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2-(1,3-Dithiolan-2-ylidene)-5-(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene(DHDA-TTP), a hybrid of BDH-TTP and BDA-TTP, and its metallic cation-radical salts†

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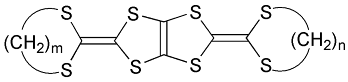
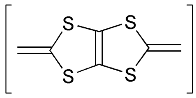
The synthesis and electrochemical properties of the DHDA-TTP donor, a hybrid of 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene (BDH-TTP) and 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (BDA-TTP), has been investigated, and its ability to form metallic cation-radical salts is elucidated.

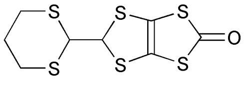
Since the discovery of the first metallic charge-transfer complex (TTF)(TCNQ),[1] TTF and its derivatives have been central to the development of organic metals and superconductors. Meanwhile, considerable research effort has been applied to the synthesis and study of non-TTF-containing donors. Although this work has resulted in the production of a good number of organic metals,[2] these metals failed to develop superconductivity. Therefore, the construction of a new π-donor system comparable to the TTF donor family requires the achievement of superconductivity. Our recent findings in this regard of (i) many metallic BDH-TTP salts stable down to low temperatures[3] and (ii) superconductivity in the β-(BDA-TTP)$_2$X (X = SbF$_6$, AsF$_6$ and PF$_6$) salts[4] demonstrate that the bis-fused 1,3-dithiol-2-ylidene (BDY) unit, contained in BDH-TTP and BDA-TTP as a common π-system, is a promising candidate for the post-TTF unit. Thus, in addition to symmetrical BDY donors such as BDH-TTP and BDA-TTP, it would be crucial to clarify whether or not the metallic or superconducting state could occur with the use of unsymmetrical BDY donors. We report here on the synthesis and electrochemical properties of DHDA-TTP, a hybrid between BDH-TTP and BDA-TTP, and also on the conducting behavior and crystal structures of its charge-transfer (CT) materials.



BDH-TTP: m = n = 2
BDA-TTP: m = n = 3
DHDA-TTP: m = 3, n = 2



BDY unit



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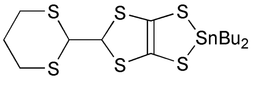

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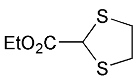

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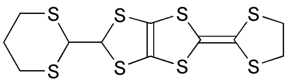

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Similarly to the synthetic route to BDA-TTP,[4] the synthesis of DHDA-TTP began with the preparation of tin dithiolate **2** from ketone **1** [MeMgBr (3.3 equiv.) in THF; then Cl$_2$SnBu$_2$ (1.0 equiv.)]. Subsequently, the Me$_3$Al (2.0 equiv.)-promoted coupling reaction of **2** with ester **3** (1.0 equiv., CH$_2$Cl$_2$, −78 °C → room temperature, overnight) gave **4** (52% overall yield from **1**), which upon oxidation with DDQ (1.1 equiv.) in refluxing toluene for 40 min led to DHDA-TTP in 85% yield.‡

Cyclic voltammetry of DHDA-TTP [0.1 M Bu$_4$NClO$_4$ in PhCN/CS$_2$ (1 : 1), Pt electrode, scan rate 50 meV s^{-1}] showed three reversible oxidation waves [E_1 = +0.67 V, E_2 = +0.87 V, E_3 = +1.35 V (V *vs.* SCE)] and another irreversible oxidation wave (E_4 = +1.53 V). The E_1 and E_2 values of DHDA-TTP are midway between the corresponding values of BDH-TTP (+0.56 and +0.82 V) and BDA-TTP (+0.72 and +0.90 V) measured under identical conditions.

DHDA-TTP reacted with TCNQ (1.0 equiv.) and its tetrafluoro analogue (TCNQF$_4$, 1.0 equiv.) in 1,1,2-trichloroethane (TCE) at room temperature to give CT complexes, whose room-temperature conductivities were, however, very low (see Table 1). Preparation of the DHDA-TTP salts listed in Table 1 was carried out in PhCl or TCE by the controlled-current electrocrystallization method.[5] The DHDA-TTP salts with linear anions and a relatively small tetrahedral anion, such as I$_3^-$, AuI$_2^-$, and BF$_4^-$, remained metallic down to 2 K. Among these salts, the AuI$_2$ salt was found to have the κ-type structure with a 4 : 1 stoichiometry by X-ray analysis. Also, the larger tetrahedral ClO$_4^-$ anion and the octahedral PF$_6^-$ and AsF$_6^-$ anions led to metallic DHDA-TTP salts, which underwent metal-to-insulator (MI) transitions near 80, 30, and 60 K, respectively. X-Ray analyses of these salts revealed that they are all the β-type salts and isostructural. On the other hand, the

Table 1 Conducting behavior of CT materials based on DHDA-TTP[a]

Acceptor	Solvent	D : A[b]	σ_{rt}/S cm^{-1}[c]
TCNQ	TCE	3 : 1	< 10^{-6}[d]
TCNQF$_4$	TCE	3 : 1	< 10^{-6}[d]
I$_3^-$	PhCl	3 : 1	53 (metallic > 2 K)
AuI$_2^-$	TCE	4 : 1[e]	7.4 (metallic > 2 K)
BF$_4^-$	TCE	2 : 1	2.3 (metallic > 2 K)
ClO$_4^-$	TCE	2 : 1[e]	9.1 (T_{MI}[f] = *ca.* 80 K)
PF$_6^-$	TCE	2 : 1	8.1 (T_{MI}[f] = *ca.* 30 K)
AsF$_6^-$	TCE	2 : 1	39 (T_{MI}[f] = *ca.* 60 K)
SbF$_6^-$	TCE	2 : 1[e]	2.6 (E_a = 16 meV)

[a] According to the controlled-current electrocrystallization method ($I = ct^2$, where I is the applied current, c is a constant, t is the growing period),[5] all the DHDA-TTP salts were prepared from DHDA-TTP (0.07 or 0.08 mmol) and the corresponding tetra-*n*-butylammonium salts (4.0 equiv.) in 16 mL of PhCl or TCE at 20 °C under nitrogen for 35 days. For the crystal growth cell and the platinum electrode used for electrocrystallization, see ref. 6. [b] Determined by elemental analysis unless otherwise noted. [c] Room-temperature conductivity measured by a four-probe technique for a single crystal unless otherwise noted. [d] Measured on a compressed pellet. [e] Determined by X-ray analysis. [f] Temperature of an MI transition.

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† Electronic supplementary information (ESI) available: selected crystallographic data. See http://www.rsc.org/suppdata/cc/b2/b200556p/

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larger octahedral SbF_6^- anion with DHDA-TTP formed a small gap semiconductor with an activation energy of 16 meV, and its preliminary X-ray analysis suggested the κ-type donor arrangement.

Fig. 1 shows the crystal structure of β-$(DHDA\text{-}TTP)_2PF_6$,§ in which the molecular packing mode is similar to those in the three isostructural superconductors β-$(BDA\text{-}TTP)_2X$ (X = SbF_6, AsF_6, and PF_6).[4] In this salt, the ethylene end group of the DHDA-TTP molecule is found essentially in the molecular plane, whereas the trimethylene end group is far out of the molecular plane. The outer dithiane ring adopts a chair conformation, and the dihedral angle around the intramolecular sulfur-to-sulfur axis is 40.6°, which is almost equal to the average value of the two corresponding angles of the BDA-TTP molecule in each BDA-TTP superconductor.[4] The DHDA-TTP molecules are stacked along [101] direction and slightly dimerized: the donor molecules alternate at the average interplanar distances of 3.66 and 3.70 Å. One pair with interplanar spacing of 3.66 Å has a slipped arrangement while the other with interplanar spacing of 3.70 Å has a nearly eclipsed arrangement. There are several intermolecular S···S contacts shorter than the van der Waals distance (3.70 Å) between stacks (Fig. 1(b)), but no short S···S contact can be observed within the stack, which is in contrast to the S···S contact patterns found in the three BDA-TTP superconductors.[4] The tight-binding band calculation, performed on the donor layer of this salt, results in the two-dimensional band dispersion relation and closed Fermi surface shown in Fig. 2. The Fermi surface of this salt is less round than those of the three BDA-TTP superconductors, suggesting the occurrence of nesting responsible for the MI transition near 30 K.

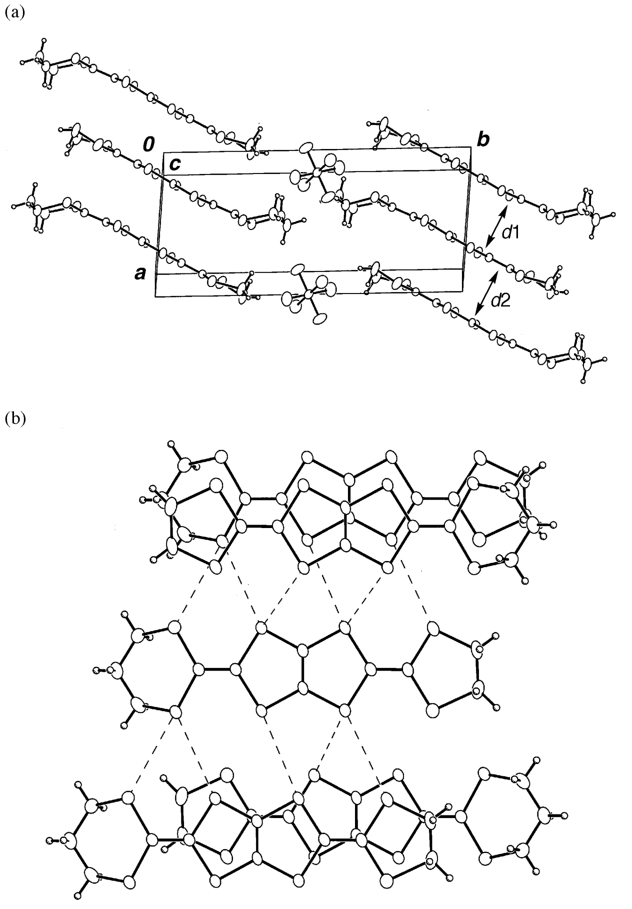

Fig. 1 Crystal structure of $(DHDA\text{-}TTP)_2PF_6$; (a) interplanar distances:$d1$ = 3.70, $d2$ = 3.66 Å; (b) intermolecular S···S contacts (< 3.70 Å) are indicated by broken lines.

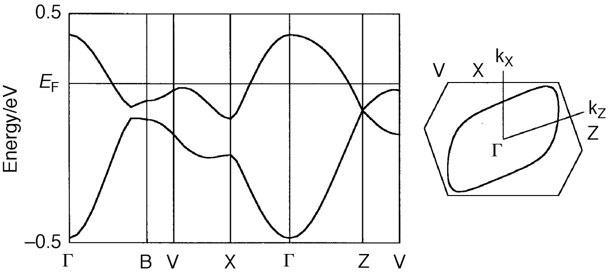

Fig. 2 Energy band structure and Fermi surface of $(DHDA\text{-}TTP)_2PF_6$.

In conclusion, application of our synthetic strategy for the symmetrical BDH-TTP and BDA-TTP donors led to the successful construction of their hybrid donor DHDA-TTP, which inherits to some extent the ability of forming stable metallic CT salts from BDH-TTP. On the other hand, the octahedral PF_6^- and AsF_6^- anions, providing the isostructural superconducting BDA-TTP salts, also give the isostructural metallic DHDA-TTP salts, which exhibit MI transitions instead of superconductivity at ambient pressure. Our effort to synthesize other unsymmetrical BDY donors currently continues, in the hope of developing new organic metals and superconductors.

Notes and references

‡ *Selected data* for DHDA-TTP: mp 212–216 °C (decomp.); δ_H (400 MHz, $CDCl_3$) 2.17–2.22 (m, 2H), 2.89–2.91 (m, 4H), 3.48 (s, 4H); *m*/*z* 398 (M^+); HRMS, calc. for $C_{11}H_{10}S_8$ 397.8548, found 397.8549; Anal. Calcd. for $C_{11}H_{10}S_8$: C, 33.13; H, 2.53. Found: C, 33.24; H, 2.51%.

§ *Crystal data* for $(DHDA\text{-}TTP)_2PF_6$: $C_{22}H_{20}S_{16}PF_6$, M = 942.32, triclinic, space group $P\bar{1}$, a = 7.930(6), b = 17.548(5), c = 6.456(2) Å, α = 96.29(3)°, β = 108.71(5)°, γ = 91.28(4)°, U = 844.1(8) Å^3, Z = 1, D_c = 1.854 g cm^{-3}, μ(Mo-Kα) = 11.25 cm^{-1}, T = 295 K, R = 0.048 and R_w = 0.043 for 3313 observed reflections with $I > 3\sigma(I)$ from 4896 unique reflections. The data were collected on an Enraf-Nonius CAD-4 diffractometer using the ω-θ scan technique to maximum 2θ of 60°. The structure was solved by direct methods and refined by full-matrix least-square analysis (anisotropic for non-hydrogen atoms). All diagrams and calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation. CCDC 178065.

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