ELECTRONIC SUPPLEMENTARY INFORMATION

FOR

Self-Assembly of Tetrathiafulvalene Derivatives at a Liquid-Solid Interface – Compositional and Constitutional Influence on Supramolecular Ordering

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SYNTHETIC PROCEDURES AND CHARACTERISATION FOR TTF COMPOUNDS AND THEIR PRECURSORS.

4-(2-Cyanoethylthio)-5-dodecylthio-1,3-dithiol-2-thione (29)

Method A: To a solution of cesium 5-(2-cyanoethylthio)-2-thioxo-1,3-dithiol-4-thiolate^[24] (27) (100 mg, 0.261 mmol) in CH₃CN (10 ml) was added 0.1 ml (0.401 mmol) of 1-bromododecane, and the mixture was brought to reflux under argon for 1 hour. An immediate change in colour from dark red to light yellow was observed. The warm solution was filtered, and upon cooling yellow needles crystallized, which were washed with diethyl ether. The mother liquor was evaporated, leaving a yellow solid which was crystallized from methanol. The total weight of 4-(2-cyanoethylthio)-5-dodecylthio-1,3-dithiol-2-thione was 100 mg (88%). M.p.: 64-66°C; FT-IR (KBr): 2950 (m), 2917 (s), 2848 (s), 2248 (w, CN), 1463 (m), 1416 (w), 1385 (w), 1323 (w), 1288 (w), 1058 (m), 1048 (s, C=S), 899 (w), 792 (w), 717 (w), 515 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃): 3.11 (t, *J*= 7.1 Hz, 2H, -SCH₂CH₂CN), 2.95 (t, *J*= 7.3 Hz, 2H, -SCH₂(CH₂)₁₀CH₃), 2.76 (t, *J*= 7.1 Hz, 2H, -CH₂CN), 1.71 (c, *J*= 7.3 Hz, 2H, -SCH₂C(H₂)₁₀CH₃), 2.76 (t, *J*= 7.1 Hz, 2H, -CH₂CN), 1.71 (c, *J*= 7.3 Hz, 2H, -SCH₂CH₂CH₂CH₃), 1.6-1.2 (m, 18H, -S(CH₂)₂(CH₂)₉CH₃), 0.90 (t, *J*=6.6 Hz, 3H, -CH₃) ppm; ¹³C NMR (62.8 MHz, CDCl₃): 210.2 (C=S), 143.1, 128.7 (C=C), 117.1 (-CN), 36.7, 31.0, 31.8, 29.6, 29.6, 29.5, 29.4, 29.3, 29.0 and 28.5 (-S(CH₂)₁₀CH₂CH₃ and -SCH₂CH₂CN), 22.6 (-CH₂CH₃), 18.8 (-SCH₂CH₂CN), 14.1 (-CH₃) ppm.

Method B: To a stirred solution of 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-thione^[24] (**26**) (1.058 g, 3.47 mmol) in CH₃CN (60 ml) under argon was added dropwise a solution of CsOH·H₂O (0.638 g, 3.80 mmol) in MeOH (6 ml) over 30 minutes. The mixture was left to stir for 30 minutes then 5.2 ml (21.66 mmol) of 1-bromododecane was added and the solution was brought to reflux for approximately 1 hour. Work-up and purification as for Method A gave 1.025 g (71%) of **29**, which had identical analytical data to the material prepared with the aforementioned method.

4-(2-Cyanoethylthio)-5-octadecylthio-1,3-dithiol-2-thione (28)

The compound was prepared as a yellow solid in an analogous way to **29** using Method B and 1bromooctadecane as the electrophilic reagent in a yield of 71%. M.p.:72°C; FT-IR (KBr): 2917 (s), 2849

(m), 2248 (w, CN), 1464 (w), 1417 (w), 1385 (w), 1288 (w), 1058 (m), (1049 (s, C=S), 954 (w), 900 (w), 717 (w), 516 (w), 463 (w) cm⁻¹; ¹H NMR(250 MHz, CDCl₃): 3.12 (t, J= 6.9 Hz, 2H, - SCH₂CH₂CN), 2.95 (t, J= 7.4 Hz, 2H, -SCH₂(CH₂)₁₆CH₃), 2.77 (t, J= 6.9 Hz, 2H, -CH₂CN), 1.8-1.2 (m, 32H, -SCH₂(CH₂)₁₆CH₃), 0.90 (t, J= 6.6 Hz, 3H, -CH₃) ppm; ¹³C NMR (62.8 MHz, CDCl₃): 210.3 (C=S), 143.5, 128.6 (C=C), 117.1 (-CN), 36.7, 32.0, 20.7, 20.6, 29.6, 29.5, 29.4, 29.1, 28.5 (-S(CH₂)₁₆CH₂CH₃ and -SCH₂CH₂CN), 22.7 (-CH₂CH₃), 18.8 (-SCH₂CH₂CN), 14.1 (-CH₃) ppm.

4-(2-Cyanoethylthio)-5-dodecylthio-1,3-dithiol-2-one (31)

A solution of 4-(2-cyanoethylthio)-5-dodecylthio-1,3-dithiol-2-thione (**29**, 500 mg, 0.992 mmol) and Hg(OAc)₂ (1.164 g, 3.653 mmol) in 50 ml of CHCl₃:HOAc 3:1 was prepared and was stirred under argon overnight. The reaction mixture was filtered through Celite to remove excess Hg(OAc)₂, and the excess acetic acid was removed by extraction with NaHCO₃ (aq, saturated, 3x60ml). The organic phase was then extracted with H₂O (3x60ml) and was then treated with decolorizing carbon. Filtering through Celite and removal of the solvent afforded a pale yellow solid. M.p: 47-48°C; FT-IR (KBr): 2954 (w), 2921 (s), 2848 (s), 2246 (w, CN), 1668 (s, C=O), 1603 (w), 1481 (w), 1460 (m), 1434 (w), 1417 (w), 1327 (w), 1295 (w), 1215 (w), 1192 (w), 1164 (w), 1124 (w), 902 (w), 883 (w), 798 (w), 757 (w), 726 (w), 644 (w), 567 (w), 555 (w), 542 (w), 500 (w), 468 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃): 3.10 (t, *J*= 7.0 Hz, 2H, -SCH₂CH₂CN), 2.92 (t, *J*= 7.4 Hz, 2H, -SCH₂(CH₂)₁₀CH₃), 2.75 (t, *J*= 7.0 Hz, 2H, -CH₂CN), 1.69 (c, *J*= 7.2 Hz, 2H, -SCH₂(CH₂)₉CH₃), 1.5-1.2 (m, 18H, -SCH₂CH₂(CH₂)₉CH₃), 0.90 (t, *J*= 6.6 Hz, 3H, -CH₃) ppm; ¹³C NMR (62.8 MHz, CDCl₃): 187.8 (C=O), 134.0 and 120.5 (C=C), 117.2 (-CN), 36.8, 31.9, 31.8, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1 and 28.5 (-S(CH₂)₁₀CH₂CH₃CH₃CH₂CH₃CN), 18.8 (-SCH₂CH₂CN), 14.1 (-CH₃) ppm.

4-(2-Cyanoethylthio)-5-octadecylthio-1,3-dithiol-2-one (30)

The compound was prepared as a white powder in an analogous way to **31** in a yield of 78%. M.p: 53-54°C; FT-IR (KBr): 2954 (w), 2920 (s), 2848 (s), 2247 (w, CN), 1668 (s, C=O), 1632 (w), 1602 (w), 1482 (w), 1461 (w), 1434 (w), 1327 (w), 1295 (w), 1278 (w), 1222 (w), 1165 (w), 1128 (w), 1023 (w),

957 (w), 903 (m), 883 (w), 800 (w), 751 (w), 726 (w), 644 (w), 567 (w), 555 (w), 543 (w), 476 (w), 461 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃): 3.10 (t, *J*= 7.1 Hz, 2H, -SC<u>H</u>₂CH₂CN), 2.92 (t, *J*= 7.4 Hz, 2H, -SC<u>H</u>₂(CH₂)₁₆CH₃), 2.75 (t, *J*= 7.1 Hz, 2H, -C<u>H</u>₂CN), 1.8-1.2 (m, 32H, -SCH₂ (C<u>H</u>₂)₁₆CH₃), 0.90 (t, *J*= 6.5 Hz, 3H, -C<u>H</u>₃) ppm; ¹³C NMR (62.8 MHz, CDCl₃): 188.8 (<u>C</u>=O), 134.0 and 120.5 (<u>C</u>=<u>C</u>), 117.2 (-<u>C</u>N), 36.8, 32.0, 31.8, 29.7, 29.6, 29.6, 29.5, 29.4, 29.1 and 28.6 (-S(<u>C</u>H₂)₁₆CH₂CH₃ and -S<u>C</u>H₂CH₂CN), 22.7 (-<u>C</u>H₂CH₃), 18.8 (-<u>C</u>H₂CN), 14.1 (-<u>C</u>H₃) ppm.

2-(2-Cyanoethylthio)-6,7-bis(methoxycarbonyl)-3-octadecyl-thiotetrathiafulvalene (4)

A solution of 4,5-bis(methoxycarbonyl)-1,3-dithiol-2-one^[29] (32, 142 mg, 0.606 mmol) and 4-(2cyanoethylene)-5-octadecylthio-1,3-dithiol-2-thione (28, 227 mg, 0.450 mmol) in freshly distilled trimethylphosphite (4 ml) was brought to reflux for 3 hours under an atmosphere of argon. A red solid precipitated from the solution upon cooling. Addition of methanol (20 ml) was performed to precipitate more material, and the suspension was filtered under suction. The resulting solid was purified by flash column chromatography (SiO₂, hexane:CH₂Cl₂ 1:1), affording 123 mg (40 %) of a red solid characterized the desired 2-(2-cyanoethylthio)-6,7-bis(methoxycarbonyl)-3-octadecylas thiotetrathiafulvalene (4); LDI-TOF/MS m/z (%): 689 (M⁺, 100); Calc. For C₃₁H₄₇NO₄S₆; 690.11 g·mol⁻¹, M.p: 82-83°C; FT-IR (KBr): 2952 (w), 2919 (s), 2850 (m), 2246 (w, CN), 1745 (m, C=O), 1708 (m, C=O), 1578 (w), 1434 (m), 1291 (s, C-O), 1093 (w), 1031 (m), 938 (w), 888 (w), 717 (w), 689 (w) cm^{-1} ; ¹H NMR (250 MHz, CDCl₃): 3.88 (s, 6H, -CO₂CH₃), 3.05 (t, J= 7.1 Hz, 2H, -SCH₂CH₂CN), 2.89 (t, J=7.2 Hz, 2H, -SCH₂(CH₂)₁₆CH₃), 2.71 (t, J=7.1 Hz, 2H, -SCH₂CH₂CN), 1.8-1.2 (m, 32H, -SCH₂(CH₂)₁₆CH₃), 0.91 (t, *J*= 6.9 Hz, 3H, -S(CH₂)₁₁CH₃) ppm.

2-(2-Cyanoethylthio)-3-octadecylthiotetrathiafulvalene (5)

A solution of 2-(2-cyanoethylthio)-6,7-bis(methoxycarbonyl)-3-octadecyl-thiotetrathiafulvalene (4) (113 mg, 0.164 mmol) and LiBr (173 mg, 0.173 mmol) in hexamethylphosphoramide (HMPA, 3 ml)

with a drop of H₂O was heated to 80°C, causing evolution of gas (CH₃Br). When no more gas evolved, the mixture was heated to 150°C for 15 minutes, causing a darkening of the solution. After cooling, H₂O (10 ml) was added, and the aqueous phase was extracted successively with hexane until the organic phase was colourless. The combined organic fractions were washed with H₂O and were dried over MgSO₄, filtered, and evaporated to dryness, leaving an orange oil, which was purified by column chromatography on alumina (hexane:CH₂Cl₂ 3:1) and crystallization from MeOH, leaving a brown solid 3 mg (3%) characterized as 2-(2-cyanoethylthio)-3-octadecylthiotetrathiafulvalene (**5**): FT-IR (KBr): 3070 (w), 2919 (s), 2851 (m), 2253 (w, CN), 1470 (w), 1377 (w), 1377 (w), 1277 (w), 115 (w), 893 (w), 775 (w), 718 (w), 645 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃): 6.37 (s, 2H, C=C<u>H</u>), 3.06 (t, *J*= 7.2 Hz, 2H, -SC<u>H₂CH₂CN), 2.89 (t, *J*= 7.2 Hz, 2H, -SC<u>H₂(CH₂)₁₆), 2.72 (t, *J*= 7.4 Hz, -SCH₂C<u>H₂CN</u>), 1.7-1.2 (m, 32H, -(C<u>H₂)₁₆CH₃), 0.91 (t, *J*= 6.6 Hz, -C<u>H₃</u>) ppm.</u></u></u>

Trans- and cis-2,6(7)-bis(2-cyanoethylthio)-3,7(6)-bis(octadecylthio)-tetrathiafulvalene (6 and 8)

A solution of 4-(2-cyanoethylthio)-5-octadecylthio-1,3-dithiol-2-one (**30**) (154 mg, 0.316 mmol) in freshly distilled trimethylphosphite (4 ml) was brought to reflux for 3 hours under an atmosphere of argon. An orange solid precipitated from the solution upon cooling. Addition of methanol (20 ml) was performed to precipitate more material, and the suspension was filtered under suction and washed with methanol. The resulting solid was purified by flash column chromatography (SiO₂, hexane:CH₂Cl₂ 1:1), affording 80 mg (50 %) of an orange solid which was proved to be the *trans* isomer (**6**) and 50 mg (30%) of an orange solid which is the *cis* isomer (**8**), based on polarity and STM studies.

6 – *trans* isomer; LDI-TOF/MS m/z (%): 942.2 (M⁺, 100); Calc. For C₄₈H₈₂N₂S₈; 942.4 g·mol⁻¹, M.p: 116-117°C FT-IR (KBr): 2957 (m), 2920 (s), 2850 (s), 2251 (w, CN), 1491 (w), 1465 (w), 1421 (w), 1384 (w), 1273 (w), 1273 (w), 1230 (w), 1122 (w), 1073 (w), 1040 (w), 895 (w), 799 (w), 773 (w), 729 (w), 465 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃): 3.06 (t, J= 7.2 Hz, 4H, -SCH₂CH₂CN), 2.90 (t, J= 7.4 Hz, 4H, -SCH₂(CH₂)₁₆), 2.73 (t, J= 7.2 Hz, 4H, -CH₂CN), 1.67 (c, J= 7.4 Hz, 4H, -SCH₂CH₂(CH₂)₁₅),

1.5-1.2 (m, 60H, $-(C\underline{H}_2)_{15}CH_3$), 0.91 (t, J= 6.5 Hz, 6H, $-C\underline{H}_3$) ppm; ¹³C NMR (62.8 MHz, CDCl₃): 134.1 (- $\underline{C}SCH_2$), 121.7 (- $\underline{C}SCH_2$), 117.5 (- $\underline{C}N$), 110.6 (central $\underline{C}=\underline{C}$), 36.5, 32.0, 31.3, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.1 and 28.5 (- $S(\underline{C}H_2)_{16}$ + $-S\underline{C}H_2CH_2CN$), 22.7 (- $\underline{C}H_2CH_3$), 18.8 (- $\underline{C}H_2CN$), 14.1 (- $\underline{C}H_3$) ppm.

8 - *cis* isomer; LDI-TOF/MS m/z (%): 942.2 (M⁺, 100); Calc. For C₄₈H₈₂N₂S₈; 942.4 g·mol⁻¹, M.p. 92-93°C; FT-IR (KBr): 2957 (m), 2920 (s), 2850 (s), 2251 (w, CN), 1491 (w), 1465 (w), 1421 (w), 1384 (w), 1273 (w), 1273 (w), 1230 (w), 1122 (w), 1073 (w), 1040 (w), 895 (w), 799 (w), 773 (w), 729 (w), 465 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃): 3.06 (t, *J*= 7.2 Hz, 4H, -SC<u>H</u>₂CH₂CN), 2.89 (t, *J*= 7.4 Hz, 4H, -SC<u>H</u>₂(CH₂)₁₆), 2.73 (t, *J*= 7.2 Hz, 4H, -C<u>H</u>₂CN), 1.67 (c, *J*= 7.4 Hz, 4H, -SCH₂C<u>H</u>₂(CH₂)₁₅), 1.5-1.2 (m, 60H, -(C<u>H</u>₂)₁₅CH₃), 0.91 (t, *J*= 6.5 Hz, 6H, -C<u>H</u>₃) ppm; ¹³C NMR (62.8 MHz, CDCl₃): 133.8 (-<u>C</u>SCH₂), 122.1 (-<u>C</u>SCH₂), 117.5 (-<u>C</u>N), 110.6 (central <u>C</u>=<u>C</u>), 36.5, 32.0, 31.3, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.1 and 28.5 (-S(<u>C</u>H₂)₁₆ + -S<u>C</u>H₂CH₂CN), 22.7 (-<u>C</u>H₂CH₃), 18.8 (-<u>C</u>H₂CN), 14.1 (-<u>C</u>H₃) ppm.

Trans and cis-2,6(7)-Bis(2-cyanoethylthio)-3,7(6)-bis(dodecylthio)tetrathiafulvalene (7 and 9)

The isomer mixture was prepared and purified in an analogous way to **6** using 4-(2-cyanoethylthio)-5dodecylthio-1,3-dithiol-2-one (**31**) (341 mg, 0.849 mmol) in freshly distilled trimethylphosphite (5 ml) for the coupling. After purification 78 mg (25%) and 103 mg (30%) of the of the *trans* (7) and *cis* (9) isomers are obtained, respectively.

7 *trans*-isomer: LDI-TOF/MS *m/z* (%): 774.4 ([M]⁺, 100); Calc. For $C_{36}H_{58}N_2S_8$; 774.2 g·mol⁻¹; FT-IR (KBr): 2951(w), 2920 (f), 2851 (m), 2250 (d, CN), 1493 (w), 1469 (w), 1422 (w), 1410 (w), 1384 (w), 1318 (w), 1277 (w), 1246 (w), 1230 (w), 1078 (w), 891 (w), 774 (w), 744 (w), 719 (w), 733 (w) cm⁻¹. ¹H NMR (250 MHz, CDCl₃): 3.06 (t, *J*= 7.3 Hz, 4H, -SC<u>H</u>₂CH₂CN), 2.90 (t, *J*= 7.3 Hz, 4H, -SC<u>H</u>₂(CH₂)₁₀), 2.72 (t, *J*= 7.3 Hz, 4H, -C<u>H</u>₂CN), 1.67 (c, *J*= 7.3 Hz, 4H, -SCH₂C<u>H</u>₂(CH₂)₉), 1.5-1.2 (m, 36H, -S(CH₂)₂(C<u>H</u>₂)₉), 0.90 (t, *J*= 6.6 Hz, 6H, -C<u>H</u>₃) ppm; ¹³C NMR (62.8 MHz, CDCl₃): 134.1 and 121.7 (-<u>C</u>SCH₂), 117.5 (-<u>C</u>N), 110.5 (<u>C</u>=<u>C</u> central), 36.5, 31.9, 31.3, 29.8, 29.7, 29.6, 29.6, 29.5, 29.4,

29.1 and 28.5 (-S(<u>C</u>H₂)₁₀ and -S<u>C</u>H₂CH₂CN), 22.7 (-S(CH₂)₁₀<u>C</u>H₂CH₃), 18.8 (-SCH₂<u>C</u>H₂CN), 14.1 (-S(CH₂)₁₁<u>C</u>H₃) ppm.

9 *cis* isomer : LDI-TOF/MS *m/z* (%): 774.4 ([M]⁺, 100); Calc. For C₃₆H₅₈N₂S₈; 774.2 g·mol⁻¹; FT-IR (KBr): 2951(w), 2920 (f), 2851 (m), 2250 (d, CN), 1493 (w), 1469 (w), 1422 (w), 1410 (w), 1384 (w), 1318 (w), 1277 (w), 1246 (w), 1230 (w), 1078 (w), 891 (w), 774 (w), 744 (w), 719 (w), 733 (w) cm⁻¹. ¹H NMR (250 MHz, CDCl₃): 3.06 (t, *J*= 7.3 Hz, 4H, -SC<u>H</u>₂CH₂CN), 2.89 (t, *J*= 7.3 Hz, 4H, -SC<u>H</u>₂(CH₂)₁₀), 2.72 (t, *J*= 7.3 Hz, 4H, -C<u>H</u>₂CN), 1.67 (c, *J*= 7.3 Hz, 4H, -SCH₂C<u>H</u>₂(CH₂)₉), 1.5-1.2 (m, 36H, -S(CH₂)₂(C<u>H</u>₂)₉), 0.90 (t, *J*= 6.6 Hz, 6H, -C<u>H</u>₃) ppm; ¹³C NMR (62.8 MHz, CDCl₃): 133.7 and 122.1 (-<u>C</u>SCH₂), 117.5 (-<u>C</u>N), 110.6 (<u>C</u>=<u>C</u> central), 36.4, 31.9, 31.3, 29.8, 29.7, 29.6, 29.6, 29.5, 29.3, 29.1 and 28.5 (-S(<u>C</u>H₂)₁₀ and -S<u>C</u>H₂CH₂CN), 22.7 (-S(CH₂)₁₀<u>C</u>H₂CH₃), 18.7 (-SCH₂<u>C</u>H₂CN), 14.1 (-S(CH₂)₁₁<u>C</u>H₃) ppm.

2,3-Bis(carboxy)-6,7-bis(octadecylthio)tetrathiafulvalene (14)

LiOH·H₂O solution (159 mg, 3.790 mmol in 5 ml H₂O) was added drop wise to a stirred solution of 2.3-bis(octadecylthio)-6.7-bis(methoxycarbonyl)tetrathiafulvalene (12)^[32] (210 mg, 0.240 mmol) in THF (20 ml). After stirring for 12 h, the mixture was diluted with diethyl ether (25 ml) and hydrochloric acid (0.5 M, 10 ml) was added. The resulting dark organic phase was dried (MgSO₄) and the resulting 2,3-bis(octadecylthio)-6,7solid 90%) purple (180)mg, was characterized as bis(carboxy)tetrathiafulvalene. LDI-TOF/MS m/z (%): 816.5 ([M-CO₂H]⁺, 35) and 772.5 ([M-2(CO₂H)]⁺, 100); Calc. For C₄₄H₇₈O₄S₆; 860.4 g·mol⁻¹; M.p. 103-104°C; FT-IR (KBr): 3413 (m), 2955 (m), 2917 (s), 2849 (s), 1667 (m), 1563 (w), 1532 (m), 1470 (m), 1423 (m), 1299 (m), 1201 (w), 888 (w), 849 (w), 774 (w), 719 (w), 673 (w), 501 (w); ¹H NMR (250 MHz, CDCl₃): 7.57 (s, 2H, -CO₂H), 3.00 (m, broad, 4H, -SCH₂), 1.7-1.2 (m, 64H, -SCH₂ (CH₂)₁₆), 1.19 (t, J= 6.9 Hz, 6H, -CH₃) ppm.

2,3-Bis(carboxy)-6,7-bis(dodecylthio)tetrathiafulavlene (15)

A solution of CsOH· (450 mg, 2.60 mmol in 5 ml H₂O) was added drop wise to a stirred solution of 2,3-bis(dodecylthio)-6,7-bis(methoxycarbonyl)tetrathiafulvalene (**13**)^[33] (154 mg, 0.214 mmol) in THF (15 ml). After stirring for 12 h, the mixture was diluted with diethyl ether (25 ml) and hydrochloric acid (0.5 M, 10 ml) was added. The resulting organic phase was dried (MgSO₄) and evaporated leaving a dark pink solid that was purified by column chromatography (SiO₂, MeOH:CH₂Cl₂ 1.5:9) obtaining 18 mg (12%) of a purple solid that was characterized as 2,3-bis(carboxy)-6,7-bis(dodecylthio)-tetrathiafulavlene. LDI-TOF/MS *m/z* (%): 648.3 ([M-CO₂H]⁺, 35) and 604.3 ([M-2(CO₂H)]⁺, 100); Calc. For C₃₂H₅₂O₄S₆; 692.2 g·mol⁻¹; M.p. 98-100°C; FT-IR (KBr): 3437 (m, -OH), 2955 (m), 2919 (s), 2849 (s), 1669 (m, C=O), 1562 (m), 1531 (m), 1467 (m), 1422 (m), 1385 (w), 1297 (m, C-O), 1201 (w), 1045 (w), 889 (w), 773 (w), 727 (w), 673 (w), 501 (w) cm⁻¹; ¹H NMR (250 MHz, acetone-d₆): 7.50 (s, 2H, -CO₂H), 2.93 (m, broad, 4H, -SCH₂), 1.7-1.2 (m, 38H, -SCH₂ (CH₂)₁₀), 0.90 (t, *J*= 6.9 Hz, 6H, -CH₃) ppm.

2,3-Bis(octadecylthio)-6-(methoxycarbonyl)tetrathiafulvalene (16)

A solution of 2,3-bis(octadecylthio)-6,7-bis(methoxycarbonyl)tetrathiafulvalene $(12)^{[32]}$ (200 mg, 0.225 mmol) and LiBr (219 mg, 2.52 mmol) in hexamethylphosphoramide (HMPA, 5 ml) with a drop of H₂O was heated to 80°C, causing evolution of gas (CH₃Br). When no more gas evolved and the mixture is at room temperature, H₂O (10 ml) was added and the aqueous phase was extracted successively with hexane until the organic phase was colourless. The combined organic fractions were washed with H₂O and were dried over MgSO₄, filtered, and evaporated to dryness, leaving an orange oil, which was purified by column chromatography on alumina (hexane) obtaining 161 mg (82%) of an orange solid characterized as **16**. LDI-TOF/MS *m/z* (%): 830.6 ([M]⁺, 100); Calc. For C₄₄H₇₈O₂S₆; 830.4 g·mol⁻¹; M.p. 76-77°C; FT-IR (KBr): 3098 (w), 2956 (m), 2916 (s), 2849 (s), 1726 (m, C=O), 1711 (m, C=O), 1568 (w), 1538 (w), 1467 (m), 1435 (w), 1256 (f, C-O), 1201 (w), 1054 (w), 943 (w), 893 (w), 834 (w), 763 (w), 720 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃): 7.37 (s, 1H, C=C<u>H</u>), 3.84 (s, 3H, -CO₂C<u>H₃</u>), 2.84 (t, *J*=7.3 Hz, 2H, -SC<u>H₂(CH₂)₁₆), 2.83 (t, *J*=7.3 Hz, 2H, -SC<u>H₂(CH₂)₁₆), 1.65 (c, *J*= 7.5 Hz, 4H, -</u></u>

SCH₂C<u>H</u>₂), 1.5-1.2 (m, 36H, -S(CH₂)₂(C<u>H</u>₂)₁₅), 0.91 (t, J= 6.5 Hz, 6H, -CH₂C<u>H</u>₃) ppm; ¹³C NMR (62.8 MHz, CDCl₃): 159.8 (-<u>C</u>O₂CH₃), 132.0 (-<u>C</u>CO₂CH₃), 128.4 and 128.2 (-<u>C</u>SCH₂), 127.5 (-CH), 111.9 and 110.1 (<u>C</u>=<u>C</u> central), 52.8 (-CO₂<u>C</u>H₃), 36.4, 32.0, 29.8, 29.8, 29.7, 29.7, 29.6, 29.4, 29.2 and 28.6 (-S(<u>C</u>H₂)₁₆), 22.7 (-<u>C</u>H₂CH₃) and 14.2 (-CH₂<u>C</u>H₃) ppm.

2,3-Bis(dodecylthio)-6-(methoxycarbonyl)tetrathiafulvalene (17)

This compound was prepared and purified in analogous way to **16** using 2,3-bis(dodedecylthio)-6,7-bis(methoxycarbonyl)tetrathiafulvalene (**13**)^[33] (723 mg, 1.016 mmol) and LiBr (975 mg, 11.226 mmol) in hexamethylphosphoramide (HMPA, 10 ml) with a drop of H₂O for the monodemethoxycarbonylation reaction in a yield of 75%. LDI-TOF/MS *m/z* (%): 662.4 ($[M]^+$, 100); Calc. For C₃₂H₅₄O₂S₆; 662.2 g·mol⁻¹; M.p. 55-58°C; FT-IR (KBr): 3098 (w), 2956 (m), 2919 (s), 2848 (s), 1726 (m, C=O), 1711 (m, C=O), 1568 (w), 1537 (w), 1466 (m), 1435 (w), 1384 (w), 1256 (f, C-O), 1200 (w), 1053 (w), 943 (w), 892 (w), 833 (w), 804 (w), 764 (w), 728 (w), 662 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃): 7.38 (s, 1H, C=C<u>H</u>), 3.84 (s, 3H, -CO₂C<u>H</u>₃), 2.84 (t, *J*=7.3 Hz, 2H, -SC<u>H₂(CH₂)₁₀), 2.83 (t, *J*=7.3 Hz, 2H, -SC<u>H₂(CH₂)₁₀), 1.65 (c, *J*= 7.5 Hz, 4H, -SCH₂C<u>H₂), 1.5-1.2 (m, 36H, -S(CH₂)₂(C<u>H₂)₉), 0.91 (t, *J*= 6.5 Hz, 6H, -CH₂C<u>H₃) ppm</u>; ¹³C NMR (62.8 MHz, CDCl₃): 159.8 (-<u>CO₂CH₃), 132.0 (-<u>C</u>CO₂CH₃), 128.4 and 128.2 (-<u>C</u>SCH₂), 127.5 (-CH), 111.8 and 110.1 (central <u>C</u>=C), 52.7 (-CO₂C<u>H₃), 36.4, 32.0, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.4, 29.2 and 28.5 (-S(C<u>H</u>₂)₁₀), 22.7 (-<u>C</u>H₂CH₃) and 14.1 (-CH₂<u>C</u>H₃) ppm.</u></u></u></u></u></u>

2,3-Bis(octadecylthio)-6-(carboxy)tetrathiafulvalene (18)

The compound was prepared as purple solid in an analogous way to **14** using 2,3-bis(octadecylthio)-6-(methoxycarbonyl)tetrathiafulvalene (**16**) (129 mg, 0.147 mmol, in 20 ml THF) and LiOH·H₂O (169 mg, 4.028 mmol in 5 ml H₂O) in a yield of 89%. LDI-TOF/MS *m/z* (%): 816.4 ($[M]^+$, 10), 772.4 ($[M-CO_2H]^+$, 100); Calc. For C₄₃H₇₆O₄S₆; 816.4 g·mol⁻¹; M.p. 97-98°C; FT-IR (KBr): 3434 (m), 2917 (s), 2849 (s), 1669 (m), 1563 (w), 1532 (m), 1470 (m), 1423 (m), 1365 (w), 1299 (m), 1201 (w), 1045 (w), 889 (w), 849 (w), 774 (w), 719 (w), 673 (w), 500 (w); ¹H NMR (250 MHz, CDCl₃): 7.58 (s, 1H, - CO₂<u>H</u>), 6.87 (s, 1H, C=C<u>H</u>), 3.00 (m, broad, 4H, -SC<u>H</u>₂), 1.7-1.2 (m, 64H, -SCH₂(C<u>H</u>₂)₁₆), 1.19 (t, *J*= 6.5 Hz, -C<u>H</u>₃) ppm.

2,3-Bis(dodecylthio)-6-(carboxy)tetrathiafulvalene (19)

The compound was prepared as purple solid in an analogous way to **14** using 2,3-bis(dodedecylthio)-6-(methoxycarbonyl)tetrathiafulvalene (**17**) (180 mg, 0.271 mmol, in 20 ml THF) and LiOH·H₂O (153 mg, 3.646 mmol in 5 ml H₂O) in a yield of 99%. LDI-TOF/MS *m/z* (%): 648.3 ($[M]^+$, 60), 604.3 ($[M-CO_2H]^+$, 100); Calc. For C₃₁H₅₂O₂S₆; 648.2 g·mol⁻¹; M.p. 96-97°C; FT-IR (KBr): 3700-3200 (d, broad, OH), 2955 (m), 2920 (s), 2850 (m), 1668 (m, C=O), 1562 (w), 1531 (w), 1467 (w), 1422 (w), 1297 (w), 1201 (w), 1045 (w), 888 (w), 848 (w), 819 (w), 773 (w), 727 (w), 673 (w), 501 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃): 7.51 (s, 1H, -CO₂H), 7.01 (s, 1H, C=C<u>H</u>), 2.84 (t, broad, 4H, -SC<u>H₂), 1.65 (c, *J*= 6.7 Hz, 4H, -SCH₂C<u>H₂), 1.50-1.20 (m, 36H, -S(CH₂)₂(C<u>H₂)₉), 0.91 (t, *J*= 6.5 Hz, -C<u>H₃) ppm.</u></u></u></u>

2,3-Bis(octadecylthio)tetrathiafulvalene (20)

Compound **20** was prepared and purified in analogous way to **5** using 2,3-bis(octadecylthio)-6,7-bis(methoxycarbonyl)tetrathiafulvalene (**12**)^[32] (512 mg, 0.576 mmol) and LiBr (714 mg, 8.221 mmol) in hexamethylphosphoramide (HMPA, 7 ml) with a drop of H₂O in a yield of 40%. LDI-TOF/MS *m/z* (%):772.6 (M⁺, 30); Calc. For C₄₂H₇₆S₆; 772.4 g·mol⁻¹; M.p. 75-76°C; FT-IR (KBr): 3064 (w), 2954 (w), 2916 (w), 2850 (s), 1470 (w), 1411 (w), 1296 (w), 1257 (w), 1084 (w), 890 (w), 793 (w), 774 (w), 758 (w), 720 (w), 646 (w), 640 (w) cm⁻¹; ¹H NMR(250 MHz, CDCl₃): 6.34 (s, 2H, C=C<u>H</u>), 2.84 (t, *J*= 7.3 Hz, 4H, -SC<u>H₂(CH₂)₁₆CH₃), 1.65 (c, *J*= 7.0 Hz, 4H, -SCH₂C<u>H₂(CH₂)₁₅CH₃), 1.5-1.2 (m, 60H, -S(CH₂)₂(C<u>H₂)₁₅CH₃), 0.91 (t, *J*= 6.2 Hz, 6H, -S(CH₂)₁₇C<u>H₃) ppm</u>; ¹³C NMR (62.8 MHz, CDCl₃): 128.0 and 119.0 (<u>C=C</u> laterals), 114.3 and 106.5 (<u>C=C</u> central), 36.3, 32.0, 29.8, 29.8, 29.7, 29.7, 29.6, 29.4, 29.2 and 28.6 (-S(CH₂)₁₆), 22.7 (-<u>C</u>H₂CH₃) and 14.1 (-CH₂<u>C</u>H₃) ppm.</u></u></u>

4,5-Bis(dodecylthio)-1,3-dithiole-2-thione (35)

To a solution of bis(tetrabutylammonium)-bis(2-thioxo-1,3-dithiole-4,5-dithiolato)zincate^[28] (25) (20.70 g, 22 mmol) in MeCN (300 ml) was added 1-bromododecane (25 ml, 97 mmol) and the mixture was refluxed for 1h. The resulting solution was cooled to room temperature and the precipitated yellow solid was separated, washed with H₂O (2 x 20 ml) and MeOH (2 x 20 ml) and recrystallised from EtOAc affording 20.02 g (85%) of yellow crystals characterized as 4,5-bis(dodecylthio)-1,3-dithiole-2-thione (**35**). M.p. 57-58°C; FT-IR (KBr): 2954 (s), 2917 (s), 2848 (s), 1470 (m), 1414 (w), 1291 (w), 1059 (s, C=S), 1028 (m), 889 (w), 824 (w), 718 (m), 517 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃): 2.89 (t, *J*= 7.3 Hz, 4H, -SCH₂), 1.69 (c, *J*= 7.5 Hz, 4H, -SCH₂CH₂), 1.50-1.20 (m, 36H, -S(CH₂)₂(CH₂)₉CH₃), 0.90 (t, *J*= 6.9 Hz, 6H, -S(CH₂)₁₁CH₃) ppm; ¹³C NMR (62.8 MHz, CDCl₃): 211.4 (C=S), 136.4 (C=C), 36.8, 32.0, 29.7, 29.7, 29.6, 29.5, 29.4, 29.1 and 28.5 (-S(CH₂)₁₀), 22.7 (-CH₂CH₃), 14.1 (-CH₃) ppm.

2,3-Bis(2-cyanoethylthio)-6,7-bis(dodecylthio)tetrathiafulvalene (11)

A solution of 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one (**33**)^[26] (356 mg, 1.26 mmol) and 4,5bis(dodecylthio)-1,3-dithiole-2-thione (**35**) (738 mg, 1.34 mmol) in freshly distilled trimethylphosphite (5 ml) was brought to reflux for 4 hours under an atmosphere of argon. An orange solid precipitated from the solution upon cooling. Addition of MeOH (20 ml) was performed to precipitate more material, and the suspension was filtered under suction. The resulting solid was purified by flash column chromatography (SiO₂, hexane:CH₂Cl₂ 1:2), affording 556 mg (54 %) of an orange solid characterized as the desired compound; LDI-TOF/MS m/z (%):774.4 (M⁺, 100); Calc. For C₃₆H₅₈N₂S₈; 774.2 g·mol⁻¹; M.p. 111°C; FT-IR (KBr): 2929 (s), 2850 (m), 2246 (d, C=N), 1469 (m), 1416 (m), 1159 (w), 889 (w), 718 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃): 3.11 (t, *J*= 7.1 Hz, 4H, -SC<u>H₂CH₂CN), 2.85 (t, *J*= 7.3 Hz, 4H, -SC<u>H₂(CH₂)₁₀), 2.80 (t, *J*= 7.1 Hz, 4H, -C<u>H₂CN), 1.66 (c, *J*= 7.6 Hz, 4H, -SCH₂C<u>H₂(CH₂)₉), 1.5-</u> 1.2 (m, 36H, -S(CH₂)₂(C<u>H₂)₉), 0.91 (t, *J*= 6.4 Hz, 6H, -C<u>H₃) ppm; ¹³C NMR (62.8 MHz, CDCl₃): 128.0 and 127.9 (-<u>C</u>SCH₂), 117.4 (-<u>C</u>N), 114.8 and 106.3 (central C=C), 36.4, 31.9, 31.3, 29.7, 29.4, 29.2 and 28.5 (-S(<u>CH₂)₁₀+ -S<u>C</u>H₂CH₂CN), 22.7 (-<u>C</u>H₂CH₃), 18.9 (-<u>C</u>H₂CN), 14.1 <u>C</u>H₃) ppm.</u></u></u></u></u></u>

4,5-Bis(docosylthio)-1,3-dithiole-2-thione

In an analogous way to **35** using bis(tetrabutylammonium)-bis(2-thioxo-1,3-dithiole-4,5dithiolato)zincate^[28] (**25**) (1.19 g, 1.27 mmol) in MeCN (100 ml) and adding 1-bromodocosane (2.26 g, 5.79 mmol) The beige solid that precipitated from the reaction mixture was filtered and washed with H₂O (2x20 ml) and MeOH (2x20ml). Recrystallisation from ethyl acetate afforded 1.75 g (85%) of yellow solid; M.p. 87-88°C; FT-IR (KBr): 2956 (w), 2917 (s), 2849 (m), 1471 (m), 1414 (w), 1291 (w), 1060 (s, C=S), 889 (w), 717 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃): 2.89 (t, *J*= 7.3 Hz, 4H, -SC<u>H₂</u>), 1.75-1.20 (m, 80H, -SCH₂(C<u>H₂</u>)₂₀), 0.91 (t, *J*= 6.3, 6H, -C<u>H₃</u>) ppm.

2,3,5,7-Tetrakis(docosylthio)-tetrathiafulvalene (22)

4,5-Bis(docosylthio)-1,3-dithiole-2-thione was treated with Hg(OAc)₂ in an analogous way to **31** to afford 4,5-docosylthio-1,3-dithiol-2-one in 78% yield. Without further his compound was coupled as for the preparation of **6** and **8** using refluxing trimethylphosphite. Recrystallisation from MeOH/CH₂Cl₂ afforded the product as an orange solid in 90% yield. M.p. 89-90°C; LDI-TOF/MS *m/z* (%): 1565.3; Calc. For C₉₄H₁₈₀S₈; 1565.2 g·mol⁻¹; FT-IR (KBr): 2956 (m), 2917 (s), 2850 (m), 1471 (m), 1416 (w), 1376 (w), 247 (w), 1038 (w), 887 (w), 717 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃): 2.84 (t, *J*= 7.5 Hz, 8H, -SCH₂), 1.75-1.20 (m, 160H, -SCH₂(CH₂)₂₀), 0.91 (t, *J*= 6.3, 12H, -CH₃) ppm.