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Controlling the Charge Carrier Dynamics by Modulating Orientation Diversity of Perovskites

Supporting Information

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Experimental Section

Time-Resolved Fluorescence Spectroscopy

A time-correlated single-photon-counting (TCSPC) system was used for measurements of spontaneous fluorescence decay. As an excitation light source, we used a mode-locked Ti: sapphire oscillator (Spectra Physics, MaiTai BB) which provides ultrashort pulse (tunable wavelenths from 710 to 990 nm with 80 fs at FWHM) with a high repetition rate of 80 MHz. This high repetition rate was reduced to 800 kHz by using a homemade pulse-picker. The pulse-picked output was frequency doubled by a 1-mm-thick BBO crystal (type-I, $\theta = 29.2$ °, EKSMA). The fluorescence was collected by a microchannel plate photomultiplier (MCP-PMT, Hamamatsu, R3809U-51) with a thermoelectric cooler (Hamamatsu, C4878) connected to a TCSPC board (Becker & Hickel SPC-130). The overall instrumental response function was about 25 ps (FWHM). A vertically polarized pump pulse by a Glan-laser polarizer was irradiated to samples, and a sheet polarizer set at an angle complementary to the magic angle (54.7 °), was placed in the fluorescence collection path to obtain polarization-independent fluorescence decays.

Flash-Photolysis Time-Resolved Microwave Conductivity Measurements

Transient photoconductivity was measured by an FP-TRMC setup. A resonant cavity with $Q \sim 2500$ was used to obtain a high degree of sensitivity in the conductivity measurement. Proving microwave frequency was set at ~9.1 GHz, such that the electric field of the microwave was sufficiently small not to disturb the translational motion of charge carriers. The observed value of photoconductivity converted to the product of the quantum yield f and the sum of charge-carrier mobilities $\Sigma\mu$ by $\phi\Sigma\mu = \Delta\sigma\ (eI_0F\text{light})^{-1}$, where e, I_0, Flight and $\Delta\sigma$ are the unit charge of a single electron, incident photon density of excitation laser (photons per m^2), a correction factor (m^{-1}) and transient photoconductivity, respectively. The sample was set at the point of electric field maximum in a resonant cavity. FP-TRMC experiments were performed at room temperature, and under N_2 saturated conditions by continuous flowing >10 min. The measurements of all the samples were performed on a quartz substrate.

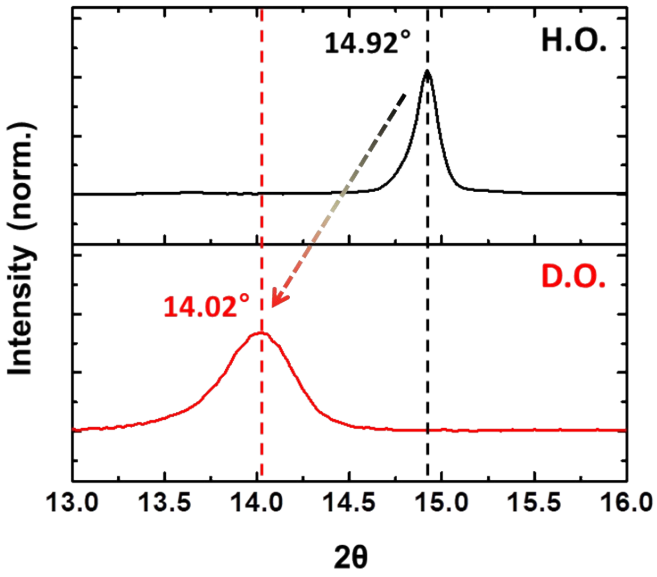

Fig. S1 XRD pattern of H.O. and D.O. perovskite films 2θ range from 13 to 16°.

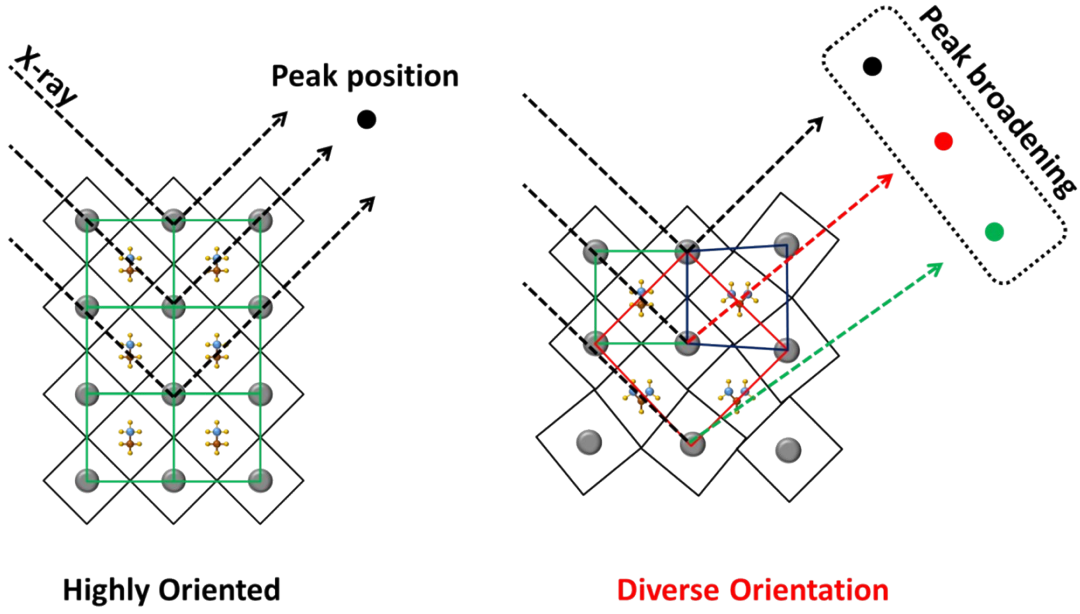

Fig. S2 Simplified illustration for the origin of XRD pattern broadening.

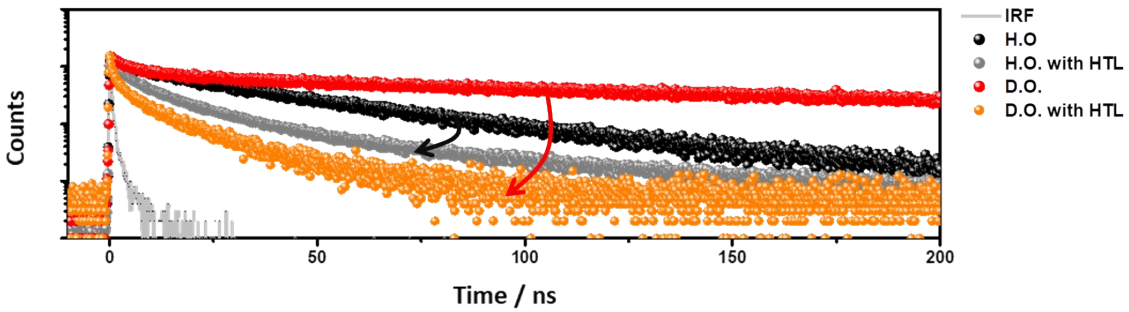

Fig. S3 Time-resolved PL decay profiles of H.O. and D.O. perovskite films with and without HTL layer at the photoexcitation of 470nm

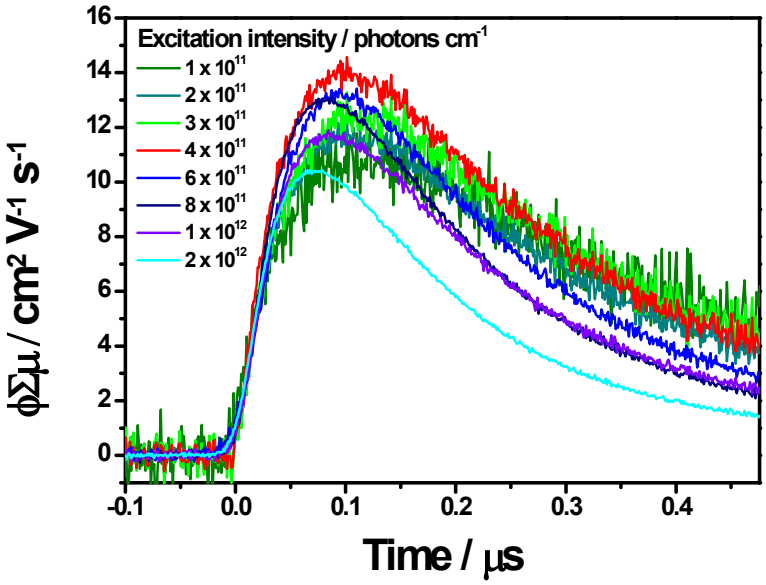

Fig. S4 Power-dependent FP-TRMC measurements for D.O. perovskite film. TRMC kinetics of D.O. upon exposure to 532 nm laser. The range of excitation intensity is 1 x 10^{11} – 2 x 10^{12} photons cm^{-2}.

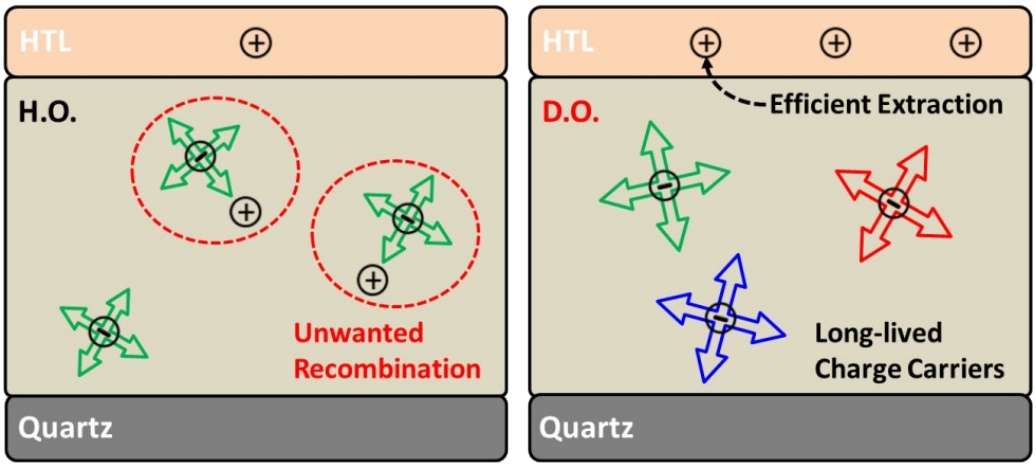

Fig. S5 Schematic illustrations of proposed behaviors of holes and electrons derived from a combination of TCSPC and FP-TRMC measurements.

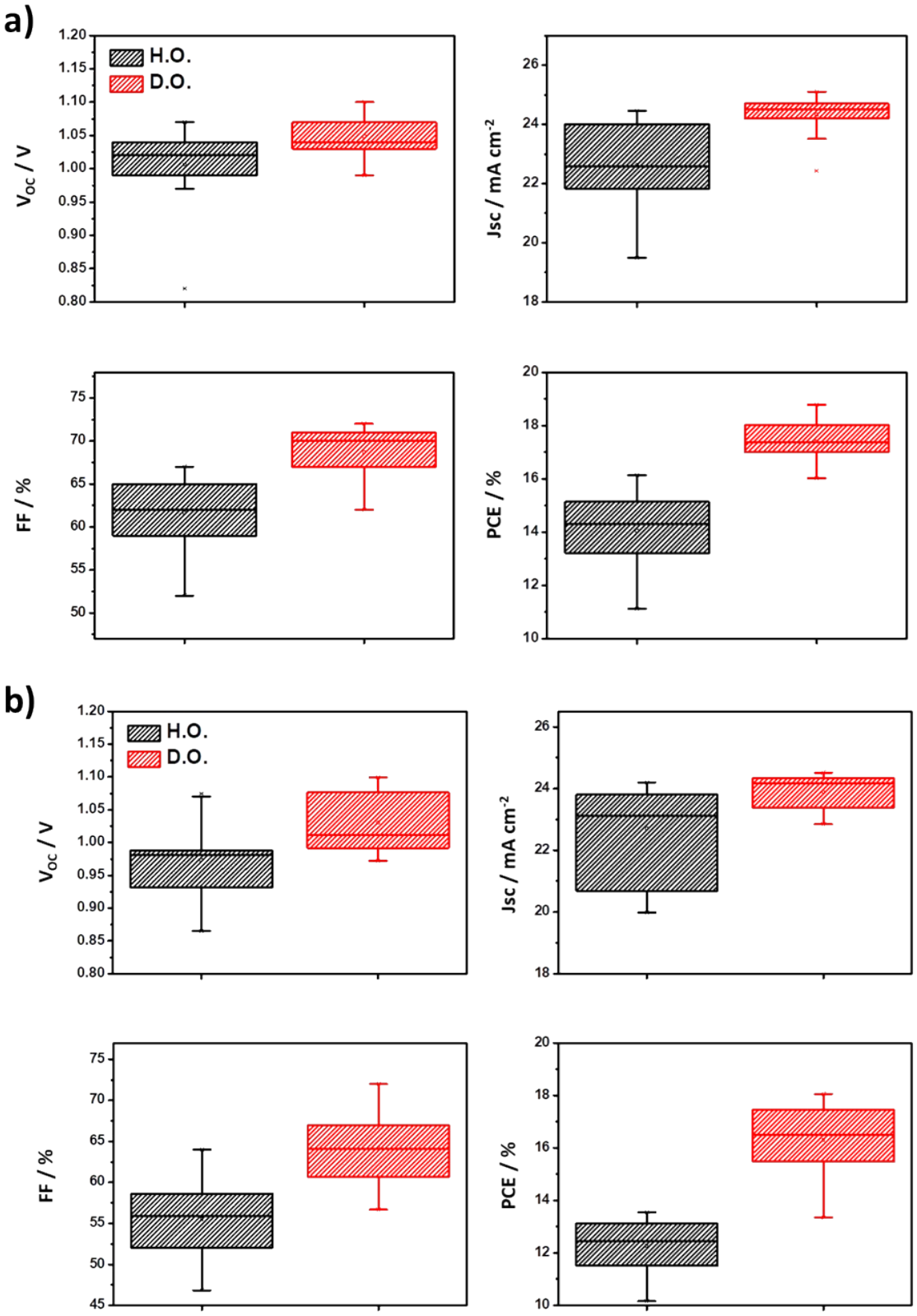

Fig. S6 Photovoltaic metrics of H.O. and D.O. perovskite solar cell devices. a) Reverse scans and b) Forward scans

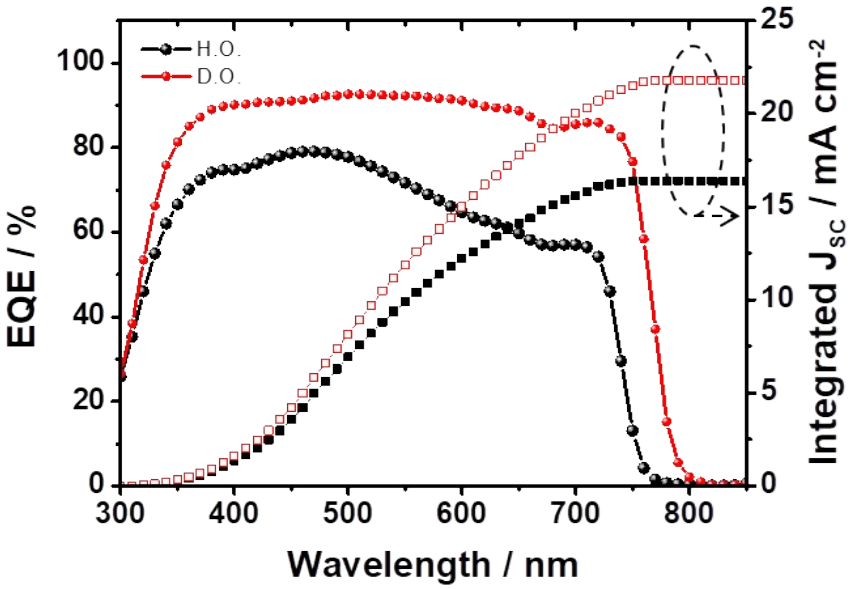

Fig. S7 External quantum efficiency (EQE) and intefrated J_{SC} spectra for the H.O. and D.O. perovskite-based solar cells.

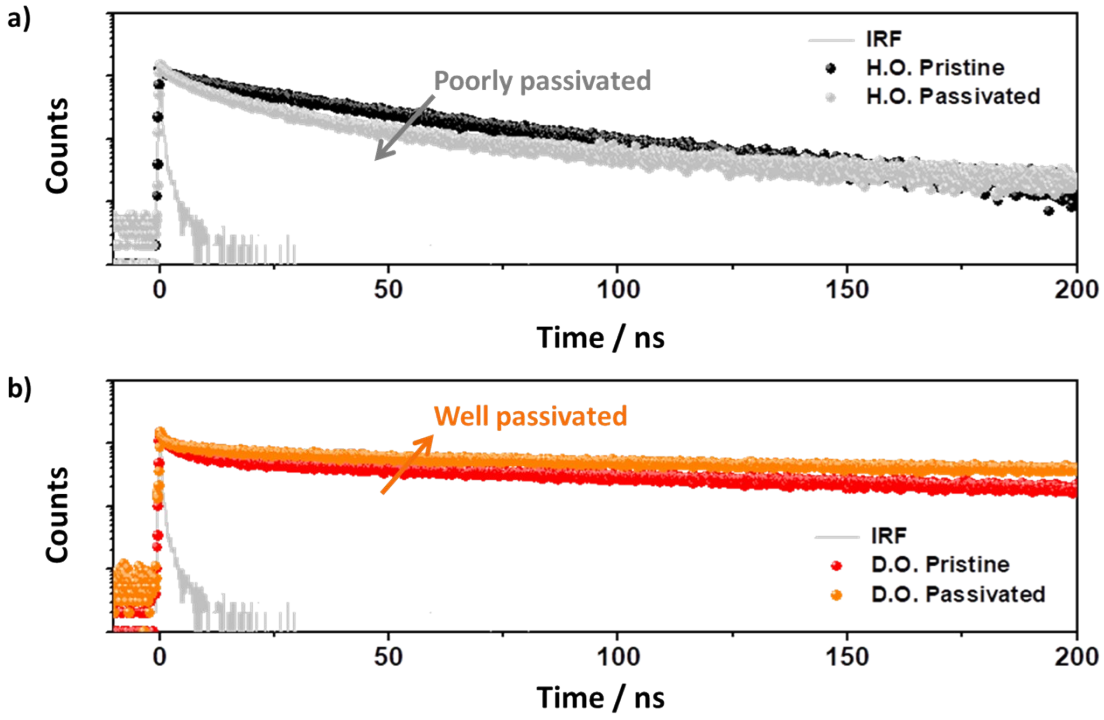

Fig. S8 Time-resolved PL decay profiles of pristine/passivated a) H.O. and b) D.O. perovskite films at the photoexcitation of 470 nm.