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Supporting information

Highly Sensitive Polymer Photodetectors with Broad Spectral Response Range from UV Light to NIR

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Content list:

1. Light intensity spectrum of the monochromatic lights through a monochromator.

The monochromatic light used in all measurements was provided by a 150 W xenon lamp coupled with a monochromator. Light intensity spectrum of the monochromatic lights through a monochromator was measured and is shown in **Fig. S1**.

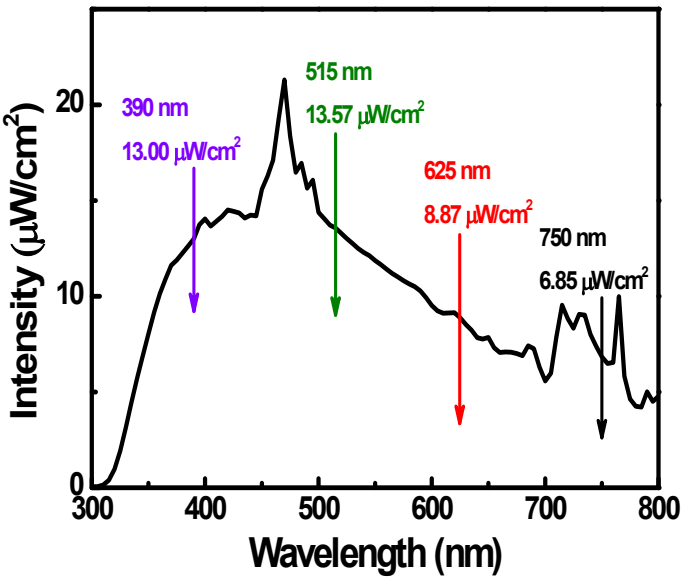
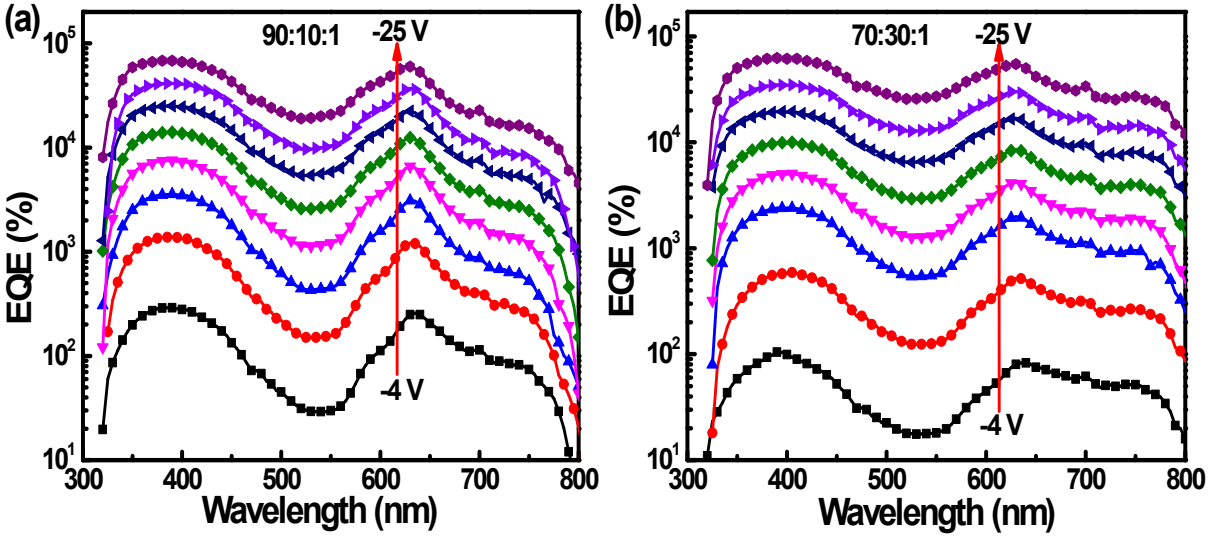


Fig. S1 Light intensity spectrum of the monochromatic lights through a monochromator.

2. EQE spectra of the PPDs with $P3HT_{100-x}$:PTB7-Th_x:$PC_{71}BM_1$ as the active layer under different applied bias, x=10, 30, 70, 90 respectively.



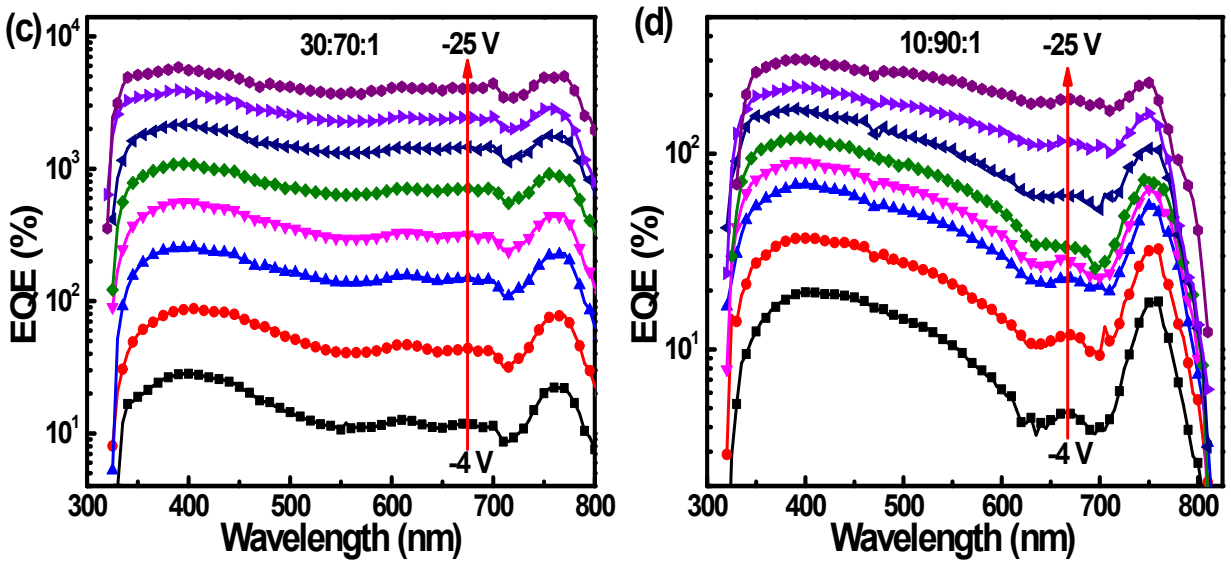


Fig. S2 EQE spectra of the PPDs under different bias from －4 V to －25 V with an interval of 3 V, (a) $P3HT_{90}$:PTB7-Th_{10}:$PC_{71}BM_1$; (b) $P3HT_{70}$:PTB7-Th_{30}:$PC_{71}BM_1$; (c) $P3HT_{30}$:PTB7-Th_{70}:$PC_{71}BM_1$; (d) $P3HT_{10}$:PTB7-Th_{90}:$PC_{71}BM_1$ as the active layer.

The EQE spectra of PPDs with $P3HT_{90}$:PTB7-Th_{10}:$PC_{71}BM_1$, $P3HT_{70}$:PTB7-Th_{30}:$PC_{71}BM_1$, $P3HT_{30}$:PTB7-Th_{70}:$PC_{71}BM_1$, $P3HT_{10}$:PTB7-Th_{90}:$PC_{71}BM_1$ as the active layer are shown in **Fig. S2.** The detailed EQE values of all the PPDs at different reverse bias and light illumination are shown in **Table S1**. It is apparent that EQE values of PPDs at 390 nm and 625 nm are monotonously decreased along with the increase of PTB7-Th doping ratio in donors. However, the EQE values of the PPDs at 750 nm are increased and then decreased along with the increase of PTB7-Th doping ratio in donors. In addition, the dips in the EQE spectral range from 490 nm to 570 nm become less and less obvious along with the increase of PTB7-Th doping ratio in donors, which should be attributed to the decreased photon harvesting by P3HT in this spectral range. However, the dip in the EQE spectral range from 600 nm to 710 nm become more and more obvious along with the increase of PTB7-Th doping ratio in donors. This phenomenon can further confirm that the EQE spectral dip should be attributed to the weakened trap-assisted hole tunneling injection.

3. The detailed EQE values of all the PPDs at different reverse bias and different wavelength light illumination.

Table S1. EQE values of the P3HT:PTB7-Th:$PC_{71}BM$ PPDs with different PTB7-Th doping ratio in donors under 390 nm, 515 nm, 625 nm and 750 nm light illumination.

P3HT:PTB7-Th:$PC_{71}BM$	λ (nm)	EQE (%)				
		−4 V	−10 V	−16 V	−22 V	−25 V
100:0:1	390	480	7,600	21,500	58,400	90,700
	515	50	1,200	4,690	15,900	27,600
	625	505	7,200	20,700	55,000	84,100
	750	13	76	256	610	850
90:10:1	390	290	3,500	14,000	41,200	68,000
	515	31	445	2,500	9,600	18,900
	625	225	2,900	11,900	35,700	59,700
	750	74	523	2,400	7,900	15,300
70:30:1	390	105	2,400	9,800	34,700	62,600
	515	18	550	2,900	12,700	25,700
	625	75	1,900	8,370	29,900	54,400
	750	51	952	4 000	14 400	27 200
50:50:1	390	98	1,840	7,600	25,700	45,500
	515	34	708	3,600	13,200	24,800
	625	72	1,400	6,190	20,900	37,800
	750	72	1,220	6,230	20,900	38,000
30:70:1	390	28	255	1,100	3,930	5,840
	515	12	152	676	2,400	3,900
	625	12	154	699	2,400	3,990
	750	20	205	868	2,800	4,880
10:90:1	390	19	70	122	222	303
	515	13	48	82	170	250
	625	4	23	38	113	186
	750	17	54	75	160	230
0:100:1	390	27	55	88	121	145
	515	23	49	82	119	143
	625	6	20	49	85	115
	750	25	51	82	116	130

4. The EQE spectra of PPDs and the absorption spectra of the active layers.

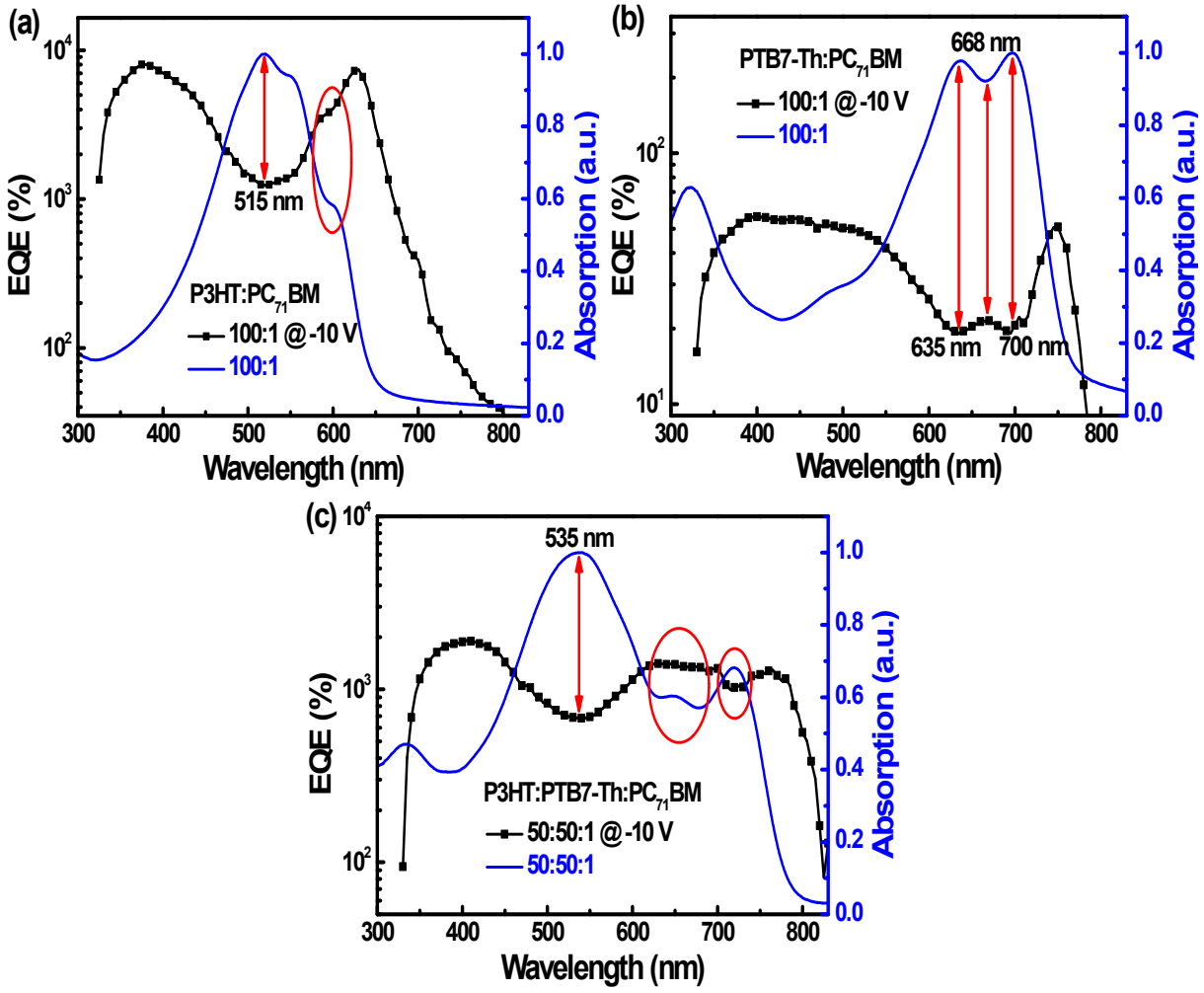


Fig. S3 EQE spectra of the PPDs with different PTB7-Th doping ratio in donors under －10 V bias, (a) $P3HT_{100}$:$PC_{71}BM_1$; (b) PTB7-Th_{100}:$PC_{71}BM_1$; (c) $P3HT_{50}$:PTB7-Th_{50}:$PC_{71}BM_1$ as the active layer.

It is apparent that the characteristics of EQE spectra of the PPDs are well accord with those of absorption spectra of the blend films. The detailed characteristics are marked in the **Fig. S3**.

5. Responsivity and detectivities of the PPDs.

The responsivity and detectivity dependence on light wavelength of all PPDs were calculated under –10 V bias and are shown in **Fig. S4.**

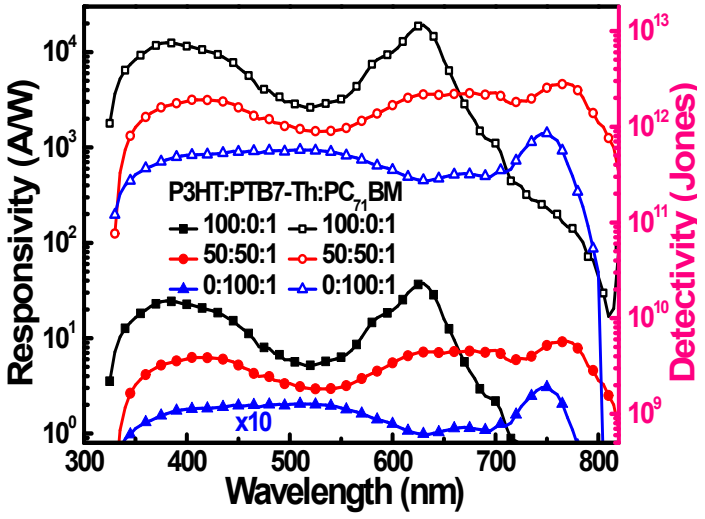


Fig. S4 The calculated specific responsivity and detectivity of the PPDs with different PTB7-Th doping ratio in donors under －10 V bias.

6. The detailed responsivity and detectivity of PPDs at different reverse bias and different wavelength light illumination.

Table S2. Responsivity and detectivity of the P3HT:PTB7-Th:$PC_{71}BM$ PPDs with different PTB7-Th doping ratio in donors under 390 nm, 625 nm and 750 nm light illumination.

P3HT:PTB7-Th:$PC_{71}BM$	λ (nm)	-10 V		-25 V	
		Responsivity (A/W)	Detectivity (Jones)	Responsivity (A/W)	Detectivity (Jones)
100:0:1	390	23.97	7.37×10^{12}	284.91	2.28×10^{13}
	625	36.54	1.12×10^{13}	423.39	3.39×10^{13}
	750	0.46	1.42×10^{11}	5.15	4.12×10^{11}
50:50:1	390	5.77	1.76×10^{12}	142.87	1.19×10^{13}
	625	7.04	2.14×10^{12}	189.74	1.58×10^{13}
	750	8.38	2.55×10^{12}	229.51	1.91×10^{13}
0:100:1	390	0.17	4.85×10^{11}	0.45	3.86×10^{11}
	625	0.10	2.79×10^{11}	0.58	4.93×10^{11}
	750	0.31	8.58×10^{11}	0.79	6.68×10^{11}

7. Current density-voltage (*J-V*) curves of the PPDs in dark and under different light illumination.

Current density-voltage (*J-V*) curves of all the PPDs were measured in dark or under 625 nm

light illumination with an intensity of 8.87 μW/cm^2 or 750 nm light illumination with an intensity of 6.85 μW/cm^2, respectively, as shown in **Fig. S4**. For the PPDs with P3HT:$PC_{71}BM$ (100:1) as the active layer, current density of the PPDs under 750 nm light illumination is comparable to that in dark, indicating that fewer holes can be injected into the active layer at this wavelength light illumination, which agrees well with the EQE spectra and the transient photocurrent of the PPDs. Meanwhile, current density of the P3HT:$PC_{71}BM$ (100:1) PPDs under 625 nm light illumination is much larger than that in dark, this phenomenon is clear evidence of enhanced hole injection assisted by trapped electrons in $PC_{71}BM$ near Al cathode due to more electrons trapped in $PC_{71}BM$ under 625 nm light illumination. Current density of the PPDs under 625 nm light illumination is decreased along with the increase of PTB7-Th doping ratio up to 50 wt % in donors, however, the current density under 750 nm light illumination is increased. For the PPDs with P3HT:PTB7-Th:$PC_{71}BM$ (50:50:1) as the active layer, current density of the PPDs under 625 nm light illumination is comparable to that under 750 nm light illumination, resulting in the similar EQE values in the large spectral range. It is apparent that the current density of the PPDs under 625 nm or 750 nm light illumination is decreased along with the further increase of PTB7-Th doping ratio in donors, which well accords with the EQE spectra of PPDs. For the active layer with relatively high PTB7-Th doping ratio in donors, fewer holes can be injected into the active layer due to the relatively large hole injection barrier from Al cathode onto the HOMO of PTB7-Th.

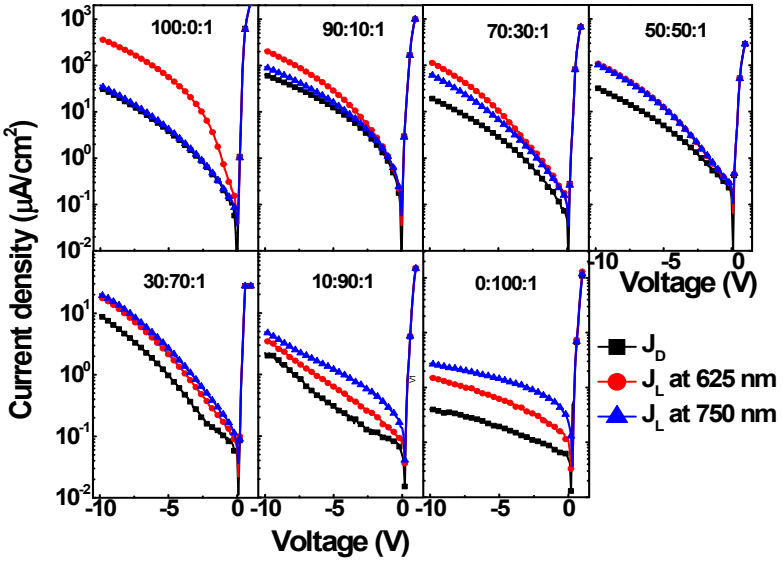


Fig. S5 Current density-voltage (*J-V*) curves of the P3HT:PTB7-Th:$PC_{71}BM$ PPDs measured in

dark or under 625 nm light illumination with intensity of 8.87 μW/cm^2 or 750 nm light illumination with intensity of 6.85 μW/cm^2, respectively.