

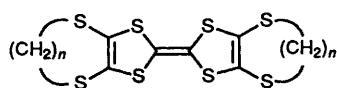
New Symmetrical Tetrathiafulvalene π -Donors Containing Nine- and Ten-membered Dithiaheterocycles

Jai D. Singh and Harkesh B. Singh*

Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India

Reactions of disodium 2-thioxo-1,3-dithiole-4,5-dithiolate (DMIT) **5** with 1,5-dibromopentane, 1,6-dibromohexane and (\pm)-1,2-dibromopropane yielded the thiones **6**, **7** and **8** respectively in good yields. Coupling of these thiones with triethyl phosphite afforded π -donors **9**, **10** and **11** respectively in moderate yields. The π -donors and their precursors have been characterised by elemental analysis, mass spectrometry, UV-VIS, IR and NMR spectroscopy. The oxidation potentials of donors **9**, **10** and **11** are reported. Preparation of the charge-transfer complexes of the donors with acceptors TCNQ and CuCl_2 and their solid state conductivity and ESR data is also presented.

$\text{Bi}(\text{1,3-dithiolo}[4,5-b][1,4]\text{dithiocyclopenten-2-ylidene})$ (BEDT-TTF) **1** has yielded a number of superconducting ion-



- 1 $n = 1$, BMDT-TTF
 2 $n = 2$, BEDT-TTF
 3 $n = 3$, BPDT-TTF
 4 $n = 4$, BBDT-TTF

radical salts.^{1,2} κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl exhibits the highest reported superconducting transition temperature ($T_c = 12.8$ K, 0.3 K bar) for this class of materials.³ In these salts, both the S...S distances in the sheet network and C-H...anion contacts play an important role in determining the solid state properties. Consequently, the synthesis and exploration of new π -donors with such characteristics is of considerable current interest.⁴ Recently we reported the synthesis and characterisation of compound **4** which incorporates the bulkier butylene residue in the exterior ring.⁵ Structural studies revealed that the molecular packing in the unit cell was similar to **2** and there were significant S...S intermolecular contacts.⁶ The unique feature of the structure was the high planarity of the C₆S₈ core which is non-planar in **2** and **3**. Very recently Shibaeva *et al.*⁷ have reported the first radical cation salt of **4** which is an 'organic metal'. Underhill *et al.*^{8,9} and others¹⁰ have reported the synthesis of some related macrocyclic cage compounds which, however, incorporate non-planar tetrathiafulvalene units. More recently condensation of **5** with 4,4'-bis(bromomethyl)-2,2'-bi-1,3-thiole to give a mixture of very sparingly soluble cyclic thiones has been reported.¹¹

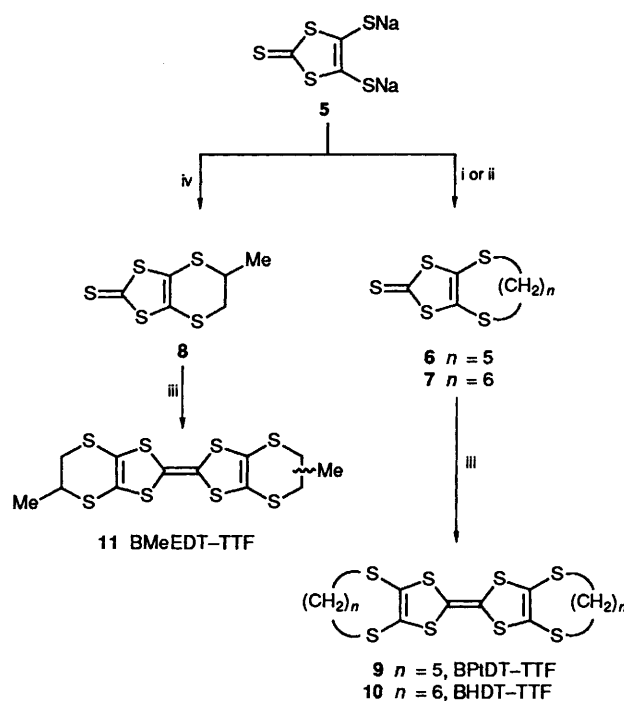
In order to further understand the structure-property relationship in this class of donors, we report the synthesis of two new π -donors **9,10** which incorporate nine- and ten-membered exterior rings respectively. Also reported herein is the modified synthesis of bi(5,6-dihydro-5-methyl-1,3-dithiolo[4,5-*b*][1,4]dithiocyclohexen-2-ylidene) (BMeEDT-TTF) **11** which is closely related to **2**. Although the synthesis of the donor **11** has been reported by Papavassiliou *et al.*,¹² very few charge-transfer complexes have been reported to date.¹³

Results and Discussion

4,5-Bis(benzylthio)-1,3-dithiole-2-thione, precursor for the preparation of the dimercapto disodium salt **5**, was prepared in much better yield by using a reported procedure¹⁴ with slight but advantageous modification. The reported procedure for the synthesis involves addition of sodium to CS₂-DMF in three

portions at -5°C . We have found that the reaction proceeded safely and smoothly when the required amount of sodium was added in one portion at room temperature.

Conventional cyclisation reactions of the dimercapto disodium salt¹⁵ **5** with 1,5-dibromopentane, 1,6-dibromohexane and (\pm)-1,2-dibromopropane in methanol at room temperature resulted in very poor yields (3–5%) of the thiones **6**, **7** and **8** respectively, along with large quantities of insoluble or soluble intractable materials. Separation of the thiones from these materials was found to be very difficult and the pure products could only be obtained by repeated column chromatography of the crude mixture using light petroleum (60–80 °C)-ethyl acetate (99:1%). The yields could not be improved by the use of either high dilution techniques or phase transfer catalysis. However, when the reactions were performed in ethanol in the temperature range -70°C to -80°C for 3–4 h followed by 3 h at room temperature, the reactions were found to be complete (monitored by TLC) during this period and the pale yellow thiones were easily obtained from crude materials by column chromatography in much better yields (Scheme 1).



Scheme 1 Reagents and conditions: (i) $\text{Br}(\text{CH}_2)_5\text{Br}$; (ii) $\text{Br}(\text{CH}_2)_6\text{Br}$; (iii) $\text{P}(\text{OEt})_3$, heat; (iv) $\text{MeCH}(\text{Br})\text{CH}_2\text{Br}$

Table 1 Cyclic voltammetric data

Compound	$E_{1/2}^1/V$	$E_{1/2}^2/V$	$\Delta E^1/V$
BEDT-TTF 2	0.54	0.96	0.42
BBDT-TTF 4	0.56	0.99	0.43
BMeEDT-TTF 11	0.51 (0.54) ^a	0.93 (0.96) ^a	0.42 (0.42) ^a
BPtDR-TTF 9	0.57 (0.59) ^a	1.03 (1.04) ^a	0.46 (0.45) ^a
BHDT-TTF 10	—	0.96 (0.99) ^a	—

^a Ag⁺/AgCl reference electrode; scan rate 100 mV s⁻¹.

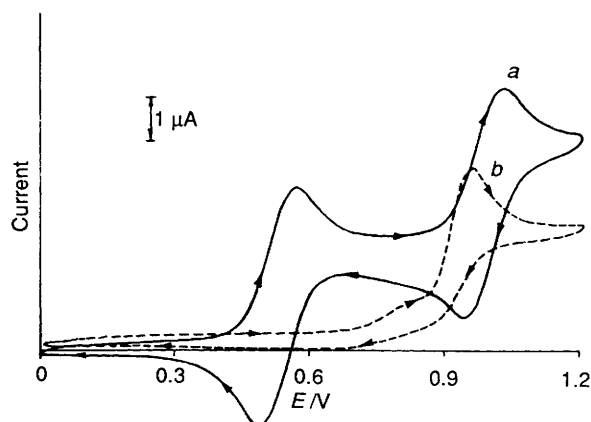


Fig. 1 Cyclic voltammograms of: (a) BPtDT-TTF 9; and (b) BHDT-TTF 10 (5×10^{-4} mol dm⁻³); tetrabutylammonium hexafluorophosphate (0.1 mol dm⁻³ in dichloromethane), scan rate 25 mV s⁻¹

The TTFs bi(5*H*-6,7,8,9-tetrahydro-1,3-dithiolo[4,5-*b*][1,4]-dithiocyclononen-2-ylidene) (BPtDT-TTF) 9, bi(5,6,7,8,9,10-hexahydro-1,3-dithiolo[4,5-*b*][1,4]dithiocyclodecen-2-ylidene) (BHDT-TTF) 10 and bi(5,6-dihydro-5-methyl-1,3-dithiolo[4,5-*b*][1,4]dithiocyclohexen-2-ylidene) (BMeEDT-TTF) 11 were obtained by coupling of the corresponding thiones 6, 7 and 8 with triethyl phosphite and purified by column chromatography (silica gel, 60–120 mesh) using dichloromethane as eluent. The π -donors and their precursors were characterised by elemental analysis, mass spectrometry, UV-VIS, IR and ¹H NMR spectroscopy. It is worth noting that TTF 10 is pale yellow in colour whereas all other TTFs of the series, 1–4 and 9, are orange–red in colour (*vide infra*). Similar yellow colours have been observed for other TTFs which have a non-planar C₆S₈ core.^{8–10}

The electrochemical redox properties of the donors have been studied by cyclic voltammetry using saturated calomel electrode as reference and the data are collected in Table 1.

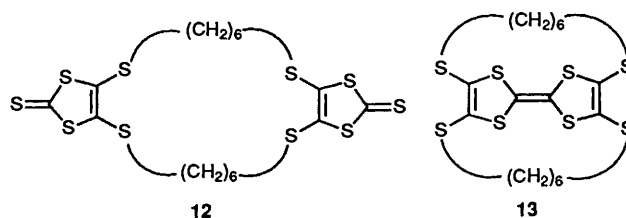
The cyclic voltammograms of 9 and 11 showed two reversible redox waves. The values of half wave potentials for 11 are slightly lower than that of 9 and are very similar to BEDT-TTF measured under identical conditions. Interestingly 10 showed only the second redox wave (Fig. 1) which was found to be irreversible. This unexpected redox behaviour of 10 is probably due to steric hindrance of the electron transfer site with the large 10-membered exterior ring.

Donors 9, 10 and 11 form 1 : 1 charge-transfer (CT) complexes with 7,7,8,8-tetracyanoquinodimethane (TCNQ). The CT complexes, BPtDT-TTF:TCNQ ($\sigma = 6.3 \times 10^{-6}$ S cm⁻¹) and BMeEDT-TTF:TCNQ ($\sigma = 9.6 \times 10^{-2}$ S cm⁻¹) are conducting while BHDT-TTF:TCNQ ($\sigma = < 10^{-6}$ S cm⁻¹) is an insulator. The degree of CT in organic conductors could be monitored by the examination of $\nu(\text{CN})$ for TCNQ.¹⁶ For the complexes synthesised the IR spectroscopic data are different from those of the components and the $\nu(\text{CN})$ band of TCNQ⁰ (2230 cm⁻¹) is observed at ~ 2220 cm⁻¹ for the TCNQ

complexes of 9 and 10 and 2200 cm⁻¹ for 11 indicating partial CT [$\text{Na}^+\text{TCNQ}^-\nu(\text{CN}) = 2180$ cm⁻¹].

The π -donors 9 and 11 could be oxidised with Cu^{II}Cl₂ to give radical cation salts with donor:CuCl₂ ratio (BPtDT-TTF)₅-(CuCl₂)₆ ($\sigma = 4.5 \times 10^{-6}$ S cm⁻¹) and (BMeEDT-TTF)₃-(CuCl₂)₆ ($\sigma = 9 \times 10^{-2}$ S cm⁻¹). The ESR spectra of all the CT complexes showed a symmetric singlet. The observed *g*-values are nearly equal to the free electron value, suggesting that the signal was due to an unpaired electron on TCNQ. ESR data of the CuCl₂ complexes indicate absence of the Cu^{II} moiety. The copper atoms in both complexes are in the diamagnetic Cu^I state and the symmetric signal observed is due to the unpaired electron on donors.¹⁷

In summary, the TTFs 1–4 and 9 incorporating 5- to 9-membered exterior rings have similar physical properties. In contrast the donor 10 having a 10-membered exterior ring shows remarkably different physical and electrochemical characteristics. This is probably due to the difference in the conformational behaviour of the exterior ring. The anomalous properties of the TTF may also be due to the phane-like structure 13 whose formation would require intramolecular



coupling of the dimeric thione 12. However, the possibility of the formation of 12 was ruled out since the mass spectrum of the thione did not exhibit any peak higher than the molecular ion of the monomeric thione 7.

Experimental

All the solvents used were dried and deoxygenated prior to use. The reactions were carried out in an inert atmosphere. M.p.s were determined with a Kettan melting point apparatus and are uncorrected. Elemental analysis was carried out with Carlo Erba elemental analyser model 1106. IR spectra were recorded as KBr pellets on a Perkin-Elmer 681 spectrometer. UV spectra were recorded on a Shimadzu UV-260 spectrophotometer (CH₂Cl₂ as solvent). Mass spectra were obtained on a JEOL D-300 mass spectrometer operating at 70 eV. ¹H NMR and ¹³C NMR spectra were recorded on Bruker 500 and Varian VXR 300 MHz instruments with Me₄Si as internal standard and CDCl₃ as solvent. Solid state ESR spectra were recorded on a Varian E-112 ESR spectrometer using tetracyanoethylene as *g*-marker at room temperature. The solid state conductivities were measured on powered samples at room temperature by the two-probe method; samples were manually compressed between two steel probes and the sample resistance monitored with a Keithley digital multimeter.¹⁸

All electrochemical experiments were performed in a one-compartment cell with platinum working and platinum wire counter electrode. The reference electrodes were Ag⁺/AgCl or saturated calomel electrode (SCE). Measurements were done on a EG and G Princeton Applied Research, Potentiostat/Galvanostat Model 273. The solutions of donors (5×10^{-4} mol dm⁻³) with tetrabutylammonium hexafluorophosphate (0.1 mol dm⁻³) as supporting electrolyte in dry dichloromethane (15 cm³) were purged with dry nitrogen and a nitrogen blanket was kept over the solutions at all times. Sweep rate varied from 25 mV s⁻¹ to 100 mV s⁻¹ over a range of 0.0 to +1.2 V. The data and voltammograms reported are for the sweep rate 25 mV s⁻¹.

Synthesis of DMIT²⁻ ligand.—The DMIT²⁻ anion was prepared according to the reported procedure¹⁴ with some modifications. To CS₂ (180 cm³) in a 1 dm³ round bottomed flask was added sodium (23 g, small pieces) under inert atmosphere at room temperature and dimethylformamide (DMF, 200 cm³) was added slowly to the stirred suspension which turned red. The mixture was stirred for 2 h to dissolve most of the sodium and finally CS₂ (25 cm³) and DMF (50 cm³) were added and the mixture stirred for an additional 3 h. The red coloured thick mass was filtered through Buchner funnel without filter paper to remove unchanged sodium and the filtrate was treated with methanol (50 cm³) to destroy unchanged sodium; excess solvent was removed under reduced pressure at a temperature below 50 °C. The resulting residue was dissolved in methanol (200 cm³) and water (100 cm³) and to this solution were rapidly added solutions of ZnCl₂ (18.0 g) in aqueous ammonia (200 cm³) and Bu₄NBr (80.0 g) in water (100 cm³). The precipitated purple crystalline material was filtered and washed with isopropyl alcohol-ether. Recrystallisation of the crude product from isopropyl alcohol-acetone (1:1) yielded [Bu₄N]₂[Zn(DMIT)₂], 67 g (29% based on Na).

The benzoyl ester of the ligand was prepared following the reported method¹⁹ by the action of benzoyl chloride on [Bu₄N]₂[Zn(DMIT)₂]. The crude ester thus obtained was recrystallised (CHCl₃-MeOH, 1:1), to give light brown needles, 57.8 g (28% based on Na). The sodium salt was generated at the time of use by a procedure reported by Underhill *et al.*¹⁵

5H-6,7,8,9-Tetrahydro-1,3-dithiolo[4,5-b][1,4]dithiocyclo-nonen-2-thione 6.—A solution of freshly generated disodium 2-thioxo-1,3-dithiolo-4,5-dithiolate **5** in absolute ethanol (500 cm³) was added dropwise to 1,5-dibromopentane (4.69 g, 20 mmol) in ethanol (500 cm³) at *ca.* -75 °C during *ca.* 4 h, and the reaction mixture was further stirred at room temperature until completion of the reaction (TLC, 3 h). The resulting viscous yellow precipitate obtained by decantation of the ethanol, was washed with ethanol and dissolved in chloroform. It was filtered and the filtrate was washed with water, dried (Na₂SO₄) and chromatographed on silica gel. Elution with light petroleum (60–80 °C)-ethyl acetate (99:1) gave the title thione **6** which was recrystallised from chloroform-ethanol (1:1) to give yellow crystal (1.68 g, 32%), m.p. 131 °C (Found: C, 35.5; H, 4.0. Calc. for C₈H₁₀S₅: C, 36.09; H, 3.75%; $\nu(\text{KBr})/\text{cm}^{-1}$ 1080 (C=S); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 359, 273 and 245; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.63 (m, 4 H, CH₂), 2.14 (m, 2 H, CH₂) and 2.90 (t, 4 H, SCH₂); $\delta_{\text{C}}(\text{CDCl}_3)$ 213.44 (C=S), 142.52 (C=C), 37.24 (SCH₂), 23.78 and 20.72 (CH₂); *m/z* 265 (M⁺, 100%).

The thiones **7** and **8** were prepared as for thione **6**.

5,6,7,8,9,10-Hexahydro-1,3-dithiolo[4,5-b][1,4]dithiocyclo-decene-2-thione.—Yellow crystal (1.33 g, 29%), m.p. 154 °C (Found: C, 38.4; H, 4.5. Calc. for C₉H₁₂S₅: C, 38.57; H, 4.28%; $\nu(\text{KBr})/\text{cm}^{-1}$ 1075 (C=S); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 382, 276 and 247; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.66 (m, 4 H, SCH₂), 1.91 (m, 4 H, SCH₂CH₂) and 2.90 (t, 4 H, CH₂CH₂); $\delta_{\text{C}}(\text{CDCl}_3)$ 212.86 (C=S), 139.94 (C=C), 36.97 (SCH₂), 25.20 and 22.30 (CH₂CH₂); *m/z* 280 (M⁺, 100%).

5,6-Dihydro-5-methyl-1,3-dithiolo[4,5-b][1,4]dithiocyclo-hexene-2-thione.—Yellow crystals (6.10 g, 64%), m.p. 53–54 °C (lit.¹² 55 °C); $\nu(\text{KBr})/\text{cm}^{-1}$ 1084 (C=S); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 406, 277 and 240; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.5 (d, 3 H, CH₃), 3.2 (d, 2 H, CH₂) and 4.0–3.5 (m, 1 H, CH); a mixture of *cis*- and *trans*-derivatives.

Bi(5H-6,7,8,9-tetrahydro-1,3-dithiolo[4,5-b][1,4]dithiocyclo-nonen-2-ylidene) (BPtDT-TTF) 9.—The thione **6** (1.59 g, 6

mmol) was taken in triethyl phosphite (10 cm³) and heated with stirring at 100–110 °C for 1 h; the solution became orange. Removal of the triethylphosphite under reduced pressure and chromatographic separation of the residue on silica gel using dichloromethane as eluent yielded BPtDT-TTF **9** as an orange solid, which was recrystallised from dichloromethane to give orange crystalline material (0.12 g, 9%; m.p. 240 °C (decomp.) (Found: C, 40.6; H, 4.5. Calc. for C₁₆H₂₀S₈: C, 41.02; H, 4.27%; $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 401, 325, 310 and 232; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.60 (m, 8 H, CH₂), 2.08 (m, 4 H, CH₂) and 2.83 (t, 8 H, CH₂); *m/z* 468 (M⁺ 99.5%).

TTFs **10** and **11** were prepared as for compound **9**.

Bi(5,6,7,8,9,10-hexahydro-1,3-dithiolo[4,5-b][1,4]dithiocyclo-decen-2-ylidene) (BHDT-TTF) 10.—Pale yellow crystals (12%); m.p. 228 °C (decomp.) (Found: C, 43.2; H, 4.9. Calc. for C₁₈H₂₄S₈: C, 43.54; H, 4.83%; $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 365, 338, 268 and 225; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.38 (m, 8 H, SCH₂CH₂), 2.35 (m, 8 H) and 3.20 (m, 8 H, CH₂CH₂); *m/z* 496 (M⁺, 64.6%).

Bi(5,6-dihydro-5-methyl-1,3-dithiolo[4,5-b][1,4]dithiocyclo-hexen-2-ylidene) (BMeEDT-TTF) 11.—Orange-red crystals (21%); m.p. 175 °C (lit.¹² 175 °C) (Found: C, 34.1; H, 3.0. Calc. for C₁₂H₁₂S₈: C, 34.95; H, 2.91%; $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 458, 322 and 263; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.46 (d, 6 H, CH₃), 2.98–3.03 (m), 3.18–3.21 (m, 2 H, CH₂) and 3.66 (m, 1 H, CH); mixture of *cis* and *trans*-derivatives.

BPtDT-TTF:TCNO.—To an acetonitrile solution (20 cm³) of BPtDT-TTF **9** (0.030; 0.063 mmol) was added a warm solution of TCNQ (0.013 g, 0.0068 mmol) in acetonitrile (10 cm³). The reaction mixture was refluxed for 2 h. During this period BPtDT-TTF was dissolved and a black crystalline material precipitated out. The reaction mixture was kept at 0 °C for few hours and the precipitated mass was filtered off, washed with hot acetonitrile and dried *in vacuo* (0.020 g, 40%; m.p. 254 °C. (Found: C, 50.4; H, 3.3; N, 9.9. C₁₆HS₈C₁₂H₄N₄ requires C, 49.98; H, 3.57; N, 8.33%; $\nu(\text{KBr})/\text{cm}^{-1}$ 2220 (C=N); $\sigma_{\text{r.t.}} = 6.3 \times 10^{-6} \text{ S cm}^{-1}$; ESR *g* 2.0035.

BHDT-TTF:TCNQ.—50%; m.p. 230–232 °C (decomp.) (Found: C, 49.3; H, 4.0; N, 7.37. C₁₈H₂₄S₈C₁₂H₄N₄ requires C, 51.4; H, 3.99; N, 7.99%; $\nu(\text{KBr})/\text{cm}^{-1}$ 2220 (C=N); $\sigma_{\text{r.t.}} = < 10^{-6} \text{ S cm}^{-1}$.

BMeEDT-TTF:TCNQ.—55%; m.p. 196 °C (Found: C, 47.2; H, 2.6; N, 8.95. C₁₂H₁₂S₈C₁₂H₄N₄ requires C, 46.73; H, 2.59; N, 9.08%; $\nu(\text{KBr})/\text{cm}^{-1}$ 2200 (C=N); $\sigma_{\text{r.t.}} = 9.6 \times 10^{-2} \text{ S cm}^{-1}$; ESR, *g* 2.00188.

Preparation of CuCl₂ Complexes with π -Donors.—To a refluxing solution of BPtDT-TTF **9** (0.020 g; 0.042 mmol) in acetonitrile (20 cm³) was added a solution of CuCl₂·2H₂O (0.007 g, 0.040 mmol) in acetonitrile (10 cm³). The colour of the solution turned from orange to brownish-black. The mixture was heated until all the BPtDT-TTF had dissolved and then concentrated to half of its volume and placed in a freezer for crystallization. The black crystalline material obtained was washed with cooled acetonitrile and dried *in vacuo*, 56%, m.p. 165 °C [Found: C, 30.8; H, 3.5. Requires C, 30.50; H, 3.17%; corresponding to formulation (BPtDT-TTF)₅(CuCl₂)₆]; $\sigma_{\text{r.t.}} = 4.5 \times 10^{-6} \text{ S cm}^{-1}$; ESR, *g* 2.0095.

BMeEDT-TTF·CuCl₂.—55%, grey powder, m.p. 185 °C [Found: C, 31.3; H, 2.4. Requires C, 31.13; H, 2.59%; corresponding to formulation (BMeEDT-TTF)₃(CuCl₂)₃]; $\sigma_{\text{r.t.}} = 9 \times 10^{-2} \text{ S cm}^{-1}$; ESR *g*, 2.00277.

Supplementary Publication.—Further data accompanies this paper in the form of a supplementary publication no. 56891 (16 pp) and comprises NMR data for **6**, **7**, **9**, **10** and **11**, CV data for **2** and **11**, and MS data for **7**.*

Acknowledgements

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* For details of the supplementary publication scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1992, issue 1.

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