

# Pyridine-Functionalised (Vinylenedithio)tetrathiafulvalene (VDT-TTF) Derivatives and Their Dithiolene Analogues

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The synthesis and characterisation of a group of vinylenedithio-TTFs bearing two or four 2- or 4-pyridyl groups are described, along with related nickel and gold bidithiolene, as potential substrates for preparing multifunctional materials. In spite of the pyridyl groups not being coplanar with the vinylenedithio-TTF cores and the significant chair-type distortions of the cores, because of the flexing of the dithiin rings, these substituted donors preserve the stacking ability of the unsub-

stituted donors in the solid state. The pyridyl substitution does not significantly change the redox potentials of these donors. Electrocrystallisation of a bis(2-pyridyl) donor with perrhenate gave a dicationic salt in which the donor is both protonated and oxidized, and the pyridinium group makes a hydrogen bond to a perrhenate ion.

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## Introduction

A significant majority of molecular conductors developed over the last decades are based on salts of the donor TTF and its derivatives. Indeed, a large number of substituted TTFs have been explored, and among them one of the most successful has been the donor bis(ethylenedithio)tetrathiafulvalene, BEDT-TTF, which when converted into radical cation salts has led to a large number of metals and some superconductors.<sup>[1]</sup> The research on this type of molecular material has recently increasingly focussed on the preparation of materials exhibiting a coexistence of conducting and magnetic properties. This has been achieved mainly by the combination of electroactive donor/acceptor units with paramagnetic counterions sited in independent sublattices.<sup>[2]</sup>

An alternative approach, expected to lead to stronger synergy between electrical and magnetic properties, relies on the use of donors, which, in addition to their electroactive role, can bind directly to paramagnetic transition metals thus providing a stronger and more direct interaction between  $\pi$  conduction and paramagnetic d electrons. However, this type of donor has been much less explored and only recently some TTF and BEDT-TTF derivatives substituted with functional

groups that can coordinate to transition metals, especially those containing N-coordinating atoms<sup>[3]</sup> and their complexes, have been described.<sup>[4]</sup> This synthetic effort has also recently been extended to the preparation of similarly substituted bidithiolene transition metal complexes, which can be seen as the inorganic analogues of TTF where the central C=C bond is replaced by a transition metal.<sup>[5]</sup>

In this context we focussed our attention on pyridine substitution in the fully unsaturated version of BEDT-TTF, bis(vinylenedithio)tetrathiafulvalene, also known as BVDT-TTF or VT, since there is a  $\pi$  system linking the metal ion binding site and the electroactive organosulfur system. In this paper we describe the synthesis and characterisation of four new pyridine-substituted vinylenedithiotetrathiafulvalenes, namely the tetra(pyridyl)-substituted symmetrical donors **3a**, **3b** and the di(pyridyl)-substituted unsymmetrical donors **4a**, **4b**, which all have the pyridyl N atoms in either the 2- or 4-positions. The electrocrystallisation of donor **4a** with  $\text{ReO}_4^-$  yielded a [**4a-H**]( $\text{ReO}_4$ )<sub>2</sub> salt, which is discussed. Furthermore, we describe the synthesis and characterisation of two new nickel and gold dithiolene complexes **6** and **7**.

## Results and Discussion

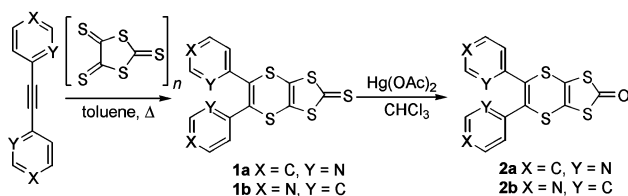
The key compounds for the syntheses of both the pyridyl-substituted donors and related bidithiolene complexes are the thiones **1a**, **1b** and the corresponding oxo compounds **2a**, **2b**, which are used as direct precursors, either by coupling or hydrolytic cleavage reactions. The thiones **1a**, **1b** were prepared by the reaction of oligo(1,3-dithiole-2,4,5-trithione)<sup>[6]</sup> with the correspondent dipyridylacetylene<sup>[7]</sup> in 80% and 83% yields, respectively (Scheme 1).

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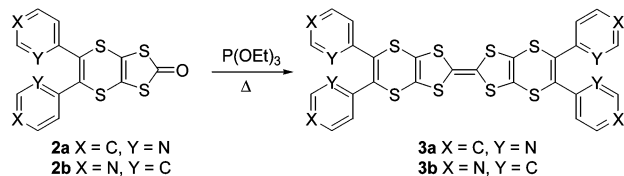
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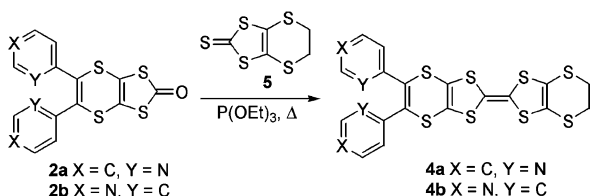
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Scheme 1. Synthesis of compounds **1a**, **1b** and **2a**, **2b**.

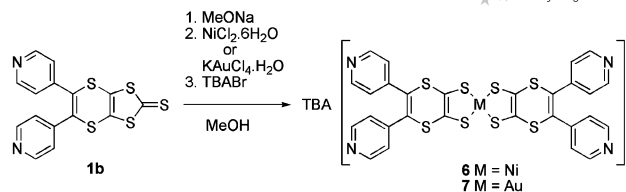
The treatment of thiones **1a** and **1b** with mercuric acetate afforded the oxo compounds **2a** and **2b** in 70% and 57% yields, respectively (Scheme 1). The best yields were obtained when the reaction times were kept short (35 min), otherwise byproducts were formed that were very difficult to separate. Homo-coupling of **2a** or **2b** in triethyl phosphite at 110 °C afforded the tetra(pyridyl)-bis(vinylenedithio)-TTF derivatives **3a** or **3b**, respectively, which precipitated from the reaction mixture, and could be purified by washing with diethyl ether (Scheme 2).

Scheme 2. Synthesis of compounds **3a** and **3b**.

Cross-coupling of the oxo compounds **2a** or **2b** with the unsubstituted thione **5** in triethyl phosphite at ca. 110 °C gave the dipyridyl donors **4a** and **4b** in 54 and 48% yields, respectively, after separation from homo-coupled products by chromatography on silica (Scheme 3).

Scheme 3. Synthesis of compounds **4a** and **4b**.

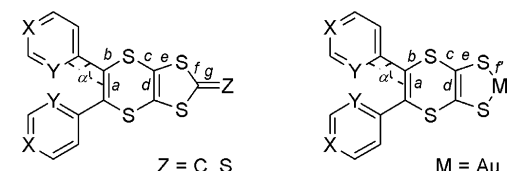
The nickel and gold monoanionic complexes **6** and **7** with four 4-pyridyl groups were obtained as tetrabutylammonium salts,  $n\text{Bu}_4\text{N}[\text{Ni}(4\text{-dpdd})_2]$  (**6**) and  $n\text{Bu}_4\text{N}[\text{Au}(4\text{-dpdd})_2]$  (**7**), respectively, following the general procedure for dithiolene synthesis illustrated in Scheme 4. The dithiolate (4-dpdd) was obtained by the cleavage of thione **1b** with a freshly prepared sodium methoxide solution, and without isolating the sodium dithiolate, a solution of nickel(II) chloride or potassium gold(III) chloride in methanol was added. The dithiolenes **6** and **7** were isolated by the addition of a methanol solution of  $n\text{Bu}_4\text{NBr}$  solution in 39% and 47% yields, respectively.

Scheme 4. Syntheses of compounds **6** and **7**.

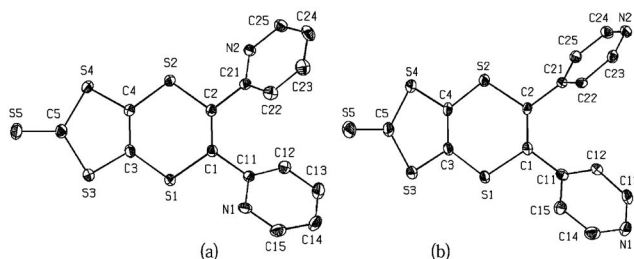
All compounds have been characterised by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy as well as CHN analysis, and the results confirm their purity and composition. It was possible to obtain X-ray crystal structure measurements of compounds **1a**, **1b**, **3b**, **4a**,  $[\mathbf{4a}\text{-H}](\text{ReO}_4)_2$  and **7**. Selected bond lengths are shown in Table 1, and details of structural measurements and, in some cases, included solvents are given in Table 4 in the Experimental Section.

Compounds **1a** and **1b** crystallise in the monoclinic space group  $P2_1/n$  and in the orthorhombic space group  $Pbca$ , respectively, each with one molecule in the asymmetric unit. The ORTEP plot of compounds **1a** and **1b** with the atom numbering scheme is shown in Figure 1. The structures of the thiones **1a** and **1b** are quite similar and have the essentially planar moiety in common, comprising atoms S1, C1, S2, S3, C2, C3, S4 and S5 (rms deviation of fitted atoms: 0.0251 Å for **1a** and 0.0294 Å for **1b**). The dithiin ring presents a flexing about the  $\text{S}\cdots\text{S}$  vector of 132° (**1a**) and 131° (**1b**). The nitrogen position does not influence the bond lengths in the organosulfur system (Table 1). Similar bond lengths have been reported for the crystal structure of 5,6-diphenyl[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-thione.<sup>[8]</sup> In both compounds there are short  $\text{S}\cdots\text{S}$  intermolecular interactions, the shortest ones being a  $\text{S}2\cdots\text{S}2\#a$  contact at 3.402 Å ( $\#a: -x, -y, -z$ ) (**1a**) and a  $\text{S}1\cdots\text{S}5\#b$  contact at 3.289 Å (**1b**) ( $\#b: 2 - x, -1/2 + y, 1/2 - z$ ).

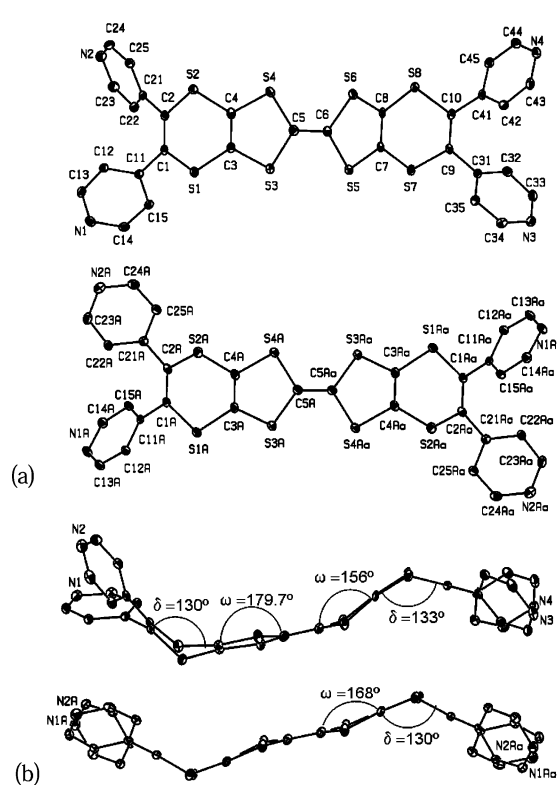
The BVDT-TTF derivative **3b** was obtained from a chloroform/hexane solution as red crystals. The structure  $\mathbf{3b}\cdot 0.66\text{CHCl}_3$  crystallises in the triclinic system, space group  $P\bar{1}$ . The asymmetric unit cell contains 1.5 donor molecules, one in a general position and one located on a centre of symmetry as well as one chloroform molecule. An ORTEP plot of the two independent molecules with the atomic numbering scheme is shown in Figure 2. The two independent molecules show flexing of 130–133° about the  $\text{S}\cdots\text{S}$  vectors in the dithiin rings, and a much lower and more variable flexing about the  $\text{S}\cdots\text{S}$  vectors in the dithiole rings (166–180°) (Figure 2b). The pyridine rings lie at 46.5° (N1A–N2A), 62.0° (N3–N4) and 57.1° (N1–N2) to each other. The best planes of the pyridine rings make angles with the adjacent  $\text{S}-\text{C}=\text{C}-\text{S}$  fragment of 60.1° (N3), 41.7° (N4), 50.2° (N1), 36.5° (N2), 44.6° (N1A) and 48.8° (N2A). The crystal structure of  $\mathbf{3b}\cdot 0.66\text{CHCl}_3$  contains layers that are perpendicular to the *c* axis formed by the donor molecules stacking close to their organosulfur groups. The pyridine rings project from both faces of the layer and the chloroform molecules lie in planes between the layers, close to the pyridine rings (Figure 3). The only intermolecular  $\text{S}\cdots\text{S}$  short contact is  $\text{S}7\cdots\text{S}2\#b$  at 3.366 Å ( $\#b: x, y, z$ ).

Table 1. Selected bond lengths [Å] and angles [°]; the angle *a* refers to the dihedral angle between the pyridine group plane and the S–C=C–S fragment.


	<b>1a</b>	<b>1b</b>	<b>3b</b> ·0.66CHCl <sub>3</sub>	<b>4a</b>	<b>[4a-H](ReO<sub>4</sub>)<sub>2</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub></b>	<b>7·CH<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O</b>		
<i>a</i>	1.336(3)	1.339(5)	1.342(4) 1.342(4)	1.348(4)	1.342(8)	1.348(9)	1.345(15)	1.340(17)
<i>b</i>	1.791(2) 1.775(2)	1.781(4) 1.790(4)	1.781(3) 1.791(3) 1.753(3)	1.802(3) 1.785(3) 1.792(3)	1.781(6) 1.791(5)	1.788(7) 1.790(6)	1.776(10) 1.776(10)	1.750(12) 1.776(13)
<i>c</i>	1.752(2) 1.750(2)	1.744(2) 1.757(4)	1.744(3) 1.747(3) 1.746(3)	1.752(3) 1.741(3) 1.738(3)	1.752(5) 1.749(6)	1.739(7) 1.727(7)	1.769(13) 1.766(12)	1.749(10) 1.768(11)
<i>d</i>	1.339(3)	1.330(5)	1.341(4) 1.334(4)	1.336(4)	1.334(8)	1.355(9)	1.316(15)	1.319(17)
<i>e</i>	1.742(2) 1.737(2)	1.745(4) 1.749(4)	1.751(3) 1.753(3) 1.753(3)	1.751(3) 1.755(3) 1.757(3)	1.752(6) 1.760(5)	1.743(7) 1.727(7)	1.774(12) 1.773(11)	1.735(13) 1.735(12)
<i>f</i>	1.733(2) 1.739(2)	1.739(4) 1.735(4)	1.757(3) 1.761(3) 1.763(3)	1.759(3) 1.771(3) 1.754(3)	1.768(5) 1.773(4)	1.721(7) 1.730(6)	2.321(3) 2.310(3)	2.311(3) 2.314(3)
<i>g</i>	1.642(2)	1.641(4)	1.348(4)	1.337(6)	1.341(7)	1.393(9)		
<i>α</i>	37.6 54.1	60.3 62.8	60.1 50.2	36.5 48.8	49.5 27.3	46.1 45.3	28.3 53.4	55.0 25.2

Figure 1. ORTEP diagram of compound **1a** (a) and **1b** (b) drawn at the 40% probability level and showing the atomic numbering scheme. H atoms were omitted for clarity.

The structure of the cross-coupled donor **4a** was also obtained by single-crystal X-ray diffraction, and an ORTEP plot with the atom numbering scheme is shown in Figure 4. The molecule is less distorted than **3b** with a flexing of just 129° about the S··S vector in the pyridyl-substituted dithiin ring. The pyridine rings lie at 48.9° to each other and at 27.3° and 49.5° to the S7–C9=C10–S8 plane. The rings are oriented so that one N lies to the edge of the molecule and one to the interior. The former forms a potential bidentate binding site with a sulfur atom of the dithiin ring. The conformation of the dihydrodithiin ring is disordered 2:1 between two approximate envelope conformations. The crystal packing consists of parallel columns of donors oriented along the *a* axis, the column arrangement is governed by the short intra-column contacts S6··S8#*a*, 3.564 Å, (#*a*: 1 + *x*, *y*, *z*) and N2··H12#*b*, 2.44 Å, (#*b*: –1 + *x*, *y*, *z*). The inter-column contacts are S8··H14#*c*, 2.88 Å, and S3··H23#*d*, 2.94 Å, (#*c*: –1/2 + *x*, 1 – *y*, 1/2 + *z*; #*d*: *x*, 1 + *y*, *z*) (Figure 5).

Figure 2. ORTEP diagrams of two independent molecules of **3b** drawn at the 40% probability level and showing (a) the atomic numbering scheme and (b) different angles about the S··S vectors in the dithiopyridine and dithiin rings. H atoms have been omitted for clarity. #*a*: 1 – *x*, –1 – *y*, 1 – *z*.

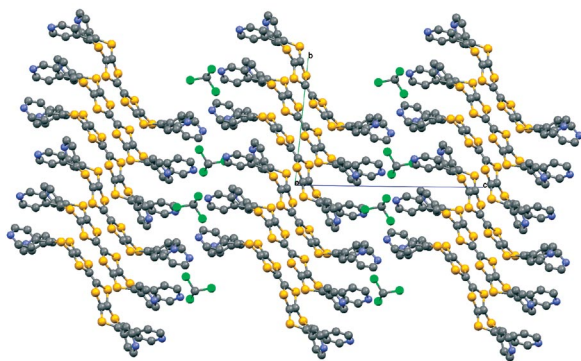


Figure 3. Packing of compound **3b**·0.66 CHCl<sub>3</sub>.

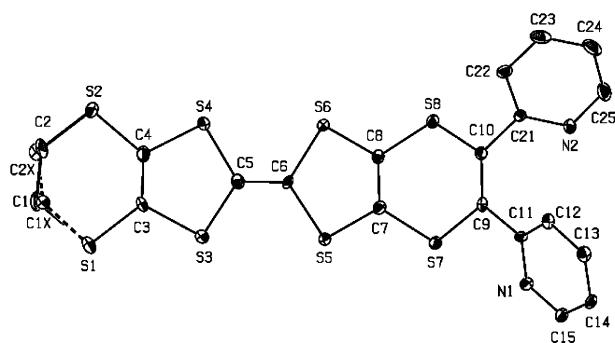


Figure 4. ORTEP diagram of compound **4a** drawn at the 40% probability level and showing the atomic numbering scheme. H atoms have been omitted for clarity.

The gold dithiolenic complex **7** crystallises in the triclinic system, space group  $P\bar{1}$ . An ORTEP plot of the anionic moiety of compound **7** with the atomic numbering scheme is shown in Figure 6. The asymmetric unit comprises two independent half anions,  $[\text{Au}(4\text{-dpdt})_2]^-$ , (each metal is located at an inversion centre), one cation,  $[\text{nBu}_4\text{N}]^+$ , and two solvent molecules (water and dichloromethane) located at general positions. The complex adopts almost perfect square-planar coordination geometry. The central cores of the anions, constituted by the metal atom and the four sulfur atoms, are essentially planar (rms deviation of fitted atoms is 0.003 Å). Im-

portant bond lengths within the  $\text{AuS}_2\text{C}_2$  metallocycle are collected in Table 1. To the best of our knowledge, this is the first example of a gold bidithiolenic complex with an unsaturated dithiolenic ring. The average Au–S bond lengths are in good agreement with values found for other Au monoanionic dithiolate complexes.<sup>[9]</sup> Within experimental uncertainty the bond lengths of the dithiolenic ring are essentially the same as in the corresponding TTF and the precursor thiones. The pyridine rings present rotations of 70.4° (N1A–N2A) and 77.5° (N1–N2) to each other. The pyridine rings and the adjacent S–C=C–S plane make angles of 28.3° (N1), 53.4° (N2), 55° (N1A) and 25.2° (N2A). The molecules flex about the S···S vector in the dithiolenic ring with an angle of 128° and 131°, a distortion that is very similar to those in **3b**. The supramolecular packing consists of parallel, mixed chains of anions alternating with cations, with the solvent molecules between the mixed chains (Figure 7). The more relevant short contacts are the short intermolecular contacts involving the C13···H25#*a*, 2.873 Å, and N2···H12#*a*, 2.688 Å, of the pyridine rings (#*a*: 1 – *x*, 1 – *y*, –*z*).

As a  $d^7$  system in a square-planar coordination, compound **6** is expected to be a paramagnetic  $S = 1/2$  system while **7**, as a  $d^8$ , is expected to be diamagnetic.<sup>[10]</sup> In fact the powder EPR spectrum of **6** shows a rhombic signal with  $g_1 = 1.999$ ,  $g_2 = 2.048$  and  $g_3 = 2.100$ , typical of monoanionic nickel bidithiolenic complexes.<sup>[11]</sup>

The redox behaviour of the new electron donors **3a**, **3b**, **4a**, **4b** and also of the dithiolenic complexes **6** and **7** were studied by cyclic voltammetry (CV) in dichloromethane. The redox potentials obtained from CV data are collected in Tables 2 and 3. For comparison, the oxidation potentials of the unsubstituted donors BEDT-TTF and BVDT-TTF are also included in Table 2. Cyclic voltammetry of the donor **3b** shows a pair of quasi-reversible redox waves centred at 0.81 V, similar to the parent unsubstituted BVDT-TTF that shows a similar process at 0.79 V. All the other donors show two pairs of reversible single-electron redox waves typical of the TTF system. These values are higher when compared with those of the related BEDT-TTF donor. The first oxidation potentials are similar to that of BVDT-TTF apart from donor **4a**, which is ca. 0.1 V lower.

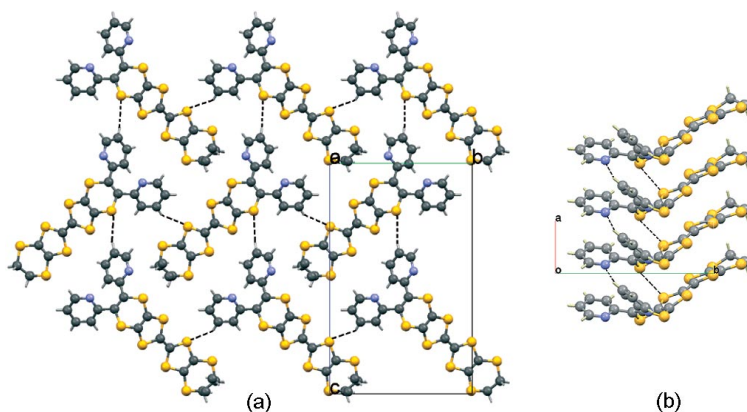


Figure 5. Crystal packing arrangement of **4a**: (a) viewed along the *a* axis, (b) one column of donors viewed along the *c* axis.

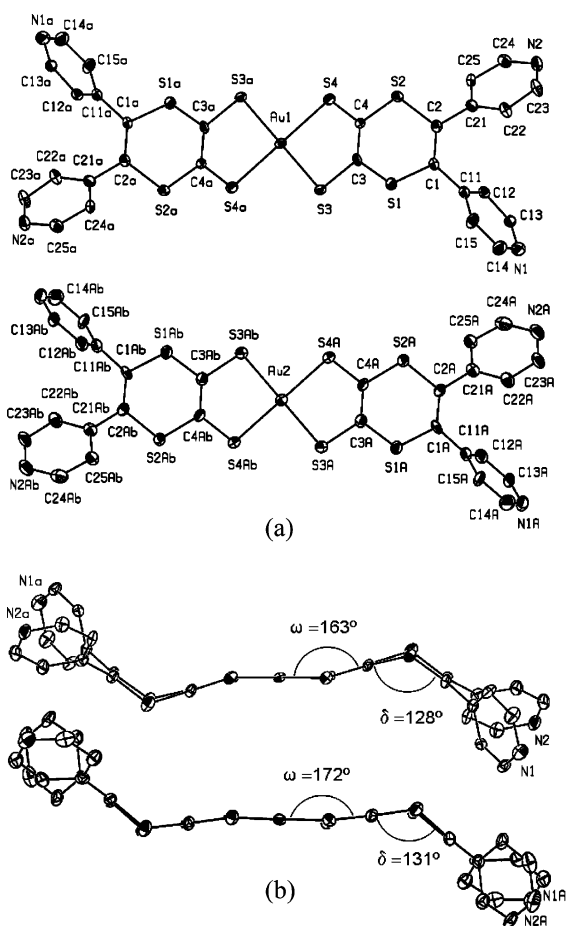


Figure 6. ORTEP plot of the monoanions  $[\text{Au}(4\text{-dpddt})_2]^-$  in  $7 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  in perpendicular (a) and parallel (b) views to the molecular plane, drawn at the 40% probability level and showing the atomic numbering scheme. H atoms have been omitted for clarity.  $a\# = -x, 1 - y, 1 - z$ ;  $b\# = 1 - x, -y, 1 - z$ .

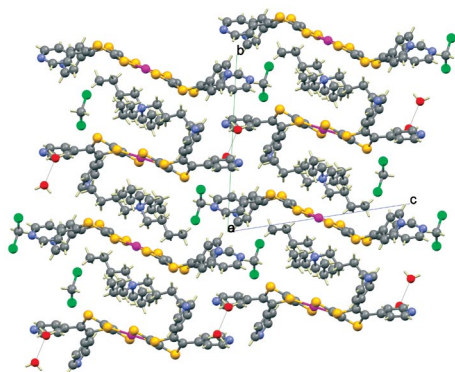


Figure 7. Two adjacent mixed chains of anions alternating with cations in compound  $7 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ , showing intermolecular short contacts involving the pyridine rings.

The CV of  $(n\text{Bu}_4\text{N})[\text{Ni}(4\text{-dpddt})_2]$  (**6**) in dichloromethane exhibits two redox processes at  $-0.31$  V and  $0.37$  V vs.  $\text{Ag}/\text{AgCl}$  and a multi-electron irreversible oxidation peak at a higher potential ( $1.2$  V). The process at  $-0.31$  V is reversible and it is ascribed to the couple  $[\text{Ni}(4\text{-dpddt})_2]^-/[\text{Ni}(4\text{-dpddt})_2]$ , in agreement with what has been observed in similar com-

Table 2. Oxidation potentials of compounds **3a**, **3b**, **4a** and **4b** measured by cyclic voltammetry.<sup>[a]</sup>

Compound	$E_{1/2}^1$ [V]	$E_{1/2}^2$ [V]
<b>3a</b>	0.77	1.12
<b>3b</b>	0.81	
<b>4a</b>	0.69	1.08
<b>4b</b>	0.75	1.07
BEDT-TTF <sup>[13]</sup>	0.49	0.89
BVDT-TTF <sup>[14]</sup>	0.79	

[a] Experimental conditions:  $\text{CH}_2\text{Cl}_2$  solutions at room temperature containing  $0.1$  M  $n\text{Bu}_4\text{NPF}_6$ , with  $\text{Ag}/\text{AgCl}$  as the reference electrode, Pt wire as a counter electrode and Pt as the working electrode; scan rate is  $100$   $\text{mV s}^{-1}$ .

Table 3. Oxi-reduction potentials  $E_{1/2}$  [V] of **6** and **7**.<sup>[a]</sup>

Compound	$E_{1/2}[\text{M}^{\text{II}}\text{L}_2]^{2-}/[\text{M}^{\text{III}}\text{L}_2]^-$	$E_{1/2}[\text{M}^{\text{III}}\text{L}_2]^-/[\text{M}^{\text{IV}}\text{L}_2]^0$
<b>6</b>	$-1.1$ <sup>[b]</sup>	$-0.31/-0.30$ <sup>[b]</sup>
<b>7</b>	$-0.93$	$0.74$
$[\text{Au}(\text{ddd})_2]$ <sup>[9b]</sup>	$-1.32$ <sup>[c]</sup>	$0.41$ <sup>[c]</sup>
$[\text{Ni}(\text{dphdt})_2]$ <sup>[15]</sup>	$-1.05$	$-0.25$
$[\text{Ni}(\text{phdt})_2]$ <sup>[15]</sup>	$-1.05$	$-0.26$
$[\text{Ni}(\text{ddd})_2]$ <sup>[15]</sup>	$-1.07$	$-0.29$

[a] Experimental conditions:  $\text{CH}_2\text{Cl}_2$  solutions at room temperature containing  $0.1$  M  $n\text{Bu}_4\text{NPF}_6$ , with  $\text{Ag}/\text{AgCl}$  as the reference electrode, Pt wire as a counter electrode and Pt as the working electrode; scan rate is  $100$   $\text{mV s}^{-1}$ . [b] Glassy carbon as the working electrode. [c]  $0.2$  M  $n\text{Bu}_4\text{NPF}_6$ , scan rate  $0.2$   $\text{V s}^{-1}$  and SCE reference electrode.

plexes. The other process at  $E_{1/2} = 0.37$  V is not fully reversible and is possibly associated with a protonated pyridine species. The irreversible oxidation peak at a higher potential can be assigned to the formation of a cationic complex as observed in the redox behaviour of  $\text{Ni}(\text{ddd})_2$  complexes.<sup>[12]</sup> Using platinum as a working electrode no visible redox process for the couple  $[\text{Ni}(4\text{-dpddt})_2]^{2-}/[\text{Ni}(4\text{-dpddt})_2]^-$  was observed, but experiments with a glassy carbon electrode revealed this process to be centred at  $-1.1$  V.

The CV of  $(n\text{Bu}_4\text{N})[\text{Au}(4\text{-dpddt})_2]$  (**7**) exhibits two quasi-reversible redox processes, at  $-0.93$  and  $0.74$  V and the CV of compound **6**, a multi-electron irreversible oxidation peak at a higher potential ( $1.1$  V) that can also be ascribed to the formation of a cationic complex. The quasi-reversible redox process with  $E_{1/2} = -0.93$  V is ascribed to the couple  $[\text{Au}(4\text{-dpddt})_2]^{2-}/[\text{Au}(4\text{-dpddt})_2]^-$  and the redox process observed at  $0.74$  V is ascribed to the couple  $[\text{Au}(4\text{-dpddt})_2]/[\text{Au}(4\text{-dpddt})_2]$ . These potentials are somewhat different from those previously found in the unsubstituted and saturated analogue  $[\text{Au}(\text{ddd})_2]$ .<sup>[9b]</sup> This difference can only partially be ascribed to different experimental conditions and may reflect the influence of the fully unsaturated dithiin ring. The moderately positive potentials associated with the couples  $[\text{Au}(4\text{-dpddt})_2]/[\text{Au}(4\text{-dpddt})_2]$  indicate that the neutral complex may be stable. But so far this complex could not be obtained either by electrocrystallisation or chemical oxidation of the monoanionic complex. These values are comparable to those observed in similar bidithiolenes also listed in Table 3 where the oxidation potentials of the complexes  $(n\text{Bu}_4\text{N})_2[\text{Ni}(\text{ddd})_2]$ ,  $(n\text{Bu}_4\text{N})_2[\text{Ni}(\text{dphdt})_2]$  and  $(n\text{Bu}_4\text{N})_2[\text{Ni}(\text{phdt})_2]$  are included. From this comparison it can be con-

cluded that no significant change in the oxidation potentials occurs with the introduction of either the phenyl or pyridine rings in the dithiolenene complex.

Preliminary electrocrystallisation studies are being made on the di- and tetra(pyridyl) donors. Electrocrystallisation of donor **4a** with perrhenate in dichloromethane gave a 1:2 salt, which could be characterised by X-ray crystallography (see Figures 8 and 9). This showed that the organosulfur system is in the +1 oxidation state and that one pyridine ring is protonated so that overall the donor is present as a dication. The protonation of one pyridine ring is supported by the wider endocyclic bond angle at N [122.8(6)°] compared to the unprotonated pyridine ring [117.0(6)°].<sup>[16]</sup> There is a hydrogen bond between the N–H of the pyridinium cation and one of the perrhenate anions [(N)–H...O: 1.85 Å; H...O–Re: 133.1°; N–H...O: 153.4°] and the O–Re bond involved in this hydrogen bond is longer [1.743(5) Å] than the other Re–O bonds in the anion [1.711(6)–1.716(6) Å]. [The bond lengths in the second perrhenate anion lie in the range: 1.710(7)–1.733(7) Å.] On oxidation the C–S bonds in the TTF core are shortened in comparison to the neutral donor, while the C=C bonds are lengthened. The empirical calculation of the charge on the TTF unit based on bond length data corresponds to a charge of +1 on the donor.<sup>[17]</sup> The two (TTF)C–S bonds in the dihydrodithiin ring are shortened, but there is no significant change for any of the other C–S bonds in the substituted dithiin ring, where there is a flexing of 122° about the S...S vector. The pyridine rings lie at 47.6° to each other and at 45–46° to the adjacent S=C=S sector of the dithiin ring. The crystal is triclinic in space group  $P\bar{1}$  with one dichloromethane molecule per unit cell located near to a centre of symmetry. The donor cations pack face to face in pairs and

lie with their main molecular axes roughly in the *c* direction with spaces between donor pairs filled by two symmetry related perrhenate anions and a dichloromethane molecule (Figure 8). The closest S...S contacts within the pair of donors are 3.398 and 3.412 Å. The hydrogen bonded perrhenates lie in a plane perpendicular to *c* surrounded on either side by protonated and unprotonated pyridine rings.

## Conclusions

The reactions of two dipyriddylenes with 1,3-dithiole-2,4,5-trithione have led to thiones that can be converted into organosulfur donors and corresponding gold and nickel bidithiolenene complexes, which bear two or four pyridyl groups. The dithiin rings in these are flexed about their S...S vectors, and the pyridyl groups are rotated relative to these rings, but this does not prevent them from forming stacks in the solid state. These new molecules are promising building blocks for preparing multifunctional materials in which conductivity and magnetism can be combined by the coordination of magnetic metal ions to the external N atoms, especially those in the 4-pyridyl systems.

The pyridyl substitution does not significantly change the redox potentials of these donors and the corresponding bidithiolenene transition metal complexes. The ability of these molecules to prepare new charge-transfer salts with interesting properties is demonstrated by a dicationic salt of a di(2-pyridyl)vinylenedithiotetrathiafulvalene donor with perrhenate obtained by electrocrystallisation in which the donor is both protonated and oxidized. Therefore protonation of the pyridine rings offers another strategy for the construction of supramolecular systems from these donors and dithiolenes. Further work is in progress involving the oxidation of these donors to produce conducting systems.

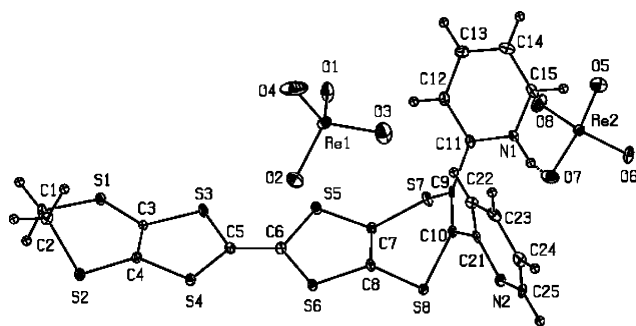


Figure 8. Molecular structure of protonated donor cation **4a** hydrogen bonded to a perrhenate ion in  $[4a\cdot H](ReO_4)_2\cdot 0.5CH_2Cl_2$ .

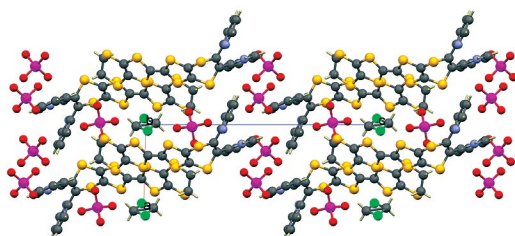


Figure 9. Crystal packing arrangement of  $[4a\cdot H](ReO_4)_2\cdot 0.5CH_2Cl_2$ , viewed along the *b* plane.

## Experimental Section

**General Remarks:** All manipulations were carried out under anaerobic conditions unless stated otherwise. All solvents were purified according to standard literature procedures.<sup>[18]</sup> Oligo(1,3-dithiole-2,4,5-trithione),<sup>[6]</sup> 4,5-bis(alkylthio)-1,3-dithiole-2-thione (**5**),<sup>[6]</sup> 2,2'-dipyriddylenes and 4,4'-dipyriddylenes were prepared by literature methods.<sup>[7]</sup> Other chemicals were commercially obtained and used without further purification. Column chromatography was carried out using silica gel (0.063 ± 0.2 mm). IR spectra were obtained with a Shimadzu FTIR-8400S or a Perkin–Elmer Spectrum 100 FT-IR spectrometer using attenuated total reflection. Elemental analyses of the compounds isolated in these studies were performed at ITN analytical services using an EA 110 CE Instruments automatic analyzer, or at London Metropolitan University by Mr S. Boyer. Melting points were performed with a Stuart Scientific SMP2 and Gallenkamp melting point apparatus. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker Aspect 3000 (300 MHz for <sup>1</sup>H) or a JEOL Eclipse (400 MHz for <sup>1</sup>H) with CDCl<sub>3</sub> as the solvent and using TMS as the internal reference. Cyclic voltammetry data were obtained using a BAS C3 cell stand at room temperature in CH<sub>2</sub>Cl<sub>2</sub> that contained *n*Bu<sub>4</sub>NPF<sub>6</sub> (10<sup>-1</sup> M) as the supporting electrolyte, with a scan rate of 100 mV s<sup>-1</sup>, platinum wire working and counter electrodes and Ag/AgCl as the reference electrode. EPR spectra were obtained at

room temperature on powder samples using a conventional X-band spectrometer (Bruker ESP 300 E) equipped with a microwave bridge ER041XK, a rectangular cavity operating in the T102 mode and a field controller ER 032M system. The modulation amplitude was kept well below the line width and the microwave power well below saturation.

**5,6-Di(pyrid-2-yl)[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-thione (1a):** A solution of 2,2'-dipyridylacetylene (0.22 g, 1.20 mmol) in toluene (40 mL) and solid 1,3-dithiole-2,4,5-trithione (0.48 g, 2.40 mmol) were stirred at reflux under a nitrogen atmosphere for 15 h. The mixture was cooled to room temperature, filtered, the solid washed with chloroform (ca. 50 mL) and the filtrate evaporated. The crude product was first purified by chromatography over silica, eluting with ethyl acetate to afford an orange band, which was collected and evaporated to yield a brown solid. This was further purified by chromatography over silica, eluting with a mixture of cyclohexane/ethyl acetate (2:1) to afford **1a** (0.36 g, 80%) as a brown solid. Crystals suitable for X-ray crystallography were grown from ethyl acetate; m.p. 207–208 °C.  $C_{15}H_8N_2S_5$  (376.5): calcd. C 47.9, H 2.1, N 7.4; found C 47.9, H 2.1, N 7.4.  $^1H$  NMR (400 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 8.6 [ddd,  $J_{H,H}$  = 4.9, 1.8, 0.9 Hz, 2 H, 6'-H], 7.5 (dt,  $J_{H,H}$  = 7.7, 1.8 Hz, 2 H, 4'-H), 7.2 (ddd,  $J_{H,H}$  = 7.6, 4.8, 1.0 Hz, 2 H, 5'-H), 6.9 (td,  $J_{H,H}$  = 7.9, 1.0 Hz, 2 H, 3'-H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 213.9 (2-C), 154.2 (2'-C), 150.0 (6'-C), 136.9 (5-C, 6-C), 136.3 (4'-C), 130.1 (3a-C, 7a-C), 124.7 (3'-C), 123.4 (5'-C) ppm. HRMS (EI): found 375.9291 [ $M$ ] $^+$ ;  $C_{15}H_8N_2S_5$  requires 375.9285. IR (ATR):  $\tilde{\nu}$  = 1578, 1563, 1455, 1428, 1063 (C=S), 992, 760, 740, 622, 505  $cm^{-1}$ .

**5,6-Di(pyrid-4-yl)[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-thione (1b):** A mixture of 4,4'-dipyridylacetylene (3.44 g, 19 mmol) and 1,3-dithiole-2,4,5-trithione (4.0 g, 20 mmol) in toluene (50 mL) were heated at reflux overnight under  $N_2$ . The mixture was cooled to room temperature and the brown precipitate filtered and washed with toluene. The filtrate was evaporated and purified by chromatography (silica gel, ethyl acetate/methanol, 1:1) to obtain the desired product (6.00 g, 83%) as a brown solid. Crystals suitable for X-ray crystallography were obtained from hot toluene; m.p. 177 °C.  $C_{15}H_8N_2S_5$  (376.5): calcd. C 47.9, H 2.1, N 7.4; found C 47.9, H 2.1, N 7.5.  $^1H$  NMR (400 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 8.5 (dd,  $J_{H,H}$  = 4.5, 1.6 Hz, 4 H, 2'-H, 6'-H), 6.9 (dd,  $J_{H,H}$  = 4.5, 1.6 Hz, 4 H, 3'-H, 5'-H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 204.0 (2-C), 150.4 (2'-C, 6'-C), 143.4 (4'-C), 135.3 (5-C, 6-C), 129.3 (3a-C, 7a-C), 123.5 (3'-C, 5'-C) ppm. HRMS (ES $^+$ ): found 376.9365 [ $M$  + H] $^+$ ;  $C_{15}H_8N_2S_5$  + H requires 376.9364. IR (ATR):  $\tilde{\nu}$  = 1579, 1543, 1403, 1071 (C=S), 1041, 1017, 847, 823, 768, 627, 602, 538, 510, 461  $cm^{-1}$ .

**5,6-Di(pyrid-2-yl)[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one (2a):** Mercuric acetate (0.105 g, 0.33 mmol) was added to a stirred solution of thione **1a** (0.083 g, 0.22 mmol) in dry chloroform (20 mL) under a nitrogen atmosphere. The suspension was stirred at room temperature for 35 min, filtered, the solid washed with dry chloroform (30 mL) and the combined filtrate washed with saturated sodium hydrogen carbonate solution (10 mL). The organic phase was dried with sodium sulfate before evaporating to give **2a** (0.055 g, 70%) as an orange gum.  $^1H$  NMR (400 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 8.6 (ddd,  $J_{H,H}$  = 4.8, 1.8, 1.0 Hz, 2 H, 6'-H), 7.5 (dt,  $J_{H,H}$  = 1.8, 7.6 Hz, 2 H, 4'-H), 7.2 (ddd,  $J_{H,H}$  = 7.6, 4.8, 1.0 Hz, 2 H, 5'-H), 6.9 (d,  $J_{H,H}$  = 7.7 Hz, 2 H, 3'-H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 192.2 (2-C), 154.4 (2'-C), 150.0 (6'-C), 136.7 (5-C, 6-C), 136.3 (4'-C), 124.7 (3'-C), 123.3 (5'-C), 120.4 (3a-C, 7a-C) ppm. HRMS (EI): found 359.9513 [ $M$ ] $^+$ ;  $C_{15}H_8N_2OS_4$  requires 359.9514. IR (ATR):  $\tilde{\nu}$  = 1668 (C=O), 1579, 1564, 1456, 1429, 993, 792, 760, 740, 622, 454  $cm^{-1}$ .

**5,6-Di(pyrid-4-yl)[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one (2b):** Mercuric acetate (0.50 g, 1.57 mmol) was added to a stirred solution of thione

**1b** (0.50 g, 1.43 mmol) in chloroform (20 mL). The mixture was stirred at room temperature for 1 h, filtered through celite and washed with  $CHCl_3$  (10 mL). The chloroform solution was washed with  $H_2O$  (20 mL), aq.  $Na_2CO_3$  (20 mL) and again with  $H_2O$  (20 mL), then dried with  $MgSO_4$ . The solvent was evaporated and column chromatography (silica gel, ethyl acetate/methanol, 9:1) was used to obtain the desired product as a white solid (0.28 g, 57%); m.p. 174–175 °C. Sometimes a yellow-brown oil is obtained.  $C_{15}H_8N_2OS_4$  (360.5): calcd. C 50.0, H 2.2, N 7.8; found C 50.1; H 2.3, N 7.8.  $^1H$  NMR (400 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 8.5 (m, 4 H, 2'-, 6'-H), 6.9 (m, 4 H, 3'-H, 5'-H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 190.8 (2-C), 150.3 (2'-C, 6'-C), 144.1 (4'-C), 135.2 (5-C, 6-C), 124.0 (3'-C, 5'-C), 120.3 (3a-C, 7a-C) ppm.  $m/z$  (ES $^+$ ): found 360.9594 [ $M$  + H] $^+$ ;  $C_{15}H_8N_2OS_4$  + H requires 360.9592; IR (ATR):  $\tilde{\nu}$  = 1674 (C=O), 1584, 1544, 1404, 1062, 990, 910, 843, 822, 786, 748, 627, 602, 538, 508  $cm^{-1}$ .

**Bis[di(2'-pyridyl)vinylenedithio]tetrathiafulvalene (3a):** The oxo compound **2a** (0.04 g, 0.11 mmol) was heated in freshly distilled triethyl phosphite (3 mL) to 100 °C under a nitrogen atmosphere for 2 h and 40 min. The reaction was cooled to room temperature overnight, filtered and the solid washed with diethyl ether (ca. 200 mL) to afford donor **3a** (0.037 g, 97%) as an orange solid; m.p. 213 °C.  $C_{30}H_{16}N_4S_8$  (688.9): calcd. C 52.3, H 2.3, N 8.1; found C 52.2, H 2.3, N 8.1.  $^1H$  NMR (400 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 8.6 (ddd,  $J_{H,H}$  = 4.9, 1.8, 1.0 Hz, 4 H, 6'-H), 7.4 (dt,  $J_{H,H}$  = 1.8, 7.6 Hz, 4 H, 4'-H), 7.2 (ddd,  $J_{H,H}$  = 7.6, 4.9, 1.0 Hz, 4 H, 5'-H), 6.9 (d,  $J_{H,H}$  = 7.8 Hz, 4 H, 3'-H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 154.7 (2'-C), 149.8 (6'-C), 137.4 [sp $^2$ C-(pyridyl)], 136.2 (4'-C), 124.6 (3'-C), 123.1 (5'-C), 122.2 (sp $^2$ -C), 118.8 (sp $^2$ -C) ppm. HRMS (ES $^+$ ): found 688.9215 [ $M$  + H] $^+$ ;  $C_{30}H_{16}N_4S_8$  + H requires 688.9213. IR (ATR):  $\tilde{\nu}$  = 1581, 1556, 1460, 1422, 1090, 1044, 994, 919, 782, 759, 742, 661, 618  $cm^{-1}$ .

**Bis[di(4'-pyridyl)vinylenedithio]tetrathiafulvalene (3b):** Oxo compound **2b** (0.30 g, 0.83 mmol) was heated in triethyl phosphite (5 mL) under nitrogen to 110 °C. An orange precipitate was observed after approximately 1 h, and the reaction was maintained at this temperature for a further 5 h. The reaction was cooled to room temperature and filtered. The solid was washed with diethyl ether (ca. 100 mL). Drying in vacuo at room temperature overnight afforded **3b** (0.27 g, 93%) as an orange solid, X-ray quality crystals were obtained from the slow diffusion of hexane to a chloroform solution; m.p. 232–233 °C.  $C_{30}H_{16}N_4S_8$  (688.9): calcd. C 52.3, H 2.3, N 8.1; found C 52.5, H 2.2, N 8.1.  $^1H$  NMR (400 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 8.5 (dd,  $J_{H,H}$  = 6.1, 1.6 Hz, 8 H, 2'-H, 6'-H), 7.0 (dd,  $J_{H,H}$  = 6.1, 1.6 Hz, 8 H, 3'-H, 5'-H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 150.3 (2'-C, 6'-C), 143.7 (4'-C), 135.8 [sp $^2$ C-(pyridyl)], 123.5 (3'-C, 5'-C), 122.6 (sp $^2$ -C), 119.1 (sp $^2$ -C) ppm. HRMS (EI): found 687.9133 [ $M$ ] $^+$ ;  $C_{30}H_{16}N_4S_8$  requires 687.9135. IR (ATR):  $\tilde{\nu}$  = 1583, 1544, 1403, 1216, 989, 917, 839, 822, 791, 763, 739, 627, 601, 537, 510  $cm^{-1}$ .

**[Di(2'-pyridyl)vinylenedithio](ethylenedithio)tetrathiafulvalene (4a):** A mixture of the oxo compound **2a** (0.40 g, 1.11 mmol) and thione **5** (1.00 g, 4.44 mmol) were stirred together in freshly distilled triethyl phosphite (15 mL) at 110 °C under a nitrogen atmosphere. After 6 h the reaction was cooled to room temperature, filtered and washed with diethyl ether (ca. 250 mL). The crude solid was purified by chromatography over silica eluting with chloroform/tetrahydrofuran (9:1) to afford **4a** (0.32 g, 54%) as a bright orange solid; m.p. 208 °C.  $C_{20}H_{12}N_2S_8$  (536.8): calcd. C 44.8, H 2.2, N 5.2; found C 44.8, H 2.2, N 5.2.  $^1H$  NMR (400 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 8.6 (ddd,  $J_{H,H}$  = 4.9, 1.8, 0.9 Hz, 2 H, 6'-H), 7.4 (dt,  $J_{H,H}$  = 1.8, 7.7 Hz, 2 H, 4'-H), 7.1 (ddd,  $J_{H,H}$  = 7.6, 4.9, 1.0 Hz, 2 H, 5'-H), 6.90 (td,  $J_{H,H}$  = 7.8, 1.0 Hz, 2 H, 3'-H), 3.3 (s, 4 H,  $CH_2$ ) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 154.6 (2'-C), 149.8 (6'-C), 137.4 (sp $^2$ C-pyridyl),

136.1 (4'-C), 124.6 (3'-C), 123.1 (5'-C), 122.1 (sp<sup>2</sup>-C), 116.2 (sp<sup>2</sup>-C), 114.2 (sp<sup>2</sup>-C), 113.7 (sp<sup>2</sup>-C), 30.1 (CH<sub>2</sub>) ppm. HRMS (EI): found 535.8763 [M]<sup>+</sup>; C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>S<sub>8</sub> requires 535.8761. IR (ATR):  $\tilde{\nu}$  = 1581, 1552, 1458, 1422, 995, 919, 769, 757, 741, 617, 484 cm<sup>-1</sup>.

**[Di(4'-pyridyl)vinylenedithio](ethylenedithio)tetrathiafulvalene (4b):** Oxo compound **2b** (0.10 g, 0.27 mmol) and thione **5** (0.30 g, 1.4 mmol) were dissolved in triethyl phosphite (10 mL) under nitrogen and heated to 110 °C for 12 h. Distillation in vacuo of the triethyl phosphite afforded the crude material, which was purified by chromatography over silica eluting with tetrahydrofuran/methanol

(5:2) to give **4b** (0.070 g, 48%) as a yellow-brown solid; m.p. 209 °C (dec.). C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>S<sub>8</sub> (536.8): C 44.7, H 2.2, N 5.2; found C 44.6, H 2.3, N 5.2. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 8.6 (d, *J*<sub>H,H</sub> = 4.4, 1.7 Hz, 4 H, 2'-H, 6'-H), 7.3 (d, *J*<sub>H,H</sub> = 4.4, 1.7 Hz, 4 H, 3'-H, 5'-H), 3.5 (s, 4 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (100 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 150.1 (2'-C, 6'-C), 143.1 (4'-C), 135.2 (sp<sup>2</sup>C-pyridyl), 123.5 (3'-C, 5'-C), 113.0 (sp<sup>2</sup>-C), 109.8 (sp<sup>2</sup>-C), 29.5 (CH<sub>2</sub>) ppm. HRMS (CI): found 536.8838 [M + H]<sup>+</sup>; C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>S<sub>8</sub> + H requires 536.8839. IR (ATR):  $\tilde{\nu}$  = 3623, 2956, 1598, 1585, 1543, 1433, 1401, 1232, 1216, 1155, 910, 866, 849, 825, 793, 769, 751, 628, 603, 540, 526, 470 cm<sup>-1</sup>.

Table 4. X-ray crystallographic data for compounds **1a**, **1b**, **3b**·0.66CHCl<sub>3</sub>, **4a**, **[4a-H](ReO<sub>4</sub>)<sub>2</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub>** and **7·CH<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O**.

Compound	<b>1a</b>	<b>1b</b>	<b>3b</b> ·0.66CHCl <sub>3</sub>
Empirical formula	C <sub>15</sub> H <sub>8</sub> N <sub>2</sub> S <sub>5</sub>	C <sub>15</sub> H <sub>8</sub> N <sub>2</sub> S <sub>5</sub>	C <sub>92</sub> H <sub>50</sub> Cl <sub>6</sub> N <sub>12</sub> S <sub>24</sub>
<i>M<sub>r</sub></i> [g mol <sup>-1</sup> ]	376.53	376.53	2305.58
<i>T</i> [K]	150(2)	150(2)	150(2)
Crystal system	monoclinic	orthorhombic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>Pbca</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	9.8246(19)	8.6146(9)	9.9124(3)
<i>b</i> [Å]	16.627(4)	10.9471(10)	12.5687(3)
<i>c</i> [Å]	10.639(2)	33.439(3)	19.2826(5)
$\alpha$ [°]	90	90	84.675(2)
$\beta$ [°]	114.832(4)	90	79.4890(10)
$\gamma$ [°]	90	90	86.139(2)
<i>V</i> [Å <sup>3</sup> ]	1577.2(6)	3153.4(5)	2348.72(11)
<i>Z</i>	4	8	1
<i>D</i> <sub>calcd.</sub> [Mg m <sup>-3</sup> ]	1.586	1.586	1.630
$\mu$ [mm <sup>-1</sup> ]	0.730	0.730	0.773
<i>F</i> (000)	768	1536	1172
Crystal size [mm]	0.42 × 0.18 × 0.10	0.22 × 0.06 × 0.02	0.30 × 0.20 × 0.09
$\theta$ range [°]	2.45 to 25.69	3.25 to 25.03	2.59 to 25.03
Index range ( <i>h,k,l</i> )	-11/11, -19/20, -12/12	-10/10, -13/13, -39/39	-11/11, -14/12, -22/22
Reflections collected/unique	8545/2985 [ <i>R</i> (int) = 0.0364]	24193/2762 [ <i>R</i> (int) = 0.1393]	21423/8123 [ <i>R</i> (int) = 0.0395]
<i>T</i> <sub>max</sub> , <i>T</i> <sub>min</sub>	0.93 and 0.75	0.99 and 0.86	0.93 and 0.82
Data/restr./param.	2985/0/199	2762/0/199	8123/0/604
G.O.F. on <i>F</i> <sup>2</sup>	1.020	0.987	0.989
<i>R</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0315, <i>wR</i> <sub>2</sub> = 0.0743	<i>R</i> <sub>1</sub> = 0.0469, <i>wR</i> <sub>2</sub> = 0.0968	<i>R</i> <sub>1</sub> = 0.0360, <i>wR</i> <sub>2</sub> = 0.0739
$\Delta\rho_{\max/\min}$ [e Å <sup>-3</sup> ]	0.345/-0.236	0.401/0.404	0.421/-0.356
Compound	<b>4a</b>	<b>[4a-H](ReO<sub>4</sub>)<sub>2</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub></b>	<b>7·CH<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O</b>
Empirical formula	C <sub>20</sub> H <sub>12</sub> N <sub>2</sub> S <sub>8</sub>	C <sub>20.50</sub> H <sub>14</sub> ClN <sub>2</sub> O <sub>8</sub> Re <sub>2</sub> S <sub>8</sub>	C <sub>45</sub> H <sub>56</sub> AuCl <sub>2</sub> N <sub>5</sub> OS <sub>8</sub>
<i>M<sub>r</sub></i> [g mol <sup>-1</sup> ]	536.80	1080.67	1207.29
<i>T</i> [K]	120(2)	120(2)	150(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	<i>Pn</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	4.1894(2)	7.7886(2)	9.7393(3)
<i>b</i> [Å]	12.7225(5)	9.2525(2)	16.3331(4)
<i>c</i> [Å]	20.5532(8)	21.0117(5)	17.1428(5)
$\alpha$ [°]	90	94.7170(10)	76.7970(10)
$\beta$ [°]	92.917(2)	90.5190(10)	78.733(2)
$\gamma$ [°]	90	103.2370(10)	81.209(2)
<i>V</i> [Å <sup>3</sup> ]	1094.06(8)	1468.36(6)	2586.93(13)
<i>Z</i>	2	2	2
<i>D</i> <sub>calcd.</sub> [Mg m <sup>-3</sup> ]	1.629	2.444	1.550
$\mu$ [mm <sup>-1</sup> ]	0.829	8.946	3.309
<i>F</i> (000)	548	1020	1220
Crystal size [mm]	0.31 × 0.09 × 0.01	0.16 × 0.07 × 0.02	0.40 × 0.18 × 0.06
$\theta$ range [°]	3.20 to 27.51	2.92 to 27.55	2.55 to 25.68
Index range ( <i>h,k,l</i> )	-5/5, -16/16, -26/26	-10/10, -12/10, -27/27	-11/11, -19/19, -20/20
Reflections collected/unique	10725/4553 [ <i>R</i> (int) = 0.0534]	21251/6699 [ <i>R</i> (int) = 0.0321]	15090/8498 [ <i>R</i> (int) = 0.0417]
<i>T</i> <sub>max</sub> , <i>T</i> <sub>min</sub>	0.99 and 0.78	0.99 and 0.71	0.83 and 0.35
Data/restr./param.	4553/0/271	6699/3/374	8498/6/566
G.O.F. on <i>F</i> <sup>2</sup>	1.097	1.032	1.071
<i>R</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0554, <i>wR</i> <sub>2</sub> = 0.107	<i>R</i> <sub>1</sub> = 0.0424, <i>wR</i> <sub>2</sub> = 0.918	<i>R</i> <sub>1</sub> = 0.0608, <i>wR</i> <sub>2</sub> = 0.1669
$\Delta\rho_{\max/\min}$ [e Å <sup>-3</sup> ]	0.712/-0.708	12.0/-3.59	3.561/-2.373



**Tetrabutylammonium salt of Bis[5,6-di(pyridin-4-yl)-1,4-dithiin-2,3-dithiolate]nickel(III),  $n\text{Bu}_4\text{N}[\text{Ni}(\text{4-pdddt})_2]$  (6):** The thione **1b** (0.1 g, 0.265 mmol) was added to a solution of sodium methoxide (0.012 g; 0.531 mmol) in methanol (5 mL). After stirring for 45 min  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.032 g, 0.133 mmol) was added. The solution was stirred for 1 h and then filtered into a solution of  $n\text{Bu}_4\text{NBr}$  (0.086 g, 0.265 mmol) in methanol (3 mL). No precipitate formation was observed. The reaction vial was opened to the air, a few  $\text{H}_2\text{O}$  drops were slowly added until incipient precipitation started and the mixture was left overnight at 4 °C. The precipitate that formed was separated from the mixture by centrifugation, washed with water, dried under vacuum ( $\text{P}_2\text{O}_5$ ) at 80 °C (dec.) and recrystallised from dichloromethane/hexane to be recovered as a microcrystalline precipitate (0.050 g, 39%); m.p. 168–170 °C.  $\text{C}_{44}\text{H}_{52}\text{NiN}_5\text{S}_8$  (966.1): C 54.7, H 5.4, N 7.2, S 26.5; found C 54.1, H 4.2, N 6.8, S 26.0.

**Tetrabutylammonium Salt of Bis[5,6-di(pyridin-4-yl)-1,4-dithiin-2,3-dithiolate]gold(III),  $n\text{Bu}_4\text{N}[\text{Au}(\text{4-pdddt})_2]$  (7):** Following the same general procedure as that used for  $n\text{Bu}_4\text{N}[\text{Ni}(\text{4-pdddt})_2]$ , the thione **1b** (0.10 g, 0.265 mmol) was dissolved in a freshly prepared methoxide solution (0.012 g, 0.531 mmol, 5 mL). The total dissolution of the thione was followed by dropwise addition of a  $\text{KAuCl}_4 \cdot 4\text{H}_2\text{O}$  methanol solution (0.0507 g; 0.133 mmol, 2 mL). The brown solution was filtered into an  $n\text{Bu}_4\text{NBr}$  methanol solution (0.086 g, 0.265 mmol, 3 mL). After the addition of a few millilitres of water the reaction vial was left for several hours at 4 °C. The brown oil that formed was recovered by centrifugation, dried under vacuum ( $\text{P}_2\text{O}_5$ ) at 80 °C (dec.) and recrystallised from dichloromethane/hexane to be recovered as a microcrystalline precipitate (0.069 g, 47%); m.p. 99–103 °C.  $\text{C}_{44}\text{H}_{52}\text{AuN}_5\text{S}_8$  (1104.4): calcd. C 47.8, H 4.7, N 6.3, S 23.2; found C 47.6, H 5.1, N 6.2, S 22.8.

**Electrocrystallisation of 4a with Perrhenate:** A solution of tetrabutylammonium perrhenate (40 mg; 0.08 mmol) in dichloromethane (25 mL) was added to an H-type electrolysis cell and **4a** (10 mg; 0.02 mmol) was added to the anode compartment. A constant current of 0.1  $\mu\text{A}$  was applied across the cell for 3 weeks and afforded small black crystals on the anode.  $\text{C}_{20}\text{H}_{12}\text{N}_2\text{S}_8 \cdot (\text{ReO}_4)_2 \cdot 0.5(\text{CH}_2\text{Cl}_2)$  (1079.6): calcd C 21.8, H 1.3, N 2.3; found C 21.9, H 0.8, N 2.3.

**X-ray Crystallographic Study:** Crystallographic data for compounds **1a**, **1b**, **3b** and **7** were collected with a Bruker AXS APEX CCD area detector diffractometer equipped with an Oxford Cryosystem low-temperature device at 150(2) K in the  $\omega$  and  $\phi$  scans mode. Data collection, cell refinement and data reduction were performed with the SMART and SAINT programs.<sup>[19]</sup> Datasets for structures **4a** and [**4a-H**]( $\text{ReO}_4$ )<sub>2</sub>·0.5 $\text{CH}_2\text{Cl}_2$  were measured with a Bruker–Nonius FR591 rotating anode equipped with 10 cm confocal mirrors at the EPSRC National Crystallography Service, Southampton University, UK, and data collection and reduction was performed with the DENZO and COLLECT programs.<sup>[20]</sup> A semi-empirical absorption correction was carried out using the program SADABS in all cases.<sup>[21]</sup> The structures were solved by direct methods using the programs SIR97<sup>[22]</sup> or SHELXS-97<sup>[23]</sup> and refined by full-matrix least-squares methods with the SHELXL-97<sup>[21]</sup> program using the WinGX<sup>[24]</sup> or XSEED<sup>[25]</sup> software packages. Non-hydrogen atoms were placed in idealised positions and allowed to refine riding on the parent C atom. Molecular graphics were prepared using the programs ORTEP<sup>[26]</sup> and Mercury.<sup>[27]</sup> A summary of the crystal data, structure solution and refinement are given in Table 4.

CCDC-723666 (for **1a**), -723667 (for **1b**), -723668 (for **3b**·0.66 $\text{CHCl}_3$ ), -723669 (for **4a**), -723670 (for [**4a-H**]( $\text{ReO}_4$ )<sub>2</sub>·0.5 $\text{CH}_2\text{Cl}_2$ ), and -723671 (for **7**· $\text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ ) contain the supplementary crystallographic data for this paper. These data can be ob-

tained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.com.ac.uk/data\\_request.cif](http://www.ccdc.com.ac.uk/data_request.cif).

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