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A new organic superconductor β-(*meso*-DMBEDT-TTF)$_2$PF$_6$†

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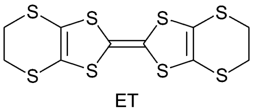
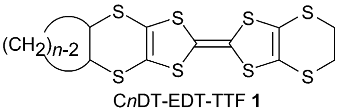
A newly synthesized donor *meso*-DMBEDT-TTF [DMBEDT-TTF = 2-(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-5,6-dihydro-5,6-dimethyl-1,3-dithiolo[4,5-*b*][1,4]dithiin] afforded a superconducting salt β-(*meso*-DMBEDT-TTF)$_2$PF$_6$, with a transition temperature at 4.3 K (onset) under a hydrostatic pressure of 4.0 kbar.

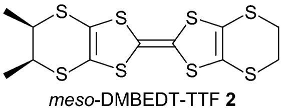
In the field of organic superconductors, ET (bis(ethylenedithio)-tetrathiafulvalene) is the most extensively studied donor as a component of organic superconductors.[1] In particular, the electronic states of the κ-type[2] salts have been systematically investigated based upon the universal phase diagram.[3] However, the Mott transition behaviour between superconducting and antiferromagnetic states has not been resolved yet. To control U/W (U: the on-site Coulomb repulsion energy) by changing the bandwidth W,[4] we have investigated donor molecules with enhanced steric hindrance, C*n*DT-EDT-TTF (n = 5, 6) **1**.[5] The results indicate (i) the stacking manners of the donor molecules for the **1a** salts are more dimeric than those of the **1b** salts because the ring for **1a** extends nearly in the molecular plane but for **1b** nearly perpendicular to the TTF skeleton, and (ii) the negative-pressure effects of the **1** salts by the cycloalkylene rings are so strong that most of the salts are semiconductor. In order to locate the systems at the boundary between metallic and insulating states, we attempted to slightly diminish the chemical pressure of **1** by *cis* substitution of two methyl groups to ET. In this communication, we report the synthesis of new donor molecule *meso*-DMBEDT-TTF **2** and its superconducting salt β-(*meso*-DMBEDT-TTF)$_2$PF$_6$.



ET



C*n*DT-EDT-TTF **1**
(n = 5; **1a**, n = 6; **1b**)



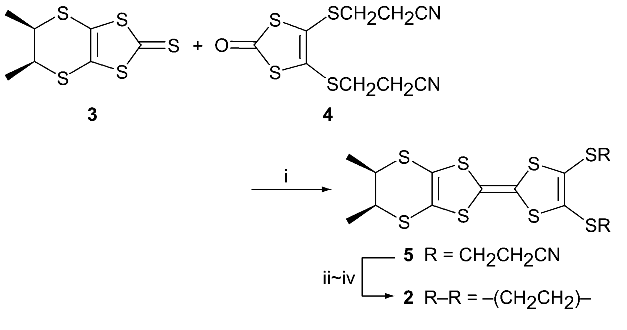
meso-DMBEDT-TTF **2**

The synthesis of **2** was carried out as shown in Scheme 1.‡ In order to avoid the contamination of non-substituted ET, the one-pot cross-coupling reaction was not adopted. The protected TTF **5** was obtained by cross-coupling reaction between **3**[6] and **4**.[7] Deprotection of **5** and subsequent treatment with zinc chloride gave the zinc complex,[8] which was alkylated *in situ* and afforded **2**. The cyclic voltammetry of **2** shows that the first (E1) and second (E2) oxidation potentials are +0.52 and +0.82 V, respectively, which are almost identical to those of ET.[1]

The PF$_6$ salt was obtained as long plate-shaped crystals by electrochemical oxidation in chlorobenzene at 0.25 μA in the presence of tetrabutylammonium hexafluorophosphate at 20 °C. The composition of this salt was determined to be 2 : 1 by EDX analysis.

X-Ray analysis revealed that this salt belongs to the triclinic space group $P\bar{1}$.§ As shown in Fig. 1(a), the PF$_6^-$ molecule locates on the inversion center and the donor molecules are in general positions, so that the unit cell contains two donor and one anion molecules. Fig. 1(b) shows that the donor arrangement is attributed to the dimeric β-type,[9] and that the calculated overlap integrals indicate the two-dimensional electronic structure similar to β-(ET)$_2$I$_3$.[10] The donor molecule has one methyl group which stands perpendicular to the donor plane since the *cis*-substituted methyl groups have to have the axial–equatorial conformation. In the case of the *trans*-isomer, (R,R)- or (S,S)-DMBEDT-TTF, the conformation of the methyl groups has to be equatorial–equatorial in preference to axial–axial due to the steric hindrance. Indeed, a superconductor κ-((S,S)-DMBEDT-TTF)$_2$ClO$_4$ (T_c = 3.0 K under 5.0 kbar)[11] has the equatorial–equatorial conformation, and maintains the flat donor shape. According to the above insight (i), it is reasonable that κ-((S,S)-DMBEDT-TTF)$_2$ClO$_4$ affords the dimeric κ-phase.

Fig. 2 shows the temperature dependence of the resistivity under hydrostatic pressures up to 4.0 kbar. At ambient pressure, the resistivity of this salt (σ_{rt} = 15 S cm^{-1}) gradually decreases with lowering temperatures down to the metal–insulator (MI) transition at 90 K with a small anomaly around 220 K. The transition temperature shifts to lower temperatures as the pressure increases, and a slight drop of resistivity around 6 K appears under 3.1 kbar. At 4.0 kbar, a rapid decrease of resistivity is observed at T_c (onset at 4.3 K and midpoint at 3.8 K), regarded as the superconducting transition. In order to confirm the superconductivity, the ac conductivity under 4.0 kbar was measured in the applied magnetic field nearly parallel to the crystal long axis. As shown in Fig. 3,



Scheme 1 *Reagents and conditions*: i, P(OEt)$_3$, 110 °C, 3 h, 52%; ii, CsOH·H$_2$O, acetone, MeOH, 0 °C; iii, ZnCl$_2$, Bu$_4$NBr, MeOH, 0 °C; iv, 1,2-dibromoethane, CH$_3$CN, reflux, 2 h, 50%.

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b4/b409631b/

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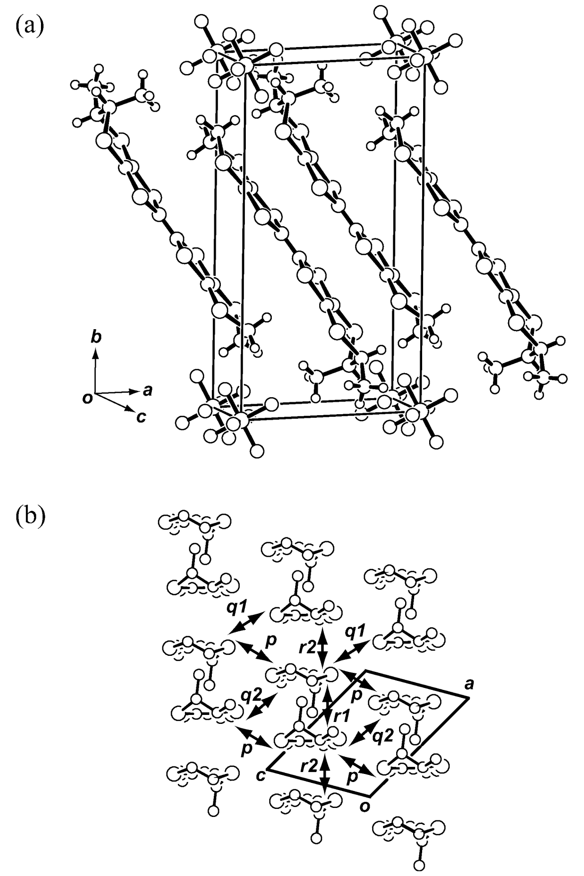

Fig. 1 (a) Crystal structure and (b) donor arrangement (hydrogen atoms are omitted for the sake of clarity) of β-(*meso*-DMBEDT-TTF)$_2$PF$_6$. Intermolecular overlap integrals ($\times$ 10^{-3}) are $r1$ = 8.24, $r2$ = 22.6, p = −4.75, $q1$ = 4.38, and $q2$ = 11.5.

T_c decreases with increasing the magnetic field, and the superconducting transition is completely suppressed above 4 T.

In conclusion, a newly synthesized donor for introducing moderate chemical pressure, *meso*-DMBEDT-TTF, afforded a superconducting salt β-(*meso*-DMBEDT-TTF)$_2$PF$_6$ with T_c = 4.3 K under 4.0 kbar. The preparations of the related salts toward the universal phase diagram of the β-type salts are now under investigation.

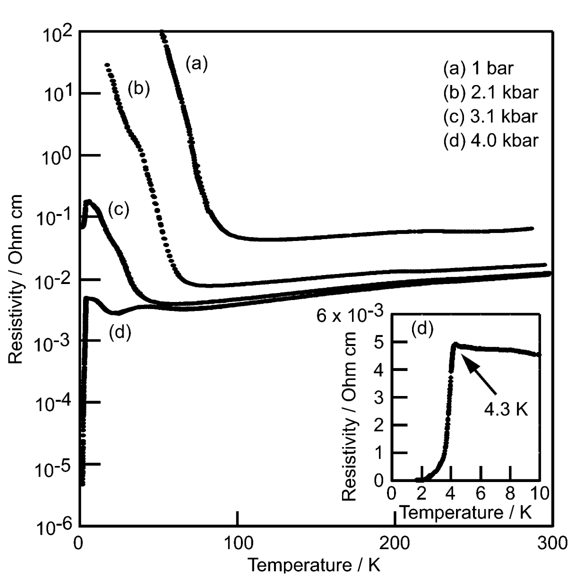

Fig. 2 Temperature dependences of the resistivity for β-(*meso*-DMBEDT-TTF)$_2$PF$_6$ under several pressures. The inset shows the superconducting transition at 4.3 K under 4.0 kbar (entry(d)).

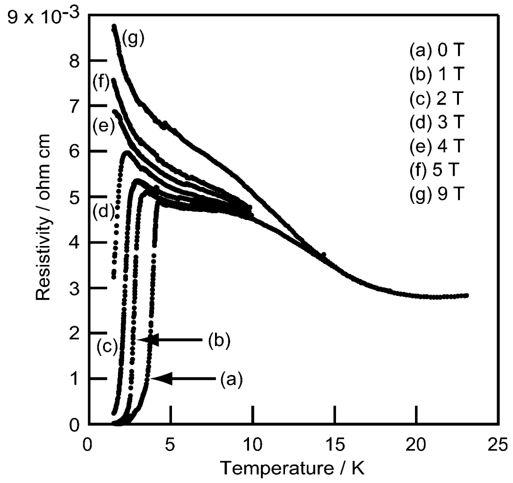

Fig. 3 Temperature dependence of the resistivity of β-(*meso*-DMBEDT-TTF)$_2$PF$_6$ under 4.0 kbar in different external magnetic fields.

Notes and references

‡ Selected data. **2**: red solid; mp 171–173 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.37 (6 H, d, J = 6.7 Hz), 3.29 (4 H, s), 3.58 (2 H, m); MS 413 (M$^+$); Anal. Calcd for $C_{12}H_{12}S_8$: C 34.92, H 2.93; found: C 34.64, H 2.92%. **5**: orange solid; mp 109–111 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.39 (6 H, d, J = 6.7 Hz), 2.73 (4 H, t, J = 7.1 Hz), 3.08 (4 H, t, J = 7.1 Hz), 3.60 (2 H, m); MS 385 (M$^+$ − 2CH$_2$CH$_2$CN); Anal. Calcd for $C_{16}H_{16}N_2S_8$: C 38.99, H 3.27, N 5.68; found C 38.86, H 3.27, N 5.46%.

§ Crystal data for (*meso*-DMBEDT-TTF)$_2$PF$_6$: $C_{24}H_{24}F_6PS_{16}$, M = 970.38, triclinic, space group $P\bar{1}$ (#2), a = 9.115(8), b = 15.649(8), c = 6.737(3) Å, α = 90.84(5), β = 109.37(5), γ = 88.87(6)°, V = 906(1) Å^3, T = 293 K, Z = 1, μ(Mo-Kα) = 1.050 mm^{-1}, D_{calc} = 1.778 g cm^{-3}, R = 0.073, R_w = 0.096, 5274 unique reflections, 1422 observed reflections [$I > 3.0\sigma(I)$]. CCDC 242446. See http://www.rsc.org/suppdata/cc/b4/b409631b/ for crystallographic data in .cif or other electronic format.

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