# Electronic Supplementary Information

# Solution-processed Organic Micro Crystal Transistor Based on Tetraceno[2,3-*b*]thiophene from a Monoketone Precursor

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#### 1. <sup>1</sup>H and <sup>13</sup>C NMR spectra









2. DSC plots



**Figure S8**. DSC profiles of tetraceno[2,3-*b*]thiophene precursor **1** at 5 deg/min heating rate by using indium as calibration.

## 3. UV/Vis spectra



**Figure S9**. UV/Vis spectra of pentacene precursor in THF  $(1.0 \times 10^{-4} \text{ M})$  under irradiated with a 1.25 mW/cm<sup>2</sup> UV lamp at 365 nm under an oxygen-free atmosphere. Measurements were take during 0 to 90 s with 10 s time interval.

4. Optical microscopic image



**Figure S10**. Optical image of microscopic crystals of tetraceno[2,3-*b*]thiophene prepared from **1**. (a) Crystal produced by heating in DCB at 130 °C; (b) crystals produced by heating CB at 130 °C; (c) crystals produced by UV irradiation in THF at 357 nm using a 1.25 mW/cm<sup>2</sup> UV lamp.



**Figure S11**. Single crystal OFET made with tetraceno[2,3-*b*]thiophene. (a) crystal obtained by heating at 130 °C in DCB; and (b) crystal obtained by UV exposure using a 1.25 mW/cm<sup>2</sup> 365 nm UV lamp in THF.



# 5. OFET characteristics

**Figure S12**. OFET characteristics based a single crystal of tetraceno[2,3-*b*]thiophene produced from **1**. (Top) A DCB solution of **1** was heated at 130 °C first, after crystallization it was then spin-coated on SiO<sub>2</sub>; (bottom) a DCB solution of **1** was spin-coated on SiO<sub>2</sub> to form a thin film first, then the film was heated at 130 °C to convert **1** to tetraceno[2,3-*b*]thiophene. (left) Output characteristics; (right) transfer characteristics recorded with  $V_{DS} = -40V$ .



**Figure S12**. Performance of measured tetraceno[2,3-*b*]thiophene single crystal FETs in histogram: upper ; single crystal from UV exposure of FET mobility (a) and on/off ratio (b), under ; single crystal from heat of FET mobility (c) and on/off ratio (d)

6. EPR spectra



**Figure S13**. EPR spectra of tetraceno[2,3-*b*]thiophene in coced H<sub>2</sub>SO<sub>4</sub> solution ( $1.0 \times 10^{-3}$  M) with O<sub>2</sub> free condition.

## 7. XRD plots



**Figure S14**. (a) XRD spectra of thin-film made with **1**; (b) the film was heated at 130 °C for 10 min; (c) simulated powder x-ray patterned of tetraceno[2,3-*b*]thiophene.