

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 terthienoquinoidal (**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-octyldihydropyrrole 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.

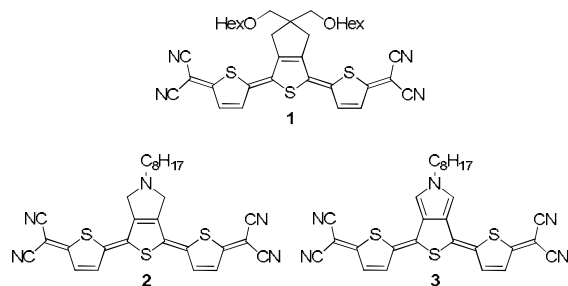


Fig. 1 Structure of thienoquinoidals (**1–3**)

Experiment

Sample Preparation

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 ($\lambda = 1.0000$ 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), $a = 8.1389(5)$, $b = 11.0698(6)$, $c = 18.102(3)$ Å, $\alpha = 76.233(6)$, $\beta = 78.218(8)$, $\gamma = 86.925(4)^\circ$, $V = 1550.6(3)$ Å³, $Z = 2$, $R = 0.1043$ for 3180 observed reflections ($I > 2\sigma(I)$) and 370 variable parameters, $wR_2 = 0.2935$ 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 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 thienoquinoidal system with the fused-pyrrole ring. These results are consistent with the data of the ¹H- and ¹³C- NMR and MALDI-TOF mass spectra.

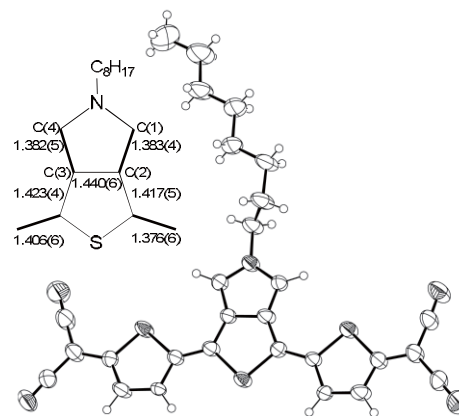


Fig. 2 ORTEP diagram of **3**. The DMF molecules are omitted for clarity. Selected bond lengths in the central thieno[3,4-*c*]pyrrole moiety are depicted in inset, where the double bond character is represented in the bold face.

References

- [1] S. Handa, et al, *J. Am. Chem. Soc.* 129, 11684 (2007).
- [2] K. Takeda, et al, *Tetrahedron Lett.* 51, 4375 (2010).
- [3] A. M. Sheldrick SHELX 97-Programs for crystal structural analysis, Göttingen, Germany, 1998.

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