

Supplementary Materials: Synthesis of New Derivatives of BEDT-TTF: Installation of Alkyl, Ethynyl, and Metal-Binding Side Chains and Formation of *Tris*(BEDT-TTF) Systems †

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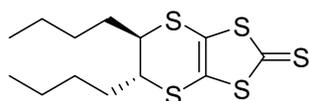
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† This paper is dedicated to the memory of Professor Peter Day FRS, who greatly encouraged and inspired our work in this area.

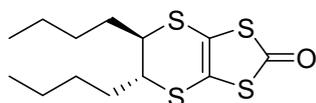
S1. Synthetic Procedures.

(+/-)-*Trans*-5,6-bis(*n*-butyl)-5,6-dihydro-1,3-dithiolo[4,5-*b*]1,4-dithiin-2-thione, **14**.



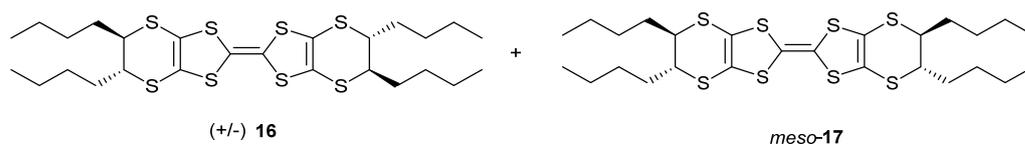
A mixture of *trans*-5-decene (5.00 g, 35.65 mmol) and trithione **10** (7.70 g, 39.21 mmol) in toluene (150 ml) was refluxed for 15 h. under nitrogen. The solvent was removed under reduced pressure and the residue purified by column chromatography (cyclohexane: toluene, 5:1) to give **14** (11.47 g, 95.0 %) as a yellow solid. m.p. 43-45°C, δ_{H} (400 MHz, CDCl₃): 3.15-3.19 (2H, m, 5-,6-*H*), 1.70-1.86 (4H, m, 2 × 1'-*H*₂), 1.47-1.57 (2H, m, 2 × 2'-*H*_a), 1.29-1.44 (6H, m, 2 × 2'-*H*_β, 2 × 3'-*H*₂), 0.92 (6H, t, *J* = 7.2 Hz, 2 × CH₃); δ_{C} (100 MHz, CDCl₃): 207.5 (C=S), 121.0 (3a- & 7a-C), 47.6 (5-, 6-C), 36.4 (2 × 1'-C), 28.8 (2 × 2'-C), 22.8 (2 × 3'-C), 14.3 (2 × CH₃); ν_{max} /cm⁻¹: 2954, 2924, 2855, 1484, 1459, 1377, 1303, 1249, 1183, 1055, 889, 818, 788, 731. Found: C, 46.48; H, 6.12%. Calc. for C₁₃H₂₀S₅: C, 46.39; H, 5.99%

(+/-)-*Trans*-5,6-bis(*n*-butyl)-5,6-dihydro-1,3-dithiolo[4,5-*b*]1,4-dithiin-2-one, **15**.



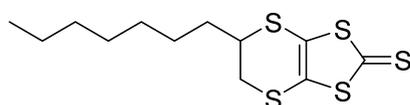
To a solution of **14** (10.00 g, 29.71 mmol) in CHCl₃ (200 ml) was added mercuric acetate (14.20 g, 44.56 mmol). After 2 h. stirring at room temperature the mixture was filtered. The filtrate was washed consecutively with saturated NaHCO₃ solution (3 × 100 ml) and water (100 ml), dried (MgSO₄) and evaporated to afford **15** as a brown oil (9.35 g, 98.2 %). δ_{H} (400 MHz, CDCl₃): 3.10-3.15 (2H, m, 5-,6-*H*), 1.71-1.87 (4H, m, 2 × 1'-*H*₂), 1.45-1.56 (2H, m, 2 × 2'-*H*_a), 1.26-1.42 (6H, m, 2 × 2'-*H*_β, 2 × 3'-*H*₂), 0.90 (6H, t, *J* = 7.2 Hz, 2 × CH₃); δ_{C} (100 MHz, CDCl₃): 189.1 (C=O), 111.3 (3a- & 7a-C), 48.9 (5-,6-C), 36.0 (2 × 1'-C), 28.7 (2 × 2'-C), 22.3 (2 × 3'-C), 13.9 (2 × CH₃); ν_{max} /cm⁻¹: 2954, 2926, 2857, 1677, 1638, 1502, 1459, 1377, 889, 807, 770, 731; HRMS (ESI) calc. for C₁₃H₂₁OS₄ ([M+H]⁺): 321.0470, found: 321.0386.

Tetrakis(*n*-butyl)-BEDT-TTF: (*rac*-5*R*,6*R*,5'*R*,6'*R* and 5*R*,6*R*,5'*S*,6'*S*), **16-17**.



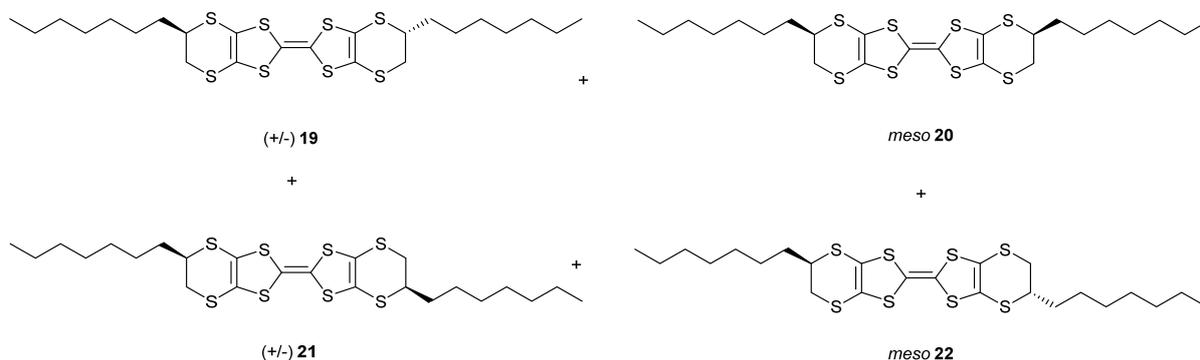
A solution of **15** (1.40 g, 4.16 mmol) in trimethyl phosphite (20 ml) was heated at 100 °C under nitrogen for overnight. Trimethyl phosphite was removed *in vacuo*, and the residue was purified by chromatography (cyclohexane/DCM 10:1) to give donor **16-17** (0.76 g, 57.1 %) as an orange oily semi-solid. δ_{H} (400 MHz, CDCl_3): 3.02-3.08 (4H, m, 5-,5'-,6-,6'-H), 1.60-1.76 (8H, m, 4 \times 1''-H₂), 1.43-1.52 (4H, m, 4 \times 2''-H _{α}), 1.24-1.37 (12H, m, 4 \times 2''-H _{β} , 4 \times 3''-H₂), 0.89 (12H, t, J = 7.2 Hz, 4 \times 4''-H₃); δ_{C} (100 MHz, CDCl_3): 111.1 (4 \times sp²-C), 110.6 (2 \times sp²-C), 48.0 (5-,5'-, 6-,6'-C), 35.8 (4 \times 1''-C), 28.7 (4 \times 2''-C), 22.3 (4 \times 3''-C), 13.9 (4 \times 4''-CH₃); $\nu_{\text{max}}/\text{cm}^{-1}$: 2952, 2924, 2855, 1702, 1459, 1377, 1328, 1226, 1107, 1003, 885, 772, 738. Found: C, 51.26; H, 6.59%. Calc. for C₂₆H₄₀S₈: C, 51.27; H, 6.62%.

(+/-)-5-(n-heptyl)-5,6-dihydro-1,3-dithiolo[4,5-b]1,4-dithiin-2-thione, **18**.



A mixture of 1-nonene (4.38 g, 34.70 mmol) and trithione **10** (4.45 g, 22.66 mmol) in toluene (120 ml) were refluxed for 15 h. under nitrogen. The solvent was removed under reduced pressure and the residue purified by column chromatography (cyclohexane: DCM, 4:1) to give **18** (6.38 g, 57.0 %) as a yellow solid, m.p. 47-49 °C. δ_{H} (400 MHz, CDCl_3): 3.57 (1H, dq, J = 2.7, 7.3 Hz, 5-H), 3.34 (1H, dd, J = 13.4, 2.7 Hz, 6-H _{α}), 3.13 (1H, dd, J = 13.3, 7.7 Hz, 6-H _{β}), 1.72-1.84 (2H, m, CH₂), 1.41-1.50 (2H, m, CH₂), 1.21-1.36 (8H, m, 4 \times CH₂), 0.87 (3H, t, J = 6.9 Hz, CH₃); δ_{C} (100 MHz, CDCl_3): 207.9 (C=S), 123.5 & 121.7 (3a- & 7a-C), 43.9 (5-C), 34.8 (6-C), 34.7 (CH₂), 31.6 (CH₂), 29.0 (CH₂), 28.9 (CH₂), 26.5 (CH₂), 22.5 (CH₂), 14.0 (CH₃); $\nu_{\text{max}}/\text{cm}^{-1}$: 2954, 2913, 2853, 1484, 1467, 1409, 1379, 1331, 1303, 1258, 1231, 1059, 1027, 1008, 908, 889, 829, 785, 718; HRMS (ESI) calc. for C₁₂H₁₉S₅ ([M+1]⁺): 323.0090, found: 323.0089. Found: C, 44.58; H, 5.59%. Calc. for C₁₂H₁₈S₅: C, 44.68; H, 5.62%.

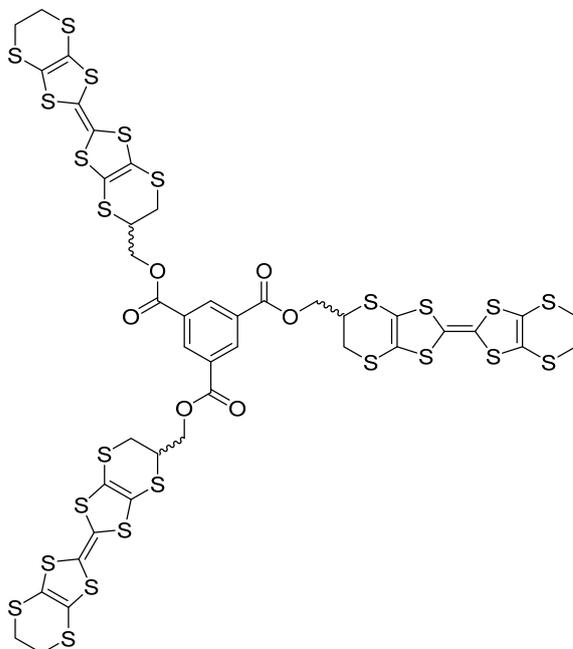
Bis(n-heptyl)-BEDT-TTF, (5,5' and 5,6' isomers, each one with *rac*-R,R and R,S stereoisomers), **19-22**.



A solution of thione **18** (1.47 g, 4.16 mmol) in trimethyl phosphite (20 ml) was heated at 90 °C under nitrogen for overnight. Trimethyl phosphite was removed *in vacuo*, the residue was purified by chromatography (cyclohexane/DCM 8:1) to give donor mixture **19-22** (0.67 g, 50.6 %) as an orange solid, m.p. 88-90 °C. δ_{H} (400 MHz, CDCl_3): 3.44 (2H, dq, J = 3.0, 7.2 Hz, 2 \times 5-H), 3.18 (2H, dd, J = 13.0, 3.0 Hz, 2 \times 6-H _{α}), 2.97 (2H, dd, J = 13.0, 7.6 Hz, 2 \times 6-H _{β}), 1.61-1.73 (4H, m, 2 \times CH₂), 1.31-1.45 (4H, m, 2 \times CH₂), 1.15-1.28 (16H, m, 8 \times CH₂), 0.81 (6H, t, J = 6.8 Hz, 2 \times CH₃); δ_{C} (100 MHz, CDCl_3): 114.3 & 112.7 (3a-,3a'-,7a-,7a'-C), 111.8 (2-,2'-C), 44.5 (5-,5'-C), 35.5 (6-,6'-C), 34.9 (2 \times CH₂), 31.7 (2 \times CH₂), 29.2 (2 \times CH₂), 29.0

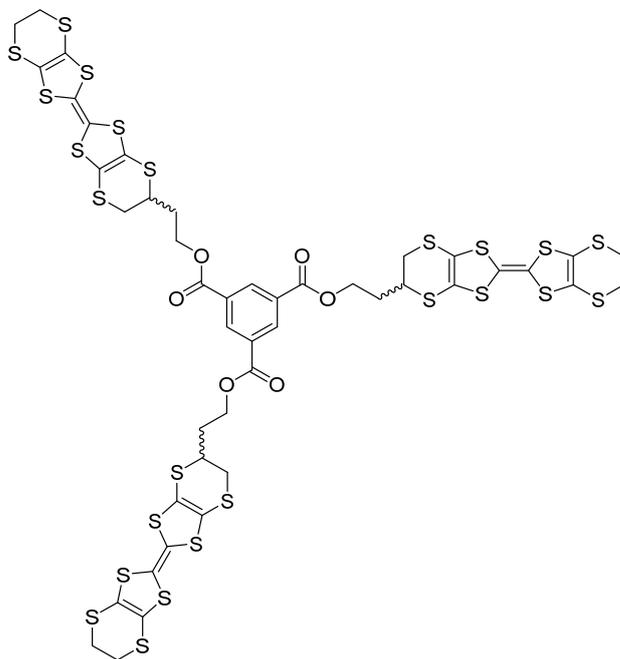
(2 x CH₂), 26.8 (2 x CH₂), 22.6 (2 x CH₂), 14.1 (CH₃); $\nu_{\max}/\text{cm}^{-1}$: 2952, 2917, 2849, 1459, 1402, 1375, 1327, 1280, 1252, 1238, 1144, 1120, 999, 910, 885, 770, 721. Found: C, 49.43; H, 6.21%. Calc. for C₂₄H₃₆S₈: C, 49.61; H, 6.25%.

Tris(BEDT-TTF-methyl) trimesate (*rac*-5*R*,5*R*,5*R* and *rac*-5*R*,5*R*,5*S*) **26**.



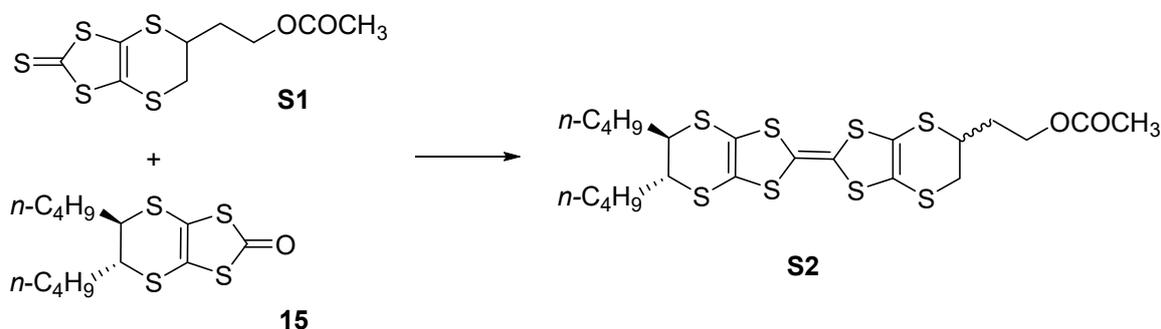
To a mixture of hydroxymethyl-BEDT-TTF^{S1} **23** (1.20 g, 2.89 mmol), trimesic acid (0.12 g, 0.57 mmol) and 4-(dimethylamino)pyridine (0.05 g) in dry DCM (50 ml), DCC (1.00 g, 4.85 mmol) was added. The resulting mixture was stirred at room temperature overnight. The precipitate formed was filtered, and washed with methanol (3 x 20 ml) and DCM (3 x 20 ml). The solid was stirred with DCM (50 ml), filtered and washed with more DCM and dried *in vacuo* to give the *tris* donor **26** (0.18 g, 22.4 %) as a brown powder, m.p. 190-192 °C (dec). Too insoluble for NMR; $\nu_{\max}/\text{cm}^{-1}$: 3078, 2912, 2175, 1979, 1723, 1647, 1444, 1406, 1373, 1331, 1284, 1225, 1107, 1041, 974, 897, 770, 730; MS (ESI) calcd for C₄₂H₃₀O₆S₂₄ ([M]⁺): 1397.5, found: 1397.5. Found: C, 35.87 H, 2.28 %. Calc. for C₄₂H₃₀O₆S₂₄: C, 36.03; H, 2.16%.

Tris(2-(BEDT-TTF)ethyl) trimesate (*rac*-5*R*,5*R*,5*R* and *rac*-5*R*,5*R*,5*S*) **27**.



To a mixture of hydroxyethyl-BEDT-TTF **24** (2.05 g, 4.78 mmol),^{S2} trimesic acid (0.25 g, 1.19 mmol) and triethylamine (15 ml) in dry THF (75 ml) cooled to 0°C, a 50% solution of *n*-propylphosphonic anhydride in ethyl acetate (3.2 ml) was added slowly. The resulting mixture was stirred for 30 min. at 0°C and then at room temperature overnight. After removal of THF, the residue was stirred with DCM (3 x 30 ml), filtered and washed with more DCM and dried *in vacuo* to give **27** (0.57 g, 33.2%) as a brown powder. m.p. 150–152°C. δ_{H} (400 MHz, THF-*d*₆): 8.84 (3H, s, 3×Ar-*H*), 4.59 (6H, m, 3×OCH₂CH₂), 3.75 (3H, m, 3×5-*H*), 3.43 (3H, dd, *J*=13.1, 3.1 Hz, 3×6-*H*_α), 3.29 (12H, s, 3×5',6'-*H*₂), 3.16 (3H, dd, *J*=13.1, 6.4 Hz, 3×6-*H*_β), 2.29 (6H, q, *J* = 6.5 Hz, 3×OCH₂CH₂); ν_{max} /cm⁻¹: 2956, 2912, 2162, 1974, 1721, 1514, 1452, 1407, 1332, 1282, 1228, 1146, 1107, 996, 886, 770, 734. Found: C, 36.35; H, 2.53%. Calc. for C₄₅H₃₆O₆S₂₄.CH₂Cl₂: C, 36.18; H, 2.52%.

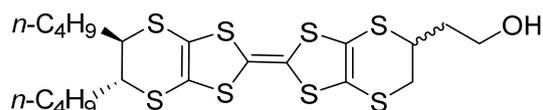
Trans-bis-5',6'-(*n*-butyl)-(5-acetoxyethyl)-BEDT-TTF (mixture of *rac*-5*R*,5'*R*,6'*R* and *rac*-5*S*,5'*R*,6'*R* stereoisomers), **S2**.



A mixture of thione **S1**^{S2} (5.95 g, 19.16 mmol) and oxo compound **15** (3.06 g, 9.55 mmol) was heated in trimethyl phosphite (60 ml) to 70 °C under nitrogen for 18 h. Trimethyl phosphite was removed *in vacuo*, the residue was purified by chromatography (chloroform/ethyl acetate 250:1) to give donor **S2** (2.44 g, 43.8%) as an orange oil. δ_{H} (400 MHz, CDCl₃): 4.15–4.30 (2H, m, OCH₂CH₂), 3.62–3.70 (1H, m, 5'-*H*), 3.34 (1H, dd, *J* = 13.3, 2.9 Hz, 6'-*H*_α), 3.04–3.12 (3H, m, 5-,6-*H* & 6'-*H*_β), 2.06–2.11 (5H, m, OCH₂CH₂ & COCH₃), 1.60–1.78 (4H, m, 2× butyl 1''-*H*₂), 1.43–1.55 (2H, m, butyl 2''-*H*_α), 1.25–1.40 (6H, m, butyl 2 × 2''-*H*_β &

3''-H₂), 0.90 (6H, t, J = 7.2 Hz, 2×CH₃); δ_c (100 MHz, CDCl₃): 170.8 (C=O), 112.9, 112.8, 112.1, 111.5 & 110.4 (sp²-C), 61.1 (OCH₂CH₂), 48.1 (5-,6-C), 40.0 (5'-C), 35.9 (butyl 2 × 1''-CH₂), 35.2 (6'-C), 33.6 (OCH₂CH₂), 28.8 (butyl 2 × 2''-CH₂), 22.3 (butyl 2 × 3''-CH₂), 20.8 (CH₃CO), 13.9 (butyl 2 × 4''-CH₃); ν_{max}/cm⁻¹: 2953, 2926, 2855, 1737, 1463, 1430, 1380, 1363, 1230, 1038, 1003, 885, 773, 731, 603; HRMS: (ES⁺) C₂₂H₃₀O₂S₈ requires 582.0017, found 582.0013. Found: C, 45.17; H, 5.23%. Calc. for C₂₂H₃₀O₂S₈: C, 45.33; H, 5.19%.

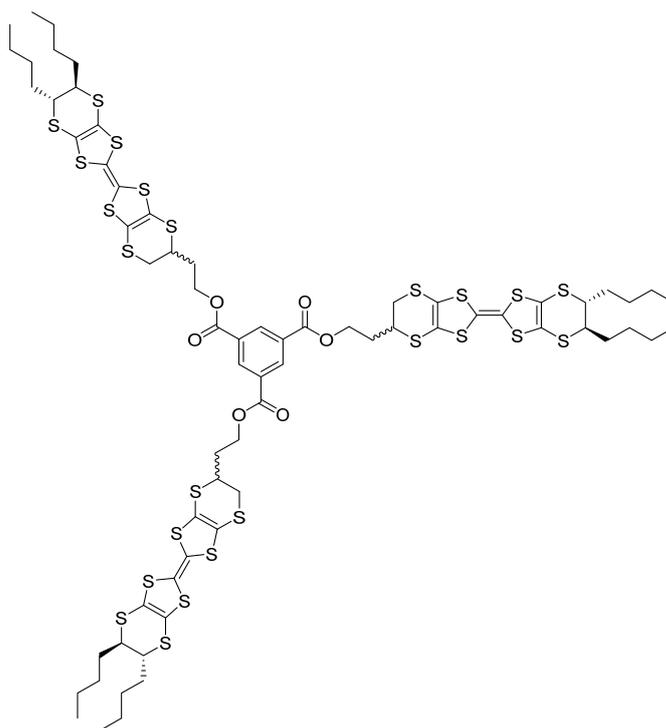
Trans-bis-5',6'-(n-butyl)-(5-hydroxyethyl)-BEDT-TTF (mixture of rac-5R,5'R,6'R and rac-5S,5'R,6'R stereoisomers) 25.



A solution of **S2** (2.44 g, 4.19 mmol) in THF (40 ml) and 20% HCl solution (18.5 ml) was stirred under nitrogen for 24 h. The solution was neutralised by the addition of solid NaHCO₃. The organic layer was collected, dried (Na₂SO₄) and purified by column chromatography (DCM/ethyl acetate 10:1) to give donor **25** (1.77 g, 78.2 %) as an orange oil. δ_H (400 MHz, CDCl₃): 3.78 (2H, t, J = 5.9 Hz, OCH₂CH₂), 3.70-3.77 (H, m, 5'-H), 3.34 (2H, dd, J = 13.2, 3.1 Hz, 6'-H_α), 3.02-3.10 (3H, m, 5-,6-H & 6'-H_β), 1.89-1.99 (2H, m, OCH₂CH₂), 1.59-1.75 (4H, m, 2 × butyl 1''-H₂), 1.41-1.52 (2H, m, 2 × butyl 2''-H_α), 1.23-1.38 (6H, m, 2 × butyl 2''-H_β & 3''-H₂), 0.87 (6H, t, J = 7.2 Hz, 2 × butyl 4''-H₃); δ_c (100 MHz, CDCl₃): 113.1, 113.0, 111.8, 111.7 & 110.9 (sp²-C), 59.7 (OCH₂CH₂), 48.3 (5-, 6-C), 40.3 (5'-C), 37.2 (OCH₂CH₂), 36.1 (2 × butyl 1''-CH₂), 35.7 (6'-C), 28.9 (2 × 2''-butyl CH₂), 22.5 (2 × butyl 3''-CH₂), 14.2 (2 × butyl 4''-CH₃); ν_{max}/cm⁻¹: 2952, 2922, 2853, 1763, 1720, 1702, 1677, 1655, 1560, 1459, 1407, 1378, 1299, 1277, 1169, 1003, 1040, 1003, 883, 772, 729; HRMS (ESI) calcd for C₂₀H₂₈OS₈ ([M]⁺): 539.9913, found: 539.9907. Found: C, 44.12; H, 5.04% Calc. for C₂₀H₂₈OS₈: C, 44.41; H, 5.22%.

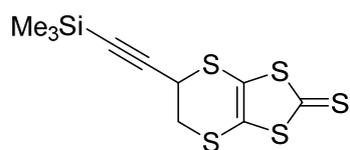
Tris(-2-(trans-5',6'-bis(n-butyl)BEDT-TTF)ethyl) trimesate 28.

(rac-5R,5R,5R and rac-5R,5R,5S – for each of these four stereoisomers there are four stereoisomers due to the possible combinations of stereochemistry at the disubstituted 5',6' bridges.)



To a mixture of hydroxyethyl donor **25** (1.11 g, 2.05 mmol), trimesic acid (0.15 g, 0.48 mmol) and triethylamine (10 ml) in dry THF (40 ml) cooled to 0°C, a 50% solution of *n*-propylphosphonic anhydride in ethyl acetate (1.3 ml) was added slowly. The resulting mixture was stirred for 30 min. at 0°C and then at room temperature overnight. After removal of THF, DCM (50 ml) and water (50 ml) were added to the residue. The organic layer was collected and washed with distilled water (100 ml) and brine (50 ml) successively, dried with MgSO₄ and then evaporated to dryness under reduced pressure. The residue was purified by column chromatography (DCM) to give donor **28** (0.57 g, 44.9 %) as an orange powder, m.p. 69–71 °C. δ_{H} (400 MHz, THF-*d*₈): 8.79 (3H, s, 3×Ar-*H*), 4.51–4.57 (6H, m, 3×OCH₂CH₂), 3.70–3.74 (3H, m, 3×5′-*H*), 3.38 (3H, dd, *J*=13.1, 2.9 Hz, 3×6′-*H*_α), 3.13 (3H, dd, *J*=13.2, 6.2 Hz, 3×6′-*H*_β), 3.08 (6H, t, *J*=5.8, 3×5,6-*H*), 2.26 (6H, q, *J*=6.2 Hz, 3×OCH₂CH₂), 1.60–1.76 (12H, m, 6 × 1″-*H*₂), 1.41–1.52 (6H, m, 6 × 2″-*H*_α), 1.23–1.39 (18H, m, 6 × 2″-*H*_α, 6 × 3″-*H*₂), 0.88 (18H, t, *J* = 7.2 Hz, 6 × 4″-*H*₃); δ_{C} (100 MHz, CDCl₃): 164.5 (C=O), 134.7 (Ar-C₃), 131.0 (Ar-C₃), 113.1, 112.6, 112.1, 111.6 & 110.3 (sp²-C), 62.7 (3 × OCH₂CH₂), 48.2 (3 × 5-6-C), 40.2 (3 × 5′-C), 35.9 (6 × 1″-CH₂), 35.4 (3 × 6′-C), 33.7 (3 × OCH₂CH₂), 28.8 (6 × 2″-CH₂), 22.3 (6 × 3″-CH₂), 14.0 (6 × 4″-CH₃); ν_{max} /cm⁻¹: 2955, 2924, 2855, 1721, 1451, 1378, 1329, 1228, 1143, 1105, 1002, 922, 918, 886, 772 737; HRMS (ESI) calc. for [M-(C₂₁H₂₈O₂S₈)-(C₂₀H₂₈OS₈)-C₄H₁₀]⁺: 609.9022, found 610.0330; calc. for [M-2(C₂₁H₂₈O₂S₈)-C₄H₁₀]⁺: 581.9072, found 582.0022; Found: C, 46.43; H, 4.78%. Calc. for C₆₉H₈₄O₆S₂₄: C, 46.59; H, 4.76%.

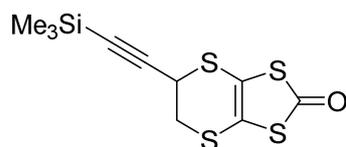
(+/-) 5-(Trimethylsilylethynyl-5,6-dihydro-1,3-dithiolo[4,5-*b*]1,4-dithiin-2-thione, **34**.



A mixture of 4-trimethylsilyl-1-buten-3-yne^{S3} **33** (5.54 g, 44.58 mmol) and trithione **10** (8.00 g, 40.74 mmol) in toluene (100 ml) were refluxed for 15 h. under nitrogen. The solvent was removed under reduced pressure and the residue purified by column chromatography (cyclohexane: ethyl acetate, 8:1) to give thione **34** (7.14 g, 54.7 %) as a yellowish

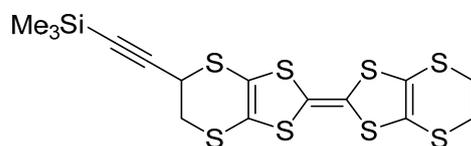
brown solid, m.p. 80–82 °C. δ_{H} (400 MHz, CDCl_3): 4.41 (1H, dd, $J = 7.3, 3.6$ Hz, 5- H), 3.49 (1H, dd, $J = 12.9, 3.6$ Hz, 6- H_{α}), 3.42 (1H, dd, $J = 12.9, 7.3$ Hz, 6- H_{β}), 0.18 (9H, s, $\text{Si}(\text{CH}_3)_3$); δ_{C} (100 MHz, CDCl_3): 207.6 (C=S), 124.4 & 123.3 (3a-,7a-C), 99.6 (C=C-Si), 93.0 (C=C-Si), 36.0 (5-C), 35.0 (6-C), 0.0 ($\text{Si}(\text{CH}_3)_3$); $\nu_{\text{max}}/\text{cm}^{-1}$: 2967, 2872, 2162, 1482, 1406, 1292, 1246, 1043, 1025, 1009, 954, 874, 833, 755; HRMS (ESI) calc. for $\text{C}_{10}\text{H}_{12}\text{S}_5\text{Si}$ ($[\text{M}+\text{H}]^+$): 320.9390, found: 320.9396.

(+/-) 5-(Trimethylsilylethynyl)-5,6-dihydro-1,3-dithiolo[4,5-b]1,4-dithiin-2-one, 35.



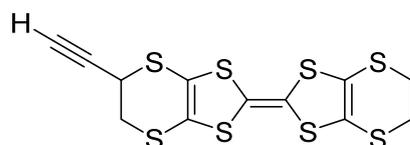
Mercuric acetate (8.88 g, 27.87 mmol) was added to a solution of thione **34** (5.95 g, 18.56 mmol) in CHCl_3 (120 ml). After 2 h. stirring at room temperature the mixture was filtered. The filtrate was washed consecutively with saturated NaHCO_3 solution (3×100 ml) and water (100 ml), dried (MgSO_4) and evaporated to afford oxo compound **35** as a brown solid (5.575 g, 98.5 %), m.p. 103–105 °C. δ_{H} (400 MHz, CDCl_3): 4.43 (1H, dd, $J = 7.3, 3.8$ Hz, 5- H), 3.51 (1H, dd, $J = 12.9, 3.8$ Hz, 6- H_{α}), 3.44 (1H, dd, $J = 12.9, 7.3$ Hz, 6- H_{β}), 0.18 (9H, s, $\text{Si}(\text{CH}_3)_3$); δ_{C} (100 MHz, CDCl_3): 189.2 (C=O), 115.3, 114.3 (3a-,7a-C), 100.0 (C=C-Si), 92.8 (C=C-Si), 37.4 (5-C), 36.4 (6-C), 0.0 ($\text{Si}(\text{CH}_3)_3$); $\nu_{\text{max}}/\text{cm}^{-1}$: 2957, 2895, 2175, 1671, 1621, 1504, 1484, 1416, 1244, 1222, 1136, 1064, 1009, 981, 958, 901, 880, 837, 756; HRMS (ESI) calc. for $\text{C}_{10}\text{H}_{12}\text{OS}_4\text{Si}$ ($[\text{M}+\text{H}]^+$): 304.9616, found: 304.9612.

(+/-)-Trimethylsilylethynyl-BEDT-TTF, 37.



A mixture of 5,6-dihydro-dithiolo[4,5-b]dithiin-2-thione **36** (5.00 g, 19.16 mmol) and oxo compound **35** (2.74 g, 9.00 mmol) was heated in trimethyl phosphite (120 ml) to 60 °C under nitrogen for 18 h. Trimethyl phosphite was removed *in vacuo*, and the residue was purified by chromatography (chloroform/ethyl acetate 250:1) to give protected donor **37** (1.97 g, 45.5%) as a yellow powder, m.p. 133–135 °C. δ_{H} (400 MHz, CDCl_3): 4.27 (1H, dd, $J = 7.7, 3.8$ Hz, 5- H), 3.35 (1H, dd, $J = 12.8, 3.8$ Hz, 6- H_{α}), 3.28 (1H, dd, $J = 12.8, 7.7$ Hz, 6- H_{β}), 3.26 (4H, s, 5',6'- H_2), 0.15 (9H, s, $\text{Si}(\text{CH}_3)_3$); δ_{C} (100 MHz, CDCl_3): 115.7, 114.9, 113.9, 113.8, 112.8 & 111.7 ($\text{sp}^2\text{-C}$), 100.4 (C=C-Si), 92.1 (C=C-Si), 36.4 (5-C), 35.6 (6-C), 30.3 (5'-,6'-C), 0.0 ($\text{Si}(\text{CH}_3)_3$); $\nu_{\text{max}}/\text{cm}^{-1}$: 2956, 2917, 2172, 1668, 1622, 1505, 1482, 1409, 1286, 1246, 1211, 1169, 1125, 1058, 983, 955, 836, 756; HRMS (ESI) calc. for $\text{C}_{15}\text{H}_{16}\text{S}_8\text{Si}$ ($[\text{M}+\text{H}]^+$): 480.8865, found: 480.8858. Found: C, 37.56; H, 3.44%. Calc. for $\text{C}_{15}\text{H}_{16}\text{S}_8\text{Si}$: C, 37.47; H, 3.35%.

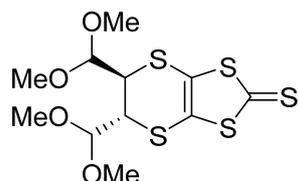
(+/-)-Ethynyl-BEDT-TTF, 38.



The protected donor **37** (0.97 g, 2.02 mmol) was stirred with potassium fluoride (0.84 g, 14.46 mmol) in a mixture of THF (40 ml) and methanol (20 ml) for 3 h. The solvent was removed *in vacuo*, the residue was stirred with methanol twice to give donor **38** (0.73 g, 88.5 %) as a brown solid, m.p. 144–146 °C. δ_{H} (400 MHz, CDCl_3): 4.32 (1H, ddd, $J = 7.2,$

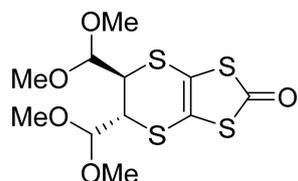
3.8, 2.5 Hz, 5-*H*), 3.38 (1H, dd, $J = 12.8, 3.8$ Hz, 6-*H* α), 3.32 (1H, dd, $J = 12.9, 7.2$ Hz, 6-*H* β), 3.29 (4H, s, 5',6'-*H* $_2$), 2.54 (1H, d, $J = 2.5$ Hz, C=C-*H*); δ_c (100 MHz, CDCl $_3$): 115.4, 114.1, 113.7, 113.7, 112.8 & 111.2 (sp 2 -C), 79.5 (C=C-*H*), 74.6 (C=C-*H*), 35.9 (5-C), 34.0 (6-C), 30.1 (5',6'-C); $\nu_{\max}/\text{cm}^{-1}$: 3262, 2958, 2915, 2118, 1665, 1552, 1507, 1405, 1283, 1259, 1171, 1124, 997, 952, 903, 875, 771, 651; HRMS (ESI) calc. for C $_{12}$ H $_8$ S $_8$ ([M+H] $^+$): 408.8470, found: 408.8465. Found: C, 35.13; H, 1.95%. Calc. for C $_{12}$ H $_8$ S $_8$: C, 35.27; H, 1.97%.

(+/-)-5,6-Bis-(dimethoxymethyl)-5,6-dihydro-1,3-dithiolo[4,5-*b*]1,4-dithiine-2-thione, 40.



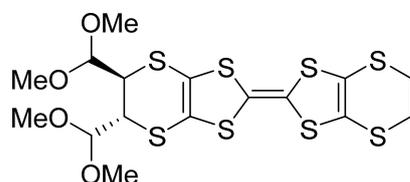
Fumaraldehyde bis(dimethylacetal) **39** (0.98 g, 5.6 mmol) and trithione **10** (2.3 g, 11.7 mmol) were heated to reflux in toluene (60 mL) under an inert atmosphere for 12 h. The reaction was cooled to room temperature and filtered, washing with dichloromethane (*ca.* 50 mL). The combined filtrate was evaporated, and the material purified by chromatography over silica eluting with cyclohexane/ethyl acetate (3:1) to afford thione **40** (0.35 g, 16.9 %) as a red-brown solid, m.p. 87-88 °C. δ_H (400 MHz, CDCl $_3$): 4.49 (2H, br d, $J = 6.9$ Hz, 2 x CH(OCH $_3$) $_2$), 3.74 (2 H, br d, $J = 6.9$ Hz, 5-,6-*H*), 3.45 (6 H, s, 2 x CH $_3$), 3.40 (6 H, s, 2 x CH $_3$); δ_c (100 MHz, CDCl $_3$): 207.8 (2-C), 122.9 (3a-, 7a-C), 104.1 (CH(OCH $_3$) $_2$), 55.9 (2 x OCH $_3$), 55.0 (2 x OCH $_3$), 45.6 (5-,6-C); ν_{\max} (ATR)/cm $^{-1}$ 2925, 2830, 1442, 1395, 1351, 1266, 1186, 1110, 1047(C=S), 957, 900, 887, 819, 726, 562, 544, 515; HRMS (EI) calc. for [C $_{11}$ H $_{16}$ O $_4$ S $_5$ +H] $^+$: 372.9725, found [M+H] $^+$ 372.9723. Found C, 35.55; H, 4.28%. C $_{11}$ H $_{16}$ O $_4$ S $_5$ requires C, 35.46; H, 4.33%.

(+/-)-5,6-Bis-dimethoxymethyl-5,6-dihydro-[1,3]dithiolo[4,5-*b*]1,4-dithiin-2-one, 41.



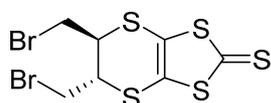
To a stirred solution of **40** (0.35 g, 0.94 mmol) in chloroform (50 mL) under an inert atmosphere, was added mercuric acetate (0.45 g, 1.4 mmol). After 1 h. the reaction was filtered, the solid washed with a little chloroform (*ca.* 20 mL) and the filtrate evaporated to afford oxo compound **41** (0.32 g, 97 %) as a red-brown solid, m.p. 81-83 °C. δ_H (400 MHz, CDCl $_3$): 4.54 (2 H, br d, $J = 6.9$ Hz, CH(CH $_3$) $_2$), 3.75 (2 H, br d, $J = 6.9$ Hz, 5-, 6-*H*), 3.47 (6 H, s, 2 x OCH $_3$), 3.42 (6 H, s, 2 x OCH $_3$); δ_c (100 MHz, CDCl $_3$): 188.7 (2-C), 113.7 (3a, 7a-C), 104.0 (CH(OCH $_3$) $_2$), 55.6 (2 x OCH $_3$), 54.8 (2 x OCH $_3$), 46.9 (5, 6-C); ν_{\max} (ATR)/cm $^{-1}$ 2938, 2831, 1658, 1627, 1507, 1443, 1356, 1270, 1188, 1110, 1060, 966, 892, 805, 749, 728, 678, 597, 546, 463; m/z (ES) $^+$ [M+NH $_4$] $^+$ 374.0223. [C $_{11}$ H $_{16}$ O $_5$ S $_4$ +NH $_4$] $^+$ requires 374.0219. Found C, 37.01; H, 4.45 %. C $_{11}$ H $_{16}$ O $_5$ S $_4$ requires C, 37.06; H, 4.52%.

(+/-)-*trans*-5,6-Bis(dimethoxymethyl)BEDT-TTF 42.



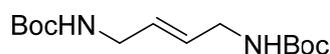
Oxo compound **41** (0.30 g, 0.84 mmol) and 5,6-dihydro-dithiolo[4,5-b]dithiin-2-thione **36** (0.57 g, 2.53 mmol) were heated to 100 °C in triethyl phosphite (15 mL) under an inert atmosphere. After approximately 30 min. an orange precipitate was observed. Heating was continued for 18 h., before cooling to room temperature. The precipitate was filtered washing with *n*-hexane (50 mL) and then chloroform (50 mL). The filtrate was evaporated affording the crude material as a deep orange oil, which was purified by chromatography over silica eluting with cyclohexane/ethyl acetate (2:1) to give the disubstituted donor **42** (0.22 g, 49 %) as a light orange solid, m.p. 131-133 °C. δ_{H} (400 MHz, CDCl₃): 4.41 (2H, d, $J = 8.0$ Hz, CH(OCH₃)₂), 3.71 (2H, d, $J = 8.0$ Hz, 5-, 6-H), 3.46 (6H, s, 2 x OCH₃), 3.39 (6H, s, 2 x OCH₃), 3.29 (4H, s, 5', 6'-H₂); δ_{C} (100 MHz, CDCl₃): 114.0, 113.8, 112.2, 111.2 (*sp*²C), 104.2 (CH(OCH₃)₂), 56.0 (2 x OCH₃), 54.7 (2 x OCH₃), 46.3 (5-, 6-C), 30.2 (5', 6'-C); ν_{max} (ATR)/cm⁻¹ 2922, 2869, 2829, 1439, 1344, 1180, 1112, 1060, 959, 914, 875, 771, 731, 563; HRMS (EI) [M]⁺ 531.9122. [C₁₆H₂₀S₈O₄]⁺ requires 531.9122, Found C, 36.21; H, 3.73%. C₁₆H₂₀O₄S₈ requires C, 36.07; H, 3.78%.

(+/-) *trans*-5,6-Bis(bromomethyl)-5,6-dihydro-1,3-dithiolo[4,5-b]1,4-dithiin-2-thione **43**.



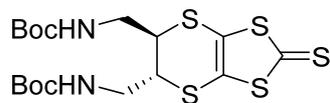
E-1,4-Dibromobut-2-ene (8.00 g, 37.4 mmol) and trithione **10** (8.10 g, 41.3 mmol) were refluxed together in toluene (200 ml) for 28 h. and then filtered and left to cool. The precipitated solid was collected and refluxed with excess chloroform containing active carbon for 30 min. Filtration and cooling gave **43** (2.36 g) as yellow crystals which were filtered off. Further material (2.59 g) was obtained by evaporation of most of the filtrate, which was collected filtration and washed with chloroform. The original filtrate was also evaporated and the residue treated as above with refluxing chloroform and active carbon, to give further product (1.97 g), giving a total yield of **43** (6.89 g, 44.9 %), yellow-orange solid, m.p. 168-170 °C, δ_{H} (400 MHz, DMSO-*d*₆): 4.16-4.21 (2H, m, 5-, 6-H), 3.85 (2H, dd, $J = 10.1, 5.3$ Hz, 5-, 6-CH_α), 3.77 (2H, t, $J = 9.7$ Hz, 5-, 6-CH_β); δ_{C} (100 MHz, DMSO-*d*₆): 207.2 (C=S), 119.4 (3a-, 7a-C), 42.5 (5-, 6-C), 34.4 (5-, 6-CH₂); ν_{max} /cm⁻¹: 3050, 1483, 1420, 1298, 1254, 1243, 1183, 1175, 1130, 1075, 1017, 910, 893, 806, 614, 575, 518, 513, 457, 442; Found: C, 20.54; H, 1.37%. Calc. for C₇H₆Br₂S₅: C, 20.49; H, 1.47%.

E-1,4-Bis-(*N*-Boc-amino)-but-2-ene, **44**.⁵⁴



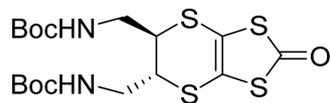
Di-*tert*-butyl dicarbonate (6.19 g, 28.36 mmol) and triethylamine (5 ml, 35.85 mmol) were added to a solution of the *E*-1,4-diaminobut-2-ene bis hydrochloride salt⁵⁵ (1.84 g, 11.7 mmol) in DCM (30 ml). The reaction mixture was stirred at room temperature overnight, filtered, and the filtrate evaporated. The residue was dissolved in DCM, and the solution washed with water (2 x 50 ml) and brine (50 ml) and dried over magnesium sulphate. Evaporation gave the product **44** as a white crystalline solid (3.09 g, 10.8 mmol, 92%), m.p. 117-119 °C. δ_{H} (400 MHz, CDCl₃): 5.58 (2H, br s, 2-, 3-H), 4.68 (2H, br, 2 x NH), 3.69 (4H, br s, 1-, 4-H₂), 1.44 (18H, s, 2 x -C(CH₃)₃); δ_{C} (100 MHz, CDCl₃): 155.7 (2 x C=O), 128.3 (2-, 3-C), 79.3 (2 x -OC(CH₃)₃), 41.8 (1-, 4-C), 28.4 (2 x C(CH₃)₃); ν_{max} : 3360, 2982, 2933, 1688, 1519, 1455, 1444, 1389, 1364, 1294, 1241, 1161, 1068, 1047, 1028, 970, 933, 864, 780, 764, 736; HRMS (ES): C₁₄H₂₆N₂O₄Na (M+Na)⁺ requires 309.1796, found 309.1782, C₂₈H₅₂N₄O₈Na (2M+Na)⁺ requires 595.3688, found 595.3687.

(+/-)-Trans-5,6-bis(N-Boc-aminomethyl)-5,6-dihydro-1,3-dithiolo[4,5-b]1,4-dithiin-2-thione, 45.



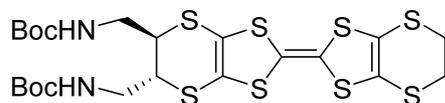
A mixture of disubstituted but-2-ene **44** (0.65 g, 2.27 mmol) and trithione **10** (0.67 g, 3.41 mmol) in toluene (30 ml) was refluxed for 24 h. The mixture was filtered and the filtrate evaporated. The residue was purified by column chromatography (3:1 cyclohexane-ethyl acetate) to yield the thione **45** as a golden crystalline solid (0.583 g, 53.5%), m.p. 149-151 °C. δ_H (400 MHz, CDCl₃): 5.04 (2H, br t, 2 x NH), 3.69 (2H, br t, 5-,6-H), 3.46 (4H, br t, 2 x NCH₂), 1.44 (18H, s, 2 x -C(CH₃)₃); δ_C (100 MHz, CDCl₃): 207.0 (2-C), 155.7 (2 x NC=O), 119.1 (3a-, 7a-C), 80.3 (2 x OC(CH₃)₃), 44.9 (2 x -CH₂N), 42.4 (5-,6-C), 28.3 (2 x OC(CH₃)₃); ν_{max} : 3319 br, 2976, 2927, 2850, 1679, 1523, 1498, 1448, 1431, 1390, 1364, 1278, 1250, 1161, 1068, 1012, 954, 882, 862, 839, 783, cm⁻¹; HRMS: (ASAP⁺) C₁₇H₂₆N₂O₄S₅ + H⁺ requires 483.0574, found 483.0574.

(+/-)-Trans-5,6-bis(N-Boc-aminomethyl)-1,3-dithiolo[4,5-b]1,4-dithiin-2-one, 46.



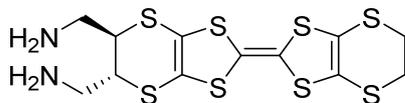
Mercuric acetate (1.33 g, 4.14 mmol) was added to a solution of thione **45** (1.00 g, 2.07 mmol) in chloroform (30 ml) and stirred at room temperature for 5 h. The mixture was filtered, and the solids washed with chloroform. The filtrate was washed with water (3 x 25 ml) and brine (25 ml) and dried over magnesium sulphate. Evaporation of solvent gave the oxo compound **46** as a fawn crystalline solid (0.60 g, 62%) m.p. 150-151 °C. δ_H (400 MHz, CDCl₃): 5.08 (2H, br s, 2 x NH), 3.62-3.68 (2H, br t, 5-,6-H), 3.44-3.58 (4H, m, 2 x NCH₂), 1.44 (18H, s, 2 x OC(CH₃)₂); δ_C (100 MHz, CDCl₃): 188.1 (2-C), 155.7 (2 x NC=O), 109.8 (3a-,7a-C), 80.2 (2 x -OCMe₃), 44.9 (2 x CH₂N), 43.7 (5-,6-C), 28.3 (2 x -C(CH₃)₃); ν_{max} : 3330, 2975, 2931, 1680, 1649, 1529, 1508, 1451, 1431, 1391, 1363, 1272, 1252, 1217, 1162, 1068, 1045, 1032, 950, 945, 892, 881, 841, 784, 763, 727, 721; HRMS: (ES⁺) C₁₇H₂₆N₂O₅S₄ + H⁺ requires 467.0803, found 467.0790.

(+/-)-Trans-5,6-(N-Boc-aminomethyl)-BEDT-TTF 47.



A mixture of oxo compound **46** (0.56 g, 1.20 mmol) and 5,6-dihydro-dithiolo[4,5-b]dithiin-2-thione **36** (0.96 g, 4.26 mmol) was heated in dry triethyl phosphite (10 ml) to 90°C for 18 h. Triethyl phosphite was removed *in vacuo* and the residue was purified by column chromatography (3:1 cyclohexane : ethyl acetate) to yield the cross coupled donor **47** as an orange powder (0.49 g, 63.5%), m.p. 141-143 °C. δ_H (400 MHz, THF-d₈): 6.68 (2H, t, J = 5.9 Hz, 2 x NH), 3.68-3.73 (2H, m, 2 x 5-,6-H), 3.33 (4H, s, 5'-,6'-H₂), 3.24-3.31 (4H, m, 2 x CH₂N), 1.38 (18H, s, 2 x C(CH₃)₃); δ_C (100 MHz, THF-d₈): 157.3 (2 x C=O), 115.0, 112.1, 111.8, 111.6 (6 x sp² C), 79.5 (2 x OC(CH₃)₃), 46.5 (2 x CHNBoc), 44.6 (5-,6-C), 31.4 (5'-,6'-C), 29.1 (2 x OC(CH₃)₃); ν_{max} : 3314 br, 2977, 2923, 1678, 1514, 1451, 1425, 1390, 1363, 1278, 1251, 1162, 1096, 1066, 1045, 1032, 1003, 953, 840, 775, 730; HRMS: Found 643.0041, C₂₂H₃₀N₂O₄S₈+H requires 643.0044. Found: C: 41.46, H: 4.77, N: 4.14%. C₂₂H₃₀N₂O₄S₈ requires C: 41.10, H: 4.70, N: 4.36%.

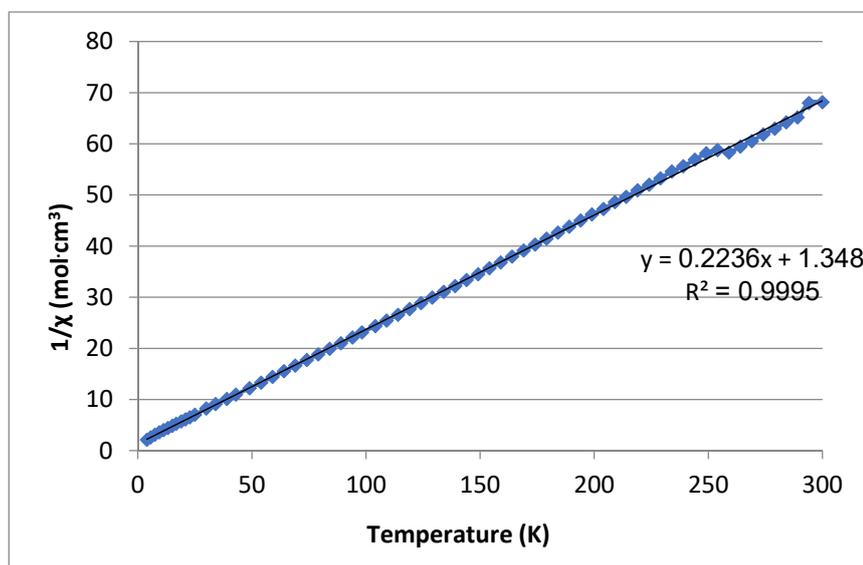
(+/-)-*Trans*-5,6-bis(aminomethyl)-BEDT-TTF, 48.

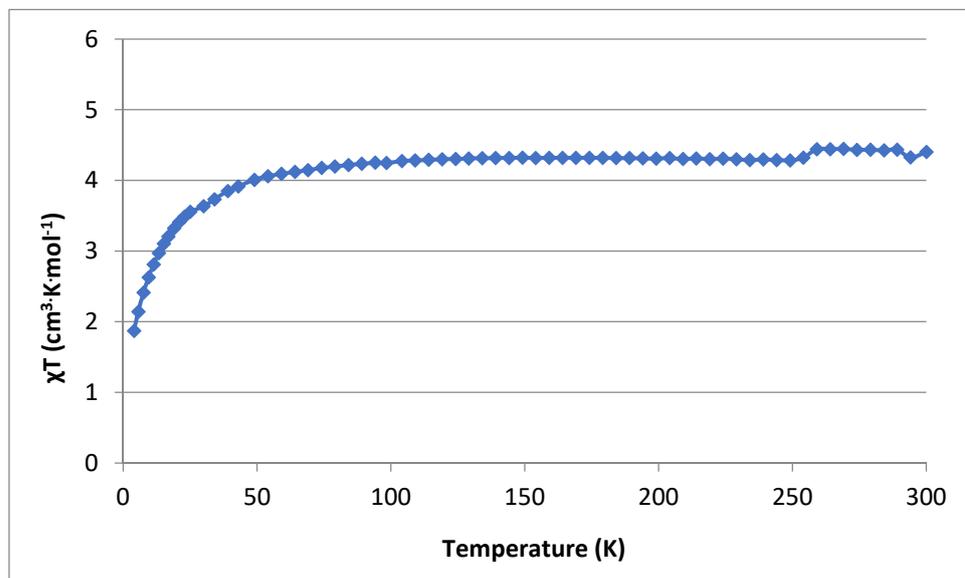
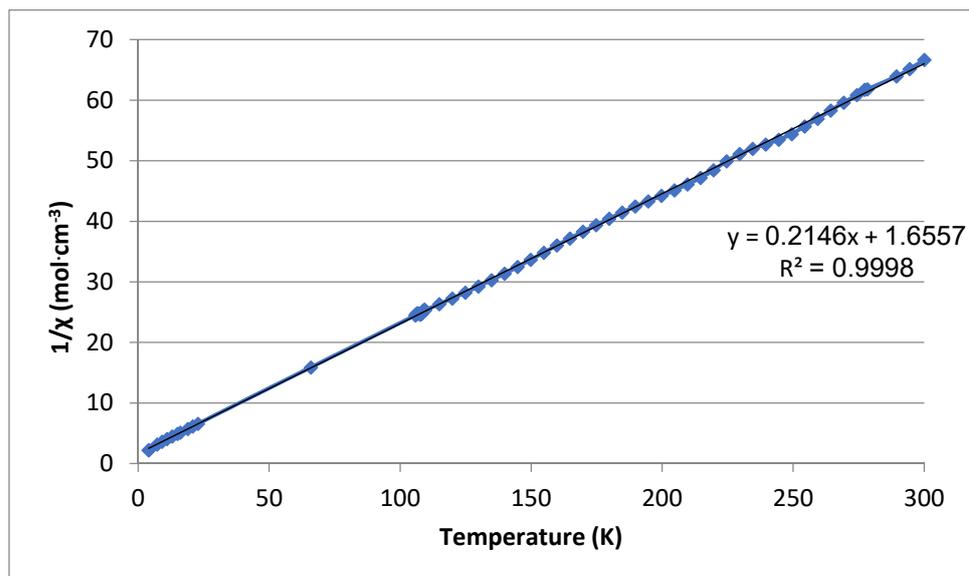


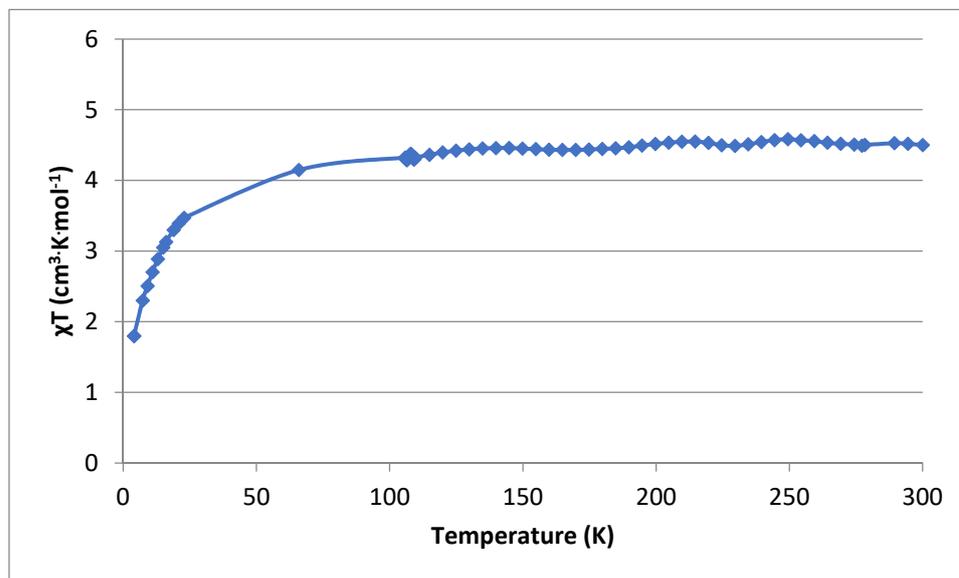
The *bis*(Boc-protected)-BEDT-TTF derivative **47** (0.13 g, 0.20 mmol) and a solution of hydrogen chloride in dioxan (2M, 4 ml) were stirred at room temperature for 2.6 h. A brown precipitate formed which was collected and washed with diethyl ether (25 ml). This solid was stirred with 1M aqueous potassium hydroxide solution (4 ml) for 1.5 h. during which time and an orange precipitate formed. The precipitate was collected and washed with cold diethyl ether (4 ml) to give the *bis*-aminomethyl donor **48** as a bright orange powder (0.069 g, 78.4 %), m.p. 126-130 °C, dec. δ_H (400 MHz, DMSO- d_6): 3.33 (2H, t, $J = 5.9$ Hz, 5-,6- H), 3.26 (4H, s, 5'-,6'- H_2), 2.95-2.97 (4H, m, 5-,6- CH_2), 1.50 (4H, br, 2 \times NH_2); δ_H (DMSO- d_6): 3.65 (2H, br t, $J = 6.0$ Hz, 5-,6- H), 3.40 (4H, s, 5'-,6'- H_2), 2.82 (2H, dd, $J = 13.3, 6.6$ Hz, 5-,6- $CH_\alpha N$), 2.73 (2H, dd, $J = 13.3, 6.3$ Hz, 5-,6- $CH_\beta N$); δ_C (100 MHz, DMSO- d_6): 112.9, 111.1, 110.0 (6 \times sp^2C), 47.0 (5-,6- C), 46.1 (2 \times CH_2N), 29.5 (5'-,6'- C); ν_{max} : 3327 br, 2911, 1573, 1559, 1508, 1465, 1423, 1401, 1374, 1319, 1284, 988, 881, 770, 617; m/z (ES $^+$): 443 (M+H) $^+$; Found C: 32.38, H: 2.97, N: 6.27%, $C_{12}H_{14}N_2S_8$ requires C: 32.55, H: 3.19, N: 6.33%.

S2. Magnetic data for 55-56.

Plot of $1/\chi v T$ (K) for 55.



Plot of χT vs T for 55.Plot of $1/\chi$ v T (K) for 56.

Plot of χT vs T for 56.

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