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Novel unsymmetrically functionalized BEDT–TTF derivatives: synthesis, crystal structure and electrochemical characterization ☆

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Abstract

Novel functionalized bis(ethylenedithio)tetrathiafulvalene (BEDT–TTF) derivatives **4** and **5** have been synthesized in good yields from cyano precursor via a cross-coupling reaction. Their redox potentials have been studied by cyclic voltammetry in a dichloromethane solution; this indicated that they are slightly weaker electron donors than BEDT–TTF. Compound **4** has been studied by X–ray crystallography; this revealed that, in the crystal, the molecules were held together by some unconventional C–H···N and C–H···S hydrogen bonds.***To cite this article: S.-X. Liu et al., C. R. Chimie 6 (2003).***

Résumé

De nouveaux dérivés fonctionnalisés du bis(éthylènedithio)tétrathiafulvalène (BEDT–TTF), **4** et **5**, ont été synthétisés avec de bons rendements à partir d'un précurseur cyano via une réaction de couplage croisé. L'étude de leurs potentiels redox par voltamétrie cyclique dans une solution de dichlorométhane indique qu'ils sont des donneurs d'électrons légèrement plus faibles que le BEDT–TTF. L'étude du composé **4** par cristallographie des rayons X révèle que, dans le cristal, la cohésion des molécules est maintenue par des liaisons hydrogène C–H···N and C–H···S non conventionnelles***Pour citer cet article : S.-X. Liu et al., C. R. Chimie 6 (2003).***

Keywords: functionalized bis(ethylenedithio)tetrathiafulvalene; crystal structure; electrochemistry

Mots clés : bis(éthylènedithio)tétrathiafulvalène fonctionnalisé ; structure cristalline ; électrochimie

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1. Introduction

The search for molecule-based materials exhibiting multiphysical properties is one of the current challenges in molecular materials science [1, 2]. Great interest is currently devoted to obtain organic/inorganic hybrid materials in which it is expected that there is long-range magnetic coupling between the localised spins on *d* orbitals of the paramagnetic transition metal ions of the inorganic part through the mobile electrons of the conducting networks (π-electrons) [3]. Consequently, our strategy involves the covalent attachment of metal-ion binding groups to BEDT–TTF derivatives and their linkage into supramolecular systems. With the appropriate choice of metal ions, the resulting system would be expected to show multiple physical properties, such as electrical conductivity or superconductivity and magnetic effects, optical and magnetic properties or spin crossover, in a synergistic way. Based on the chemistry of thiapendione, synthetic approaches to symmetrically functionalised BEDT–TTF derivatives have been realised in our group in order to prepare novel organic conducting materials featuring TTF moieties within metal binding ligand systems [4]. Herein, we describe a short and efficient synthetic route to two new unsymmetrically functionalized BEDT–TTF derivatives **4** and **5**, together with their electrochemical properties as well as the crystal structure of compound **4**.

2. Results and discussion

2.1. Syntheses

In general, several strategies for the preparation of unsymmetrically functionalised BEDT–TTF derivatives are possible [5]. The most widely used method is via the phosphite-mediated cross coupling of two appropriate chalcogenones leading to a mixture from which the desired species must be separated from the symmetrical by-products [6]. However, some BEDT–TTF derivatives are not successfully available by the simple procedure of refluxing their corresponding thiones/ones in the presence of a phosphorous (III) compound, [P(OMe)$_3$, P(OEt)$_3$ or P(Ph)$_3$] [7]. Furthermore, this classical synthesis is problematic, suffering from disadvantages, such as low yields, tedious separations, multistep procedures, and/or expensive starting materials [8]. Therefore, an alternative strategy has been adopted by several groups. The key compound in this case is the 4,5-bis(2'-cyano-ethylsulfanyl)-4',5'-ethylenedithiotetrathiafulvalene **3**, which can be readily prepared as described [9] by treatment of equimolecular amounts of 4,5-ethylenedithio-1,3-dithiole-2-thione **1** and 4,5-bis(2'-cyanoethylsulfanyl)-1,3-dithiol-2-one **2** at 100 °C in neat P(OEt)$_3$ (Fig. 1). Then compound **3** can simply be deprotected by a basic reagent [10] and, subsequently, by appropriate alkylations, to give two new functionalized BEDT–TTF derivatives **4** and **5** in good yields (Fig. 2).

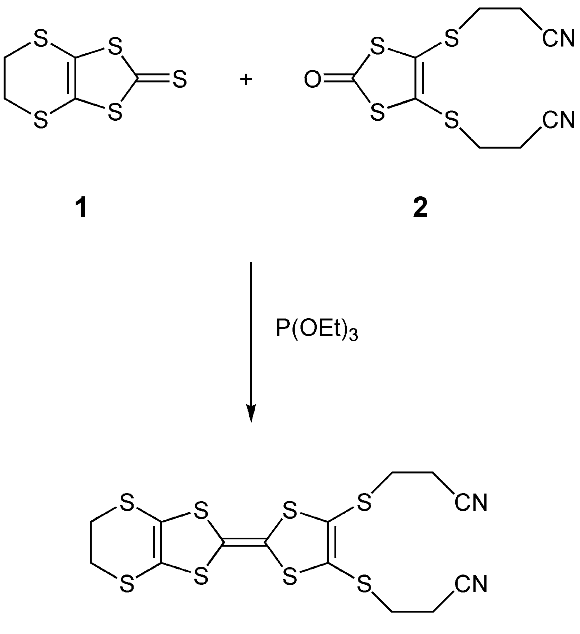

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Fig. 1. A synthetic route for the preparation of key compound **3**.

2.2. Electrochemical studies

The redox potentials of new donors **4** and **5** were measured in dichloromethane by cyclic voltammetry. Their cyclic voltammetric data are collected in Table 1 together with those of BEDT–TTF for comparison. In each case, two reversible single-electron oxidation waves are observed, typical of the TTF system corresponding to $E^{1/2}{}_1$ and $E^{1/2}{}_2$ in Table 1. In general, the values of **4** and **5** are slightly raised as compared to those of BEDT–TTF, which is probably due to the

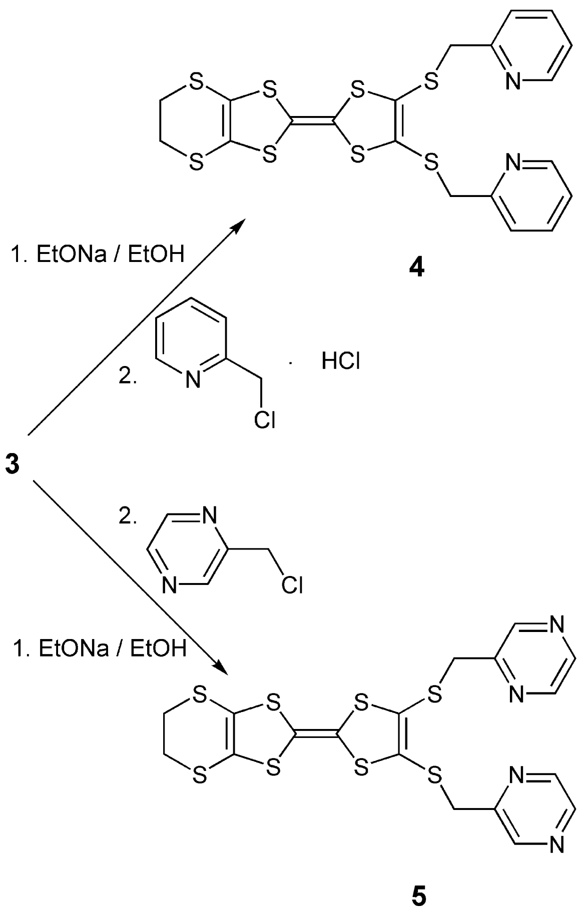

Fig. 2. A short and efficient synthetic route for the preparation of BEDT–TTF derivatives **4** and **5**.

Table 1
Cyclic voltammetric data[a]

E (V)	**4**	**5**	BEDT–TTF
$E^{1/2}{}_1$	0.58	0.56	0.52
$E^{1/2}{}_2$	0.97	0.90	0.94

[a] Conditions: all oxidation potential were determined in CH_2Cl_2 under N_2 at room temperature containing 0.1 M Bu_4NPF_6, with Ag/AgCl as reference electrode and Pt as working electrode; scan rate 100 mV s^{-1}.

electron-withdrawing effect of the pyridine and pyrazine units. These results also show that the presence of the pyridine or pyrazine units relatively far away from the TTF core on the side chains $–SCH_2–C_5H_4N$ and $–SCH_2–C_4H_3N_2$ respectively, has only a very weak influence on their values.

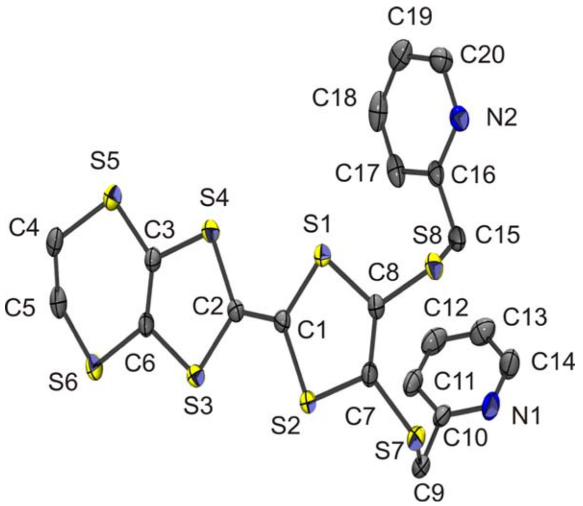

Fig. 3. ORTEP drawing of compound **4** showing 50% probability thermal ellipsoids and the atom-numbering scheme.

2.3. Crystal structure of donor 4

BEDT–TTF derivatives **4** and **5** have been characterized by elemental analysis, ^1H NMR and ^{13}C NMR as well as IR spectroscopy (see the Experimental section). The single crystal X-ray structure of **4** is depicted in Fig. 3 and the selected bond distances and angles are given in Table 2. TTF core of compound **4** is nearly planar with a dihedral angle of 1.94(9)° between the two five-membered rings (S1, S2, C1, C7, C8 and S3, S4, C2, C3, C6).

In the crystal lattice, the molecules are linked by a network of some unconventional C–H··N and C–H··S hydrogen bonds (Fig. 4 and Table 3). Interestingly, the ‘BEDT–TTF’ and the pyridine moieties of **4** are arranged in two separate columns. Within the ‘BEDT–TTF column’, some S··S contacts in the range 3.832–4.296 Å are observed, and the interplanar separation of 6.03 Å is rather large, dictated by the bulky substituents (Fig. 5). In the ‘pyridine column’, the pyridine rings involving atom N2, of symmetry related molecules, are separated by an inter-planar stacking distance of ca 4.02 Å.

In conclusion, two novel unsymmetrically functionalized BEDT–TTF derivatives **4** and **5** were synthesized and characterized. Their redox potentials were determined by cyclic voltammetry in CH_2Cl_2 solution and results revealed they were slightly weaker donors than BEDT–TTF. A crystal structure analysis was carried out for compound **4**, showing an interesting mo-

Table 2
Selected bond distances (Å) and bond angle (°) for **4**

S(1)–C(1)	1.7508(16)	S(6)–C(5)	1.805(2)
S(1)–C(8)	1.7511(16)	S(7)–C(7)	1.7454(16)
S(2)–C(7)	1.7544(16)	S(7)–C(9)	1.824(2)
S(2)–C(1)	1.7552(16)	S(8)–C(8)	1.7490(16)
S(3)–C(6)	1.7501(17)	S(8)–C(15)	1.8297(19)
S(3)–C(2)	1.7559(16)	C(1)–C(2)	1.341(2)
S(4)–C(3)	1.7489(16)	C(3)–C(6)	1.340(2)
S(4)–C(2)	1.7540(16)	C(4)–C(5)	1.507(3)
S(5)–C(3)	1.7457(17)	C(7)–C(8)	1.345(2)
S(5)–C(4)	1.7991(18)	C(9)–C(10)	1.494(3)
S(6)–C(6)	1.7450(16)	C(15)–C(16)	1.498(2)
C(1)–S(1)–C(8)	95.71(7)	C(7)–S(7)–C(9)	100.20(8)
C(7)–S(2)–C(1)	95.59(8)	C(8)–S(8)–C(15)	101.55(8)
C(6)–S(3)–C(2)	94.80(8)	C(2)–C(1)–S(1)	122.98(13)
C(3)–S(4)–C(2)	95.09(8)	C(2)–C(1)–S(2)	122.99(13)
C(3)–S(5)–C(4)	99.86(8)	S(1)–C(1)–S(2)	113.98(9)
C(6)–S(6)–C(5)	101.42(8)	C(1)–C(2)–S(4)	122.61(13)
C(1)–C(2)–S(3)	122.43(13)	S(4)–C(2)–S(3)	114.92(9)

lecular packing pattern. The binding ability to transition metal ions, the formation of charge-transfer complexes and ion radical salts of these promising new donors is currently under investigation in our laboratory and will be published in due course.

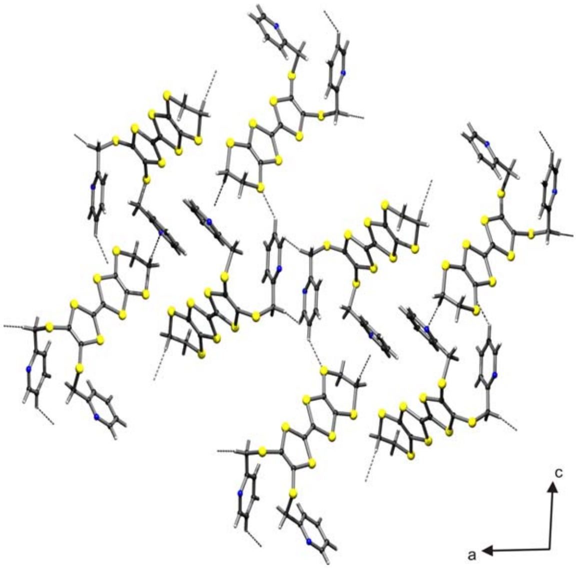

Fig. 4. Crystal structure (*ac* projection) of compound **4** showing the unconventional hydrogen bonds.

3. Experimental Section

3.1. Synthesis

3.1.1. General methods and instrumentation

Reactions requiring air- and/or water-sensitive manipulations were conducted under argon with dry, freshly distilled solvents. Unless stated otherwise, all other reagents were purchased from commercial sources and used without additional purification. 2-chloromethylpyrazine [11], 4,5-ethylenedithio-1,3-dithiole-2-thione (**1**) [12], 4,5-bis(2'-cyanoethylsulfanyl)-1,3-dithiol-2-one (**2**) [12] and 4,5-bis-(2'-cyano-ethylsulfanyl)-4',5'-ethylenedithiotetrathiafulvalene (**3**) [9] were prepared according to literature procedures. Unless otherwise specified, all ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ at 300 MHz and 75 MHz, respectively. Melting points are reported in degrees Celsius and are uncorrected. Elemental analyses were performed on an EA 1110 Elemental

Table 3
Some unconventional hydrogen bond distances [Å] and bond angles [°] for **4**

Donor–H··Acceptor	D··A	D–H··A
C(4)–H(4B)··N(2)	3.487(2)	170.45
C(9)–H(9B)··N(1)	3.339(3)	147.50
C(13)–H(13A)··S(6)	3.550(2)	133.53

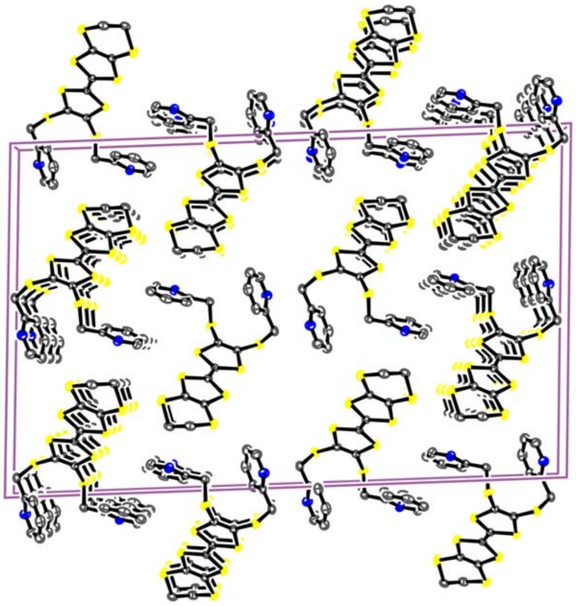

Fig. 5. Crystal packing (*ac* projection) of compound **4**.

Analyser CHNS Carlo Erba Instruments. FT–IR data were collected at a resolution of 4 cm^{-1}. Cyclic voltammetric measurements were conducted on a VA-Stand 663 electrochemical analyser. Mass spectra were recorded on a Micromass AutoSpec spectrometer using FAB or EI. Analytical TLC was carried out on Merck Silica gel 60 F254 coated aluminium foil; the same type of silica was used for columns.

3.1.2. Thiolate deprotection-alkylation procedure

A solution of 0.5 M EtONa/EtOH (8 ml) was added with a syringe to a suspension of 4,5-bis(2'-cyanoethylsulfanyl)-4',5'-ethylenedithiotetrathiafulvalene (**3**) (0.465 g, 1 mmol) in anhydrous degassed EtOH (27 ml) under Argon. After being stirred at room temperature for 4 h, the mixture was reacted with a solution of the appropriate alkyl halide (12 mmol) in anhydrous degassed EtOH (24 ml), and then the mixture was stirred overnight. H_2O was added to quench the reaction, and the reaction mixture was then extracted with CH_2Cl_2. The combined organic extracts were washed, dried over $MgSO_4$, filtered, and concentrated in vacuo to give a dark-brown oil which was purified by flash chromatography on silica gel, initially with CH_2Cl_2 (to remove any unreacted alkyl halide as well as unwanted by-products), and then with 10:1 CH_2Cl_2/ethyl acetate, unless mentioned, to give the desired product.

4,5-bis(2-pyridylmethylsulfanyl)-4',5'-ethylenedithiotetrathiafulvalene **(4).** Yield: 80%. Colour: brown. Melting point: 105 °C. ^{1}H NMR: δ 3.29 (s, 4H), 4.02 (s, 4H), 7.14–7.25 (m, 4H), 7.59–7.65 (dt, J = 2 Hz, J = 8 Hz, 2H), 8.54–8.55 (d, J = 4 Hz, 2H); ^{13}C NMR: 156.4, 149.7, 136.7, 129.2, 123.3, 122.4, 113.9, 113.6, 108.7, 42.3, 30.2. IR (KBr, cm^{-1}): 1590, 1568, 1471, 1435, 1406, 1149, 1085, 1046, 994, 771, 743. Mass spectrum (EI) *m/z*: 540 (M^+). Anal. calcd for $C_{20}H_{16}N_2S_8$: C, 44.42; H, 2.98; N, 5.18. Found: C, 44.71; H, 2.96; N, 5.18.

4,5-bis(2-pyrazylmethylsulfanyl)-4',5'-ethylenedithiotetrathiafulvalene (**5**). After work-up, the resulting dark-brown residue was subjected to column chromatography, eluting initially with a gradient of 20–100% ethyl acetate in CH_2Cl_2 and then with MeOH / ethyl acetate (1:2) to give **5.** Yield: 63%. Colour: Dark brown. Melting point: 90 °C. ^{1}H NMR: δ 3.29 (s, 4H), 4.03 (s, 4H), 8.50 (m, 6H); ^{13}C NMR: 152.4, 144.6, 144.3, 143.4, 129.2, 113.8, 111.9, 110.5, 39.4, 30.1; IR (KBr, cm^{-1}): 1526, 1473, 1400, 1287, 1215, 1173, 1112, 1055,1018, 881, 772. Mass spectrum (FAB) *m/z*: 542 (M^+). Anal. calcd for $C_{18}H_{14}N_4S_8 \cdot 0.25EtOAc$: C, 40.40; H, 2.85; N, 9.91. Found: C, 40.50; H, 2.73; N, 9.85.

3.2. X-ray crystallography

$C_{20}H_{16}N_2S_8 \cdot 0.5\ (C_4H_8O_2)$, M_W = 584.88, monoclinic, space group $C2/c$, a = 36.0971(19), b = 6.0257(2), c = 22.8424(13) Å, β = 92.850(4)°, V = 4962.3(4) Å^3, Z = 8, d_{calc} = 1.566 g cm^{-3}, μ(Mo Kα) = 0.740 mm^{-1}. 28 000 reflections measured, 5447 independent reflections, 4744 observed reflections ($I > 2\ \sigma(I)$), final $R1$ = 0.0303 (observed data), $wR2$ = 0.827 (all data).

Suitable crystals were obtained as red-brown plates by slow evaporation of a CH_2Cl_2 / CH_3COOEt solution of **4**. The intensity data were collected at 153 K (–120 °C) on a Stoe Mark II–Image Plate Diffraction System [13] using Mo Kα graphite monochromated radiation (λ = 0.710 73 Å). Image plate distance 120 mm, ω oscillation scans 0–180° at ϕ 0°, and ω oscillation scans 0–60° at ϕ 90°, step $\Delta\omega$ = 1°, 2θ range 1.91–54.78°, $d_{max} - d_{min}$ = 21.331 – 0.772 Å. The structure was solved by direct methods using the programme SHELXS-97 [14]. The refinement and all further calculations were carried out using SHELXL-97 [15]. The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least squares on F^2. A series of electron density peaks were located along the 2-fold axes, parallel to the crystallographic *b* axis, but it could not be identified clearly as a particular solvent molecule, for example ethylacetate. The SQUEEZE routine in PLATON [16] was used to modify the HKL file, and indicated an empty volume of approximately 503 Å^3 per unit cell, corresponding to 126 electrons per unit cell. This electron density was equated to half a molecule of ethylacetate per molecule of **4**.

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, as supplementary material No. CCDC 196642 and can be obtained by contacting the CCDC (fax: (+44) 1223 336 033; email: deposit@ccdc.cam.ac.uk).

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