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Improved stability of a metallic state in benzothienobenzothiophene-based molecular conductors: An effective increase of dimensionality with hydrogen bonds

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A dihydroxy-substituted benzothienobenzothiophene, BTBT(OH)$_2$, was synthesized, and its charge-transfer (CT) salt, *β*-[BTBT(OH)$_2$]$_2$ClO$_4$, was successfully obtained. Thanks to the introduced hydroxy groups, a hydrogen-bonded chain structure connecting the BTBT molecules and counter anions was formed in the CT salt, which effectively increases the dimensionality of the electronic structure and consequently leads to a stable metallic state.

In the field of functional molecular materials, increasing the dimensionality of the electronic structures has been an important issue for realization not only of stable metallic or superconducting states,[1] but also of next generation electronic materials/devices.[2] A charge-transfer (CT) complex (TTF)(TCNQ) (TTF: tetrathiafulvalene, TCNQ: tetracyanoquinodimethane) is known as the first organic metal, however, its one-dimensional (1D) character causes a metal-insulator transition at 53 K.[3] This so-called 1D instability has successfully been overcome by the chemical modification of the TTF skeleton, such as the introduction of additional chalcogen substituents, leading to stable metallic states and even superconducting states.[4]

Recently, as a new class of molecular conductor without the TTF skeleton, a CT salt (BTBT)$_2$PF$_6$ (BTBT: [1]benzothieno[3,2-*b*][1]benzothiophene, Chart 1) and its analogues were developed.[5] Interestingly, in spite of lesser sulphur atoms in the π-conjugated skeleton, these BTBT-based CT salts exhibit metallic behaviour with a significantly high room temperature conductivity ($\sigma_{\mathrm{r.t.}}$ ~ 4100 S cm^{-1}) and also large thermoelectric power factor with a large bandwidth.[5b] These results have reminded us of the importance of the exploration of such new classes of molecular conductors.[6] These BTBT salts, however, change to an insulator at low temperatures, due to an abrupt resistivity jump resulting from 1D nature of the crystal/electronic structures.[5] Unfortunately, this 1D instability has not completely been suppressed by substituting the sulphur atoms with selenium ones with a larger atomic orbital.[7] Therefore, another kind of chemical modification is required to realize a stable metallic state in the BTBT-based molecular conductors.

Hydrogen bonds (H-bonds) are frequently used as a powerful tool to control and regulate the crystal structures of molecule-based functional materials.[8–12] In some TTF-based conductors, the H-bonding interactions also enabled to control the CT states and conducting properties, in addition to the molecular arrangements.[9–11] Moreover, our group has recently demonstrated that catechol-fused TTF derivatives (Cat-TTF, Chart 1) provide several kinds of unique H-bonded molecular conductors by taking advantage of strong H-bonding ability of the catechol moiety.[12]

From these aspects, in this study, we have designed a new BTBT molecule with a catechol substructure, **BTBT(OH)$_2$**[13] (Chart 1), and consequently succeeded in the synthesis of its CT salt ***β*-[BTBT(OH)$_2$]$_2$ClO$_4$**. Thanks to the two hydroxy groups introduced at the 2,3-positions, a H-bonded chain structure connecting the BTBT molecules and counter anions was formed in the CT salt, which effectively increases the

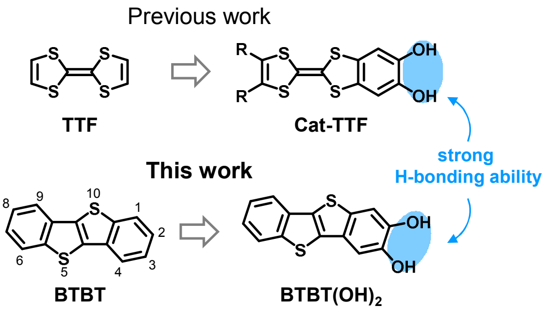

Chart 1 Molecular design of **Cat-TTF**[12] and **BTBT(OH)$_2$** from **TTF** and **BTBT**.

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† Electronic Supplementary Information (ESI) available: Additional information for synthesis, electrochemical measurement, theoretical calculation, X-ray analysis, bond length analysis, and resistivity measurement. CCDC 1529671-1529675 contain the supplementary crystallographic information for **5a**, **5b**, **BTBT(OMe)$_2$**, **[BTBT(OH)$_2$]$_2$·H$_2$O**, and ***β*-[BTBT(OH)$_2$]$_2$ClO$_4$**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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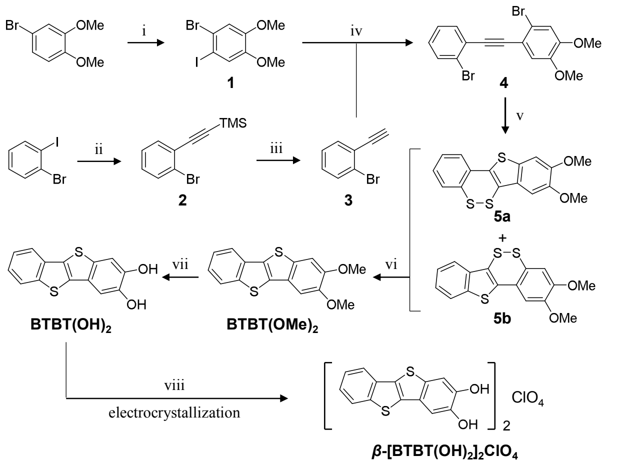

Scheme 1 Synthesis of **BTBT(OH)$_2$** and ***β*-[BTBT(OH)$_2$]$_2$ClO$_4$**. *Reagents and conditions*: (i) H_5IO_6, I_2, MeOH, reflux, 9 h, 95%; (ii) $PdCl_2(PPh_3)_2$, CuI, Et_3N, TMS-acethylene, THF, reflux, 2 h, 96%; (iii) K_2CO_3, MeOH, CH_2Cl_2, r.t., 3h, 92%; (iv) $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, reflux, 9 h, 83%; (v) *t*-BuLi, sulphur powder, $K_3[Fe(CN)_6]$, THF, −78 °C - r.t., overnight, 14% for **5a**, 15% for **5b**; (vi) Cu, 250 °C, 20 min, 84%; (vii) BBr_3, CH_2Cl_2, 0 °C - r.t., 6 h, 92%, (viii) *n*-$Bu_4N\cdot$ ClO_4, CH_2Cl_2, r.t., 2 µA, 48 h.

dimensionality of the electronic structure and consequently leads to a stable metallic state.

The synthetic route for the donor molecule **BTBT(OH)$_2$** is depicted in Scheme 1 (see Supplementary Information for details). The asymmetric unit **4** was prepared by the conventional Sonogashira cross-coupling reaction of the iodobenzene derivative **1** with the phenyl acetylene derivative **3**. Treatment of **4** with *t*-BuLi followed by sulphur powder and potassium hexacyanoferrate(III) afforded the thieno[3,2-*c*][1,2]dithiin compounds as an isomeric mixture of **5a** and **5b** in moderate yields.[14,15] The copper-mediated dechalcogenation of the mixture of **5a** and **5b** provided a single product **BTBT(OMe)$_2$** in 84% yield. Finally, demethylation of the methoxy groups with boron tribromide gave the target compound **BTBT(OH)$_2$** in 92% yield. Surprisingly, such BTBT derivatives functionalized at the 2,3-positions are unknown,[16] although a lot of BTBT derivatives have been designed and synthesized so far.[17] Therefore, our present synthetic strategy will be effective to explore a new class of functionalized BTBT derivatives.

In cyclic voltammetry, **BTBT(OH)$_2$** showed one irreversible oxidation wave (Fig. S1 in Supplementary Information). The onset oxidation potential (E_{onset}) is 0.88 V (vs. SCE), which is lower than that of the unsubstituted BTBT (1.18 V). This means that electron-donating ability is significantly enhanced by the introduction of the hydroxy groups into the BTBT backbone, as suggested by DFT calculations.[18]

The electrocrystallization of **BTBT(OH)$_2$** in the presence of tetra-*n*-butylammonium perchlorate gave needle-like black crystals of the ClO$_4$ salt, namely ***β*-[BTBT(OH)$_2$]$_2$ClO$_4$**. The crystallographic data are listed in Table S1, and the crystal structure is depicted in Fig. 1. This salt crystalizes in a monoclinic system, space group *C*2/*c*, in which one BTBT molecule in the general position and a half of the ClO$_4$ anion located on the two-fold axis are crystallographically independent (Fig.1a). Since the unit cell contains eight BTBT molecules and four anions, the donor:anion stoichiometry is deduced to be 2:1. This means that the BTBT molecule is in a partially oxidized state with a +0.5e charge, as also supported by the bond length analysis (Table S2). Therefore, **BTBT(OH)$_2$** is expected to form a 3/4-filled band structure (discussed below). As shown in Fig. 1b, the BTBT molecule is almost planar and forms a head-to-tail-type uniform stack along the *b*-axis with the interplanar spacing of 3.326 Å (corresponding to the half-length of the *b*-axis). It is noteworthy that two kinds of [O−H···O]-type H-bonding interactions were observed between the hydroxy groups of the donor and the ClO$_4$ anion (O1−O4 and O2−O3 in Fig. 1c); the O···O distances are 2.809(7) Å (O1−O4) and 2.783(5) Å (O2−O3), which are much shorter than the sum of the van der Waals radii of oxygen atoms (3.04 Å). Consequently, an infinite 1D H-bond-chain structure is formed along the *c*-axis (Fig. 1c).[12a] In this arrangement, very weak C−H···S interactions (H···S distances: ~ 3.05 Å, green lines in Fig. 1c) are also found in the side-by-side direction of the donor molecule. As a result of these intermolecular interactions, **BTBT(OH)$_2$** produces a sheet-type molecular arrangement (Fig. 1d). In this sheet, **BTBT(OH)$_2$** stacks in a "ring-over-bond" manner (represented as the black and gray molecules in Fig. 1a and 1d) along the *b* axis, leading to a so-called *β*-type molecular arrangement[19] (thus termed ***β*-(BTBT(OH)$_2$)$_2$ClO$_4$**). The transfer integrals, which correspond to intermolecular interactions between the neighbouring molecules,[20] are largest in the stacking direction *b* (91.0 meV) and relatively smaller in the diagonal directions *p* (–2.77 meV), *q* (–13.6 meV), and *r* (–13.1 meV), as shown in the caption of Fig. 1d. Also, there are no meaningful donor-donor interactions between the sheets, due to the presence of the anion layer.

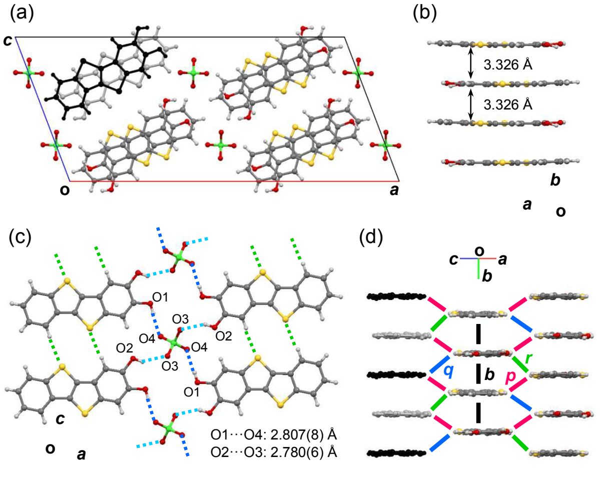

Fig. 1 Crystal structures of ***β*-[BTBT(OH)$_2$]$_2$ClO$_4$**, viewed along (a) the *b* axis (the black and gray molecules: overlap mode), (b) the *c* axis, (c) the stacking direction (blue broken line: O−H···O H-bonding patterns, green broken line: C−H···S interactions), and (d) the molecular long axis (ClO$_4$ anions are omitted for clarity). Transfer integrals: $b = 91.0$, $p = -2.77$, $q = -13.6$, $r = -13.1$ meV.

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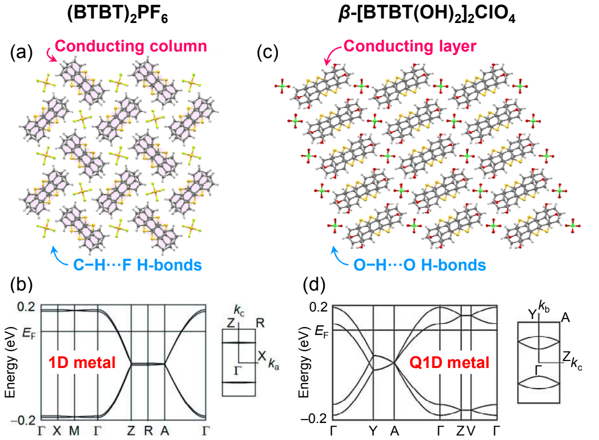

Fig. 2 (a, c) Molecular arrangements and (b, d) electronic band structures in $(BTBT)_2PF_6$[5] and **β-$[BTBT(OH)_2]_2ClO_4$**, respectively.

The effect of the H-bond interactions in the crystal of **β-$(BTBT(OH)_2)_2ClO_4$** is further disclosed by comparing the crystal structures of **β-$(BTBT(OH)_2)_2ClO_4$** and the parent salt $(BTBT)_2PF_6$. As shown in Fig. 2a, the BTBT molecules in $(BTBT)_2PF_6$ form windmill-type columnar structures with effective π-π interactions. There are, however, no effective interactions between the columns, due to the existence of C−H···F contacts between the donor molecule and the PF_6 anion.[5] As a result, the columnar arrangement produces a typical 1D electronic structure with a flat Fermi surface (Fig. 2b).[21] On the other hand, the π-stacking columns in the present salt **β-$(BTBT(OH)_2)_2ClO_4$** (Fig. 1b) are connected with the O−H···O H-bonding interactions through the ClO_4 anions (Fig. 2c). A resultant Fermi surface is warped in the 3/4-filled band structure (Fig. 2d), which means the formation of a quasi-one-dimensional (Q1D) electronic structure in **β-$(BTBT(OH)_2)_2ClO_4$**.[22] This enhancement of the electronic structure from 1D to Q1D is also evidenced by comparing the anisotropy of the transfer integrals. $(BTBT)_2PF_6$ has a strong interaction within the π-stacking column (87 meV), however, the interstack interaction is negligibly small (≈1.4 meV).[5] On the other hand, the present **β-$(BTBT(OH)_2)_2ClO_4$** has the substantial interstack interactions (q, r ≈ 13 meV), in addition to the strong intrastack one (b = 91 meV), as described before. Thus, the intrastack/interstack anisotropy is significantly decreased from 60 (= 87/1.4) in $(BTBT)_2PF_6$ to 7 (= 91/13) in **β-$(BTBT(OH)_2)_2ClO_4$**. A similar decrease is observed in the 1D and Q1D TTF conductors, that is, 100 for (TTF)(TCNQ) and 10 for $(TMTSF)_2PF_6$, respectively.[23] These results clearly indicate that the dimensionality of the electronic structure is successfully enhanced by the introduction of the H-bonding interactions.

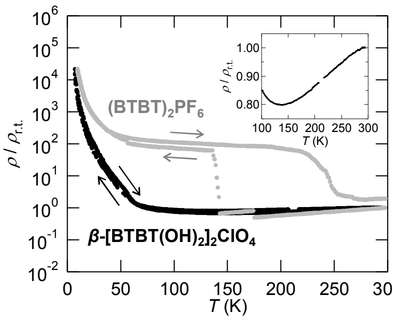

Fig. 3 Temperature dependence of the electrical resistivity for **β-$[BTBT(OH)_2]_2ClO_4$** (black) and $(BTBT)_2PF_6$ (gray)[5], measured along the molecular stacking direction. The values are normalized with that at room temperature ($\rho_{r.t.}$). Inset: magnified data in the metallic region of **β-$[BTBT(OH)_2]_2ClO_4$**.

The increase of the dimensionality of the electronic structure significantly influenced the electrical conducting properties. Figure 3 shows temperature dependence of the electrical resistivity in **β-$(BTBT(OH)_2)_2ClO_4$**, together with that in $(BTBT)_2PF_6$, where the values are normalized with that at room temperature ($\rho_{r.t.}$). The crystal of **β-$(BTBT(OH)_2)_2ClO_4$** shows a relatively low room-temperature electrical resistivity ($\rho_{r.t.}$ ≈ 5.5 × 10^{-3} Ω cm), which decreases with decreasing temperature down to 135 K (the inset of Fig. 3). This temperature dependence indicates that this salt is metallic above 135 K, and more importantly, this metallic state is more stable than that of $(BTBT)_2PF_6$. This is because this salt does not show an abrupt resistivity jump, as seen in $(BTBT)_2PF_6$ at 150 K.[5] Therefore, we have proved that the increase of the dimensionality caused by the H-bond interactions brings about the stabilization of metallic state in BTBT-based conductors. On further cooling, this salt finally undergoes a metal-insulator-like transition around 60 K, after entering the semiconducting state at 135 K. A similar transition without hysteresis has also been observed in $(BTBT)_2PF_6$ at around 50 K.[5] Investigation on the low-temperature insulating state as well as the realization of a more stabilized metallic state are currently underway.

In conclusion, we have successfully synthesized a new benzothienobenzothiophene (BTBT) derivative with 2,3-dihydroxy groups, **$BTBT(OH)_2$**, and realized a stable metallic state in a quasi-one-dimensional charge-transfer salt **β-$(BTBT(OH)_2)_2ClO_4$**. Strong H-bonding ability of the catechol-type hydroxy groups has played a crucial role in the formation of an infinite one-dimensional H-bonded chain structure, which leads to the increase of the dimensionality of the electronic structure and the stable metallic state. These results demonstrate that functionalized BTBT derivatives are promising electron donors in molecular conductors. We believe that this study will pave a new way to design and develop high-dimensional BTBT-based materials/devices[24] with interesting conducting properties (*e.g.* superconductivity and high carrier mobility).

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