Chemistry

Characterization and structural analysis of thieno[3,4-c]pyrrole-incorporated quinoidal terthiophene with dicyanomethylene termini

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Introduction
7,7,8,8-Tetracyanoquinodimethane (TCNQ) and its related compounds have been known as superior electron-accepting molecules and widely studied in the field of charge-transfer complexes. Owing to their low-lying LUMO energy levels, the TCNQ-type compounds have recently focused as n-channel organic semiconductors. Cyclopentene-annulated terthienuquinoidal (1), which is one of classes of the n-channel organic semiconductors, have afforded air-stable, solution-processed n-channel FETs with electron mobility of 0.16 cm²/Vs [1].

To strengthen the intermolecular interaction, we have designed a new thienoquinoidal system 2 by modifying the central fused-octylidihydropyrrole ring to form a planar structure. However, the synthetic result of 2 indicated the existence of its oxidized compound 3 with the unambiguous electronic structure [2]. Thus we characterized the structure of 3 by the X-ray analysis.

Experiment

The quinoidal compound (3) was prepared according to our report [2]. Single crystals of 3 suitable for the X-ray structural analysis were obtained by careful recrystallization from N,N-dimethylformamide (DMF).

Single crystal X-ray analysis

The crystals of 3 contain the DMF molecules as a crystal solvent, and the single crystal X-ray structural analysis was conducted at 200 K to avoid the efflorescence of the crystals. The measurement was made on a Rigaku DSC imaging plate system by using Si-monochromated synchrotron (λ = 1.0000 Å). The structure was solved by the direct method using SHELX-97 [3]. All atoms except for the hydrogen atoms were refined anisotropically, and the hydrogen atoms were calculated.

Crystallographic data for 3·DMF: C31H30N6OS3 (598.82), black needles, 0.30 x 0.05 x 0.02 mm³, triclinic, space group P-1 (#2), α = 8.1389(5), β = 11.0698(6), γ = 18.102(3) Å, α = 76.233(6), β = 78.218(8), γ = 86.925(4)º, V = 1550.6(3) Å³, Z = 2, R = 0.1043 for 3180 observed reflections (I > 2σ(I)) and 370 variable parameters, wR2 = 0.2935 for all data.

Characterization and structural analysis

The molecular structure of 3 obtained by the X-ray structural analysis is depicted in Fig. 2. The π-framework of 3 containing the thieno[3,4-c]pyrrole ring forms a planar structure. Focused on the bond lengths of the the thieno[3,4-c]pyrrole moiety, the bond length alternation is observed; the carbon–carbon bond lengths in the fused-pyrrole ring are 1.382(5) and 1.383(4) Å for C(1)–C(2) and C(3)–C(4) bands, respectively, which is rational to be attribute to the double bond character. Thus, 3 was well-characterized as the novel thienoquiloidal system with the fused-pyrrole ring. These results are consistent with the data of the ¹H- and ¹³C- NMR and MALDI-TOF mass spectra.

References