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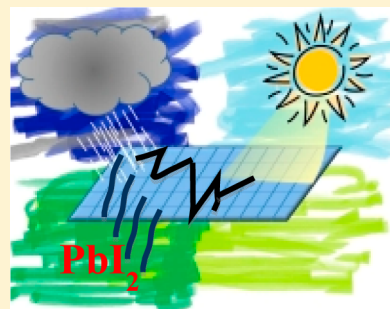
Rain on Methylammonium Lead Iodide Based Perovskites: Possible Environmental Effects of Perovskite Solar Cells

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S Supporting Information

ABSTRACT: The great promise of hybrid organic–inorganic lead halide perovskite (HOIP)-based solar cells is being challenged by its Pb content and its sensitivity to water. Here, the impact of rain on methylammonium lead iodide perovskite films was investigated by exposing such films to water of varying pH values, simulating exposure of the films to rain. The amount of Pb loss was determined using both gravimetric and inductively coupled plasma mass spectrometry measurements. Using our results, the extent of Pb loss to the environment, in the case of catastrophic module failure, was evaluated. Although very dependent on module siting, even total destruction of a large solar electrical power generating plant, based on HOIPs, while obviously highly undesirable, is estimated to be far from catastrophic for the environment.



Lead is a naturally occurring metal found in compounds in small quantities (50–400 ppm) in the earth's crust. However, although lead can be found in all parts of our environment, much of it comes from human activities including burning of fossil fuels, mining and manufacturing of consumer goods such as (secondary) batteries, ammunition, soldering, piping (cf. plumbing), and electronic devices. Exposure to lead can lead to severe health effects ranging from cardiovascular and developmental diseases to neurological and reproductive damage. For these reasons, the lead content of gasoline, paints and ceramic products, sealing, and water pipe solder has been limited, and its concentrations have been dramatically reduced in recent years. The maximum accepted levels of lead in drinking water and air were set to 15 and 0.15 $\mu\text{g/L}$, respectively, by the U.S. EPA.¹ This is why, when there is a potential of introducing a new source of lead contaminant into the environment, one should be particularly careful, and the ways that lead might leach into the natural and human environment should be explored and eliminated or at least minimized.

Organic lead halide perovskites recently emerged into the world of solar cells and have taken it by storm, with efficiencies of small-area cells (defined by small areas of one of the contacts) above 20%² and small “modules” already being tested in laboratories.³ The ease of chemical tunability,^{4,5} its hydrogen-bonding directed self-assembly (and, possibly, self-healing),^{6,7} and solution processability turn these perovskite-based cells into excellent candidates for either a new inexpensive absorber, as a top cell in a tandem system,⁸ or simply the hitherto missing affordable high-voltage photovoltaic (PV) cell.

However, the exact same properties also have a downside as these materials are easily dissociated in the presence of highly polar solvents such as water.⁹ Taking into account that solar panels will normally be placed in the open field or on the

rooftops of homes, their exposure to precipitation is unavoidable. Moreover, although all current (and probably future) solar panels will be encapsulated to minimize degradation and decomposition, one should also consider the effect that damaged panels might have when exposed to rain, as was done for, for example, CdTe cells.¹⁰ Here, we have simulated a worst-case scenario in which a damaged “cell” ($\text{CH}_3\text{NH}_3\text{PbI}_3$ deposited on mesoporous alumina) is exposed to rain and monitor the leaching out of the lead into the surroundings.

When water interacts with, for example, methylammonium lead iodide, ($\text{CH}_3\text{NH}_3\text{PbI}_3$), a decomposition reaction takes place where the $\text{CH}_3\text{NH}_3\text{I}$ is decomposed (possibly through intermediate products) to HI (hydriodic acid), and CH_3NH_2 (methylamine), which initially formed it. PbI_2 (lead iodide), which remains behind, has a solubility product on the order of 10^{-8} , which is much higher than those of other common heavy metal compounds used in solar cells. CdS, PbS, and CdTe have K_{sp} values ranging from $1 \cdot 10^{-27}$ to 1×10^{-34} ,¹¹ and because those are binary compounds rather than the three-atom PbI_2 , the relevant Cd solubilities are up to about 14 orders of magnitude smaller than that of Pb from PbI_2 . Thus, we cannot dismiss the possibility that lead might find its way into the effluent and from there in groundwater in significant quantities.

We conducted a series of experiments aimed to examine how much of the active layer will be rinsed from the cell and eventually find its way to the soil or groundwater. For that purpose, $\sim 12 \text{ mm} \times 30 \text{ mm}$ samples of $\text{CH}_3\text{NH}_3\text{PbI}_3$ on mesoporous alumina electrodes were fabricated using a literature procedure¹² and rinsed with water with a pH ranging from 4.2 to 8.1. The amount of $\text{CH}_3\text{NH}_3\text{PbI}_3$ rinsed was

Received: March 10, 2015

Accepted: April 7, 2015

calculated from gravimetric analysis based on substrate weight differences before and after rinsing, and the effluent water was tested for Pb content in the solution by inductively coupled plasma mass spectrometry (ICP-MS) analysis.

The dark-brown-colored samples became yellow almost immediately (within a few seconds) upon contact with the water. Most of the visible color disappeared by the end of the 1 h rinsing procedure, although some traces remained. When $\text{CH}_3\text{NH}_3\text{PbI}_3$ is exposed to water vapor, it eventually changes color from black to yellow. The early literature describes hydrated materials, if prepared or cooled below $\sim 40^\circ\text{C}$.^{13,14} Such phases convert back to the black, dehydrated phase when heated (e.g., at 100°C). The product of exposure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ to water vapor in humid air in the absence of light has been associated with a hydrate,¹⁵ described by Vincent et al.¹⁴ In the presence of supra-band-gap light, the product is PbI_2 . We carried out experiments to distinguish between the hydrated phase and PbI_2 (which cannot convert back to the perovskite upon annealing because it lacks the methylammonium salt). We found that even a very short exposure to liquid water (a few second dip in water) causes the loss of CH_3NH_3^+ (with I^- as the counterion). Figure 1 shows a $\text{CH}_3\text{NH}_3\text{PbI}_3$ film

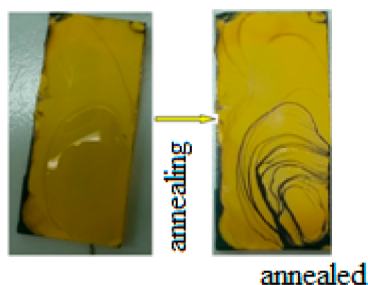


Figure 1. Perovskite film after treatment with water as described above; 0.4 mL of water is applied over a period of 5 min (left) and after annealing at 100°C for 10 min (right).

after 5 min of exposure to simulated rain (~ 0.4 mL of water gradually applied over that time). The black/dark brown initial color was completely changed to yellow (except at some edges of the sample where water probably did not reach efficiently). After annealing at 100°C for 10 min, most of the sample remained yellow; some dark lines did form, which is presumably due to heterogeneities in the coverage of the sample by the water, meaning that a small proportion of $\text{CH}_3\text{NH}_3\text{I}$ still remained in the film. In fact, if the perovskite was dipped into water (instead of the gradual exposure to simulate rain, as described above), the color change occurred essentially immediately and was, even after just a few seconds, irreversible, that is, the product was PbI_2 and not a hydrated perovskite. This fast conversion also implies a very rapid reconstruction of the perovskite, probably by removal of $\text{CH}_3\text{NH}_3\text{I}$ through fast out-diffusion. The result of this experiment was the same regardless of whether the experiment was carried out under room light or in the dark (see ref 15 discussed above, where light affected the course of the reaction of the perovskite with water vapor (over a much longer time)). Finally, X-ray diffraction of films rinsed with water showed only PbI_2 and no peaks from the hydrated perovskite (Figure SI-2, Supporting Information). It is clear that the reaction of the perovskite with water vapor and with liquid water progresses differently. This can be explained by the removal of CH_3NH_3^+ and I^- by liquid water, while reaction by water vapor requires

sublimation of the $\text{CH}_3\text{NH}_3\text{I}$ for its removal. In addition, optical absorption spectra of the yellow films obtained after treatment with liquid water were identical (in terms of the absorption onset) to those of PbI_2 films (see Figure SI-1 in the Supporting Information).

Early experiments showed poor agreement between the mass of Pb lost by the rinsing treatment as measured gravimetrically and that measured by ICP-MS (typically only 60–70% of the Pb loss measured by weighing was detected in the solution; see Table 1). ICP-MS measures ions in solution but does not

Table 1. Percent Loss in Pb, Measured Gravimetrically, from the Samples after Rinsing, and the Percentage of That Loss Measured by ICP-MS as a Function of Added AcH

	volume AcH added (μL)	% Pb mass loss by rinse	$[\text{Pb (ICP-MS)}/\text{Pb (mass loss)}] \times 100$
trial 1	0	71.8 ± 10.4	59.9 ± 9.6
	120		74.8 ± 12.3
trial 2	0	66.0 ± 6.1	67.1 ± 6.1
	240		93.4 ± 7.8

detect solid (including colloidal) particles. To increase the solubility of the PbI_2 , we added acetic acid (AcH) to the effluent solution. Table 1 shows the percentage of Pb, detected by ICP-MS, compared to the Pb lost measured gravimetrically as a function of added AcH. Table 1 shows only the average values of either 9 or 10 separate samples; the same table, including all raw data and separate samples, is given in the Supporting Information, Table SI-1.

First, we look at the effluent samples with no added AcH. We divided these samples into two separate blocks (labeled trial 1 and trial 2 in the table), 1 of 9 samples and 1 of 10, which reflects the groups in which the experiments were carried out, to provide an idea of the reproducibility of these results; see Table SI-1 (Supporting Information). The average gravimetric data giving the % loss of Pb upon rinsing from the two blocks are fairly close ~ 72 and 66% . There is a much larger sample-to-sample variation, from ~ 58 to 88% , for the individual samples (Table SI-1, Supporting Information). The variation between individual samples is not too surprising; it will depend on many factors, in particular, detachment of small visible solid pieces of PbI_2 , which we have noted to occur on occasion.

Comparing these gravimetric data with the ICP-MS measurements (the ratio of Pb measured by ICP-MS to that measured by gravimetry is given in % in the last column of Table 1; ideally, this should be 100% for full agreement), we find considerable disagreement between the two measurements of the same samples, with, on average, in one block $\sim 60\%$ of the gravimetrically measured Pb found by ICP-MS and $\sim 67\%$ in the other block. The moderate difference between the two blocks can be explained to a large extent by the two outliers in the first block ($<50\%$). However, the more important issue was, How much can we trust the overall measurements with such a large disagreement between the two methods?

As we noted earlier, ICP-MS does not detect Pb in the solid form (e.g., colloids). It was shown that PbI_2 colloids form when Pb^{2+} and I^- ions are mixed, even at concentrations where the PbI_2 is expected to be soluble.¹⁶ Excess I^- was present in these experiments, which might affect the solubility. This could decrease the solubility because of the common ion effect or it might actually increase it due to complexation. Therefore, it is reasonable to suspect that some of the Pb in the effluent might

be present as colloidal PbI_2 . A qualitative green, 540 nm laser test of the (visually clear) effluent solution exhibited strong scattering, which infers the presence of colloidal particles in the effluent solution. To minimize the possibility of colloid formation, we added AcH, which is a complexant for Pb, to the effluent. Table 1 shows that this increases the amount of lead measured by ICP-MS and, therefore, the agreement between the two methods. For 120 μL of AcH added per effluent sample (3 mL), the percentage of Pb measured by ICP-MS relative to that with the gravimetric method (last column) increased to $\sim 75\%$ (from $\sim 64\%$ for the average of all of the AcH-free samples taken together) and $\sim 92\%$ for the 240 μL addition of AcH. This reasonable agreement between the two methods provides confidence that the measurements are meaningful. The remaining difference can be due to the sum of a number of experimental steps: inaccuracies in weight measurements (the difference between two measurements is taken); differences in moisture adsorption of the samples (minimized by repeated weighing until no change in weight was observed between weighing); mechanical effects of the rinsing procedure (e.g., disintegration of parts of the treated films); and, of course, that possibly some solid PbI_2 is still present.

Another possibility for loss of Pb is precipitation of some Pb compound, either in the solution or on the walls of the glass vessels. We therefore performed experiments to check this possibility, carrying out sequential ICP-MS measurements (on the same solution) within 1–3 h after the rinsing process, after 24 h, and then after 48 h. As shown in Figure 2, there was an

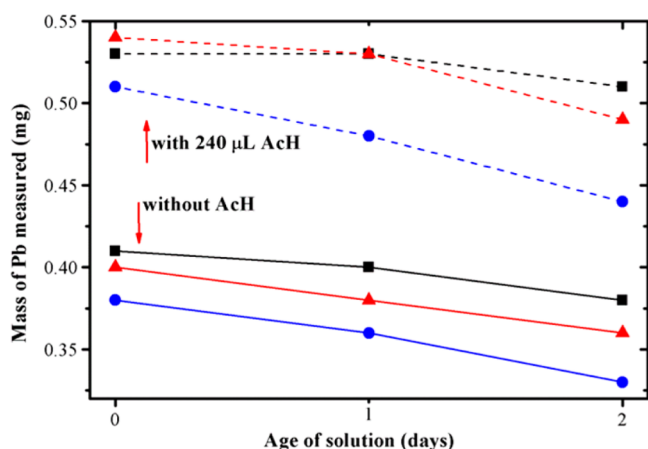


Figure 2. Amount of Pb detected in the effluent solution (three different samples with AcH and three without) by ICP-MS, measured within 1–3, 24, and 48 h after the rinsing process. In solutions with added AcH, 240 μL of AcH was added to 3 mL of solutions as before. The full data table is given in Table SI-2 (Supporting Information).

appreciable drop in the measured Pb, particularly between the 1 and 2 day measurements, suggesting that precipitation in the rinsing solution can indeed affect the ICP-MS measurements. Note that except for samples used to obtain the data in Figure 2 and Table SI-2 (Supporting Information), all other samples described in this work were measured within the range of 1–12 h after the rinsing process (a larger number of samples was measured in these other experiments, thus requiring a longer time between carrying out the rinsing procedure and the ICP-MS measurements).

The pH of rainwater can vary considerably. For that reason, we repeated the previous experiments with acidic (pH 4.2) and

alkaline (pH 8.1) “rain”, prepared as described in the Experimental Methods section (Table 2). There is only a

Table 2. As Table 1 Using Water with Three Different pH Values, 4.2, 6, and 8.1, and 240 μL of AcH Added to All Samples^a

pH	% Pb mass loss by rinse	[Pb (ICP-MS)/Pb (mass loss)] \times 100
6.0	67.5 \pm 5.7	94.9 \pm 9.9
8.1	69.0 \pm 4.5	93.2 \pm 5.0
4.2	71.9 \pm 4.1	89.4 \pm 20.0

^aThe full table is given in Table SI-3 (Supporting Information).

small, and probably not meaningful, difference between the gravimetric % loss of Pb using the pH 6.0 and 8.1 water (67.5 and 69.0%, respectively) and a somewhat larger (maybe meaningful) difference between the pH 6.0 and 4.2 water (67.5 and 72.0%, respectively). It is not surprising that the more acidic rain dissolves the PbI_2 somewhat more rapidly, although the solubility of the PbI_2 may also depend on the actual species in the rain (e.g., nitric acid will dissolve the PbI_2 better than sulfuric acid, the most common components of “acid rain”). However, the main conclusion here is that, over the pH range used here, the difference, if any, is not pronounced.

To sum up the simulated rain experiments, it is obvious from these results that, unless efforts are made to contain the loss of lead before or soon after the onset of rain (e.g., by exposing the damaged module(s) to a small amount of soluble sulfide solution, which would convert the Pb to highly insoluble PbS (about 11 orders of magnitude less Pb in solution compared to the iodide), which could then be removed), essentially all of the lead will be leached out eventually and this conclusion will hold regardless of the variation in our data.

To analyze the impact of exposed or broken solar panels based on perovskite materials on the soil below it and, thus, on the environment, we will consider first a solar field (a large area of panels installed in an open space); a 1 m^2 panel of perovskite-based solar cell would contain less than 1 g of lead (for a 300 nm thick $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer, the typical thicknesses for good cells, it would be ~ 0.4 g). A panel with broken encapsulation and incomplete sealing by subsequent layers on top of the perovskite, such as charge-selective conductors and metallic contacts, will, in the worst case, result in the dissolution of essentially all of the Pb that it contained to the ground below it, as we have shown here. Assuming an average soil density of 1.5 g/mL , this will cause the lead concentration in the first cm of ground below the panel to increase by ~ 70 ppm. Typical Pb levels in soil vary from <10 –30 ppm for natural “uncontaminated” soil to 50–200 ppm (in some cases, much higher) in urban areas.¹⁷ With continued rainfall, the Pb concentration will continue to drop as the Pb is distributed more widely through the depth of the soil, although for many types of soil, the lead will remain concentrated in the top several cm due to its tendency to be strongly adsorbed on soil particles (meaning a Pb concentration of ~ 20 ppm in this layer, which in itself is a form of remediation since the Pb would remain there for a longer time which would greatly improve the possibility for removing contaminated soil). Therefore, such a pollution scenario cannot be considered even close to disastrous, although, naturally, any release of Pb and resulting increase (even if not large) in the background lead pollution should be avoided. Obviously, other consid-

erations will have to be taken into account when installing such panels near groundwater reservoirs or surface water sources and maybe also for rooftop panels.

To put things into perspective, we consider a very current alternative. A medium to fairly large sized clean coal-burning power station, generating 1 GW, emits over its 20 years lifetime (20 GW-yr energy supplied) between 100 and >1000 kg of lead to the air (plus a much larger quantity in the solid byproducts, some of which is dumped as waste, as well as many other heavy metals such as Hg and Cd, all of which we do not consider here).¹⁸ Assuming lead-free storage of PV-generated electricity, the perovskite PV cell equivalent for this constantly occurring contamination of our environment, assuming 1 g of Pb/m² (an upper limit) of 15% efficiency (solar power to AC electrical power) in the array of PV modules, required to provide 20 GW-yr equivalent continuous power (assuming a ~20% equivalent operation time, i.e., conversion from peak power to continuous power), is a field containing ~30 tons of lead. Therefore, taking the lower value (the lowest that we could find, ref 18a) of 100 kg of Pb emission for a coal station, if over 20 years less than one module out of 300 breaks, there will be a reduction in Pb emission to the environment compared with the best presently available coal-generation station. Concerning module disposal at the end of module life, First Solar, the main manufacturer of CdTe-based PVs, has been operating a reclamation and recycling program for the past decade for their modules,¹⁹ and such a program can be anticipated for Pb perovskite cells if they become commercial. Pb already has one of the highest overall recycling rates among nonprecious metals, >50% worldwide and >20% in the U.S.A.²⁰

In conclusion, rain falling on CH₃NH₃PbI₃ perovskite-based solar cells with a damaged encapsulation will result in complete irreversible decomposition of the absorber layer. Furthermore, dipping experiments indicate that due to the moderate solubility of lead iodide in water, with time, a significant amount or even all of the Pb will be solubilized and find its way into the environment. If the leached out lead spreads and does not concentrate in a limited volume of groundwater, eventually the amount of added lead to the environment is small, in comparison to the natural occurrence of lead. If it does not spread out because of strong adsorption by the topsoil, then as already suggested, this in itself a form of remediation. Still, for the large-scale scenario that we have considered, one must consider the possible implications of implementing lead halide perovskite solar cells for each specific scenario. This scenario can be mitigated to a greater or lesser extent if other components of the cell on top of the perovskite (e.g., hole conductor and contacts) are impermeable to water. Our experiments represent a worst-case scenario where the perovskite is completely exposed.

EXPERIMENTAL METHODS

CH₃NH₃PbI₃ was deposited on <50 nm particle size alumina on FTO-glass by spin-coating a solution of 1:1 CH₃NH₃I and PbI₂ in *N,N*-dimethylformamide. The resulting films were heated at 100 °C for 10 min. The films were weighed, and the substrate weight was subtracted to give the weight of the perovskite. Eighteen MΩ deionized water (pH 6.0) was used to simulate rain except for those experiments where a different pH "rain" (pH 4.2 or 8.2) was used using HNO₃ or NaOH, respectively. The rain was fed to the sample lying in a funnel placed over a vial by a syringe pump at a rate of 5 mL/h for 1 h. This simulated 1 h of heavy rain or 3 h of moderate rain. It

should be noted that actual cells would also be covered with other layers (e.g., hole conductor, contact) so that these experiments should be considered a worse-case scenario. After acidification with HNO₃ (and usually also AcH to better solubilize the PbI₂, as described in the text), the Pb concentration was measured by ICP-MS. The experimental procedures are described in more detail in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

Experimental details, optical spectra, tables of full analytical details, and XRD spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Leona M. and Harry B. Helmsley Charitable Trust, the Israel National Nano-Initiative, the Israel Ministry of Science, and the Nancy and Stephen Grand Center for Sensors and Security for partial support. D.C. holds the Sylvia and Rowland Schaefer Chair in Energy Research.

REFERENCES

- (1) USA Environmental Protection Agency *Lead Laws and Regulations*. <http://www2.epa.gov/lead/lead-laws-and-regulations> (retrieved on 12/01/2015).
- (2) National Center for Photovoltaics (NCPV) *Research Cell Efficiency Records*. http://www.nrel.gov/ncpv/images/efficiency_chart.jpg (retrieved on 11/02/2015).
- (3) Matteocci, F.; Razza, S.; Giacomo, F. D.; Casaluci, S.; Mincuzzi, G.; Brown, T. M.; D'Epifanio, A.; Licoccia, S.; Carlo, A. D. Solid-State Solar Modules Based on Mesoscopic Organometal Halide Perovskite: A Route Towards the Up-Scaling Process. *Phys. Chem. Chem. Phys.* **2014**, *16*, 3918–3923.
- (4) Eperon, G. E.; Stranks, S. D.; Menelaou, C.; Johnston, M. B.; Herz, L.; Snaith, H. Formamidinium Lead Trihalide: A Broadly Tunable Perovskite for Efficient Planar Heterojunction Solar Cells. *Energy Environ. Sci.* **2014**, *7*, 982–988.
- (5) Noh, J. H.; Im, S. H.; Heo, J. H.; Mandal, T. N.; Seok, S. I. Chemical Management for Colorful, Efficient, and Stable Inorganic–Organic Hybrid Nanostructured Solar Cells. *Nano Lett.* **2013**, *13*, 1764–1769.
- (6) Mitzi, D. B. Solution-Processed Inorganic Semiconductors. *J. Mater. Chem.* **2004**, *14*, 2355–2365.
- (7) Mitzi, D. B.; Dimitrakopoulos, C. D.; Kosbar, L. L. Structurally Tailored Organic–Inorganic Perovskites: Optical Properties and Solution-Processed Channel Materials for Thin-Film Transistors. *Chem. Mater.* **2001**, *13*, 3728–3740.
- (8) Hodes, G. Perovskite-Based Solar Cells. *Science* **2013**, *342*, 317–318.
- (9) Frost, J. M.; Butler, K. T.; Brivio, F.; Hendon, C. H.; van Schilfegaarde, M.; Walsh, A. Atomistic Origins of High-Performance in

Hybrid Halide Perovskite Solar Cells. *Nano Lett.* **2014**, *14*, 2584–2590.

(10) Zweibel, K.; Moskowitz, P.; Fthenakis, V. *Thin-Film Cadmium Telluride Photovoltaics: ES&H Issues, Solutions, and Perspectives*, Prepared under Task No. PV804401; National Renewable Energy Laboratory (NREL): Golden, CO, 1998; pp 1–4.

(11) Patnaik, P. *Handbook of Inorganic Chemicals*; McGraw-Hill: New York, 2003.

(12) Edri, E.; Kirmayer, S.; Henning, A.; Mukhopadhyay, S.; Gartsman, K.; Rosenwaks, Y.; Hodes, G.; Cahen, D. Why Lead Methylammonium Tri-iodide Perovskite-Based Solar Cells Require a Mesoporous Electron Transporting Scaffold (but Not Necessarily a Hole Conductor). *Nano Lett.* **2014**, *14*, 1000–1004.

(13) Weber, D. $\text{CH}_3\text{NH}_3\text{PbX}_3$, a Pb(II)-System with Cubic Perovskite Structure. *Z. Naturforsch.* **1978**, *33* (b), 1443–1445.

(14) Vincent, B. R.; Robertson, K. N.; Cameron, T. S.; Knop, O. Alkylammonium Lead Halides. Part 1. Isolated PbI_6^{4-} ions in $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$. *Can. J. Chem.* **1987**, *65*, 1042–1046.

(15) Christians, J. A.; Miranda Herrera, P. A.; Kamat, P. V. Transformation of the Excited State and Photovoltaic Efficiency of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite upon Controlled Exposure to Humidified Air. *J. Am. Chem. Soc.* **2015**, *137* (4), 1530–1538.

(16) Roy, A.; Sarma, D. D.; Sood, A. K. Spectroscopic Studies on Quantum Dots of PbI_2 . *Spectrochim. Acta* **1992**, *48A*, 1779–1787.

(17) Penn State Extension. <http://extension.psu.edu/plants/crops/esi/lead-in-soil> (2015).

(18) (a) Technical Note – Estimating Lead (Pb) Emissions from Coal Combustion Sources. <http://www.epa.gov/ttn/amtic/files/ambient/pb/EstimatingPbFromCoal.pdf> (May 27, 2011). (b) Ito, S.; Yokoyama, T.; Asakura, K. Emissions of Mercury and Other Trace Elements from Coal-Fired Power Plants in Japan. *Sci. Total Environ.* **2006**, *368*, 3970402. (c) 10 Harsh Realities of the US Coal Industry. http://desmogblog.com/sites/beta.desmogblog.com/files/10_Harsh_Realities_of_the_US_Coal_Industry.pdf (2015).

(19) The Recycling Advantage. <http://www.firstsolar.com/en/technologies-and-capabilities/recycling-services> (2015).

(20) Graedel, T. E.; Allwood, J.; Birat, J.-P.; Buchert, M.; Hagelüken, C.; Reck, B. K.; Sibley, S. F.; Sonnemann, G. What Do We Know about Metal Recycling Rates? *J. Industr. Ecol.* **2011**, *15*, 355–366.