

Supplementary Information

PCBM doped with fluorene-based polyelectrolytes as electron transporting layer for improving performance of planar heterojunction perovskite solar cells

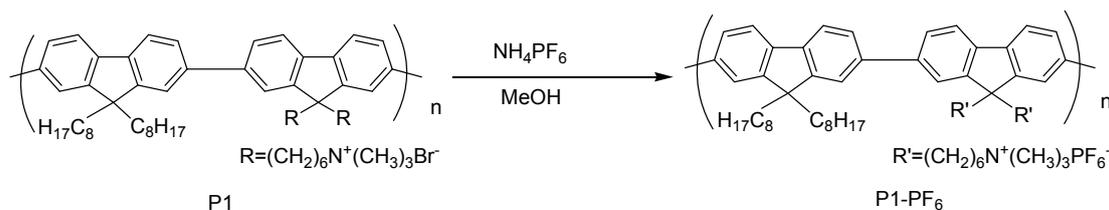
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Materials

Poly(3,4-ethylenedioxy thiophene):poly(styrene sulfonate) (PEDOT:PSS) aqueous solution (Clevios™ P VP AI 4083) was purchased from Heraeus Precious Metals GmbH & Co. KG. PCBM (purity 99%) was purchased from Solenne B. V., Netherlands. Methylammonium iodide (CH₃NH₃I or MAI) was synthesized in the laboratory according to the previous literature.¹ The ionic polyfluorene derivative P1-PF₆ was synthesized by ionic exchange from its precursor which was prepared according to the previous literature.² The synthetic route to P1-PF₆ is shown in Scheme 1, and the detailed procedure is described as follows. To a solution of the precursor polymer (100 mg) in methanol (20 mL) was slowly added a solution of ammonium hexafluorophosphate (0.4 g, 4.8 mmol) in methanol (20 mL). The mixture was stirred at room temperature for 48 hr, followed by removing the solvent by rotary evaporation. The previous step was repeated for 4 to 5 times to achieve high percentage of ionic exchange from Br⁻ to PF₆⁻ groups. The final product P1-PF₆ was collected and dried in an oven to give a yellow solid (90 mg, 75%). Other chemicals including reagents and solvents were purchased from Alfa Aesar or Acros and used without further purification.



Scheme 1. Synthesis of P1-PF₆ by ionic exchange reaction.

Characterization methods

Gel permeation chromatography (GPC) assembled from a Viscotek VE3850 RI detector and three columns in series were used to measure the molecular weights of polymers relative to polystyrene standards at 35 °C. Differential scanning calorimetry (DSC) was performed on a Seiko DSC 6200 unit with a heating/cooling rate of 5 °C/min. Thermal gravimetric analysis (TGA) was undertaken on a Seiko TG/DTA 7200 instrument with a heating rate of 10 °C/min. The electron spectroscopy for chemical analysis (ESCA) was performed with an ULVAC-PHI PHI 5000 Versaprobe II instrument. The current density–voltage (J–V) characteristics of the photovoltaic devices were recorded using a Keithley 2400 source measuring unit under a simulated AM 1.5G light (USHIO UXL-10S, Xe 1000W) at 100 mW/cm². The electrical conductivities of the thin films were measured using a four-point probe setup with a Keithley 2400 source measuring unit. PL quenching measurement was performed on a spectrophotometer (Princeton Instruments Acton 2150) equipped with a He-Cd laser (325/442 nm). The UPS spectra were obtained with a hemispherical electron energy analyzer (ULVAC-PHI PHI 5000 Versaprobe II). He I ($h\nu = 21.22$ eV) discharge lamp was used as an excitation source. Cross-sectional images of devices were performed on a JEOL 6700F SEM. The surface morphologies of the films were investigated using a Bruker Innova AFM with the tapping mode. Time-resolved PL decay experiments were carried out using a EasyLife X bench top fluorescence lifetime system equipped with a high-power blue LED as excitation source (403 nm).

Characterization of P1-PF₆

The number- and weight-average molecular weights of P1-PF₆ were determined by GPC technique to be 3.4×10^4 and 1.06×10^5 g/mol, respectively. The thermal properties of P1-PF₆ was analysed with DSC and TGA, and the corresponding thermograms are shown in Fig. S1 and S2, respectively. No obvious thermal behavior was found in the range of -50–200 °C. The thermal decomposition temperature (T_d , defined at 5% weight loss) is found at 306 °C. The above results indicate that P1-PF₆ possesses good thermal stability during device fabrication and photovoltaic evaluation. The ESCA experiment was used to examine the ionic exchange of the polymer,³ and the corresponding spectra of the precursor polymer P1 and ionic polymer P1-PF₆ are depicted in Fig. S3. The clear N *1s* signal at 400 eV and Br *3s*, *3p*, *3d* signals at 260, 180, 80 eV reveal the presence of trimethylammonium bromide $-\text{N}(\text{CH}_3)_3\text{Br}$ group. After ionic exchange, the existence of N *1s* signal and newly formed F *1s*, *2s* signals at 700, 20 eV, and P *2s*, *2p* signals at 195, 150 eV are observed, while Br signals are vanished, referring to successful replacement of Br⁻ by PF₆⁻. The solubility test was also performed that provided evidence of ionic exchange. The precursor polymer P1 is soluble in highly polar solvents, such as methanol, dimethyl sulfoxide, and DMF. After ionic exchange, the solubility of the resulting polymer P1-PF₆ is significantly decreased in methanol; instead, it can be dissolved in chloroform, indicating change of nature of ionic polymers. According to the ESCA spectra and solubility test, we conclude that the conversion of counterions from Br⁻ to PF₆⁻ was nearly completed after ionic exchange for 4 to 5 times, as described in the previous section.

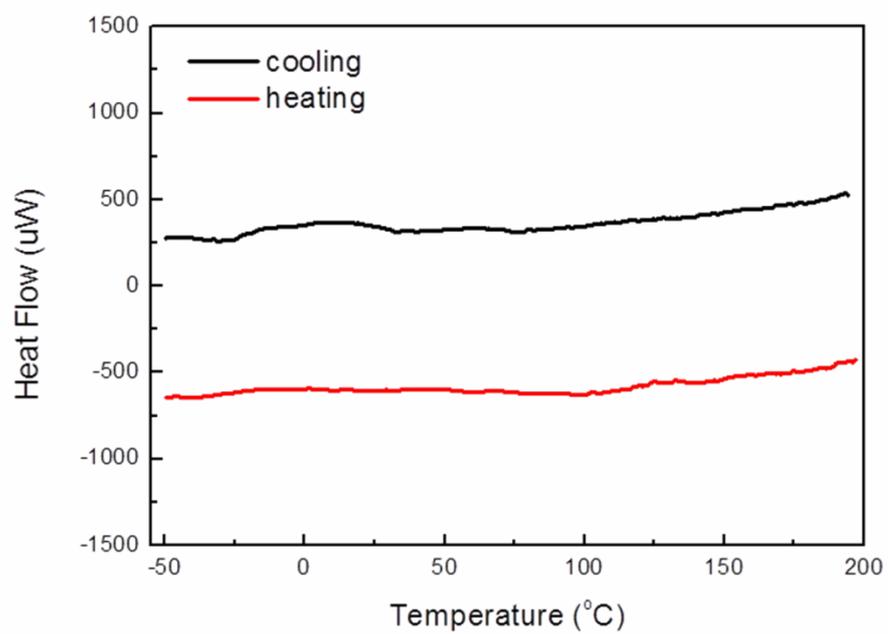


Fig. S1. DSC thermograms of P1-PF₆.

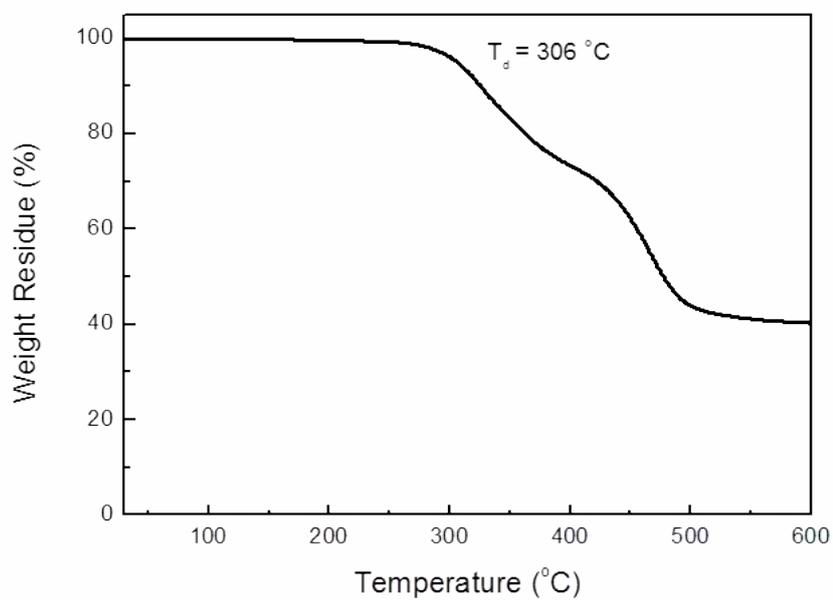


Fig. S2. TGA thermogram of P1-PF₆.

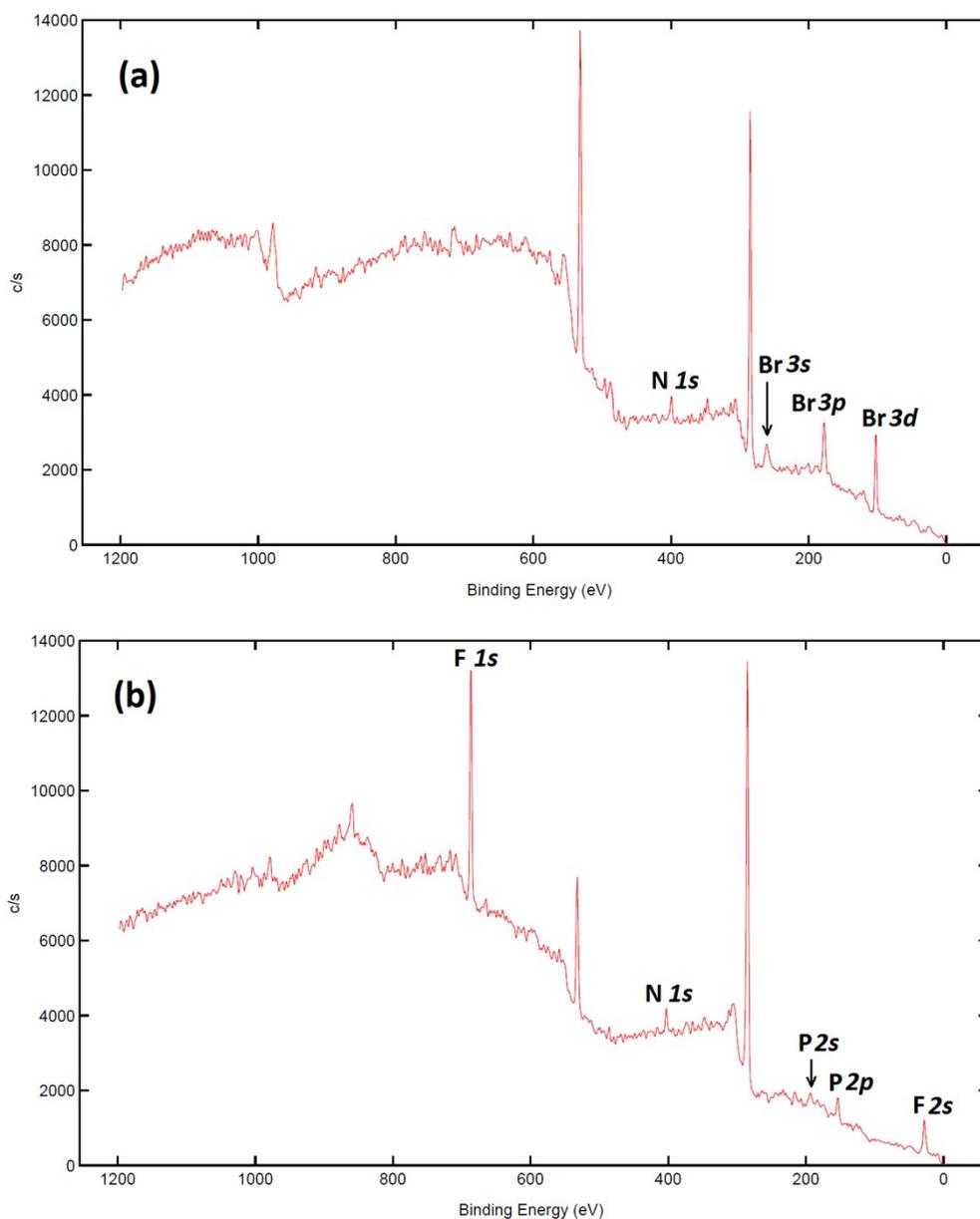


Fig. S3. ESCA spectra of the polymers (a) P1 and (b) P1-PF₆.

Device fabrication

ITO substrates ($7 \Omega/\square$) were cleaned sequentially with detergent, de-ionized water, acetone, and isopropyl alcohol (IPA) in an ultrasonic cleaner for 30 min, followed by ultraviolet-ozone exposure for 15 min. PEDOT:PSS was spin-cast on the cleaned ITO substrates at 5000 rpm for 30 sec and dried at 90 °C for 30 min. The perovskite layer was prepared via single-step coating process. A mixture of PbI₂ (400 mg), CH₃NH₃I (159 mg), and DMSO (60 μ L) in

DMF (1 mL) was heated to 60 °C for 30 min to reach complete reaction.¹ The above solution was then spin-coated on the PEDOT:PSS layer at 5000 rpm for 30 sec, and 150 μ L of diethyl ether was dripped on the rotating substrate in 3 sec. The next step is to deposit ETL on the perovskite layer. First, two individual solutions of PCBM in chloroform (20 mg/mL) and P1-PF₆ in chloroform (2 mg/mL) were prepared. Second, 20, 100, or 180 μ L of P1-PF₆ solutions were taken and mixed with 750 μ L of PCBM solution, and chloroform was added to the above three solutions to reach total volume of 1 mL for each, followed by spin-coating on the perovskite layer at 3000 rpm for 30 sec to form doped PCBM layers, namely PCBM:P1-PF₆ (20), PCBM:P1-PF₆ (100), and PCBM:P1-PF₆ (180). Pure PCBM solution (15 mg/mL in chloroform) was also spin-coated into thin film as ETL for comparison. Finally, Ag electrodes were deposited on ETL by thermal evaporation under a base pressure of 10⁻⁶ torr. The active area of each device is 4 mm².

Device Performance

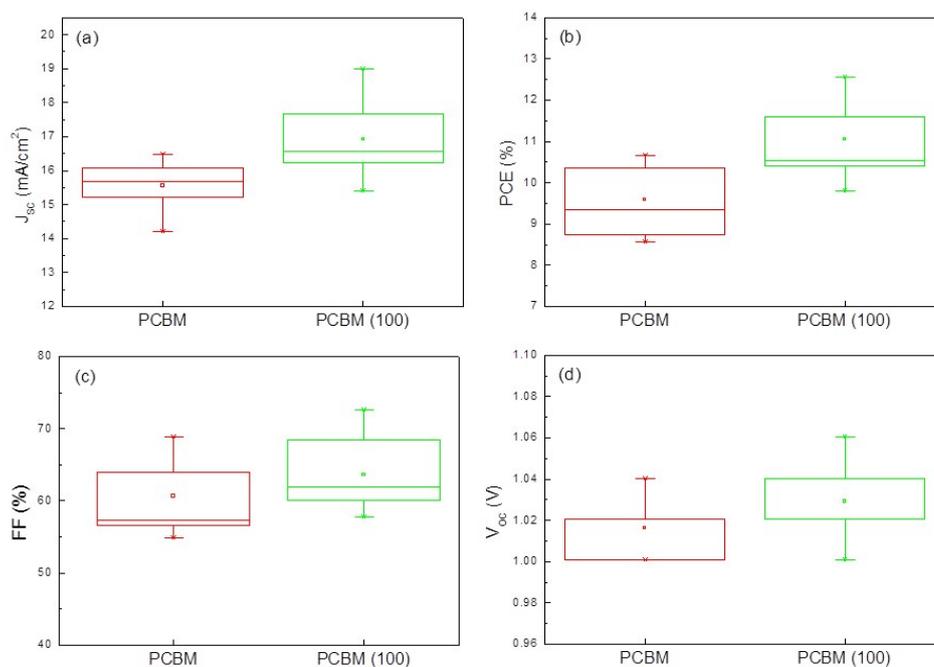


Fig. S4. Performance variation represented as a standard box plot in (a) J_{sc} , (b) PCE , (c) FF , and (d) V_{oc} from 14 devices using pure and P1-PF₆ (100)-doped PCBM as ETL.

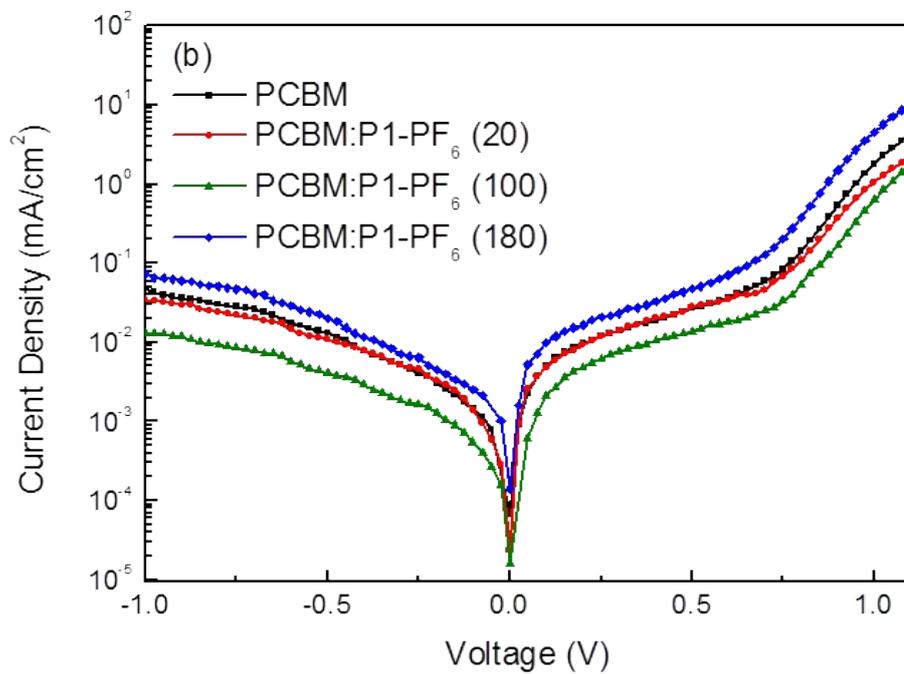
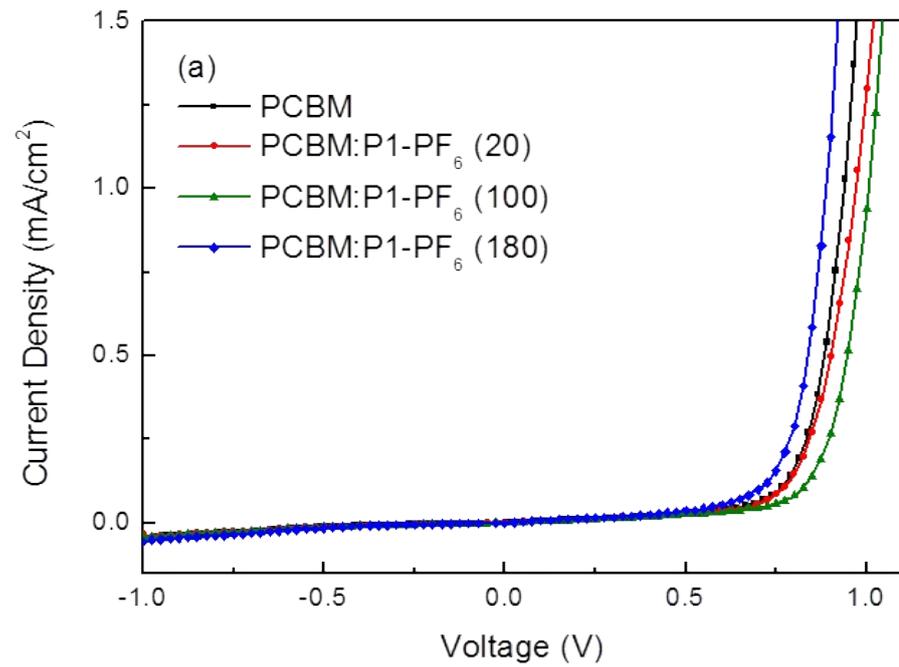


Fig. S5. (a) (b) J-V characteristics of all devices in the dark.

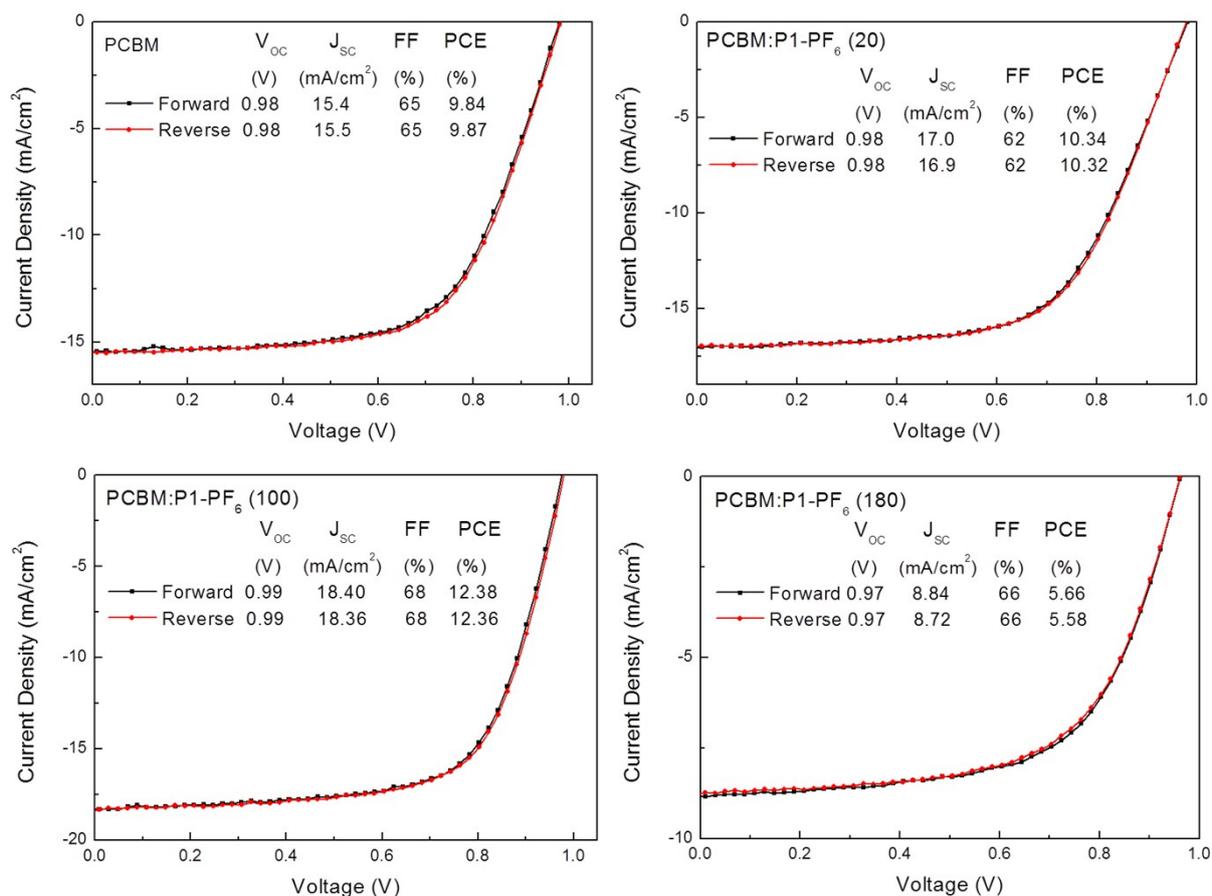


Fig. S6. J-V characteristics of all devices under forward and reverse scans with a scanning rate of 0.2 V/s.

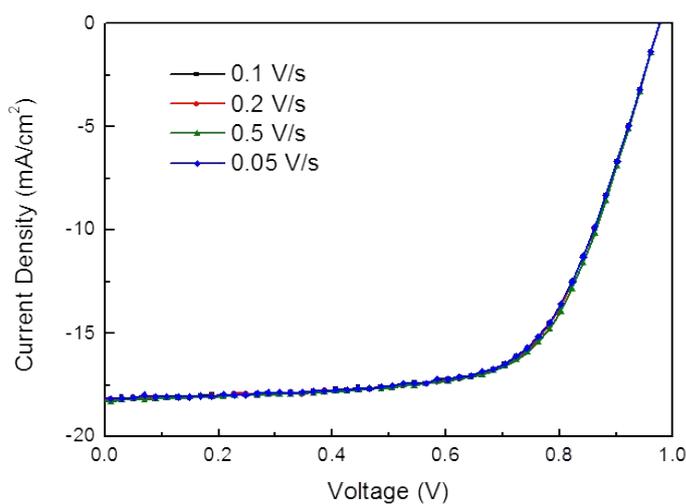


Fig. S7. J-V characteristics of the device based on PCBM:P1-PF₆ (100) under different voltage sweep rates of 0.05, 0.1, 0.2, and 0.5 V/s.

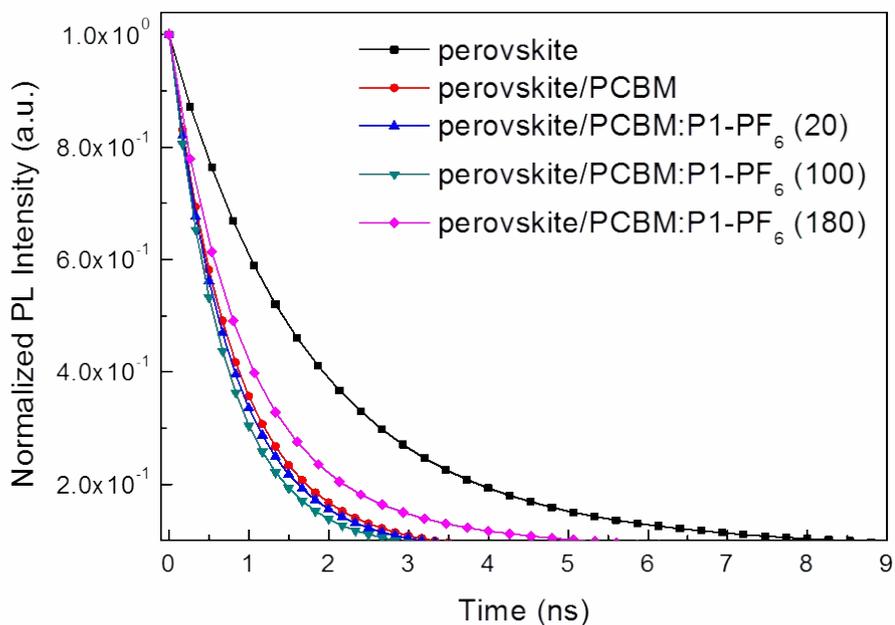


Fig. S8. Time-resolved PL decay curves of pure perovskite, perovskite/PCBM, and perovskite/P1-PF₆-doped PCBM films.

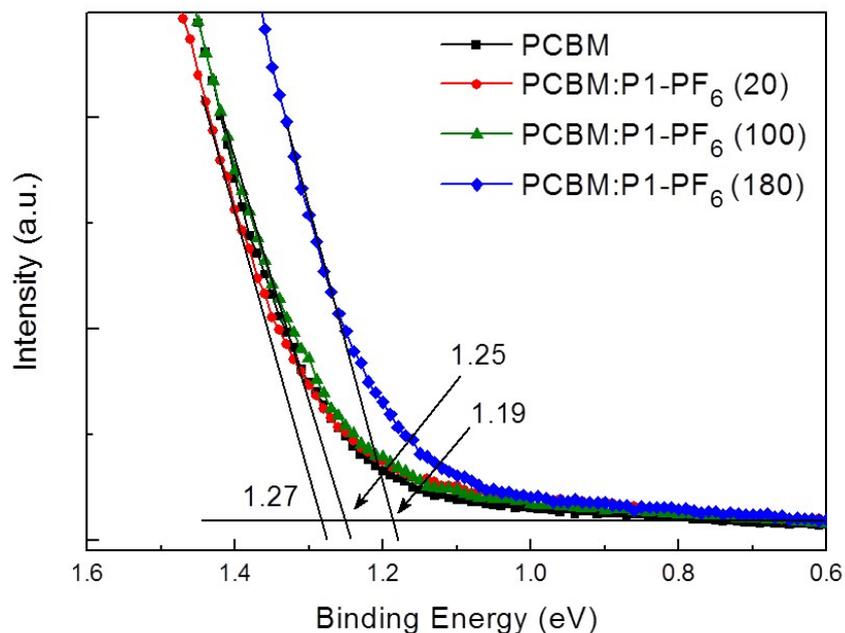


Fig. S9. UPS spectra of pure and P1-PF₆-doped PCBM for low binding energy region. Binding energy cutoffs of PCBM and PCBM:P1-PF₆ are indicated.

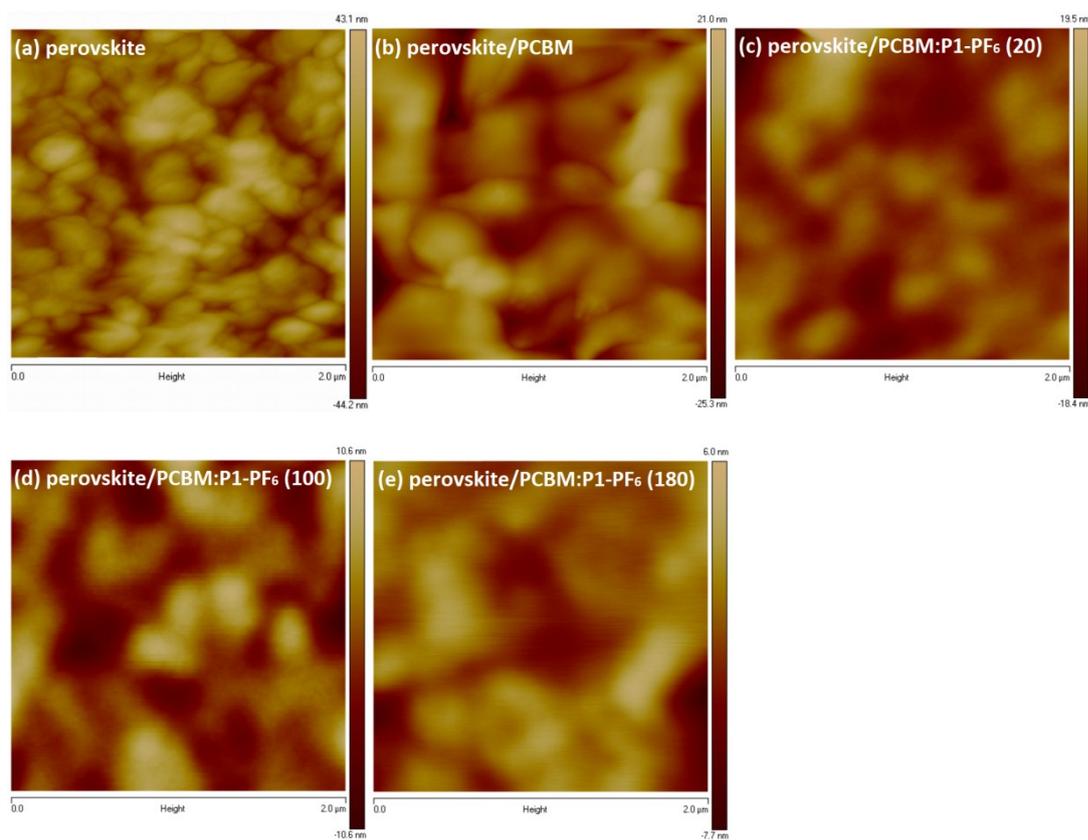


Fig. S10. Surface topographic AFM images of (a) pure perovskite, (b) perovskite/ PCBM, (c) perovskite/PCBM:P1-PF₆ (20), (d) perovskite/PCBM:P1-PF₆ (100), and (e) perovskite/PCBM:P1-PF₆ (180) films.

References

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