Facile Syntheses of 4-(2-Cyanoethylthio)-1,3-dithiole-2-thione and New Electron Donors with Two TTF Units and Compounds with Bis(1,3-dithiole-2-thione) Groups

Chunyang Jia, Deqing Zhang,* Xuefeng Guo, Shuhui Wan, Wei Xu, Daoben Zhu*

Organic Solids Laboratory, Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China
E-mail: dqzhang@infoc3.icas.ac.cn

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Abstract: The synthetic conditions for the preparation of 4-(2-cyanoethylthio)-1,3-dithiole-2-thione (**1**) from $TBA_2{\cdot}[Zn(dmit)_2]$ were studied. Compound **1** was used to synthesize new electron donors with two tetrathiafulvalene (TTF) units. Other interesting compounds that are good precursors for tetrathiafulvalenophanes were also easily prepared from $TBA_2{\cdot}[Zn(dmit)_2]$.

Key words: electron donors, tetrathiafulvalene, cyclophane, 1,3-dithiole-2-thione, 1,3-dithiole-2-thione-4,5-dithiolate

As the key compound for the preparation of tetrathiafulvalene (TTF) derivatives, 4,5-bis(alkylthio)-1,3-dithiole-2-thiones can be conventionally synthesized from the zinc complex of 1,3-dithiole-2-thione-4,5-dithiolate {$TBA_2{\cdot}[Zn(dmit)_2]$, TBA: tetrabutylammonium} or the anion of 1,3-dithiole-2-thione-4,5-dithiolate generated in situ.[1] In comparison, its analogue, 4-alkylthio-1,3-dithiole-2-thione is not easily accessible.[2] We have just recently reported that 4-alkylthio-1,3-dithiole-2-thione can be synthesized easily starting from $TBA_2{\cdot}[Zn(dmit)_2]$ and electrophilic reagents such as 3-bromopropionitrile in the presence of pyridine hydrochloride.[3] Since 2-cyanoethyl is a good protecting group for thiolates,[4] 4-(2-cyanoethylthio)-1,3-dithiole-2-thione (**1**) is a suitable precursor for the preparation of new electron donors (Figure 1). For example, **1** can be converted easily to 4-(2-cyanoethylthio)-1,3-dithiole-2-one (**2**) with $Hg(OAc)_2$, and new electron donor molecules such as **3** and **4** with 2-cyanoethyl group can be prepared through the cross-coupling of **2** and 4,5-ethylenedithio-1,3-dithiole-2-thione and 4,5-bis(methylthio)-1,3-dithiole-2-thione, respectively, in the presence of trialkyl phosphite.[5] By removal of the 2-cyanoethyl group from **3** and **4** and subsequently reaction with bis-electrophilic reagents, new electron donors such as **5**–**9** (Figure 1) with two TTF units can be obtained from the easily accessible reactants in a rather straightforward way. These electron donors are interesting for studies of organic conductors since higher than one dimensional and different stoichiometric charge-transfer complexes may result from them.[6] In particular, they may be useful for the construction of molecular spin-ladder systems.[7] In addition, interesting compounds that are good precursors for tetrathiafulvalenophanes[8] can be also easily prepared based on the unusual reaction of $TBA_2{\cdot}[Zn(dmit)_2]$.[3] Herein we report the syntheses of **1** under different conditions and compounds with bis(1,3-dithiole-2-thione) groups by the facile approach described by us recently[3] as well as the synthesis of new electron donors with two TTF units. Oxidation potentials of these new electron donors are also described.

It was assumed that 4,5-dimercapto-1,3-dithiole-2-thione (**10**)[3,9] was the important intermediate compound for the formation of **1** starting from $TBA_2{\cdot}[Zn(dmit)_2]$ and 3-bromopropionitrile as shown in Scheme 1. But, when the reaction was performed in the presence of four equivalents (based on $TBA_2{\cdot}[Zn(dmit)_2]$) of acids such as acetic acid and *p*-toluenesulfonic acid, compound **1** was not detected in the reaction mixture. By reducing the amounts of acids, only 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione (**11**) separated out in rather low yield and again compound **1** was not found in the reaction mixture. Thus, it may be inferred that pyridine hydrochloride would be a suitable reagent, while it is a mild acid and its conjugate base – pyridine is a mild base, and is essential for the reaction to generate **1** (Scheme 1). Besides pyridine hydrochloride, several commercially available ammonium salts and the mixture of sodium acetate and acetic acid (in 1:1 molar ratio) were tried for the reaction under the same condition as in the case of pyridine hydrochloride (see Table 1). For comparison, the yields of **1** and **11** generated from the reaction (Scheme 1) in the presence of pyridine hydrochloride were also included in Table 1. In the cases of ammonium chloride and the mixture of sodium acetate and acetic acid, compound **1** was not formed and only compound **11** was obtained in a low yield. This may be attributed to the low solubilities of ammonium chloride and sodium acetate in the reaction medium (MeCN). But, it may be also due to the weak acidic character of ammonium chloride and weak basic character of sodium acetate. On the contrary, the results indicated that the hydrochloride salts of triethylamine, aniline and *p*-diaminobenzene can be employed for the reaction (Scheme 1) to induce the formation of **1**. It is expected that other organic ammonium salts can be also used for the reaction to generate compound **1**.

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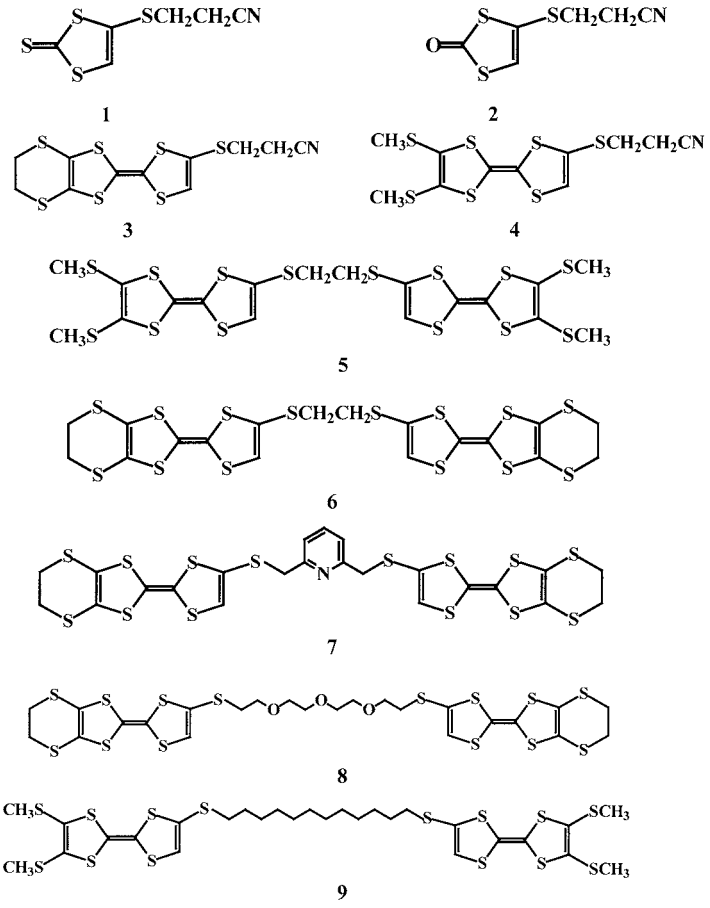
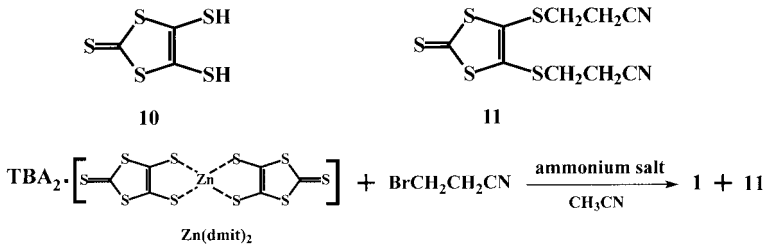


Figure 1 The structures of compounds **1**–**9**

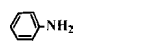


Scheme 1 Synthesis of compound **1**

As an example, the effect of the quantity of pyridine hydrochloride used on the yield of **1** was studied (Table 1). When the molar ratio of pyridine hydrochloride versus $TBA_2{\cdot}[Zn(dmit)_2]$ was less than four, the yield of **1** was lower and more **11** was produced. But, if the molar ratio of pyridine hydrochloride versus $TBA_2{\cdot}[Zn(dmit)_2]$ was larger than four, the yield of **1** was not increased largely. The optimal molar ratio was about four. This may be explained as following: four equivalents of pyridine hydrochloride probably converted most of the $TBA_2{\cdot}[Zn(dmit)_2]$ into **10** and liberate the free base (pyridine) which may be involved in the further reaction of **10** to generate **1**. If limited amounts of pyridine hydrochloride were used, probably $TBA_2{\cdot}[Zn(dmit)_2]$ was only partially transformed into **10**, and the rest of $TBA_2{\cdot}[Zn(dmit)_2]$ will react directly with 3-bromopropionitrile to give **11**. Consequently, the yield of **1** will be lowered. In short, compound **1** can be synthesized from the easily accessible reactants with four equivalents of an organic ammonium salt in ca. 70% yield.

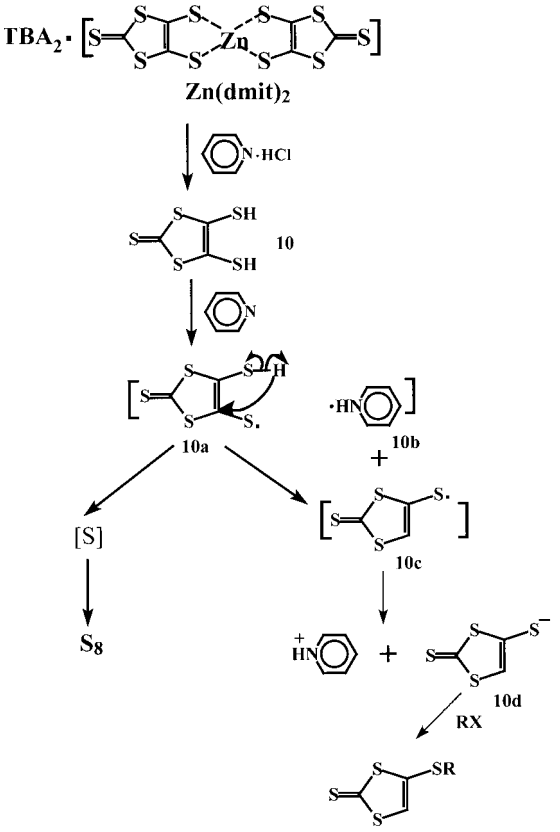
Based on the above observations and the previous results,[3,9] the following mechanism was tentatively suggested for the unusual reaction of $Zn(dmit)_2$ ion (Scheme 2). Compound **10** was supposed to be the key intermediate. Probably with the help of pyridine, homo-cleavage of S–H bond generates radical intermediates **10a** and **10b**. From **10a**, further cleavage of the neighboring S–H bond and intramolecular migration of hydrogen radical would lead to the radical intermediate **10c** and free sulfur. This is in accordance with the separation of S_8 in the reaction mixture. Electron-transfer reaction between **10b** and **10c**

Table 1 Yields of **1** and **11** for the Reaction (Scheme 1) in the Presence of Different Ammonium Salts and the Mixture of Sodium Acetate and Acetic Acid

Product	CH_3CO_2Na	NH_4Cl		NEt_3				
	AcOH		HCl	HCl	HCl	HCl	HCl	HCl
1	0[a]	0[a]	58%[a]	35%[a]	63%[a]	70%[a]	35%[b]	72%[c]
11	~35%	~35%	45%	61%	25%	17%	47%	13%

[a] The reaction was performed with 4 equivalents of ammonium salts and a mixture of NaOAc and AcOH, and the yields were based on the $[Zn(dmit)_2]$.
[b] The reaction was performed with 1 equivalent of pyridine hydrochloride.
[c] The reaction was performed with 10 equivalents of pyridine hydrochloride.

should afford 4-thio-1,3-dithiole-2-thione anion (**10d**), which will react with suitable electrophilic reagents to produce the analogues of **1**.



Scheme 2 The possible reaction mechanism for the unusual reaction of $Zn(dmit)_2$ ion

Since the 2-cyanoethyl group can be easily removed under basic condition,[4] **1** is a potentially good starting compound for the synthesis of new electron donors and related interesting molecules. For instance, **1** was converted to **2** with $Hg(OAc)_2$, and **3** and **4** can be prepared by the conventional cross-coupling procedure effected by tri(isopropyl) phosphite in yields of 73 and 56%, respectively (Scheme 3). The deprotection of 2-cyanoethyl group resulted in the formation of the corresponding thiolates in situ, which subsequently reacted with bis-electrophilic reagents such as 1,2-dibromoethane to afford new electron donors with two TTF units **5**–**9**. Analogues of these new electron donors were synthesized by different multi-step approaches.[10]

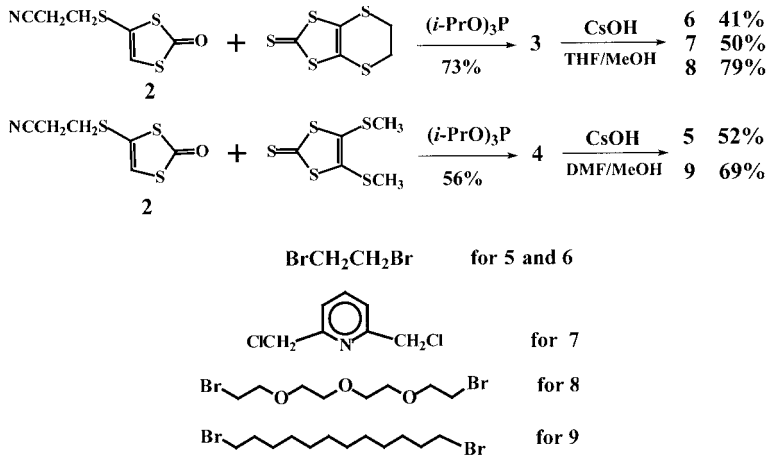
The oxidation potentials of these new electron donors were measured with cyclic voltammetry, and the results are summarized in Table 2. As examples, the cyclic voltammograms of **7** and **9** are shown in Figure 2. For **5**, **6** and **7**, three distinct redox-waves were observed. By comparing with the electrochemical behaviors of analogous electron donors described previously,[11] the first two waves might correspond to two one-electron redox processes, and the third was probably due to a two-electron redox process. On the other hand, only two redox waves were detected for **8** and **9**, which implied that the two TTF units were independent and they could be oxidized simultaneously. Investigations of their charge-transfer salts are in progress.

Table 2 Redox Potentials of **3**–**9** Measured by Cyclic Voltammetry[a]

Compound	$E_{1/2}^1$(V)	$E_{1/2}^2$(V)	$E_{1/2}^3$(V)
3	0.49	0.85	–
4	0.52	0.88	–
5	0.37	0.48	0.80
6	0.38	0.52	0.81
7	0.40	0.54	0.86
8	0.44	0.81	–
9	0.46	0.86	–

[a] All measurements were performed in CH_2Cl_2 containing 0.1 M Bu_4NPF_6, with SCE as the reference electrode, platinum as working and counter electrodes.

Under similar conditions, $TBA_2{\cdot}[Zn(dmit)_2]$ reacted directly with bis-electrophilic reagents such as 1,3-dibromopropane in the presence of pyridine hydrochloride to afford compounds **12** and **13** with bis(1,3-dithiole-2-thione) groups (see Scheme 4). The yields of **12** and **13**



Scheme 3 Synthesis of new electron donors **5**–**9**

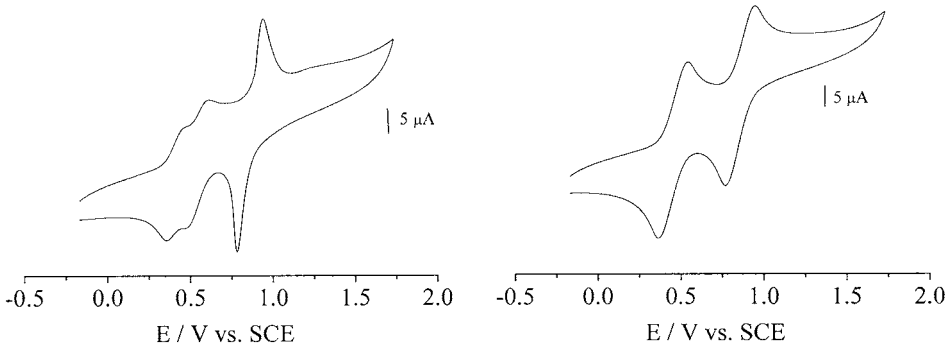
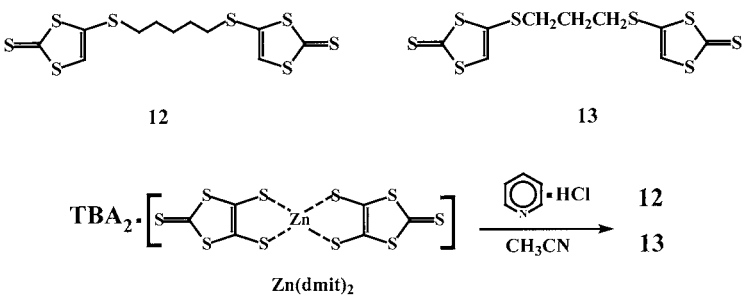


Figure 2 Cyclic voltammograms of **7** (left) and **9** (right)

were low (about 20%), which was probably due to the formation of compounds with only one 1,3-dithiole-2-thione group. Although the yields were not high, the present approach to compounds with bis(1,3-dithiole-2-thione) groups was rather simple in terms of the easiness to obtain the reactants and perform the reaction and separation in comparison with the synthetic method for their analogues.[10a] Efforts are underway to optimize the reaction condition and hence improve the yields. These compounds (e.g. **12** and **13**) are good precursors for the tetrathiafulavenophanes and other interesting molecules with TTF units.[8]

In summary, on the basis of our recent work, a facile and efficient approach to **1** was developed and the synthetic conditions were studied. Its synthetic applications were demonstrated by the efficient preparations of new electron donors **5**–**9** with two TTF units. Compounds like **12** and **13** with bis(1,3-dithiole-2-thione) groups can also be synthesized from $TBA_2{\cdot}[Zn(dmit)_2]$ in a simple manner.

Melting points were measured with an XT4-100 microscope apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Unity 200 (Varian) and Bruker 300 MHz instruments. IR spectra were recorded on a Pekin-Elmer 2000 FT-IR spectrometer. Mass spectra were recorded on AEI-MS50 for EI-MS, KYKY-ZH-P-5 for FAB-MS and Beflex III for TOF-MS. Elemental analyses were per-



Scheme 4 Synthesis of compounds **12** and **13**

formed on a Carlo-Erba-1106 instrument. Cyclic voltammetric measurements were carried out on an EGDG PAR 370 system.

Pyridine hydrochloride and 1,12-dibromodecane were purchased from Acros Chemicals. 1,11-Dibromo-3,6,9-trioxoundecane was synthesized from tetraethylene glycol, Ph_3P and CBr_4 with the conventional method. TBA·[Zn(dmit)$_2$] was prepared according to Ref.[1]. All other chemicals and solvents were from Beijing Chemical Company, and were used as received. The petroleum ether used had a bp range of 60–90 °C.

4-(2-Cyanoethylthio)-1,3-dithiole-2-thione (1)
This was prepared as described in Ref. 3. Different organic amine salts as well as NH_4Cl and NaOAc/AcOH were tried and the results are summarized in Table 1.

4-(2-Cyanoethylthio)-1,3-dithiole-2-one (2)
To a solution of compound **1**[3] (0.27 g, 1.23 mmol) in CH_2Cl_2 (45 mL) was added $Hg(OAc)_2$ (1.18 g, 3.69 mmol) and the mixture was stirred at 20 °C for 1 h. The white precipitate was removed by filtration through Celite and the filtrate was washed with CH_2Cl_2. The solvent was removed to afford compound **2** as a colorless powder; yield: 200 mg (80%); mp 56–57 °C.

FT-IR (KBr): 2247 (C≡N), 1632 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 2.75 (t, *J* = 6.8 Hz, 2 H, CH_2S), 3.06 (t, *J* = 6.8 Hz, 2 H, CH_2CN), 7.12 [s, 1 H, CH=CS(S)].

MS(EI): *m*/*z* = 203 (M^+).

Anal. Calcd. for $C_6H_5NOS_3$: C 35.45; H 2.48; N 6.89; Found: C 35.29; H 2.37; N 6.77.

Compound 3
A solution of compound **2** (0.5 g, 2.46 mmol) and 4,5-bis(ethylenethio)-1,3-dithiole-2-thione (1.66 g, 7.39 mmol) in tri(isopropyl) phosphite (20 mL) was heated to 120 °C under N_2 and stirred at this temperature for 3 h. Column chromatography of the crude reaction mixture, after the removal of excess tri(isopropyl) phosphite under reduced pressure, on silica gel with CH_2Cl_2–petroleum ether (1:1, v/v) afforded compound **3** as a red powder; yield: 681 mg (73%); mp 119–120 °C.

FT-IR (KBr): 2248 cm^{-1} (C≡N).

^{1}H NMR ($CDCl_3$): δ = 2.73 (t, *J* = 6.9 Hz, 2 H, CH_2S), 3.02 (t, *J* = 6.9 Hz, 2 H, CH_2CN), 3.34 (s, 4 H, CH_2CH_2), 6.61 [s, 1 H, CH=CS(S)].

MS (EI): *m*/*z* = 379 (M^+).

Anal. Calcd for $C_{11}H_9NS_7$: C, 34.80; H, 2.39; N, 3.69. Found: C, 34.55; H, 2.28; N, 3.32.

Compound 4
This was prepared in a similar way as for **3** and isolated as a red powder; yield: 56%; mp 102–104 °C.

IR (KBr): 2251 cm^{-1} (C≡N).

^{1}H NMR ($CDCl_3$): δ = 2.42 (s, 6 H, SCH_3), 2.58 (t, *J* = 7.3 Hz, 2 H, CH_2S), 2.93 (t, *J* = 7.3 Hz, 2 H, CH_2CN), 6.61 [s, 1 H, CH=CS(S)].

MS (EI): *m*/*z* = 381 (M^+).

Anal. Calcd for $C_{11}H_{11}NS_7$: C, 34.62; H, 2.91; N, 3.67. Found: C, 34.80; H, 2.82; N, 3.58.

Compound 5; Typical Procedure
To a solution of **4** (0.19 g, 0.5 mmol) in THF (20 mL) under N_2 was added a solution of CsOH·H_2O (0.994 g, 0.59 mmol) in MeOH (10 mL). The mixture was stirred for 0.5 h at r.t., and then 1,2-dibromoethane (0.02 mL, 0.25 mmol) in THF (5 mL) was added. After stirring for 12 h, the mixture was concentrated in vacuo. The product was subjected to column chromatography with a mixture of petroleum ether–CH_2Cl_2 (2:1, v/v) affording **5** as a yellow crystalline solid. The crude product was recrystallized from $CHCl_3$–hexane to give yellow micro-needles of **5**; yield: 0.089 g (52%); mp 160–162 °C.

IR (KBr): 2922, 2854, 1636, 1495, 1417, 1261 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.44 (s, 12 H, SCH_3), 2.96 (s, 4 H, SCH_2CH_2S), 6.43 [s, 2 H, CH=CS(S)].

MS (TOF): *m*/*z* = 682 (M^+).

Anal. Calcd for $C_{18}H_{18}S_{14}$: C, 31.68; H, 2.66; Found: C, 31.53; H 2.55.

Compounds **6**–**9** were prepared similar to **5**.

6
Yield: 41%; yellow micro-needles; mp 113–115 °C.

IR (KBr): 2920, 1645, 1417, 1288 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.95(s, 4 H, SCH_2CH_2S), 3.29 (s, 8 H, CH_2CH_2), 6.43 [s, 2 H, CH=CS(S)].

MS (EI): *m*/*z* = 678 (M^+).

Anal. Calcd for $C_{18}H_{14}S_{14}$: C, 31.83; H, 2.08. Found: C, 31.80; H, 2.09.

7
Yield: 50%; yellow powder; mp 164–166 °C.

IR (KBr): 3067, 2922, 1632, 1587, 1452, 1407 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.29 (s, 8 H, CH_2CH_2), 4.05(s, 4 H, SCH_2), 6.22 [s, 2 H, CH=CS(S)], 7.15 (d, *J* = 5.8 Hz, 2 H, pyridine ring), 7.62 (t, *J* = 5.8 Hz, 1 H, pyridine ring).

FAB-MS: *m*/*z* = 756 (M + 1).

Anal. Calcd for $C_{23}H_{17}NS_{14}$: C, 36.57; H, 2.27; N, 1.86. Found: C, 36.65; H, 2.21; N, 1.73.

8
Yield; 79%; red oil.

IR (KBr): 2920, 2865, 1554, 1469, 1409 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.93 (t, *J* = 4.8 Hz, 4 H, SCH_2), 3.28 (s, 8 H, CH_2CH_2), 3.63 ('br's, 8 H, OCH_2CH_2O), 3.66 (t, *J* = 4.8 Hz, 4 H, OCH_2), 6.42 [s, 2 H, CH=CS(S)].

MS(TOF): *m*/*z* = 811 (M + 1).

Anal. Calcd for $C_{24}H_{26}S_{14}O_3$: C, 35.53; H, 3.23. Found: C, 35.38; H, 3.20.

9
Yield: 69%; red-brown powder; mp 88–89 °C.

IR (KBr): 2921, 2850, 1555, 1485, 1426 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.22–1.38 (m, 16 H, CH_2), 1.48–1.72 (m, 4 H, CH_2), 2.43 (s, 12 H, SCH_3), 2.74 (t, *J* = 7.6 Hz, 4 H, SCH_2), 6.33 [s, 2 H, CH=CS(S)].

MS(TOF): *m*/*z* = 822 (M^+).

Anal. Calcd for $C_{28}H_{38}S_{14}$: C, 40.84; H, 4.65. Found: C, 41.27; H, 4.71.

Compound 12
To a solution of TBA$_2$·[Zn(dmit)$_2$] (940 mg, 1.0 mmol) in MeCN (50 mL) weree added 1,5-dibromopentane (0.14 mL, 1.0 mmol) and pyridine hydrochloride (462.2 mg, 4.0 mmol). The mixture was heated to 50–60 °C and stirred for 2 h at this temperature. The resulting mixture was filtered hot and the remaining solid was further washed with CH_2Cl_2 (3 × 20 mL) for complete extraction of the

product. The combined filtrate and washings were decolorized by use of activated charcoal. After removal of the solvent, column chromatography of the crude reaction mixture on silica gel with CH_2Cl_2–petroleum ether (1:4, v/v) as eluent afforded compound **1** as a yellow solid (72 mg, 18%); mp 80–82 °C.

IR (KBr): 1432, 1060, 1046 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.60–1.90 (m, 6 H, $CH_2CH_2CH_2$), 2.85 (t, *J* = 7.2 Hz, 4 H, SCH_2), 7.02 [s, 2 H, CH=CS(S)].

MS(EI): *m*/*z* = 400 (M^+).

Anal. Calcd for $C_{11}H_{12}S_8$: C, 33.97; H, 3.02, Found: C, 32.59; H, 2.79.

Compound 13

This was prepared according to the same procedure as above; yield: 21%; yellow powder; mp 72–73 °C.

IR (KBr): 1413, 1331, 1264, 1186, 1061 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.01 (quint, *J* = 7.4 Hz, 2 H, CH_2), 2.93 (t, *J* = 7.4 Hz, 4 H, SCH_2), 7.07 [s, 2 H, CH=CS(S)].

MS(EI): *m*/*z* = 372 (M^+).

Anal. Calcd for $C_9H_8S_8$: C, 29.04; H, 2.17. Found: C, 29.20; H, 2.10.

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