

*Supporting Information for*

**High-Performance, Stable Organic Field-Effect Transistors Based on**

**trans-1,2-(dithieno[2,3-*b*:3',2'-*d*]thiophene)ethene \*\***

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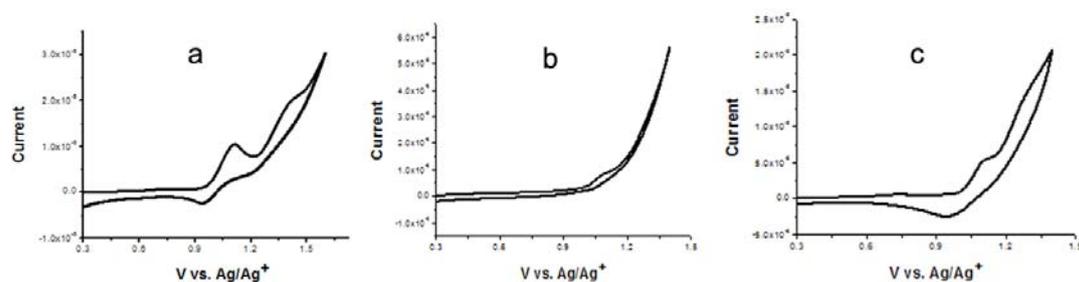
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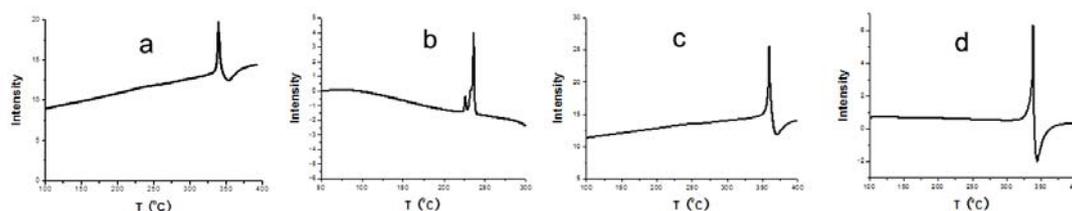
1. Characteristics of the compounds
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3. Packing model of compound **3** in the thin film on the substrate
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## 1. Characteristics of the compounds

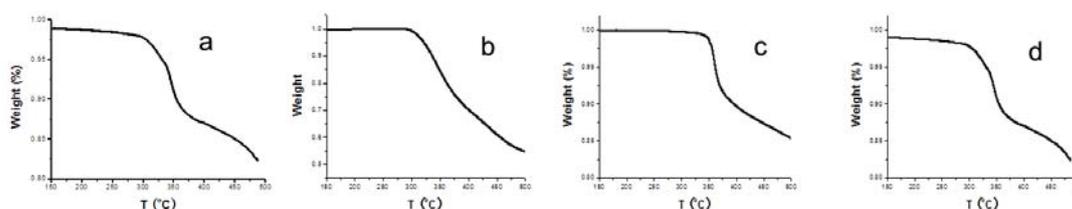
General:  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in deuterated solvent on a Bruker ADVANCE 400 NMR spectrometer and a Bruker ADVANCE 600 NMR spectrometer.  $^1\text{H}$  NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. EI-MS spectra were obtained on a Shimadzu QP-2010 spectrometer and MALDI-TOF-MS were determined on a Bruker BIFLEX III Mass spectrometer. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. THF was freshly distilled from sodium prior to use.



S1. Cyclic voltammogram of compound **2**, **3** and **4**. a, **2**; b, **3**; c, **4**.



S2. Differential scanning calorimetry (DSC) thermogram of fused-ring dimmers with a scan of  $10\text{ }^\circ\text{C}/\text{min}$ . a, **1**; b, **2**; c, **3**; d, **4**.



S3. TGA measurements for fused-ring dimmers with a scan of 10 °C/min under nitrogen flow. a, **1**; b, **2**; c, **3**; d, **4**.

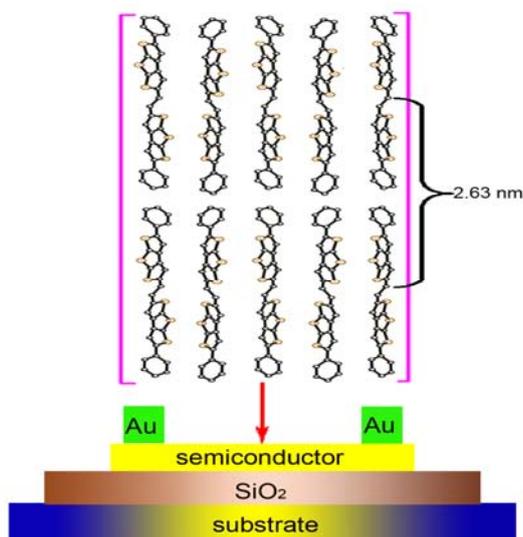
## 2. X-ray crystallographic analysis of compound **3** and **4**

The X-ray crystal structures analysis were made on a Bruker SMART CCD diffractometer, using graphite-monochromated MoK $\alpha$  radiation ( $\lambda$ ) 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 **3**: C<sub>30</sub>H<sub>16</sub>S<sub>6</sub>, M=568.79, crystal size: 0.08×0.08×0.02mm<sup>3</sup>, monoclinic, space group P2(1)/c,  $a= 26.259 (5)$ ,  $b= 7.3600 (15)$ ,  $c= 6.1739 (12)$ ,  $\alpha= 90.00$ ,  $\beta= 94.51$ ,  $\gamma= 90.00$ ,  $V= 1189.5 (4)\text{Å}^3$ ,  $Z=2$ ,  $\rho= 1.588 \text{ mg/cm}^3$ ,  $2\Theta_{\text{max}}= 25.02$ . Of 5304 reflections, 2053 were unique ( $R_{\text{int}}= 0.0964$ ). GOF= 1.019, 163 parameters,  $RI= 0.0822$ ,  $wR_2= 0.1493$ .

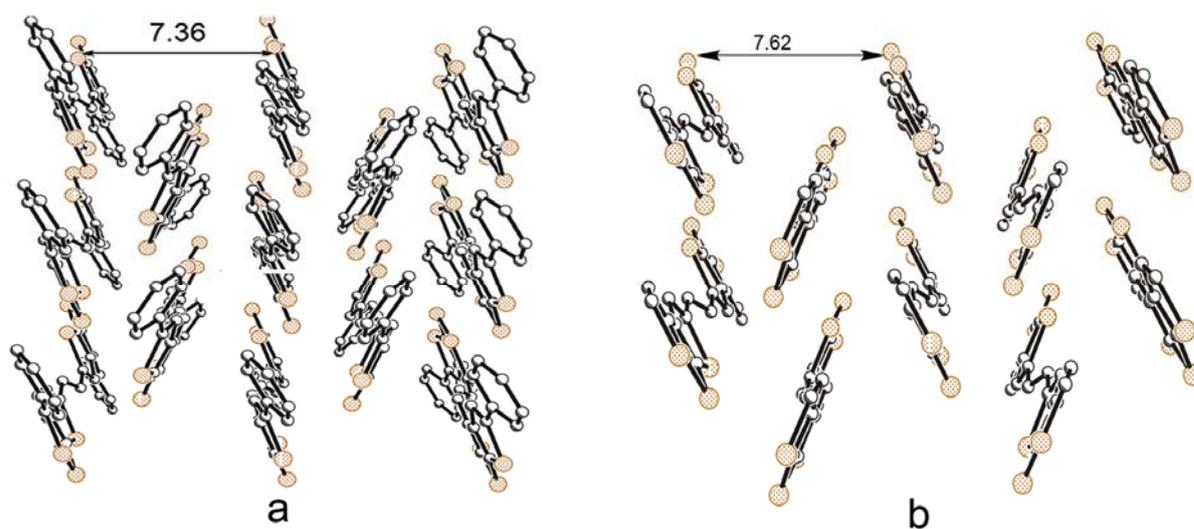
Crystallographic data for compound **4**: C<sub>26</sub>H<sub>12</sub>S<sub>8</sub>, M=580.84, crystal size: 0.14×0.02×0.02mm<sup>3</sup>, triclinic, space group P1,  $a= 6.0327 (12)$ ,  $b= 13.627 (3)$ ,  $c= 15.260 (3)$ ,  $\alpha= 107.89 (3)$ ,  $\beta= 96.87 (3)$ ,  $\gamma= 91.74 (3)$ ,  $V= 1182.2 (4)\text{Å}^3$ ,  $Z=2$ ,  $\rho= 1.632 \text{ mg/cm}^3$ ,  $2\Theta_{\text{max}}= 25.02$ . Of 6903 reflections, 2509 were unique ( $R_{\text{int}}= 0.0864$ ). GOF= 1.018, 307 parameters,  $RI= 0.0750$ ,  $wR_2= 0.1546$ .

## 3. Packing model of the compound **3** in the thin film on the substrate



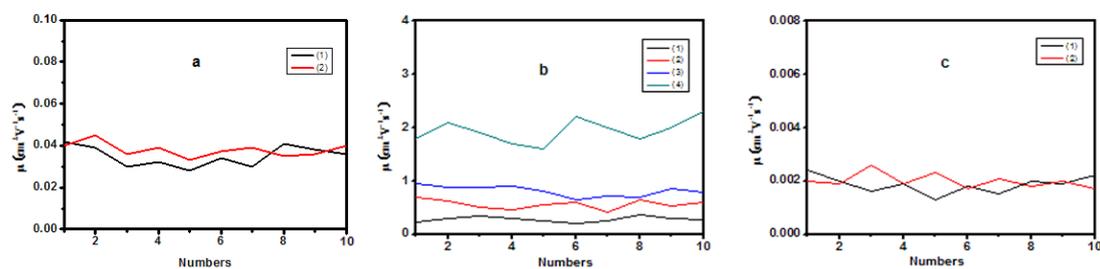
S4. Packing model of compound 3 in the thin film on the substrate.

#### 4. Packing arrangements of compound 1 and 3 along b-axis



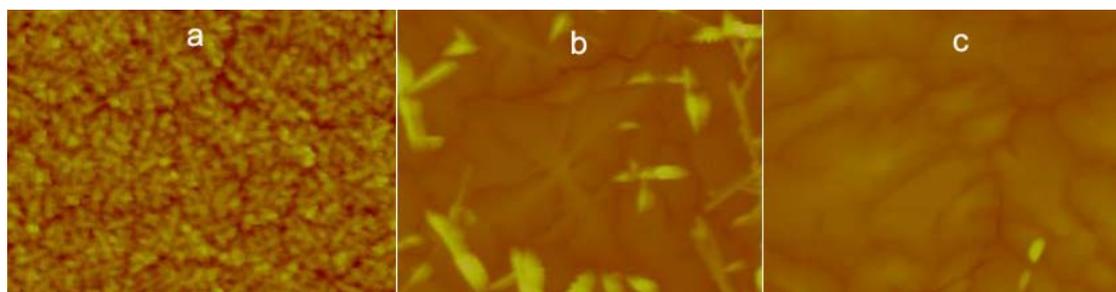
S5. Crystal Packing of the compounds. a, 3; b, 1.

#### 5. The statistical mobility of 2, 3, 4

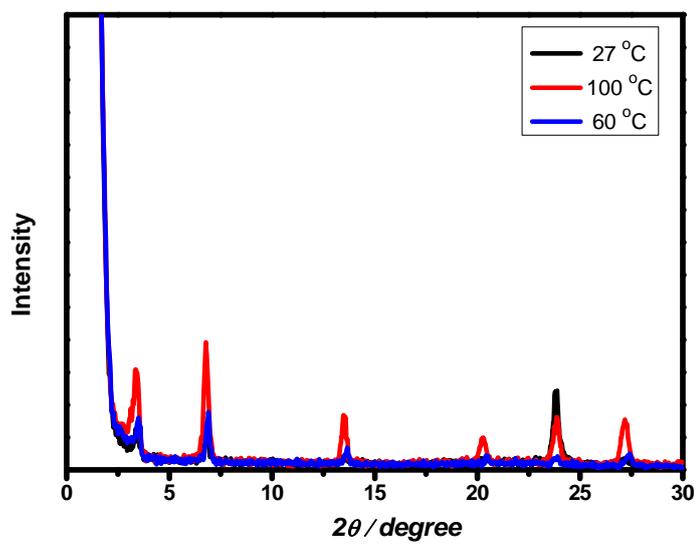


S6. The statistical mobility of the compounds at different temperatures. a, 2 (1, 27°C; 2, 100/27°C); b, 3 (1, 27°C; 2, 60°C; 3, 100°C; 4, 100/27°C); c, 4 (1, 27°C; 2, 100/27°C);

#### 5. AFM images of compound 3 at different temperatures



S7. AFM images of compound 3 at different temperatures. a, 27°C; b, 60°C; c, 100°C;



S8. XRD images of compound 3 at different temperatures. a, 27°C; b, 60°C; c, 100°C;