Electronic Supplementary Information (ESI)

Electrochemically Induced Iodine Migration in Mixed Halide Perovskites: Suppression through Chloride Insertion

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Experimental Methods

Materials

All chemicals were used as acquired without additional purification. Methylammonium chloride (MACl, Sigma Aldrich), methylammonium bromide (MABr, Greatcell Solar), methylammonium iodide (MAI, Greatcell Solar), lead chloride ($PbCl_2$, 99.99%, Sigma-Aldrich), lead bromide ($PbBr_2$, 99.99%, Sigma-Aldrich), lead iodide (PbI_2, 99.99%, 10 mesh bead, Alfa-Aesar), diethyl ether (anhydrous 99.8%, Sigma-Aldrich), dimethylformamide (DMF, anhydrous 99.8%, Sigma-Aldrich), dimethyl sulfoxide (DMSO, anhydrous 99.9%, Sigma-Aldrich), fluorine-doped tin oxide conducting glass (FTO, Pilkington glass).

Preparation of Triple-Halide (Cl/Br/I) Perovskite Films

The triple-halide (Cl/Br/I) perovskite films were prepared by following the previously reported literature precedence.[1-3] The preparation of perovskite films was carried out in a glovebox (< 10 ppm H_2O) unless otherwise stated. Square-shaped FTO substrates (2.5 cm × 2.5 cm) were used for fabricating the perovskite films. The triple-halide perovskite films with a chemical formula of $MAPb(Cl_xBr_{0.5(1-x)}I_{0.5(1-x)})_3$, wherein x is Cl concentration, were prepared by dissolving stoichiometric amount of precursors of PbX_2 ($PbCl_2$ + $PbBr_2$ + PbI_2) and MAX (MACl + MABr + MAI) in mixed anhydrous DMF:DMSO solvents at a volume ratio of 4:1 to make a 0.6 M (Pb^{2+}) precursor solution. The stoichiometric ratio of halide precursors (Cl/Br/I) was systematically varied in the Cl concentration (x) range of 0—10 % while maintain the equimolar ratio of Br/I = 1:1. The mixed precursor solutions were vigorously stirred for 1 hr at room temperature in glovebox until the solution became transparent. The precursor solutions were subsequently syringe-filtered through polytetrafluoroethylene membrane filter (0.2 μm pore size, G8549141, Whatman). A 50 μL of precursor solution was statically applied onto the FTO substrate followed by spin-casting at 4000 rpm for 25 s with an acceleration of 1200 rpm. A 0.5 mL of diethyl ether was rapidly injected as antisolvent at 10 s after spinning. The films were transferred to a preheated hot plate and treated at 100 °C for 5 minutes. The films were then taken out from the hot plate, cooled down at room temperature, and stored in the glovebox until further use.

Electrochemical measurements

Electrochemical measurements were performed with a Gamry potentiostat in a standard three-electrode setup in which the FTO/perovskite electrodes served as the working electrode, a Pt mesh (1 cm^2) as the counterelectrode (cleaned by "Piranha solution", water, and finally DCM), and a Ag/AgCl wire as a pseudo-reference electrode. The Ag/AgCl pseudo-reference electrode was prepared by depositing AgCl on Ag wire surface. Calibration of the pseudoreference electrode was performed by measuring the formal potential of the ferrocene/ferrocenium redox couple reaction in DCM (0.001 M ferrocene and 0.01 M Bu_4NPF_6)

with a scan rate of 50 mV s^{-1}. The formal potential was determined to be E = 0.37 ± 0.05 V with respect to our Ag/AgCl electrode.[1,4] The electrochemical cells were assembled in ambient conditions and then purged with nitrogen for 10 minutes to ensure inert conditions in the assembled cells.

Steady-State Absorption Measurements

Steady-state absorption measurements were carried out using a Varian Cary 50 bio spectrophotometer in the wavelength of 450—750 nm. The difference absorption (ΔA) spectra were obtained by subtracting the spectrum at 0 s as a reference from the spectra acquired at later time. Spectroelectrochemical measurements were performed by recording the steady-state absorption spectra under potentiostatic (chronoamperometry) and potentiodyanmic (linear sweep voltammetry) conditions.
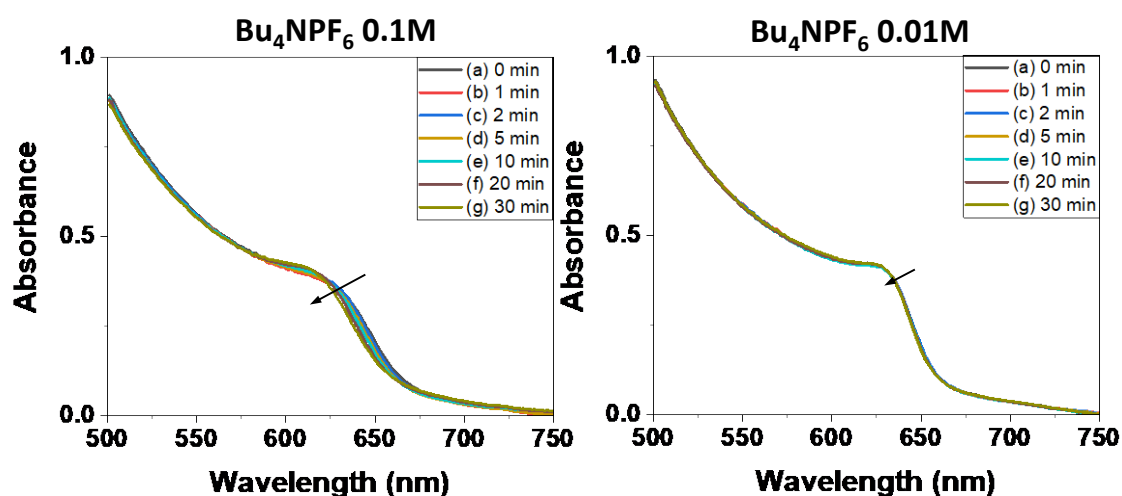

Fig. S1 (A,B) Absorption changes of mixed halide perovskite films with 0% Cl on FTO upon immersing the films in Bu$_4$NPF$_6$/DCM electrolyte with different electrolyte concentration of 0.1 M (A) and 0.01 M (B).
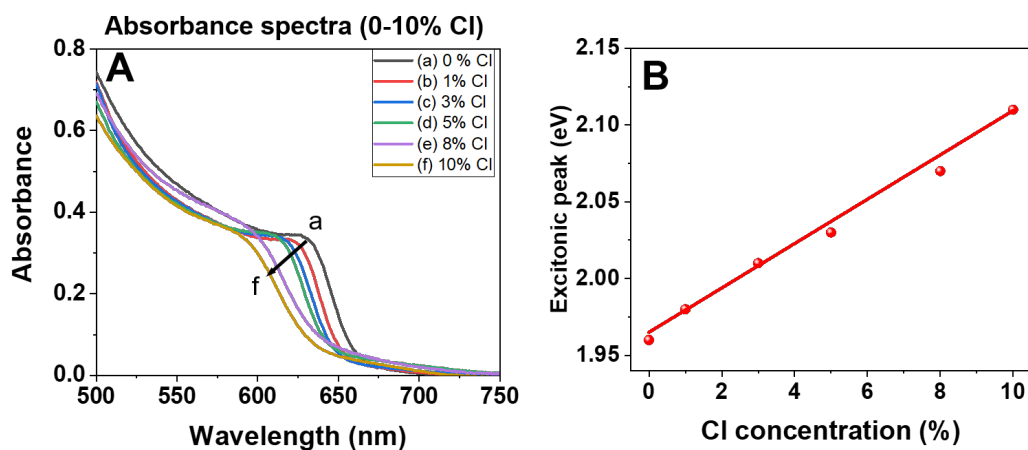
Fig. S2 (A) Absorbance spectra of mixed halide perovskites films on FTO with different Cl concentration from 0-10% (a-f). **(B)** The excitonic peak dependence of mixed halide perovskite film MAPb(Cl$_x$Br$_{0.5(1-x)}$I$_{0.5(1-x)}$)$_3$ containing different Cl concentration. The excitonic peak which corresponds to bandgap shows a shift of 0.15 eV as we increase Cl concentration from 0 -10%.
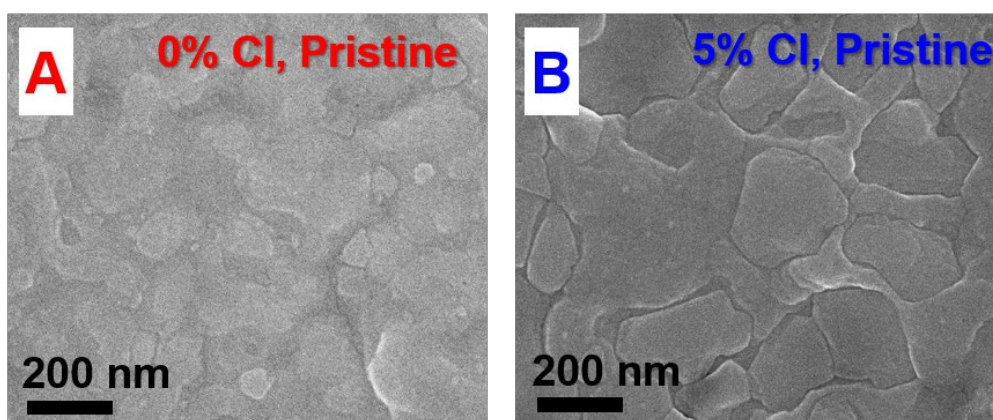

Fig. S3 SEM images of MAPb(Cl$_x$Br$_{0.5(1-x)}$I$_{0.5(1-x)}$)$_3$ film (A) with 0% Cl and (B) with 5% Cl deposited on FTO glass before subjecting to electrochemical treatment (pristine films).
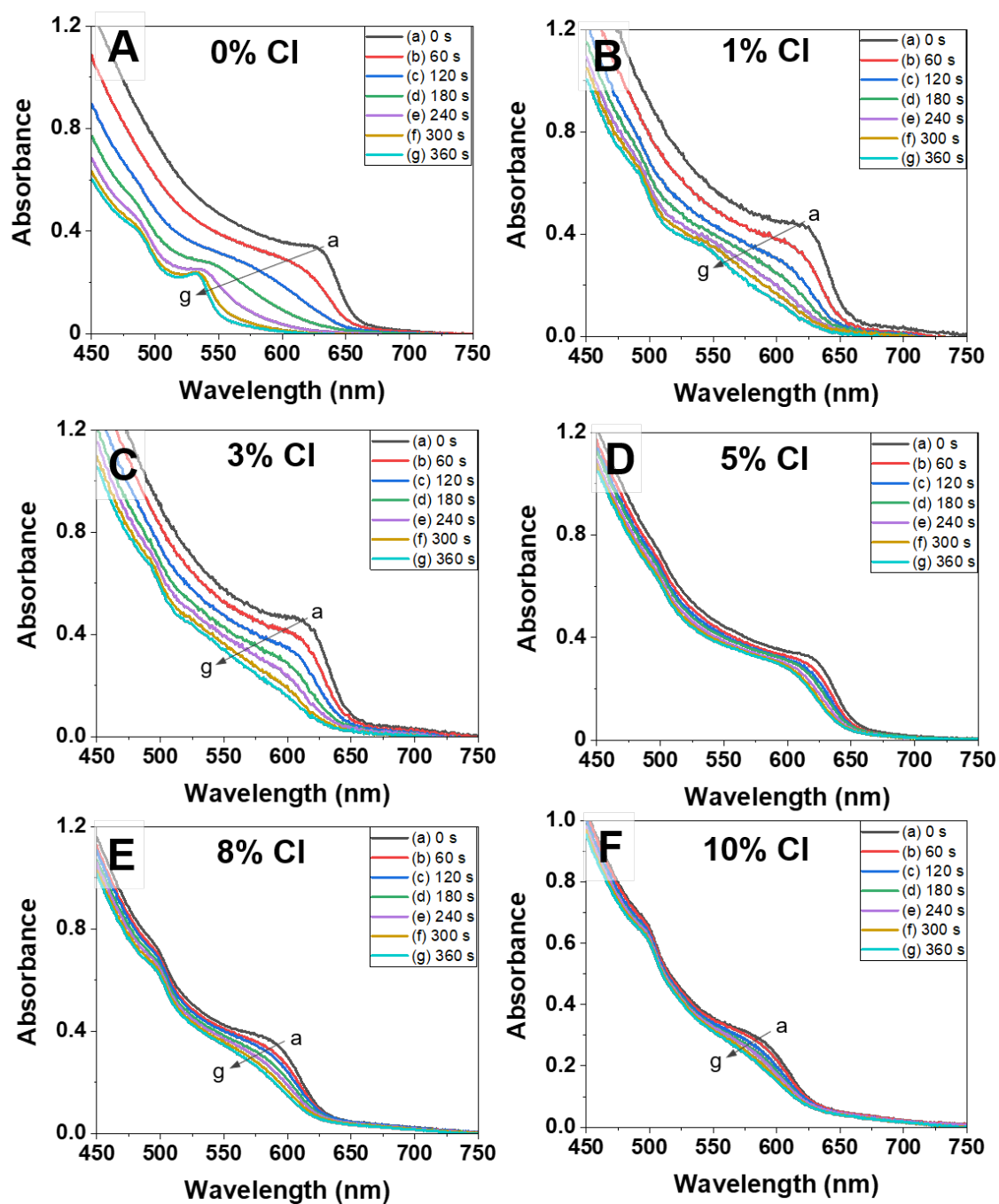
Fig. S4 (A-F) Absorbance changes recorded for the FTO/MAPb($Cl_xBr_{0.5(1-x)}I_{0.5(1-x)}$)$_3$ films with different Cl concentration of 0% Cl (A), 1% Cl (B), 3% Cl (C), 5% Cl (D), 8% Cl (E), and 10% Cl (F) during potentiostatic treatment at anodic bias of 1.0 V versus Ag/AgCl in 0.01 M Bu$_4$NPF$_6$/DCM electrolyte with different treatment time from 0-360 s (a-g).
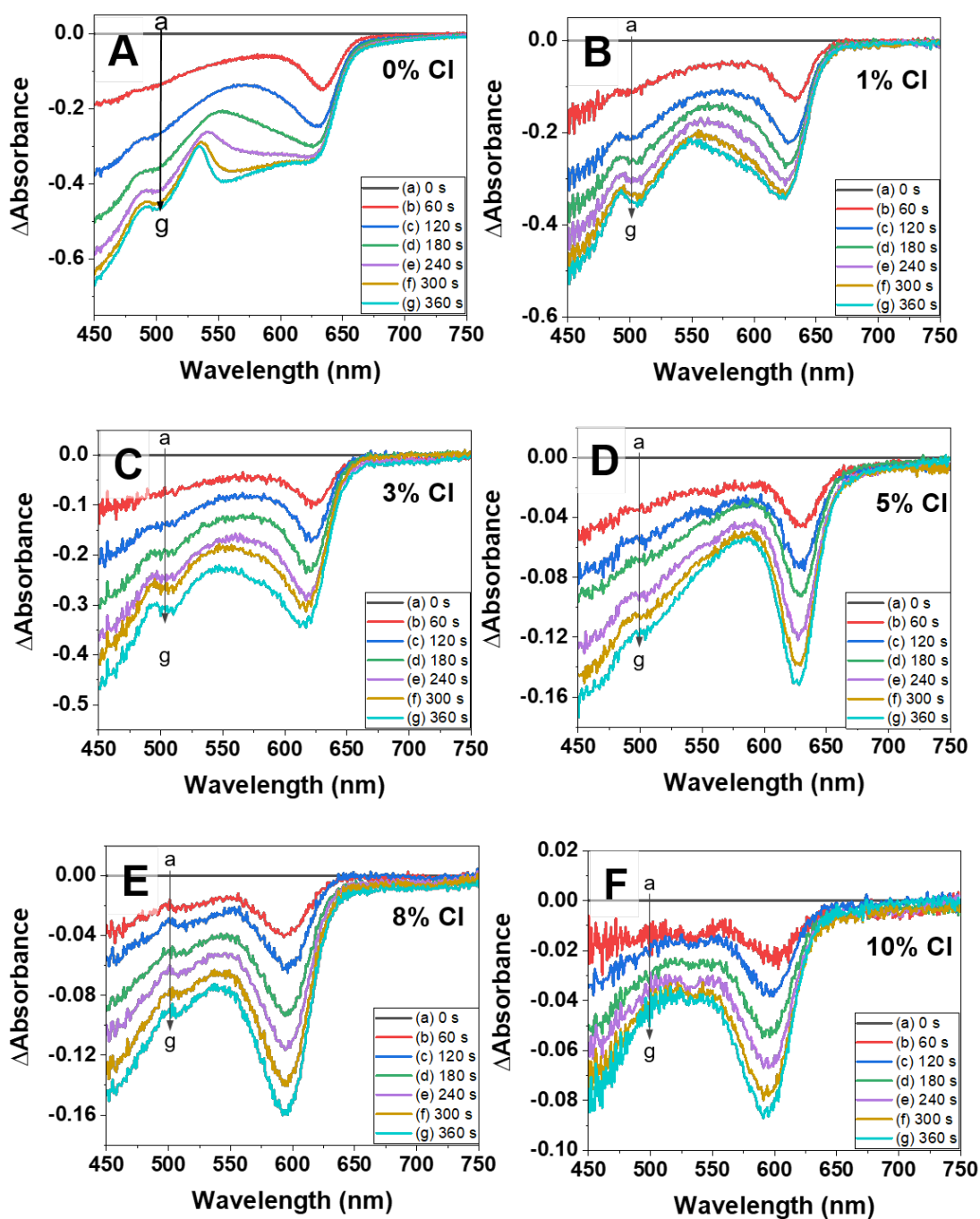
Fig. S5 (A-F) Difference absorption spectra recorded for the FTO/ MAPb($Cl_xBr_{0.5(1-x)}I_{0.5(1-x)})_3$ films with different Cl concentration of 0% Cl (A), 1% Cl (B), 3% Cl (C), 5% Cl (D), 8% Cl (E), 10% Cl (F) under anodic bias of 1.0 V versus Ag/AgCl in 0.01 M Bu_4NPF_6/DCM electrolyte with different treatment time from 0-360 s (a-g). The absorption spectrum at 0s serves as a reference to obtain the difference absorption spectra.
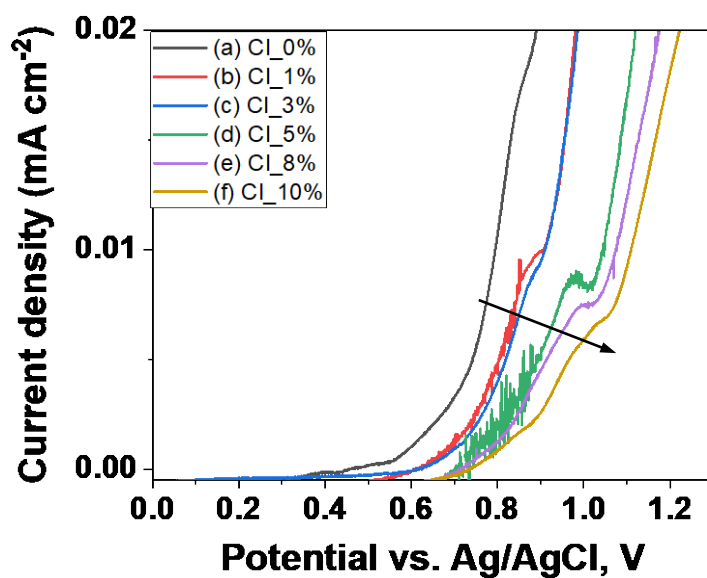
Fig. S6 Magnified linear sweep voltammograms acquired for the FTO/MAPb(Cl$_x$Br$_{0.5(1-x)}$I$_{0.5(1-x)}$)$_3$ films with different Cl concentration from 0-10% (a-f) with a scan rate of 5 mV/s in the voltage range of 0-1.44 V vs Ag/AgCl in 0.01 M Bu$_4$NPF$_6$/DCM electrolyte.
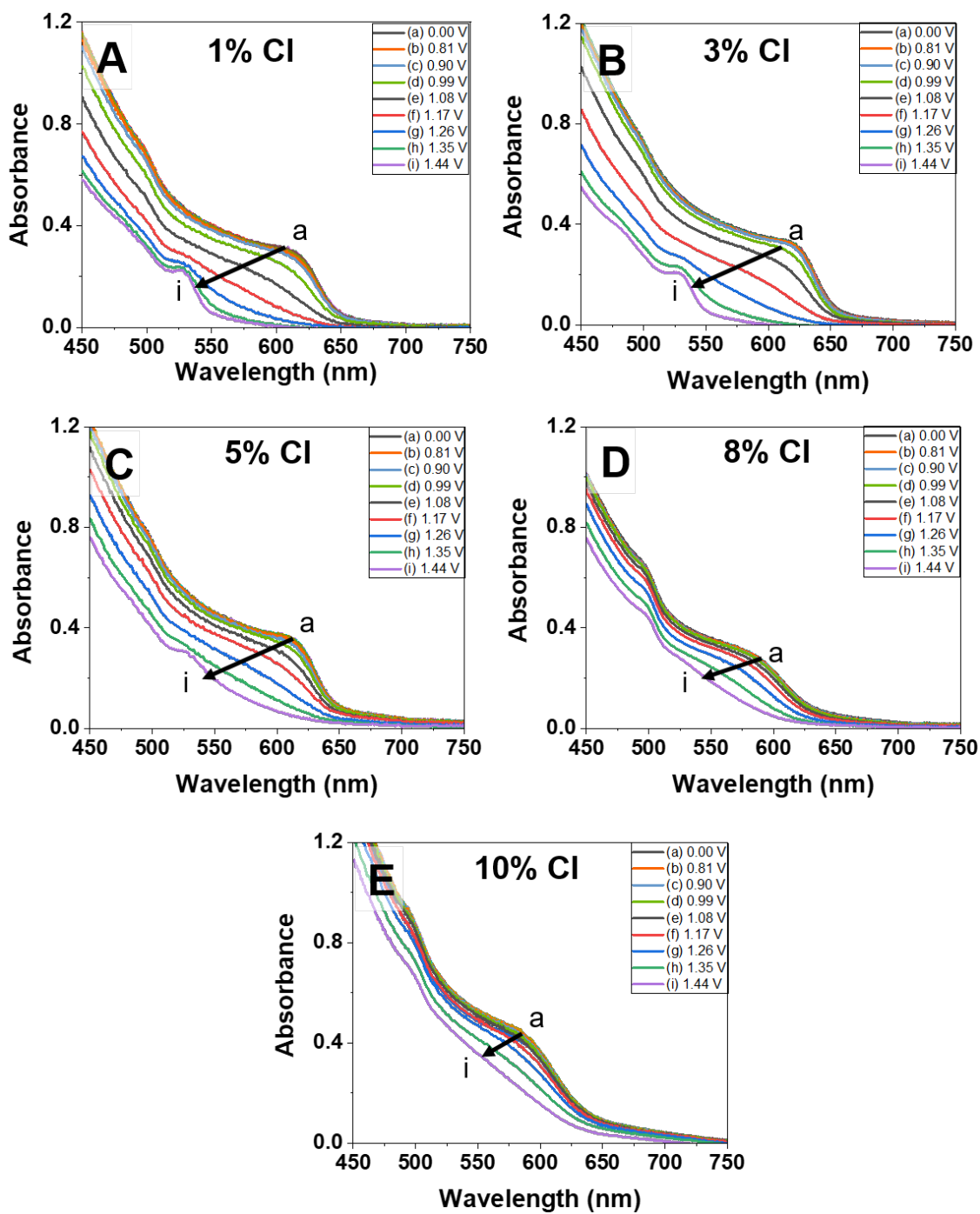
Fig. S7 (A-D) Absorption spectra changes recorded during stepwise application of potential between 0 V and + 1.44 V (a-i) versus Ag/AgCl in 0.01 M Bu_4NPF_6/DCM electrolyte for the FTO/MAPb($Cl_xBr_{0.5(1-x)}I_{0.5(1-x)}$)$_3$ films with different Cl concentration of 1% Cl (A), 3 % Cl (B), 5% Cl (C), 8% Cl (D), and 10% Cl (E).

References

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