

## Supporting Information

### Air-stable n-channel organic field-effect transistors based on a sulfur rich $\pi$ -electron acceptor

Agathe Filatre-Furcate,<sup>a,b\*</sup> Toshiki Higashino,<sup>a</sup> Dominique Lorcy,<sup>b</sup> and Takehiko Mori<sup>a\*</sup>

#### Band integral calculations

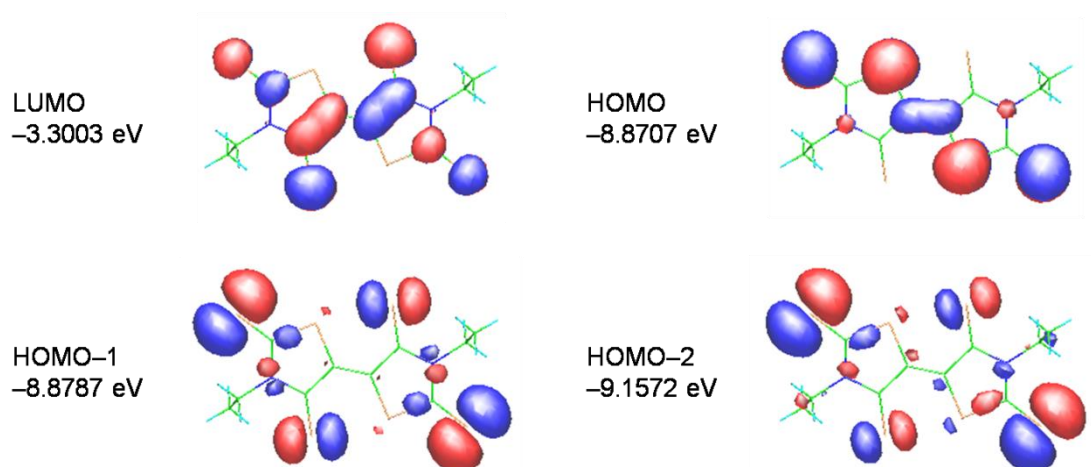
The intermolecular transfer integrals  $t_i$  are calculated on the basis of the intermolecular overlaps of HOMO and LUMO obtained from MOPAC, the AM1 molecular orbital calculation (Table S1).<sup>24</sup> As depicted in Fig. S1, the HOMO and LUMO are  $\pi$ -like, but two  $\sigma$ -like orbitals coming from the sulfur lone pairs (HOMO-1 and HOMO-2) are located very close to the HOMO level.<sup>14</sup> For the HOMO-HOMO transfers, the stacking interaction ( $a$ ) is overwhelmingly large, in agreement with the  $\pi$ -stacking structure, because the HOMO is largely populated on the ring sulfur atoms. However, the intercolumnar interactions  $b1$  and  $q$  amount to one tenth of the stacking interaction. These interactions come from the large population on the terminal thioketone atoms, and mediate the characteristic interactions along the molecular long ( $c$ ) axis. The intracolumnar LUMO-LUMO interaction  $a$  is not very large due to the cancellation of the twisted overlaps (Fig. 3c), but the intercolumnar interactions  $b1$  and  $b2$  are large because the LUMO is largely populated on the side thioketones. These interactions form the connection along the  $b$  axis. It is noteworthy that there are many short S-S distances not only along the stacking ( $a$ ) axis but also along the other two ( $b$  and  $c$ ) axes. The HOMO-1 and HOMO-2 afford many considerable intercolumnar interactions, though the intracolumnar interaction of HOMO-2 is large. Since the energy levels are very close, these levels are expected to form three-

dimensional energy bands as a whole. Accordingly, the intermolecular interactions are possible in three different directions owing to the short S-S interactions between the thioketones, as well as the  $\pi$  stacking.

**Table S1.** Transfer integrals and S-S distances.

mode	LUMO (meV)	HOMO (meV)	HOMO-1 (meV)	HOMO-2 (meV)	S-S ( $\text{\AA}$ )
<i>a</i>	-4.109	175.9	27.24	-117.1	<sup>a</sup>
<i>b1</i>	-18.48	1.794	-7.034	11.08	3.841
<i>b2</i>	-74.46	1.704	-44.09	14.23	3.451
<i>c1</i>	8.825	-22.29	39.28	-48.31	3.341
<i>c2</i>	0.2785	-1.439	-0.6403	-2.157	4.683
<i>p</i>	-12.02	-0.08579	-10.11	-9.662	3.452
<i>q</i>	-8.628	22.83	-2.673	0.9613	4.159

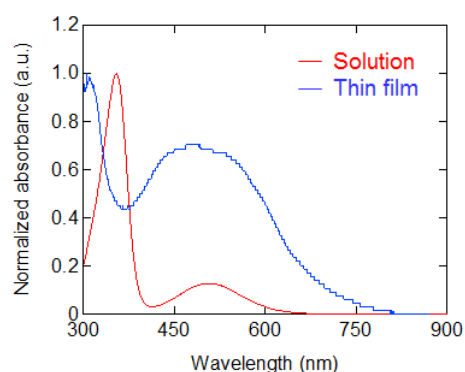
<sup>a</sup> Designated in Fig. 3c.



**Figure S1.** Molecular orbitals obtained from MOPAC, the AM1 molecular orbital calculation.

## Optical properties

UV/vis spectra of a  $10^{-5}$  M chloroform solution and a 20 nm thin film deposited on a glass substrate were collected on a SHIMADZU UV-1800 UV-VIS spectrometer (Fig. S2). The considerable change in the thin film demonstrates strong intermolecular interaction in the solid, related to the intermolecular sulfur-sulfur contacts.

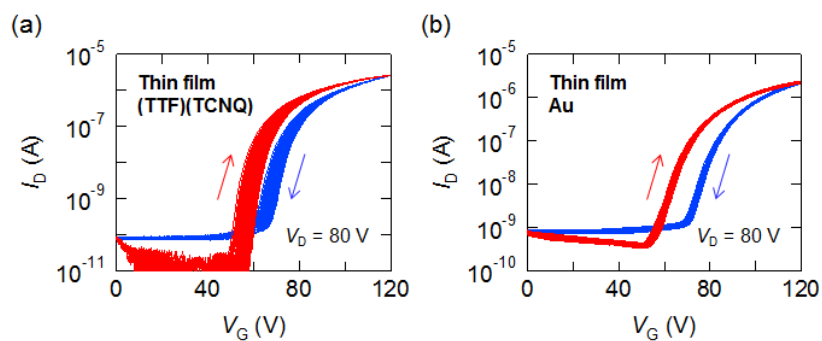


**Figure S2.** UV/vis spectra of DEBTTT measured for a solution (red) and a thin film (blue).

## Device fabrication

The sulfur electron rich acceptor was purified by sublimation under a vacuum of  $10^{-4}$  Pa at about  $140^{\circ}\text{C}$ . Transistors were fabricated onto n-doped Si substrates with a thermally grown  $\text{SiO}_2$  dielectric layer (300 nm,  $C = 11.5 \text{ nF/cm}^2$ ). For the thin-film device, the passivation layer tetratetracontane ( $\text{C}_{44}\text{H}_{90}$ , TTC,  $\epsilon = 2.5$ ) was evaporated under a vacuum of  $10^{-3}$  Pa on the substrates with a thickness of 20 nm,<sup>20</sup> where the resulting overall capacitance of the gate dielectrics was  $10.4 \text{ nF/cm}^2$ .<sup>S1</sup> The organic semiconductor with a thickness of 50 nm was vacuum evaporated. The top-contact electrodes were patterned by thermal deposition of Au (50 nm) and (TTF)(TCNQ) charge-transfer salt (220 nm) using a shadow mask; the channel length ( $L$ ) and width ( $W$ ) were 100  $\mu\text{m}$  and 1000  $\mu\text{m}$ , respectively. The temperature of the alumina crucible is  $130^{\circ}\text{C}$  for (TTF)(TCNQ), which is prepared by mixing in hot acetonitrile

solutions of the component molecules.<sup>8,9</sup> For the single-crystal device, the polystyrene (PS,  $\epsilon = 2.5$ , 100 nm) layer was deposited by spin coating (3000 rpm, and 30 sec) from a solution of PS (20 mg) in toluene (1 mL) on the silicon surface,<sup>S2</sup> where the resulting overall capacitance was 7.6 nF/cm<sup>2</sup>. Needle-like black crystals recrystallized from DEBTTT/chlorobenzene solution were fixed on the PS layer using EtOH. Carbon paste (DOTITE, XC-12) was deposited at both ends of the single crystals as source-drain electrodes. The transistor characteristics were measured under the vacuum of 10<sup>-4</sup> Pa and ambient conditions just after the fabrication, by using a Keithley 4200 semiconductor parameter analyzer, and the mobility was evaluated from the transconductance in the saturated region. The transistor characteristics were measured after ten weeks for the thin film and six weeks for the single crystal under vacuum and after additional four weeks under ambient conditions. After that, one hundred cycles of bias-stress test in air was carried out as shown in Fig. 5c and S3.



**Figure S3.** One-hundred cycles of transfer curves in the thin-film devices with (a) (TTF)(TCNQ) and (b) Au electrodes.

### Thin film properties

X-ray diffraction patterns of thin films of DEBTTT (50 nm) deposited on TTC (20 nm)|SiO<sub>2</sub> substrates were obtained by a Phillips X'Pert-Pro-MRD with a

monochromated CuK $\alpha$  radiation ( $\lambda = 1.541838 \text{ \AA}$ ) in air. AFM images of thin films of DEBTTT on TTC (20 nm)|SiO<sub>2</sub> were taken by an SII scanning probe microscope system SPI3800 and SPA-300 by using an Si<sub>3</sub>N<sub>4</sub> cantilever in air.

## References

- [S1] K.-J. Baeg, Y.-Y. Noh, J. Ghim, B. Lim and D.-Y. Kim, *Adv. Funct. Mater.*, 2008, **18**, 3678.
- [S2] M.-H. Yoon, H. Yan, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2005, **127**, 10388.