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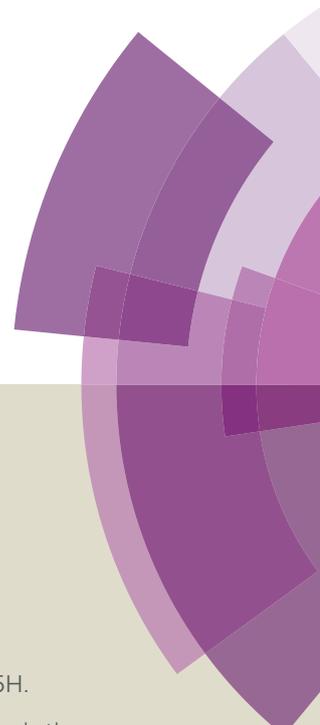
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COMMUNICATION

Insights into the Liquid State of Organo-Lead Halide Perovskites and Their New Roles in Dye-sensitized Solar Cells

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Received 00th January 2012,
Accepted 00th January 2012Qiong Wang^a, Jung-Ho Yun^a, Meng Zhang^a, Hongjun Chen^a, Zhi-Gang Chen^b, and Lianzhou Wang^{a*}

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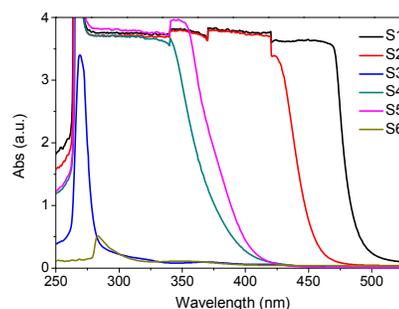
Here we report organo-lead halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ solution can be used as new liquid electrolyte in dye-sensitized solar cells (DSCs). We find that the presence of inorganic octahedra of $[\text{PbX}_6]^{4-}$ (X = I or Cl, or a combination of them) in this perovskite solution can not only remarkably improve the device stability but also enhance photo-response of DSCs.

Solid-state lead halide perovskite films, used as either sensitizers¹⁻⁴ or hole collectors⁵⁻⁷ in solid-state solar cells (SSCs) or heterojunction solar cells, have attracted intensive attention. Organic-inorganic hybrid perovskite materials combine the advantageous characteristics of crystalline inorganic solids with those of organic molecules within a molecular-scale composite. It endows the hybrid materials with structure flexibility, special magnetic, electrical and optical properties, and solution processability.⁸ It has been reported that thermal annealing conditions can largely affect the crystallization and morphology of the solution-processed perovskite thin films, and finally greatly influence the performance of SSCs based on perovskite as absorbers.⁹ However, properties of lead halide perovskites in solutions at room temperature have been much less studied, and how these perovskites exist and behave under liquid condition is not clear.

In this work, we address this question by firstly studying their optical properties. $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ solution was prepared by mixing $\text{CH}_3\text{NH}_3\text{I}$ and PbCl_2 with a molar ratio of 3:1 in *N,N*-dimethylformamide (DMF) solvent according to the reference.² The formation of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ perovskite was confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM) characterizations (See supporting information). It is known that PbI_2 has different solubilities in water and DMF. In water, PbI_2 salt is dissociated into Pb^{2+} and I^- ions; while in DMF solvent, $[\text{PbI}_6]^{4-}$ octahedra are formed and at the edges of these octahedra, two iodine atoms are replaced by oxygen atoms from DMF, which is denoted as solvated $\text{PbI}_2\cdot\text{DMF}$.¹⁰ Because PbI_2 in water and DMF exhibit different absorbance spectra, therefore, to define the possible formation of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ in DMF, the absorbance spectra of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x\text{-DMF}$ solution were studied by UV-Vis

characterization in comparison with $\text{CH}_3\text{NH}_3\text{I-DMF}$, $\text{PbI}_2\text{-DMF}$ and $\text{PbI}_2\text{-water}$. (Figure 1) It can be seen that UV-Vis spectrum of 3.3 mM $\text{PbI}_2\text{-DMF}$ resembles absorbance spectrum of 10 mM $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ that contains 3.3 mM lead halide precursor in DMF. In comparison, absorbance spectra of $\text{PbI}_2\text{-water}$ and $\text{CH}_3\text{NH}_3\text{I-DMF}$ exhibit totally different properties from that of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x\text{-DMF}$ solution. Note that because of very strong absorbance of solutions of S1, S2, S4, and S5, the intensities of these samples have exceeded the up-limitation of the UV-Vis spectrometer. As discussed above, PbI_2 salt is dissociated into Pb^{2+} and I^- in water, and $\text{CH}_3\text{NH}_3\text{I}$ is dissociated into CH_3NH_3^+ and I^- ions in DMF, thus, it can be concluded that lead and halide in $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x\text{-DMF}$ do not exist as free Pb^{2+} and I^- ions but as inorganic octahedra, $[\text{PbX}_6]^{4-}$ (X = I or Cl, or a combination of them).

Figure 1. UV-Vis spectra of 1 M $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x\text{-DMF}$ (S1), 100 mM $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x\text{-DMF}$ (S2), 100 mM $\text{CH}_3\text{NH}_3\text{I-DMF}$ (S3), 10 mM $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x\text{-DMF}$ (S4), 3.3 mM $\text{PbI}_2\text{-DMF}$ (S5) and saturated $\text{PbI}_2\text{-water}$ (S6).



By adjusting the solution concentration of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x\text{-DMF}$, it is found that at low concentration, the solution is yellowish, transparent and stable (1 M in DMF), while increasing concentration (2 M in DMF) leads to the formation of a gel-like structure (photos in Scheme 1). Based on the UV-Vis study and observation of the solutions, we speculate that the inorganic parts, $[\text{PbX}_6]^{4-}$ are mostly isolated and largely surrounded by organic parts and DMF solvent at low concentration whereas the inorganic octahedra might get connected with each other by sharing the same halide to form larger clusters when the concentration goes higher; eventually the solution

is transformed into a gel. Scheme 1 proposes the possible constitution changes of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ in DMF. To make things straightforward, the interactions between the inorganic parts and the DMF molecules are not expressed.

Scheme 1. Illustration of possible composition of methylammonium lead halide perovskite in DMF solution.

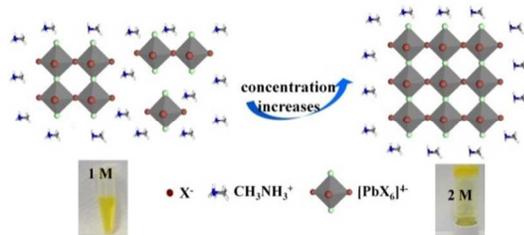
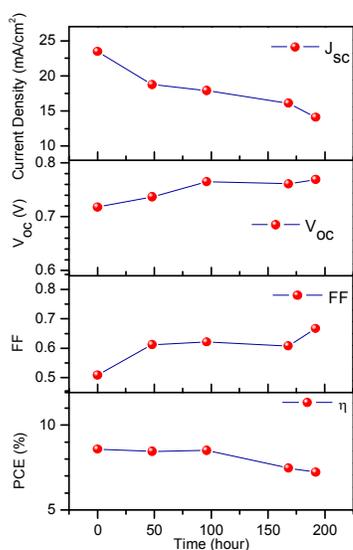


Figure 2. Stability test of optimized $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ -DSCs stored in air at room temperature.



In the following, we try to determine the impact of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ -DMF on the electric properties of the solution. Dye-sensitized solar cells (DSCs) were chosen for this test because of the relatively facile fabrication process and comparatively good understanding of their working mechanisms.¹¹⁻¹⁴ DSCs based on iodine electrolyte have been fully researched, and the redox mediators of I^-/I_3^- have been identified as being responsible for the regeneration of dye.¹⁵ Because of the iodide containing nature of the lead halide perovskite, it would be quite interesting to investigate how such perovskite behaves as an electrolyte in DSCs. We also use its precursor $\text{CH}_3\text{NH}_3\text{I}$ in DMF under the same DSC assembly condition for comparison. Photovoltaic studies given in the supporting information show that the power conversion efficiency (PCE) of $\text{CH}_3\text{NH}_3\text{I}$ -DSCs rapidly declines from 4.14 % to below 1 % merely in ten minutes due to the fast decrease of short-circuit current density (J_{sc}) under illumination. However, $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ -DSCs exhibit considerably better stability. As shown in Figure 2, in the first 100 hours, only a slight decrease in PCE of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ -DSCs is observed. Our understanding on $\text{CH}_3\text{NH}_3\text{I}$ -based electrolyte, is that free I^- ions could be firstly oxidized to I_n^- , and then to I_m^- ($n < m$).¹⁶ Thus during the working process of $\text{CH}_3\text{NH}_3\text{I}$ -DSCs, I_m^- can be depleted instantly and cannot be generated quickly enough, as a result the excited dye cannot be effectively reduced to their ground

states;¹⁷ which subsequently lead to diminished current density. In contrast, the stable PCE performance in the DSCs assembled with $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ electrolyte highlights the unique roles of inorganic species of $[\text{PbX}_6]^{4-}$ in $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ solution. It is observed that the stability of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ -DSCs also is better than that of DSCs based on conventional iodine electrolyte (I_2 -DSCs), which is mainly attributed to the less volatile property of the solvent used in $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ electrolyte.

Another role of the inorganic part of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ is revealed by the photovoltaic (PV) features of the DSCs. Figure 3 and Table 1 present the PV characteristics of optimized $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ -DSCs and I_2 -DSCs. Influences of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ concentrations, additives and film thickness of photoanodes on performance of DSCs are given in the supporting information. The incident photon to current conversion efficiency (IPCE) measurement of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ -DSCs and I_2 -DSCs shows that the typical IPCE peak of N719-sensitized solar cells in wavelength ranging from 300 nm to 350 nm is absent in $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ -DSCs (Figure 3b). Meanwhile, $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ -DSCs present enhanced IPCE in wavelength ranging from 350 nm to 500 nm. It is uncertain if the missed IPCE peak from 300 nm to 360 nm is due to back transfer of photo-generated electrons from N719 dye to $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ electrolyte or due to the reason that the excited states of N719 molecules by high energies cannot be effectively reduced to their ground states by $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ electrolyte.

Figure 3. a) Current density-potential (J - V) curves and b) IPCE results of optimized $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ -DSCs and I_2 -DSCs. (Note that no mask is used for the photovoltaic measurement in this work)

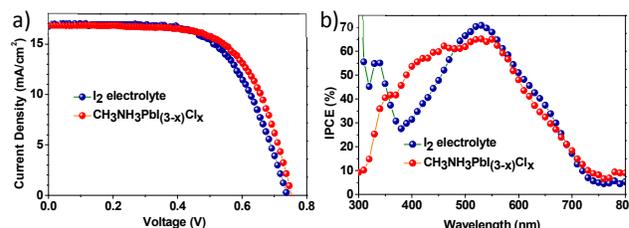


Table 1. Photovoltaic parameters of optimized devices, measured under AM 1.5G one sun with light intensity of 100 mW/cm².

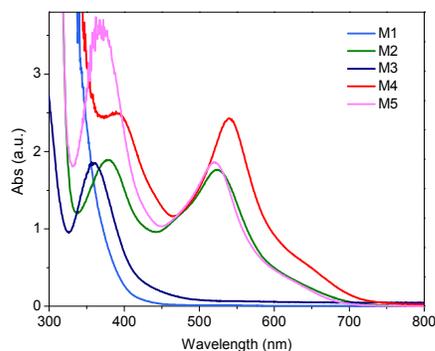
Conditions	η /%	FF	V_{oc} /V	J_{sc} /(mA/cm ²)
$\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$	8.19	0.646	0.75	16.87
I_2 electrolyte	7.76	0.626	0.74	16.76

The enhancement of IPCE for $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ -DSCs in certain wavelength ranges is of more interest to us. As detected by UV-Vis (Figure 4), light absorbance reveals that for the mixture of N719 and $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ solution, absorbance features of N719 are retained, and more importantly, the absorbance is highly enhanced, even though 10 mM of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ solution barely exhibit any absorbance in the wavelength range of 400 nm to 700 nm. On the other hand, the absorbance of the mixtures of N719 and iodine electrolyte does not show noticeable interaction between them at all. This difference reiterates the obvious interplays between N719 dye and $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ solution. In fact, it has been reported that organic cations in dye molecules can be incorporated between the MX_4^- ($M = \text{Sn}$ or Pb ; $X = \text{Cl}$, Br , I) perovskite sheets.⁸ Nevertheless, the charge/energy transfer between TiO_2 photoanodes, N719 and methylammonium lead halide perovskite is still not clear. It is possible that the light absorbance of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ that are adsorbed on TiO_2 photoanodes can transfer photo-induced electrons

to TiO₂ photoanodes directly or they could enhance the absorbance of N719 sensitizer to contribute to photocurrent indirectly. IPCE of CH₃NH₃PbI_(3-x)Cl_x-DSC without any N719 dye loaded on TiO₂ photoanodes is given in Figure S7. It can be seen that a small value (~25%) is observed at wavelength around 350 nm. Because TiO₂ nanoparticles also have absorbance in the wavelength below 400 nm,¹⁸ we cannot conclude that the IPCE value at 350 nm given in Figure S7 is devoted by light absorbance of methylammonium lead halide perovskite electrolyte. But the other peak, even though it has a smaller value, centred at 750 nm should be dedicated by photo-induced electrons of CH₃NH₃PbI_(3-x)Cl_x electrolyte that inject to the conduction band of TiO₂ photoanodes.

On the ground of above observations, we tend to conclude that the contribution to photocurrent in CH₃NH₃PbI_(3-x)Cl_x-DSCs by CH₃NH₃PbI_(3-x)Cl_x electrolyte should be majorly come from its interactions with the sensitizer. To better understand this issue, the possible interactions between N719 dye and other lead halide perovskite (CH₃NH₃PbI₃ and CH₃NH₃PbBr₃), are also detected by UV-Vis spectra. (Figure S8) Fourier transform infrared spectroscopy (FTIR) characterizations reveal new absorbance peaks for CH₃NH₃PbI₂Cl, CH₃NH₃PbI₃ and CH₃NH₃PbBr₃ powders after mixing with N719 dye, indicating the formation of new bonds (Figure S9). Yet further investigation is still needed to determine the molecule forces between the sensitizer and methylammonium lead halide perovskites in the future work.

Figure 4. UV-Vis absorbance of 10 mM CH₃NH₃PbI_(3-x)Cl_x (M1), 0.167 mM N719 (M2), iodine electrolyte diluted by 600 times (M3), 0.167 mM N719 mixed with 10 mM CH₃NH₃PbI_(3-x)Cl_x (M4), and 0.167 mM N719 mixed with iodine electrolyte diluted by 600 times(M5).



Conclusions

In summary, we found that the inorganic octahedra species of [PbX₆]⁴⁻ in methylammonium lead halide perovskite as a new role of electrolyte can significantly improve the stability of CH₃NH₃PbI_(3-x)Cl_x-DSCs, compared with DSCs using CH₃NH₃I as an electrolyte. Compared with DSCs based on well-studied iodine electrolyte with I⁻/I₃⁻ as redox shuttles, charge/energy transfer between TiO₂ photoanodes, N719 sensitizer and methylammonium lead halide perovskite electrolyte has resulted in enhanced IPCE of CH₃NH₃PbI_(3-x)Cl_x-DSCs in some wavelengths. In addition to the established roles of organo-lead halide perovskites as either solid-state sensitizers or hole collector, the findings reported herein add new functionalities to the library of this class of perovskites. Further fundamental understanding of this new solution system in regards of

interactions between dye sensitizer and perovskites is a worthwhile investigation in the future.

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Notes and references

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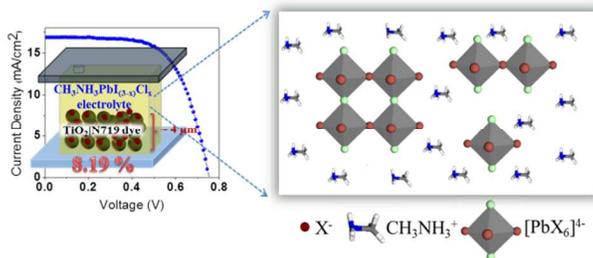
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†Electronic Supplementary Information (ESI) available: [Experimental conditions, XRD and TEM characterizations, discussion on film thickness, concentrations and additives on performance of CH₃NH₃PbI_(3-x)Cl_x-DSCs, photovoltaic characterizations of CH₃NH₃PbI_(3-x)Cl_x-DSCs and CH₃NH₃I-DSCs, IPCE of DSCs without N719 dye loaded on photoanodes, UV-Vis characterization and FTIR characterizations].

See DOI: 10.1039/c000000x/

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Table of Contents Graphic



We report organo-lead halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ solution as a new type of liquid electrolyte in dye-sensitized solar cells (DSCs) delivering an efficiency of 8.19%.