Supplementary material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information for

Synthesis, Packing Arrangement and Transistor Performance of Dimers of Dithienothiophenes

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Contents

1. UV-spectra of fuse-ring dimers

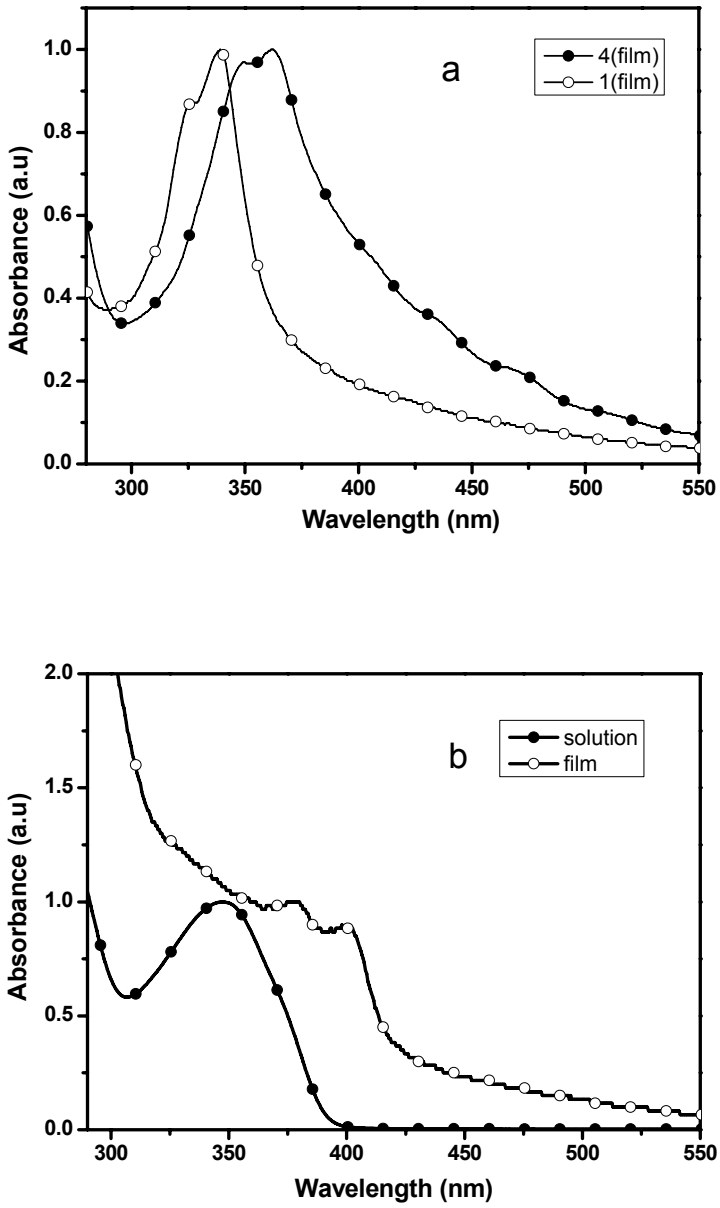

Figure 1. Optical absorption spectra of fused-ring dimers in solution and vacuum deposited films on quartz. a: **1**, **4**; b: **2**;

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 ($TBAPF_6$) dissolved in THF was employed as the

supporting electrolyte. THF was freshly distilled over $LiAlH_4$ prior to use.

2. CV-spectra of fuse-ring dimers

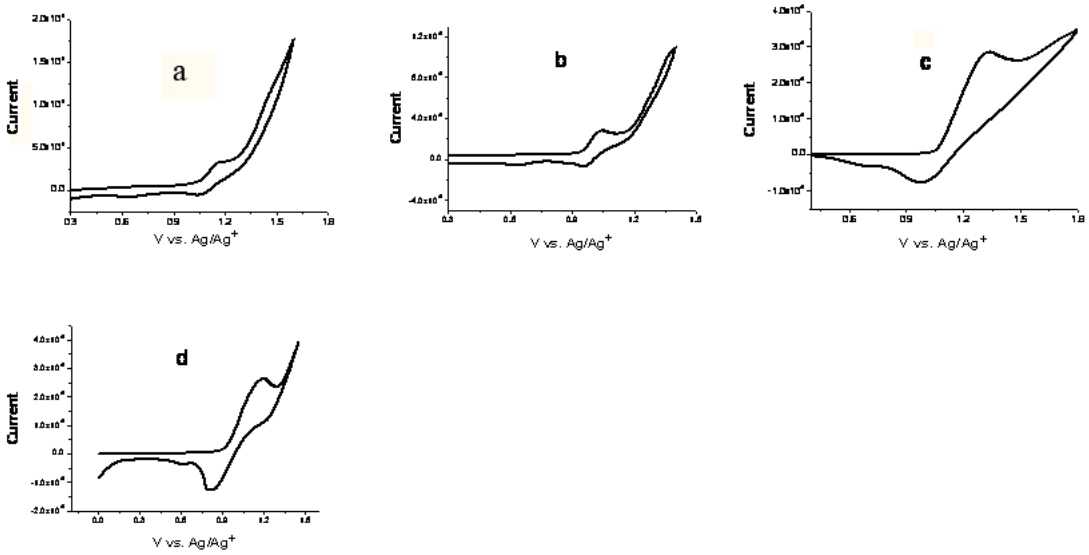

Figure 2. Cyclic voltammogram of fused-ring dimers. a, **1**; b, **4**; c, **3**; d, **6**.

3. DSC measurement of fuse-ring dimers

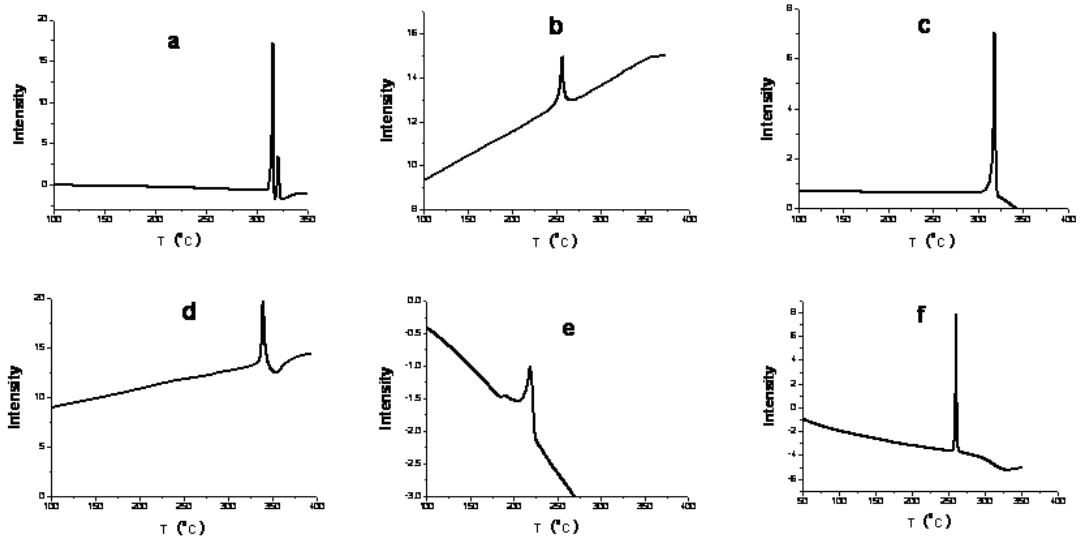

Figure 3. Differential scanning calorimetry (DSC) thermogram of fused-ring dimers with a scan of 10 °C/min. a, **1**; b, **2**; c, **4**; d, **5**; e, **3**; f, **6**.

4. TGA measurement of fuse-ring dimers

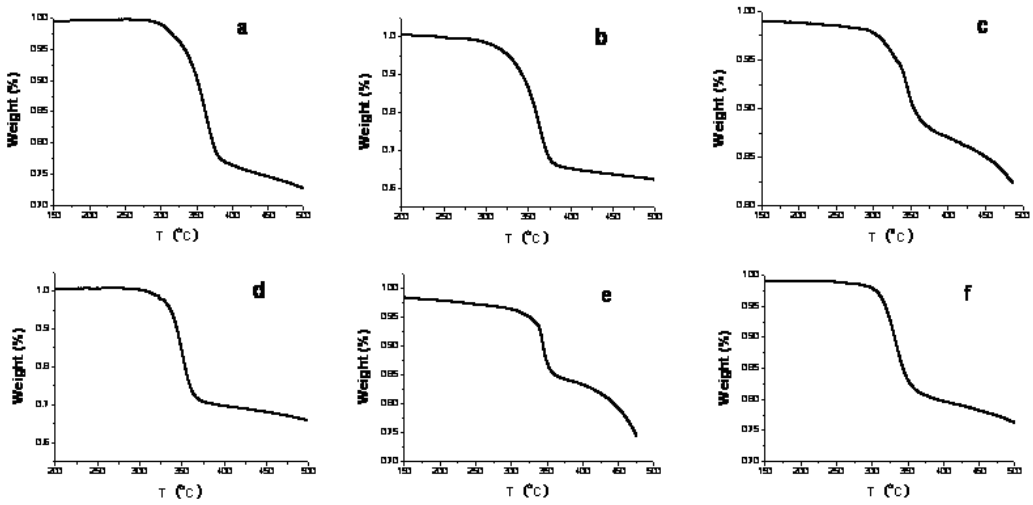

Figure 4. TGA measurements for fused-ring dimers with a scan of 10 ˚C/min under nitrogen flow. a, **1**; b, **2**; c, **5**; d, **4**; e, **3**; f, **6**.

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**: $C_{18}H_8S_6$, M=416.6, crystal size: 0.14×0.12×0.01mm^3, monoclinic, space group P_121/n_1, 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.