



## Application of luminescence downshifting materials for enhanced stability of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>(1-x)Cl<sub>3x</sub> perovskite photovoltaic devices

Anizelli, Helder Scapin; Stoichkov, Vasil; Fernandes, Ricardo Vignoto; Duarte, Jose Leonil; Laureto, Edson; Kettle, Jeffrey; Visoly-Fisher, Iris; Katz, E. A.

### Organic Electronics

DOI:

[10.1016/j.orgel.2017.06.056](https://doi.org/10.1016/j.orgel.2017.06.056)

Published: 01/10/2017

Peer reviewed version

[Cyswllt i'r cyhoeddiad / Link to publication](#)

*Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA):*

Anizelli, H. S., Stoichkov, V., Fernandes, R. V., Duarte, J. L., Laureto, E., Kettle, J., Visoly-Fisher, I., & Katz, E. A. (2017). Application of luminescence downshifting materials for enhanced stability of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>(1-x)Cl<sub>3x</sub> perovskite photovoltaic devices. *Organic Electronics*, 49, 129-134. <https://doi.org/10.1016/j.orgel.2017.06.056>

#### Hawliau Cyffredinol / General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

#### Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

## **Application of luminescence downshifting materials for enhanced stability of $\text{CH}_3\text{NH}_3\text{PbI}_{3(1-x)}\text{Cl}_{3x}$ perovskite photovoltaic devices**

Helder Scapin Anizelli<sup>1</sup>, Vasil Stoichkov<sup>2</sup>, Ricardo Vignoto Fernandes<sup>1</sup>, José Leonil Duarte<sup>1</sup>, Edson Laureto<sup>1\*</sup>, Jeff Kettle<sup>2</sup>, Iris Visoly-Fisher<sup>3,4</sup> and Eugene A. Katz<sup>3,4</sup>

<sup>1</sup> Departamento de Física, Centro de Ciências Exatas, Universidade Estadual de Londrina, 86051-990 Londrina, PR, Brazil

<sup>2</sup> School of Electronic Engineering, Bangor University, Dean St., Bangor, Gwynedd, LL57 1UT, Wales, UK

<sup>3</sup> Department of Solar Energy and Environmental Physics, Swiss Institute for Dryland Environmental and Energy Research, J. Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sede Boker Campus, 84990, Israel

<sup>4</sup> Ilse Katz Inst. of Nano-Science and Technology, Ben-Gurion University of the Negev, Be'er Sheva 84105, Israel

\* contact author: laureto@uel.br

### **Abstract**

The application of luminescent down shifting (LDS) layers as alternative UV filters for  $\text{CH}_3\text{NH}_3\text{PbI}_{3(1-x)}\text{Cl}_{3x}$  perovskite solar cell (PSC) devices is reported. A combination of photo-absorption measurements and of device decay measurements during light soaking are used to verify the stability. The application of a UV filter or LDS layer was able to significantly retard photo-induced degradation with ~18% drop in device power conversion efficiency (PCE) observed over 30 hours for non-encapsulated devices, which **is** compared to ~97% for an unfiltered device, also without encapsulation. Whilst the PCE of the PSC device decreases with the application of the LDS layer, the drop is not as significant as when a commercial UV filter is used. Considering that UV filters will be essential for the commercialization of PSCs, the work provides evidence that the LDS layer can act as an alternative UV filter in PSCs and can limit the drop in PCE **that** can be expected from the inclusion of a UV filter, thus providing an added benefit over commercial UV filters.

**Keywords:** perovskite; degradation; luminescence downshifting; stability; solar cells

## 1. Introduction

Perovskite based solar cells (PSCs) have attracted significant attention of PV researchers over the past seven years<sup>1-4</sup>, primarily by the simplicity of manufacture and rapid advancement of the power conversion efficiency (PCE), which has risen from 3 to 22.1%<sup>5</sup>. Perovskites-based absorbers within PSCs have the general formula  $ABX_3$ <sup>6</sup>, where A is an organic cation, typically methyl ammonium ( $CH_3NH_3$ ); B is an inorganic cation, usually lead (II); and X is a halide (I, Br or Cl)<sup>7</sup>. Several studies have shown that using mixed halides, resulting in compositions like  $CH_3NH_3PbI_xBr_{1-x}$  or  $CH_3NH_3PbI_xCl_{1-x}$ , may lead to improvement in the electronic properties of the films and in the device performance<sup>8-11</sup>. For example, the carrier diffusion length increases an order of magnitude with the addition of chloride, which is associated with a lower amount of structural defects in the compound<sup>12</sup>.

Despite the high performance demonstrated by the PSCs, they have been shown to possess poorer long term stability compared to other PV technologies. The degradation of the devices is caused by a number of environmental factors including intensity of UV and visible light, humidity and temperature<sup>13-16</sup>. These processes can be mitigated by a number of preparation techniques including addition of environmental barrier layers and UV filters<sup>17</sup>, as well as by optimizing active layer materials to develop more robust absorbers<sup>18</sup> or control of grain size in the films<sup>19,20</sup>. This second strategy requires a careful study of the changes in the optical and morphological properties of the films caused by the action of stressors.

Various solar cells technologies make use of luminescent materials to improve the device PCE<sup>21-28</sup>. In particular, some materials make use of the Luminescence Down Shifting (LDS) effect, that concerns the absorption of photons with higher energy and the subsequent energy **downshift** through their emission by photoluminescence. For better results, the materials must have a high emission efficiency, and its optical absorption band should not overlap with the absorption of the active layer in the device. Thus, LDS layers absorb higher-energy photons and convert the wavelength to one that is closer to the maximum external quantum efficiency (EQE) of the solar cell. In PSCs, **previous reports** have employed phosphor materials to improve the performance of PSCs by the LDS effect<sup>22, 29, 30</sup>. In addition to the PCE enhancements, since LDS layers absorb photons of higher energy, it is possible to select luminescent materials whose optical absorption is in the UV region of the solar spectrum. In this way, LDS could also impact the long-term stability by reducing harmful UV absorption in the active layer. Whilst the same role could be fulfilled by a UV filter, the LDS layer **does not** block the incident UV light and 'recycles' it to be used ~~as~~ for photocurrent generation.

This work investigates the impact of photo-degradation of  $CH_3NH_3PbI_{3(1-x)}Cl_{3x}$  films and solar cells made on their basis, under illumination of simulated sunlight (1 sun, AM1.5G). The degradation kinetics was evaluated with and without UV filters and the effectiveness of a

LDS layer for UV-filtering was assessed. The LDS material was selected to ensure the luminescent emission occurs at wavelengths where the perovskite cell has a high EQE. The performance and stability of the PSCs made using the LDS layer are reported.

## 2. Experimental

### 2.1 LDS layer and UV filter

A series of luminescent materials were evaluated from a previous study according to an optimization process reported by Fernandes et al.<sup>31</sup>. These included a range of 10 LDS materials, from metal complexes to organic dyes. The relevant aspects to considering the LDS application of the materials were their optical properties, processability, commercial availability and cheapness. The material selected for this work was Kremer fluorescent blue (KB), which is based upon a Triazine-toluene sulfonamide-paraformaldehyde-based resin. The LDS material was dissolved with PMMA into anisole at a concentration of 8% by weight. The layers were deposited by spin coating onto the top facing side of a fused silica substrates and annealed for 15 minutes at 60 °C. The average film thickness was measured to be 300 nm. Table I shows the values for the figures of merit (FOM) calculated for PMMA:KB films. The detailed definition of the parameters listed in Table I was given in a previous work<sup>31</sup>.

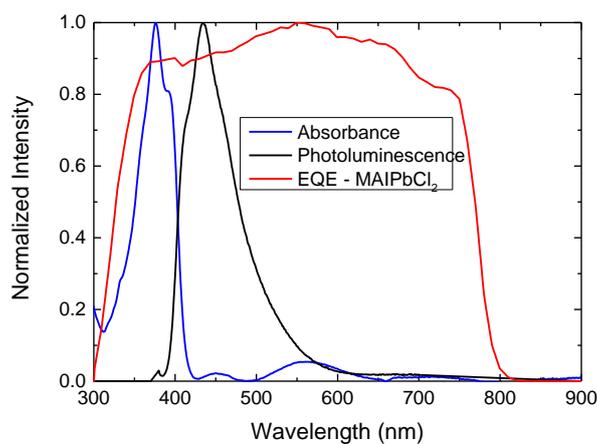
Figure of Merit (FOM)	RO	ASM	ESM	PA	PLQY	UV
Value (%)	9.2	40	78.2	8.7	5.7	12.2

**Table I** – Figures of merit for PMMA:KB luminescent layer. RO: radiative overlap; ASM: absorption spectral matching; ESM: emission spectral matching; PA: parasitic absorption; PLQY: photoluminescence quantum yield; UV: UV coverage.

The calculations of the FOMs were based on absorbance and photoluminescence (PL) spectra of the PMMA:KB layer, and on the External Quantum Efficiency (EQE) curve of the perovskite-based device, as shown in Figure 1. PL was measured with a Horiba Scientific Fluoromax 4 spectrofluorometer, with excitation at 375 nm (at the maximum of optical absorption of the layer). EQE spectra were recorded using a Bentham TMC300 monochromator, with

measurements taken every 1 nm using a Stanford Research System SR830 lock-in amplifier. As seen in Fig. 1, the optical absorption of the PMMA:KB layer is between 350-420 nm, so this should prevent any UV light in this region entering the absorber layer.

For control, a UV filter was supplied from Solaronix (Switzerland), which cuts off light with wavelengths less than 390nm.



**Figure 1** – Normalized absorbance (blue line) and photoluminescence (black line) of PMMA:KB layer, and EQE curve of a  $CH_3NH_3Pb_{3(1-x)}Cl_{3x}$ -based photovoltaic device (red line).

## 2.2 Perovskite film and solar cell preparation

Methylammonium Iodide (MAI, code 14965-49-2) and Lead (II) Chloride ( $PbCl_2$ , code 7758-95-4) were purchased from Lumtec (Taiwan) with 99.999% purity. Dimethyl sulphoxide (DMSO, code 67-68-5) and Isopropyl alcohol (IPA, code 67-63-0) were purchased from Sigma-Aldrich (UK). Anisole (#495 A8) was supplied by MicroChem. All products were used as received.

For photo-degradation studies, glass substrates were cleaned in ultrasound bath by immersion for 5 minutes in deionised water, acetone and finally IPA. Lastly the substrates were dried under nitrogen flux and oxygen-plasma treated for 5 minutes. Methylammonium iodide (MAI) solution was prepared by dissolving the solid in IPA with proportion of 30 mg/ml, and stirred for 15 min in ambient temperature.  $PbCl_2$  was dissolved into DMSO at a concentration of

300 mg/ml and stirred at 70 °C for 20 min. The absorber deposition was undertaken in a glove box (with water and oxygen concentrations below 0.1 ppm) using the two-step sequential deposition method. The PbCl<sub>2</sub> solution was spin-coated at 6000 rpm and dried for 20 min at 90 °C. After drying the substrates were left to cool down to room temperature before the next layer was deposited. A solution of MAI was then spin-coated at 6000 rpm, after which the samples were again placed on a hotplate set to 90 °C and annealed for 20 min.

The devices analysed in this work were manufactured onto indium-tin oxide (ITO) coated glass substrates which were coated with a layer of PEDOT:PSS (AI4083). Subsequently, the absorber was deposited inside a glove box by spin-coating using the two-step procedure described above. The acceptor was 6,6-phenyl-C71-butyric acid methyl ester (PC<sub>71</sub>BM) dissolved in chlorobenzene (30 mg/ml). Finally, thermal evaporation of 100 nm of silver (Ag) was deposited to form the cathode of the device.

### 2.3 Photo-degradation and device characterisation

All measurements were undertaken in an air-conditioned room with relative humidity of 35 ± 5 % and ambient temperature of 20 ± 5 °C. For photo-degradation studies, samples were kept at a constant temperature of 60 °C whilst simultaneously exposing to a Solar Simulator with an output power of 100 mW/cm<sup>2</sup> and AM 1.5G spectrum (calibrated using a silicon reference cell from RERA, Netherlands). Absorbance measurements were taken every 10 min.

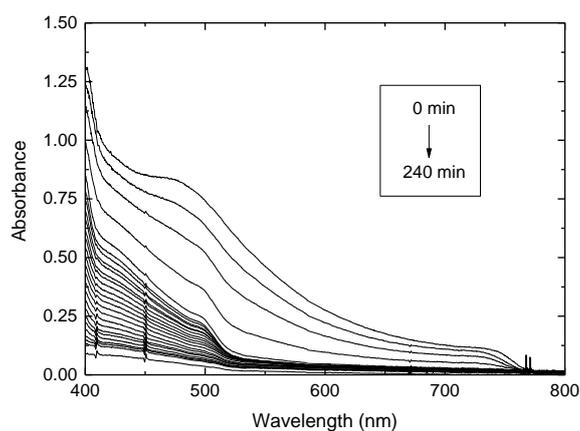
The PSC current density-voltage (J-V) curves were measured for six devices illuminated by the same solar simulator. For this work, three configurations were used whereby the light facing side of the device was covered with a UV filter, PMMA:KB LDS layer or without filtration. For stability tests, the devices were constantly light soaked illumination interrupted for the J-V measurements made every 5 minutes. The test corresponded to the ISOS-L-2 protocol<sup>32</sup>.

## 3. Results and Discussion

### 3.1 Photo-degradation of absorber layers

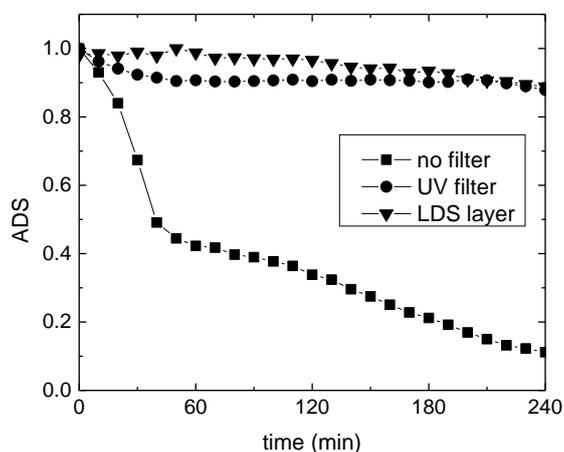
Figure 2 shows the evolution of the UV-Vis light absorption of the non-encapsulated photoactive perovskite layer under illumination by 1 sun irradiance at ambient atmosphere. Initially the spectrum had the typical characteristics of optical absorption of lead iodide-chloride perovskites<sup>33</sup>. However, with the continuous sunlight exposure, a loss of absorbance in the region between 540-780 nm and the emergence of an absorption shoulder around 520 nm are in evidence.

This is related to the formation of  $\text{PbI}_2$  compound, as shown by Manser et al.<sup>34</sup>. Hu et al.<sup>16</sup> also indicated that this absorption peak is due to the emergence of  $\text{PbI}_2$  as the main by-product of  $\text{MAPbI}_2$  degradation<sup>27</sup>, which was corroborated by O'Mahony et al. who showed that the combined effect of light and oxygen plays a major and significant role in the degradation process<sup>35</sup>.



**Figure 2** – Evolution of the UV-Vis light absorption of the unencapsulated  $\text{MAIPbCl}_2$  film under AM1.5G illumination as a function of the irradiation time. The temperature of the sample was maintained at 60 °C during all measurements.

Recently a quantity called Absorption Degradation State (ADS), which is equal to the ratio of the number of absorbed solar photons (from the AM 1.5G spectrum) for the degraded sample to that of the fresh sample was introduced to quantify the degradation of the optical absorption spectra of organic<sup>36,37</sup> and perovskite-based<sup>38</sup> photovoltaic materials. Here, the ADS values were calculated over the 400-800 nm range of the absorbance spectra. Figure 3 shows the ADS variation for the films exposed to simulated sunlight. For samples where no UV filtration was undertaken (square symbols), degradation was rapid with absorption values decreasing to 10% of the original value recorded after four hours of exposure.



**Figure 3** – Evaluation of the Absorption Degradation State (ADS) parameter in the range of 400-800nm for non-encapsulated film (squares), and for films with UV filter (circles) and with PMMA:KB luminescent layer (triangles). The temperature of the samples was maintained at 60 °C during all measurements.

The stability issue has been addressed by several recent reviews<sup>14, 21, 39</sup>. In all these works, the relevant factors that are indicated to lead to perovskite film deterioration are moisture, oxygen, UV radiation, and temperature. All of these factors were present in the experiment related to the sample without UV filtration, which can explain the fast degradation of the film observed by its decreased absorbance along all visible spectrum.

However, by using UV filtration (by a commercial source, or with the PMMA:KB LDS layer), it is clear that degradation is significantly reduced. After 240 min of irradiation, the ADS of the film under with UV filter drops to only around 90% of the original value, thus, providing evidence that the use of UV filters can be an effective strategy to increasing the lifespan perovskite absorber layers.

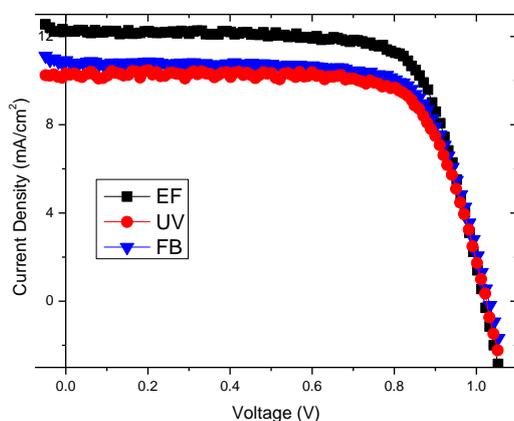
The effectiveness of the UV filtering may affect the retarding degradation pathways. Firstly, it can reduce the formation of oxygen atom radical and/or ozone which attack the perovskite layer<sup>40</sup>. In this case, the light and oxygen induce the formation of halide anions through donation of electrons to the surrounding oxygen. The anions generate free radicals that deprotonate the methylammonium cation and form the highly volatile  $\text{CH}_3\text{NH}_2$  molecules that escape and leave pure  $\text{PbI}_2$  behind<sup>41</sup>. This degradation pathway is supported by the data in figure 2, where the formation of  $\text{PbI}_2$  is seen with the absorption peak. Secondly, UV excitation is known

to lead to photolysis which creates organic breakages. Last but not least is the protection provided by the layers (commercial UV filter and PMMA:KB film) against moisture ingress in the perovskite absorber. Habisreutinger et al. showed the role of a PMMA layer on the top of a  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  film under thermal stress to preserve its optical properties<sup>42</sup>. It is likely that both affects are being retarded by the use of an LDS filter in this instance.

The benefit of the LDS filter for the PSCs performance needs to be evaluated. As observed by Kettle et al.<sup>36</sup>, commercial UV filters are generally composed of inorganic oxide compounds with relatively high refractive index. The difference in the refractive index between the filter material and the substrate of the photovoltaic device may result in significant losses (around 20%) in the device performance. However in the case of the LDS layer, the refractive index is primarily determined by the PMMA, which is approximately the same value as the glass substrate.

### 3.2 Effect of the LDS layer on efficiency and stability of perovskite-based devices

In order to evaluate the photo-degradation effects on devices, PSCs were manufactured in accordance with the experimental procedure. Figure 4 shows the current density-voltage curve of PSCs under AM1.5G simulated sunlight with  $100 \text{ mW/cm}^2$  of irradiance for devices without UV filtration, with the LDS layer and with the commercial UV filter.



**Figure 4** – Current density-voltage plots for perovskite-based devices under  $100 \text{ mW/cm}^2$  AM1.5G simulated sunlight: without filtration (EF), i.e. without filters (squares), with UV filter (circles), and with PMMA:KB (FB) luminescent layer (triangles). The temperature of the devices was maintained at  $60^\circ\text{C}$  during all measurements.

Commented [JK1]: Why 'EF'? What does it stand for?

The values for the electrical parameters of the cells are shown in Table II. As can be seen, the use of UV filter or LDS layer led to a slight decrease in the  $J_{SC}$  value of the cell, which resulted in lower PCE when compared to ~~with~~ the device without UV filtration. The drop in performance when compared to the reference device is to be expected as the  $CH_3NH_3PbI_{3(1-x)}Cl_{3x}$  PSC has a high spectral response between 300 and 800nm, as presented in Figure 1. Therefore, the application of a UV filter will limit the photo current that is generated in the UV region in an unfiltered cell and this accounts for the drop in PCE as seen in Table II. Likewise, the absorbance of the LDS layer is mainly restricted to the UV region (see Figure S2 in the supplementary material) and the absorption will reduce the photo-generation in the 300-400nm region of the spectrum, as is the case for the UV filter. **However, the luminescence of the LDS layers occurs randomly in all directions and therefore light will be also lost in the direct opposite to the active layer and also towards the edges of the device. In addition, losses will occur as the PLQY of thin films is much less than 100%. So even though the photoluminescence of the LDS layer will generate additional carriers, due to the losses, the photocurrent should not increase relative to a non-filtered PSC.** However, it is evident from the data in Table II that LDS layer resulted in better  $J_{SC}$  and PCE values when compared with devices made with a commercial UV filter. Therefore, there is still an added-value of using an LDS layer as the performance drop in UV filtering is not as severe as the application of a commercial UV filter.

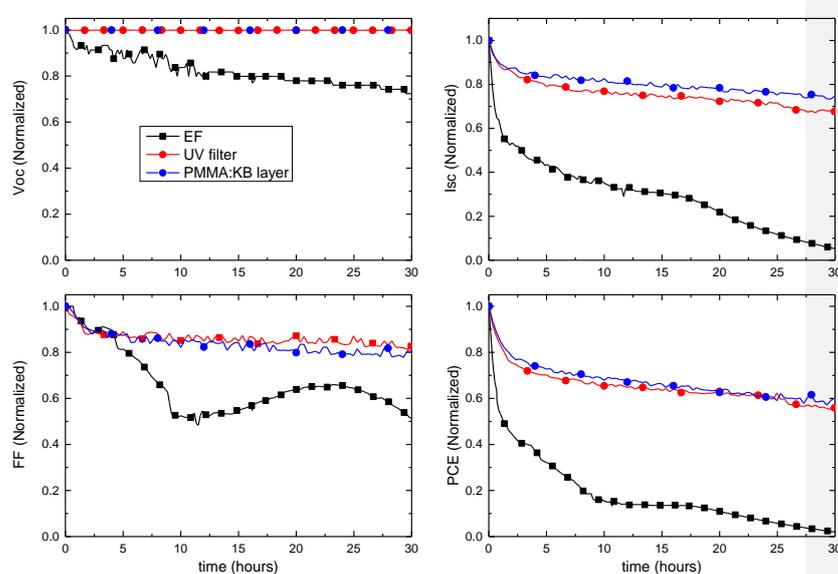
Parameter	AM1.5G	with UV filter	with LDS layer
$V_{oc}$ (V)	1.022	1.021	1.033
$I_{sc}$ (mA)	0.856	0.723	0.764
FF	0.745	0.735	0.722
PCE (%)	9.31	7.76	8.14

Commented [JK2]: You need to add s.d. to this table?

**Table II** – Electrical parameters of cells exposed to 1 sun irradiance without spectral filtration, with a commercial UV filter and with the PMMA:KB LDS layer. The results are an average value from six devices.

Despite some reduction in the PSC performance from adding an LDS filter, the stability should be enhanced as a result of UV filtration. Fig. 5 shows the evolution of the electrical parameters ( $I_{sc}$ ,  $V_{oc}$ , FF and PCE) with the exposure time under AM1.5G illumination. It is clear that both UV filtering using the commercial filter or PMMA:KB layer significantly improves the longevity of the devices. For example, after 30 hours of exposure without filtration to the sunlight, the PCE of unfiltered device decreases to around 5% of the original value, whereas for the devices with PMMA:KB layer the PCE value was around 65% of its initial value. In the timeframe of this

test, there appears no difference between the stability of the cells with the commercial UV filter and the LDS layer. This result shows an improvement on the data reported recently by Cui et al., who used a magnesium based luminescent compound<sup>29</sup>. Thus, by using figure of merits, as described in the experimental section, to better identify suitable LDS layers, improved stability can be found. Organic dyes such as KB are cheaper and commercially available, which makes them a very promising option for use both as LDS layer and as UV protective layer in PSCs.



**Figure 5** – Evolution of electrical parameters with irradiation time (AM1.5G) for devices without filtration to sunlight, with a commercial UV filter and with the PMMA:KB LDS layer: (a) open circuit voltage, (b) short-circuit current, (c) fill factor and (d) PCE. The values are the mean obtained of three devices, and were normalized for better comparison. The temperature of the devices was maintained at 60 °C during all measurements.

**Commented [JK3]:** I would add error bars to these graphs - you can make some scientific estimate of experimental error

## Conclusion

In this paper, we present a study of the application of LDS/UV filters to improve the photo-stability of perovskite absorber films which were produced by a two-step deposition method using  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{PbCl}_2$ . Stability tests were carried out at 60 °C for non-encapsulated films and

devices under standard AM1.5G solar spectrum irradiation. Both a commercial UV filter and a ~~layer of~~ luminescent down shifting (LDS) layer of Kremer Blue dispersed in PMMA matrix were used in order to protect the perovskite film from UV-induced degradation and were able to significantly retard the photo-induced degradation process. This layer was subsequently used in PSC devices utilizing the beneficial effect of LDS, which led to an improvement in the photocurrent produced by the solar cell as compared with devices under UV filter. Because they are cheaper and commercially available, organic dyes such as Kremer Blue dispersed in PMMA, which have strong optical absorption in the UV region of the electromagnetic spectrum, may be a promising alternative for the preparation of protective layers and for use of the LDS effect in solar cells based on perovskite thin films.

### **Acknowledgements**

The authors from UK and Brazil would like to thank the Royal Academy of Engineering for the financial support via the Newton exchange, which funds collaboration between these countries. HSA, RVF, JLD and EL would like to thank CNPq and CAPES for the financial support. VS would like to thank Sêr Cymru National Research Network for funding his PhD studies. IVF and EAK are grateful to the Adelis foundation and Israel's Ministry of National Infrastructures, Water and Energy Resources (grant no. 0399202/215-11-037) for partial support of the research. EAK also thanks the United States – Israel Binational Science Foundation. As a final point, the authors VS and HAS contributed equally to the experimental work in this paper.

## References

1. Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C., Long-range balanced electron-and hole-transport lengths in organic-inorganic CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. *Science* **2013**, *342* (6156), 344-347.
2. Bretschneider, S. A.; Weickert, J.; Dorman, J. A.; Schmidt-Mende, L., Research update: physical and electrical characteristics of lead halide perovskites for solar cell applications. *APL Materials* **2014**, *2* (4), 040701.
3. Green, M. A.; Jiang, Y.; Soufiani, A. M.; Ho-Baillie, A., Optical Properties of Photovoltaic Organic-Inorganic Lead Halide Perovskites. *The journal of physical chemistry letters* **2015**, *6* (23), 4774-4785.
4. Habibi, M.; Zabihi, F.; Ahmadian-Yazdi, M. R.; Eslamian, M., Progress in emerging solution-processed thin film solar cells-Part II: Perovskite Solar Cells. *Renewable and Sustainable Energy Reviews* **2016**, *62*, 1012-1031.
5. Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D., Solar cell efficiency tables (version 48). *Progress in Photovoltaics: Research and Applications* **2016**, *24* (7), 905-913.
6. Peng, G.; Xu, X.; Xu, G., Hybrid organic-inorganic perovskites open a new era for low-cost, high efficiency solar cells. *Journal of Nanomaterials* **2015**, *2015*.
7. Graetzel, M.; Park, N.-G., Organometal halide perovskite photovoltaics: a diamond in the rough. *Nano* **2014**, *9* (05), 1440002.
8. Cao, C.; Zhang, C.; Yang, J.; Sun, J.; Pang, S.; Wu, H.; Wu, R.; Gao, Y.; Liu, C., Iodine and Chlorine Element Evolution in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>-x Cl<sub>x</sub> Thin Films for Highly Efficient Planar Heterojunction Perovskite Solar Cells. *Chemistry of Materials* **2016**, *28* (8), 2742-2749.
9. Xie, F.; Su, H.; Mao, J.; Wong, K. S.; Choy, W. C., Evolution of Diffusion Length and Trap State Induced by Chloride in Perovskite Solar Cell. *The Journal of Physical Chemistry C* **2016**.
10. Luo, S.; Daoud, W. A., Crystal Structure Formation of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>-xCl<sub>x</sub> Perovskite. *Materials* **2016**, *9* (3), 123.
11. Su, Z.; Hou, F.; Jin, F.; Wang, L.; Li, Y.; Zhu, J.; Chu, B.; Li, W., Hole transporting material-free and annealing-free thermal evaporated planar perovskite solar cells with an ultra-thin CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>-xCl<sub>x</sub> layer. *Organic Electronics* **2015**, *26*, 104-108.
12. Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J., Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. *Science* **2013**, *342* (6156), 341-344.
13. Beiley, Z. M.; McGehee, M. D., Modeling low cost hybrid tandem photovoltaics with the potential for efficiencies exceeding 20%. *Energy & Environmental Science* **2012**, *5* (11), 9173-9179.
14. Yang, J.; Kelly, T. L., Decomposition and Cell Failure Mechanisms in Lead Halide Perovskite Solar Cells. *Inorganic Chemistry* **2016**.
15. Shahbazi, M.; Wang, H., Progress in research on the stability of organometal perovskite solar cells. *Solar Energy* **2016**, *123*, 74-87.
16. Hu, L.; Shao, G.; Jiang, T.; Li, D.; Lv, X.; Wang, H.; Liu, X.; Song, H.; Tang, J.; Liu, H., Investigation of the interaction between perovskite films with moisture via in situ electrical resistance measurement. *ACS applied materials & interfaces* **2015**, *7* (45), 25113-25120.
17. Lin, X.; Luo, H.; Jia, X.; Wang, J.; Zhou, J.; Jiang, Z.; Pan, L.; Huang, S.; Chen, X., Efficient and ultraviolet durable inverted polymer solar cells using thermal stable GZO-AgTi-GZO multilayers as a transparent electrode. *Organic Electronics* **2016**, *39*, 177-183.
18. Habisreutinger, S. N.; McMeekin, D. P.; Snaith, H. J.; Nicholas, R. J., Research Update: Strategies for improving the stability of perovskite solar cells. *APL Materials* **2016**, *4* (9), 091503.
19. Yen, H.-J.; Liang, P.-W.; Chueh, C.-C.; Yang, Z.; Jen, A. K. Y.; Wang, H.-L., Large Grained Perovskite Solar Cells Derived from Single-Crystal Perovskite Powders with Enhanced Ambient Stability. *ACS Applied Materials & Interfaces* **2016**, *8* (23), 14513-14520.

20. Misra, R. K.; Ciannaruchi, L.; Aharon, S.; Mogilyansky, D.; Etgar, L.; Visoly-Fisher, I.; Katz, E. A., Effect of Halide Composition on the Photochemical Stability of Perovskite Photovoltaic Materials. *ChemSusChem* **2016**, *9* (18), 2572-2577.
21. Wang, D.; Wright, M.; Elumalai, N. K.; Uddin, A., Stability of perovskite solar cells. *Solar Energy Materials and Solar Cells* **2016**, *147*, 255-275.
22. Chander, N.; Khan, A.; Chandrasekhar, P.; Thouti, E.; Swami, S. K.; Dutta, V.; Komarala, V. K., Reduced ultraviolet light induced degradation and enhanced light harvesting using YVO4: Eu<sup>3+</sup> down-shifting nano-phosphor layer in organometal halide perovskite solar cells. *Applied Physics Letters* **2014**, *105* (3), 033904.
23. Ahmed, H.; Doran, J.; McCormack, S., Increased short-circuit current density and external quantum efficiency of silicon and dye sensitised solar cells through plasmonic luminescent down-shifting layers. *Solar Energy* **2016**, *126*, 146-155.
24. Alonso-Álvarez, D.; Ross, D.; Klampaftis, E.; McIntosh, K. R.; Jia, S.; Storiz, P.; Stolz, T.; Richards, B. S., Luminescent down-shifting experiment and modelling with multiple photovoltaic technologies. *Progress in Photovoltaics: Research and Applications* **2015**, *23* (4), 479-497.
25. Chander, N.; Sardana, S. K.; Parashar, P. K.; Khan, A.; Chawla, S.; Komarala, V. K., Improving the short-wavelength spectral response of silicon solar cells by spray deposition of YVO 4: Eu 3+ downshifting phosphor nanoparticles. *IEEE Journal of Photovoltaics* **2015**, *5* (5), 1373-1379.
26. Griffini, G.; Bella, F.; Nisic, F.; Dragonetti, C.; Roberto, D.; Levi, M.; Bongiovanni, R.; Turri, S., Multifunctional Luminescent Down-Shifting Fluoropolymer Coatings: A Straightforward Strategy to Improve the UV-Light Harvesting Ability and Long-Term Outdoor Stability of Organic Dye-Sensitized Solar Cells. *Advanced Energy Materials* **2015**, *5* (3).
27. Pintossi, D.; Iannaccone, G.; Colombo, A.; Bella, F.; Välimäki, M.; Väisänen, K. L.; Hast, J.; Levi, M.; Gerbaldi, C.; Dragonetti, C., Luminescent Downshifting by Photo-Induced Sol-Gel Hybrid Coatings: Accessing Multifunctionality on Flexible Organic Photovoltaics via Ambient Temperature Material Processing. *Advanced Electronic Materials* **2016**, *2* (11).
28. Yue, J.; Xiao, Y.; Li, Y.; Han, G.; Zhang, Y.; Hou, W., Enhanced photovoltaic performances of the dye-sensitized solar cell by utilizing rare-earth modified tin oxide compact layer. *Organic Electronics* **2017**, *43*, 121-129.
29. Cui, J.; Li, P.; Chen, Z.; Cao, K.; Li, D.; Han, J.; Shen, Y.; Peng, M.; Fu, Y. Q.; Wang, M., Phosphor coated NiO-based planar inverted organometallic halide perovskite solar cells with enhanced efficiency and stability. *Applied Physics Letters* **2016**, *109* (17), 171103.
30. Bella, F.; Griffini, G.; Correa-Baena, J.-P.; Saracco, G.; Grätzel, M.; Hagfeldt, A.; Turri, S.; Gerbaldi, C., Improving efficiency and stability of perovskite solar cells with photocurable fluoropolymers. *Science* **2016**, aah4046.
31. Fernandes, R. V.; Bristow, N.; Stoichkov, V.; Anizelli, H. S.; Duarte, J. L.; Laureto, E.; Kettle, J., Development of multidye UV filters for OPVs using luminescent materials. *Journal of Physics D: Applied Physics* **2017**, *50*.
32. Reese, M. O.; Gevorgyan, S. A.; Jørgensen, M.; Bundgaard, E.; Kurtz, S. R.; Ginley, D. S.; Olson, D. C.; Lloyd, M. T.; Morvillo, P.; Katz, E. A.; Elschner, A.; Haillant, O.; Currier, T. R.; Shrotriya, V.; Hermenau, M.; Riede, M.; R. Kirov, K.; Trimmel, G.; Rath, T.; Inganäs, O.; Zhang, F.; Andersson, M.; Tvingstedt, K.; Lira-Cantu, M.; Laird, D.; McGuinness, C.; Gowrisanker, S.; Pannone, M.; Xiao, M.; Hauch, J.; Steim, R.; DeLongchamp, D. M.; Rösch, R.; Hoppe, H.; Espinosa, N.; Urbina, A.; Yaman-Uzunoglu, G.; Bonekamp, J.-B.; van Breemen, A. J. J. M.; Girotto, C.; Voroshazi, E.; Krebs, F. C., Consensus stability testing protocols for organic photovoltaic materials and devices. *Solar Energy Materials and Solar Cells* **2011**, *95* (5), 1253-1267.
33. Colella, S.; Mosconi, E.; Fedeli, P.; Listorti, A.; Gazza, F.; Orlandi, F.; Ferro, P.; Besagni, T.; Rizzo, A.; Calestani, G.; Gigli, G.; De Angelis, F.; Mosca, R., MAPbI<sub>3</sub>-xCl<sub>x</sub> Mixed Halide Perovskite for Hybrid Solar Cells: The Role of Chloride as Dopant on the Transport and Structural Properties. *Chemistry of Materials* **2013**, *25* (22), 4613-4618.
34. Manser, J. S.; Saidaminov, M. I.; Christians, J. A.; Bakr, O. M.; Kamat, P. V., Making and Breaking of Lead Halide Perovskites. *Accounts of chemical research* **2016**, *49* (2), 330-338.

35. O'Mahony, F. T. F.; Lee, Y. H.; Jellett, C.; Dmitrov, S.; Bryant, D. T. J.; Durrant, J. R.; O'Regan, B. C.; Graetzel, M.; Nazeeruddin, M. K.; Haque, S. A., Improved environmental stability of organic lead trihalide perovskite-based photoactive-layers in the presence of mesoporous TiO<sub>2</sub>. *Journal of Materials Chemistry A* **2015**, *3* (14), 7219-7223.
36. Tromholt, T.; Manceau, M.; Helgesen, M.; Carlé, J. E.; Krebs, F. C., Degradation of semiconducting polymers by concentrated sunlight. *Solar Energy Materials and Solar Cells* **2011**, *95* (5), 1308-1314.
37. Visoly-Fisher, I.; Mescheloff, A.; Gabay, M.; Bounioux, C.; Zeiri, L.; Sansotera, M.; Goryachev, A.; Braun, A.; Galagan, Y.; Katz, E., Concentrated sunlight for accelerated stability testing of organic photovoltaic materials: towards decoupling light intensity and temperature. *Solar Energy Materials and Solar Cells* **2015**, *134*, 99-107.
38. Misra, R. K.; Aharon, S.; Li, B.; Mogilyansky, D.; Visoly-Fisher, I.; Etgar, L.; Katz, E. A., Temperature-and component-dependent degradation of perovskite photovoltaic materials under concentrated sunlight. *The journal of physical chemistry letters* **2015**, *6* (3), 326-330.
39. Zhao, X.; Park, N.-G., Stability Issues on Perovskite Solar Cells. *Photonics* **2015**, *2* (4).
40. Leijtens, T.; Eperon, G. E.; Pathak, S.; Abate, A.; Lee, M. M.; Snaith, H. J., Overcoming ultraviolet light instability of sensitized TiO<sub>2</sub> with meso-superstructured organometal tri-halide perovskite solar cells. *Nature Communications* **2013**, *4*, 2885.
41. Niu, G.; Li, W.; Meng, F.; Wang, L.; Dong, H.; Qiu, Y., Study on the stability of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films and the effect of post-modification by aluminum oxide in all-solid-state hybrid solar cells. *Journal of Materials Chemistry A* **2014**, *2* (3), 705-710.
42. Habisreutinger, S. N.; Leijtens, T.; Eperon, G. E.; Stranks, S. D.; Nicholas, R. J.; Snaith, H. J., Carbon Nanotube/Polymer Composites as a Highly Stable Hole Collection Layer in Perovskite Solar Cells. *Nano Letters* **2014**, *14* (10), 5561-5568.

Supplementary Information

**Application of luminescence downshifting materials for enhanced stability of  $\text{CH}_3\text{NH}_3\text{PbI}_{3(1-x)}\text{Cl}_{3x}$  perovskite photovoltaic devices**

Helder Scapin Anizelli<sup>1</sup>, Vasil Stoichkov<sup>2</sup>, Ricardo Vignoto Fernandes<sup>1</sup>, José Leonil Duarte<sup>1</sup>, Edson Laureto<sup>1\*</sup>, Jeff Kettle<sup>2</sup>, E.A. Katz<sup>3,4</sup>, I. Visoly-Fisher<sup>3,4</sup>

<sup>1</sup> Departamento de Física, Centro de Ciências Exatas, Universidade Estadual de Londrina, 86051-990 Londrina, PR, Brazil

<sup>2</sup> School of Electronic Engineering, Bangor University, Dean St., Bangor, Gwynedd, LL57 1UT, Wales, UK

<sup>3</sup> Department of Solar Energy and Environmental Physics, Swiss Institute for Dryland Environmental and Energy Research, J. Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sede Boker Campus, 84990, Israel

<sup>4</sup> Ilse Katz Inst. of Nano-Science and Technology, Ben-Gurion University of the Negev, Be'er Sheva 84105, Israel

\* contact author: laureto@uel.br

S1- Transmittance of the commercial UV filter (Solaronix - Switzerland)

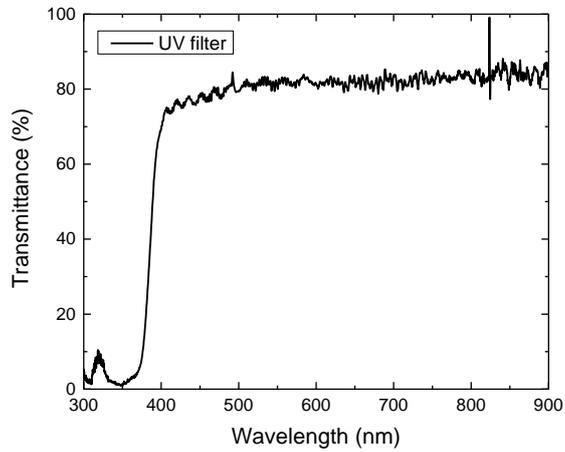


Figure S1 – Absolute transmittance of the commercial UV filter from 300-900nm  
S2- Absorption of the LDS filter consisting of Kremer blue dispersed into PMMA a

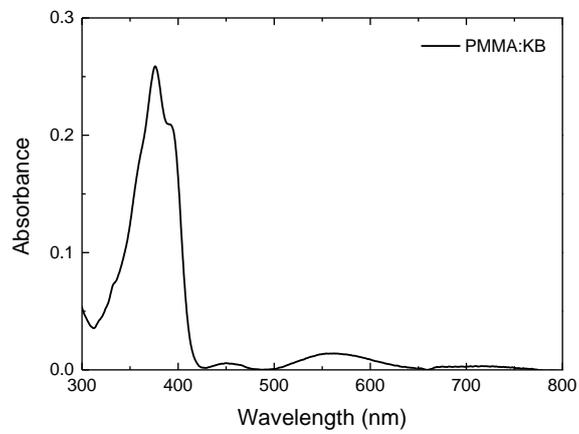


Figure S2 – Absorbance of PMMA:KB film used as LDS layer in this work.