Supporting Information

Lewis Acid-Base Adduct Approach for High Efficiency Perovskite Solar Cells

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Experimental details

Material synthesis

$HC(NH_2)_2I$. $HC(NH_2)_2I$ (FAI) was synthesized according to the method described elsewhere [1]. 30 mL of hydroiodic acid (57 wt.% in water, Sigma-Aldrich) was reacted with 15 g of formamidinium acetate (99%, Aldrich) at 0 ^oC. After stirring for 2 h, dark yellow precipitate was obtained by evaporating the solvent at 60 ^oC using rotary evaporator. The solid was washed with diethyl ether and recrystallized from anhydrous ethanol. Resulting white precipitate was dried under vacuum for 24 h at 60 ^oC and stored under Ar atmosphere.

PbI_2•DMSO adduct. 461 mg of PbI_2 (99.9985%, Alpha Aesar) was dissolved in 2 mL of *N,N*-dimethylsulfoxide (DMSO, 99.5%, Sigma-Aldrich), to which 10 mL of anhydrous ethanol (SAMCHUN, 99.5%) was added. The precipitation was filtered and dried in vacuum oven for 1 h, which was used for infrared (IR) spectrocopy measurement.

FAI•PbI_2•DMSO adduct. 461 mg of PbI_2, 172 mg of FAI and 78 mg of DMSO were dissolved in 600 mg of *N,N*-dimethylformamide (DMF) (Sigma-Aldrich, 99.8%), to which 10 mL of diethyl ether (SAMCHUN, 99.0%) was added. The precipitation was filtered and dried in vacuum oven for 1 h, which was used for infrared (IR) spectrocopy measurement.

PbI_2•thiourea adduct. 461 mg of PbI_2 and 76 mg of thiourea (Sigma-Aldrich, ≥99.0%) were dissolved in 600 mg of DMF, to which 10 mL of diethyl ether was added. The precipitation was filtered and dried in vacuum oven for 1 h, which was used for infrared (IR) spectrocopy

measurement.

FAI•PbI_2•thiourea adduct. 461 mg of PbI_2, 172 mg of FAI and 76 mg of thiourea were dissolved in 600 mg of DMF, to which 10 mL of diethyl ether was added. The precipitation was filtered and dried in vacuum oven for 1 h at 80 ^oC, which was used for infrared (IR) spectrocopy measurement.

Device fabrication

All the devices were prepared in ambient condition without controlling the humidity. Fluorine-doped tin oxide (FTO) glass (Pilkington, TEC-8, 8Ω/sq) was cleaned by detergent followed by washing with acetone and sonication in ethanol bath for 15 min. ca. 60 nm-thick compact TiO_2 blocking layer was deposited on the FTO glass by spin-coating of 0.1 M titanium diisopropoxide bis(acetylacetonate) (Aldrich, 75 wt% in isopropanol) solution in 1-butanol (Aldrich, 99.8%) three times. The substrate was dried on hot plate at 125 ^oC for 5 min between each coating, and finally annealed at 500 ^oC for 20 min. To enhance the wettability, compact TiO_2-caoted FTO glass was treated with UV-Ozone for 10 min before spin-coating of perovskite solution. Perovskite solution was prepared by dissolving 1 mmol of PbI_2 (461 mg) and FAI (172 mg) in 600 mg of DMF, in which 1 mmol of dimethyl sulfoxide (DMSO) (78 mg) or thiourea (76 mg) was added to form the corresponding adduct. The solution was filtered using syringe filter having 0.45 μm pore size (Whatman) before use. To control the adduct ratio between DMSO and thiourea, corresponding amount of solution containing DMSO and thiourea was mixed. FAI•PbI_2•($DMSO_{1-x}$$thiourea_x$) adduct film was formed by spin-coating of 30 μL of corresponding perovskite solution at 4000 rpm for 30 s, in which 500 μL of diethyl ether was dropped on spinning substrate after 10 s. The adduct film was converted to $FAPbI_3$ film by heat-treatment at 50 ^oC for 3 min and 150 ^oC for 30 min. Spiro-MeOTAD layer was formed from the solution prepared by dissolving 72.3 mg of spiro-MeOTAD in 1 mL of chlorobenzene, to which 28.8 μL of 4-tert-butyl pyridine and 17.5 μL of lithium bis(trifluoromethanesulfonyl)imide solution (520 mg Li-TFSI in 1 mL acetonitrile (Sigma-Aldrich, 99.8%)) were added. Spiro-MeOTAD was deposited by dropping 20 μL of spiro-MeOTAD solution on spinning substrate at 3000 rpm. Gold was thermally evaporated and used as a counter electrode.

Characterization

Current density-voltage curve was obtained using a Keithley 2400 source meter under AM 1.5G one sun illumination (100 mW/cm^2), which was simulated by solar simulator (Oriel Sol 3A classAAA) equipped with 450 W Xenon lamp (Newport 6280NS). NREL-calibrated Si solar cell equipped with KG-2 filter was used to adjust the light intensity. The device was covered with a metal aperture with active area of 0.125 cm^2 during the measurement. External quantum efficiency (EQE) was measured by a specially designed EQE system (PV measurement Inc.), in which monochromatic beam was generated from a 75 W Xenon source lamp (USHIO, Japan). EQE data were collected at DC mode without bias light. Absorption spectra were measured by UV-vis spectrometer (PerkinElmer, lamda35). The Fourier transform infrared spectra (FT-IR) were measured using Bruker Vertex 70 spectrometer equipped with MIRacle Micro ATR accessory. Capacitance-frequency (*C-f*) curve was obtained using impedance spectroscopy (IS) with PGSTAT 128N (Autolab, Eco-Chemie). 20 mV of AC sinusoidal voltage was applied with frequency ranging from 1 MHz to 1 Hz at short-circuit condition. For IS measurement under illumination, LED white source was used to provide 80 mW/cm^2 of light intensity. Thermogravimetric analysis (TGA) was carried out by TG/DTA 7300 (SEICO INST.). X-ray diffraction patterns were collected by X-ray diffractometer (D8 advance with DAVINCI, Bruker Corporation) using Cu Kα radiation at a scan rate of 2.4 ^{o}/min. Time-integrated and time-resolved photoluminescence (PL) was measured by a fluorescence lifetime spectrometer (Quantaurus-Tau C11367-12, HAMAMATSU). The films were photo-excited by 464 nm laser with peak power of 231 mW and pulse duration of 53 ps (PLP-10, HAMAMATSU) pulsed at frequency of 2 MHz. The PL was detected by high sensitivity photon counting near IR detector.

Reference

[1] Lee, J.-W; Kim, D.-H; Kim, H.-S; Seo, S.-W.; Cho, S. M.; Park, N.-G. Formamidinium and Cesium Hybridization for Photo- and Moisture-Stable Perovskite Solar Cell. *Adv. Energy Mater.* **2015**, DOI: 10.1002/aenm.201501310.