Enhanced Electron Transport in Heterojunction Sn-Perovskite Solar Cells Assisted by [6,6]-Phenyl-C61-butyric Acid Methyl Ester as a Dopant

Ajay Kumar Baranwal, *# Huan Bi,# Gaurav Kapil, Takeshi Kitamura, Liang Wang, Jiaqi Liu, Qing Shen, Shuzi Hayase*

Info-Powered Energy System Research Center, The University of Electro-Communications,

1-5-1 Chofugaoka, Chofu, Tokyo, 182-8585, Japan

Email: ajaybaranwal@uec.ac.jp; hayase@uec.ac.jp

# equal contribution

Experimental details: All chemicals were used as received without any purification. Laser etching was performed to make a pattern on FTO glass. PEDOT:PSS (AI4083) was purchased from Clavious. Dimethylformamide (DMF), dimethyl sulfoxide, chlorobenzene, Tin Iodide (99.99%, perovskite grade), ethylenediammoinum diiodide ($EDAI_2$), diethylammonium iodide, germanium iodide, cesium iodide, tin fluoride, and tin metal powder (45 µm) were purchased from sigma Aldrich. PCBM (99%) was purchased from nanom spectra, Japan.

PEDOT:PSS was coated on 2cm×2cm FTO glass at ambient air condition at 5000 rpm/50 seconds and subsequently heat treatment was performed at 150 °C/20 minutes. The samples were then transferred inside glove box filled with N_2. 4 ml stock solution of 1M $(Cs_{0.02}(FA_{0.9}DEA_{0.1})_{0.98})_{0.98}EDA_{0.01}SnI_3$ + 10% SnF_2+ 5% GeI_2 + 20 mg Sn powder was prepared inside glove box with DMF:DMSO (4:1 v/v) mixed solvent. Addition of Sn-metal powder was essential to attain the required photoelectric performance. This perovskite solution was placed for overnight stirring. 1 ml of this solution was poured into another PCBM containing vial such that PCBM concentration was maintained to 1mM, 3mM and 10mM. After 1 hours stirring, each perovskite solution was filtered with 45 µm PTFE filter. 50 µl of this solution was dropped onto PEDOT:PSS coated FTO glass. The spin program to run this FTO glass was set to 5000 rpm/50 seconds, and 500 µl of chlorobenzene as antisolvent was dropped quickly at 15 second at the start of spinning process. Perovskite coated FTO glass was heat treated at 70 °C/20 minutes. As a next step, perovskite surface was dynamically coated with 15mM EDA solution dissolved in chlorobenzene. Further samples were baked at 70 °C/5 minutes. This assembly was transferred to thermal evaporation system where 30 nm C60 and 7 nm BCP were deposited consequently in a chamber at 10-5 Pa. The semi prepared devices were transferred to another chamber where 130 nm of silver electrodes were thermally deposited at 10-5Pa. UV-vis absorption spectra was measured using instrument V-570, JASCO. Photo-yield spectroscopy was measured using Bunkoukeiki KV 205-HK ionization system with photon energy variation from 4 eV to 6.5 eV. Fermi level was measured using Riken keiki FAC-2 inside glove box. XRD pattern was measured using Ultima III, Rigaku co. limited. X-ray photoelectron spectroscopy were measured using JPS-9200 Jeol limited. Surface images of fabricated films were captured using Field emission scanning electron microscopy (FESEM) HITACHI 4800. Roughness of

film using atomic force morphology using JSPM-5200, JEOL. Contact angle measurement setup DCA-VZ, Kyowa was used to measure the water contact angle. IMPS, IMVS, TPV, TPC and EIS spectra were measured using Piaos setup of Fluxim. Solar cell photoelectric performance was measured inside N2 filled glove box applying a black metal mask of 0.10cm2 opening area, using instrument CEP-2000SRR, Bunkoukeiki Inc, AM 1.5G, 100mW/cm^2. The intensity of lamp was calibrated with silicon solar cell. Incident photon to collected electron (IPCE) was measured using Bunkokeiki CEP-2000SRR (300W Xenon lamp with a monochromator, Newport 74010).

Vienna ab Initio Simulation Package (CP2K) was used to perform DFT calculations.[1] The exchange-correlation energies of generalized gradient approximation were followed from Perdew-Burke-Ernzerh. 400 eV was set for energy cutoff for plane-wave. At last, visualization was performed using VESTA by constructing 3×3×3 super cell.[2]

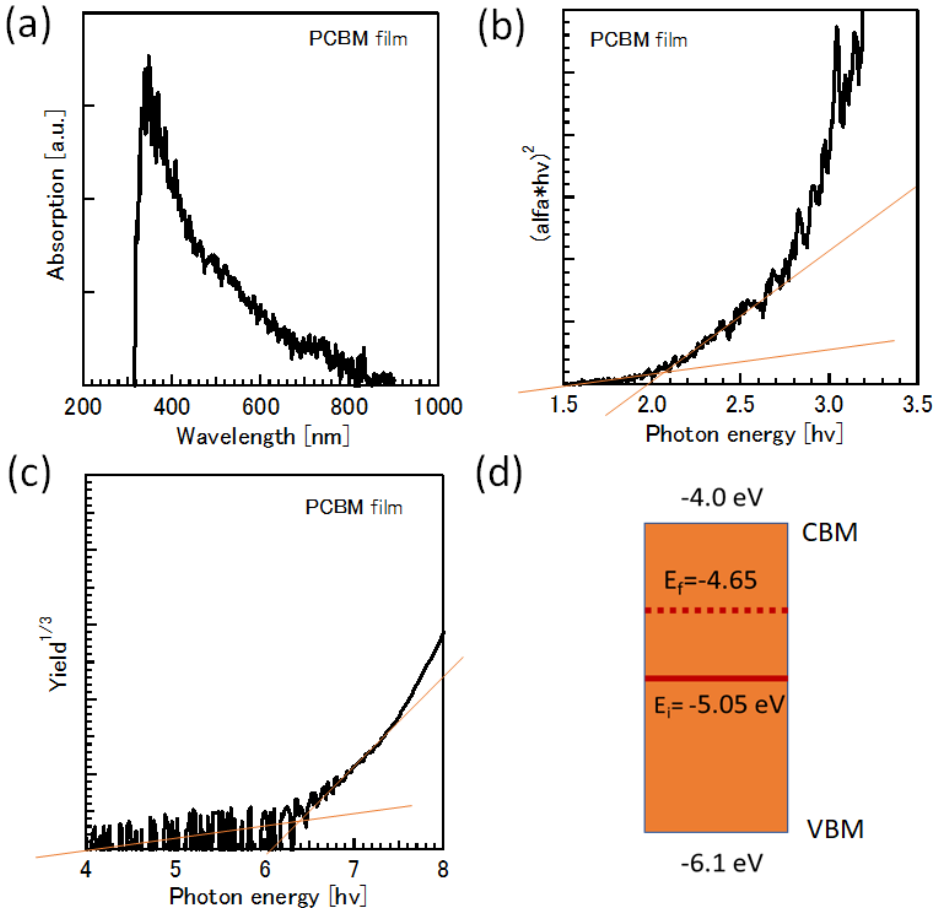

Figure S1: Thin film of PCBM with DMF:DMSO (4:1 v/v) solvent **(a)** UV-vis absorption spectra **(b)** Tauc plot **(c)** PYS spectra **(d)** Energy diagram showing fermi level, Valence band maximum and conduction band minimum values.

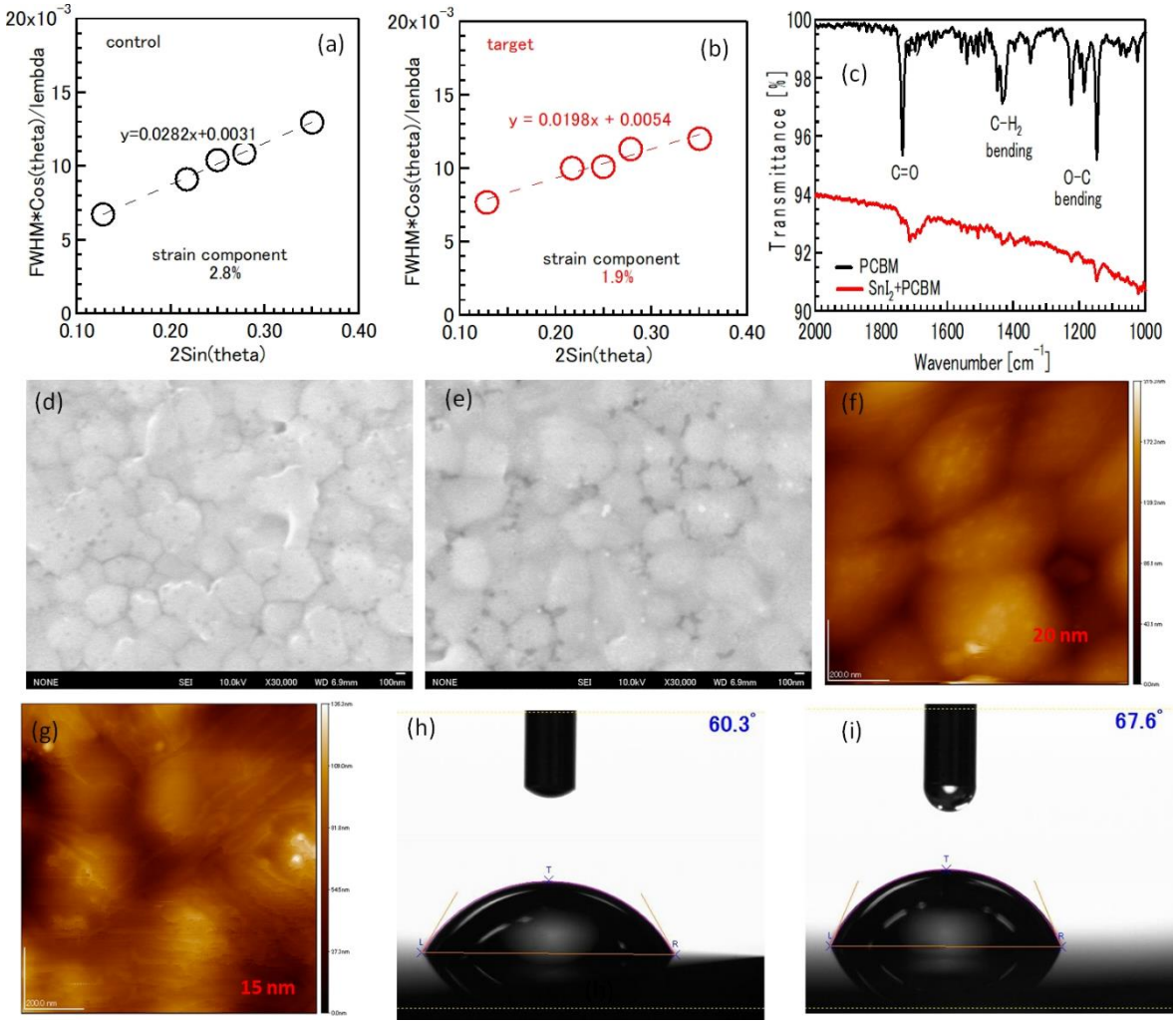

Figure S2: (a) (b) Williamson-Hall plot **(c)** FTIR spectra of PCBM and SnI_2mixed PCBM **(d)** surface morphology of THP film **(e)** surface morphology of PCBM-THP film **(f)** AFM image of THP film **(g)** AFM image of PCBM-THP film **(h)** water contact angle of THP film **(i)** water contact angle of PCBM-THP film.

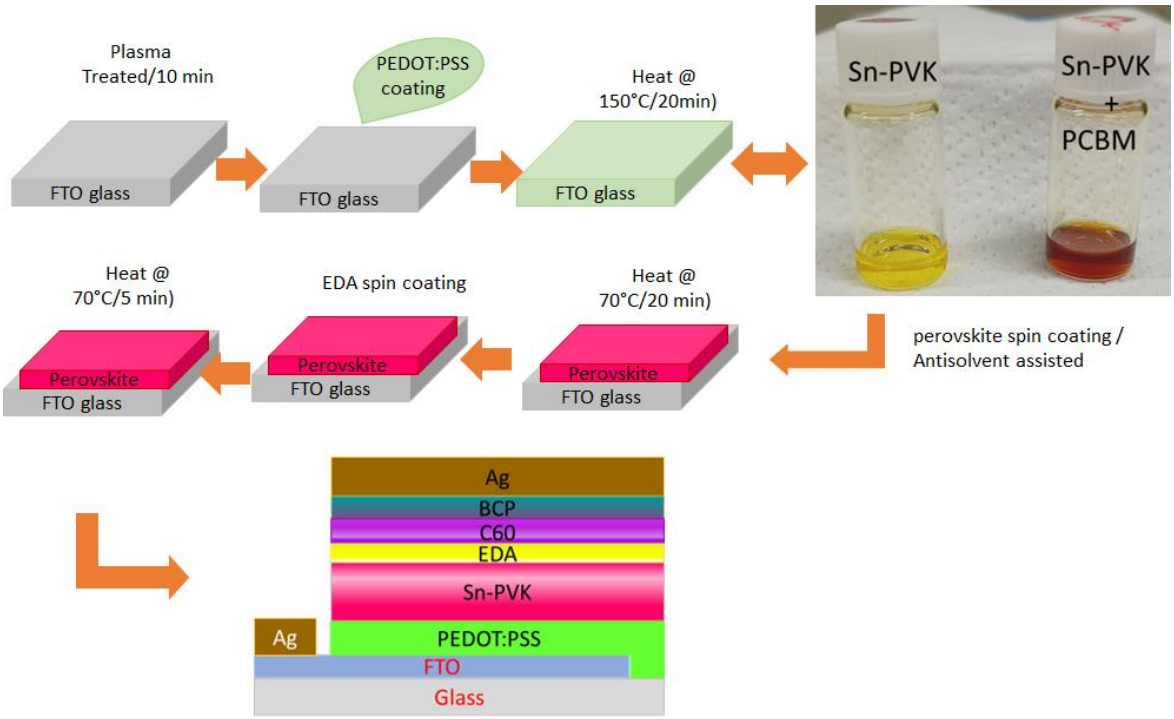

Figure S3: Tin halide perovskite solar cell fabrication process and device structure.

Table S I: Time resolved photoluminescence decay curve profile fitting data. Films were fabricated on FTO glass.

	τ	τ 1	A1	τ 2	A2	A1/A2	Electron transfer rate [/s] [3]
Control	12.65	6.69	503.98	15.72	418.22	1.20	0.94×10^{8}
1mM	9.47	4.39	556.98	12.11	388.91	1.43	
3mM	8.65	3.63	540.32	11.08	365.43	1.48	2.1×10^{8}
10mM	13.61	6.31	460.56	16.19	508.03	0.90	
Control (glass)	13.27	8.70	699.6	18.21	307.8		

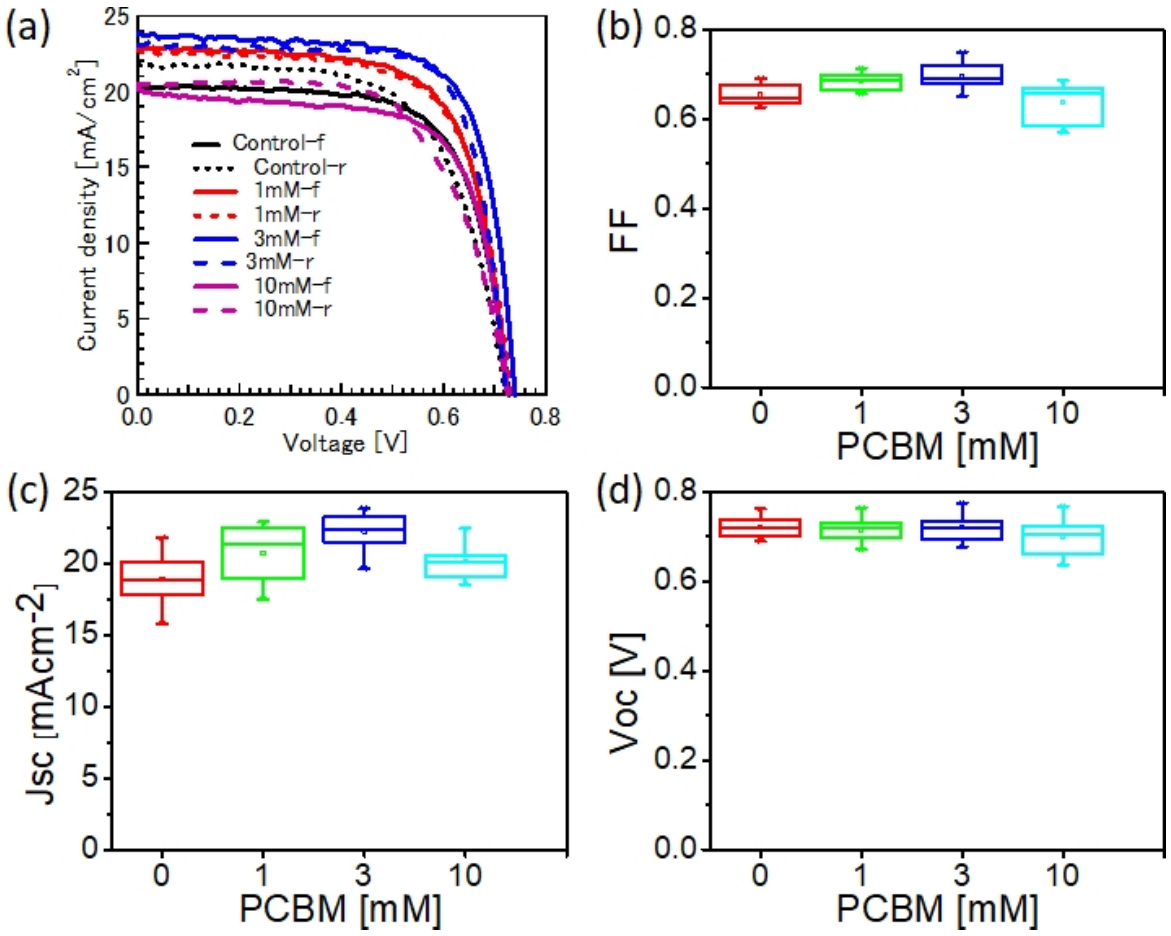

Figure S4: Box plot showing photoelectric performance variation with respect to PCBM as a dopant **(a)** Efficiency **(b)** Fill factor **(c)** Short circuit current density **(d)** Open circuit voltage. Ten devices were fabricated in each condition.

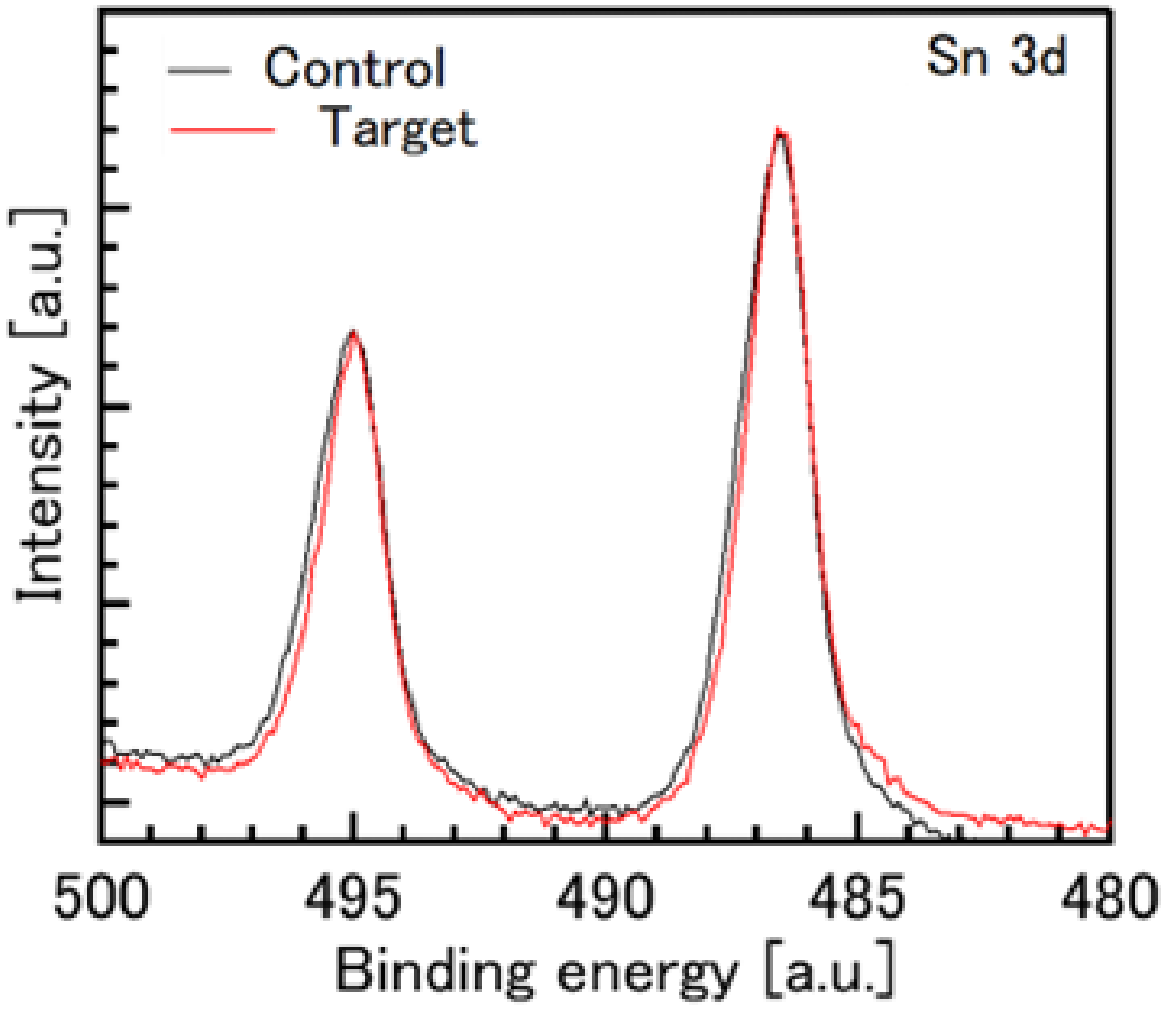

Figure S5: Sn 3d spectra of control and target tin halide perovskite films.

References:

1. Kühne, T. D.; Iannuzzi, M.; Del Ben, M.; Rybkin, V. V.; Seewald, P.; Stein, F.; Laino, T.; Khaliullin, R. Z.; Schütt, O.; Schiffmann, F.; Golze, D.; Wilhelm, J.; Chulkov, S.; Bani-Hashemian, M. H.; Weber, V.; Borštnik, U.; Taillefumier, M.; Jakobovits, A. S.; Lazzaro, A.; Pabst, H.; Müller, T.; Schade, R.; Guidon, M.; Andermatt, S.; Holmberg, N.; Schenter, G. K.; Hehn, A.; Bussy, A.; Belleflamme, F.; Tabacchi, G.; Glöß, A.; Lass, M.; Bethune, I.; Mundy, C. J.; Plessl, C.; Watkins, M.; VandeVondele, J.; Krack, M.; Hutter, J. CP2K: An Electronic Structure and Molecular Dynamics Software Package - Quickstep: Efficient and Accurate Electronic Structure Calculations. *J Chem Phys* **2020**, *152* (19). https://doi.org/10.1063/5.0007045.

2. Momma, K.; Izumi, F. *VESTA 3* for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. *J Appl Crystallogr* **2011**, *44* (6), 1272–1276. https://doi.org/10.1107/S0021889811038970.

3. Chen, M.; Kapil, G.; Li, Y.; Kamarudin, M. A.; Baranwal, A. K.; Nishimura, K.; Sahamir, S. R.; Sanehira, Y.; Li, H.; Ding, C.; Zhang, Z.; Shen, Q.; Hayase, S. Large Synergy Effects of Doping, a Site Substitution, and Surface Passivation in Wide Bandgap Pb-Free ASnI2Br Perovskite Solar Cells on Efficiency and Stability Enhancement. *J Power Sources* **2022**, *520*, 230848. https://doi.org/10.1016/j.jpowsour.2021.230848.