### Supporting information for:

# Preparation and Ambipolar Transistor Characteristics of Co-crystal Microrods of Dibenzotetrathiafulvalene and Tetracyanoquinodimethane

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# **Experimental Section**

#### **Materials**

Dibenzotetrathiafulvalene (DBTTF) and tetracyanoquinodimethane (TCNQ) were purchased from Sigma-Aldrich Company and used as received.

# **Preparation of Microrods**

0.5 mL chloroform solution of DBTTF (~ 4 mM) was fast injected into 0.5 mL chloroform solution of TCNQ (~ 4 mM). The mixed solution was shaken vigorously for 30 s and maintained for 5 minutes. Then, 3 mL n-hexane was added slowly to the surface of the mixed chloroform solution. The resulting two-layer mixture was stored at room temperature for 12 h without disturbance. The final solution was transparent and the brown precipitates were collected at the bottom. For the fabrication of devices, the precipitates could be dispersed by shaking the mixed solution for several seconds.

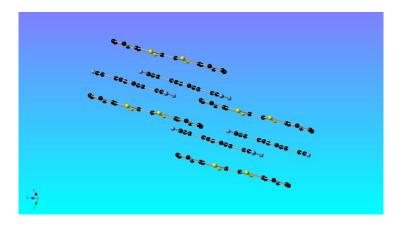
# Device Fabrication

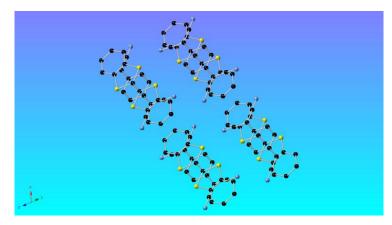
Source-drain gold electrodes were fabricated by photolithography and electron beam deposition of Au on Si substrate with 300 nm thick SiO<sub>2</sub>. A drop of the mixed solution with dispersed microrods is directly deposited on the prepatterned substrate. Randomly, some of microrods could be attached to the Au electrodes, which bridge the source and drain electrodes. The devices were then annealed at 393 K in vacuum

oven for 2 h to remove the solvent thoroughly. All the measurements were carried out with a Keithley 4200 SCS and standard probe station at ambient conditions in the shielded box and at room temperature.

*Measurements* SEM images were taken with a Hitachi s-4800 scanning electron microscope. STEM mapping analysis was performed by Quanta 400 FEG scanning electron microscope. TEM images were recorded using a Tecnai G2 F20 S-TWIN transmission electron microscope. XRD patterns were performed using a D8-discover Bruker X-ray diffractometer with Cu Kα radiation ( $\lambda = 1.5418$  Å). UV-vis-NIR spectra were recorded by a lambda750 spectrophotometer with a 60 mm integrating sphere for the measurement of solid samples deposited on quartz in the form of film. Raman spectra were obtained by LabRAM HR high resolution Raman microscope with a focused laser (632 nm).

Fig. S1 Chemical structures of DBTTF and TCNQ.





**Fig. S2** Schematic structures of triclinic crystal of DBTTF-TCNQ viewed along the [11-1] direction (top) and [011] direction (bottom), respectively.