ADVANCED MATERIALS

Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.201707001

Mixed Valence Perovskite $Cs_2Au_2I_6$: A Potential Material for Thin-Film Pb-Free Photovoltaic Cells with Ultrahigh Efficiency

Lamjed Debbichi, Songju Lee, Hyunyoung Cho, Andrew M. Rappe, Ki-Ha Hong, Min Seok Jang, and Hyungjun Kim**

Supporting Information

Mixed valence perovskite $Cs_2Au_2I_6$: a potential material for thin-film Pb-free photovoltaic cells with ultra high-efficiency

Lamjed Debbichi,[a],† Songju Lee,[b],† Hyunyoung Cho,[b] Andrew M. Rappe,[c] Ki-Ha Hong,[d] Min Seok Jang,[b], and Hyungjun Kim,[a],[e]**

[a] Dr. L. Debbichi, Prof. H. Kim
Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-Ro, Yuseong-Gu, Daejeon 34141, Korea
E-mail: linus16@kaist.ac.kr

[b] S. Lee, H. Cho, Prof. M. S. Jang
School of Electrical Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-Ro, Yuseong-Gu, Daejeon 34141, Korea
E-mail: jang.minseok@kaist.ac.kr

[c] Prof. A. M. Rappe
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, United States

[d] Prof. K.-H. Hong
Department of Materials Science and Engineering, Hanbat National University, 125 Dongseo-Daero, Yuseong-Gu, Daejeon 34158, Korea

[e] Prof. H. Kim
Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-Ro, Yuseong-Gu, Daejeon 34141, Korea
E-mail: linus16@kaist.ac.kr

† L.D. and S.L are equally contributed to this work

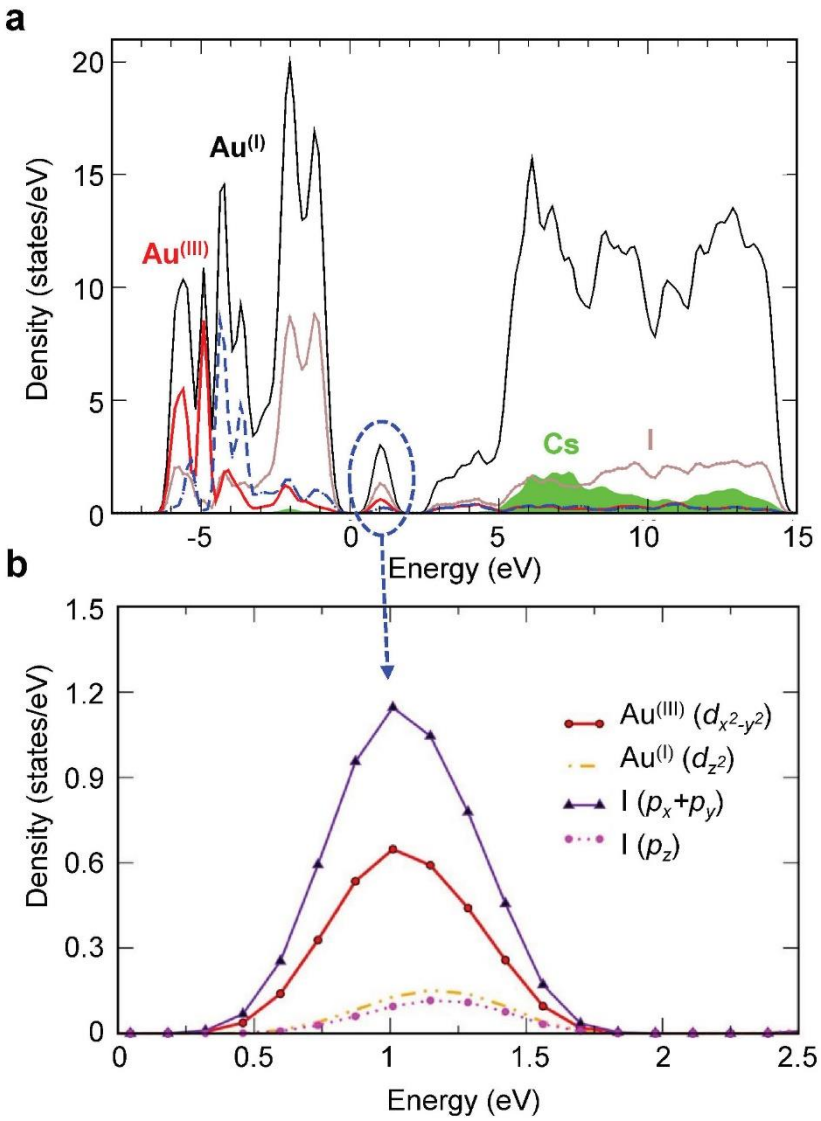

Figure S1. (a) Total and atomic partial density of states (DOS) of the $Cs_2Au_2I_6$ structure. The Fermi level is set at zero energy. (b) Partial DOS of the intermediate band (IB) is magnified. IB mostly consists of d_{x2-y2} orbital of Au^{III} and $p_{x/y}$ orbital of I, implying the dominant contribution from the trivalent Au^{III}-I_4 unit.

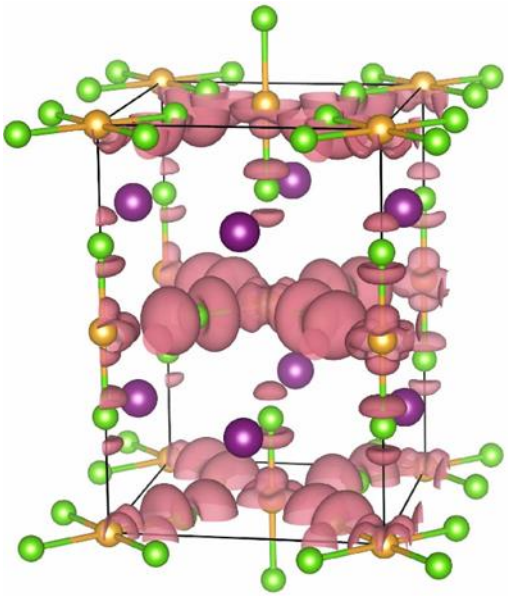

Figure S2. Real-space visualization of the intermediate band (IB) of the $Cs_2Au_2I_6$ structure. Charge density isosurface is shown with the isovalue of 0.0012 e/Bohr^3.

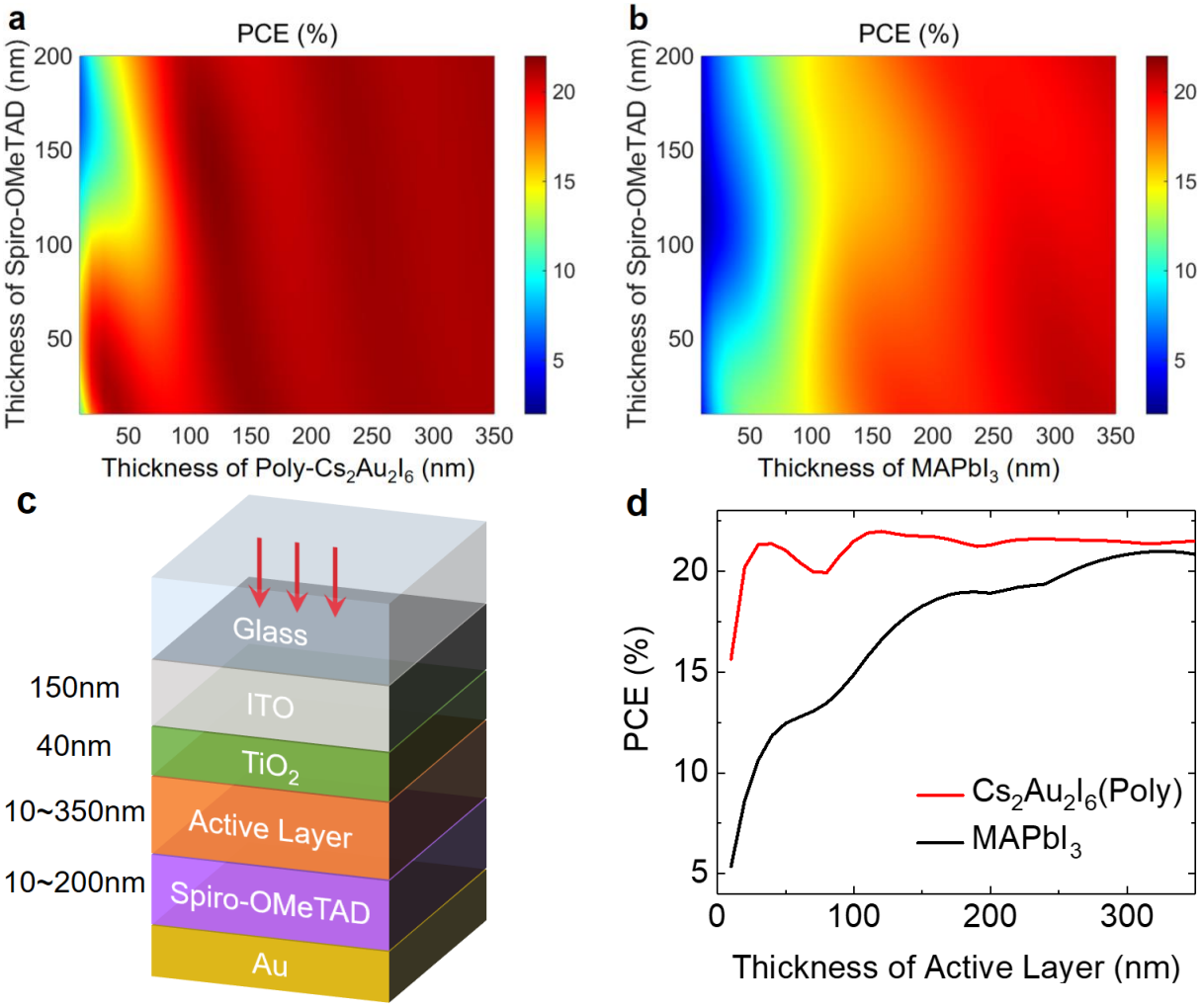

Figure S3. Dependence of photoconversion efficiency (PCE) on the thickness of Spiro-OMeTAD and the active layer of solar cell device based on (a) poly-$Cs_2Au_2I_6$ and (b) $MAPbI_3$. (c) Schematic of full solar cell device structure (Glass / ITO(150nm) / TiO_2(40nm) / Active layer(10~350nm) / Spiro-OMeTAD(10~200nm) / Au). (d) PCE of optimized structure with varying active layer thickness.

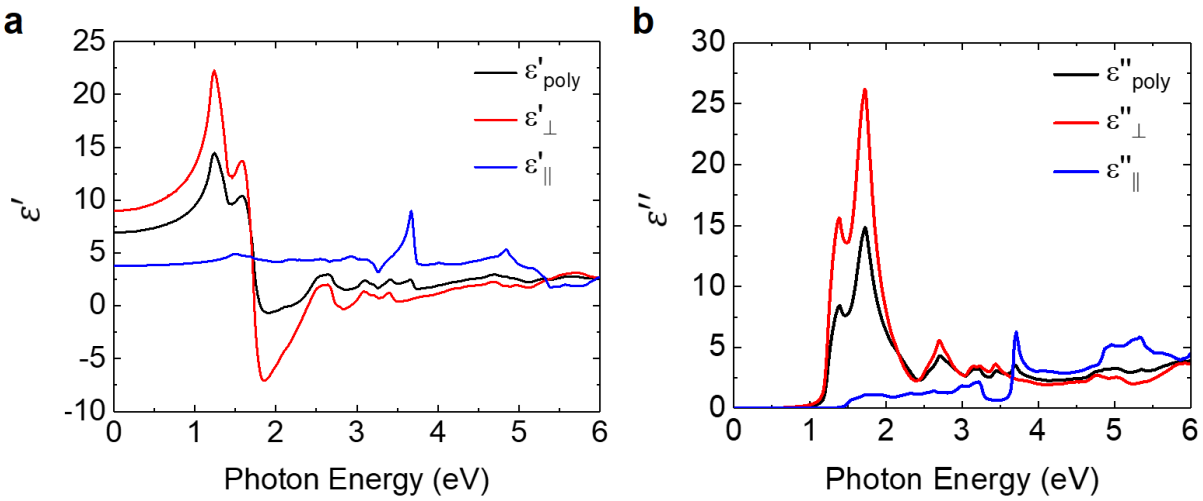

Figure S4. Real (a) and imaginary (b) part of electric permittivity of single (red curve for $E \perp c$ and blue curve for E // c) and poly (black curve) crystalline $Cs_2Au_2I_6$ as functions of photon energy. PBE calculated ε'' is shifted by 0.42 eV (reproducing HSE bandgap of 1.21 eV), which is utilized to obtain ε' by using Kramers-Kronig transform.

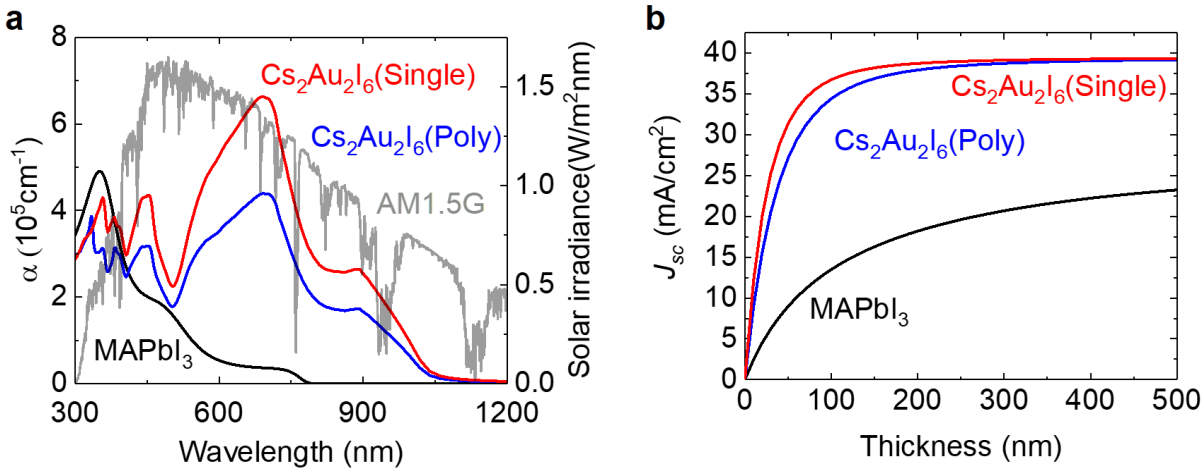

Figure S5. ε' and ε'' values shown in Figure S4 are used to obtain (a) absorption spectrum of $MAPbI_3$, poly-$Cs_2Au_2I_6$, and single-$Cs_2Au_2I_6$ which are indicated by black, blue and red line respectively, and (b) estimated short circuit current density (J_{sc}), assuming single-path absorption.

TABLE I. DFT optimized lattice constants (*a*, *c*), cell volume (*V*), and inter-atomic distances of the $Cs_2Au_2I_6$, calculated using PBE. For the comparison, the corresponding experimental values are also listed. All distances are in Å and volumes are in $Å^3$.

	This work	Exp.[a]
a	8.39	8.284
C	12.34	12.092
V	869.04	829.8
Au^{III}-I	2.703	2.646
Au^{I}-I	2.625	2.586

[a]N. Matsushita, H. Kitagawa, N. Kojima, *Acta Crystallogra. Sect. C* **1997**, *53*, 663.