Three-Dimensional Sulfur-Based π-Donor: A Novel Dimeric TTF Derivative of a Cross-Cyclophane Type

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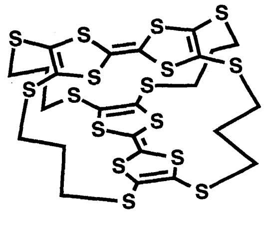
A novel dimeric TTF derivative (**1**) of a cross-cyclophane type was prepared through an intramolecular coupling of a cyclic tetramer of alkylated dmit. The crystal structure of **1**·TCNQ indicates a unique sheet structure of **1** through *face-to-face* and two types of *side-by-side* interactions. Cyclic voltammetric measurement of **1** suggests the presence of intramolecular interaction between two donor units.

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 Tc superconductivity or soft ferromagnetism.[1]

Searching for a TTF family with higher dimensionality in reference to intermolecular interactions, dimeric TTF derivatives in which two TTF skeletons are connected by single or double methylenedithio chains have been prepared.[2] The conformation of donors in their salts is often of a cyclophane-type, exhibiting characteristic intermolecular interactions. Therefore, design of a dimeric donor with a different mutual orientation has become of current interest. Here we report preparation of a cross-typed cyclophane donor, in which two TTF skeletons are connected in a cross orientation by four trimethylenedithio chains (**1**), [3] and discuss the characteristic intra- and intermolecular interactions based on the unique molecular structure.



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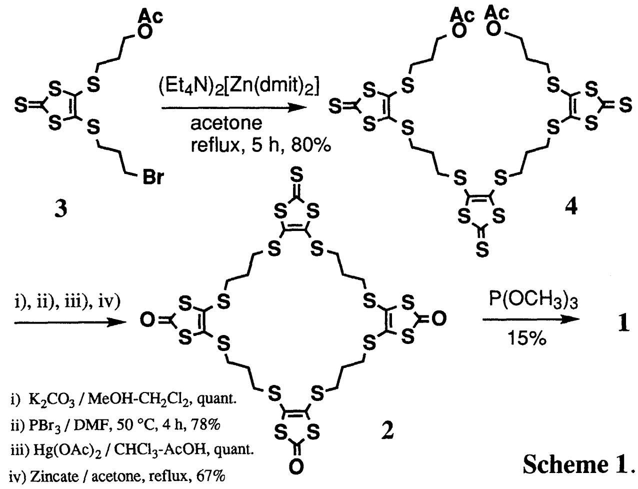
Preparation of the cross-cyclophane donor **1** was accomplished *via* a cyclic tetramer of alkylated dmit (triketo-thione **2**) as a key intermediate. Addition of alkylated dmit (**3**) with bromo and acetyloxy groups at the terminal carbons to an acetone solution of zincate afforded an acyclic trimer **4** (Scheme 1). After thiones and terminal acetyloxy groups were converted to ketones and bromines, respectively, the acyclic trimer allowed to react with zincate to give the cyclic tetramer **2** in good yield. Intramolecular coupling of **2** between carbonyl or thiocarbonyl groups at the diagonal sites by trimethylphosphite afforded the desired product **1**.[4]

Single crystals (black needles) of CT complex (1:1)[5] between donor **1** and TCNQ were obtained by slow evaporation from chloroform solution. X-ray crystallographic analysis reveals that two TTF moieties of **1** are located in an orthogonal manner each other, and four inner sulfur atoms of each donor unit above and below are nearly superimposed (S···S distances 5.13 ~ 5.87 Å) (Figure 1).[6] If sixteen sulfur atoms of **1** 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 2. Although the donor units of the neutral **1** are bent based on the electronic repulsion,[7] they are supposed to become flat when **1** is oxidized to the cation radical $\mathbf{1}^{+\bullet}$, as it is the case in BEDT-TTF.



Scheme 1.

Cyclic voltammogram of donor **1** was measured in benzonitrile to show significant electronic interaction between two donor units in the oxidized states.[8] Four reversible redox waves appear at $E_{1/2}$ = 0.64, 0.77, 1.07 and 1.18 V in the voltammogram. Although the oxidation potentials are slightly shifted to higher values compared with those of BEDT-TTF ($E_{1/2}$ = 0.58, 0.88 V), the splitting between the first and the second oxidation potentials is only 0.13 V, suggesting the decrease of on-site Coulombic repulsion due to the presence of two interacting donor units.

Characteristics of the cross-cyclophane donor **1** are summarized

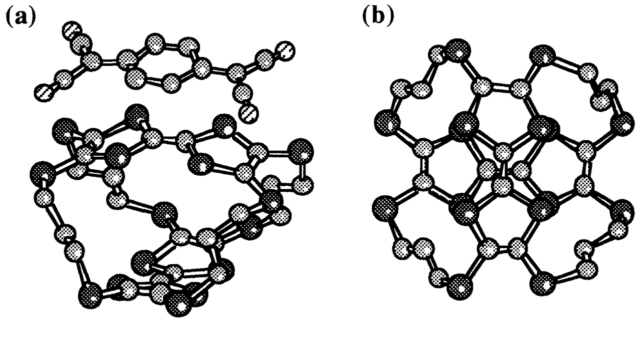


Figure 1. (a) Molecular structures of **1**·TCNQ complex.
(b) Top view of cross-cyclophane TTF **1**.

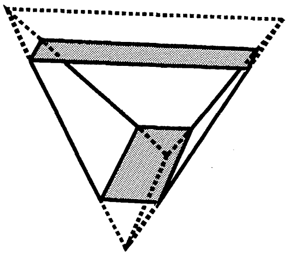


Figure 2. Hexahedral structure derived from tetrahedron by slicing two orthogonal edges.

as follows. First, although the interaction between two donor units is small in the neutral state, judged from the intramolecular S···S distances, it becomes significant during the redox processes. The result can be explained by an idea that the interplanar distance between the donor units is shortened in the oxidized states, accompanied by flattening of the $TTF^{+\bullet}$ units. Second, donor **1** has a possibility to exhibit an intermolecular interaction along the long axis of the donor unit, while such a type of interaction is lacking in BEDT-TTF. In fact, donor **1** in the CT complex with TCNQ forms an intermolecular dimer through a *face-to-face* interaction, and the dimers are arranged in an array along the *a* axis through *side-by-side* interactions. Besides, donors in the array interact along the *b* axis with those in adjacent arrays in both sides, forming a sheet structure (Figure 3).

In summary, we have prepared a novel cross-cyclophane donor **1**, which exhibits not only *face-to-face* but also two kinds of *side-by-side* intermolecular interactions. Such a type of overlap is not found in crystals of BEDT-TTF radical ion salts and can only be achieved by utilizing the artificial dimeric donor. Crystal structures and physical properties of radical ion salts of donor **1** are of great interest in this respect.

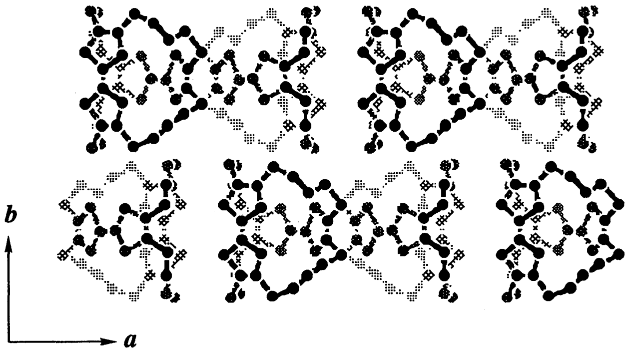


Figure 3. Sheet structure of donors **1** in the CT complex, viewed normal to the *ab* plane.

References and Notes

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4 **1:** MS m/z 824 (M^+); mp > 240 °C (decomp.); ^{1}H-NMR ($CDCl_3$, ppm) δ 2.88-2.76 (m, 16H, CH_2S), 2.24-2.16 (m, 8H, CH_2); ^{13}C-NMR ($CDCl_3$, ppm) δ 125.0, 112.9, 34.3, 32.6; UV (CH_2Cl_2), λ_{max} = 262, 314, 338, 380(sh) nm.

5 The degree of charge transfer was estimated to be only 0.05 based on the frequency shift of CN stretching in IR. Thus the complex can be regarded nearly as a neutral complex ($\sigma_{rt} = 10^{-8}$ Scm^{-1}).

6 Crystallographic data for **1**·TCNQ: formula, $C_{36}H_{28}N_4S_{16}$; fw = 1029.61; monoclinic, Space group *C* 2; a = 18.652(8), b = 20.331(5), c = 12.756(4) Å, β = 109.74(2)°; V = 4553(3) $Å^3$; Z = 4; D_{calcd} = 1.50 g cm^{-3}; radiation, Mo Kα (λ = 0.71073Å); unique obsd. data, 2967; R = 0.068.

7 When the molecular structure is observed precisely, two donor units are not equivalent: One of the donor units (bent angles 18.6 and 19.0 degree) interacts with TCNQ and the other unit (bent angle 8.9 and 30.1 degrees) interacts with a donor unit of the adjacent donor molecule.

8 Cyclic voltammogram was measured at 100 mV/sec in benzonitrile solution of 0.1 M TBAP *vs.* Ag/AgCl.