 (w), 1512 (w), 1463 (m), 1377 (w), 1287 (w), 1248 (w), 1173 (w), 1030 (w), 878 (w), 825 (w), 825 (w), 721 (w). UV/VIS ($CHCl_3$): λ_{max} = 336 nm, 372. Fluorescence ($CHCl_3$): λ_{em} (λ_{ex}) = 513 nm (326). CV (THF, NBu_4PF_6): $E_{1/2}^{red1}$ = -1.93 V (Fc), $E_{1/2}^{red2}$ = -2.10 V (Fc), $E_{1/2}^{red3}$ = -2.33 V (Fc). MS (MALDI): *m/z* (%) = 641.09 (100) $[M+H]^+$, 640.08 (49) $[M]^+$. HR-MS (MALDI$^-$): *m/z* = 641.0900. Calc. for ($C_{34}H_{21}N_6O_2S_3$): 641.0888.

1,4-Dithiophen-2-yl-triptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]thiadiazole) (11).



4 **S2** **11**

Dibromotriptycenetristhiadiazole **4** (20 mg, 0.034 mmol) and the boronic acid **S2** (44 mg, 0.34 mmol), were packed under argon and a degassed mixture of THF (1 mL) and aqueous K_2CO_3 solution (1 M, 1 mL) was added. The solution was degassed for 2 min and tris(dibenzylidenacetone)dipalladium(0) (3 mg, 0.003 mmol 10 mol%) and tri-*tert*-butylphosphonium tetrafluoroborate (4 mg, 0.014 mmol, 23 mol%) were added. After heating under argon for 19 h at 80 °C the solution was cooled to room temperature and DCM (10 mL) was added. The organic phase was washed with sat. aq. NaCl (2 x 5 mL), dried over Na_2SO_4 and the solvent removed in vacuo. The residue was purified by flash column chromatography (SiO_2, petroleum ether:ethyl acetate = 7:1, R_f = 0.16) to obtain 17 mg (84%) of bisthienyltriptycene **11** as orange solid with m.p. 335 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.07 ppm (s, 4H, Ar-*H*), 7.75 (dd, ^3J = 5.1 Hz,^4J = 1.0 Hz, 2H, 20-*H*), 7.49 (dd, ^3J = 3.4 Hz, ^4J = 1.1 Hz, 2H, 18-*H*), 7.43 (dd, ^3J = 3.5 Hz, ^3J = 5.1 Hz, 2H, 19-*H*), 6.35 (s, 2H, bridgehead-*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 154.3 ppm (Ar-*C*=N-6,7,13,14), 153.7 (Ar-*C*=N-2,3), 143.0 (*C*-5',8',11,16), 141.3 (*C*-1',4'), 134.8 (*C*-17), 130.0 (*C*-18), 128.2 (*C*-20), 127.9 (*C*-19), 123.3 (*C*-1,4), 116.7 (Ar-*C*-H), 50.3 (*C*-9,10). IR (ATR): $\tilde{\nu}$ = 3356 cm^{-1} (w), 3086 (w), 2921 (m), 2851 (m), 1724 (w), 1660 (w), 1633(w), 1525 (m), 1463 (m), 1429 (m), 1364 (w), 1320 (w), 1267 (w), 1223 (m), 1193(m), 1126 (m), 1066 (w), 1040 (w), 924 (w), 902 (m), 858 (m), 839 (s), 780 (m), 696(s), 664 (w), 634 (w). UV/VIS ($CHCl_3$): λ_{max} = 336 nm, 387. Fluorescence ($CHCl_3$): λ_{em} (λ_{ex}) = 541 nm (326). CV (THF, NBu_4PF_6): $E_{1/2}^{red1}$ = -1.85 V (Fc). MS (MALDI): *m/z* (%) = 592.98 (100) $[M+H]^+$, 591.97 (12) $[M]^+$. HR-MS (MALDI$^+$): *m/z* = 591.9709. Calc. for ($C_{28}H_{13}N_6S_5$): 591.9727.

3. ^{1}H and ^{13}C NMR spectra of all new compounds

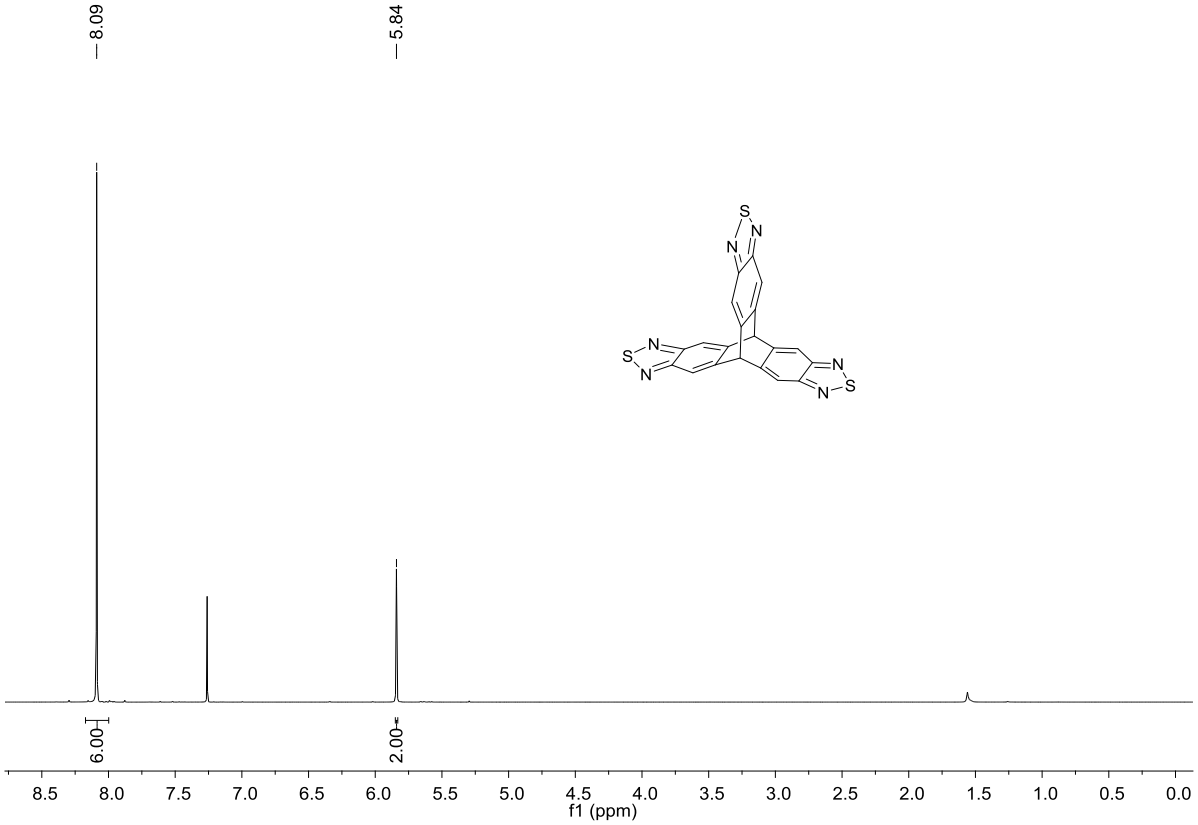


Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of triptycene[2,3-c:6,7-c':13,14-c'']tris([1,2,5]thiadiazole) (**2**).

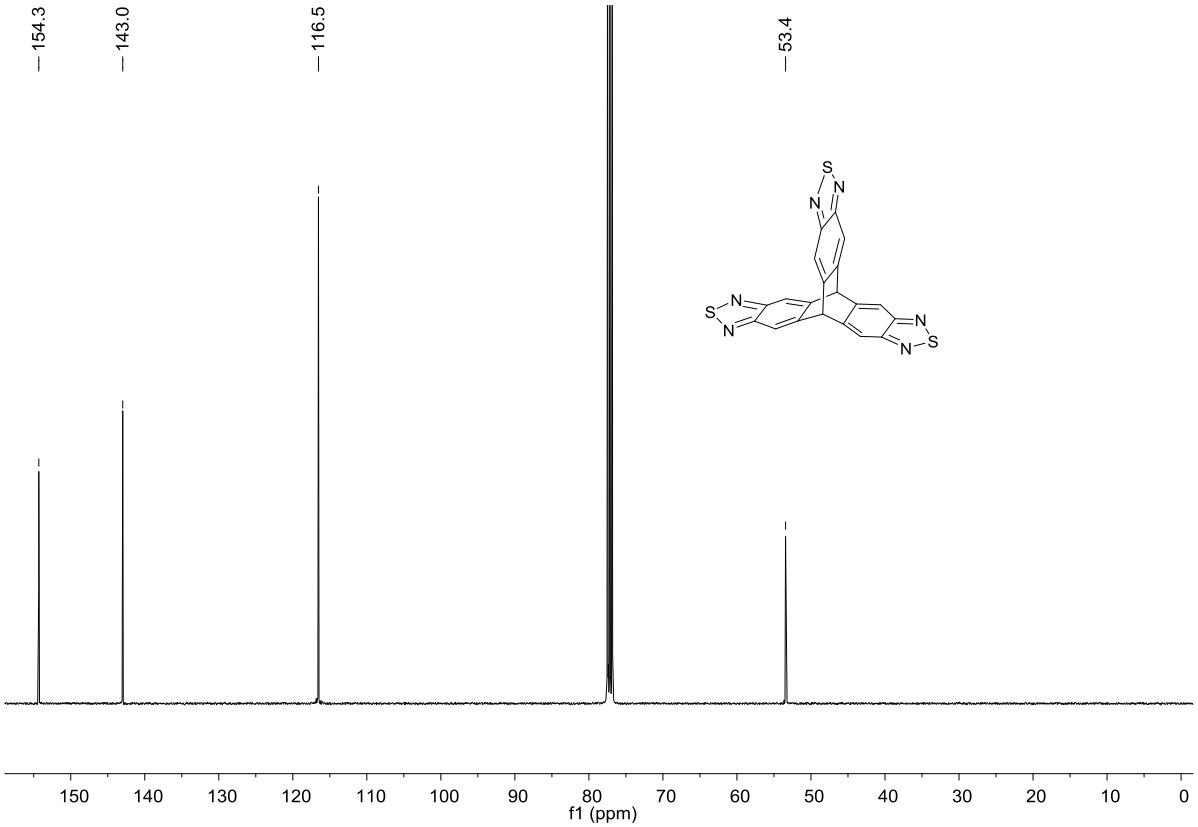


Figure S2. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of triptycene[2,3-c:6,7-c':13,14-c'']tris([1,2,5]thiadiazole) (**2**).

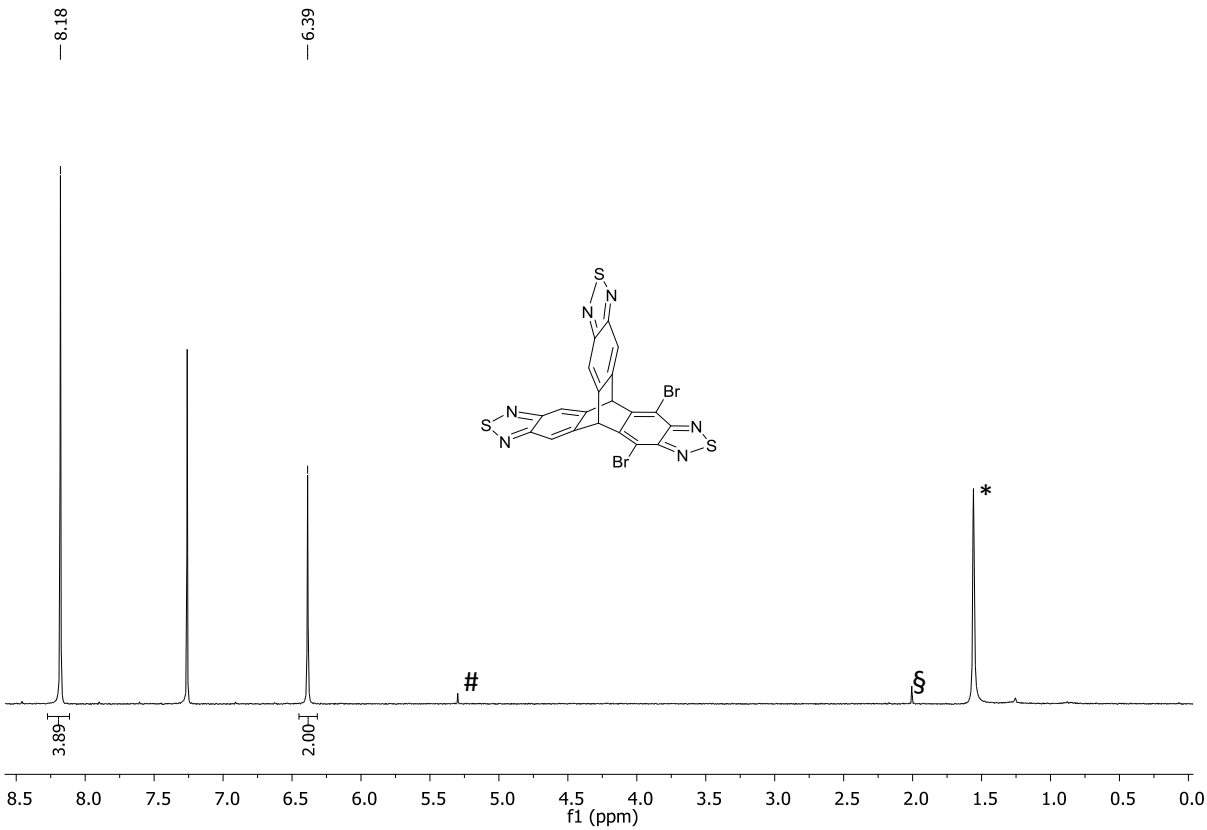


Figure S3. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 1,4-dibromotriptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]thiadiazole) (**4**). Residual solvent signals #: DCM, §: MeCN, *: H_2O.

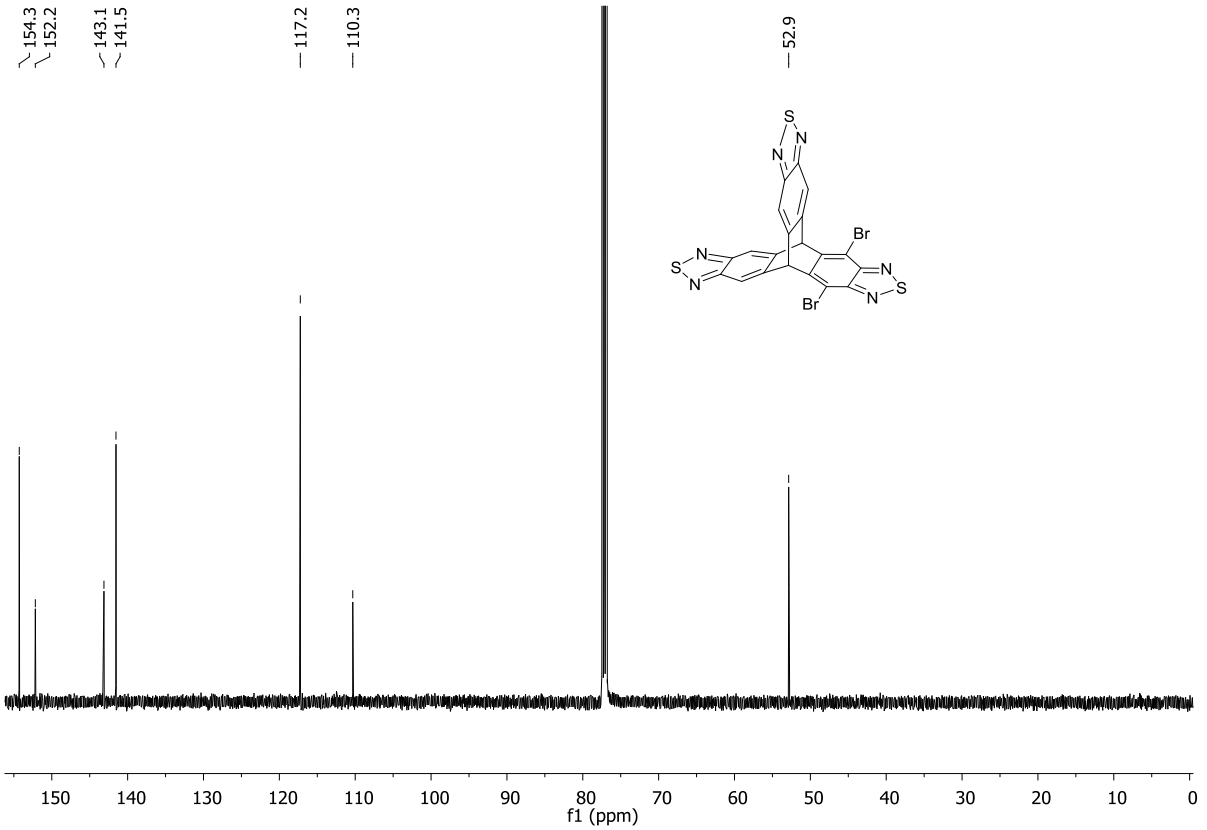


Figure S4. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1,4-dibromotriptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]thiadiazole) (**4**).

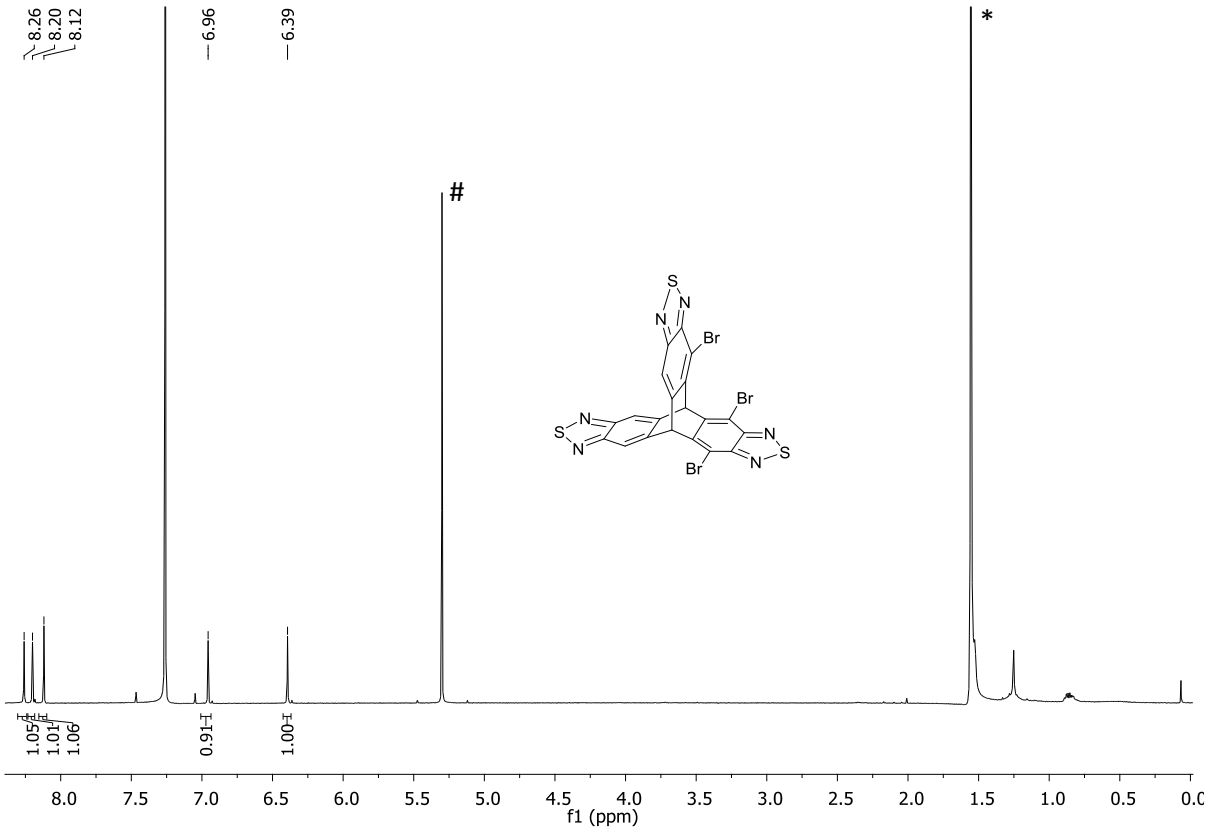


Figure S5. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 1,4,5-tribromo-triptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]-thiadiazole) (**6**). Residual solvent signals #: DCM, *: H_2O.

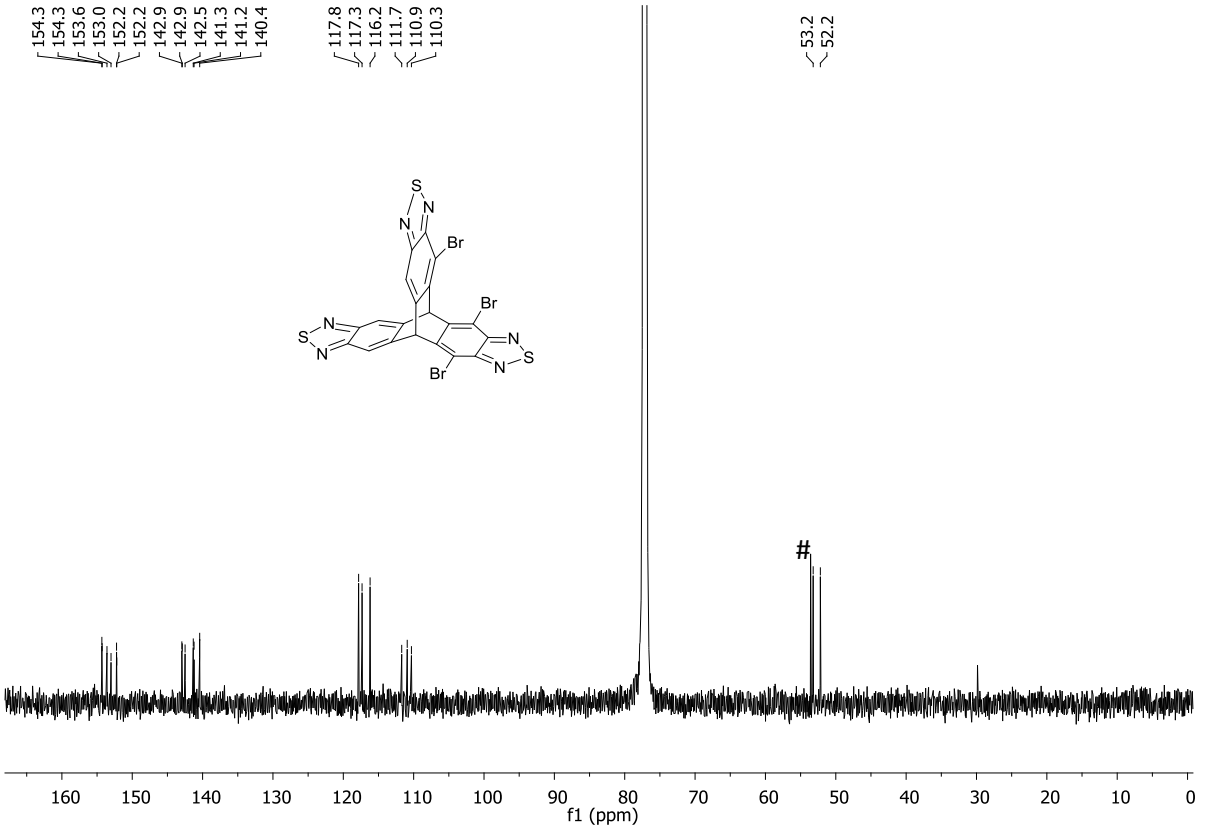


Figure S6. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of 1,4,5-tribromo-triptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]-thiadiazole) (**6**). Residual solvent signals #: DCM.

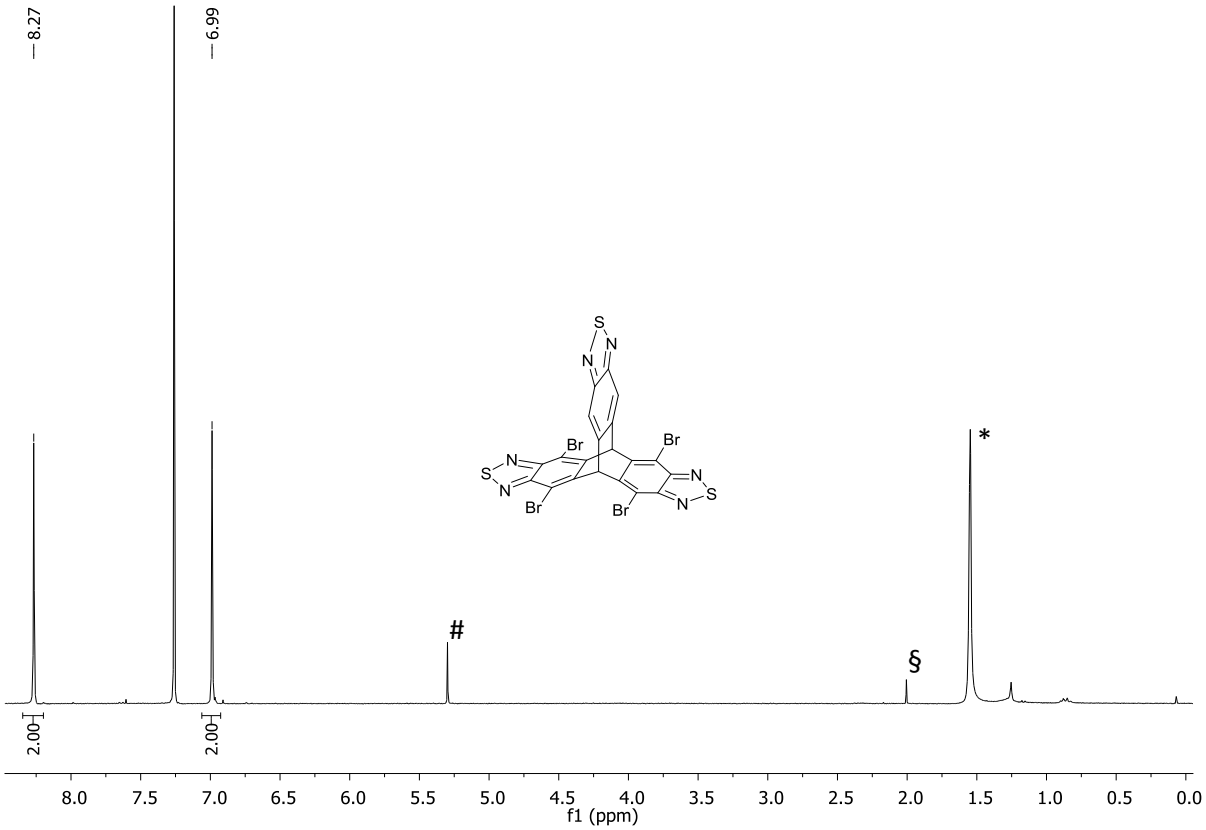


Figure S7. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 1,4,5,8-tetrabromotriptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]-thiadiazole) (**5**). Residual solvent signals #: DCM, §: MeCN, *: H_2O.

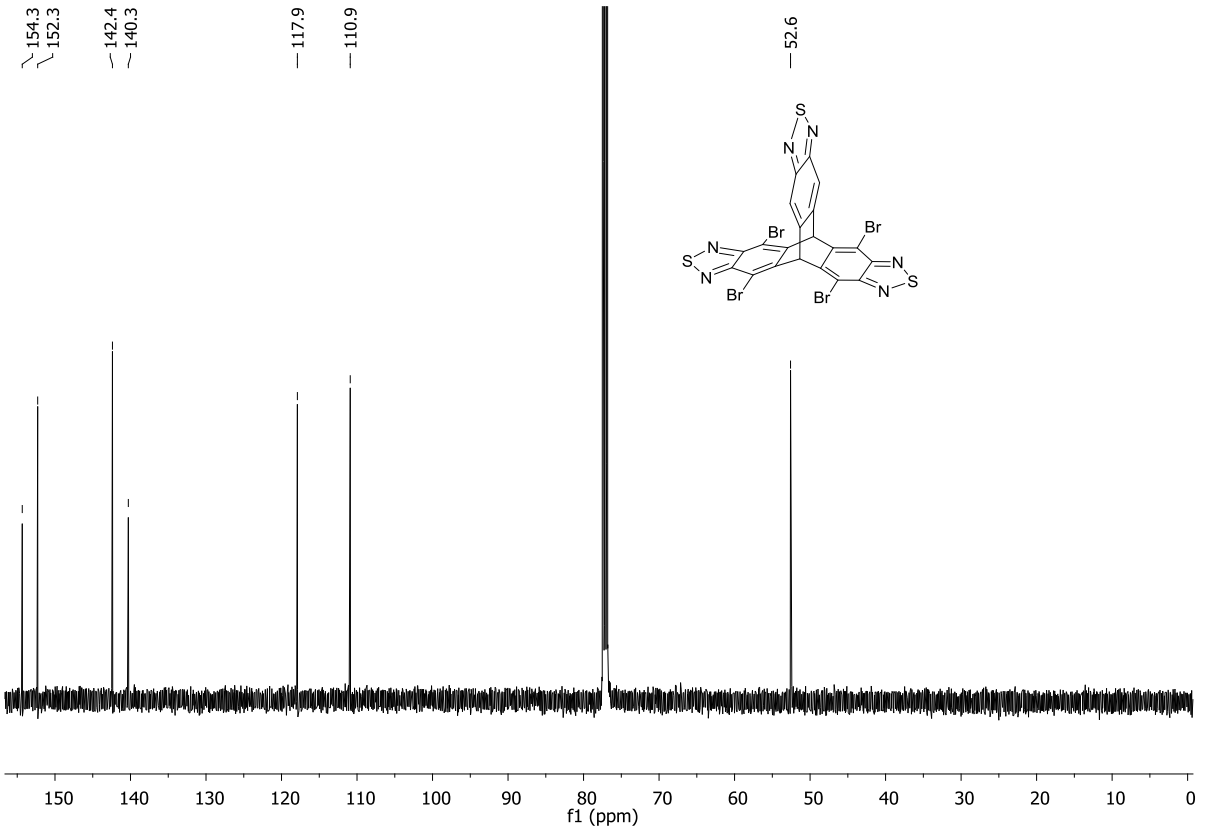


Figure S8. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1,4,5,8-tetrabromotriptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]-thiadiazole) (**5**).

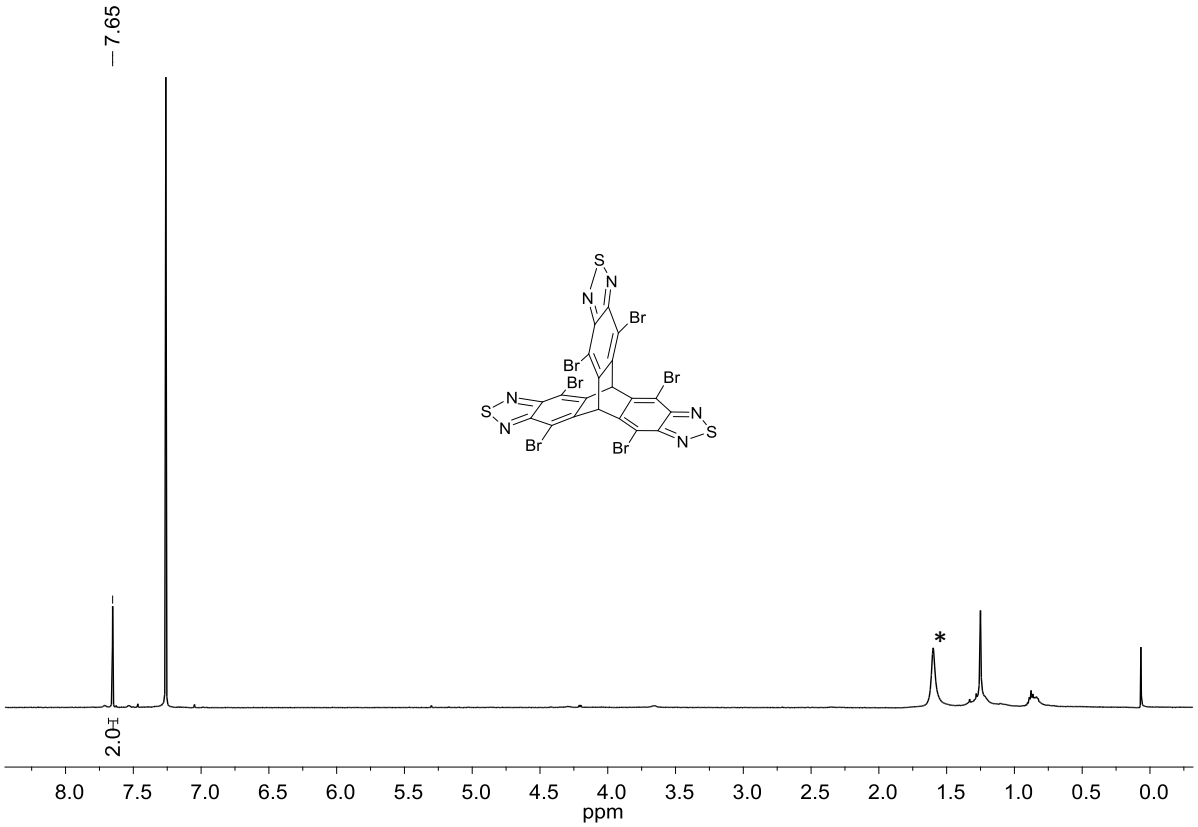


Figure S9. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 1,4,5,8,12,15-hexabromotriptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]thiadiazole) (**3**). The asterisk marks residual H_2O.

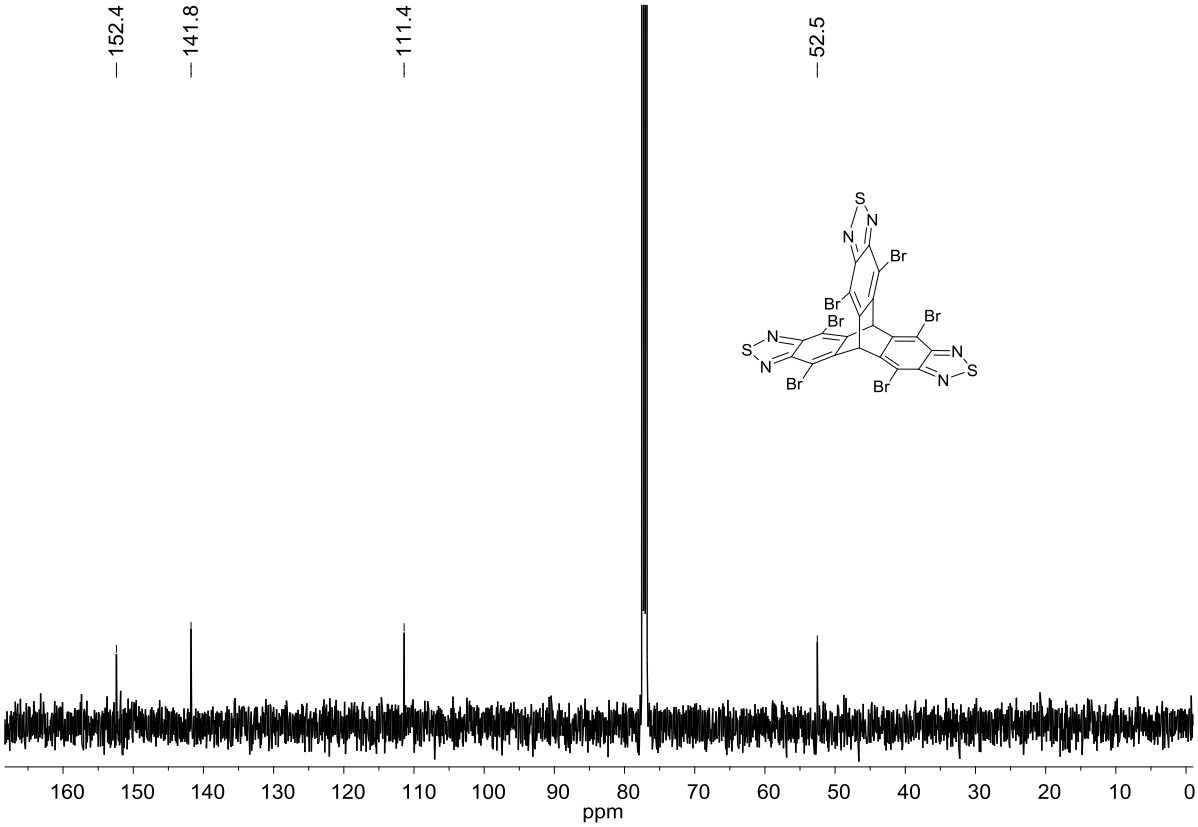


Figure S10. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1,4,5,8,12,15-hexabromotriptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]thiadiazole) (**3**).

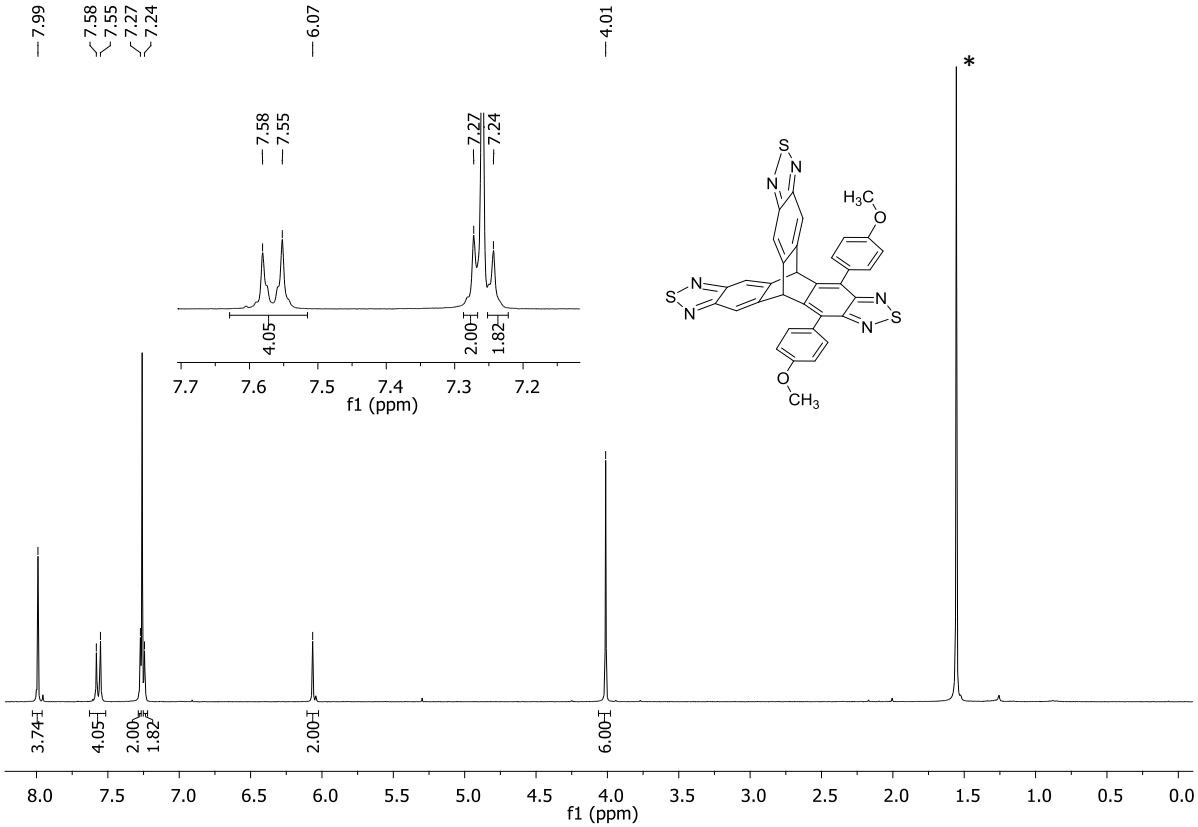


Figure S11. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) 1,4-Di(*p*-methoxyphenyl)-triptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]thiadiazole) (**10**). The asterisk marks residual H_2O.

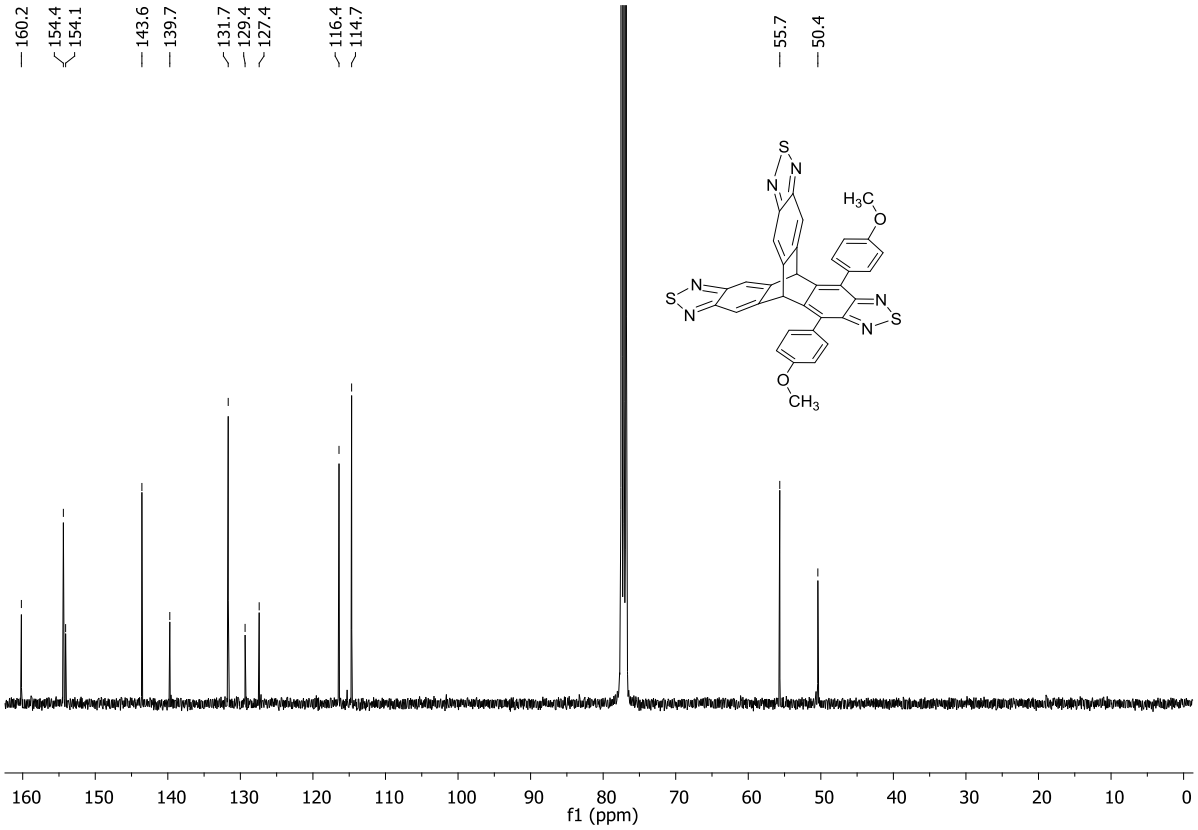


Figure 12. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1,4-Di(*p*-methoxyphenyl)-triptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]thiadiazole) (**10**).

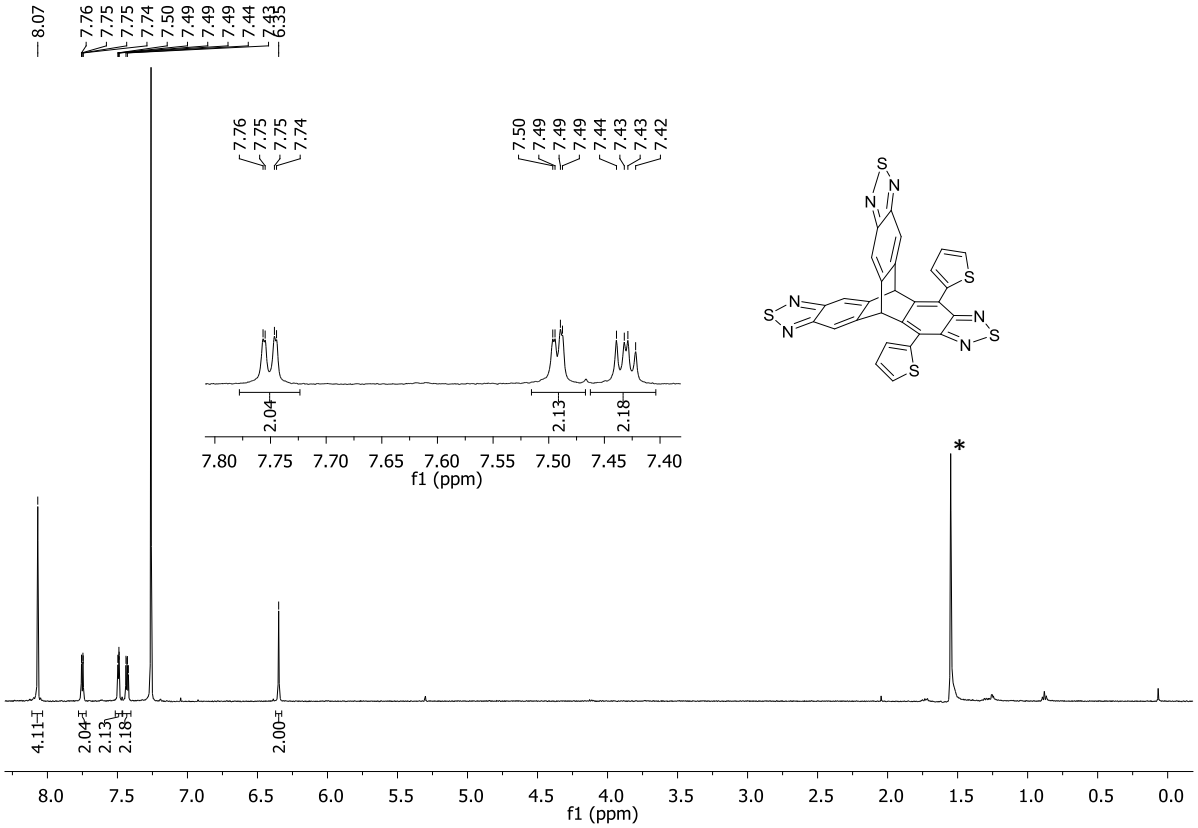


Figure S13. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 1,4-dithiophen-2-yl-triptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]thiadiazole) (**11**). The asterisk marks residual H_2O.

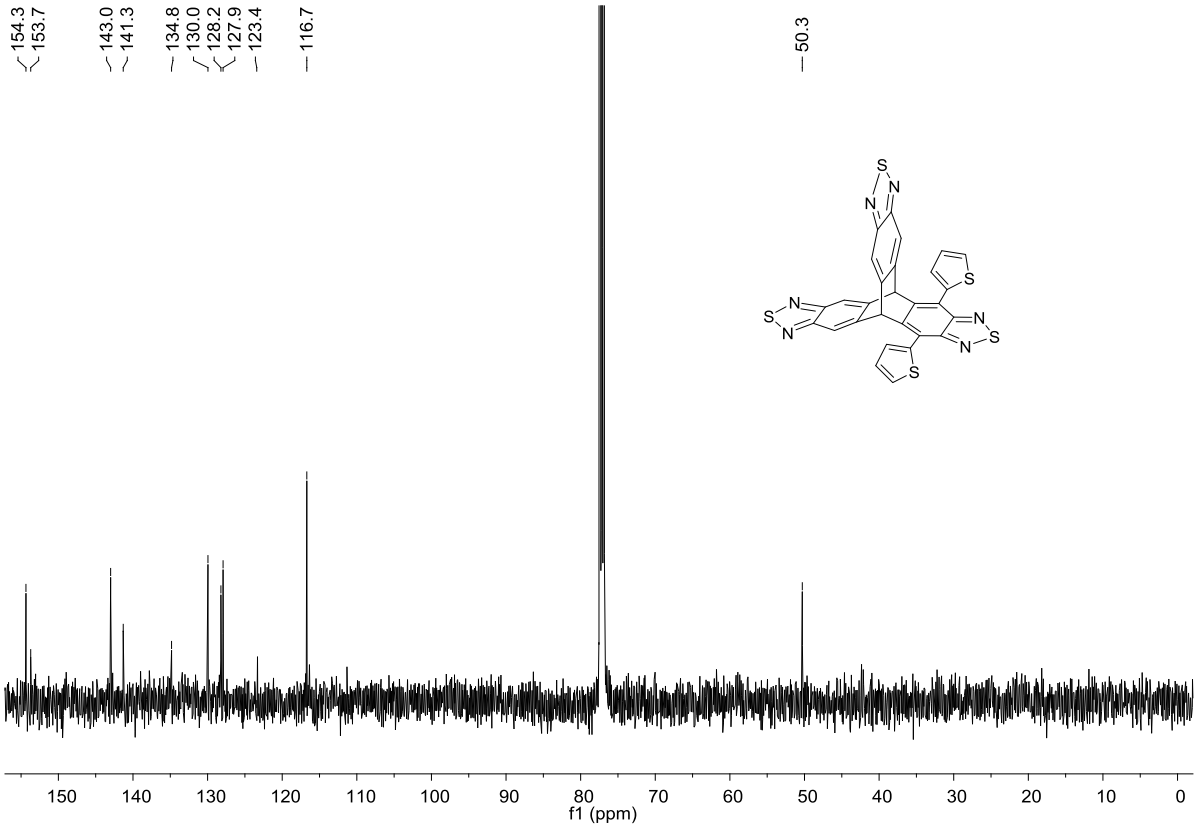


Figure S14. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of 1,4-dithiophen-2-yl-triptycene[2,3-c:6,7-c':13,14-c"]tris([1,2,5]thiadiazole) (**11**).

4. UPLC-MS Chromatograms

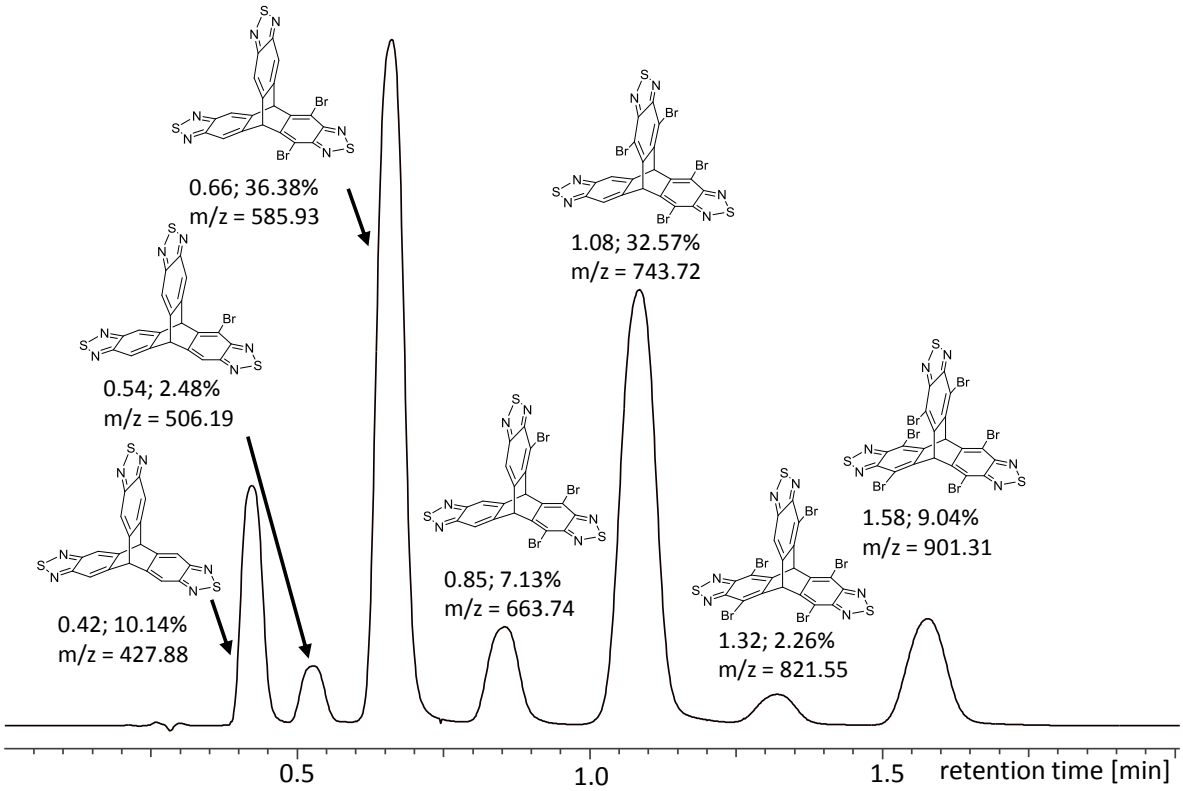


Figure S15. UPLC-MS chromatogram detected at 330 nm (H_2O/MeCN 30/70 → 10/90) for the crude product of the reaction with the following conditions: neat, 150 eq. Br_2; 12 eq. Fe; 40 °C; 14 h. Below the molecular structures the retention time (min), the relative integrals and the detected *m/z* values are given. Please note that the relative integrals are not corrected by the exctinction coefficients of the compounds.

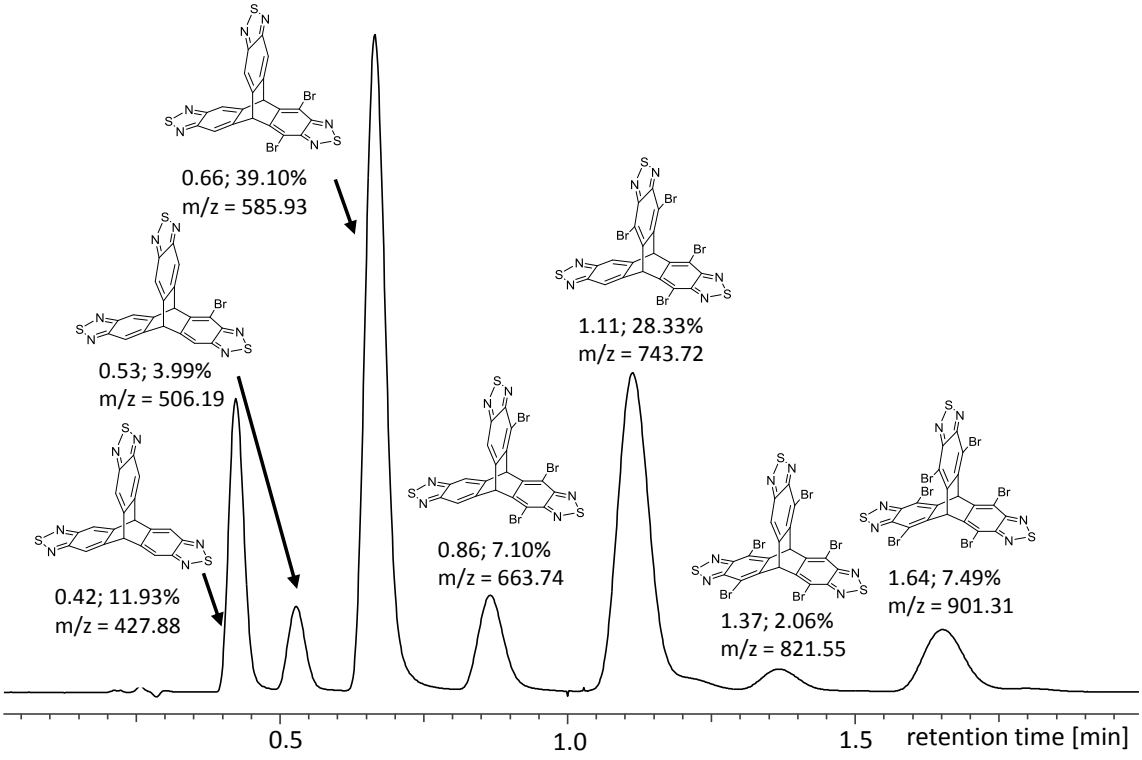


Figure S16. UPLC-MS chromatogram detected at 330 nm (H_2O/MeCN 30/70 → 10/90) for the crude product of the reaction with the following conditions: neat, 34 eq. Br_2; 6 eq. Fe; 55 °C; 2 h. Below the molecular structures the retention time (min), the relative integrals and the detected *m/z* values are given. Please note that the relative integrals are not corrected by the exctinction coefficients of the compounds.

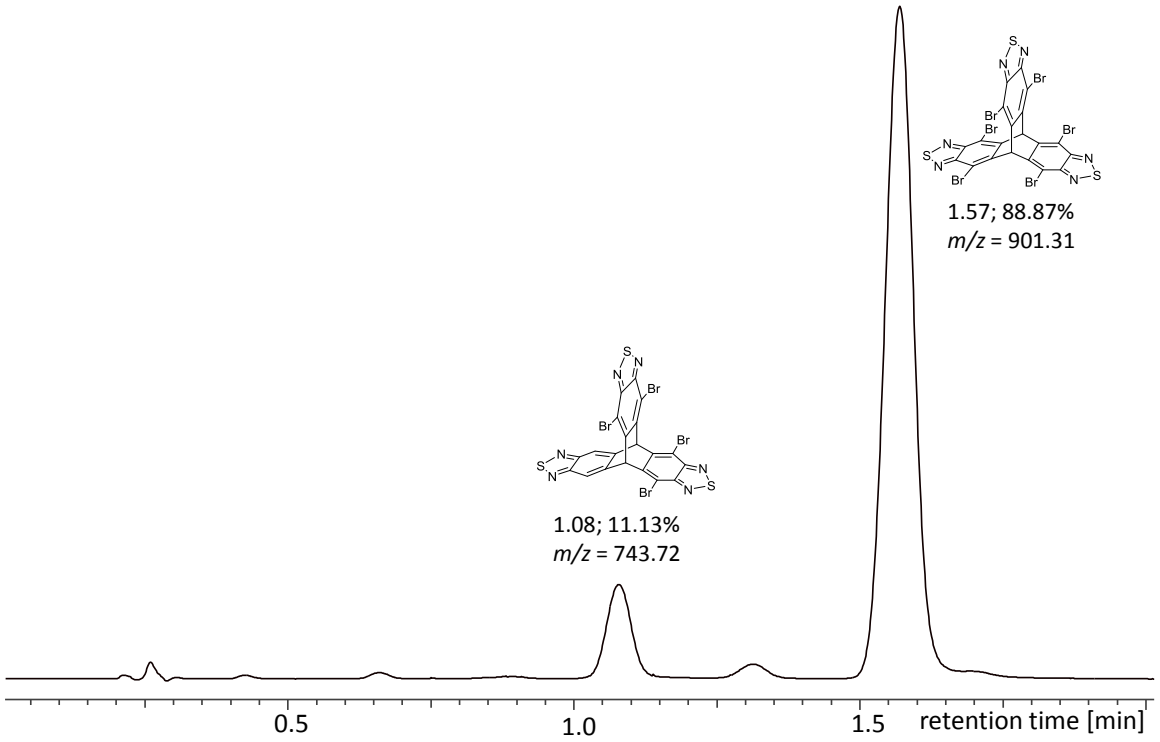


Figure S17. UPLC-MS chromatogram detected at 330 nm (H_2O/MeCN 30/70 → 10/90) for the crude product of the reaction with the following conditions: neat, 600 eq. Br_2; 12 eq. Fe; 55 °C; 140 h. Below the molecular structures the retention time (min), the relative integrals and the detected *m/z* values are given. Please note that the relative integrals are not corrected by the exctinction coefficients of the compounds.

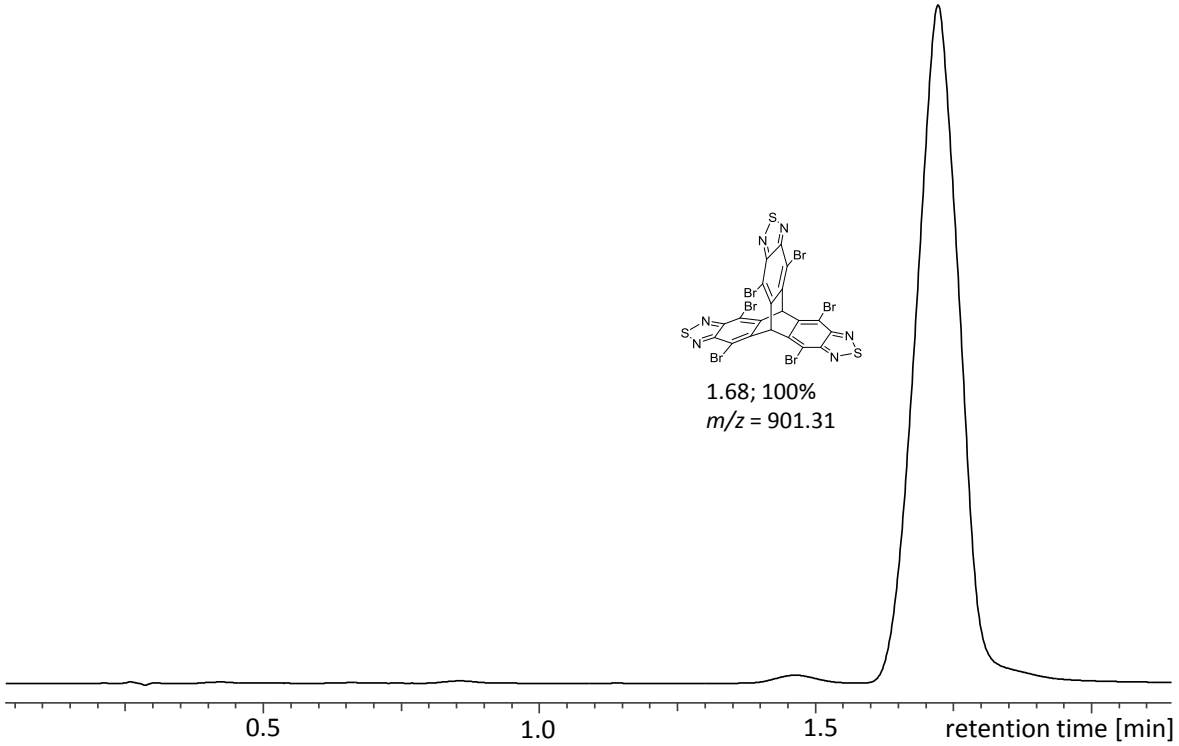


Figure S18. UPLC-MS chromatogram detected at 330 nm (H_2O/MeCN 30/70 → 10/90) for the crude product of the reaction with the following conditions: neat, 50 eq. Br_2; HBr (47%); 140 °C; 24 h. Below the molecular structure the retention time (min), the relative integral and the detected *m/z* value is given. Please note that the relative integrals are not corrected by the exctinction coefficients of the compounds.

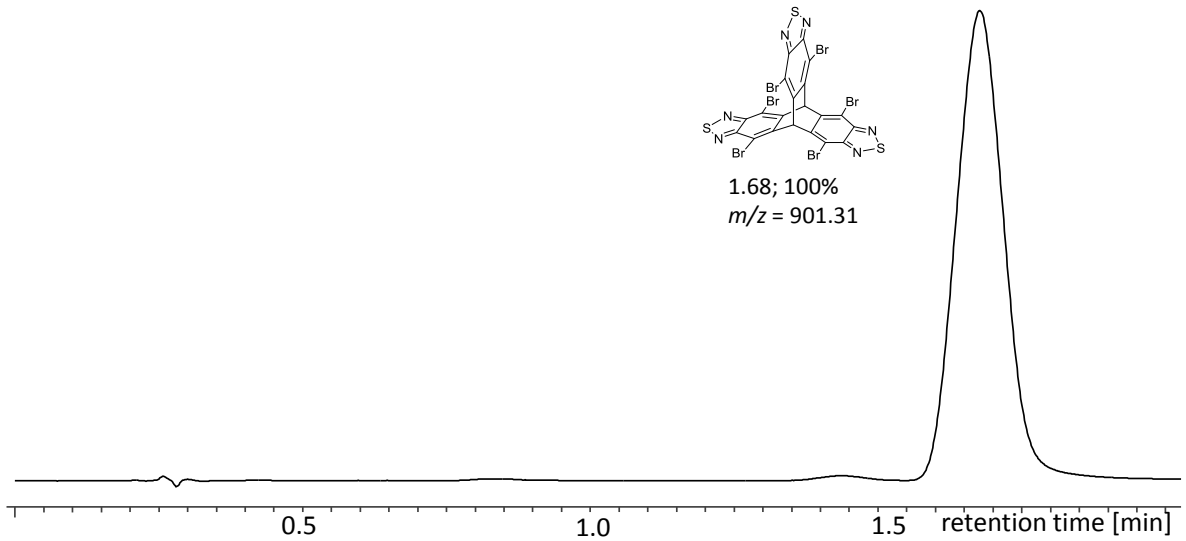


Figure S19. UPLC-MS chromatogram detected at 330 nm (H_2O/MeCN 30/70 → 10/90) for the crude product of the reaction with the following conditions: neat, 50 eq. Br_2; 6 eq. $FeCl_3 \cdot 6H_2O$; 55 °C; 26 h. Below the molecular structure the retention time (min), the relative integral and the detected *m/z* value is given. Please note that the relative integrals are not corrected by the exctinction coefficients of the compounds.

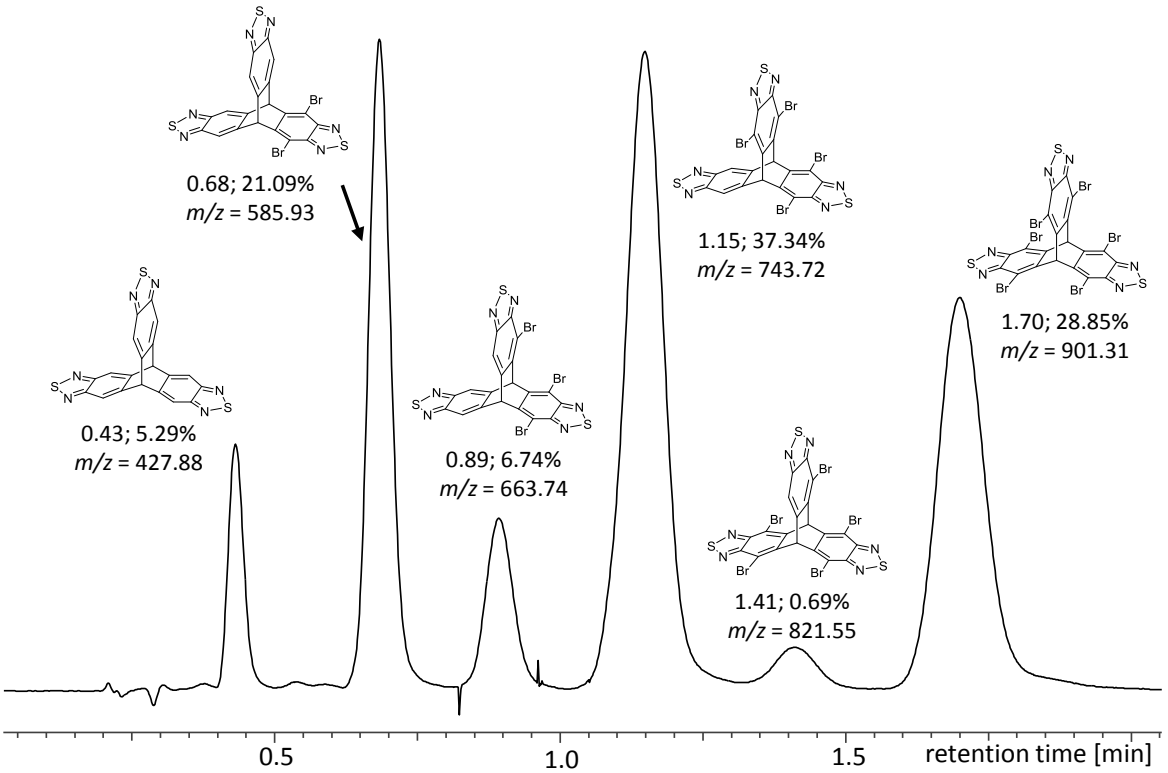


Figure S20. UPLC-MS chromatogram detected at 330 nm (H_2O/MeCN 30/70 → 10/90) for the crude product of the reaction with the following conditions: neat, 50 eq. Br_2; 6 eq. $FeCl_3$; 55 °C; 21 h. Below the molecular structures the retention time (min), the relative integrals and the detected *m/z* values are given. Please note that the relative integrals are not corrected by the exctinction coefficients of the compounds.

5. Crystal Structure Analyses of Compounds 10 and 11

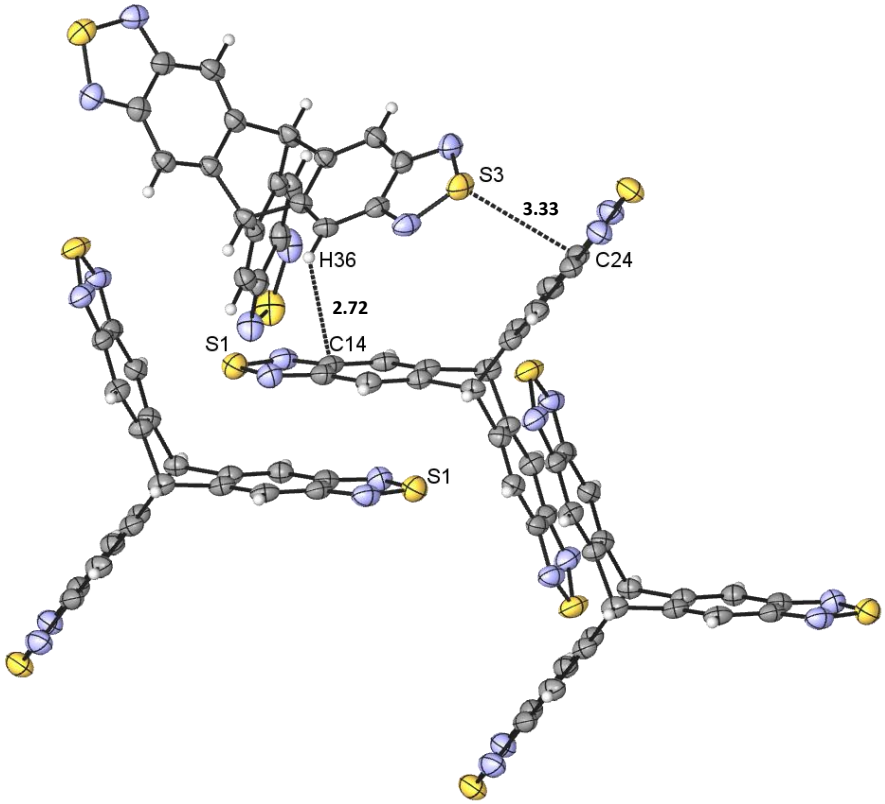


Figure S21. X-ray Crystal Structure Analysis of **2** showing CH-π and chalcogen-π stacking.

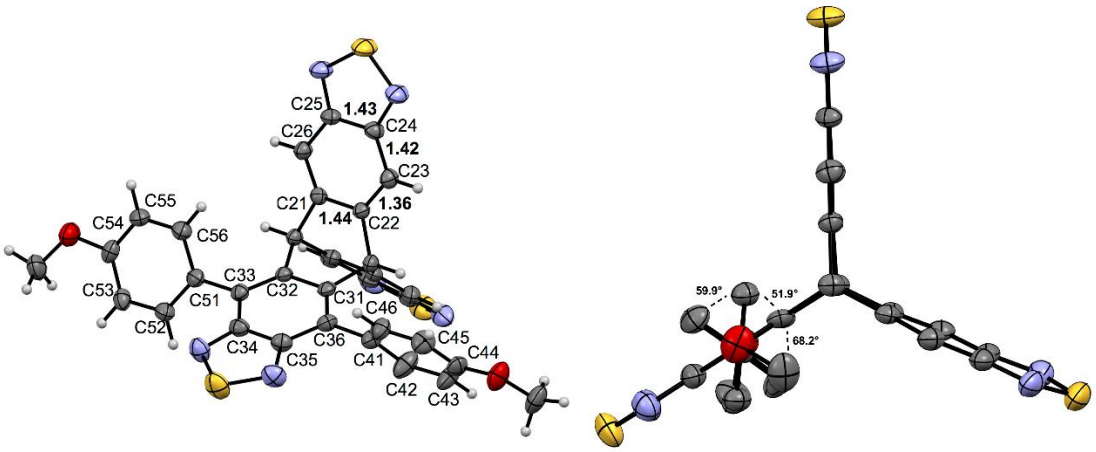


Figure S22. X-ray Crystal Structure Analysis of **10**. (left) C-C-bond lengths (Å) on the phenyl ring; (right) view along the axis through the bridgehead atoms of compound **10**.

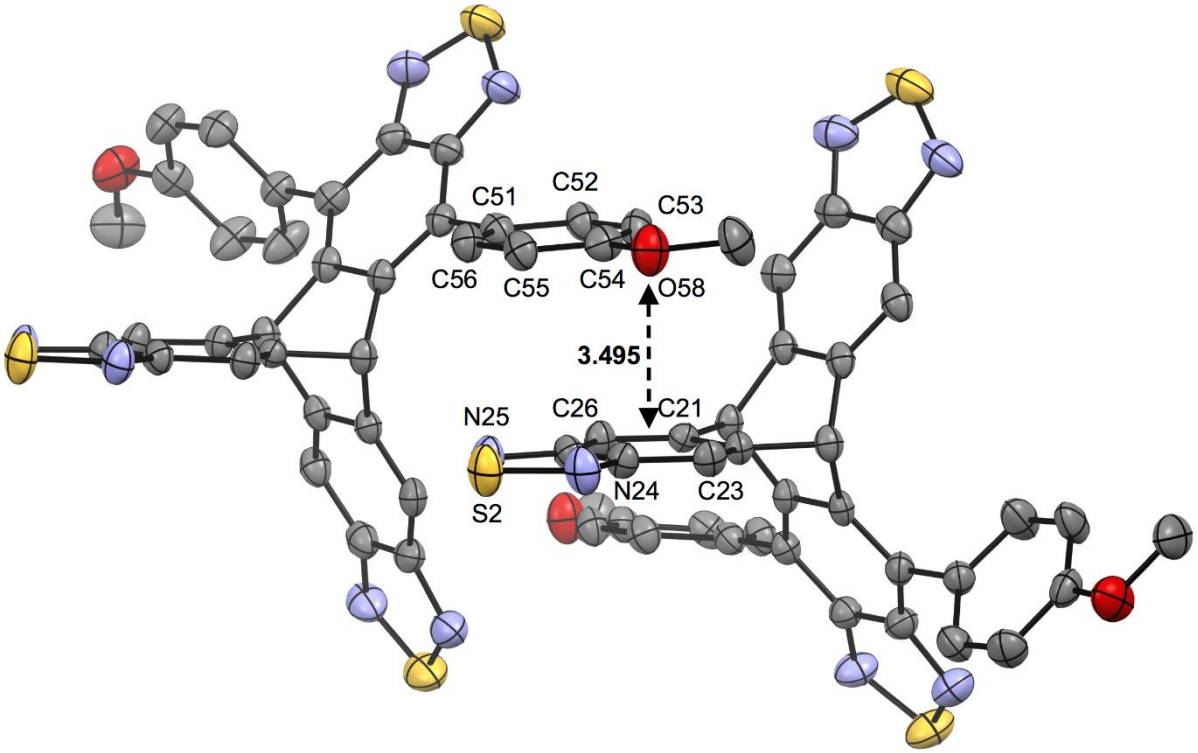


Figure S23. Distance between the two π-planes (Å) of two adjacent molecules of compound **10**.

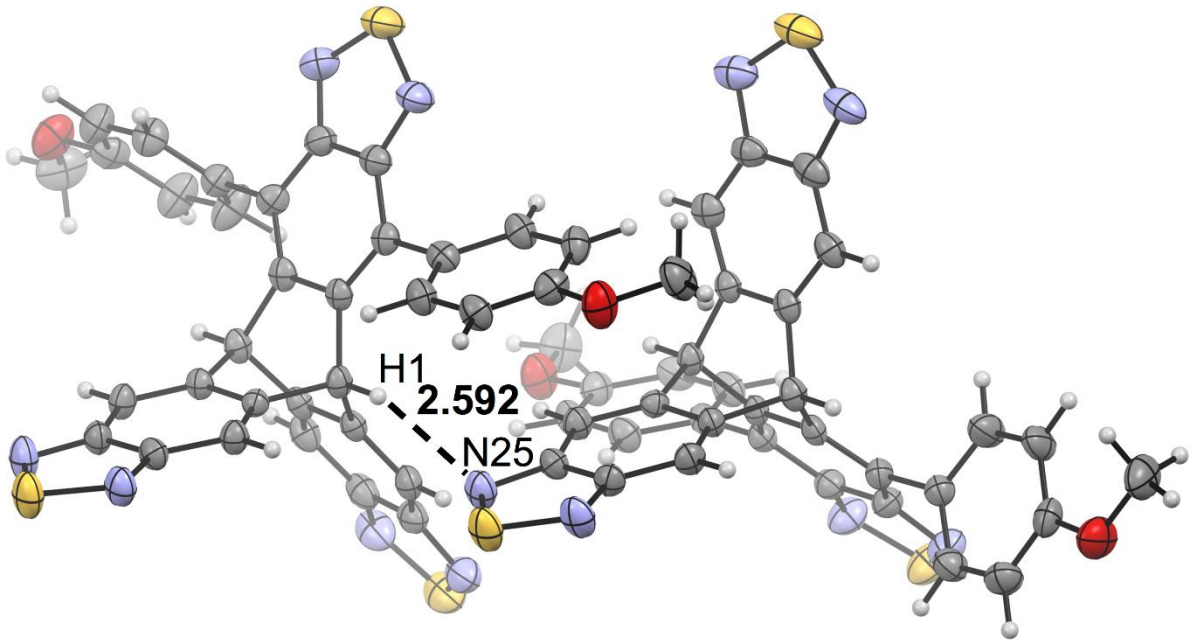


Figure S24. N-H-Distance (Å) between two adjacent molecules of compound **10**.

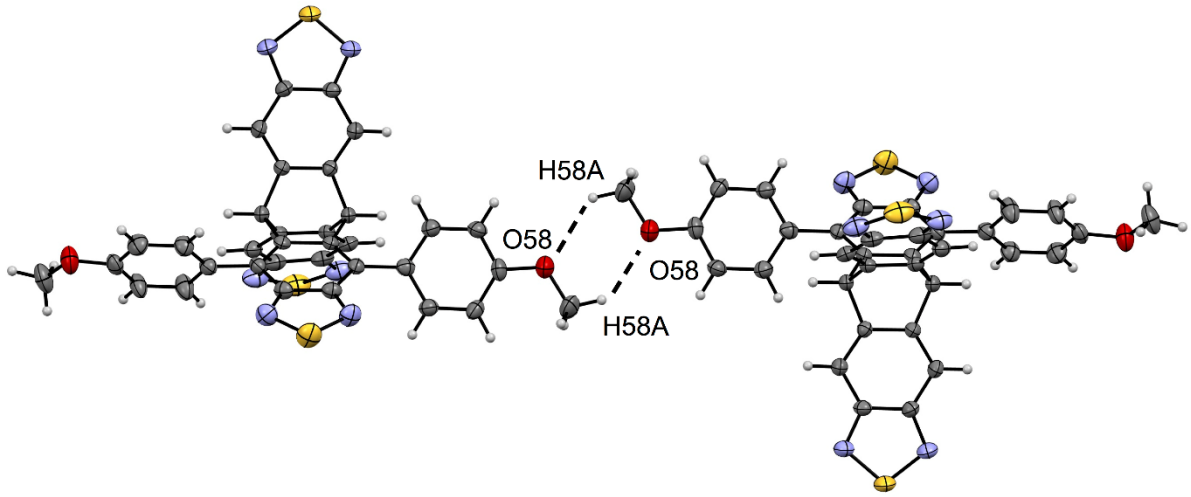


Figure S25. X-ray Crystal Structure Analysis of **10**. Methoxy-methoxy-interaction between two adjacent molecules of compound **10**.

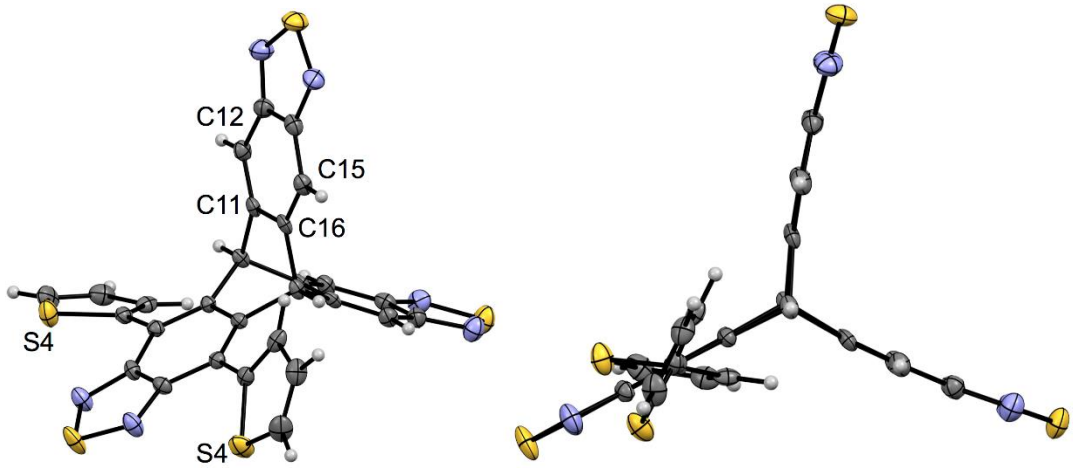


Figure S26. X-ray Crystal Structure Analysis of **11**. (left) ORTEP-illustration; (right) view along the axis through the bridgehead atoms of compound **11**.

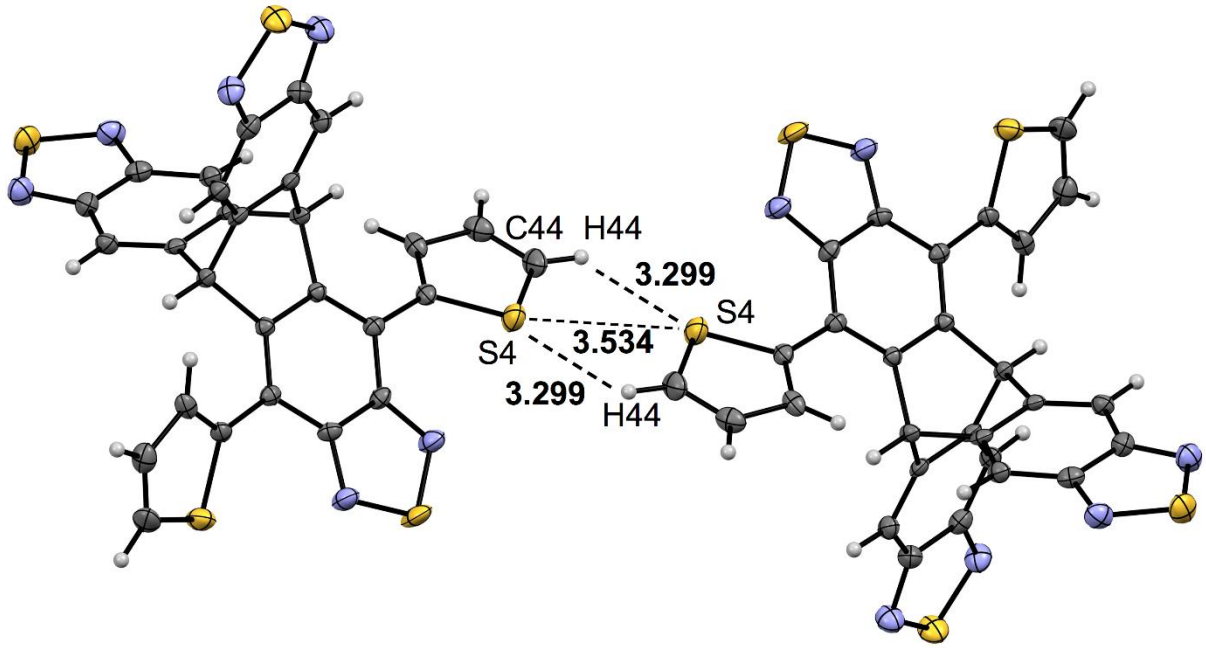


Figure S27. Thiophene-thiophene-interaction (Å) between two adjacent molecules of compound **11**.

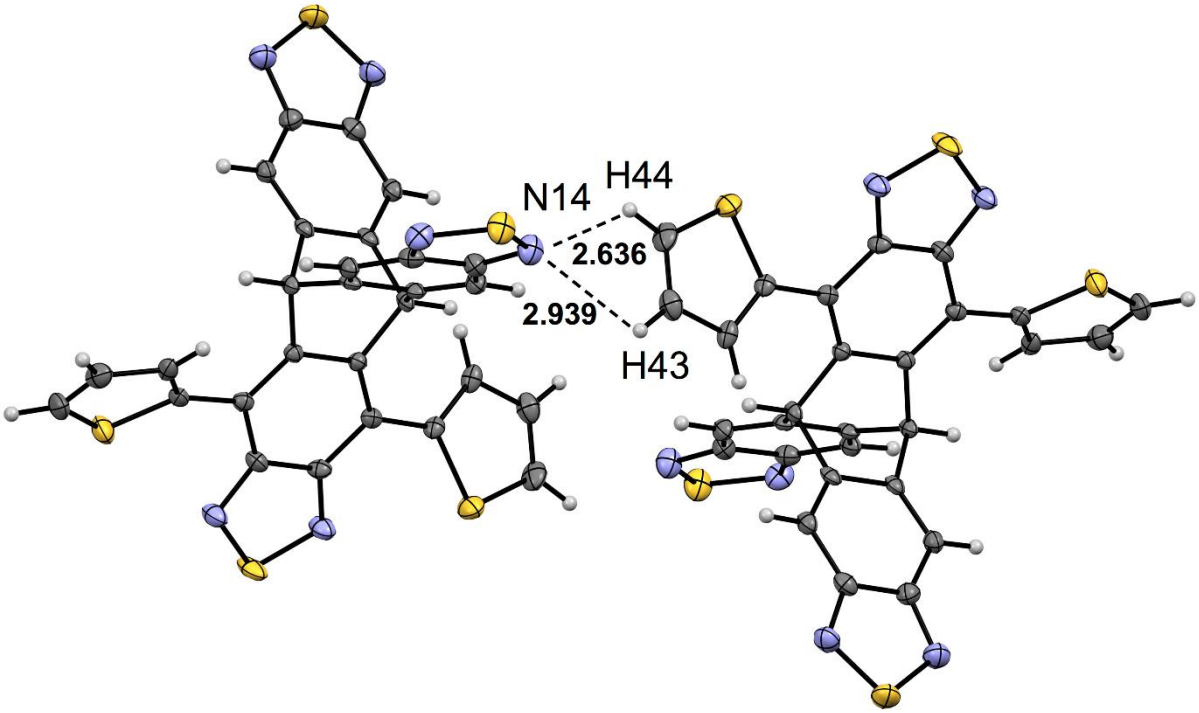


Figure S28. X-ray Crystal Structure Analysis of **11**. N-H-Distance (Å) between two adjacent molecules of compound **11**.

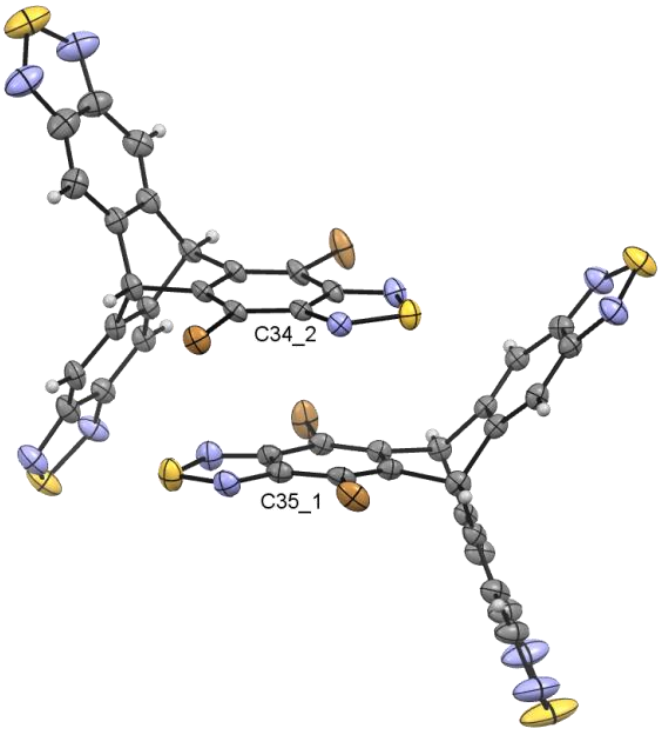


Figure S29. X-ray Crystal Structure Analysis of **4,** showing the π-π stacking. The distance between the π-planes is *d* = 3.79 Å.

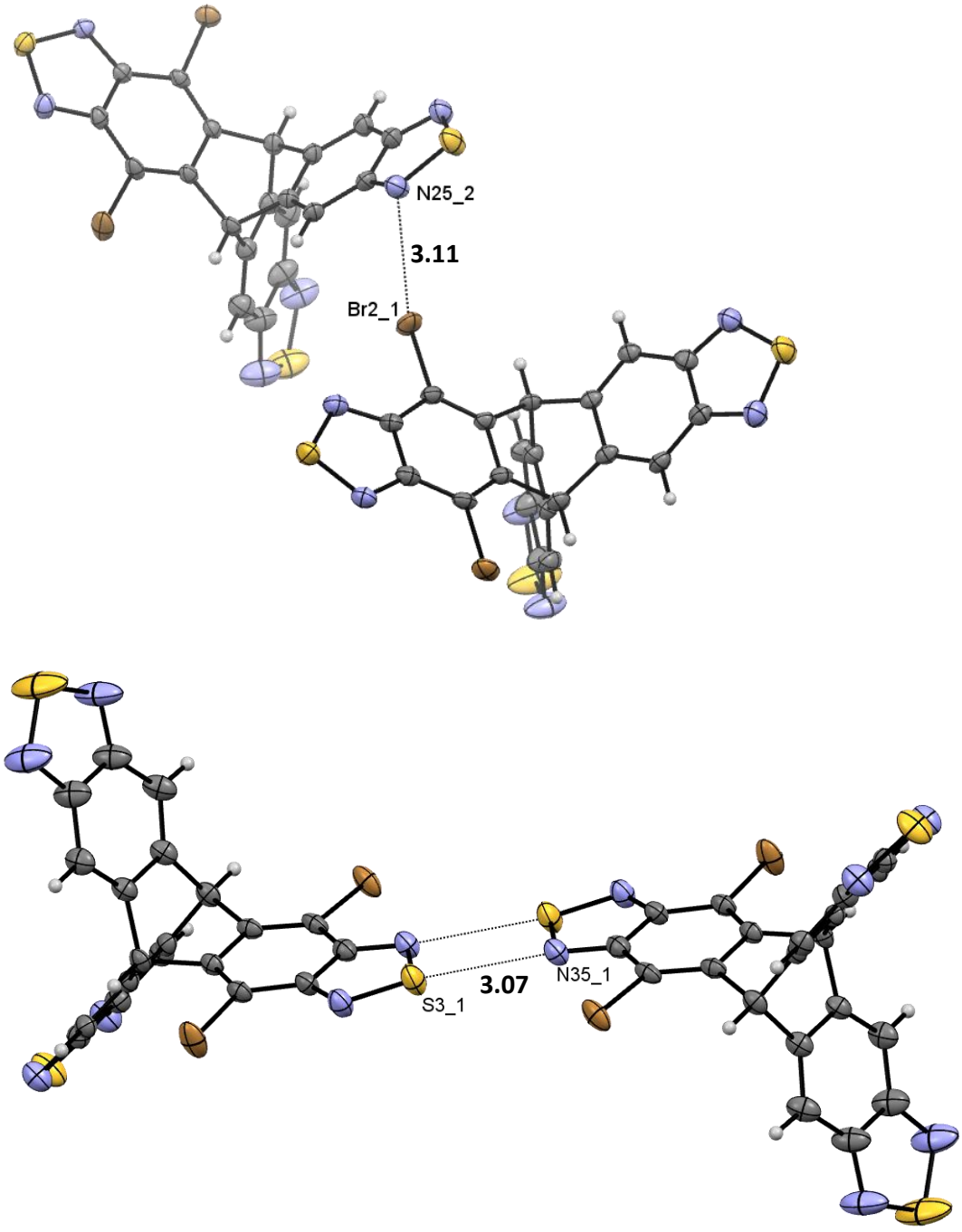


Figure S30. X-ray Crystal Structure Analysis of **4,** showing halogen bonding (top) and pnicogen interactions (bottom).

6. References

[S1] Mastalerz, M.; Sieste, S.; Cenić, M.; Oppel, I. M. *J. Org. Chem.* **2011**, *76*, 6389–6393.