New Cyclohexeno-fused Tetrachalcogenofulvalenes and an Electron Correlated TCNQ Salt

Naoki Sakurai,[†],[††] Hatsumi Mori,*[†] Shoji Tanaka,[†] and Hiroshi Moriyama*[††]
[†]*International Superconductivity Technology Center, Shinonome, Koto-ku, Tokyo 135-0062*
[††]*Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274-8510*

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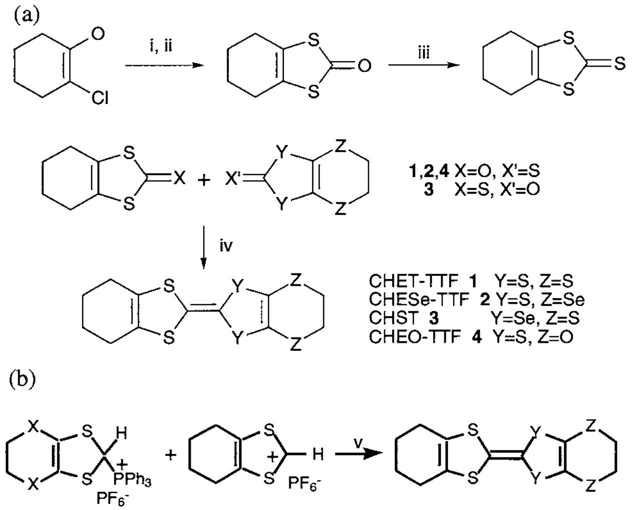
New cyclohexeno-fused donors, CHET-TTF **1**, CHESe-TTF **2**, CHST **3** and CHEO-TTF **4**, have been synthesized and the prepared **1** • TCNQ is electron correlated system with two-dimensional electronic structure by a tight-binding band calculation, where magnetic susceptibility is retained in Curie-like behavior down to 2 K.

Within the field of organic conductors, the control of electronic state is common interest, and the pivotal roles of (1) dimensionality and (2) electronic correlation parameter (U/W, U; on-site Coulomb repulsion energy, W; bandwidth) are well established. It is widely recognized that the chemical modifications by the introduction of functional group and the substitution to the larger chalcogen atoms are effective to control the solid state. Most of EDT-TTF (ethylenedithio-TTF) salts so far investigated form low dimensional conductors, where their ground states are a non-magnetic insulating phase[1] except the strongly dimerized $(EDT\text{-}TTF)_4Cu_2Br_4$.[2] Therefore, in order to increase the dimensionality of EDT-TTF salts by means of the introduction of an annulated tetramethylene group and control correlation parameter by the introduction of Se atom in TTF skeleton, new cyclohexeno-fused donors, tetramethylene-(ethylenedithio)TTF (CHET-TTF) **1**, tetramethylene(ethylenediseleno)TTF (CHESe-TTF) **2**, tetramethylene(ethylenedithio)diselenadithiafulvalene (CHST) **3** and tetramethylene(ethylenedioxy)TTF (CHEO-TTF) **4**, have been synthesized not only by the cross-coupling reactions with $P(OEt)_3$, but also by the Wittig reactions. It is characteristic that present cyclohexeno-fused donors have the same framework as BEDT-TTF which provides many stable metallic conductors and superconductors.[3] In this paper, the syntheses of new donors, the crystal and electronic structure analyses, and the resistivity and magnetic susceptibility measurements of **1** • TCNQ are reported in order to investigate the effect of the introduction of annulated tetramethylene group.



Scheme 1. *Reagents and conditions:* i, Pr^iOCSSK, acetone, reflux, 3 h; ii, H_2SO_4, 0 °C, 2 h (52%); iii, P_2S_5, toluene, reflux, 2.5 h (86%); iv; $P(OEt)_3$, 110 °C, 5 h; v, NEt_3, MeCN, rt, 1 h.

Donors, **1**-**4**, were synthesized by the cross coupling reactions with $P(OEt)_3$ [yield; **1** 8%, **2** 2%, **3** 8%, **4** 8%] (Scheme (a)). The reactants ketone and thione were prepared by modified methods of literatures.[4] The yields were low, however, so that we investigated the other method shown in Scheme (b).[5] These Wittig reactions were favorable for syntheses of **1** and **2** with higher yields, 69% and 59%, respectively.[cf., **3**(8%) and **4**(0%)]

The oxidation potentials of the corresponding symmetrical donors, EDT-TTF and **1**-**4** measured by cyclic voltammetry are shown in Table. The values of E1, E2 and ΔE of **1**-**4** are close to the average values of those of corresponding symmetrical donors. It suggests that present donors have good donor abilities and that these complexes tend to form highly correlated systems owing to the relatively large ΔE.

The black plate crystal of **1** • TCNQ was prepared by slow-cooling of concentrated chlorobenzene solution. The four-probe conductivity measurement along the c*-axis at room temperature of **1** • TCNQ is 0.8 S cm^{-1} and the activation energy is 50 meV. The C≡N stretching frequency of TCNQ (2201 cm^{-1})[6] and redox potentials of **1** and TCNQ[6] indicate $TCNQ^{0.5\text{-}0.6\text{-}}$, similar to that of BEDT-TTF • TCNQ.[7] The crystal structure of **1** • TCNQ is depicted in Figure 1.[8] The segregated donor layer and acceptor sheet stack along the b-axis. As for the donor sheet, the tetramethylene part is not sandwiched by two stacking donors and allocated out of the column due to the hindrance of eight H atoms bonded to C9-C12 atoms, so that the donors are strongly dimerized. Moreover, the positional disorder of S1/C10 and S2/C9 is observed by 17% due to the similarity of S and CH_2 part, partially related to the semiconducting behavior. The donor

Table. Half-wave oxidation potentials[a]

Donors	$E^1_{1/2}$/V	$E^2_{1/2}$/V	ΔE/V[b]
OMTTF[c]	0.31	0.76	0.45
CHEO-TTF **4**	0.36	0.75	0.39
CHESe-TTF **2**	0.42	0.80	0.38
CHET-TTF **1**	0.43	0.81	0.38
BO[d]	0.45	0.77	0.32
EDT-TTF	0.46	0.82	0.36
CHST **3**	0.50	0.84	0.34
BEDT-TTF	0.52	0.82	0.30
BEDSe-TTF[e]	0.53	0.83	0.30
BETS[f]	0.68	0.88	0.20

[a]0.1 M Bu_4NClO_4 in PhCN, Pt electrode, 25 °C, scan rate 100 mV s^{-1}, V vs. SCE. [b]$\Delta E = E^2_{1/2}\text{-}E^1_{1/2}$. [c]OMTTF = octamethylene-TTF. [d]BO = bis-(ethylenedioxy)TTF. [e]BEDSe-TTF = bis(ethylenediseleno)TTF. [f]BETS = bis(ethylenedithio)tetraselenafulvalene.

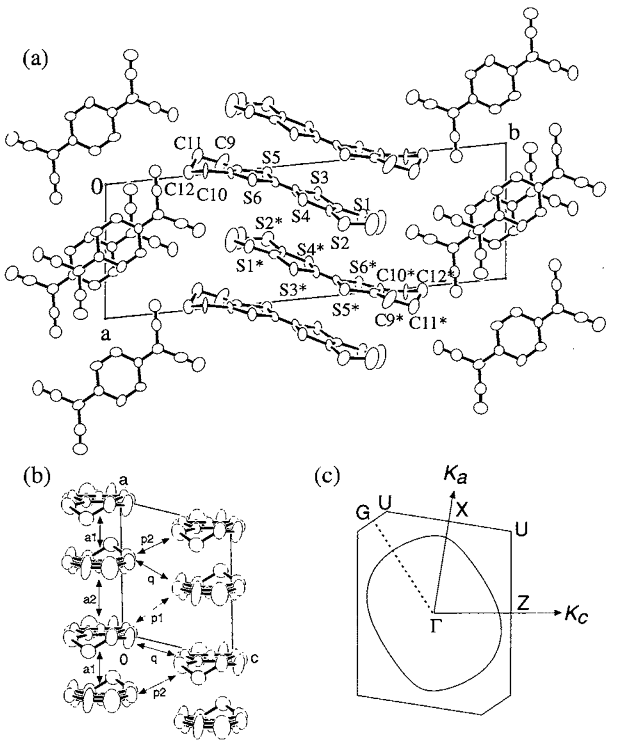


Figure 1. (a) Crystal structure, (b) donor arrangement and (c) Fermi surface of the donor part for CHET-TTF • TCNQ. The calculated overlap integrals (x10^{-3}) of the HOMO of CHET-TTF$^{0.5+}$ without taking account of disorder are a1 = 14.3, a2 = 20.3, p1 = 8.4, p2 = 3.8 and q = -2.4.

arrangement as shown in Figure 1(b) is the face-to-face dimerized stacking mode, which is similar to that of β-(BEDT-TTF)$_2$I$_3$.[9] The electronic structure was estimated by the band calculation based on the tight binding approximation.[10] As shown in Figure 1(c), the calculated Fermi surface of the donor part is two-dimensional with the band width of 0.92 eV, whereas TCNQ part shows completely one dimensionality. Owing to the relatively large on-site Coulomb interaction of **1** and dimerization of donors, **1** • TCNQ is electron correlated system even though the band width is not particularly narrow. The magnetic susceptibility measurement indicates that the value at room temperature is 8.2x10^{-4} emu mol^{-1} and the Curie-like behavior is retained down to 2 K with a small increase of χT at low temperatures (Figure 2).

In conclusion, we have synthesized new cyclohexeno-fused donors, **1-4**, not only by the cross coupling reactions with P(OEt)$_3$, but also by the Wittig reactions with high yields. The prepared complex, **1** • TCNQ, has segregated sheets, where the calculated electronic structure of the donor part is two-dimensional. By the introduction of annulated tetramethylene group to the EDT-TTF molecule, the higher dimensional salt, **1** • TCNQ, could be obtained, where the magnetic susceptibility is retained down to 2 K. The incorporation of the Se atoms in this system is under progress.

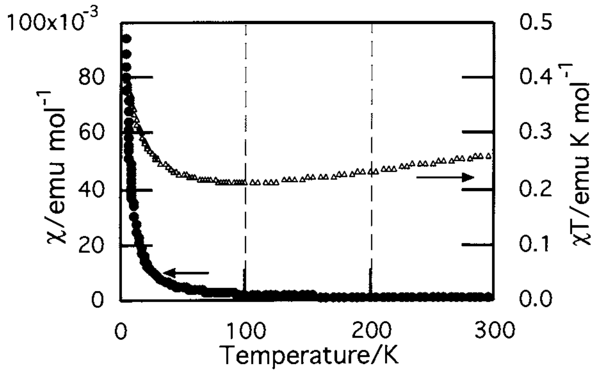


Figure 2. Temperature dependence of magnetic susceptibility for CHET-TTF • TCNQ.

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References and Notes

1 H. Mori, N. Sakurai, S. Tanaka, and H. Moriyama, *Bull. Chem. Soc. Jpn.*, **72**, 683 (1999); R. Kato, H. Kobayashi, and A. Kobayashi, *Chem. Lett.*, **1989**, 781; T. Mori and H. Inokuchi, *Solid State Commun.*, **70**, 823 (1989); A. Hountas, A. Terzis, G. C. Papavassilou, B. Hilti, M. Burkle, C. W. Meyer, and J. Zambounis, *Acta Cryst.*, **C46**, 228 (1990); T. Kondo, L. A. Kushch, H. Yamochi, and G. Saito, *Mat. Res. Soc. Symp. Proc.*, **488**, 921 (1998).

2 H. Mori, I. Hirabayashi, S. Tanaka, T. Mori, and Y. Maruyama, *Synth. Met.*, **70**, 877 (1995); H. Mori et al., private communication.

3 For recent progress in molecular conductors, see Proceeding of International Conference on Science and Technology of Synthetic Metals (ICSM '98), *Synth. Met.*, **102-103** (1999).

4 J. Larsen and C. Lenoir, *Synthesis*, **1989**, 134; J. P. Ferraris, T. O. Poehler, A. N. Bloch, and D. O. Cowan, *Tetrahedron Lett.*, **27**, 2553 (1973); R. Mayer and B. Gebhardt, *Chem. Ber.*, **97**, 1298 (1964); P. J. Nigrey, *Synth. Met.*, **27**, B365 (1988); P. J. Nigrey and B. Morosin, *Synth. Met.*, **27**, B481 (1988); K. Hartke and T. Lindenblatt, *Synthesis*, **1990**, 281; R. Kato, H. Kobayashi, and A. Kobayashi, *Synth. Met.*, **41-43**, 2093 (1991).

5 K. Akiba, K. Ishikawa, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2674 (1978); A. J. Moore and M. R. Bryce, *Synthesis*, **1991**, 26; T. K. Hansen, M. V. Lakshmikantham, M. P. Cava, R. M. Metzger, and J. Becher, *J. Org. Chem.*, **56**, 2720 (1991); A. J. Moore and M. R. Bryce, *Synthesis*, **1997**, 407.

6 J. S. Chappel, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler, and D. O. Cowan, *J. Am. Chem. Soc.*, **103**, 2442 (1981); G. Saito and J. P. Ferraris, *Bull. Chem. Soc. Jpn.*, **53**, 2141(1980).

7 Y. Iwasa, K. Mizuhashi, T. Koda, Y. Tokura, and G. Saito, *Phys. Rev. B*, **49**, 3580 (1994); T. Mori and H. Inokuchi, *Solid State Commun.*, **59**, 355 (1986).

8 Crystal data for CHET-TTF • TCNQ: $C_{24}H_{16}N_4S_6$, Mw = 552.78, triclinic, space group P$\bar{1}$ (no.2), a = 7.965(4), b = 23.44(1), c = 6.589(4) Å, α = 93.61(5), β = 98.62(5), γ = 95.15(4)°, V = 1207(1) Å^3, Z = 2, Dc = 1.52 g cm^{-3}, μ = 5.89 cm^{-1}, R (Rw) = 0.105 (0.112) for independent 3202 reflections [I > 5.00 σ(I)].

9 T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, *Chem. Lett.*, **1984**, 957.

10 T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **57**, 627(1984).