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The X-Ray Crystal Structure of a Charge-transfer Complex Derived from a Non-planar, Bulky, and Conformationally Flexible Donor Compound

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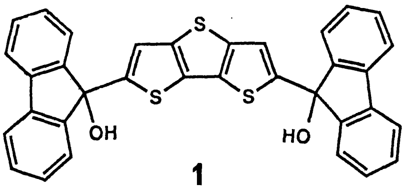
Bis(9-hydroxyfluorenyl)-substituted dithienothiophene afforded a crystalline charge-transfer complex with 2,3-dichloro-5,6-dicyanobenzoquinone. The crystal structure was revealed by an X-ray analysis to be composed of a cage-like dimeric unit of the donor molecules which are alligned in a segregated columnar stack.

One of the fundamental requirements for formation of conducting organic charge-transfer complexes is an effective overlap of the π-electron system for an efficient charge transport. Therefore, most of the component organic donor and acceptor compounds have been designed based on planar π-systems and their two-dimensional modifications. On the other hand, three-dimensional design of planar π-moieties in a donor molecule has not attracted much attention so far. The rigid cage-like molecules1) based on tetrathiafulvalene (TTF) may be regarded as such structural modifications and a compound of the extreme case in this line should be buckminsterfullerene (C_{60}). We now demonstrate that bis(9-hydroxyfluorenyl)dithieno[3,2-b:2',3'-d]thiophene (**1**) as a donor species (D) forms a crystalline charge-transfer complex, in which a cage-like dimeric unit constitutes a novel molecular arrangement of a -DD-DD-DD-DD-stacking motif in the crystal.

The molecule of **1** is comprised of a rigid backbone and bulky substituents, therefore is an excellent host compound for crystalline host-guest inclusion complexes.2) Despite this irregular structure as a donor component, **1** formed a charge-transfer complex with dichlorodicyano-



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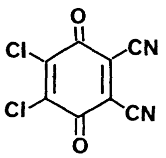

DDQ

benzoquinone (DDQ), since dithieno[3,2-b:2',3'-d]thiophene (**2**) moiety has a low ionization potential.3) When **1** was recrystallized with DDQ from dichloromethane,4) a three-component complex comprised of the 2:1:1 stoichiometry of **1**:DDQ:H_2O has been isolated as dark greenish crystals.5)

An X-ray analysis was carried out for a needle-like single crystal of the complex.6) A stereoview of the crystal packing is shown in Fig. 1. The donor (D) and acceptor (A) molecules are aligned in a -D-D-A-D-D-A- stacking column along the a axis.7) The planar dithienothiophene rings in the dimeric D_a and D_b molecules overlap with the intermolecular spacing of 3.71 Å. The overlapping pattern of the dimer is shown in Fig. 2. Molecules D_a are twisted to molecules D_b by 61.1° to avoid steric repulsion of the bulky fluorenyl substituents. Thus, the donor molecules D_a and D_b form a cage-like structure with both the dithienothiophene and the fluorenyl planes facing outside the dimeric block. The hydroxyl group of molecule D_a is connected to that of molecule D_b by the hydrogen bond (O---O; 2.87 Å).

The molecular axis of DDQ (the line O=C---C=O) is twisted to the longer molecular axis of the dithienothiophene moiety of D_a by 3.0° and to that of D_b by 58.1°, respectively. The interplanar distances between D_a---A and D_b---A is 3.25 Å and 3.41 Å, respectively (Fig. 2). Water molecules are accommodated close to D_b molecules and are connected to the OH group of D_b molecules by the hydrogen bonds (O---O: 2.75, 2.92 Å).

Even though a mixed stack is seen along the a axis, along the c axis the dimeric donor molecules are aligned in a segregated columnar stack (Fig. 3). The fluorenyl π-planes of D_b molecules form a face-to-face array along the stacking direction with the inclination from each other by 4.5°. Thus, a segregated columnar stack is realized, even in the charge-transfer complex composed of the donor molecule bearing bulky and rotational-free fluorenyl substituents.

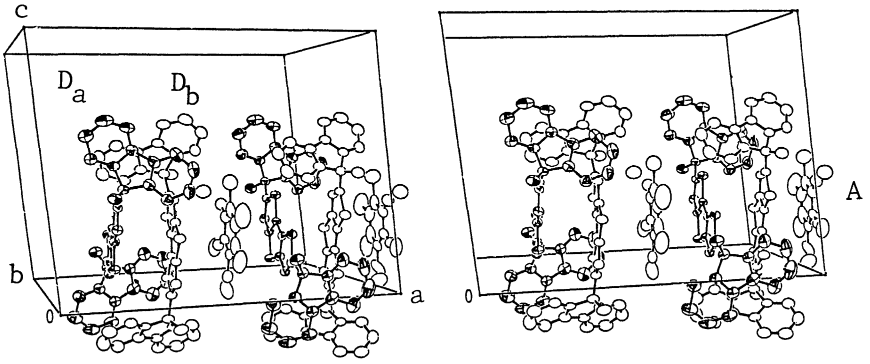

Fig. 1. Stereoview of the crystal structure of complex $(\mathbf{1})_2(DDQ)(H_2O)$ along the b axis.

There are no significant differences in the bond lengths and angles between D_a and D_b molecules. The differences in the bond length from the neutral to cationic forms of the dithieno[3,2-b:2',3'-d]thiophene moeity are observed for the inner C=C bonds; the value of 1.386 Å and 1.389 Å for D_a and D_b, respectively, in the charge-transfer complex are obviously longer than those in neutral **2** (1.374 Å)[8] and **1** (1.376 Å).[2] This is explained by considering the nodal properties of the HOMO of the skeleton[9] and suggests that the positive charge appears to be localized on the inner C=C bonds. The room temperature conductivity of a single crystal sample was low, below 10^{-6} S cm^{-1}.

This study suggests a potential importance of non-planar, bulky, and conformationally flexible molecules as a donor or acceptor component to explore new molecular solids. Even such ragged compounds could afford a segregated columnar stacking in their charge-transfer complexes.

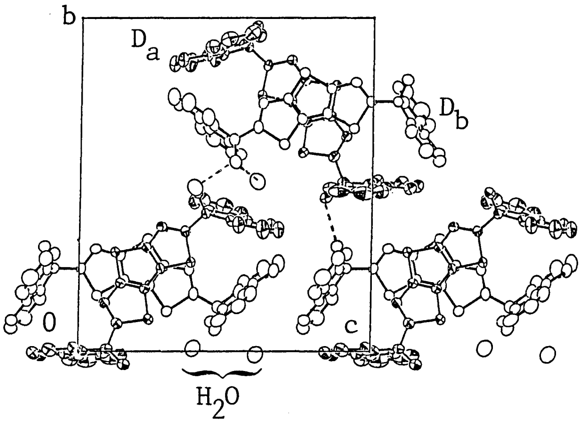

Fig. 2. Molecular overlapping of **1** molecules, D_a and D_b, viewed along the a axis. Hydrogen bonds are indicated by dotted lines.

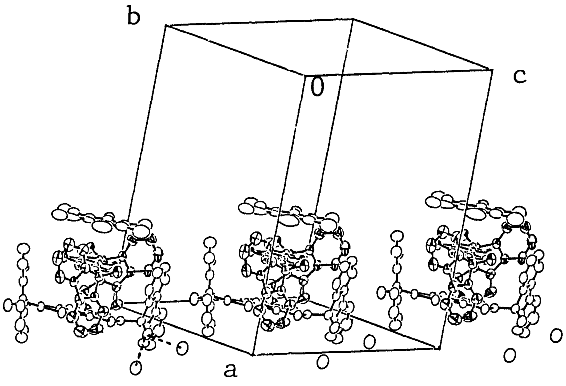

Fig. 3. Columnar stack of **1** along the c axis.

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The backbone compound, **2**, forms a charge-transfer complex with TCNQ. We have carried out an X-ray analysis for this complex and revealed a mixed columnar stack of the donor and acceptor species. Details should be published elsewhere.

4) Electronic spectra of the solution show a low-energy absorption band at 810 nm attributable to a charge-transfer transition.

5) Water is assumed to come from the solvent which was not completely dried.

6) Crystal data: $(C_{34}H_{20}O_2S_3)_2(C_8N_2O_2Cl_2)(H_2O)$, M=1358.59, space group $P2_1/a$, a=20.762(9), b=18.691(8), c=16.240(2) Å, β=95.91(3), V=6269(4) $Å^3$, Z=4, Dc=1.420 gcm^{-1}. Intensity data were collected by a Rigaku AFC-5 automatic four-circle diffractometer with monochromated Mo-K_α radiation. A total of 15379 reflections with $2\theta<55°$ were obtained, of which independent 7893 reflections with $F_o>3\sigma(F_o)$ were used for the structure determination. The structure was solved by direct methods using SHELXS 86$^{10)}$ and refined by UNICS-III$^{11)}$ program for 1007 parameters. The R and R_W factors are 8.01 and 8.00, respectively.

7) Some other -DD-A-DD-A- stacks have been reported; see, for example: K. Kobayashi, M. Takahashi, and H. Kobayashi, J. Chem. Soc., Perkin Trans. 2, **1988**, 427; F. Iwasaki, S. Hironaka, N. Yamazaki, and K. Kobayashi, Bull. Chem. Soc. Jpn., in press; K. Kobayashi, Y. Mazaki, and F. Iwasaki, Synthetic Metals, **27**, B309 (1988).

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