

Supporting Information

Highly Efficient Ligand-Modified Manganese Ions Doped CsPbCl₃ Perovskite Quantum Dots for Photon Energy Conversion in Silicon Solar Cells

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Experimental section

Materials:

Cs₂CO₃ (99.9%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), oleylamine (OAm, 70%), PbCl₂ (99.99%), MnCl₂ (99.99%), toluene (ACS grade, Fischer), dodecyl dimethylammonium chloride (DDAC) were all purchased from Sigma-Aldrich and were used as starting materials without further purification.

Preparation of the Cs-Oleate Precursor

0.8 g of Cs₂CO₃ was loaded into a mixture of 30 mL of ODE and 2.5 mL of OA, then heated to 200 °C until the white powder was completely dissolved. After that, the mixture was kept at 120 °C for 1h under vacuum. Note that, during the synthesis of perovskite QDs, the temperature of the Cs-oleate mixture should be kept at least at 120 °C to avoid precipitation.

Synthesis of CsPbCl₃ perovskite QDs

PbCl₂ (0.6 mmol), OAm (3 mL), OA (3 mL), and ODE (10 mL) were added to a 50-

mL 3-neck round bottomed flask and were evacuated and refilled with N₂ followed by heating the solution to 120 °C for 1 hour. The solution was then increased to 200 °C. Then the Cs-oleate (1 mL) was swiftly injected and after 30s the solution was cooled with an ice bath.

Synthesis of Mn²⁺ ions doped CsPbCl₃ perovskite QDs

PbCl₂ (0.3 mmol) and DDAC (0-0.30mmol) were dissolved into ODE (10 mL) OAm (3 mL) and OA (1.5 mL) at 120°C for 30 minute under purging N₂ gas, then MnCl₂ (0.15 mmol) and OA (1.5mL) was adeded into the mixture, the temperature kept at 120°C for 1h. After complete dissolution, the temperature was raised to 200°C under purging N₂ gas. The as-prepared Cs-oleate (1 mL) was then injected into the contents promptly, after 30s, which was immediately transferred to an ice-water bath.

Lastly, all the samples were centrifuged at 5000 rpm for 10 min and the supernatant was discarded. The precipitate was dispersed in toluene and then centrifuged again at 10000 rpm for 10 min. The resultant QDs were redispersed in toluene for second time.

Fast anion-exchange reaction

PbBr₂ as anion sources were mixed with ODE (5 mL) in a 25 mL 3-neck flask and kept under vacuum at 120 °C for 15 minutes. Dried OA and OAm (0.2 mL each) were injected at 120 °C under the protection of N₂. The anion source after complete solubilisation was added to the Mn²⁺ ions doped CsPbCl₃ QD (1 mmol) solution dropwise at 120 °C. After reaction for 5 min, QDs were isolated by centrifugation. The supernatant was discarded and the precipitate was dispersed in hexane and centrifuged again.

Fabrication of perovskite QDs coated silicon solar cells

The Mn²⁺ ions doped perovskite QDs (0.3 mmol, 0.5 mmol, 0.7 mmol) were

dispersed in 50 mL hexane solution. The silicon solar cell was dropped vertically into the solution and placed in an oven at 30 °C for 4h. With the slow volatilizing of hexane, the Mn²⁺ ions doped perovskite QDs were self-assembled on the surface of silicon solar cell.

Measurement of PCE of silicon solar cells coated with perovskite QDs

To control the effective area, a nontransparent mask with square shaped aperture (1 cm*1 cm) was used. The mask dimensions were adjusted to fit inside a frame built around the device substrate. The frame also hinders the light from entering through the sides of the substrate. A precision electronic caliper was used to measure the edges of the aperture and calculate the area assuming that the aperture was perfect square. The solar cell devices were tested under a Class A solar simulator (ABET Sun 2000) at AM1.5 and 100 mW/cm² illumination conditions calibrated with a reference Silicon cell (RERA Solutions RR-1002), using a Keithley 2400 as a source-meter in ambient condition without sealing for J-V measurements from +1.5 V to -1.5 V. The scan speed 0.1 V/s.

Characterization

UV/vis–NIR absorption spectra were measured with a Shimadzu UV-3600PC UV/vis–NIR scanning spectrophotometer in the range from 300 to 2000 nm. Patterns were recorded in thin film mode on a Bruker AXS D8 diffractometer using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). The morphology of the products was recorded with a Hitachi H-8100IV transmission electron microscope (TEM) under an acceleration voltage of 200 kV. The samples were imaged in EFTEM mode with a 20eV energy slit inserted around the zero energy loss of electrons to acquire high-resolution TEM (HRTEM) micrographs. Trace-Metal Analysis was carried out using inductively coupled plasma optical emission spectrometry (ICP-OES) on a Varian720-ES ICP-optical emission spectrometer. Dried powdered samples of NCs were the first acid

digested in a microwave and then diluted prior to measurements. ICP-OES measurements with a detection limit ranging from parts per million (ppm) to parts per billion (ppb) were performed twice on separately synthesized NP samples (synthesized under identical reaction conditions) and standard deviations were calculated accordingly. In the measurements of luminescent dynamics, the samples were pumped using a laser-system consisting of a Nd:YAG pumping laser (1064 nm), a third-order Harmonic-Generator (355 nm) and a tunable optical parameter oscillator (OPO, Continuum Precision II 8000) with a pulse duration of 10 ns, a repetition frequency of 10 Hz and a line width of 4–7 cm^{-1} . A visible photomultiplier (350–850 nm) combined with a double-grating monochromator was used for spectral collection. X-ray photoelectron spectroscopy (XPS) was performed with an ESCALab220i-XL electron spectrometer from VG Scientific. Monochromatic Al $K\alpha$ X-ray ($h\nu = 1486.6$ eV) was employed for analysis with an incident angle of 30° with respect to the surface normal. FTIR spectra were obtained using a Nicolet iS50 FT-IR spectrometer. The solar cell devices were tested under a Class A solar simulator (ABET Sun 2000) at AM1.5 and 100 mW/cm^2 illumination conditions calibrated with a reference Silicon cell (RERA Solutions RR-1002), using a Keithley 2400 as a source-meter in ambient condition without sealing for J - V measurements from +1.5 V to -1.5 V. IPCE was measured at AC mode under bias light using a IPCE system (PV measurement Inc.) with a computerized setup consisting of Solar Cell Quantum Efficiency — Solar-Cell Scan100.

Photoluminescence quantum yields (PLQY). The PLQYs of the samples were acquired using an integrating sphere incorporated into a spectrofluorometer (FLS980, Edinburgh Instruments). Absolute photoluminescence quantum yield measurements were performed on colloidal PQD samples dispersed in hexane placed in a sealed 1 cm path length quartz cuvette and positioned in a teflon-based integrating sphere using a custom cuvette holder. The samples were directly excited with a 365 nm Xe lamp and attenuated with neutral density filters, as necessary. Excitation power was measured through a power meter to calculate excitation power.

Quantum yield was then calculated by using the Edinburgh L980 software package, which was calculated based on the following equation:

$$PLQY = \frac{N_{em}}{N_{abs}} = \frac{\int I_{sample}(\lambda) - I_{ref}(\lambda) d\lambda}{\int E_{ref}(\lambda) - E_{sample}(\lambda) d\lambda}$$

where “I” indicates the spectrally corrected intensity of the emitted light, “E” indicates the spectrally corrected intensity of the excitation light, “sample” indicates measurements of QD samples, and “ref” indicates measurements of a reference cuvette containing neat hexane.

Our PLQY equipment was calibrated using the recognized dye emission standards, which was in good agreement with literature values: Rhodamine 6G – Measured (91.1%), Literature (90-92%).

Supplementary Figures:

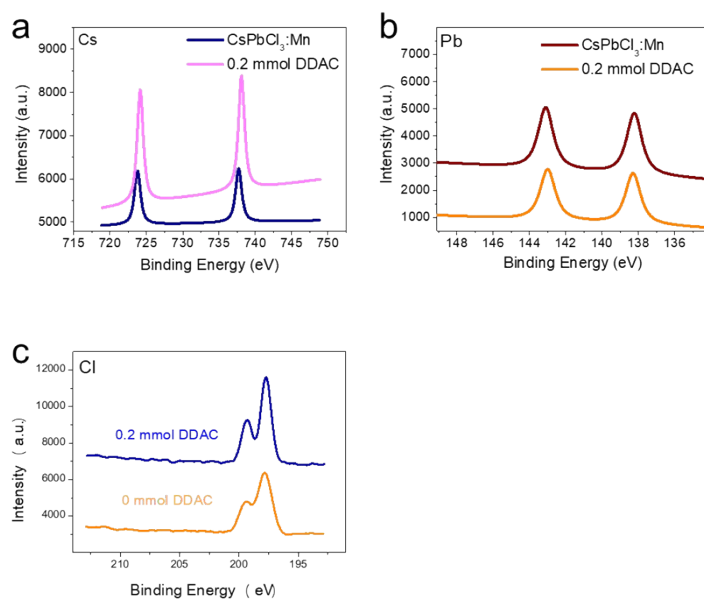


Figure S1. (a-c) Corresponding high-resolution XPS analysis corresponding to Cs, Pb, Cl element, respectively.

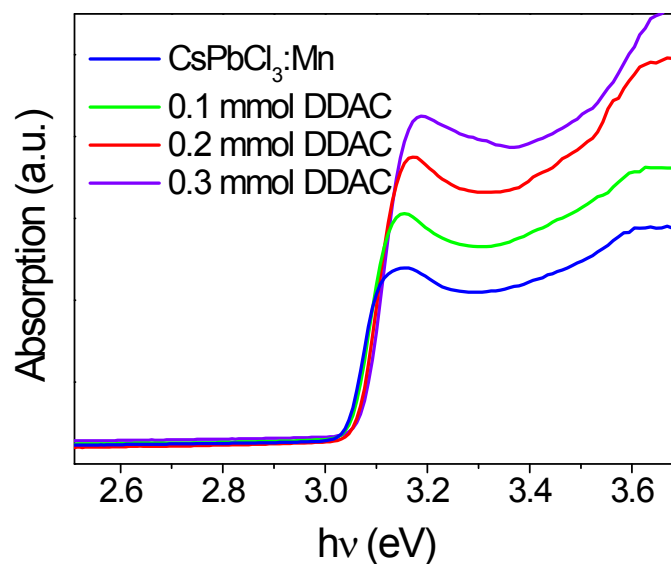


Figure S2. Tauc plots of Mn²⁺ ions doped CsPbCl₃ QDs with different concentrations of DDAC.

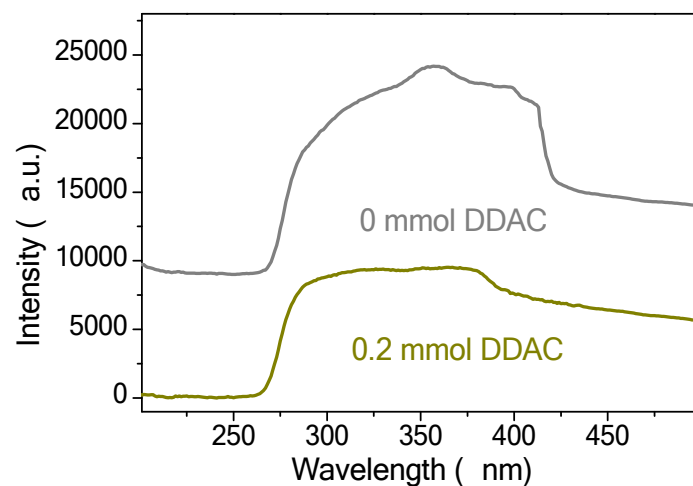


Figure S3. Excitation spectra of Mn^{2+} ions doped CsPbCl_3 QDs and with 0.2 mmol DDAC, respectively.

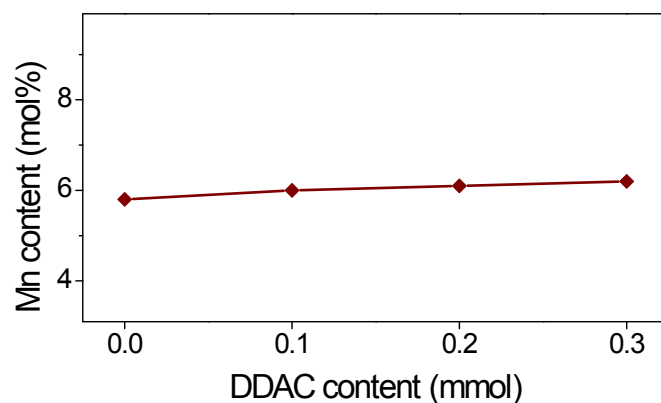


Figure S4. Mn doping mole content (obtained from ICP-MS) in Mn^{2+} ions doped CsPbCl_3 QDs versus DDAC content.

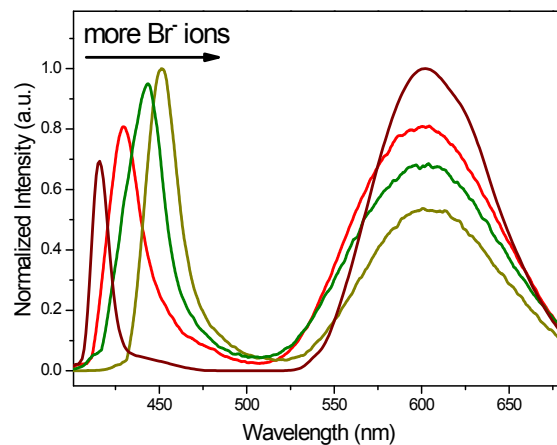


Figure S5. PL emission spectra of Mn^{2+} doped QDs with 0.1 mmol DDAC added Br^- source.

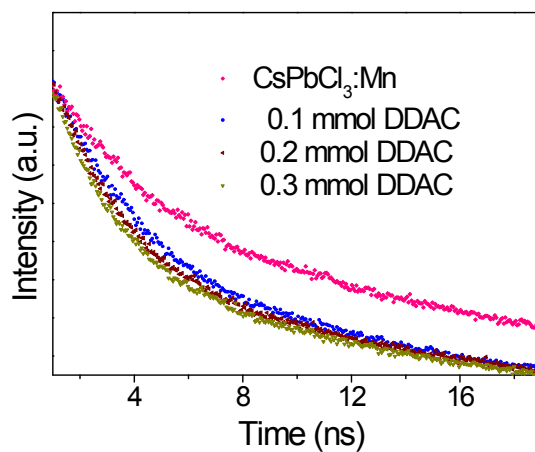


Figure S6. Emission decay curves of the excitonic transition monitored at 410 nm.

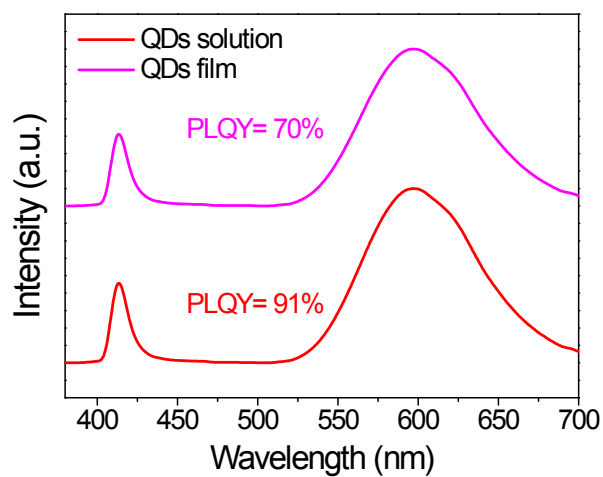


Figure S7. PL spectra of Mn^{2+} ions doped CsPbCl_3 QDs with addition of 0.2 mmol DDAC toluene solution and film.

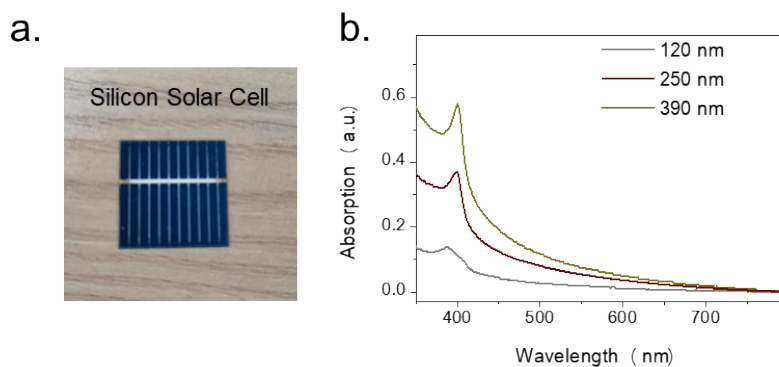


Figure S8. (a) Picture of silicon solar cell. (b) Absorption spectra of QD films with different thicknesses.

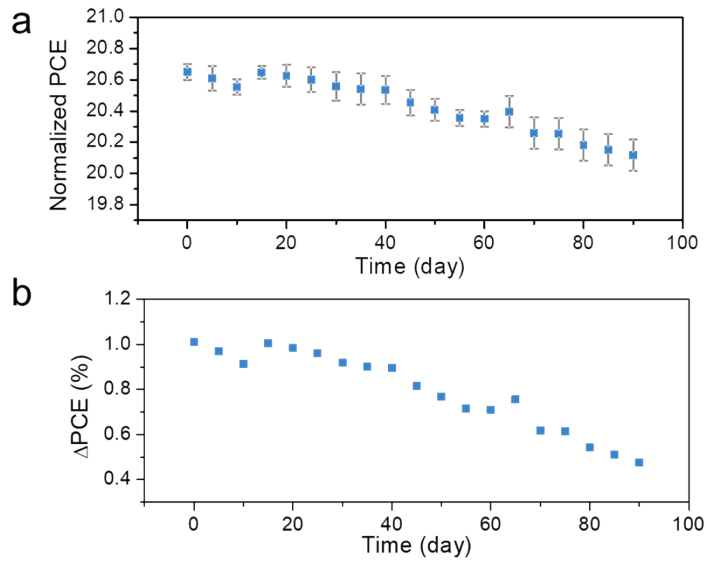


Figure S9. (a) PCEs of a single SSC and SSC with perovskite converters as a function of time. (b) Δ PCE as a function of time in Figure S9b. Δ PCE is defined as the increase of PCE after introducing the perovskite converter compared to the pristine silicon solar cell.

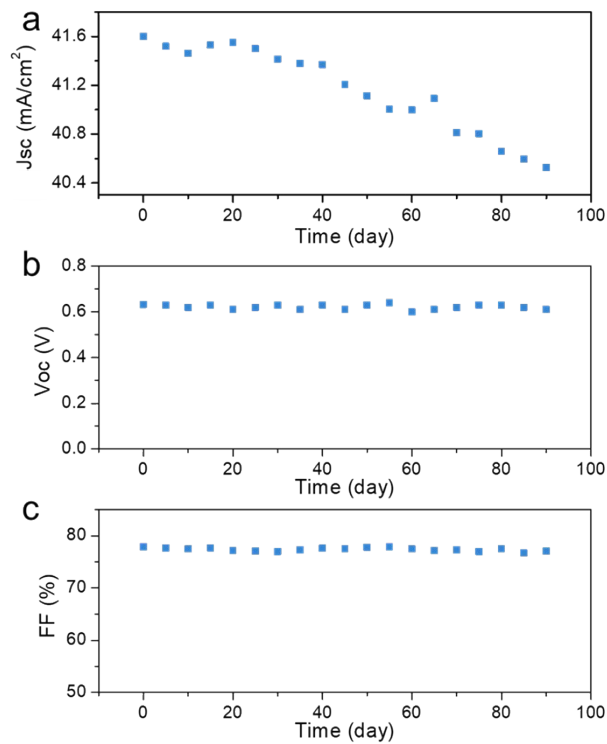


Figure S10. (a-c) Variation of J_{sc} , V_{oc} and FF as a function of time.

Table S1. Typical Mn²⁺ ions doped CsPbCl₃ QDs.

Year	synthetic method	PL Peak position (nm)	PLQY (%)	application	Ref
2016	hot-injection	600	60	—	1
2017	hot-injection	590	60	perovskite solar cells	2
2017	isocrystalline shell growth	~ 600	40	—	3
2018	Fast Room-Temperature Cation Exchange	610	18.3	—	4
2018	Ce ³⁺ /Mn ²⁺ -codoped hot-injection	~ 600	75	phosphor-converted WLEDs	5
2018	microwave-assisted hot injection	~ 600	65	—	6
2019	a versatile sol–gel method at room temperature	607	50.5	phosphor-converted WLEDs	7
2020	DDAC added hot-injection	602	91	Silicon solar cells	This work

Reference

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