Facile Synthesis of Novel Functionalized Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) Derivatives

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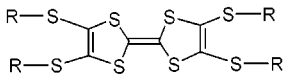
Abstract: An improved and efficient synthetic route to four functionalized bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) derivatives **2**−**5** is reported. Tetrathiolate **1** was readily prepared from 2,2′-bis(1,3,4,6-tetrathiapentalen-5-one) under carefully controlled conditions. Subsequent reaction of **1** with selected primary alkyl halides affords new functionalized BEDT-TTF derivatives in good yields.

Since 1985, the syntheses of new functionalized tetrathiafulvalene (TTF) derivatives have paved the way for the use of the TTF system as a building block within the wider context of supramolecular and materials chemistry,[1] for example, as redox-active components in Langmuir−Blodgett (LB) films, molecular sensors, molecular shuttles and switches, wires, multistage assemblies, and dendritic macromolecules. As a consequence, considerable attention has been paid to molecular systems containing a redox-active functionality, as well as a host unit capable of cation binding.[2,3] Recently, we have been exploring an approach to design and synthesize suitably functionalized bis(ethylenedithio)-tetrathiofulvalene (BEDT-TTF) derivatives in order to prepare novel organic conducting materials featuring TTF moieties within metal-binding ligand systems. Herein, we describe an improved, short, and efficient synthetic route to the known compound **2**, as well as the preparation of three new functionalized BEDT-TTF derivatives **3**−**5** (Figure 1).

In general, there are two main strategies for the preparation of functionalized BEDT-TTF derivatives. The most widely used method is via the coupling of two 1,3-dithiole-2-thiones or -2-ones (Scheme 1). However, some BEDT-TTF derivatives are not successfully available by the simple procedure of refluxing their corresponding thiones/ones in the presence of a phosphorus(III) compound, [$P(OMe)_3$, $P(OEt)_3$, or PPh_3].[4] Furthermore, this classical synthesis is a multistep procedure starting from CS_2, resulting in very poor yields of the target molecules.[5] Therefore, an alternative strategy has been adopted by several groups. The key step in this case relies on the generation of the tetraanion **1**, which is very air and moisture sensitive. Previously, a variety of precursors to



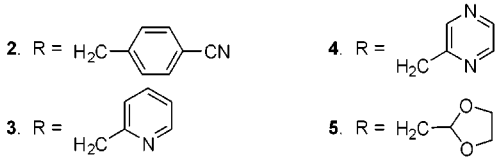
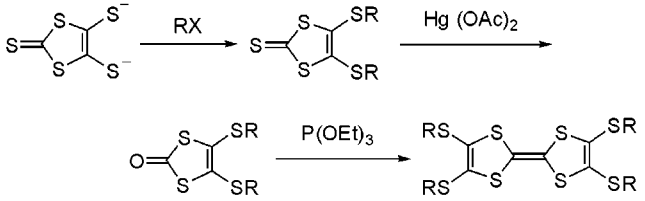


Figure 1. Structures of tetraalkylthiotetrathiafulvalenes.

Scheme 1. Classic Synthetic Route for the Preparation of BEDT-TTF Derivatives



1 have been reported.[6−8] Unfortunately, all of them are problematic, suffering from disadvantages such as low yields, tedious separations, multistep procedures, and/or expensive starting materials. Thus, the detailed investigation of functionalized BEDT-TTF derivatives is still largely unexplored. On the basis of the chemistry of thiapendione, an alternative, sufficiently general, and convenient synthetic procedure was required for the preparation of functionalized BEDT-TTF derivatives (Scheme 2). The tetraanion **1** can be readily prepared from 2,2'-bis(1,3,4,6-tetrathiapentalen-5-one) under carefully controlled conditions. The nucleophilic displacement reaction of **1** with primary alkyl halides gives, in one step, the corresponding BEDT-TTF derivatives in good yields. Compound **2** can be readily prepared via this route in a 75% overall yield from dithiapendione. This is a marked improvement on the 37% yield previously reported for the preparation of this compound via the self-coupling of its corresponding 1,3-dithiole-2-one.[5]

The novel feature of the donors **3**−**5** is that they contain an additional functionality, which has been incorporated with the following specific roles in mind. (i) Interactions in the radical cation salts between the N or O groups and the anions may promote better anion ordering (as they may enhance inter- and intrastack interactions) and produce a more cohesive crystal structure. (ii) Complexation reactions should provide unprecedented opportunities for the attachment of a wide range of transition metals to the donor system, which may induce a change in the electronic properties of the redox center.

All of these BEDT-TTF derivatives have been characterized by elemental analysis, ^{1}H NMR, and ^{13}C NMR,

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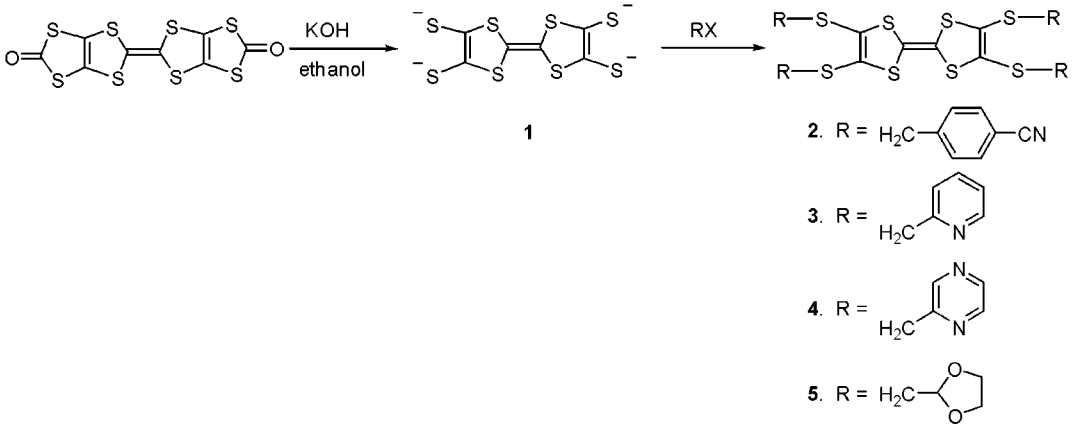
Scheme 2. Improved and Efficient Synthetic Route for the Preparation of BEDT-TTF Derivatives



as well as IR spectroscopy. The single-crystal *X*-ray structure of compound **3** will be reported elsewhere[9] soon.

In conclusion, this protocol provides not only a versatile and convenient pathway to new TTF derivatives in good overall yields and high purity but also paves the way for the attachment of many functional groups to the core of the donor framework. As discussed previously, the construction of redox-active supramolecular systems has received considerable attention since such compounds may act as host molecules.[1] The ability to bind transition metal ions and the formation of charge transfer complexes and ion radical salts of these promising new donors are currently under investigation in our laboratory and will be published in due course.

Experimental Section

General. Reactions requiring air- and/or water-sensitive manipulations were conducted under nitrogen with dry, freshly distilled solvents. Unless stated otherwise, all other reagents were purchased from commercial sources and used without additional purification. 2-Chloromethylpyrazine,[10] 1,3,4,6-tetrathiapentalene-2,5-dione (thiapendione),[11,12] and 2,2'-bis(1,3,4,6-tetrathiapentalen-5-one) (dithiapendione)[13] were prepared according to literature procedures. Unless otherwise specified, all ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ at 300 and 75 MHz, respectively. Melting points are reported in degrees Celsius and are uncorrected. Elemental analyses were performed on an Exeter Analytical CE-440 elemental analyzer. FT-IR data were collected at a resolution of 4 cm^{-1}. Mass spectra were recorded on a Micromass AutoSpec spectrometer using FAB. Analytical TLC was carried out on Merck Silica gel 60 F254 coated aluminum foil; the same type of silica was used for columns.

Preparation of Tetrapotassium 2,2'-Bis(1,3-dithiole-4,5-disulfide) (1). A mixture of dry ethanol (150 mL), KOH (15 g), and dithiapendione (1.5 g) was stirred for 10 h under nitrogen. The resulting suspension was filtered under nitrogen to give a pink powder. After drying under vaccum, the crude product[14] (2.8 g) was stored in a glovebox and used without any further purification.

General Procedure for the Alkylation Reaction of Tetrapotassium 2,2'-Bis(1,3-dithiole-4,5-disulfide) (1). To a solution of **1** in dry DMF (40 mL) was added an excess of the appropriate alkyl halide, and then the mixture was stirred for 1 day in a glovebox at room temperature, unless otherwise stated. H_2O was added to quench the reaction, and the reaction mixture was then extracted with $CHCl_3$. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo to give a dark-brown oil that was purified by flash chromatography on silica gel, initially with CH_2Cl_2 (to remove any unreacted alkyl halide as well as unwanted byproducts) and then with 1:1 CH_2Cl_2/ethyl acetate, unless mentioned, to give the desired product. The overall yield is given on the basis of dithiapendione.

4,4′,5,5′-Tetrakis(4-cyanobenzylthio)tetrathiafulvalene (2). Reaction of **1** (0.40 g) with 4-bromomethyl-benzonitrile (2.00 g) gave an orange powder **2** (0.33 g, 75%): mp 188−190 °C; ^{1}H NMR (DMSO-d_6) δ 4.15 (s, 8H), 7.41−7.44 (d, J = 9 Hz, 8H), 7.78−7.81 (d, J = 9 Hz, 8H); ^{13}C NMR (DMSO-d_6) δ 142.9, 132.4, 129.9, 128.7, 118.6, 110.2, 66.8; IR (KBr, cm^{-1}) 2226, 1606, 1502, 1414, 847, 823. Anal. Calcd for $C_{38}H_{24}N_4S_8$: C, 57.55; H, 3.05; N, 7.06. Found: C, 57.33; H, 3.00; N, 7.08.

4,4′,5,5′-Tetrakis(2-pyridylmethylthio)tetrathiafulvalene (3). To a solution of KOH (1.68 g) in dry ethanol (30 mL) was added 2-bromomethylpyridine hydrobromide (3.75 g). After the mixture was stirred for 10 min, compound **1** (1.20 g) and DMF (25 mL) were added. After stirring for 2 days, the solution was worked up in the same manner as **2**. The brown crystalline compound **3** was obtained (0.71 g, 61%): mp 113−115 °C; ^{1}H NMR δ 4.03 (s, 8H), 7.14−7.18 (m, 4H), 7.23−7.26 (m, 4H), 7.58−7.63 (m, 4H), 8.51−8.54 (m, 4H); ^{13}C NMR δ 156.4, 149.5, 136.8, 129.1, 123.3, 122.4, 110.3, 42.1; IR (KBr, cm^{-1}) 1590, 1567, 1471, 1434, 1413, 1149, 1085, 1048, 994, 771, 747; MS (FAB) *m*/*z* (relative intensity) 697 (M)$^+$ (22). Anal. Calcd for $C_{30}H_{24}N_4S_8$: C, 51.70; H, 3.47; N, 8.04. Found: C, 51.35; H, 3.51; N, 8.11.

4,4′,5,5′-Tetrakis(2-pyrazylmethylthio)tetrathiafulvalene (4). To a suspension of **1** (1.80 g) in DMF (40 mL) was added 2-chloromethylpyrazine (2.83 g). After workup, the resulting dark-brown residue was subjected to column chromatography, eluting initially with a gradient of 50−100% ethyl acetate in CH_2Cl_2 and then with MeOH/ethyl acetate (1:5) to give **4** (0.48 g, 30%) as an orange solid: mp 93−95 °C; ^{1}H NMR δ 4.05 (s, 8H), 8.50−8.55 (m, 12H); ^{13}C NMR δ 152.3, 144.6, 144.2, 143.4, 129.2, 110.5, 39.4; IR (KBr, cm^{-1}) 1577, 1526, 1474, 1401, 1314, 1263, 1220, 1188, 1157, 1122, 1054, 1018, 873, 836, 769; MS (FAB) *m*/*z* (relative intensity) 701 (M)$^+$ (23). Anal. Calcd for $C_{26}H_{20}N_8S_8$: C, 44.55; H, 2.88; N, 15.98. Found: C, 44.42; H, 2.92; N, 16.29.

4,4′,5,5′-Tetrakis(1,3-dioxolyl-2-methylthio)tetrathiafulvalene (5). A mixture of **1** (0.50 g), 2-bromomethyl-1,3-dioxolane (3.00 mL), and DMF (40 mL) was stirred for 2 days. The resulting deep-orange solution was eluted from a silica gel column with CH_2Cl_2/ethyl acetate (2:1) to afford an orange

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(14) Purification and characterization of this compound are difficult since it decomposes on exposure to air. Approximate analysis (EDX) of this crude tetrapotassium salt gave a 1:1 molar ratio of K to S. This implies that about half of the salt is most probably a mixture of KOH and KOEt. These impurities are not problematic for subsequent nucleophilic displacement reactions.

powder **5** (0.31 g, 66%): mp 83−85 °C; ^{1}H NMR δ 2.99 (d, J = 4 Hz, 8H), 3.86−3.89 (m, 8H) 3.97−3.99 (m, 8H), 5.07−5.11 (m, 4H); ^{13}C NMR δ 128.0, 110.5, 102.4, 65.4, 39.3; IR (KBr, cm^{-1}) 2890, 1742, 1417, 1381, 1227, 1128, 1040, 1017, 979, 891; MS (FAB) m/z (relative intensity) 677 $(M)^+$ (4). Anal. Calcd for $C_{22}H_{28}O_8S_8$: C, 39.04; H, 4.17. Found: C, 39.09; H, 4.01.

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