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Supporting Information for

Introducing Optically Polarizable Molecules into Perovskite Solar Cells with Simultaneously Enhanced Spin-Orbital Coupling, Suppressed Non-Radiative Recombination and Improved Transport Balance towards Enhancing Photovoltaic Actions

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Experiment

Device Fabrication.

PEDOT:PSS (Heraeus 4083) was spun on a pre-cleaned ITO substrate at a speed of 4000 round per minute (rpm) for 60 seconds. The film was then annealed at 150 °C for 15 min. The MAPbI_{3-x}Cl_x precursor solution was prepared by mixing MAI, PbI₂ and PbCl₂ (Xi' An Polymer Light Technology Corp) with a molar rate (1.4:1.25:0.15) in mixture of dimethylsulfoxied (DMSO) and γ -butyrolactone (GBL) with a volume rate (3:7). The solution was stirred at 60 °C for 12 hours and then coated on the PEDOT:PSS/ ITO substrate by a consecutive two-step spin-coated process at 1000 and 4000 rpm for 10 and 31 s, respectively. During the second spin-coating step, the substrate was treated by 400 µl chlorobenzene (CB, Sigma Aldrich) drop-coating. The substrate was annealed on a hot plate at 100 °C for 5 min. The solution of PCBM (25 mg/ml in CB) was spin-coated on the top of the perovskite film at 3000 rpm for 60 s. The PEI modification layer was spin-coated on top at 5000 rpm for 30 s from isopropanol solution (0.05 wt%). Finally, a 60 nm thick silver layer was thermal evaporated through a shadow mask to define the active area of the device (~2×2 mm²). For depositing UBHJ perovskite-ITIC films, 0.5 mg ITIC was dissolved in 1 ml perovskite precursor solution. To prepare GBHJ films, ITIC was pre-dissolved in the dripping solvent (CB) with a concentration of 1 mg/ml. Supporting information Figure S10 shows the optimization of ITIC concentration.

Characterization.

J-V curves were measured using a solar simulator (Zolix SS150A) with a source meter (Keysight B2912A) at 100 mW/cm², AM 1.5G illumination, and a calibrated Si-reference cell. The J-V curves were measured by forward (reverse bias (-0.2 V) \rightarrow forward bias (1.2 V)) or reverse (forward bias (1.2 V) \rightarrow reverse bias (-0.2 V)) scan. The step voltage was fixed at 7 mV and the scan speed was fixed at 100 mV/s. The top-view morphologies of perovskite films were measured with a Hitachi S-4800 field-emission scanning electron microscope (SEM). A thin layer of Au was deposited on top of the perovskite film for conductivity requirement. An acceleration voltage of 5KV was used to minimize electron beam damage. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) experiment was conducted on a TOF.SIMS 5-100 (ION-TOF GmbH). Bil were used as the primary beam and positive ions were detected. Cs+ ions with 2 keV ion energy were used to sputter the sample. A scan area of 100×100 um was analyzed with Bi ions with 30 keV ion energy. Ultraviolet-visible spectra were measured by a Shimadzu UV/Vis 2600 spectrophotometer in the 400-800 nm wavelength range. Solution samples were prepared by dissolving ITIC or ITIC with PbI2 in DMF. Films were deposited on Glass/ PEDOT:PSS substrates like device fabrication. Spin effects of Jsc was measured using a 532 nm laser at 10 mW/cm², a source meter (Keithley 2400), and a silicon reference solar cell. The beam from laser passes vertically through a polarizer and a quarter wave plate, then illuminating to a solar cell. We convert between linear polarized and circular polarized light by adjusting the angle of the quarter wave plate. Steady-state photoluminescence spectra were recorded with a Jobinyvon Horiba Fluorolog-3 fluorometer system with excitation at 480 nm from film surface. Time-resolved photoluminescence experiments were conducted using the single photon counting system, and the samples were excited by a pulsed laser diode with a 480 nm wavelength from film surface. Thermal admittance spectroscopy (TAS) was measured by using an Agilent E4990A LCR meter with alternating voltage of 30 mV. The frequency dependent capacitance was measured from 100 Hz to 10 MHz with zero bias in dark. The voltage dependent capacitance was measured from -0.2 to 1.3 V with a frequency of 100 kHz in dark. Fourier transform infrared spectroscopy (FTIR) was characterized by using VERTEX 70 Spectrometer from Brucker Optics. The samples used ITIC MAPbI3 mixed power and pure ITIC power. The ITIC MAPbI3 mixed power was prepared by dissolving MAPbI₃ power into ITIC chlorobenzene and stirring for 1 hour at 60 °C, then the black solid was achieved after removing the solvent. The electron mobility was measured with a space-charge limited current (SCLC) model using the Mott-Gurney law by constructing the electron-only device (ITO/ TiO₂/ Perovskite/ PCBM/ Ag).



Figure S1. Water contact angles measured on the surfaces of ITIC (blue) and PCBM (brown) films.



Figure S2. IPCE spectra of solar cells with PHJ (black) perovskite, UBHJ (red) and GBHJ (blue) perovskite-ITIC.



Figure S3. *J-V* curves measured under 100 mW/cm² AM 1.5 illumination in both forward (short circuit to open circuit) and reverse (open circuit to short circuit) direction for PHJ (\mathbf{a}), UBHJ (\mathbf{b}) and GBHJ (\mathbf{c}) devices.



Figure S4. Stabilized photocurrent density obtained while holding the solar cells at 0.88 V for 300 s.



Figure S5. UV-vis absorption spectra of pure (black), UBHJ(red) and GBHJ (blue) perovskite films formed on glass.



Figure S6. (a) The Nyquist plots of solar cells with PHJ (black) perovskite, UBHJ (blue) and GBHJ (brow) perovskite-ITIC, the fitting curves are denoted by the red lines. (b) The fitting model of equivalent circuit.



Figure S7. a)UV-vis absorption spectra and b) steady-state PL spectroscopy of ITIC film formed on glass with 480 nm green laser as excitation source.



Figure S8. *J-V* curves measured under dark for solar cells with PHJ (black) perovskite, UBHJ (blue) and GBHJ (green) perovskite-ITIC.



Figure S9. *J-V* curve measured under 100 mW/cm² AM 1.5 illumination for the device consists of ITO/ PEDOT:PSS / CH₃NH₃PbI_{3-x}Cl_x/ ITIC/ PEI/Ag.



Figure S10. *J-V* curves measured under 100 mW/cm² AM 1.5 illumination for various concentration of ITIC doping solutions (a) and dripping solution (b).