Supporting Information

Two-Dimensional Cross-Linked Polythiophene Network

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1. Carrier concentration and mobility measured by Hall method.

**Experimental details:** The experiment was carried out using Ecopia HMS-3000. Temperature is set at 300 K. The current $I = 1 \mu$A. Thickness $d = 1.3$ nm. Strength of magnetic field $B = 0.556$ T.

**Results:** Hole concentration $p = -2.094 \times 10^{19}$ cm$^{-3}$. Hall mobility $\mu = 2.451$ cm$^2$·V$^{-1}$·s$^{-1}$.

2. Figures

![Diagram of CVD equipment](image)

Figure S1. A CVD equipment used in the 2DPT growth.
Figure S2. SEM image of a 2D polythiophene film on Cu foil. Scale bar, 100 μm.

Figure S3. Overall thickness distribution of the 2DPT samples after CVD growth for 20, 30, 40, 50, 60 min. Each sample is measured for 10 times.

Figure S4. (a) OM image of the transferred sample grown without TBB cross-linking precursor. (b) Raman spectrum of the sample grown on Cu foil without
TBB. (c) Raman spectrum of the sample after transfer as shown in (a). Scale bar, 20 μm.

Figure S5. Full-range XPS spectrum acquired from 2DPT grown on Cu foil.

Figure S6. Sheet resistance of 1 to 4 layers of stacked 2DPT without doping.
Figure S7. SEM image of a pentacene film near the electrode/channel interface. The insets are corresponding AFM images in each region. Scale bars are 2 μm (SEM image) and 1 μm (AFM images).

Figure S8. Contact resistance measurement of pentacene OFET based on different bottom-contacted electrodes.