Electronic Supplementary Information (ESI)

Annealing-free highly crystalline solution-processed molecular metal oxides for efficient single-junction and tandem polymer solar cells

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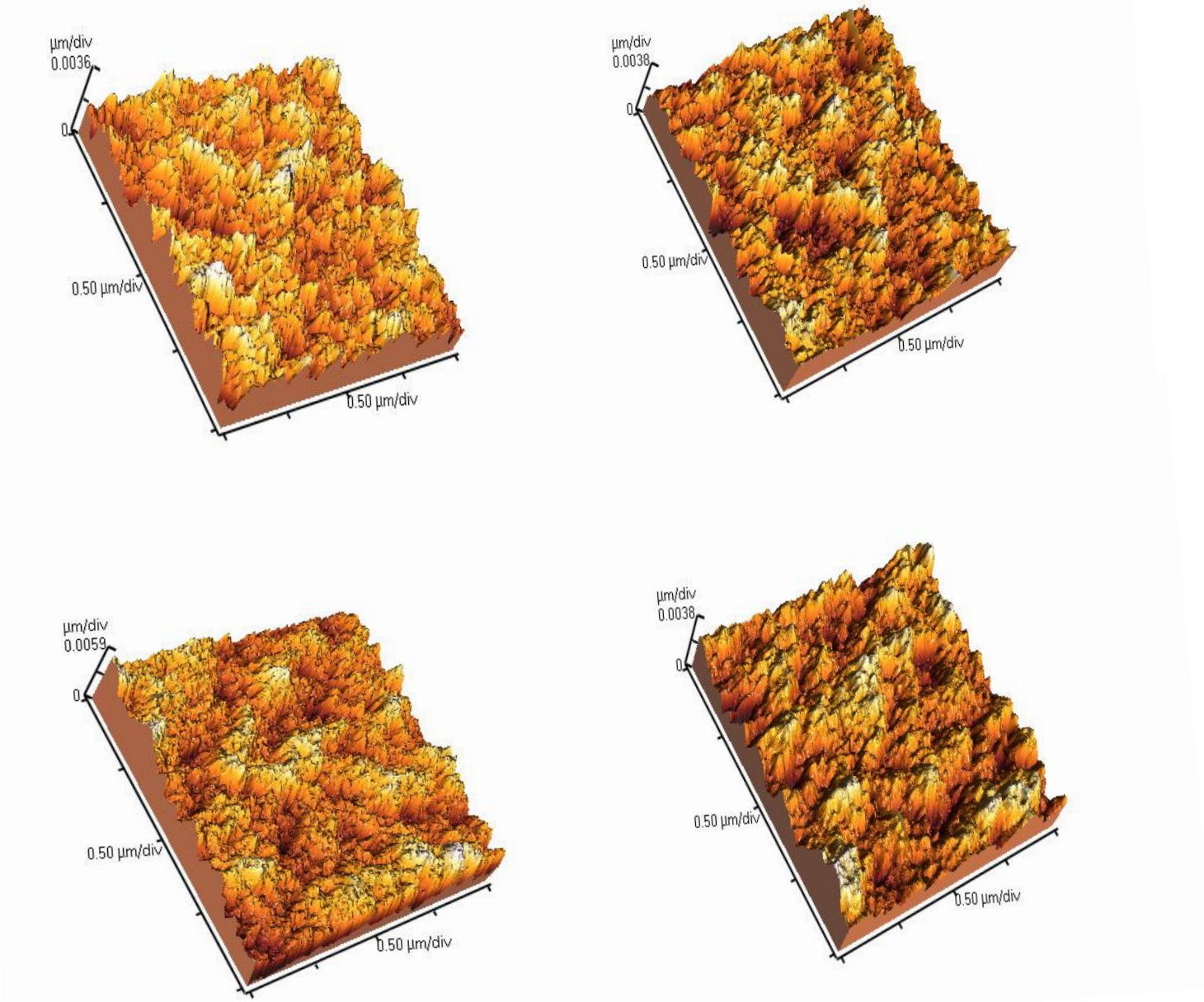


Figure S1 3D AFM topographies of PW-POM 12, PMo-POM 12, P_2W-POM18 and P_2Mo-POM 18 (from top left clockwise) films with a thickness of 50 nm.

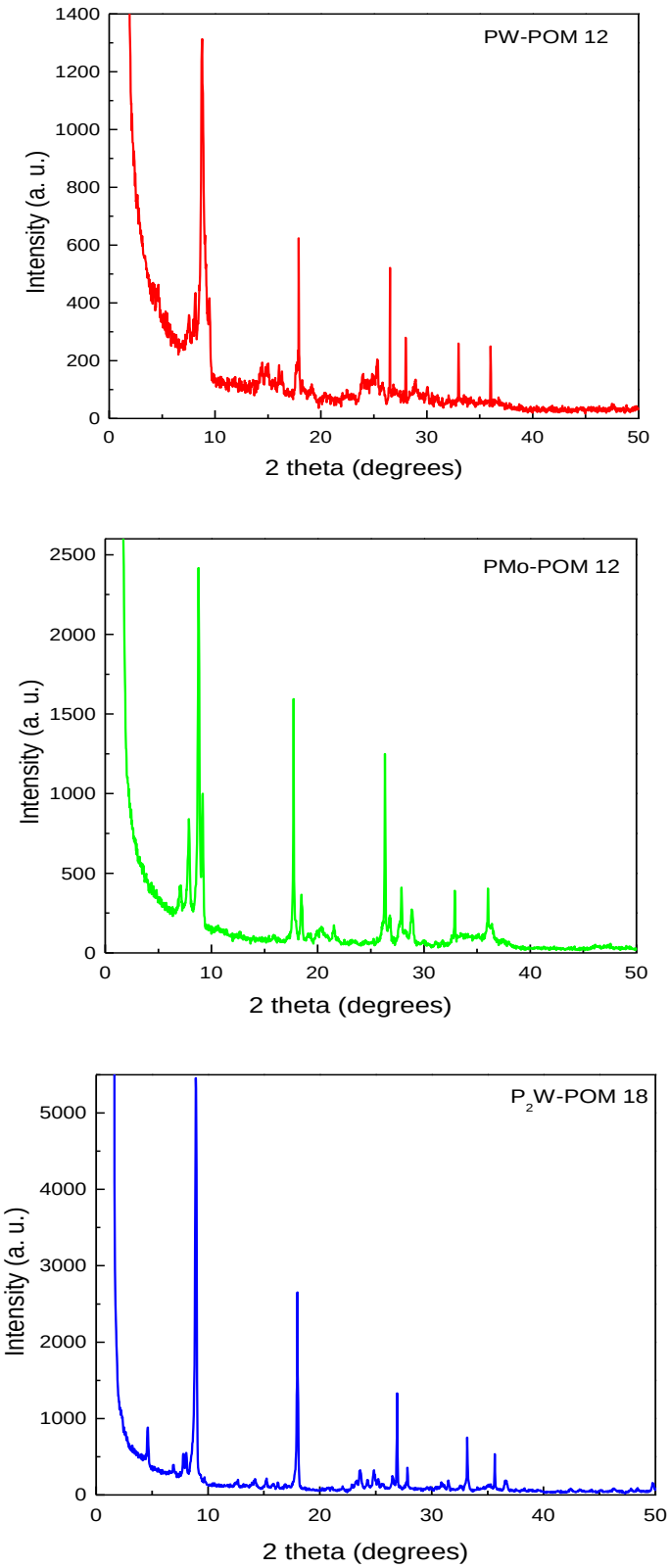


Figure S2 XRD patterns of different POM films 60 nm thick deposited via spin-coating from methanol solutions without any post deposition annealing treatment.

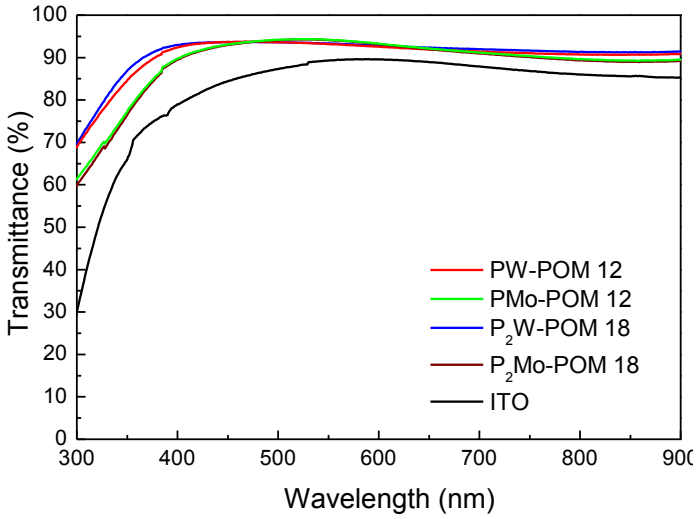


Figure S3 Transmittance spectra of 60 nm annealing-free POM films deposited on quartz substrates via spin-coating from methanol solutions. The spectrum of ITO on glass is also shown for comparison.

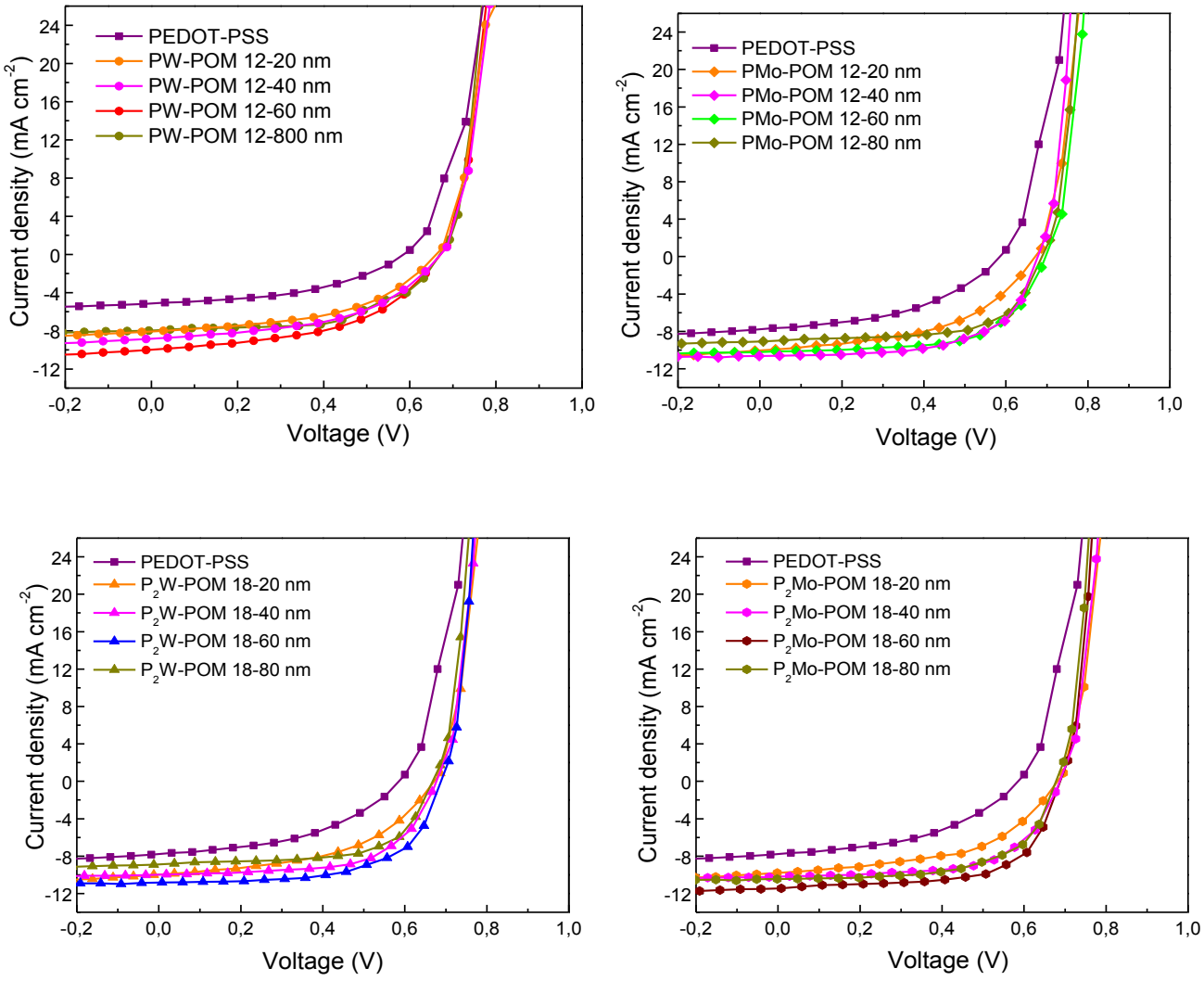


Figure S4 POMs thickness study: J-V curves of P3HT:$PC_{71}BM$-based OPVs with different thicknesses POM HELs and 40 nm thick ZnO ETL.

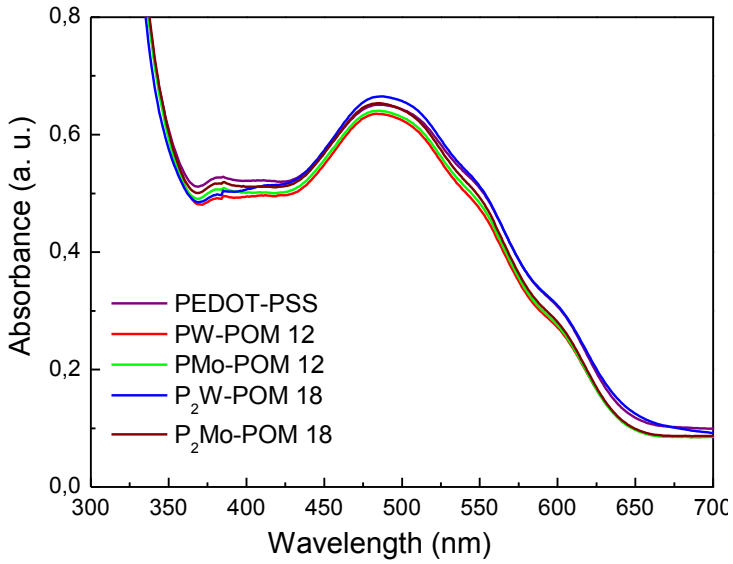


Figure S5 UV/vis absorption spectra of 120 nm P3HT:$PC_{71}BM$ films deposited on different POM layers and on PEDOT-PSS.

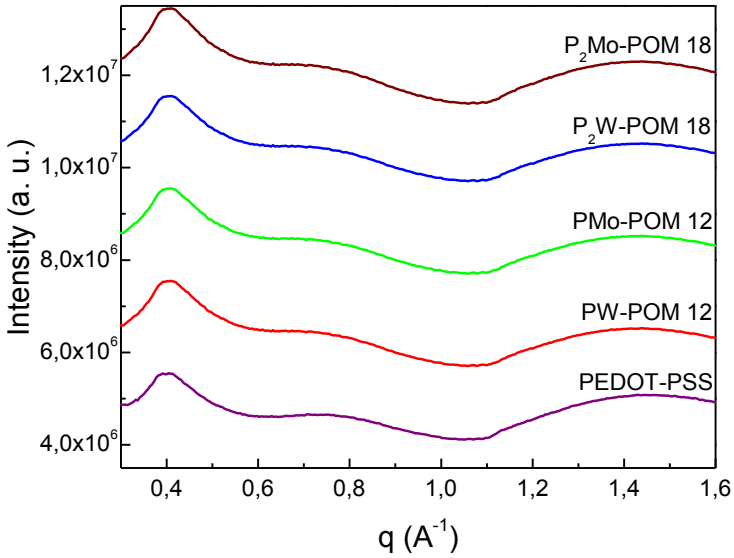


Figure S6 Grazing incidence X-ray scattering (GIWAXS) of P3HT:$PC_{71}BM$ films (as cast, in order to directly probe morphological changes caused by the underlayer) spin-cast from a 18 mg mL^{-1} solution in CB deposited onto different layers (on POMs and on PEDOT-PSS). The data are presented with arbitrary units and have been shifted for clarity. The region selected for integration is from q = 0.3 to 1.6 $Å^{-1}$. The peaks observed at q~0.39 $Å^{-1}$ and ~0.75 $Å^{-1}$ are the (100) and (200) peaks of the P3HT component, respectively. The peak observed at q~1.42 $Å^{-1}$ originates from crystalline $PC_{71}BM$. (GIWAXS was employed on the BM26B-DUBBLE beamline (λ = 1.033 Å, sample-to-detector distance of 2.1 m using a Pilatus 1M 981× 1043 pixel detector with pixel size 172 μm) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France).

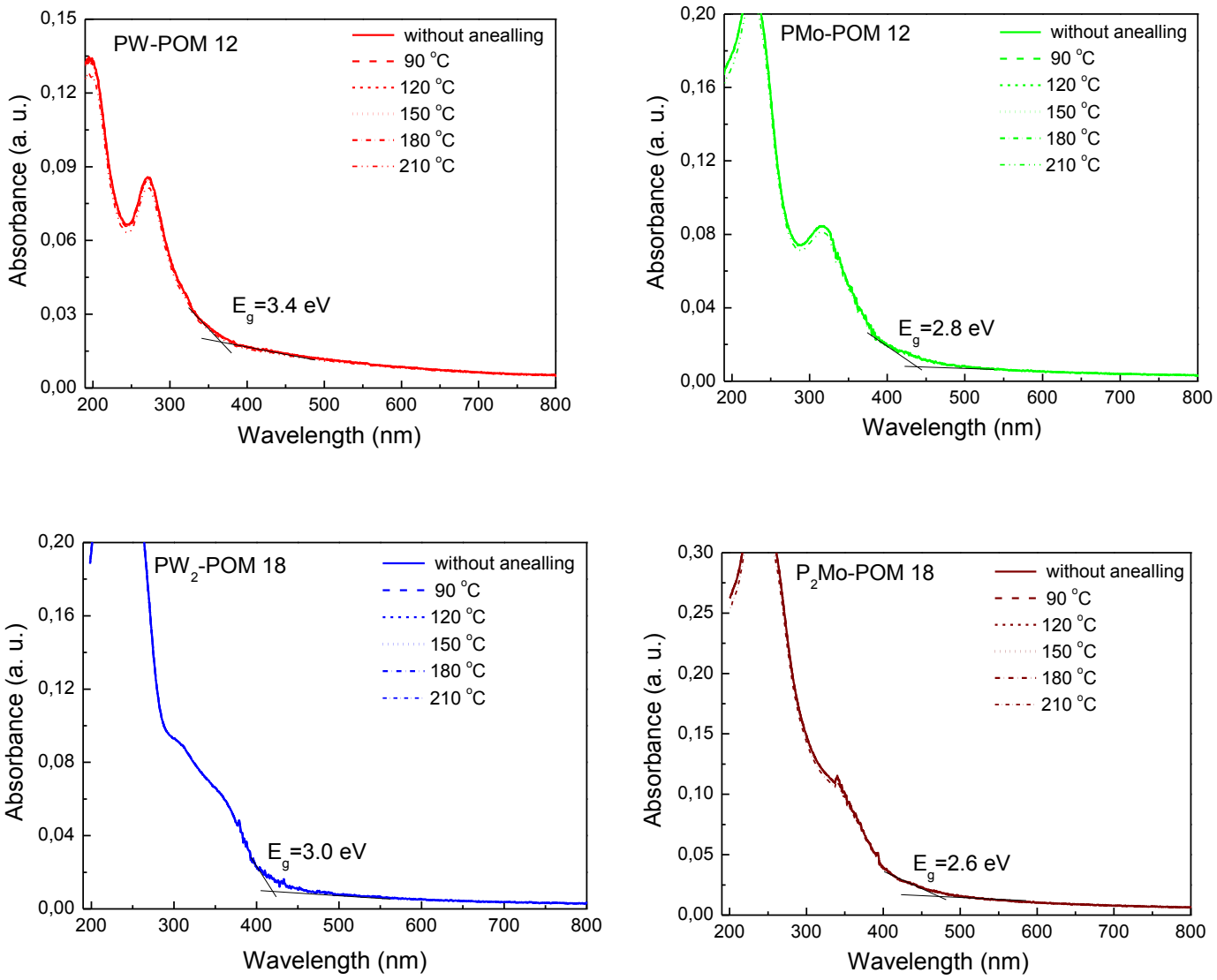


Figure S7 Absorption spectra of 60 nm POM films deposited on quartz substrates via spin-coating from their methanol solution. Films were either annealing-free for the estimation of their optical energy gap or annealed at elevated temperatures to study their thermal stability.

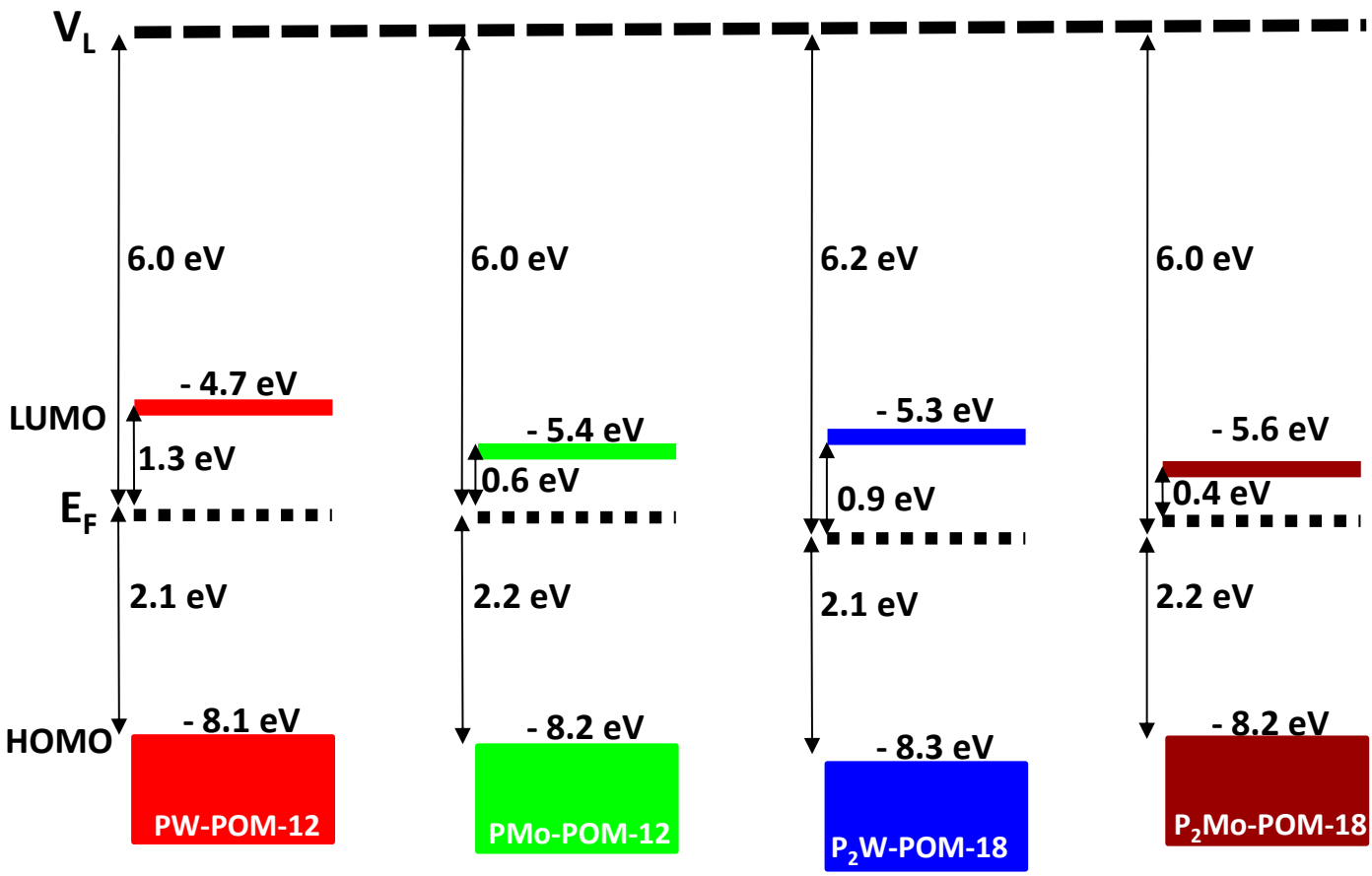


Figure S8 The energy levels of POMs as derived from the UPS measurements shown in the main manuscript (Figure 4) and the UV-vis absorption measurements shown above (Figure S7). According to the energy levels shown here, POMs are n-type materials since the distance of their Fermi level from their LUMO is smaller compared with the distance from the HOMO.

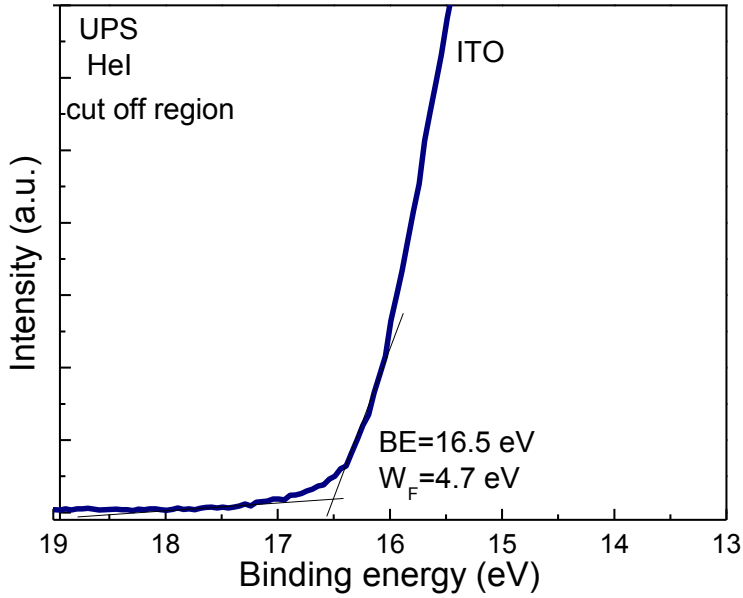


Figure S9 UPS secondary electron cut-off spectrum of ITO.

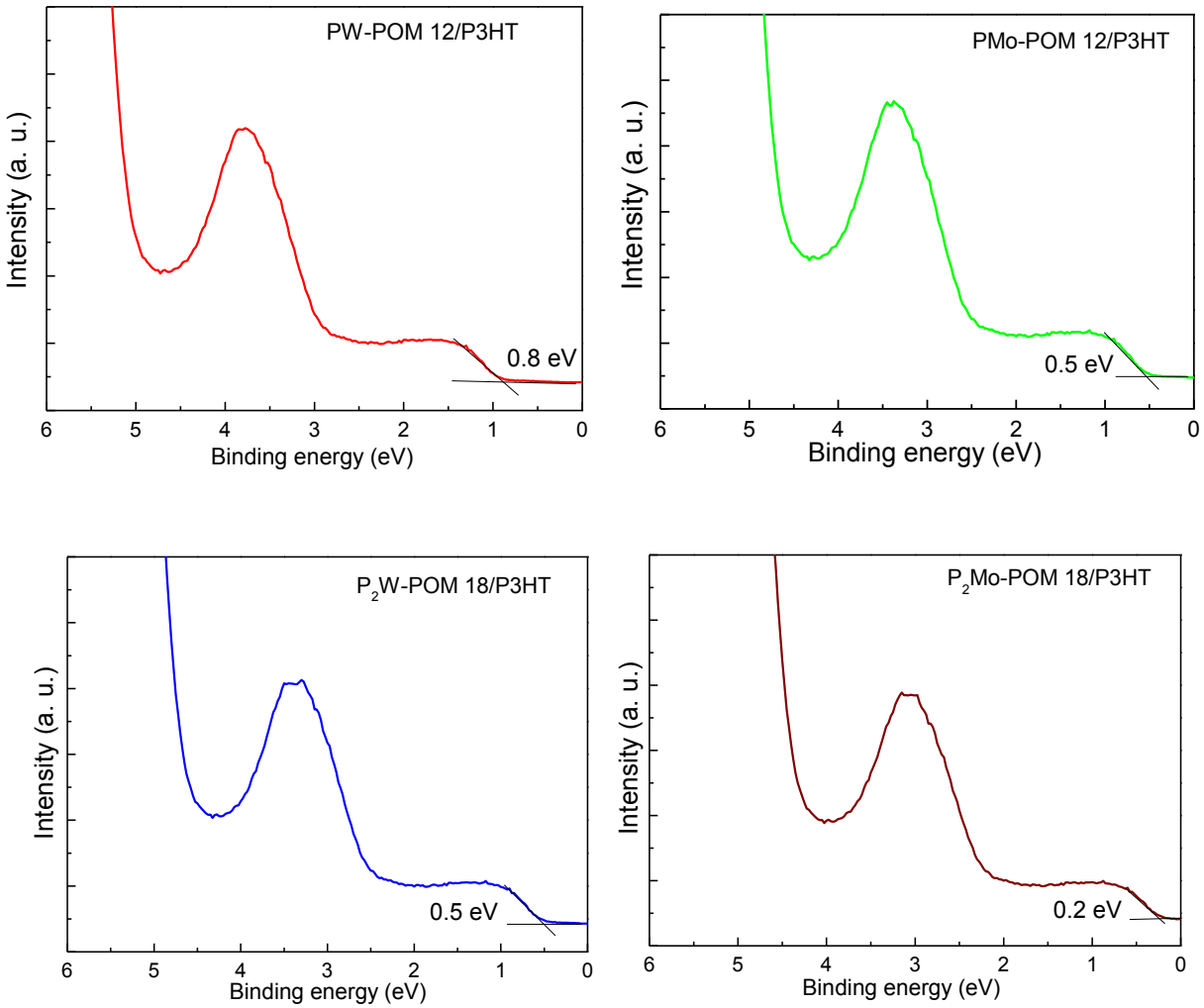


Figure S10 HOMO region of the UPS spectra of thin (about 3 nm) P3HT films on different POM layers.

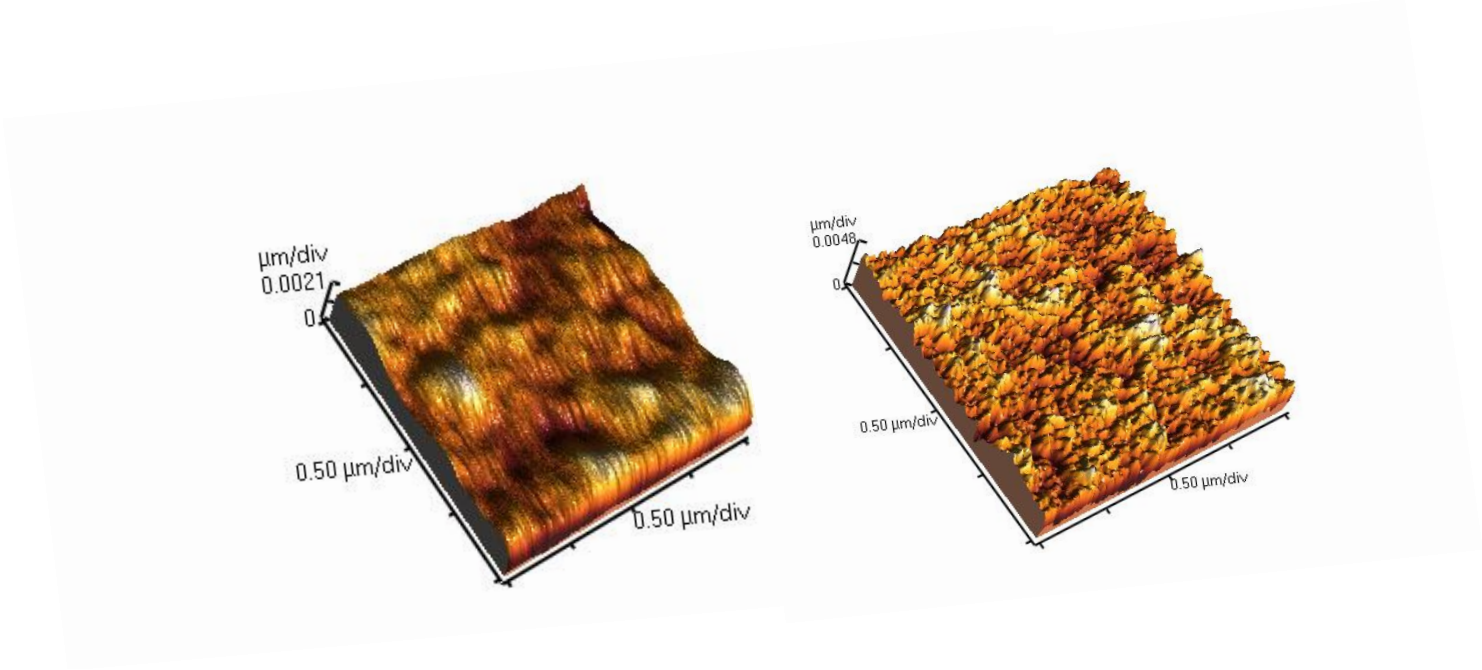


Figure S11 AFM 3D topographies of P3HT:$IC_{60}BA$ (left) and P_2Mo-POM 18 on P3HT:$IC_{60}BA$ (which has been subjected to methanol treatment prior to deposition of the POM layer).

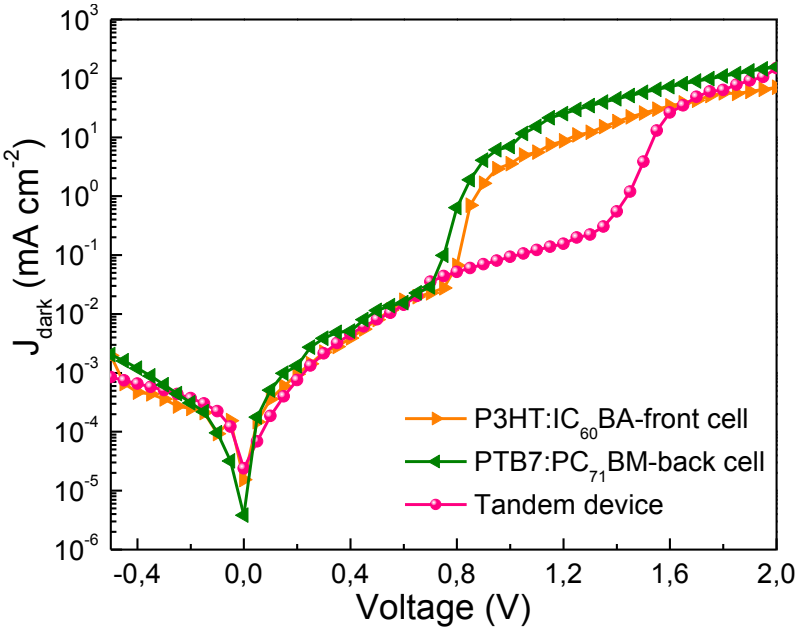


Figure S12 Dark J-V curves of P3HT:$IC_{60}BA$-front cell, PTB7:$PC_{71}BM$-back cell and Tandem device. The values of series resistance estimated for each cell are: 2.8 Ω cm^2, 3.3 Ω cm^2 and 8.6 Ω cm^2 for the individual front sub-cell, the back sub-cell and the tandem device, respectively.

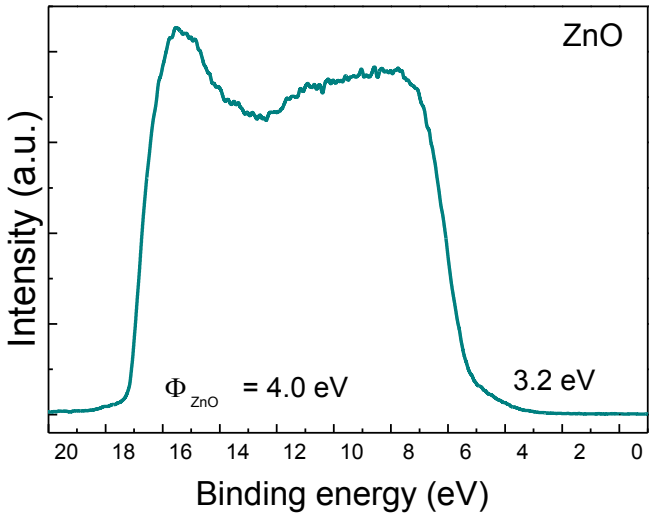
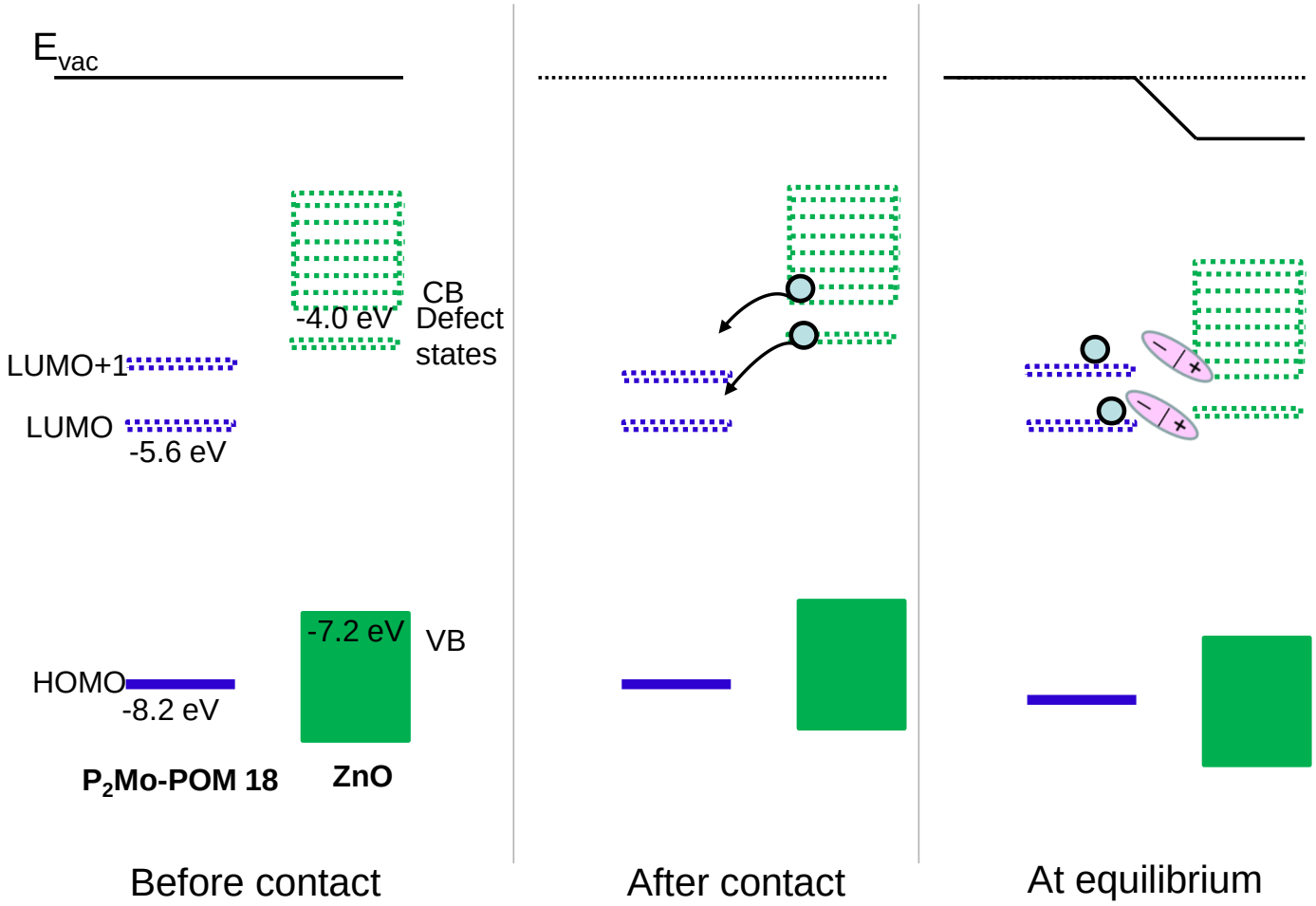


Figure S13 UPS spectrum of 40 nm thick ZnO films.



S14 Illustration of vacuum level shift *via* the formation of an interfacial dipole due to electron transfer from the conduction band (CB) and/or defect states of ZnO to the LUMO (and/or LUMO+1) level of POM.