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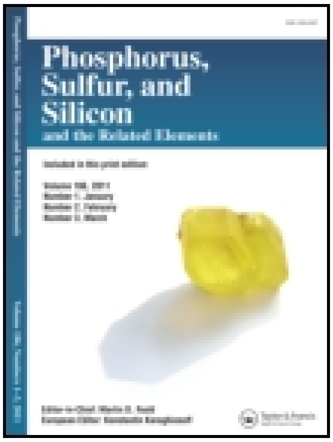

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PREPARATION AND ELECTROCHEMICAL PROPERTIES OF A NEW ORGANIC DONOR BIS-(HYDROXYMETHYLETHYLENEDITHIO)-TETRATHIAFULVALENE

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PREPARATION AND ELECTROCHEMICAL PROPERTIES OF A NEW ORGANIC DONOR BIS-(HYDROXYMETHYLETHYLENE-DITHIO)-TETRATHIAFULVALENE

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Preparation and characterization of a new organic donor molecule bis(hydroxymethylethylenedithio)-tetrathiafulvalene is reported. Cyclic voltammogram (Figure 1) of the donor molecule shows two reversible redox processes in n-Bu_4NBF_4/DMF system at half-wave potentials of 0.64 and 0.81 V *vs* SCE, respectively, which are higher than those of the well-known organic donor molecule bis(ethylenedithio)-tetrathiafulvalene with the corresponding values of 0.60 and 0.73 V , respectively. In addition, the π-donor ability of some related donor molecules of the same series is compared and the effects of solvents on the half-wave potentials of the donors are studied.

Keywords: Organic electron donor; synthesis; electrochemistry

INTRODUCTION

In 1984, the first sulfur-based organic charge transfer (CT) salt β-$(ET)_2I_3$ with Tc = 1.5 K at ambient pressure was reported [ET = BEDT-TTF = bis(ethylenedithio)-tetrathiafulvalene].[1] Soon after, it was found that the compound could exist in low- and high-temperature superconducting states with Tc = 1.5 and 8 K, respectively.[2] 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-based salts and chemical modification of the cation radical system itself. Both approaches appeared to be rather

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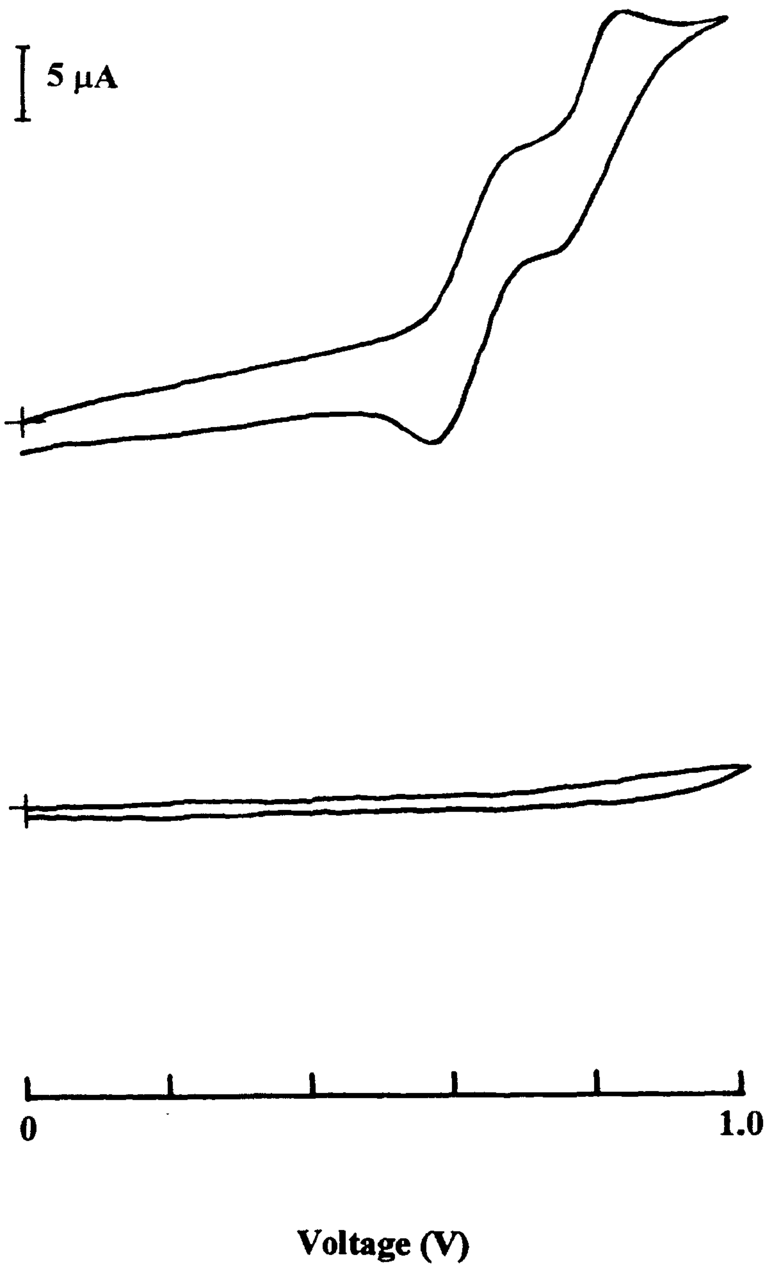


FIGURE 1 Cyclic voltammograms of HMET (upper) and the blank (bottom) in DMF using TBABF$_4$ as the supporting electrolyte at scan rate of 50 mV/s. V *vs* SCE.

fruitful, which led to the increase of the number of the ET- or its derivative-based organic superconductors up to over 40 and to the enhancement of their Tc up to 12.8 K, the highest known to date. Presently, the ET- or its derivative-based CT salts remain the main objects in the search for new organic superconductors. Since the presence of 2-dimensional S · · · S networks and C-H · · · (anion) interactions in the cation radical salts is important in determining the solid-state properties, many synthetic efforts have been devoted to systematically varying the structure of ET with consequential 'fine tuning' of the ionization potential, symmetry, size, and S · · · S intermolecular contacts.[3] In this paper, we will report the preparation and electrochemical property of a new ET derivative: bis(hydroxymethylethylenedithio)-tetrathiafulvalene (HMET). The guidelines for the design of such target molecule are as follows: first, the electron donating hydroxymethyl substituents may be expected to enhance the π-donor ability of the ET core and, thanks to the —OH group, should favor the hydrogen bond formation[4] and furthermore, should favor the S · · · S intermolecular interactions in the related salts, thus possibly increasing their dimensionality; second, due to the —OH group, it should be possible to prepare some kind of polymers and some unusual physical properties may be expected after complexing or doping the polymer with some suitable counter anions.

EXPERIMENTAL

General instrumentation and descriptions: IR spectra were recorded on a Perkin Elmer 683 Infrared spectrophotometer in the region of 4000–200 cm^{-1} as KBr pellets. UV-Vis spectra was recorded on a Hitachi 340 spectrophotometer. MS spectra were recorded on a MS-50 spectrometer (EI, 70 eV). Elemental analyses were performed by the Analysis & Measurement Center of the Institute with a Carlo Erba 1106 apparatus. Thin Layer Chromatography (TLC) analyses were carried out with home-made silica gel plates using $CHCl_3$/petroleum ether (b.p 60–90°C) mixtures. Cyclic voltammetric measurements at slow potential scan rates (10–100 mVs^{-1}) were carried out as described in the literature.[5] DMF or acetonitrile was used as the solvent and Bu_4NBF_4 or Bu_4NClO_4 was used as the supporting electrolyte in 0.1 $molL^{-1}$. The measurements were performed on solutions containing 2×10^{-3} $molL^{-1}$ donor molecules. All reagents were commercially available. All solvents were dried and purified prior to use according to standard procedures. All temperatures quoted are uncorrected.

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

The precursor compound, **3**, was prepared as described in the literature.[6]

4,5-bis(benzoylthio)-1,3-dithiole-2-thione, $(dmit)(COPh)_2$

The preparation of $(dmit)(COPh)_2$, **4**, was carried out according to the literature with the yield of 80.7%.[6]

4,5-(hydroxymethylethylenedithio)-1,3-dithiole-2-thione, 6

0.45 g metallic Na (19.5 mmol) was dissolved in 50 mL of methanol then $(dmit)(COPh)_2$, **4** (3.95 g, 9.7 mmol) was added to the mixture under Ar. After stirring for 7 h at room temperature under Ar, 4 mL 2,3-dibromopropanol (8.48 g) and 150 mL ethanol were 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 ethanol to give 1.2 g (48%) of yellow crystals. M.p 191–192°C. MS (EI, 70 eV) *m/z* 254; IR (KBr, cm^{-1}) 3410 (m), 2910 (w), 1055 (s), 1027 (m). UV-Vis (ethanol, λ_{max}, nm) 212.1, 264.3, 376.8. *Anal.* calcd for $C_6H_6S_5O$ C, 28.36; H, 2.36; S, 62.98; O, 6.30%; found C, 28.35; H, 2.30; S, 63.09; O, 6.65%.

4,5-(hydroxymethylethylenedithio)-1,3-dithiole-2-one, 7

A boiling solution of mercuric acetate (2.51 g, 7.8 mmol) in 50 mL of acetic acid was slowly added, with stirring, to a solution of **6** (1.0 g, 3.9 mmol) in 100 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 well washed with water and dried over Na_2CO_3. The solvent was removed by rotary evaporation. Yellow precipitate was filtered off and washed with water (4 × 20 mL), recrystallized from ethanol to give 0.8 g (85.4%) of yellow needle-like crystals. M.p 117–119°C. MS *m/e* (EI, 70 eV) 238. IR (KBr, cm^{-1}): 3464 (m), 2920 (w), 1664 (m), 1606 (s), 1220 (w), 897 (m), 747 (m). UV-Vis (ethanol, λ_{max}, nm): 218.7, 280.2. *Anal.* calcd for $C_6H_6S_4O_2$: C, 30.25; H, 2.52; S, 53.78; found: C, 30.40; H, 2.27; S 53.24%.

Bis(hydroxymethylethylenedithio)-tetrathiafulvalene (HMET), 8

4,5-(hydroxymethylethylenedithio)-1,3-dithiole-2-one (1.0 g) was added to a mixture of 100 mL toluene and 3 mL of $P(OEt)_3$. After refluxing for 20 h, the mixture was concentrated under reduced pressure. The resulting yellow powder was filtered and washed with cold methanol to give crystalline yellow powder. Column chromatography (chloroform/petroleum ether 1:1 v/v) afford 150 mg of the pure product **8** in 13.4% yield. M.p. 269–270. Ms (EI, 70 eV) *m/z* 444. IR (KBr, cm^{-1}): 3504 (m), 3402 (m), 2913 (m), 1401 (w), 1220 (m), 1022 (m). UV-Vis ($CHCl_3$, λ_{max}, nm): 248 (sh), 268.5, 304, 320 (sh), 335, 402. *Anal.* calcd for $C_{12}H_{12}S_8O_2$: C, 33.40; H, 2.70; S, 57.60; found: C, 33.11; H, 2.48; S, 57.13%.

Bis(propylenedithio)-tetrathiafulvalene (PT), bis(butylenedithio)-tetrathiafulvalene (BT), ET, 4,5-dimethyl-4′,5′-ethylenedithio-1,3-deselena-1′,3′-dithiafulvalene (DMET) and 3,4;3′,4′-tetra(methylthio)-2,5;2′,5′-tetrathiafulvalene (TTM-TTF)

The above donors were synthesized according to the reported procedures.[7]

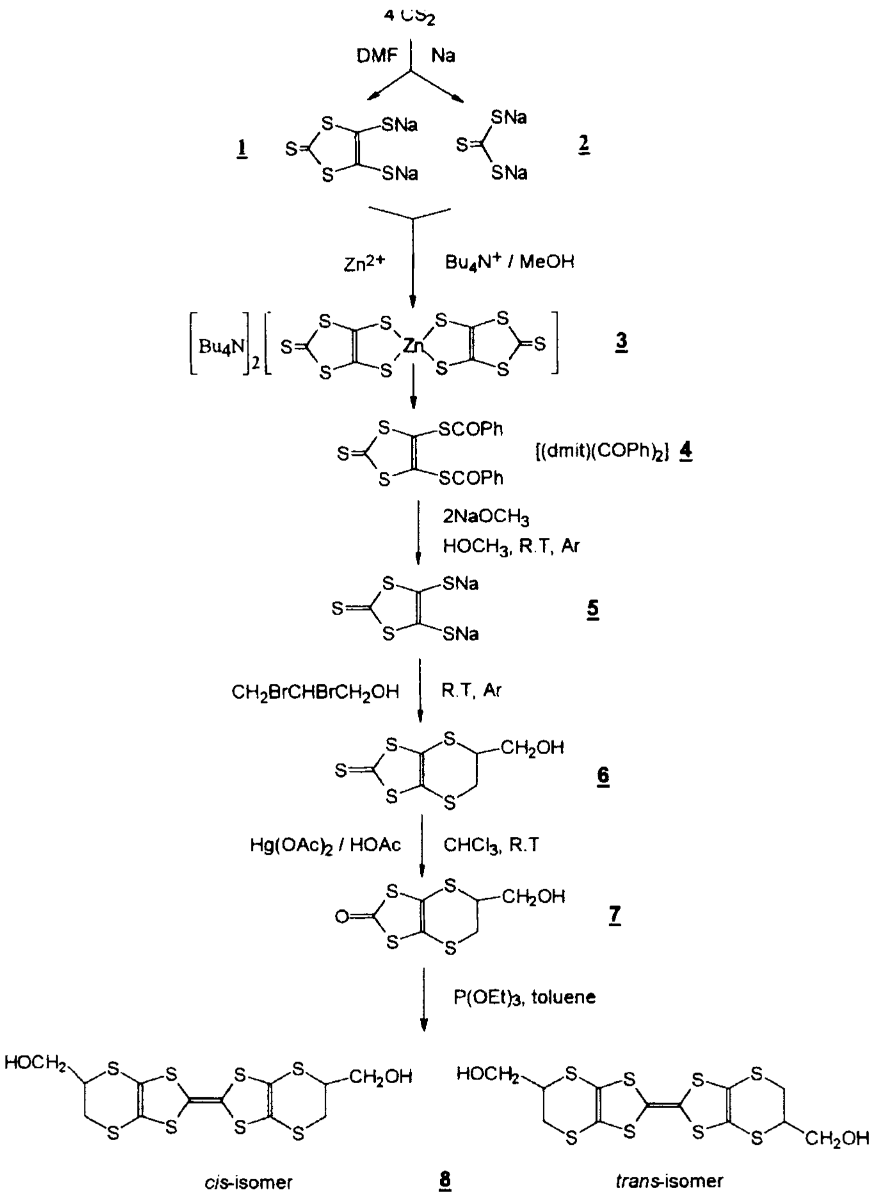
RESULTS AND DISCUSSION

Synthesis

The donor molecule HMET was prepared by the following procedure shown in the Scheme.

This route,[8] which is a classic one for the synthesis of ET-derivatives, starts from CS_2 followed by the reaction of 1,3-dithiole-2-thione-4,5-dithiolate with (±)-2,3-dibromopropanol afforded 4,5-(hydroxymethylethylenedithio)-1,3-dithiole-2-thione, which was then desulfurised to the corresponding dithiolone with mercury acetate and phosphite coupled to give the target compound as a mixture of two geometrical isomers. All of our efforts to separate these isomers by common column chromatography and high pressure liquid chromatography (HPLC) proved to be unsuccessful.

In the route, the key step lies in the preparation of the 1,3-dithiole-2-thione with high yield. However, due to the air-sensitivity and difficulty to be stored of the versatile dianion, **1**, and 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-(hydroxymethylethylenedithio)-1,3-


4 CS2
DMF
Na
1
2
Zn2+
Bu4N+ / MeOH
3
[(dmit)(COPh)2] 4
2NaOCH3
HOCH3, R.T, Ar
5
CH2BrCHBrCH2OH
R.T, Ar
6
Hg(OAc)2 / HOAc
CHCl3, R.T
7
P(OEt)3, toluene
cis-isomer
8
trans-isomer

dithiole-2-thione, one should first isolate the 1,3-dithiole-2-thione-4,5-dithiolate anion **1** from the trithiocarbonate anion by means of stabilizing the dianion with zinc chloride to form a bischelate-zinc complex, $(n\text{-}Bu_4N)_2Zn(dmit)_2$, where dmit is dimercapto-isotrithione or 1,3-dithiole-2-thione-4,5-dithiolate, followed by treating the bischelate-zinc complex 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, purified sodium salt of the dianion can be regenerated (see the Scheme).

Electrochemical Behavior

The desirable features in the design of related tetrathiafulvalene (TTF) π-donors for use in the preparation of conducting CT salts are an increased electronic polarisability and decreased band occupancy, both of which are favourable toward diminishing energetically costly electron-electron correlations which inhibit electrical transport.

The figure shows the cyclic voltammogram of the new donor HMET in $n\text{-}Bu_4NBF_4$/DMF system at 50 mV/s. It is observed that there exist two reversible redox processes with half-wave potentials ($E_{1/2}$) at about 0.64 and 0.81 V *vs* SCE, respectively. In order to evaluate the donor ability of HMET and investigate the solvent effect, Table I presents the $E_{1/2}$ values of the donor and some other related donor molecules of the same series in different solutions. As a result, we can notice that the solvent shows great effects on the $E_{1/2}$ values and furthermore, for all the donors studied, the $E^1{}_{1/2}$ values in DMF are higher than those in acetonitrile, while, the $E^2{}_{1/2}$ values in DMF are lower than those in acetonitrile with the exception of TTM-TTF. However, both the scan rate and electrolyte exhibit little effect on the $E_{1/2}$ values.

To our surprise, we found that the π-donor ability of HMET is smaller than that of ET even though the hydroxymethyl substituent is an electron donating group. This may be explained as that HMET is greatly disordered near the ethylene group as expected.[10] The $E^1{}_{1/2}$ values in DMF for the donors are in the series HMET ~ BT > DMET ~ TTM-TTF ~ ET > TTF and the trend for $E^2{}_{1/2}$ values follows the same way. In acetonitrile, the trend for $E^1{}_{1/2}$ values are in the series HMET ~ PT > ET > TTM-TTF > TTF and for the $E^2{}_{1/2}$ values the trend is HMET ~ PT > ET > TTF>TTM-TTF. This smaller π-donor ability for HMET may lead to a smaller CT if complexed with some suitable acceptors and hence should decrease the band occupancy in the crystalline state. Moreover, the difference between $E^1{}_{1/2}$ and $E^2{}_{1/2}$, *i.e.*, $\Delta E_{1/2}$ values for the donor remains small, which is important to allow desirable double-occupancy fluctuations in the conducting state. However, all of our efforts to grow

TABLE I Half-wave potentials of the new donor HMET and some related donor molecules of the same series in different voltammetric conditions

Donor	*solvent*	*scan rate*[a]	*electrolyte*	$E^{1}_{1/2}$[b]	$E^{2}_{1/2}$[b]	$E^{2}_{1/2}-E^{1}_{1/2}$
HMET	DMF	50	TBABF$_4$[c]	0.64	0.81	0.17
	DMF	100	TBAClO$_4$	0.64	0.80	0.16
	DMF	50	TBAClO$_4$	0.64	0.80	0.16
	CH$_3$CN	50	TBABF$_4$	0.59	0.88	0.29
	CH$_3$CN	100	TBABF$_4$	0.59	0.88	0.29
BT	DMF	50	TBABF$_4$	0.64	0.82	0.18
	DMF	20	TBABF$_4$	0.64	0.82	0.18
PT	CH$_3$CN		TEAClO$_4$[d]	0.580[e]	0.861[e]	0.281
ET	DMF	100	TBABF$_4$	0.60	0.73	0.13
	DMF	50	TBABF$_4$	0.60	0.74	0.14
	DMF	20	TBABF$_4$	0.60	0.73	0.13
	DMF	10	TBABF$_4$	0.61	0.73	0.12
	CH$_3$CN		TEAClO$_4$	0.532[e]	0.773[e]	0.241
DMET	DMF	50	TBABF$_4$	0.61	0.73	0.12
	DMF	20	TBABF$_4$	0.61	0.73	0.12
	DMF	10	TBABF$_4$	0.61	0.73	0.12
TTM-TTF	DMF	50	TBABF$_4$	0.61	0.74	0.13
	DMF	20	TBABF$_4$	0.61	0.73	0.12
	DMF	10	TBABF$_4$	0.61	0.74	0.13
	CH$_3$CN		TEAClO$_4$	0.496[e]	0.668[e]	0.172
TTF	DMF	50	TBABF$_4$	0.39	0.63	0.24
	CH$_3$CN		TEAClO$_4$	0.342[e]	0.721[e]	0.379

[a] in mV/s.

[b] reversible oxidations, the resulting values are given in V *vs* SCE.

[c] TBA = tetrabutylammonium.

[d] TEA = tetraethylammonium.

[e] reversible oxidations *vs* Ag/Ag$^+$ (0.1 N in acetonitrile) with a glassy carbon electrode as the working electrode, the resulting values are given in V *vs* SCE.[9]

crystalline CT salts with such counter anions as I_3^- or its analogous or CuSCN/SCN$^-$ proved to be unsuccessful. This may be explained by the fact that the donor exists as a mixture of two geometrical isomers:[10] 7,7′-dihydroxymethyl bis(ethylenedithio)-tetrathiafulvalene and 7,8′-dihydroxymethyl bis(ethylenedithio)-tetrathiafulvalene, as shown in the Scheme, which is evidenced by HPLC analysis but is impossible to be separated.

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