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Novel Molecular Conductors Based on Cyclopenteno-TTP Showing Strong Self-aggregation

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Several molecular conductors based on CP-TTP, where CP-TTP is 2-(4,5-cyclopenteno-1,3-dithiol-2-ylidene)-5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene, have been prepared. X-ray structure analyses revealed that all the CP-TTP conductors obtained so far have β-type array of the donors regardless of the counter anions. Among them, the ReO_4^- and $Au(CN)_2^-$ salts exhibited metallic conducting behavior down to 10 K.

Control of molecular packing in molecular conductors is of significant importance, because electronic structures and resultant conducting behavior strongly depend on molecular packing. However, we have found that bis-fused TTF donor 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) (Chart 1) and its derivatives have yielded a large number of molecular complexes retaining their metallic conductivity down to liquid helium temperature.[1] X-ray structure analyses of various BDT-TTP salts have revealed that BDT-TTP has a tendency to form a uniform β-type molecular packing,[1,2] in which the molecules form face-to-face stacks connected by several S···S contacts along the side-by-side direction. On the other hand, introduction of appropriate substituents on a BDT-TTP framework is known to affect the molecular packing. For example, CH-TTP, which is designed by annelation with a cyclohexene ring, affords a radical cation salt with a nonstacked κ-type arrangement.[3] The cyclohexene ring adopts a half-chair conformation, and the two terminal carbon atoms deviate in the opposite direction for the π plane of BDT-TTP. A dimethyl-substituted BDT-TTP analog, DM-TS-TTP, however, yields a molecular metal with β-type donor packing.[4] The methyl groups of DM-TS-TTP lay in the π plane. In this connection, molecular conductors based on cyclopenteno-TTP (CP-TTP) are of interest to elucidate the correlation of molecular structure and molecular packing in conducting materials, because the cyclopentene ring adopts an envelope conformation and has an intermediate steric hindrance between cyclohexene and methyl groups. Although the synthesis of CP-TTP was reported in 1997,[5] there has been no example of a CP-TTP conductor whose crystal structures was determined. In this letter, we report structures and electrical properties of $(CP\text{-}TTP)_3(ReO_4)(PhCl)_{0.5}$, $(CP\text{-}TTP)_4[Au(CN)_2](THF)$, and $(CP\text{-}TTP)_4(AsF_6)(DCE)_2$.

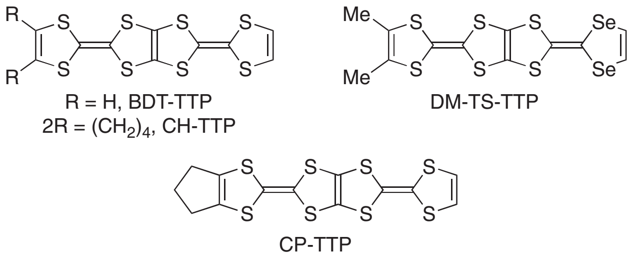

Chart 1.

CP-TTP was prepared according to the literature.[5] Galvanostatic electrocrystallization of CP-TTP at 0.2 µA using ^{n}Bu$_4$N·X (X = ReO_4, $Au(CN)_2$, and AsF_6) as the electrolytes at 50 °C gave plate-like single crystals. X-ray structure analyses[6,7] of the obtained salts are carried out, and their crystallographic data are summarized in Table 1. The $Au(CN)_2^-$ salt crystallizes in a monoclinic system with the space group $C2/c$, while the

Table 1. Crystallographic data of CP-TTP conductors

	$(CP\text{-}TTP)_3(ReO_4)(PhCl)_{0.5}$	$(CP\text{-}TTP)_4[Au(CN)_2](THF)$	$(CP\text{-}TTP)_4(AsF_6)(DCE)_2$
Solvent[a]	PhCl	THF	DCE
D:A:Solv.	3:1:0.5	4:1:1	4:1:2
Appearance	Black plate	Black plate	Black plate
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	17.0970(9)	37.606(8)	10.392(3)
b/Å	19.485(1)	12.129(3)	21.049(6)
c/Å	8.5565(5)	15.507(4)	8.628(3)
α/°	92.701(8)	90	91.385(6)
β/°	108.922(6)	94.447(5)	99.839(7)
γ/°	75.659(6)	90	91.863(5)
V/Å^3	2610.7(3)	7052(3)	1857.6(10)
Z	2	4	1
$R1$; $wR2$ [$I > 2\sigma(I)$]	0.0590; 0.1420	0.0876; 0.1885	0.0511; 0.1241
GOF	1.099	1.030	1.030

[a]PhCl: chlorobenzene; THF: tetrahydrofuran; DCE: 1,2-dichloroethane.

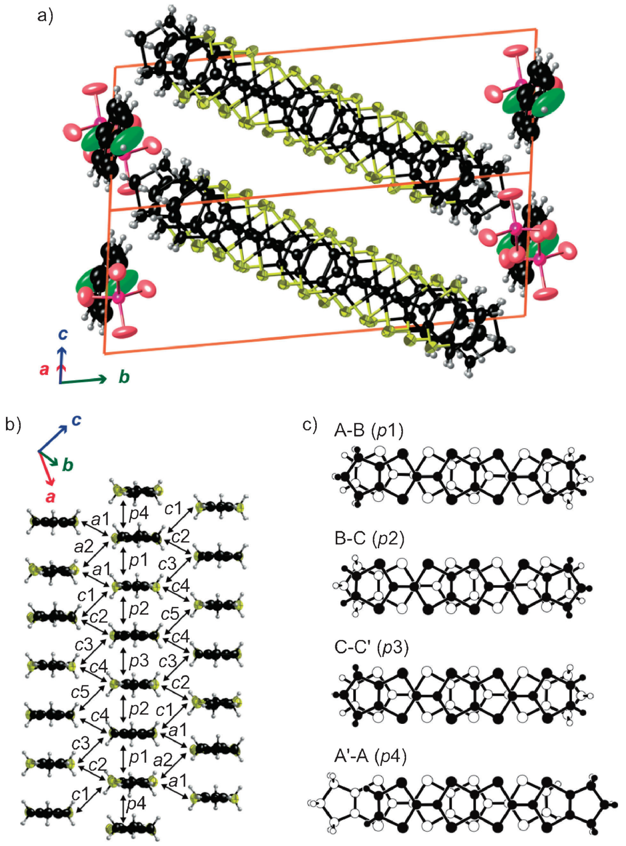

Figure 1. (a) Crystal structure of $(CP\text{-}TTP)_3(ReO_4)(PhCl)_{0.5}$ viewed along the a–c axis. (b) Donor sheet structure viewed along the molecular long axis, and (c) overlap modes in the stack. The calculated intermolecular overlaps between HOMOs ($\times 10^{-3}$) are $p1 = -25.4$, $p2 = -24.0$, $p3 = 23.7$, $p4 = 24.1$, $a1 = -0.03$, $a2 = -8.5$, $c1 = -8.5$, $c2 = 0.4$, $c3 = -10.4$, $c4 = -0.2$, and $p5 = 8.9$.

others crystallize in a triclinic system with the space group $P\bar{1}$. All the salts include the solvent used for electrocrystallization. The ratio of the donor (D), the anion (A), and the solvent (Solv.) are different from each other. Thus, the ReO_4^- salt has a composition of $D_3A(Solv.)_2$, while the $Au(CN)_2^-$ and AsF_6^- salts have a composition of $D_4A(Solv.)$ and $D_4A(Solv.)_2$, respectively. In all the materials, the donors form conducting sheets, each of which are divided by the insulating layers composed of the anions and the solvents.[7] The cyclopentene ring of CP-TTP has high planarity, the deviation distances of the terminal cyclopentene carbons from the BDT-TTP plane are 0.00(1)–0.36(1) Å. Figure 1a shows the crystal structure of the ReO_4^- salt as a representative. All the salts obtained so far have a donor packing similar to β-type (Figures 1b, 2a, and 2c). The unsymmetrical donor molecules are stacked in a head-to-tail manner in all the salts, and the overlap mode in the stack is the ring-over-bond type. However, stacking patterns are a little different from each other.

Three donor molecules, which are denoted as A, B, and C, are crystallographically independent in $(CP\text{-}TTP)_3(ReO_4)(PhCl)_{0.5}$. Each anion and chlorobenzene are crystallographically unique. A center of inversion is located on the six-membered ring of the solvent molecule to show the crystallographic disorder. The donors are stacked in a zig-zag pattern with an A–B–C–C′–B′–A′-type sixfold periodicity. The interplanar distances are 3.55–3.72 Å, and the slip distances along the donor long axis are almost the same at 1.5–1.6 Å (Figure 1c). As a result, the ReO_4^- salt is classified in $\beta_{\bar{6}0}$.[8] The intrastack overlap integrals $p1$, $p2$, $p3$, and $p4$ (24.0–25.3 $\times 10^{-3}$) are similar, suggesting that this salt has almost uniform stacking. There are many short interstack S···S contacts of 3.457(2)–3.585(2) Å less than the sum of the van der Waals radii (3.60 Å).[9] On the other hand, the $Au(CN)_2^-$ and AsF_6^- salts contain two crystallographically independent donor molecules A and B. The donors are stacked in an A–B–A′–B′-type four molecule period for the $Au(CN)_2^-$ salt, indicating the presence of two intrastack overlaps $c1$ and $c2$ (Figures 2a and 2b). In this salt, the slip distance along the molecular long axis for $c2$ (4.8 Å) is larger than that for $c1$ (1.4 Å). As a result, the donors are electronically dimerized along the stacking direction ($c1 = 25.0 \times 10^{-3}$ and $c2 = 18.5 \times 10^{-3}$). Since the stacks have twofold repetition along the transverse direction, the donor sheet structure of the $Au(CN)_2^-$ salt is designated as $\beta_{42\times2}$. Differently from the $Au(CN)_2^-$ salt, two crystallographically independent molecules A and B are stacked with a fourfold period of A–B–B′–A′ for $(CP\text{-}TTP)_4(AsF_6)(DCE)_2$. The interplanar distances and the slip distances along the donor long axis for the AsF_6^- salt are 3.58 and 1.4 Å for $p1$, 3.51 and 1.7 Å for $p2$, and 3.46 and 4.9 Å for $p3$, respectively (Figures 2c and 2d). The overlap integral $p3$ (17.6×10^{-3}) is about three quarters of the others ($p1 = -23.8 \times 10^{-3}$ and $p2 = 24.0 \times 10^{-3}$) due to larger slip distance along the donor long axis of $p3$ compared with those of the other overlaps. The A–B–B′–A′-type tetramers are divided by the large slip at $p3$, and the AsF_6^- salt is classified in β_{41}-phase similar to $(CPTM\text{-}TTP)_4AsF_6$.[10]

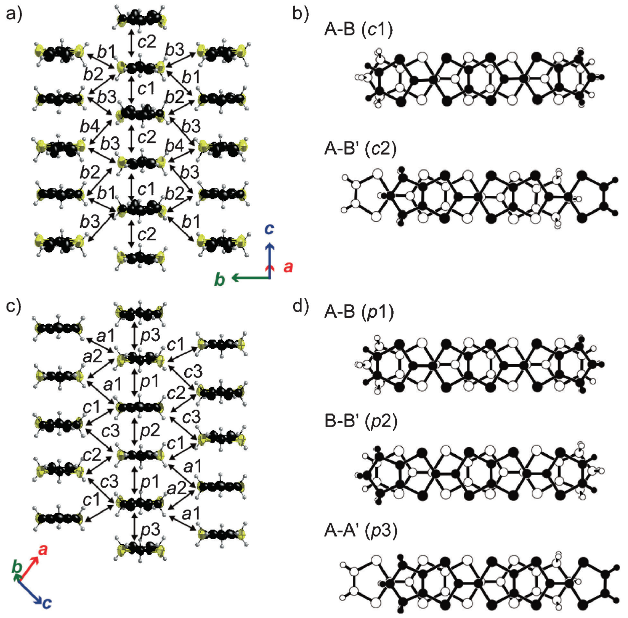

Figure 2. Donor sheet structure viewed along the molecular long axis for (a) $(CP\text{-}TTP)_4[Au(CN)_2](THF)$ and (c) $(CP\text{-}TTP)_4(AsF_6)(DCE)_2$. Overlap modes in the stack in (b) $(CP\text{-}TTP)_4[Au(CN)_2](THF)$ and (d) $(CP\text{-}TTP)_4(AsF_6)(DCE)_2$. The calculated overlap integrals are summarized in Table S1.[7]

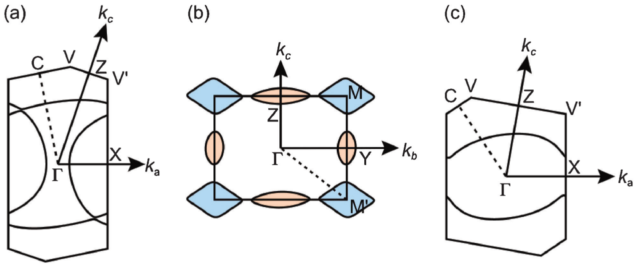

Figure 3. The calculated Fermi surfaces of (a) (CP-TTP)$_3$(ReO$_4$)(PhCl)$_{0.5}$, (b) (CP-TTP)$_4$[Au(CN)$_2$](THF), and (c) (CP-TTP)$_4$(AsF$_6$)(DCE)$_2$.

Table 2. Electrical properties of CP-TTP conductors

Anion	D:A	σ_{rt}/S cm^{-1}	Conducting property[a]
ReO$_4^-$	3:1	160	Metallic down to 10 K
Au(CN)$_2^-$	4:1	310	Metallic down to 10 K
AsF$_6^-$	4:1	19	$T_c = 180$ K ($E_a = 0.019$ eV)

[a] T_c is defined as the temperature at which the resistivity shows the minimum. Activation energy (E_a) is calculated by Arrhenius plot of the semiconducting region.

Figure 3 shows the calculated Fermi surfaces of the ReO$_4^-$, Au(CN)$_2^-$, and AsF$_6^-$ salts. The calculated Fermi surface of the ReO$_4^-$ salt is closed, suggesting this material is a two-dimensional metal due to large side-by-side interactions (about one-thirds of the intrastack interaction). On the other hand, the Au(CN)$_2^-$ salt is suggested to have one electron pocket centered at M point and two hole pockets centered at Y and Z points. In contrast, the calculated Fermi surface of the AsF$_6^-$ salt is open, being characteristic of a quasi-one-dimensional metal.

The electrical conductivities of CP-TTP conductors are measured on a single crystal using a four-probe technique, and their electrical properties are summarized in Table 2. The ReO$_4^-$ and Au(CN)$_2^-$ salts exhibited high conductivity of 160 and 310 S cm^{-1} at room temperature, respectively. They show metallic temperature dependence of the resistivity down to 10 K, although there are several resistivity jumps for the ReO$_4^-$ salt (Figure 4). It is consistent with their calculated Fermi surfaces as mentioned above. On the other hand, the room temperature conductivity of the AsF$_6^-$ salt (19 S cm^{-1}) is one order smaller than those of the ReO$_4^-$ and Au(CN)$_2^-$ salts. The resistivity of the AsF$_6^-$ salt shows temperature-independent behavior down to 180 K, and then the AsF$_6^-$ salt exhibits semiconducting behavior with small activation energy (0.019 eV) below 180 K.[11] It is noteworthy that CP-TTP affords molecular conductors with β-type molecular packing regardless of the shape of the counter anions; however, the stacking patterns are a little different from each other. The electronic structure and the conducting behavior of β-CP-TTP conductors vary according to the stacking pattern.

In summary, three kinds of molecular conductors have been obtained from CP-TTP. The results obtained from this work indicate that CP-TTP shows self-aggregation similar to BDT-TTP, because the steric hindrance of the cyclopentene ring is not too large to diminish the self-aggregation of BDT-TTP. However, the electronic structure and the conducting behavior are different from each other. Further investigations, in particular, correlation between molecular structures and molecular packing patterns by means of theoretical calculation are actively in progress.

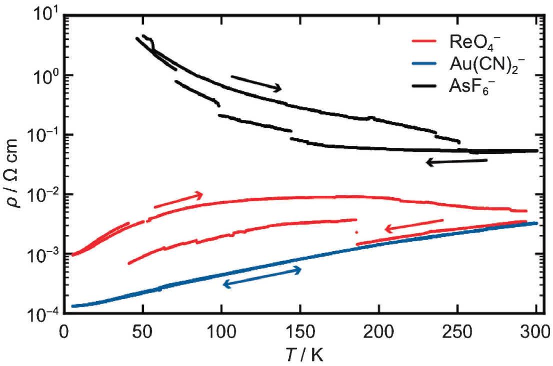

Figure 4. Conducting behavior of (CP-TTP)$_3$(ReO$_4$)(PhCl)$_{0.5}$, (CP-TTP)$_4$[Au(CN)$_2$](THF), and (CP-TTP)$_4$(AsF$_6$)(DCE)$_2$.

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11 To investigate the origin of the semiconducting behavior of AsF$_6^-$ salt, we performed crystal structure analysis at 100 K; however, no distinct difference in the lattice parameters and the bond length was observed. The origin of the semiconducting nature of AsF$_6^-$ salt is unclear at present, and the discussion of the origin will be reported elsewhere along with other physical properties.