

New Electron Donors for Organic Metals: the Synthesis of Highly Conjugated Bis-(1,3-dithiole) Derivatives

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Routes to bis-(1,3-dithiole) derivatives with extended conjugation between the two heterocyclic rings are described. Compound (17) has been prepared in three steps from benzene-1,2-dithiol. Compounds (27) and (30), both prepared from 2,6-bis(bromomethyl)naphthalene, could not be isolated, but have been characterised as salts or complexes.

During the decade since the discovery of high electrical conductivity and other remarkable solid-state properties in the charge-transfer complex of tetrathiafulvalene (TTF) (1) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) there has been intense interest in the preparation of new electron-donor and -acceptor molecules and a large number of organic metals are now known.¹

Synthetic work towards new donors has followed two main lines: (i) replacement of one or more sulphur atoms of TTF with selenium or tellurium, and (ii) substitution of cyclic or acyclic groups at the carbon atoms of TTF. Thus molecules such as TMTSF (2), DBTTF (3), DBTTFe (4), and BEDT-TTF (5) have been prepared and their complexes described in a plethora of papers.¹ Currently, compounds (2) and (5) are at the forefront of the field as they both form salts which are superconducting at very low temperatures.^{1b}

With many donors and acceptors now available a clearer picture is emerging as to why some charge-transfer complexes have metallic properties in the solid state. It is widely agreed that three major prerequisites for high electrical conductivity in a complex are (i) segregated stacks of donor and acceptor molecules, (ii) extensive π -electron delocalisation along these stacks, and (iii) *partial* charge-transfer from donor to acceptor. The electronic properties are highly anisotropic with delocalised electrons forming a conduction band whose width is determined by the interactions between neighbouring molecules. We have a continuing interest in the synthesis of new molecules designed to meet these requirements and in this paper we describe the synthesis of bis(dithiole) donors with extended conjugation between the heterocyclic rings. These donors offer the desirable features of more widely spaced sites of maximum spin relative to TTF (1) and, hence, less Coulombic repulsion in the doubly ionised state, and, in some cases, a certain amount of disorder is possible due to rotation about C-C bonds that link the dithiole rings.²

The work published to date on dithiole donors with extended conjugation between the rings is restricted to compounds (6)—(14) and it is worthwhile collating the references here. The preparation of compound (6) is claimed in an early patent but no details are given.³ The air-sensitive diphenyl derivative (7) forms an iodine complex of low conductivity [room temperature conductivity, σ_{rt} , 8.5×10^{-5} ($\Omega \text{ cm}^{-1}$)] and possibly complexes with TCNQ and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in solution.⁴ Tetramethyl derivative (8) forms salts with TCNQ, ClO_4^- , and BF_4^- , the last two being metallic at room temperature [σ_{rt} , 10 ($\Omega \text{ cm}^{-1}$)].⁵ Diphenyl compound (9) has been studied by two groups^{6,7} and forms an insulating complex with DDQ and possibly a complex with TCNQ.⁶ Phenyl-substituted derivatives of system (10) were first reported ten years ago,⁸ but only recently have the parent derivatives (10)⁹ and (11)¹⁰ been described. As expected, cyclic voltammetry shows that Coulombic repulsion in the dication of

compound (10) is decreased when compared with the dication of TTF (1).⁹ 1,1,4,4-Tetrathiabutadiene derivatives with saturated dithiole and dithiane rings, (12) and (13), had been studied previously and are very weak donors; compound (12) forms a π -complex and an ion-radical salt with the very strong acceptor tetrafluoro-TCNQ.¹¹ Salts of TCNQ and DDQ with the extensively conjugated bis(dithiole) (14) have recently been reported.¹² We now describe the synthesis of donors (17), (27) and (30); the last two are unstable and have been characterised either as salts or complexes.

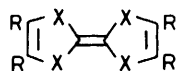
Our route to donor (17), a vinyllogue of DBTTF (3), is shown in Scheme 1.¹³ Reaction of 2 mol equiv. of benzene-1,2-dithiol with 2,5-dimethoxytetrahydrofuran, or with succinaldehyde, gave compound (15) with a saturated linkage between the heterocyclic rings. Hydride abstraction from compound (15) using trityl hexachloroantimonate afforded the salt (16), which was readily deprotonated by triethylamine to yield compound (17), as a slightly air-sensitive crystalline solid. The overall yield of compound (17) for the three steps was 70%. Essentially the same route to (17) has been reported independently by Yoshida and co-workers.¹⁴

Cyclic voltammetry of donor (17) shows two reversible one-electron waves at 0.26 and 0.41 eV (*vs.* s.c.e.). U.v. spectra confirmed the presence of the neutral, radical-cation, and dication species of compound (17) (see Experimental section). Compound (17) is a better donor than DBTTF (3) and the reduction potential for (17) falls within a narrow range (*ca.* -0.1 to +0.4 eV) which favours incomplete charge-transfer from donor to TCNQ.¹⁴ In accord with this, the black 1:1 complex formed between donor (17) and TCNQ is metallic at room temperature [σ_{rt} (powdered sample), 5 ($\Omega \text{ cm}^{-1}$)]. This complex is of interest as it is one of the first highly conducting complexes to be formed from a TTF-type donor that can adopt a non-planar conformation due to free rotation about the central C-C single bond.[†] However, as yet crystals of the complex have not been obtained and powdered samples of the complex tend to decompose on storage as judged by a drop in conductivity with time.

We next turned our attention to the 2,2'-(naphthalene-2,6-diylidene)bis(1,3-dithiole) system (NBDT) with a conjugated naphthoquinonoid unit between the dithiole rings, and, following precedents set for compounds (7)⁴ and (8),⁵ the tetramethyl derivative (27) (TM-NBDT) and diphenyl derivative (30) (DP-NBDT) seemed promising targets.¹⁵

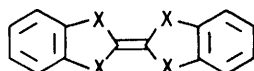
Our route to compound (27) is shown in Scheme 2. Treatment of 2,6-bis(bromomethyl)naphthalene (18) with

[†] Yoshida and co-workers (ref. 14) report that an X-ray structure of a dimethyl derivative of (17) is in progress. During the preparation of this manuscript metallic TCNQ complexes of selenium-containing analogues of (10) were reported (Z. Yoshida, H. Awaji, and T. Sugimoto, *Tetrahedron Lett.*, 1984, **25**, 4227).



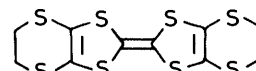
(1) X = S, R = H (TTF)

(2) X = Se, R = Me (TMTSF)

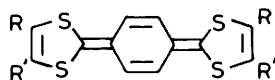


(3) X = S (DBTTF)

(4) X = Te (DBTTeF)



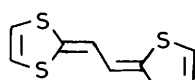
(5) BEDT-TTF



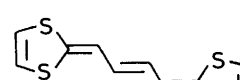
(6) R = R' = H

(7) R = H, R' = Ph (or isomer)

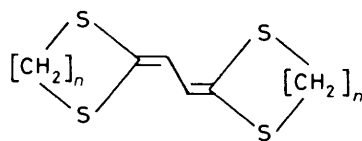
(8) R = R' = Me

(9) RR' = (CH=CH)₂

(10)

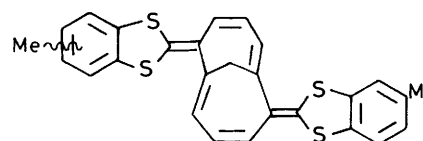


(11)

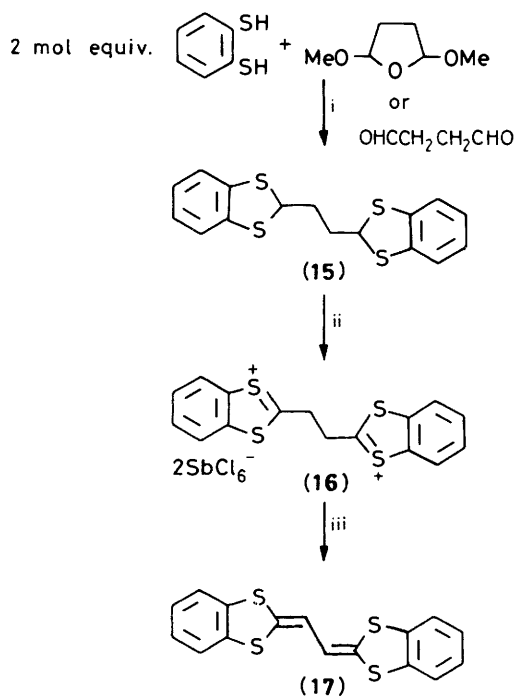


(12) n = 2

(13) n = 3



(14)



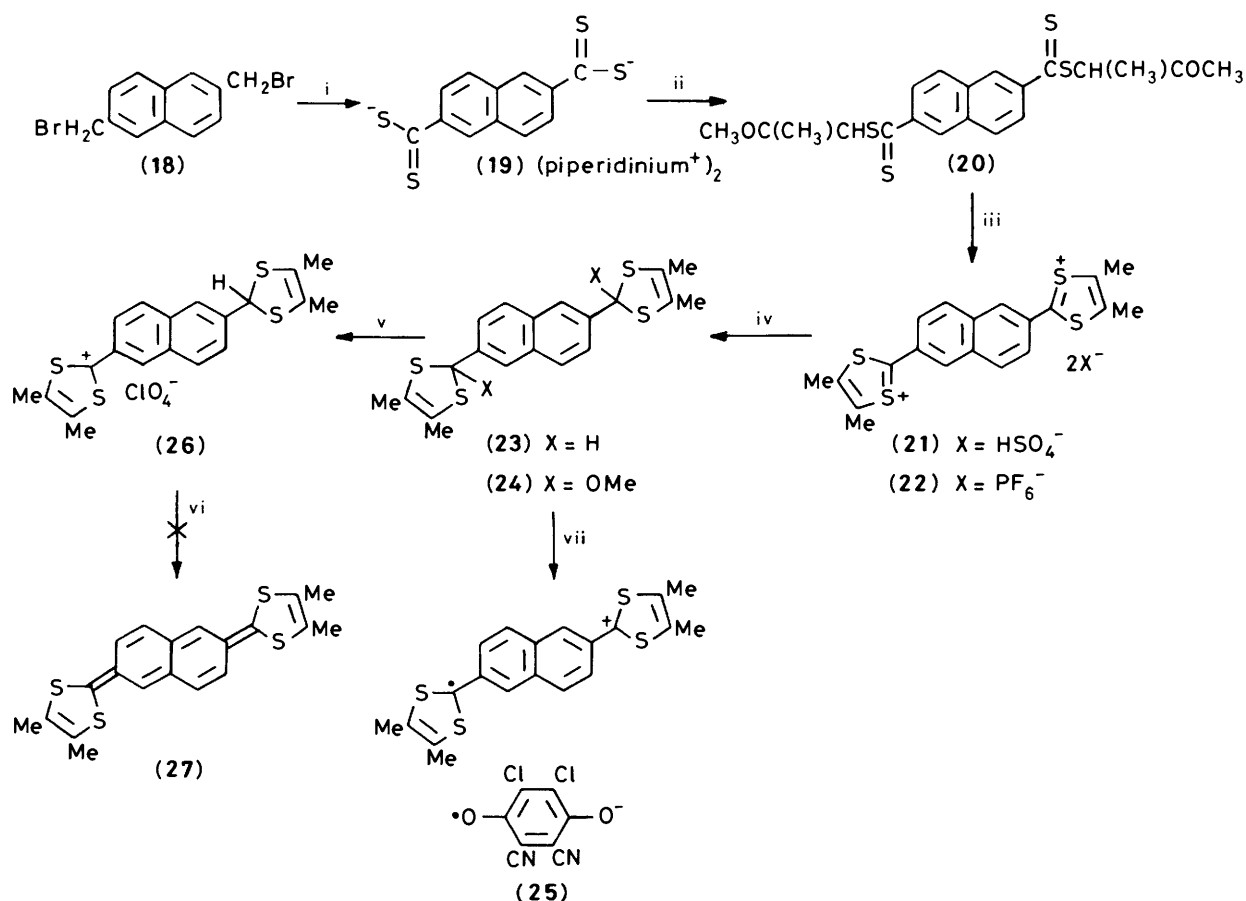
Scheme 1. Reagents: i, toluene-4-sulphonic acid; ii, trityl hexachloroantimonate; iii, triethylamine

sulphur under basic conditions as described by Ueno *et al.*⁴ led to the corresponding bis(dithiocarboxylic) acid which was unstable, but could be conveniently isolated and purified as the dipiperidinium salt (19). The presence of the CS₂⁻ group in salt (19) was confirmed by a band in the i.r. spectrum at 1 000 cm⁻¹. Salt (19) reacted readily with 3-chlorobutan-2-one at room temperature to afford diester (20). Dissolution of the diester in

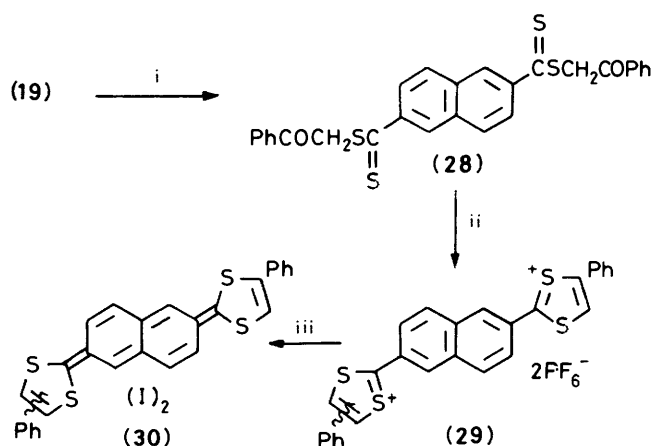
conc. sulphuric acid caused rapid cyclisation with dehydration to yield the bis-(1,3-dithiolium) salt (21) which was purified as the bis(hexafluorophosphate) salt (22). The methyl protons of structure (22) are observed as a singlet at δ_H 2.8 in the ¹H n.m.r. spectrum; this downfield shift with respect to the normal value for CH₃-C=C protons is consistent with the cationic structure of compound (22). Treatment of dication salt (22) with sodium borohydride in ethanol, or sodium methoxide in methanol, yielded compounds (23) and (24), respectively. The overall yield for the preparation of (23) from (18) is 10%. Attempts to dehydrogenate dihydro compound (23) to TM-NBDT (27) using 2 mol equiv. of DDQ yielded a highly insoluble brown powder, which was identified from analytical and spectroscopic data as a 1 : 1 salt of the quinol radical anion and the TM-NBDT radical-cation, (25). In particular the i.r. spectrum of compound (25) showed no carbonyl absorption of DDQ but a strong absorption band at 1 554 cm⁻¹ assigned to the phenoxyl radical. The salt gave a strong singlet in the e.s.r. spectrum (*g* 2.0003). Similar data have been used to identify the quinol salt of bis(dithiole) (9).⁶

Reaction of dihydro compound (23) with 1 mol equiv. of DDQ in 70% perchloric acid⁴ yielded monocation salt (26) in high yield, but attempts to convert salt (26) into TM-NBDT (27) by reaction with triethylamine gave an intractable mixture of products.

DP-NBDT (30) has been approached by a directly analogous route (Scheme 3). Thus salt (19) was treated with 2 mol equiv. of phenacyl bromide to yield diester (28), which cyclised to dication, again isolated as the bis(hexafluorophosphate) salt (29). The ¹H n.m.r. spectrum of the dication of compound (29) [as the bis(trifluoroacetate)salt] shows a singlet from the 1,3-dithiolium ring protons at δ_H 8.85 appropriate for a cationic structure [*cf.* δ_H 9.05 for the dication of structure (7)].⁴ Addition of the dication of (29) to a solution of excess of lithium iodide in acetone gave a black, amorphous solid for which analytical data suggested a stoichiometry (DP-NBDT)₁(I)₂. The complex exhibited a strong e.s.r. signal, and the u.v. spectrum showed a bathochromic shift consistent with the highly conjugated



Scheme 2. Reagents: i, S_8 -NaOMe, followed by HCl-piperidine; ii, $MeCH(Cl)COCH_3$; iii, c. H_2SO_4 , followed by 60% HPF_6 ; iv, $NaBH_4$ or NaOMe; v, 1 mol equiv. $DDQ-HClO_4$; vi, NEt_3 ; vii, 2 mol equiv. DDQ



Scheme 3. Reagents: i, $PhCOCH_2Br$; ii, H_2SO_4 , followed by 60% HPF_6 ; iii, Lil

quinonoid structure of DP-NBDT (**30**) (λ_{max} . 655 and 1 030 nm) and decisively different from that of the aromatic precursor (**29**). As yet this iodine complex has not been obtained crystalline and conductivity measurements on a powdered sample showed the material is an insulator [$\sigma_{ri} < 10^{-5} (\Omega \text{ cm})^{-1}$]. The formation of iodine complexes in this way has been described previously and explained by electron transfer from iodide anion to the dithiole dication followed by further aggregation of iodine moiety.⁴

Attempts to isolate an iodine complex of TM-NBDT (**27**)

were unsuccessful. Addition of dication salt (**22**) to a solution of lithium iodide in acetone resulted in considerable darkening of the solution and the appearance of u.v. bands indicative of a highly conjugated structure, but on evaporation of the solution only starting materials were recovered.

DP-NBDT (**30**) forms a complex with TCNQ, the characterisation of which will be reported separately.

Experimental

N.m.r. spectra were recorded on a Bruker HX90E spectrometer with tetramethylsilane as internal standard. Mass spectra were recorded on an A.E.I. MS9 spectrometer. I.r. spectra were recorded as Nujol mulls, unless otherwise stated, using a Perkin-Elmer 577 instrument. U.v. spectra were obtained on an SP8-100 spectrophotometer. Microanalyses were obtained on a Perkin-Elmer CHN 240 elemental analyser. M.p.'s were recorded on a Kofler micro-heating stage and are uncorrected.

Preparation of Compound (15).—A solution of benzene-1,2-dithiol¹⁶ (2.8 g, 2.0 mmol), 2,5-dimethoxytetrahydrofuran (1.3 g, 1.0 mmol), and toluene-4-sulphonic acid (400 mg) in methanol (10 ml) was stirred at room temperature for 16 h. After the mixture had been cooled to 0°C the solid product was collected and washed with methanol to yield *compound* (**15**) (6.8 g, 97%) as crystals, m.p. 130–131°C (Found: C, 57.7; H, 4.3. $C_{16}H_{14}S_4$ requires C, 57.5; H, 4.2%); m/z 334 (M^+); δ_H ($CDCl_3$) 7.26–6.95 (8 H, AA'-BB'), 4.97–4.71 (2 H, m), and 2.13–2.05 (4 H, m).

When succinaldehyde was used instead of dimethoxytetra-

hydrofuran, reaction on the same scale as that described above yielded compound (15) (70% yield).

Preparation of Dication Bis(hexachloroantimonate) (16).—A solution of compound (15) (1.7 g, 0.05 mol) and trityl hexachloroantimonate (5.8 g, 0.1 mol) in dichloromethane (30 ml) was stirred and heated under reflux for 12 h. After the solution had cooled and been treated with ether the solid was collected and identified as the bis(hexachloroantimonate) (16) (4.8 g, 95%). A small portion was recrystallised from aqueous ethanol to yield a brown powder, m.p. 200 °C (decomp.) (Found: C, 19.3; H, 0.9. $C_{16}H_{12}Cl_{12}S_4Sb_2$ requires C, 19.2; H, 1.2%).

Preparation of Bis-(1,3-benzodithiole-2-ylidene)ethane (17).—A mixture of dication salt (16) (2.0 g, 2 mmol) and triethylamine (1.5 ml, excess) in acetonitrile (15 ml) was stirred overnight at room temperature. Partial evaporation of solvent yielded a brown solid only sparingly soluble in most organic solvents. Recrystallisation from dimethylformamide afforded compound (17) as orange crystals that darkened in air (510 mg, 80%), m.p. 225 °C (decomp.) (Found: C, 57.9; H, 3.0. $C_{16}H_{10}S_4$ requires C, 58.2; H, 3.0%; m/z 330 (M^+); $\delta_H(CS_2)$ 7.24–6.90 (8 H, br s) and 5.86 (2 H, s). Cyclic voltammetry of donor (17) in benzonitrile showed two reversible one-electron oxidation waves at 0.26 and 0.41 V versus s.c.e. U.v. spectra of donor (17): $\lambda_{max.}(PhCN)$ 360sh (log ϵ 4.72), 374 (4.81), and 392 nm (4.94); (17) radical-cation: $\lambda_{max.}$ 320 (4.31), 345sh (4.22), 460sh (3.70), 565 (4.75), 665 (4.28), and 782 nm (4.07); (17) dication: $\lambda_{max.}$ 460 nm (4.66).

Preparation of Dipiperidinium Salt (19).—A mixture of elemental sulphur (3.8 g, 0.12 mol) and sodium methoxide [from Na, 5.5 g (0.12 mol)] in methanol (100 ml) was refluxed for 1 h. 2,6-Bis(bromomethyl)naphthalene (18)¹⁷ (10.0 g, 0.03 mol) was then added in portions to the mixture. After being refluxed overnight the mixture was cooled and the solvent was evaporated off to yield the disodium salt of the tetrathioacid (dianion) of compound (19). This was dissolved in water to give a dark solution. On acidification with HCl a solid precipitated which was filtered off under a blanket of nitrogen and partially dried. The resultant solid was dissolved in dichloromethane, the solution was filtered, and piperidine was added to the dark filtrate at 0 °C until precipitation was complete. The solid was collected and washed thrice with ether to yield dipiperidinium salt (19) as orange crystals, (7.1 g, 50%), m.p. 152–155 °C (Found: C, 59.4; H, 6.3; N, 6.7. $C_{22}H_{28}N_2S_4$ requires C, 58.9; H, 6.3; N, 6.3%; $\nu_{max.}(Nujol)$ 1 000 cm^{-1} (CS_2^-).

Preparation of Compound (20).—A solution of 3-chlorobutan-2-one (4.3 g, 0.02 mol) in methanol (50 ml) was added dropwise to a stirred suspension of the dipiperidinium salt (19) (4.5 g, 0.01 mol) in methanol (50 ml). After the mixture had been stirred at 20 °C for 12 h, the red precipitate was collected and recrystallised from acetonitrile to yield compound (20) (2.1 g, 50%) as red needles, m.p. 181–183 °C (Found: C, 57.2; H, 4.6. $C_{20}H_{20}O_2S_4$ requires C, 57.1; H, 4.8%; m/z 420 (M^+); $\nu_{max.}$ 1 700 (C=O) and 1 216 cm^{-1} (C=S); $\delta_H(CDCl_3)$ 7.6–8.5 (6 H, m), 4.95 (2 H, q), 2.36 (6 H, s), and 1.63 (6 H, d).

Preparation of Bis(hexafluorophosphate) Salt (22).—Compound (20) (2.0 g) was dissolved in stirred conc. H_2SO_4 (5 ml) at 0 °C. The solution was allowed to warm to room temperature and then diluted with acetone to precipitate the di(hydrogen sulphate) salt (21). This was collected by filtration and dissolved in 60% hexafluorophosphoric acid (20 ml). Dilution with acetone yielded salt (22) (2.0 g, 62%) as a brown powder, m.p. > 300 °C (Found: C, 36.0; H, 2.9; F, 32.9. $C_{20}H_{18}F_{12}P_2S_4$ requires C, 35.5; H, 2.7; F, 33.7%);

$\delta_H(CF_3CO_2H)$ 8.1–8.7 (6 H, m) and 2.75 (12 H, s); $\lambda_{max.}(CH_3CN)$ 325 and 442 nm.

Preparation of Compound (23).—A stirred suspension of salt (22) (380 mg, 0.5 mmol) in ethanol (10 ml) was treated at room temperature with sodium borohydride (80 mg, 1.05 mmol) added in portions during 15 min. After a further 1 h at room temperature the solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The solution was filtered and the filtrate was evaporated to yield compound (23) as a brown powder (134 mg, 62%) (Found: C, 63.2; H, 5.8; S, 32.7%; M^+ , 388.0448. $C_{20}H_{20}S_4$ requires C, 61.9; H, 5.4; S, 33.0%; M , 388.0448; $\delta_H[(CD_3)_2SO]$ 7.5–8.0 (6 H, m), 5.60 (2 H, s), and 1.80 (12 H, s).

Preparation of Compound (24).—To a solution of salt (22) (380 mg, 0.5 mmol) in methanol (15 ml) at room temperature was added sodium methoxide (108 mg, 4 mol equiv.). The mixture was stirred for 4 h. Water was then added and the mixture was extracted with chloroform. The organic layer was separated, dried ($MgSO_4$), and evaporated under reduced pressure to yield dimethoxy compound (24) (100 mg, 40%) as a white solid, m.p. > 290 °C. An analytical sample was recrystallised from methanol (Found: C, 59.1; H, 5.3. $C_{22}H_{24}O_2S_4$ requires C, 58.9; H, 5.4%; m/z 448 (M^+); $\delta_H(CDCl_3)$ 7.7–8.2 (6 H, m), 3.44 (6 H, s), and 1.95 (12 H, s).

Preparation of Complex (25).—A solution of dihydro compound (23) (200 mg, 0.5 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (230 mg, 1.0 mmol) in benzene (5 ml) was refluxed for 2 h. The solution was cooled and filtration separated the highly insoluble salt (25) (70 mg, 20%) (Found: C, 54.6; H, 3.2; N, 4.7; S, 20.2. $C_{28}H_{18}Cl_2N_2O_2S_4$ requires C, 54.9; H, 2.9; N, 4.6; S, 20.9%; $\nu_{max.}(KBr)$ 1 554 cm^{-1} (phenoxy radical band), C=O absent; e.s.r. (powder) singlet, g 2.0003; $\lambda_{max.}(CH_3CN)$ 330, 430, 640, and 785 nm.

Preparation of Perchlorate Salt (26).—A mixture of compound (23) (200 mg, 0.5 mmol) and DDQ (115 mg, 0.5 mmol) in 70% perchloric acid was stirred at 50 °C overnight. The mixture was cooled and diluted with water and then poured into acetone to precipitate salt (26) (205 mg, 81%), m.p. ca. 200 °C (decomp.) (Found: C, 43.7; H, 3.1; S, 23.7. $C_{20}H_{20}ClO_4S_4$ requires C, 43.5; H, 3.6; S, 23.2%; $\delta_H(CF_3CO_2H)$ 7.7–8.4 (6 H, m), 5.4 (1 H, s), 2.5 (6 H, s), and 1.82 (6 H, s).

Reaction of salt (26) with either 1 mol equiv. or an excess of triethylamine in acetonitrile gave a complex mixture of products from which nothing could be purified.

Preparation of Compound (28).—Following the procedure detailed above for compound (20), dipiperidinium salt (19) (2.2 g, 5 mmol) and α -bromoacetophenone (2.0 g, 10 mmol) yielded compound (28) (1.5 g, 60%) as red crystals, m.p. 184–187 °C (Found: C, 65.2; H, 4.2. $C_{28}H_{20}O_2S_4$ requires C, 65.1; H, 3.9%; m/z 516 (M^+); $\delta_H[(CD_3)_2SO]$ 7.5–8.5 (16 H, m) and 4.80 (4 H, br s).

Preparation of Dication Salt (29).—Following the procedure described above for the salt (22), compound (28) (500 mg) afforded dication salt (29) (260 mg, 35%), m.p. 250 °C (decomp.) (Found: C, 43.8; H, 1.9; F, 30.0. $C_{28}H_{18}F_{12}P_2S_4$ requires C, 43.6; H, 2.1; F, 29.6%; $\delta_H(CF_3CO_2H)$ 8.85 (2 H, s), 8.10–8.70 (6 H, m), 7.55–8.10 (10 H, m); $\lambda_{max.}(CH_3CN)$ 225, 249, 342, and 465 nm.

Preparation of (DP-NBDT)-Iodine Complex (30).—Dication salt (29) (100 mg) was added to a solution of lithium iodide (excess) in acetone (10 ml) and the resultant dark green solution

was heated under reflux for 1 h. The solution was then cooled and the black precipitate was collected and washed with cold acetone to afford complex (30) (44 mg, 46%), m.p. >290 °C (Found: C, 46.0; H, 2.1; I, 33.8. $C_{28}H_{18}I_2S_4$ requires C, 45.6; H, 2.45; I, 34.5%); λ_{max} (acetonitrile) 650 and 1 030 nm. Attempted purification by recrystallisation was unsuccessful.

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