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Electronic, redox and charge transport properties of an unusal hybrid structure: a bis(septithiophene) bridged by a fused tetrathiafulvalene (TTF)

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Supplementary Information

General. LDA was purchased from Aldrich and titrated against menthol with 2,2'-bipyridyl as indicator before use. NBS was purchased from Aldrich and recrystallised from water and dried under vacuum, $Pd(PPh_3)_4$ was made prior to use and stored under N_2. Unless otherwise stated all other reagents were sourced commercially and used without further purification. Dry solvents were obtained from a solvent purification system (SPS 400 from Innovative Technologies) using alumina as drying agent. Melting points were taken using a TA Instruments DSC Q1000 differential Scanning Calorimeter and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 apparatus at 500.13 and 125.76 MHz. Chemical shifts are given in ppm; all *J* values are in Hz. Elemental analyses were obtained on a Perkin-Elmer 2400 analyser. MS LDI-TOF spectra were run on a Shimadzu Axima-CFR spectrometer (mass range 1-150000 Da). TGA analysis was performed using a Perkin Elmer Thermogravimetric Analyzer TGA7 under a constant flow of helium.

Electrochemistry. CV measurements were performed on a CH Instruments 660A electrochemical workstation with *iR* compensation using anhydrous dichloromethane as the solvent. The electrodes were glassy carbon, platinum wire, and silver wire as the working, counter, and reference electrodes, respectively. All solutions were degassed (Ar) and contained monomer substrates in concentrations *ca.* 10^{-4} M, together with n-Bu_4NPF_6 (0.1 M) as the supporting electrolyte. All measurements are referenced against the $E_{1/2}$ of the Fc/Fc^+ redox couple. Spectroelectrochemical experiments were conducted on ITO glass. Absorption spectra and CIE coordinates were recorded on a Unicam UV 300 instrument.

Experimental Section

2-Bromo-3-hexylthiophene:

Under exclusion of light, NBS (22.65 g, 134.58 mmol) was added portionwise to a stirred solution of 3-hexylthiophene (23.95 g, 134.58 mmol) in 1:1 chloroform/glacial acetic acid mixture (400 ml). The reaction was left to stir overnight at room temperature before being poured into H_2O (200 ml). The aqueous phase was extracted with dichloromethane (DCM) (3 × 150 ml), and the combined organic phases were washed with satd. $NaHCO_3$ soln. (4 × 250 ml), and water (4 × 250 ml) before drying ($MgSO_4$), and evaporation of the solvent under reduced pressure to give the crude product as a brown oil. The oil was purified via distillation under high vacuum (kugelrohr, b.p. 95 °C at 6.8×10^{-2} mbar) to give a colourless oil (32.71 g, 98%).

^1H NMR ($CDCl_3$): δ = 7.18 (1H, d, J = 5.60), 6.80 (1H, d, J = 5.60), 2.57 (2H, t, J = 7.60), 1.58 (2H, quintet), 1.32 (6H, m), 0.90 (3H, t, J = 6.60)

^{13}C NMR ($CDCl_3$): δ = 142.2, 128.5, 125.3, 109.0, 31.8, 29.9, 29.6, 29.1, 22.8, 14.3

MS (CI): *m/z* = 246 $[M]^+$

2-Bromo-3-hexyl-5-methylthiophene (2):

Under N_2, 2-bromo-3-hexylthiophene (32.71 g, 132.32 mmol) was dissolved in dry THF (150 ml) and cooled to -40°C before dropwise addition of lithium diisopropylamide monotetrahydrofuran (LDA.THF) (1.5 M solution in cyclohexane, 88.20 ml, 132.32 mmol). The mixture was stirred at -40 °C for 30 min before dropwise addition of MeI (22.54 g, 158.79 mmol) at the same temperature. The reaction mixture was allowed to come to room temperature and stirred for 24 h, then hydrolysed before extraction with Et_2O (3 × 125 ml), drying ($MgSO_4$) and removal of solvent under reduced pressure. The crude product was purified via distillation under high vacuum (kugelrohr, b.p. 113 °C at 6.8×10^{-2} mbar) to give a pale yellow oil (31.33 g, 91 %).

^{1}H NMR ($CDCl_3$): δ = 6.47 (1H, m, J = 1.00), 2.48 (2H, t, J = 7.75), 2.39 (3H, d, J = 1.00), 1.54 (2H, quintet), 1.31 (6H, m), 0.89 (3H, t, 7.00)

^{13}C NMR ($CDCl_3$): δ = 142.0, 139.5, 126.6, 105.3, 31.9, 29.9, 29.7, 29.1, 22.8, 15.8, 14.3

MS (CI): *m/z* = 261 $[M + H^+]^+$

Elemental Analysis: Found C, 50.06; H, 6.65; S, 11.98; Br, 29.70 Calculated: C, 50.59; H, 6.52; S, 12.27; Br, 30.62

3-Hexyl-5-methyl-2,2'-bithiophene (3):

Under N_2, thiophene (5.36 g, 63.71 mmol) was dissolved in THF (50 ml) and cooled to -60 °C before dropwise addition of n-BuLi (2.5 M in hexanes) (25.5 ml, 63.71 mmol). After stirring for 30 min, a suspension of $ZnCl_2$ (8.68 g, 63.71 mmol) in THF (65 ml) was added to the lithiated thiophene via syringe at -60 °C before being allowed to attain room temperature. The 2-thienylzinc bromide solution thus formed was added *via* cannula to **2** (13.87 g, 53.09 mmol) and $Pd(PPh_3)_4$ (1.54 g, 1.33 mmol) in THF (50 ml) and the mixture was heated to reflux overnight then allowed to cool to room temperature before filtration and treatment with 2N HCl. The aqueous phase was then extracted with Et_2O (300 ml) and the combined organic phases were washed with H_2O (2×150 ml) and brine (2×150 ml) before drying ($MgSO_4$). Evaporation of the solvent under reduced pressure yielded a crude yellow oil which was purified via distillation under high vacuum (kugelrohr, b.p. 125 °C at 6.8×10^{-2} mbar) before column chromatography (silica, petroleum) to give pure **3** as a colourless oil (9.54 g, 67%).

^{1}H NMR ($CDCl_3$): δ = 7.26 (1H, dd, J = 4.50, J = 1.75), 7.05 (2H, m), 6.61 (1H, m, J = 1.00), 2.68 (2H, t, J = 8.00), 2.46 (3H, d, J = 3.50), 1.60 (2H, quintet, J = 7.87), 1.31 (6H, m), 0.90, (3H, t, J = 7.00)

^{13}C NMR ($CDCl_3$): δ = 139.8, 138.3, 136.9, 128.5, 128.2, 127.4, 125.6, 124.9, 31.9, 30.9, 29.5, 22.8, 15.4, 14.3

MS (CI): *m/z* = 265 $[M + H^+]^+$

5'-Bromo-3-hexyl-5-methyl-2,2'-bithiophene (4):

Under exclusion of light, NBS (4.65 g, 26.13 mmol) was added portionwise to a stirred solution of **3** (6.91 g, 26.13 mmol) in 1:1 chloroform/glacial acetic acid mixture (200 ml). The reaction was left to stir for 3 h at room temperature before being poured into H_2O (350 ml). The aqueous phase was extracted with DCM (3 × 125 ml) and the combined organic phases were washed with satd. $NaHCO_3$ soln. (3 × 200 ml) and water (3 × 200 ml) before drying ($MgSO_4$). Evaporation of the solvent under reduced pressure gave the crude product as brown oil. The oil was purified via distillation under high vacuum (kugelrohr, b.p. 185 °C at 6.8×10^{-2} mbar) to give a light yellow oil (8.62 g, 96 %).

^{1}H NMR ($CDCl_3$): δ = 6.99 (1H, d, J = 4.00), 6.79 (1H, d, J = 4.00), 6.59 (1H, m, J = 1.00), 2.63 (2H, t, J = 8.25), 2.44 (3H, d, J = 1.00), 1.58 (2H, quintet, J = 7.50), 1.30 (6H, m), 0.90 (3H, t, J = 7.00)

^{13}C NMR ($CDCl_3$): δ = 140.5, 138.9, 138.4, 130.3, 128.5, 127.3, 125.8, 111.3, 31.9, 30.9, 29.4, 22.8, 15.5, 14.3

MS (CI): *m/z* = 343 $[M + H^+]^+$

5-Methyl-3-hexyl-2,2’:5’,2’’-terthiophene (5):

Compound **4** (4.33 g, 12.57 mmol) and $Pd(dppf)Cl_2.CH_2Cl_2$ (103 mg, 0.126 mmol) were placed under N_2 and dissolved in dry THF (75 ml) before being cooled to 0 °C. Thiophen-2-yl-magnesium bromide (1.0 M solution in THF, 13.83 ml, 13.83 mmol) was added slowly and the reaction mixture was stirred for 1 h at room temperature. The reaction was hydrolysed with satd. NH_4Cl soln. (50 ml), which was followed by the addition of hexane (125 ml). Et_2O (400 ml) was added before the organic phase was washed with water (3 × 250 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give the crude product which was purified via column chromatography (silica, petroleum/DCM 10:1) and finally by distillation under high vacuum (kugelrohr, b.p. 240 °C at 6.8×10^{-2} mbar) to give a bright yellow oil (3.85 g, 88 %).

^{1}H NMR ($CDCl_3$): δ = 7.21 (1H, dd, J = 5.00, J = 1.00), 7.18 (1H, dd, J = 3.50, J = 1.00), 7.10 (1H, d, J = 3.50), 7.03 (1H, dd, J = 5.50, J = 3.00), 6.95 (1H, d, J = 3.50), 6.61 (1H, m), 2.70 (2H, t, J = 7.75), 2.46 (3H, d, J = 0.50), 1.63 (2H, quintet, J = 7.88), 1.32 (6H, m), 0.90 (3H, t, J = 6.5)

^{13}C NMR ($CDCl_3$): δ= 140.0, 138.5, 137.5, 136.7, 135.9, 128.7, 128.0, 127.7, 124.5, 124.1, 123.7, 31.9, 30.8, 29.6, 29.5, 22.8, 15.4, 14.3

MS (MALDI): *m/z* = 346 $[M]^+$

Elemental Analysis: Found C, 65.98; H, 6.32; S, 27.58 Calculated: C, 65.90; H, 6.36; S, 27.75

5-Methyl-3-hexyl-2,2’:5’,2’’-terthiophene-5’’-carboxaldehyde (6):

Under N_2, compound **5** (3.32 g, 9.57 mmol) in dry THF (50 ml) was cooled to 0 °C. *n*-BuLi (2.5 M in hexanes, 5.0 ml, 12.43 mmol) was added dropwise and the reaction was stirred at 0 °C for 15 min. Dry DMF (909 mg, 12.43 mmol) was added and the reaction was heated to reflux for 2.5 h. The mixture was poured into water (300 ml) and extracted with ethyl acetate (3 × 200 ml), before the combined organic extracts were washed with water (3 × 200 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification was achieved via column chromatography (silica, DCM/petroleum 2:1) to yield the product as, red/orange crystals which may be recrystallised from hexane (2.96 g, 83 %). m.p. 60 - 61 °C.

^{1}H NMR ($CDCl_3$): δ= 9.87 (1H, s), 7.68 (1H, d, J = 4.00), 7.30 (1H, d, J = 3.50), 7.24 (1H, d, J = 4.00), 7.01 (1H, d, J = 4.00), 6.63 (1H, m, J = 1.00), 2.71 (2H, t, J = 7.75), 2.46 (3H, d, J = 1.00), 1.63 (2H, quintet, J = 7.62), 1.33 (6H, m), 0.89 (3H, t, 7.00)

^{13}C NMR ($CDCl_3$): δ= 182.6, 147.36, 141.6, 140.8, 139.3, 139.0, 137.6, 134.9, 128.9, 127.5, 126.7, 126.3, 124.0, 31.9, 30.7, 29.7, 29.4, 22.8, 15.5, 14.3

MS (MALDI): *m/z* = 375 $[M + H^+]^+$, 397 $[M + Na^+]^+$

Elemental Analysis: Found C, 63.76; H, 5.99; S, 25.83 Calculated: C, 64.13; H, 5.92; S, 25.68

(2-Thioxo-1,3-dithiole-4,5-diyl)bis((3''-hexyl-5''-methyl-[2,2':5',2''-terthiophen]-5-yl)methanone) (7)

Under N_2, vinylene trithiocarbonate (326 mg, 2.43 mmol) was dissolved in dry THF at -55 °C. LDA.THF (1.5 M solution in cyclohexane, 1.78 ml, 2.67 mmol) was added and the reaction was stirred for 20 min at -55 °C. **6** (1.00 g, 2.67 mmol) was added dropwise as a solution in dry THF (10 ml) before the reaction was stirred for a further 20 min at -55 °C. A second equivalence of LDA.THF (1.5 M solution in cyclohexane, 1.78 ml, 2.67 mmol) was added and the reaction was stirred for 15 min at -55 °C. The cooling bath temperature was reduced to -80 °C, and a second equivalence of **6** (1.00 g, 2.67 mmol) in dry THF (10 ml) was added and the reaction was allowed to continue until the reaction temperature was -50 °C whereupon the reaction was allowed to attain RT without external cooling. The reaction mixture was poured into a solution of saturated $NaHCO_3$ (60 ml) to which KBr (6.00 g) was added. The product was extracted with ethyl acetate (3 × 60 ml) and the combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuo and the residue was purified via column chromatography (silica, DCM then ethyl acetate) to obtain the mono and diol respectively in order of elution. The diol was obtained as a red solid and was reacted immediately. The diol (2.19 g) was dissolved in DCM (80 ml) and to this a ten-fold excess (w/w) of MnO_2 (21.9 g) was added portionwise yet quickly and the mixture stirred for 1 min at RT before being filtered immediately through a plug of silica (*ca.* 2.5 × 5 cm thick) eluting DCM (approx. 200 ml). The solvent was removed under reduced pressure to yield **7** as a deep-red tar-like solid (1.29 g, 60 %). The material was used without further purification, though an analytical sample was obtained via precipitation from hot DCM with hexane to give a red powder. T_g = 27.6 °C, m.p. 83 - 84 °C.

^{1}H NMR ($CDCl_3$): δ = 7.62 (1H, d, *J* = 4.00), 7.22 (1H, d, *J* = 4.00), 7.12 (1H, d, *J* = 4.50), 6.96 (1H, d, *J* = 4.00), 6.61 (1H, m, *J* = 1.00), 2.67 (2H, t, *J* = 7.75), 2.44 (3H, d, *J* = 0.50), 1,60 (2H, quintet, *J* = 7.75), 1.33 (6H, m), 0.89 (3H, t, *J* = 7.00)

^{13}C NMR ($CDCl_3$): δ = 207.86, 175.17, 150.07, 144.22, 141.03, 139.98, 139.70, 139.57, 136.92, 134.21, 129.02, 127.43, 127.38, 126.28, 124.24, 31.86, 3066, 29.71, 29.43, 22.80, 15.50, 14.30

MS (MALDI): *m/z* = 879 [M^+]

Elemental Analysis: Found C, 58.69; H, 4.51; S, 32.91 Calculated: C, 58.73; H, 4.81; S, 32.82

(2-Oxo-1,3-dithiole-4,5-diyl)bis((3''-hexyl-5''-methyl-[2,2':5',2''-terthiophen]-5-yl)methanone) (8)

7 (1.29g, 1.47 mmol) was dissolved in 3:1 DCM/glacial acetic acid mixture (150 ml) before addition of mercury(II) acetate (0.65 g, 2.05 mmol). The mixture was stirred overnight at room temperature before being filtered through a plug of silica eluting DCM. The filtrate was washed with water (2 × 200 ml) and saturated $NaHCO_3$ solution (2 × 200 ml) before the solvent was removed under reduced pressure.

Purification was achieved via column chromatography (silica, DCM/hexane 2:1) to give a dark red tar-like solid (1.26 g, 99%). An analytical sample was obtained via precipitation from hot DCM with hexane to give a bright red powder. T_g = 22.5 °C, m.p. 76 - 77 °C.

^{1}H NMR ($CDCl_3$): δ = 7.59 (1H, d, J = 4.00), 7.21 (1H, d, J = 4.00), 7.12 (1H, d, J = 4.00), 6.95 (1H, d, J = 3.50), 6.61 (1H, m, J = 1.00), 2.67 (2H, t, J = 8.00), 2.44 (3H, d, J = 0.50), 1,60 (2H, quintet, J = 7.75), 1.33 (6H, m), 0.89 (3H, t, J = 7.00)

^{13}C NMR ($CDCl_3$): δ = 187.3, 176.8, 149.8, 140.9, 140.0, 139.8, 139.5, 136.8, 135.5, 134.3, 129.0, 127.4, 127.2, 126.3, 124.1, 31.8, 30.6, 29.7, 29.4, 22.8, 15.5, 14.3

MS (MALDI): m/z = 863 [M^+]

Elemental Analysis: Found C, 59.85; H, 4.68; S, 29.82 Calculated: C, 59.82; H, 4.90; S, 29.71

4,6-Bis(3''-hexyl-5''-methyl-[2,2':5',2''-terthiophen]-5-yl)thieno[3,4-d][1,3]dithiol-2-one (9)

Compound **8** (1.26 g, 1.47 mmol), phosphorus pentasulfide (1.63 g, 7.33 mmol) and sodium hydrogen carbonate (616 mg, 7.33 mmol) were stirred together in 1,4-dioxane under N_2. The reaction was heated from 60 – 90 °C over 30 min, then stirred at 90 °C for 3 h. The reaction mixture was then allowed to cool to room temperature and water was added (10 × 10 ml portions) (**CAUTION!** H_2S and CO_2 gas evolution). The resulting suspension was heated to reflux for 1 h before being allowed to cool and stirred overnight at room temperature. The precipitate was filtered off over a glass sinter and washed with copious amounts of water before being dried under a stream of air. The precipitate was washed through the sinter with copious CS_2 before drying over Na_2SO_4 and removal of solvent under reduced pressure. The crude material was purified via column chromatography (silica, CS_2) then precipitation from hot chloroform with hexane to give **9** as fine purple crystals with a metallic lustre. (872 mg, 69 %). Recrystallisation may be achieved from dichloromethane to yield larger crystals. T_d = 400 °C, m.p. 112 - 113 °C.

^{1}H NMR ($CDCl_3$): δ = 7.12 (3H, m), 6.96 (1H, d, J = 4.00), 6.62 (1H, m, J = 1.00), 2.70 (2H, t, J = 7.75), 2.46 (3H, s), 1,60 (2H, quintet, J = 7.37), 1.34 (6H, m), 0.90 (3H, t, J = 7.00)

^{13}C NMR ($CDCl_3$): δ= 191.88, 140.05, 138.55, 138.28, 136.80, 135.24, 132.79, 128.78, 128.03, 125.76, 125.74, 125.44, 124.50, 124.16, 124.02, 31.91, 30.69, 29.71, 29.50, 22.84, 15.47, 14.34

MS (MALDI): *m/z* = 863 [M^+]

Elemental Analysis: Found C, 59.48; H, 4.65; S, 33.66 Calculated: C, 59.82; H, 4.90; S, 33.43

4,4',6,6'-Tetrakis(3''-hexyl-5''-methyl-[2,2':5',2''-terthiophen]-5-yl)-2,2'-bithieno[3,4-d][1,3]dithiolylidene (1)

9 (750 mg, 872 µmol) was dissolved in dry triethylphosphite (20 ml) and heated at 125 °C for 4 days. The crude product forms as a red precipitate which was filtered then washed with hexane and dried under a stream of air. The precipitate was then washed through the sinter with CS_2 before removal of solvent under reduced pressure. The material was purified via column chromatography (silica, CS_2) prior to precipitation from hot chloroform with hexane (286 mg, 39 %). A sample suitable for crystallographic analysis was obtained by slow evaporation of a DCM/CS_2 3:2 mixture. T_d = 399 °C

^{1}H NMR (CD_2Cl_2/CS_2 (3:1)): δ= 7.48-6.55 (20H, brm), 2.74-2.44 (20H, brm), 1.64-1.60 (8H, brm), 1.40-1.32 (24H, brm), 0.95-0.91 (12H, brm)

MS (MALDI): *m/z* = 1694 [M^+]

Elemental Analysis: Found C, 60.27; H, 4.95; S, 34.03 Calculated: C, 60.95; H, 5.00; S, 34.06

Crystallography

Intensity data were recorded on a Nonius KappaCCD diffractometer driven by COLLECT[1] and DENZO[2] software. Structures were determined using the direct methods procedure in SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97[3]. Full details of data collection and structure determination have been deposited with the Cambridge Crystallographic Data Centre with deposition numbers CCDC 783815 and CCDC 783816 for compounds **1** and **9**.

Crystal data for **1** at 120(2) K with MoKa (λ = 0.71073Å). $C_{86}H_{84}S_{18}.CS_2$,*M* = 1770.74, Monoclinic, *P*2$_1$/*c, a* = 11.7929(2), *b* = 12.7339(3), *c* = 15.5721(4) Å, α = 82.8950(10)°, *β* = 74.031(2)°, γ = 66.263(2)°, *V* = 2057.80(8) Å^3, *Z* = 1, 37249 measured reflections, 9158 unique reflections (*R*int = 0.0498), *R* = 0.0532, *wR* = 0.1385.

Crystal data for **9** at 120(2) K with MoKa (λ = 0.71073Å). $C_{43}H_{42}OS_9$, *M* = 478.58, Monoclinic, *P*2$_1$/*c, a* = 18.4493(18), *b* = 16.6052(16), *c* = 14.1055(12) Å, *β* = 99.196(2)°, *V* = 4265.7(7) Å^3, *Z* = 4, 51176 measured reflections, 9743 unique reflections (*R*int = 0.1372), *R* = 0.1478, *wR* = 0.2442.

1. R. Hooft, *Collect: Data Collection Software, Nonius B.V.*, **1998**.
2. Z. Otwinowski and W. Minor, *Methods in Enzymology,* **1997**, *276*, 307.
3. G.M. Sheldrick, *Acta Crystallographica*, **2008**, A64, 112-122.