## Supporting information for

# Insights into the Liquid State of Organo-Lead Halide

### Perovskites and Their New Roles

#### in Dye-sensitized Solar Cells

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#### **Experimental section**

*CH*<sub>3</sub>*NH*<sub>3</sub>*PbI*<sub>(3-x)</sub>*Cl<sub>x</sub> electrolyte preparation*: CH<sub>3</sub>NH<sub>3</sub>I was synthesized by reacting 33.70 ml of methylamine (33% in absolute ethanol, Aldrich) and 31.09 ml of hydroiodic acid (55 wt% in water, Sigma-Aldrich) in 250 ml round bottomed flask at 0 °C for 2 h with stirring. The precipitate was recovered by evaporation at 50 °C for 1 h. The product, methyl ammonium iodide CH<sub>3</sub>NH<sub>3</sub>I, was washed with diethyl ether by stirring the solution for 30 min, which was repeated three times, and then finally dried at 60 °C in vacuum oven for 24 h. The synthesized powder CH<sub>3</sub>NH<sub>3</sub>I of certain amount was mixed with PbCl<sub>2</sub> (Aldrich) at 3:1 mole ratio in 1 ml N,N-Dimethylformamide (anhydrous, Sigma-Aldrich) with different additives of 4-tert-butylpyridine (96%, Aldrich), Lithium bis(trifluoromethylsyfonyl)imde salt (99.95%, Aldrich), or guanidinium thiocyanate ( $\geq$  99%, Sigma) inside the glove box, followed by filtering using 13 mm diameter and 0.45 µm pore PVDF syringe filter (Whatman), which was stored in air and used later as an electrolyte.

 $CH_3NH_3PbI_{(3-x)}Cl_x$  characterizations: UV-vis absorbance spectra of perovskite solutions were measured by Jasco V-650 spectrophotometer. X-ray diffraction (XRD) patterns of  $CH_3NH_3PbI_{(3-x)}Cl_x$  perovskite were recorded on a Rigaku Miniflex with cobalt K $\alpha$  radiation, and the result was then converted to copper target. Transmission electron microscope (TEM) images were obtained by Tecnai F20. Fourier transform infrared spectroscopy (FTIR) absorbance spectra were collected from Nicolet FTIR spectrometer.

*Fabrication of DSSCs*: A compact layer was deposited onto  $SnO_2$ :F conductive glass substrate (FTO, 15  $\Omega$  cm<sup>-2</sup> or 8  $\Omega$  cm<sup>-2</sup>, Dyesol company) by immersing glass into 40 mM TiCl<sub>4</sub> aqueous solution (0.57 ml of TiCl<sub>4</sub>, diluted in 100 ml water) at 70 °C for 30 min. One layer of TiO<sub>2</sub> paste (Dyesol company) was deposited on top by doctor-blade method and then sintered at 450 °C for 30 min, followed by post-treatment of 40 mM TiCl<sub>4</sub> aqueous solution at 70 °C for 30 min and sintered at 450 °C for another 30 min. With no specifications, the post-treatment of photoanodes were not conducted. Then  $TiO_2$  photoanodes were immersed into 0.5 mM N719 (Dyesol company) in mixture of acetonitrile (anhydrous, 99.8%, Sigma-Aldrich) and tert-butanol (anhydrous, 99.5%, Sigma-Aldrich) at volume ratio of 1:1 and kept for 24 h. Meanwhile Pt-counter electrodes were prepared by spin-coating 10 mM H<sub>2</sub>PtCl<sub>4</sub> solution on FTO and sintered at 400 °C for 15 min. Subsequently, the dye-loaded TiO<sub>2</sub> electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a spacer of 30 µm thickness (Surlyn, Du Pont), and then filled with liquid electrolyte introduced *via* vacuum back-filling. Iodine based electrolyte was purchased from Dyesol company and used as received. The active area was 0.09 cm<sup>2</sup>. All processes were conducted in air.

*Characterizations of DSCs*: The cross-sectional morphology and top views of the photoanodes were observed by scanning electron microscopy (SEM, JEOL 7001). The photocurrent density-voltage (*J-V*) curves were measured using an AM 1.5 solar simulator (Oriel) equipped with a 300 W xenon light source (Newport). The light intensity of the solar simulator was calibrated by using a thermal power meter (Newport, 1918-c). Keithley model 2420 digital source meter is used to supply an external bias to the cell. The incident photon-to-current conversion efficiency (IPCE) was recorded on a Newport 1918-c power meter under the irradiation of a 300 W xenon light tower (Newport) with an Oriel Cornerstone<sup>T</sup> 260  $\frac{1}{4}$  m monochromator (Oriel) in DC mode.

**Figure S1.** a) X-ray Diffraction (XRD) pattern of  $CH_3NH_3PbI_{(3-x)}Cl_x$  spin-coated on a glass slide: prior to the measurement, the prepared sample was heat treated on a hot plate at 100 °C for 45 min. b) TEM and high resolution (HR-TME) images of  $CH_3NH_3PbI_{(3-x)}Cl_x$  perovskite prepared by drying drops of the solution on Cu grids.



**Figure S2:** SEM characterizations of  $TiO_2$  photoanodes used in DSCs: a-c) cross-sectional images of photoanodes of 7.1 µm, 4.2 µm and 3.8 µm; d-f) high magnifications of photoanodes in (a-c) correspondingly. Photoanodes in c) and f) have been post-treated by  $TiCl_4$  aqueous solution and are used for the optimized devices.



**Figure S3:** Current density-potential (*J-V*) curves of  $CH_3NH_3PbI_{(3-x)}Cl_x$ -DSCs prepared with different concentrations of  $CH_3NH_3PbI_{(3-x)}Cl_x$  in solution with 0.192 M of LiTFSI and 0.198 M of TBP as additives.



Table S1. Influences of concentrations of  $CH_3NH_3PbI_{(3-x)}Cl_x$  on performance of DSCs

Concentrations	η/%	FF	V <sub>oc</sub> / V	J <sub>sc</sub> /(mA/cm <sup>2</sup> )
0.05 M	0.18	0.158	0.387	2.96
1.0 M	5.03	0.512	0.696	14.10
1.9 M	5.75	0.450	0.706	18.11
2.8 M	5.96	0.457	0.711	18.36

**Figure S4:** Current density-potential (*J-V*) curves of  $CH_3NH_3PbI_{(3-x)}Cl_x$ -DSCs with same photoanodes of 4 µm but different additives in electrolytes: "ADT-0" stands for no additives in electrolyte; "ADT-1" stands for additives of LiTFSI and TBP under concentrations of 0.064 M and 0.198 M, respectively; "ADT-2" stands for additives of LiTFSI and TBP under concentrations of 0.192 M and 0.198 M, respectively; "ADT-3" stands for additives of GITC and TBP under concentrations of 0.1 M and 0.5 M, respectively.



**Table S2.** Photovoltaic performance of  $CH_3NH_3PbI_{(3-x)}Cl_x$ -DSCs based on different additive conditions.

Conditions	η/%	FF	V <sub>oc</sub> / V	J <sub>sc</sub> /(mA/cm <sup>2</sup> )
ADT-0	3.07	0.380	0.662	12.19
ADT-1	4.68	0.495	0.684	13.83
ADT-2	5.03	0.512	0.696	14.10
ADT-3	5.67	0.531	0.730	14.63

**Figure S5.** Current density-potential (*J-V*) curves of  $CH_3NH_3PbI_{(3-x)}Cl_x$ -DSCs with different film thickness.



**Table S3.** Photovoltaic performance of  $CH_3NH_3PbI_{(3-x)}Cl_x$ -DSCs with different film thickness. Further decrease in the thickness of the photoanodes will not further improve the performance of DSCs because the amount of N719 loading on the thinner photoanodes will be badly influenced and the light harvesting will be decreased.

Conditions	η/%	FF	V <sub>oc</sub> / V	J <sub>sc</sub> /(mA/cm <sup>2</sup> )
7 µm-CH <sub>3</sub> NH <sub>3</sub> PbI <sub>(3-x)</sub> Cl <sub>x</sub>	5.55	0.434	0.733	17.46
4 $\mu$ m-CH <sub>3</sub> NH <sub>3</sub> PbI <sub>(3-x)</sub> Cl <sub>x</sub>	7.66	0.612	0.756	16.58

**Figure S6.** Current density-potential (*J-V*) curves of DSCs that are prepared employing  $CH_3NH_3I$  as an electrolyte in comparison with  $CH_3NH_3PbI_{(3-x)}Cl_x$  as an electrolyte with same concentrations and additives.



**Table S4.** Photovoltaic performance of DSCs based on  $CH_3NH_3I$  electrolyte in comparison with  $CH_3NH_3PbI_{(3-x)}Cl_x$  electrolyte under same conditions.

Conditions	η/%	FF	V <sub>oc</sub> / V	J <sub>sc</sub> /(mA/cm <sup>2</sup> )
CH <sub>3</sub> NH <sub>3</sub> I	4.14	0.399	0.697	14.89
ADT-3	5.67	0.531	0.730	14.63

**Figure S7.** IPCE characterizations of  $CH_3NH_3PbI_{(3-x)}Cl_x$ -DSCs that contained no N719 sensitizer adsorbed on the photoanodes.



Figure S8. UV-Vis absorbance of 10 mM  $CH_3NH_3PbBr_3$ , 0.167 mM N719, 10 mM  $CH_3NH_3PbBr_3$  in mixture of 0.167 mM N719, 10 mM  $CH_3NH_3PbI_3$ , 0.042 mM N719, and 10 mM  $CH_3NH_3PbI_3$  in mixture of 0.042 mM N719.



**Figure S9.** FTIR of a)  $CH_3NH_3PbBr_3$  powder before and after mixing with N719, b)  $CH_3NH_3PbI_3$  powder before and after mixing with N719, c)  $CH_3NH_3PbICl_2$  powder before and after mixing with N719 and d) comparisons of mixtures in a), b) and c) with N719. New absorbance peak is marked with asterisk (\*).<sup>a)</sup>



Note: a) CH<sub>3</sub>NH<sub>3</sub>PbICl<sub>2</sub>, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, and CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> powders were prepared by grounding powders of CH<sub>3</sub>NH<sub>3</sub>I and PbCl<sub>2</sub> (1:1), CH<sub>3</sub>NH<sub>3</sub>I and PbI<sub>2</sub> (1:1), and CH<sub>3</sub>NH<sub>3</sub>Br and PbBr<sub>2</sub> (1:1) respectively. Mixtures of CH<sub>3</sub>NH<sub>3</sub>PbICl<sub>2</sub>-N719, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>-N719, and CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>-N719 were prepared by mixing perovskite solutions with N719 dissolved in DMF. Then collect the precipitates after centrifuge. All powders were dried under 70 °C in a vacuum oven for 2 hours before FTIR measurement.