Electronic Supplementary Information for

Synthesis, Packing Arrangement and Transistor Performance of Dimers of Dithienothiophenes
Lei Zhang†, Lin Tan†, Wenping Hu†, and Zhaohui Wang†

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solid, Chinese Academy of Sciences, Beijing, 100190, China and Graduate School of the Chinese Academy of Sciences, Beijing, 100190, P. R. China

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1. UV-spectra of fuse-ring dimers

![UV-spectra of fuse-ring dimers](image)

**Figure 1.** Optical absorption spectra of fused-ring dimers in solution and vacuum deposited films on quartz. a: 1, 4; b: 2.

Cyclic voltammograms (CVs) were recorded on a Zahner IM6e electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/Ag⁺ electrode as the reference electrode, and ferrocene/ferrocenium as an internal potential marker. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) dissolved in THF was employed as the
supporting electrolyte. THF was freshly distilled over LiAlH₄ prior to use.

2. CV-spectra of fuse-ring dimers

![Figure 2](image)

Figure 2. Cyclic voltammogram of fused-ring dimers. a, 1; b, 4; c, 3; d, 6.

3. DSC measurement of fuse-ring dimers

![Figure 3](image)

Figure 3. Differential scanning calorimetry (DSC) thermogram of fused-ring dimers with a scan of 10 °C/min. a, 1; b, 2; c, 4; d, 5; e, 3; f, 6.

4. TGA measurement of fuse-ring dimers
5. X-ray crystallographic analysis of compound 4

The X-ray crystal structures analysis were made on a Bruker SMART CCD diffractometer, using graphite-monochromated MoKα radiation (λ) 0.7107 Å. The data were collected at 113 K and the structures were refined by full-matrix least-square on $F^2$. The computations were performed with SHELXL-97 program. All-hydrogen atoms were refined anisotropically.

Crystallographic data for compound 4: C$_{18}$H$_8$S$_6$, M=416.6, crystal size: 0.14×0.12×0.01mm$^3$, monoclinic, space group P$_{2}1/n$, $a$= 6.1973 (12), $b$= 4.7149 (7), $c$= 27.494 (5), $α$= 90.00, $β$= 95.383, $γ$= 90.00, $V$= 799.80 (2)Å$^3$, $Z$=2, $ρ$= 1.730mg/cm$^3$, 2Θmax= 27.85. Of 6967 reflections, 1886 were unique ($R_{int}$= 0.0458). GOF= 1.104, 110 parameters, RI= 0.0419, wR$_2$= 0.0837. CCDC 680799. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.