Supporting Information for:

Sensitized Molecular Triplet and Triplet Excimer Emission in 2D Hybrid Perovskites

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Figure S1. The XRD patterns of $(NMA_{0.2}PEA_{0.8})_2PbBr_4$ (upper panel) and NMA_2PbBr_4 (lower panel) perovskite thin films



Figure S2. The NMA₂PbBr₄ film TA kinetics probed for the naphthalene triplets (³Nap*; 435nm) at two different pump pulse energy densities.

Materials and Methods

Materials. Lead (II) bromide (99.99%) and HBr (48 wt.%, in water) were purchased from TCI. Phenylethylammonium bromide (99.99%) was purchased from Xi'an polymer Light Technology Corp. N,N-Dimethylformamide (DMF; 99%) was purchased from J&K Scientific LTD. Naphthalene methylamine (98%) was purchased from Energy Chemical.

Naphthalenemethylammonium bromide (NMABr). NMABr was synthesized by adding HBr (48wt% in water) into Naphthalene methylamine in ethanol at 0 °C (molar ratio of amine to HBr = 1:1.2). The crude product was obtained by slowly evaporating the solvent under reduced pressure. The white precipitate was dissolved in ethanol and recrystallized by slowly adding diethyl ether. The small crystals were further washed with diethyl ether several times before drying them in vacuum oven. After drying overnight, they were all transferred into a nitrogen-filled glove box and sealed under nitrogen for further use.

Film preparation. The quartz substrate was washed sequentially with detergent, deionized water, acetone and ethanol by ultrasonication for 30 min and then was UV–ozone cleaned for 20 min. The perovskite precursor was prepared by mixing PbBr₂ with respective amine salt (1:2 molar ratio) in anhydrous DMF: (PEA)₂PbBr₄ (PPB) was prepared with 2 mM of PEABr and 1 mM of PbBr₂; (NMA)₂PbBr₄ (NPB) was prepared with 2 mM of NMABr and 1 mM of PbBr₂; mixed-cation perovskite PNPB was prepared by mixing the above two precursor solutions using nominal ratios. The

precursor was continuously stirred at room temperature overnight. To deposit the perovskite film, precursor solution (60 μ L) was dropped onto the precleaned quartz substrate and quickly spin-coated at 4000 rpm for 30 s. The film was thermally annealed at a hot plates at 100 °C for 10 min in N₂ filled glove box.

Characterizations. Thin film X-ray diffraction (XRD) was carried out on Empyrean-100. Absorption spectrum was obtained by using Agilent Cary 5000 UV-Vis-NIR. Phosphorescence spectrum were recorded on Cary Eclipse Fluorescence Spectrometer. Phosphorescence mode was operated at 0.2 ms delay time and 5 ms gate time. Phosphorescence lifetime was measured on FLS1000 Spectrometer. All measurements were conducted under ambient air.

Transient absorption (TA). The femtosecond pump-probe TA measurements were performed using a regenerative amplified Ti:sapphire laser system (Coherent; 800 nm, 70 fs, 6 mJ/pulse, and 1 kHz repetition rate) as the laser source and a Femto-100 spectrometer (Time-tech spectra) as the spectrometer. Briefly, the 800 nm output pulse from the regenerative amplifier was split in two parts with a 50% beam splitter. The transmitted part was used to pump an Optical Parametric Amplifier (OPA; TOPAS) which generated a wavelength-tunable laser pulse from 250 nm to 2.5 µm as pump beam. The reflected 800 nm beam was split again into two parts. One part with less than 10% was attenuated with a neutral density filter and focused into a 2 mm thick sapphire or CaF2 window to generate a white light continuum (WLC) used for probe beam. The probe beam was focused with an Al parabolic reflector onto the

sample. After the sample, the probe beam was collimated and then focused into a fiber-coupled spectrometer with CMOS sensors and detected at a frequency of 1 KHz. The intensity of the pump pulse used in the experiment was controlled by a variable neutral-density filter wheel. The delay between the pump and probe pulses was controlled by a motorized delay stage. The pump pulses were chopped by a synchronized chopper at 500 Hz and the absorbance change was calculated with two adjacent probe pulses (pump-blocked and pump-unblocked).

Time-resolved PL. PL decay was measured using a time-resolved photoluminescence (u-PL) upconversion set-up (Chimera, Light conversion) and a Pharos laser (1030 nm,100 kHz, 230 fs pulse-duration; Light conversion). Briefly, the fundamental 1030 nm laser pulse was split into two parts. One part was used to pump a TOPAS OPA to generate wavelength-tunable excitation pulses; the other was used as the gate pulse. The emitted light was collected by lens and focused into a BBO crystal together with the 1030 nm gate pulse to generate the up-converted signal via sum-frequency-generation (SFG). The up-converted photons were focused onto the entrance slit of a monochromator and then detected by the spectrometer. The fluorescence decay curve was obtained by delaying the gate pulse using a mechanical delay stage.

Kinetics fitting

The decay curve for the (PEA)₂PbBr₄ (PPB) u-PL was fitted by a 2-exponential decay function, mainly accounting for hole trapping processes. In contrast, the PPB XB decay curve needed to be fitted by a 3-exponential function, due to co-contributions of electron and hole to the XB. The average lifetime τ_{ave} was calculated according to the following equation:

$$\tau_{ave} = \frac{\sum_{i} A_{i} \tau_{i}}{\sum_{i} A_{i}}$$
(S1),

where A_i and τ_i are the amplitude and lifetime, respectively, of the *i*-th exponential component.

The $(NMA)_2PbBr_4$ (NPB) u-PL was also fitted by a 2-exponential decay function, accounting for ultrafast hole transfer processes from the inorganic layer to naphthalene. The NPB XB decay curve, XB(t), was fitting to the following equation:

$$XB(t) = 0.3 \cdot uPL(t) + 0.7 \cdot \sum_{i} A_{i} e^{-t/\tau_{i}}$$
 (S2),

where uPL(t) is the fitting curve for the u-PL decay of NPB, the multi-exponential decay describes electron transfer from the inorganic layer to naphthalene cation radical, and 0.3 (0.7) is the hole (electron) contribution to the XB feature. Note that the reported hole contribution to the XB of lead bromide perovskites varies from 0.25 (ref¹) to 0.33 (ref²). Here we find that the factor 0.3 can successfully fit out data.

All the fitting parameters are listed in Table S1.

	τ_1 (ps)	A_1 (%)	$ au_2$ (ps)	<i>A</i> ₂ (%)	$ au_3$ (ps)	A3 (%)	$ au_{\rm ave}({\rm ps})$
PPB u-PL	2.1±0.0	69	66.5±2.0	31	-	-	22
PPB XB	3.3±0.2	37	38.8±1.6	46	493±36	16	98.9
NPB u-PL	0.6±0.0	96	31.7±5.7	4	-	-	2.0
NPB XB (electron)	11.8±0.7	36	84.6±5.3	45	1030±90	20	245

Table S1. Fitting parameters for different samples.

References for SI:

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(2) Wu, K.; Liang, G.; Shang, Q.; Ren, Y.; Kong, D.; Lian, T. Ultrafast Interfacial Electron and Hole Transfer from CsPbBr3 Perovskite Quantum Dots. *J. Am. Chem. Soc.* **2015**, *137*, 12792-12795.