Supporting Information

Gamma Rays Induced Degradation in the Triple-cation Perovskite Solar Cells

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Experimental Details

Preparation of thin films and photovoltaic cells

Glass/ITO substrates (Kintek, 15 Ohm/sq.) were cleaned manually with toluene and acetone, sonicated in deionized water, acetone and isopropyl alcohol (IPA) for 10 min each, dried with air and subjected to additional plasma cleaning for 300 sec. A 1:1 solution of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS, Clevios PH) in deionized water was deposited statically on the cleaned substrates and spin-coated at 3000 rpm for 20 sec. Subsequently, samples were annealed for 20 min at 165 C in the air. The following procedures were performed entirely inside the nitrogen glove box to avoid exposure of the samples to the ambient atmosphere. 172.0 mg of formamidinium iodide (FAI), 507.1 mg of PbI_2, 22.2 mg of methylammonium bromide (MABr) and 73.4 mg of $PbBr_2$ were dissolved in 1 mL of 4:1 DMF/DMSO solvent mixture. Separately 390.0 mg of CsI in 1 mL of DMSO was prepared and 70 µl of that precursor was added to the mixture described above. The precursor solution was stirred for 2 hours at 75 °C for complete dissolving of all the components. 25 µL of the solution was deposited (dynamically) at 6000 rpm following by quenching with 60 µL of toluene (dropped 55 sec after perovskite precursor) applied at the same spin-coating frequency. The deposited $Cs_{0.15}MA_{0.10}FA_{0.75}Pb(Br_{0.17}I_{0.83})_3$ films were annealed for 3 min at 100 °C, which led to the development of a dark brown color. [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) was used as traditional electron transport material in perovskite solar cells. $PC_{61}BM$ (40 mg) was dissolved in 1 mL of chlorobenzene under stirring at 45 °C overnight and spin-coated at 2000 rpm. The samples were left for drying within 10 min inside the glove box before loading into the vacuum chamber for deposition of the top electrodes. Silver electrodes (100 nm) were evaporated in high vacuum (10-6 mbar) through a shadow mask defining the active area of each device as ~0.16 cm^2. The current-voltage characteristics of the devices were measured using Advantest 6240A source-measurement unit under the simulated 100 mW cm-2 AM1.5G solar irradiation provided Newport Verasol AAA class solar simulator. The intensity of the illumination was adjusted using a reference silicon diode of a known spectral response. The obtained current density (J_{sc}) values were reconfirmed by integrating the EQE spectra against the standard AM1.5G spectrum. The EQE spectra were measured using self-made setup based on optical components from LOMO instruments (Russia) and electrical equipment from Stanford Research Instruments.

Radiation stability tests

Radiation stability tests were performed in parallel for three different sets of samples: Glass/ITO/PEDOT:PSS; Glass/ITO/PEDOT:PSS/perovskite and Glass/ITO/PEDOT:PSS/ perovskite/$PC_{61}BM$. The prepared samples were packed in three layers of Al lamination foil (used to form cases for pouch-type Li-ion batteries) inside the argon glove box. Note that the packaging material was transparent for gamma rays. Each set consisted of 10 samples, which were exposed to 100, 200, 300, 400 and 500 Gy (2 samples per dose) with ^{137}Cs γ-ray source (Eγ = 662 keV) with a dose rate of 2.5 Gy/min. Two reference samples were left fresh, packed and exposed to the ambient atmosphere for the same time as irradiated samples. After exposure of the samples to γ-rays (or to the ambient atmosphere for the reference ones), they were introduced back in the glove box and the package was opened under the inert atmosphere. The samples (irradiated + reference) were further processed in one batch as described in the previous section to complete the p-i-n type perovskite solar cells of the following architecture: Glass/ITO/PEDOT:PSS/perovskite/$PC_{61}BM$/Ag. Characterization of the device was performed as described above.

Film characterization

The X-ray diffraction patterns were collected using Bruker XRD with Cu K_α source. Measurements were carried out in a fixed illumination mode with no rotation in the range of 5-60 degrees. Cypher ES microscope (Asylum Research, CA) was used to measure the surface potential and topography of the samples. The measurements were performed in a tapping mode under dry inert Ar atmosphere in a MBraun glovebox with O_2 and H_2O concentrations < 0.1 ppm. The samples were grounded through the ITO with conductive silver paint. Other details of the technique were reported previously.[19] UV-vis spectra were measured in inert atmosphere using AvaSpec-2048-2UV-VIS fiber spectrometer integrated with MBraun glove box. PL spectra were measured in inert atmosphere using Horiba spectrometer with 532 nm laser as excitation.

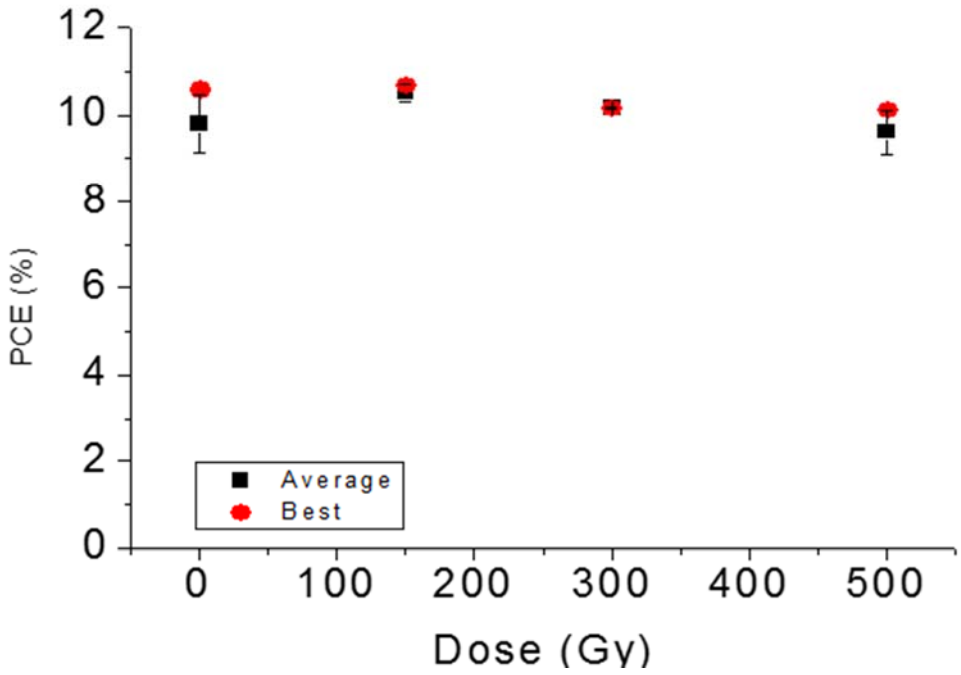
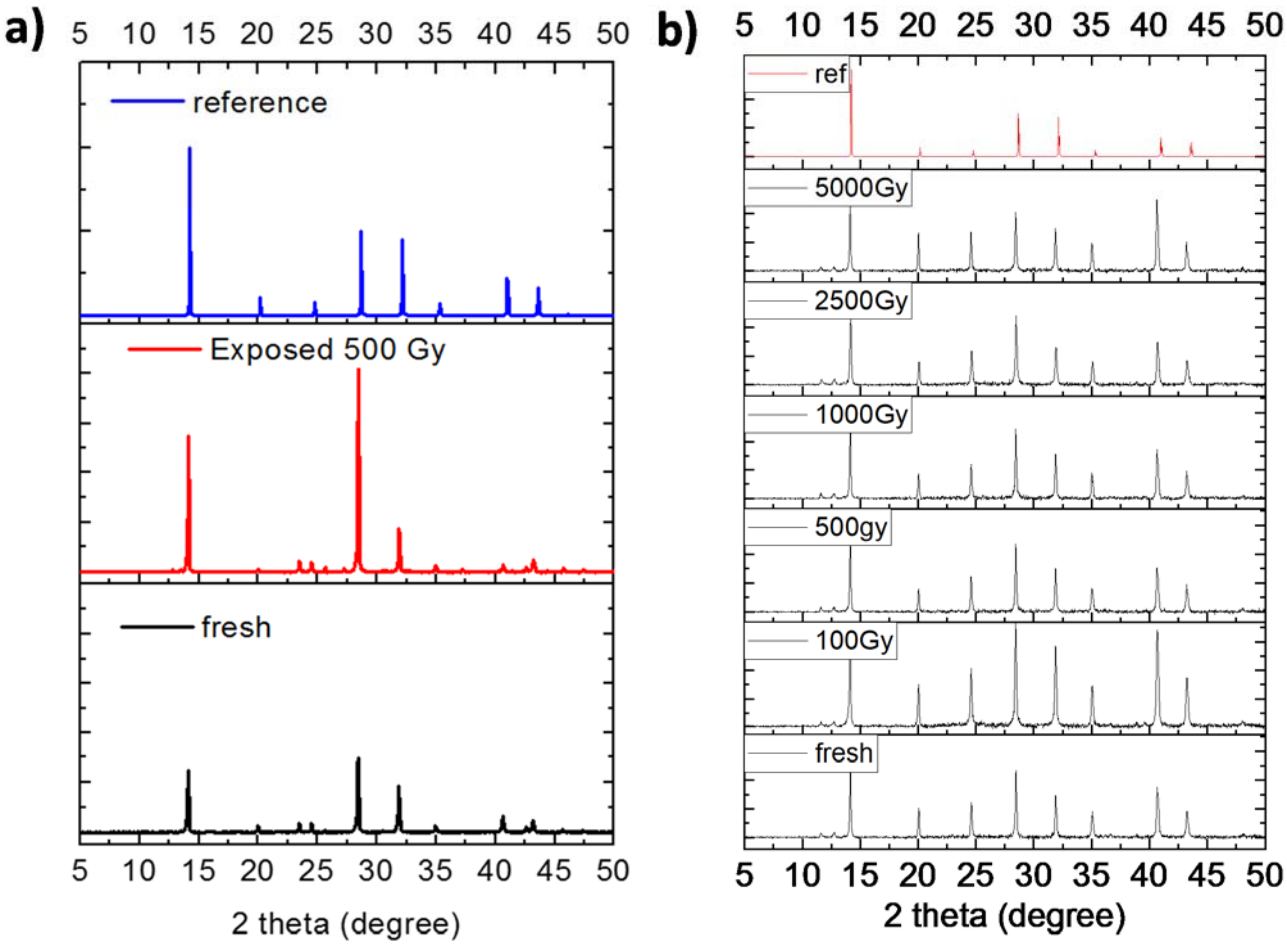


Figure S1. Power conversion efficiency of the devices based on the glass/ITO/PEDOT:PSS samples exposed to gamma rays as a function of the radiation dose.



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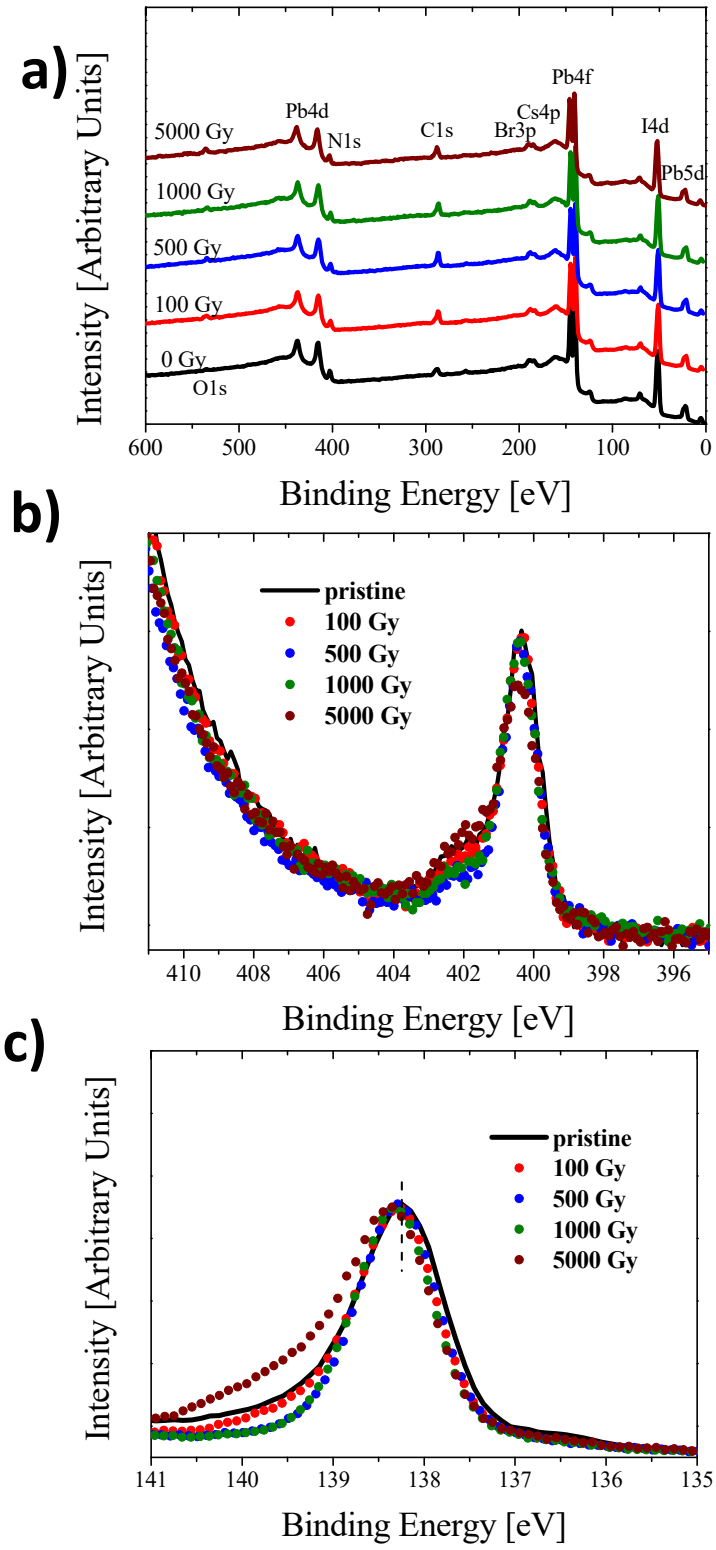

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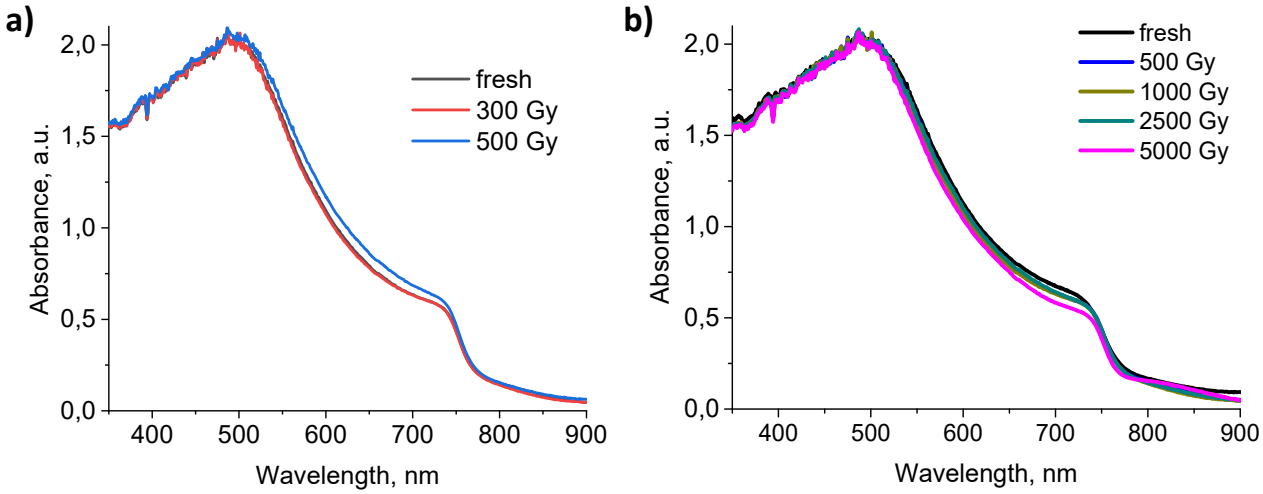

Figure S4. UV-vis spectra of the fresh and exposed (300 Gy and 500 Gy) Glass/ITO/PEDOT:PSS/perovskite samples (a). Evolution of the optical characteristics of the glass/perovskite samples under 100-5000 Gy radiation exposure (b).

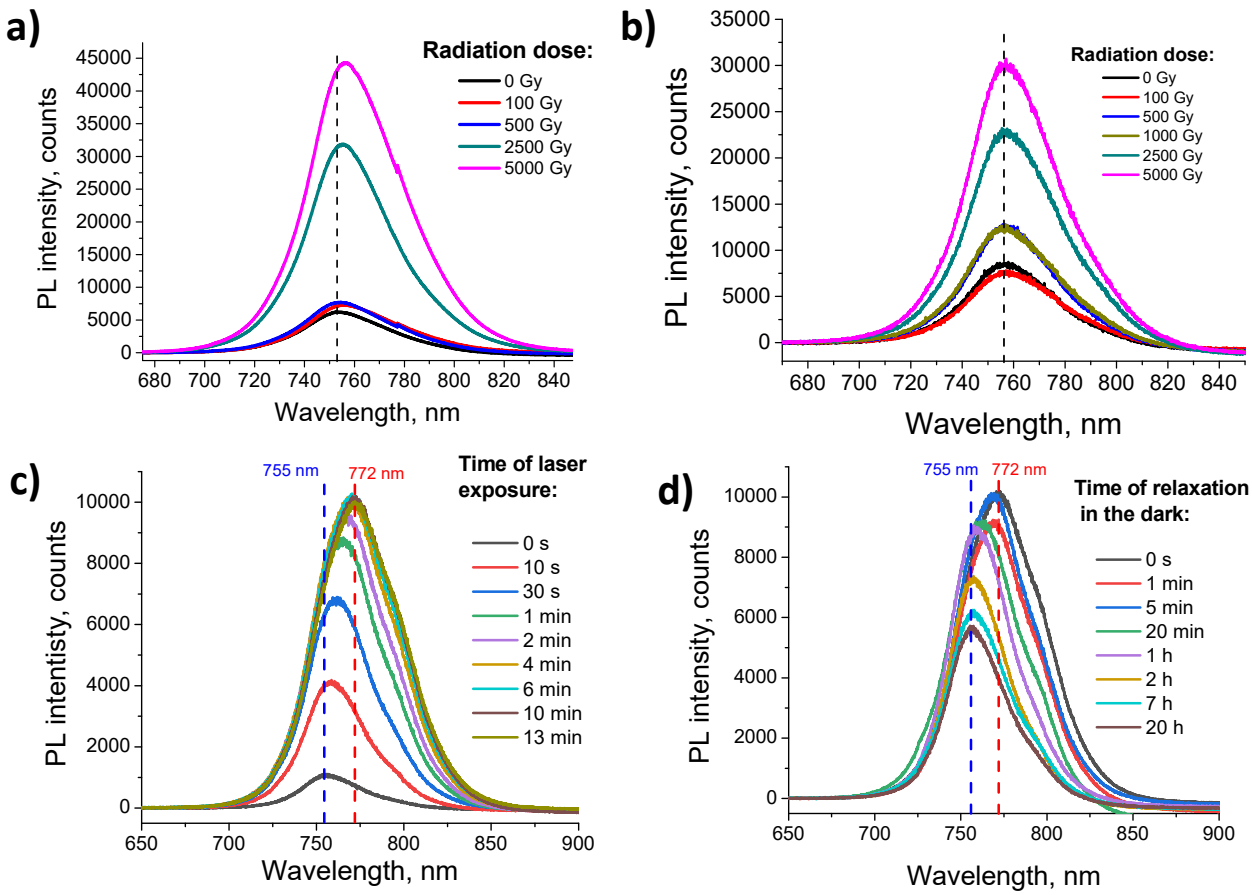

Figure S5. PL dynamics in the perovskite films induced by gamma rays (a-b) and green (532 nm) laser (c-d). Strong increase in the PL intensity accompanied with the red-shift of the emission band maximum as revealed 1 h after the radiation exposure (a) and the spectra of the same samples measured 2 weeks later showing a significant relaxation of the gamma rays-induced effects (b). Laser-induced PL dynamics in the perovskite sample characteristic for the Hoke effect (c) and its relaxation while storing the sample in the dark (d).

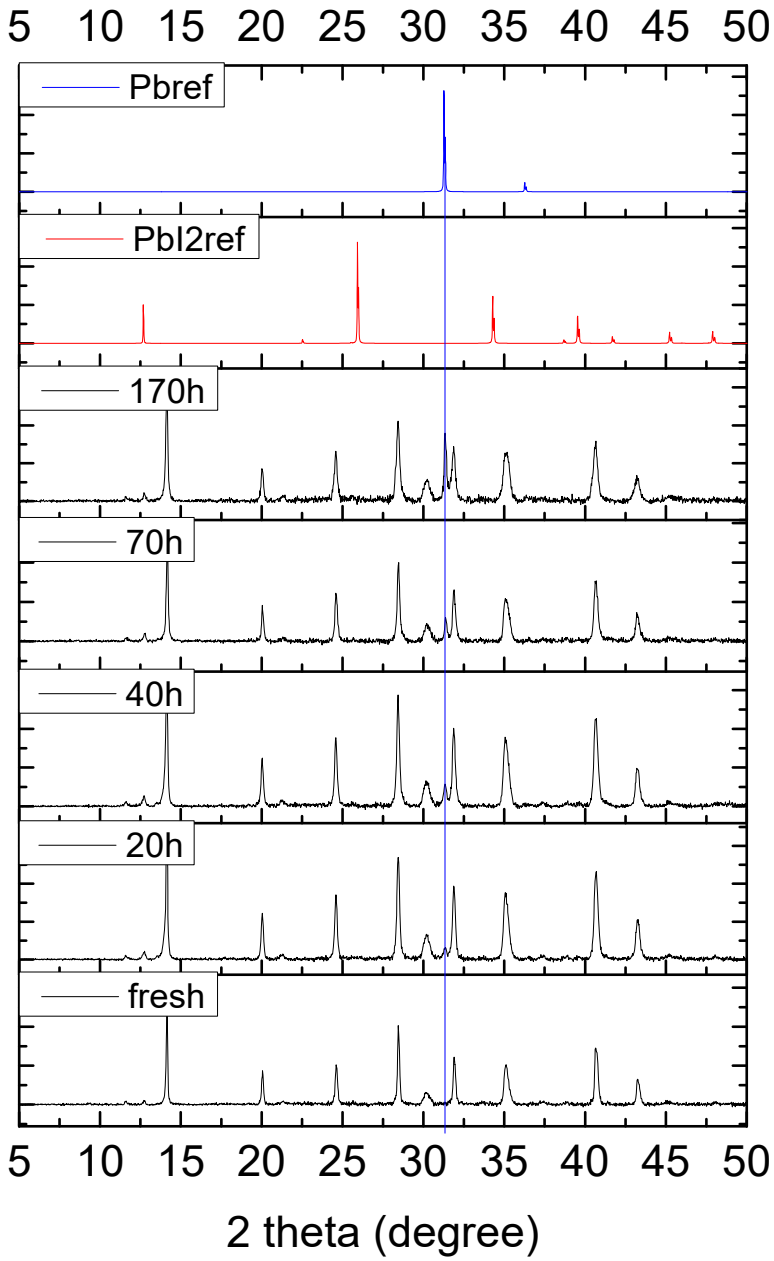

Figure S6. The dynamics of the XRD patterns for the Glass/perovskite sample exposed to white light illumination inside under inert atmosphere the glove box. Vertical blue line highlights the appearance of the peak characteristic for metallic lead (Pb(0)).

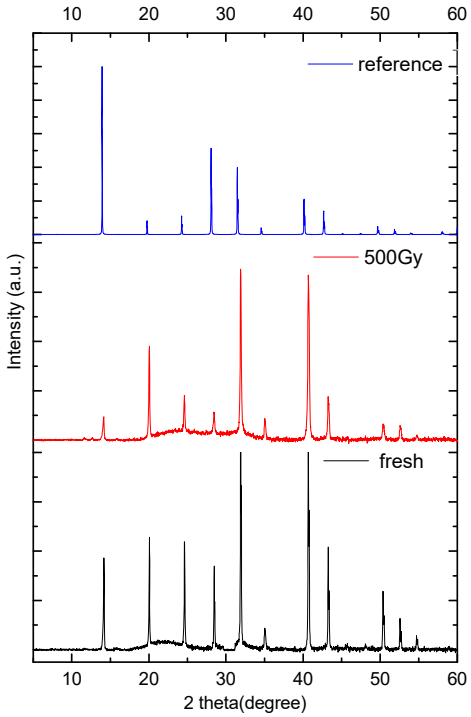

Figure S7. XRD patterns of the reference and 500 Gy exposed Glass/ITO/ PEDOT:PSS/perovskite/$PC_{61}BM$ samples. The reference XRD pattern of $MAPbI_3$ films is shown for comparison.

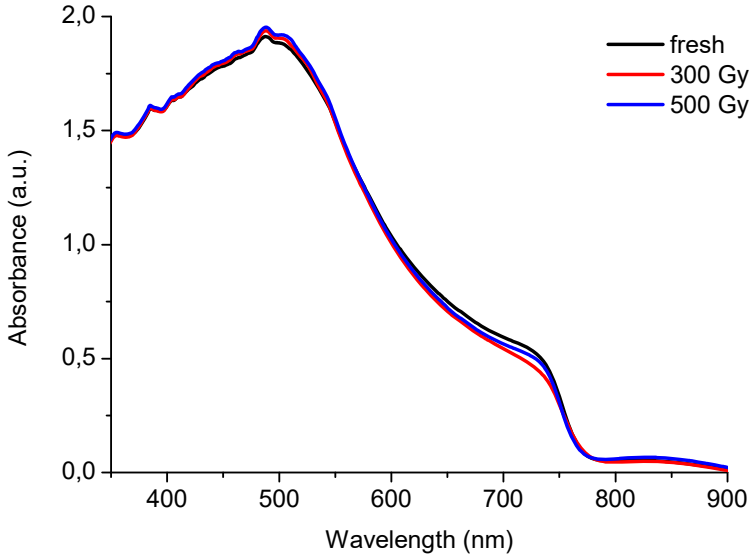

Figure S8. UV-vis spectra of glass/ITO/PEDOT:PSS/perovskite/$PC_{61}BM$ films exposed to 0-500 Gy.

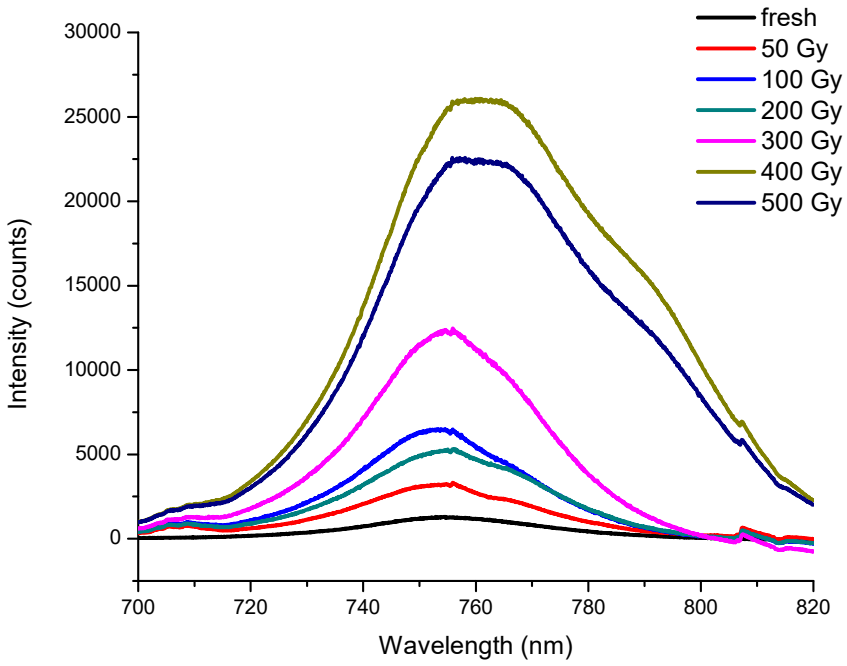

Figure S9. Photoluminescence spectra of glass/ITO/PEDOT:PSS/perovskite/$PC_{61}BM$ films exposed to 0-500 Gy.

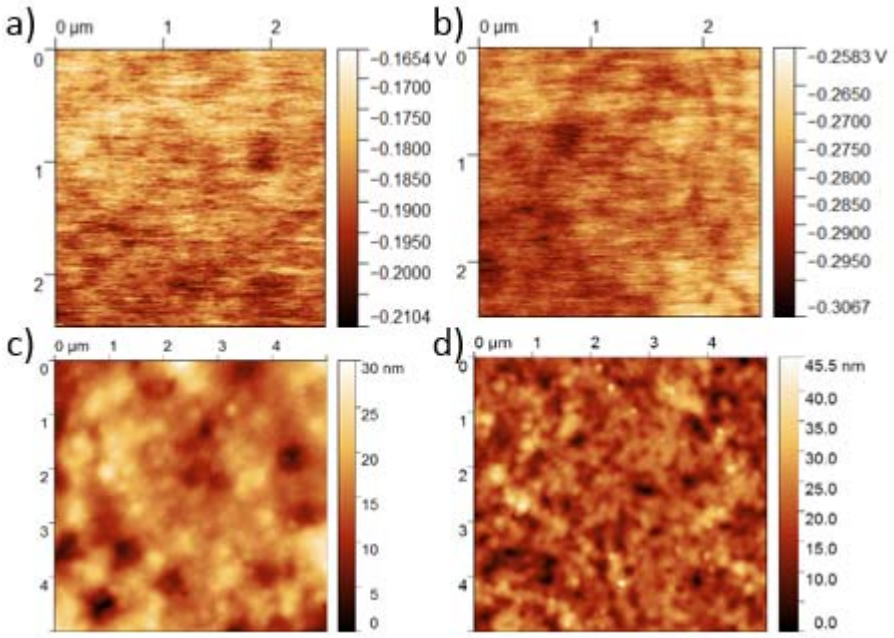

Figure S10. Surface potential (a, b) and topography (c,d) images of the reference (a,c) and exposed to 500 Gy (b, d) Glass/ITO/PEDOT:PSS/perovskite/$PC_{61}BM$ samples.

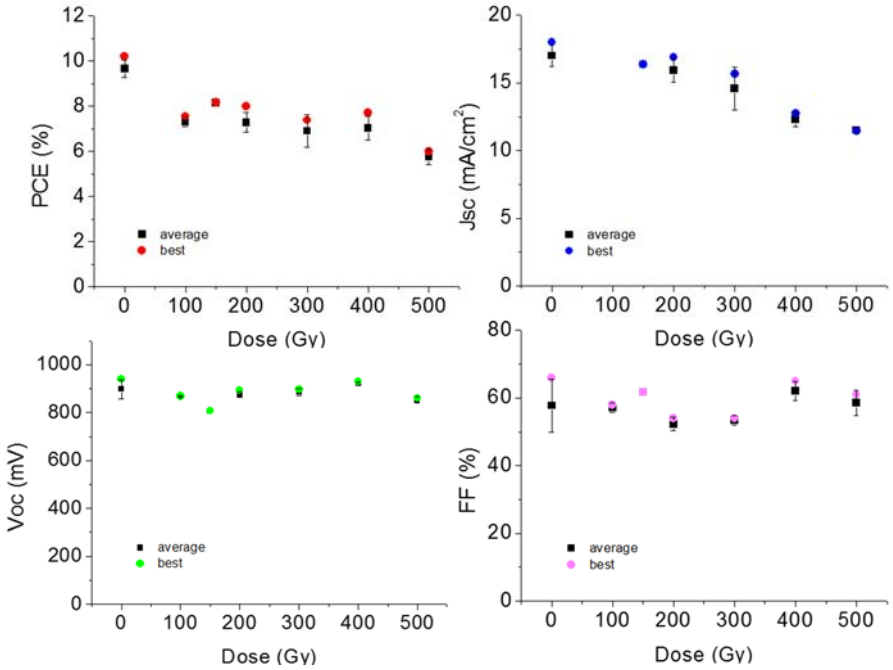

Figure S11. Characteristics of the devices as functions of the gamma radiation dose delivered to the glass/ITO/PEDOT:PSS/perovskite samples before assembling the solar cells.

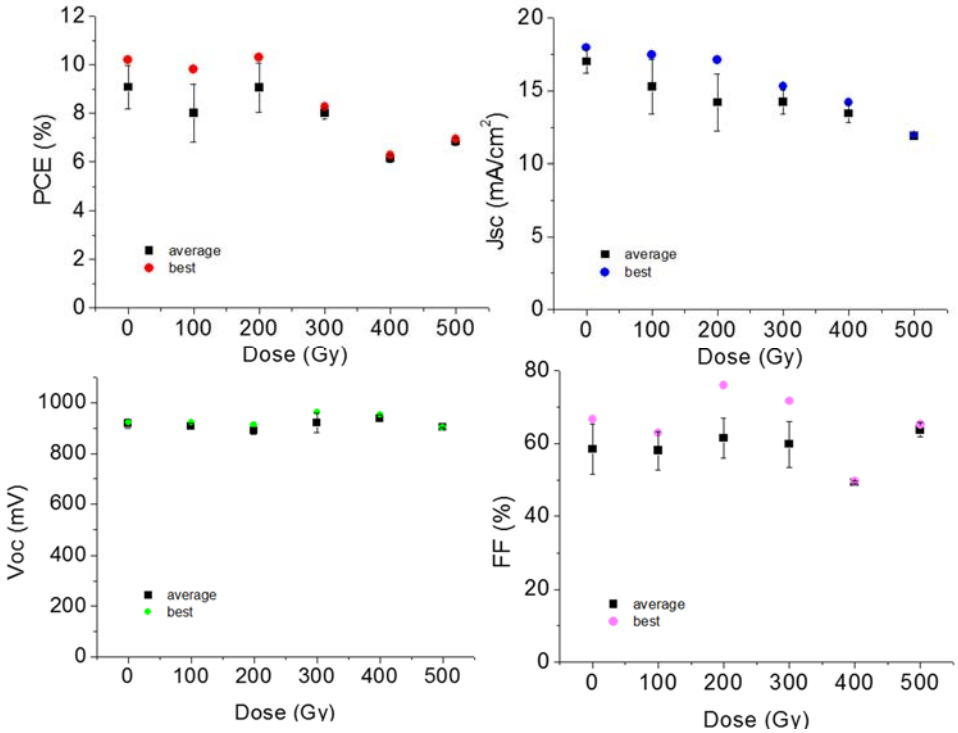

Figure S12. Characteristics of the devices as functions of the gamma radiation dose delivered to the glass/ITO/PEDOT:PSS/perovskite/$PC_{61}BM$ samples before assembling the solar cells.

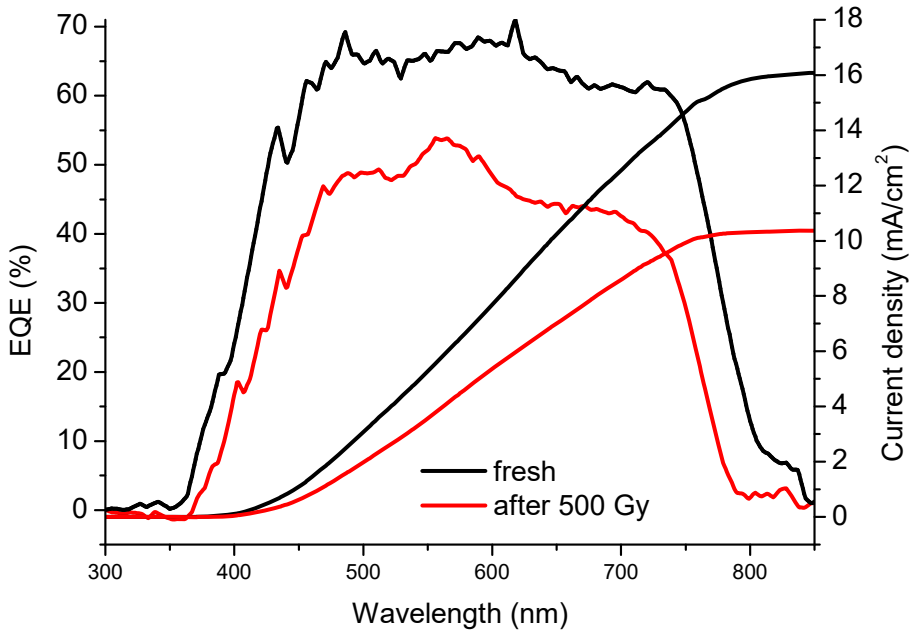

Figure S13. EQE spectra of the solar cells fabricated using reference glass/ITO/PEDOT:PSS/perovskite/$PC_{61}BM$ samples and exposed to 500 Gy dose of gamma rays.

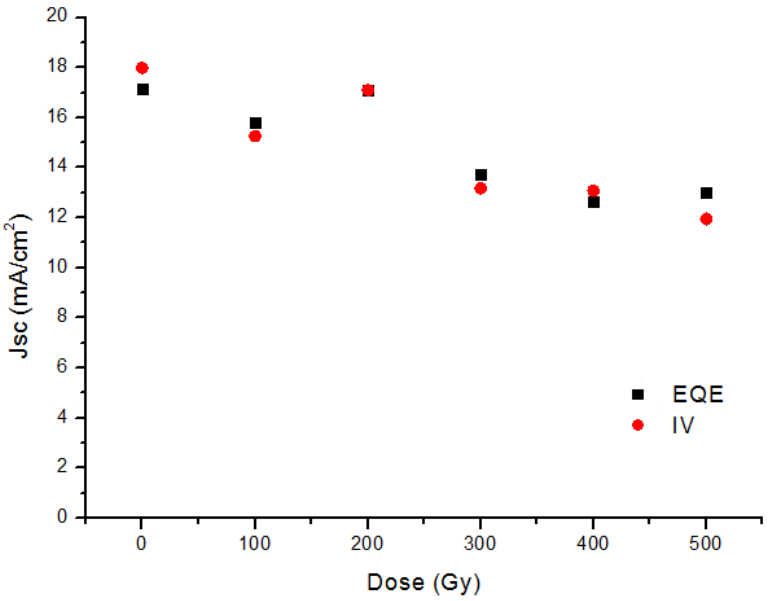

Figure S14. Comparison of J_{sc} values obtained from IV measurements and by integration of EQE against the standard AM1.5G solar spectrum for solar cells assembled using glass/ITO/PEDOT:PSS/perovskite samples exposed to different doses of radiation.

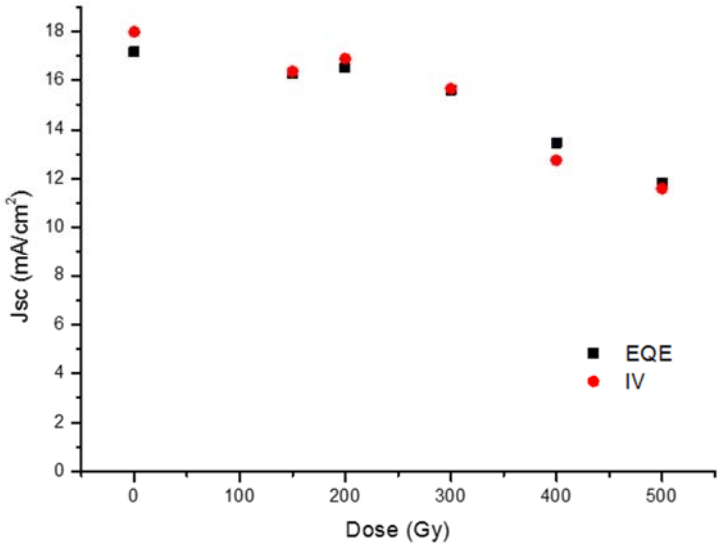

Figure S15. Comparison of J_{sc} values obtained from IV measurements and by integration of EQE against the standard AM1.5G solar spectrum for solar cells assembled using glass/ITO/PEDOT:PSS/perovskite/$PC_{61}BM$ samples exposed to different doses of radiation.

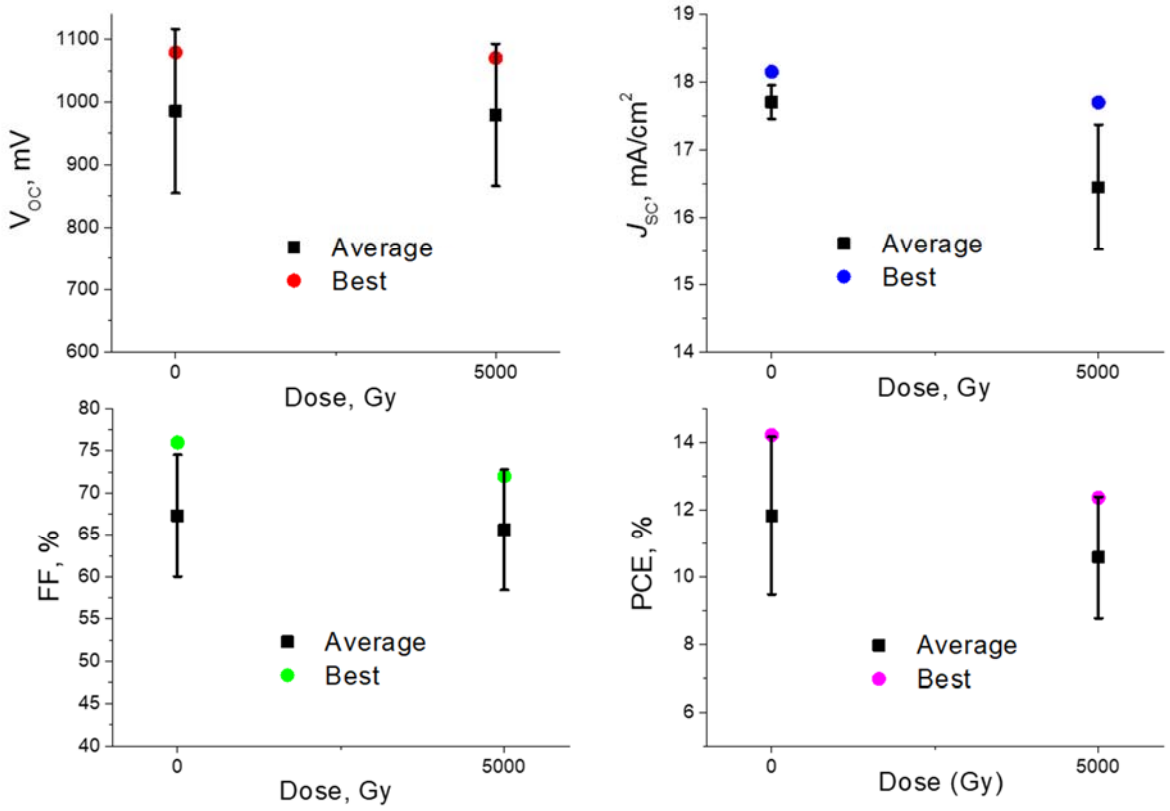

Figure S16. Characteristics of p-i-n glass/ITO/PEDOT:PSS/perovskite/$PC_{61}BM$/Ag solar cells fabricated using two different batches of $PC_{61}BM$: pristine (left column) and exposed to 5000 Gy of gamma rays (right column).