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STRUCTURE AND PROPERTY OF CROSS-CYCLOPHANE TWIN DONORS

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Abstract Cross-cyclophane twin donors, in which long axes of TTF units are fixed in a cross orientation by four ethylenedithio (*x*-CPTD (II)) and four trimethylenedithio (*x*-CPTD (III)) chains, were designed and prepared. Although the donor ability of *x*-CPTD (II) was low due to a heavy bending of the donor units, that of *x*-CPTD (III) was the same as BEDT-TTF. The crystal structures of a charge transfer complex, *x*-CPTD (III) •TCNQ, and an ion radical salt, *x*-CPTD (III)• Br (1,1,2-TCE)$_2$, revealed that *x*-CPTD (III) has an ability to construct characteristic self-assembled structures, recognizing a size and a shape of acceptors or counter ions. The almost isotropic conducting property ($\sigma_{r.t.}^{//a} = 1.0 \times 10^{-2}$ S • cm^{-1}, $\sigma_{r.t.}^{//c} = 5.5 \times 10^{-3}$ S • cm^{-1}) of the ion radical salt was interpreted based on the unique molecular structure of *x*-CPTD (III).

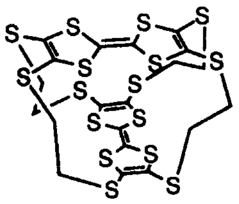
Keywords: Twin donor, BEDT-TTF, charge transfer complex, anion radical salt, cyclophane.

INTRODUCTION

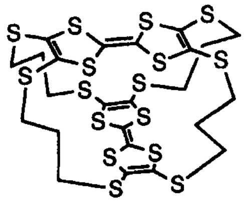
Truncated dodecahedral structure of C_{60} (I_h) enables an isotropic three-dimensional intermolecular interaction in its anion salts or CT complexes, leading to prominent physical properties, such as high T_c superconductivity or soft ferromagnetism.[1] Searching for a TTF family with higher dimensionality[2] in reference to intermolecular interactions, dimeric TTF derivatives,[3] twin donors, in which two TTF skeletons are connected by single or double methylenedithio or ethylenedithio chain(s), have been prepared.[4,5] Although conformation of the dimeric donors is flexible, the cyclophane-type conformers of twin donors are often observed in their ion radical salts, exhibiting characteristic intermolecular interactions.

As an extension along this line, we are interested, in particular, in a cross-type twin donors, in which two long axes of donor units are fixed in an orthogonal orientation, according to the following reasons.[6] First, this type of orientation of donors can hardly be encountered in charge transfer complexes or ion radical salts.[7] Second, the cross-type donor may have a chance to interact not only along the stacking direction but also in a two-dimensional fashion through intermolecular S···S contacts between sulfur atoms at four corners of the upper and lower donor units. Thus we have designed a cross-cyclophane twin donor (*x*-CPTD), in which long axes of two TTF units are fixed in a cross orientation by four ethylenedithio (*x*-CPTD (II)) and trimethylenedithio (*x*-CPTD (III)) chains.

Such donors have multi-redox states due to the presence of two donor units, interacting electronically. If the energy splitting between the different oxidation states is small, the valence fluctuation may exist in their ion radical salts, leading to intriguing electromagnetic properties.



x-CPTD (II)



x-CPTD (III)

Here we report preparations of *x*-CPTD (II, III) and structures and properties of a charge transfer complex and an ion radical salt formed by *x*-CPTD (III). The characteristic crystal structures of the neutral donors and those of the charge transfer complex and the ion radical salt reveal that the cross-cyclophane twin donors can be regarded as a unique building block for constructing supramolecular assemblies,[8] exhibiting prominent physical properties.

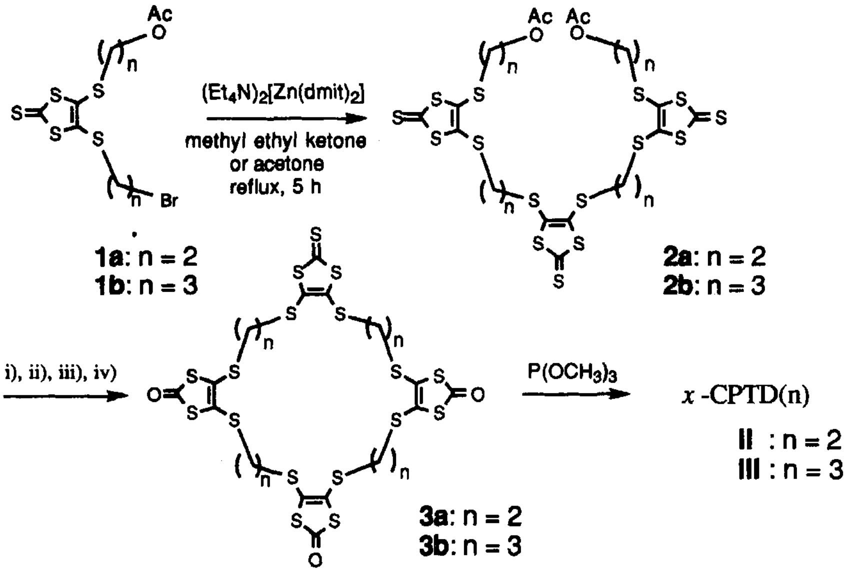
RESULTS

Preparation of *x*-CPTD (II, III)

x-CPTD (II, III) with four ethylendithio or trimethylenedithio chains were prepared *via* a cyclic tetramer of alkylated dmit[9] (triketo-thione **3**) as a key intermediate according to Scheme I. Addition of alkylated dmit (**1**) to an acetone solution of zincate[10] afforded an acyclic trimer **2**. After thiones and terminal acetoxy groups were converted to ketones[9,11] and bromides,[12] respectively, the acyclic trimer was reacted with zincate to give the cyclic tetramer **3**. Intramolecular double-coupling of **3** between carbonyl or thiocarbonyl groups at the diagonal sites by trimethylphosphite afforded the desired products *x*-CPTD (II, III) in reasonably high yields.

Crystal structures of neutral *x*-CPTD (II, III)

Crystal structures of the neutral donors, *x*-CPTD (II) and *x*-CPTD (III), were revealed by X-ray crystallography (Figure 1). In the crystal of *x*-CPTD (II) (yellow prism, monoclinic,



i) K_2CO_3 / MeOH-CH_2Cl_2, quant.
ii) PBr_3 / DMF, 50 °C
iii) $Hg(OAc)_2$ / $CHCl_3$-AcOH, quant.
iv) Zincate / acetone, reflux

SCHEME I Synthetic route of *x*-CPTD (n).

C2/c), a half of the donor molecule is an asymmetric unit. On the other hand, there are two independent donor molecules (A, B) in the crystal of *x*-CPTD (III) (orange-yellow prism, tetragonal, $P4_1$) As shown in the top views of *x*-CPTD (II, III) (Figure 1a), the two donor units are fixed in a cross orientation. Although four sulfur atoms of each of TTF units above and below are superimposed, the intramolecular S···S distances are as remote as 6.16 Å in *x*-CPTD (II), and 5.85, 5.45 Å in *x*-CPTD (III), suggesting that there are almost no intramolecular electronic interactions between two donor units in the neutral state. The bent angles of the upper and lower donor sites of *x*-CPTD (II) are 30.7 degrees and 37.8 degrees, respectively, while the corresponding bent angels of *x*-CPTD (III) are reduced to the range of 15.8-29.0 degrees (Figure 1b).

These cross-cyclophane donors, *x*-CPTD (II, III), form characteristic supramolecular structures, reflecting polyhedral shapes with sulfur atoms at each corner. Namely, *x*-CPTD (II) are arranged in a corrugated column with a *face-to-face* interaction at tetrathioethylene moieties at both sides. These corrugated columns run in parallel along the *c*-axis (Figure 2). While two independent molecules of *x*-CPTD (III) are located by two four-fold axes, respectively. A pair of independent molecules is on the *ab* plane, forming a sheet structure by translational symmetry (Figure 3).

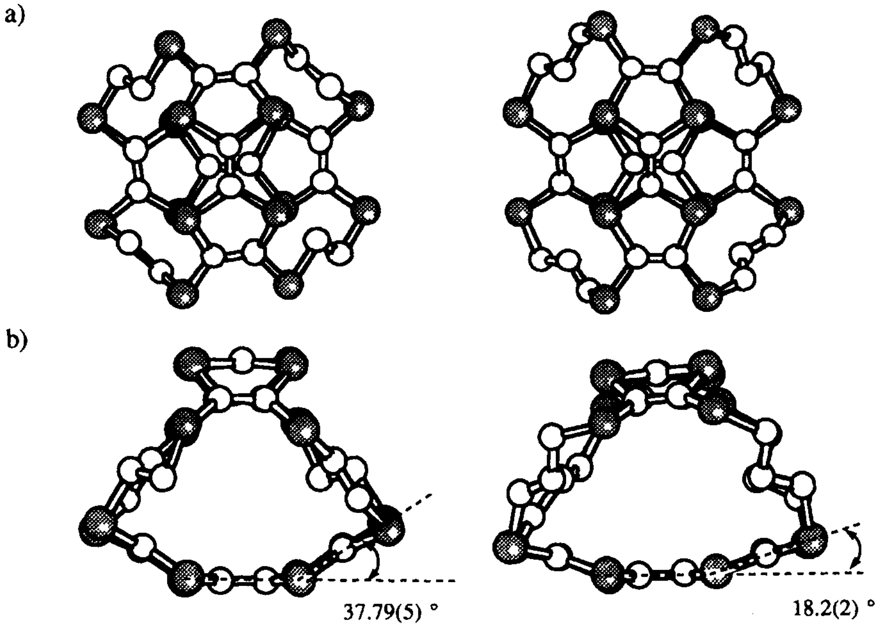


FIGURE 1 a) Molecular structures of *x*-CPTD viewed from the top of *x*-CPTD (II) (left) and of *x*-CPTD (III) (A type) (right).
b) Molecular structures of *x*-CPTD viewed from the side of *x*-CPTD (II) (left) and of *x*-CPTD (III) (A type) (right).

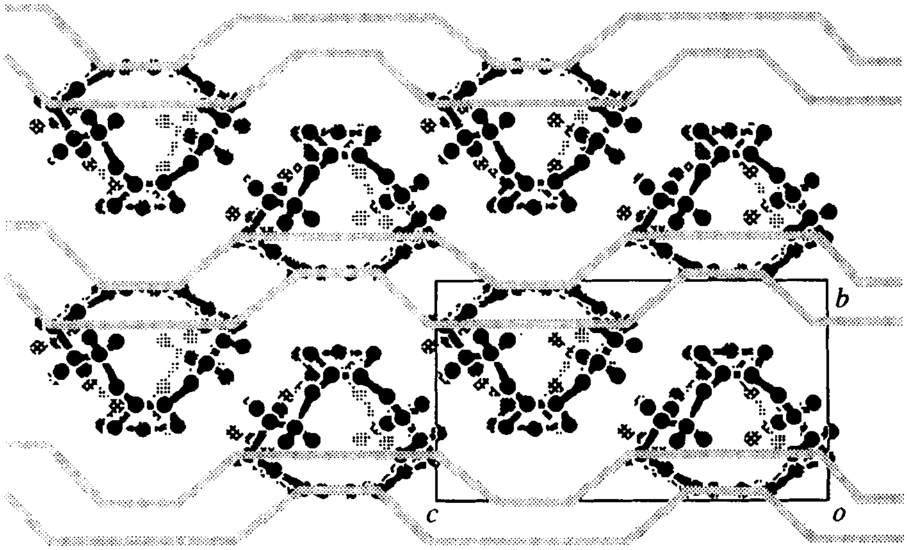


FIGURE 2 Corrugated columns in the neutral crystal of *x*-CPTD (II).

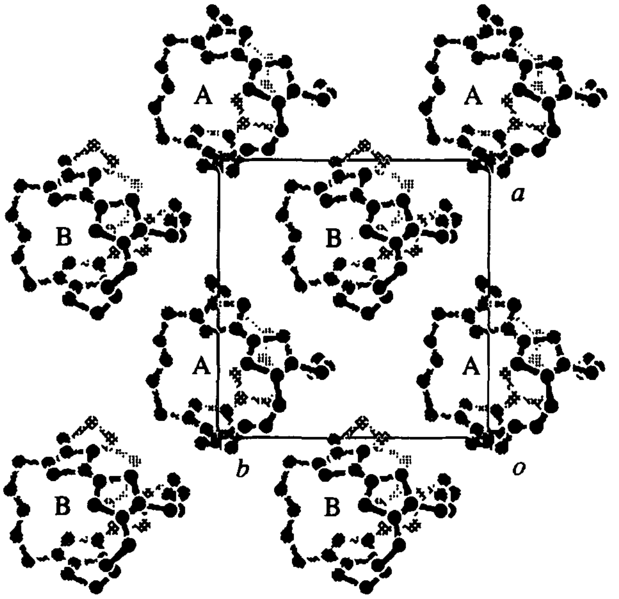


FIGURE 3 Sheet structure on the *ab* plane in the neutral crystal of *x*-CPTD (III).

Redox Potentials of *x*-CPTD (II, III)

Cyclic voltammograms of donors, *x*-CPTD (II) and *x*-CPTD (III), were measured in benzonitrile. The oxidation wave of *x*-CPTD (II) was irreversible and the corrected oxidation potential was as high as 0.94 V *vs.* Ag/AgCl (Table I).

TABLE I Redox potentials of BEDT-TTF and *x*-CPTD (II, III).

	$E_{1/2}^1$	$E_{1/2}^2$	$E_{1/2}^3$	$E_{1/2}^4$
BEDT-TTF	0.58	0.88	-	-
x-CPTD(II)	$0.94^{\text{irr.}}$	-	-	-
x-CPTD(III)	0.64	0.77	1.07	1.18

Reference electrode Ag/AgCl; Supporting electrolyte TBA • ClO_4 0.1 mol dm^{-3}/ PhCN; Reference Fc/Fc^+ = 0.52 V; Scanning rate 200 mV sec^{-1}.
Average of the oxidation and reduction potentials for $D^0 \rightleftharpoons D^+ + e$ ($E_{1/2}^1$), $D^+ \rightleftharpoons D^{2+} + e$ ($E_{1/2}^2$), $D^{2+} \rightleftharpoons D^{3+} + e$ ($E^{1/2}{}_3$), and $D^{3+} \rightleftharpoons D^{4+} + e$ ($E_{1/2}^4$) are shown.

On the other hand, four reversible redox couples appeared in *x*-CPTD (III) at $E_{1/2}$ = 0.64, 0.77, 1.07 and 1.18 V *vs.* *Ag* / AgCl in the voltammogram (Figure 4). Although the redox potentials are slightly shifted to higher values compared with those of BEDT-TTF ($E_{1/2}$ = 0.58, 0.88 V), the donor ability of *x*-CPTD (III) is considered to be almost the same as BEDT-TTF.

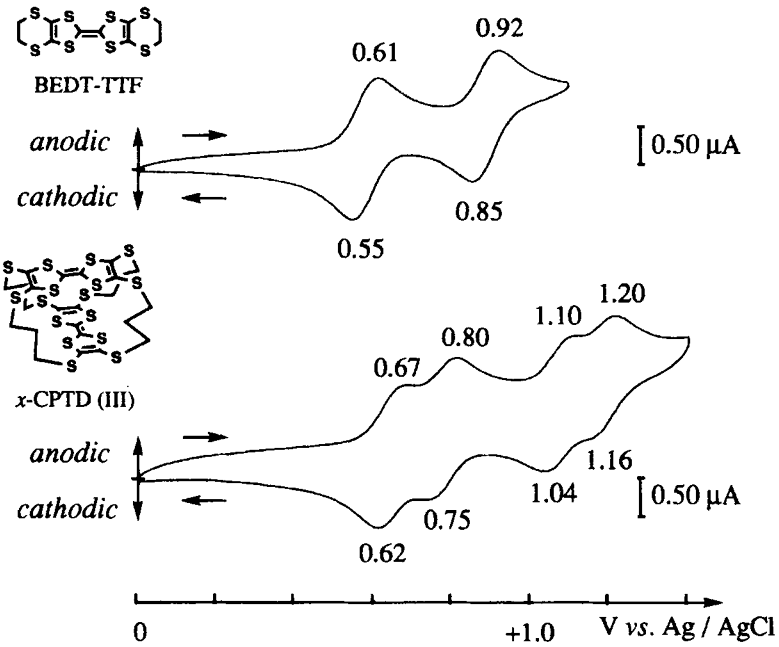


FIGURE 4 Redox potentials of BEDT-TTF (above) and those of *x*-CPTD (III) (below). BEDT-TTF (2.6 mol dm^{-3}/PhCN), *x*-CPTD (III) (2.4 mol dm^{-3}/PhCN).

Crystal structure of a CT complex of *x*-CPTD (III) with TCNQ

Single crystals (black needles, monoclinic, *C*2) of a CT complex (1:1) between donor *x*-CPTD (III) and TCNQ were obtained by slow evaporation from chloroform solution. The shape of the donor is almost the same as that of the neutral donor (intramolecular S···S distances 5.13 ~ 5.87 Å). When the molecular structure is looked precisely, two donor units are not equivalent. One of the donor units with the bent angles of 18.3 and 19.3 degrees overlaps with TCNQ (Figure 5a), and the other unit with the bent angles of 8.9 and 21.2 degrees forms a *face-to-face* dimer of donors (Figure 5b).

The *face-to-face* dimers (intermolecular S···S distances 3.64 ~ 3.70 Å) are arranged in an array along the *a*-axis through *side-by-side* interactions (intermolecular S···S distances 3.85 Å). Besides, donors in the array are arranged along the *b*-axis with those in adjacent arrays at both sides, forming a sheet structure (Figure 6). TCNQ molecules are located in between layers. The UV-VIS-NIR spectrum of the complex in a KBr pellet showed an absorption at λ_{max} = 630, 1270 nm, which can be assigned to the charge transfer band. The degree of the charge transfer, however, is considered to be small, because the CN stretching frequency of 2224 cm^{-1} is almost the same as that of the neutral TCNQ.[13] This may be due to the poor overlap (interplanar distance 3.45 Å) between the donor and TCNQ as shown in Figure 5a.

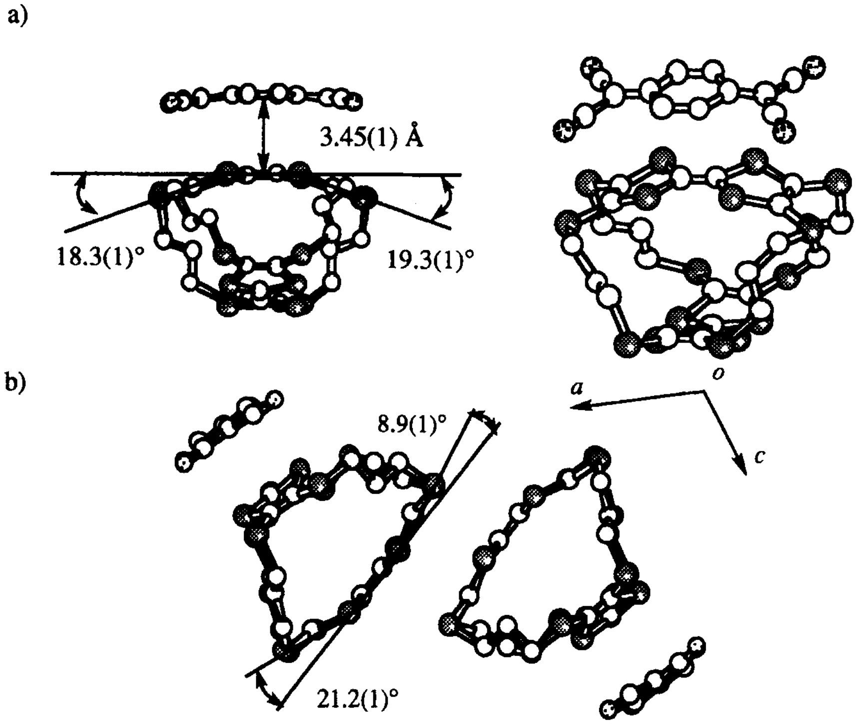


FIGURE 5 Molecular structures of *x*-CPTD (III) in the CT complex with TCNQ.
a) Overlap between TCNQ and one of the donor units.
b) *Face-to-face* overlap between two neighboring donors, viewed along the *b*-axis.

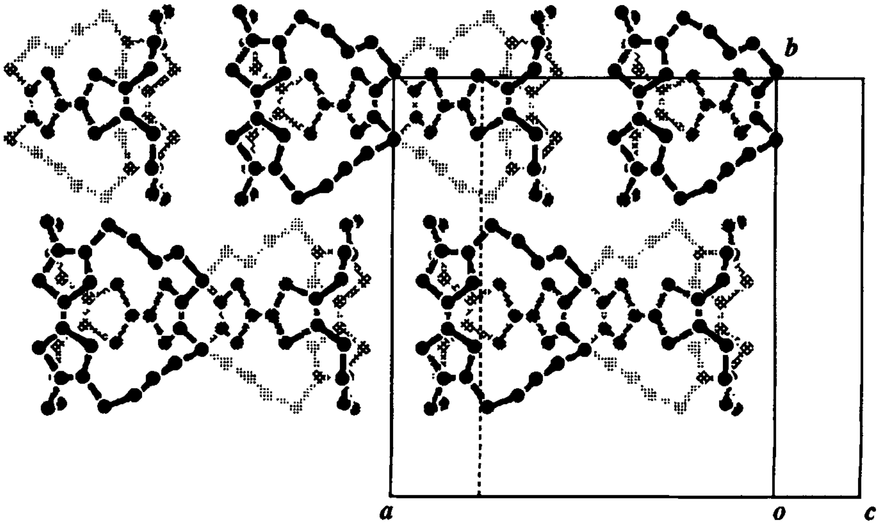


FIGURE 6 Sheet structure constructed by the *face-to-face* dimer, viewed normal to the *ab* plane. TCNQ molecules are not shown for clarity.

Crystal structure of ion radical salt of *x*-CPTD (III)

Ion radical salts (black block, tetragonal, $P4_1$) of donor *x*-CPTD (III) was prepared through galvanostatic electrocrystallization in 1,1,2-trichloroethane (TCE) solution, using tetra-*n*-butylammonium bromide (TBA • Br) as a supporting electrolyte. The chemical composition of the salt was determined by the elemental analysis to be *x*-CPTD (III):Br: 1,1,2-TCE = 1:1:2.

Although the donor units of the neutral *x*-CPTD (III) are bent based on the electronic repulsion, they are supposed to become flat when *x*-CPTD (III) is oxidized to the cation radical, *x*-CPTD $(III)^{+\bullet}$, as it is the case in BEDT-TTF. In fact, the bent angle of *x*-CPTD $(III)^{+\bullet}$ was decreased to *ca.* 8 degrees (Figure 7a). As a result, the intramolecular S···S distance between donor units was reduced to *ca.* 4.5 Å.

The donors are overlapped in a *face-to-face* manner, although the arrangement was shifted by a half of the donor unit. The *face-to-face* dimers are located *side-by-side* to form a cavity among them. Bromide anion and solvent molecules are incorporated in the cavity (Figure 7b). The donors thus form a sheet structure, and the donor sheets are stacked, sliding by a half of the donor unit along the *a*- and the *b*-axes. There are intermolecular S···S contacts (3.6-3.8 Å) between sulfur atoms at the four corners of the donor units of the rectangular shape above and below, respectively. Since the long axes of the donor units are orthogonal each other, there are two orthogonal conduction paths along the *a*- and the *b*-axes.

Conductive property of *x*-CPTD (III) •Br $(1,1,2\text{-TCE})_2$

Conductivity of the salt was measured by a four-probe method both along the *a*- or *b*-axis and the *c*-axis. The conductivity at room temperature was 1.0×10^{-2} S•cm^{-1} along the *a*- or *b*-axis and 5.5×10^{-3} S • cm^{-1} along the *c*-axis. The temperature dependence of conductivity indicates that the salt exhibits a semiconducting behavior. The activation energy along the *a*- or *b*-axis was estimated to be 0.75 eV from the Arrhenius plot.

DISCUSSIONS

x-CPTD as a building block for a supramolecular assembly

The molecular structure of *x*-CPTD is unique as a building block to construct a supramolecular assembly.[8] If sixteen sulfur atoms of *x*-CPTD are connected by hypothetical bonds, they form a hexahedral sulfur cluster. This structure is obtained by slicing two orthogonal edges of tetrahedron as shown in Figure 8a. Thus the molecular structure of *x*-CPTD can be regarded as an edge-sliced tetrahedron. Such a molecule is likely to form a sheet structure, being arranged in the *upside-down* manner alternately (Figure 8b).

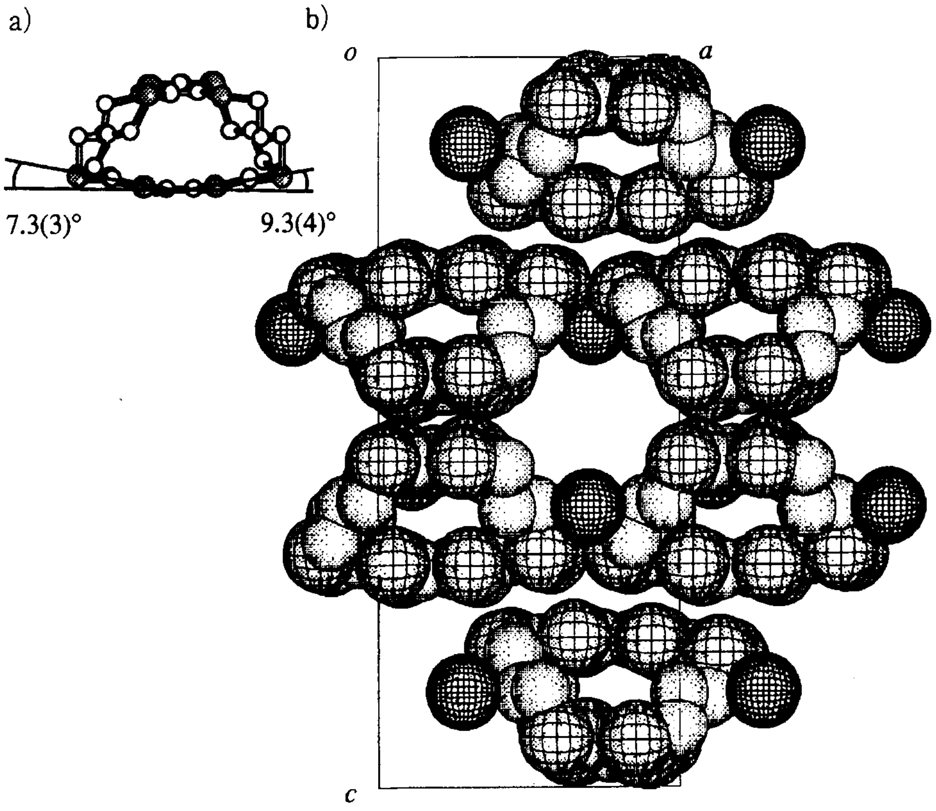


FIGURE 7 a) Molecular structure of *x*-CPTD (III) in the ion radical salt, *x*-CPTD (III) • Br (1,1,2-TCE)$_2$.
b) Crystal structure of *x*-CPTD (III)•Br (1,1,2-TCE)$_2$.
Solvent molecules are not shown because of the heavy disorder.

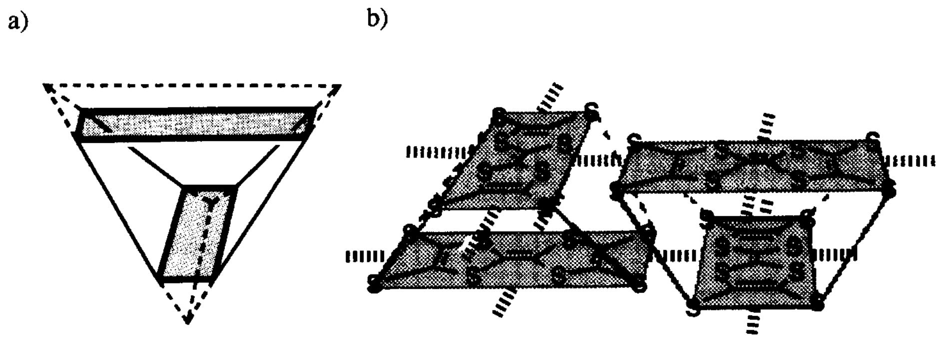


FIGURE 8 a) Shape of *x*-CPTD (III) of an edge-sliced tetrahedron.
b) Sheet structure composed of *x*-CPTD (III).

When the molecular structures of *x*-CPTD (II) and *x*-CPTD (III) are compared, the ethylenedithio bridges are considered to be too short to keep the TTF unit flat. The bent angle of 37.8 degrees is almost comparable with those of a cyclophane-type donor reported by Müllen.[14] Reflecting the deformation of the TTF unit, the oxidation potential of *x*-CPTD (II) is as high as 0.94 V *vs.* Ag/AgCl. Since the bent angles of *x*-CPTD (III) is much released and its redox potentials are similar to those of BEDT-TTF, *x*-CPTD (III) is considered to be adequate for preparing CT complexes and ion radical salts.

The molecular shape of *x*-CPTD was found to be changed depending on the oxidation states. In the neutral state, the donor unit is bent heavily at the central tetrathioethylene. On the other hand, the donor units of *x*-CPTD (III) become almost flat in its ion radical salt. As a result, the intramolecular S···S distance decreases to *ca.* 4.5 Å.

Characteristics of the structure of the self-assembled *x*-CPTD

In the neutral crystals of *x*-CPTD (II, III), the donors are arranged in a *face-to-face* manner, although the mode of overlap is different between *x*-CPTD (II) and *x*-CPTD (III). We noticed that donor *x*-CPTD (III) has an ability of constructing a characteristic self-assembled structure not only in the neutral crystal but also in CT complexes and ion radical salts, recognizing the size and the shape of acceptors or counter ions. When an acceptor is flat in shape, the donor molecules have a tendency to be arranged in a *side-by-side* and *upside-down* manner, forming a sheet structure, and flat acceptors are like to superpose on the layer (Figure 9a).

On the other hand, when a counter ion is spherical in shape, the donors have a tendency to form a *face-to-face* dimer and the dimers are arranged *side-by-side* to construct a cavity. In such a case, the cavity may incorporate large spherical counter ions and sometimes even solvent molecules (Figure 9b).

Characteristics of the electronic structure of *x*-CPTD (III)

Although the intramolecular electronic interaction is small in the neutral state, the cyclic voltammogram of *x*-CPTD (III) showed a splitting between the first and second redox potentials of 0.13 V. The splitting is too small to be regarded as on-site Coulombic repulsion of the donor unit, but should be derived from the intramolecular electronic interaction between two donor units.[2]

The electronic structure of *x*-CPTD (III) of various oxidation states can be expressed in terms of a partial molecular orbital method (Scheme II). Interaction between *homos* of two donor units induces the splitting between HOMO and NHONO of the donor. The first one-electron oxidation removes an electron from HOMO to afford a cation radical ($D^{+\bullet}$-D^0). The second oxidation can occur either from SOMO or NHOMO, depending on the energy difference (ΔE) between the relevant orbitals and the on-site

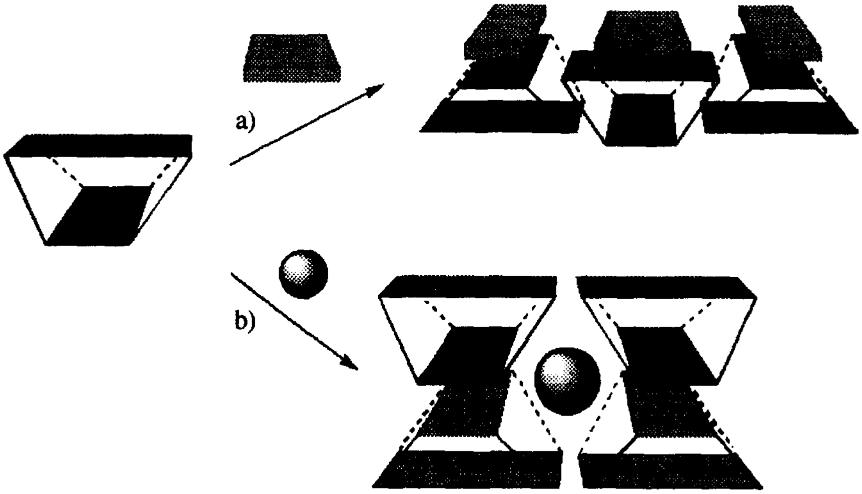
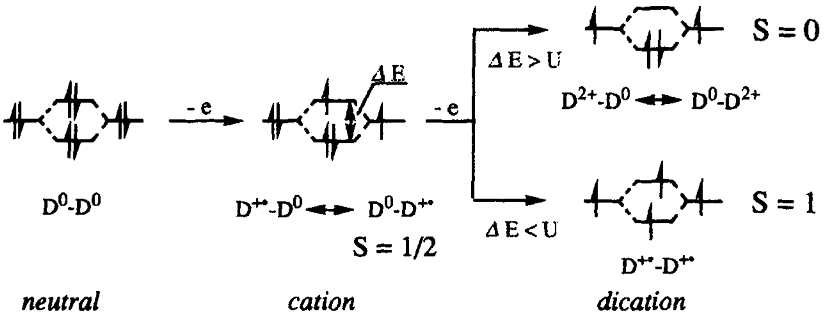


FIGURE 9 a) Self-assembled structure of the CT complex of *x*-CPTD (III), the donor sheet being imposed by acceptors of a flat shape.
b) Self-assembled structure of the ion radical salt of *x*-CPTD (III), including counter ions in a cavity.

Coulombic repulsion (U). If $\Delta E > U$, the second oxidation should occur from SOMO to give a closed-shell dication (D^{2+}-D^0). On the other hand, if $U > \Delta E$, the second oxidation removes an electron from NHOMO, affording an open-shell dication diradical ($D^{+\bullet}$-$D^{+\bullet}$) of the triplet ground state. Although through-bond interaction between two donor units can not be ignored in these oxidized species. The possibility of the dual oxidation states for the doubly oxidized species is especially intriguing in respect of the magnetic properties of the ion radical salts. The relative stability between the closed-shell dication and the dication diradical may be heavily dependent on the conformation of the doubly oxidized species.



SCHEME II Oxidation states and electronic structures of *x*-CPTD (III).

Conductivities of the salt along the *a*- and *b*-axes are the same ($\sigma_{r.t.} = 1.0 \times 10^{-2}$ S • cm^{-1}) and that along the *c*-axis is not significantly different ($\sigma_{r.t.} = 5.5 \times 10^{-3}$ S • cm^{-1}). This result suggests that the electronic interaction along the stacking axis is reasonably large, despite the relatively long intramolecular S···S distance of *ca.* 4.5 Å. It may be concluded that the conductivity is almost isotropic, reflecting the unique molecular structure of *x*-CPTD (III).

SUMMARY

Construction of a supramolecular structure is the recent topic in materials science. Although quite a few numbers of magnificent supramolecular structures have been reported, there are only a few cases which exhibit prominent physical properties or functionalities. In the current study, however, a donor molecule of a block-type shape was utilized as a building block of a supramolecular structure. Consequently, the characteristic molecular assembly constructed by *x*-CPTD exhibits a semiconductive property with the almost isotropic conductivity. This conducting behavior is supposed to reflect the shape of the donor molecule. Besides, the prominent electromagnetic properties may also be manifested, if the contribution of the dication state with dual electronic configurations becomes significant to the electronic structure of its ion radical salts.

EXPERIMENTAL

General Procedures

NMR spectra were recorded on a JEOL GSX-α-500 spectrometer, operating at 500 and 125 MHz for ^{1}H and ^{13}C, respectively. UV-VIS-NIR and IR spectra were recorded on a JASCO V-570 UV/VIS/NIR spectrometer and a Perkin-Elmer 1640 spectrometer, respectively.

Melting points were recorded on a Shimadzu DSC-50 differential scanning calorimeter. Mass spectra were recorded on a JEOL JMX-SX102 instrument. Microanalyses were performed at the Elemental Analysis Center of the Department of Chemistry, Faculty of Science, The University of Tokyo. Gel permeation chromatography (GPC) were performed on a series of JAIGEL 1H-40 and 2H-40 columns with a flow of 13.5 mL • min^{-1} of chloroform on an LC908-C60 Liquid Chromatography of Japan Analytical Industry Co. Ltd.

Unless noted otherwise, all starting materials were obtained from commercial suppliers and were used without further purification. Acetone and methyl ethyl ketone were dried over calcium sulfate. Trimethylphosphite was treated with sodium, then decanted and distilled. 1,1,2-TCE was shaked with sulfuric acid, passed through an alumina column, and distilled under a reduced pressure.

Cyclic voltammograms (CV) were measured in benzonitrile (PhCN) at room temperature in the presence of tetra-*n*-butylammonium perchlorate ($TBA \cdot ClO_4$) as an electrolyte with a platinum working electrodes, using a potentiostat/galvanostat HAB 151 (HOKUTO DENKO Ltd.). An Ag /AgCl electrode (BAS co., Ltd.) was used for a reference electrode, scanning rate was 200 $mV \cdot s^{-1}$.

X-ray data were collected by a Rigaku AFC-5S or AFC-7R four-circle diffractometer by using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) at room temperature. The structures were solved by a direct method (SHELX–86[15]) and were refined for all non–hydrogen atoms with anisotropic temperature factors by a block–diagonal least–squares method (UNICS–III[16]). The coordinates of hydrogen atoms were recalculated after an each refinement cycle with the isotropic temperature factor of 4.0 Å^2.

The electrical conductivity was measured by the four probe method, using gold paste for attaching gold wires (ϕ 25 μm) to the samples.

Preparation of *x*-CPTD (II, III)

4-(3-Acetoxypropylthio)-5-(3-bromopropylthio)-1,3-dithiole-2-thione (1b): Zincate,[10] $(Et_4N)_2[Zn(dmit)_2]$ (dmit[9] = 4,5-dimercapto-1,3-dithiole-2-thione), was mixed with 3-bromopropanol and 3-bromopropyl acetate in acetone. The mixture was refluxed for 1 day to give 4-(3-acetoxypropyl)-5-(3-hydroxy-propyl)-dmit. Methyl ethyl ketone was used instead of acetone for the preparation of **1a**. Bromination of the dmit derivative with phosphorus tribromide in *N,N*-dimethylformamide (DMF) at 50 °C afforded **1b** in 35% (**1a** in 31%) yield based on zincate.

α,ω-Bis(3-acetoxypropylthio) dmit trimer (2b): A 300 mL flask was charged with 3.00 g (7.15 mmol) of **1b**, 1.28 g (1.78 mmol) of zincate, and 300 mL of acetone. Methyl ethyl ketone was used instead of acetone for the preparation of **2a**. The mixture was refluxed for 1 day under nitrogen, then filtered. The filtrate was concentrated on a rotary evaporator to yield crude reaction products. The crude reaction products were purified by column chromatography on 150-200 mesh silica gel (50 g, elution with CH_2Cl_2/ hexane, 4:1) to furnish 2.43 g (78%) of **2b** as dark red oil.

2b: ^{1}H NMR ($CDCl_3$/TMS): δ 4.19 (t, 4H), 3.04 (td, 8H), 2.98 (t, 4H), 2.08 (s, 6H), 2.06 (t, 4H), 2.04 (quintet, 4H); ^{13}C NMR ($CDCl_3$): δ 210.5, 210.2, 170.9, 137.6, 136.1, 134.7, 62.2, 35.0, 35.0, 33.4, 29.2, 28.8, 20.9.

2a: yield 77%; ^{1}H NMR ($CDCl_3$): δ 4.30 (t, 4H), 3.19-3.14 (m, 8H), 3.15 (t, 4H), 2.09 (s, 6H); Anal. Calcd for $C_{21}H_{22}O_4S_{15}$: C, 30.8; H, 2.7. Found: C, 31.3; H, 2.6.

Cyclic dmit tetramer (triketo-thione 3b): Treatment of **2b** with potassium carbonate in methanol-dichloromethane[17] followed by bromination led to a 76% yield of α,ω-bis(3-bromopropyl) dmit trimer. Treatment of the dibromide with mercuric acetate gave the acyclic dibromo-triketone in quantitative yield.[9,11]

A 100 mL flask was charged with 327 mg (0.37 mmol) of acyclic dibromo-triketone, 135 mg (0.19 mmol) of zincate, and 100 mL of acetone. Methyl ethyl ketone was used instead of acetone for the preparation of **3a**. The mixture was refluxed for 1 day under nitrogen. The resulting yellow-orange solid was collected by vacuum filtration, washed on the filter using water and acetone successively, and dried to yield 234 mg (69%) of **3b** as yellow solid.

3b: ^{1}H NMR ($CDCl_3$/TMS): δ 3.10-2.98 (m, 16H), 2.09-1.95 (m, 8H)

3a: yield 77%; ^{1}H NMR ($CDCl_3$/TMS): δ 3.25-3.15 (m , 16H).

Cross-cyclophane twin donor (*x*-CPTD (III)): A 10 mL flask was charged with 1.91 g (2.11 mmol) of **3b** and 20 mL (23.7 mmol) of trimethylphosphite. The mixture was heated at 120 °C for 12 hr under nitrogen followed by removal of the solvent under a reduced pressure to yield black oil. The crude reaction product was purified by column chromatography on 150-200 mesh silica gel (50 g, elution with CH_2Cl_2/ hexane, 10: 1) and by GPC (retention time 63 min., 13.5 mL / min.) to give orange powder. Crystallization of the powder from $CHCl_3$ gave 0.36 g (20%) of orange-yellow crystals.

***x*-CPTD (III):** mp. > 240 ℃(decomp); IR (KBr): 1486m, 1439m, 1416s, 777s; ^{1}H NMR ($CDCl_3$/TMS): δ 2.88-2.76 (m, 16H), 2.24-2.16 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 125.0, 112.9, 34.3, 32.6; FAB HRMS Calcd for $C_{24}H_{24}S_{16}$: 823.7410. Found: *m/z* 823.7319; UV (CH_2Cl_2), λ_{max} (log ε) = 262 (4.48), 314 (4.32), 338 (4.42), 380 (sh) (3.80) nm.

***x*-CPTD (II):** yield 67%; mp. > 255 ℃; IR (KBr): 1417s, 1269s, 772s; ^{1}H NMR ($CDCl_3$/TMS): δ 3.24-3.15 (m, 8H), 2.91-2.82 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 130.0, 122.8, 37.1; FAB HRMS Calcd for $C_{20}H_{16}S_{16}$: 767.6784. Found: *m/z* 767.6730; UV (CH_2Cl_2), λ_{max} (log ε) = 262 (4.52), 333 (4.48), 375 (sh) (3.83) nm.

Preparation of *x*-CPTD (III) • TCNQ

The charge transfer complex of *x*-CPTD (III) with TCNQ was obtained by addition of a solution of 1.24 mg (6.07 μmol) of TCNQ in 10 mL of $CHCl_3$ to a solution of 5.00 mg (6.06 μmol) of *x*-CPTD (III) in 10 mL of $CHCl_3$. Slow evaporation of the solvent afforded black needle-like crystals after *ca.* 2 weeks.

***x*-CPTD (III) • TCNQ:** Anal. Calcd for $C_{36}H_{28}S_{16}N_4$: C, 41.99; H, 2.74; S, 49.83; N, 5.44. Found: C, 41.89; H, 3.20; S, 50.04; N, 5.61.

Preparation of *x*-CPTD (III) • Br (1,1,2-TCE)$_2$

Single crystals of *x*-CPTD (III) • Br were obtained by galvanostatic anodic oxidation of 4.2 mg (5.1 μmol) of *x*-CPTD (III) in 18.0 mL of 1,1,2-TCE containing 31.5 mg (96.2 μmol) of TBA • Br as a supporting electrolyte in a H-type cell equipped with platium electrodes. The anode and cathode in the cell were separated by a glass filter. A constant current of 0.3 μA was applied. Black blocks of Br salts (*x*-CPTD (III) • Br (1,1,2-TCE)$_2$) were obtained after 15 days. The crystals were collected on a glass filter, and washed with purified 1,1,2-TCE.

***x*-CPTD (III) • Br (1,1,2-TCE)$_2$:** Anal. Calcd for $C_{28}H_{30}S_{16}Br_1Cl_6$: C, 28.69; H, 2.58; S, 43.76; Cl, 18.15; Br, 6.82; N, 0. Found: C, 28.56; H, 2.60; S, 43.28; Cl, 18.31; Br, 6.76; N, 0.

Crystallographic data

Crystallographic data for ***x*-CPTD (II)**: formula, $C_{20}H_{16}S_{16}$; $M = 769.31$; monoclinic, Space group $C2/c$; $a = 17.719(6)$, $b = 9.959(4)$, $c = 17.609(4)$ Å, $\beta = 91.91(2)°$; $V = 3106(2)$ Å^3; $Z = 4$; $D_{calcd} = 1.65$ g cm^{-3}; radiation, Mo-$K\alpha$ ($\lambda = 0.71073$ Å); unique obsd. data, 1645; $R = 0.061$. ***x*-CPTD (III)**: formula, $C_{24}H_{24}S_{16}$; $M = 825.41$; tetragonal, Space group $P4_1$; $a = 15.340(2)$, $c = 30.166(3)$ Å; $V = 7098(2)$ Å^3; $Z = 8$; $D_{calcd} = 1.55$ g cm^{-3}; radiation, Mo-$K\alpha$ ($\lambda = 0.71073$ Å); unique obsd. data, 3286; $R = 0.066$. ***x*-CPTD (III) • TCNQ**: formula, $C_{36}H_{28}N_4S_{16}$; $M = 1029.61$; monoclinic, Space group $C\,2$; $a = 18.652(8)$, $b = 20.331(5)$, $c = 12.756(4)$ Å, $\beta = 109.74(2)°$; $V = 4553(3)$ Å^3; $Z = 4$; $D_{calcd} = 1.50$ g cm^{-3}; radiation, Mo-$K\alpha$ ($\lambda = 0.71073$ Å); unique obsd. data, 2967; $R = 0.068$. ***x*-CPTD (III) • Br (1,1,2-TCE)$_2$**: formula, $C_{28}H_{30}S_{16}Br_1Cl_6$; $M = 1172.13$; tetragonal, Space group $P\,4_1$; $a = 12.425(3)$, $c = 29.919(7)$ Å; $V = 4619(3)$ Å^3; $Z = 4$; $D_{calcd} = 1.930$ g cm^{-3}; radiation, Mo-$K\alpha$ ($\lambda = 0.71073$ Å); unique obsd. data, 2384; $R = 0.107$.

DEDICATION

This paper is dedicated to Professor Fumio Ogura and Professor Yusei Maruyama in honor of their retirements from successful academic careers in Hiroshima University and in Institute for Molecular Science, respectively.

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