Thienoquinonoid-extended Analogues of Bis(alkylenedithio)tetrathiafulvalenes and their Conductive Complexes

Kazuko Takahashi* and Kensuke Tomitani

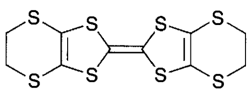
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980-77, Japan

Three thienoquinonoid-extended analogues of bis(alkylenedithio)tetrathiafulvalenes, which are symmetric and unsymmetric conjugation-elongated donors, are synthesized and TCNQ complexes of these donors are proved to exhibit a metallic temperature dependence or a fairly high room temperature conductivity even when measured on compressed powder samples.

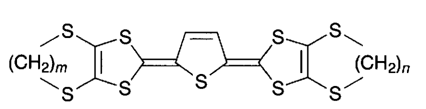
Bis(ethylenedithio)tetrathiafulvalene (BEDT–TTF) has been recognized as the most promising synthetic component of organic superconductors owing to its ability to produce two-dimensional conducting layers[1] with high superconducting transition temperatures (T_c).[2] Recently, it has been pointed out that the T_cs of BEDT–TTF superconductors are proportional to the volume of the most effective space (V_{mes}) for the carrier distribution in the donor layer, which is composed of the C_6S_8 skeleton and intra-donor–layer overlaps between the atomic orbitals of the C_6S_8 π-systems.[3] Donor molecules with a more elongated π-system than that of BEDT–TTF have been required[3] in order to increase the V_{mes} and then to obtain high T_c organic superconductors. 2,5-bis(4,5-Ethylenedithio-1,3-dithiol-2-ylidene)-2,5-dihydrothiophene (BEDT–BDTT, **1**), that is the 2,5-thienoquinonoid-extended analogue of BEDT–TTF, would be a promising donor to satisfy such a requirement, since the large $C_{10}S_9$ moiety of BEDT–BDTT may contribute effectively to increase the V_{mes} in the conducting donor-layer of its metallic salts. With this motivation, herein we report the successful synthesis and electrochemical properties of three new conjugation-elongated donors with four outer-chalcogen atoms, **1**, **2** and **3**, and the electrical properties of their conducting complexes. An elongated BEDT–TTF analogue, in which the central C=C bond of BEDT–TTF is replaced by an ethanediylidene moiety, has been synthesized by several groups,[4] but the electric properties of its complexes have not yet been reported.

The new donors **1**, **2**, and **3** were synthesized according to the routes shown in Scheme 1. The cross-coupling reactions of **4**[5] with 2 equiv. of **5a** and **5b** afforded mono-capped ketones **6a** (44%) and **6b** (40%) with small amounts of bis-capped compounds **7** (17%) and **9** (3%), respectively. The second step, cross-coupling reactions of **6a** and **6b** with 3 equiv. of **5a** and **5b**, yielded bis-capped intermediates **7** (40%) and **9** (30%), respectively.† When **6b** was allowed to react with 3 equiv. of **5a**, the unsymmetric intermediate **8** was obtained in 34% yield, but in a lower yield of *ca.* 10% in the reaction of **6a** with **5b**. Chloranil has proved to be the most effective dehydrogenation reagent for **7**, **8** and **9** giving **1** (64%), **2** (60%), and **3** (73%) in fairly good yields.‡

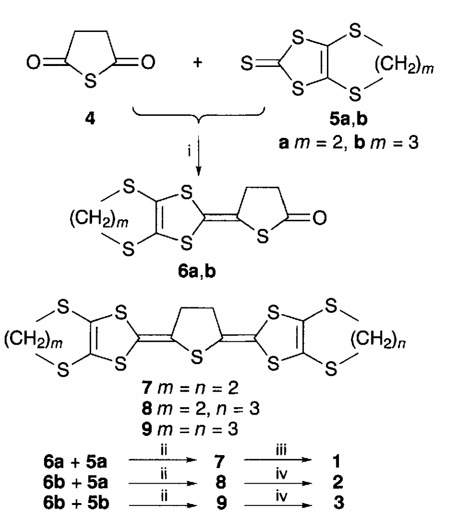
The donors **1–3** are air-stable and exhibited two pairs of reversible one-electron redox waves in their CV (Fig. 1). The E_1^{ox} values of **1–3** (Table 1) are lower by 0.26–0.28 V than that of BEDT–TTF, indicating that the electron-donating ability is significantly enhanced by the elongation with the thienoquinon-



BEDT–TTF



1 BEDT–BDTT; $m = n = 2$
2 EP–BDTT; $m = 2, n = 3$
3 BPDT–BDTT; $m = n = 3$



Scheme 1 *Reagent and conditions*: i, $P(OMe)_3$ in PhH, reflux, 6 h; ii, $P(OMe)_3$ in PhH, reflux, 18 h; iii, chloranil (1.4 equiv.) in xylene, reflux, 4 h; iv, chloranil (1.1 equiv.) in xylene, reflux, 3 h

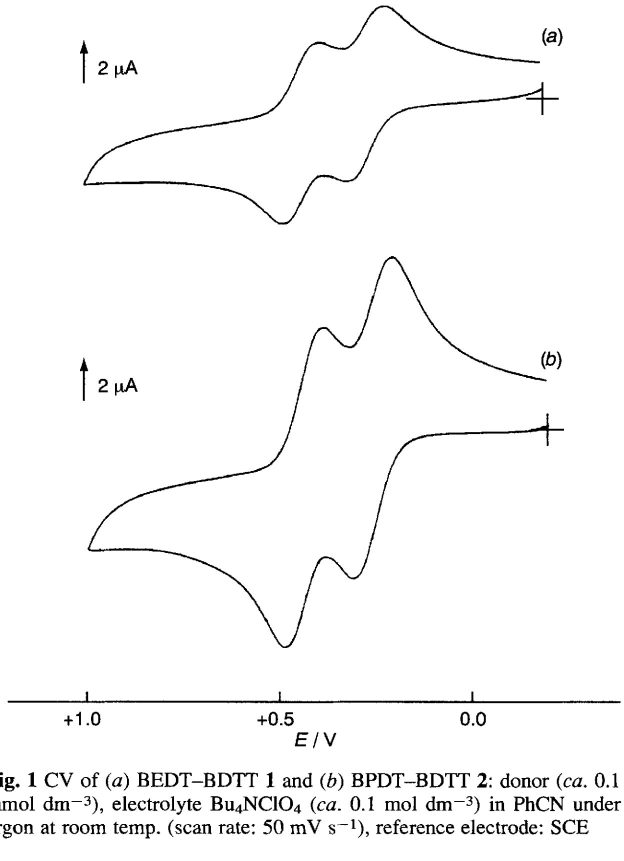


Fig. 1 CV of (*a*) BEDT–BDTT **1** and (*b*) BPDT–BDTT **2**: donor (*ca.* 0.1 mmol dm^{-3}), electrolyte Bu_4NClO_4 (*ca.* 0.1 mol dm^{-3}) in PhCN under argon at room temp. (scan rate: 50 mV s^{-1}), reference electrode: SCE

Table 1 Electrochemical data of donors and physical properties of their TCNQ complexes

	Electrochemical property[a]				Conductivity[b] and IR band[c] of the TCNQ complex			
Donor	E_1^{ox}	E_2^{ox}	ΔE^{ox}	log K_{sem}	$D:A$[d]	σ/Scm^{-1}	ν_{CN}/cm^{-1}	ν_{CT}/cm^{-1}
1	+0.26	+0.34	0.17	2.88	1 : 1	16	2197	3000 (br)
2	+0.24	+0.42	0.18	3.05	1 : 1	1.8	2189	3000 (br)
3	+0.26	+0.44	0.18	3.05	1 : 1	1.4	2189	3000 (br)
BDTT	+0.11	+0.34	0.23	3.90	1 : 1	6.9×10^{-3}	2125, 2152	5500 (br)
BEDT–TTF	+0.52	+0.83	0.31	5.25	—	—	—	—

[a] Potentials are given in V *vs.* SCE, determined by CV, 1.0 mmol dm^{-3} solutions in PhCN with 0.1 mol dm^{-3} Bu_4NCl_4 : 50 mV s^{-1}. [b] Four-probe method on a compaction pellet measured at room temp. [c] ν_{CN} of TCNQ: 2224 cm^{-1}. [d] Determined by elemental analysis.

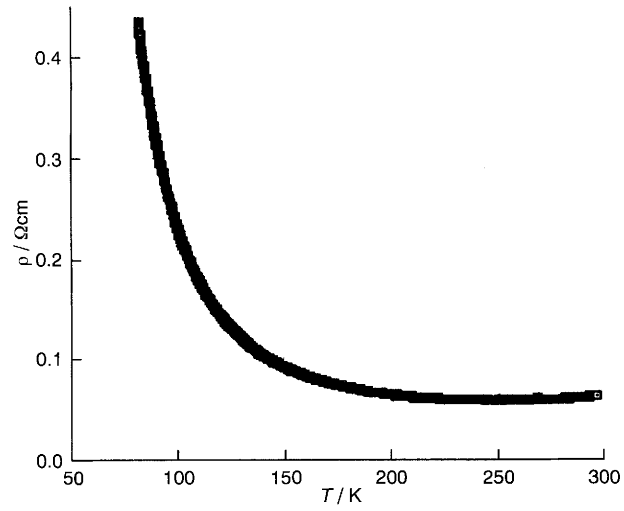


Fig. 2 Temperature dependence of the resistivity of the 1 : 1 TCNQ complex of BEDT–BDTT, **1** measured on a compaction pellet

oid moiety. The E_1^{ox} values of **1–3** are higher by 0.13–0.15 V than that of 2,5-bis(1,3-dithiol-2-ylidene)-2,5-dihydrothiophene (BDTT) having no outer-chalcogen atom.[6] The positive charge appears to be delocalizing effectively on the outer-chalcogen atoms in the dications of **1–3**, since the $\Delta E^{ox} = (E_2^{ox}–E_1^{ox})$ values of **1–3** are smaller than that of BDTT.

All these three donors **1–3** formed 1 : 1 molecular complexes with TCNQ, whose electric conductivities and characteristic IR bands are summarized in Table 1 along with the values for the TCNQ complex of BDTT measured under the same conditions. Interestingly, the room temperature conductivities of TCNQ complexes of **1–3** are 10^4–10^3 times higher than that of the TCNQ complex of BDTT. Moreover, the TCNQ complex of BEDT–BDTT showed a metallic temperature dependence of the conductivity down to 248 K and exhibited a semiconducting behaviour with very low activation energy of E_a = 0.023 eV at the temperature range of 240–80 K on the compressed pellet (Fig. 2). Thus the single crystal of the salt is expected to show metallic behaviour down to much lower temperatures.§

Thus, donors **1–3** are the first examples of the conjugation-elongated analogues of bis(alkylenedithio)tetrathiafulvalenes[4,7] providing high or metallic conducting complexes.

The solid state electronic spectra of the TCNQ salts of **1–3** in KBr showed a very broad intrastack CT absorption band[8] at around 3000 cm^{-1} indicating that these salts possess a segregated stacking mode in a mixed valence state. The degrees of CT estimated primarily from ν_{CN} values (Table 1) using Chappell's equation[9] are partial mode with Z = 0.61 for the TCNQ salt of **1** and 0.79 for the salts of **2** and **3**.

This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Molecular Conductors (No. 06243203) from the Ministry of Education, Science and Culture, Japan and by the grant from the Shorai Foundation for Science and Technology.

Received, 13th December 1994; Com. 4/07566H

Footnotes

† BEDT–TTF was formed as a by-product in 10–20% yields in these reactions.

‡ *Selected physical data*: (^{1}H NMR data: in CS_2–$CDCl_3$; UV–VIS data in THF) for **1**: dark red brown powder, mp 170–175 °C (decomp.) ^{1}H NMR (200 MHz) δ 3.33 (8H, s, SCH_2CH_2S) and 6.30 (2H, s, thiH-3,4); MS *m/z* 466 (M$^+$); UV λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) 504 (4.35), 473 (4.28) and 279 (4.13). **2**: dark-brown powder, mp 139–140 °C (decomp.); ^{1}H NMR (600 MHz) δ 2.35 (2H, m, H-β), 2.70 (4H, t, H-α), 3.31 (4H, s, SCH_2CH_2S) and 6.28 (2H, br., thiH-3,4); MS *m/z* 480 (M$^+$); UV λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) 501 (4.50), 474 (4.45) and 274 (4.18). **3**: red brown powder, mp 240–241 °C (decomp.); ^{1}H NMR (200 MHz) δ 2.42 (4H, m, H-β), 2.71 (8H, t, H-α) and 6.25 (2H, br., thiH-3,4); MS *m/z* 494 (M$^+$); UV λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) 496 (4.60), 474 (4.58) and 271 (4.25).

§ Donors **1–3** have a bow-shaped structure, so the intrastack interactions may be somewhat weakened and the interstack interactions along the transverse direction may be strengthened comparatively. Such a donor may provide somewhat unstable metals which transfer easily to high T_c organic superconductors.

References

1 G. Saito, *Phosphorus Sulfur Silicon Relat. Elem.*, 1992, **67**, 345; G. Saito, *Pure Appl. Chem.*, 1987, **59**, 999.

2 J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. S. Crouch, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung and M.-H. Whangbo, *Inorg. Chem.*, 1990, **29**, 3272; J. M. Williams, A. J. Schultz, U. Geiser, K. D. Carlson, A. M. Kini, H. H. Wang, W.-K. Kwok, M.-H. Whangbo and J. E. Schirber, *Science*, 1991, **252**, 1501.

3 H. Yamochi, T. Komatsu, N. Matsukawa, G. Saito, T. Mori, M. Kusunoki and K. Sakaguchi, *J. Am. Chem. Soc.*, 1993, **115**, 11319.

4 T. K. Hansen, M. V. Lakshmikantham, M. P. Cava, R. M. Metzger and J. Becher, *J. Org. Chem.*, 1991, **56**, 2720; A. J. Moore, M. R. Bryce, D. J. Ando and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1991, 320; V. Yu. Khodorkovskii, L. N. Veselova and O. Ya. Neiland, *Khim. Geterotsikl. Soedin*, 1990, 130.

5 H. J. Jakobsen, E. H. Larsen and S. -O. Lawesson, *Tetrahedron*, 1963, **19**, 1867.

6 K. Takahashi, T. Nihira and K. Tomitani, *J. Chem. Soc., Chem. Commun.*, 1993, 1617.

7 T. K. Hansen, M. V. Lakshmikantham, M. P. Cava and J. Becher, *J. Chem. Soc., Perkin Trans. 1*, 1991, 2873.

8 J. B. Torrance, B. A. Scott and F. B. Kaufman, *Solid State Commun.*, 1975, **17**, 1369; J. Tanaka, M. Tanaka, T. Kawai, T. Takabe and O. Maki, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2358.

9 J. S. Chappell, A. N. Block, W. A. Bryden, M. Maxfield, T. O. Poehler and D. O. Cowan, *J. Am. Chem. Soc.*, 1981, **103**, 2442.