



# Perovskite Quantum Dots: A New Absorber for Perovskite- Perovskite Tandem Solar Cells

## Preprint

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# Perovskite Quantum Dots. A New Absorber for Perovskite-Perovskite Tandem Solar Cells

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**Abstract** — The nanoscale phase stabilization of CsPbI<sub>3</sub> quantum dots allows for the advantageous manipulation of its phase diagram. We show that these all inorganic halide perovskite nanocrystals can be used to fabricate colloidal perovskite quantum dot solar cells with incredibly low voltage losses. Despite recently emerging on the photovoltaic scene, CsPbI<sub>3</sub> quantum dot solar cells have already achieved approximately 85% of their Shockley-Queisser limit open-circuit voltage, among the lowest voltage loss achieved for any material with a band gap of 1.7 eV, excepting III-V semiconductors. The low losses in these devices recently led to a world record certified quantum dot solar cell efficiency of 13.4%. While single junction thin film perovskite solar cells have surpassed 22% power conversion efficiency, perovskite-perovskite tandem solar cells offer the potential for power conversion efficiencies exceeding 30%. However, to accomplish this ambitious goal, perovskite solar cells must be designed with incredibly low losses and the appropriate band gaps, which differ from the ideal band gap for single junction perovskite solar cells. In this respect, the incredibly low voltage loss and tunable band gap of CsPbI<sub>3</sub> quantum dots make them ideally suited for all-perovskite tandem solar cell applications.

## I. INTRODUCTION

Halide perovskites offer the potential to revolutionize the photovoltaic (PV) landscape with their unique combination of efficiency and manufacturability.[1]–[3] While most of the research community’s focus has thus far been on the development of halide perovskite polycrystalline thin films, the recent advent of CsPbI<sub>3</sub> quantum dots (QD) opened a new area of materials research,[4] particularly following the demonstration of their nanoscale phase stability and application in optoelectronic devices.[5]

While the power conversion efficiency (PCE) of single-junction perovskite photovoltaics has reached 22.7%, [6] the development of perovskite-perovskite tandem solar cells represents a feasible path toward a 30% efficient solution-processed PV module.[7] While the highest efficiency single-junction perovskite solar cells have band gaps of 1.5-1.6 eV,[8] band gaps of 1.22 eV, the lowest band gap thus far achieved with standard halide perovskites, and 1.7-1.9 eV are required for high efficiency tandem solar cells.[7], [9] Therefore, the design of low loss perovskite solar cells in these band gap regions is critical for the realization of high efficiency tandem solar cells.

While all inorganic halide perovskites, such as CsPbI<sub>3</sub> and CsPbI<sub>3-x</sub>Br<sub>x</sub> remove the compositional instabilities associated

with volatile organic cations such as methylammonium (MA), [10], [11] the phase transitions in these all inorganic materials are more problematic than those in MAPbI<sub>3</sub> because they are no longer simply rotations of the corner-sharing [PbI<sub>6</sub>]<sup>4-</sup> octahedra [12] but rather are a change from 3-dimensional networks of corner-sharing [PbI<sub>6</sub>]<sup>4-</sup> octahedra to 1-dimensional chains of edge-sharing octahedra which coincides with large changes in optical absorption.[13]

CsPbI<sub>3</sub> QD solar cells (QDSC) show tremendous promise as wide band gap cells because their small size changes the phase diagram of the material, stabilizing the desired crystalline phase of the material (corner-sharing [PbI<sub>6</sub>]<sup>4-</sup> octahedra).[5], [14] Additionally, they have open circuit voltages ( $V_{OC}$ ) exceeding 1.2 V for 1.7 eV band gap, among the lowest  $V_{OC}$  deficit of any non-III-V material. Figure 1 demonstrates the low voltage deficit by comparing the  $V_{OC}$  of record devices of common PV technologies [15] to their theoretical  $V_{OC}$  under 1 Sun conditions, as calculated by the Shockley-Queisser limit.[16]

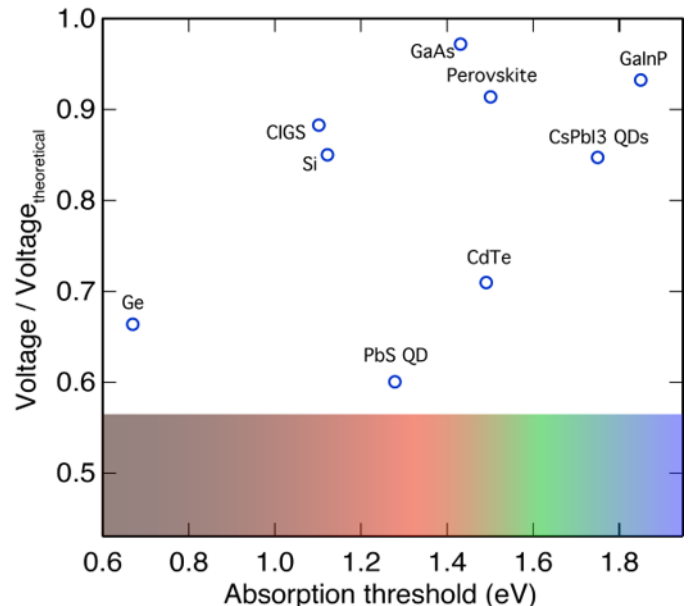


Fig. 1.  $V_{OC}$  deficit of several different PV technologies reported as the percent of the Shockley-Queisser limit voltage achieved for the given band gap.

Moreover, as has been demonstrated in other QDSCs, most notably in PbS,[17] the band gap of the CsPbI<sub>3</sub> QD absorber

can be readily tuned simply by tuning the QD size, and this band gap shift is retained in complete QDSCs.[5] Importantly, the size tunability of the band gap of CsPbI<sub>3</sub> means that these solar cell materials do not suffer from the same deleterious effects of halide segregation found in mixed halide thin film perovskites of similar band gaps.[18]–[20]

By improving the QD coupling of CsPbI<sub>3</sub> QD films, we have been able to achieve a world record certified quantum dot solar cell efficiency of 13.4%.[14] CsPbI<sub>3</sub> QDs have now been implemented into high-efficiency, transparent device stacks which exhibit high transmission at photon energies >1.75 eV. These semi-transparent CsPbI<sub>3</sub> QDSCs are well-suited for applications as a top-cell for all-perovskite tandem solar cells.

## II. EXPERIMENTAL

Synthesis of CsPbI<sub>3</sub> QDs can be carried out following previously reported methods.[5], [21] Following synthesis, washing of the QDs was performed using methyl acetate (MeOAc), as previously reported.[5] This washing step removes excess precursor materials and is critical to maintaining phase-stable CsPbI<sub>3</sub>. [5] The long-chain ligands covering the surface of the QDs following synthesis allow these materials to be easily suspended in non-polar solvents; however, they are electronically insulating. Electronically coupled CsPbI<sub>3</sub> films were fabricated as previously reported.[14] All fabrication steps were carried out under ambient conditions with approximately 10-20% relative humidity. Briefly, the films were deposited in a layer-by-layer approach in which (i) a concentrated solution of the washed CsPbI<sub>3</sub> QDs was cast onto a substrate by spin-coating from octane, (ii) the film was briefly (2-4 s) dipped in a saturated solution of Pb(NO<sub>3</sub>)<sub>2</sub> in MeOAc, and then (iii) dipped in a neat MeOAc solution. These steps can be repeated multiple times to tune the QD film thickness (typically 3-4 layers). Lastly, (iv) the QD film was immersed in a saturated solution of formamidinium iodide (FAI) in ethyl acetate for 10 s to improve QD coupling and film mobility.[14]

CsPbI<sub>3</sub> solar cells were fabricated by first depositing a compact TiO<sub>2</sub> layer, as described previously,[14] on a cleaned FTO substrate and then depositing the CsPbI<sub>3</sub> QD film onto the TiO<sub>2</sub> as described above. Spiro-OMeTAD (2,2',7,7'-tetrakis(N,N-dip-methoxyphenylamino)-9,9'-spirobifluorene) was then deposited by spin-coating from a chlorobenzene solution with added lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and 4-*tert*-butylpyridine (tBP).[14] Following spiro-OMeTAD deposition the devices were allowed to remain in air overnight before depositing the top electrode. In both cases, 15 nm of MoO<sub>x</sub> was evaporated. The opaque top electrode was Al,[22] deposited by thermal evaporation, while the transparent top electrode was a sputtered zinc oxide-based transparent conducting oxide (TCO).

## III. RESULTS AND DISCUSSION

The device architectures and representative current density-voltage (*J-V*) scans for standard opaque and transparent devices are shown in Figure 2. From a reverse *J-V* scan, the opaque device had a short-circuit current (*J*<sub>SC</sub>) of 15.88 mA/cm<sup>2</sup>, a *V*<sub>OC</sub> of 1.170 V, a fill factor (FF) of 0.770, and a power conversion efficiency (PCE) of 14.30 %. Similarly, the transparent device had a *J*<sub>SC</sub> of 13.66 mA/cm<sup>2</sup>, a *V*<sub>OC</sub> of 1.190 V, a FF of 0.732, and a PCE of 11.90 %.

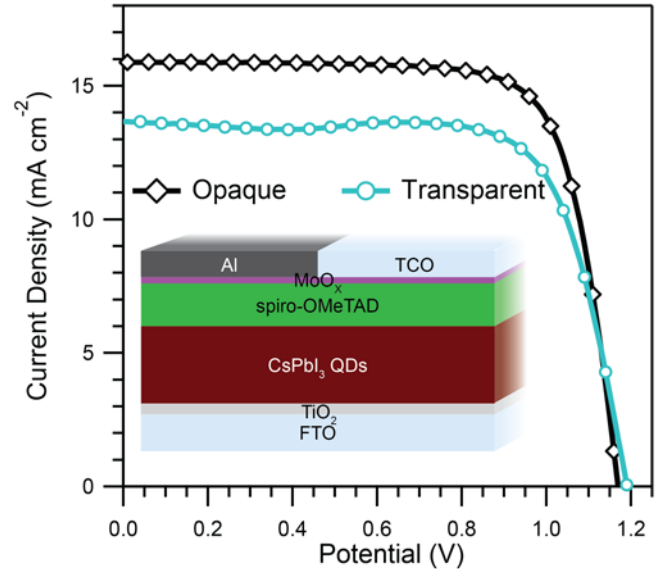


Fig. 2. *J-V* scans showing the performance of opaque and transparent CsPbI<sub>3</sub> QDSCs. The inset shows the two device architectures used for these devices (opaque, left; transparent, right).

The performance of these solar cells, which have a band gap of 1.71 eV, as calculated from the absorption onset by Tauc analysis, are promising for tandem solar cell applications; however, long wavelength transparency is critical for the eventual coupling of these devices with an efficient low band gap bottom cell. Transmission measurements (Figure 3) were taken of the transparent CsPbI<sub>3</sub> solar cell device stack to elucidate parasitic optical losses. The transmission spectra of the complete device stacks show good transmission at energies less than 1.7 eV with a maximum value of over 70% and an average value of 66 % between 1.7 and 1.25 eV. It is anticipated that the optical transmittance of these devices can be further improved by the implementation of new hole transport materials with lower optical absorbance than spiro-OMeTAD, for example the recently reported hole transport material EH44.[23]

## IV. SUMMARY

Perovskite-perovskite 2-terminal tandem solar cells require the simultaneous development of narrow and wide band gap perovskite solar cells which can be fully integrated. We

propose CsPbI<sub>3</sub> QD solar cells as a novel material for the wide band gap absorber due to their promising performance, extremely  $V_{OC}$  deficit, and the absence of halide phase segregation which plagues I/Br<sup>-</sup> alloys. The high transmission and low voltage loss of CsPbI<sub>3</sub> QD solar cells in this work shows their potential. Moreover, the fact that these materials are processed from non-polar organic solvents, such as octane and methyl acetate, could facilitate 2-terminal tandem solar cell processing and perhaps remove the need for a TCO barrier layer between the two subcells.[9] With the advances shown, the realization of perovskite tandem solar cells with performance surpassing Si is well within reach.

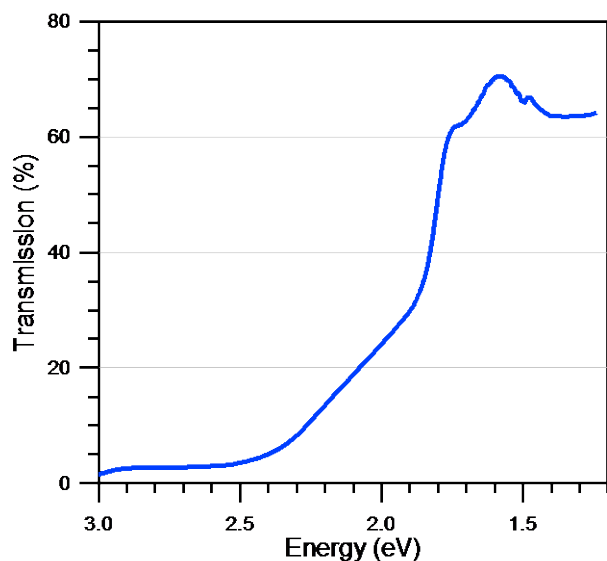


Fig. 3. Transmission spectra of a transparent contact CsPbI<sub>3</sub> QDSC showing high transmission of low energy (<1.7 eV) light.

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#### REFERENCES

- [1] M. A. Green and A. Ho-Baillie, “Perovskite Solar Cells: The Birth of a New Era in Photovoltaics,” *ACS Energy Lett.*, vol. 2, no. 4, pp. 822–830, Apr. 2017.
- [2] B. Dou *et al.*, “High-Performance Flexible Perovskite Solar Cells on Ultrathin Glass: Implications of the TCO,” *J. Phys. Chem. Lett.*, vol. 8, no. 19, pp. 4960–4966, Oct. 2017.
- [3] J. S. Manser, J. A. Christians, and P. V. Kamat, “Intriguing optoelectronic properties of metal halide perovskites,” *Chem. Rev.*, vol. 116, no. 21, pp. 12956–13008, Nov. 2016.
- [4] H. Huang, M. I. Bodnarchuk, S. V. Kershaw, M. V. Kovalenko, and A. L. Rogach, “Lead Halide Perovskite Nanocrystals in the Research Spotlight: Stability and Defect Tolerance,” *ACS Energy Lett.*, vol. 2, no. 9, pp. 2071–2083, 2017.
- [5] A. Swarnkar *et al.*, “Quantum dot-induced phase stabilization of a-CsPbI<sub>3</sub> perovskite for high-efficiency photovoltaics,” *Science*, vol. 354, no. 6308, pp. 92–95, 2016.
- [6] NREL, “Research Cell Record Efficiency Chart.” [Online]. Available: <https://www.nrel.gov/pv/assets/images/efficiency-chart.png>.
- [7] M. T. Hörlantner *et al.*, “The Potential of Multijunction Perovskite Solar Cells,” *ACS Energy Lett.*, vol. 2, no. 10, pp. 2506–2513, 2017.
- [8] W. S. Yang, B. Park, E. H. Jung, and N. J. Jeon, “Iodide management in formamidinium-lead-halide based perovskite layers for efficient solar cells,” *Science*, vol. 356, no. 6345, pp. 1376–1379, 2017.
- [9] G. E. Eperon *et al.*, “Perovskite-perovskite tandem photovoltaics with optimized band gaps,” *Science*, vol. 354, no. 6314, pp. 861–865, Nov. 2016.
- [10] D. Nenon *et al.*, “Structural and chemical evolution of methylammonium lead halide perovskites during thermal processing from solution,” *Energy Environ. Sci.*, vol. 9, pp. 2072–2082, 2016.
- [11] R. E. Beal *et al.*, “Cesium Lead Halide Perovskites with Improved Stability for Tandem Solar Cells,” *J. Phys. Chem. Lett.*, vol. 7, no. 5, pp. 746–751, 2016.
- [12] L. T. Schelhas *et al.*, “Monitoring a silent phase transition in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> solar cells via operando X-

- ray diffraction,” *ACS Energy Lett.*, vol. 1, no. 5, pp. 1007–1012, 2016.
- [13] J. Lin *et al.*, “Thermochromic halide perovskite solar cells,” *Nat. Mater.*, 2018.
- [14] E. M. Sanehira *et al.*, “Enhanced mobility CsPbI<sub>3</sub> quantum dot arrays for record-efficiency, high-voltage photovoltaic cells,” *Sci. Adv.*, vol. 3, no. 10, p. eaao4204, Oct. 2017.
- [15] IEEE, “Interactive: Record-Breaking PV Cells.”
- [16] S. Rühle, “Tabulated values of the Shockley–Queisser limit for single junction solar cells,” *Sol. Energy*, vol. 130, pp. 139–147, Jun. 2016.
- [17] A. R. Marshall, M. R. Young, A. J. Nozik, M. C. Beard, and J. M. Luther, “Exploration of metal chloride uptake for improved performance characteristics of PbSe quantum dot solar cells,” *J. Phys. Chem. Lett.*, vol. 6, no. 15, pp. 2892–2899, Aug. 2015.
- [18] S. Draguta *et al.*, “Rationalizing the light-induced phase separation of mixed halide organic–inorganic perovskites,” *Nat. Commun.*, vol. 8, no. 1, p. 200, 2017.
- [19] M. C. Brennan, S. Draguta, P. V. Kamat, and M. Kuno, “Light-Induced Anion Phase Segregation in Mixed Halide Perovskites,” *ACS Energy Lett.*, p. acsenergylett.7b01151, 2017.
- [20] E. T. Hoke, D. J. Slotcavage, E. R. Dohner, A. R. Bowring, H. I. Karunadasa, and M. D. McGehee, “Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics,” *Chem. Sci.*, vol. 6, no. 1, pp. 613–617, 2015.
- [21] L. Protesescu *et al.*, “Nanocrystals of cesium lead halide perovskites (CsPbX<sub>3</sub>, X = Cl, Br, and I): Novel optoelectronic materials showing bright emission with wide color gamut,” *Nano Lett.*, vol. 15, no. 6, pp. 3692–3696, Jun. 2015.
- [22] E. M. Sanehira *et al.*, “Influence of electrode interfaces on the stability of perovskite solar cells: Reduced degradation using MoO<sub>x</sub>/Al for hole collection,” *ACS Energy Lett.*, vol. 1, no. 1, pp. 38–45, Jul. 2016.
- [23] J. A. Christians *et al.*, “Tailored interfaces of unencapsulated perovskite solar cells for >1,000 hour operational stability,” *Nat. Energy*, vol. 3, no. 1, pp. 68–74, Jan. 2018.