Electronic supplementary information

Extending the Light Response Range of Organic Photoelectric Synaptic Transistors by p-Doping

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Materials

All the materials were used without further purification. o-Dichlorobenzene (o-DCB, 99%) was purchased from Sigma-Aldrich. Poly(3-hexylthiophene-2,5-diyl) (P3HT, $M_w = 20,000-35,000, 99.99\%$) was purchased from Xi'an Yuri Solar Co., Ltd.. 2,3,5,6-Tetrafluoro-7,7',8,8'-tetracyanoquinodimethane (F₄TCNQ, 97%) was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd.

Device fabrication

Organic optosynaptic semiconductor devices with bottom-gate contact structure were prepared by using 300 ± 10 nm heavy P-doped silicon wafers with SiO₂ as gate dielectrics. Silicon substrate (0.001–0.005 $\Omega \cdot cm$; 15 × 15 mm², Suzhou Jingxi Electrontics and Technology Company), was washed with a piranha solution under sonication for 20 min, followed by ultrasonic cleaning with deionized water, ethanol, acetone and isopropyl alcohol for 15 min, and finally the washed silicon wafers were stored in isopropyl alcohol. After the silicon wafers were dried with N₂ gas stream and treated with UV-O₃ for 15 min, the 30 nm thick gold source drain electrode was evaporated through a mask in a vacuum chamber < 1 × 10⁻⁴ Pa by thermal evaporation. The channel length was 200 µm and the width was 23.4 mm. After the clean silicon wafer with gold electrode is treated with UV-O₃ for 15 min, it was laid on the bottom of a crystallizing dish and placed in the oven at 110°C for 2 min. Then, 4 mg of hexamethyldisilazane (HMDS) was placed in a 2 mL of vial. The vial was placed in the center of the crystallization dish to achieving a self-assembled layer on the substrate.

First, F4TCNQ was dissolved in o-DCB with a concentration of 1 mg/mL at 80°C for 12 h to

obtain solution A. Then, P3HT was dissolved in o-DCB and solution A with the concentration of P3HT fixing at 5.46 mg/mL. The mixed solutions were prepared according to the molar ratio of

the compounds (m_{F4TCNQ}:m_{P3HT} = x:100 (x=0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10)). After the mixed solution

(5.46 mg/mL) was spin-coated at 1000 rpm for 80 s, the obtained was annealed at 110 $^{\circ}C$ in N_2 gas for 30 min.

For the 3 \times 3 and 10 \times 10 array devices, the array masks were used, and the fabrication condition is the same as that for used for the single device. The mixed solution was also spin-coated on the self-assembly layer, and then annealed in N₂ gas.

Characterization of semiconducting films

The absorption spectra of the films were measured using the UV-Vis spectrophotometer (UV3600, Shimadzu, Japan). X-ray photoelectron spectra (XPS) were tested by Thermo Scientific K-Alpha using an Al K α source. Ultraviolet photoelectron spectra (UPS) were tested by Thermo Scientific Nexsa using a He ultraviolet source. Cyclic voltammetry (CV) was performed in a solution of tetra-n-butylammonium hexafluorophosphate (0.1 M) in acetonitrile on a CHI 604E electrochemical workstation with a three-electrode system at a scan rate of 100 mV/s. P3HT and doped P3HT were deposited on a Pt plate electrode by dipping the electrode into the corresponding solutions and then dried under the ambient condition. Pt wire and Ag/AgNO₃ were used as the counter electrode and reference electrode, respectively. Time-resolved photoluminescence (TRPL) was measured with a Horiba Fluorolog-3 time-correlated single photon counting equipment at an excitation of 485 nm. The surface morphology and roughness of the active layer films was measured using an Atomic Force Microscope (AFM, Keysight 5500, formerly Agilent, Agilent Technologies, Inc.). The film thickness was measured using a Bruker Dektak XT surface profilometer.

Device characterizations

The electrical and synaptic properties of FP-n in air were tested using a Semiconductor Parameter Analyzer (PDA FS-Pro), and the electrical properties under a nitrogen atmosphere were tested by the Keithley 4200 SCS Semiconductor Parameter Analyzer. The temperature test was performed by Keithley 2636 after heating the device to a target temperature and holding it in air for 2 min. The self-assembly process of FP-n was carried out in an oven.

Supplementary Figures and Tables



Fig. S1 The preparation of the active layer solution. From left to right, are the active layer solutions of F_4TCNQ :P3HT with molar doping ratios of 0%, 0.1%, 0.5%, 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, in that order



Fig. S2 Absorption spectra of the thin films obtained by the spin-coating active layer solutions with different F_4TCNQ doping ratios.



Fig. S3 The FP-6 device was heated from the bottom using a hot plate to investigate the effect of temperature variations on the generated excitatory post-synaptic current (Δ EPSC) ($V_{\rm G} = -10$ V, $V_{\rm DS} = -10$ V, laser wavelength = 1550 nm).



Fig. S4 (a) I_{DS} of FP-6 device in dark state and light state ($V_G = -10$ V, $V_{DS} = -10$ V, laser wavelength = 1550 nm, P = 37.2 mW/mm²). (b) Noise current (i_{noise}) of the FP-6 device under -10 V bias ($V_G = -10$ V).



Fig. S5 Photocurrent of the FP-6 device measured under different irradiance intensities. ($V_G = -10 \text{ V}$, $V_{DS} = -10 \text{ V}$, laser wavelength = 1550 nm).



Fig. S6 XPS spectra comparing elemental compositions of pristine P3HT and P3HT films doped with 6% F_4TCNQ : (a) F 1s; (b) N 1s; (c) S 2p.



Fig. S7 CV measurements of the frontier orbital energy levels (HOMO and LUMO) for the active layer films with varying doping ratios. (a) Calibration of the standard electrode potential using ferrocene as a reference. (b) Frontier orbital energy levels of P3HT determined from CV. (c) Frontier orbital energy levels of $m(F_4TCNQ):m(P3HT) = 6\%$ determined from CV.

Based on the reduction and oxidation potential onsets, the HOMO and LUMO energy levels of P3HT and 6%

(F₄TCNQ:P3HT) were calculated by using the equation:

 $E_{HOMO/LUMO} = - 4.82 - \varphi_{ox/red} eV$

P3HT: LUMO = -4.82 - (-1.32 - 0.06) eV = -3.44 eV P3HT: HOMO = -4.82 - (0.54 - 0.19) eV = -5.17 eV 6% doping: LUMO = -4.82 - (-1.28 - 0.06) eV = -3.48 eV

6% doping: HOMO = -4.82 - (0.35 - 0.19) eV = -4.98 eV



Fig. S8 (a) The I_{DS} - V_G curve of P3HT and P3HT exposed to air ($V_{DS} = -50$ V). (b) The I_{DS} - V_{DS} curve of P3HT. (c) The I_{DS} - V_{DS} curve of P3HT exposed to air. (d) The I_{DS} - V_G curves of FP-6 in dark and under 1550 nm light illumination at a fixed gate voltage of -10 V ($V_{DS} = -50$ V). (e) The I_{DS} - V_{DS} curve of FP-6 device in dark. (f) The I_{DS} - V_{DS} curve of FP-6 device under 1550 nm light illumination.



Fig. S9 Atomic Force Microscope (AFM) height images of (a) P3HT and (b) $m(F_4TCNQ):m(P3HT) = 6\%$ films. The scan size is 5 μ m × 5 μ m.



Fig. S10 Optical response of FP-6 device to light pulses with different wavelengths and intensities ($V_{\rm G} = -10$ V, $V_{\rm DS} = -10$ V).



Fig. S11 The FP-6 device's photoresponse to 450 nm light pulses with different intensities ($V_{\rm G} = -10$ V, $V_{\rm DS} = -10$ V).



Fig. S12 The minimum resolution of FP-6 devices in response to 450 nm light illumination ($V_{\rm G} = -10$ V, $V_{\rm DS} = -10$ V).



Fig. S13 PPF index of FP-6 device with spike time interval at 532 nm ($V_G = -10$ V, $V_{DS} = -10$ V).



Fig. S14 (a) Waveform of STDP. (b) Synaptic weight change under different spike-timing differences $\Delta T (V_{DS} = -10 \text{ V})$.



Fig. S15 (a) EPSC of FP-6 device before and after optical burn-in test ($V_G = -10$ V, $V_{DS} = -10$ V, laser wavelength = 1550 nm, P = 37.2 mW/mm²). (b) EPSC of FP-6 device before and after thermal aging test ($V_G = -10$ V, $V_{DS} = -10$ V, laser wavelength = 1550 nm, P = 37.2 mW/mm²).



Fig. S16 Illustration of learning-experience behavior, demonstrating that a small amount of pulse stimulation can effectively restore the memory current following the forgetting process ($V_{\rm G} = -10$ V, $V_{\rm DS} = -10$ V, laser wavelength = 450 nm, P = 1.6 mW/mm²).



Fig. S17 Excitatory post-synaptic current (Δ EPSC) response of the FP-6 device to external optical information in 26-letter Morse code ($V_{\rm G} = -10$ V, $V_{\rm DS} = -10$ V, laser wavelength = 1550 nm, P = 37.2 mW/ mm², "dot ": 0.2 s, "dash ": 0.3 s).



Fig. S18 Uniformity testing of 10×10 synaptic array devices: (a) Real picture of the array. (b) The image of a single device. (c) The virtual diagram of the array device. (d) Dark state current values of 25 random devices at operating voltages $V_{\rm G} = -10$ V, $V_{\rm DS} = -10$ V (laser wavelength = 1550 nm, P = 37.2 mW/ mm²).

Doping ratio of F_4 TCNQ in P3HT by mole	Average thickness based on three samples (nm)
0	23.9
0.1:100	24.0
0.5:100	22.9
1:100	23.2
2:100	23.7
3:100	22.1
4:100	24.4
5:100	24.1
6:100	23.8
7:100	24.1
8:100	23.1
9:100	23.5

Table S1 Summary of the active layer film thickness of FP-n devices (n indicates the molar doping ratio of the solution).