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Supporting Information

for

Eco-friendly and high-efficiency luminescent solar concentrators

enabled by Green-Emissive manganese halide hybrids

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EXPERIMENTAL SECTION

Material.

Tetramethylammonium bromide ((CH₃)₄NBr, 98%), Tetraethylammonium bromide ((C₂H₅)₄NBr, 98%), Tetrabutylammonium bromide (C₄H₉)₄NBr, 98%), Benzyl trimethyl ammonium bromide (C₁₀H₁₆NBr, 98%), Manganese bromide tetrahydrate (MnBr₂ · 4H₂O, 99%) and Polyethylene oxide (HO (CH₂CH₂O) nH, Mv ~ 300,000), were purchased from Macklin. Methanol (CH₃OH, AR), Ether (C₂H₅OC₂H₅, AR), Dichloromethane (CH₂Cl₂, AR), and Toluene (C₇H₈, AR) were purchased from Sinopharm. Bathocuproine (BCP) was purchased from TCl. Methylammonium iodide (MAI), PbI₂, PCBM, phenylethyl-ammonium iodide (PEAI) and NiO nanoparticles were purchased from Advanced Election Technology Co., Ltd. Dimethyl sulfoxide (DMSO, 99.8%), N,N-dimethylformamide (DMF, 99.8%) ,Isopropanol (IPA, 99.7%) and Ethyl Acetate (EAC) were purchased from J&K Scientific.

All chemicals are commercially available. All reagents and pharmaceuticals were not further purified except $MnBr_2 \cdot 4H_2O$. $MnBr_2 \cdot 4H_2O$ should be dehydrated before use. The specific operation is to heat $MnBr_2 \cdot 4H_2O$ in an oven at 140 °C for 24 h, and the dehydrated $MnBr_2$ appears pink block.

Growth of manganese halide single crystals

The commonly used slow evaporation solvent growth crystal method was employed for the growth of single crystals, the procedure involved adding 2mmol of A (A = tetramethylammonium bromide, tetraethylammonium bromide, tetrabutylammonium bromide, benzyl trimethyl ammonium bromide) and 1 mmol of anhydrous manganese bromide (MnBr₂) to 2 mL of methanol solution, followed by stirring at room temperature until the solution became clear. The clarified solution was filtered into a 5 mL beaker with a 0.22 μ m organic filter head, which was placed in an oil bath vessel set to 40°C. After a few days, the single crystal in the beaker was collected and rinsed with ether to obtain the centimeter-level green transparent single crystal.

Fabrication of LSCs.

Glass cleaning: The glass substrate used in the experiment is electronic grade ultrawhite glass, with dimensions of 20 mm \times 20 mm \times 2 mm, 140 mm \times 100 mm \times 2 mm, respectively. The glasses were first cleaned in an aqueous detergent solution, deionized water, acetone, and then isopropanol with ultrasound for15min in turn. Subsequently, it was treated in UV-ozone for 20 min.

Preparation method of (BTMA)₂MnBr₄-based LSC: 0.4296 g anhydrous MnBr₂(2 mmol) and 0.9206 g BTMA (4 mmol) were added to 1 mL of the deionized aqueous solution, stirred well at room temperature until clear. The film was prepared using a one-step spin-coating process: at a speed of 2000 rpm/min for 20s and then annealed on a heating plate at 80°C for more than 6 h.

 $(BTMA)_2MnBr_4@PEO$ -based LSC preparation method: 0.4296 g anhydrous MnBr₂ (2 mmol) and 0.9206 g BTMA (4 mmol) were added to 1 mL of deionized aqueous solution, stirred well at room temperature until clear. Subsequently, weigh an appropriate amount of polyethylene oxide (PEO) into the solution (~2 wt%), and stir at room temperature for more than 24 h to obtain a viscous transparent solution. Using the same treatment steps and process preparation as before.

Preparation method of large-area (BTMA)₂MnBr₄@PEO-based LSC: 1.718 g of anhydrous MnBr₂ (8 mmol) and 3.682 g of BTMA (16 mmol) were added to 4 mL of deionized aqueous solution. The mixture was stirred well at room temperature until it became clear. Subsequently, an appropriate amount of PEO weighing approximately 4 wt% was added to the solution. The mixture was stirred at room temperature for more than 24 hours, resulting in the formation of a viscous translucent solution. The solution was then prepared using blade coating, with the scraper thickness set to 500 μ m.

MAPbI₃-based PSCs fabrication

Glass/ITO substrates were cleaned thoroughly by sequential ultra-sonication for 20 min in a detergent solution, distilled water, alcohol, and acetone. The NiO hole transport layer was formed by spin-coating NiO nanoparticles (20mg/mL, in distilled water) onto the ITO substrate at 3000 rpm. for 30 s, then annealed at 100 °C for 10 min

in an air environment and then transferred to a nitrogen-filled glovebox. Subsequently, perovskite was then deposited with the anti-solvent one-step method: an 80µL 1.5 M MAPbI₃ precursor solution (a mixture of PbI₂: MAI =1.05:1 by molar ratio and DMF: DMSO= 4:1 by volume) was spin-coated at 5000 rpm for 30 s, followed by quickly drop-casting diethyl ether (1000 µL) as an anti-solvent within 10s. For the surface treatment, PEAI with the concentration of 1 mg/ml in IPA was spin-coated on top (5000 rpm, 20 s) and annealed at 100 °C for 5 min. Then, the PCBM solution (15 mg/mL, in chlorobenzene) was spin-coated on top of the PEAI layer as an electron transport layer at 2000 rpm for 20 s and annealed at 70 °C for 10 min. Sequentially, the saturated solution of BCP in methanol was dynamically spin-coated on the PCBM layer at 5000 rpm for 20 s and annealed at 70 °C for 10 min. Finally, the device was conducted by thermally evaporating Ag (150 nm) at a rate of 0.5 Å s⁻¹ in a vacuum chamber ($<5 \times 10^{-4}$ Pa).

Measurement and Characterization.

The Bruker-AXS D8 X Discover with the Cu K α radiation ($\lambda = 1.54102$ Å) was used to collect powder X-ray powder diffraction spectra. The single crystal diffraction data were collected by Bruker D8 Venture single crystal diffractometer, the X-ray radiation source target was Cu K α ($\lambda = 1.54184$ Å) and the single crystal test temperature was 293K. The absorption and reflection spectra were obtained by using aUV-3600 UV/vis/NIR spectrophotometer from Shimadzu. The Photoluminescence (PL) and Photoluminescence Excitation (PLE) spectra were measured with the HORIBA FLOUESCENCE MAX type fluorescence spectrophotometer. Quantum yield (PLQY) and time-resolved spectroscopy (TRPL) of samples were tested at room temperature using the UK Edinburgh FLS1000 spectrometer. The J-V curves of the LSC/PV system and PV cell are from the solar cell I-V test system, which consists of a solar simulator, Keithley 2400 source meter, probe station, I-V test software, and display.

Supplementary Note 1. The η_{PCE} of LSC calculation $^{1,\,2}$

The η_{PCE} can also be calculated by the following equation:

$$\eta_{PCE} = \frac{J_{LSC-S} \times FF \times V_{OC}}{P_0}$$

where J_{LSC-S} is normalized over the surface area of the LSC ($J_{LSC-S} = I_{LSC}/A_{surface}$ =($J_{LSC} \times A_{edge}$)/ $A_{surface}$), V_{OC} is the open-circuit voltage, FF is the fill factor, and P_0 is the integrated solar power density (100 mW·cm²).

Supplementary Note 2. The η_{abs} of LSC calculation

The η_{abs} is solar absorbance of the LSC, which can be calculated using the below equation:

$$\eta_{abs} = \frac{\int_{0}^{\infty} Sin(\lambda) \times (1 - e^{-\alpha(\lambda)d}) d\lambda}{\int_{0}^{\infty} Sin(\lambda) d\lambda}$$
$$\alpha = \ln(10) \times \frac{A}{d}$$

where α is the absorption coefficient, Sin is the Sun irradiance, d is the effective length and A is the absorption of the LSC



Figure S1. single crystals in natural light and ultraviolet light (a)(TMA)₂MnBr₄. (b)TEA₂MnBr₄.
(c)TBA₂MnBr₄. (d) (BTMA) ₂MnBr₄.



Figure S2. Ball-and-stick model of [MnBr₄]²⁻ in (BTMA)₂MnBr₄.



Figure S3. Comparison of XRD and structure fitting data of single crystal powder: (a) (TMA)₂MnBr₄. (b) (TEA)₂MnBr₄. (c) (TBA)₂MnBr₄. (d) (BTMA)₂MnBr₄.



Figure S4. (a) PL and PLE of $(TMA)_2MnBr_4$; (b) PL and PLE of $(TEA)_2MnBr_4$; (b) PL and PLE of $(TBA)_2MnBr_4$; (d) PL and PLE of $(BTMA)_2MnBr_4$.



Figure S5. (BTMA)₂MnBr₄-based LSC light-emitting layer PL and PLE



Figure S6. Photographs for the (TEA)₂MnBr₄-based LSC under UV light



Figure S7. Comparison of (BTMA)2MnBr4-based LSC with (BTMA)2MnBr4@PEO-based LSC



Figure S8. Schematic diagram of the PL attenuation test setup for LSC



Figure S9. Normalized PL light Spectral contrast.



Figure S10. Schematic of the coupling test of LSC and $MAPbI_3$ solar cells



Figure S11. Photographs for the LSC with 140mm×100mm×2mm size under UV light

sample	τ1	A1(%)	τ2	A2(%)	$ au_{ExpDec2}(\mu s)$	τ _{ExpDec1} (μs)
TMA ₂ MnBr ₄	214.82	20.30	369.66	79.70	349.69	338.89
TBA_2MnBr_4	397.45	50.35	397.44	49.65	397.44	397.19
TEA ₂ MnBr ₄	209.88	11.43	383.25	88.57	371.80	364.28

Table S1 (TMA)₂MnBr₄ , (TBA)₂MnBr₄ and (TEA)₂MnBr₄ single and double exponential fitting

 Table S2 Summary of Reported Hybrid manganese halides

sample	peak position (nm)	Fwhm(nm)	lifetime (µs) 293 K	PLQY (%)	shortest Mn−Mn distance (Å)	Exciton binding energy(meV)
TMA_2MnBr_4	522	52	338.89	54.48	8.08, 8.15	176.48
TEA ₂ MnBr ₄	515	46	364.28	99.72	9.36, 9.45	419.15
TBA_2MnBr_4	516	48	397.20	67.48	9.19, 12.82	/
BTMA ₂ MnBr ₄	520	51	644.71	99.59	9.59, 9.72	/

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