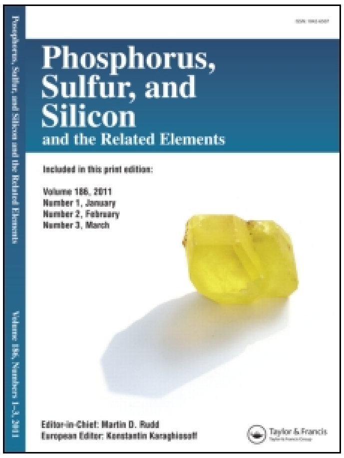

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STUDY ON THE SYNTHESIS OF THE ELECTRON DONOR MOLECULE OF [BIS(ETHYLENEDITHIO)-TETRATHIAFULVALENE] (BEDT-TTF)

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STUDY ON THE SYNTHESIS OF THE ELECTRON DONOR MOLECULE OF [BIS(ETHYLENEDITHIO)-TETRATHIAFULVALENE] (BEDT-TTF)

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Two kinds of synthetic methods for the organic donor molecule BEDT-TTF or ET [bis(ethylenedithio)-tetrathiafulvalene] are reviewed and compared. Through detailed and systematic studies of the synthesis of BEDT-TTF, a convenient, reliable, ready and high-yield synthetic procedure is presented, which is superior to the methods reported to date in terms of the yield and reproducibility.

Key words: Electron donor, BEDT-TTF, ET, synthesis, synthetic metal.

INTRODUCTION

The first organic metal, reported in 1954,[1] was a perylene-bromine complex ($\text{Per}\cdot\text{Br}_x$, $\sigma \approx 1\ \text{S}\cdot\text{cm}^{-1}$). While this finding may be considered as the first, a real burst in research on organic conductors did not occur until after the discoveries of the powerful pi-molecular acceptor tetracyano-*p*-quinodimethane (TCNQ),[2] in 1960, and the sulfur-based electron donor tetrathiofulvalene (TTF) in 1970,[3] and finally in 1972 their combination to form the high conductivity pi-molecular donor-acceptor complex TTF-TCNQ.[4,5] It was the breakthrough that aroused the interest of chemists, physicists, and theorists, many of whom began to work in the field of organic synthetic metals. For decades beginning in 1970, research focused on the synthesis of a large number of new TTF and TCNQ derivatives[6,7] in addition to other electron donor and acceptor systems, which led to the discovery of the first molecular organic superconductor, quasi-1-D $(\text{TMTSF})_2\text{PF}_6$ ($T_c = 0.9$ K at $P = 12$ kbar) in 1979.

The discovery of superconductivity in the Se-based organic donor system containing simple charge compensating monovalent anion acceptors has greatly stimulated studies of promising S-based systems. One such donor system is bis(ethylenedithio)-tetrathiafulvalene (abbreviated to BEDT-TTF, and commonly referred to as "ET").[8] Great interest in the salts of this electron donor was generated after the 1982 report that $(\text{ET}_2\text{ClO}_4(\text{TCE})_{0.5}$ was metallic from room temperature down to 1.4 K.[9] This finding was soon followed by the discovery, in 1983, of the first S-based pressure-induced ($P = 4.5$ kbar) superconductivity ($T_c = 2$ K) in $(\text{ET})_2\text{ReO}_4$.[10] However, the attempts of increasing the number of ET-based superconductors with tetra- and octahedral anions, which worked so well in the case of Bechgaard salts, appeared to be unsuccessful.

In 1984, the first sulfur organic superconductor with $T_c = 1.5$ K at ambient pressure was synthesized.[11] It was an ET salt with the linear anion I_3^-, i.e. β-

$(ET)_2I_3$. Soon after, it was found that the compound could exist in low- and high-temperature superconducting states with $T_c = 1.5$ K and 8 K, respectively.[12] The further progress in the search for organic superconductors was much affected by these results. The quest developed in two directions: variations of the anions in the ET salts and chemical modifications of the cation radical system itself. Both approaches appeared to be rather fruitful and led to the increase of the number of organic superconductors up to over 40 and to the enhancement of their critical temperature up to 12.8 K,[13] especially, in which more than 20 organic superconductors,[13,14] including those with the highest T_c values, are charge-transfer salts derived from the electron donor molecule ET. The ET salts remain the main objects in the search for new superconductors at present day.

Although the synthesis of ET was originally reported early in 1978,[8] and another synthetic procedure reported in 1983,[15] the synthesis of ET was chosen for our detailed study because it is the best organic electron donor known to date. Most of those, who have been or will be working in this field have to synthesize the donor ET or its analogies, so it deserves to study its synthesis in detail and explore a better synthetic procedure with convenient conditions. Based on the comparison of the synthetic entries into the donor ET, a really more convenient, reliable, ready and high-yield synthetic procedure is presented, which is superior to the methods reported to date.

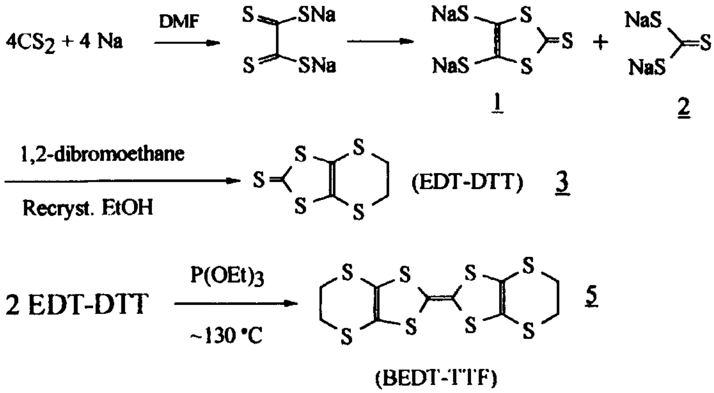
RESULTS AND DISCUSSION

During the intervening ten-year hiatus, numerous modifications and improvements to the original synthesis of ET were reported.[15] These methods could be basically divided into two kinds in terms of the starting materials.

A. Carbon Disulfide (CS_2) Route

This method was originally reported by M. Mizuno *et al.*[8] without a detailed description of the synthetic procedures. They synthesized the donor molecule, using CS_2 as starting material, by the direct phosphite coupling of the 1,3-dithiole-2-thione. After that, more detailed synthetic procedures of the dithiolethione or/and its desulfurised compound dithiolone with mercury acetate were presented by G. Steimecke *et al.* in 1979[16] and K. Hartke *et al.* in 1980,[17] respectively, both via the reduction of CS_2 with the use of Kalium. A slightly simple preparative procedure which involves the reduction of CS_2 with metallic sodium was also developed in 1985[18] by J. A. Williams *et al.* as indicated in Scheme I.[19]

In Scheme I, the versatile dianion 1, which can be conveniently generated from the reduction of CS_2 either electrically[20] or with the use of an alkali metal[16] in DMF, can lead to many S-based organic donors. But first, it is air-sensitive and difficult to store, it is usually generated in situ and used directly; second, a slight complication occurs due to the concomitant formation of a trithiocarbonate anion, 2, which tends to polymerization and thus lower the yield and leads to slightly difficult to purify the precursor 4,5-ethylenedithio-1,3-dithiole-2-thione, 3. So we must first isolate the 1,3-dithiole-2-thione-4,5-dithiolate anion, 1, from the trithio-



SCHEME I

carbonate anion, 2: (1) stabilizing the anion 1 with zinc chloride to form a bischelate-zinc complex, $(NR_4)_2Zn(dmit)_2$, where dmit is dimercapto-isotrithione or 1,3-dithiole-2-thione-4,5-dithiolate and R = *n*-Bu or Et. The zincate then reacts with 1,2-dibromoethane to produce 4,5-ethylenethio-1,3-dithiole-2-thione, 3, which upon coupling in neat triethylphosphite yields ET; (2) treating 1 with benzoyl chloride yields 4,5-bis(benzoylthio)-1,3-dothiole-2-thione. Upon adding sodium methoxide to 4,5-bis(benzoylthio)-1,3-dothiole-2-thione, the purified sodium salt of 1 is regenerated.

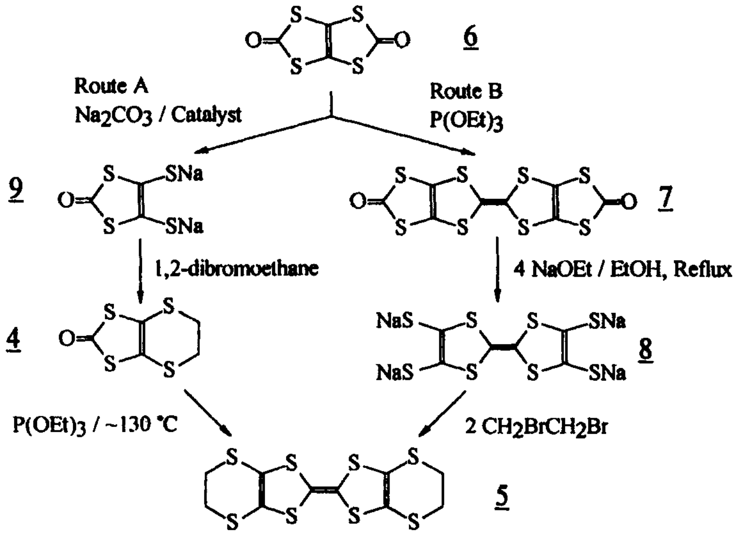
B. Thiapendione Route

IBM group (R. R. Schumaker *et al.*) reported the synthesis of ET and related donor molecules in 1983,[15] starting from a reaction of 1,3,4,6-tetrathiapentalene-2,5-dione (thiapendione) with a phase-transfer catalyst and a weak base, Na_2CO_3, in a water-benzene mixture.

Thiapendione, which is a very important building block for donor synthesis, can be made (1) by refluxing dichloroacetate with potassium O-isopropyldithiocarbonate in acetone followed by acid-initiated cyclization[21]; (2) from the zincate, after reacting with thiophosgene and then mercury acetate.[22] In general, there are two routes for various donors synthesizing starting from the dione, as shown in Scheme II.

In route A, the central step involves the use of a weak base, Na_2CO_3, and a phase-transfer agent to selectively cleave one carbonyl group in order to generate the dithiolate anions, 9.[23] By adding 1,2-dibromoethane to 9, 4,5-ethylenedithio-1,3-dithiole-2-one, 4, are produced, which undergoes facile coupling in neat phosphite affording ET.

In route B, the key step lies in the coupling of thiapendione in refluxing toluene with triethylphosphite[22,24,25,26] and the purification of the dimerized system dithiapendione, 7.[26] Reaction of 7 under Ar with 4 mol equiv of sodium ethoxide in refluxing ethanol afforded the corresponding air-sensitive tetrathiolate salt, 8, which could be subsequently converted on addition of 1,2-dibromoethane to ET. In our course of exploring the chemistry of the dithiapendione as a means for synthesizing



BEDT-TTF

SCHEME II

TABLE I
Coupling conditions of the thiapendione as a function of the yield of the dithiapendione

No.	Solvent	Cp (M)	Ct (M)	Reflux-time (h)	Yield (%)
1	benzene	0.02	0.04	24	0.0
2	toluene	0.02	0.04	4	54.0
3	toluene	0.10	0.20	22	62.0
4	toluene	0.13	1.00	5*	85.3

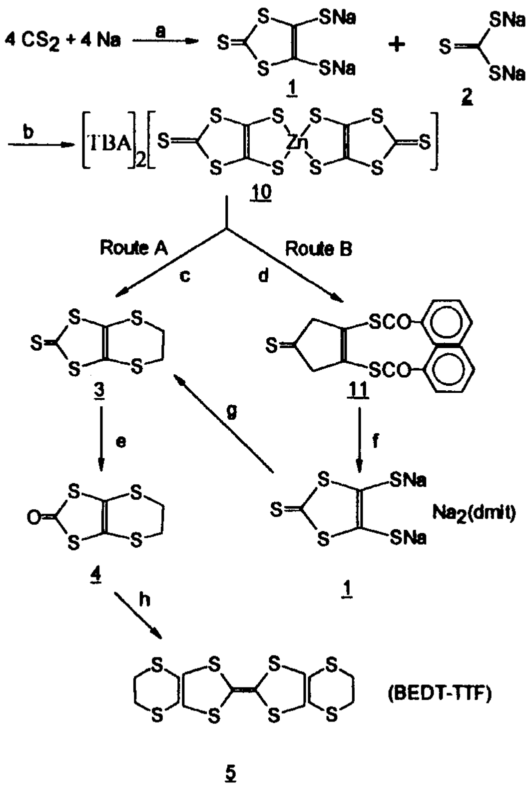
Cp=concentration of thiapendione, Ct=concentration of triethyl phosphite, * greatly affected by the concentration of triethyl phosphite

novel solid-state materials, we have studied the coupling reaction of the thiapendione to form purer dithiapendione with higher yield and great successes have achieved, shown in Table I. However, in the last step in the route B of Scheme II, the product ET is hard to be purified and the yield is unusually low. Hence, this route could not be a good one for the synthesis of ET.

In Table I, we can notice that benzene is not a suitable solvent in the coupling of thiapendione to dithiapendione. This is contrasted to the results reported by R. R. Schumaker *et al.*[24]

IBM method (Route A in Scheme II) is assumed to be broadly applicable to the synthesis of the related donor molecules, and deserves to be studied in detail. However, comparing these methods, the method shown in Scheme I is better than that in Scheme II from the following reasons: (1) the starting material, CS_2, can be obtained on a large scale and very cheap. Therefore, the succeeding synthesis can be made on a large scale. On the other hand, a large-scale synthesis of the dione is not only difficult, but its synthesis requires several days. Although the dione can be commercially obtained, it is expensive. Furthermore, the dione sensitizes and produces skin rashes on some individuals; (2) all of the reaction products in Scheme I can be easily purified by recrystallization or chromatography. On the other hand, the products in Scheme II, either route A or route B, must be purified by column chromatography, followed by recrystallization, moreover, the precursor itself (dithiapendione) in route B (Scheme II) is very difficult to recrystallization from common solvents, such as toluene, chlorobenzene, THT, ethanol, due to its very low solubility. Thus, a much longer time is required for the purification work. The loss of the products during these procedures is also a serious problem.

The method shown in Scheme I is a classic one, but the yield of ET was usually low for the multi-step process, polymerization of the trithiocarbonate dianion, 2, and lack of detailed, high-yield and reproducible synthetic conditions for reference.



a. DMF, Ar, Reflux, 4-5h

b. $ZnCl_2$ / CH_3OH, $NH_3 \cdot H_2O$, n-Bu_4NBr / H_2O, R.T., 72~77 %

c. CH_2BrCH_2Br, acetone, Reflux 15-72h, 50~97 %

d. PhCOCl, acetone, R.T., 1h, 81~85 %

e. $Hg(OAc)_2$ / HOAc, $CHCl_3$, R.T., 5h, 81~94 % f. CH_3ONa / MeOH, Ar, R.T, 2h

g. CH_2BrCH_2Br, R.T, 54~84 % h. $P(OEt)_3$ / Toluene, Reflux, 3-20h, 49~86 %

SCHEME III

Concerning the synthetic chemistry of ET, we have studied each reaction step of the synthesis of ET in detail and found a better procedure with convenient and easy-controlled synthetic conditions, as shown in Scheme III.

In Scheme III, $[TBA]_2[Zn(dmit)_2]$ can be readily prepared.[16] We found that the yield was nearly constant varying between 72 and 77%, shown in Table II.

The key step in Scheme III lies in the preparation of 4,5-ethylenedithio-1,3-dithiole-2-thione with high purity, high yield and convenient synthetic conditions. Through detailed and comparative studies of this reaction step, we have found that it is better to synthesize 4,5-ethylenedithio-1,3-dithiole-2-thione by refluxing the acetone solution of $(Bu_4N)_2Zn(dmit)_2$ (0.02 M) and 1,2-dibromoethane for about 50 hrs (see Table III).

In order to enhance the yield of ET, it is better to convert the thioxo group in the dithiolethione to an oxo group with mercury acetate. Table IV shows that the ratio of mercuric acetate:thione, 3, must be at least 2:1.

Upon coupling the half-units 4,5-ethylenedithio-1,3-dithiole-2-one, 4, with triethylphosphite in toluene yields ET as red crystals, then recrystallized twice from chlorobenzene giving purer red crystals. We found that the yield was greatly affected by the reaction temperature and time (see Table V).

In Table V, we can notice that the best reaction time could be around 16 hrs at about 110°C.

TABLE II

Reaction conditions of the reduction of CS_2 with the use of Na as a function of the yield of $[TBA]_2[Zn(dmit)_2]$

No	DMF (mL)	Reflux-time (h)	Yield (%)
1	100	5	77.2
2	200	5	72.4
3	200	5	73.4
4	200	5	74.2
5	200	4	73.9

TABLE III

Reaction conditions of $(Bu_4N)_2Zn(dmit)_2$ and 1,2-dibromoethane as a function of the yield of 4,5-ethylenedithio-1,3-dithiole-2-thione

No	Equiv	Reflux-time (h)	Yield (%)
1	1 : 2	24	50.6
2	1 : 4	40	63.3
3	1 : 4	50	96.7
4	1 : 4	72	96.7
5	1 : 4	15*	97.0

Equiv=$(Bu_4N)_2Zn(dmit)_2$: 1,2-dibromoethane in mole, * concentrated acetone solution of the Zn salt (0.04 M)

TABLE IV

Oxidation conditions of 4,5-ethylenedithio-1,3-dithiole-2-thione as a function of the yield of 4,5-ethylenedithio-1,3-dithiole-2-one

No.	Equiv	Reaction-time (h)	Yield (%)
1	1 : 2.0	5	80.8
2	1 : 2.5	5	81.1
3	1 : 2.5	5	84.6
4	1 : 2.4	5	86.3
5	1 : 1.1	5	47.8*
6	1 : 2.5	5	94.1
7	1 : 2.2	5	93.8

Equiv=precursor : mercuric acetate in mole, * Incomplete oxidation evendenced by TLC and MS (EI) m/e 224

TABLE V

Coupling conditions of 4,5-ethylenedithio-1,3-dithiole-2-one as a function of the yield of the product BEDT-TTF

No.	Equiv	Reflux-time (h)	Yield (%)
1	1 : 2	5	48.8
2	1 : 2	10	59.1
3	1 : 2.7	14	81.3
4	1 : 2.7	16	85.3
5	1 : 2.7	18	86.1

Equiv=precursor : triethyl phosphite in mole

TABLE VI

Yield of BEDT-TTF produced by different methods

Method	Yield (%)	Reference
CS_2 route	44-45	8
	85	this work[a]
	56	this work[b]
Thiapendione route	not reported	15
	50	27[c]

[a] refer to the yield of the final step, [b] overall yield, [c] overall yield

In conclusion, the yield of the product BEDT-TTF produced according to the method shown in Scheme III is higher than that of both M. Mizuno *et al.*[8] and R. R. Schumaker *et al.*[15] as well as H. Mueller *et al.*,[27] tabulated in Table VI.

EXPERIMENTAL DETAILS

General instrumentation and descriptions: FT-IR spectra were recorded on a Bruker IFS-113V Fourier Transform Infrared spectrophotometer in the region of 4000–400 cm^{-1} as KBr pellets at room temperature in addition to compounds of 3, 4, and 10, the IR spectra of which were recorded on a Perkin Elmer 683 Infrared spectrophotometer in the region of 4000–200 cm^{-1} as KBr pellets. UV-Vis spectrum was recorded on a HITACHI 340 spectrophotometer in ethanol solution at room temperature. MS spectra were recorded on a MS-50 spectrometer (EI, 70 eV). Elemental analyses were performed by the Analysis & Measurement Center of our institute with a Carlo Erba1106 apparatus. Thin Layer Chromatograph (TLC) analyses were carried out with homemade silica gel plates using $CHCl_3$/petroleum ether (b.p 60–90°C) mixtures. All reagents were commercially available and purified before use. All solvents were dried and purified prior to use according to standard procedures. All temperatures quoted are uncorrected.

Synthesis of bis(tetrabutylammonium)-bis(1,3-dithiole-2-thione-4,5-dithiolato)-Zinate (i.e.,. Zn salt), $(n\text{-}Bu_4N)_2Zn(dmit)_2$, 10

The precursor compound, 10, was prepared according to the literature.[16] M.p 169–172°C. IR (KBr, cm^{-1}): 2960 (s), 2938 (s), 2870 (m), 1485 (m), 1475 (m), 1460 (m), 1410 (vs), 1380 (m), 1170 (vw), 1150 (vw), 1100 (vw), 1055 (s), 1030 (vs), 994 (m), 890 (m), 795 (vw), 740 (w), 530 (w), 464 (s), 397 (w), 320 (m). UV-Vis (ethanole, λ_{max}, nm): 223.7, 308.7, 376.0 (vw), 477.3. Anal. calc. for $C_{38}H_{72}N_2S_{10}Zn$: C, 48.39; H, 7.69; N, 2.97; found : C, 48.41; H, 7.54; N 3.06%.

Synthesis of 2,5,7,9-tetrathiabicyclo[4,3,0]non-1(6)-en-8-thione, 3[16]

Bis(tetrabutylammonium)-bis(1,3-dithiole-2-thione-4,5-dimercapto) Zincate, 10, (10 g, 10.6 mmol) and 1,2-dibromoethane (4 mL, 43.6 mmol) were stirred and refluxed in 500 mL of acetone for 50 hrs. The solvent was removed under reduced pressure and 400 mL of water was added. The product was filtered off and washed with water (5 × 50 mL), methanol (3 × 5 mL), acetone (1 × 5 mL), dried in air affording 4.6 g (96.7%) of yellow crystals, m.p 123–124°C. MS m/e (EI, 70 eV) 224. IR (KBr, cm^{-1}): 2960 (vw), 1480 (m), 1400 (w), 1060 (s), 1040 (m), 1012 (w), 920 (w), 870 (m), 525 (w), 460 (w), 355 (w). UV-Vis (ethanole, λ_{max}, nm): 222.2, 276.1, 403.8. Anal. calc. for $C_5H_4S_5$: C, 26.76; H, 1.80; S 71.44; found: C, 26.52; H, 1.76; S 71.68%.

Synthesis of 2,5,7,9-tetrathiabicyclo[4,3,0]non-1(6)-en-8-one, 4

A boiling solution of mercuric acetate (32.7 g, 0.102 mol) in 150 mL of acetic acid was slowly added, with stirring, to a solution of 3 (9.2 g, 0.041 mol) in 600 mL of chloroform. After vigorous stirring for 5 h at room temperature and standing for 1 h, the white precipitate was filtered off and washed with chloroform (4 × 20 mL). The filtrate was evaporated under reduced pressure and then 250 mL of distilled water was poured into the residue. Yellow precipitate was filtered off and washed with water (4 × 20 mL), methanol (3 × 5 mL) to give 8.0 g (94.1%) of yellow crystals, 4, m.p 129–130°C. MS m/e (EI, 70 eV) 208. IR (KBr, cm^{-1}): 2970 (vw), 2920 (vw), 1670 (w), 1630 (s), 1602 (s), 1500 (m), 1415 (m), 1010 (w), 920 (w), 880 (w), 870 (m), 750 (w), 570 (vw), 540 (vw), 470 (w), 400 (w), 380 (w). UV-Vis (ethanole, λ_{max}, nm): 236.1, 290.7. Anal. calc. for $C_5H_4S_4O$: C, 28.82; H, 1.93; S, 61.56; found: C, 28.68; H, 1.91; S 61.81%.

Synthesis of 4,5-bis(benzoylthio)-1,3-dithiole-2-thione, $(dmit)(COPh)_2$, 11[16]

The preparation of $(dmit)(COPh)_2$, 11, was carried out according to the literature,[16] but the yield is higher, around 81–85% (60–70% in Reference 16), m.p 143–145°C. MS m/e (EI, 70 eV) 406. IR (KBr, cm^{-1}): 1690 (s), 1672 (m), 1450 (w), 1204 (s), 1177 (w), 1060 (s), 1000 (w), 897 (m), 884 (s), 777 (w), 768 (w), 687 (m), 679 (m), 473 (w). UV-Vis (ethanole, λ_{max}, nm): 211.8, 249.2, 364.3. Anal. calc. for $C_{17}H_{10}S_5O_2$: C, 50.21; H, 2.47; S, 39.43; found: C, 49.95; H, 2.71; S 39.75%.

Synthesis of 2,5,7,9-tetrathiabicyclo[4,3,0]non-1(6)-en-8-thione, 3, from 11

0.12 g metallic Na (5.2 mmol) was dissolved in 50 mL of methanol then $(dmit)(COPh)_2$, 11 (1.0 g, 2.46 mmol) was added to the mixture. After stirring for 7 h at room temperature, 1,2-dibromoethane (0.22 mL, 2.5 mmol) was added into the red solution with stirring for another 24 h at room temperature. The yellow precipitate was filtered off and washed well with water (5 × 10 mL), recrystallized from methanol to give 0.3 g (54.3%) of yellow crystals, m.p 123–124°C.

Synthesis of thiapendione, 6

Thiapendione, 6, was prepared by the reported method.[21]

Synthesis of dithiapendione, 7

Dithiapendione, 7, was prepared by the method of R. R. Schumaker *et al.*[24]

Synthesis of bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), 5, from 4[8,15]

2,5,7,9-tetrathiabicyclo[4,3,0]non-1(6)-en-8-one (1.0 g) was added to a solution of 25 mL toluene and 1.7 mL of $P(OEt)_3$. After refluxing for 16 hrs, the red crystals was filtrate off and washed with methanol (3 × 10 mL), recrystallized twice from chlorobenzene giving 0.87 g (85.3%) purer red crystals. MS m/e (EI, 70 eV) 384. IR (KBr, cm^{-1}): 2961 (m), 2922 (s), 1636 (w), 1409 (s), 1385 (m), 1284 (s), 1022 (w), 918 (m), 772 (s), 500 (w). UV-Vis (ethanole, λ_{max}, nm): 227.1, 317.2, 340 (sh). Anal. calc. for $C_{10}H_8S_8$: C, 31.22; H, 2.10; S, 66.68; found: C, 31.46; H, 2.07; S, 66.54%.

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