Electronic Supplementary Material (ESI) for CrystEngComm.

Synthesis and Structures of Polyiodide Radical Cation Salts of Donors Combining Tetrathiafulvalene with Multiple Thiophene or Oligo-thiophene Substituents.

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Supplementary Information.

1. **Synthesis of Donors.**
2. **Synthesis of Radical Cation Salts.**
3. **Cyclic Voltammetry and Conductivity Measurements.**
4. **X-ray Crystallography.**

Experimental

General. All chemicals were purchased from Sigma Aldrich and used as received. Solution NMR spectra were measured on a Jeol ECLIPSE 400 spectrometer at 400 MHz for ^{1}H and at 100.6 MHz for ^{13}C using $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard unless otherwise stated, and measured in p.p.m. downfield from TMS with coupling constants reported in Hz. IR spectra for donors were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer using Attenuated Total Reflection sampling on solids or oils and are reported in cm^{-1}. IR spectra for donor cations were measured on a Nicolet iS50 FR-IR spectrometer using a Specac Golden Gate single diamond ATR. UV-vis spectra were measured on a Agilent Technologies Cary 8454 UV-vis spectrometer. Chemical analysis data were obtained from Mr Stephen Boyer, London Metropolitan University. *Tetrakis*(thiophen-2-ylthio)TTF **15A** was prepared as described.[S1.]

3-Iodothiophene. *n*-BuLi solution (1.6 M, 34.5 mL, 55.3 mmol) was added dropwise to a solution of 3-bromothiophene (8.20 g, 50.3 mmol) in dry hexane:diethyl ether (75:15 mL) at -78 °C. After stirring for 3 h. at -78 °C, iodine (12.12 g, 47.8 mmol) was added in portions to the reaction mixture. The solution was allowed to warm up to room temperature and stirred overnight. The white mixture was filtered and the solids washed with hexane. The organic phase was washed with $Na_2S_2O_3$ solution, water (3 x 100 mL) and brine (2 x 50 mL) and was dried over $MgSO_4$. Filtration and evaporation of the solvent gave a brownish oil which was purified by column chromatography with (hexane) to give **2** (9.70 g**,** 92%) as colourless oily crystals. δ_H (400 MHz, $CDCl_3$): 7.41 (1H, dd, *J* = 3.0, 1.8 Hz, 2-*H*), 7.20 (1H, dd, *J* = 5.0, 3.0 Hz, 5-*H*), 7.11 (1H, dd, *J* = 5.0, 1.8 Hz, 4-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 134.7 (4-*C*), 128.6 (2-*C*), 127.3 (5-*C*), 77.1 (3-*C*).

4,5-Bis(thiophen-3’-ylthio)-1,3-dithiole-2-thione 14B.

A mixture of zinc complex **13**[S2] (2.33 g, 3.25 mmol), 3-iodothiophene (3.00 g, 14.3 mmol), Cu_2O (100 mg, 0.65 mmol), ethyl acetoacetate (180 µL, 1.42 mmol), and anhydrous DMF (8 mL) was heated to 120 °C and refluxed overnight under N_2. Dichloromethane (100 mL) was added to the cooled mixture, which was washed with water (5 x 50 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated. The resulting brown oil was purified by column chromatography (petroleum ether : DCM (4:1)) to give **14B** (1.93 g, 82%) as a yellow-orange solid, m.p. 102-103 °C; δ_H (400 MHz, $CDCl_3$): 7.55 (2H, dd, *J* = 3.0, 1.3 Hz, 2 x 2’-*H*), 7.42 (2H, dd, *J* = 5.0, 3.0 Hz, 2 x 5’-*H*), 7.14 (2H, dd, *J* = 5.0, 1.3 Hz, 2 x 4’-*H*); δ_H (400 MHz, $CDCl_3$): 210.9 (*C*=S), 134.7 (2 x 3’-*C*), 130.6 (2 x 4’-*C*), 130.1 (2 x 2’-*C*), 127.6 (2 x 5’-*C*), 126.4 (4,5-*C*); ν_{max}/cm^{-1}: 3088, 3086, 3058, 1456, 1389, 1351, 1196, 1051,1023,1010, 889, 853, 774, 758, 682. Found: C, 36.21 ; H, 1.58 %. Calc. for $C_{11}H_6S_7$: C, 36.44; H, 1.67 %.

4,4',5,5'-Tetrakis(thiophen-3’’-ylthio)-tetrathiafulvalene 15B.

Thione **14B** (0.60 g, 1.65 mmol) (2 mL) was stirred in trimethyl phosphite at 90 ^{o}C for 12 h. The reaction was left to cool to RT, and the trimethyl phosphite was removed. The reddish oil was purified by column chromatography (petroleum ether : DCM (3:1)) to give **15B** (0.49 g, 90%) as red crystals, m.p. : 211-214 ^{o}C; δ_H (400 MHz, $CDCl_3$): 7.40 (4H, dd, *J* = 3.0, 1.3 Hz, 4 x 2’’-*H*), 7.35 (4H, dd, *J* = 5.0, 3.0 Hz, 4 x 5’’-*H*), 7.07 (4H, dd, *J* = 5.0, 1.3 Hz, 4 x 4’’-*H*); δ_C (100 MHz, $CDCl_3$): 130.4 (4 x 4”-*C*), 128.2 (4 x 2”-*C*), 127.6 (4-,4’-,5-,5’-*C*), 127.2 (4 x 3”-*C*), 126.7 (4 x 5”-*C*), 109.5 (2-,2’-*C*); ν_{max}/cm^{-1}: 3093, 3090, 3086, 1479, 1401, 1395, 1351, 1196, 1095, 1074, 891, 849, 771, 712. Found: C, 40.04; H, 1.74 %. Calc. for $C_{22}H_{12}S_{12}$: C, 39.97; H, 1.83 %.

4,5-*Bis*(2’,2”-bithiophen-5’-ylthio)-1,3-dithiole-2-thione, 14C.

Zinc complex **13** (3.76 g, 5.2 mmol) and 2-iodo-2,2’-bithiophene[S3] (7.65 g, 26.2 mmol) with catalyst copper(I) oxide (120 mg) and ligand ethyl acetoacetate (0.3 mL) were heated in DMF (10 mL) for 18 h under nitrogen. The reaction mixture was cooled to room temperature and poured into DCM (100 mL). The resulting mixture was washed with distilled water (3×30 mL) and brine (30 mL) successively and then dried with $MgSO_4$. The product was purified by chromatography (hexane: chloroform, 8:1 gradually changed to 1:1) to give the thione **14C** (4.06 g, 73.6 %) as a yellow-green crystals, m.p. 123-125 °C. δ_H (400 MHz, $CDCl_3$): 7.28 (2H, dd, J = 1.1, 5.0 Hz, 2 × 5’’-*H*), 7.26 (2H, d, J = 3.8 Hz, 2 × 4’-*H*), 7.21 (2H, dd, J = 1.1, 3.7 Hz, 2 × 3’’-*H*), 7.09 (2H, d, J = 3.8 Hz, 2 × 3’-*H*), 7.04 (2H, dd, J = 3.7, 5.1 Hz, 2 × 4’’-*H*); δ_C (100 MHz, $CDCl_3$): 210.0 (*C*=S), 144.4 (2 × 2’-*C*), 137.6 (2 × 4’-*C*), 136.0 (2 × 2’’-*C*), 135.4 (4-,5-*C*), 128.0 (2 × 4’’-*C*), 126.6 (2 × 5’-*C*), 125.7 (2 × 5’’-*C*), 124.9 (2 × 3’’-*C*), 123.9 (2 × 3’-*C*); ν_{max}/cm^{-1}: 3099, 3091, 3080, 3065, 1433, 1414, 1059, 839, 794, 693. Found: C, 43.34; H, 1.76. Calc. for $C_{19}H_{10}S_9$: C, 43.32; H, 1.91%.

Tetrakis(2”,2”’-bithiophen-5”-ylthio)-TTF, 15C.

Thione **14C** (1.80 g, 2.93 mmol) was heated in trimethyl phosphite (20 mL) to 90 ^{o}C under nitrogen for 18 h. The precipitate formed was filtered, and washed with methanol (3 x 20 mL). The solid was stirred with refluxing chloroform for 18 h, filtered and washed with more chloroform and dried *in vacuo* to give **15C** (1.15 g, 68.0 %) as a bright orange powder, m. p. 225-226 °C. δ_H (400 MHz, THF-d_8): 7.38 (2H, dd, J = 1.1, 5.1 Hz, 4 × 5’’-*H*), 7.25 (2H, m, 4 × 3’’-, 4 × 4’-*H*), 7.13 (2H, d, J = 3.7 Hz, 4 × 3’’-*H*), 7.02 (2H, dd, J = 3.7, 5.2 Hz, 4 × 4’-*H*); δ_C (100 MHz, THF-d_8,10,000 scans): 144.5 (2 × 2’’-*C*), 137.5 (2 × 4’’-*C*), 137.0 (2 × 2’’’-*C*), 128.3 (2 × 4’’’-*C*), 128.0 (4-,5- or 2 x 5”-C), 126.0 (2 × 5’’’-*C*), 125.1 (2 × 3’’’-*C*), 124.2 (2 × 3’’-*C*); ν_{max}/cm^{-1}: 3100, 3079, 3070, 1415, 1215, 1199, 885, 839, 824, 799, 767, 706, 692, 684, 532, 486, 466, 452, 412. Found: C, 46.01; H, 1.96. Calc. for $C_{38}H_{20}S_{16}$: C, 46.12; H, 2.04%.

4,5-*Bis*(5”-hexyl-2’,2”-bithiophen-5’-ylthio)-1,3-dithiole-2-thione, 14D.

Zinc complex **13** (1.33 g, 1.85 mmol) and 5’-hexyl-5-iodo-2,2’-bithiophene[S4] (3.01 g, 8.00 mmol) with catalyst copper(I) oxide (40 mg) and ligand ethyl acetoacetate (0.2 mL) were heated in DMF (10 mL)) to 120 ^{o}C for 18 h under nitrogen. The reaction mixture was cooled to room temperature and poured into DCM (100 mL). The resulting mixture was washed with distilled water (3×30 mL) and brine (30 mL) successively and then dried with $MgSO_4$. The product was purified by chromatography (cyclohexane: chloroform, 2:1) to give the thione as **14D** (1.60 g, 60.8 %) as a yellow powder. m.p. 94-96 °C. δ_H (400 MHz, $CDCl_3$): 7.17 (2H, d, J = 3.9 Hz, 2 × 4’-*H*), 6.97 (2H, d, J = 3.6 Hz, 2 × 3’’-*H*), 6.95 (2H, d, J = 3.8 Hz, 2 × 3’-*H*), 6.65 (2H, d, J = 3.5 Hz, 2 × 4’’-*H*), 2.75 (4H, t, J = 7.5 Hz, 2 × Ar-CH_2), 1.65 (4H, m, 2 × CH_2), 1.35 (4H, m, 2 × CH_2), 1.29 (8H, m, 4× CH_2), 0.88 (6H, t, J = 6.8 Hz, 2×CH_3); δ_C (100 MHz, $CDCl_3$): 209.8 (*C*=S), 146.7 (2 × 5’’-*C*), 144.9 (2 × 2’-*C*), 137.5 (2 × 4’-*C*), 135.2 (4-,5-*C*), 133.2 (2 × 2’’-*C*), 125.6 (2 × 5’-*C*), 124.8 (2 × 4’’-*C*), 124.4 (2 × 3’’-*C*), 122.8 (2 × 3’-*C*), 31.4 (2 x CH_2), 31.3 (2 x CH_2), 30.0 (2 x CH_2), 28.6 (2 x CH_2), 22.4 (2 x CH_2), 14.0 (2 x CH_3); ν_{max}/cm^{-1}: 2953, 2918, 2849, 1512, 1459, 1425, 1200, 1051, 978, 885, 870, 808, 781, 719. Found: C, 53.46; H, 4.78. Calc. for $C_{31}H_{34}S_9$: C, 53.56; H, 4.93%.

***Tetrakis*(5’’’-hexyl-2’’,2’’’-bithiophen-5’’-ylthio)-TTF, 15D.**

Thione **14D** (0.70 g, 1.00 mmol) in trimethyl phosphite (10 mL) was heated to 90 °C under nitrogen for 18 h. The trimethyl phosphite was evaporated and the residue purified by chromatography (cyclohexane:chloroform 3:1 increasing to 1:1) to give donor **15D (**0.38 g, 57.6 %) as an orange-brown powder, m.p. 168-170 °C. δ_H (400 MHz, $CDCl_3$): 7.14 (4H, d, J = 3.7 Hz, 4 × 4’’-*H*), 6.98 (4H, d, J = 3.6 Hz, 4 × 3’’’-*H*), 6.95 (4H, d, J = 3.7 Hz, 4 × 3’’-*H*), 6.67 (4H, d, J = 3.6 Hz, 4 × 4’’’-*H*), 2.78 (8H, t, J = 7.6 Hz, 4 × Ar-CH_2), 1.67 (8H, m, 4 × CH_2), 1.37 (8H, m, 4 × CH_2), 1.31 (16H, m, 8 × CH_2), 0.89 (12H, t, J = 6.9 Hz, 4 × CH_3); δ_C (100 MHz, $CDCl_3$): 146.4 (4 × 5’’’-*C*), 143.9 (4 × 2’’-*C*), 136.7 (4 × 4’’-*C*), 133.8 (4 × 2’’’-*C*), 127.8 (4-,4’-,5-,5’-*C*), 127.1 (4 × 5’’-*C*), 124.9 (4 × 4’’’-*C*), 124.2 (4 × 3’’’-*C*), 122.9 (4 × 3’’-*C*), 109.2 (2-,2’-*C*), 31.5 (8 x CH_2), 30.1 (4 x CH_2), 28.7 (4 x CH_2), 22.5 (4 x CH_2), 14.1 (4 x CH_3); ν_{max}/cm^{-1}: 3067, 2956, 2921, 2852, 1509, 1465, 1459, 1426, 1321, 1213, 1194, 973, 887, 870, 797, 785, 766, 734, 723, 656, 509, 452, 420. Found: C, 56.18; H, 5.24 %. Calc. for $C_{62}H_{68}S_{16}$: C, 56.15; H, 5.17%.

4,5-*Bis*(5’’’-hexyl-5’,2’’,5’’,2’’’-terthiophen-2’-ylthio)-1,3-dithiole-2-thione, 14E.

Zinc complex **13** (1.07 g,1.49 mmol) and 5”-hexyl-2-iodo-5,2’,5’,2’’-terthiophene^{S5} (3.03 g, 6.61 mmol) with catalyst copper(I) oxide (40 mg) and ligand ethyl acetoacetate (0.2 mL) in DMF (10 mL) were heated to 120 °C for 18 h under nitrogen. After cooling to room temperature, methanol (30 mL) was added and the precipitated solid filtered off and washed with more methanol. The solid was purified by chromatography eluting with chloroform to give the thione **14E** (2.06 g, 79.0 %) as a yellow powder, m.p. 139-141 °C. δ_H (400 MHz, $CDCl_3$): 7.25 (2H, d, J = 3.8 Hz, 2 × Ar-*H*), 7.08 (2H, d, J = 3.8 Hz, 2 × Ar-*H*), 7.05 (2H, d, J = 3.8 Hz, 2 × Ar-*H*), 7.00 (4H, d, J = 3.9 Hz, 4 × Ar-*H*), 6.68 (2H, d, J = 3.6 Hz, 2 × Ar-*H*), 2.79 (4H, t, J = 7.4 Hz, 2 × Ar-CH_2), 1.67 (4H, m, 2 × CH_2), 1.38 (4H, m, 2 × CH_2), 1.31 (8H, m, 4 × CH_2), 0.89 (6H, t, J = 7.0 Hz, 2 × CH_3); δ_C (100 MHz, $CDCl_3$): 210.1 (*C*=S), 146.1, 144.2, 138.3, 137.6 (Ar-C_8), 135.4 (4-,5-*C*), 133.9, 133.8, 126.4, 125.4, 124.9, 123.8, 123.5, 123.5 (Ar-C_{16}), 31.5 (4 x CH_2), 30.1 (2 x CH_2), 28.7 (2 x CH_2), 22.5 (2 xCH_2), 14.0 (2 x CH_3); ν_{max}/cm^{-1}: 3066, 2955, 2923, 2853, 1506, 1475, 1447, 1423, 1376, 1210, 1204, 1202, 1056, 1015, 980, 920, 889, 862, 851, 789, 734. Found: C, 54.68; H, 4.29 . Calc. for $C_{39}H_{38}S_{11}$: C, 54.51; H, 4.46%.

Tetrakis(5””’-hexyl-5’’,2’’’,5’’’,2’’’’-terthiophen-2’’-ylthio) TTF, 15E.

Thione **14E** (0.92 g, 1.05 mmol) in trimethyl phosphite (20 mL) was heated to 90 °C under nitrogen for 18 h. The trimethyl phosphite was evaporated and the residue washed with methanol and dissolved in hot 1,1,2,2-tetrachloroethane (40 mL) and cooled to room temperature, filtered and washed with 1,1,2,2-tetrachloroethane and chloroform and dried *in vacuo* to give donor **15E (**0.61 g, 69.5 %) as a very poorly soluble pale orange-brown powder, m.p. 234-236 dec. °C. δ_H (400 MHz, $CDCl_3$): 7.08 (4H, d, J = 3.3 Hz, 4 × Ar-*H*), 6.95 (4H, d, J = 3.8 Hz, 4 × Ar-*H*), 6.93 (4H, d, J = 3.8 Hz, 4 × Ar-*H*), 6.86 (8H, d, J = 3.6 Hz, 8 × Ar-*H*), 6.58 (4H, d, J = 3.2 Hz, 4 × Ar-*H*), 2.76 (8H, t, J = 7.5 Hz, 4 × Ar-CH_2), 1.66 (8H, m, 4 × CH_2), 1.38 (8H, m, 4 × CH_2), 1.31 (16H, m, 8 × CH_2), 0.89 (12H, t, J = 6.9 Hz, 4 × CH_3); ν_{max}/cm^{-1}: 3065, 2956, 2922, 2853, 1507, 1459, 1445, 1428, 1420, 1414, 1376, 1365, 1220, 1203, 1195, 1067, 1054, 1033, 981, 969, 912, 890, 865, 852, 787, 769, 733, 653, 544, 519, 481, 470, 456. Found: C, 56.47; H, 4.51. Calc. for $C_{78}H_{76}S_{20}$: C, 56.62; H, 4.63%.

4,5-_Bis_(thiophen-2”-yl)(vinyldithio)TTF 17A.

Oxo compound **16**^{S6} (0.50 g, 2.43 mmol) and thione **14A**^{S1} (0.40 g, 0.89 mmol) in trimethyl phosphite (10 mL) were heated together to 90 °C under nitrogen for 18 h. After evaporating the trimethyl phosphite, the oily brown residue was purified by chromatography (cyclohexane:ether, 3:1) to give a red oil which was stirred with a small amount of ether to give the cross-coupled donor **17A** (0.13 g, 22.6 %) as an orange powder, m.p. 93-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.48 (2H, dd, J = 5.2, 1.1 Hz, 2 x 5’’-*H*), 7.32 (2H, dd, J = 3.3, 1.1 Hz, 2 x 3’’-*H*), 7.04 (2H, m, 2 x 4’’-*H*), 6.49 (2H, s, 5’-,6’-H); ^{13}C NMR (100 MHz, $CDCl_3$): 136.0 (2 x 3’’-*C*), 131.8 (2 x 5’’-*C*), 129.5 (2 x 2’’-*C*), 127.7 (2 x 4’’-*C*), 127.5 (4-,5-*C*), 124.5 (5’-,6’-*C*), 118.9 (3’a-,7’a-*C*), 115.9, 113.5 (2-,2’-C); $\upsilon_{max.}$: 3096, 3078, 3021, 1656, 1562, 1542, 1510, 1397, 1215, 988, 903, 849, 833, 804, 768, 711, 694, 669, 500, 438. Found: C, 36.69; H, 1.44. Calc. for $C_{16}H_8S_{10}$: C, 36.90; H, 1.55 %.

4,5-_Bis_(thiophen-2”-yl)(ethylenedithio)TTF, 19A.

Thione **14A**^{S1} (1.40 g, 3.86 mmol), and oxo compound **18** (2.01 g, 9.64 mmol) were heated together in trimethyl phosphite at 70 °C under nitrogen for 18 h. After evaporation of trimethyl phosphite, the residue was purified by chromatography, eluting with 1:1 cyclohexane/chloroform, to give the unsymmetrical donor **19A** (0.99 g, 49.0%) as a yellow powder, m.p. 104-106 °C. δ_H (400 MHz, $CDCl_3$): 7.47 (2H, dd, J = 1.3, 5.4 Hz, 2 × 5’’-*H*), 7.31 (2H, dd, J = 1.3, 3.7 Hz, 2 × 3’’-*H*), 7.03 (2H, dd, J = 3.6, 5.3 Hz, 2 × 4’’-*H*), 3.23 (4H, s, 5’-,6’-H_2); δ_C (100 MHz, $CDCl_3$): 135.9 (2 × 3’’-*C*), 131.7 (2 × 5’’-*C*), 129.7 (2 × 2’’-*C*), 127.7 (2 × 4’’-*C*), 127.6 (4,5-*C*), 113.9 (3a’,7a’-*C*), 113.6 & 108.4 (2-,2’-*C*), 30.1 (5’-,6’-*C*); ν_{max}/cm^{-1}: 3096, 3084, 3070, 2966, 2927, 1400, 1335, 1284, 1216, 1124, 1084, 1054, 985, 915, 883, 845, 835, 769, 710, 564, 503. Found: C, 36.65; H, 1.91. Calc. for $C_{16}H_{10}S_{10}$: C, 36.76; H, 1.93%.

Bis(2”,2”’-bithiophen-5”-ylthio)(ethylenedithio)-TTF, 19C.

Thione **15C** (1.95 g, 3.70 mmol) and unsubstituted oxo compound **18** (2.07 g, 9.93 mmol) were heated in trimethyl phosphite (30 mL) under nitrogen to 110 °C for 18 h. The reaction mixture was cooled to room temperature then filtered and washed with chloroform. The solvent and trimethyl phosphite were removed *in vacuo*, and the residue purified by chromatography (cyclohexane:chloroform 2:1) to give donor **19C** (1.14 g, 44.8 %) as a bright orange-pink powder, m.p. 146-148 °C. δ_H (400 MHz, $CDCl_3$): 7.24 (2H, dd, J = 1.1, 5.2 Hz, 2 × 5’’’-*H*), 7.21 (2H, d, J = 3.8 Hz, 2 × 4’’-*H*), 7.19 (2H, dd, J = 1.1, 3.7 Hz, 2 × 3’’’-*H*), 7.07 (2H, d, J=3.8, 2 × 3’’-*H*), 7.01 (2H, dd, J=3.7, 5.1, 2 × 4’’’-*H*), 3.20 (4H, s, 5’-,6’-H_2); δ_C (100 MHz, $CDCl_3$): 143.4 (2 × 2’’-*C*), 136.7 (2 × 4’’-*C*), 136.4 (2 × 2’’’-*C*), 128.0 (2 × 5’’-*C*), 127.9 (2 × 4’’’-*C*), 127.6 (4-,5-*C*), 125.3 (2 × 5’’’-*C*), 124.6 (2 × 3’’’-*C*), 123.7 (2 × 3’’-*C*), 113.9 (3a’,7a’-*C*), 113.1 & 108.7 (2-,2’-*C*), 30.1 (5’-,6’-*C*); ν_{max}/cm^{-1}: 3010, 3080, 3067, 3031, 2960, 2918, 1418, 1285, 1214, 1196, 893, 883, 835, 824, 799, 772, 696, 534. Found: C, 42.00; H, 2.02 %. Calc. for $C_{24}H_{14}S_{12}$: C, 41.95; H, 2.05%.

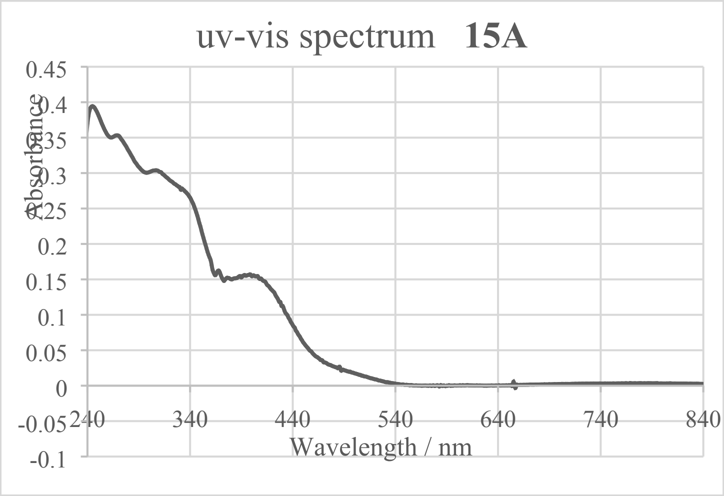
Attempted synthesis of 4,5-*Bis*(5’,2’’,5’’,2’’’-terthiophen-2’-ylthio)-1,3-dithiole-2-thione.
Zinc complex **13** (2.35 g, 3.27 mmol) and 2-iodo-5,2’,5’,2’’-terthiophene[S3] (5.40 g, 14.43 mmol) with catalyst copper(I) oxide (75 mg) and ligand ethyl acetoacetate (0.2 mL) were heated in DMF (10 mL) to 120 ^{o}C for 18 h under nitrogen. The precipitate was filtered, and washed with distilled water (3 x 20 mL) and methanol (3 x 20 mL) and dried *in vacuo* to give the mono-substituted thione, *5-(2’,2’’,5’’,2’’’-terthiophen-5’-ylthio)-2-thioxo-1,3-dithiole-4-thiol*, brown powder, m.p.163-165 °C ,which was highly insoluble in common organic solvents, ν_{max}/cm^{-1}: 3069, 1421, 1053, 1019, 981, 891, 833, 792, 695, 510, 456. Found: C, 40.38; H, 1.74 %. Calc. for $C_{15}H_8S_8$: C, 40.51; H, 1.81%.

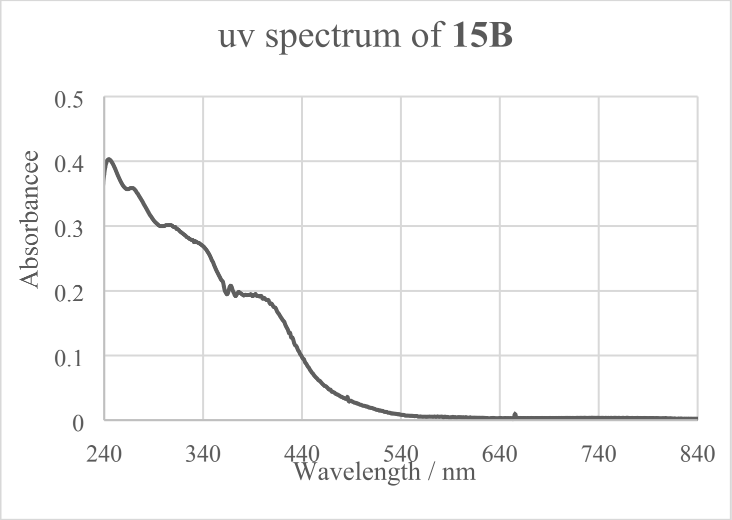
***Bis*(5’’’-hexyl-2’’,2’’’-bithiophen-5’’-ylthio)(ethylenedithio)-TTF, 19D.**
Thione **14D** (0.70 g, 0.98 mmol) in trimethyl phosphite (10 mL) was heated to 90 ^{o}C under nitrogen for 18 h. The trimethyl phosphite was evaporated and the residue purified by chromatography (cyclohexane:chloroform 3:1 increasing to 1:1) to give donor **19D (**0.38 g, 57.6 %) as a bright pale orange powder, m.p. 97-99 °C. δ_H (400 MHz, $CDCl_3$): 7.18 (2H, d, J = 3.7 Hz, 2 × 4’’-*H*), 7.01 (2H, d, J = 3.6 Hz, 2 × 3’’’-*H*), 6.98 (2H, d, J = 3.7 Hz, 2 × 3’’-*H*), 6.69 (2H, d, J = 3.6 Hz, 2 × 4’’’-*H*), 3.20 (4H, 2 × 5’,6’-*H*), 2.79 (4H, t, J = 7.6 Hz, 2 × Ar-CH_2), 1.67 (4H, m, 2 × CH_2), 1.37 (4H, m, 2 × CH_2), 1.31 (8H, m, 4 × CH_2), 0.89 (6H, t, J = 6.8 Hz, 2 × CH_3); δ_C (100 MHz, $CDCl_3$): 146.4 (2 × 5’’’-*C*), 144.1 (2 × 2’’-*C*), 136.8 (2 × 4’’-*C*), 133.8 (2 × 2’’’-*C*), 127.6 (4-,5-*C*), 127.1 (2 × 5’’-*C*), 124.9 (2 × 4’’’-*C*), 124.3 (2 × 3’’’-*C*), 122.9 (2 × 3’’-*C*), 113.9 (3a’-,7a’-*C)*, 113.4 & 108.4 (2’-,2-*C*), 31.5 (2 x *C*H_2), 30.1 (2 x *C*H_2), 30.0 (2 x *C*H_2), 28.7 (2 x *C*H_2), 22.5 (2 x *C*H_2), 14.1 (2 x *C*H_3); ν_{max}/cm^{-1}: 3066, 2954, 2924, 2850, 1510, 1459, 1424, 1213, 1040, 989, 969, 889, 870, 799, 771. Found: C, 50.48; H, 4.39. Calc. for $C_{36}H_{38}S_{12}$: C, 50.55; H, 4.48%.

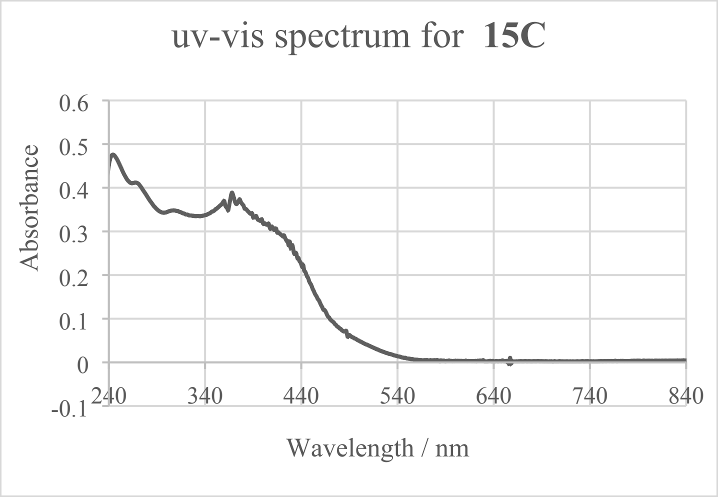
***Bis*(5’’’’-hexyl-5’’,2’’’,5’’’,2’’’’-terthiophen-2’’-ylthio) (ethylenedithio)TTF, 19E.**
Thione **14E** (1.11 g, 3.70 mmol) and unsubstituted oxo compound **18** (0.70 g, 9.93 mmol) were heated with trimethyl phosphite (20 mL) under nitrogen to 110 ^{o}C for 18 h. After evaporation of trimethyl phosphite, the residue was purified by chromatography eluting with cyclohexane/chloroform (2:1 changing to 1:1) to give donor **19E** (0.50 g, 38.7 %) as an orange powder, m.p. 144-146 °C. δ_H (400 MHz, $CDCl_3$): 7.21 (2H, d, J = 3.8 Hz, 2 × Ar-*H*), 7.07 (2H,

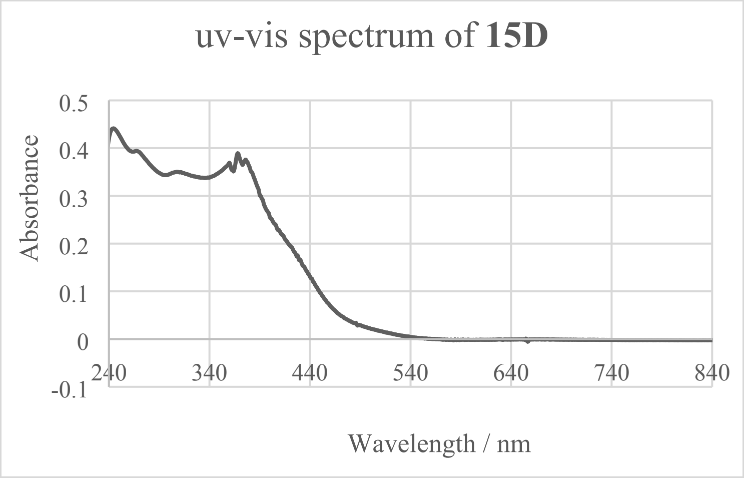
d, J = 3.8 Hz, 2 × Ar-*H*), 7.04 (2H, d, J = 3.8 Hz, 2 × Ar-*H*), 6.99 (2H, d, J = 3.8 Hz, 2 × Ar-*H*), 6.98 (2H, d, J = 3.5 Hz, 2 × Ar-*H*), 6.68 (2H, d, J = 3.5 Hz, 2 × Ar-*H*), 3.22 (4H, s, 5’,6’-*H*), 2.79 (4H, t, J = 7.5 Hz, 2 × 5’’’’-C*H₂*), 1.66 (4H, m, 2 × C*H₂*), 1.37 (4H, m, 6 × C*H₂*), 1.31 (8H, m, 6 × C*H₂*), 0.89 (6H, t, J = 7.0 Hz, 2 × C*H₃*); δ_C (100 MHz, $CDCl_3$): 145.9, 143.3, 137.8 (Ar-C_6), 136.8 (4-,5-*C*), 134.3, 134.1, 127.9, 127.8, 125.2, 124.8, 123.6, 123.5, 123.4 (Ar-C_{18}), 113.9 (2-*C*), 113.2 (3a’-,7a’-*C*), 108.7 (2’-*C*), 31.5 (4 x CH_2), 30.2 (2 x CH_2), 30.1 (5’-,6’-*C*), 28.7 (2 x CH_2), 22.5 (2 x CH_2), 14.0 (CH_3); ν_{max}/cm^{-1}: 3066, 2955, 2918, 2872, 2851, 1508, 1466, 1459, 1447, 1422, 1408, 892, 849, 791, 765, 733, 723, 682, 479, 465 Found: C, 51.39; H, 3.97. Calc. for $C_{44}H_{42}S_{14}$: C, 51.83; H, 4.15%.

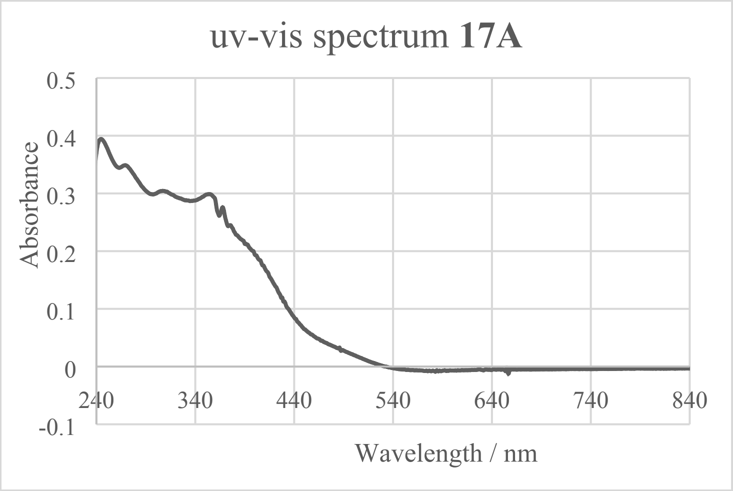
UV-Vis Spectra for donors.

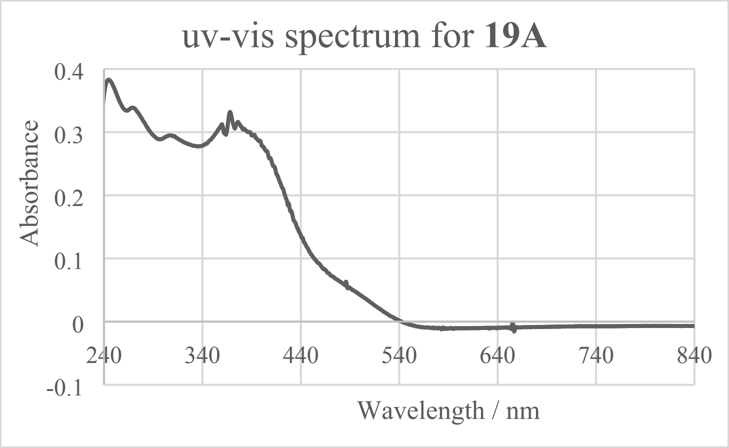


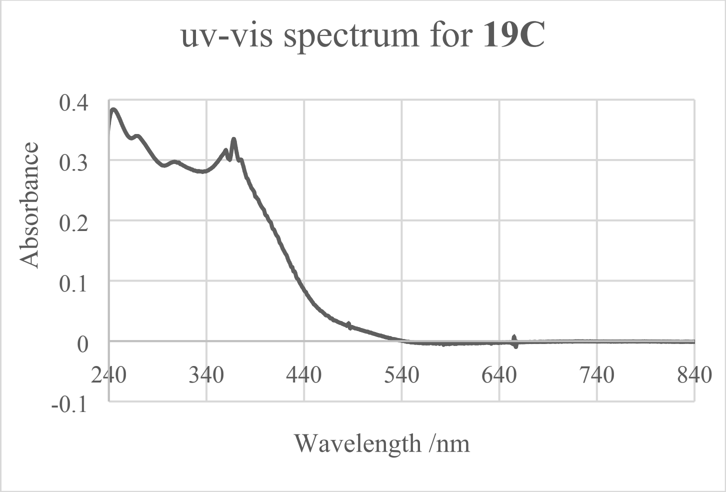



uv-vis spectrum for **15C**


uv-vis spectrum of **15D**


uv-vis spectrum **17A**


uv-vis spectrum for **19A**
Absorbance
0.4
0.3
0.2
0.1
0
-0.1
240
340
440
540
640
740
840
Wavelength / nm


uv-vis spectrum for **19C**
Absorbance
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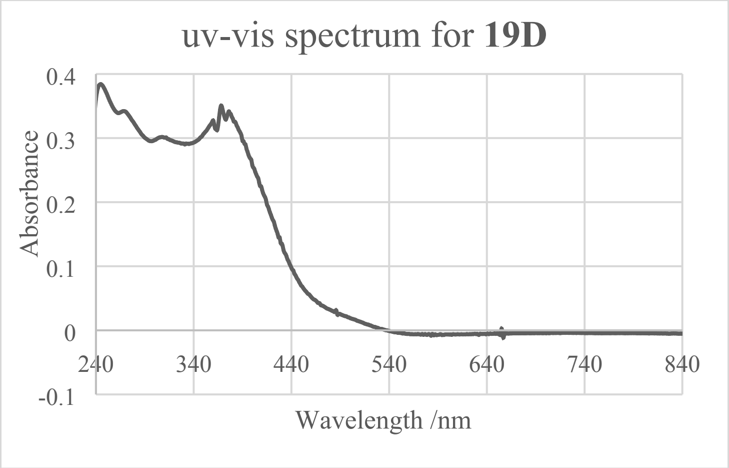
0.2
0.1
0
-0.1
240
340
440
540
640
740
840
Wavelength /nm


uv-vis spectrum for **19D**
Absorbance
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0.3
0.2
0.1
0
-0.1
240
340
440
540
640
740
840
Wavelength /nm

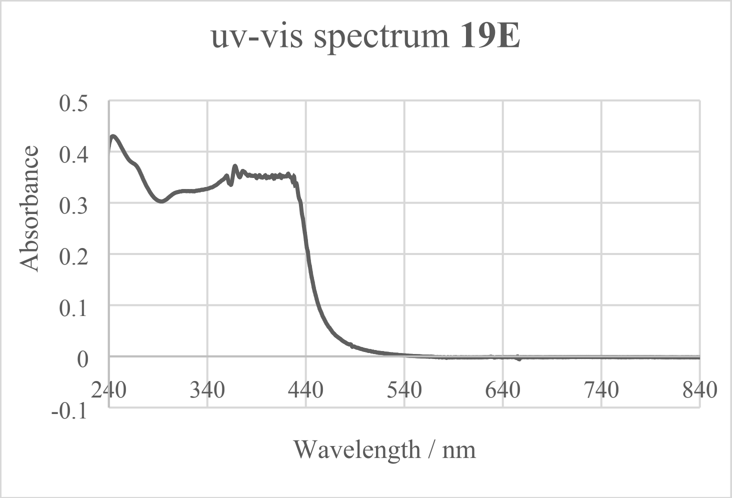


Figure S1. Ultra-violet/visible spectra of donors **15A-15D, 17A, 19A** and **19C-19E.**

Radical Cation Salts.

Single crystals of radical cation salts were grown by slow diffusion as follows:

Synthesis of 15A.I_5. Iodine (10 mg, 3.94 x 10^{-2} mmol) in hexane (5 mL) was layered over donor **15A** (5 mg, 7.5 x 10^{-3} mmol) in DCM (5 mL) and left to diffuse over a period of one week. Large black rhombohedral crystals of **15A**.I_5 were collected.); ν_{max}/cm^{-1}: 3090, 3077, 1411, 1409, 1324, 1281, 1214, 1171, 1130, 1078, 1050, 1019, 985, 915, 886, 845, 810, 708.

Synthesis of 15B.I_5. Iodine (10.1 mg, 3.96 x 10^{-2} mmol) in hexane (3 mL) was layered over donor **15B** (5 mg, 7.58 x 10^{-3} mmol) in DCM (3 mL) with layers of DCM (2 mL) and hexane (2 mL) layered in between. After 5 days some small black crystalline blocks of **15B**.I_5 were collected. ν_{max}/cm^{-1}: 3089, 3076, 1403, 1392, 1329, 1198, 1095, 1076, 1026, 920, 889, 854, 808, 766, 683.

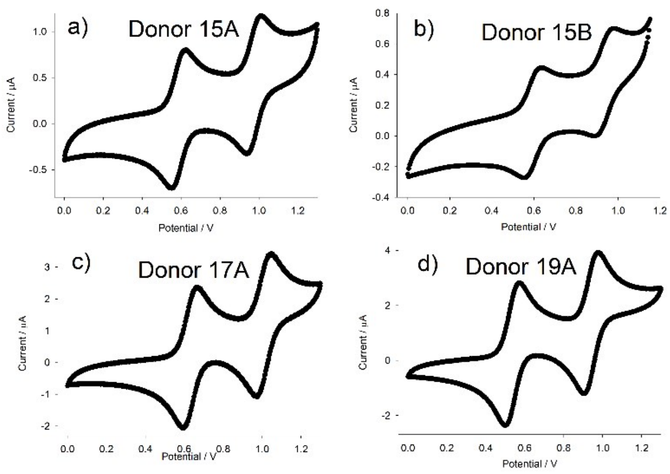
Synthesis of 17A.I_3.1.5I_2. Iodine (10.36 mg, 3.94 x 10^{-2} mmol) in hexane (3 mL) was layered over donor **17A** (7.2 mg, 1.38 x 10^{-2} mmol) in DCM (3 mL) with hexane (2 mL) layered between and left to diffuse. After 5 days thin black plates of **17A**.I_3.1.5I_2 were collected. ν_{max}/cm^{-1}: 3092, 3077, 1413, 1393, 1327, 1224, 1209, 1096, 1078, 1054, 1014, 986, 969, 890, 844, 769, 705.

Synthesis of (19A)$_2$.I_5.I_3. Iodine (10 mg 3.94 x 10^{-2} mmol) in hexane (5 mL) was layered over donor **19A** (5 mg, 9.58 x 10^{-3} mmol) in DCM (5 mL) and left to diffuse over a period of 3 days. Black needle crystals of (**19A**)$_2$.I_5.I_3 were collected. ν_{max}/cm^{-1}: 3070, 2959, 1445, 1411, 1393, 1324, 1281, 1266, 1214, 1175, 1130, 1082, 1055, 1019, 981, 915, 886, 845, 807, 708.

Synthesis of 19A.I_3.: Black block crystals of this salt were collected from the same experiment as (**19A**)$_2$.I_5.I_3**.** ν_{max}/cm^{-1}: 3089, 3073, 1449, 1412, 1393, 1328, 1281, 1226, 1175, 1081, 1059, 1019, 986, 885, 845, 713, 700.

Synthesis of 19C.I_5.0.5I_2. Iodine (10 mg, 3.94 x 10^{-2} mmol) in hexane (5 mL) was layered over donor **19C** (5 mg, 7.29 x 10^{-3} mmol) in DCM (5 mL) and left to diffuse over a period of 4 weeks. Large black crystalline plates of **19C**.I_5.0.5I_2 were collected.

Cyclic voltammetry measurements. Electrochemical investigations using cyclic voltammetry were carried out using a µ-Autolab III potentiostat controlled with GPES software. A three-electrode system was used consisting of a platinum disk working electrode (3 mm diameter), a platinum foil counter electrode and a silver/silver chloride reference electrode. The working electrode was polished with 0.5 µm alumina paste, rinsed and dried prior to all measurements. All voltammograms were performed at ambient temperature (~20°C) and the solution was degassed with nitrogen for 10 min prior to the measurement. Measurements were taken in a solution containing approximately 0.01 mM of the donor in 0.1M tetrabutylammonium hexafluorophosphate/DCM at a scan rate of 100 mV s^{-1}.



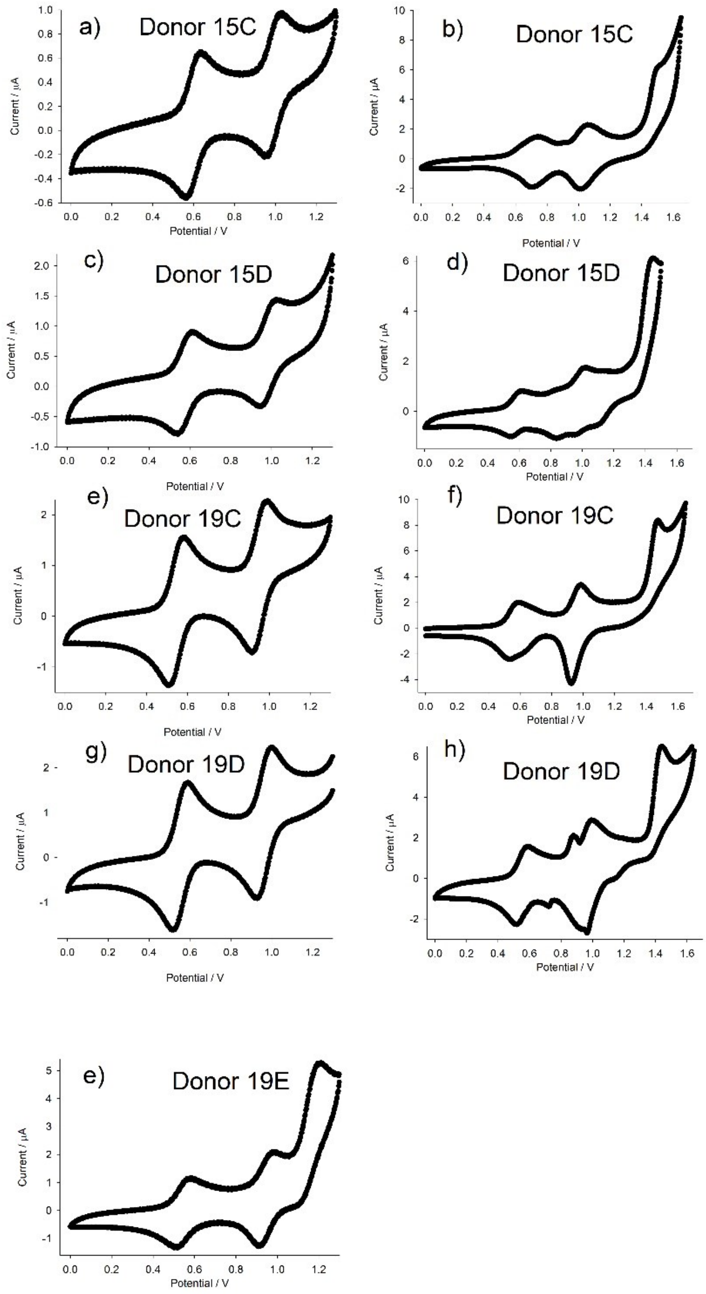


Figure S2. Cyclic voltammograms for **15A-15D**, **17A**, **19A** and **19C-19E.**

Conductivity measurements.

Two-probe DC transport measurements were made on several crystals of each radical-cation salt. Gold wires (15 μm diameter) were attached to the crystal, and the attached wires were connected to an eight-pin integrated circuit plug with carbon conductive cement. Measurements at room temperature for all six radical-cation salts shows that all of them have a room temperature resistance too high to be measured using a Keithley 2401 digital multimeter (>200 MOhms).

Single Crystal X-ray Diffraction

X-ray single crystal diffraction measurements were performed using a Rigaku Oxford Diffraction Excalibur System equipped with a Sapphire detector at 150 K using CrysalisPro software.[S7] All non-H atoms were located using direct methods[S8] and difference Fourier syntheses. Hydrogen atoms were placed and refined using a geometric riding model. All fully occupied non-H atoms were refined with anisotropic displacement parameters, unless otherwise specified. Crystal structures were solved and refined using the Olex2 software package[S9] with SHELXL[S10] (structure refinement) and SHELXS or SHELXT[S11] (structure solution). CIF files were checked using checkCIF,[S12] CCDC 2011618-2011623 contains the supplementary data for compounds **15A**.I_5, **15B**.I_5, **17A.**I_3.1.5I_2, **19A**.I_5.I_3, **19A**.I_3 and **19C**.I_5.0.5I_2. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Molecular illustrations were prepared with Mercury.[S13]

References.

S1. J. Sun, X. Lu, J. Shao, Z. Cui, Y. Shao, G. Jiang, W. Yu and X. Shao, *RSC Advances*, 2013, **3**, 11093-10196.

S2. C. Wang, A. S. Batsanov, M. R. Bryce and J. A. K. Howard, *Synthesis*, 1998, 1615-1618.

S3. U. Boas, A. Dhanabalan, D. R. Greve andE. W..Meijer, *Synlett*, 2001, **5**, 634-636.

S4. Q. Meng, J. Gao, R. Li, L. Jiang, C. Wang, H. Zhao, C. Liu, H. Li and W. Hu, *J. Mater. Chem*., 2009, **19**, 1477-1482.

S5. M. Funahashi and J.-I. Hanna, *Adv. Mater*., 2005, **17**, 594-598.

S6. T. Nakamura, S. Iwasaka, H. Nakano, K. Inoue, T. Nogami and H. Mikawa, *Bull. Chem. Soc. Jpn*, 1987, **60**, 365-368; J. Garin, R. Andreu, J. Orduna and J. Royo, *Synth. Met*., 2001, **120**, 749-750.

S7. Agilent (2014). CrysAlis PRO. Agilent Technologies Ltd, Yarnton, Oxfordshire, England.

S8. G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr*., **2008**, *64*, 112-122.

S9. 10 a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr*., **2009**, *42*, 339-341; b) O. V. Dolomanov, A. J. Blake, N. R. Champness, M. Schroder, *J. Appl. Crystallogr*,. **2003**, *36*, 1283-1284.

S10. G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem*. **2015**, *71*, 3-8.

S11. G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2015**, *71*, 3-8.

S12. http://checkcif.iucr.org.

S13. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Cryst*., **2006**, *39*, 453-457.