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Supporting information

Organo metal halide perovskites effectively photosensitize the production of singlet oxygen ($^1\Delta_g$)

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Experimental Section

Materials. Methyl ammonium bromide (CH_3NH_3Br = MABr, 99.9%), lead (II) bromide ($PbBr_2$, 99.99% trace metals basis), N,N-dimethylformamide (DMF, anhydrous, 99.8%), toluene anhydrous (99.5%), chloroform anhydrous (99.5%), diphenylisobenzofuran (DPBF, 99.5%) were purchased from Sigma-Aldrich. Chloroform (>99%) and toluene (>99%). Octylamine (approximate C_{18}-content 80-90%) was purchased from Acros Organics. Oleic acid (97%) was purchased from VWR Chemicals.

Instruments. The UV-Vis electronic absorption spectra were obtained by using either Lambda 950 of Perkin-Elmer or Black CXR-SR-50 of StellnarNet Inc. Time resolved NIR and Vis photoluminescence were recorded by Fluorolog-3 fluorescence spectrometer of Horiba Scientific. Steady state Vis photoluminescence was measured by FLS920 fluorescence spectrometer of Edinburgh Instruments.

Perovskites nano particles (NPs) preparation. The synthesis were carried out according to reported method for $CH_3NH_3PbX_3$ (X=I, Br) with slight modification.[22] All syntheses were carried out at room temperature in air with average room humidity ~60%.

$MAPbBr_3$ NPs. CH_3NH_3Br (0.0088 g, 0.1 mmol) and $PbBr_2$ (0.0367 g, 0.1 mmol) were dissolved in 2.5 mL DMF containing 250 µL of the oleic acid and 10 µL octylamine. Next, 50 µL of this mixture was injected into 5 mL of toluene or chloroform. Bright green light-emitting NPs were formed immediately after fast agitation. After centrifugation at 8000 rpm for 5 min, the clear liquid part was used for various measurements.

Methods

Perovskites NC characterization.

TEM. TEM and HRTEM images were obtained from a TEM Tecnai F30 (FEI company) high-resolution transmission electron microscope (300 kV acceleration voltage, 0.20 nm point resolution, and 0.102 line resolution), equipped with a LaB6 filament and a CCD camera with an image size of 2048×2048 pixels. TEM samples were prepared by casting one drop of the perovskites NPs in toluene onto a standard copper grid coated with a continuous amorphous carbon film, it is washed twice by n-hexane to remove oleic acid and then dried in vacum. The size distribution and thicknesses of NPs were obtained from the TEM image with ImageJ software.

X-ray Powder Diffraction (XRD). X-ray powder diffraction was obtained by the classical ex situ Bragg–Brentano geometry using a Rigaku Smartlab powder diffractometer with filtered Cu-Kα radiation and equipped with scintillation detector and two-dimensional silicon array detector. Sample preparation is as following. The concentrated toluene NP solution was centrifuged to get solid NPs, and the obtained solid NPs were washed twice by dispersing in n-hexane and centrifuged to get solid NPs again. The dried powder was used for XRD measurements.

XPS. The XPS analyses were carried out on a PHI 5000 Versa Probe spectrometer using monochromatic Al K(alpha) X ray source (100um 25W 15kV). Survey scan analyses were carried out by scanning a 100um X ray beam in a 100 x 1400 micron square rectangular area. The analyzer pass energy is selected as 280.0 eV and step size of 1.0 eV. High resolution analyses were carried out with same X ray settings and analysis area, while analyzer pass energy is selected at 69. 0 eV (step size of 0.125eV). Spectra have been charge corrected to the main line of the carbon 1s spectrum (adventitious carbon) and set to BE of 284.8 eV.

TGA. TGA (Thermo-gravimetric analysis) measurement was carried out with a Mettler-Toledo TGA thermal analyzer under purified nitrogen gas flow with a 10 ^{o}C min^{-1} heating rate.

Photophysics. The absorption and photoluminescence spectra, photoluminescence quantum yields and photoluminescence lifetimes were investigated at room temperature ca 21 ^{o}C.

Steady-state photoluminescence spectra and quantum yields were acquired on a FLS920 of Edinburgh Instruments, the excitation wavelength of 470 nm was employed for both fluorescein and perovskites NPs. All spectra were corrected for the sensitivity of the photo-multiplier tube. The photoluminescence quantum yield (Φ_f) was calculated by using Eq. (1),[23, 24]

$$\Phi_{\mathrm{f}} = \Phi_{\mathrm{f}}^{0} \cdot \frac{\mathrm{F_s}}{\mathrm{F_0}} \cdot \frac{\mathrm{A_0}}{\mathrm{A_s}} \frac{n_s^2}{n_0^2}, \qquad \text{Eq. (1)}$$

in which **F** is the integrated fluorescence intensity, **A** is the absorbance at excitation wavelength, n is the refractive index of the solvent used, the subscript 0 stands for a reference compound and s represents samples. Fluorescein was used as the reference (Φ_{f}^{0}= 0.92 in 0.1 M NaOH aq. solution).[24] The sample and reference solutions were prepared with the same absorbance (A_i) at the excitation wavelength (near 0.09 per cm).

Photoluminescence lifetime was measured by time-correlated single photon counting method (Horiba Scientific, Fluorolog-3 spectrophotometer) with excitation at 485 nm diode laser (50 ps FWHM) and emission was monitored at 510 nm. The lifetime values were fit by biexponential decay function $I(t)=A+B_1\exp(-t/\tau_1) +B_2\exp(-t/\tau_2)$.

Singlet oxygen NIR phosphorescence. The NIR steady state photoluminescence spectra were recorded by Fluorolog-3 spectrophotometer equipped with an electronic cooled InGaAs detector (900-1700 nm) with excitation at 400 nm using a standard 1 cm quartz cuvettes. Both the emission and excitation slits were adjusted to their maxima. A long pass filter of 1000 nm was placed between a sample and the detector for all NIR experiments to filter away any stray light and the second harmonic of the excitation light with wavelengths shorter than 1000 nm. For singlet oxygen lifetime measurements, the excitation source is changed to a 1 μs flash lamp (450 nm, 1 mW), the emission at 1270 nm was monitored.

Singlet oxygen chemical trapping. Singlet oxygen quantum yield (Φ_Δ) were determined using the well known chemical trapping method.[25] Typically, a 3 mL toluene that contains perovskites NPs and 20 μM diphenylisobenzofuran (DPBF) was irradiated at 473 nm by a LED light under air (or oxygen) saturated condition. Φ_Δ value was obtained by the relative method using Eq. (2):

$$\Phi_\Delta = \Phi_\Delta^{\mathrm{ref}} \frac{k}{k^{\mathrm{ref}}} \frac{I_a^{\mathrm{ref}}}{I_a}, \qquad \text{Eq. (2)}$$

where $\Phi_\Delta^{\mathrm{ref}}$ is the singlet oxygen quantum yield for the reference standard I_2-TMBDP (2,6-diiodotetramehylBODIPY, $\Phi_\Delta{}^R$=0.96 in toluene) with excitation at 473 nm),[26] k and k^{ref} are the DPBF photo-bleaching rate constants in the presence of the respective sample and the reference standard, respectively; I_a and $I_a{}^{\mathrm{ref}}$ are the rates of light absorption at the irradiation wavelength of 473 nm by the samples and the reference standard, respectively. Their ratio can be obtained by Eq. (3).

$$\frac{I_a^{\mathrm{ref}}}{I_a} = \frac{1-10^{-A_{\mathrm{ref}}}}{1-10^{-A}}, \qquad \text{Eq. (3)}$$

In which, A and A_{ref} is the absorbance of a sample and the reference compound at excitation wavelength 473 nm, respectively. DPBF degradation was monitored by UV-vis absorption spectrum. The error in the determination of Φ_Δ was ~10% (determined from several Φ_Δ values).

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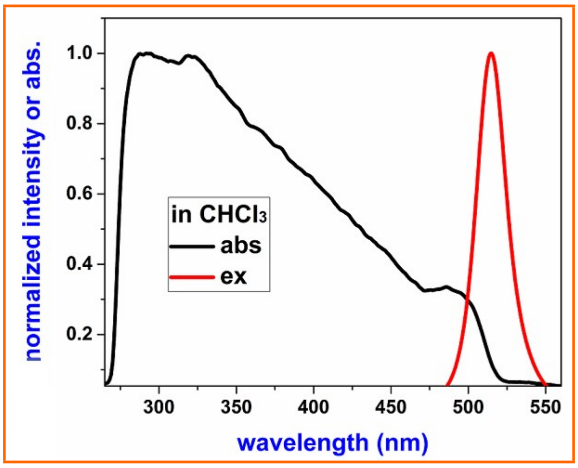

Figure S1. The absorption and emission spectra of $MAPbBr_3$ NPs in $CHCl_3$ (excitation wavelength is 440 nm for em. spectrum).

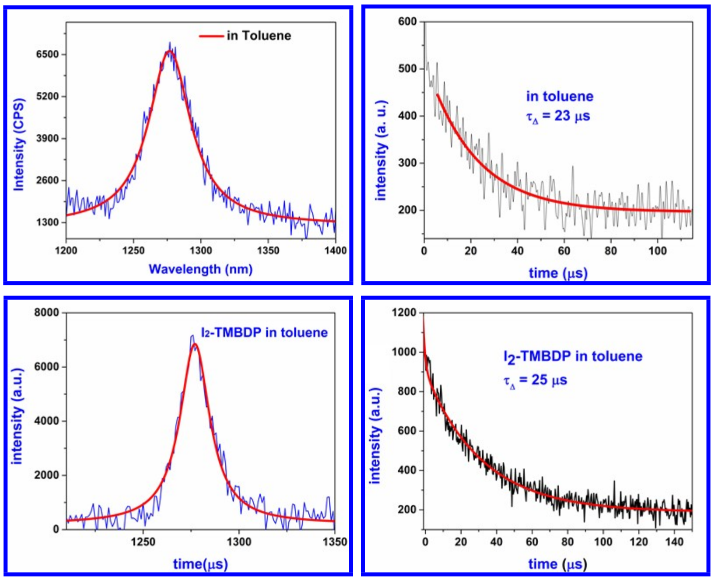

Figure S2. The NIR emission spectrum and emission decay of $MAPbBr_3$ NPs in toluene (Top). The bottom is the NIR emission spectrum and emission decay of I_2-TMBDP in toluene. Excitation wavelength is 440 nm (the absorbance at this wavelength is 0.30).

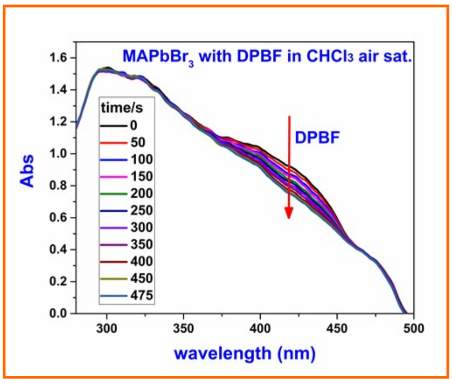

Figure S3. the change of DPBF (10 μM) absorption spectra in chloroform in the presence of perovskite NPs.

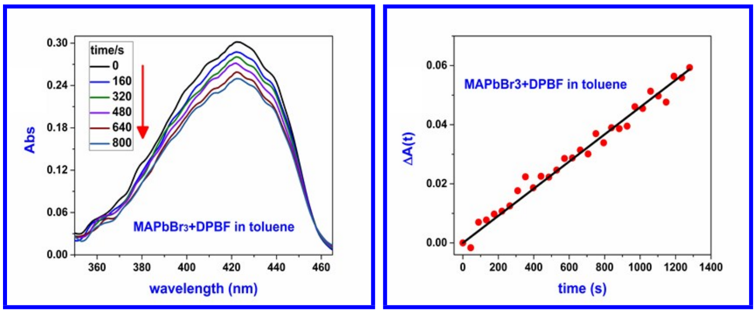

Figure S4. Left: the change of DPBF (15 μM) absorption spectra in toluene after subtracting the absorption spectrum of perovskite NPs. **Right:** the plotting of ΔA(t) = A(0)-A(t) at 420 nm against time t for the measurement in toluene, A(t) is the absorbance at time t at 420 nm. Pure DPBF absorption decrease is obtained by subtracting the constant absorption of the perovskites NPs.

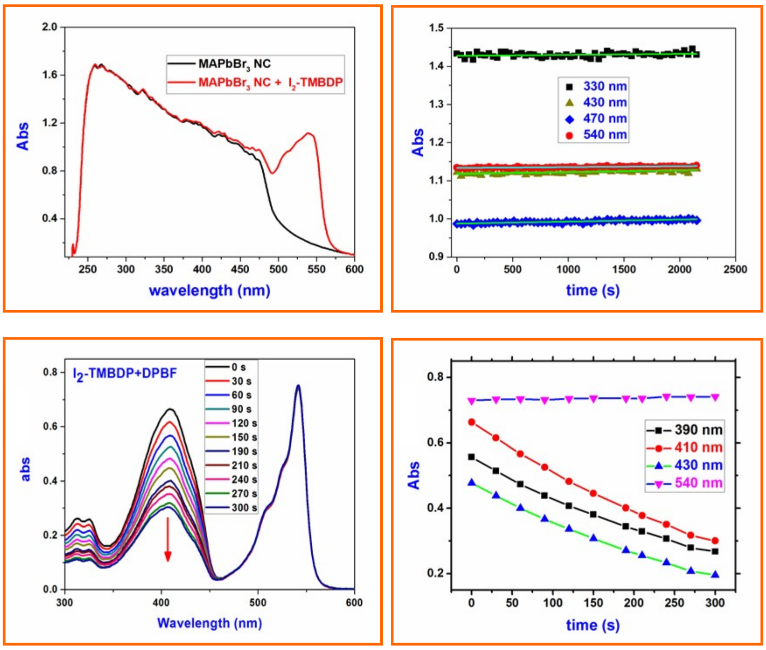

Figure S5. Top figures show that MAPbBr$_3$ NCs are stable to singlet oxygen generated by the I$_2$-TMBDP photosensitizer (10 μM) with photo excitation at 540 nm in toluene. **Top left:** the absorption spectra of MAPbBr$_3$ NCs in the presence and absence of I$_2$-TMBDP; **Top right:** the absorbance change of MAPbBr$_3$ NCs (330, 430, 470 nm) in toluene with 540 nm light irradiation time. **Bottom** figures show that DPBF decomposed quickly by singlet oxygen generated by the I$_2$-TMBDP photosensitizer (10 μM) with photo excitation at 540 nm in toluene. **Bottom left:** the decrease of absorption spectra of DPBF in the presence of I$_2$-TMBDP; **Bottom right:** the absorbance change of DPBF (390, 410, 430 nm) in toluene with 540 nm light irradiation time.

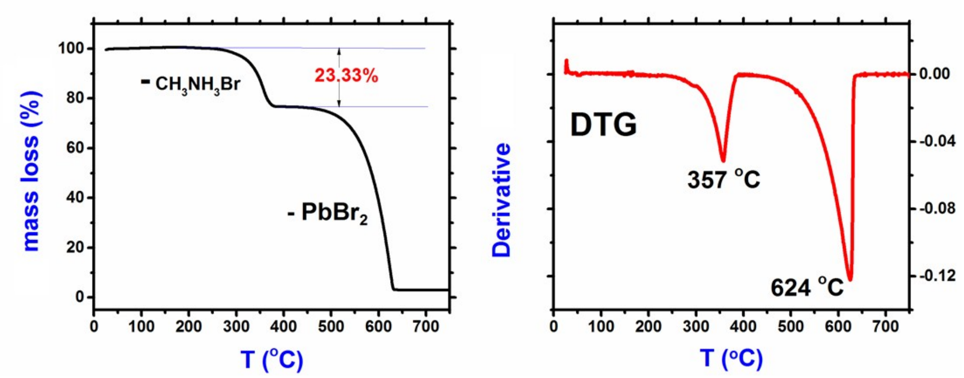

Fig. S6. TGA (left) and corresponding DTG (right) of MAPbBr$_3$ NPs (9.0 mg) under purified nitrogen gas flow with a 10 ^{o}C min^{-1} heating rate.

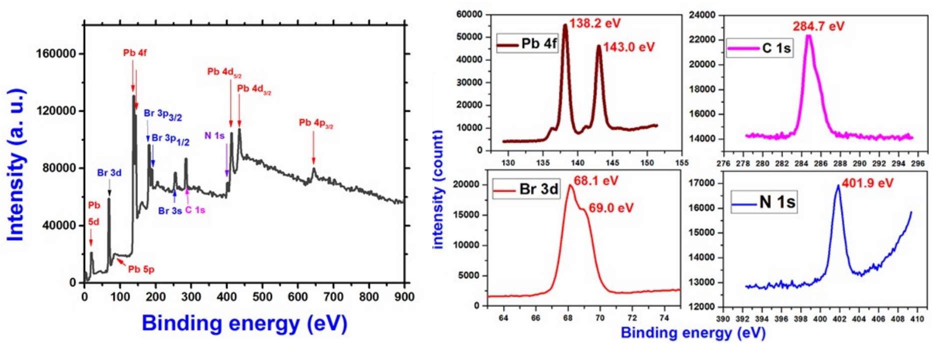

Fig. S7. Left: HR-XPS survey scan of the $MAPbBr_3$ NPs from 0-900 eV. **Right**: HR-XPS narrow scan for specific Pb, C, Br and N, respectively.