

Alq3 (Tris(8-hydroxyquinolinato)aluminium) as Selective N-Type Contact for FAMAPIBr Perovskite Solar Cell with Efficient Energy Transfer to Increase the Solar Cell Photocurrent

Maria Méndez,^a and Emilio Palomares^{a,b}

(SUPPORTING INFORMATION)

^aThe Institute of Chemical Research of Catalonia (ICIQ). The Barcelona Institute of Science and Technology (BIST). Avda. Països Catalans, 16. Tarragona. E-43007. Spain.

^bICREA. Passeig Lluís Companys, 23. Barcelona. E-08010. Spain

† To whom the correspondence must be address: epalomares@icq.es

Solar cell preparation

Substrate preparation. The fluorine-doped tin oxide-coated glass substrates (FTO, sheet resistance $8 \Omega/\text{cm}^2$) were previously etched using Zn powder (Alfa Aesar 98%) and a 2 M solution of HCl according to the desired pattern. Then, the FTOs substrates were sequentially cleaned in an ultrasound bath using Hellmax soap in deionized water, deionized water and ethanol. They were dried and treated with UV/Ozone. After 20 min of treatment, compact TiO_2 was made from 0.65 ml of Ti(IV) isopropoxide (Sigma Aldrich 97%) and 0.38 ml of acetylacetone (Sigma Aldrich) mixed in 5 ml of ethanol and spin coated at 3000 rpm for 60 s over the FTO, and the substrates were then sintered at 500°C for 30 min. Afterwards, 10, 25 and 50 nm of tris(8-hydroxyquinolinato) aluminium (Alq3) was deposited by thermal evaporation on c- TiO_2 with the exception of one used as reference cell.

$\text{FA}_{1-x}\text{MA}_x\text{Pb}(\text{I}_{1-y}\text{Br}_y)_3$ deposition. The perovskite solution was prepared by mixing PbI_2 (Sigma Aldrich 99%), PbBr_2 (Sigma Aldrich 99.999%), FAI and MABr in a mixed solvent of DMF and DMSO with a volume ratio of 4:1. FAI and MABr were synthesized following a previous report of D. Bi et al.¹. The solution with 1.35 M Pb^{2+} (PbI_2 and PbBr_2) contained the following molar ratios: 0.85:0.15 for $\text{PbI}_2/\text{PbBr}_2$, 1:1 for MABr/ PbBr_2 and 1.16 for PbI_2/FAI . The perovskite layer was deposited by spin coating 80 μl on compact titania: first, 3000 rpm for 50 s at $400 \text{ rpm}\cdot\text{s}^{-1}$; second, 2000 rpm for 10 sec at $400 \text{ rpm}\cdot\text{s}^{-1}$. 100 μl of chlorobenzene was dropped on the spinning substrate during the first spin-coating step 20 s before the end of the procedure. The substrates were heated at 100°C for 1h on a hotplate.

Spiro-OMeTAD and contact metal deposition. After cooling down to room temperature, the Spiro-OMeTAD (1-Material) was subsequently deposited on top of the perovskite layer by spin coating at 3000 rpm for 45 s. 72.3 mg of Spiro-OMeTAD was dissolved in 1 ml of chlorobenzene, with the addition of 30mM bis(trifluoromethanesulfonyl)imide (from a stock solution of 520 mg/ml of LiTFSI in acetonitrile) and 200 mM tert-butylpyridine. Finally, FK209 tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III)tris(bis(trifluoromethylsulfonyl)imide); the molar ratio for FK209 and Spiro-OMeTAD was 0.03. Finally, 120 nm of silver was deposited by thermal evaporation. The perovskite and hole transporting material were deposited into a glove box with $\text{O}_2/\text{H}_2\text{O} < 0.1 \text{ ppm}$.

Solar cell characterization

The current density vs voltage (J-V) curves were obtained using a Sun 200 solar simulator (150 W, ABET Technologies), with the appropriate filters to simulate the AM 1.5G solar spectrum. The light intensity was calibrated with a silicon photodiode (NREL) to obtain $100 \text{ mW}\cdot\text{cm}^{-2}$ of light intensity. The IV curves were registered with a Keithley digital 2400 Source Meter and plotted automatically with a home-built Labview© software. The scan rate conditions were $81 \text{ mV}\cdot\text{s}^{-1}$. PIT-PV, PIT-PC and PIDC measurements were carried out using a white light LED ring LUXEON® Lumileds and the signal is measured in an oscilloscope Yokogawa DLM2052 registering drops in voltage. All devices were measured in a sealed holder under a N_2 atmosphere. All measured Voc decays were performed in steady state according to the Voc stabilization time of each device. The measurement of incident photon-to-current conversion efficiency (IPCE) was plotted as a function of the excitation wavelength using the incident light from a 300 W xenon lamp (ILC Technology), which was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd.).

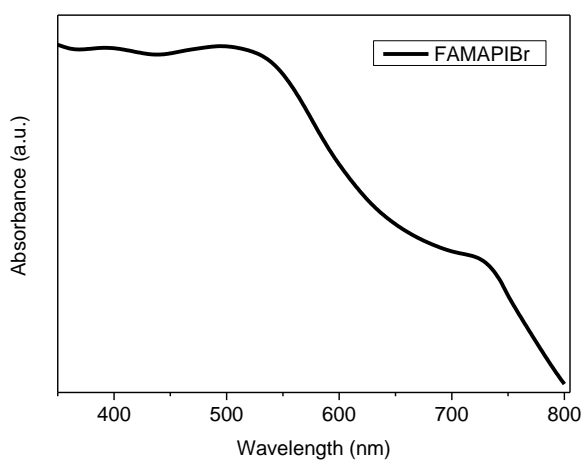
For the UV, PL and TCSPC experiments, Alq3, FAMAPIBr and Alq3 coated FAMAPIBr films were deposited on glass. The UV-Visible and fluorescence spectra were recorded on a Shimadzu Corporation UV 2401 and on Spectrofluorimeter Fluorolog Horiba Jobin Yvon. The PL spectrum was recorded by exciting the Alq3 film deposited on glass at 405 nm with a standard Xenon lamp. Finally, the Time Correlated Single Photon Counting (TCSPC) was recorded in an Edinburgh Instruments© LifeSpec-II spectrometer with a PMT detector and a laser excitation source pulsed at 405 nm. For studying the energy transfer from Alq3 to FAMAPIBr the samples were illuminated under ambient conditions from the glass face and monitored either at 540 or at 780 nm. The FAMAPIBr film was illuminated from the film face and monitored 780 nm.

S1. Summary of the mean values and the standard deviation of the devices below the performance parameters of the highest performance.

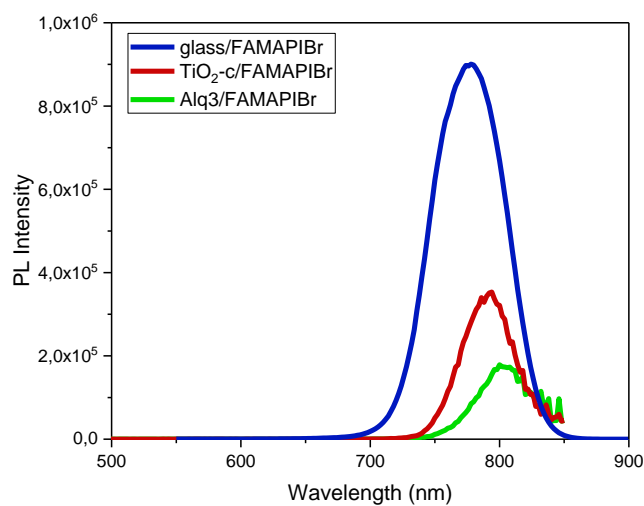
Device - ETL	Scan	Jsc (mA/cm ²)	Voc (V)	FF	PCE (%)
TiO ₂ -c/Alq3-10nm		23	0.775	0.43	7.71
	Mean	22.98 ± 0.91	0.820 ± 0.06	0.38 ± 0.03	6.9 ± 0.65
		22.85	0.90	0.53	11.02
Mean	Rev	22.70 ± 0.84	0.919 ± 0.04	0.47 ± 0.05	9.40 ± 1.44
TiO ₂ -c/Alq3-25nm		22.45	0.853	0.44	8.51
	Mean	21.7 ± 1.10	0.79 ± 0.03	0.37 ± 0.04	6.53 ± 1.25
		22.36	0.950	0.53	11.45
	Mean	21.46 ± 1.13	0.900 ± 0.03	0.48 ± 0.04	9.38 ± 1.50
TiO ₂ -c/Alq3-50nm		24.93	0.793	0.41	8.13
	Mean	24.81 ± 1.78	0.766 ± 0.04	0.34 ± 0.06	6.52 ± 1.63
		Rev	24.24	0.954	0.53

Mean		24.23 ± 2.02	0.927 ± 0.03	0.45 ± 0.07	10.11 ± 1.90
Ref Cell		24.87	1.020	0.42	10.76
	Fw				
Mean		22.78 ± 2.02	0.96 ± 0.07	0.35 ± 0.06	7.87 ± 2.29
		24.30	1.065	0.53	13.83
	Rev				
Mean		22.43 ± 1.82	1.007 ± 0.07	0.44 ± 0.08	10.29 ± 2.99

S2. Absorption of FAMAPIBr film deposited on glass.



S3. Steady-state photoluminescence measurements of FAMAPIBr layer on glass, TiO₂-c and Alq₃.



1. D. Bi, W. Tress, M. I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J.-P. Correa Baena, J.-D. Decoppet, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel and A. Hagfeldt, *Journal*, 2016, **2**.