

Supporting Information: Improved Environmental Stability of Organic Lead Trihalide Perovskite-based photoactive-layers in the presence of mesoporous TiO₂

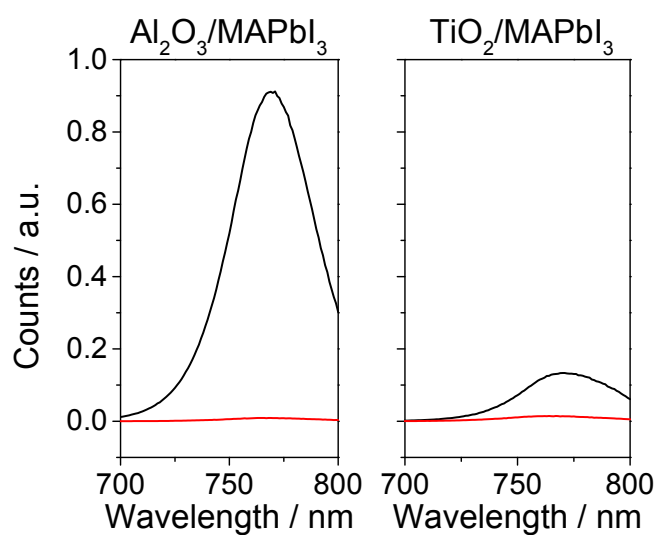


Figure S1 – Schematic to illustrate the photoluminescence quenching in Al₂O₃/MAPbI₃ and TiO₂/MAPbI₃ structures in the absence (black) and presence (red) of spiro-OMeTAD hole transporting material.

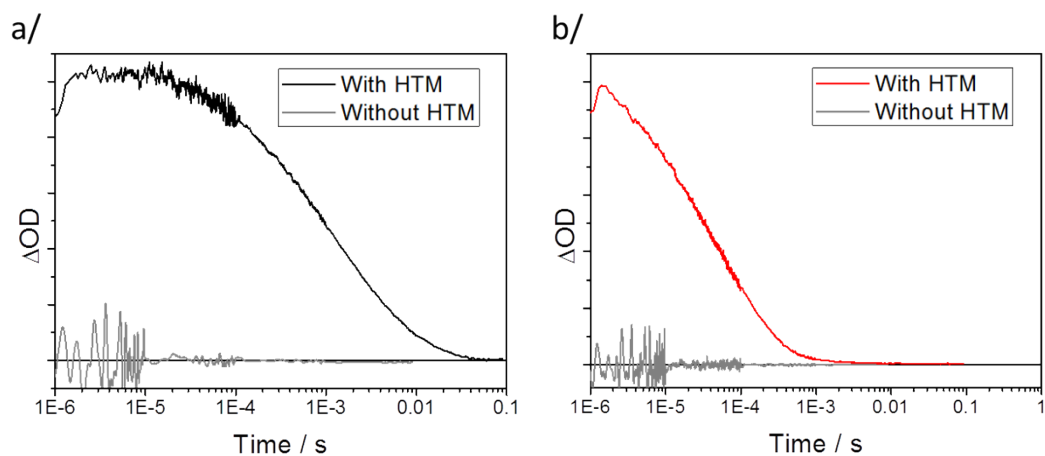


Figure S2. Shows transient kinetics monitored at 1600 nm following pulsed laser excitation (at 567 nm) in the absence and presence of a spiro-OMeTAD hole-transport material (HTM) in TiO_2 (left figure) and Al_2O_3 (right figure) based architectures. These data confirm that the positive signal at 1600nm is due to the transient existence of oxidized spiro-OMeTAD.

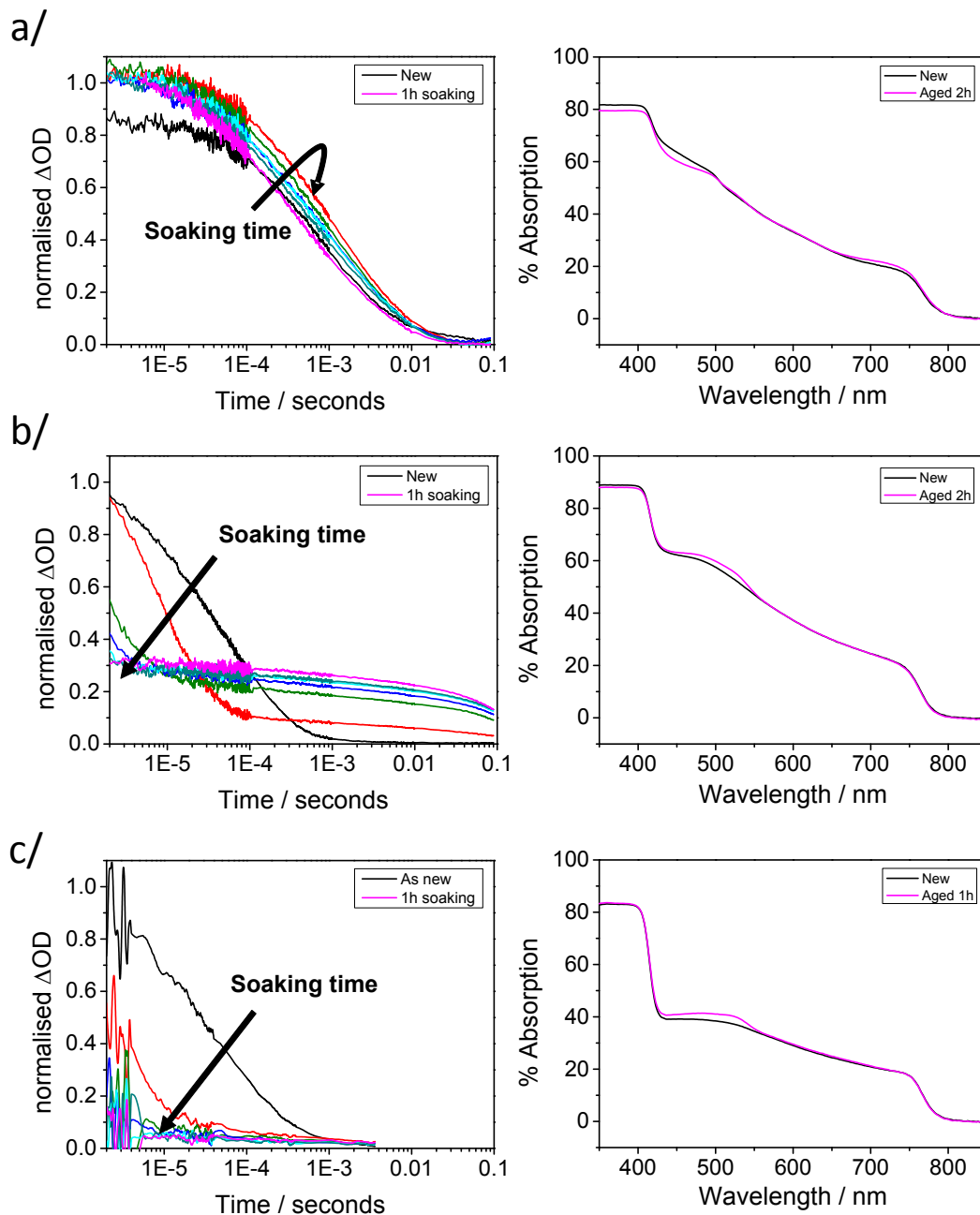


Figure S3 – Decay in transient absorption of *spiro*-OMeTAD holes at 1600 nm (left) and steady- state UV- vis absorption spectra (right) for a/ glass/mp-TiO₂/MAPbI₃/*spiro*-OMeTAD, b/ glass/mp-Al₂O₃/MAPbI₃/*spiro*-OMeTAD and c/ glass/MAPbI₃/*spiro*-OMeTAD as a function of soaking time in ambient light and air. All measurements recorded under flowing nitrogen. The black trace represents the pristine film, with red, green, blue, turquoise, pink and teal representing subsequent measurements recorded at regular intervals over the course of 1 hour. Laser photoexcitation was at 567 nm with an energy density of 24.5 $\mu\text{J cm}^{-2}$.

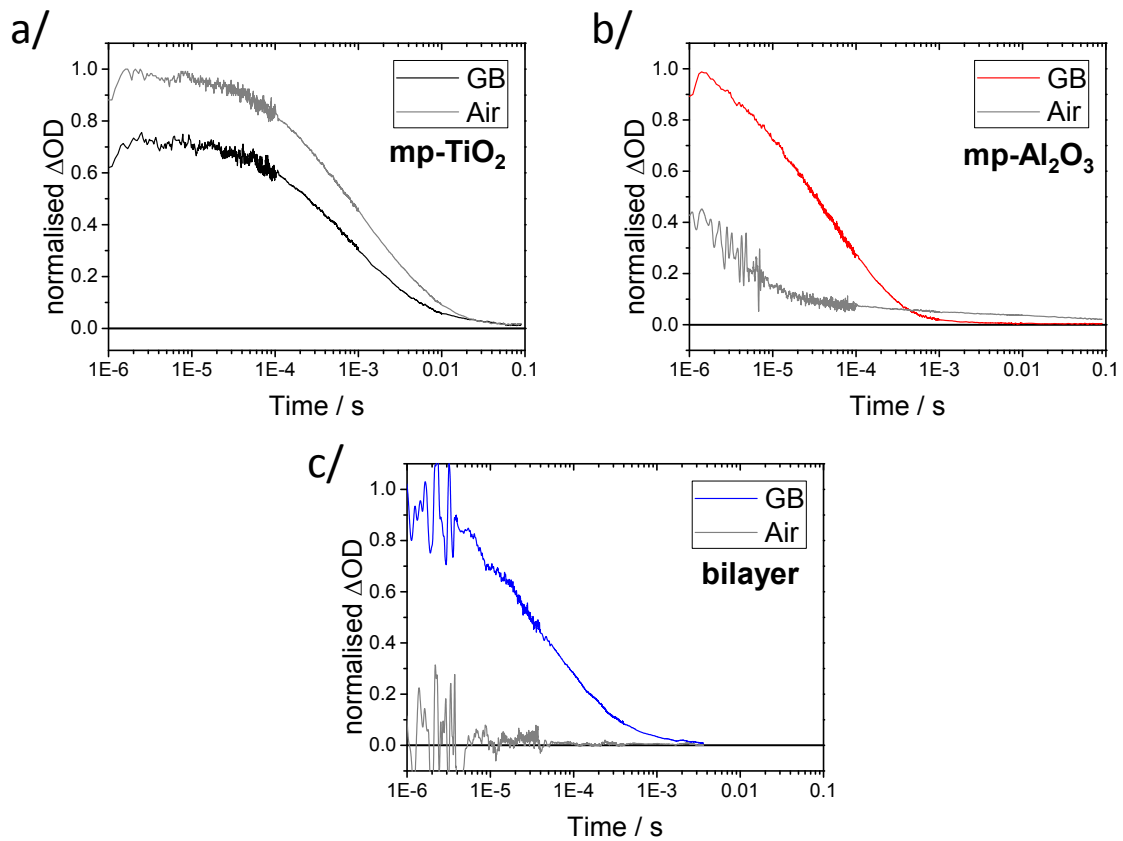


Figure S4 – Transient absorption signal at 1600 nm of as new MAPbI₃/spiro-OMeTAD films prepared in a glovebox (coloured) and in ambient conditions (grey) for the following architectures: a/ mesoporous TiO₂/ MAPbI₃/spiro-OMeTAD, b/ Al₂O₃/MAPbI₃/spiro-OMeTAD, MAPbI₃/spiro-OMeTAD bilayer. Laser excitation energy density = 25 $\mu J cm^{-2}$ at 567 nm.

Average device performance	V _{oc} (V)	J _{sc} (mA cm ⁻²)	Efficiency (%)	FF
TiO ₂ Before	-0.815	18.681	10.037	65.924
Al ₂ O ₃ Before	-0.952	17.481	10.119	60.689
TiO ₂ aged (72hrs dry air and light)	-0.816	15.509	7.286	57.68
Al ₂ O ₃ aged (72hrs dry air and light)	-0.854	11.886	5.032	58.68

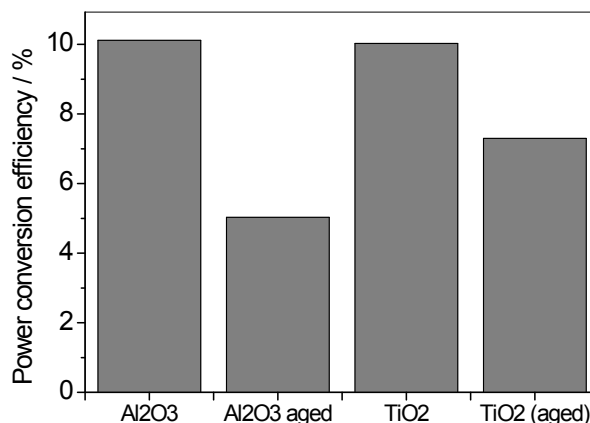


Figure S5 – Devices based on mesoporous TiO₂/ MAPbI₃/spiro-OMeTAD and mesoporous Al₂O₃/MAPbI₃/spiro-OMeTAD structures. The data shown here is an average of 11 devices. Table above gives device performance parameters before and after ageing. The data presented here suggests that the Al₂O₃/MAPbI₃/spiro-OMeTAD devices are more prone to oxygen and light exposure than the TiO₂/MAPbI₃/spiro-OMeTAD devices. The devices reported in this study were fabricated as follows. To make the organolead halide perovskite photovoltaic solar cells FTO glass had a compact layer of TiO₂ deposited by spin-coating a weakly acidic solution containing 0.25 mM titanium (IV) isopropoxide in ethanol. The layer was then sintered at 500 °C for 30 minutes on a hotplate before slowly cooling to room temperature. The resulting layer thickness of the dense TiO₂ coating is approximately 50 nm. For titania based devices a TiO₂ scaffold was deposited by spin coating a diluted paste of TiO₂ nanoparticles and subsequent sintering at 450 °C to give a film thickness of 350nm. For alumina based devices an Al₂O₃ porous scaffold was deposited by spin-coating a suspension of <50 nm Al₂O₃ nanoparticles in isopropanol before drying at 150 °C for 30 minutes. A perovskite precursor solution containing methylammonium iodide and PbI₂ (3:1 molar ratio) was spin coated onto the scaffolds and annealed on a hotplate at 100 °C for 90 minutes in a <0.1 ppm O₂ and H₂O atmosphere. The hole transport layer (HTL) was deposited by spin-coating a solution containing 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (Spiro-OMeTAD) onto the perovskite surface. Au was evaporated onto the HTL layer using a Kurt J. Lesker Nano 36. For device testing the cells were masked to a 2.5x2.5mm area. All the devices were stored and measured unsealed.