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Crystal Structure and FET Characteristics of an n-Type Thiophene/Phenylene Co-oligomer of 1,4-Bis{5-[4-(trifluoromethyl)phenyl]thiophen-2-yl}benzene

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The crystal structure of a thiophene/phenylene co-oligomer of 1,4-bis{5-[4-(trifluoromethyl)phenyl]thiophen-2-yl}benzene ($AC5-CF_3$) has been investigated. The crystals are monoclinic with space group $P2_1/c$. The crystals of $AC5-CF_3$ function as an n-type semiconductor. This has been confirmed on a field-effect transistor device configuration.

Various molecular semiconductors have been proposed and synthesized during the past decades. These are potentially useful for optoelectronic devices including field-effect transistors (FETs) and light-emitting diodes.[1] Most of the molecular semiconductors so far act as p-type semiconductors or have been designed to function as such. Recently however, organic synthesis has provided a variety of n-type molecular semiconductors.[2] Nonetheless, the design and synthesis of complicated molecular structures are often necessary for those materials to function as n-type semiconductors.

Having these circumstances as a background, we have recently developed new n-type materials based upon thiophene/phenylene co-oligomers (TPCOs).[3] The materials are characterized by the presence of trifluoromethyl groups on either terminal of the TPCO molecules. Of these, we focus our attention upon 1,4-bis{5-[4-(trifluoromethyl)phenyl]thiophen-2-yl}benzene ($AC5-CF_3$); see Figure 1a for its structural formula. Crystals of its parent molecule, 1,4-bis(5-phenylthiophen-2-yl)benzene (AC5),[4] function as a p-type semiconductor; their charge-transport properties are well-documented.[5,6] Thus the same TPCO backbone can evenly produce the two types of polarities with the carrier conduction according to the presence (or absence) of the trifluoromethyl groups. In the present studies we show the crystallographic structure of $AC5-CF_3$[7,8] and the initial characterization of its charge transport examined on the FET device configuration.

The crystals were made in the vapor phase following a previously published method.[6] These crystals were used for both the crystal structure analysis and transport study. Figures 1b–1d show the molecular and crystal structures of $AC5-CF_3$. The crystals are monoclinic with space group $P2_1/c$. Related structures are found for many TPCO materials[9] as well as other straight oligomers.[10] Also like other TPCO molecules, the crystals of $AC5-CF_3$ form a molecular layered structure along the molecular long axis (*a* axis in the present studies) and assume a herringbone array[9–11] that spreads parallel to the bottom crystal plane (*bc* plane). The molecular axis (defined by a straight line connecting the two carbon atoms in the CF_3 groups) crosses the normal to the bottom *bc* plane at an angle of 14.26°. It is well-established that this structure is advantageous to the FET devices.[12]

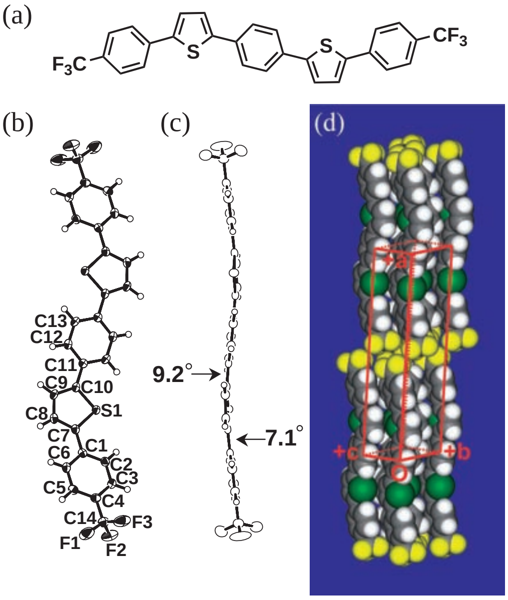

Figure 1. Molecular and crystal structures of $AC5-CF_3$. (a) Structural formula; (b) ORTEP diagrams with atomic numbering; (c) side view of the molecule; (d) crystal structure. Numerals in (c) denote dihedral angles (see text).

Table 1 summarizes and compares the lattice constants of $AC5-CF_3$ and AC5.[9d] Of the listed lattice constants, the short and medium axes determine the lateral molecular packing scheme. Resemblance in the crystal structures is evident, indicating the closely related molecular packing in these two crystals. The long axis reflects the length of the molecules that are disposed nearly vertical to the bottom crystal plane. Regarding AC5, half of the long axis represents the molecular length because $Z = 4$. For $AC5-CF_3$, $Z = 2$, reflecting the presence of the center of symmetry within a single molecule (see Supporting Information). The difference between a of $AC5-CF_3$ and $c/2$ of AC5 is 3.61 Å. This difference corresponds to two times the van der Waals radii between a CF_3 group and a hydrogen.[13]

The deviation from the symmetry of C_{2h} for $AC5-CF_3$ molecules is relatively small. The dihedral angle between the two least-squares planes of the central phenylene and adjacent thiophene is 9.2°. That between the thiophene and end phenylene is

Table 1. Comparison of lattice constants (Å) between AC5-CF_3 and AC5 crystals

Compound	Short axis[a]	Medium axis[a]	Long axis[a]
AC5-CF_3	5.7989(19) [*c*]	7.472(2) [*b*]	25.237(8) [*a*]
AC5[b]	5.7903(10) [*a*]	7.4954(13) [*b*]	43.262(7) [*c*]

[a]Numbers in parentheses denote the standard deviation; characters in angled bracket represent each axis of the crystals. [b]Ref. 9d.

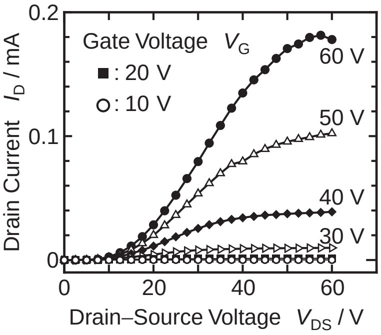

Figure 2. Device performance of an AC5-CF_3 crystal FET.

7.1° (see Figure 1c). As a result each molecule sags so that the laterally nearest-neighbor molecules can nestle one another closely against their zigzag backbones.

We made an FET by laminating the prefabricated device substrate with the crystal. The substrate comprised a silicon wafer on the SiO_2 gate dielectric (300-nm thick) of which Cr/Au source and drain electrodes were vacuum-deposited. Electrical measurements were carried out at room temperature under pressures ranging 1.0×10^{-3} to 5.3×10^{-3} Pa. Figure 2 indicates a typical device performance. It is characterized by the increasingly large drain currents noted with larger positive drain and gate voltages. This observation obviously reflects the n-type transistor feature. We estimated the *electron* mobility to be $1.6 \times 10^{-2}\,cm^2\,V^{-1}\,s^{-1}$ from the transfer characteristics,[14] even though the threshold voltage was somewhat high (≈21 V) and the convex-downward behavior[5] was noticed around the origin. We confirmed the mobilities at a similar level using another two devices; these were 1.7×10^{-2} and $3.9 \times 10^{-2}\,cm^2\,V^{-1}\,s^{-1}$. These mobilities are contrasted with the *hole* mobility of $2.1 \times 10^{-2}\,cm^2\,V^{-1}\,s^{-1}$ for crystals of parent molecules AC5 measured and recorded under air.[6] The switch of the polarities is associated with the lowering in both the LUMO and HOMO levels of AC5-CF_3 (determined at a semiempirical level[15]) by ca. 0.4 eV relative to AC5.

The crystallographic feature common to AC5-CF_3 and AC5 is summarized as that the crystals consist of the molecular layered structure with the closely related molecular packing. The herringbone structure laterally spreads over each layer (see Figure 1d) with the herringbone angles being 40.19 and 45.37° for AC5-CF_3 and AC5,[9d] respectively. Takimiya et al.[2a] showed that the same molecular backbone produces the two polarities according to presence or absence of substituent CF_3 groups. The electron mobility, however, was an order of magnitude lower than the hole mobility. It has, therefore, remained unclear whether the related molecular packing produces the two polarities at an even mobility level. In the present studies we have in fact been successful in realizing this by using the AC5-CF_3 crystals that comprise the same AC5 backbones arranged in a herringbone array.

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7 Intensity data from a Bruker SMART-CCD diffractometer (Mo Kα). Crystallographic data for AC5-CF_3; $C_{28}H_{16}F_6S_2$, MW 530.53, monoclinic, $P2_1/c$, $a = 25.237(8)$, $b = 7.472(2)$, $c = 5.7989(19)$ Å, $\beta = 94.186(6)°$, $V = 1090.6(6)$ Å^3, $Z = 2$, $D_{calcd} = 1.616\,g\,cm^{-3}$, $T = 183$ K. 5324 reflections measured, 1917 unique reflections [R(int) = 0.0652]. $R_1 = 0.0598$ [$I \geq 2.0\sigma(I)$], $wR_2 = 0.1540$ (all data), GOF = 1.039 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-717649. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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