Supporting Information for

Mechanism of Ultrafast Energy Transfer between the Organic-Inorganic Layers in Multiple-Ring Aromatic Spacers for 2D Perovskites

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Preparation of 1-pyrenyl-methylammonium bromide:

1-Pyrenyl-methylamine were dissolved in the required amount of isopropanol and stirred about 30 min at room temperature. Then hydrobromic (47%) were added in one portion, whereupon the hydrobromide precipitates immediately. There was still 30 min stirred, and the precipitate formed was filtered off, washed with isopropanol and finally with diethyl ether and dried in vacuum.

**Preparation of 1-pyrenyl-methylammonium iodide:**

1-Pyrenylmethylamine were dissolved in the required amount of isopropanol (approx. 40 mL). For a complete solution, about 30 min. be stirred at room temperature. Then 0.183 mL (1.38 mmol) HI (57%) were added in one portion, whereupon the hydroiodide precipitates immediately. (The hydriodic acid was present as a 57% aqueous solution, which was stabilized with 1.5% hypophosphorous acid and was therefore freshly distilled shortly before use. After the distillation, the acid changes colour very quickly due to light and small amounts of dust or the like red-brown.) Another 30 min stirred, and the precipitate formed was filtered off, washed with isopropanol and finally with diethyl ether and dried in vacuum. During all manipulations, care was taken to ensure that there was only a little incidence of light.

SEM, Schemes and XRD spectra of $(BA)_2Pb(Br_{0.7}I_{0.3})_4$, $(NMA)_2Pb(Br_{0.7}I_{0.3})_4$ and $(PMA)_2Pb(Br_{0.7}I_{0.3})_4$ thin films:
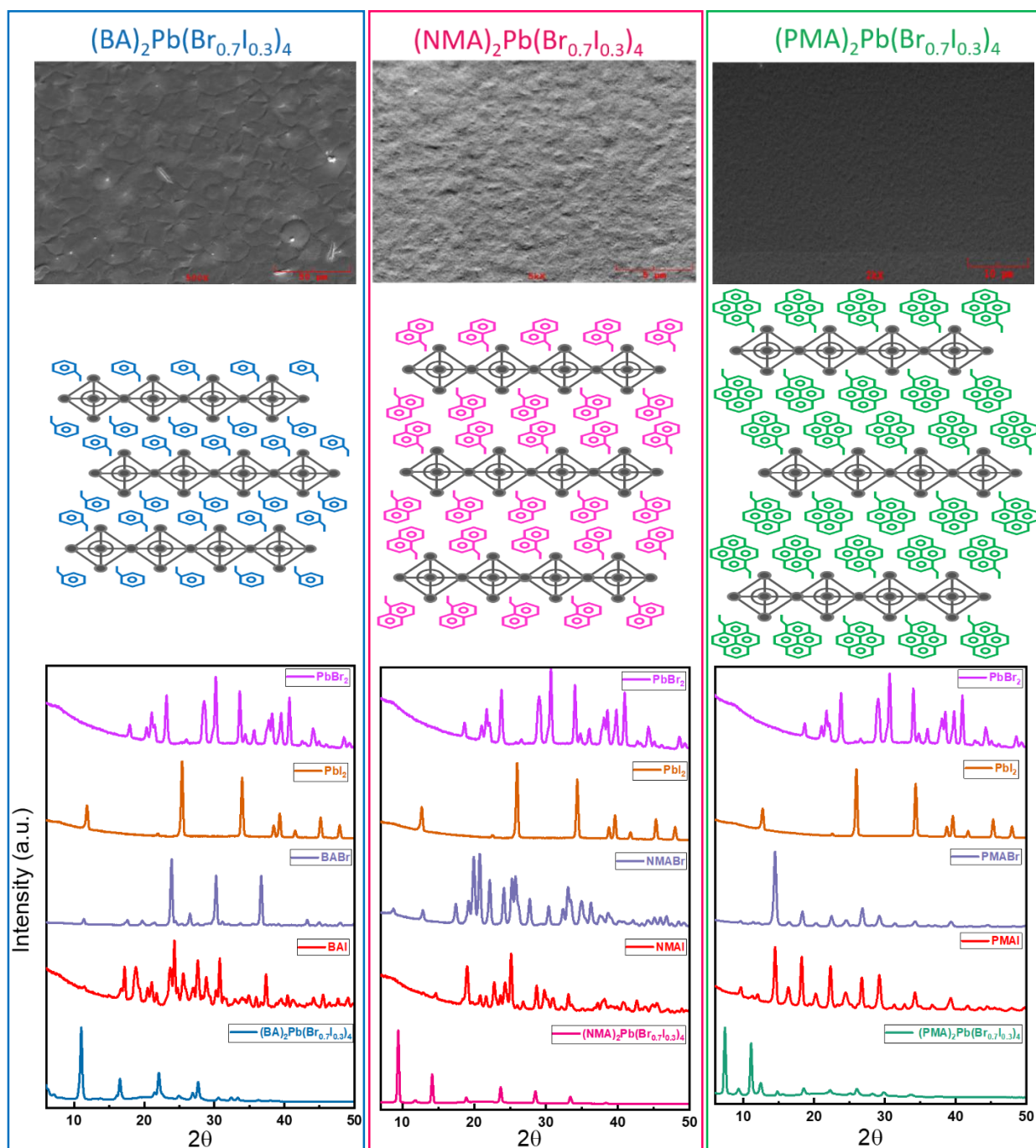
Fig. S1 Scanning-electron Microscope images of all films. XRD patterns of $PbBr_2$ and PbI_2 powders (the same for all samples). Benzylammonium bromide, benzylammonium iodide powders, and $(BA)_2Pb(Br_{0.7}I_{0.3})_4$ film in the left panel; 1-naphthylmethylammonium bromide, 1-naphthylmethylammonium iodide powders, and $(NMA)_2Pb(Br_{0.7}I_{0.3})_4$ film in the middle panel; 1-pyrenemethylammonium bromide and 1-pyrenemethylammonium iodide powders and $(PMA)_2Pb(Br_{0.7}I_{0.3})_4$ film in the right panel. All powders exposed in ambient air.

TCSPC measurements:
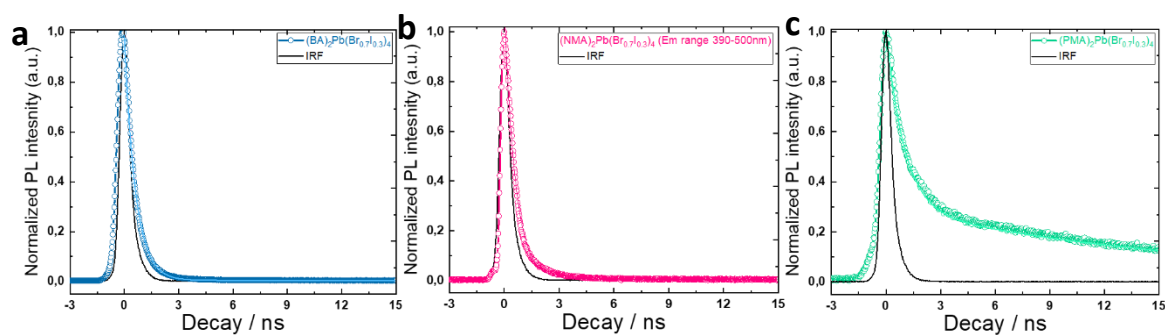
Fig. S2 Photoluminescence (PL) decay of (a) $(BA)_2Pb(Br_{0.7}I_{0.3})_4$, (b) $(NMA)_2Pb(Br_{0.7}I_{0.3})_4$ and (c) $(PMA)_2Pb(Br_{0.7}I_{0.3})_4$ thin films deposited on quartz substrates with excitation at 320 nm at room temperature measured by TCSPC.

Table S1. Photoluminescence (PL) decay time coefficients of all samples. Values in parentheses give the relative amplitude.

Films	τ_1 (ns) (A_1)	τ_2 (ns) (A_2)
$(BA)_2Pb(Br_{0.7}I_{0.3})_4$	0.61 (100%)	
$(NMA)_2Pb(Br_{0.7}I_{0.3})_4$ (390-500 nm)	0.60 (100%)	
$(PMA)_2Pb(Br_{0.7}I_{0.3})_4$	0.98 (72%)	17.1 (28%)

Excitation density-dependent measurements:

OPTIMUS (www.optimusfit.org) has been used to perform the global lifetime analysis for these measurements[1]. The samples were pumped by 387 nm and probed by a white-light continuum to reveal the transient changes in absorption (ΔA). The samples were measured at room temperature.

For $(BA)_2Pb(Br_{0.7}I_{0.3})_4$, a bi-exponential decay function was sufficient to obtain a satisfactory global fit between 400 and 650 nm. In Fig. S3, the bleach signal of the lead halide-based exciton bleach at 404 nm is shown, exemplarily.
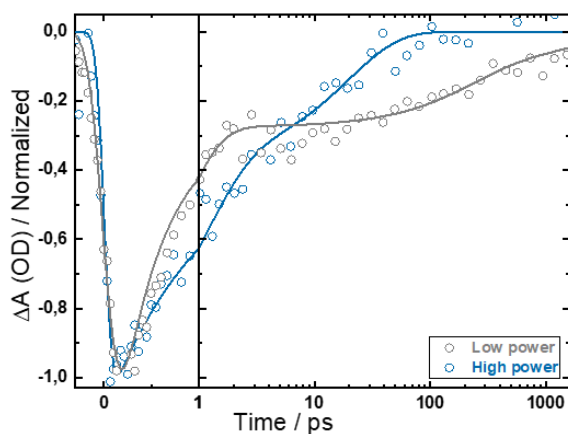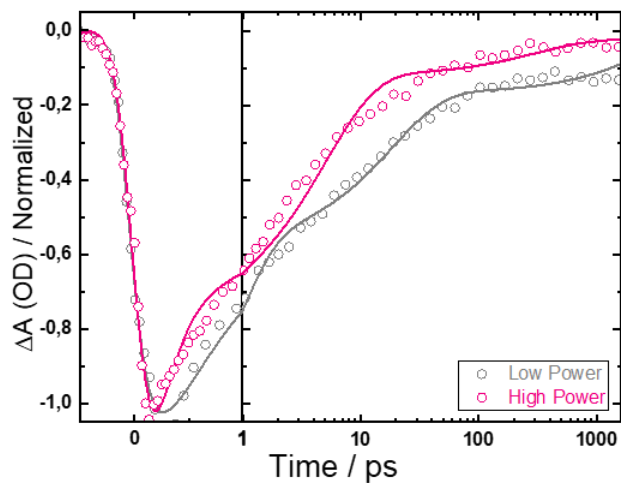

Fig. S3 $(BA)_2Pb(Br_{0.7}I_{0.3})_4$ kinetic traces excited by 387 nm and probed at 404 nm at two different pump pulse energies.

Table S2. Time constants in ps resulting from the global fit analysis for different excitation densities of $(BA)_2Pb(Br_{0.7}I_{0.3})_4$ probed at 404 nm.

Power ($\mu J/cm^2$)	τ_1 (ps) (A_1)	τ_2 (ps) (A_2)
146	1 (70 %)	32 (30%)
81	0.52 (70%)	506 (30%)

For $(NMA)_2Pb(Br_{0.7}I_{0.3})_4$, a tri-exponential decay function and signal offset (τ_4 = infinity) was required to obtain a satisfactory global fit between 400 and 650 nm. In Fig S4, the bleach signal of the lead halide-based exciton bleach at 419 nm is shown, exemplarily.
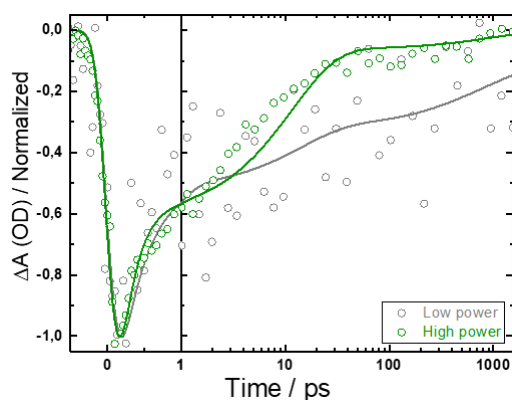

Fig. S4 $(NMA)_2Pb(Br_{0.7}I_{0.3})_4$ kinetic traces excited by 387 nm and probed at 419 nm at two different pump pulse energies.

Table S3. Time constants in ps resulting from the global fit analysis for different excitation densities of $(NMA)_2Pb(Br_{0.7}I_{0.3})_4$.

Power ($\mu J/cm^2$)	τ_1 (ps) (A_1)	τ_2 (ps) (A_2)	τ_3 (ps) (A_3)	τ_4 (ps)
162	0.20 (30%)	5 (48%)	288 (15%)	Infinity (7%)
81	0.26 (27%)	9.7 (48%)	670 (13%)	Infinity (12%)

For $(PMA)_2Pb(Br_{0.7}I_{0.3})_4$, a tri-exponential decay function and signal offset (τ_4 = infinity) was required to obtain a satisfactory global fit between 400 and 650 nm. In Fig. S5, the bleach signal of the lead halide-based exciton bleach at 418 nm is shown, exemplarily.

Fig. S5 $(PMA)_2Pb(Br_{0.7}I_{0.3})_4$ kinetic traces excited by 387 nm and probed at 418 nm at two different pump pulse energies.

Table S4. Time constants in ps resulting from the global fit analysis for different excitation densities of $(PMA)_2Pb(Br_{0.7}I_{0.3})_4$.

Power ($\mu J/cm^2$)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)
146	0.2 (40%)	8.6 (45%)	196 (10%)	Infinity (5%)
81	0.36 (40%)	14 (25%)	500 (19%)	Infinity (17%)

SI References

(1)   Slavov, C.; Hartmann, H.; Wachtveitl, J. Implementation and Evaluation of Data Analysis Strategies for Time-Resolved Optical Spectroscopy. *Anal. Chem.* **2015**, *87* (4), 2328–2336. https://doi.org/10.1021/ac504348h.