Electronic Supplementary Information (ESI)

Highly Sensitive All-polymer Photodetectors with Ultraviolet-visible to Near-infrared Photo-detection and its Application as Optical Switch

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Experimental section

Device fabrication: The patterned indium tin oxide (ITO) coated glass substrates (~10 Ω per square) were cleaned via sequential sonication in detergent, de-ionized and ethanol and then blow-dried by high-purity nitrogen. All pre-cleaned ITO substrates were treated by oxygen plasma for 1 minute to improve their work and clearance. Subsequently, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) function (PEDOT:PSS, purchased from H.C. Starck co. Ltd.) solution was spin-coated on ITO substrates at 5000 RPM for 40 s and dried at 150 °C for 15 min in atmospheric air. Then ITO substrates coated with PEDOT:PSS films were transferred into a high-purity nitrogen-filled glove box. The P-TPD (purchased from 1 material) was dissolved in chlorobenzene to prepare 1 mg/ml and 2 mg/ml pure solution. The employed materials PMBBDT (received from Prof. W. Li's group),¹ N2200 (purchased from Organtec Materials Inc.) were dissolved in chlorobenzene to prepare 8mg/ml blended solutions. The weight ratios of PMBBDT:N2200 blended solution are 100:1, 100:3, 100:5, 100:7, 100:9. For the PM-APPDs without P-TPD layer, the blended solutions were spin-coated on the PEDOT:PSS/ITO substrate with 800 RPM for 30 s to prepare photoactive layers with the thickness about 250 nm. The prepared photoactive layers were annealed on a hot platform at 100 °C for 10 min to dry the wet blended films. For the device with P-TPD layer, the 1 mg/ml and 2 mg/ml P-TPD solutions were spin-coated on the PEDOT:PSS/ITO substrate with 4000 RPM for 30 s to prepare hole transport layers with the thickness about 10 nm and 20 nm, respectively. The prepared P-TPD layers were annealed on a hot platform at 100 °C for 5 min. Then, the photoactive layers were spin-coated on P-TPD layer with the process mentioned above. Under 10-4 Pa condition in vacuum chamber, 70 nm Au film was finally deposited onto the active layers based on the thermal evaporation method. The photoactive area of the PM-APPDs is defined by the vertical overlap of ITO and Au electrode, approximate 3.8 mm2 in this study.

Device characterization: Current versus voltage (I-V) curves of the PM-APPDs was scanned by using a Keithley-2400 source meter. A monochromatic light can be obtained by the combination of a 150 W xenon lamp with a monochromator. The monochromatic light intensity spectrum was measured by utilizing a Thorlabs S120VC power meter. The UV-visible absorption spectra and the transmittance spectra were recorded by a SHIMADZU UV-3101 PC spectrophotometer. The photoactive layer thickness was measured using an AMBIOS Technology XP-2 stylus profilometer. The LDR of the PM-APPDs was measured under monochromatic light of 650 nm generated by diode laser. The incident light intensity was manipulated by utilizing different neutral density filters. The electrochemical impedance spectroscopy (EIS) was performed by Zahner Electrochemical Workstation. Transient photocurrent (TPC) of PM-APPDs was measured through a 803 nm light souce with 50 Hz pulse and an oscilloscope with 2.5 KHz sample rate.

| Device structure | Spectral | $J_{\rm d}$ (A cm ⁻²) | D^*_{\max} (Jones) | $R_{\rm max}$ (A/W) | EQE _{max} (%) | Ref. |
|--------------------------------|-------------|-----------------------------------|--|---------------------|------------------------|------|
| | region (nm) | (V) | (V) | (V) | (V) | |
| ITO/ZnO/PBDB-T: | | | | | | |
| PNDI-FT10 (2:1, | 300-850 | 1.1×10 ⁻⁸ (-3) | 5.8×10 ¹² (-3) ^{a)} | 0.34 (-3) | 65 (-3) | 2 |
| w/w)/P3HT/MoO ₃ /Ag | | | | | | |
| ITO/PEDOT:PSS/NT40:N | 300-850 | 4.85×10 ⁻¹⁰ (0.1) | 2.61×10 ¹³ (-0.1) ^{a)} | 0.33 (-0.1) | 58 (-0.1) | 3 |
| 2200(2:1, w/w)/PFN-Br/Al | | | | | | |
| ITO/PEDOT:PSS/PTzBI- | 300-850 | 3.77×10 ⁻⁹ (-0.1) | 9.07×10 ¹² (-0.1) ^{a)} | 0.25 (-0.1) | 55 (-0.1) | 4 |
| Ph/N2200/Ca/Al | | | | | | |
| ITO/PEDOT:PSS/P3HT:P | 300-800 | ~3.1×10 ⁻⁵ (-5) | 1.1×10 ¹² (-5) ^{b)} | 8 (-5) | 2200 (-5) | 5 |
| Z1 (100:4, w/w)/Al | | | | | | |
| ITO/PEDOT:PSS/PBDB- | 300-800 | ~8.5×10 ⁻⁶ (-10) | 1.0×10 ¹² (-10) ^{b)} | ~8 (-20) | 1470 (-20) | 6 |
| T:PZ1 (100:3, w/w)/Al | | | | | | |
| | | | | | | |

Table S1. The fundamental figures of merit of recently reported PM-PPDs all-polymer PPDs.

^{a)} the D* was estimated by the dark current; ^{b)} the D* was calculated by measured noise current.



Fig. S1. The absorption spectra of the PMBBDT:N2200 (100:3, w/w) blend film.



Fig. S2. The EQE spectra of the PM-PPDs under different applied bias.

Obviously, the EQE values of PM-APPDs are dramatically enhanced along with the increase of the applied voltage, which should be due to the strengthened hole tunneling injection and hole transport under large applied voltage. Meanwhile, maximal EQE value of optimal PM-APPDs arrives to 20700% under 4 V applied voltage, which is one of the largest values of the reported PM-APPDs under the same applied voltage.



Fig. S3. The twenty periods TPCs of the PM-APPDs with and without P-TPD layer.

The TPCs of PM-APPDs with and without P-TPD layer are nearly overlap in twenty periods, indicating the similar response time of the PM-APPD with and without P-TPD layer.



Fig. S4. The NEP spectra of the PM-APPDs with and without P-TPD layer under 2 V bias.

It is obvious that the NEP values of PM-APPDs with ~ 10 nm P-TPD layer are about 5 times lower than that of PM-APPDs without P-TPD layer. The minimum NEP of $2.6 \times 10-13$ and $1.3 \times 10-12$ W Hz-1/2 are obtained for the PM-APPDs with ~ 10 nm P-TPD layer and with P-TPD layer under 2 V applied voltage.

Reference

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