PREPARATION AND PROPERTIES OF TRIS(1,3-DITHIOLE) DONORS CONTAINING THIOPHENE SPACER UNITS†

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Abstract - Novel tris(1,3-dithiole) donors (**4**) and (**5**) containing thiophene spacer units have been prepared. The cyclic voltammograms indicate that **4** and **5** are oxidized to trication radicals and tetracations, respectively, and on-site Coulombic repulsion in the dication state is reduced. An electroactive polymer was formed from **4c**. The donors (**4**) and (**5**) gave conducting charge-transfer complexes with iodine.

Recently much attention has been focused on the development of new electron donors which lead to organic conductors.[1] One of the recent trends involves the insertion of an extending and π-conjugating spacer group between two 1,3-dithiole units in order to decrease on-site Coulombic repulsion in the dication state and increase electron donating ability.[2] Although there have been reported many such extended bis(1,3-dithiole) donors, molecules which possess more than three 1,3-dithiole moieties are little known.[3] Such molecules are expected to exhibit interesting electrochemical properties owing to the configuration as well as the number of 1,3-dithiole units. We have now prepared novel tris(1,3-dithiole) donors (**4**) and (**5**) containing thiophene units as spacer. The donors (**4a**-**d**) and (**5a**-**d**) were synthesized by a Wittig-Horner reaction of the corresponding carbanions derived from phosphonate esters (**3**)[4] with aldehyde (**1**)[5] or ketone (**2**)[6] in 27, 69, 54, 72, 26, 54, 52, and 47% yields, respectively. The structures of new compounds were determined on the basis of the spectral data and elemental analyses.[7]

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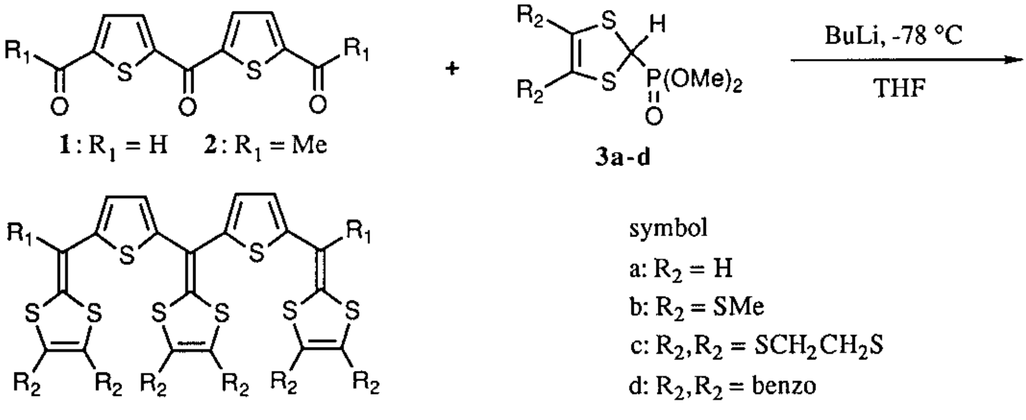
†Dedicated to Prof. Rolf Huisgen on the occasion of his 75th birthday.



1: R_1 = H **2**: R_1 = Me

3a-d

4a-d: R_1 = H **5a-d**: R_1 = Me

symbol
a: R_2 = H
b: R_2 = SMe
c: R_2,R_2 = SCH_2CH_2S
d: R_2,R_2 = benzo

The cyclic voltammograms (CV) in benzonitrile[8] reveal that the donors (**4**) and (**5**) are oxidized to trication radicals and tetracations, respectively. The data are summarized in Table 1. The donors (**4**) and (**5**) showed two and three pairs of redox waves, respectively. The first redox waves are assigned to a quasi reversible one-step two-electron oxidation process which can be resolved into nearly overlapped two waves in dichloromethane for **4c,d** and **5c,d**. This indicates that on-site Coulombic repulsion in the dication states is reduced. The absence of the third oxidation wave in the case of the donors (**4**) suggests that the methyl groups of **5** play an important role in the stabilization of the trication radical states. The E_1 values for **4** and **5** are higher than that for tetrathiafulvalene (TTF) in spite of extension of π-conjugation, indicating that they are weaker electron donors than TTF.

Table 1. Oxidation potentials[a] of donors (**4**) and (**5**)

Donor	E_1	E_2	E_3
4a	0.48[b]	0.82[c]	-
4b	0.58[b]	0.92[c]	-
4c	0.58[b]	0.91[c]	-
4d	0.66[b]	1.02[c]	-
5a	0.50[b]	0.88	1.22[c]
5b	0.59[b]	0.90	1.18[c]
5c	0.59[b]	0.92	1.22[c]
5d	0.68[b]	1.04	1.30[c]
TTF	0.45	0.86	-

[a] Measured in benzonitrile, V *vs*. SCE. [b] Two-electron process. [c] Irreversible wave, peak potential.

In the case of **4c**, when dichloromethane was used as solvent on the CV measurement, the peak current increased steadily with the repetition of scans as shown in Figure 1. This observation indicates that an electroactive polymer (**6**) is formed on the surface of electrode. Other donors did not give any polymers under the same condition. A similar electrochemical behavior of an extended 1,3-dithiole donor was reported recently.[3a] The peak current of the polymer (**6**) is proportional to the scan rate in the potential range of -0.5 to 1.3 V *vs*. SCE, indicating that the electrode reactions of the films are phenomenologically equivalent to that of a surface-attached redox species.[9] The oxidation peak potential (0.85 V *vs*. SCE in CH_2Cl_2, Pt) of the polymer (**6**) is higher than that of the monomer (**4c**), indicating that π-conjugation does not extend efficiently along the polymer chain probably due to steric interactions. This is supported by the fact that the absorption maximum (404 nm) of the polymer film on an indium-tin oxide (ITO) conducting glass electrode in the neutral state is blue-shifted compared with that of the monomer (464 nm). An additional absorption peak was observed at 815 nm in the doped state.

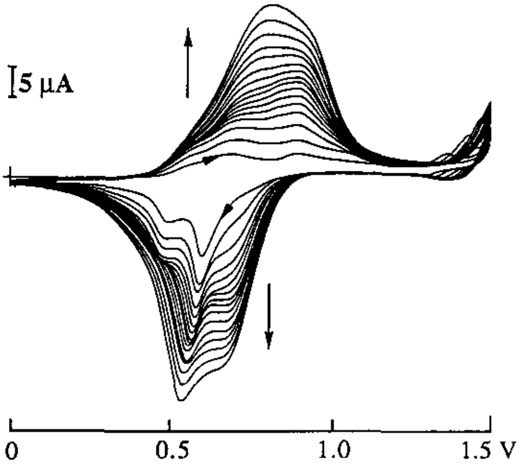
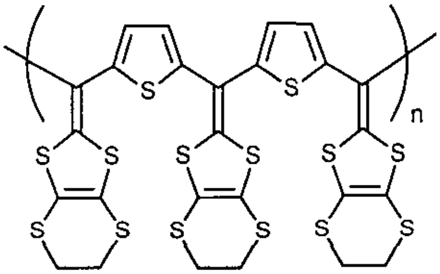


Figure 1. Successive voltammograms of **4c** in dichloromethane; Pt electrode.



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The donors (**4**) and (**5**) afforded charge-transfer complexes with iodine except for **4b**. The electrical conductivities of these complexes measured by a two-probe method on compressed pellets were 10^{-2} to 10^{-5} S cm^{-1}. On the other hand, no tetracyanoquinodimethane complex was obtained probably due to the unfavorable conformational flexibilities for the molecular stacking and the high oxidation potentials of the donors. The electrochemical oxidation of them under the various conditions gave only small amounts of semiconducting salts as black powder.

REFERENCES AND NOTES

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5. This was synthesized from bis(5-formyl-2-thienyl)methane by the similar method for the preparation of the ketone (**2**).
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7. Satisfactory elemental analyses were obtained for the new compounds. Typical example, **4b**: mp 145-147 °C (chloroform/hexane), ir (KBr) 2916, 1563, 1498, 798 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$) δ 2.42, 2.43, and 2.44 (each 6H, s, SCH_3), 6.64 (2H, s, -CH=), 6.80 (2H, d, J = 4.0 Hz, thienyl), 6.89 (2H, d, J = 4.0 Hz, thienyl); ms (FAB) *m/z* 784 (M^+); uv (CH_2Cl_2) λmax (log ε) 432 (4.56), 455 (4.51, sh) nm; Anal. Calcd for $C_{26}H_{24}S_{14}$: C, 39.76; H, 3.08. Found: C, 39.64; H, 3.06.
8. Measured at a Pt electrode in benzonitrile with 0.1 mol dm^{-3} Bu_4NBF_4 as a suporting electrolyte and saturated calomel electrode (SCE) as a reference electrode; scan rate 100 mV s^{-1}.
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