

2,5-Bis(1,3-dithiol-2-ylidene)-2,5-dihydrothiophene and its Bis(alkylthio) Derivatives: a New Synthetic Approach to Thienoquinonoid-extended Tetrathiafulvalenes and their Conductive Complexes

Kazuko Takahashi,* Takayasu Nihira and Kensuke Tomitani

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

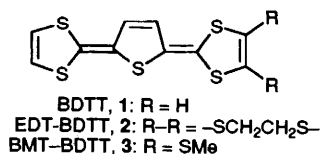
Bis(dithiolylidene)dihydrothiophene and its unsymmetrically substituted bis(alkylthio) derivatives, giving stable radical cations and dications on two-step one-electron oxidations, have been efficiently synthesized by convenient methods and electrical properties of their conductive complexes are described.

On the basis of molecular design strategies for stabilizing the dicationic state of donors by reducing the intramolecular Coulomb repulsive energy, many conjugation-extended tetrathiafulvalene (TTF) analogues involving a π -linking bridge between the two 1,3-dithiole rings have been synthesized.^{1,2} Nevertheless, most of these extended TTFs with a hydrocarbon π -bridge consisting of more than two sp^2 carbons¹ favour the dication state over the radical cation state. We have already synthesized 2,5-bis(4,5-benzo-1,3-dithiol-2-ylidene)-2,5-dihydrothiophenes³ and 2,2'-(thiophene-2,5-diyl)bis(4,5-dimethyl-1,3-dithiolium) bis(tetrafluoroborate)⁴ giving stable radical cations, but this synthetic methodology is of limited scope, and only dibenzo derivatives and dication salts of tetramethyl or diphenyl derivatives were synthesized. After many fruitless efforts, we have now found new advantageous methods applicable widely for the systematic synthesis of various modified bis(dithiolylidene)dihydrothiophene (BDTT)-type donors, by which unsubstituted BDTT itself **1**

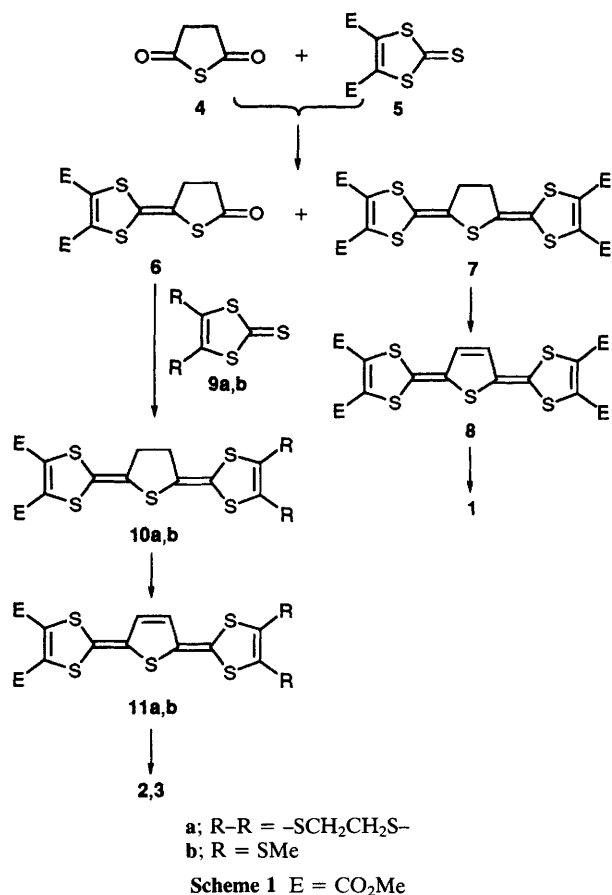
and unsymmetrically substituted EDT-BDTT **2** and BMT-BDTT **3**[†] have successfully been synthesized. We report here the synthesis and electrochemical properties of these new donors, and electrical conductivities of their charge-transfer complexes.

The synthetic routes are outlined in Scheme 1. The anhydride **4**, conveniently available by the pyrolysis of 2,5-di-*tert*-butoxythiophene,⁵ was allowed to react with 3 equiv. of 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione **5** in the presence of excess of trimethyl phosphite in refluxing benzene to afford **6** (m.p. 114–116 °C) and **7** (m.p. 212–214 °C) in 58 and 11% yields, respectively, along with tetrakis(methoxycarbonyl)tetrathiafulvalene.

The bis-capped **7** was also obtained in 57% yield by an analogous cross-coupling reaction of **6** with **5**. Reaction of **7** with 1 equiv. of dichlorodicyanobenzoquinone (DDQ) in refluxing xylene yielded **8** (m.p. 227–229 °C) in 98% yield which was smoothly demethoxycarbonylated with lithium



[†] Superconductors or organic metals based on unsymmetrical TTF derivatives have been reported: G. C. Papavassiliou, G. A. Mousdis, J. S. Zambounis, A. Terzis, A. Hountas, B. Hilti, C. W. Mayer and J. Pfeiffer, *Synth. Metals*, 1988, **27**, B379; K. Kikuchi, K. Murata, Y. Honda, T. Namiki, K. Saito, H. Anzai, K. Kobayashi, T. Ishiguro and I. Ikemoto, *J. Phys. Soc. Jpn.*, 1987, **56**, 4241.



bromide monohydrate in hexamethylphosphoric triamide (HMPA)⁶ at 95 °C and then at 155 °C to give unsubstituted BDTT **1** in 91% yield.‡ When **6** was allowed to react with 3 equiv. of 4,5-ethylenedithio-1,3-dithiole-2-thione **9a** in refluxing toluene containing an excess of trimethyl phosphite, the unsymmetrically capped compound **10a** (m.p. 191–193 °C) was obtained in 55% yield. By the similar cross-coupling reaction of **6** and **9b** was obtained the bis(methylthio) derivative **10b** (m.p. 118–120 °C) in 53% yield. Both **10a** and **10b** were dehydrogenated with DDQ in refluxing xylene to afford **11a** (m.p. 179–181 °C) and **11b** (m.p. 150–151 °C) in 53 and 65% yields, respectively. The unsymmetrical **2** and **3** were obtained in 63 and 60% yields, respectively,‡ by heating **11a** and **11b** with an excess of lithium bromide monohydrate in HMPA. This method can be applied to the synthesis of a

‡ Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds. Selected physical data for 1: reddish violet microcrystals, m.p. (decomp.) 149–150 °C; ¹H NMR (200 MHz, C₆D₆) δ 5.28 (2H, d, *J* 6.5 Hz, dithiH-4 or 5), 5.36 (2H, d, *J* 6.5 Hz, dithiH-5 or 4) and 6.06 (2H, s, thiH-3,4); ¹³C NMR (50 MHz, C₆D₆) δ 118.0 (dithiC-2), 118.6 (dithiC-4 or 5), 119.0 (dithiC-5 or 4), 124.7 (thiC-2,5) and 127.3 (thiC-3,4); UV (tetrahydrofuran) λ_{max}/nm (log ε) 462 (4.51) and 489 (4.58); MS *m/z* 286 (M⁺, 100%). 1²⁺ (2BF₄⁻ salt): dark yellow powder, m.p. 190–195 °C (decomp.); ¹H NMR (200 MHz, CF₃CO₂D) δ 8.36 (2H, s, thiH-3, 4) and 9.10 (4H, s, dithiH-4,5); ¹³C NMR (50 MHz, CF₃CO₂D) δ 137.2 (thiC-3,4), 138.7 (thiC-2,5), 142.6 (dithiC-4,5) and 186.8 (dithiC-2). 2: dark brown microcrystals, m.p. 188–190 °C; ¹H NMR (600 MHz, C₆D₆) δ 2.13 (4H, AA'BB'-type m, -SCH₂CH₂S-), 5.22 (1H, d, *J* 6.5 Hz, dithiH-4 or 5), 5.30 (1H, d, *J* 6.5 Hz, dithiH-5 or 4), 5.98 (1H, d, *J* 5.5 Hz, thiH-3 or 4) and 6.01 (1H, d, *J* 5.5 Hz, thiH-4 or 3); UV (tetrahydrofuran) λ_{max}/nm (log ε) 470 (4.43) and 496 (4.48); MS *m/z* 376 (M⁺, 100%). 3: reddish brown microcrystals, m.p. 102–105 °C; ¹H NMR (200 MHz, C₆D₆) δ 1.78 (3H, s, SMe), 1.83 (3H, s, SMe), 5.27 (1H, d, *J* 6.5 Hz, dithiH-4 or 5), 5.34 (1H, d, *J* 6.5 Hz, dithiH-5 or 4), 6.04 (1H, d, *J* 5.5 Hz, thiH-3 or 4) and 6.10 (1H, d, *J* 5.5 Hz, thiH-4 or 3); UV (tetrahydrofuran) λ_{max}/nm (log ε) 466 (4.45) and 492 (4.48); *m/z* 378 (M⁺, 100%).

Table 1 Cyclic voltammetric data^a for BDTT-donors **1**, **2**, **3**, **11a**, **11b**, **8** and TTF

Compound	<i>E</i> ₁	<i>E</i> ₂	Δ <i>E</i> (= <i>E</i> ₂ - <i>E</i> ₁)	log <i>K</i> _{sem}
TTF	+0.36	+0.77	0.41	6.95
1	+0.11	+0.34	0.23	3.90
2	+0.18	+0.38	0.20	3.39
3	+0.19	+0.37	0.18	3.05
11a	+0.35	+0.55	0.20	3.39
11b	+0.34	+0.55	0.21	3.56
8	+0.47	+0.67	0.20	3.39

^a Potentials are given in V vs. standard calomel electrode (SCE) and were determined for 1.0 mmol dm⁻³ solutions in PhCN with 0.1 mol dm⁻³ Bu₄NClO₄ at room temperature (scan rate: 50 mV s⁻¹). *E*₁ and *E*₂ values are the average of peak potentials of the reversible anodic and cathodic segments of the cycle.

variety of other modified donors by using various derivatives of 1,3-dithiole-2-thione or 1,3-diselenole-2-selenone and heterocyclic dicarbonyl compounds.

The cyclic voltammograms of all the new donors **1**, **2** and **3** in benzonitrile exhibited clearly separated two reversible one-electron oxidation waves. Half-wave oxidation potentials *E*₁ and *E*₂, Δ*E* (= *E*₂ - *E*₁), and log *K*_{sem} values determined by cyclic voltammetry are summarized in Table 1 along with those of TTF measured under the same conditions. The *E*₁ value of **1** is lower by 0.25 V than that of TTF, demonstrating that the donor character is strengthened by introduction of the thienoquinonoid linking bridge. BDTT **1** is one of the most powerful donors among TTFs and their extended analogues. The *E*₁ values of **2** and **3** are higher by 0.07–0.08 V than that of **1**, indicating that the donor ability is slightly reduced by the alkylthio substitution at the 1,3-dithiole ring. Owing to the electron-attracting property of the ester groups, the *E*₁ values of **11a** and **11b** are higher than those of **2** and **3**, and are near to that of TTF. The Δ*E* values for **1**, **2** and **3** are smaller by 0.18–0.23 V than that of TTF, and are indicative of decreased Coulombic repulsions in the dicationic state as expected. However, the Δ*E* and log *K*_{sem} values of **1**, **2** and **3** are significantly larger than those of other extended TTFs involving a hydrocarbon π-linking bridge¹ which undergo one-step two-electron oxidation to the dicationic state. The Δ*E* values of **1**, **2** and **3** are larger than those of 2,5-bis(dithiafulvenyl)-thiophenes or -furans in which conformational changes have occurred during the redox reactions^{2a-d} and quasi-reversible redox waves or nearly coalescent two-electron waves have been observed in some cases by cyclic voltammetry.^{2d} The thermodynamic stabilization of the radical cations of our BDTTs is ascribed to the distribution of an unpaired electron over all three rings, and as a result conformational changes associated with rotation of the 1,3-dithiole rings about the intercyclic bonds would be difficult. Indeed the hyperfine splitting constants for the thienyl ring protons (0.071 mT) and for the 1,3-dithiole ring protons (0.089 mT) are comparable with each other in the ESR spectrum (*g* = 2.0073) of **1** in dichloromethane. We measured the absorption spectrum of the radical cation **1**^{•+} formed by the electrochemical oxidation of **1** in acetonitrile (Fig. 1).

The dicationic salt **1**²⁺,‡ isolated by oxidation of **1** with NOBF₄ in dichloromethane, shows a strong fluorescence emission at 530 nm in acetonitrile with a quantum yield φ_f of 0.56,§ indicating that these donors exist in rigid and coplanar conformations in their dicationic states even in solution. The same is true for the neutral species, because each of the two

§ The fluorescence emission of **1** was presented by us at the 63th Annual Meeting of the Chemical Society of Japan, March, 1992, Abstr. II, 1246.

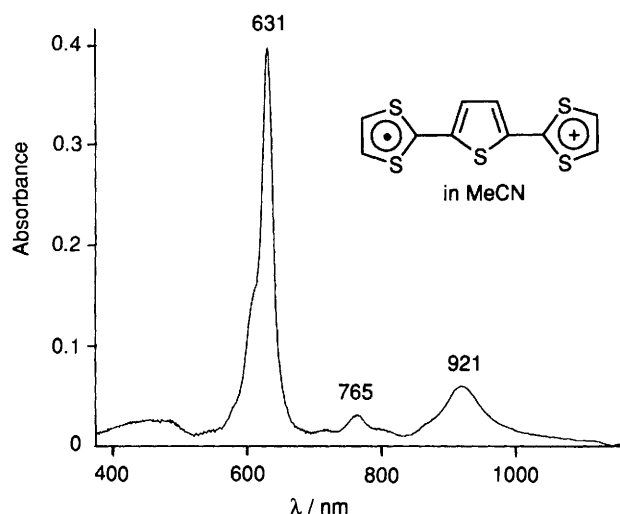


Fig. 1 Electronic spectrum of radical cation of thienoquinonoid-extended TTF $1^{\bullet+}$ in MeCN

1,3-dithiole ring protons in **1**, **2** and **3**, as well as each of the two methyl protons in **3**, exhibit different chemical shifts in their ^1H NMR spectra, suggesting that the 1,3-dithiole rings in these donors do not rotate around the intercyclic bonds in solution. Thus the BDTT donors reported here are of particular importance as novel highly extended redox systems undergoing only electron transfer.

Donors **1**, **2** and **3** are soluble in conventional organic solvents and gave molecular complexes with electron acceptors, whose electrical properties measured by the two-probe method on compressed powder samples are summarized in Table 2 along with the ΔE (D, A) values.⁷ The donor **1** appears to be too electron-donating for tetracyanoquinodimethane (TCNQ) to form a partial 1:1 charge-transfer (CT) complex. The conductivity of the TCNQ complex of **1** is relatively low. On the other hand, the conductivities of the TCNQ complexes of **2** and **3** are almost 1000 and 100 times higher, respectively, than that of the TCNQ complex of **1**. This can be ascribed to the enhancement of intra- or inter-stack interactions in the complexes via the chalcogen atoms located at the edges of these donors, and also to the slightly weaker electron donating abilities of **2** and **3** than **1**, which can form a partial CT complex with TCNQ. Further efforts to obtain single crystals of radical salts with various inorganic counter anions by electrochemical methods are in progress.

Table 2 Stoichiometries, room temperature resistivities, and ΔE (D, A) values for the complexes of **1**, **2** and **3** with electron acceptors^a

Donor	Acceptor	Stoichiometry ^b donor : acceptor	Resistivities ^c $\rho_{r.t.}/\Omega \text{ cm}$	ΔE (D, A)/V
1	TCNQ	2:3	2.1×10^4	-0.07
2	TCNQ	3:2	28	0.00
3	TCNQ	1:1	260	+0.01
1	Chloranil	1:1	1.2×10^3	+0.07
1	I_3	1:2	1.3×10^7	—
2	I_3	1:2	8.3×10^5	—

^a Prepared by mixing two hot solutions of the donor and acceptor in conventional organic solvents. ^b Determined by elemental analysis of the complexes. ^c Two-probe method on compressed powder samples.

We thank Dr K. Akiyama and Professor Y. Ikegami of Tohoku University for measuring the ESR and fluorescence spectra. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan and by a grant from the Hayashi Memorial Foundation for Female Natural Scientists.

Received, 2nd June 1993; Com. 3/03135G

References

- Z. Yoshida, T. Kawase, H. Awaji and S. Yoneda, *Tetrahedron Lett.*, 1983, **24**, 3473; M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1675; Y. Yamashita, Y. Kobayashi and T. Miyashi, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1052; A. J. Moore and M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1*, 1991, 157; Y. Yamashita, S. Tanaka and M. Tomura, *J. Chem. Soc., Chem. Commun.*, 1993, 652.
- (a) T. K. Hansen, M. V. Lakshmikantham, M. P. Cava, R. E. Niziurski-Mann, F. Jensen and J. Becher, *J. Am. Chem. Soc.*, 1992, **114**, 5035; (b) A. S. Benahmed-Gasmi, P. Frere, B. Garrigues, A. Gorgues, M. Jubault, R. Carlier and F. Texier, *Tetrahedron Lett.*, 1992, **33**, 6457; (c) J. Roncali, M. Giffard, P. Frere, M. Jubault and A. Gorgues, *J. Chem. Soc., Chem. Commun.*, 1993, 689; (d) K. Takahashi, T. Nihira, M. Yoshifuji and K. Tomitani, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 2330.
- K. Takahashi, T. Nihira, K. Takase and K. Shibata, *Tetrahedron Lett.*, 1989, **30**, 2091.
- K. Takahashi and T. Nihira, *Tetrahedron Lett.*, 1989, **30**, 5903.
- H. J. Jakobsen, E. H. Larsen and S.-O. Lawesson, *Tetrahedron*, 1963, **19**, 1867.
- S. Yoneda, T. Kawase and Z. Yoshida, *J. Org. Chem.*, 1979, **44**, 1728.
- G. Saito and J. P. Ferraris, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2141.