

## Electronic Supplementary Information

### Molecular Antenna Tailored Organic Thin-film Transistor for Sensing Application

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**Device Fabrication and Characterization.** A heavy n-doped Si wafer with 50 nm SiO<sub>2</sub> (~60 nF cm<sup>-2</sup>) was utilized to fabricate low-voltage operating devices. The substrates were cleaned with deionized (DI) water, alcohol, and acetone respectively, and then immersed in piranha solution (98% sulfuric acid blended with 30% H<sub>2</sub>O<sub>2</sub> at a ratio of 7:3) for 30 min, rinsed by DI water and dried in nitrogen flow. Afterwards, the substrates were modified with a self-assembled octadecyltrichlorosilane (OTS, Sigma-Aldrich) monolayer at 120 °C under vacuum atmosphere. PDPP3T (Solarmer Co., 5 mg mL<sup>-1</sup>, toluene solvent) was spin-coated onto the substrate at a speed of 4000 rpm. After spin-coating, the films were annealed at 150 °C for 15 min in a glovebox. Bottom-gate top-contact (BGTC) OFETs were fabricated by thermally evaporating gold (Au) drain-source electrodes (30 nm) onto the PDPP3T layer. The channel length and width of the device were 200 μm and 4800 μm, respectively. To protect the source and drain electrodes from direct contact with testing electrolytes, silicon monoxide (SiO, 80 nm) was thermally deposited on the Au electrodes to form a passivation layer except for the probe contacts.

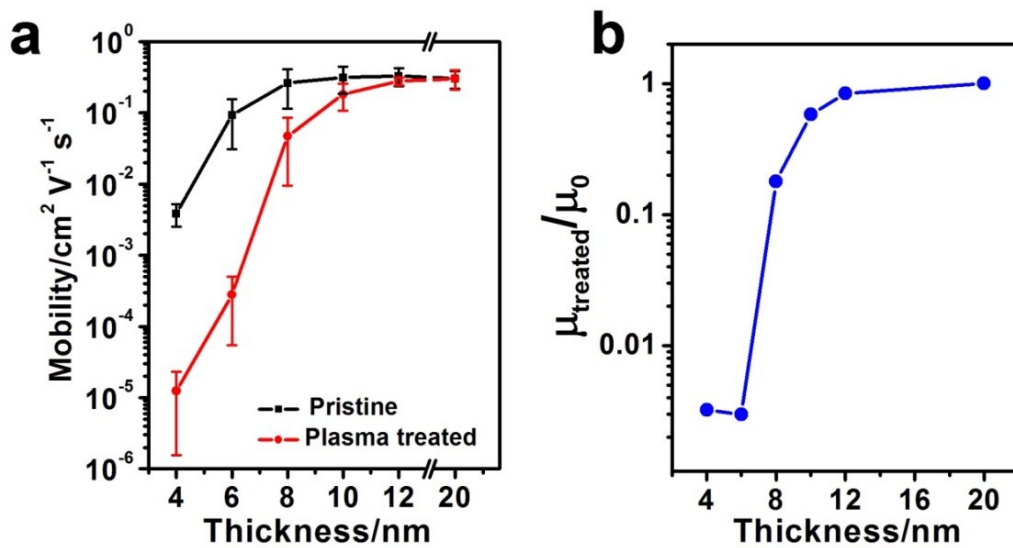
Prior to the biological functionalization process, the semiconductor films were treated by oxygen plasma (Plasma technology GmbH. MiniFlecto®) at a fixed

pressure of 0.3 mbar, power of 24 W for 2 min. Therefore functional group tailored PDPP3T surfaces were realized. Afterwards, the devices were immediately stored in 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) and N-hydroxy-succinimide (NHS) (20 mg mL<sup>-1</sup> for EDC and 6 mg mL<sup>-1</sup> for NHS) mixture solution for 20 min and then washed with PBS (10 mM) for three times to activate the carboxyl groups. The devices were further incubated in apyrase (Sigma-Aldrich, EC 3.6.1.5) solution (0.1 mg mL<sup>-1</sup>) buffered by Dulbecco's phosphate buffered saline (D-PBS, 1X, pH 7.4) for 1 hr. At the end of surface functionalization process, the devices were rinsed with DI water three times and blown dry in a nitrogen flow.

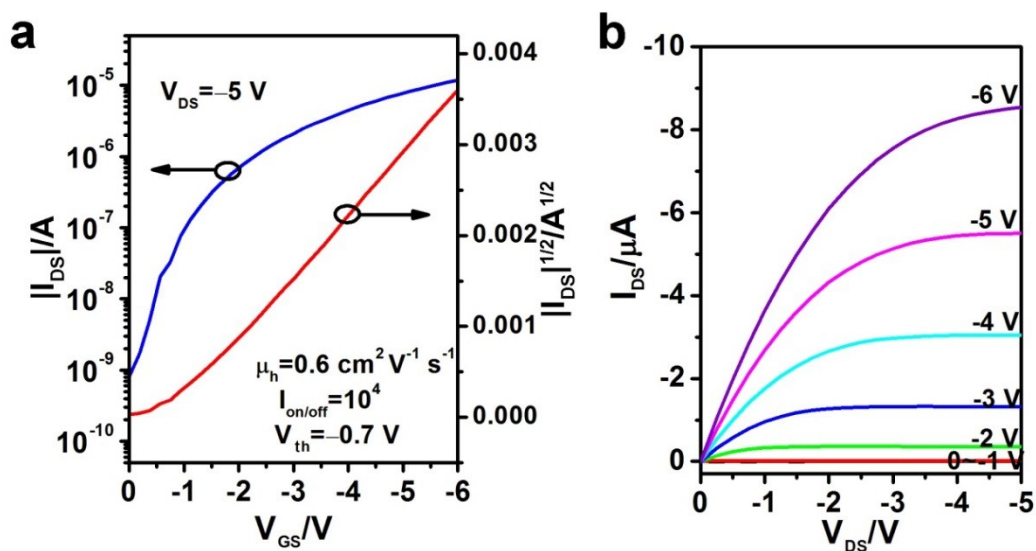
The measurement of the transistor and device sensing performances were performed using a semiconductor parameter analyzer (Agilent B1500A) at ambient conditions. 30  $\mu$ L solutions for recording the sensing responses were introduced onto or withdrawn from the channel area using a micropipette for each time. Solutions for ATP, ADP or AMP (Sigma-Aldrich, 99%) detection were prepared in a pH adjusted buffered media (0.1 mM HEPES, 5 mM CaCl<sub>2</sub>, pH 7.0). The baseline current was typically recorded after 100 s constant source-drain and gate biases ( $V_{DS}=-1$  V,  $V_{GS}=-3$  V) prior to the sensing measurements.

**AFM Characterization.** Atomic force microscopy (AFM) images were measured by using a Nanoscope IIIa AFM (Digital Instruments) with tapping mode.

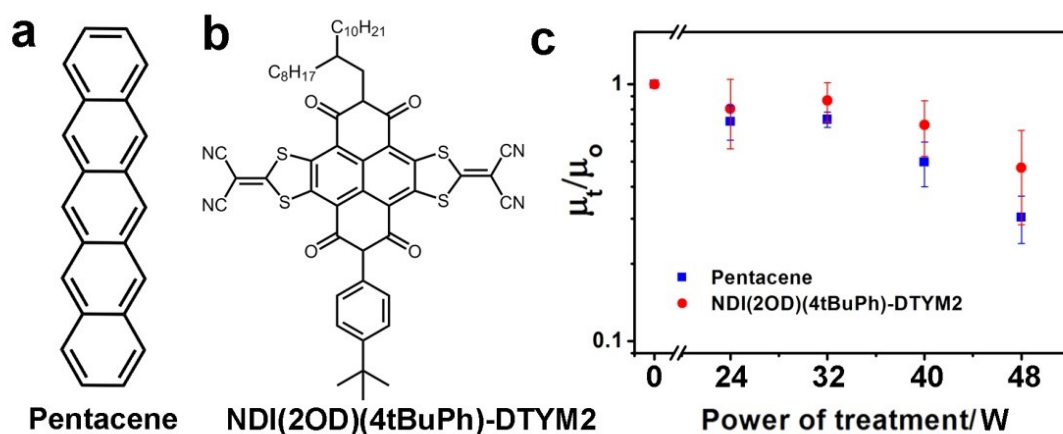
**UPS and XPS Characterization.** The UPS and XPS measurements were carried out in a Kratos ULTRA AXIS DLD ultrahigh vacuum photoelectron spectroscopy with a base pressure of better than  $2 \times 10^{-9}$  Torr. An unfiltered He-discharge lamp (21.22 eV) and a monochromatic Al K $\alpha$  X-ray (1486.6 eV) excitation sources were utilized for UPS and XPS analysis, respectively. The samples for photoemission characterization were obtained by spincoating the OSC solution on  $1 \times 1$  cm<sup>2</sup> silicon wafers. The energy resolution for UPS measurement was 100 meV as estimated from the Fermi edge of an Ar<sup>+</sup> sputtered clean Au substrate. The samples were negatively biased at 9.0 V for the electron analyzer to obtain the secondary electron cutoff (SECO) spectra. The Fermi edge was calibrated from a UPS spectrum of the clean Au substrate.



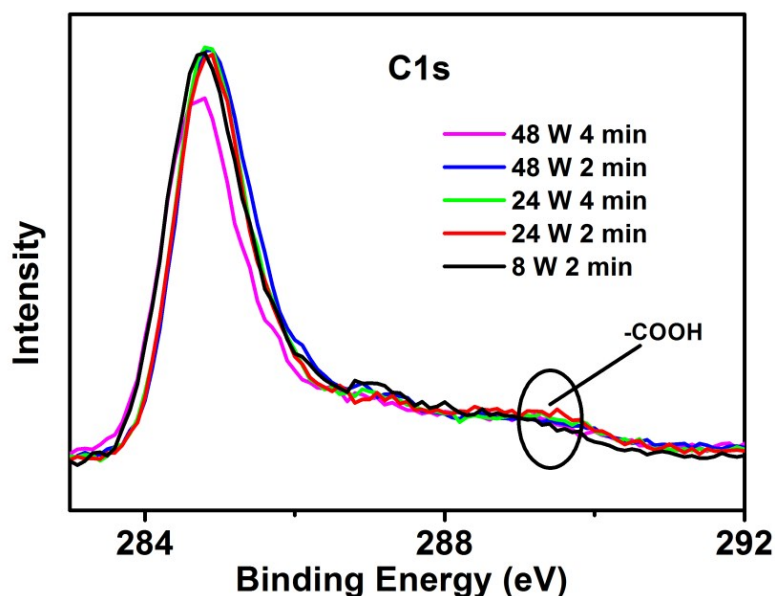
**Fig. S1** (a) The relationship of thickness dependent mobility of PDPP3T based transistor before and after  $\text{O}_2$  plasma treatment (24 W for 2 min). (b) Thickness dependent relative change in mobility of PDPP3T based transistor after plasma treatment (24 W, 2 min).



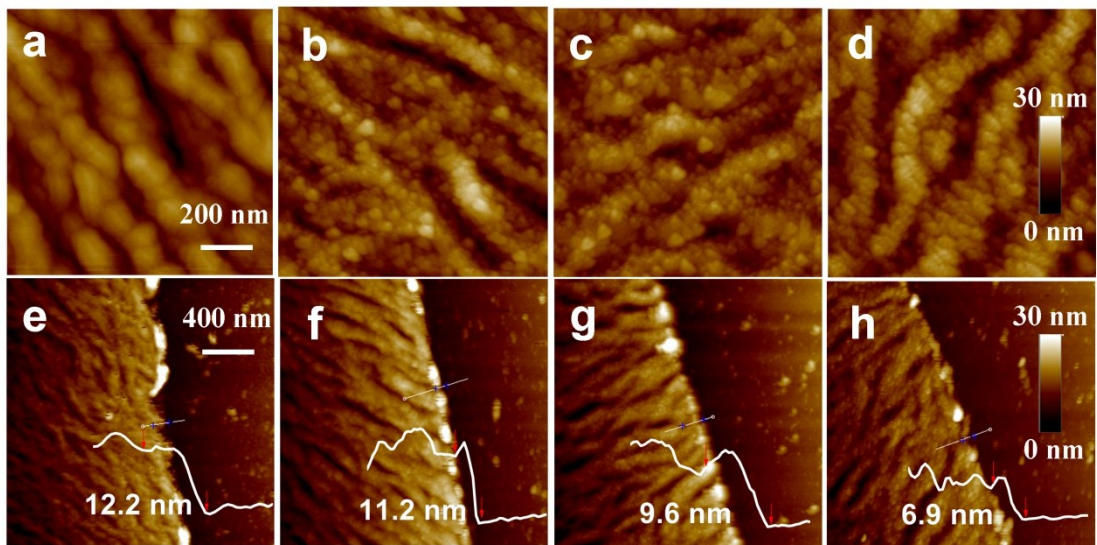
**Fig. S2** (a) Transfer and (b) output curve of PDPP3T based OTFTs with active layer thickness of 12 nm.



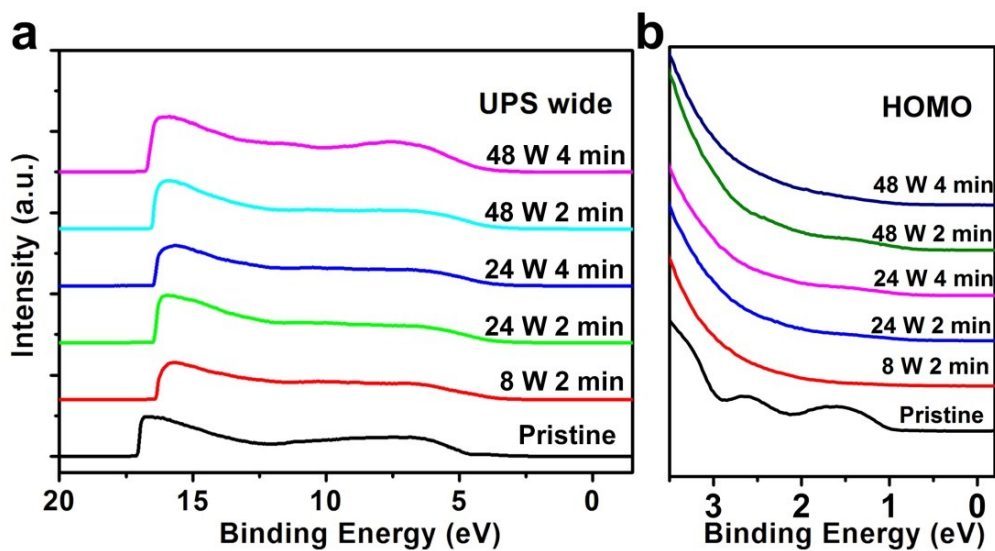
**Fig. S3** Chemical structure of (a) pentacene, and (b) NDI(2OD)(4tBuPh)-DTYM2. (c) Relative change in mobility after O<sub>2</sub> plasma treatments with different power and a fixed treatment time of 2 min. Pentacene based thin film (20 nm in thickness) were prepared by thermal evaporation and NDI(2OD)(4tBuPh)-DTYM2 based thin film (12 nm in thickness) were prepared by spin-coating (5 mg mL<sup>-1</sup> in chloroform).



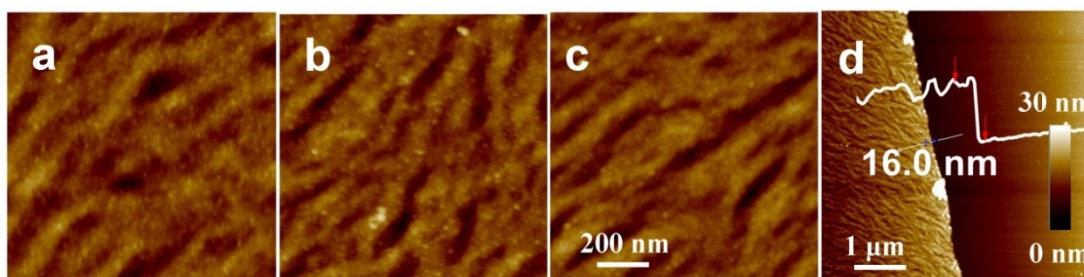
**Fig. S4** C 1s spectra of PDPP3T thin films upon O<sub>2</sub> plasma treatment at different treatment powers and exposure times.



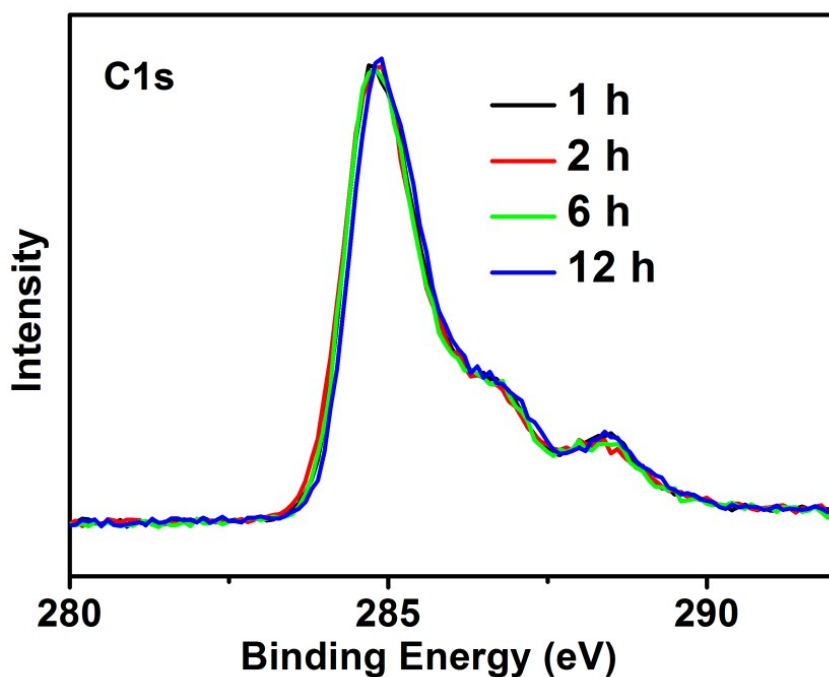
**Fig. S5** AFM images of a pristine PDPP3T film (a), (e) before and after plasma treatment at (b), (f) 24 W for 2 min, (c), (g) 48 W for 2 min, and (d), (h) 48 W for 4 min.



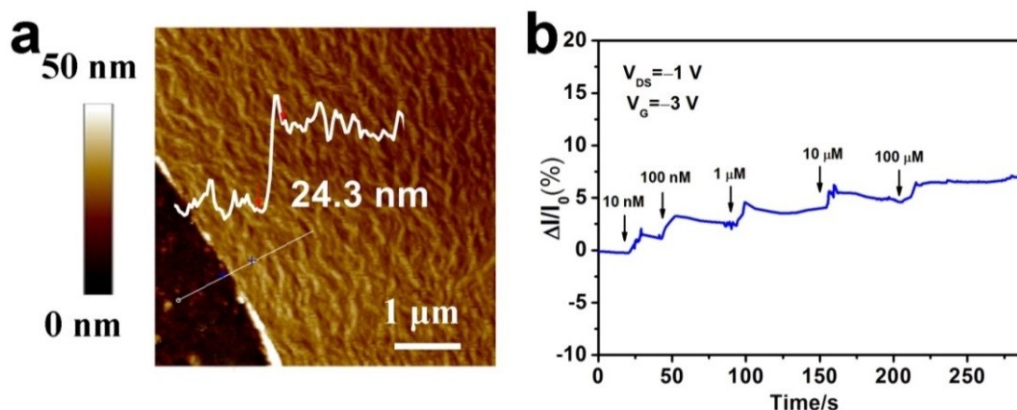
**Fig. S6** (a) Wide scan spectra and (b) low binding energy region (HOMO region) of UPS of PDPP3T films upon different O<sub>2</sub> plasma treatments.



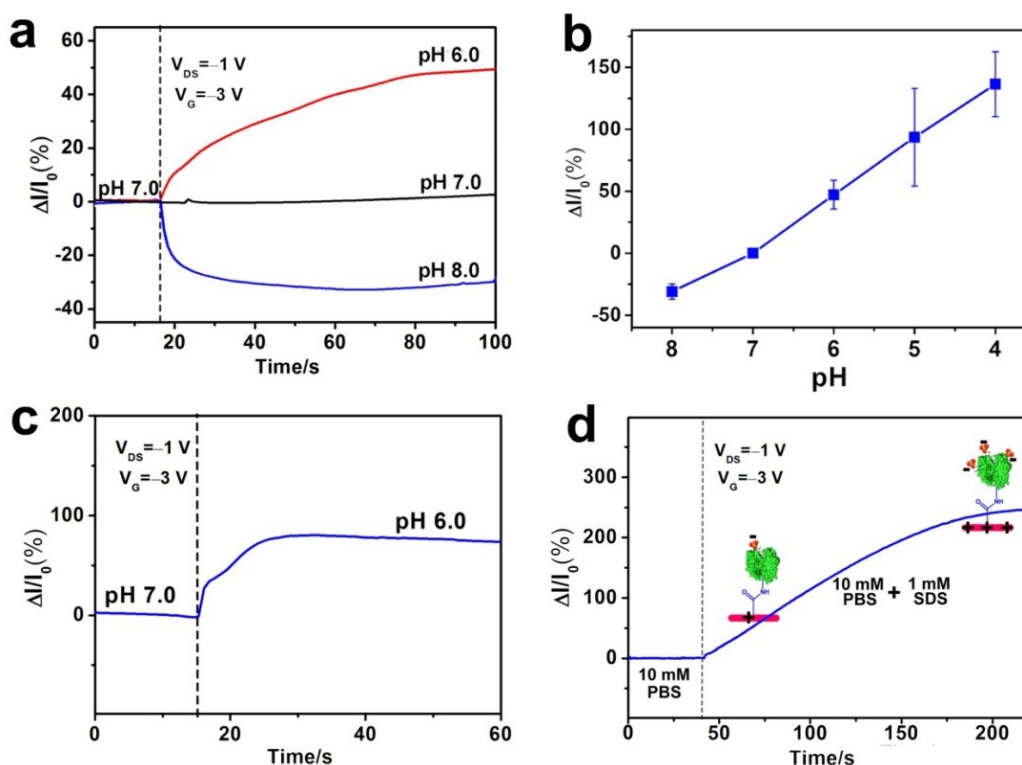
**Fig. S7** AFM images of O<sub>2</sub> plasma treated PDPP3T films after apyrase functionalization for (a) 1 h, (b) 6 h, and (c) 12 h. (d) AFM images of O<sub>2</sub> plasma treated PDPP3T films after apyrase functionalization for 12 h. The thickness increases from 11.2 nm to 16.0 nm, which corresponds to the attachment of an apyrase monolayer. The molecular diameter of apyrase (M<sub>w</sub>=49 kDa) was estimated to be ~5 nm.



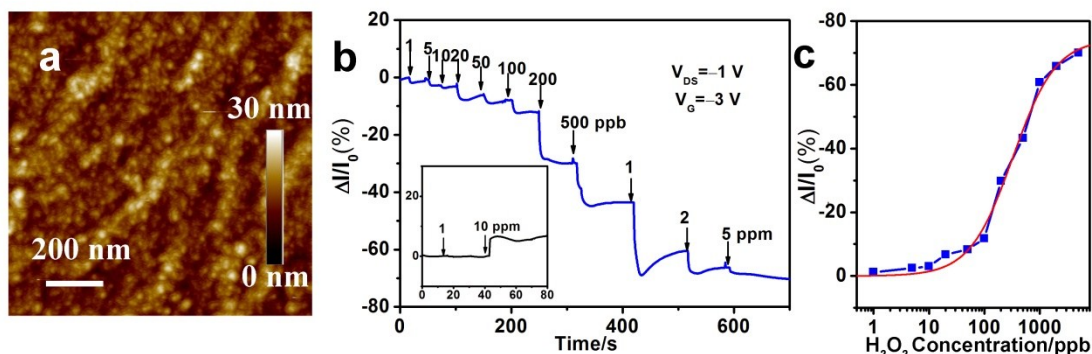
**Fig. S8** C 1s spectra of apyrase modified PDPP3T films with different functionalization time.



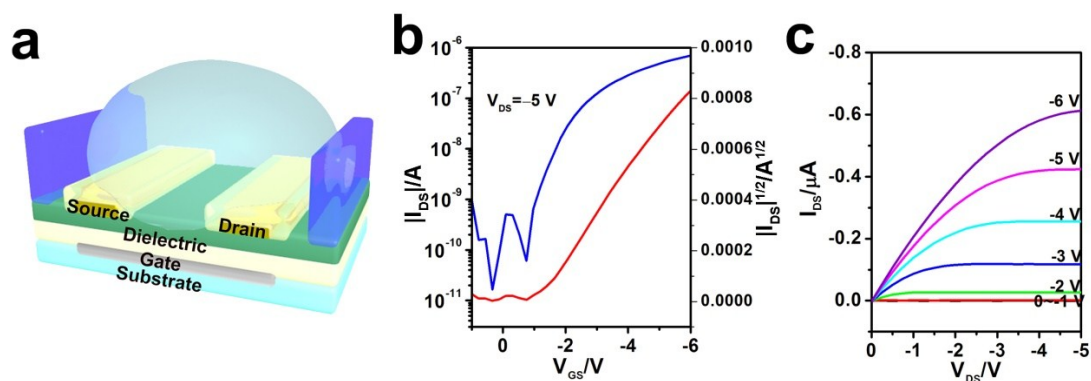
**Fig. S9** (a) AFM image of a PDPP3T film with a thickness of 24 nm. (b) Real-time sensing  $I_{DS}$  responses to ATP with concentration ranging from 10 nM to 100  $\mu$ M.



**Fig. S10** (a) Real time  $\Delta I/I_0$  of untreated PDPP3T films to varied pH values (10 mM PBS buffer). (b) Statistic  $\Delta I/I_0$  versus pH ranging from 8.0 to 4.0 of five individual devices. (c) Real time  $\Delta I/I_0$  of an apyrase functionalized device when the pH value changes from 7.0 to 6.0 (0.1 mM HEPES, 5 mM  $\text{CaCl}_2$ ). (d) Real time  $\Delta I/I_0$  of an apyrase functionalized device to the addition of SDS (1 mM in 10 mM PBS buffer, pH 7.4).

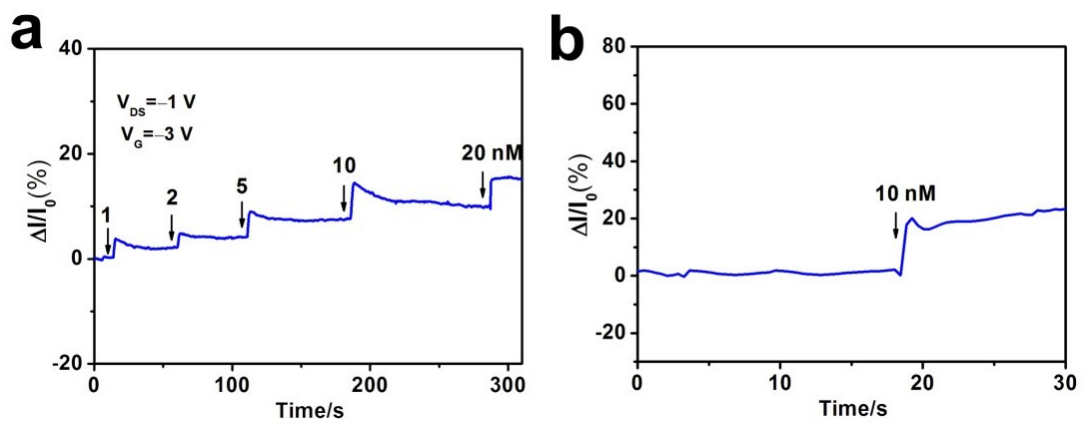


**Fig. S11** (a) AFM images of a PDPP3T film functionalized by catalase. The functionalization is realized by immersing the device in a PBS (10 mM, pH 7.4) buffered catalase (Sigma-Aldrich, EC 1.11.1.6, 0.1 mg mL<sup>-1</sup>) solution for over 1 h. (b) Real-time sensing response of catalase functionalized device to H<sub>2</sub>O<sub>2</sub> (buffered PBS media, 0.1 mM, pH 7.4) with different concentrations. Inset: real-time sensing current response of an untreated PDPP3T device to H<sub>2</sub>O<sub>2</sub>. (c) H<sub>2</sub>O<sub>2</sub> concentration dependent relative current change of catalase functionalized device.



**Fig. S12** (a) Schematic illustration of a flexible sensor with aluminum (Al) gate (30 nm) and parylene dielectric (50 nm) on a PET substrate. (b) Transfer and (c) output curves of a PDPP3T OFET with parylene dielectric layer. The Al gate was thermally evaporated on the substrate and the parylene layer was deposited by an SCS Labcoater (PDS 2010).





**Fig. S13** (a) Real time  $I_{DS}$  responses of a flexible sensing pixel to a series of ATP concentrations. (b) A flexible sensing device driven by two batteries, where the  $V_{DS}$  and  $V_{GS}$  were fixed to be  $-1.5$  and  $-3.0$  V, respectively.