Supporting Information

CsPbI₂Br Quantum Dots Integration for High Performance Organic Photovoltaics and Photodetectors

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Device Fabrication and Characterization

Materials

PM6, D18, L8-BO and PDINN were purchased from Solarmer Materials (Beijing) Inc. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS, Clevios AI 4083) was purchased from Heraeus, Germany. Pre-patterned high-transmittance ITO-glass substrate (resistance ∼12 Ω sq⁻¹, maximum transmittance ∼94% at ∼550 nm, size of 20 × 15 × 0.7 mm³) was purchased from You Xuan Ltd. (China). Other reagents and solvents were purchased from commercial sources and used as received.

Synthesis of CsPbI₂Br PQDs
Synthesis of precursor:

The experimental environment was first dehumidified for 20 min. 125 mg of cesium carbonate (Cs₂CO₃) was weighed with a weighing paper into a 50 ml three-necked flask. Next, 12.5 ml of 1-Octadecene (ODE) and 0.5 ml of Oleic Acid (OA) were taken with a pipette gun and added into the flask. The temperature was increased to 120 °C with a circulating water vacuum pump, kept stirring and heated for 20 min, then nitrogen was introduced and the temperature was increased to 150 °C

until the reaction solution became clarified.

Synthesis of PQDs:

166.4 mg of lead iodide and 66 mg of bromine iodide were placed in a three-necked flask, 12.5 ml of ODE was added and heated in a vacuum at 120°C for 30 min. Next, a stream of nitrogen was passed through and 1.25 ml each of oleyl amine and oleic acid was added using a syringe. After the powders were completely dissolved at 170°C, 2 ml of the precursor solution, which had been heated to 150°C in advance, was taken and injected rapidly, and the flask was removed after 5-8 s of reaction and placed in ice water to cool down. For the subsequent purification process, the reaction solution was mixed with methyl acetate at 1:3, centrifuged at 8000 rpm for 5 min, and then the precipitate was taken and dissolved in hexane. This step was repeated two times to obtain 4 ml of PQDs dispersion dissolved in hexane. The dispersion was dried at 70°C before use and then dissolved in chloroform. The mixing time with the organic solution should be less than 30 min.[2, 3]

Fabrication of Organic Solar Cells and Organic Photodetectors

All organic diodes were fabricated in a bulk heterojunction (BHJ) structure (ITO/PEDOT:PSS/Active Layer/PDINN/Ag). ITO glass substrates were cleaned by sequential sonication in deionized water, ethanol, and isopropyl alcohol for 10 mins each. Then these ITO glass substrates were further treated with ultraviolet/ozone for another 30 mins after drying at 120 °C on a hotplate in air. PEDOT:PSS solution was spin-coated onto ITO glass substrates at a speed of 5000 rpm and annealed at 150 °C for 10 mins in air to get 20 nm PEDOT: PSS film. PM6 and L8-BO were mixed and dissolved in chloroform at a concentration of 6 mg/ml and 7 mg/ml respectively, and following with stirring in N_2 glovebox overnight. Before spin coating the active layer, 1,4-diiodobenzene (DIB, equal weight with acceptor) was added as additive in organic active layer solutions. For active layer with PQDs, $CsPbI_2Br$ QDs were dissolved in chloroform and introduced into active layer solution with a concentration of 0.3 mg/ml. The active layer was deposited on top of the PEDOT:PSS layer by spin-coating to obtain films in the glovebox, and then films were treated with thermal annealing at 85°C for 3 min. PDINN (1.2 mg/mL) in MeOH solution was spin-coated at 3000 rpm onto the active layer to get 10 nm electron transport layer. Finally, devices were transferred to an evaporation chamber where 100 nm Ag was thermally

evaporated through a shadow mask under high vacuum to form the anode. The size of the active area for devices defined by the overlapping of anode and cathode is 6.625 mm^2 defined by the overlapping of anode and cathode.

Characterization

Film absorption spectra were obtained by using a UV-visible spectrophotometer (HITACHI, Japan). The thickness and dielectric constant of films were obtained by using a spectroscopic ellipsometer (J. A. Woollam, USA). Current density-voltage (*J-V*) measurements were performed under AM 1.5G (100 mW cm^{-2}) using a Newport 3A solar simulator (Newport, USA) at room temperature in air, and the light intensity was calibrated using a standard silicon reference cell certified by the National Renewable Energy Laboratory (NREL, USA). *J-V* characteristics were measured with a programmed software developed by Ossila Ltd. (UK) and a source meter unit (2612B, Keithley, USA). An aperture mask was placed over the device to accurately define an area of 4 mm^2 for each pixel. External quantum efficiency (EQE) was measured with an EQE system (Zolix, China) equipped with a standard Si diode. GIWAXS measurements were conducted at beamline BL16B1 at the Shanghai Synchrotron Radiation Facility in China. Steady-state photo-luminescence (PL) spectra were obtained using a PL microscopic spectrometer (Flex One, Zolix, China), with a 405 nm CW laser as the excitation source. Time-resolved photo-luminescence (TRPL) spectroscopy was measured using a time correlated single-photon counting spectrofluorometer (PicoQuant, Germany) with a 405 nm laser. Transmission Electron Microscope (TEM) images and the electron diffraction patterns were gained using a high-resolution transmission electron microscope (JEOL, Japan) operated at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250Xi using a 500 μm X-ray spot for XPS analysis. Water contact angle and surface energy was performed using a water contact angle measurement system (Attension Theta Lite). The Mott-Schottky (MS) analyses were carried out under the dark state condition, with the bias range of 0.2 V to 1 V, and frequency of 10 kHz. Electrochemical Impedance Spectroscopy (EIS) and MS conducted on the ModuLab XM electrochemical workstation (AMETEK U.K.). The noise-current-frequency measurement, linear dynamic range (LDR), frequency response and transient photocurrent measurement of OPDs were determined by an optical sensor characteristic analyzer (Enli Technology Co., Ltd., China) with a square-wave pulse of 633 nm laser diode.

In Situ Spectroscopic Ellipsometry

In situ spectroscopic ellipsometry measurements were conducted to probe the molecular aggregation dynamics of NFAs through mapping their extinction coefficient (k) evolutions during the film formation process, which were extracted using a Kramers–Kronig consistent B-spline model where k locating at 780 nm refer to the characteristic absorption peak L8-BO. All films show a thickness reduction from 2500 nm (wet film) to ≈150 nm (dry film) within 3.5 s. This process can be classified into three stages: stage 1 is related to the evaporation of free solvent and densification of acceptor molecules; stage 2 is associated with the rapid ordering of molecules; stage 3 refers to the slow evaporation of the residual solvent in which the molecular organization in the film is almost completed.

Responsibility

$$R = \frac{EQE * \lambda}{1240}$$

(1)

The responsibility of OPDs were calculated through the equation shown above, where λ is the wavelength of the incident light in nanometer.

Dielectric constant

$$\varepsilon = (n + ik)^2$$

(2)

The dielectric constant of films was calculated through the equation shown above via ellipsometry. Here the dielectric constant could be extracted by fitting B-Spline layer from spectroscopic ellipsometer (J. A. Woollam, USA), where n is refractive index, k is extinction coefficient. The ε_r of PM6:L8-BO optoelectronic devices with and without PQDs are 2.93 and 2.32, respectively.
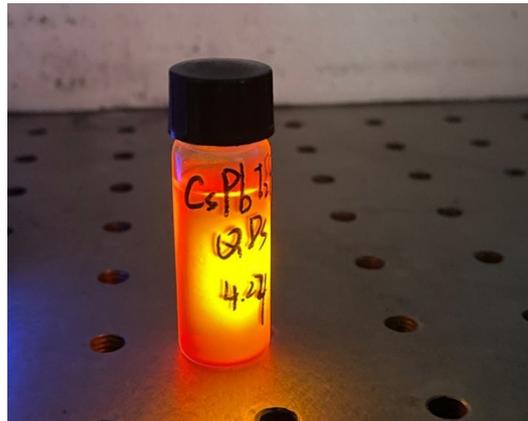
Supporting Figures and Tables

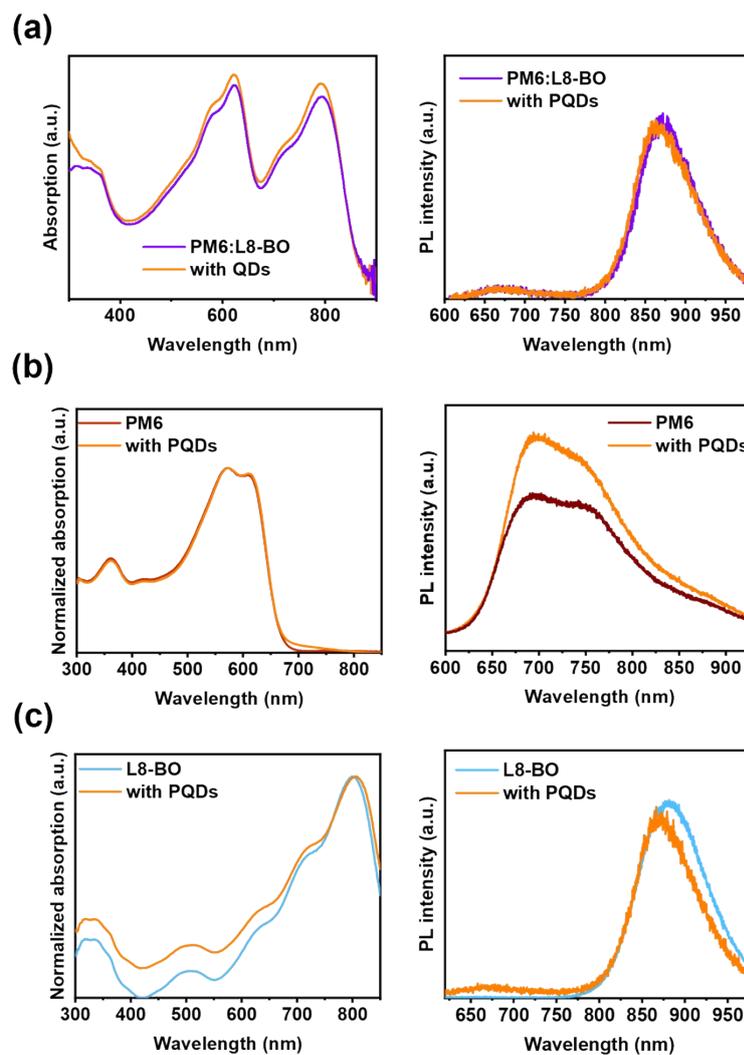**Figure S1**. CsPbI$_2$Br PQDs under ultraviolet radiator

Figure S2. Absorption and PL spectra of (a) PM6:L8-BO, (b) PM6 and (c) L8-BO films with or
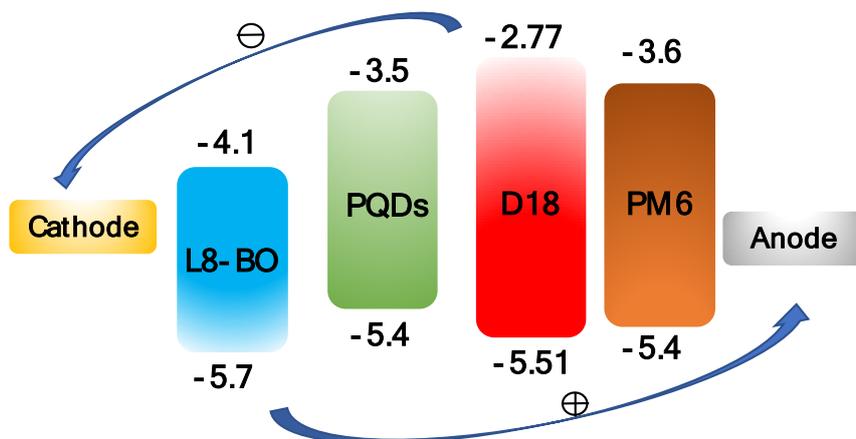
without PQDs.

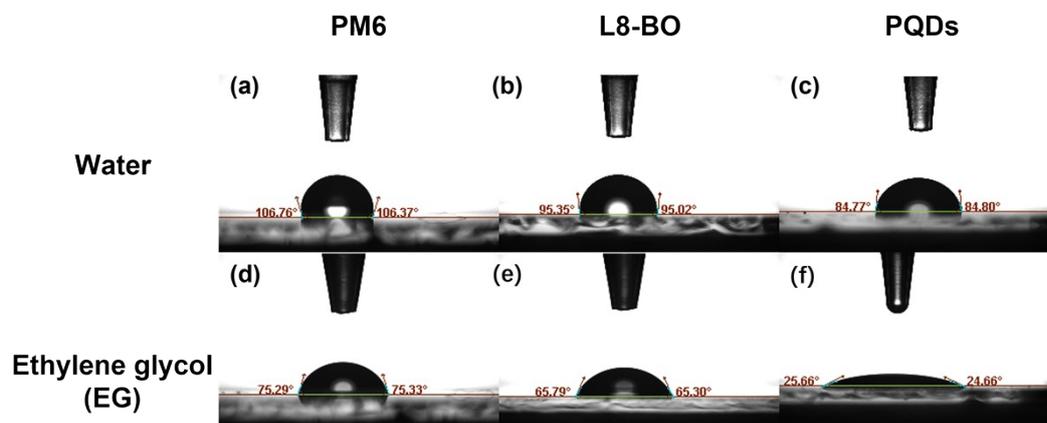**Figure S3**. Schematic diagram of energy levels of organic photodiodes.

Figure S4. Contact angle images of (a, d) PM6, (b, e) L8-BO, (c, f) PQDs neat films with water or ethylene glycol droplet on top
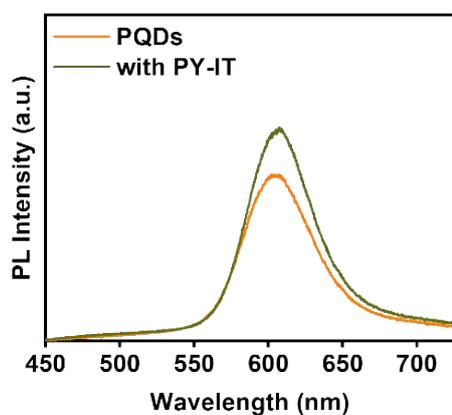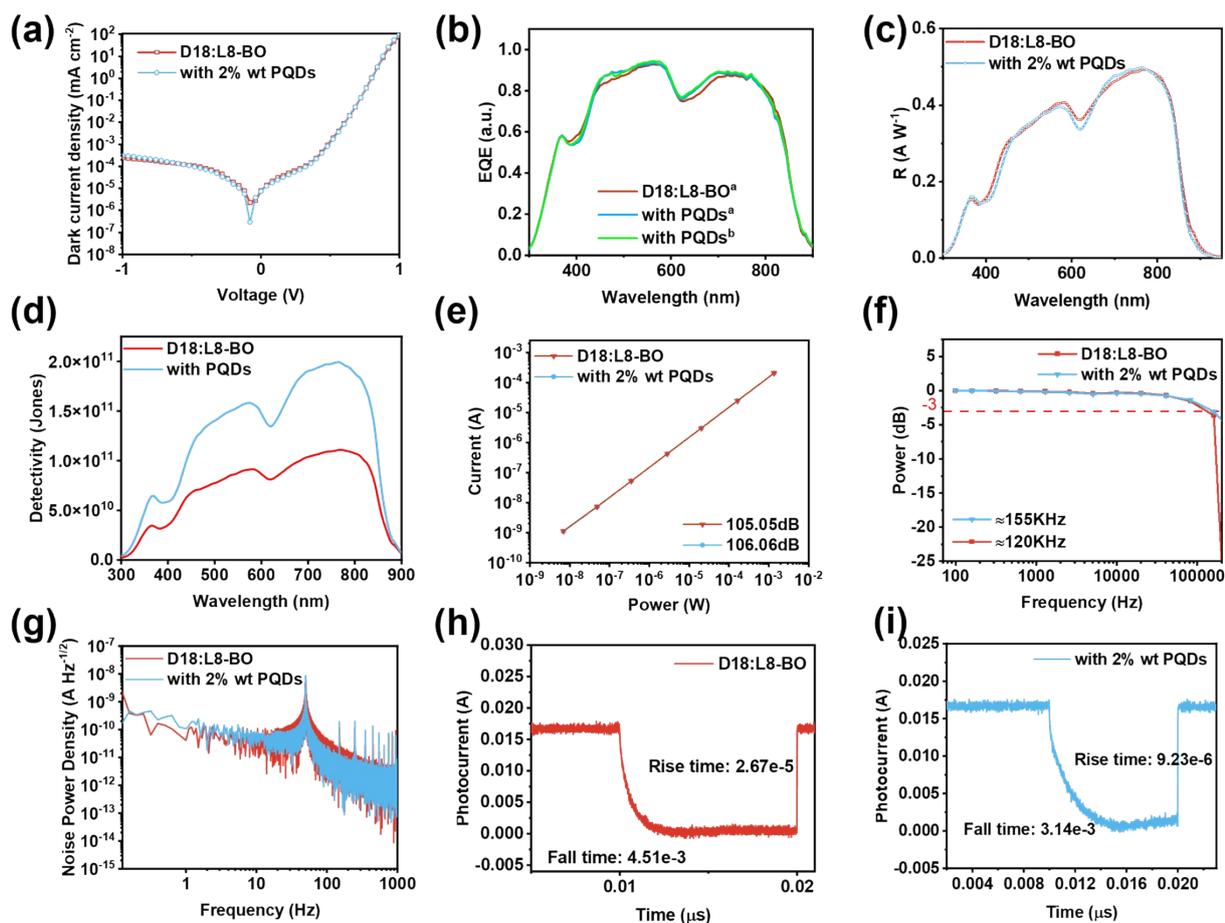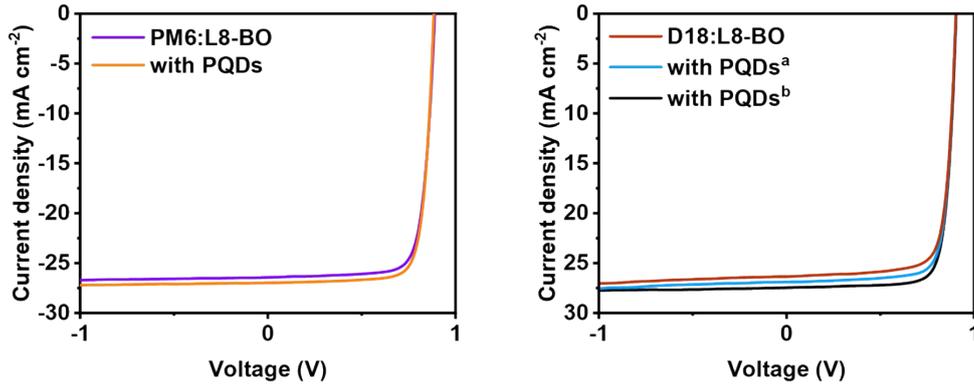

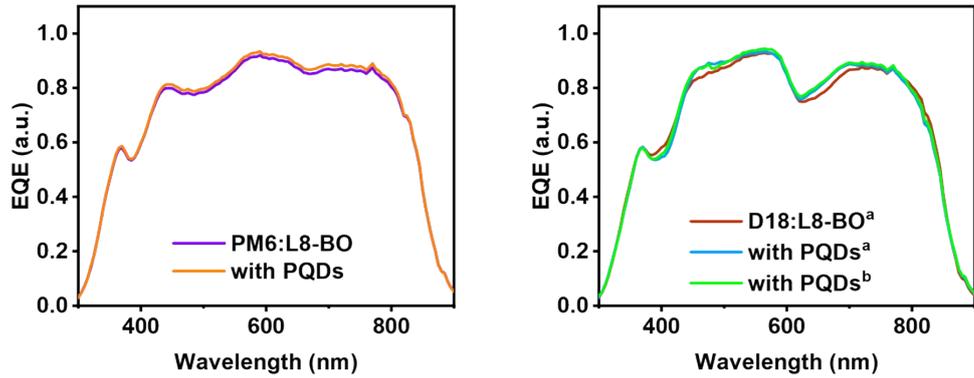**Figure S5**. PL spectra of $CsPbI_2Br$ QDs films with or without PY-IT.

Figure S6. OPDs performances of D18:L8-BO devices including (a) dark current density, (b) EQE spectra, (c) responsibility, (d) detectivity, (e) LDR, (f) cut-off frequency, (g) noise current density and (h, i) rise/fall time with or without PQDs.
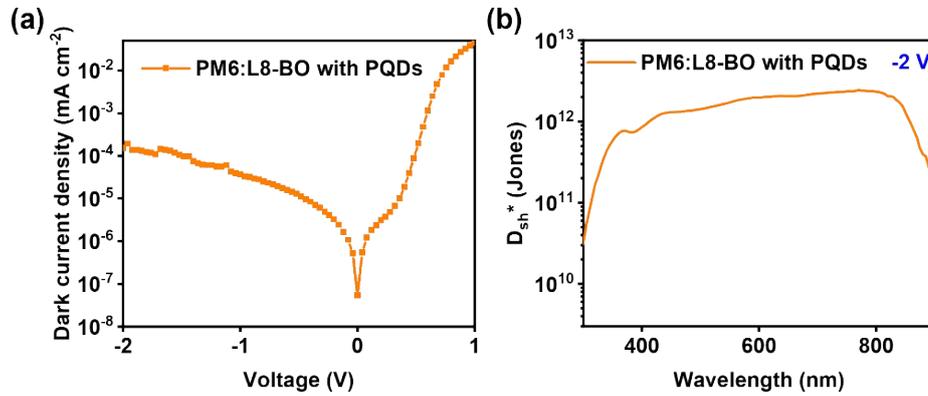
Figure S7. (a) J-V curves and (b) EQE spectra of PM6:L8-BO and D18:L8-BO with or without PQDs.

Figure S8. (a) Dark current density and (b) $D_{sh}*$ of PM6:L8-BO with PQDs devices at -2 V bias.

Table S1. Summary of contact angles (θ), and surface tensions (γ) of PM6, L8-BO, CsPbI$_2$Br PQDs neat films, and compatibility (χ) of PM6, L8-BO with PQDs.

Materials	Contact angles (°) with Water	Contact angles (°) with EG	γ (mN/m)	χ
PM6	106.6	75.3	21.1	-
L8-BO	95.2	65.5	26.5	-
PQDs	84.8	25.2	38.0	-
PM6:PQDs	-	-	-	2.5
L8-BO:PQDs	-	-	-	1.0

Table S2. Summary of electrochemistry parameters of OPDs

BHJ	PQDs in blend	R_s (Ω)	R_p (Ω)	C (F)	W_d (nm)
PM6:L8-BO	w/o	83	706	1.4×10^{-9}	85
	2 % wt	75	784	1.6×10^{-8}	129

Note: The values were measured from 10 individual devices.

Table S3. Complete semiconductor parameters of PM6:L8-BO based devices.[4, 5]

	PM6:L8-BO	**with 2% wt PQDs**
R_s (Ω)	83.46	75.18
R_p (Ω)	705.8	783.6
C (F)	1.4×10^{-9}	1.6×10^{-8}
W_d (nm)	85	129
V_{bi} (V)	0.75	0.74
T (nm)	92	93
$|k|$	1.41×10^{18}	2.05×10^{18}

REFERENCES

[1] J. S. Pedersen and P. Schurtenberger, *Macromolecules*, 1996, **29**, 7602–7612.

[2] W. Miao, C. Guo, D. Li, T. Li, P. Wang, Y. Yang, D. Liu and T. Wang, *Sol. RRL*, 2021, **5**, 2100499.

[3] K. Vighnesh, S. Wang, H. Liu and A. L. Rogach, *ACS Nano*, 2022, **16**, 19618–19625.

[4] Y. Wang, B. Jia, J. Wang, P. Xue, Y. Xiao, T. Li, J. Wang, H. Lu, Z. Tang, X. Lu, F. Huang and X. Zhan, *Adv. Mater.*, 2020, **32**, 2002066.

[5] J. Yuan, X. Zhang, J. Sun, R. Patterson, H. Yao, D. Xue, Y. Wang, K. Ji, L. Hu, S. Huang, D. Chu, T. Wu, J. Hou and J. Yuan, *Adv. Funct. Mater.*, 2021, **31**, 2101272.