Lead-Free Dion−Jacobson Tin Halide Perovskites for Photovoltaics
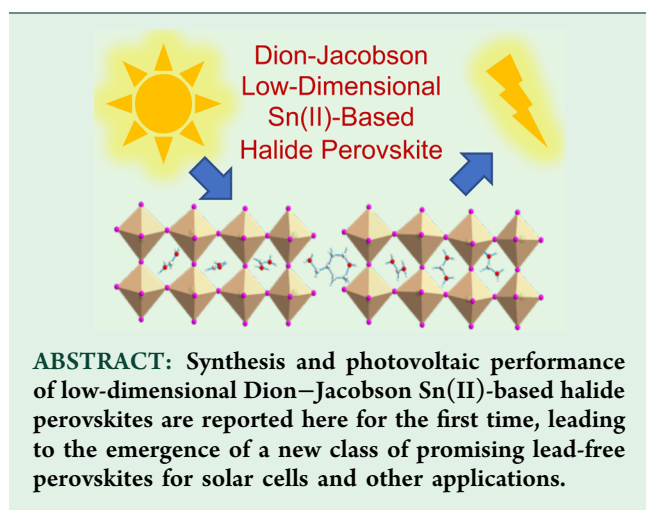
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S *Supporting Information*

ABSTRACT: Synthesis and photovoltaic performance of low-dimensional Dion−Jacobson Sn(II)-based halide perovskites are reported here for the first time, leading to the emergence of a new class of promising lead-free perovskites for solar cells and other applications.
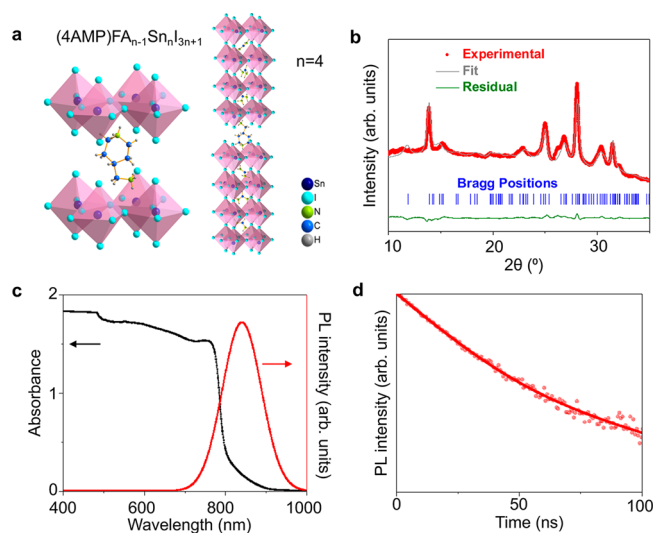

Figure 1. DJ Sn-based halide perovskite $(4AMP)(FA)_{n-1}Sn_nI_{3n+1}$ ($n = 4$): (a) schematic crystal structure; (b) experimental XRD pattern (powder) with Rietveld refinement (Bragg positions and residual), showing a possible crystal structure with space group Ia and lattice parameters $a = 8.978$ Å, $b = 8.966$ Å, $c = 59.656$ Å, $\alpha = \Upsilon = 90°$, and $\beta = 91.109°$; (c) absorption and steady-state PL spectra (powder); and (d) time-resolved PL spectrum (powder).

Perovskite solar cells (PSCs) based on Pb-containing organic−inorganic halide perovskites have now achieved a record power conversion efficiency (PCE) of 23.3% within a relatively short period of time.[1,2] However, the toxicity of Pb is likely to be a serious hurdle in the path toward future commercialization of PSCs.[3,4] Several elements such as Sn(II),[5] Bi(III),[6] Sb(III),[7] and Ti(IV)[8,9] with relatively lower toxicity are being considered for replacing Pb(II) in PSCs. To date, Sn-based PSCs have shown the most promising PCE.[5] However, it has been argued that Sn-vacancies form easily in Sn(II)-based perovskites, which results in metallic conductivity.[10] Furthermore, Sn(II) readily oxidizes to Sn(IV), leading to poor air stability, inadequate optoelectronic properties, and, thus, lower device PCE.[11] In order to overcome these issues, we report the synthesis of a new type of Dion−Jacobson (DJ) Sn(II)-based low-dimensional perovskite, $(4AMP)(FA)_{n-1}Sn_nI_{3n+1}$, and demonstrate its first use in PSCs with a promising PCE of over 4%. Here FA is formamidinium $(HC(NH_2)_2^+)$, 4AMP is 4-(aminomethyl)piperidinium, and n is the number of octahedra layers in the perovskite-like stack. The discovery of this new lead-free perovskite is inspired by the previous first report of lead-based DJ halide perovskites by Mao et al.[12]

The DJ Sn(II)-based halide perovskite structure of $(4AMP)(FA)_{n-1}Sn_nI_{3n+1}$ is illustrated in Figure 1a. It features aligned divalent ($+2$) interlayer organic spacers, instead of the staggered interlayer monovalent ($+1$) organic spacers in the more popular Ruddlesden−Popper (RP) phases.[12] Bulk crystalline powders of $(4AMP)(FA)_{n-1}Sn_nI_{3n+1}$ ($n = 1−4$) perovskites were prepared by the simple solution-casting method, using the experimental procedure described in the Supporting Information. Rietveld refinement of the XRD pattern of the most representative $(4AMP)(FA)_3Sn_4I_{13}$ ($n = 4$) sample is presented in Figure 1b, confirming the expected DJ perovskite crystal structure. The direct comparison between the experimental and simulated XRD patterns is shown in Figure S1, where there is good match of the Bragg positions. The observed background in the experimental XRD pattern can be attributed to the presence of

some amorphous material. (More comprehensive analyses of the crystal structures of all other DJ phases will be performed in the future.) The $(4AMP)(FA)_3Sn_4I_{13}$ perovskite shows reasonable absorption characteristics, with edge at 860 nm, as shown in Figure 1c. The calculated band structure using density functional theory (DFT) shows a consistent value, similar to the RP phase case,[13] and reveals a slight indirect character of the bandgap (Figure S2). This material also shows a strong, well-resolved steady-state photoluminescence (PL) peak at 840 nm. Surprisingly, the PL lifetime is as long as 18.56 ns, which is significantly longer than those observed in other Sn(II)-based perovskite materials (hundreds of picoseconds to a couple of nanoseconds).[5] The PL peak (Figure 1c) suggests an optical bandgap of 1.47 eV. We have further investigated the effect of n on the optical absorption of these DJ perovskites, results from which are shown in Figures S3 and 1c. An increase of n, from 1 to 4, results in a systematic red-shift of the absorption edge and the PL peak. This is because of the change of the dimensionality of the perovskite crystal structure from 2D to "quasi-2D", similar to the case of RP phases in the $(PEA)_2(FA)_{n-1}Sn_nI_{3n+1}$ system.[5]

PSCs based on $(4AMP)(FA)_3Sn_4I_{13}$ were then fabricated to evaluate their potential in PV applications. The printable hole-transporting layer (HTL)-free triple-mesoscopic PSC architecture is adopted.[14] The corresponding energy-level diagram is schematically shown in Figure 2a. Figure 2b presents the current
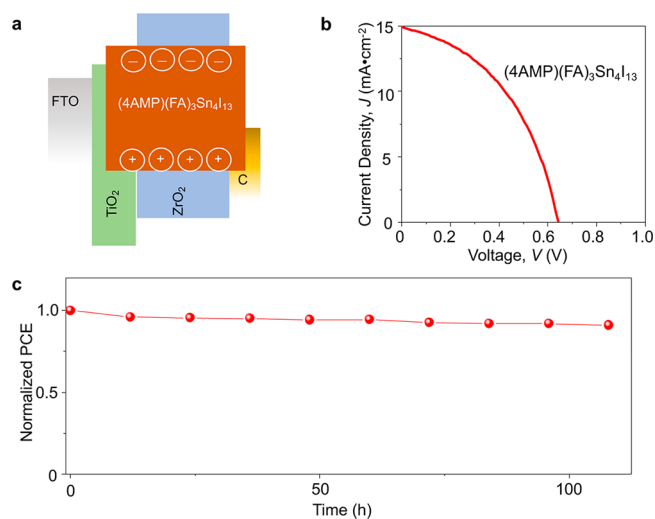

Figure 2. (a) Energy-level diagram for DJ Sn(II)-based HTL-free PSCs. (b) Typical $J-V$ curves for a $(4AMP)(FA)_3Sn_4I_{13}$ ($n = 4$) HTL-free PSCs. (c) PCE stability of a $(4AMP)(FA)_3Sn_4I_{13}$-based HTL-free PSC as a function of storage duration (in N_2 atmosphere, at 45 °C, under 1-sun illumination).

density−voltage ($J-V$) curves of a PSC. A promising PCE of 4.22% is obtained, with J_{SC} of 14.90 mA·cm^{-2}, V_{OC} of 0.64 V, and FF of 0.443. The V_{OC} can be improved by tailoring the n value. For example, Figure S4 shows that V_{OC} is increased to 0.80 V when $n = 1$. Therefore, there is room for further improvement in the PCE of these PSCs based on DJ Sn(II)-based perovskites. The PCE of the unencapsulated $(4AMP)(FA)_3Sn_4I_{13}$ PSC was also tracked periodically, with the device exposed to 1 sun illumination in N_2 atmosphere at 45 °C for 100 h. Only 9% decay of the initial PCE is observed, demonstrating the promising device stability.

In closing, the synthesis and use of DJ Sn(II)-based halide perovskites for stable, lead-free PVs have been demonstrated

here for the first time. We envision DJ Sn(II)-based perovskites having the following potential advantages: (i) possible reduced propensity for the formation of Sn-vacancies; (ii) enhanced stability due to the stronger interlayer bonding by divalent organic spacers, compared to the relatively weaker van der Waals bonding in the case of monovalent organic spacers in RP phases; and (iii) possible improvement in photocarriers transport due to the divalent organic spacers that reduce the overall organic content.[15]

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergy-lett.8b02051.

Experimental procedure and additional results (PDF)

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Notes
The authors declare no competing financial interest.

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