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Supporting Information

Balancing the performance and stability in organic photodiodes with all polymer active layer

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Content

1. Photoelectron spectroscopy in air (PESA) measurements

Photoelectron spectroscopy in air (PESA) measurements were recorded using a Riken Keiki PESA spectrometer with a power setting of 10 nW and a power number of 0.3. Samples for PESA were prepared on glass substrates.[1]

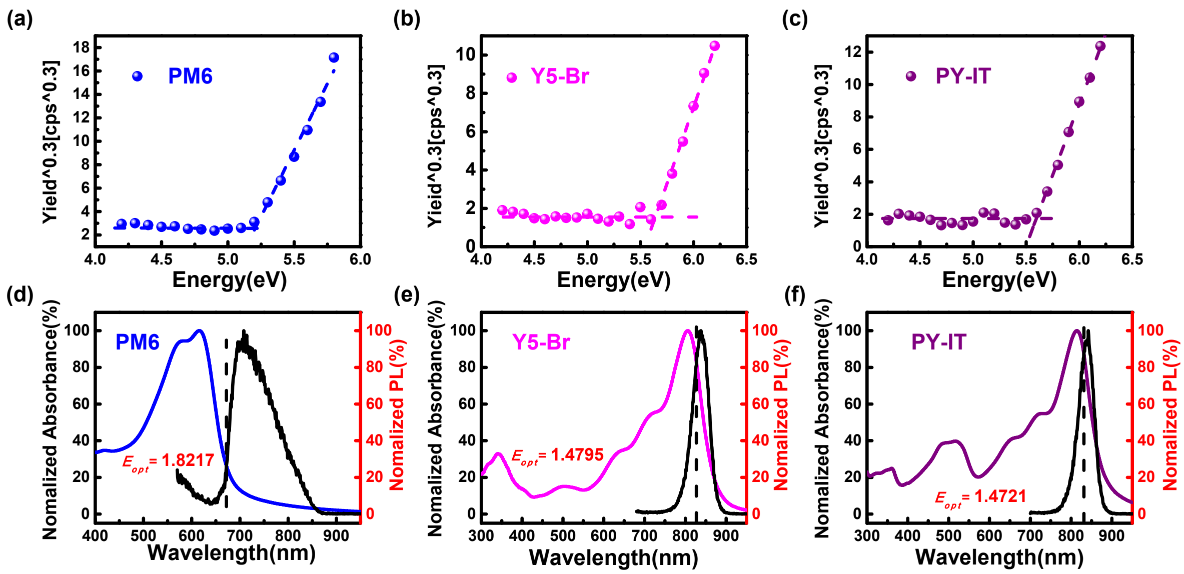

Fig. S1. The energy levels of (a) PM6, (b) Y5-Br and (c) PY-IT were investigated using a Photoelectron spectroscopy (PESA) in air. The normalized UV-Vis absorption and PL emission (black) spectra of (d) PM6, (e) Y5-Br and (f) PY-IT, respectively.

Table S1. The energy levels of materials were investigated using PESA.

Material	**E_{HOMO} (eV)**	**E_g^{opt} (eV)**	**E_{LUMO} (eV)**
PM6	−5.22	1.82	−3.40
Y5-Br	−5.64	1.48	−4.16
PY-IT	−5.59	1.47	−4.12

2. Device Characterization

Current density-voltage ($J-V$) curves of the devices were measured in a nitrogen-filled glove box using a Keithley 2400 Source Meter with an Enlitech solar simulator at AM 1.5G (100 mW cm^{-2}). The light intensity was calibrated using a standard single crystal silicon reference cell (with KG5 filter, purchased from PV Measurement to bring spectral mismatch to unity). The external quantum efficiency (EQE) was measured by a certified incident photon to electron conversion (IPCE) equipment (QE-R) from Enli Technology Co., Lt.

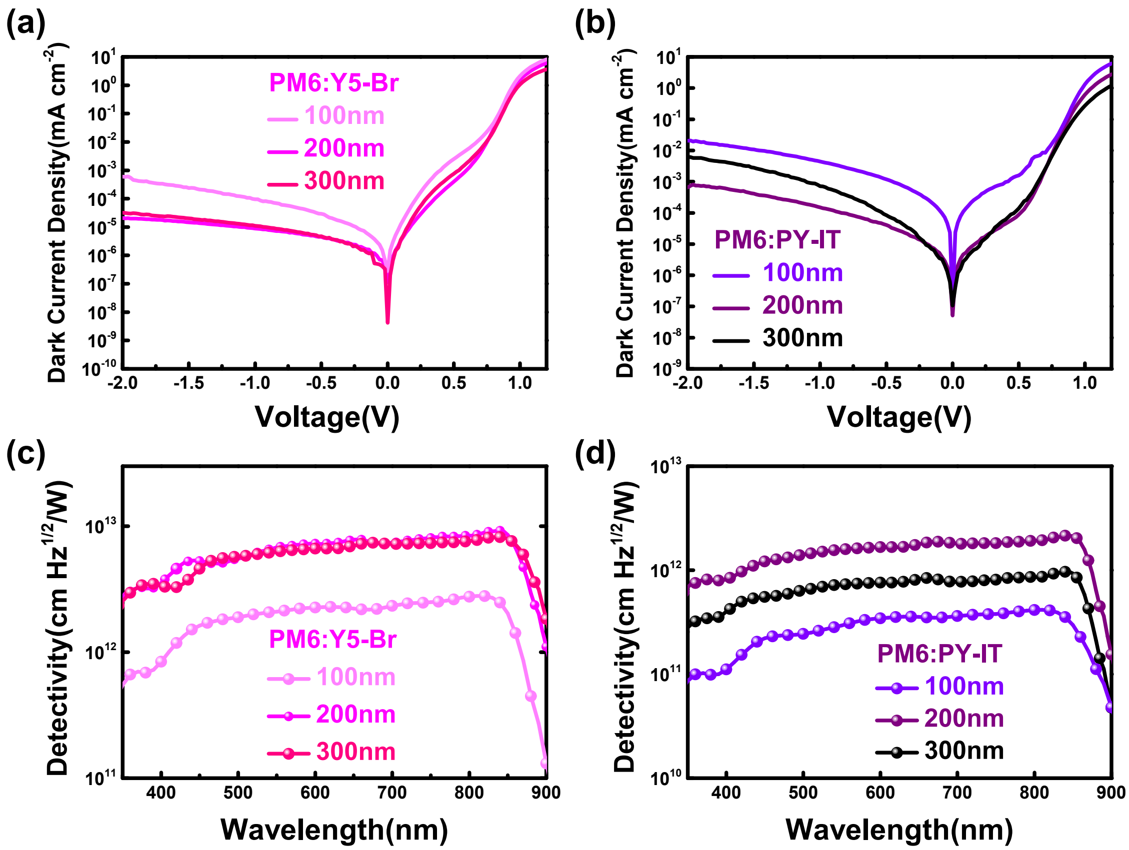

Fig. S2. (a, b) Dark $J-V$ characteristics; (c, d) Detectivity of the OPDs with PM6:Y5-Br and PM6:PY-IT depending on thickness of photosensitive layers.

3. UV-Vis Absorption

UV-Vis absorption spectra of different blend films were recorded on a PerkinElmer LAMBDA 365 UV-Vis spectrophotometer.

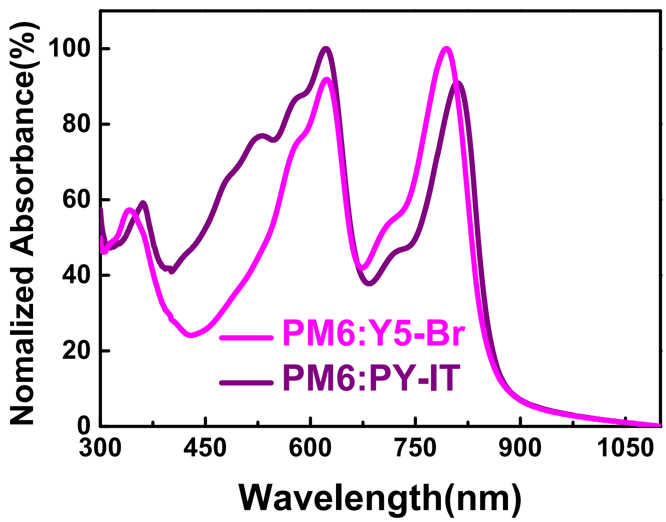

Fig. S3. Normalized UV-Vis absorbance spectra of PM6:Y5-Br and PM6:PY-IT in films.

4. SCLC Measurements

Electron-only and hole-only devices were fabricated for the $J-V$ measurements. The structure of electron-only device was ITO/ZnO/BHJ/PDIN/Ag and the hole-only was ITO/PEDOT:PSS/BHJ/MoO_3/Ag.[2] The single-carrier device was connected to a Source Measure Unit (Keithley, Model 236 SMU) which provides DC voltage to the electron-only devices. The $J-V$ values of different DC voltages can be detected and recorded through SMU, and trap density extracted by the space-charge-limited-current (SCLC) method.[3]

5. Photoluminescence measurements

The photoluminescence of the films were measured by a OmniFluo990LSP equipped with an integrating hemisphere at an excitation wavelength of 580 nm or 750 nm.

6. Atomic Force Microscopy (AFM) Imaging

A Dimension Icon atomic force microscope (AFM) from Bruker was used to image the active layers in tapping mode. The photosensitive layers were coated over PEDOT:PSS by methods described in Section of Device Fabrication.

7. Transmission Electron Microscopy (TEM) Characterization

Using PEDOT:PSS as a sacrificial layer on a glass substrate, the spun-cast film was peeled from the substrate by dissolving the PEDOT:PSS layer in water and then transferred onto a 50-mesh copper grid (Electron Microscopy China), and viewed by a spherical aberration-corrected electron microscope (Titan ETEM G2 E-Twin) operated at an acceleration voltage of 300 keV.

8. Grazing Incidence Wide-angle X-ray Scattering

Grazing-incidence wide-angle X-ray scattering (GIWAXS) was measured at a Pohang Light Source (Korea), beam line 3C. The incidence angle (0.1^{o} ~ 0.14^{o}) was carefully selected to allow for complete penetration of the X-rays into the film.[4]

Table S3. Fitting data obtained from GIWAXS in the in-plane (IP) and out-of-plane (OOP) directions of PM6:PY-IT blend films.

Component	Peak	Peak Location(Å^{-1})	d-Space(Å)	FWHM(Å^{-1})	Crystal Coherence Length(Å)
PM6:PY-IT As-cast	(IP) (100)	0.29	21.67	0.05	117.80
	(OOP) (010)	1.33	4.72	0.38	14.9
	(OOP) (010)	1.63	3.85	0.27	20.9
PM6:PY-IT Annealed	(IP) (100)	0.29	21.67	0.05	117.80
	(OOP) (010)	1.37	4.59	0.37	15.3
	(OOP) (010)	1.64	3.83	0.27	20.9

Table S4. Fitting data obtained from GIWAXS in the in-plane (IP) and out-of-plane (OOP) directions of PM6:Y5-Br blend films.

Component	Peak	Peak Location(Å^{-1})	d-Space(Å)	FWHM(Å^{-1})	Crystal Coherence Length(Å)
PM6:Y5-Br As-cast	(IP) (100)	0.29	21.67	0.06	102.80
	(OOP) (010)	1.52	4.13	0.56	10.1
	(OOP) (010)	1.64	3.83	0.23	24.6
PM6:Y5-Br Annealed	(IP) (100)	0.29	21.67	0.06	102.80
	(OOP) (010)	1.42	4.42	0.32	17.7
	(OOP) (010)	1.67	3.76	0.26	21.7

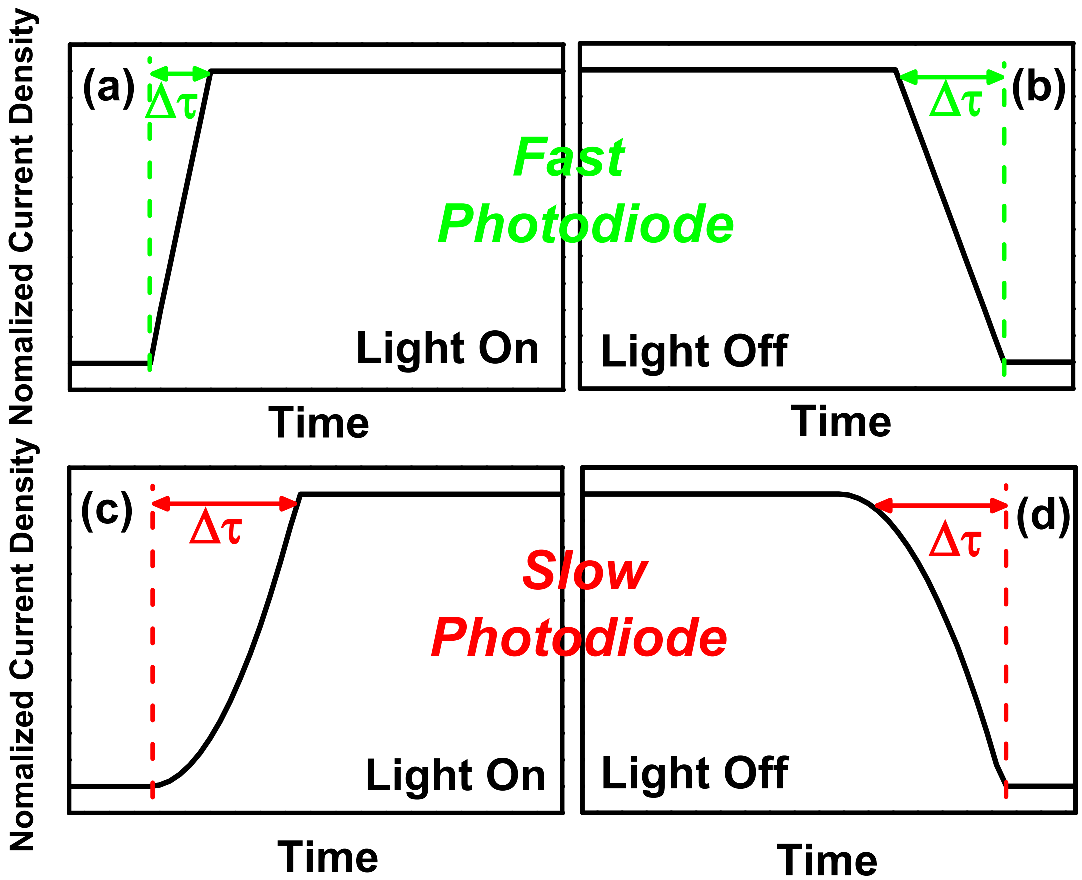

Fig. S4. Schematic illustration of the on-off response from fast and slow photodiodes.

9. References

1. Y. Firdaus, L. P. Maffei, F. Cruciani, M. A. Müller, S. Liu, S. Lopatin, N. Wehbe, G. O. N. Ndjawa, A. Amassian, F. Laquai and P. M. Beaujuge, *Adv Energy Mater*, 2017, **7**, e1700834.
2. J. Lv, H. Tang, J. Huang, C. Yan, K. Liu, Q. Yang, D. Hu, R. Singh, J. Lee, S. Lu, G. Li and Z. Kan, *Energy Environ. Sci.*, 2021, **14**, 3044-3052.
3. X. Meng, C. H. Y. Ho, S. Xiao, Y. Bai, T. Zhang, C. Hu, H. Lin, Y. Yang, S. K. So and S. Yang, *Nano Energy*, 2018, **52**, 300-306.
4. H. Tang, T. Xu, C. Yan, J. Gao, H. Yin, J. Lv, R. Singh, M. Kumar, T. Duan, Z. Kan, S. Lu and G. Li, *Adv Sci*, 2019, **6**, e1901613.