Supplementary information

Chemically and physically enhanced adhesion for robust interfaces in all-soft vertical organic photodetectors

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Experimental Section

Materials

PDMS (Sylgard 184, silicone elastomer) was purchased from Dow-Corning. Dimethyl sulfoxide (DMSO; >99.9%), Tergitol 15-s-9, polyurethane diol solution (PUD; average M_n ~320, 88 wt% in H_2O), dichloromethane (DCM; >99.5%), chloroform (CF; >99.5%), polyethylenimine 80% ethoxylated solution (PEIE; $M_W = 110{,}000$, 37 wt% in H_2O), (3-glycidyloxypropyl)trimethoxysilane (GPTMS), poly(3-hexylthiophene-2,5-diyl) (P3HT; $M_W = 50{,}000 - 100{,}000$), [6,6]-Phenyl-$C_{71}$-butyric acid methyl ester ($PC_{71}BM$) were purchased from Sigma-Aldrich. (3-aminopropyl)triethoxysilane (APTES) was purchased from Thermo Fisher Scientific. Polyimide (PI) film was purchased from Alphaflon. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Heraeus Clevios PH1000) was purchased from Ossila. Isopropyl alcohol (IPA) was purchased from Sanchun Chemical. All materials were used as received without further purification process.

Preparation of PUD/PEDOT:PSS and PEIE solutions

For the preparation of the PUD/PEDOT:PSS solution, PEDOT:PSS was mixed with 1 wt% Tergitol 15-s-9, 5 wt% DMSO, and the desired content (wt%) of PUD. The mixture was gently stirred at 400 rpm for 30 mins and subsequently stored in a refrigerator at 4°C until needed. The PEIE solution was prepared by dissolving PEIE in IPA at a concentration of 1 wt%. This solution was stirred at 400 rpm for 10 mins and then refrigerated at 4°C before use.

Preparation of P3HT-NFs:$PC_{71}BM$/PDMS solution

Firstly, liquid PDMS was prepared with a 10:1 weight ratio of base and curing agent. Then, the PDMS precursor was dissolved in DCM with a concentration of 160 mg/ml to prepare PDMS solution. P3HT and $PC_{71}BM$ were dissolved in DCM at a concentration of 4 mg/ml and heated at 90 °C for 30 mins. Thereafter, P3HT solution was kept in the refrigerator at 4 °C for 12 h resulting in the formation of the P3HT nanofibrils (P3HT-NFs), as reported.[1-3] The P3HT-NFs and $PC_{71}BM$ solutions were mixed in a 1:1 volume ratio, followed by blending with PDMS solution at a 10:1

volume ratio. The final mixture maintained a total weight ratio of the P3HT-NFs and $PC_{71}BM$ to PDMS at 1:4.

Fabrication of all-soft v-OPD

The fabrication of the all-soft v-OPD began with the preparation of liquid PDMS mixed at a 15:1 weight ratio of base to curing agent. The liquid PDMS was spin-casted onto a glass substrate at 400 rpm for 30 s and then solidified at 100°C in a convection oven for 30 mins. The prepared PDMS substrates were treated by UV-O_3 for 20 mins. Subsequently, two separate UV-O_3 treated PDMS substrates were immersed in solutions of GPTMS and APTES (2 wt% in DI water) for 30 mins each, to prepare anode and cathode substrates, respectively, followed by drying with N_2 gas. PI-based shadow masks with the desired patterns, prepared using a programmable cutting machine (Silhouette Portrait 3, Silhouette America Inc.), were laminated onto the GPTMS-PDMS and APTES-PDMS, respectively, to define the electrode areas. For the anode, a PUD/PEDOT:PSS solution was spin-casted at 1500 rpm for 30 s onto the GPTMS-PDMS with a shadow mask, followed by a 5 min heating at 80°C after shadow mask removal, completing the anode substrate preparation. The cathode was formed by spin-casting a PEIE solution at 4000 rpm for 30 s immediately after the formation of the PUD/PEDOT:PSS layer, followed by annealing for 10 min at 80°C after shadow mask removal. Next, the desired volume of the P3HT-NFs:$PC_{71}BM$/PDMS solution was drop-casted onto the cathode and thermally annealed at 120°C for 20 min to form the soft light-sensing layer (approximately 1.5 μm-thick), completing the cathode substrate preparation. Finally, the anode and cathode substrates were aligned and vertically assembled using a customized aligner, and the resultant device was heated at 80°C for 10 mins to ensure robust chemical interfacial adhesion of the device.

Characterization of materials and devices

The electrical properties of the PUD/PEDOT:PSS electrodes and the P3HT-NFs:$PC_{71}BM$/PDMS light-sensing layer were characterized by a semiconductor analyser (4200-SCS, Keithley Instruments Inc.) and LCR meter (E4980A, Keysight Technologies Inc.). For the characterization under the mechanical strains, programmable stretching machine

(Bending&stretchable machine system, SNM Korea) was additionally utilized. A spectrophotometer (V-670, JASCO Inc.) was employed to characterize the transmission and absorption properties of the electrodes and light-sensing layers in the visible light region. The mechanical properties of the substrates, electrodes, and light-sensing layers were characterized using a motorized force tester (ESM 750, Mark-10 Corp.) equipped with force gauges (M5-2 or M7-50, Mark-10 Corp.), which were selectively used depending on the force levels. The device characteristics of the all-soft v-OPDs were measured with precision source/measure unit (B2912B, Keysight Technologies Inc.) and white light emitting diode (MCWHL5, Thorlab Inc). The customized stretcher was additionally used for characterize device performance under mechanical strains.

References

1 J. Y. Oh, M. Shin, T. I. Lee, W. S. Jang, Y. Min, J.-M. Myoung, H. K. Baik and U. Jeong, *Macromolecules*, 2012, **45**, 7504-7513.

2 H. Park, S. Kim, J. Lee, I. Lee, S. Bontapalle, Y. Na and K. Sim, *Nat. Electron.*, 2024, **7**, 39-50.

3 K. Sim, Z. Rao, H. J. Kim, A. Thukral, H. Shim and C. Yu, *Sci. Adv.*, 2019, **5**, eaav5749.

Supplementary Figures.

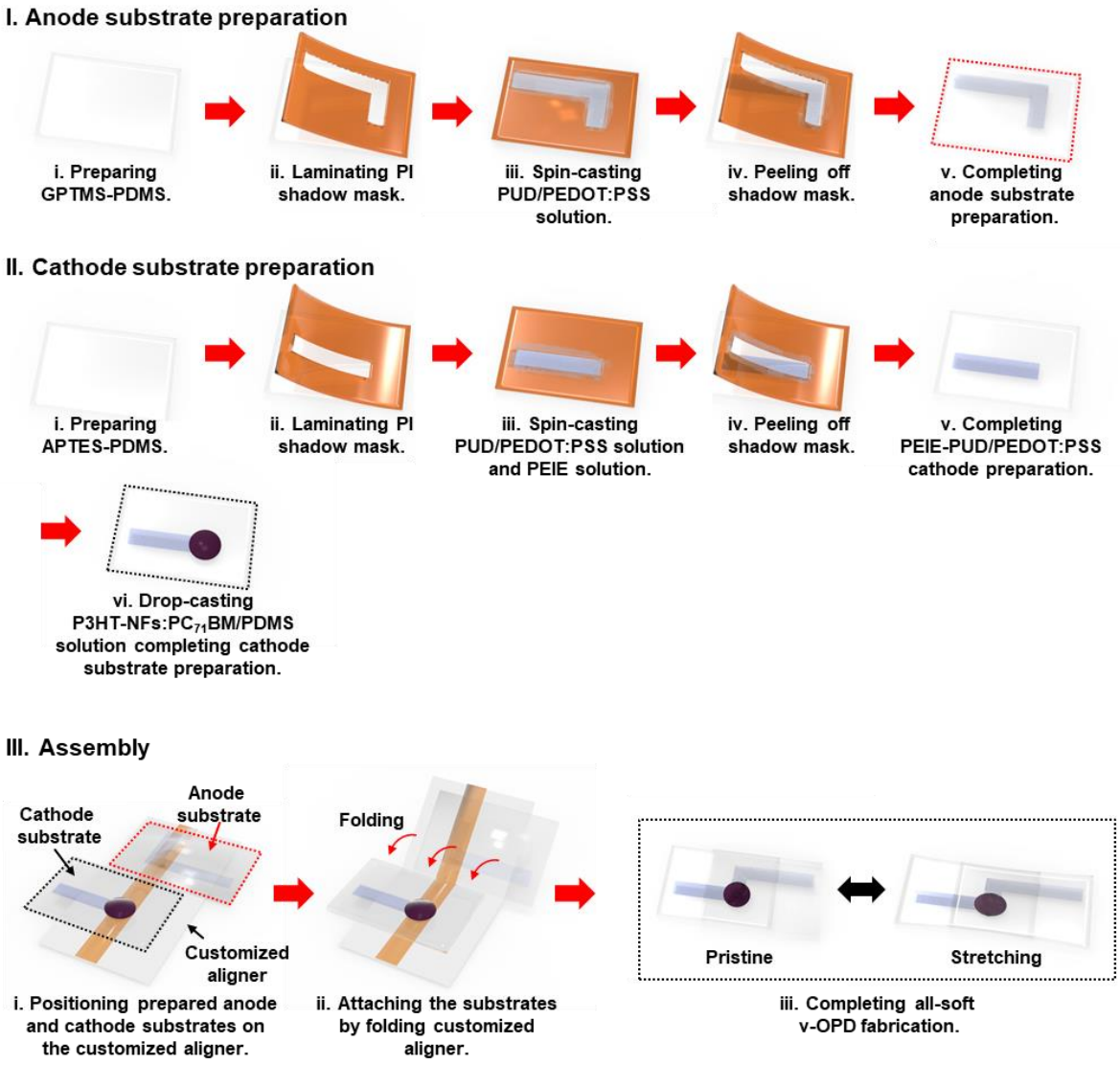

Fig. S1 A schematic fabrication process of the all-soft v-OPDs.

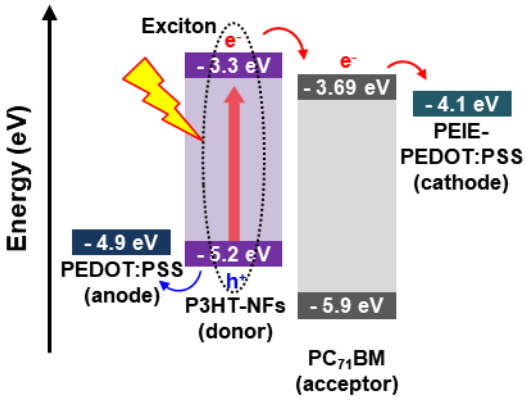

Fig. S2 The energy diagram of the all-soft v-OPDs. When visible light illuminates the all-soft v-OPDs, photons are primarily absorbed by P3HT-NFs (electron donor), generating excitons. These excitons diffuse and dissociate at the interfaces of P3HT-NFs and $PC_{71}BM$ (electron acceptor), resulting in free charge carriers. Finally, holes and electrons transport through the P3HT-NFs and $PC_{71}BM$ phases, respectively, and are collected by the anode and cathode.

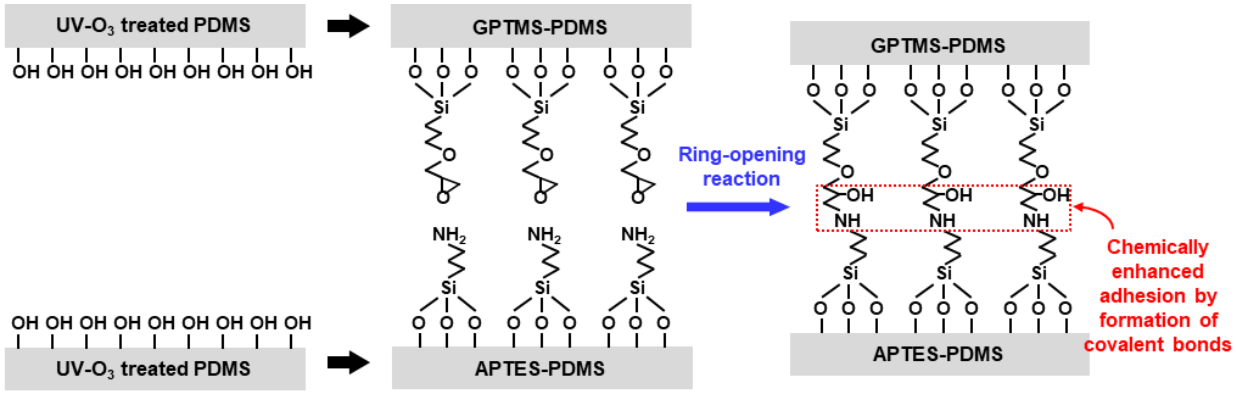

Fig. S3 A schematic mechanism of the chemically enhanced adhesion between GPTMS-PDMS and APTES-PDMS.

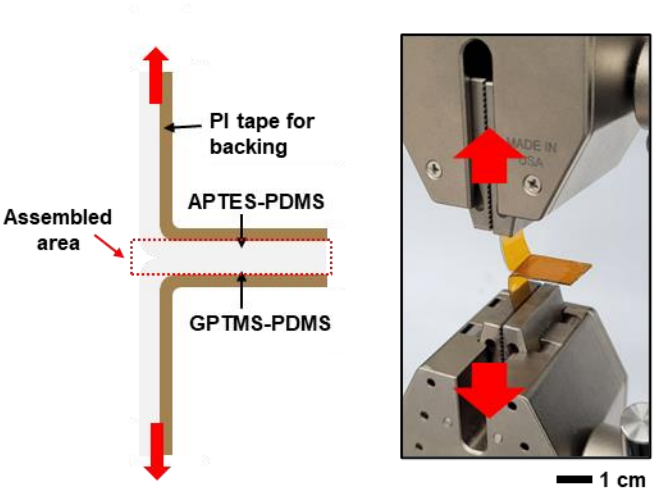

Fig. S4 A schematic (left) and an optical image (right) of the t-peeling for the assembled PDMS.

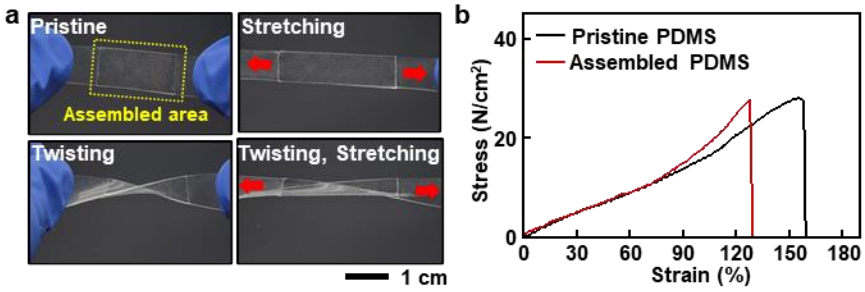

Fig. S5 Mechanical characteristics of the assembled PDMS. (a) Optical images of the assembled PDMS under various deformations. **(b)** The stress-strain curves of the pristine and assembled PDMS.

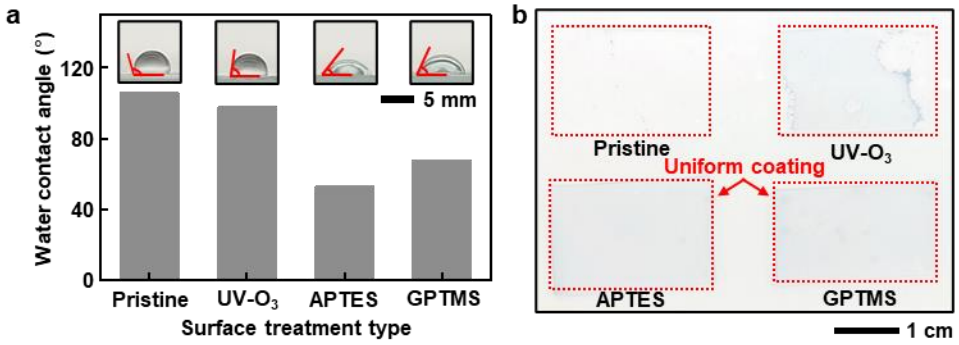

Fig. S6 Uniform coating of the PUD/PEDOT:PSS electrodes on the silane-treated PDMS. (a) Comparison of water contact angles on the PDMS surface treated with various methods. Inset is the corresponding images. **(b)** Comparison of coating uniformity of the electrodes on the PDMS surface-treated with various methods. Note that 15 wt% of PUD was incorporated into the PUD/PEDOT:PSS electrodes.

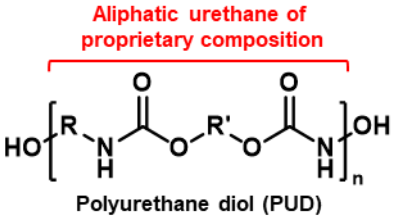

Fig. S7 The molecular structure of the PUD.

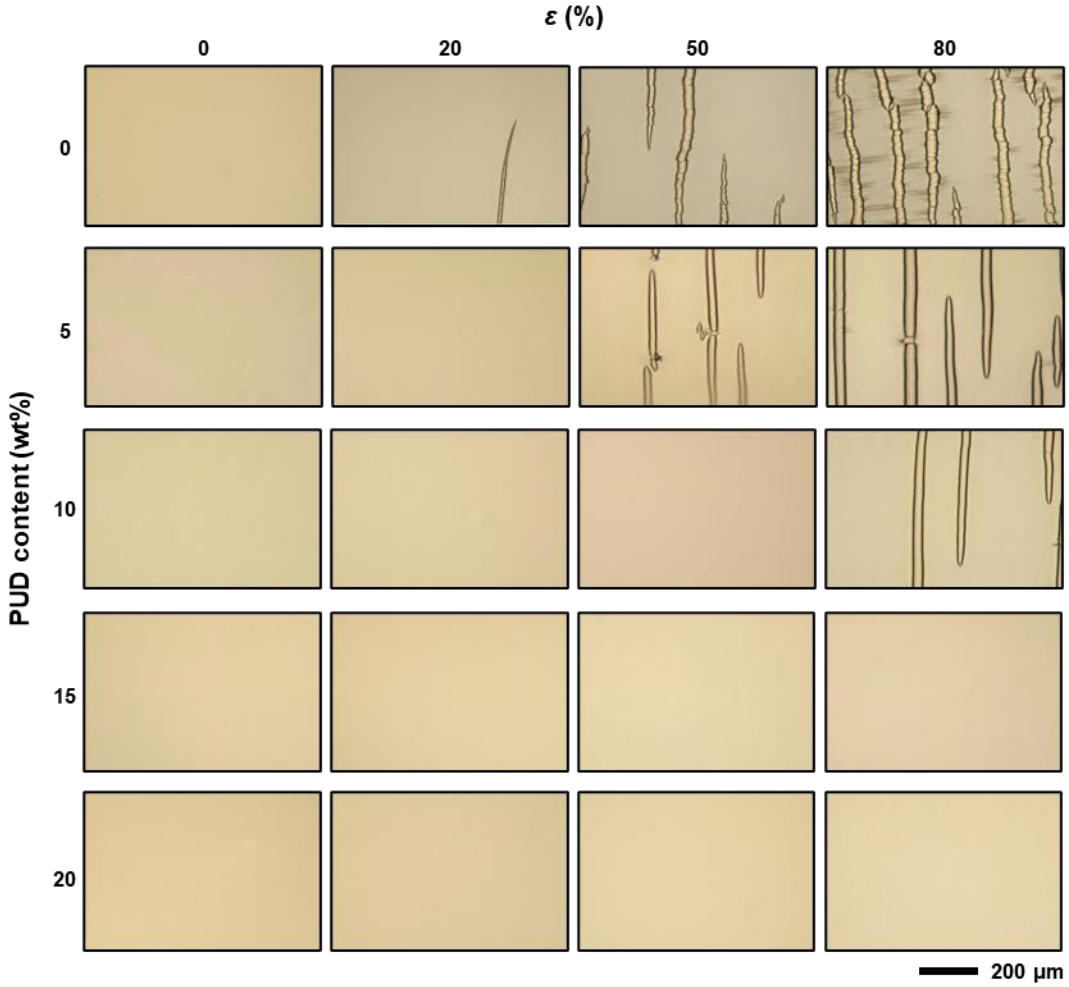

Fig. S8 Optical microscopic images of the PUD/PEDOT:PSS electrodes with different PUD content under the mechanical strains (*ε*).

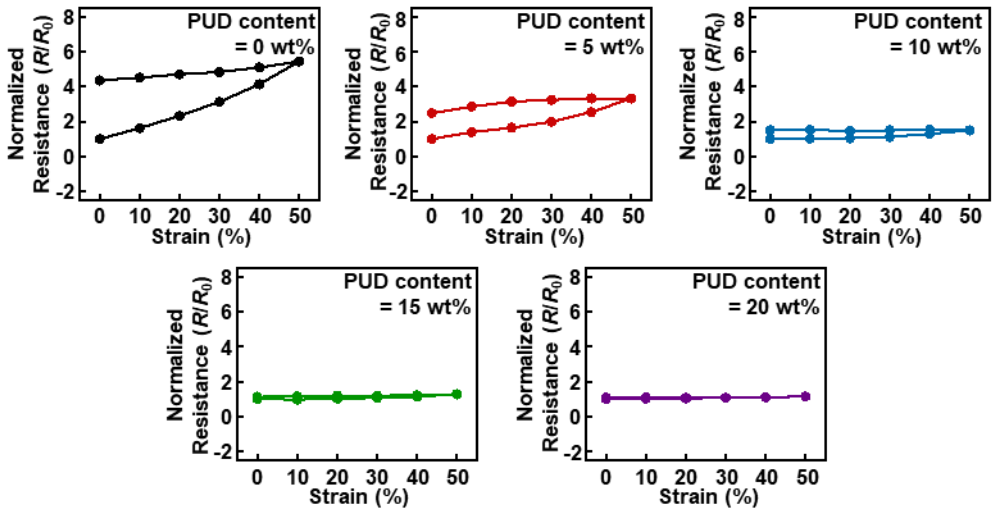

Fig. S9 Normalized resistance hysteresis of the PUD/PEDOT:PSS electrodes with different PUD content.

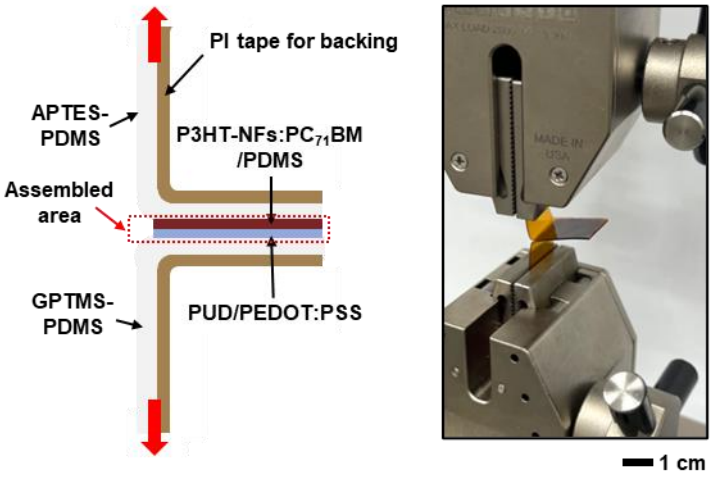

Fig. S10 A schematic (left) and an optical image (right) of the t-peeling test between the light-sensing layers and the electrodes.

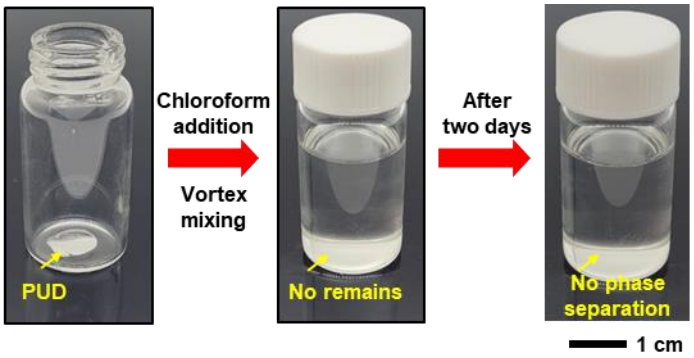

Fig. S11 Optical images of the PUD dissolution in the chloroform.

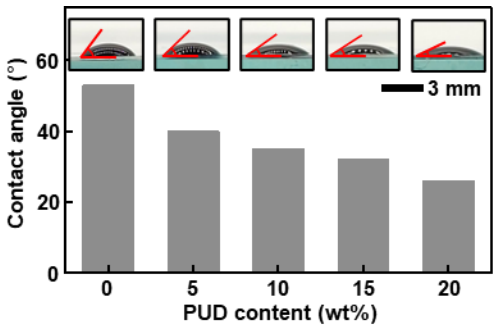

Fig. S12 Contact angles of P3HT-NFs:$PC_{71}BM$/PDMS solution on the PUD/PEDOT:PSS electrodes with different PUD content.

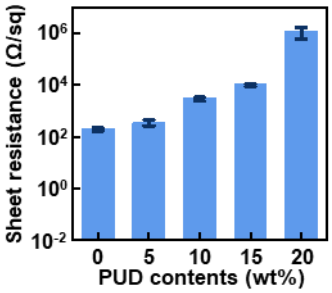

Fig. S13 The sheet resistance of the PUD/PEDOT:PSS electrodes with different PUD content. (*n* = 5)

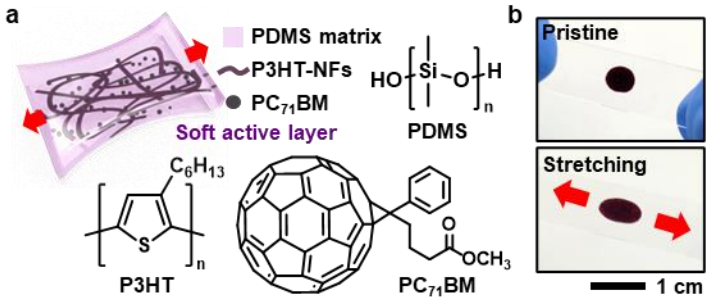

Fig. S14 Soft light-sensing layer. (a) A schematic of the soft light-sensing layer and composing molecules. **(b)** Optical images of the soft light-sensing layer under mechanical stretching.

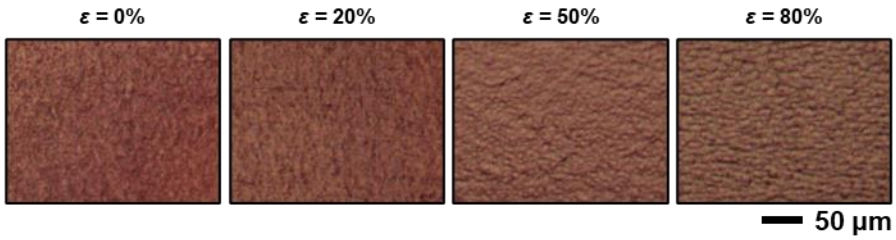

Fig. S15 Optical microscopic images of the soft light-sensing layer under various mechanical strains (ε).

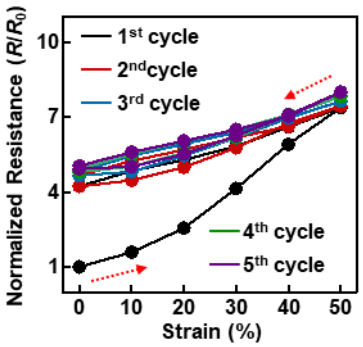

Fig. S16 Normalized resistance hysteresis of the soft light-sensing layer during 5 cycles of cyclic stretching.

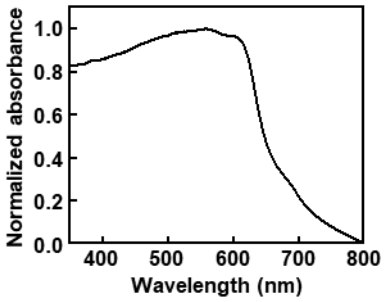

Fig. S17 The UV-Vis absorption spectrum of the soft light-sensing layer.

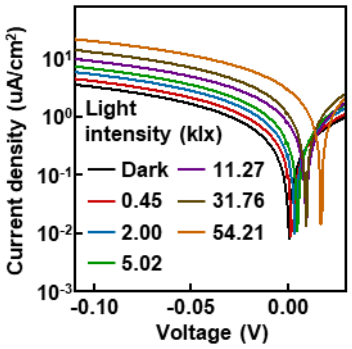

Fig. S18 Current profiles of the all-soft v-OPDs in the dark and under various intensities of light illumination.

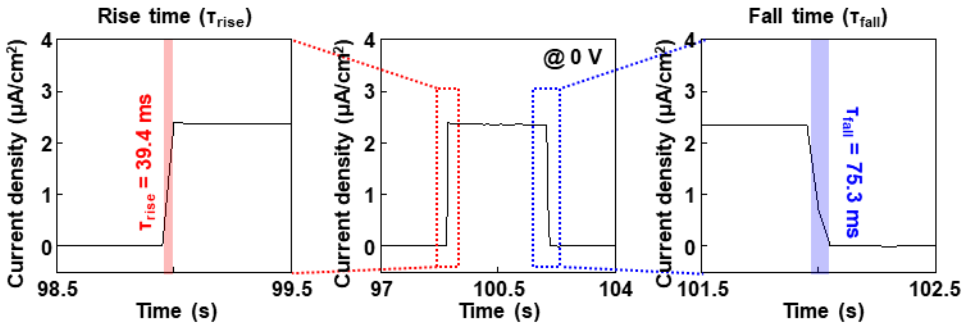

Fig. S19 The response time of the all-soft v-OPDs.

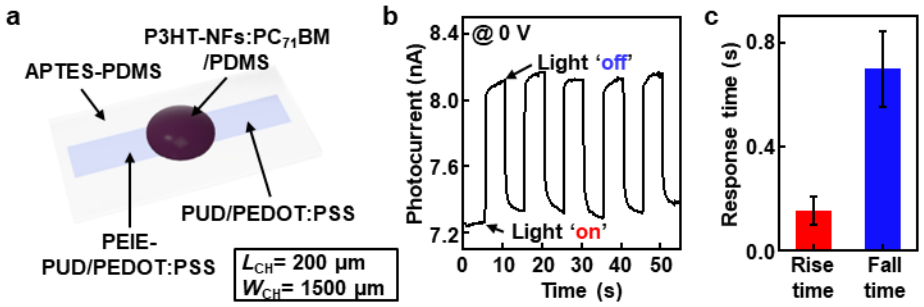

Fig. S20 Device performance of the planar-type all-soft organic photodetector. (a) A schematic of the planar-type all-soft organic photodetectors. **(b)** The dynamic photoresponse of the device during 5 light on/off cycles at 0 V (Intensity of the light: 52.85 klx). **(c)** The response time of the device (n = 5).