DOI: 10.1002/ejoc.200600392

Synthesis and Characterization of Novel Tetrathiafulvalene-Type Electron Donors Bearing Two Pyridine Groups

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Keywords: Synthetic methods / TTF / X-ray diffraction / Cyclic voltammetry

The syntheses of seven new tetrathiafulvalene (TTF) derivatives substituted by two pyridine groups and their characterization by the usual methods are described. Cyclic voltammetry of all the compounds showed two one-electron reversible waves with redox potentials comparable to other pyridine-substituted TTF molecules. X-ray crystal structures were solved for five compounds. In all the molecular structures the pyridine groups lie out of the central TTF plane but are located on the same side of that plane.

Introduction

One of the current objectives in the field of conducting materials derived from tetrathiafulvalene (TTF) is to incorporate, within the same solid, two distinct physical properties such as magnetism and electronic conductivity while seeking to establish a magnetic coupling between the conduction electrons and the spins.[1] Most of such studied π–d materials have so far been based on organic salts composed of TTF radical cations and transition-metal anions acting as sources of conducting π- and d-electrons, respectively. As an alternative, paramagnetic transition-metal complexes involving redox-active ligands, such as pyridine-type heterocycles,[2–4] dithiolate,[5] acetylacetonate,[6] or phosphane substituents[7] covalently linked to TTF derivatives, have recently been studied. Magnetic transition-metal complexes with such ligands seem to be good candidates for increasing the interactions between the conducting electrons of ligands and the localized spins of the metal atom through coordination bonds.[1c] Although a large number of hybrid complexes have been reported, only a few have successfully been oxidized, showing an insulating behaviour arising from dimerization[4] and a lack of highly ordered stacking[7d] in the donor sublattice. Therefore, it is still a major challenge for synthetic chemists to design new π-donors containing coordinating substituents for constructing and controlling the self-assembly of molecular building blocks in an ordered manner and for obtaining materials with the desired structure, stability and physical properties. We present here the syntheses, spectroscopic characterizations, redox properties and X-ray structure analyses of a series of TTF-type molecules bearing two pyridine units.

Results and Discussion

Synthesis

The new series of electron donors **2a**, **3a** and **2b**–**6b** substituted by two pyridine rings were synthesized from the corresponding bis(cyanoethyl) precursors **1** (Scheme 1). These precursors, containing selenium and sulfur atoms, were first synthesized according to literature procedures.[8–11] Compounds **1** were then converted into the target molecules **2**–**6** through a deprotection/realkylation process:[12] the two cyanoethyl protecting groups were removed using an excess of sodium ethoxide in ethanol and the bis(thiolates) and bis(selenolates) thus formed were subsequently treated with the appropriate alkylating agents to give the expected compounds **2**–**6**.

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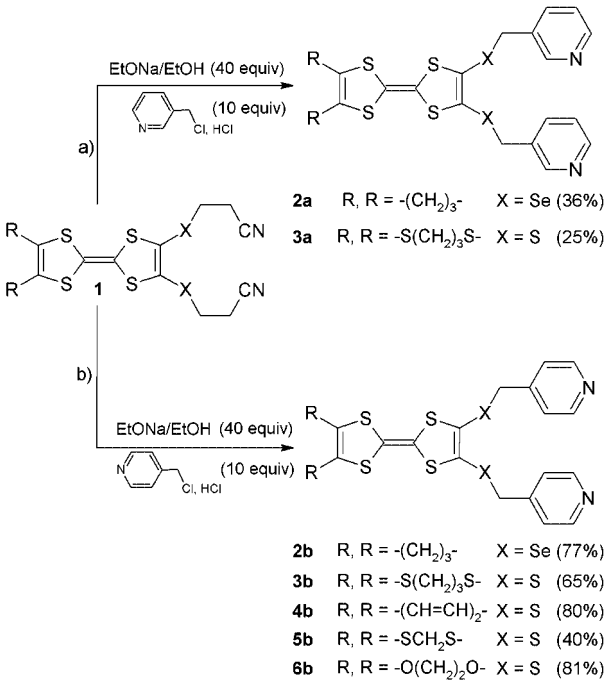

Scheme 1.

X-ray Structure Determination

ORTEP drawings of the X-ray structures of **2a**, **2b** and **4b**–**6b** are shown in Figure 1 and selected bond lengths are given in Table 1. For all the compounds discussed below, the S1–S2–C3–C4–S3–S4 atoms belonging to the TTF skeleton form the TTF mean plane whereas the six atoms of the NC_5 ring constitute the pyridyl mean planes.

Table 1. Selected bond lengths [Å].

	2a	2b	4b	5b	6b
C(1)–C(2)	1.334(6)	1.334(6)	1.349(4)	1.347(4)	1.335(7)
C(1)–S(1)	1.757(4)	1.761(4)	1.760(3)	1.760(3)	1.757(5)
C(2)–S(2)	1.758(4)	1.767(4)	1.765(3)	1.759(3)	1.757(5)
C(3)–C(4)	1.340(5)	1.356(6)	1.338(5)	1.339(4)	1.341(6)
C(3)–S(2)	1.754(4)	1.756(4)	1.757(3)	1.756(3)	1.758(6)
C(3)–S(1)	1.762(4)	1.760(4)	1.761(4)	1.750(3)	1.743(5)
C(4)–S(3)	1.764(4)	1.768(4)	1.759(3)	1.765(3)	1.760(6)
C(4)–S(4)	1.771(4)	1.758(4)	1.753(4)	1.762(4)	1.751(5)
C(5)–C(6)	1.320(5)	1.334(7)	1.406(5)	1.336(5)	1.312(8)
C(5)–S(3)	1.742(4)	1.748(4)	1.746(4)	1.746(4)	1.746(5)
C(6)–S(4)	1.740(4)	1.751(4)	1.761(3)	1.752(3)	1.745(6)

Compound 2a

The two pyridyl rings are located on the same side of the TTF mean plane. An angle of 39.5(2)° is observed between them, while the $N1C_5$ and $N2C_5$ rings form angles of 81.70(11) and 43.13(16)°, respectively, with the TTF mean plane. A significant short intermolecular contact occurs between two sulfur atoms from two adjacent molecules [S3···S3 = 3.453(2) Å]. Two TTF planes are packed along the *a*-direction, the shorter contacts being the *a*-parameter.

Compounds 2b, 4b and 5b

These three molecules are isostructural. Neither short S···S contacts nor TTF packing are observed between adjacent molecules. The two pyridyl rings are localized on the same side of the TTF mean plane with similar angles between the calculated mean planes: angles of 38.29(19), 41.10(14) and 38.44(14)° are observed between the two rings for **2b**, **4b** and **5b**, respectively. The $N1C_5$ ring forms an angle of 73.24(10), 73.88(7) and 73.88(7)° with the TTF mean plane in **2b**, **4b** and **5b**, respectively; likewise this mean

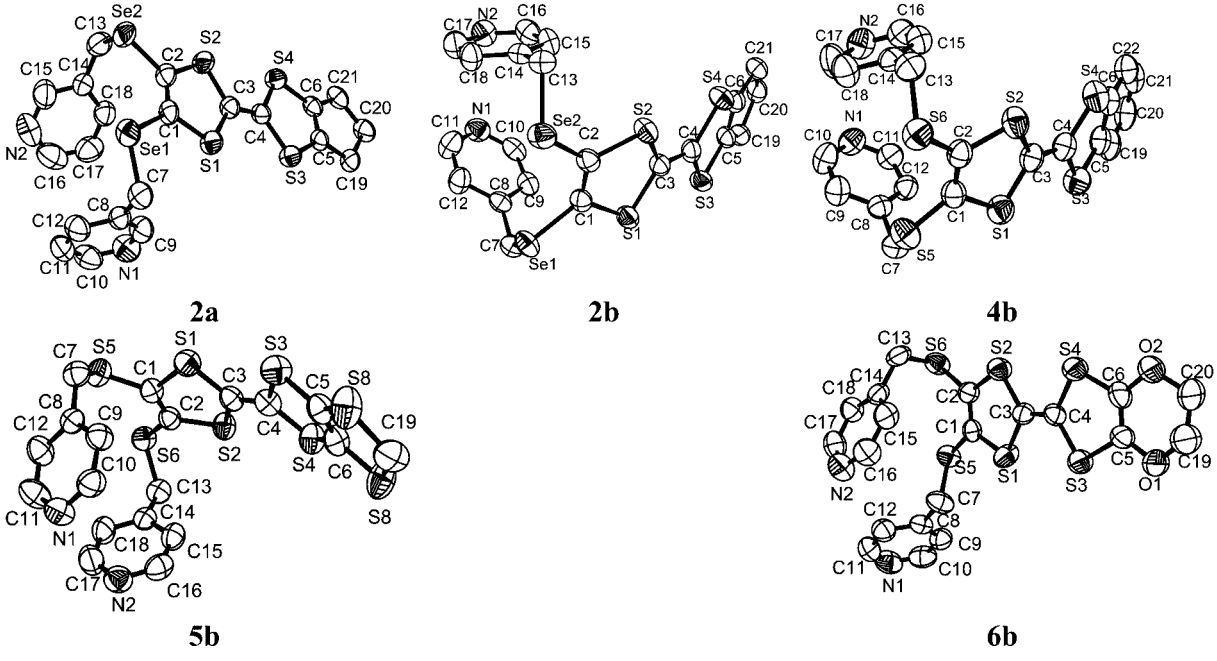

Figure 1. ORTEP diagram at the 50% probability level and atomic numbering schemes for **2a**, **2b**, **4b**, **5b** and **6b**.

plane forms an angle of 69.18(9), 69.17(9) and 72.61(6)° with $N2C_5$ in **2b**, **4b** and **5b**, respectively.

Compound 6b

In this molecule, the two pyridyl rings form an angle of 86.53(15)°, while the $N1C_5$ and $N2C_5$ rings form an angle with the TTF mean plane of 59.23(18) and 41.80(17)°, respectively. The shortest intermolecular contacts are in the van der Waals range and occur between two oxygen atoms of the ethylenedioxo fragments [O2···O2 2.992(8) Å] belonging to molecules lying in the same plane.

Redox Potentials

All the redox potentials were measured by cyclic voltammetry using platinum electrodes with an SCE as a reference electrode in dichloromethane solutions containing n-Bu_4PF_6 (0.1 M) and a scan rate of 100 mV s^{-1}. As expected, two reversible redox waves were observed.[2d,11c] The oxidation potentials (E_{OX1}, E_{OX2}) are given in Table 2 and compared with those of BEDT-TTF used as a reference. These values were found comparable to those reported for similar TTF derivatives containing pyridyl substituents.[2b–2d] Only compounds **2a** and **2b**, in which the electron-donating effect due to the peripheral ring [R,R = –$(CH_2)_3$–] is compensated for by the electron-donating effect of the pyridine rings, exhibit E_{OX1} values close to those of BEDT-TTF. All the other compounds are more difficult to oxidize due to a combination of the electron-withdrawing effects of the pyridine rings and of the heterocycles or benzo groups attached on the other side of the TTF core. Note also that the position of the nitrogen atom of the pyridine ring in either the *para* or the *meta* position has no effect on the redox potential value as shown by the E_{OX1} values of **2a**, **2b** (0.44 V) and **3a**, **3b** (0.61 V), respectively.

Table 2. Oxidation potentials measured by cyclic voltammetry.[a]

Compound	E_{OX1}[V]	E_{OX2}[V]
2a	0.44	0.87
3a	0.61	0.98
2b	0.44	0.87
3b	0.61	0.98
4b	0.64	1.00
5b	0.80	1.05
6b	0.80	1.05
BEDT-TTF	0.43	0.84

[a] Solvent: dichloromethane. Electrolyte: 0.1 M Bu_4NPF_6. Scan rate: 100 mV s^{-1}. Reference electrode: SCE. Working electrode: platinum.

Conclusions

A new series of TTF derivatives bearing two 3- or 4-pyridyl groups as side-chains has been synthesized and characterized. Their oxidation potentials and structures were determined by cyclic voltammetry and by X-ray diffraction. The synthesis of their coordination complexes with various transition metals is the subject of current investigations.

Experimental Section

General Procedures: All solvents were dried and distilled according to standard procedures; all experiments were carried out under argon. An ethanolic solution of sodium ethoxide prepared from Na (0.92 g) in anhydrous EtOH (40 mL) was added dropwise to a solution of **1** (1 mmol) in an anhydrous and degassed mixture of CH_2Cl_2/EtOH (50 mL, 3:1) at room temperature under argon. The colour of the reaction mixture changed from orange to brown during 6 h of stirring. Then, the appropriate alkyl halide (10 mmol) was added under argon, and the mixture was stirred overnight. The mixture was quenched with water and extracted with CH_2Cl_2, the organic layer was dried with $MgSO_4$, filtered, and concentrated in vacuo to afford a yellow-brown oil which was purified by column chromatography on silica gel, eluting initially with CH_2Cl_2 for **2a** and **3a** and with Et_2O for **2b**–**6b** and then with an ethyl acetate/methanol (2:1) mixture. Evaporation of the solvent in vacuo and crystallisation of the oil isolated from CH_2Cl_2/hexane (1:1) yielded the pure target compounds as powders. Single crystals were also obtained by slow evaporation of the solvents as described below.

Characterization: All the compounds were characterized by the usual analytical methods: ^{1}H and ^{13}C NMR (HMBC and HMQC) spectra were recorded with a Bruker Avance (300 and 500 MHz) spectrometer and all chemical shifts are referenced to Me_4Si (J values are given in Hz). Melting points were measured with a Kofler melting points apparatus. Cyclic voltammetry measurements were carried out with a Potentiostat eDAQ instrument. Elemental analyses were performed with a Microanalyser Flash EA1112 CHNS/O apparatus. IR spectra were measured with a Bruker Equinox 55 spectrometer. Mass spectra were measured with a JEOL JMS-700 spectrometer with nitrobenzyl alcohol as matrix. Single crystals of the title compounds were mounted on an Enraf–Nonius four-circle diffractometer equipped with a CCD camera and a graphite-monochromated Mo-K_α radiation source (λ = 0.71073 Å). Data collection was performed at room temperature. No absorption correction was performed and structures were solved with SHELXS-97 and refined with SHELXL-97[13] by full-matrix least-squares methods on F^2. Crystallographic data are summarised in Table 3. CCDC-604173 to -604177 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4,5-Bis(3-picolylseleno)-4′,5′-trimethylenetetrathiafulvalene (2a): The reaction was carried out starting with 4,5-bis(2-cyanoethylseleno)-4′,5′-trimethylenetetrathiafulvalene (510 mg, 1 mmol). Recrystallization was carried out by slow concentration of a hot mixture of CH_2Cl_2/hexane (1:1). Compound **2a** was obtained as brown crystals; yield 204 mg (36%); m.p. 116 °C. ^{1}H NMR ($CDCl_3$): δ = 2.40–2.45 (m, 2 H, CH_2), 2.51–2.57 (m, 4 H, CH_2), 3.91 (s, 4 H, CH_2Se), 7.19–7.23 (m, 2 H, pyridine), 7.51–7.55 (m, 2 H, pyridine), 8.46–8.49 (m, 4 H, pyridine) ppm. ^{13}C NMR (HMBC, HMQC, $CDCl_3$): δ = 27.69 ($CH_2CH_2CH_2$), 30.01 (CH_2Se), 30.18 ($CH_2CH_2CH_2$), 109.79 (C=C, ylidene), 121.34, 121.39 (SeC=CSe), 123.39 (CH, pyridine), 133.05 (CH_2C=CCH_2), 133.59 (C=CH), 136.36 (CH, pyridine), 148.54 (CH, pyridine), 150.04 (CH, pyridine) ppm. MS (FAB): found for $C_{21}H_{18}{}^{32}S_4{}^{80}Se_2N_2$ $[M]^{+\cdot}$ 586. $C_{21}H_{18}S_4Se_2N_2$ (584.56): calcd. C 43.14, H 3.10, N 4.79; found C 43.13, H 3.22, N 4.91. IR (KBr):

Table 3. Crystal data and structure refinement for **2a**, **2b** and **4b**–**6b**.

Compound	**2a**	**2b**	**4b**	**5b**	**6b**
Formula	$C_{21}H_{18}N_2S_4Se_2$	$C_{21}H_{18}N_2S_4Se_2$	$C_{22}H_{16}N_2S_6$	$C_{19}H_{14}N_2S_8$	$C_{20}H_{16}N_2O_2S_6$
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$	$C2/c$	$P2_1/c$
a [Å]	6.1790(1)	32.9622(9)	33.2641(10)	32.4218(12)	5.7072(3)
b [Å]	10.4634(2)	9.4119(2)	9.3094(4)	9.4909(3)	16.2133(10)
c [Å]	34.5966(8)	14.4659(4)	14.4259(4)	14.2989(6)	24.1363(15)
β [°]	91.649(1)	96.940(1)	96.956(3)	96.797(2)	93.831(3)
Z	4	8	8	8	4
μ [mm^{-1}]	3.693	3.706	0.630	0.828	0.635
Total reflns.	6967	17042	8341	8582	5992
Unique reflns.	4406	4905	4305	4434	3774
R(int)	0.0295	0.0926	0.0337	0.0292	0.0641
R_1[a] [$I > 2\sigma(I)$]	0.0424 [2877]	0.0511 [3479]	0.0438 [2511]	0.0421 [2846]	0.0616 [2128]
wR_2[b]	0.0900	0.1218	0.1011	0.0974	0.1300
R_1[a] [all data]	0.0819	0.0786	0.0929	0.0797	0.1247
wR_2[b]	0.1047	0.1387	0.1254	0.1150	0.1626

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}$.

$\tilde{\nu}_{max}$ = 3551, 3480, 3413, 3236, 2851, 1638, 1617, 1572, 1477, 1422, 1310, 1184, 1094, 1024, 819, 805, 762, 709, 630, 430 cm^{-1}.

4,5-Bis(3-picolylthio)-4′,5′-trimethylenedithiotetrathiafulvalene (3a): The reaction was carried out starting with 4,5-bis(2-cyanoethylthio)-4′,5′-trimethylenedithiotetrathiafulvalene (478 mg, 1 mmol). Compound **3a** was obtained as brown crystals; yield 120 mg (25%); m.p. 138 °C. ^{1}H NMR ($CDCl_3$): δ = 2.35–2.47 (m, 2 H, CH_2), 2.66–2.74 (m, 4 H, CH_2), 3.82 (s, 4 H, CH_2), 7.20–7.30 (m, 2 H, pyridine), 7.56–7.57 (m, 2 H, pyridine), 8.40–8.67 (m, 4 H, pyridine) ppm. ^{13}C NMR (HMBC, HMQC, $CDCl_3$): δ = 33.09 (CH_2CH_2S), 34.39 (CH_2CH_2S), 37.79(CH_2S), 109.97, 114.00 (C=C, ylidene), 123.56 (CH, pyridine), 129.24 ($CSCH_2C$), 130.50 ($CSCH_2CH_2CH_2$), 132.58 (C=CH), 136.48 (CH, pyridine), 148.86 (CH, pyridine), 150.02 (CH, pyridine) ppm. MS (FAB): found for $C_{21}H_{18}{}^{32}S_8N_2$ $[M]^{+\cdot}$ 554. $C_{21}H_{18}S_8N_2$ (554.91): calcd. C 45.45, H 3.27, N 5.05; found C 45.41, H 3.25, N 5.08. IR (KBr): $\tilde{\nu}_{max}$ = 3552, 3479, 3414, 3235, 1637, 1617, 1575, 1475, 1420, 1275, 1187, 1025, 894, 713, 628, 477 cm^{-1}.

4,5-Bis(4-picolylseleno)-4′,5′-trimethylenetetrathiafulvalene (2b): The reaction was carried out starting with 4,5-bis(2-cyanoethylseleno)-4′,5′-trimethylenetetrathiafulvalene (510 mg, 1 mmol). Recrystallization was carried out by slow concentration of a solution in ethyl acetate/methanol (2:1). Compound **2b** was obtained as brown crystals; yield 434 mg (77%); m.p. 134 °C. ^{1}H NMR ($CDCl_3$): δ = 2.36–2.48 (m, 2 H, CH_2), 2.49–2.59 (m, 4 H, CH_2), 3.84 (s, 4 H, CH_2Se), 7.13 (d, ^3J = 4.81 Hz, 4 H, pyridine), 8.51 (d, ^3J = 4.27 Hz, 4 H, pyridine) ppm. ^{13}C NMR (HMBC, HMQC, $CDCl_3$): δ = 27.70 ($CH_2CH_2CH_2$), 30.20 ($CH_2CH_2CH_2$), 31.71 (CH_2Se), 109.31 (C=C, ylidene), 121.77, 121.95 (SeC=CSe), 123.85 (CH, pyridine), 133.04 ($CH_2C=CCH_2$), 146.69 (C=CH), 149.92 (CH, pyridine) ppm. MS (FAB): found for $C_{21}H_{18}{}^{32}S_4{}^{80}Se_2N_2$ $[M]^+$ 586. $C_{21}H_{18}S_4Se_2N_2$ (584.56): calcd. C 43.14, H 3.10, N 4.79; found C 43.14, H 3.10, N 3.25. IR (KBr): $\tilde{\nu}_{max}$ = 3548, 3478, 3415, 2847, 1598, 1557, 1495, 1449, 1415, 1225, 991, 812, 764, 616, 559 and 461 cm^{-1}.

4,5-Bis(4-picolylthio)-4′,5′-trimethylenedithiotetrathiafulvalene (3b): The reaction was carried out starting with 4,5-bis(2-cyanoethylthio)-4′,5′-trimethylenedithiotetrathiafulvalene (429 mg, 0.90 mmol). Compound **3b** was obtained as brown crystals; yield 314 mg (30%); m.p. 157 °C. ^{1}H NMR ($CDCl_3$): δ = 2.41–2.49 (m, 2 H, CH_2), 2.68–2.72 (m, 4 H, CH_2), 3.77 (s, 4 H, CH_2), 7.17 (d, ^3J = 5.81 Hz, 4 H, pyridine), 8.55 (d, ^3J = 5.88 Hz, 4 H, pyridine) ppm. ^{13}C NMR (HMBC, HMQC, $CDCl_3$): δ = 33.11 (CH_2CH_2S), 34.37 (CH_2CH_2S), 39.38 (CH_2S), 109.76, 114.37 (C=C, ylidene), 123.83 (CH, pyridine), 129.13 ($CSCH_2C$), 130.46 ($CSCH_2CH_2CH_2$), 145.60 (C=CH), 150.08 (CH, pyridine) ppm. MS (FAB): found for $C_{21}H_{18}{}^{32}S_8N_2$ $[M]^+$ 554. $C_{21}H_{18}S_8N_2$ (554.91): calcd. C 45.45, H 3.27, N 5.05; found C 45.43, H 3.30, N 5.10. IR (KBr): $\tilde{\nu}_{max}$ = 3547, 3476, 3415, 1636, 1617, 1600, 1503, 1412, 1275, 1133, 1109, 992, 889, 813, 770, 619, 483 cm^{-1}.

4,5-Bis(4-picolylthio)-4′,5′-benzotetrathiafulvalene (4b): The reaction was carried out starting with 4,5-bis(2-cyanoethylthio)-4′,5′-benzotetrathiafulvalene (424 mg, 2.36 mmol). Recrystallization was carried out by slow concentration of a solution in CH_2Cl_2/petroleum ether (2:1). Compound **4b** was obtained as yellow crystals; yield 385 mg (80%); m.p. 168 °C. ^{1}H NMR ($CDCl_3$): δ = 3.87 (s, 2 H, CH_2), 7.12–7.14 (m, 2 H, benzene), 7.16 (d, ^3J = 5.78 Hz, 4 H, pyridine), 7.23–7.26 (m, 2 H, benzene), 8.54 (d, ^3J = 5.89 Hz, 4 H, pyridine) ppm. ^{13}C NMR (HMBC, HMQC, $CDCl_3$): δ = 39.35 (CH_2), 108.06, 113.44 (C=C, ylidene), 122.00 (CH, benzene), 123.85 (CH, pyridine), 126.11 (CH, benzene), 129.22 ($CSCH_2C$), 136.30 (HCC=CCH), 145.66 (C=CH), 150.07 (CH, pyridine) ppm. MS (FAB): found for $C_{22}H_{16}{}^{32}S_6N_2$ $[M]^+$ 500. $C_{22}H_{16}S_6N_2$ (500.77): calcd. C 52.77, H 3.22, N 5.59; found C 52.66, H 3.20, N 5.54. IR (KBr): $\tilde{\nu}_{max}$ = 3552, 3412, 1616, 1601, 1561, 1444,1433, 1417, 1115, 992, 868, 816, 772, 744, 677, 573, 479 cm^{-1}.

4,5-Bis(4-picolylthio)-4′,5′-methylenedithiotetrathiafulvalene (5b): The reaction was carried out starting with 4,5-bis(2-cyanoethylthio)-4′,5′-methylenedithiotetrathiafulvalene (500 mg, 1.1 mmol). Recrystallization was carried out by concentration of a hot solution in CH_2Cl_2/hexane (1:1). Compound **5b** was obtained as yellow crystals; yield 205 mg (40%); m.p. 141 °C. ^{1}H NMR ($CDCl_3$): δ = 3.77 (s, 2 H, CH_2), 4.94 (s, 4 H, CH_2), 7.95 (d, ^3J = 5.90 Hz, 4 H, pyridine), 8.53 (d, ^3J = 5.97 Hz, 4 H, pyridine) ppm. ^{13}C NMR (HMBC, HMQC, $CDCl_3$): δ = 39.36 (SCH_2S), 45.22 (SCH_2C), 117.61, 118.31 (C=C, ylidene), 123.94 (CH, pyridine),124.21 ($CSCH_2C$), 129.22 ($CSCH_2S$), 145.52 (C=CH), 150.15 (CH, pyridine) ppm. MS (FAB): found for $C_{19}H_{14}{}^{32}S_8N_2$ $[M]^+$ 526. $C_{19}H_{14}S_8N_2$ (526.86): calcd. C 43.31, H 2.68, N 5.32; found C

43.55, H 2.73, N 5.16. IR (KBr): $\tilde{\nu}_{max}$ = 3555, 3416, 3234, 1638, 1616, 1600, 1412, 1384, 1114, 890, 812, 770, 621, 484 cm^{-1}.

4,5-Bis(4-picolylthio)-4′,5′-ethylenedioxytetrathiafulvalene (6b): The reaction was carried out starting with 4,5-bis(2-cyanoethylthio)-4′,5′-ethylenedioxytetrathiafulvalene (124 mg, 2.87 mmol). Recrystallization was carried out by slow concentration of a solution in ethyl acetate/methanol (2:1). Compound **6b** was obtained as red-orange crystals; yield 118 mg (81%); m.p. 125 °C. ^{1}H NMR ($CDCl_3$): δ = 3.77 (s, 2 H, CH_2), 4.94 (s, 4 H, CH_2), 7.95 (d, ^3J = 5.9 Hz, 4 H, pyridine), 8.53 (d, ^3J = 5.97 Hz, 4 H, pyridine) ppm. ^{13}C NMR (HMBC, HMQC, $CDCl_3$): δ = 39.36 (SCH_2S), 45.22 (SCH_2C), 117.61, 118.31 (C=C, ylidene), 123.94 (CH, pyridine),124.21 ($CSCH_2C$), 129.22 ($CSCH_2S$), 145.52 (C=CH), 150.15 (CH, pyridine) ppm. MS (FAB): found for $C_{20}H_{16}{}^{32}S_6N_2O_2$ $[M]^+$ 508. $C_{20}H_{16}S_6N_2O_2$ (508.75): calcd. C 47.22, H 3.17, N 5.51; found C 46.84, H 3.11, N 5.57. IR (KBr): $\tilde{\nu}_{max}$ = 3549, 3479, 3413, 1653,1617, 1596, 1559 1411, 1166, 1083, 949, 866, 835, 816, 772, 658, 572, 498, 486 cm^{-1}.

Acknowledgments

This work was supported by the CNRS, the EU through MAGMANet and la Région Bretagne (projects SIE no. 05012917 and PRIR no. 05013053). N. B. thanks the Algerian and French Ministries of Education for a scholarship.

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Received: May 3, 2006
Published Online: July 25, 2006

