Electronic Supplementary Information (ESI) for:

# Boosting the electron mobility of solution-grown organic single

# crystals via reducing the amount of polar solvent residues

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### **Experiment section:**

#### Crystal growth and characterization.

6,13-bis(triisopropylsilylethynyl)-5,7,12,14-tetraazapentacene (TIPS-TAP) was prepared following the reported procedures<sup>1</sup> and purified by recrystallization from ethyl acetate twice. TIPS-TAP single crystals were grown in ambient condition using the dropletpinned crystallization (DPC) method<sup>2</sup> onto the divinyltetramethyldisiloxanebis(benzocyclobutene) (BCB)-covered highly doped silicon substrates (1 cm<sup>2</sup>) with 300 nm SiO<sub>2</sub>. BCB (Dow Chemicals) thin-layers were spin-coated from a mesitylene (Fluka) solution ( $V_{BCB}$ :  $V_{mesitylene} = 1:30$ ) and, subsequently, thermally crosslinked on a hotplate in a N<sub>2</sub> glovebox. A TIPS-TAP solution (10  $\mu$ L) in a specific solvent was dropped onto a silicon substrate (1 cm<sup>2</sup>) with a smaller piece of silicon wafer ( $0.4 \times 0.4$  cm<sup>2</sup>, pinner) to pin the solution droplet. The concentration of the various solutions is 0.3 mg/mL for hexane (TCI, HPLC) and 0.4 mg/mL for dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) (Aladdin, HPLC) and chloroform (CHCl<sub>3</sub>) (Labor, HPLC), respectively. A slightly low concentration (0.3 mg/mL) in hexane was used because of the low solubility of TIPS-TAP in hexane. As a 0.4 mg/mL solution in hexane was used, large crystals precipitated (Fig. S1b). The silicon substrate was placed on a Teflon slide inside a Petri-dish (35 mm  $\times$  10 mm) sealed with parafilm, allowing the solvent to slowly evaporate on a hotplate of  $25 \pm 1$  °C. Solution dried within ten minutes and aligned crystals formed. The morphology of the crystals was characterized by optical microscopy (OM) (Nikon LV100 POL) and atomic force microscopy (AFM) (Veeco 3D). Crystal thickness and width were measured by AFM from 20 ribbons. In order to examine the bottom surface of the crystals contacting the substrates, the crystals were gently peeled off from the substrate after being spin-coated with a thin layer of polyvinyl alcohol (PVA).<sup>3</sup> The PVA film was from an aqueous solution (PVA concentration = 15 wt%) and dried thoroughly overnight. The crystalline structures were examined by selected-area electron diffraction (SAED) (JEOL 1400) and the elemental composition was analyzed by X-ray Photoelectron Spectroscopy (XPS) for the crystals before and after heat treatment under 100 °C in a N<sub>2</sub> glovebox for two hours. The XPS was measured in an integrated ultrahigh vacuum system equipped with multitechnique surface analysis system (Thermo ESCALAB 250Xi).

#### FETs fabrication and measurement.

FETs were constructed in a top-contact, bottom-gate configuration by depositing electrodes (90 nm Au as both of the source and drain electrodes) using shadow masks (50  $\mu$ m channel length (*L*) and 1 mm width (*W*)). The real *W/L* value was measured (Fig. 2b) to calculate the mobility values. The devices were characterized before and after the heat treatment in a N<sub>2</sub> glovebox using a Keithley 4200-SCS semiconductor parameter analyzer. For heat treatment, FETs were typically heated under 100 °C in a N<sub>2</sub> glovebox for two hours before being cooled down naturally. For comparison, the devices were also heated at 80 °C and 120 °C. The measured capacitance of the BCB-covered SiO<sub>2</sub>/Si substrates was 10 nF/cm<sup>2</sup>, and was used for mobility calculation.

# **Supporting figures**



**Fig. S1.** Morphology of single crystals grown from hexane solutions. (a,b) OM images of TIPS-TAP crystals. The concentration of the solutions is 0.3 mg/mL for a and 0.4 mg/mL for b, respectively.



**Fig. S2.** Morphology and FET characteristics of TIPS-TAP single crystals grown from CH<sub>2</sub>Cl<sub>2</sub> solutions. (a) An OM image of the crystals. (b) An OM image of the crystals between crossed-polarizers. (c,d) Typical transfers of the FETs: (c) as-prepared; (d) heat-treated. (e,f) Histograms of 21 FETs' electron mobility of as-prepared (e, on-to-off current radio  $(I_{on}/I_{off}) > 10^5$  and threshold voltages  $(V_T)$  between 62 and 76 V) and heat-treated (f,  $I_{on}/I_{off} > 10^6$ , and  $V_T$  between 67 and 83 V).



**Fig. S3.** XPS analysis in the energy range of the Cl 2p signal. (a) An XPS spectrum for the as-prepared crystals, showing the signal of Cl 2p. (b) An XPS spectrum for the heat-treated crystals. There is no obvious signal of Cl 2p.



**Fig. S4.** Effect of the heat treatment temperatures on the electron mobilities. Electron mobilities of 13 devices heat-treated at 80 °C, 100 °C and 120 °C are shown. For comparison, the initial mobility without heating is also shown.

## References

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