

Electronic Supplementary Information

In situ Near-Ambient Pressure X-ray Photoelectron Spectroscopy Reveals the Effects of Water, Oxygen and Light on the Stability of PM6:Y6 photoactive layers.

Qilun Zhang,^{*a,b} Yongzhen Chen,^a Xianjie Liu^a and Mats Fahlman^{a,b}

^a Laboratory of Organic Electronics, Department of Science and Technology (ITN) ,Linköping University, SE-60174 Norrköping, Sweden. E-mail: qilun.zhang@liu.se.

^b Wallenberg Wood Science Center, Department of Science and Technology (ITN) ,Linköping University, SE-60174 Norrköping, Sweden. E-mail: qilun.zhang@liu.se.

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Materials

All OPV materials were purchased from Solarmer Energy, Inc. PEDOT:PSS (Clevios™ P VP Al 4083) was purchased from Heraeus Materials. PDINN was purchased from 1-Material. The other materials and solvents were commercially available. All the materials were used as received.

Experiment Methods

Organic film and solar cell preparation

The thin films (≈ 50 nm) were spin-coated onto Au from 8 mg/mL and 12 mg/mL in chloroform solutions under nitrogen atmosphere in dark condition, then sealed and transferred with illumination shield, into the load lock chamber of the ultrahigh vacuum (UHV) system used for the experiments. The blend films were prepared with the same conditions as the active layer used in devices. All substrates were cleaned by sonication in isopropyl alcohol before spin coating.

The OSC device with normal structure is Glass/ITO/PEDOT:PSS/Active layer/PDINN/Ag. The pre-cleaned ITO substrate with the same procedure mentioned in photoelectron spectroscopy measurement was treated with UV-Ozone for 20 min. The anode buffer layer PEDOT:PSS (Baytron P VP Al 4083) was spin-coated onto ITO-coated glass substrates, followed by annealing at 120 °C for 20 min to remove the water. The thickness of the PEDOT:PSS layer was around 35 nm, as determined by a Dektak 6M surface profilometer. For blend active layer in device, PM6:Y6 mixed solution was made with a concentration of 16 mg/mL and a mass ratio of 1:1.2 in chloroform. The quasi-bilayer device was fabricated with sequentially spin-coating PM6 (8 mg/mL) dissolved in chlorobenzene, and Y6 (10 mg/mL) dissolved in chloroform. Thermal annealing at 85 °C was carried out for 10 min. After deposited with about 8 nm PDINN, the coated substrates were directly transferred to a vacuum deposition system mounted inside of the glove box. The cathode Ag (100 nm) was thermally evaporated via a shadow mask under vacuum at 3×10^{-7} mbar. The effective device area is 0.044 cm². J–V characteristics were recorded by a Paios platform under illumination of an AM1.5 solar simulator with an intensity of 100 mW/cm² in the glovebox. The light intensity was determined by a standard silicon photodiode.

NAP-XPS

Photoelectron spectroscopy characterizations were performed at the SPECIES beamline at MAX IV. The beamline is equipped with an APPES end station, which allows surface sensitive characterization of solid-liquid interfaces at a pressures up to 25 mbar in the energy range of 27–1500 eV. The data presented here were recorded at pressures below 10^{-10} mbar in the analysis chamber, when we refer to UHV condition/back to UHV in the text. The photon energy of 830 eV for F1s, 545 eV for N1s, 435eV for C1s, 310 eV for S2p and 70 eV for VB were used, respectively, with the pass energy of 50 eV and slit width if 50 μ m. In all cases, the spectral resolution was limited by the sample. The incident photon angle was 54 degrees, and the photoelectron emission angle was 90 degrees, both relative to the plane of the sample substrate. The beamline and end station are described in detail in refs^{1,2}. Exposure to oxygen and water experiment was carried out in the NAP cell with a base pressure of 1 mbar. In all cases, a series of spectra were recorded at different time intervals, different exposure times and different spots of the film under synchrotron radiation to avoid beam damage. For clarity of presentation, only one representative data set per sample environment is shown. It should be noted that Y6* as a supply sample for water combine with NIR illumination have slightly different starting N1s feature compared to other scenario, as shown in Fig. S3, their response to water and NIR illumination exposure has the same trend.

The detailed procedure and parameters for XPS data analysis/fitting in S2p and N1s. In S2p fitting, the doublet separation, area ratios and full width at half maximum (FWHM) are constrained to 1.2 ± 0.005 eV, about 2:1, and 0.8 ± 0.005 respectively. The additional peaks marked with S* are fixed with the S2p_{3/2} component at 164.31 eV to have comparable change for all the scenarios. For N1s fitting, the position of the exposure induced additional N1s peak is also fixed in relation to the two main peaks, i.e., the same binding energy difference in this case, the change of spectral feature due to the exposure can be clearly extracted, e.g., the relative intensity changes between the two main N1s components, and the increase of the additional N1s feature.

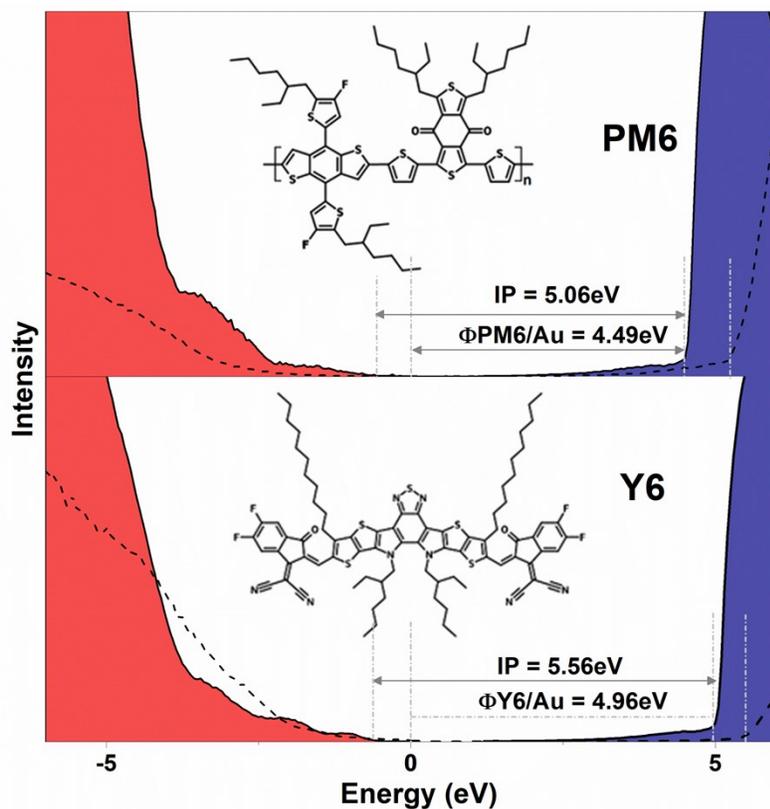


Figure S1. The chemical structures of the donor PM6 and acceptor Y6 with the corresponding UPS spectra measured by home-made PES(He I). The error bar of the measurement is ± 0.05 eV. The secondary electron cut-off feature with blue pattern is shifted by the incident photon energy to show the position of the vacuum level relative to the Fermi level (located at 0 eV). The dot line in the spectra refers to the substrates.

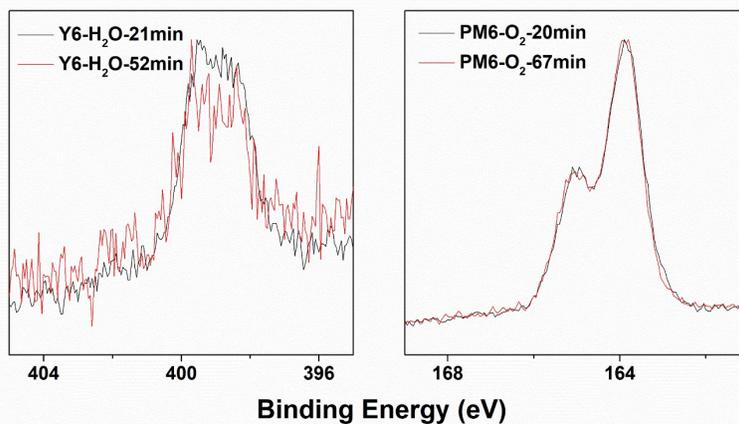


Figure S2. The N1s and S2p core level spectra of Y6 and PM6 under different expose time to water and O₂.

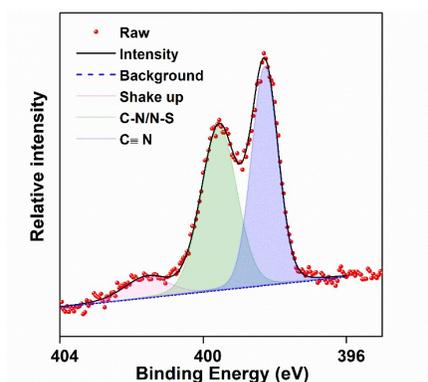


Figure S3. The N1s core level spectrum of the supply Y6 sample in UHV.

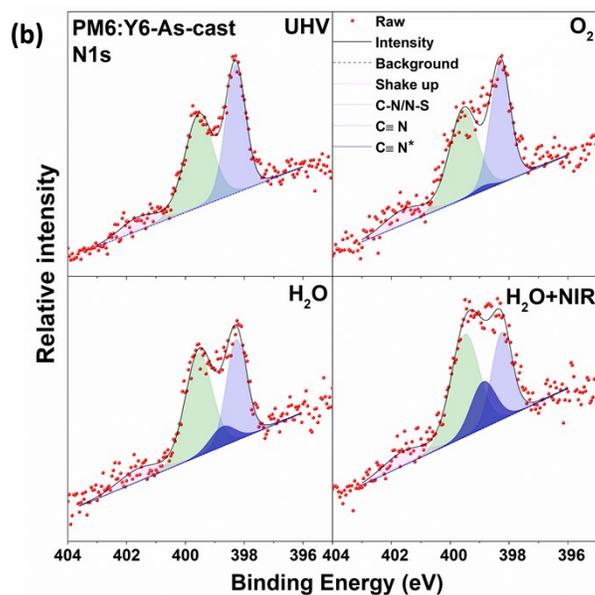
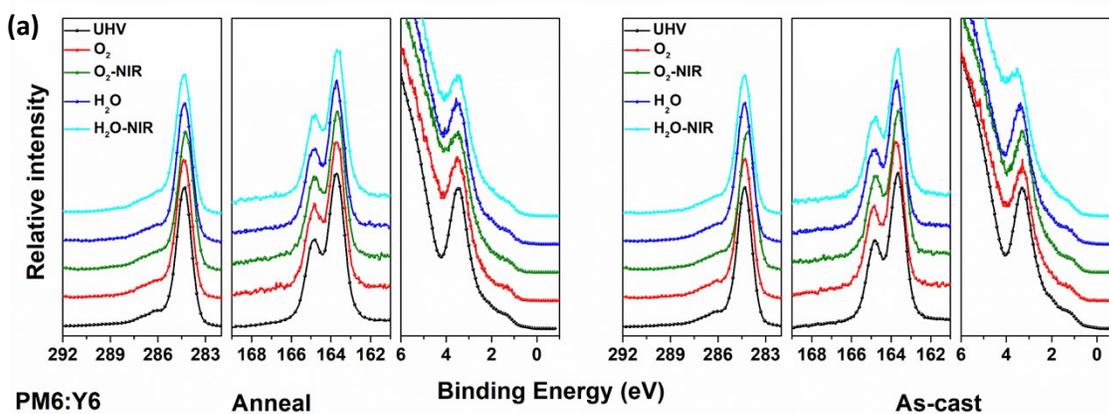


Figure S4. (a) XPS C1s, S2p and VB spectra of PM6:Y6 films, left for annealed film and right for as-cast film, (b) Evolution of XPS N1s core level spectra and their deconvolution of as-cast PM6:Y6 film under exposure to O₂, water and illumination.

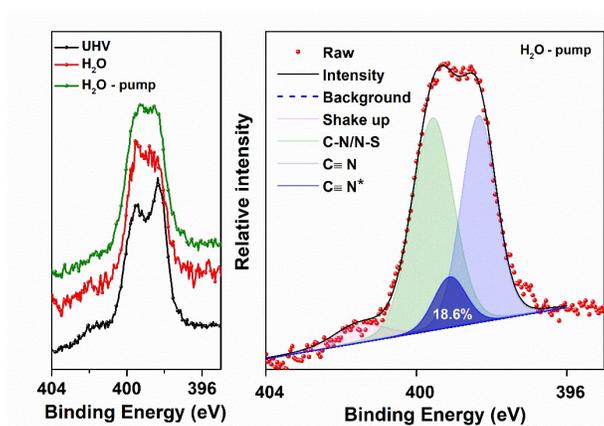


Figure S5. The evolution of N1s core level spectra of Y6 film after pumped water (left) and the fitted spectra (right).

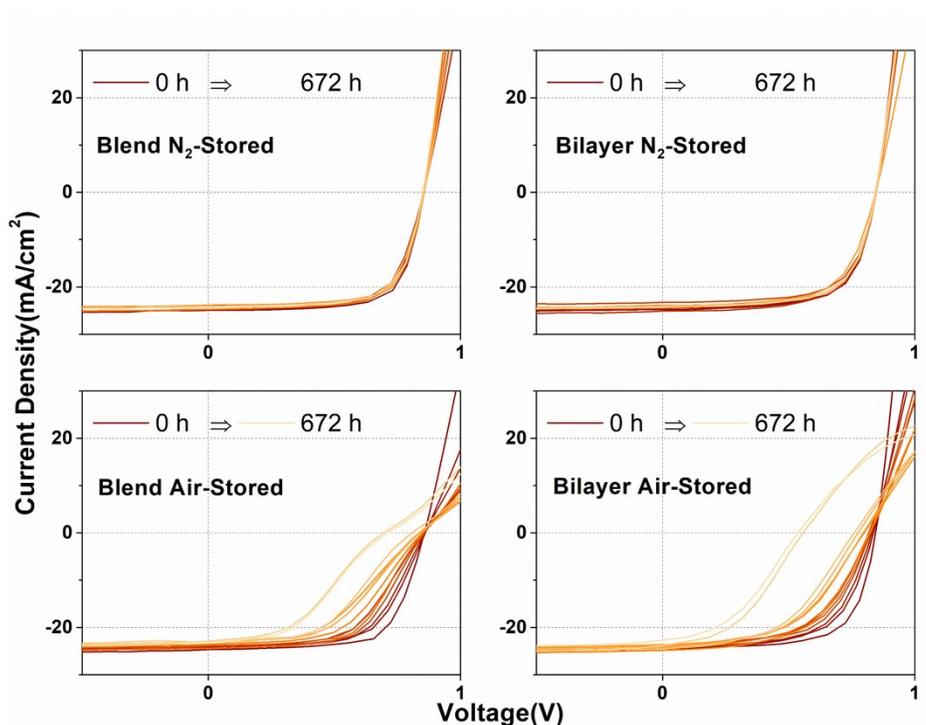


Figure S6. The J-V curves of OSCs with blend BHJ and bilayer BHJ active layers stored in glovebox (N₂-stored) and fume hood (air-stored) for 672 hours degradation.

1. J. Schnadt, J. Knudsen, J. N. Andersen, H. Siegbahn, A. Pietzsch, F. Hennies, N. Johansson, N. Mårtensson, G. Öhrwall and S. Bahr, *J. Synchrotron Radiat.*, 2012, **19**, 701-704.
2. J. Knudsen, J. N. Andersen and J. Schnadt, *Surf. Sci.*, 2016, **646**, 160-169.