Supporting information

Small molecule-based tandem solar cells with solution-processed and *vacuum*-processed photoactive layers.

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General:

DPP(TBFu)$_2$ was purchased from Lumtec Ltd. (Lumtec Ltd. Taiwan) and was further purified by flash column chromatography. 2,4-bis[4-(*N,N*-diisobutylamino)-2,6-dihydroxyphenyl] squaraine (SQ) was synthesized following the procedure of Tian *et al.*[25] PC$_{70}$BM was purchased from Solenne (Solenne BV, the Netherlands). High purity (99.9%) CHCl$_3$ was used for the active layer deposition. Aluminium (99.999%), MoO$_3$ (99.99% trace metal basis), BCP (97%) and LiF (99.995%) were purchased from Sigma-Aldrich. C$_{60}$ (>99%) was purchased from MER Corp., Texas. BCP was sublimed twice prior to use and Al, MoO3, LiF and C60 were used as received.

Device Fabrication:

Prepatterned Indium Tin Oxide (ITO) 5 Ohm/square (PSiOTec, Ltd., UK) sodalime glass substrates were first rinsed with acetone to remove the residual photoresist layer. The substrates were then placed in a teflon holder and sequentially sonicated in acetone (1 × 10 min) and isopropanol (2 × 10 min), and finally dried under a flow of Nitrogen. The ITO substrates where ozone-treated in a UV-ozone cleaner for 30 mins in ambient atmosphere, and subsequently coated in air with a layer of filtered (0.45 mm, cellulose acetate) solution of Poly(3,4-

ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS, HC Starck Baytron P) (4500 rpm 30 seconds followed by 3500 rpm 30 seconds). The PEDOT:PSS film was dried at 120 ºC under inert atmosphere for 15 min. Active layers were spin-coated (8000 rpm) in air over the PEDOT:PSS layer from a 12 mg/ml (total concentration) solution of DPP(TBFu)$_2$ and PC$_{70}$BM (6:4 w/w ratio). The approximate thickness of the active layer was 45 nm.

The solvent annealing step was carried out straight after deposition of the active layer by exposing the films to a saturated vapour of solvent in a closed vessel. The vessel (100 ml) was filled with 5 ml of CH_2Cl_2 and left sealed for 10 min. prior to the SVA step to ensure the atmosphere was saturated with solvent. The substrates were exposed to the solvent vapours from 15 seconds to several minutes by placing them in the solvent vessel.

The interlayer and back sub-cell layers were deposited by thermal evaporation in an ultra high vacuum chamber (1×10^{-6} mbar). To avoid short circuit between the sub-cells the interlayer was evaporated through a shadow mask covering an area slightly larger than the final device area (figure 1). The SQ, C60 and BCP were evaporated through an area largely covering the interlayer. The aluminium cathode was evaporated through a shadow mask leading to devices with an area of 9 mm^2 (figure1). LiF (0.6 nm), MoO_3 (20 nm) and Al (100 nm) were deposited at a rate of 0.1 Å/s, 0.3 Å/s and 0.5-1 Å/s respectively. SQ (6 nm), C60 (40 nm) and BCP (10 nm) were deposited at an average rate of 0.2 Å/s, 0.5 Å/s and 0.2 Å/s respectively. Following fabrication, the films were maintained under a Nitrogen atmosphere and stored in the dark until used.

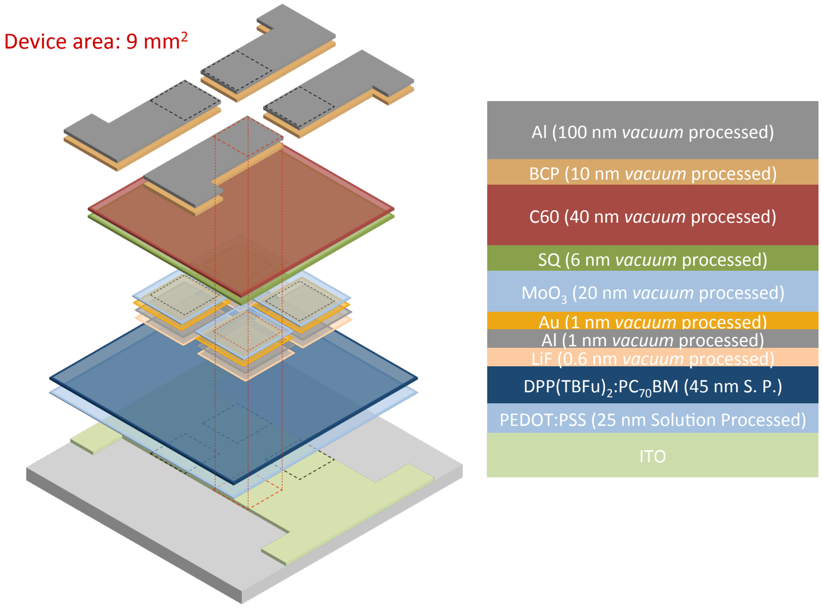

Figure S1: 3D depiction of the device's architecture.

Device Characterization:

The UV-Vis absorption of films was measured using a Shimadzu UV-1700 spectrophotometer. The J-V characteristics of the devices were measured using a Sun 2000 Solar Simulator (150 W, ABET Technologies). The illumination intensity was measured to be 100 mW/cm^2 with a calibrated silicon photodiode (NREL). The appropriate filters were utilised to faithfully simulate the AM 1.5G spectrum. The applied potential and cell current were measured with a Keithley 2400 digital source meter. The current to voltage (*J–V* curve) was plotted automatically with a home-built Labview© software. The EQE (External Quantum Efficiency) was measured using a home made set up consisting of a 150 W Oriel Xenon lamp, a motorized monochromator and a Keithley 2400 digital source meter. The photocurrent and irradiated light intensity were measured simultaneously and processed with a home-built Labview© software. The thickness of the films was measured with a stylus profilometer Ambios Tech. XP-1, by scratching the film in the middle of the substrate.

MoO_3 thickness optimization

The optimization of the MoO3 thickness was carried out on SQ:C60 devices having the same architecture than the back sub-cell. The thickness of MoO_3 was varied from 1 to 20 nm (Figure S2, table S1).

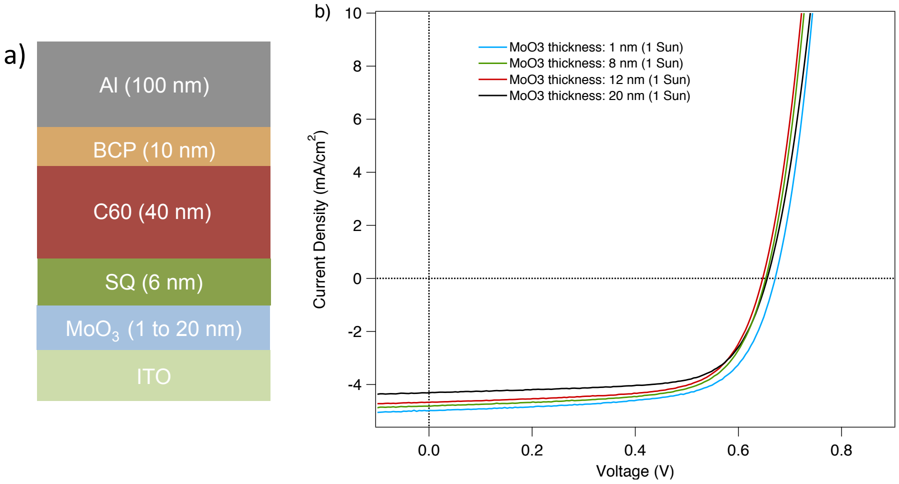

Figure S2. *J-V* characteristics of SQ:C60 devices comprising MoO_3 layers varying from 1 to 20 nm in thickness.

Table S1: *J-V* parameters of SQ:C60 devices comprising MoO_3 layers varying from 1 to 20 nm in thickness.

MoO_3 thickness	J_{SC}	V_{OC}	FF	PCE
1 nm	4.98	0.669	67	2.21
8 nm	4.82	0.648	67	2.09
12 nm	4.67	0.643	67	2.02
20 nm	4.31	0.653	69	1.94