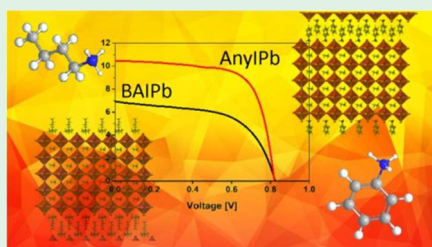


Conjugated Organic Cations to Improve the Optoelectronic Properties of 2D/3D Perovskites

Jesús Rodríguez-Romero, Bruno Clasen Hames, Iván Mora-Seró,*^{1b} and Eva M. Barea*

Institute of Advanced Materials (INAM), Universitat Jaume I, 12006 Castelló, Spain

S Supporting Information



ABSTRACT: Use of $C_6H_5NH_3I$ as an organic cation instead of $CH_3(CH_2)_3NH_3I$ in the synthesis of 2D/3D perovskites $(C_6H_5NH_3I)_2(CH_3NH_3I)_{n-1}(PbI_2)_n$ leads to a material with significantly improved photovoltaic and optoelectronic properties with respect to the common butylammonium iodide-based perovskite, which is one of the most studied materials so far.

Two-dimensional (2D) hybrid perovskites (HPVKs) are structures alternating organic and inorganic layers, arising from inclusion of a large organic cation providing Goldschmidt's tolerance factor higher than 1.¹ This fact generates separation of a determined number of inorganic layers (n), which can range from 1 to ∞ , which corresponds to a 3D arrangement. A variation of this pure organic–inorganic structure can be obtained by addition of a small organic cation, MA ($CH_3NH_3^+$) in most cases, providing a Goldschmidt's tolerance factor adequate for perovskite formation, making it so the inorganic part becomes a hybrid structure. These organic–inorganic hybrid structures are called 2D/3D HPVKs. Actually, 2D/3D perovskite-based solar cells have emerged as an alternative to pure 3D perovskites with the aim to improve their long-term stability, which is a key factor in future device commercialization.^{2–3} In the last years, several studies have been reported on 2D/3D perovskites prepared using mainly two ammonium salts: (i) phenylethylammonium iodide (PEA), with 4.73% efficiency for a layered material ($n = 3$)⁴ and 15.3% for a quasi-3D material ($n = 60$)⁵ and (ii) butylammonium iodide (BAI) (4.02–12.52%, observed only in layered materials, i.e., $n \leq 5$).^{6–8} Recently, 1 year stable 2D/3D perovskite-based devices fabricated using 5-ammonium valeric acid iodide with an efficiency up to 11% have been shown.² It is clear that development in the photovoltaic performance is impressive; however, considering the number of organic molecules that can

be introduced as ammonium salts within the perovskite structure, the results obtained so far can be considered very limited because, in general, the studies have focused only on aliphatic nonconjugated ammonium salts.

We report the synthesis of 2D/3D HPVKs $(C_6H_5NH_3I)_2(CH_3NH_3I)_{n-1}(PbI_2)_n$ ($n = 1–5$), hereafter AnyIPb_{*n*}, using anilinium iodide ($C_6H_5NH_3I$) and its performance in a complete perovskite solar cell; see the SI for material preparation. At the same time, comparative studies using the well-known 2D/3D perovskite $(BuNH_3I)_2(MAI)_{n-1}(PbI_2)_n$, hereafter BAIPb_{*n*}, were carried out.⁵ The films were prepared by modification of the successful hot casting method.⁷ The XRD pattern for the first perovskite films, fabricated without posterior annealing, shows a peak at 12.72° (PbI_2 005 reflection), which is indicative of incomplete formation of the perovskite lattice (Figure S1). To overcome this drawback, different annealing times for perovskite films were studied, with 10 min as the most adequate time. The two characteristic peaks for layered structures at 14.2 and 28.52°, associated with (111) and (202) crystallographic planes, can also be observed; see Figure S1.⁵

The current–potential ($J–V$) curves for the champion devices (for each one of the n evaluated, i.e., $n = 1–5$) are plotted in Figure 1a,b for cells prepared with AnyIPb_{*n*} and BAIPb_{*n*} perovskites, respectively. $J–V$ curves show a systematic increase in the power conversion efficiency (PCE) from $n = 1$ to 5 for both HPVK systems, and in all cases, the performance of the device with anilinium exhibits significantly higher performance than its respective reference prepared with BAI. The conversion efficiency values obtained for the AnyIPb_{*n*} family devices are 0.66 ($n = 1$) to 5.94% ($n = 5$) (see Table S3), while the BAIPb_{*n*} family exhibits photoconversion efficiencies from 0.01 ($n = 1$) to 3.02% ($n = 5$) (Table S4). This evolution of the photovoltaic behavior with n is a clear indicator of the 2D/3D structure of the material formed.⁹ Great improvement comparing both kinds of devices was observed at the photocurrent J_{sc} . In the case of AnyIPb_{*n*} devices, J_{sc} ranges from 1.2 ($n = 1$) to 10.46 mA/cm² ($n = 5$). BAIPb_{*n*} cells present a J_{sc} higher than 6 mA/cm² just for $n = 5$, while for AnyIPb_{*n*}, this threshold is overcome for $n \geq 2$. The use of anilinium instead of BAI also improves the fill factor (FF) and photovoltage (V_{oc}); see Tables S3 and S4. Whereas the

Received: July 24, 2017

Accepted: August 2, 2017

Published: August 2, 2017

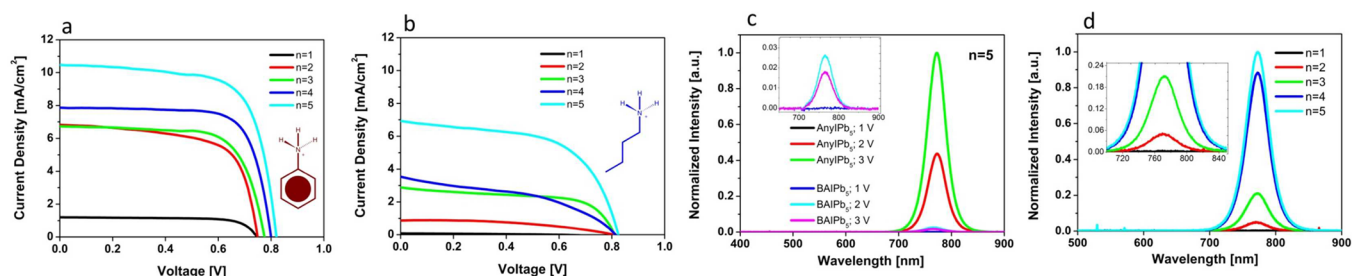


Figure 1. J - V curves of champion devices prepared with (a) AnyIPb_{*n*} and (b) BAIPb_{*n*} 2D/3D HPVK layers; the photovoltaic parameters are depicted in Tables S3 and S4. (c) EL obtained from devices prepared with both AnyIPb_{*n*} and BAIPb_{*n*} at different applied bias. (d) EL obtained for AnyIPb_{*n*} samples with different *n* at 3 V applied bias.

increase of FF is significant for the entire *n* range, augmentation of V_{oc} is especially significant for low *n*.

In addition to improvement of the performance of solar cells by use of AnyIPb_{*n*} 2D/3D HPVKs, the goodness of this new 2D/3D material for development of another kind of optoelectronic device has also been analyzed. Perovskites have been increasingly applied in a wide range of areas, including photodetectors,¹⁰ optical amplifiers,¹¹ lasers,¹² and light-emitting diodes (LEDs),¹³ due to their incredible optoelectronic properties based on the low nonradiative recombination. Considering that the TiO₂ and spiro-OMeTAD layers used respectively as the electron and hole selecting contact can be also used as efficient injecting layers,¹⁴ electroluminescence (EL) measurements were performed comparing the two photoactive materials AnyIPb_{*n*} and BAIPb_{*n*}. Figure 1c shows the response of the devices under different applied bias. It can be clearly appreciated that the ELs of AnyIPb_{*n*} devices are practically 2 orders of magnitude higher than those for BAIPb_{*n*}-based devices at the same applied voltage. The same effect can be observed for devices prepared with *n* = 3; see Figure S2. However, in this case, no EL signal was detected for BAIPb_{*n*}.

Analysis of samples with different *n* also provides interesting conclusions. The optical absorption spectra of each of the families studied show significant differences (Figure S3a,b). While for the BAIPb_{*n*} family the spectra exhibit the corresponding progression of the excitonic band as we move from *n* = 1 to 3,⁵ the AnyIPb_{*n*} family shows an impressive red shift for the band edge from *n* ≥ 2, suggesting that the excitons are practically ionized into free carriers, even for films with *n* = 2. In fact, no shift of the EL at 772 nm is observed for AnyIPb_{*n*} samples for *n* ≥ 2 (see Figure 1d), suggesting a common electronic state from which the radiative recombination is carried out.^{9,15} That effect is really interesting, demonstrating that the systems combine both imperative requirements to be used as photovoltaic material: good charge transport and high stability.^{8,15} Recently, this behavior was observed in the BAIPb_{*n*} family, but it was observed from *n* = 3 to 5.⁹ 2D/3D HPVKs evolve to 3D behavior as *n* increases, and the use of conjugated molecules as anilinium produces faster evolution and allows one to obtain significant efficiencies with relatively low *n*; see Figure 1a.

In summary, we report for the first time the synthesis of AnyIPb_{*n*} 2D/3D HPVK and its implementation in optoelectronic devices as solar cells and LEDs. The use of conjugated anilinium cation enhances significantly the performance of both kinds of devices. The higher photoconversion and photoemission efficiencies observed, compared to the BAIPb_{*n*} HPVK, can be attributed to an increase of the electronic transport properties of the material, as suggested by the higher J_{sc} without a deleterious effect on the nonradiative recombination, as pointed out by the increase of EL and V_{oc} . Concerning optoelectronic

properties, the absence of emission or absorption shifts, obtained through UV-vis spectroscopy and EL, suggests that the excitons for *n* ≥ 2 films are practically ionized into free carriers. Consequently, AnyIPb_{*n*} is a good candidate in the fabrication of optoelectronic devices. Although 2D/3D HPVKs show higher stability than the 3D counterparts, they present an important drawback of lower performance due to transport property limitations. This work reflects the undoubted interest of the use of conjugated cations to improve the transport properties of 2D/3D HPVKs and could have important implications in the field.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenerylett.7b00654.

Experimental methods. Photovoltaic parameters. XDR. EL of *n* = 3. Absorbance. (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: sero@uji.es (I.M.-S.).

*E-mail: barea@uji.es (E.M.B.).

ORCID

Iván Mora-Seró: 0000-0003-2508-0994

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

See the Supporting Information.

■ REFERENCES

- (1) Goldschmidt, V. M. *Naturwissenschaften* **1926**, *14*, 477–485.
- (2) Grancini, G.; et al. *Nat. Commun.* **2017**, *8*, 15684.
- (3) Mei, A.; et al. *Science* **2014**, *345*, 295–298.
- (4) Smith, I. C.; et al. *Angew. Chem.* **2014**, *126*, 11414–11417.
- (5) Quan, L. N.; et al. *J. Am. Chem. Soc.* **2016**, *138*, 2649–2655.
- (6) Cao, D. H.; et al. *J. Am. Chem. Soc.* **2015**, *137*, 7843–7850.
- (7) Tsai, H.; et al. *Nature* **2016**, *536*, 312–316.
- (8) Koh, T. M.; et al. *Chem* **2017**, *2*, 326–327.
- (9) Blancon, J.-C.; et al. *Science* **2017**, *355*, 1288–1292.
- (10) Dou, L.; et al. *Nat. Commun.* **2014**, *5*, 5404.
- (11) Suárez, I.; et al. *Adv. Mater.* **2015**, *27*, 6157–6162.
- (12) Xing, G.; et al. *Nat. Mater.* **2014**, *13*, 476–480.
- (13) Tan, Z.-K.; et al. *Nat. Nanotechnol.* **2014**, *9*, 687–692.
- (14) Jaramillo-Quintero, O. A.; et al. *J. Phys. Chem. Lett.* **2015**, *6*, 1883–1890.
- (15) Cohen, B.-E.; et al. *Adv. Funct. Mater.* **2017**, *27*, 1604733.