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New electron donors: BEDT-TTF derivatives bearing a pyridine group; synthesis, crystal structure, electrochemical studies and the formation of charge transfer complexes

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Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) derivatives **1a**,**b** and **2a**,**b** containing a pyridine group have been synthesized and their redox potentials have been studied by cyclic voltammetry in dichloromethane solution, which indicate that they are weaker electron donors than BEDT-TTF. Compound **2b** has been studied by X-ray crystallography, which revealed a column-packing pattern in its crystal lattice. The charge transfer (CT) complexes formed between these new donors and tetracyanoquinodimethane (TCNQ), 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone (DDQ) as well as cupric chloride ($CuCl_2$) have been investigated. Among them the CT complexes $\mathbf{1b}_{1.1}$·TCNQ and **1a**·$CuCl_2$ show conductivity in the semiconducting range at room temperature ($\sigma_{rt} = 1.6 \times 10^{-3}$ S cm^{-1} for $\mathbf{1b}_{1.1}$·TCNQ, 4.3×10^{-3} S cm^{-1} for **1a**·$CuCl_2$ measured on a compressed pellet). From the results of X-ray photoelectron spectroscopy (XPS) and conductivity measurements, we suggest that charge transfer and coordination contact coexist in the complex **1a**·$CuCl_2$.

Introduction

Since discovery of the first organic metal TTF–TCNQ (TTF: tetrathiafulvalene, TCNQ: tetracyanoquinodimethane) in 1972,[1] great progress has been achieved in the field of organic conductors and superconductors.[2] Nowadays, efforts are still being devoted to the chemical modification of the donor of the TTF series, for enhancement of the intermolecular interactions among electron donors and acceptors (or counter anions), which is essential for stabilizing the conducting and superconducting state (suppressing the Peierls distortions) at low temperature. Such studies include replacing the sulfur atoms of TTF by more orbitally diffuse selenium atoms (*e.g.* tetramethyltetraselenafulvalene, TMTSF)[3] and substituting the four hydrogen atoms by sulfur rich substituents (*e.g.* bis(ethylenedithio)tetrathiafulvalene, BEDT-TTF)[4] to increase the chance of contact. These efforts have led to the discovery of more than forty organic superconductors with a highest critical temperature of 12.8 K.[5] Another trend developed recently is introducing a hydroxy group or other functional groups into donor molecules to set up intermolecular hydrogen bonds[2b,6] to increase the intermolecular interactions in the materials. From a similar consideration, our project is aimed at introducing a coordination group such as pyridine into the BEDT-TTF molecule to enhance the intermolecular interactions between electron donors and counter anions in the crystal of their charge transfer (CT) complexes by the formation of coordination bonds between the coordination groups and the metallic atoms of counter anions. Furthermore, such electron donors containing coordination groups may form special supermolecular structures with inorganic metallic ions through the coordination effect (self-assembly). Recently, for studies on conducting Langmuir–Blodgett (LB) films,[7] J. Y. Becker *et al.* prepared several ethylenedithiotetrathiafulvalene (EDT-TTF) derivatives bearing a pyridine or *N*-methylpyridine group as a hydrophilic tail, which should be favorable for the formation of LB films. In this paper we will report the synthesis, crystal structure and electrochemical studies on new electron donors (**1a**,**b** and **2a**,**b**) containing a pyridine group. We will also discuss preliminary investigations on their CT salts formed with TCNQ and 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone (DDQ) as well as cupric chloride ($CuCl_2$).

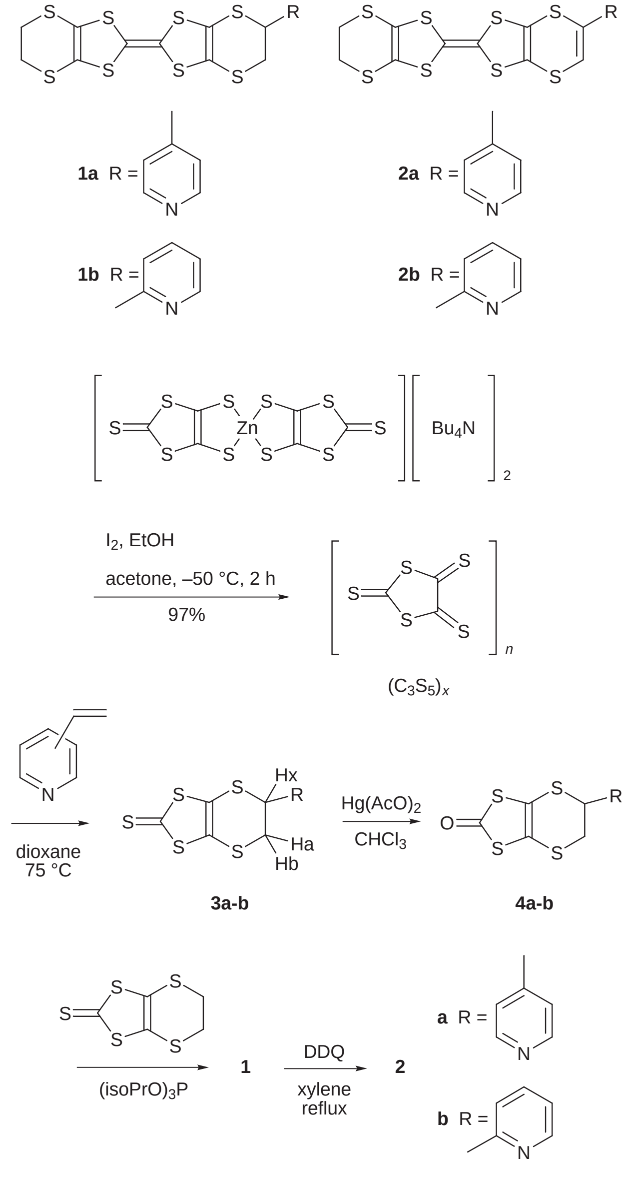
Results and discussion

Synthesis of BEDT-TTF derivatives

Synthesis of the target molecules **1a**,**b** and **2a**,**b** started from trithione oligomer $(C_3S_5)_x$, oligo(4,5-dihydro-1,3-dithiole-2,4,5-trithione), as shown in Scheme 1, which was prepared by the oxidation of bis(tetrabutylammonium) bis[2-thioxo-1,3-dithiole-4,5-bis(thiolato)]zincate with iodine.[7] This oligomer undergoes thermal depolymerization on heating to give the unstable 4,5-dihydro-1,3-dithiole-2,4,5-trithione monomer, which acts as an effective 4π component to form Diels–Alder adducts with dienophiles.[8] Accordingly, the oligomer reacted with 4-vinylpyridine and 2-vinylpyridine leading to the key intermediate compounds **3a** and **3b** in yields of 15 and 20% after recrystallization. Compounds **3a** and **3b** were converted to compounds **4a** and **4b** by a conventional method[9] in high yield. The cross coupling reaction of 4,5-ethylenedithio-1,3-dithiole-2-thione[10] and compounds **4a**,**b** in the presence of triisopropyl phosphite afforded the target compounds **1a** and **1b** in yields of 26 and 25% after recrystallization from 1,2-dichloroethane. The homo-coupling products of **4a**,**b** have been observed in the mass spectra of the reaction mixture, but have not been isolated; they are expected to be a mixture of isomers. The above coupling reaction was also conducted using 4,5-ethylenedithio-1,3-dithiol-2-one instead of the corresponding thione, but isolation of the target compounds was much more difficult due to the formation of side products such as BEDT-TTF. In contrast, in the coupling reaction with 4,5-ethylenedithio-1,3-dithiole-2-thione the formation of BEDT-TTF was largely suppressed.

Dehydrogenation of **1a** and **1b** was carried out by treatment with an excess of DDQ in refluxing xylene (mixture of isomers) to give compounds **2a** and **2b** in yields of 20 and 44% after chromatography on silica gel with dichloromethane–ethyl acetate (1 : 1). Charge transfer complexes were found to be formed during the reaction, which lowered the reaction yields.

In the ^{1}H-NMR spectra of **3b** and **4b** a typical ABX hydrogen–hydrogen coupling system was observed, a quadruplet for the pyridine ring linked methine proton (X) ($\delta =$ 4.90–5.10 ppm) and four doublets for the adjacent methylene protons (AB) ($\delta =$ 3.60–3.95 ppm). For compounds **3a** and **4a**



Scheme 1

as well as **1a** and **1b**, however, the methylene protons (AB) were found to be a doublet.

Electrochemical studies

The redox potentials of new electron donors **1a**,**b** and **2a**,**b** were measured in dichoromethane by cyclic voltammetry. Their cyclic voltammetric data are collected in Table 1 together with those of BEDT-TTF for comparison. For **1a** and **1b** as well as **2a** and **2b**, two reversible single-electron oxidation waves are observed, corresponding to $E^{1/2}{}_1$ and $E^{1/2}{}_2$ in Table 1. The values of **1a** and **1b** are slightly raised as compared to those of BEDT-TTF, which is probably due to the electron withdrawing effect of the pyridine units. The results also indicate that **2a** and **2b** are even more difficult to oxidize than **1a** and **1b**. This may be accounted for by the cooperative effect of conjugation and the electron withdrawing behavior of pyridine. From the data in Table 1, it can also be concluded that the substituent position of the pyridine has no significant effect on the electrochemical behavior of these BEDT-TTF derivatives.

Table 1 Cyclic voltammetric data of **1a**,**b** and **2a**,**b** (10^{-4} mol l^{-1} in CH_2Cl_2, $TBAPF_6$ as supporting electrolyte, Pt electrode as working electrode, scan rate 50 mV s^{-1}, reported voltage *vs.* SCE)

E/V	1a	1b	2a	2b	BEDT-TTF
$E^{1/2}{}_1$	0.45	0.45	0.50	0.48	0.43
$E^{1/2}{}_2$	0.82	0.87	0.89	0.89	0.84

Crystal structure of 2b

Crystallographic data of **2b** are presented in the Experimental section and selected bond lengths and angles are listed in Table 2. Fig. 1 shows the molecular structure of **2b**. Apparently, compound **2b** in the crystal adopts a non-planar conformation. The TTF moiety shows a boat conformation, folding along the S(3)···S(4) and S(5)···S(6) vectors by 10.7 and 27.2° respectively. The planar pyridine ring forms a dihedral angle of 26.3° with the adjacent S(7)C(9)C(10)S(8) moiety. The C(7)C(8)S(8)C(10)C(9)S(7) ring is folded along the S(7)···S(8) vector by 40.0°. The bond lengths and angles of **2b** are all in the normal range, and are similar to those of BEDT-TTF.[11] The bond length of C(9)–C(10) is 1.329(7) Å, typical for carbon–carbon double bonds,[12] which further confirms the dehydrogenation position.

In the crystal lattice of **2b** (Fig. 2), molecules are stacked in columns. Interestingly, 'BEDT-TTF' and the pyridine moiety of **2b** are arranged in two columns separately. Within the 'BEDT-TTF column', short S···S contacts in the range 3.425(1)–3.554(1) Å are observed and neighboring molecules are displaced toward each other. In the 'pyridine column' adjacent pyridine rings are planar with an inter-planar distance of about 3.818 Å. Thus, if the pyridine part of the compound **2b** is considered to be an electron acceptor, the crystal structure of **2b** is very similar to those of organic conductors and superconductors.

Charge transfer complexes

By directly mixing **1a** or **1b** with TCNQ or DDQ black polycrystals or powders were obtained. These should be the CT complexes formed between **1a** (or **1b**) with TCNQ (or DDQ). The stoichiometric ratio of these CT complexes was determined based on elemental analysis as indicated in Table 3. Their room-temperature conductivities measured on a compressed pellet are also listed in Table 3, and only the conductivity of the complex $\mathbf{1b}_{1.1}$·TCNQ was in the semi-conducting range. The cyano group stretching frequencies of the TCNQ complexes of **1a** and **1b** (Table 3) are shifted to low wavenumbers with respect to that of TCNQ (2222 cm^{-1}); this is due to the influence of the delocalised radical anion in the complex.[13]

When **2a** and **2b** were treated with TCNQ and DDQ under the same conditions as for **1a** and **1b**, no black precipitate was obtained. This observation suggested that the electron donating abilities of **2a** and **2b** were lower than those of **1a** and **1b**, which was fully in accordance with the results of electrochemical studies.

In addition, we also conducted a preliminary study of the complexes of these new donors with metallic compounds, taking advantage of the coordination ability of the pyridine group. As an example, the complex formed between **1a** and $CuCl_2·2H_2O$ in dichloromethane was studied by X-ray photoelectron spectroscopy (XPS). The binding energies (BE) of Cu($2p_{3/2}$), Cl($2p_{3/2}$), N(1s) and S($2p_{3/2}$) in the complex, compound **1a** and $CuCl_2$ are listed in Table 4. There are two kinds of sulfur atoms with different BE (166.17 and 163.90 eV) in the complex in the approximate ratio of 1:11, and the former has a significantly increased energy while the latter remains at almost the same energy as in **1a**. This result may suggest that charge transfer occurs between parts of the donor molecules and copper chloride, which is further confirmed by the conductivity measurement for this complex (Table 3). The

Table 2 Selected bond lengths (Å) and angles (°) for compound **2b**

S(1)–C(1)	1.759(6)	S(6)–C(8)	1.736(5)	S(4)–C(4)	1.741(5)
S(3)–C(3)	1.744(5)	S(6)–C(6)	1.762(5)	S(4)–C(5)	1.745(5)
S(3)–C(5)	1.760(5)	S(7)–C(7)	1.737(5)	S(2)–C(4)	1.746(5)
N–C(11)	1.396(7)	S(7)–C(9)	1.796(5)	S(2)–C(2)	1.797(6)
C(1)–C(2)	1.491(9)	S(5)–C(6)	1.750(5)	S(1)–C(3)	1.739(5)
C(3)–C(4)	1.342(7)	S(5)–C(7)	1.764(5)	C(9)–C(10)	1.329(7)
C(5)–C(6)	1.323(6)	S(8)–C(10)	1.743(5)	C(9)–C(11)	1.463(6)
C(7)–C(8)	1.332(7)	S(8)–C(8)	1.763(5)	C(11)–C(12)	1.342(7)
C(8)–S(6)–C(6)	92.3(2)	C(3)–C(4)–S(4)	117.0(4)	C(7)–C(8)–S(6)	118.9(4)
C(7)–S(7)–C(9)	98.5(2)	C(3)–C(4)–S(2)	127.5(4)	C(7)–C(8)–S(8)	120.9(3)
C(10)–S(8)–C(8)	99.9(2)	C(6)–C(5)–S(3)	122.4(4)	S(6)–C(8)–S(8)	119.7(3)
C(4)–S(4)–C(5)	95.6(2)	S(4)–C(5)–S(3)	113.7(3)	C(10)–C(9)–C(11)	124.9(4)
C(4)–S(2)–C(2)	101.0(3)	C(5)–C(6)–S(5)	123.9(4)	C(10–C(9)–S(7)	121.1(4)
C(3)–S(1)–C(1)	101.8(3)	C(5)–C(6)–S(6)	123.3(4)	C(11)–C(9)–S(7)	114.0(3)
C(11)–N–C(15)	117.8(5)	C(8)–C(7)–S(7)	125.6(4)	C(9)–C(10)–S(8)	124.7(4)
C(2)–C(1)–S(1)	115.0(5)	C(8)–C(7)–S(5)	115.3(3)	C(12)–C(11)–N	122.9(4)
C(4)–C(3)–S(1)	129.2(4)	S(7)–C(7)–S(5)	118.9(3)		

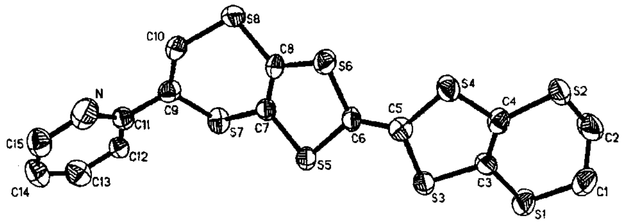


Fig. 1 Molecular structure of compound **2b**.

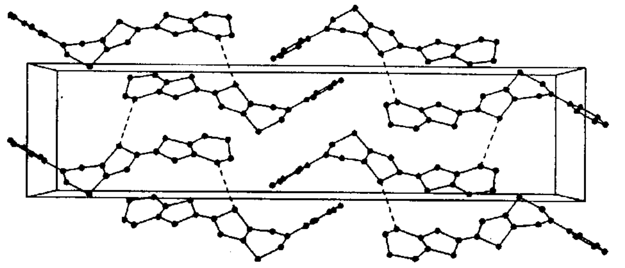


Fig. 2 Crystal packing of compound **2b**.

Table 3 Physical data of the CT complexes

Donor, D	Acceptor, A	D:A[a]	ν_{CN}/cm^{-1}	σ_{rt}[b]/S cm^{-1}
1a	TCNQ	1.1:1	2182	2.24×10^{-8}
1a	DDQ	3:1		$<10^{-8}$
1b	TCNQ	1.1:1	2181	1.60×10^{-3}
1b	DDQ	2:1		$<10^{-8}$
1a	$CuCl_2$	1:1		4.3×10^{-3}

[a] Determined based on elemental analysis. [b] Room-temperature conductivity measured on a compressed pellet.

N(1s) BE in the molecular donor is 399.21 eV, but in the salt it is shifted to 399.87 eV. This may be due to the coordination effect between the nitrogen atom of the donor molecule and the copper atom of $CuCl_2$.

Attempts to obtain single crystals of the CT complexes mentioned above are still under way. The preparation of CT complexes of these new electron donors with other acceptors and counter anions by electrochemical and diffusion methods is also in progress.

Table 4 Binding energies (eV) of Cu($2p_{3/2}$), Cl($2p_{3/2}$), N(1s) and S($2p_{3/2}$) of **1a**, CT complex **1a**·$CuCl_2$ and $CuCl_2$

Compound	Cu($2p_{3/2}$)	Cl($2p_{3/2}$)	N(1s)	S($2p_{3/2}$)
1a			399.21	163.96
1a·$CuCl_2$	934.38, 932.51	198.95, 197.62	399.87	166.17 (8%), 163.90 (92%)
$CuCl_2$	934.3	199.5		

Summary

Four novel pyridine-substituted BEDT-TTF derivatives (**1a**,**b** and **2a**,**b**) were synthesized and characterized. Their redox potentials were determined by cyclic voltammetry in CH_2Cl_2 solution and the results revealed that they were weaker donors than BEDT-TTF. A crystal structure analysis was carried out for compound **2b**; an interesting molecular packing pattern was observed. Preliminary results on CT complexes of these new donors with TCNQ and DDQ as well as $CuCl_2$ are presented. Further investigations on CT complexes based on these new donors are in progress.

Experimental

X-Ray crystallography†

A single crystal of **2b** with the size of 0.4 × 0.4 × 0.15 mm suitable for X-ray structure analysis was obtained from 1,2-dichloroethane. Intensity data were collected on a Rigaku AFC-6 four-circle diffractometer with graphite monochromated Mo-Kα radiation ($\lambda=0.71069$ Å) using the 2θ-ω scan mode ($3° < 2\theta < 52°$). All collected reflections are unique. Refined cell parameters were obtained from the setting angles of 15 reflections with $2\theta \geqslant 22°$. Intensities were corrected for Lp effects and theoretical absorption corrections. A total of 3025 reflections were collected, 2157 reflections with $I > 2\sigma(I)$ were considered as observed. The structure was solved by direct methods and refined using SHELXL software (Siemens SHELXL PLUS, PC version).[14] All non-H atoms were refined anisotropically using full-matrix least squares refinement based on F^2 with weights of the form given in eqn. (1).

$$w = 1/[\sigma^2(F_o^2) + (0.1426P)^2 + 0.0000P]$$
$$\text{where } P = (F_o^2 + 2F_c^2)/3 \qquad (1)$$

Hydrogen atoms are included and all H-atom parameters refined. Convergence to $R = 0.0646$ ($R_w = 0.1956$) was obtained using 219 variable parameters. The final value of S is 1.004. Crystal data: $C_{15}H_9NS_8$; crystal system: orthorhombic, space group: *Pbca*; cell parameters: $a = 11.448(5)$, $b = 35.680(10)$, $c = 8.632(3)$ Å; $Z = 8$; $D_{calcd} = 1.732$ g cm^{-3}; $F(000) = 1872$.

Synthesis

General. Melting points were measured with an XT_4–100_X microscope apparatus and are uncorrected. ^{1}H-NMR spectra

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†CCDC reference number 1145/150. See http://www.rsc.org/suppdata/jm/1999/1245/for crystallographic files in .cif format.

were recorded on a UNITY 200 (Varian) instrument. Infrared spectra were recorded on a Perkin-Elmer SYSTEM 2000 FT-IR spectrometer. Mass spectra were determined with the instruments AEI-MS50 for EI-MS, KYKY-ZH-P-5 for FAB-MS and BEFLEX III for TOF-MS. Elemental analyses were performed on a Carlo-Erba-1106 instrument. Cyclic voltammetric measurements were conducted on an EGDG PAR 370 System.

Chemicals. The $(C_3S_5)_x$ oligomer was synthesized by the method described in ref. 8. Triisopropyl phosphite (Acros Chemicals) was used without purification. All solvents were dried by standard procedures.

4,5-(4-Pyridylethylenedithio)-1,3-dithiole-2-thione 3a

4-Vinylpyridine (1.05 ml, 10 mmol) was added to a stirred suspension of oligomeric 4,5-dihydro-1,3-dithiole-2,4,5-trithione (1.7 g) in dioxane (15 ml). The mixture was heated to 75 °C and stirred for 1.5 h at this temperature. The resulting mixture was filtered hot, and the remaining solid was further washed with CH_2Cl_2 (3 × 10 ml) for complete extraction of the product. The filtrate and washings were treated with activated charcoal. The solvent was evaporated under vacuum on a rotary evaporator. The resulting solid was recrystallized from acetonitrile–dichloromethane (3 : 1) to give **3a** as yellow crystals (0.4 g) in 15% yield, mp 129–131 °C (dec). Anal. calcd for $C_{10}H_7NS_5$: C, 39.84; H, 2.34; N, 4.64. Found: C, 39.71; H, 2.06; N, 4.36%. *m/z* (FAB) 302 ($M^+ + 1$); $\delta_H(CDCl_3)$: 3.54 (2H, d, *J* 3.3), 4.74 (1H, dd), 7.34 (2H, d, *J* 5.6), 8.67 (2H, d, *J* 5.6); $\nu_{max}(KBr)/cm^{-1}$: 1595, 1559, 1488 and 1064.

4,5-(2-Pyridylethylenedithio)-1,3-dithiole-2-thione 3b

Thione **3b** was prepared from 2-vinylpyridine by an analogous procedure to that used for the synthesis of compound **3a** and isolated as yellow crystals in 20% yield, mp 122–124 °C. Anal. calcd for $C_{10}H_7NS_5$: C, 39.84; H, 2.34; N, 4.64. Found: C, 39.59; H, 2.16; N, 4.48%. *m/z* (EI) 301 (M^+); $\delta_H(CDCl_3)$: 3.60–3.95 (2H, m), 4.95 (1H, dd), 7.28–8.60 (4H, m); $\nu_{max}(KBr)/cm^{-1}$: 1582, 1567, 1486, 1469, 1431 and 1058.

4,5-(4-Pyridylethylenedithio)-1,3-dithiol-2-one 4a

To a solution of thione **3a** (0.5 g, 1.66 mmol) in $CHCl_3$ (25 ml), $Hg(AcO)_2$ (1.5 g, 4.8 mmol) was added. The resulting solution was stirred at room temperature for 1 h. The precipitate was filtered off and the filtrate washed with water (3 × 10 ml). After drying (Na_2SO_4) the solvent was evaporated and the resulting solid was recrystallized from acetonitrile to give **4a** as white crystals (0.39 g, 83% yield), mp 132–133 °C. Anal. calcd for $C_{10}H_7NOS_4$: C, 42.08; H, 2.47; N, 4.91. Found: C, 42.09, H, 2.22; N, 4.65%. *m/z* (FAB) 286 ($M^+ + 1$); $\delta_H(CDCl_3)$: 3.56 (2H, d, *J* 11.4), 4.74 (1H, dd), 7.34 (2H, d, *J* 6.0), 8.67 (2H, d, *J* 6.0); $\nu_{max}(KBr)/cm^{-1}$: 1671, 1625, 1597 and 1504.

4,5-(2-Pyridylethylenedithio)-1,3-dithiol-2-one 4b

Compound **4b** was prepared from thione **3b** by an analogous procedure to that used for the synthesis of compound **4a** and isolated as white crystals in 80% yield, mp 102–104 °C. Anal. calcd for $C_{10}H_7NOS_4$: C, 42.08; H, 2.47; N, 4.91. Found: C, 42.07, H, 2.19; N, 4.72%. *m/z* (EI) 285 (M^+); $\delta_H(CDCl_3)$: 3.60–4.95 (2H, m), 4.95 (1H, dd), 7.30–8.60 (4H, m); $\nu_{max}(KBr)/cm^{-1}$: 1678, 1615, 1585, 1501, 1469, 1142 and 901.

4,5-Ethylenedithio-4′,5′-(4-pyridylethylenedithio)tetrathiafulvalene 1a‡

Compound **4a** (0.57 g, 2 mmol) and 4,5-ethylenedithio-1,3-dithiole-2-thione (1.34 g, 6 mmol) were suspended in triisopropyl phosphite (30 ml). The mixture was heated up to 120–130 °C under nitrogen atmosphere and stirred for a further 2 h. The resulting mixture was allowed to cool to room temperature and methanol (50 ml) was added. The mixture was further cooled in a refrigerator. A yellow solid precipitated out which was filtered off, washed with methanol, then recrystallized from 1,2-dichloroethane to give **1a** as a yellow solid (0.24 g, 26% yield). Mp 187–188 °C (dec). Anal. calcd for $C_{15}H_{11}NS_8$: C, 39.01; H, 2.40; N, 3.03. Found: C, 38.71; H, 2.32; N, 2.95%. *m/z* (FAB) 461 (M^+); $\delta_H(CDCl_3)$: 3.30 (4H, s), 3.42 (2H, d, *J* 6.7), 4.64 (1H, dd), 7.32 (2H, d, *J* 5.0), 8.62 (2H, d, *J* 5.0); $\nu_{max}(KBr)/cm^{-1}$: 2914, 1597, 1443 and 1023.

4,5-Ethylenedithio-4′,5′-(2-pyridylethylenedithio)tetrathiafulvalene 1b

1b was synthesized by a similar method to **1a** and isolated as a yellow solid in 25% yield. Mp 173–175 °C (dec). Anal. calcd for $C_{15}H_{11}NS_8$: C, 39.01; H, 2.40; N, 3.03. Found: C, 38.49; H, 2.16; N, 2.80%. *m/z* (TOF) 461 (M^+); $\delta_H(DMSO\text{-}d_6)$: 3.38 (4H, s), 3.75 (2H, m), 5.00 (1H, dd), 7.35–8.58 (4H, m); $\nu_{max}(KBr)/cm^{-1}$: 1584, 1505, 1468, 1056 and 848.

4,5-Ethylenedithio-4′,5′-(4-pyridylethenylenedithio)tetrathiafulvalene 2a

A solution of DDQ (80 mg, 0.35 mmol) in xylene (isomer mixture) (5 ml) was added dropwise under argon over 20 min to a solution of **1a** (92 mg, 0.2 mmol) in mixed xylenes (20 ml) under reflux. After an additional 10 min, the reaction mixture was allowed to cool to room temperature, then filtered and the remaining solid was washed with CH_2Cl_2. Evaporation of solvents from the filtrate and washing afforded an oily brown residue, which was chromatographed on silica gel with dichloromethane–ethyl acetate (1 : 1) as the eluent. The product was further purified by recrystallization from 1,2-dichloroethane to give **2a** as an orange solid (18 mg, 20% yield). Mp 222–224 °C (dec). Anal. calcd for $C_{15}H_9NS_8$: C, 39.19; H, 1.97; N, 3.05. Found: C, 38.76; H, 1.72; N, 2.82%. *m/z* (EI) 459 (M^+); $\delta_H(CDCl_3)$: 3.34 (4H, s), 6.95 (1H, s), 7.43 (2H, d, *J* 6.2), 8.64 (2H, d, *J* 6.2); $\nu_{max}(KBr)/cm^{-1}$: 2919, 1587, 1408 and 803.

4,5-Ethylenedithio-4′,5′-(2-pyridylethenylenedithio)tetrathiafulvalene 2b

2b was synthesized by a similar procedure to that for compound **2a** and isolated as an orange solid in 44% yield, mp 204–206 °C (dec). Anal. calcd for $C_{15}H_9NS_8$: C, 39.19; H, 1.97; N, 3.05. Found: C, 38.91; H, 1.97; N, 2.88%. *m/z* (EI) 459 (M^+); $\delta_H(CDCl_3)$: 3.32 (4H, s), 7.34 (1H, s), 7.60–8.60 (4H, m); $\nu_{max}(KBr)/cm^{-1}$: 2922, 1623, 1581, 1460, 1434, 1022 and 761.

Preparation of CT complexes

To a solution of the donor (1 equiv.) in dichloromethane under reflux, a hot solution of TCNQ or DDQ (1 equiv.) in acetonitrile was added. The mixture was heated gently under reflux for 30 min before cooling. After several hours the charge transfer complexes were collected by filtration.

1a with TCNQ: mp > 300 °C. $\nu_{max}(KBr)/cm^{-1}$: 3419, 2182, 2123, 1733, 1690, 1631, 1571, 1505, 1414, 1346, 1282, 1179,

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‡IUPAC name: 5,5′,6,6′-tetrahydro-5-(4-pyridyl)-2,2′-bi([1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene). Related compounds **2**–**4** can be named similarly.

1107. C, 47.92; H, 2.37; N, 10.68 (Anal. calcd for $C_{28.5}H_{16.1}N_{5.1}S_{8.8}$: C, 48.07; H, 2.43; N, 10.22%).

1a with DDQ: mp >300 °C. ν_{max}(KBr)/cm^{-1}: 3417, 3025, 2214, 1629, 1590, 1455, 1410, 1255, 1201, 1171, 1035. The composition of this CT complex was determined to be $\mathbf{1a}_3$·DDQ based on the elemental analysis: C, 38.92; H, 1.71; N, 4.04 (Anal. calcd for $C_{38}H_{22}Cl_2N_4O_2S_{16}$: C, 39.50; H, 2.05; N, 4.34%).

1b with TCNQ: mp >300 °C. ν_{max}(KBr)/cm^{-1}: 4324, 2924, 2181, 1632, 1571, 1434, 1355, 1174, 1114. The composition of this CT complex was determined to be $\mathbf{1b}_{1.1}$·TCNQ based on the elemental analysis: C, 47.52; H, 2.66; N, 10.89 (Anal. calcd for $C_{28.5}H_{16.1}N_{5.1}S_{8.8}$: C, 48.07; H, 2.43; N, 10.22%).

1b with DDQ: mp >300 °C. ν_{max}(KBr)/cm^{-1}: 3418, 3022, 2220, 1622, 1579, 1444, 1348, 1170, 1107. The composition of this CT complex was determined to be $\mathbf{1b}_2$·DDQ·$(CH_3CN)_{1.5}$ based on the elemental analysis: C, 41.41; H, 2.45; N, 5.64 (Anal. calcd for $C_{41}H_{26.5}Cl_2N_{5.5}O_2S_{16}$: C, 40.63; H, 2.20; N, 6.36%).

Preparation of the complex of 1a with $CuCl_2$

A solution of $CuCl_2·H_2O$ (34 mg, 0.02 mmol) in acetonitrile (5 ml) was added to a hot solution of **1a** (46 mg, 0.1 mmol) in dichloromethane (5 ml). The resulting mixture was stirred overnight at room temperature. The precipitate was collected by filtration; **1a**·$CuCl_2$ was obtained as a black solid after drying under vacuum. Mp >300 °C. Anal. calcd for $C_{15}H_{11}Cl_2NS_8Cu$: C, 30.22; H, 1.86; N, 2.35. Found: C, 29.71; H, 1.66; N, 1.97%.

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