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Dielectric polarization effect and transient relaxation in FAPbBr$_3$ films before and after PMMA passivation

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S1. Methods

Synthesis of $FAPbBr_3$ film

0.077 g $MABr_2$ and 0.3 g $PbBr_2$ were dissolved in 1 ml of DMF, and the precursor solution was obtained after ultrasonication for 0.5 hr. Then, The precursor solution was spin-coated onto the CaF_2 substrate, first 3 s to 1000 rpm, then 2000 rpm for 5 s. Chlorobenzene was added dropwise to assist film formation during the spin coating. The spin-coated film is annealed at 80°C for 0.5 hr to obtain final film sample.

Synthesis of $FAPbBr_3$–PMMA film

The prepared $FAPbBr_3$ film is placed on the spin coater, and the PMMA dissolved in chlorobenzene is added dropwise on the film, first to reach 1000 rpm in 3s, then spin coating for 5s at 2000 rpm. The spin-coated film was annealed at 80 °C for 0.5 hr to obtain final film sample.

Steady-state and time-resolved spectroscopy

Visible absorption spectra were measured on a CARY 100 BIO UV-vis spectrophotometer. Fourier Transform Infrared (FTIR) spectra in the region of 400 - 4000 cm^{-1} were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Electron) with 0.12 cm^{-1} spectral resolution, for the samples that were spin coated onto a 2-mm thick CaF_2 optical windows. The relevant photoluminescence (PL) spectra and micro-Raman spectra were obtained through a laser confocal PL microscope system (Acton SP2500, Olympus BX51M, Princeton Instruments, Trenton, NJ, USA) using 633 nm and 405 nm continuous-wave (CW) lasers as excitation sources, respectively. The phase purity of the sample was analyzed via x-ray diffraction (XRD, Bruker, Karlsruhe).

The time-resoled fluorescence spectra and stimulated emission spectra were obtained by a frequency-doubled Ti: Sapphire femtosecond laser system (Legend, Coherent) with emission wavelength of 400 nm, equipped with a high-resolution streak camera system (Hamamatsu C10910).

Ultrafast pump-probe spectroscopy

The femtosecond infrared (fs-IR) transient absorption spectroscopy has previously been described in detail.[1] Briefly, an ultrafast Ti: Sapphire laser (Spectra-Physics) was used to pump two separate optical parametric amplifiers (OPAs). The first OPA (Spectra-Physics) was used to generate a mid-IR pulse with wavelength centered at 6 μm and ca. 55 fs duration, which was attenuated to weak pulse energy level and used as the probe in the fs-IR experiment. A second OPA (TOPAS, Light Conversion) was used to generate a visible pulse with wavelength centered at 530 nm with pulse energy of 100 $\mu J/cm^2$, and the pulse was used to excite the band edge of $FAPbBr_3$ film. The visible pump pulse has a spot size with 250-μm diameter at the sample, while the IR probe pulse is focused at the sample with a spot size of 100-μm diameter to examine the ultrafast generation and dynamics of electrons and holes. The time delay in the visible pump and IR probe experiment was adjusted using a computer-controlled translation stage (LNR150, THORLABS). A mercury cadmium telluride (MCT) array detector (Infrared Systems/Infrared Associates) was used through an IR monochromator (JYHORIBA) in the fs-IR experiment.

S2. Additional experimental data

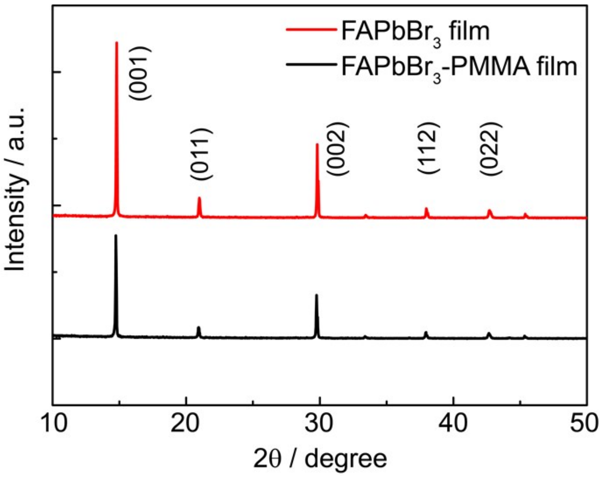

Figure S1. X-ray diffraction patterns of FAPbBr$_3$ film and FAPbBr$_3$-PMMA film.

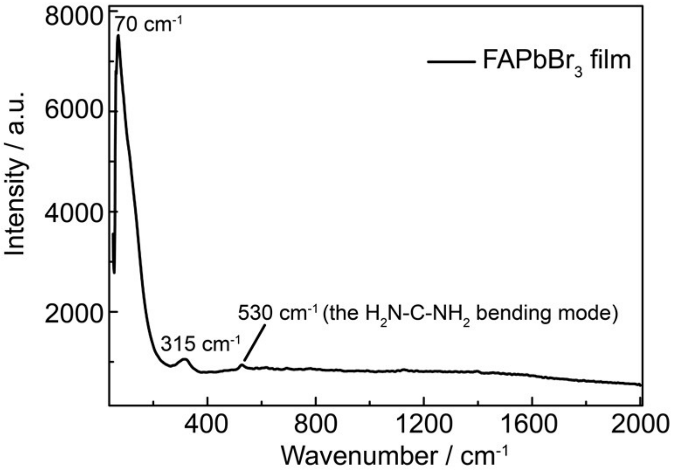

Figure S2. Raman spectrum of FAPbBr$_3$ film. In order to eliminate the influence of fluorescence, we plated a gold film about 10 nm thick on the surface of the perovskite film. The excitation light was a 633 nm continuous laser. There is a broad band of low-frequency vibration mode in the range of 30 - 380 cm^{-1}. The weaker the independent peak at 315 cm^{-1} is, the greater the degree of amorphization of the film. The peak at 530 cm^{-1} was tentatively attributed to the H$_2$N-C-NH$_2$ bending vibration.[2]

S3. Quantum-chemistry calculations

Formamidinium (FA) molecule was geometry optimized and followed by normal-mode vibrational analysis using the density functional theory (DFT) at the level of B3LYP/6-31+G(d).[3, 4] In order to identify whether there are dielectric charges formed around the FA molecules in the FAPbBr$_3$ film systems, Neutral, positively charged, and negatively changed FA species were considered and the obtained computational results were compared. Charge carriers may gather due to the dielectric polarization at the organic-inorganic interface, and thus causes a charged FA group. The multiple charged FA molecules were also calculated to mimic the situation of the spectral fingerprint change under the influence of carrier concentration. The harmonic vibrational frequencies of these FA species were obtained using a frequency scaling factor of 0.9636,[5] and the corresponding simulated IR spectra with Lorentzian line broadening (FWHM= 11 cm^{-1}) in the C=N stretching vibration region were given in Figure S3a. The C=N vibrational frequency-shift data of these species compared to neutral molecular spectrum were shown in Figure S3b. All calculations were carried out using Gaussian 09.[6] It should be pointed out that frequency and linewidth differences between the calculated and experimental IR spectra exist, which is simply due to our simplified FA model and the FA molecules in actual neighborhood that is quite complicated. However, the results in Figure S3b We aim to qualitatively illustrate the effect of the presence of charges on the vibration frequency of organic vibrating groups.

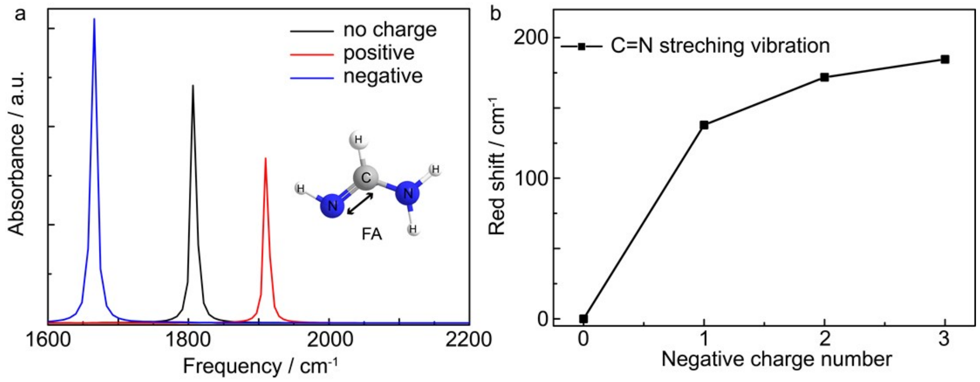

Figure S3. (a) Computed IR spectrum of the C=N stretching vibration of neutral, positively and negatively changed FA molecules. Spectral lines were broadened using Lorentzian function with full width at half maximum of 11 cm^{-1} (b) Relative to neutral FA molecules, the relationship between the red shift of the C=N stretching vibration peak position of negatively charged FA molecules and the number of charges.

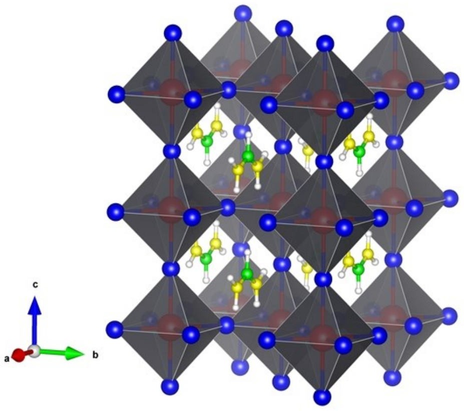

Figure S4. The lattice structure of $FAPbBr_3$ perovskite, which is composed of an organic FA ion layer and an inorganic $PbBr_2$ layer superimposed.

Table S1. Kinetics fitting parameters for the photoluminescence (PL), the C=N stretching, and polaron dynamics shown in Figures 1, 2 and 3.

	Sample	τ_1 (A_1)	τ_2 (A_2)
PL decay	$FAPbBr_3$ film	2.6±0.1 ps (0.7)	48.7±0.3 ps (0.3)
	$FAPbBr_3$-PMMA film	200.6±1.7 ps (0.67)	2500±10.0 ps (0.33)
C=N stretching vibration	$FAPbBr_3$ film	295.1±2.0 ps	-
	$FAPbBr_3$-PMMA film	497.5± 3.8 ps	-
Polaron	$FAPbBr_3$ film	10.2±0.3 ps (0.45)	279.6±5.8 ps (0.55)
	$FAPbBr_3$-PMMA film	36.8±0.8 ps (0.62)	512.4±22.4 ps (0.38)

Table S2. Kinetics fitting parameters of power dependence shown in Figure 4.

	Excitation pulse energy	τ_1 (A_1)	τ_2 (A_2)
Polaron ($FAPbBr_3$-PMMA film)	100 mJ/cm^2	36.8±0.8 ps (0.62)	512.4±22.4 ps (0.38)
	200 mJ/cm^2	22.7±0.7 ps (0.61)	280.5±11.6 ps (0.39)
	400 mJ/cm^2	3.1±0.1 ps (0.68)	152.2±3.5 ps (0.32)
C=N stretching vibration ($FAPbBr_3$-PMMA film)	100 mJ/cm^2	49.8±3.8 ps	-
	200 mJ/cm^2	1486.3±37.0 ps	-
	400 mJ/cm^2	2578.0±59.0 ps	-
Polaron ($FAPbBr_3$ film)	100 mJ/cm^2	29.8±1.3 ps (0.4)	262.3±5.6 ps (0.6)
	200 mJ/cm^2	12.7±0.5 ps (0.39)	153.9±11.6 ps (0.61)
	400 mJ/cm^2	4.7±0.1 ps (0.54)	114.5±1.6 ps (0.46)
C=N stretching Vibration ($FAPbBr_3$ film)	100 mJ/cm^2	603.2±23.5 ps	-
	200 mJ/cm^2	1234.1±39.6 ps	-
	400 mJ/cm^2	6595.1±494.1 ps	-

S4. References for SI

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