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Yasushi Morita [a], Eigo Miyazaki [a], Suguru Maki [a], Jiro Toyoda [a], Hideki Yamochi [b], Gunzi Saito [b] & Kazuhiro Nakasuji [a]

[a] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan

[b] Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan

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Synthesis of New 2,7-Diiodo-1,6-dithiapyrene and Crystal Structures of its Charge-Transfer Salts

YASUSHI MORITA[a], EIGO MIYAZAKI[a], SUGURU MAKI[a], JIRO TOYODA[a], HIDEKI YAMOCHI[b], GUNZI SAITO[b] and KAZUHIRO NAKASUJI[a]

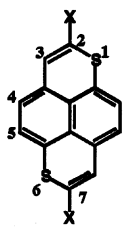
[a]*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan and*
[b]*Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan*

We have designed and synthesized 2,7-diiodo-1,6-dithiapyrene (DIDTPY) as a first halogenated DTPY derivative. The X-ray structural analyses showed that the charge-transfer salts, (DIDTPY)(PF_6) and (DIDTPY)$_{1.5}$($AuBr_2$), possessed dimeric pairs of the cationic donor molecules and columnar stack of donor molecules, respectively. The conductivity of the compressed pellet for (DIDTPY)$_{1.5}$($AuBr_2$) exhibited a semiconducting behavior ($\sigma_{rt} = 2 \times 10^{-2}$ Scm^{-1}).

Keywords: 1,6-dithiapyrene; halogen-halogen interaction; charge-transfer salt; semiconductor; dimensionality

INTRODUCTION

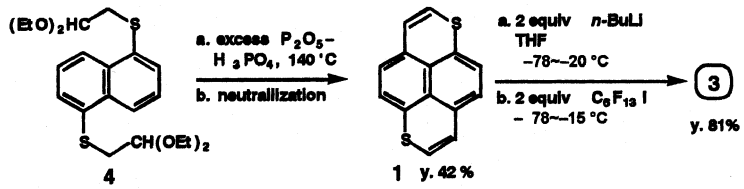
Charge-transfer (CT) complexes and radical salts based on the TTF-type donors play an important role in the area of the organic conductors. In order to extend and create a new class of the physical properties and molecular functionalities, the design and synthesis of the electronically active organic π-electronic system are recognized as one of the key elements. We have focused on the peri-condensed Weitz-type donors, and synthesized 1,6-dithiapyrene (DTPY, **1**) and 2,7-bis(methylthio)DTPY (MTDTPY, **2**)[1–3]. Interestingly, the CT complexes, **2**–bromanil and **2**–chloranil, became the first organic molecular metals which were not based on TTF- and TCNQ-component molecules[3]. However, these complexes exhibited metal-insulator transition at 125 K for **2**–bromanil and 240 K for **2**–chloranil due to the low dimensionalities of the conducting columns. For the purpose of enhancing the dimensionalities by the introduction of multi-functional interactions, we have newly designed 2,7-diiodo-1,6-dithiapyrene (DIDTPY, **3**) as a first halogenated DTPY derivative[4]. We here describe the preparation and the crystal structures of DIDTPY and its CT salts, $(DIDTPY)(PF_6)$ and $(DIDTPY)_{1.5}(AuBr_2)$.



1; X=H, DTPY
2; X=SCH_3, MTDTPY
3; X=I, DIDTPY

RESULTS AND DISCUSSION

Our continuous and elaborate synthetic efforts for DTPY (**1**) have enabled the practical improvement for the preparation of **1** in 42% chemical yield from **4** with a reproducible manner. The new di-iodinated DTPY **3** was prepared as a light orange powder by the treatment of **1** with *n*-BuLi followed by the iodination by using tridecafluorohexyl iodide (Scheme 1).



Scheme 1 Synthetic method of di-iodinated DTPY **3**

Cyclic voltammogram of **3** in DMF showed two reversible oxidation potentials, which demonstrated that the donor ability of **3** was reduced compared with that of **1** and TTF, owing to the electron-withdrawing nature of the iodine atoms (Table 1).

TABLE 1 Oxidation Potentials (V vs. Fc/Fc^+)[a]

	3	**1**	TTF
E^{ox1}	0.13	–0.04	–0.10
E^{ox2}	0.42	0.27	0.15
ΔE	0.29	0.31	0.25

[a]1 mM solution (for **3**) and 3 mM solution (for **1** and TTF) in DMF with 0.1 M Et_4NClO_4 supporting electrode on gold working electrode and Pt counter electrode at room temperature; scan rate = 100 mV/s.

The CT salts, $(DIDTPY)(PF_6)$ and $(DIDTPY)_{1.5}(AuBr_2)$, were obtained as dark green and black crystals by the electrocrystallization in THF solution under a constant current of ca. 3 and 5 μA, respectively. The crystal data of both salts are summarized in Table 2.

TABLE 2 Crystal Data of the CT salts

Compound	(DIDTPY)(PF_6)	(DIDTPY)$_{1.5}$($AuBr_2$)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	8.6134(1)	10.5037(9)
b, Å	9.1880(2)	11.573(1)
c, Å	11.7918(5)	11.681(1)
α, deg	76.751(4)	68.268(2)
β, deg	73.804(2)	66.912(4)
γ, deg	86.7777(6)	76.709(5)
V, Å^3	872.29(5)	1207.3(2)
Z	2	2
R-value	0.117	0.049

The crystal of (DIDTPY)(PF_6) was fundamentally composed of the $A^-D^+D^+A^-$ stack, in which the cation D^+ formed the dimer structure with no noticeable intradimer S···S contacts (D^+, cationic donor; A^-, PF_6^-; see Figure 1). On the other hand, the short interatomic I···F contacts (3.32 and 3.39 Å) were observed between the cation D^+ and PF_6^- (the sum of van der Waals radii, 3.45 Å). The conductivity of the compressed pellet was 8 x 10^{-5} Scm^{-1} (E_a = 240 meV).

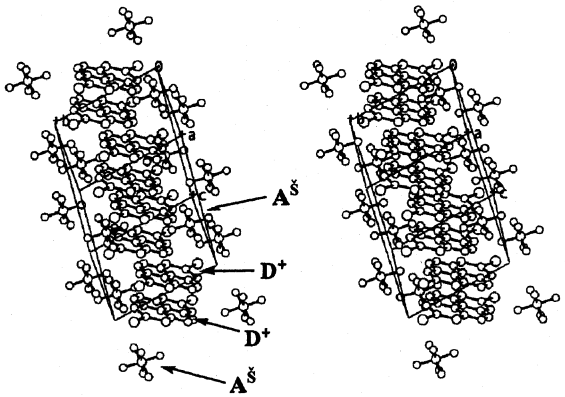


FIGURE 1 Stereoview of (DIDTPY)(PF_6) salt

The stereoview of the crystal structure of $(DIDTPY)_{1.5}(AuBr_2)$ is shown in Figure 2. The DIDTPY formed the columnar stack along the [101] direction, which was composed of the weak dimer of the cation molecule (D^+) and neutral DIDTPY (D^0). The interplanar distances between D^+ and D^+ and between D^+ and D^0 were 3.45 Å and 3.54 Å, respectively. In the cation dimer, there were the short intrastack S···S (3.54 Å) and I···I (3.90 Å) contacts which were slightly shorter than the van der Waals contacts 3.70 and 4.00 Å, respectively. In addition, the short interatomic I···Br contacts were observed between D^+ and A^- (3.30 and 3.62 Å) and between D^0 and A^- (3.54 Å, the sum of van der Waals radii, 3.83 Å). The crystal structure of the $AuBr_2$ salt can be rationalized by the interplay between the CT interactions and a variety of halogen-halogen interactions as well as the short S···S contacts. The room-temperature conductivity of the compressed pellet was 2×10^{-2} Scm^{-1} with semiconducting behavior (E_a = 180 meV).

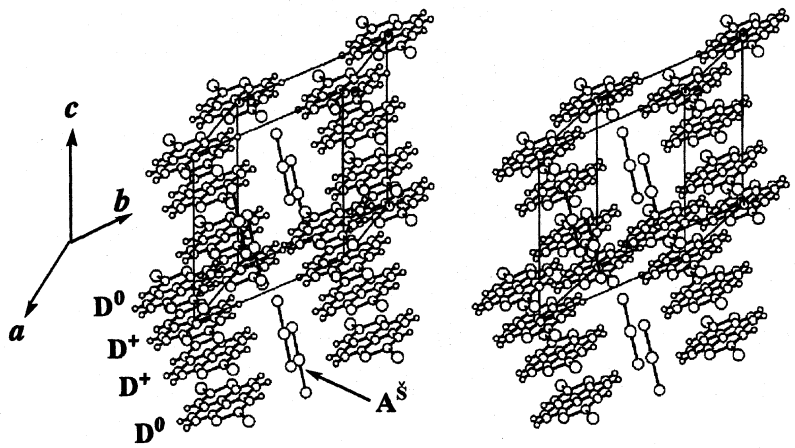


FIGURE 2 Stereoview of $(DIDTPY)_{1.5}(AuBr_2)$ salt

In summary, we have synthesized DIDTPY as a first halogenated

DTPY derivative and determined the crystal structures of two CT salts, (DIDTPY)(PF_6) and (DIDTPY)$_{1.5}$($AuBr_2$). We demonstrated that the introduction of the heteroatomic-substituents should provide a unique opportunity to construct the multi-functional interactions in the DTPY-based CT salts. Our improved synthesis of DTPY and chemical derivatization by the heteroatomic functional groups may contribute to the development of the new physical properties and functionalities in the area of the organic materials.

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