

## Supplementary data

**Synthesis of the DOTVAnT:** LDA (1.5 M in cyclohexane, 3.2 mL, 5.75 mmol) was added dropwise to a stirred solution of 2,6-bis(diethylphosphorylmethyl)anthracene (1.4 g, 2.92 mmol) in anhydrous THF (50 mL) at -78 °C under nitrogen. The mixture was stirred for 1 h and then 5-dodecylthiophene-2-carbaldehyde (2.30 g, 8.20 mmol) in THF (20 mL) was added dropwise over a period of 10 min. After the mixture was stirred for 2 h at -78 °C and for 12 h at roomtemperature, 5 mL of water was added and the solvent was evaporated. The residue was washed with water and MeOH. The desired product was separated by washing.

The synthesis of 2,6-bis(diethylphosphorylmethyl)anthracene can be found further in ref. [13].

**High-resolution mass spectrometry (HRMS):** Calcd. for  $C_{50}H_{66}S_2$  730.4606. Found: 730.4604. Anal. Calcd.: C, 82.13; H, 9.10; S, 8.77; Found: C, 82.11; H, 9.06; S, 8.83.

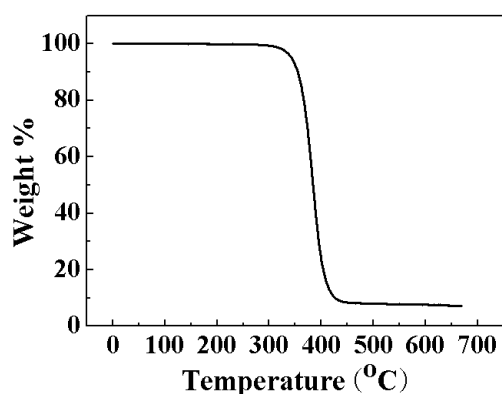
**Gelation test:** DOTVAnT (10 mg) and the solvent (1ml) were put in a vial (10 ml) and heated until the solid DOTVAnT was completely dissolved. Then, the resulting solution were cooled down. About a minute after cooling, yellow solid-like organogels were formed.

**Device fabrication and electrical measurement of single-nanofiber transistors of DOTVAnT:** We fabricated a 1D single-nanofiber of DOTVAnT organic transistor with a bottom-contact geometry. We used the heavily doped-silicon wafer as a gate electrode and HMDS-treated  $SiO_2$  layer (thickness of  $\sim 300$  nm) as a gate dielectric. Cr/Au (2nm/40 nm) was thermally evaporated as the source and drain electrodes and patterned by photolithography and a lift off method. The resulting bottom-contact substrates consist of arrays of  $1000 \times 1000$   $\mu m$  square electrodes with 5 or 10  $\mu m$  channel gap. Then, well-dispersed nanofibers of DOTVAnT in chloroform (0.01 mg/mL) were spin-coated at  $\sim 3000$  rpm onto the patterned electrode substrate. To find a single-nanofiber bridged between the source and the drain electrodes, we used an polarized optical microscope. Then, the electrical

characterization of a single-nanofiber transistor was performed at room temperature in the air using a Keithley 4200-SCS semiconductor analyzer. The ratio of the width to the length, W/L of a nanofiber was characterized by a field-emission scanning electron microscope (FE-SEM, JSM7401F, JEOL). We also confirmed that there was only one nanofiber bridged between a source and a drain in the single-nanofiber transistors by a AFM. Field-effect mobility ( $\mu$ ) was extracted in the saturation regime ( $V_{DS} = -30$  V) in the plot of the square-root of drain current vs.  $V_{GS}$  using the following equation:

$$I_{DS} = \frac{WC_i}{2L} \mu (V_{GS} - V_T)^2$$

Where  $I_{DS}$  is the source-drain saturation current;  $C_i$  ( $1.1 \times 10^{-8}$  F) is the capacitance of the HMDS-treated  $\text{SiO}_2$  insulator, W/L is the ratio of the width of the nanofiber to its channel length across the source-drain electrodes.  $V_{GS}$  and  $V_T$  are the gate-source and threshold voltages, respectively.



**Fig. S1** Thermal gravimetric analysis (TGA) of DOTVAnT.

The absorption spectra of a DOTVAnT dissolved in toluene were recorded on an Agilent 8453 spectrometer. The cyclic voltammograms of the DOTVAnT dissolved in dichlorobenzene with tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ , 0.1M) as supporting electrolytes were measured on a CHI 700C electrochemical instrument at a

scan rate of 100mV/s. Counter and working electrodes were Pt electrodes and the reference electrode was a Ag/AgCl. All the potentials were calibrated with the standard ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple ( $E^{1/2} = + 0.26$  V).

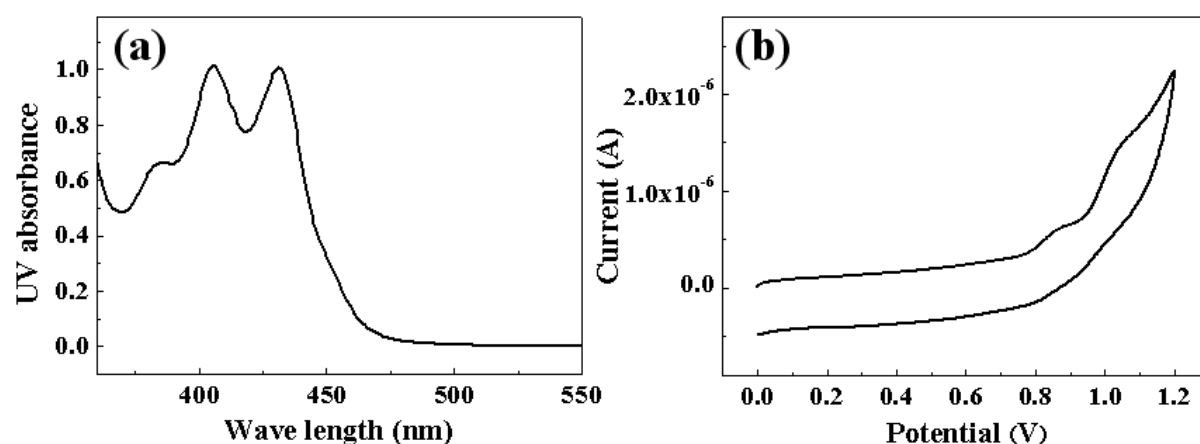


Fig. S2 a) UV-Vis absorption spectra and b) a cyclic voltammogram of DOTVAnT.

- XRD analyses were carried out with a Rigaku ( $\lambda=1.5418$  Å, 298K) x-ray instrument.

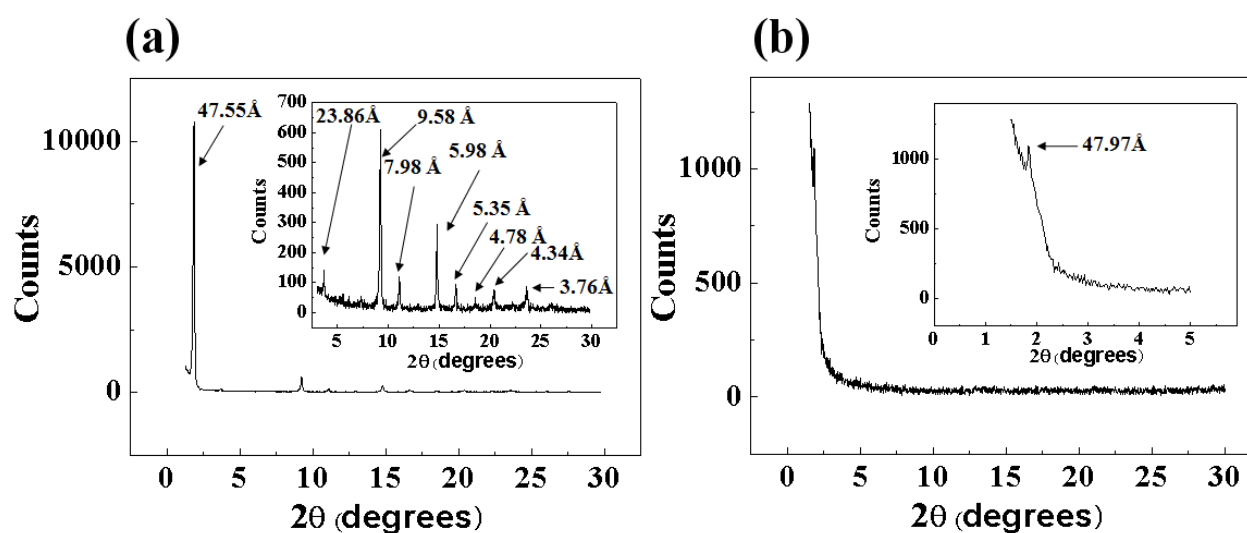


Fig. S3 X-ray diffraction patterns of DOTVAnT xerogel (a) and film (b). The inset shows the enlarged part of the portion ranging from (a)  $5^\circ$  to  $30^\circ$  and (b)  $1.5^\circ$  to  $5^\circ$ , respectively.

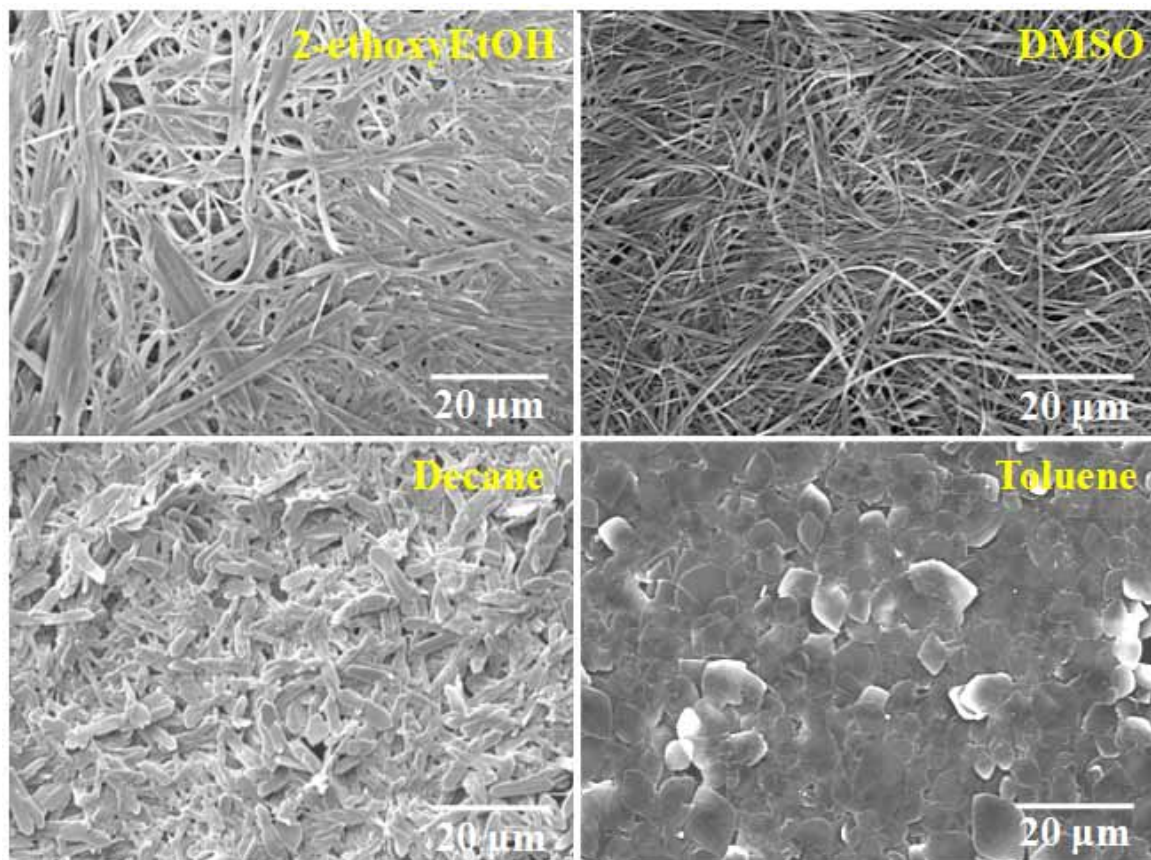


Fig. S4 SEM images of DOTVAnT in various solvents.

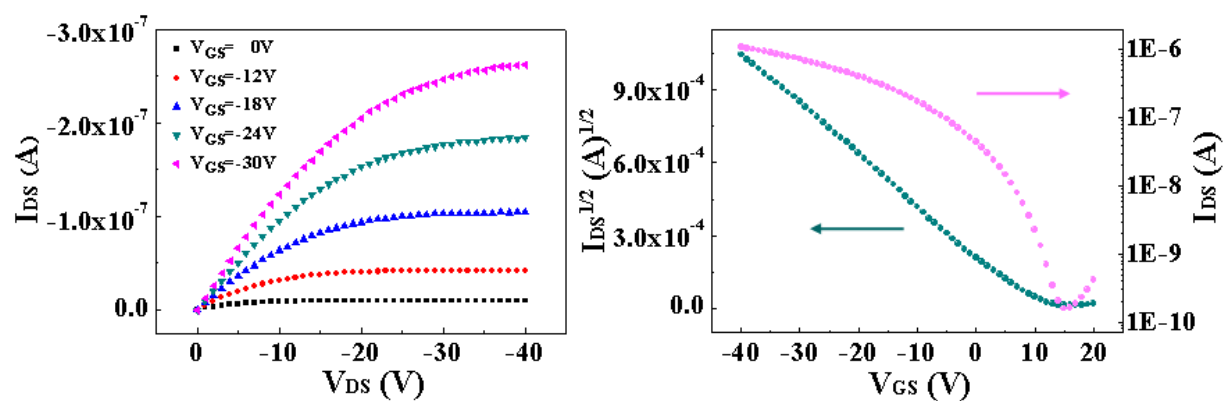
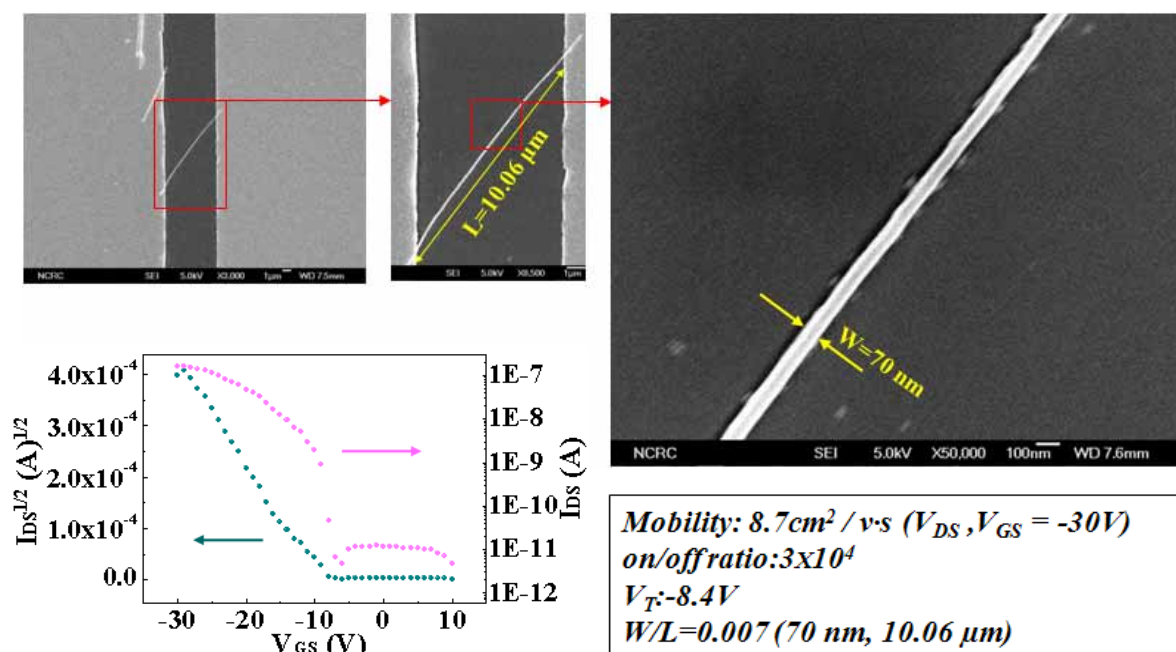


Fig. S5 Output & transfer characteristics of a OTFTs based on DOTVAnT films.



**Fig. S6** Single-nanofiber transistors of DOTVAnT with 70 nm width. It exhibited extremely high mobility (up to  $8.7 \text{ cm}^2/\text{V}\cdot\text{s}$ ). However, we hardly get its output I-V characteristics of  $I_{DS}$  vs.  $V_{DS}$ . Further studies on such a single-nanofiber transistors with less than tens of nanometer are in progress.