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# **Supporting Information**

# Single-Crystal Field-Effect Transistors based on a Fused-Ring Electron Acceptor with High Ambipolar Mobilities

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#### 1. Materials and measurements

Fused-ring electron acceptor Y6 used in this work was purchased from Solarmer Inc. Beijing. UV-vis absorption spectra were measured with Hitachi (Model U-3010) UVvis spectrophotometer in a 1 cm quartz cell. Single crystals data collections were performed at the SSRF BL17U beamline, using graphite-monochromated Mo K $\alpha$ radiation (0.71073 Å). Using Olex2, these structures were solved with the ShelXS and refined with the ShelXL-97 refinement package using Least Squares minimization.

The microscope images of all the aligned microcrystal arrays were acquired by an optical microscope (Vision Engineering Co., UK), which was coupled to a CCD camera. Atomic force microscopy (AFM) measurements were carried out with a Nanoscope IIIa instrument (Digital Instruments). X-ray diffraction (XRD) was measured on a D/max2500 with a CuK $\alpha$  source ( $\kappa = 1.541$  Å). TEM observation was carried out with a JEOL 1011 JEM-2100F microscope operated at 200 kV.

#### 2. Single-crystal X-ray diffraction analysis.

The single-crystal X-ray diffraction data for **Y6** were collected at 173 K on a Bruker SMART CCD area detector with graphite monochromated MoK/ $\alpha$  radiation ( $\lambda = 0.71073$  Å). All calculations were performed using the SHELXL and the CrystalStructure crystallographic software package.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1975854. The single crystal Xray crystallographic data were summarized in **Table S1**.

compound	Y6
Empirical formula	$C_{82}H_{86}N_8O_2S_5$
Formula weight	1451.94
Temperature (K)	293(2) K
Wavelength (Å)	0.71073
Crystal system	Triclinic

Table S1. Crystallographic data of fused-ring electron acceptor *rac*-Y6.

Space group	P-1
a (Å)	14.4691(4)
b (Å)	21.1859(7)
<b>c</b> (Å)	30.8424(10)
α (°)	109.352(3)
β (°)	96.264(2)
γ (°)	98.409(2)
Volume (Å <sup>3</sup> )	8697.7(5)
Density (mg/m <sup>3</sup> )	0.745
Crystal size (mm <sup>3</sup> )	$0.20\times0.17\times0.12$
No. of formula units per unit cell	4
Absorption coefficient (mm <sup>-1</sup> )	1.525
F(000)	1976
Theta range for data collection (°)	2.253 to 66.500
Limiting indices	-17<=h<=16, -24<=k<=25, -36<=l<=35
<b>Reflections collected</b>	70956
Independent reflections	13237
R (int)	0.1139
Goodness-of-fit on F <sup>2</sup>	1.049
Final R [I>2sigma(I)]	R1 = 0.1117, wR2 = 0.2909
R indices (all data)	R1 = 0.1410, wR2 = 0.3136



**Figure S1**. (a) The deformed configuration of **Y6** single crystal. (b) Intramolecular S····O=C interactions (green) in **Y6** single crystal. (c) The existence of M-isomer and P-isomer in **Y6** single crystal (green for M-isomer and purple for P-isomer). (d) Different types of intermolecular  $\pi$ - $\pi$  stacking interactions between adjacent **Y6** molecules (blue for IC···IC, yellow for DTT-BT···DTT-BT and green for IC···DTT-BT).



#### 3. Morphology and packing motif characterization.

**Figure S2.** (a) AFM images and (b) optical microscopy images of *rac*-Y6 single-crystalline micro-ribbons.



**Figure S3**. (a) Out-of-plane XRD patterns of **Y6** micro-ribbons. (b) The SAED patterns of *rac*-**Y6** micro-ribbons.

#### 4. Devices fabrication and characterization.

The single-crystalline micro- ribbons of rac-Y6 were prepared by a slowly selfassembling from a chloroform solution (0.2 mg/mL) under a certain solvent pressure in a closed jar.<sup>1</sup> Micrometer-sized single crystals were slowly grown on the octadecyltrichlorosilane (OTS)-modified SiO<sub>2</sub>/Si substrates with the solution evaporation. Thin films of the Y6 were spin-coated from chloroform solution (5 mg/mL, 3000 r/min, 40-60 nm) onto Si/SiO<sub>2</sub> (300 nm) substrates modified with octadecyltrichlorosilane (OTS). Source/drain electrodes with optimal width/length (W/L) of 1400 µm/50 µm, electrodes were sputtered and patterned by a lift-off technique. SiO<sub>2</sub>/Si wafers used here were cleaned orderly with deionized water, piranha solution ( $H_2SO_4/H_2O_2 = 2:1$ ), deionized water, isopropyl alcohol, and finally were blown dry with high-purity nitrogen gas. OTS-modified SiO<sub>2</sub>/Si wafers was carried out with the vapor-deposition method: the cleaned wafers were dried under vacuum at 90 °C for 0.5 h to eliminate the moisture. When the temperature decreased to 70 °C, a small drop of OTS was dropped onto the wafers. Subsequently, this system was heated to 120 °C for 2 h under vacuum. OTS-modified SiO2/Si wafers used here were cleaned with n-hexane, chloroform and isopropyl alcohol in sequence, and finally were blown dry with high-purity nitrogen gas.

All OFETs devices were measured in insert atmosphere and were recorded with a Keithley 4200-SCS semiconductor parameter analyzer and a Micromanipulator 6150 probe station at room temperature. The mobilities were calculated from the saturation region in the transfer curves with the following equation:  $I_{DS} = (W/2L) C_{i\mu} (V_{GS}-V_{TH})^2$ , where  $I_{DS}$  is the drain–source current, W is the channel width, L is the channel length,  $\mu$  is the field-effect mobility,  $C_i$  is the capacitance per unit area of the gate dielectric layer, and  $V_{GS}$  and  $V_{TH}$  are the gate voltage and threshold voltage, respectively. This equation defines the important characteristics of mobility ( $\mu$ ) and threshold voltage ( $V_{TH}$ ), which could be deduced by the equation from the plot of current–voltage.



**Figure S4.** Typical transfer (a for p-type, b for n-type) and output curves (c for p-type, d for n-type) of representative thin film OFET devices of *rac*-**Y6**.

All OPTs devices were measured in insert atmosphere and were recorded with a Keithley 4200-SCS semiconductor parameter analyzer and a Micromanipulator 6150

probe station at room temperature. Photocurrent on/off ratio (P) is calculated from  $P = (I_{light} - I_{dark})/I_{dark}$ , photoresponsivity (R) is calculated from  $R = (I_{light}-I_{dark})/S P_{input}$  and  $D^*$  is given by  $D^* = R/(2eJ_d)^{1/2}$ , where  $I_{light}$  and  $I_{dark}$  are the source–drain current under illumination and in the dark condition, S is the area of OPTs device,  $P_{input}$  is the incident optical power, e is the unit of charge and  $J_d$  is the dark current density.



Figure S5. N-type output curves of OPTs based on Y6 with  $V_{DS} = 60$  V under dark condition or different laser intensities. (a) for thin film and (b) for single crystal.

## **References:**

1. H. Dong, S. Jiang, L. Jiang, Y. Liu, H. Li, W. Hu, E. Wang, S. Yan, Z. Wei, W. Xu and X. Gong, *J. Am. Chem. Soc.*, 2009, **131**, 17315-17320.