Complete Sequential Functionalization of Monopyrrolo[tetrathiophenalenes

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Abstract: Introduction of aldehyde and ketone functional groups into the \( \alpha \)-positions of monopyrrolo[tetrathiophenalenes provides a novel method for a stepwise and selective penta-functionalization of monopyrrolo[tetrathiophenalene derivatives.

Key words: aldehyde, functionalization, ketone, pyrrole, tetrathiophenalene

Tetrathiophenalene\(^1\) (TTF, Figure 1) is a well established molecule whose interest goes beyond the field of materials chemistry. Its derivatives were originally prepared as strong electron-donor molecules for the development of electrically conducting materials.\(^2,3\) In the last decades, large synthetic efforts have been devoted to the preparation of molecular, macromolecular,\(^4\) and supramolecular\(^5\) systems based on TTF and its derivatives. The ongoing quest for these materials has promoted much research in the development of new TTF building blocks which are nowadays used in systems such as cyclophanes,\(^6\) chemical sensors,\(^7\) catalysts,\(^8\) switches,\(^9\) and electronic devices.\(^10\) Thus, one of the most successful modifications has been the annelation of a pyrrole ring directly onto the TTF skeleton affording (Figure 1) the monopyrrolo[3,4-\(d\)]tetrathiophenalenes (MPTTF) 2. Derivatives of MPTTF, such as 3 (Scheme 1) carrying cyanoethyl thiolate and tosyl protecting groups, have proven to be some of the most useful building blocks in TTF chemistry.\(^11\)

On account of effective N- and S-alkylations, it is possible to functionalize (Figure 2a) the MPTTF unit in the 5-, 4'-, and 5'-positions and several cyclophanes,\(^12\) cage molecules,\(^13\) and amphiphilic bistable \([2]\)rotaxanes\(^14\) have been prepared from MPTTF building blocks. However, the potential for functionalizing the MPTTF unit in its 4- and 6-position (Figure 2b) has only very recently been pursued\(^15\) and has mainly been conducted under strongly basic conditions\(^16\) using LDA rendering this method less convenient for the preparation of systems containing functional groups sensitive to strong base. Although the progress in molecular, macromolecular, and supramolecular TTF chemistry has been revolutionized by an ongoing development of new TTF building blocks there is still a quest for further developments allowing new and even more complicated TTF systems to be prepared under mild conditions.

Here, we report such an accomplishment by describing a synthetic method that allows the MPTTF building block 3 to be functionalized sequentially in all of its five possible attachments sites under mild conditions in a chronological manner as shown in Scheme 1. Firstly, the MPTTF building block can be functionalized in two separate steps at position I and II, followed by functionalization at position III. Finally, the two \( \alpha \)-positions, i.e., positions IV and V, on the pyrrole ring can be functionalized in a stepwise manner by the introduction of either dithiocacetol or dithioketal substituents which act as masked aldehyde or ketone functional groups, respectively. Introduction of such reactive handles in the IV- and V-positions creates not only novel MPTTF derivatives, but also potentially useful building blocks on account of the wide range of chemical reactions – such as oxidation and reduction reactions,\(^17\) Wittig reactions,\(^18\) and imine\(^19\) formation to mention just a few examples – which can be carried out on aldehyde and ketone functionalities.

Generally, carbonyl functional groups can be introduced into the \( \alpha \)-position of pyrrole derivatives in a single syn-
thetic step by reactions such as the Vilsmeier formylation. Unfortunately, these types of reactions only allow one carbonyl group to be introduced because of the strong deactivating effect of carbonyl groups toward subsequent electrophilic aromatic substitution reactions. However, bisacylated pyrrole derivatives can be accessed by a synthetic approach reported by Barbero and co-workers in the early 1990’s. In a two step synthetic procedure α,α’-bisacylation can be carried out by 1) treatment of pyrrole derivatives with benzodithiol-2-ylium tetrafluoroborate salts; followed by 2) deprotection of the resulting dithioacetals or dithioketals affording the bisacylated pyrrole derivatives. By combining this method with the well established N- and S-alkylations of MPTTF derivatives, we have devised a synthetic protocol for sequential functionalization of the MPTTF building block at all of its five possible attachments sites as outlined in Scheme 2. Treatment of with one equivalent of cesium hydroxide generates the MPTTF-monothiolate selectively, without interfering with the tosyl protecting group. This MPTTF-monothiolate can thereafter be alkylated with an alkylating reagent (R1X) affording the alkylthio-MPTTF derivative. The tosyl protecting group on the MPTTF unit can be removed by using sodium methoxide and the resultant pyrrole nitrogen in can be alkylated with a third alkylating reagent (R3X) providing the MPTTF derivative. Further functionalization of the MPTTF unit to the bis-aldehyde/ketone can be achieved (Scheme 2) in three separate steps. Firstly, a bisthioacetal/bisthioketal group can be introduced by treatment of 7 with the benzodithiol-2-ylium tetrafluoroborate salt carrying R4. Secondly, another bisthioacetal/bisthioketal group can be introduced by treatment of 9 with the benzodithiol-2-ylium tetrafluoroborate salt carrying R5 affording the MPTTF derivative. Finally, the two bisthioacetal/bisthioketal protecting groups in 11 can be removed using mercury(II) acetate giving the pentafunctionalized MPTTF derivative.

In principle two different alkyl groups (R1 and R2) can be introduced (Scheme 1) into position I and II by deprotection of the two cyanoethyl thiolate protecting group followed by realkylation of the resulting thiolates. However, for simplicity we have chosen to alkylate these two positions with identical alkylating reagents as shown in Scheme 1. In this paper, pentyl bromide (C5H11Br) was used as the alkylating reagent which could be coupled with the MPTTF building block following its in situ (THF/MeOH) deprotection with one equivalent of cesium hydroxide monohydrate (CsOH·H2O) to give in 79% yield. Subsequently, the remaining cyanoethyl protecting group in was deprotected using one equivalent of CsOH·H2O followed by addition of C5H11Br, which effected the second deprotection/alkylation sequence, affording 14 in 82% yield. Deprotection of the tosyl group was carried out in near quantitative yield by stirring at 50 °C in a 1:1 mixture of THF–MeOH in the presence of an excess of sodium methoxide. Introduction of the alkyl (methyl and propyl) groups onto the pyrrole nitrogen of...
the TTF derivative 15 was easily carried out (Scheme 3) at 0 °C by deprotonation with sodium hydride followed by reaction with either methyl iodide or propyl bromide. Both products 16 and 17 were easily purified and obtained in high yields of 96% and 93%, respectively.

Functionalization of the MPTTF derivatives 16 and 17 at the 4-position could be achieved selectively (Scheme 4) by controlling the reaction conditions. Treatment of 16 with one equivalent of 1,3-benzodithiol-2-ylium tetrafluoroborate (18) in acetonitrile and pyridine as base gave the dithioacetal 20 in 53% yield; the reaction was completed within one hour. Similarly, the reaction of 16 with one equivalent of 2-phenyl-1,3-benzodithiol-2-ylium tetrafluoroborate (19) under identical conditions gave the dithioacetal 21 in a 65% yield. In both cases, electrophilic aromatic substitution took place at both the 4- and 6-positions thus reducing the yield of the desired products. It should also be noted that under these conditions, the reaction did not go to completion and consequently a small amount of starting material was isolated during purification. Similar reactions were carried out on the N-propyl derivative 17 and the products 22 and 23 were obtained in good yields of 61% and 75%, respectively.

Deprotection of the dithioacetals (20 and 22) and dithioketals (21 and 23) into their corresponding aldehydes (24 and 26) and ketones (25 and 27) were achieved (Scheme 4) by using mercury(II) acetate in DMSO at 100 °C. All the reactions took place within 2 hours and the products were obtained in good yields (69–78%).

The syntheses of the dialdehydes (32 and 34) and diketones (33 and 35), i.e., functionalization at both the 4- and 6-positions, were carried out in two alternative ways. The first strategy (Scheme 4, Method B) employed the MPTTF derivatives (20–23) as starting material and an excess of the respective salts (18 and 19) with either stirring at room temperature or by stirring under reflux. Thus 20 was reacted with 2.5 equivalents of 1,3-benzodithiol-2-ylium tetrafluoroborate (18) in acetonitrile to yield the bis-dithioacetal 28. The propyl analogue 22 reacted under similar conditions to give 30. It was envisaged that 2-phenyl-1,3-benzodithiol-2-ylium tetrafluoroborate (19) would show similar reactivity with 21 and 23 under the conditions described above. In the case of 21 the product 29 was easily formed at room temperature in good yields. However, when identical conditions were applied on 23, only a small amount of product 31 was obtained as indicated by TLC analysis. Consequently, a larger amount of 2-phenyl-1,3-benzodithio-2-ylium tetrafluoroborate (19) (up to 5 equiv) was added and a good yield was obtained only after heating the mixture under reflux for 10 hours. Compounds 28 to 31 were obtained in moderate to good yields (60–80%).

In the second strategy (Scheme 4, Method A), bis-functionalization of the MPTTF derivatives 16 and 17 directly at the 4- and 6-positions was carried out in a one-pot reaction. Thus, compounds 16 and 17 were reacted with 1,3-benzodithiol-2-ylium tetrafluoroborate (18) at room temperature and afforded the products 28 and 30, respectively. Also, the reaction of 16 with excess 2-phenyl-1,3-benzodithiol-2-ylium tetrafluoroborate (19) proceeded smoothly and product 29 was obtained in a reasonable yield. However, harsher conditions (5 equiv of 19 and 10 h of heating under reflux) had to be used when 17 was reacted with 2-phenyl-1,3-benzodithiol-2-ylium tetrafluoroborate (19) to obtain 31. The difference can most likely be attributed to steric hindrance. All products were obtained in reasonable yields (48–74%).

Finally, deprotection (Scheme 4) of the bisdithioacetals 28 and 30 and bisdithioketals 29 and 31 into their respective aldehydes (32 and 34) and ketones (33 and 35) were carried out by using mercury(II) acetate in DMSO at 100 °C. The reactions took place within two hours and all products were obtained in good yields (72–78%).

In conclusion, we have successfully developed a synthetic method that allows the MPTTF building block 3 to be functionalized sequentially in all of its five possible positions under mild conditions. The synthetic routes allow selective introduction of either one or two aldehyde or ketone functional groups on the MPTTF unit depending on the reaction conditions used. It can therefore be extrapolated that five totally different groups can be introduced using this sequence of reactions, a finding which undeni-
ably is important for the future development of molecular and supramolecular systems based on TTF.

All reactions were carried out under an anhyd argon atmosphere in an oven dried round bottomed flask. Chemicals were purchased from commercial sources and were used as received except com-

pounds 3 and 19 which were prepared according to literature

procedures. Solvents were dried according to literature proce-

dures.23 TLC was carried out using aluminium sheets pre-coated

with silica gel 60 F254 (Merck 5554). The plates were inspected un-

der UV light (254 nm) and, if required, developed in I2 vapor. Col-

umn chromatography was carried out using silica gel 60F (Merck

9385, 0.040–0.063 mm). Melting points were determined on a Bü-

chi melting point apparatus and are uncorrected. 1H NMR (300

MHz) and 13C NMR (75 MHz) spectra were recorded on a Gemini-

300BB instrument, using TMS or the residual solvent as the internal

standard which were assigned on the basis of Nudelman.24 Fourier

transform matrix-assisted laser-desorption/ionization mass spec-

trometry (FT–MALDI–MS) was performed on an IonSpec 4.7 tesla

Ultima Fourier Transform mass spectrometer, utilizing a 2,5-dihy-

droxybenzoic acid (DHB) matrix. Microanalyses were performed

by the Atlantic Microlab, Inc., Atlanta, Georgia, USA.

2-[4-(2-Cyanoethylthio)-5-pentylthio-1,3-dithiole-2-yliden]-5-

tosyl-(1,3)-dithiolo[4,5-c]pyrrole (13)

A solution of compound 3 (0.28 g, 0.50 mmol) in anhyd THF (40

mL) was degassed (N 2, 10 min) and a solution of CsOH·H 2O

(88 mg, 0.53 mmol) in anhyd MeOH (1 mL) was added dropwise

over a period of 1 h. The mixture was stirred for 15 min and C5H11Br

(91 mg, 0.074 mL, 0.60 mmol) was added in one portion. The reac-

tion mixture was stirred for a further 5 h. The solvent was evaporat-

ed and the resulting yellow residue was dissolved in CH 2Cl2

(100 mL), washed with H2O (3 × 50 mL) and dried (MgSO4). Evap-

oration of the solvent gave a yellow solid, which was purified by

column chromatography (250 mL SiO2, ∆ = 6 cm; CH2Cl2–cyclo-

hexane, 9:1) to give the title compound 13 as a yellow powder;

yield: 0.23 g (79%); mp 105–109 °C.

1H NMR (CDCl3/TMS): δ = 0.90 (t, 3 H, J = 7.0 Hz), 1.25–1.45 (m,

4 H), 1.57–1.70 (m, 2 H), 2.41 (s, 3 H), 2.67 (t, 2 H, J = 7.4 Hz),

2.85 (t, 2 H, J = 7.4 Hz), 3.01 (t, 2 H, J = 7.3 Hz), 6.94 (s, 2 H), 7.30

(d, 2 H, J = 8.2 Hz), 7.73 (d, 2 H, J = 8.2 Hz).

13C NMR (CDCl3/TMS): δ = 13.9, 18.6, 21.6, 22.1, 29.4, 30.5, 31.2,

36.3, 111.2, 111.3, 113.5, 117.4, 118.3, 121.5, 126.8 (two overlapping

peaks), 126.9, 130.1, 133.4, 135.2, 145.5.

FT–MALDI-MS: m/z (%) = 583 (M+, 90).
2-[4-[5-Bis(pentylthio)-1,3-dithiole-2-yliden]-5-tosyl-(1,3)-dithiolo[4,5-c]pyrrole (14)
A solution of compound 13 (0.20 g, 0.34 mmol) in anhyd THF (40 mL) was degassed (N2, 10 min) and a solution of CsOH·H2O (60.0 mg, 0.36 mmol) in MeOH (1 mL) was added dropwise over a period of 1 h. The mixture was stirred for 15 min and CH3Br (56 mg, 0.046 mL, 0.37 mmol) was added in one portion and the reaction mixture was stirred for 5 h. The solvent was evaporated and the resulting yellow residue was dissolved in CH2Cl2 (70 mL), washed with H2O (2×50 mL) and dried (MgSO4). Evaporation of the solvent gave a yellow solid, which was purified by column chromatography (200 mL SiO2, δ = 6 cm; cyclohexane·CH2Cl2, 3:2) to give the title compound 14 as a yellow powdery solid; yield: 0.17 g (82%); mp 80–83 °C (Lit.22 79–81 °C).

H NMR (CDCl3/TMS): δ = 8.09 (t, 6 H, J = 1.7 Hz), 1.25–1.45 (m, 8 H), 1.61 (quintet, 4 H, J = 7.2 Hz), 2.41 (s, 3 H), 2.79 (t, 4 H, J = 7.4 Hz), 6.92 (s, 2 H), 7.29 (d, 2 H, J = 8.3 Hz), 7.72 (d, 2 H, J = 8.3 Hz).


FT-MALDI-HRMS: m/z calcd for C19H27NS6 (461.0462); found, 461.0469 (M+, 9%).

Anal. Calcd for C19H27NS6 (461.0462): C, 49.42; H, 5.89; N, 3.03; S, 41.66. Found: C, 49.55; H, 5.92; N, 3.03; S, 41.80.

5-Propyl-2-[4,5-bis(pentylthio)-1,3-dithiole-2-yliden]-(1,3)-dithiole[4,5-c]pyrrole (17)
Compound 15 (2.40 g, 5.30 mmol) was dissolved in anhyd DMF (20 mL) and the solution degassed with N2 for 15 min. C,H5Br (6.60 g, 50 mmol) was added, the mixture cooled to 0 °C in an ice/salt bath whereupon hexane washed NaH (0.69 g, 17.2 mmol) was added. The reaction mixture was stirred for 1 h at 0 °C, poured onto ice, extracted with CH3Cl (3×50 mL), and the extracts were dried (MgSO4). Evaporation of the solvent gave the crude product, which was purified by column chromatography (400 mL SiO2, δ = 6 cm; CH2Cl2–petroleum ether, 1:1) to give the title compound 17 as a yellow oil; yield: 2.49 g (93%).

1H NMR (CDCl3/TMS): δ = 0.92 (t, 9 H, J = 7.1 Hz), 1.29–1.42 (m, 8 H), 1.62 (quintet, 4 H, J = 7.2 Hz), 1.75 (sextet, 2 H, J = 7.3 Hz), 2.82 (t, 2 H, J = 7.2 Hz), 3.80 (br s, 2 H, J = 6.96) (s, 2 H).

13C NMR (CDCl3/TMS): δ = 11.1, 13.9, 22.1, 29.4, 30.7, 30.9, 36.2, 112.3, 118.5 (2 overlapping peaks), 127.4 (2 overlapping peaks).

FT-MALDI-MS: m/z (%) = 489 (M+, 100).

FT-MALDI-HRMS: m/z calcd for C21H31NS6 (489.0775); found, 489.0765.

Anal. Calcd for C21H31NS6 (489.0775): C, 51.49; H, 6.38; N, 3.08; S, 41.92. Found: C, 51.67; H, 6.51; N, 2.88; S, 39.42.

2-[4-[5-Bis(pentylthio)-1,3-dithiole-2-yliden]-1-(3,3-dimethyl)-1,3-dithiole[4,5-c]pyrrole (15)
A solution of compound 14 (2.41 g, 4.01 mmol) in anhyd THF (120 mL) and anhyd MeOH (40 mL) was degassed (N2, 15 min); NaOMe (25% solution in MeOH; 9.1 mL, 2.16 g, 40.0 mmol) was added in one portion. The yellow mixture was heated at 50 °C for 1 h. After cooling to r.t., H2O (200 mL) was added, the mixture was extracted with CH2Cl2 (3×100 mL) and the extracts were dried (MgSO4). Evaporation of the solvent gave an orange oil, which was purified by column chromatography (500 mL SiO2, δ = 6 cm; CH2Cl2·cyclohexane 1:1) to give the title compound 15 as an orange oil; yield: 1.75 g (98%); mp 96–98 °C (Lit.22 92–94 °C).

H NMR (CDCl3/TMS): δ = 0.90 (t, 6 H, J = 1.7 Hz), 1.25–1.45 (m, 8 H), 1.63 (quintet, 4 H, J = 7.2 Hz), 2.82 (t, 4 H, J = 7.4 Hz), 6.60 (d, 2 H, J = 2.3 Hz), 8.19 (s, 1 H).

13C NMR (CDCl3/TMS): δ = 13.9, 22.1, 29.4, 30.6, 36.2, 109.7, 111.5, 119.8, 120.0, 127.3.

5-Methyl-2-[4,5-bis(pentylthio)-1,3-dithiole-2-yliden]-(1,3)-dithiole[4,5-c]pyrrole (16)
Compound 15 (2.20 g, 4.92 mmol) was dissolved in anhyd DMF (20 mL) and the solution degassed with N2 for 15 min. MeI (0.69 g, 49.22 mmol) was added; the mixture cooled to 0 °C in an ice/salt bath whereupon hexane washed NaH (0.69 g, 17.22 mmol) was added. The reaction mixture was stirred for 1 h and then purged with N2 to evaporate the excess MeI. The mixture was poured onto ice, extracted with CH2Cl2 (3×50 mL) and dried (MgSO4). Evaporation of the solvent gave the crude product, which was purified by column chromatography (400 mL SiO2, δ = 6 cm; CH2Cl2·petroleum ether, 1:1) to give the title compound 16 as a yellow oil; yield: 2.20 g (96%).

H NMR (CDCl3/TMS): δ = 0.92 (t, 6 H, J = 7.0 Hz), 1.28–1.46 (m, 8 H), 1.63 (quintet, 4 H, J = 7.0 Hz), 2.83 (t, 4 H, J = 7.0 Hz), 3.65 (br s, 3 H), 6.42 (s, 2 H).

13C NMR (CDCl3/TMS): δ = 13.9, 22.3, 29.4, 30.7, 36.2, 37.2, 113.4, 118.8 (2 overlapping peaks), 127.4 (2 overlapping peaks).

FT-MALDI-MS: m/z (%) = 461 (M+,* 90).

FT-MALDI-HRMS: m/z calcd for C14H17NS5 (461.0449), 461.0462; found, 461.0449.
H. Gopee et al.  

\textbf{PAPER}  

\begin{table}[h]  
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\begin{tabular}{|c|c|c|}  
\hline  
\textbf{Compound} & \textbf{1H NMR (CDCl$_3$/TMS)}: & \textbf{13C NMR (CDCl$_3$/TMS)}: \\
\hline  
\textbf{17} & $\delta = 0.85-0.96$ (m, 9 H), 1.25-1.41 (m, 8 H), 1.65 (quintet, 4 H, $J = 7.2$ Hz), 1.75 (sextet, 2 H, $J = 7.0$ Hz), 2.78 (t, 2 H, $J = 7.2$ Hz), 3.79 (br s, 2 H), 6.38 (s, 1 H), 6.44 (s, 1 H), 7.05 (dd, 2 H, $J = 9.1, 3.3$ Hz), 7.23 (dd, 2 H, $J = 9.1, 3.3$ Hz) & $\delta = 11.1, 13.9$ (2 overlapping peaks), 22.2 (2 overlapping peaks), 25.4 (2 overlapping peaks), 29.4 (2 overlapping peaks), 30.7 (2 overlapping peaks), 36.2 (2 overlapping peaks), 49.0, 119.9, 120.1, 120.3, 120.9, 122.5 (2 overlapping peaks), 126.1 (2 overlapping peaks), 127.1, 127.3, 127.4. \\
\hline  
\textbf{22} & $\delta = 0.87-0.97$ (m, 6 H), 1.29-1.44 (m, 8 H), 1.56-1.71 (m, 4 H), 2.83 (m, 4 H), 3.60 (br s, 3 H), 6.44 (s, 1 H), 7.09 (dd, 2 H, $J = 8.9, 3.2$ Hz), 7.24 (dd, 2 H, $J = 8.9, 3.2$ Hz), 7.28-7.37 (m, 3 H), 7.59-7.66 (m, 2 H) & $\delta = 11.0, 14.0$ (2 overlapping peaks), 22.2 (2 overlapping peaks), 29.4 (2 overlapping peaks), 30.6 (2 overlapping peaks), 30.7 (2 overlapping peaks), 36.2 (2 overlapping peaks), 49.3, 116.6, 122.6, 126.3 (2 overlapping peaks), 127.5, 127.6, 127.8, 128.7 (2 overlapping peaks), 128.8 (2 overlapping peaks), 137.5, 138.3, 138.5. \\
\hline  
\textbf{25} & $\delta = 0.70$ (m, 6 H), 1.29-1.42 (m, 8 H), 1.56-1.71 (m, 4 H), 2.83 (m, 4 H), 3.60 (br s, 3 H), 6.53 (s, 1 H), 7.08 (dd, 2 H, $J = 9.0, 3.1$ Hz), 7.25 (dd, 2 H, $J = 9.0, 3.1$ Hz), 7.28-7.33 (m, 3 H), 7.61–7.65 (m, 2 H) & $\delta = 11.0, 14.0$ (2 overlapping peaks), 22.2 (2 overlapping peaks), 29.4 (2 overlapping peaks), 30.6 (2 overlapping peaks), 30.7 (2 overlapping peaks), 36.2 (2 overlapping peaks), 49.3, 116.6, 122.6, 126.3 (2 overlapping peaks), 127.5, 127.6, 127.8, 128.7 (2 overlapping peaks), 128.8 (2 overlapping peaks), 137.5, 138.3, 138.5. \\
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5-Propyl-2-[4,5-bis(pentylthio)-1,3-dithiole-2-yldien]-(1,3)-dithiole[4,5,c]pyrrole-4-carboxaldehyde (26)

Compound 22 (0.20 g, 0.31 mmol) was dissolved in DMSO (20 mL) and the solution stirred at 100 °C. Hg(OAc)₂ (1.00 g, 3.11 mmol) was then added in one portion and the mixture stirred at the same temperature for a further 1 h (TLC analysis was performed after treatment of an aliquot with an aq solution of KI). The reaction mixture was allowed to cool to r.t. and an aq solution of KI (30 mL, 10%) was then added. The mixture was extracted with CH₂Cl₂ (3 × 50 mL), the extracts were filtered through celite, and dried (MgSO₄). Evaporation of the solvent gave the crude product, which was purified by column chromatography (500 mL SiO₂, 6 cm; CH₂Cl₂–petroleum ether, 1:1) to give the title compound 26 as a yellow oil; yield: 0.11 g (70%).

¹H NMR (CDCl₃/TMS): δ = 0.87–0.95 (m, 9 H), 1.10–1.59 (m, 8 H), 1.61–1.68 (m, 4 H), 1.79 (sextet, 2 H, J = 7.0 Hz), 2.80 (t, 4 H, J = 7.0 Hz), 4.17 (t, 2 H, J = 7.2 Hz), 6.68 (s, 1 H), 9.56 (s, 1 H).

¹³C NMR (CDCl₃/TMS): δ = 13.9 (2 overlapping peaks), 22.2 (2 overlapping peaks), 24.8 (2 overlapping peaks), 29.3 (2 overlapping peaks), 29.4 (2 overlapping peaks), 30.6 (2 overlapping peaks), 36.2, 93.2, 117.8, 120.5, 120.8, 123.9, 127.1, 127.8, 155.0, 175.9.

Complete Sequential Functionalization of Monopyrrolotetraethiafulvalenes

5-Propyl-2-[4,5-bis(pentylthio)-1,3-dithiole-2-yldien]-(1,3)-dithiole[4,5,c]pyrrole-4-ylphenylmethanone (27)

Compound 23 (0.25 g, 0.35 mmol) was dissolved in DMSO (30 mL) and the solution stirred at 100 °C. Hg(OAc)₂ (0.11 g, 3.48 mmol) was then added in one portion and the mixture stirred at the same temperature for a further 1 h (TLC analysis was performed after treatment of an aliquot with an aq solution of KI). The reaction mixture was allowed to cool to r.t. and an aq solution of KI (30 mL, 10%) was then added. The mixture was extracted with CH₂Cl₂ (3 × 50 mL), the combined extracts filtered through celite, and dried (MgSO₄). Evaporation of the solvent gave the crude product, which was purified by column chromatography (600 mL SiO₂, 6 cm; CH₂Cl₂–petroleum ether, 1:4) to give the title compound 27 as a red brown oil; yield: 0.14 g (70%).

¹H NMR (CDCl₃/TMS): δ = 0.85–0.89 (m, 9 H), 1.25–1.41 (m, 8 H), 1.61 (quintet, 4 H, J = 7.1 Hz), 1.78 (sextet, 2 H, J = 7.2 Hz), 2.73 (t, 2 H, J = 7.1 Hz), 2.80 (t, 2 H, J = 7.1 Hz), 4.27 (br, 2 H), 6.76 (s, 1 H), 7.50 (dd, 2 H, J = 7.2 Hz, 7.0 Hz), 7.60 (d, 1 H, J = 7.2 Hz) 7.70 (d, 2 H, J = 7.0 Hz).

¹³C NMR (CDCl₃/TMS): δ = 11.0, 13.9, 22.2, 24.9, 28.9, 29.3, 29.4, 29.7, 30.6, 31.2, 36.3, 38.1, 51.2, 111.6, 118.9, 121.2, 127.3, 127.7, 128.4 (2 overlapping peaks), 128.8 (2 overlapping peaks), 132.3 (2 overlapping peaks), 138.5, 185.3.

FT-MALDI-MS: m/z (%) = 517 (M⁺, 100).

FT-MALDI-HRMS: m/z calc for C₂₈H₃₅NS₈: 517.07244; found: 517.0708.

5-Propyl-2-[4,5-bis(pentylthio)-1,3-dithiole-2-yldien]-(1,3)-dithiole[4,5,c]pyrrole-4-y1-phenylmethanone (27)

Compound 24 (0.50 g, 0.16 mmol) and 1,3-benzodithiol-2-ylidium tetrafluoroborate (18) (0.078 g, 0.33 mmol) were dissolved in MeCN (20 mL) at 50 °C. Anhyd pyridine (0.1 mL, 1.2 mmol) was then added to the dark red solution and the mixture stirred for 20 minutes at r.t. The reaction mixture was diluted with CH₂Cl₂ (20 mL). H₂O (100 mL) was added, extracted with CH₂Cl₂ (3 × 50 mL), and the extracts were dried (MgSO₄). Evaporation of the solvent gave the crude product, which was purified by column chromatography (700 mL SiO₂, 6 cm; CH₂Cl₂–petroleum ether, 1:4) to give the title compound 28 as an orange yellow solid; yield: 0.10 g (80%); mp 70–73 °C.

¹H NMR (CDCl₃/TMS): δ = 0.89 (t, 6 H, J = 7.3 Hz), 1.28–1.39 (m, 8 H), 1.58 (quintet, 4 H, J = 7.0 Hz), 2.78 (t, 4 H, J = 7.0 Hz), 3.59 (br s, 3 H), 6.25 (s, 2 H), 7.07 (dd, 4 H, J = 9.0, 3.3 Hz), 7.23 (dd, 4 H, J = 9.0, 3.3 Hz).

¹³C NMR (CDCl₃/TMS): δ = 14.1, 22.3, 29.6, 30.8, 32.4, 46.4, 48.9, 120.3, 122.8 (2 overlapping peaks), 126.2 (2 overlapping peaks), 127.5, 137.1 (2 overlapping peaks).

FT-MALDI-MS: m/z (%) = 765 (M⁺, 100).

FT-MALDI-HRMS: m/z calc for C₃₃H₃₅NS₁₀: 764.9971; found: 765.0013.

4,6-Bis-(2-phenylbenzo-1,3-dithio-2-yl)-5-methyl-2-[4,5-bis(pentylthio)-1,3-dithiole-2-yldien]-(1,3)-dithiole[4,5,c]pyrrole (29)

Method A:

Compound 16 (0.30 g, 0.65 mmol) and 2-phenyl-1,3-benzodithiol-2-yldium tetrafluoroborate (19) (1.02 g, 3.25 mmol) were dissolved in MeCN (50 mL) at 50 °C. Anhyd pyridine (0.3 mL, 3.7 mmol) was then added to the dark red solution and the mixture stirred under reflux for 10 h. The reaction mixture was diluted with CH₂Cl₂ (20 mL). H₂O (100 mL) was added, extracted with CH₂Cl₂ (3 × 50 mL), and the extracts were dried (MgSO₄). Evaporation of the solvent gave the crude product, which was purified by column chromatography (700 mL SiO₂, 6 cm; CH₂Cl₂–petroleum ether, 1:4) to give the title compound 29 as a yellow solid; yield: 0.26 g (45%); mp 109–110 °C.

Method B:

Compound 20 (0.10 g, 0.16 mmol) and 1,3-benzodithiol-2-yldium tetrafluoroborate (18) (0.078 g, 0.33 mmol) were dissolved in MeCN (20 mL) at 50 °C. Anhyd pyridine (0.1 mL, 1.2 mmol) was then added to the dark red solution and the mixture stirred for 20 minutes at r.t. The reaction mixture was diluted with CH₂Cl₂ (20 mL). H₂O (100 mL) was added, extracted with CH₂Cl₂ (3 × 50 mL), and the extracts were dried (MgSO₄). Evaporation of the solvent gave the crude product, which was purified by column chromatography (700 mL SiO₂, 6 cm; CH₂Cl₂–petroleum ether, 1:4) to give the title compound 28 as an orange yellow solid; yield: 0.40 g (49%); mp 71–72 °C.

Method B:

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FT-MALDI-MS: m/z (%) = 917 (M+, 30).

FT-MALDI-HRMS: m/z calc for C_{16}H_{25}N_{30} 917.0597; found, 917.0572.

Anal. Calc. for C_{16}H_{25}N_{30} (917.6): C, 58.85; H, 4.72; N, 1.52; S, 34.91. Found: C, 58.86; H, 4.91; N, 1.54; S, 34.71.

4,6-Bis(phenyl-1,3-dithiol-2-yl)-5-propyl-2-[4,5-bis(pentylthio)-1,3-dithiole-2-ylidene]-1(3)-dithiole[4,5-c]pyrrole (31)

Method A:

Compound 17 (0.40 g, 0.82 mmol) and 1,3-benzodithiol-2-ylium tetrafluoroborate (18) (0.49 g, 2.04 mmol) were dissolved in MeCN (50 mL) at 50 °C. Anhyd pyridine (0.3 mL, 3.7 mmol) was then added to the dark red solution and the mixture stirred for 20 min at r.t. The reaction mixture was diluted with CH2Cl2 (20 mL), H2O (100 mL) was added, extracted with CH2Cl2 (3 × 50 mL) and the extracts were dried (MgSO4). Evaporation of the solvent gave the crude product, which was purified by column chromatography (500 mL SiO2, Ω = 6 cm; CH2Cl2–petroleum ether, 1:1) to give the title compound 30 as a yellow solid; yield: 0.074 g (60%), mp 136–138 °C.

Method B:

Compound 22 (0.10 g, 0.16 mmol) and 1,3-benzodithiol-2-ylium tetrafluoroborate (18) (0.49 g, 0.23 mmol) were dissolved in MeCN (20 mL) at 50 °C. Anhyd pyridine (0.1 mL, 1.2 mmol) was then added to the dark red solution and the mixture stirred for 20 min at room temperature. The reaction mixture was diluted with CH2Cl2 (20 mL), H2O (100 mL) was added, extracted with CH2Cl2 (3 × 50 mL) and the extracts were dried (MgSO4). Evaporation of the solvent gave the crude product, which was purified by column chromatography (500 mL SiO2, Ω = 6 cm; CH2Cl2–petroleum ether, 1:1) to give the title compound 30 as a yellow solid; yield: 0.074 g (60%), mp 136–138 °C.

4,6-Bis(phenyl-1,3-dithiol-2-yl)-5-propyl-2-[4,5-bis(pentylthio)-1,3-dithiole-2-ylidene]-1(3)-dithiole[4,5-c]pyrrole (31)

Method A:

Compound 17 (0.50 g, 1.02 mmol) and 2-phenyl-1,3-benzodithiol-2-ylium tetrafluoroborate (19) (0.81 g, 2.55 mmol) were dissolved in warm MeCN (50 mL). Anhyd pyridine (0.4 mL, 4.9 mmol) was then added to the dark red solution and the mixture stirred under reflux for 10 h. The reaction mixture was diluted with CH2Cl2 (20 mL), H2O (100 mL) was added, extracted CH2Cl2 (3 × 50 mL) and the extracts were dried (MgSO4). Evaporation of the solvent gave the crude product, which was purified by column chromatography (400 mL SiO2, Ω = 6 cm; CH2Cl2–petroleum ether, 1:1) to give the title compound 31 as a yellow solid; yield: 0.85 g (74%); mp 98–99 °C.

Anal. Calc. and FT-MALDI-MS:

\[
\begin{align*}
\text{FT-MALDI-MS: m/z (%) = 917 (M+, 30).} \\
\text{FT-MALDI-HRMS: m/z calc for C}_{16}\text{H}_{25}\text{N}_{30} \text{ 917.0597; found, 917.0572.} \\
\text{Anal. Calc. for C}_{16}\text{H}_{25}\text{N}_{30} (917.6):} & C, 58.85; H, 4.72; N, 1.52; S, 34.91. \text{ Found: C, 58.86; H, 4.91; N, 1.54; S, 34.71.}
\end{align*}
\]

4,6-Bis(phenyl-1,3-dithiol-2-yl)-5-propyl-2-[4,5-bis(pentylthio)-1,3-dithiole-2-ylidene]-1(3)-dithiole[4,5-c]pyrrole (31)

Method B:

Compound 23 (0.10 g, 0.14 mmol) and 2-phenyl-1,3-benzodithiol-2-ylium tetrafluoroborate (19) (0.11 g, 0.36 mmol) were dissolved in warm MeCN (50 mL). Anhyd pyridine (0.1 mL, 1.2 mmol) was then added to the dark red solution and the mixture stirred under reflux for 10 h. The reaction mixture was diluted with CH2Cl2 (20 mL), H2O (100 mL) was added, extracted CH2Cl2 (3 × 50 mL) and the combined organic phases were dried (MgSO4). Evaporation of the solvent gave the crude product, which was purified by column chromatography (400 mL SiO2, Ω = 6 cm; CH2Cl2–petroleum ether, 1:1) to give the title compound 31 as a yellow solid; yield: 0.10 g (78%); mp 97–99 °C.

1H NMR (CDCl3/TMS): δ = 0.25 (t, 3 H, J = 7.3 Hz), 0.91 (t, 6 H, J = 7.1 Hz), 1.30–1.42 (m, 10 H), 1.61 (quintet, 4 H, J = 7.1 Hz), 2.81 (t, 4 H, J = 7.1 Hz), 3.60 (br, 2 H), 7.08 (dd, 4 H, J = 8.9, 3.0 Hz), 7.20–7.31 (m, 10 H), 7.53 (dd, 4 H, J = 8.9, 3.0 Hz).

13C NMR (CDCl3/TMS): δ = 34.91. Found: C, 59.87; H, 5.10; N, 1.56; S, 33.97.

5-Methyl-2-[4,5-bis(pentylthio)-1,3-dithiole-2-ylidene]-1(3)-dithiole[4,5-c]pyrrole-4,6-dicarbaldehyde (32)

Compound 28 (0.30 g, 0.39 mmol) was dissolved in DMSO (20 mL) and the solution stirred at 100 °C. Hg(OAc)2 (1.25 g, 3.91 mmol) was then added in one portion and the mixture stirred at the same temperature for a further 1 h (TLC analysis was performed after treatment of an aliquot with anaq solution of KI). The reaction mixture was allowed to cool to r.t. and anaq solution of KI (30 mL, 10%) was added. The mixture was extracted with CH2Cl2 (3 × 50 mL), the combined extracts filtered through celite, and dried (MgSO4). Evaporation of the solvent gave the crude product, which was purified by column chromatography (400 mL SiO2, Ω = 6 cm; CH2Cl2–petroleum ether, 1:1) to give the title compound 32 as a deep purple solid; yield: 0.15 g (72%); mp 93–95 °C.

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Evaporation of the solvent gave the crude product, which was purified by column chromatography (400 mL SiO₂, Ω = 6 cm; CH₂Cl₂–petroleum ether, 4:1) to give the title compound 33 as a deep red solid; yield: 0.11 g (75%), mp 97–100 °C.  

H NMR (CDCl₃/TMS): δ = 0.89 (t, 3 H, J = 7.1 Hz), 1.26–1.38 (m, 8 H), 1.57 (quintet, 4 H, J = 7.1 Hz), 2.74 (t, 4 H, J = 7.1 Hz), 4.03 (br s, 3 H), 7.54 (dd, 4 H, J = 7.4, 6.9 Hz), 7.67 (d, 2 H, J = 7.4 Hz), 7.81 (d, 4 H, J = 6.9 Hz).  

13C NMR (CDCl₃/TMS): δ = 13.9, 22.1, 29.3, 30.5, 36.1, 36.7, 112.7, 116.8, 127.5, 128.5, 129.0, 129.5, 133.3, 137.4, 186.1.  

FT-MALDI-MS: m/z (%) = 697 (M⁺, 100%).  

FT-MALDI-HRMS: m/z calcd for C₁₅H₉₁NO₂S₆: 697.1300; found: 697.1298.  

Anal. Calcd for C₁₅H₉₁NO₂S₆: C, 60.22; H, 5.63; N, 2.06; S, 26.99.  

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