

Supporting Information

Integration of Light-harvesting Complexes into the Polymer Bulk Heterojunction P3HT/PCBM Device for Efficient Photovoltaic Cells

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Preparation of LHCIIB and free thylakoid pigments

LHCIIB was isolated from 10-14 day old pea seedlings according to the method described in Krupa et al (1987). Leaves were homogenized in precold solution containing 400 mM sorbitol, 50 mM tricine/NaOH (pH7.8). After filtering through four layers of cheesecloth, the suspension was centrifuged at 7000×g for 10 min at 4 °C. The pellet was resuspended in cold buffer containing 50 mM sorbitol, 5 mM EDTA (pH 7.8) and centrifuged at 10,000×g for 10 min at 4 °C. The pellet was resuspended in cold water and the density of the suspension adjusted to 0.8 mg Chl/ml. Upon dissolving the thylakoid membrane by adding Triton X-100 (5% (w/v)) to a final detergent concentration of 0.7% (w/v), the LHCIIB was precipitated by adding 20 mM MgCl₂ and 100 mM KCl. The pellet was suspended in water again and the process was repeated until the Chl *a/b* ratio of the LHCIIB extract was about 1.3.

Part of the homogenate was used to extract total thylakoid pigments by acetone under dim light. The homogenate was centrifuged at 6000×g (10 min). The pellet was suspended in acetone and centrifuged at 15000×g (10 min). The pigment solution in acetone was then partitioned into diethyl ether and dried in a rotary evaporator

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(Heidolph, Germany).

(Krupa, Z., et al., Development at cold-hardening temperatures. The structure and composition of purified rye light harvesting complex II. *Plant Physiol.*, 1987. 84: p. 19-24.)

Characterizations The ultraviolet–visible (UV) spectra of the samples were recorded on a PerkinElmer Lambda 750 spectrophotometer. Fluorescence measurement for photoluminescence (PL) of the polymers was carried out on a Hitachi F-7000 PC spectrofluorophotometer with a xenon lamp as the light source. Cyclic voltammograms (CV) were performed in a three-electrode cell using platinum electrodes at a scan rate of 50 mV s⁻¹ and a Ag/Ag⁺ (0.1 M of AgNO₃ in acetonitrile) reference electrode in an anhydrous and nitrogen-saturated solution of 0.1 M tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) in acetonitrile. Under these conditions, the onset oxidation potential ($E_{1/2}^{ox}$) of ferrocene was -0.02 V versus Ag/Ag⁺. The HOMO energy level of polymers was determined from the oxidation onset of the second scan from CV data. It is assumed that the redox potential of Fc/Fc⁺ has an absolute energy level of -4.60 eV to vacuum. The energy of HOMO level was calculated according to the eqs1; the electrochemically determined band gaps were deduced from the difference between onset potentials from oxidation and reduction of copolymers as depicted in eq 2.

$$E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{ox}} + 4.62) \text{ (eV)} \quad (1)$$

$$E_{\text{gap}}^{\text{EC}} = (E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}) \text{ (eV)} \quad (3)$$

Annealing of films was conducted by heating in the setting temperature for 30 min, followed by cooling to room temperature at a cooling speed of 1 deg/min. All the thermal treatments were performed under ambient atmosphere. Microscopy was performed on a Zeiss LSM 510 Confocal Laser Scanning Microscope.

Device Fabrication and Characterization

Normal Structure: ITO-coated glasses were cleaned with acetone and isopropyl alcohol. After the substrates were dried with air, they were treated with UV ozone for

5 min. PEDOT:PSS (Baytron AI 4083) was spin-cast on the cleaned ITO as received and baked at 140 °C for 10 min. The blend solutions of the P3HT (purchased from Rieke Metals, used as received) and PCBM (purchased from Nano-C, used as received), blending as 1:1 wt %, 25 mg/mL in chlorobenzene, were prepared by stirring of the solution for 24 h in a glovebox and spin-cast at 1000 rpm for 30 s. Alternatively, LHCIIB layers was coated on the PEDOT:PSS or P3HT/PCBM through spray deposition. Subsequently, the substrates are rinsed thoroughly with water for 5 s, dried in a stream of nitrogen, and then stored under an argon atmosphere, to prepare the substrate for deposition of the semiconducting protective coating. The thicknesses of all the films were measured by a Dektak profiler with an accuracy of ± 1 nm. 0.8 nm of LiF and 100 nm of Al were deposited sequentially at 5×10^{-7} Torr. All devices were characterized under ambient conditions, and the typical illumination intensity was 100 mW/cm^2 (AM 1.5G Oriel solar simulator). The spectral mismatch factor was calculated by comparison of the solar simulator spectrum and the AM 1.5 spectrum at room temperature. The IPCE spectra for the PSCs were measured on an IPCE measuring system. National Institute of Standards and Technology (NIST) calibrated UV-enhanced silicon, and germanium photodetectors were used to calibrate the measurements.

Inverted Structure: Inverted solar cells were fabricated on ITO-coated glass substrates. The ITO-coated glass substrates were first cleaned with detergent, ultrasonicated in water, acetone and isopropyl alcohol, and subsequently dried overnight in an oven. The ZnO precursor solution was spin-cast on top of the ITO-glass substrate. The films were annealed at 150 °C for 1 h in air. The ZnO film thickness was approximately 40 nm, as determined by a profilometer. The ZnO-coated substrates were transferred into a glove box. A solution containing a mixture of P3HT:PCBM (1:1, w/w) in a chlorobenzene solvent with a concentration of 20 mg mL^{-1} was spin-cast on top of ZnO films. The polymer–fullerene films were heated at 120 °C for 30 min. Then, a layer of LHCIIB film was deposited on top of the active layer. Finally, the anode (Ag, ≈ 60 nm) was deposited through a shadow

mask by thermal evaporation in a vacuum of about 5×10^{-7} Torr.

Solvent annealing: P3HT and PCBM were blended to make 1:1 wt %, 25 mg ml⁻¹ solution, dissolved in 1,2-dichlorobenzene (DCB). The blend was stirred for 12 h at 40 °C in the glove box. The active layer was obtained by spin-coating the blend at 650 r.p.m. for 60 s and then 1500 r.p.m for 1s. And the thickness of film was about 200 nm, as measured with a Dektak profilometer. Spin-coating at 650 r.p.m. left the films wet for slow growth, which were then dried in covered glass petri dishes to control the growth of the activelayer films. And the solvent evaporation time is all about 30min, judging by visual inspection of the change in film color when it solidifies from the liquid phase.

Thermal treatment: The preannealed treatment is conduct where the active layer is annealed under a nitrogen atmosphere at 120°C for 30 min before a 60 nm thick Ag (cathode) layer is evaporated on top of the active layer.

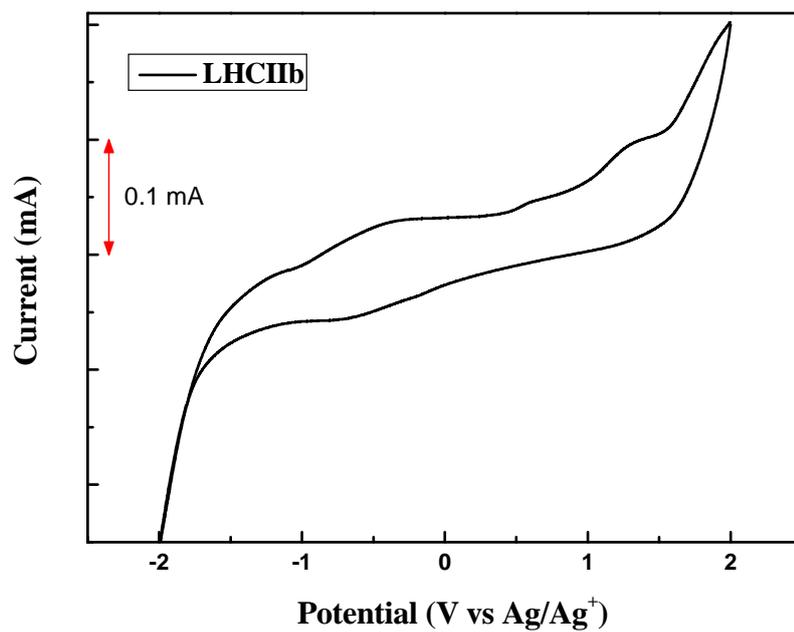


Figure S1. Cyclic voltammetry (CV) of the LHCIb thin film, measured in a 0.1 M solution of Bu_4NPF_6 in CH_3CN with a Pt electrode and a Ag/AgNO_3 reference electrode.

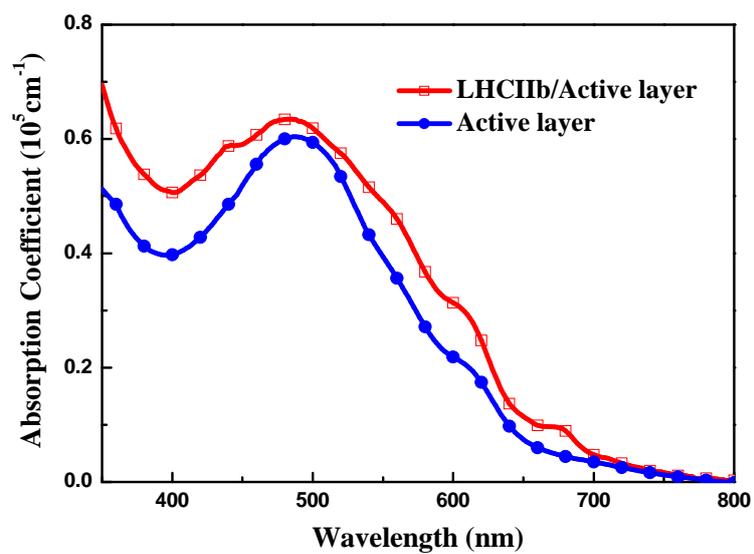


Figure S2. Absorption spectra of the thin films of P3HT:PCBM (1:1, w/w) active layer and their bilayer films with LHCIIB.

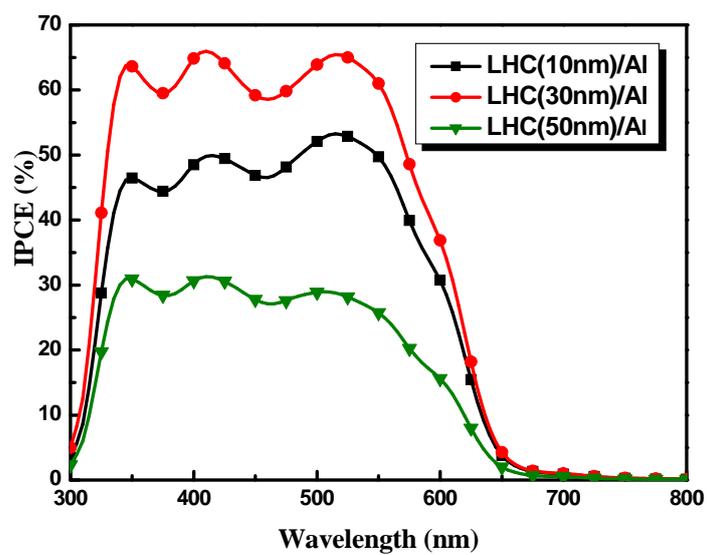


Figure S3. Incident photon-to-current efficiency (IPCE) of photovoltaic cells based on cell C (ITO/ZnO/P3HT:PCBM/LHCIIb/Ag) after preannealing with different LHCIIb layer thickness.