Supporting Information

Controllable Growth of Centimeter-Scale 2D Crystalline Conjugated Polymers for Photonic Synaptic Transistors

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Note S1. The reason to choose chloroform as solvent

Selecting appropriate growth-assisting solvent is the key point in this experiment. A low-boiling-point solvent, chloroform, was adopted as the growth assistant and the growth mechanism was further discussed. The reason to choose chloroform was that the solubility parameter of chloroform was much closer to the conjugated polymer and its low boiling point would make it easier to evaporate. Through the self-shearing force generated from the evaporation, ordered conjugated polymer films could be obtained. The evaporate rate of the liquid follows a formula relating to the boiling point.

$$u = (p/\rho_1)[\mu/(2\pi RT)]^{1/2}$$

Where p is the saturated vapor pressure of the liquid, ρ_1 is the density, μ is the molar mass of the liquid and R is a constant value equals to 8.31 J mol^{-1} K^{-1}. Substitute the fundamental physical properties of chloroform into the formula, an evaporate rate of 0.397 cm s^{-1} at room temperature can be obtained, which is the highest value among the common-used crystal growing assistants (Table S1). In order to realize the 2D growth of conjugated polymers, a space-confined growth need to be realized.

Table S1. Evaporate rates of several common-used solvents.

Solvents	Saturated vapor pressure (p, kPa)	Density (ρ_1, kg m^{-3})	Molar mass (μ, kg mol^{-1})	Evaporate rate (u, cm s^{-1})
Toluene	4.89 kPa	0.87×10^3	92.14×10^{-3}	0.014
Chlorobenzene	1.33 kPa	1.10×10^3	112.56×10^{-3}	0.004
1,2-dimethylbenzene	1.33 kPa	0.88×10^3	106.16×10^{-3}	0.004
Chloroform	2.12 kPa	1.48×10^3	119.38×10^{-3}	0.397

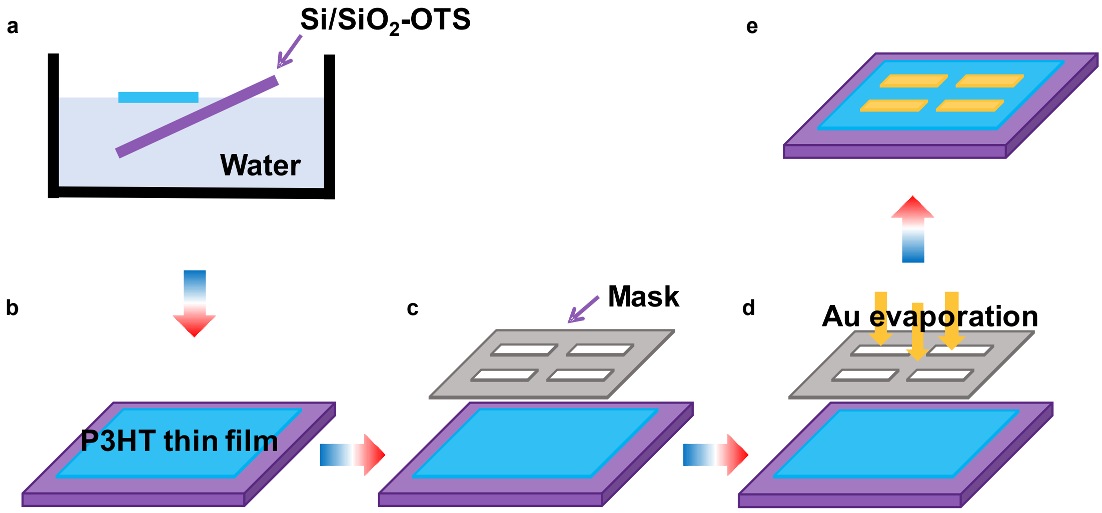

Figure S1. The OFETs preparation process. (a) Transfer the floating P3HT film on the substrate of Octadecyltrichlorosilane (OTS)-modified Si/SiO_2. (b) The schematic diagram of P3HT thin film on the substrate after the transfer. (c) Masks are applied to cover the thin film. (d) Then thermal evaporation of gold is executed, where the thickness of gold is controlled around 60 nm. (e) After the thermal evaporation, remove the mask and the array-type OFET devices can be obtained.

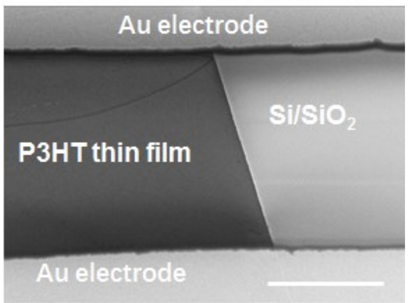

Figure S2. SEM image of the device with bottom-gate structure. Scale bar: 10 μm.

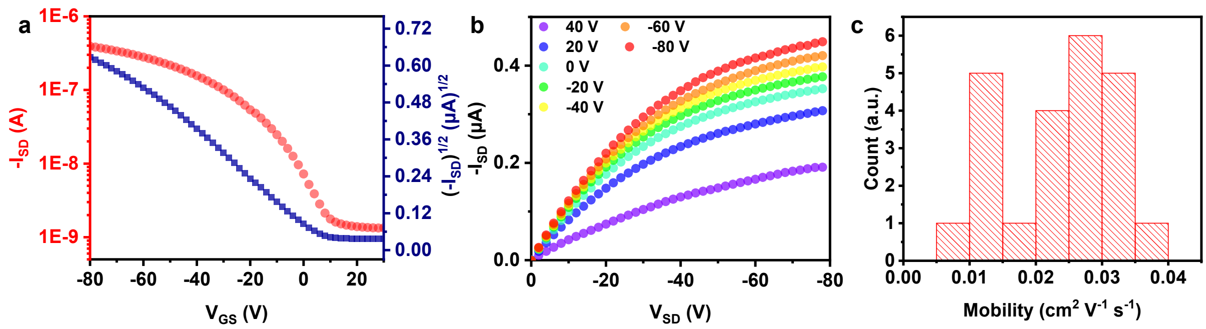

Figure S3. The electrical properties of P3HT crystals. (a) The representative transfer curve of the device. Drain voltage = -80 V. Red curve represents the actual value of I_{SD} along the change of gate voltage while blue curve is the square root of that value. (b) The representative output curves of the device. (c) Distribution of the mobility based on 23 devices from different batches.

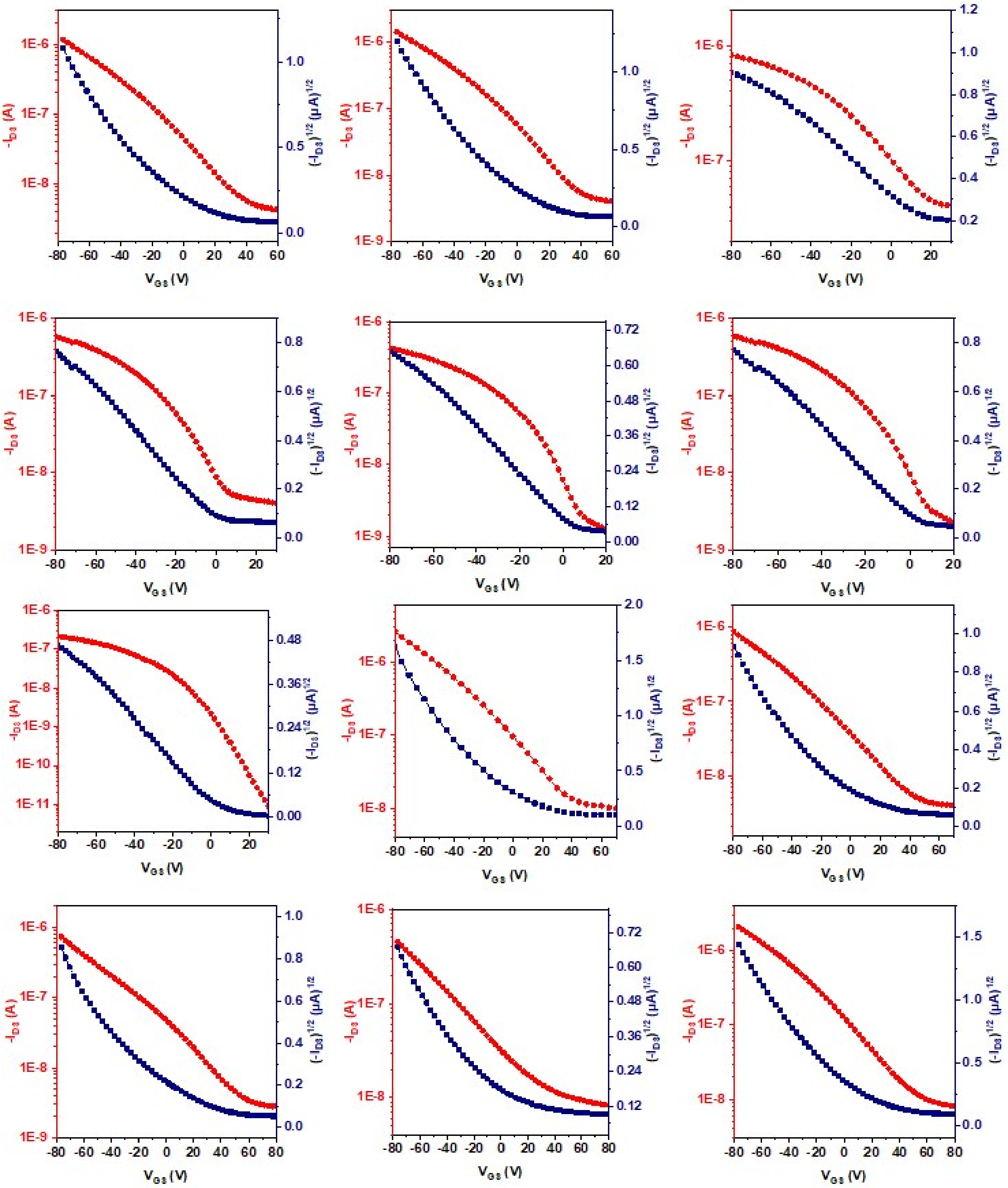

Figure S4. All the 23 transfer curves tested from the randomly selected devices (12 of them). Red curve represents the actual value of I_{SD} along the change of gate voltage while blue curve is the square root of that value.

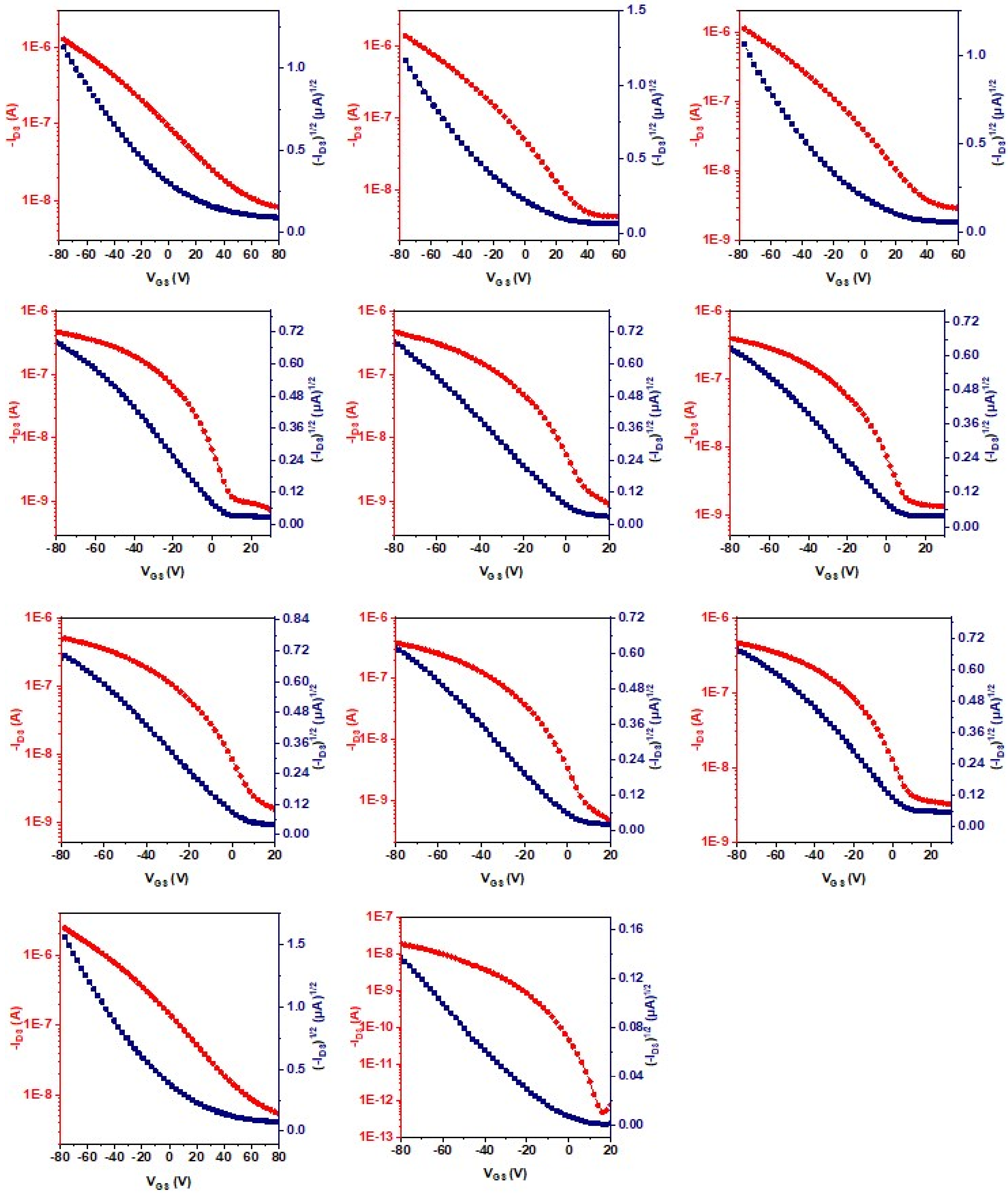

Figure S5. All the 23 transfer curves tested from the randomly selected devices (residual 11 of them).

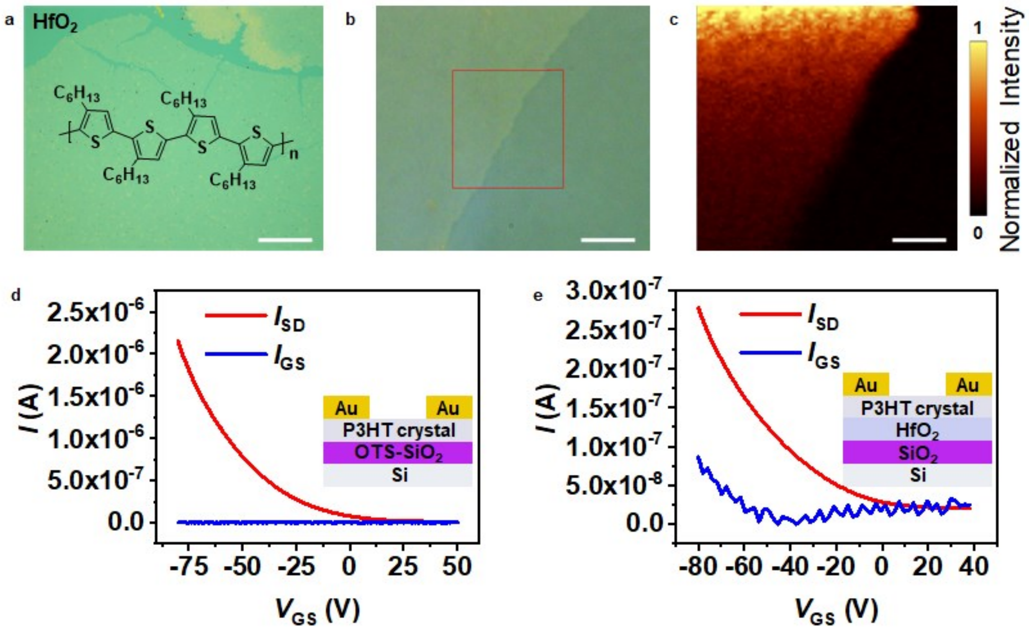

Figure S6. Characterization of P3HT thin film on the substrate of HfO_2. (a) The microscopic picture of P3HT thin film. Scale bar: 200 μm. (b) Red circle: selected area to do Raman mapping. Scale bar: 10 μm. (c) The mapping result of 1447 cm^{-1} peak. The scale bar is 4 μm. The comparation of leakage currents (I_{GS}) and source-drain currents (I_{SD}) within the configuration of (d) Au/P3HT crystal/OTS-SiO_2/Si and (e) Au/P3HT crystal/HfO_2/SiO_2/Si.

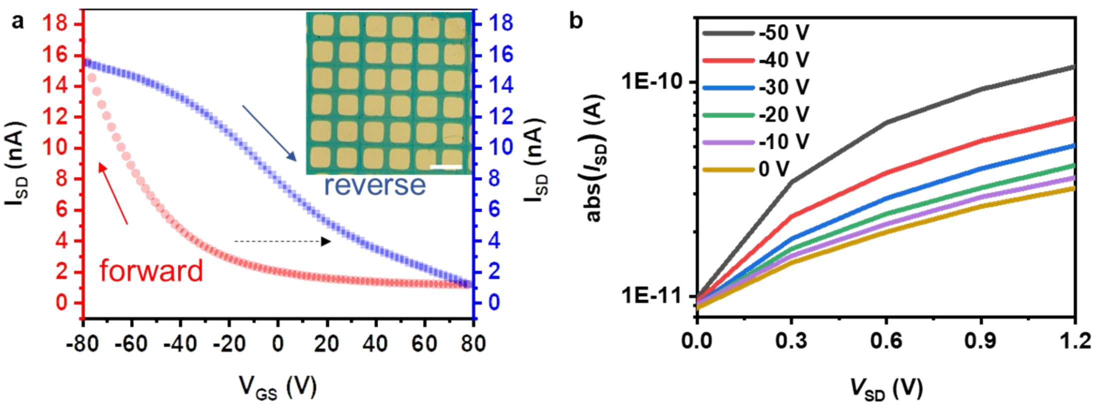

Figure S7. (a) The hysteresis curve of the device based on P3HT/HfO_2, which exhibits a clockwise hysteresis. The threshold voltage value shows a positive shift as the dotted arrow shows. Inset is the microscopic image of the P3HT/HfO_2-based device array. The scale bar is 200 μm. (b) *I*-*V* output curve of the device.

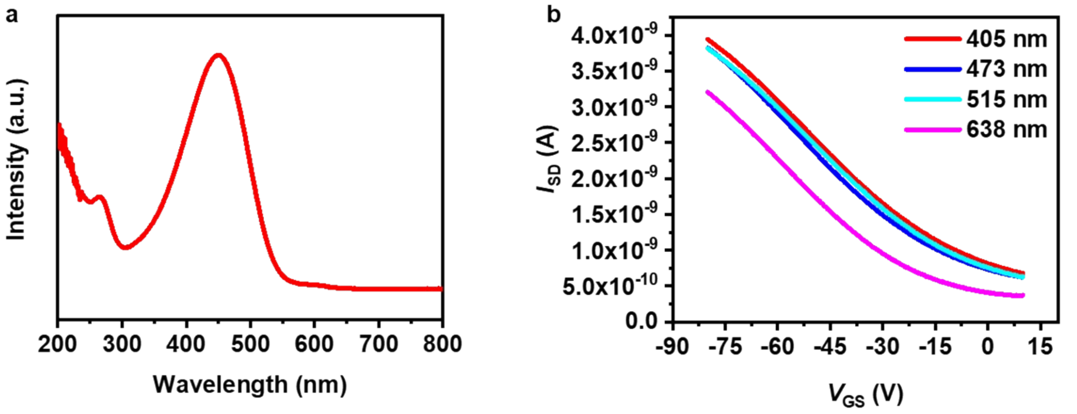

Figure S8. (a) UV-*vis* spectra of as-produced P3HT crystal. (b) Light currents of the device with response to four different-wavelength light sources, 405 nm, 473 nm, 515 nm and 638 nm.

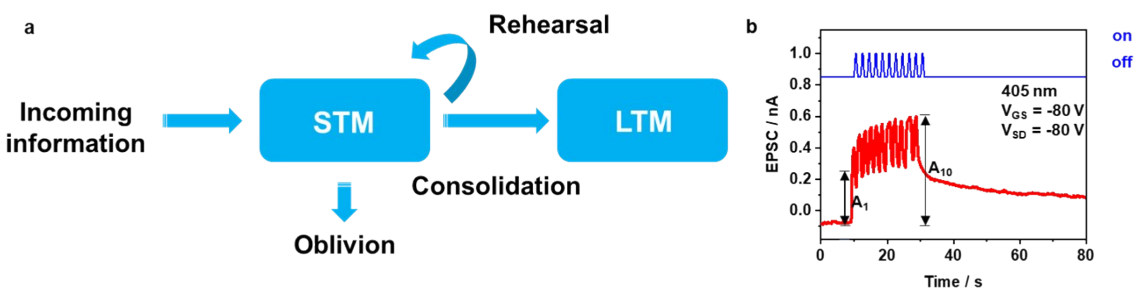

Figure S9. Memory consolidation and synaptic learning. (a) Schematic diagram of the biological memory consolidation process in human brain, where STM equals to short-term memory while LTM corresponding to long-term memory. In the artificial synapse, STM and LTM are described as STP and LTP. (b) Preliminary LTP of the photonic synaptic transistor based on P3HT/HfO_2. The postsynaptic currents after the first and tenth illuminations are defined as A_1 and as A_{10}, respectively.

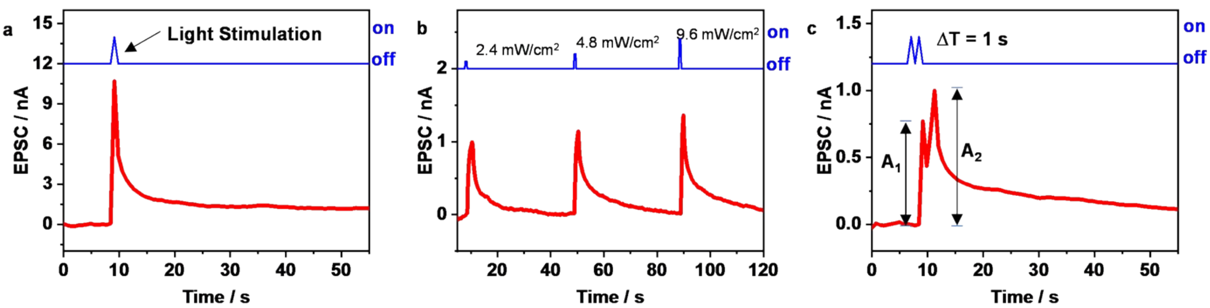

Figure S10. Performance of the photonic synaptic devices based on P3HT/HfO_2 in the air. (a)

STP curve of the device after a light stimulation of 4.8 mW cm^{-2} with a constant V_{GS} of -80 V and V_{SD} of -80 V. (2) Light-intensity-dependent STP curve of the device after a series of stimulation (2.4 mW cm^{-2}, 4.8 mW cm^{-2}, 9.6 mW cm^{-2}). (c) PPF curve of the device when light intensity is 4.8 mW cm^{-2} and interval is 1 s. V_{GS} = -80 V, V_{SD} = -80 V.