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Synthesis and Electrochemical Studies on BEDT-TTF Derivatives with Hydroxyl Groups

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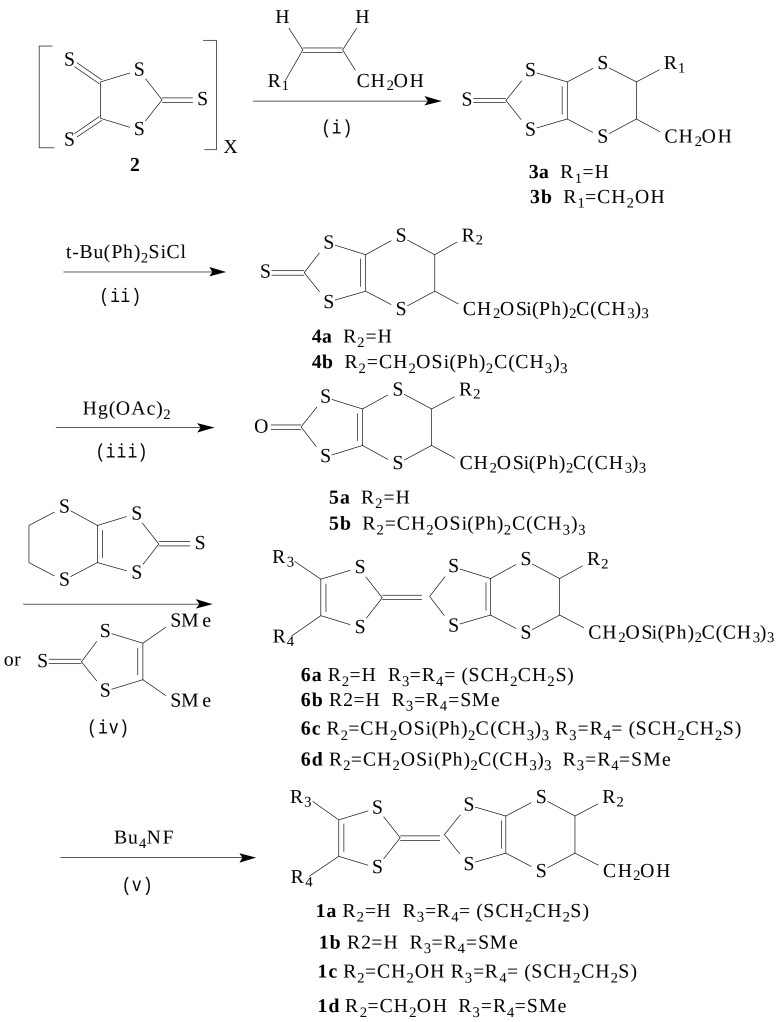
Abstract: New electron donors with hydroxyl groups were synthesized and characterized spectroscopically. Their redox potentials were determined with cyclic voltammetry, and the comparison with BEDT-TTF [Bis(ethylenedithio)tetrathiafulvalene] in this aspect was made. These results indicated that the new electron donors had similar electron-donating capabilities as BEDT-TTF.

Keywords: Electron donor, hydroxyl group, hydrogen bond, redox potential.

Since the finding of organic conductor in 1973 and organic superconductor in 1980, great progress has been achieved[1] in the field of organic conductors and superconductors. Much effort is still being devoted to this field, and several significant results have been obtained by subtle modifications of BEDT-TTF, such as, the substitution of peripheral sulfur atoms with selenium (BETS)[2] and oxygen (BEDO)[3]atoms, the extra-substitution with hydroxyl , amide, pyridine groups[4] *etc*., all of them are aimed to increase the dimensions of the materials by enhancing the intermolecular interaction, Recently, we have paid great attention to new electron donors with hydroxyl groups since electron donors bearing hydroxyl groups would give rise to two or three dimensional materials through hydrogen bonds, which can form among electron donor molecules and acceptors or counter anions. We have reported the synthesis and related investigation of the electron donor with four hydroxyl groups previously[5]. In this paper we will describe the synthesis and electrochemical studies on four new electron donors with hydroxyl groups. The synthesis of new electron donors **1 (a-d)** (see **scheme 1**) started from trithione oligomer $(C_3S_5)_x$ **2** which was prepared by the oxidation of bis (tetrabutylammonium)bis-[2-thioxo-1,3-dithiole-4,5-bis(thiolato)] zincate with iodine[6]. Compounds **3 (a-b)** were synthesized by [4+2] cycloaddition between ally alcohol and 2-butene-1,4-diol, respectively, with trithione oligomer, which decomposed to give the unstable 4,5-dihydro -1,3-dithiole-2,4,5-trithione monomer under heating. Similar strategy was employed for the preparation of alkyl substituted 4,5-ethylenedithio-1,3-dithiole-2-thione[7]. Efforts were also made to synthesize **3 (a-b)** by the nucleophilic substitution reaction between DMIT anion and corresponding dibromoalkyl alcohols, but there were no target compounds in the reaction mixture as indicated by analytical results of thin layer chromatography and the mass spectrum.

Scheme 1



Reagents and Conditions: (i) 1,4-dioxane, 100^0C; (ii) dry DMF, N_2, room temperature; (iii) CH_2Cl_2; (iv) $P(i\text{-}PrO)_3$, N_2, 140^0C; (v) CH_2Cl_2, N_2, room temperature.

The trialkylphosphite mediated coupling of 1,3-dithiole-2-thiones is standard chemistry in the construction of TTF derivatives. However, direct coupling of compounds **3 (a-d)** was failed probably because of the side-reaction between hydroxyl groups and trialkyl phosphite although triisopropanyl phosphite instead of triethyl phosphite was used to hinder such side reaction. Thus, **3 (a-b)** were converted to **4 (a-b)** to protect the hydroxyl groups with *tert*-butyldiphenylchlorosilane. Oxidation of **4 (a-b)** with mercuric acetate gave **5 (a-b)** in high yield. The cross coupling reaction between **5 (a-b)** and corresponding 1,3-dithiole-2-thiones afforded compound **6 (a-d)** in moderate yield. Deprotection of **6 (a-d)**, using tertbutylammonium fluoride in CH_2Cl_2, afforded target molecules **1 (a-d)** in analytically pure form after isolation with column chromatography on silica gel. Since the target molecules **1 (a-d)** were easily and quickly oxidized in crude reaction mixture under air, the deprotection step should be performed under nitrogen atmosphere and tertbutylammonium fluoride should not be largely excess. The chemical structure of **1 (a-d)** were confirmed by spectroscopic data (^{1}H-NMR, MS) and elemental analysis[8].

The redox behaviors of compounds **1 (a-d)** were investigated by cyclic voltammetry and the data were collected in **Table 1**. They all exhibited two quasi-reversible redox waves. For comparison, the corresponding redox potentials of BEDT-TTF were also measured under the same condition and listed in **Table 1**. It can be seen that compounds **1 (a-d)** show similar electron-donating capacities as BEDT-TTF. It further indicated that the substituted hydroxyl groups of **1 (a-d)** have no significant influence on the electron-donation properties and they all should be good precursors for organic conductors.

Table 1 The redox potentials of compounds **1 (a-d)** and BEDT-TTF [solvent: CH_2Cl_2, voltage vs. SCE, electrolyte: $TBAPF_6$ ($0.1 mol.l^{-1}$),]

compound	$E^1_{1/2}$ (V)	$E^1_{1/2}$ (V)
1a	0.46	0.88
1b	0.48	0.87
1c	0.48	0.88
1d	0.48	0.85
ET	0.48	0.89

In conclusion, new electron donors **1 (a-d)** were synthesized and characterized. Their redox potentials were determined and they have similar electron-donating capabilities. The preparation of CT salts based on **1 (a-d)** and relevant physical studies are in progress.

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References and Notes

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8 Compound **3a**: m.p. 88-89 ^{0}C; ^{1}H-NMR ($CDCl_3$): δ (ppm) 3.96 (2H, m), 3.89 (1 H, m), 3.40 (2H, m); MS (EI) 254 (M^{+}); Anal. Calc. for $C_6H_6OS_5$: C, 28.33; H, 2.38; S, 63.01; Found C, 28.59; H, 2.25; S, 63.25. Compound **3b**: m.p. 143-145 ^{0}C; ^{1}H-NMR ($CDCl_3$): δ (ppm) 4.10 (4 H, m), 3.94 (2 H, m), MS (EI) 284 (M^{+}), Anal. Calc. for $C_7H_8O_2S_5$ C, 29.89; H, 2.73; Found C, 29.57; H, 2.82. Compound **1a**: m.p. 160-161 ^{0}C; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.84 (2H, m), 3.78 (1H, m), 3.30 (2H, m), 3.28 (4H, t); MS (TOF) 414 (M^{+}); Anal. Calc. for $C_{11}H_{10}OS_8$. C, 31.88; H, 2.41; S, 61.84; Found C, 32.18; H, 2.53; S, 61.42. Compound **1b**: red oil. ^{1}H-NMR ($CDCl_3$) δ (ppm) 3.85 (2H, m), 3.80 (1H, m), 3.27 (2H, m), 2.43 (6H, s). MS (EI) 415.8648254. Compound **1c**: m.p. 196-197 ^{0}C, ^{1}H-NMR ($CDCl_3$) δ (ppm) 4.05 (4H, m), 3.93 (2H, m), 3.28 (4H, t). MS (EI) 444 (M+); Anal. Calc. for $C_{12}H_{12}O_2S_8$ C, 32.43; H, 2.70; S, 57.65; Found C, 32.33; H, 2.77; S, 57.44. Compound **1d**: m.p. 138-139 ^{0}C ^{1}H-NMR ($CDCl_3$) δ (ppm) 3.95 (4H, m), 3.85 (2H, m), 2.42 (6H, s). MS (TOF) 446 (M+). Anal. Calc. for $C_{12}H_{14}O_2S_8$ C,32.29; H, 3.14; S. 57.40, Found C, 32.29; H, 3.20; S, 57.37.

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