Comment on ZAAC Article z201800267 (On the Demystification of "$HPbI_3$" and the Peculiarities of the Non-innocent Solvents H_2O and DMF)

Henning A. Höppe*[a]

1 The Setting

The study by *Harald Hillebrecht* and *Michael Daub* on *On the demystification of "$HPbI_3$" and the peculiarities of the non-innocent solvents H_2O and DMF* in *Z. Anorg. Allg. Chem.* presents a very important contribution to the treatment of inconsistencies regarding a precursor highly relevant for modern solar cells.

Since this contribution refers to the possible misinterpretation in previous publications of other authors I thought it might be worth commenting this publication from an independent point-of-view.

2 Assessment Regarding the Corrections

The authors of the manuscript – *Harald Hillebrecht* and *Michael Daub* – charge previous publications[1–5] for the possible misinterpretation of data, namely:

- Feng Wang, Hui Yu, Haihua Xu, and Ni Zhao, *Advanced Functional Materials* **2015**, *25*, 1120 (DOI: 10.1002/adfm.201404007)

- Shuping Pang, Yuanyuan Zhou, ZaiweiWang, Mengjin Yang, Amanda R. Krause, Zhongmin Zhou, Kai Zhu, Nitin P. Padture, and Guanglei Cui, *J. Am. Chem. Soc.* **2016**, *138*, 750 (DOI: 10.1021/jacs.5b11824).

- Mingzhu Long, Tiankai Zhang, Yang Chai, Chun-Fai Ng, Thomas C. W. Mak, Jianbin Xu, and Keyou Yan, *Nature Communications* **2016**, 13503 (DOI: 10.1038/ncomms13503).

- Taiyang Zhang, M. Ibrahim Dar, Ge Li, Feng Xu, Nanjie Guo, Michael Grätzel, and Yixin Zhao, *Science Advances* **2017**, *3*, e1700841 (DOI: 10.1126/sciadv.1700841).

- Yuanyuan Zhou and Nitin P. Padture, *ACS Energy Letters* **2017**, *2*, 2166 (DOI: 10.1021/acsenergylett. 7b00667).

Considering the results presented in the manuscript by *Hillebrecht* and *Daub* and those of the charged publications the allegations specified mainly in the Introduction are apparently justified. For instance, recording vibrational spectra or a simple – sometimes blamed as *outdated* – chemical elemental analysis of the ominous $HPbI_3$ samples in combination with basic chemical knowledge would have safely prevented the authors from their erroneous interpretation of the correct data.

The manuscript by *Daub* and *Hillebrecht* nicely demonstrates how experimental results may mock even renowned scientists, especially then, when these data seemingly support certain initial false hypotheses. It reminds every researcher of being more critical with the own conclusions drawn from data and taking into account alternative explanations. It is also highly advisable to be more critical with conclusions drawn by colleagues.

The really exciting results presented in this manuscript in *Z. Anorg. Allg. Chem.* deserve broad attention due to their relevance to the field and their quality as such. Especially the authors of the initially mentioned publications should consult and consider the hints given therein with care.

My independent estimation yields a few simple consequences, which should be drawn:

(1) The publication by Feng Wang, Hui Yu, Haihua Xu, and Ni Zhao, *Advanced Functional Materials* **2015**, *25*, 1120 (DOI: 10.1002/adfm.201404007) should be withdrawn due to wrong interpretation of data. For instance, the interpretation of X-ray diffraction data is not state-of-the-art. Moreover, the lack of any evidence for the presence of "$HPbI_3$" like an elemental analysis or a vibrational spectrum rises concerns. Thus the authors knowingly present misleading information for other research groups reproducing their precursor.

(2) The publication by Mingzhu Long, Tiankai Zhang, Yang Chai, Chun-Fai Ng, Thomas C. W. Mak, Jianbin Xu, and Keyou Yan, *Nature Communications* **2016**, 13503 (DOI: 10.1038/ncomms13503) should be withdrawn due to severely false interpretation of data in combination with lack of evidence for the chemical composition of both samples. Also in this manuscript bad mistakes occurred during crystal structure determinations – for instance that "$HPbI_3$" and "$HPbI_3$·DMF" show the same unit cell, by the way ignoring that these cells are the same as found previously for hexagonal dimethylammonium lead iodide $(CH_3)_2NH_2PbI_3$, with astonishingly similar PXRD intensities. A further obvious mistake is the failure to not per-

[a] Lehrstuhl für Festkörperchemie
Universität Augsburg
Universitätsstraße 1
86159 Augsburg, Germany

form a simple elemental analysis and record conventional vibrational spectra.

(3) I strongly recommend the editorial boards of all journals of the other alleged publications to consult the corrections made in the herein commented manuscript and consider adding a respective comment to the online published publication abstracts.

References

[1] F. Wang, H. Yu, H. Xu, N. Zhao, *Adv. Funct. Mater.* **2015**, *25*, 1120 .

[2] S. Pang, Y. Zhou, Z. Wang, M. Yang, A. R. Krause, Z. Zhou, K. Zhu, N. P. Padture, G. Cui, *J. Am. Chem. Soc.* **2016**, *138*, 750.

[3] M. Long, T. Zhang, Y. Chai, C.-F. Ng, T. C. W. Mak, J. Xu, K. Yan, *Nat. Commun.* **2016**, 13503.

[4] T. Zhang, M. Ibrahim Dar, G. Li, F. Xu, N. Guo, M. Grätzel, Y. Zhao, *Sci. Adv.* **2017**, *3*.

[5] Y. Zhou, N. P. Padture, *ACS Energ. Lett.* **2017**, *2*, 2166 .