# **Supporting information**

Donor-acceptor co-assembled supramolecular nanofibers with high and well-balanced ambipolar charge transport properties under ambient conditions.

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# **Supporting information**

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#### 1. Experimental section

#### 1.1. Preparation of TCAT/PDI-13 co-assembled supramolecular nanofibers

We firstly prepared a final concentration of  $1 \times 10^{-4}$  M of equimolar TCAT and PDI-13 with cyclohexane in a 5 mL screw type vial, and then placed the closed vial over a hot plate at 100 °C until it completely dissolved to give a homogenous and clear solution. The resulting hot solution was cooled to room temperature thus forming macroscopic flocs and finally the dilute solution of flocculation was casted on a required substrate to obtain the entangled nanofibers.

# **1.2. SBN-OFET** devices Fabrication and characterization and photoresponsivity measurement

Bottom-gate top-contact FETs based on single bundle nanofibers of TCAT/PDI-13 complex were fabricated, using a doped n-type silicon wafer as the gate electrode, Au electrodes as the source and drain electrodes, and OTS-modified SiO<sub>2</sub> as the dielectric layer. Firstly, single bundle nanofibers of TCAT/PDI-13 complex were deposited on an OTS/SiO<sub>2</sub>/Si substrate by spin-casting the dilute solution of flocculation prepared as above mentioned. Secondly, Au drain and source electrodes (~50 nm-thick) were deposited on the single-bundle nanofibers by thermal evaporation with an organic ribbon as a shadow mask. Finally, the organic ribbon mask was peeled off to obtain a gap between the source and drain electrodes. Electrical transport properties were measured under ambient conditions by using a semiconductor analyzer (Keithley 4200).

For photoresponsivity measurement, the SBN-OFET devices of TCAT/PDI-13 co-assembled supramolecular nanofibers were remeasured with a white light stimulation at an optical power of 4.56 mWcm<sup>-2</sup>, and the photocurrent responses depend on the gate voltages were recorded.

#### 2. UV/Vis spectrum



Figure S1. A) UV/Vis spectra of TCAT, PDI-13 and TCAT/PDI-13 recorded in the cyclohexane of  $1 \times 10^{-6}$  M under ambient conditions; B) UV/Vis spectra of these three samples in nanofibers state.

### **3.** Photoluminescence spectrum



Figure S2. Photoluminescence spectra recorded during the course of adding PDI-13 to

the cyclohexane solution of TCAT ( $1 \times 10^{-6}$  M) at room temperature.



## 4. Line-cut profiles of 2D-GIWAXS (out-of-plane)



Figure S3. Out-of-plane line-cut profiles from 2D-GIWAXS patterns

## 5. Line-cut profiles of 2D-GIWAXS (in-plane)





Figure S4. In-plane line-cut profiles from 2D-GIWAXS patterns

# 6. 1D-GIXRD spectra



Figure S5. 1D-GIXRD of TCAT, PDI-13 and TCAT/PDI-13 co-assembled nanofibers

#### 7. Schematic diagram and Optical microscopy image of SBN-OFET



Figure S6. (A) Schematic diagram of the device structure. (B) Optical microscopy image of the single-bundle nanofibers based OFET (SBN-OFET) fabricated from TCAT/PDI-13 co-assembled nanofibers.

#### 8. Output characteristics of SBN-OFET



Figure S7. Output characteristics of the representative SBN-OFET fabricated from TCAT/PDI-13 co-assembled nanofibers.