

## Supporting Information

### High ON/OFF Ratio Single Crystal Transistors based on Ultrathin Thienoacene Microplates

Xiaoli Zhao,<sup>a</sup> Tengfei Pei,<sup>a</sup> Bin Cai,<sup>a</sup> Shujun Zhou,<sup>a</sup> Qingxin Tang,<sup>\*a</sup> Yanhong Tong,<sup>\*a</sup> Hongkun Tian,<sup>\*b</sup> Yanhou Geng<sup>b</sup> and Yichun Liu<sup>a</sup>

<sup>a</sup> Key Laboratory of UV Light Emitting Materials and Technology under Ministry of Education, Northeast Normal University, Changchun 130024, P. R. China

<sup>b</sup> State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

E-mail: tangqx@nenu.edu.cn; tongyh@nenu.edu.cn; hktian@ciac.ac.cn

#### **1. The highly ordered structure and the absence of grain boundary defects in organic single crystals are favorable for high mobility, while dramatically improve the off-state current and hence lower the ON/OFF ratio.**

The ON/OFF ratio is related to on-state current and off-state current. The current is related to the defect number. In comparison with organic single crystal, a lot of defects and boundary are present in organic thin film, which can capture the carriers, resulting in the decrease of current. When the device work in a high current (on-state current), the movable carrier number is large so that the captured carriers is negligible. Therefore, defects have the weak effect on the on-state current. However, when the device is on the off state, the movable carrier number is small. The number of those trapped carriers by the defects is not negligible compared with the total carrier number in the off state. The defects affect the off-state current much more dramatically than the on-state current. Therefore, we address “The highly ordered structure and the absence of grain boundary defects in organic single crystals are favorable for high mobility, while dramatically improve the off-state current and hence lower the organic single crystals will ON/OFF ratio.” On the other hand, previous publications have experimentally shown that the organic single crystal devices generally yield the lower ON/OFF ratio than their film counterparts, for example,  $10^4$  vs  $10^6$  for R-6T,  $10^4$  vs  $10^5$  for CuPc, and  $10^6$  vs  $10^8$  for pentacene in single crystal and thin film transistors, respectively.<sup>18</sup>

#### **2. The linear current-voltage characteristics at low source-drain bias (Figure. 4d) is consistent with a relatively low Schottky barrier to hole injection and thus low contact resistance,<sup>3b</sup> which possibly related to which possibly related to the ultrathin dimension of the crystal and the “gold film stamping” electrode fabrication technique.**

When the Ph5T2 semiconductor contact with the Au electrodes, the low HOMO energy level will result in a barrier for hole injection. However, the injection barrier is not only determined by the mismatching of the work function of the electrode and the HOMO energy level. In our experiments, the linear output characteristics in the onset of the curves suggests a relatively low hole injection barrier. We believe that the low Schottky hole injection barrier could be

ascribed to: i) The ultrathin single crystal dimension. For the top-contact devices, the source-drain current  $I_{SD}$  need cross the thickness of organic semiconductor for two times, which increases the parasitic resistance and limits the carrier injection and transport.<sup>41</sup> In our experiments, those ultrathin microplates were used as the semiconductor layer, which decreases parasitic resistance and improves carrier injection efficiency. ii) The electrode stamping technology. The conventional electrodes fabrication technique is to deposit the metal on the semiconductor for top-contact devices. Inevitably, the thermal irradiation damages the semiconductor surface and possibly increases the carrier injection barrier. In our experiments, all Ph5T2 single crystal FETs were fabricated by the “gold film stamping” technology.<sup>42</sup> Small pieces of Au film were peeled off from the silicon substrate and transferred onto microplates as the source/drain electrodes. The small pieces of Au film formed good contact with the microplate by van der Waals force. The contact between electrodes and semiconductor is the physical contact without the thermal-radiation damage. The smooth surface of the ultrathin microplate (Figure 2b<sub>4</sub>) and Au film ensure the intimate contact between the single crystal and electrodes, which effectively improves carrier injection. Therefore, the output curves in Figure. 4d, 5d and S1b look perfect.

**Table S1.** A detailed performance list for the reported organic single crystal field-effect transistors.

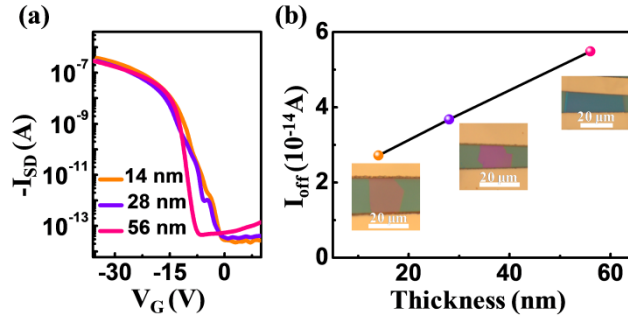
Semiconductor	ON/OFF <sup>a</sup>	$V_G$ (V) <sup>b</sup>	$\mu$ ( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ ) <sup>c</sup>	$V_T$ (V) <sup>d</sup>	Condition	Ref.
perylene	10-10 <sup>2</sup>	-100-0	9.62×10 <sup>-4</sup>	-20	—	[1]
rubrene	10 <sup>2</sup>	-20-10	1.12	-0.3	—	[2]
DPh-21DNTT	10 <sup>2</sup>	—	8.7×10 <sup>-2</sup>	-3	—	[3]
DPh-21DNTT	10	—	6.1×10 <sup>-2</sup>	20	—	[3]
2TBPZ	10 <sup>3</sup>	-120-20	0.36	—	—	[4]
PBBTZ2	7×10 <sup>3</sup>	-60-20	0.014	-1.9	air	[5]
tetracene	10 <sup>3</sup>	-3-1	6×10 <sup>-5</sup>	-1.6	vacuum	[6]
1,2-DNTT	10 <sup>3</sup>	—	2.4	-33	air	[7]
perylene	10 <sup>4</sup>	-160-0	0.12-0.25	—	air	[8]
TTPZn	>10 <sup>4</sup>	-140-0	0.32	—	air	[9]
6T	10 <sup>4</sup>	-100-30	0.075	6.4	air	[10]
TMPC	10 <sup>4</sup>	-100-20	1	-3	—	[11]
rubrene	>10 <sup>4</sup>	-110-0	0.1-1	0	air	[12]
H2TPOPP	10 <sup>4</sup>	-50-0	1.8×10 <sup>-3</sup>	-14.5	air	[13]
CuPc	10 <sup>4</sup>	-40-2	1	-6	air	[14]
BP2T	10 <sup>4</sup>	-30-15	0.66	-3.9	—	[15]
CuPc	10 <sup>4</sup>	-30-0	0.19-0.36	—	—	[16]
rubrene	10 <sup>4</sup>	-15-20	15-30	15	air	[17]
F <sub>16</sub> CuPc	6×10 <sup>4</sup>	-15-10	0.2	-5.5	air	[18]
Rubrene	10 <sup>4</sup>	-1-4	—	1	—	[19]
2,1-DNTT	10 <sup>4</sup>	—	0.8	-8	air	[7]
C8-DPNDF	10 <sup>4</sup> -10 <sup>5</sup>	-150-50	1.5-3.6	-100	—	[20]
DPNDF	10 <sup>5</sup>	-100-100	1.3	-10	—	[20]
ICZ	10 <sup>5</sup>	-150-0	0.52	—	air	[21]
DTT-12	10 <sup>5</sup>	-80-0	1.8	—	—	[22]
C12-BBICZ	10 <sup>5</sup>	-50-10	1.5	-4.7	air	[23]
PBBTZ3	9×10 <sup>5</sup>	-30-10	0.4	-6.3	air	[24]
BPEA	10 <sup>5</sup>	-25-2.5	0.03-0.73	—	air	[25]
THF	2×10 <sup>5</sup>	-20-10	2.1	-7	air	[24]
DT-TTF	7×10 <sup>5</sup>	—	1.4	0.4	air	[26]
DCT	10 <sup>5</sup>	—	1.6	—	—	[27]
rubrene	10 <sup>6</sup>	0-200	15	0	vacuum	[28]
2TBPH	10 <sup>6</sup>	-120-20	0.12	—	—	[4]
rubrene	10 <sup>6</sup>	-100-20	4.6	-2.1	—	[29]
PBBTZ1	1.9×10 <sup>6</sup>	-60-30	3.6	6.7	air	[5]
pentacene	5×10 <sup>6</sup>	-50-30	0.3	5	vacuum	[30]
BNEA	10 <sup>6</sup>	-25-10	0.01-0.52	—	air	[25]
rubrene	10 <sup>6</sup>	-4-0	2×10 <sup>-3</sup>	-0.4	vacuum	[6]
rubrene	10 <sup>7</sup>	-60-90	0.6	—	—	[31]
DBTDT	10 <sup>7</sup>	-80-0	0.6-1.8	-30	air	[32]
DTT-8	10 <sup>7</sup>	-80-0	10.2	-20	air	[22]
rubrene	10 <sup>7</sup>	-55-0	1.7	-12-1	argon	[33]
tetracene	2×10 <sup>7</sup>	-50-0	0.15	-10	vacuum	[34]
Anthradithiophe	10 <sup>7</sup>	-40-20	1	—	—	[35]
C8-BTBT	10 <sup>7</sup>	-40-5	5.2	-18.9	air / vacuum	[36]
rubrene	10 <sup>5</sup> -10 <sup>8</sup>	-70-20	19	-5-5	air	[37]
tetracene	10 <sup>5</sup> -10 <sup>8</sup>	-100-10	2.4	-40-10	air	[37]
DNTT	>10 <sup>8</sup>	-50-10	8.3	0	air	[38]
diF-TESADT	1×10 <sup>8</sup>	-40-20	6	2	nitrogen	[39]
tetracene	>10 <sup>9</sup>	-100-50	0.1	—	—	[40]

<sup>a</sup> ON/OFF ratio; <sup>b</sup> sweep range of gate voltage; <sup>c</sup> carrier mobility; <sup>d</sup> threshold voltage

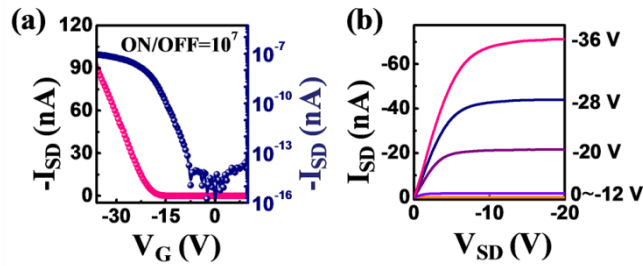
**Table S2.** A detailed performance list for Ph5T2 single crystal field-effect transistors with different thicknesses.

Thickness (nm)	ON Current (A) <sup>a</sup>	OFF Current (A) <sup>b</sup>	ON/OFF	$V_T$ (V)	$\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
14	$-3.808781 \times 10^{-7}$	$-2.71883 \times 10^{-14}$	$1.4 \times 10^7$	-11	0.204
28	$-2.869523 \times 10^{-7}$	$-3.67726 \times 10^{-14}$	$7.8 \times 10^6$	-12	0.088
56	$-2.465333 \times 10^{-7}$	$-5.48801 \times 10^{-14}$	$4.5 \times 10^6$	-10	0.029

<sup>a</sup> on-state current; <sup>b</sup> off-state current



**Fig. S1** (a) Semi-log plots of the drain current  $I_{SD}$  vs. gate voltage  $V_G$  for Ph5T2 transistors with different thicknesses. (b) Thickness dependence of the off-state current of the Ph5T2 transistors. The insets are the optical images of the devices with different crystal colors.



**Fig. S2** (a, b) Transfer and output characteristics of Ph5T2 transistor based on an individual single crystal microplate on the Si/SiO<sub>2</sub> substrate measured at  $V_{SD} = -5$  V in air at room temperature. A maximum carrier mobility of up to 0.15 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> can be obtained on Si/SiO<sub>2</sub> substrate. The threshold voltage and ON/OFF ratio is -20 V and 10<sup>7</sup>, respectively.

- [1] J. W. Lee, H. S. Kang, M. K. Kim, K. Kim, M. Y. Cho, Y. W. Kwon, J. Joo, J. I. Kim and C. S. Hong, *J. Appl. Phys.*, 2007, **102**, 124104.
- [2] K. Kim, M. K. Kim, H. S. Kang, M. Y. Cho, J. Joo, J. H. Kim, K. H. Kim, C. S. Hong and D. H. Choi, *Synth. Met.*, 2007, **157**, 481.
- [3] Y. Kunugi, T. Arakawa, M. Tsutsui and K. Okamoto, *J. Photopolym. Sci. Technol.*, 2012, **25**, 285.
- [4] M. H. Hoang, D. H. Choi and S. J. Lee, *Synth. Met.*, 2012, **162**, 419.
- [5] Z. Wei, W. Hong, H. Geng, C. Wang, Y. Liu, R. Li, W. Xu, Z. Shuai, W. Hu and Q. Wang, D. Zhu, *Adv. Mater.*, 2010, **22**, 2458.
- [6] M. J. Panzer and C. D. Frisbie, *Appl. Phys. Lett.*, 2006, **88**, 203504.
- [7] Y. Kunugi, T. Arai, M. Tsutsui, H. Maeda and K. Okamoto, *J. Photopolym. Sci. Technol.*, 2010, **23**, 323.
- [8] H. Jiang, K. K. Zhang, J. Ye, F. Wei, P. Hu, J. Guo, C. Liang, X. Chen, Y. Zhao, L. E. McNeil, W. Hu and C. Kloc, *small*, 2013, **9**, 990.
- [9] M. H. Hoang, Y. Kim, S.-J. Kim, D. H. Choi and S. J. Lee, *Chem. Eur. J.*, 2011, **17**, 7772.
- [10] G. Horowitz, F. Garnier, A. Yassar, R. Hajlaoui and F. Kouki, *Adv. Mater.*, 1996, **8**, 52.
- [11] A. L. Briseno, R. J. Tseng, S. Li, C. Chu, Y. Yang, E. H. L. Falcao, F. Wudl, M. Ling, H. Z. Chen, Z. Bao, H. Meng and C. Kloc, *Appl. Phys. Lett.*, 2006, **89**, 222111.
- [12] V. Podzorov, V. M. Pudalov and M. E. Gershenson, *Appl. Phys. Lett.*, 2003, **82**, 1739.
- [13] P. Ma, Y. Chen, X. Cai, H. Wang, Y. Zhang, Y. Gao and J. Jiang, *Synth. Met.*, 2010, **160**, 510.
- [14] R. Zeis, T. Siegrist and C. Kloc, *Appl. Phys. Lett.*, 2005, **86**, 22103.
- [15] M. Ichikawa, H. Yanagi, Y. Shimizu, S. Hotta, N. Suganuma, T. Koyama and Y. Taniguchi, *Adv. Mater.*, 2002, **14**, 1272.
- [16] W. Liu, B. L. Jackson, J. Zhu, C.-Q. Miao, C.-H. Chung, Y. J. Park, K. Sun, J. Woo and Y.-H. Xie, *Acs Nano*, 2010, **4**, 3927.

- [17] M. Uno, Y. Tominari and J. Takeya, *Org. Electron.*, 2008, **9**, 753.
- [18] Q. X. Tang, H. X. Li, Y. L. Liu and W. P. Hu, *J. Am. Chem. Soc.*, 2006, **128**, 14634.
- [19] D. Braga, M. Campione, A. Borghesi and G. Horowitz, *Adv. Mater.*, 2010, **22**, 424.
- [20] C. Mitsui, J. Soeda, K. Miwa, H. Tsuji, J. Takeya and E. Nakamura, *J. Am. Chem. Soc.*, 2012, **134**, 5448.
- [21] H. Jiang, H. Zhao, K. K. Zhang, X. Chen, C. Kloc and W. Hu, *Adv. Mater.*, 2011, **23**, 5075.
- [22] Y. S. Yang, T. Yasuda, H. Kakizoe, H. Mieno, H. Kino, Y. Tateyama and C. Adachi, *Chem. Commun.*, 2013, **49**, 6483.
- [23] K. S. Park, S. M. Salunkhe, I. Lim, C.-G. Cho, S.-H. Han and M. M. Sung, *Adv. Mater.*, 2013, **25**, 3351.
- [24] Y. Zhou, T. Lei, L. Wang, J. Pei, Y. Cao and J. Wang, *Adv. Mater.*, 2010, **22**, 1484.
- [25] C. Wang, Y. Liu, Z. Ji, E. Wang, R. Li, H. Jiang, Q. Tang and H. Li, W. Hu, *Chem. Mater.*, 2009, **21**, 2840.
- [26] M. Mas-Torrent, M. Durkut, P. Hadley, X. Ribas and C. Rovira, *J. Am. Chem. Soc.*, 2004, **126**, 984.
- [27] H. Moon, R. Zeis, E. Borkent, C. Besnard, A. J. Lovinger, T. Siegrist, C. Kloc and Z. Bao, *J. Am. Chem. Soc.*, 2004, **126**, 15322.
- [28] T. Takahashi, T. Takenobu, J. Takeya and Y. Iwasa, *Appl. Phys. Lett.*, 2006, **88**, 033505.
- [29] A. L. Briseno, R. J. Tseng, M. M. Ling, E. H. L. Falcao, Y. Yang, F. Wudl and Z. Bao, *Adv. Mater.*, 2006, **18**, 2320.
- [30] V. Y. Butko, X. Chi, D. V. Lang and A. P. Ramirez, *Appl. Phys. Lett.*, 2003, **83**, 4773.
- [31] A. L. Briseno, S. C. B. Mannsfeld, M. M. Ling, S. Liu, R. J. Tseng, C. Reese, M. E. Roberts, Y. Yang, F. Wudl and Z. Bao, *Nature*, 2006, **444**, 913.
- [32] R. Li, L. Jiang, Q. Meng, J. Gao, H. Li, Q. Tang, M. He, W. Hu, Y. Liu and D. Zhu, *Adv. Mater.*, 2009, **21**, 4492.

- [33] C. Goldmann, S. Haas, C. Krellner, K. P. Pernstich, D. J. Gundlach and B. Batlogg, *J. Appl. Phys.*, 2004, **96**, 2080.
- [34] V. Y. Butko, X. Chi and A. P. Ramirez, *Solid State Comm.*, 2003, **128**, 431.
- [35] M. M. Payne, S. R. Parkin, J. E. Anthony, C. Kuo and T. N. Jackson, *J. Am. Chem. Soc.*, 2005, **127**, 4986.
- [36] C. Liu, T. Minari, X. Lu, A. Kumatani, K. Takimiya and K. Tsukagoshi, *Adv. Mater.*, 2011, **23**, 523.
- [37] C. Reese, W.-J. Chung, M.-M. Ling, M. Roberts and Z. Bao, *Appl. Phys. Lett.*, 2006, **89**, 202108.
- [38] S. Haas, Y. Takahashi, K. Takimiya and T. Hasegawa, *Appl. Phys. Lett.*, 2009, **95**, 022111.
- [39] O. D. Jurchescu, S. Subramanian, R. J. Kline, S. D. Hudson, J. E. Anthony, T. N. Jackson and D. J. Gundlach, *Chem. Mater.*, 2008, **20**, 6733.
- [40] C. R. Newman, R. J. Chesterfield, J. A. Merlo and C. D. Frisbie, *Appl. Phys. Lett.*, 2004, **85**, 422.
- [41] Y. Zhang, H. Dong, Q. Tang, Y. He and W. Hu, *J. Mater. Chem.* 2010, **20**, 7029.
- [42] Q. Tang, Y. Tong, H. Li, Z. Ji, L. Li, W. Hu, Y. Liu and D. Zhu, *Adv. Mater.* 2008, **20**, 1511.