Supporting Information

“Power conversion efficiency improvement of planar organic photovoltaic cells using an original hybrid electron transporting layer.”

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Supporting information S.1.

S.1.1. Organic photovoltaic scheme

![Organic photovoltaic scheme diagram](image)

Electron transporting Layer: Alq₃ or K/Alq₃.

**Figure S1.** Organic photovoltaic scheme

S.1.2. Organic molecules

![Organic molecules](image)

**Figures S2.** Organic molecules

S1
S.1.3. Longitudinal structure

Figure S3. Longitudinal structure (taken by J. C. Bernède)

The averaged value of the resistivity was around $5 \times 10^7 \, \Omega \, \text{cm}$ in the case of Alq$_3$ layer and $3.5 \times 10^4 \, \Omega \, \text{cm}$ in the case of K/Alq$_3$ structure. It confirms that the presence of K decreases the resistivity of the EBL by three orders of magnitude.

Supporting information S.2. Organic photovoltaic cells deposition process:

After scrubbing with soap, the ITO coated glass substrates were rinsed in running deionised water. Then the substrates were dried with an argon flow and loaded into a vacuum chamber.

All the layers were deposited in a vacuum of $10^{-4} \, \text{Pa}$. The thin film deposition rates and thicknesses were measured \textit{in situ} with a quartz monitor.

Following earlier studies, the deposition rate and final thickness were $0.05 \, \text{nm/s}$ and $6 \, \text{nm}$ for MoO$_3$, $16 \, \text{nm}$ and $0.03 \, \text{nm/s}$ for SubPc, $0.05 \, \text{nm/s}$ and $40 \, \text{nm}$ for C$_{60}$ and $0.1 \, \text{nm/s}$, $9 \, \text{nm}$ for Alq$_3$. After organic thin film deposition, the aluminium top electrodes were thermally evaporated, without breaking the vacuum, through a mask with $2 \, \text{mm} \times 8 \, \text{mm}$ active areas.

Supporting information S.3. Electrical characterization of the organic photovoltaic cells:

S.3.1. Electrical characterization was performed with an automated I-V tester, in the dark and under sun global AM 1.5 simulated solar illumination. Performances of photovoltaic cells were measured using a calibrated solar simulator (Oriel 300W) at $100 \, \text{mW/cm}^2$ light intensity adjusted with a PV reference cell ($0.5 \, \text{cm}^2$ CIGS solar cell, calibrated at NREL, USA).

Measurements were performed at an ambient atmosphere. All devices were illuminated through TCO electrodes.

The slopes of the electrical characteristics at the short circuit point and at the open circuit voltage are the inverse values of the shunt resistance ($R_{sh}$) and the series resistance ($R_s$) cell respectively.

S.3.2. External Quantum Efficiency (EQE) was also measured on apparatus built up in our laboratory. The measurements of incident photon-to-current conversion efficiency are done with monochromatic continuous light without modulation. The measurement duration for a given wavelength was long enough to reach a steady-state value and to minimize noise.

Supporting Information S.4. Organic stacked layers characterizations

S.4.1. The morphology of the layers was observed by scanning electron microscopy (SEM). The surface and layer cross sections were observed through scanning electron microscopy with a field emission scanning electron microscope (JSM JEOL 7600F). Secondary electron images (SEI)
and backscattered electron images (BEI) have been done. The presence of K in the films has been checked by energy dispersive spectrometry (EDS) with a BRUKER Quantax silicon drift detector (SDD) mounted to the SEM.

S.4.2. AFM images of the films were taken ex-situ at atmospheric pressure and room temperature. All measurements have been performed in Tapping Mode™ on a MultiMode8 SPM AFM (Bruker). A crystal silicon probe of type TESPA (NanoWorld) with an imaging resonance frequency around 320 KHz was used. The elastic coefficient was 40 N/m, the scanning frequency is 1 Hz, and the scanning range was 10 μm×10 μm (512 lines). The obtained AFM images were analyzed with Gwyddion2.53 software, which is mainly used for statistical analyses of surface characteristics.

S.4.3. Optical transmission spectra were recorded using a a UV/visible spectrometer (PERKIN ELMER Lambda 1050 spectrophotometer). The optical absorption has been measured at wavelengths of 1 to 0.30 μm.

S.4.4. XPS measurements were carried out at room temperature on an Axis Nova spectrometer (Kratos Analytical) using the Al Kα line (1486.6 eV) as the excitation source. Survey spectra were acquired at pass energies of 80 eV (energy resolution of 0.87 eV). Data analysis was performed using CasaXPS software. Binding energy for the C 1s hydrocarbons peak was set at 285 eV in the calibration procedure.

Supporting Information S.5. Complementary experimental results

S.5.1. Optical density of SubPc and C_{60} layers

![Figure S.5.1. Optical density of SubPc and C_{60} layers](image-url)
S.5.2. EDS analysis

![Figure S5.2. Spectre EDS of a structure Glass/ITO (100 nm)/K (1.5 nm)/Alq₃ (9 nm)](image)

S.5.3. Surface visualization of ITO/Alq₃(9 nm) (a) and ITO/K (1.5 nm)/Alq₃ (9 nm) (b)

![Figure S5.3. Surface visualization of ITO/Alq₃(9 nm) (a) and ITO/K (1.5 nm)/Alq₃ (9 nm) (b)](image)
S.5.4. AFM image (10 x 10 μm) of a cathode ITO/K (2.5 nm)/Alq3 (9 nm)

Figure S.5.4. AFM image (10 x 10 μm) of a cathode ITO/K (2.5 nm)/Alq3 (9 nm)

S.5.5. Transmission spectra of ITO/Alq3 (-----) and ITO/K/Alq3 (---)

Figure S5.5. Transmission spectra of ITO/Alq3 (-----) and ITO/K/Alq3 (---)
S.5.6. Cross section visualization of active organic layers (C₆₀/SubPc) deposited onto (a) ITO/Alq₃ (9 nm), (b) ITO/K (1.5 nm) and ITO/K (1.5 nm)/Alq₃ (9 nm).

Figure S.5.6. Cross section visualization of active organic layers (C₆₀/SubPc) deposited onto (a) ITO/Alq₃ (9 nm), (b) ITO/K (1.5 nm) and (c) ITO/K (1.5 nm)/Alq₃ (9 nm).

S.5.7. SEM image of a structure C₆₀/SubPc deposited onto ITO/K (1.5 nm)/Alq₃ (9 nm) EBL.
Secondary electron (a) and backscattered electron (b) images. 

**Figure S.5.7.** SEM image of a structure $C_{60}/$SubPc deposited onto ITO/K (1.5 nm)/Alq$_3$ (9 nm) EBL.

In order to obtain some more information on small amount present at the surface of the structures we take photos of their surface using the backscattered electron detector of the SEM at low accelerating voltage (5KV). It is known that, using this mode, the heaviest component appears brightest than the lightest component. Therefore it can be deduced from the images that the amounts distributed over the films have the same composition than the rest of the layer since there is no large contrast visible in the backscattered electron image except for the darkest parts of the image resulting from the orientation of the surface elements.

S.5.8. XPS spectra of C1s window with K2p clearly visible in the case of ITO/K/Alq$_3$, the Alq$_3$ thickness being 40 nm and that of K 5 nm.

![XPS spectra graph](image_url)

**Figure S.5.8.** XPS spectra of C1s window with K2p clearly visible in the case of ITO/K/Alq$_3$, the Alq$_3$ thickness being 40 nm and that of K 5 nm.
The valence band value of ITO/Alq₃ is situated at around 1.82 eV below the Fermi level. When K is introduced, the valence band value of ITO/K/Alq₃ shift towards 2.70 eV.