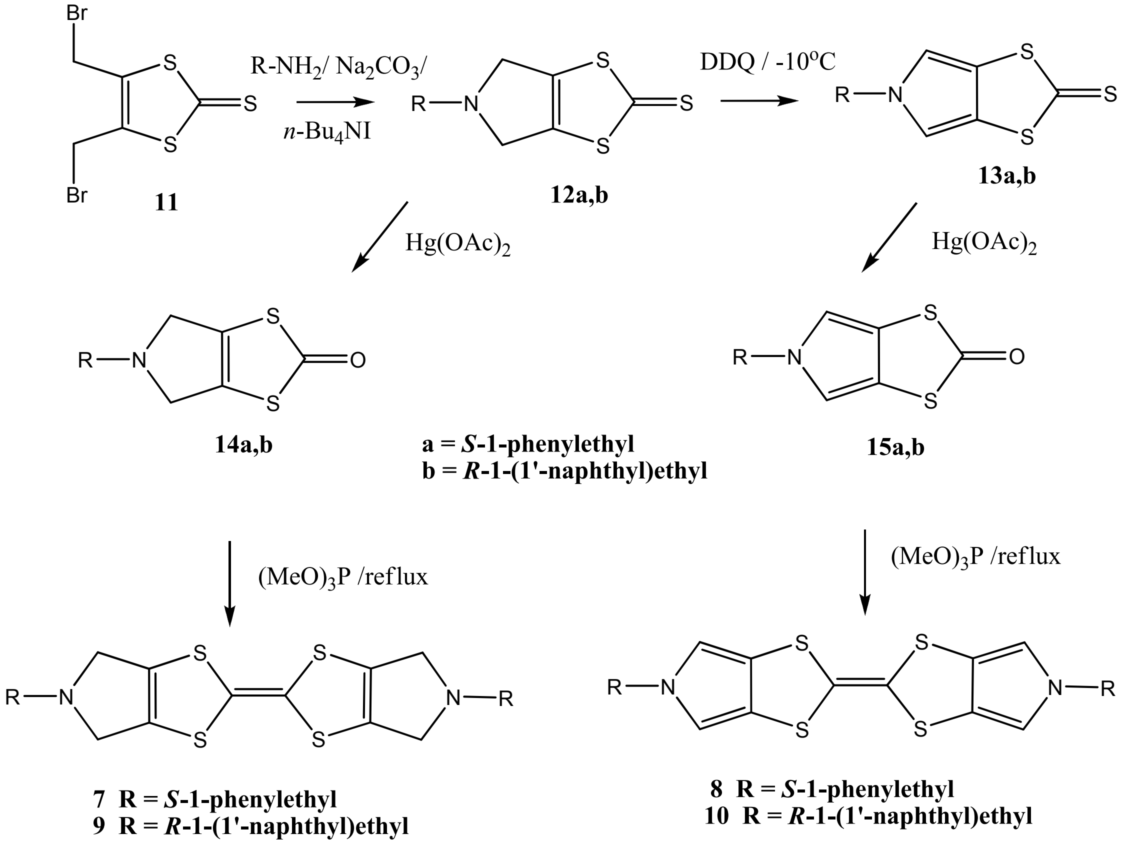
Supplementary Material

Experimental.

General. NMR spectra were measured on a JEOL ECLIPSE 400 spectrometer at 400 MHz for ^{1}H and at 100 MHz for ^{13}C and measured in p.p.m. downfield from TMS with coupling constants reported in Hz. IR spectra were recorded on Perkin Elmer Spectrum 100 FT-IR Spectrometer with a Universal ATR accessory, and are reported in cm-^{1} Optical rotation data were measured on a PerkinElmer 241 polarimeter. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre at the University of Swansea. Chemical analysis data were obtained from Mr Stephen Boyer, London Metropolitan University. X-ray diffraction datasets were measured by the EPSRC National Crystallography Service at Southampton University. Flash chromatography was performed on 40-63 silica gel (Merck).



11

12a,b

13a,b

14a,b

15a,b

a = *S*-1-phenylethyl
b = *R*-1-(1'-naphthyl)ethyl

7 R = *S*-1-phenylethyl
9 R = *R*-1-(1'-naphthyl)ethyl

8 R = *S*-1-phenylethyl
10 R = *R*-1-(1'-naphthyl)ethyl

S,S-Bis (2,5-dihydro-N-(1-phenylethyl)pyrrolo[3,4-d])tetrathiafulvalene, 7.

S-4,6-Dihydro-5-(1-phenylethyl)-1,3-dithiolo[4,5-c]pyrrolo-2-thione, 12a

(*S*)-(-)-α-Methylbenzylamine (1.7mL, 13.1mmol) was added dropwise to a mixture of 4,5-bis(bromomethyl)-1,3-dithiole-2-thione (4.00g, 12.5mmol), sodium carbonate (3.00g, 28.3mmol) and tetrabutylammonium iodide (0.47g, 1.3mmol) in THF (50mL). The resulting mixture was refluxed under nitrogen overnight. After removal of solvent, the residue was treated with ethyl acetate and 1M HCl solution to precipitate the product which was collected by filtration and washed with water and acetone to yield the thione **12a** as a yellow solid (1.32g, 35.8%). m.p. 199-201°C (dec.); δ_H (DMSO-d$_6$, 125° C): 7.64 (2H, d, J = 7.6 Hz, 2'-,6'-*H*), 7.40 (3H, m, 3'-,4'-,5'-*H*), 4.61 (1H, br m, C*H*CH$_3$), 4.33 (2H, br d, J = 12.0 Hz, 4-,6-H_α), 4.20 (2H, br d, J = 12.0 Hz, 4-,6-H_β), 1.90 (3H, d, J = 6.9 Hz, CH_3); δ_C (CDCl$_3$, 25°C): 218.6 (2-*C*), 136.6, 134.9, 129.3, 129.1, 128.0 (Ar-C_6+3a-,6a-*C*), 65.0 (4,6-*C*), 56.7 (*C*HCH$_3$), 18.7 (*C*H$_3$); ν_{max} (ATR): 2973, 2873, 1419, 1379, 1332, 1140, 1075, 1050, 992, 793, 772, 700, 546, 492, 486, 450, 413, 386cm^{-1}; *m/z*: (ES) 280 [M]$^+$; HRMS (ES) found: 280.0284, $C_{13}H_{13}NS_3$ requires: 280.0283; found C, 55.80; H, 4.55; N, 4.97%, $C_{13}H_{13}NS_3$ requires C, 55.87; H, 4.69; N, 5.01%; $^{293}[\alpha]_D$ = -7.0° (c = 0.2, DMSO).

S-4,6-Dihydro-5-(1-phenylethyl)-1,3-dithiolo[4,5-c]pyrrole-2-one, 14a

Mercuric acetate (2.80g, 8.79mmol) was added to a solution of the thione **12a** (1.50g, 5.37mmol) in chloroform (200mL) and the reaction mixture was stirred overnight, filtered and the solid residue washed with chloroform. The combined filtrates were concentrated in *vacuo* and the residue was purified by flash chromatography (SiO$_2$, eluting with cyclohexane:chloroform (4:1)) to yield the oxo compound **14a** as a pale orange solid (1.21g, 86.6%); m.p. 95-97°C; δ_H (CDCl$_3$): 7.37 (4H, m, Ar-H_4), 7.30 (1H, m, Ar-H_1), 3.98 (2H, m, 4-,6-H_α), 3.88 (2H, m, 4-,6-H_β), 3.87 (1H, q, J = 6.6 Hz, C*H*CH$_3$), 1.38 (3H, d, J = 6.6 Hz, CH_3); δ_C (CDCl$_3$): 195.5 (*C*=O), 144.1, 128.6, 127.4, 127.0 (Ar-C_6), 125.8 (3a-,6a-*C*), 64.7 (*C*HCH$_3$), 57.2 (4-,6-*C*), 22.9 (*C*H$_3$); ν_{max} (ATR): 2972, 2772, 1668, 1614, 1513, 1490, 1450, 1375, 1326, 1310, 1137, 1121, 1076, 1052, 965, 937, 815, 766, 699, 544cm^{-1}; *m/z*: (ES) 264 $[M]^+$; HRMS (ES) found: 264.0509, $C_{13}H_{13}NOS_2$ requires: 264.0511; found C, 59.14; H, 6.00; N, 5.37%, $C_{13}H_{13}NOS_2$ requires C, 59.28; H, 6.11; N, 5.32%; $^{293}[\alpha]_D = -18.5^o$ (c = 0.4, $CHCl_3$).

S,S-Bis (2,5-dihydro-N-(1-phenylethyl)pyrrolo[3,4-d])tetrathiafulvalene 7.

A mixture of oxo compound **14a** (1.21g, 4.59mmol) and freshly distilled trimethyl phosphite (100mL) was heated to reflux for 48h. The reaction mixture was left to cool to room temperature. The orange crystals of the product **7** were collected by filtration and washed with ethyl acetate and then dried in *vacuo* (256mg, 38.8%); m.p. 187-189°C (dec.); δ_H ($CDCl_3$): 7.26 (8H, m, 2×Ar-H_4), 7.19 (2H, m, 2×Ar-H_1), 3.64 (2H, q, J = 6.6 Hz, 2×C*H*), 3.53 (4H, m, 4-,4'-,6-,6'-H_α), 3.43 (4H, m, 4-,4'-,6-,6'-H_β), 1.32 (6H, d, J = 6.6 Hz, 2×CH_3); δ_C ($CDCl_3$): 144.4, 129.6, 128.6, 127.1 (2×Ar-C_6), 127.3 (3a-,3a'-,6a-,6a'-*C*), 117.4 (2-,2'-*C*), 65.2 (2×*C*HCH_3), 55.9 (4-,4'-,6-,6'-*C*), 22.9 (2×*C*H_3); ν_{max} (ATR): 2973, 2885, 2789, 1489, 1450, 1367, 1322, 1305, 1278, 1206, 1178, 1158, 1135, 1078, 1058, 1028, 957, 902, 837, 759, 698, 548cm^{-1}; *m/z*: (EI) 494 $[M]^+$; HRMS (EI) found: 494.0970, $C_{26}H_{26}N_2S_4$ requires: 494.0973; found C, 63.06; H, 5.38; N, 5.49%, $C_{26}H_{26}N_2S_4$ requires C, 63.12; H, 5.30; N, 5.66%; $^{293}[\alpha]_D = -44.5^o$ (c = 0.2, $CHCl_3$).

2 *S,S*-Bis (N-(1-phenylethyl)pyrrolo[3,4-d])tetrathiafulvalene, 8.

S-5-(1-Phenylethyl)-1,3-dithiolo[4,5-c]pyrrole-2-thione, 13a.

A stirred solution of thione **12a** (3.94g, 14.10mmol) in chloroform (200mL) was cooled to -15°C/-10°C and DDQ (3.20g, 14.10mmol) dissolved in benzene (80mL) was added dropwise and resulted in a dark suspension. The mixture was stirred for 2 h. then treated with 1M sodium carbonate solution. The mixture was extracted with dichloromethane (2 x 50 ml), and the combined organic solution was washed with 1M sodium carbonate solution and water and dried over magnesium sulfate. The filtrate was evaporated in *vacuo*, and the residue was purified by flash chromatography (SiO_2, eluting with petroleum ether:DCM (1:1)) to yield the thione **13a** as an orange oil (1.64g, 41.9%). δ_H ($CDCl_3$): 7.26 (3H, m, 3'-,4'-,5'-*H*), 7.08 (2H, m, 2'-,6'-*H*), 6.69 (2H, s, 4-,6-*H*), 5.26 (1H, q, J = 7.1 Hz, C*H*CH_3), 1.90 (3H, d, J = 7.1 Hz, CH_3); δ_C ($CDCl_3$): 219.6 (2-*C*), 141.4, 128.8, 128.1, 125.9 (Ar-C_6), 122.9 (3a-,6a-*C*), 110.7 (4-,6-*C*), 59.8 (*C*HCH_3), 21.8 (CH_3); ν_{max} (ATR): 3060, 3027, 2977, 1483, 1452, 1361, 1295, 1123, 1043, 1004, 862, 757, 696, 634, 522, 497cm^{-1}; *m/z*: (ES) 278 $[M]^+$; HRMS (ES) found: 278.0130, $C_{13}H_{11}NS_3$ requires: 278.0126; found C, 56.28; H, 3.90; N, 5.13%, $C_{13}H_{11}NS_3$ requires C, 56.28; H, 4.00; N, 5.05%; $^{293}[\alpha]_D = +31.6^o$ (c = 0.64, $CHCl_3$).

S-5-(1-Phenylethyl)-1,3-dithiolo[4,5-c]pyrrole-2-one, 15a.

Mercuric acetate (2.80g, 8.79mmol) was added to a solution of the thione (1.64g, 5.91mmol) **13a** in chloroform (100mL). The reaction mixture was stirred overnight, filtered and the solid residue washed with chloroform. The combined filtrates were concentrated in *vacuo* and the residue was purified by flash chromatography (SiO_2, eluting with cyclohexane:DCM (1:1)) to yield the oxo compound **15a** as an orange solid (1.11g, 71.8%); m.p. 62-64^{o}C (dec.); δ_H ($CDCl_3$): 7.25 (3H, m, 3',-4'-,5'-*H*), 7.07 (2H, m, 2'-,6'-*H*), 6.71 (2H, s, 4-,6-*H*), 5.24 (1H, q, J = 6.9 Hz, C*H*CH_3), 1.77 (3H, d, J = 6.9 Hz, CH_3); δ_C ($CDCl_3$): 196.6 (*C*=O), 141.8, 128.8, 128.0, 125.9 (Ar-C_6), 112.5 (4-,6-*C*), 112.3 (3a-,6a-*C*), 59.3 (*C*HCH_3), 21.9 (CH_3); ν_{max} (ATR): 3153, 3019, 2978, 1699, 1634, 1622, 1492, 1452, 1380, 1352, 1289, 1202, 1127, 1058, 1005, 839, 763, 722, 699, 623, 542, 515cm^{-1}; *m/z*: (EI) 261 $[M]^+$; found C, 59.77; H, 4.35; N, 5.46%, $C_{13}H_{11}NOS_2$ requires C, 59.74; H, 4.25; N, 5.36%; $^{293}[\alpha]_D = +4.2^o$ (c = 0.88, $CHCl_3$).

S,S-Bis (N-(1-phenylethyl)pyrrolo[3,4-d])tetrathiafulvalene, 8.

A mixture of oxo compound **15a** (949mg, 3.63mmol) and freshly distilled trimethyl phosphite (35mL) was heated to reflux for 50h. The reaction mixture was concentrated in *vacuo* and the residue was purified by flash chromatography (SiO_2, eluting with cyclohexane:DCM (1:1)) to yield the donor **8** as a yellow solid (472mg, 53.0%); m.p.

172-174°C; δ_H (CDCl$_3$): 7.23 (6H, m, 2×Ar-*H$_3$*), 7.04 (4H, m, 2×Ar-*H$_2$*), 6.45 (4H, s, 4-,4'-,6-,6'-*H*), 5.12 (2H, br, 2×C*H*CH$_3$), 1.71 (6H, d, J = 6.9 Hz, 2×C*H$_3$*); δ_C (CDCl$_3$): 142.5 (br), 128.7, 127.7, 125.8 (2×Ar-*C$_6$*), 119.0 (4-,4'-,6-,6'-*C*), 112.0 (br, 2-,2'-3a-,3a'-,6a-,6a'-*C*), 58.8 (br, 2×*C*HCH$_3$), 22.2 (br, 2×*C*H$_3$); ν_{max} (ATR): 2972, 2926, 1453, 1373, 1360, 1297, 1260, 1139, 1123, 1074, 1044, 1008, 991, 915, 792, 776, 757, 703, 693, 606, 544, 520, 493cm^{-1}; *m/z*: (EI) 490 [M]$^+$; HRMS (EI) found: [M]$^+$ 490.0659, $C_{26}H_{22}N_2S_4$ requires: 490.0660; found C, 63.55; H, 4.37; N, 5.60%, $C_{26}H_{22}N_2S_4$ requires C, 63.51; H, 4.52; N, 5.71%; $^{293}[\alpha]_D$ = +48.1° (c = 0.4, CHCl$_3$).

R,R-Bis(2,5-dihydro-N-(1-naphthylethyl)pyrrolo[3,4-d])tetrathiafulvalene, 9

R-4,6-Dihydro-5-(1-(naphth-1'-yl)ethyl)-1,3-dithiolo[4,5-c]pyrrole-2-thione, 12b.

A mixture of (*R*)-(+)-1-(1-naphthyl)ethylamine (5.1mL, 31.5mmol), 4,5-bis(bromomethyl)-1,3-dithiole-2-thione (9.59g, 31.0mmol), sodium carbonate (7.00g, 66.0mmol) and tetrabutylammonium iodide (1.20g, 3.2mmol) in THF (100mL) was refluxed under nitrogen atmosphere overnight. After removal of solvent, the residue was treated with ethyl acetate and 1M HCl solution to precipitate the product. The product was collected by filtration and washed with water and acetone to yield the thione **12b** as a yellow solid (8.04g, 81.4%); m.p. 202-205°C (dec.); δ_H (DMSO-d$_6$): 8.38 (1H, br, Ar-*H$_1$*), 8.15 (1H, br, Ar-*H$_1$*), 7.98 (2H, br, Ar-*H$_2$*), 7.59 (3H, br, Ar-*H$_3$*), 5.85 (1H, br, C*H*CH$_3$), 4.82 (2H, br, 4-,6-*H$_\alpha$*), 3.99 (2H, br, 4-,6-*H$_\beta$*), 1.68 (3H, br, C*H$_3$*); ν_{max} (ATR): 2974, 2929, 1513, 1438, 1412, 1391, 1378, 1333, 1251, 1172, 1140, 1118, 983, 853, 793, 775, 732, 624, 568, 536, 493cm^{-1}; *m/z*: (ES) 330 [M]$^+$; HRMS (ES) found: 330.0440, $C_{17}H_{15}NS_3$ requires: 330.0439, $^{293}[\alpha]_D$ = -75.4° (c = 0.2, DMSO).

R-4,6-Dihydro-5-(1-naphthylethyl)-1,3-dithiolo[4,5-c]pyrrole-2-one, 14b.

Mercuric acetate (1.45g, 4.55mmol) was added to a solution of the thione **12b** (1.00g, 3.03mmol) in chloroform (150mL), and the mixture stirred overnight. The reaction mixture was filtered and the solid residue was washed with chloroform. The combined filtrates were concentrated in *vacuo* to yield the oxo compound **14b** as a pale orange oil (0.87g, 91.5%); δ_H ($CDCl_3$): 8.37 (1H, d, J = 7.9 Hz, Ar-H_1), 7.79 (1H, dd, J = 7.6, 1.9 Hz, Ar-H_1), 7.68 (1H, d, J = 8.2 Hz, Ar-H_1), 7.56 (1H, d, J = 6.9 Hz, Ar-H_1), 7.40 (3H, m, Ar-H_3), 4.44 (1H, q, J = 6.5 Hz, C*H*CH_3), 3.79 (4H, m, 4-,6-H_2), 1.38 (3H, d, J = 6.5 Hz, CH_3); δ_C ($CDCl_3$): 196.1 (*C*=O), 139.6, 134.0, 130.8, 128.9, 127.8, 125.9, 125.5, 125.4, 124.9, 123.4 (Ar-C_{10}), 125.7 (3a-,6a-*C*), 61.7 (*C*HCH_3), 57.2 (4-,6-*C*), 21.9 (*C*H_3); ν_{max} (ATR): 3046, 2971, 2790, 1750, 1673, 1614, 1587, 1509, 1451, 1371, 1318, 1233, 1182, 1138, 1123, 939, 800, 776, 529cm^{-1}; *m/z*: (ES) 314 $[M]^+$; HRMS (ES) found: 314.0670, $C_{17}H_{15}NOS_2$ requires: 314.0668; $^{293}[\alpha]_D = +38.9^o$ (c = 1.1, $CHCl_3$).

R,R-Bis (2,5-dihydro-N-(1-naphthylethyl)pyrrolo[3,4-d])tetrathiafulvalene, 9

A mixture of oxo compound **14b** (2.66g, 8.49mmol) and freshly distilled trimethyl phosphite (70mL) was heated to reflux for 62h. The solvent was removed under *vacuo* and ethyl acetate (20 ml) was added to the residue and heated to reflux for 30 min. The mixture was cooled to room temperature and the yellow solid product was collected by filtration, washed with ethyl acetate and dried in *vacuo* (1.03 g, 40.6%); m.p. 182-184ºC; δ_H ($CDCl_3$): 8.38 (2H, d, J = 7.7 Hz, 2×Ar-H_1), 7.79 (2H, dd, J = 7.7, 1.9 Hz, 2×Ar-H_1), 7.68 (2H, d, J = 8.1 Hz, 2×Ar-H_1), 7.56 (2H, d, J = 6.9 Hz, 2×Ar-H_1), 7.40 (6H, m, 2×Ar-H_3), 4.45 (2H, q, J = 6.6 Hz, 2×C*H*CH_3), 3.57 (8H, m, 4-,4'-,6-,6'-H_2), 1.46 (6H, d, J = 6.6 Hz, 2×CH_3); δ_C ($CDCl_3$): 139.8, 134.0, 130.8, 128.8, 127.6, 125.8, 125.5, 125.4, 124.9, 123.5 (2×Ar-C_{10}), 129.6 (3a,3a'-6a-,6a'-C), 117.0 (2-,2'-C), 62.0(*C*HCH_3), 56.0 (4-,4'-,6-,6'-C), 21.9 (CH_3); ν_{max} (ATR): 2974, 2929, 2872, 1512, 1440, 1414, 1378, 1345, 1333, 1140, 1118, 1076, 1051, 983, 793, 773, 733, 701, 493cm^{-1}; *m/z*: (CI) 591 $[M-3H]^+$ (2), 222 (100); found C, 68.69; H, 4.97; N, 4.61%, $C_{34}H_{30}N_2S_4$ requires C, 68.65; H, 5.08; N, 4.71%; $^{293}[\alpha]_D = +14.0^o$ (c = 0.6, $CHCl_3$).

4 *R,R*-Bis (N-(1-naphthylethyl)pyrrolo[3,4-d])tetrathiafulvalene, 10.

R-5-(1-naphthylethyl)-1,3-dithiolo[4,5-c]pyrrole-2-thione, 13b

A stirred suspension of thione **12b** (3.70g, 11.23mmol) in chloroform (150mL) was cooled to -15^{o}C~-10^{o}C and DDQ (3.50g, 15.41mmol) dissolved into benzene (100 mL) was added dropwise to give a dark suspension. The mixture was stirred overnight and then treated with 1M sodium carbonate solution. The mixture was extracted with dichloromethane (3 x 50 ml), and the combined organic solution was washed with 1M sodium carbonate solution and water and dried over magnesium sulfate. The filtrate was evaporated *in vacuo*, and the residue was purified by flash chromatography (SiO_2, eluting with petroleum ether:DCM (1:1)) to yield the thione **13b** as a yellow solid (3.12g, 84.8%); m.p. 189-191^{o}C (dec.); δ_H ($CDCl_3$): 7.83 (2H, m, 6'-,7'-*H*), 7.79 (1H, d, J = 8.3 Hz, 4'-*H*), 7.45 (2H, m, 5'-,8'-*H*), 7.40 (1H, t, J = 7.7 Hz, 3'-*H*), 7.24 (1H, d, J = 7.19 Hz, 2'-*H*), 6.70 (2H, s, 4-,6-*H*), 6.06 (1H, q, 7.0 Hz, C*H*CH_3), 1.94 (3H, d, J = 7.0 Hz, CH_3); δ_C ($CDCl_3$): 219.4 (*C*=S), 136.1, 133.9, 130.5, 129.3, 129.2, 127.0, 126.1, 125.4, 123.6, 122.1 (Ar-C_{10}), 123.1 (3a-,6a-*C*), 110.9 (4-,6-*C*), 56.3 (*C*HCH_3), 22.0 (*C*H_3); ν_{max} (ATR): 2977, 2926, 2853, 1707, 1620, 1596, 1507, 1485, 1468, 1393, 1372, 1363, 1298, 1237, 1204, 1165, 1126, 1046, 1034, 1001, 993, 871, 859, 799, 775, 758, 721, 638, 594, 567, 524, 500cm^{-1}; *m/z*: (EI) 327 $[M]^+$; found C, 62.20; H, 3.98; N, 4.21%, $C_{17}H_{13}NS_3$ requires C, 62.35; H, 4.00; N, 4.28%; $^{293}[\alpha]_D = -154.1^{o}$ (c = 0.80, $CHCl_3$).

R-5-(1-Naphthyethyl)-1,3-dithiolo[4,5-c]pyrrole-2-one, 15b

Mercuric acetate (5.20g, 16.3mmol) was added to a solution of the thione **13b** (3.50g, 10.69mmol) in chloroform (150mL) and the reaction mixture was stirred overnight. The mixture was filtered and the solid residue washed with chloroform. The combined filtrates were concentrated in *vacuo* and the residue was purified by flash chromatography (SiO_2, eluting with petroleum ether:DCM (1:1)) to yield the oxo compound **15b** as a yellow solid (2.42g, 72.7%); m.p. 143-145^{o}C; δ_H ($CDCl_3$): 7.84 (2H, m, 6'-,7'-*H*), 7.78 (1H, d, J = 8.2 Hz, 4'-*H*), 7.45 (2H, m, 5'-,8'-*H*), 7.38 (1H, t, J = 7.4 Hz, 3'-*H*), 7.22 (1H, d, J = 7.2 Hz, 2'-*H*), 6.73 (2H, s, 4-,6-*H*), 6.03 (1H, q, 6.9 Hz, C*H*CH$_3$), 1.92 (3H, d, J = 6.9 Hz, C*H$_3$*); δ_C (CDCl$_3$): 182.3 (*C*=O), 136.6, 133.9, 130.6, 129.1, 129.1, 126.9, 126.0, 123.5, 122.2, 122.1 (Ar-*C$_{10}$*), 112.8 (4-,6-*C*), 112.4 (3a-,6a-*C*), 55.9 (*C*HCH$_3$), 22.0 (*C*H$_3$); ν_{max} (ATR): 3117, 2973, 2924, 1698, 1629, 1509, 1489, 1377, 1355, 1292, 1201, 1121, 1094, 1017, 839, 803, 779, 765, 648, 622, 545, 522, 506cm^{-1}; *m/z*: (EI) 311 [M]$^+$; found C, 65.68; H, 4.21; N, 4.38%, $C_{17}H_{13}NS_2O$ requires C, 65.56; H, 4.21; N, 4.50%; $^{293}[\alpha]_D$ = -89.7° (c = 0.70, CHCl$_3$).

Bis (N-(1-naphthyethyl)pyrrolo[3,4-d])tetrathiafulvalene, 10.

A mixture of oxo compound **15b** (2.31g, 7.42mmol) and freshly distilled trimethyl phosphite (50mL) was heated to reflux for 50h. The reaction mixture was cooled to room temperature, and the precipitated yellow donor **10** was collected by filtration, washed with ethyl acetate and dried in *vacuo* (0.90g, 41.0%); m.p. >250ºC (dec.); δ_H (CDCl$_3$): 7.86 (2H, m, 2×Ar-*H$_1$*), 7.80 (2H, m, 2×Ar-*H$_1$*), 7.74 (2H, d, J = 8.2 Hz, 2×Ar-*H$_1$*), 7.44 (4H, m, 2×Ar-*H$_2$*), 7.36 (2H, t, J = 7.63 Hz, 2×Ar-*H$_1$*), 7.15 (2H, d, J = 7.0 Hz, 2×Ar-*H$_1$*), 6.48 (4H, s, 4-,4’,-6-,6’-*H*), 5.95 (2H, br, 2×C*H*CH$_3$), 1.85 (6H, d, J = 6.9 Hz, 2×C*H$_3$*); δ_C (CDCl$_3$): 137.4, 133.8, 130.5, 130.5, 129.0, 126.7, 125.8, 125.5, 123.4, 122.4 (2×Ar-C$_{10}$), 119.1 (4-,4’-,6-,6’-*C*), 111.4 (br, 2-,2’-3a-,3a’-,6a-,6a’-*C*), 55.8 (*C*HCH$_3$), 21.8 (*C*H$_3$); ν_{max} (ATR): 3065, 2980, 1599, 1511, 1485, 1374, 1359, 1294, 1253, 1238, 1198, 1170, 1118, 1091, 1020, 991, 199, 775, 760, 722, 648, 612, 569, 531, 505, 459cm^{-1}; *m/z*: (EI) 590 [M]$^+$; HRMS (EI) found: [M]$^+$ 590.0977, $C_{34}H_{26}N_2S_4$ requires: 590.0973; found C, 68.97; H, 4.33; N, 4.67%, $C_{34}H_{26}N_2S_4$ requires C, 69.11; H, 4.44; N, 4.74%; $^{293}[\alpha]_D$ = -239.0° (c = 0.2, THF).

X-Ray Crystallography.

Datasets were measured at 120 K by the EPSRC NCS, University of Southampton, on Bruker –Nonius diffractometer equipped with a FR591 rotating anode and a Bruker-Nonius Roper CCD detector. Structures were solved with SHELXS-97 and refined with SHELXL-97. Compared to the donors **7** and **9**, the bond lengths in most parts of the pyrrole rings of **10** and **12** are notably shorter, e.g. C-N, 1.358-1.384 Å compared to

1.474-1.494 Å and unfused C-C bonds 1.358-1.372 Å compared to 1.481-1.502 Å, while the bond at the ring fusion is longer 1.404-1.417 Å compared to 1.335-1.343 Å, all in accord with the formation of a delocalized π structure in the pyrrole ring. Tetra(ethyl)BEDT-TTF has been reported to resolve on crystallization to give tetragonal crystals with space group $P4_32_12$, but in this case there are no S---S contacts within the layers perpendicular to the *c* axis.[1]

1. A.M. Kini, J.P. Parakka, U. Geiser, H.-H. Wang,F.Rivas, E. DiNino, S. Thomas, J.D. Dudek, J. M. Williams, *J. Mater. Chem.,* **1999**, *9*, 883.