Stable, bromine-free, tetragonal perovskites with 1.7 eV bandgaps via Asite cation substitution

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Experimental Section

Chemicals

PbI₂ beads (99.999%) and CsI powder (99.999%), and anhydrous solvents were purchased from Sigma-Aldrich. DMAI and GuaI were purchased from GreatCell Solar (Australia). All salts and solvents were used as received without any further purification.

Preparation of perovskite solution

The Cl-capped TiO₂ was prepared following procedures reported elsewhere.^{S1}

For the CsDMA and CsGua perovskite, PbI_2 , CsI and DMAI or PbI₂, CsI and GuaI were dissolved in a DMSO/DMF (1:1) mixture solution. The final concentration was 1M and the solution was spin-coated at 6000 rpm for 60 s, 0.3 mL chlorobenzene was dropped as antisolvent 20 s before the end.

The Spiro-OMeTAD solution was prepared in chlorobenzene with 65 mg/mL Spiro-OMeTAD and 20 μ L/mL tert-butylpyridine, as well as 70 μ L/mL bis(trifluoromethane)sulfonimide lithium salt (170 mg/mL in acetonitrile).

For the 40% Br perovkskite, the perovskite layer is $Cs_{0.12}MA_{0.05}FA_{0.83}Pb(I_{0.6}Br_{0.4})_3^2$. The perovskite films were deposited with a two-step spin-coating procedure. The first step was 2000 rpm for 10 s and the second step was 6000 rpm for 40 s. Chlorobenzene (100 µL) was dropped during the second spin-coating step at 20 s before the end of the procedure.

Perovskite solar cell fabrication

Pre-patterned indium tin oxide (ITO, TFD Devices) coated glass slides were cleaned with acetone and isopropanol. After drying the ITO substrates, the Cl-capped TiO₂ was spin-coated on ITO substrates, and annealed on a hot plate at 150°C for 30 min in ambient air. The preparation method of the Cl-capped TiO₂ solution is reported elsewhere.^{S1} The perovskite films were deposited onto the TiO₂ substrates with a two-step spin coating procedure. The first step was 1000 rpm for 10 s with an acceleration of 200 rpm/s and the second step was 6000 rpm for 80 s with a ramp-up of 2000 rpm/s. Chlorobenzene (200 µL) was dropped on the spinning substrate during the second spin-coating step at 20 s before the end of the procedure. The substrates were then transferred onto a hotplate and heated at 30-50°C for 10 min. The spiro layer was deposited by dropping 70 µL of spiro solution and spin-coating at 4,000 rpm for 30 s. Finally, 10 nm MoO3 and 120 nm Ag was deposited by thermal evaporation.

Solar cell characterization

The *J-V* characteristics were measured using a Keithley 2400 sourcemeter under the illumination of a solar simulator (Newport, class A) at a light intensity of 100 mW/cm² in N₂ atmosphere (Sciencetech class A). Unless otherwise stated, the *J-V* curves were measured with a scanning rate of 100 mV s-1 (voltage step of 10 mV and delay time of 100 ms). An aperture shade mask with area of 4.9 mm² was placed in front of the solar devices,

respectively, to avoid overestimation of the photocurrent density. The steady-state PCE, PCE(t), was measured by setting the bias voltage to the V_{MPP} and then tracking the current density. The V_{MPP} at maximum power point was determined from the *J-V* curve. A spectral mismatch factor of 1 was used for all *J-V* measurements. EQE measurements were performed using an in-house built system with monochromatic light and a white bias light (~0.1 Sun). The photodiode used for the calibration of EQE measurements was calibrated by Newport. For the stability tests and aging tests at continuous MPP operation under 1 Sun, a white LED was used as an illumination source. Measurements were carried out in nitrogen, fixing the voltage at V_{MPP} and then tracking the current output.

Other characterizations

High-resolution SEM images were obtained using Hitachi SU5000 scanning electron microscope at 3 keV. XRD patterns were obtained using a Rigaku MiniFlex 600 diffractometer equipped with a NaI scintillation counter and using monochromatized Copper K α radiation ($\lambda = 1.5406$ Å). Photoluminescence (PL) was measured using a Horiba Fluorolog time correlated single-photon-counting system with photomultiplier tube detectors. The excitation source is a laser diode at a wavelength of 504 nm. The instrument used for XPS analysis is a PHI 5500 Multi-Technique system. The X-ray is generated from a monochromatic aluminum K α source with a radiation energy of 1486.7 eV. XPS was performed with a take-off angle of 75° in an ultra-high vacuum environment with a base pressure of approximately 10⁻⁹ torr. TGA experiments were conducted using a PerkinElmer Pyris 1 TGA. Sample preparation: about a 1.23 mg of perovskite powder was taken on a platinum sample pan. TGA was performed by an equilibration step at 25 °C for 15 minutes and later heated to 750°C with a heating rate of 10°C/min under nitrogen.



Figure S1. XPS of N signal in $Cs_{0.7}DMA_{0.3}$ perovskite.



Figure S2. XRD of pure CsPbI₃ film after aging in air for 30 min.



Figure S3. TGA of Cs_{0.7}DMA_{0.3}PbI₃



Figure S4. Cross-sectional SEM image of CsDMA perovskite

	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)
Cs _{0.8} DMA _{0.2} PbI ₃	0.95	19.16	48.6	8.85
Cs _{0.7} DMA _{0.3} PbI ₃	1.19	18.4	69.4	15.2
Cs _{0.5} DMA _{0.5} PbI ₃	0.85	15.76	53.4	7.12

 Table S1. Performance of different CsDMA solar cells



Figure S5. J-V of CsDMA solar cell with different DMA concentration.



Figure S6. J-V of CsGua solar cell.



Figure S7. J-V of CsMAFA solar cell with 40% Br.

References

(S1) Tan, H. *et al.* Efficient and stable solution-processed planar perovskite solar cells via contact passivation. *Science* **355**, 722-726 (2017).

(S2) Tan, H. *et al.* Dipolar cations confer defect tolerance in wide-bandgap metal halide perovskites. *Nat. Commun.* 9, 3100 (2018).