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Supporting Information

for

Cesium Functionalized Pectin as Cathode Interlayer for Polymer Solar Cells

Han Xu, Zicheng Ding, Lu Zhang, Jun Liu, Junli Hu*, Yichun Liu**

H. Xu, Prof. J. L. Hu, Prof. Y. C. Liu
Centre for Advanced Optoelectronic Functional Materials Research, Key Laboratory for UV Light-Emitting Materials and Technology of the Ministry of Education, Northeast Normal University, Changchun 130024, P. R. China
*E-mail: hujl100@nenu.edu.cn, ycliu@nenu.edu.cn
H. Xu, Z. C. Ding,L. Zhang, Prof.J. Liu
State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China
*E-mail: liujun@ciac.ac.cn

Experimental Section

Synthesis of PeCs: Pectin (5 mg, pectin from apple, Sigma Aldrich) and Cs_2CO_3 (0.75 mg, Energy Chemical) are stirred in 5 mL de-ionized water at room temperature for 12 hours. Then ethanol (35 mL) were added to the solution to make PeCs precipitate out. The solid was collected by centrifuge and dried at 90 ^{o}C for 3 hours.

PSC device fabrication and measurement: Poly[N-9″-hepta-decanyl-2,7-carbazolealt-5,5-(4′,7′-di-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) was synthesized in our laboratory. [6,6]-phenyl C71-butyric acid methyl ester ($PC_{71}BM$) was purchased from American Dye Source. Devices with the structure of ITO/CIL/Photoactive Layer/MoO_3/Al were fabricated on pre-cleaned Indium tin oxide (ITO) glass substrates.ITO glass substrates were cleaned by sequential ultrasonication in detergent, deionized water, acetone, and isopropyl alcohol, followed by dried at 120 ^{o}C for 30 min and treated with UV-ozone for 20 minutes. PeCs aqueous solution (0.4 mg mL^{-1}) was spin-coated on the ITO substrates at 2000 rpm for 1 minute and annealed at 150 ^{o}C for 20 minutes. The substrates were then transferred to a nitrogen-filled glove box. The photoactive layer was spin-coated from the *o*-dichlorobenzene solution (in total 17.5 mg mL^{-1}) of PCDTBT:$PC_{71}BM$ (1:4 by weight) at 700 rpm for 3 minutes and annealed at 80 ^{o}C for 10 minutes. Then 20 nm thickness layer of MoO_3 was deposited on top of it under the vacuum of 2×10^{-4} Pa. Finally, Al (100 nm) was deposited on top of the MoO_3 layer. The active area of each device was 8.0 mm^2. The *J-V* curves of the devices were measured by using a computer-controlled Keithley 2400 source meter under 100 mW cm^{-2} AM 1.5G simulated solar light illumination provided by a XES-70S2-CE Class Solar Simulator (Japan, SAN-EI Electric Co., Ltd.). The EQE spectra were measured under the short-circuit condition with a lock-in amplifier (SR830, Stanford Research System) at a chopping frequency of 280 Hz during illumination with monochromatic light from a xenon lamp.

Instrumentation: AFM in tapping mode was performed on a SPI 3800N Probe Station (Seiko Instruments Inc., Japan). The sample for AFM measurement was prepared as the device condition by spin-coating the PeCswater solution (0.4 mg mL^{-1})

onto ITO substrates at 2000 rpm for 1 minute and thermal annealed at 150 °C for 20 minutes. The UPS and XPS measurements were carried out by using a VG Escalabmkll spectrometer (UK) with a He I (21.2 eV for UPS) discharge lamp and Al Kα irradiation source (1486.7 eV for XPS) excitation. The film sample UV-Vis absorption spectra and transmittance spectra were measured with a PerkinElmer Lambda 35 UV-Vis spectrometer. The sample for UV-Vis absorption measurement was made by dispersing PeCs in de-ionized water with a concentration of 0.4 mg mL^{-1}. Film samples used for UPS, XPS and UV-Vis transmittance spectra measurements were made by spin-coating of PeCs in aqueous solution on ITO glass substrates using the same parameters as for PSC device fabrication. The morphologies of the Cs_2CO_3 and PeCs films were observed by optical microscopy (Zeiss Axio Imager A2m, Carl Zeiss, Germany). The samples for optical microscopy were prepared by spin-coating the Cs_2CO_3 dispersion (50 mg mL^{-1}) and the PeCs dispersion (0.4 mg mL^{-1}) onto silicon wafers at 2000 rpm for 1 minute. The pH values were measured by a pH meter (pHS-3C, Leici, China). Thermal gravimetric analysis (TGA) was performed under a N_2 flow with a Perkin-Elmer-TGA 7 system.

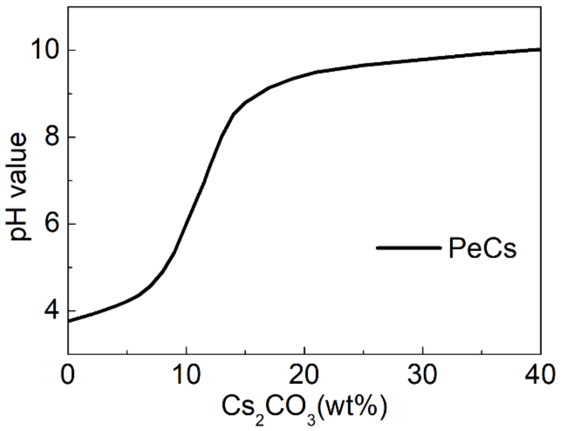

Fig. S1. Dependence of the pH value of pectin aqueous solution on the amount of Cs_2CO_3.

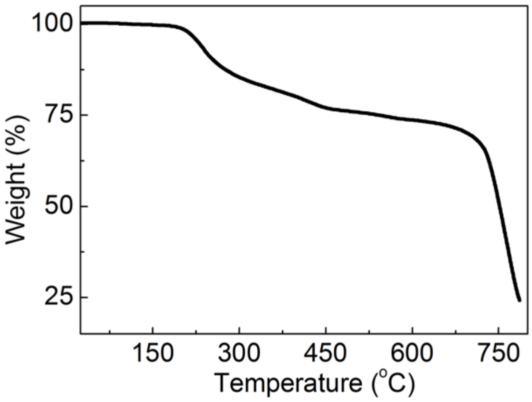

Fig. S2. TGA curve of PeCs under nitrogen atmosphere. TGA shows that the decompositiontemperature (T_d) of PeCs at 5% weight loss is 229 °C.

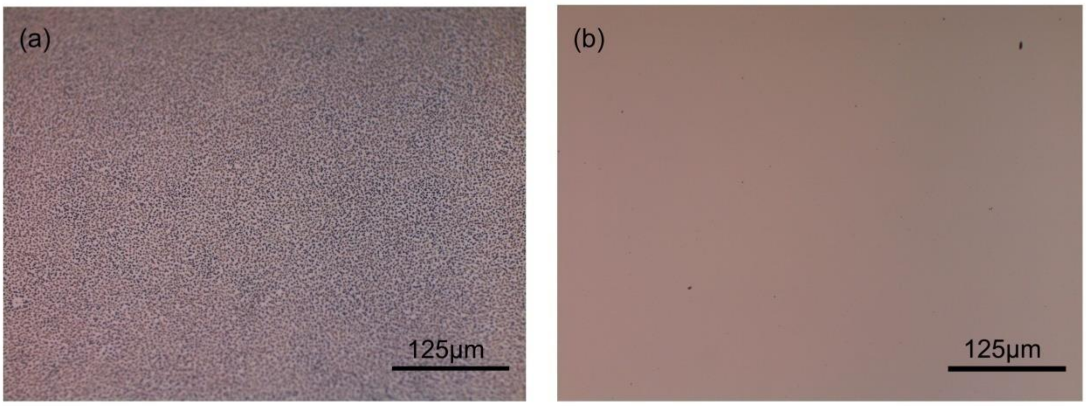

Fig. S3. The optical microscope images of the film spin-coated on Si substrates with aqueous solution of (a) Cs_2CO_3 or (b) PeCs. The surface of PeCs is smooth and the surface of Cs_2CO_3 is rough.

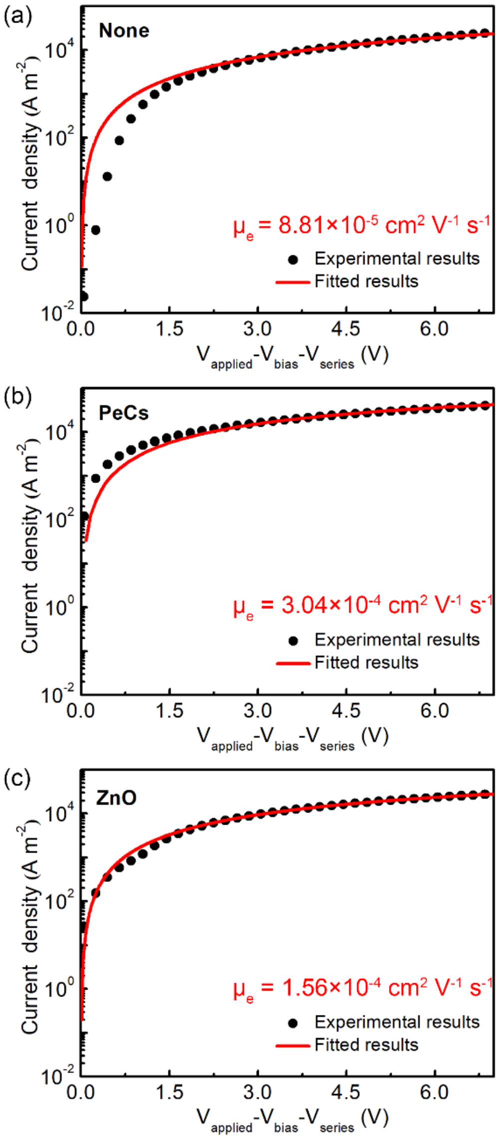

Fig. S4. SCLC fittings of the electron-only devices based on PCDTBT:PC$_{71}$BM photoactive layer with (a) none, (b) PeCs and (c) ZnO as CILs.

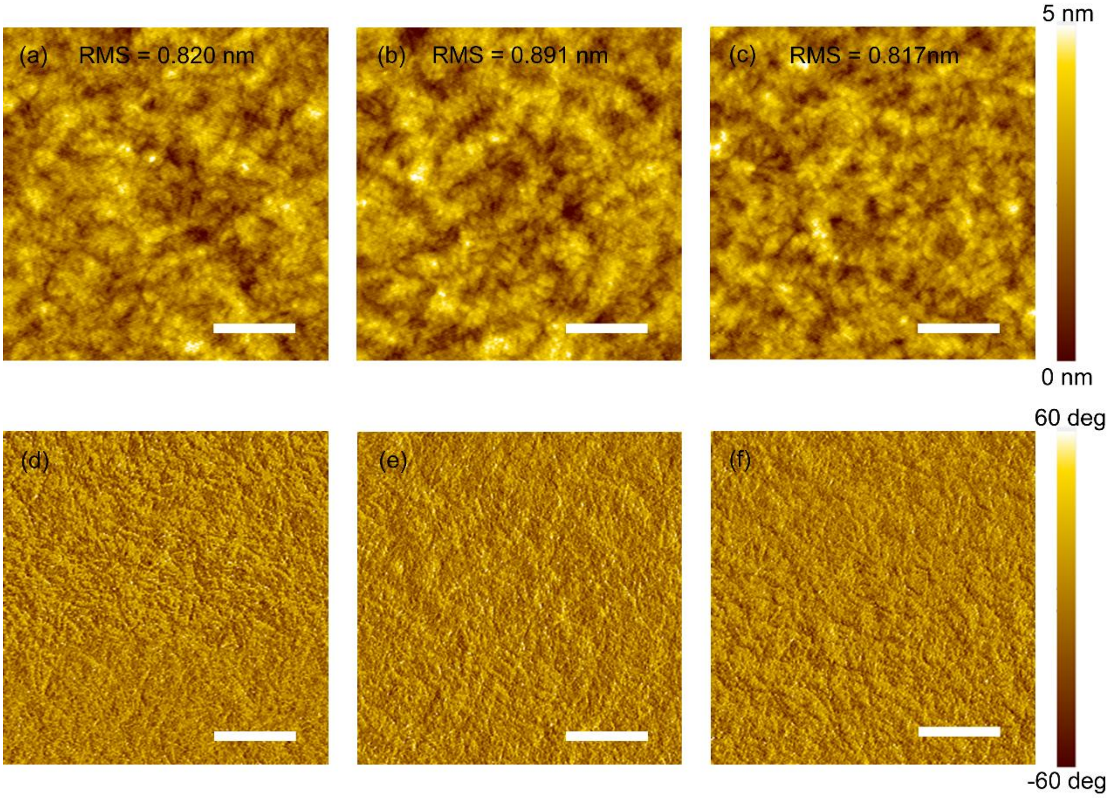

Fig. S5. AFM height images of the PCDTBT:$PC_{71}BM$ photoactive layer on (a) ITO, (b) ITO/PeCs and (c) ITO/ZnO substrates. AFM phase images of the PCDTBT:$PC_{71}BM$ photoactive layer on (d) ITO, (e) ITO/PeCs and (f) ITO/ZnO substrates. The scale bar is 500 nm.