SUPPLEMENTARY INFORMATION

Effect of Selective Interactions at the Interface of Polymer-Oxide Hybrid Solar Cells

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Figure S1 Devices with 2-MP and TBP interlayer: J-V characteristics under standard AM 1.5 illumination condition of a hybrid TiO₂/P3HT solar cell provided with 2-mercaptopyridine (green squares) and 4-tert-butylpyridine interlayer (blue stars). For comparison, the J-V curves of TiO₂/P3HT solar cells without the interlayer (red triangles) and with 4-MP interlayer (black circles) are reported. The figures of merit are reported in Table S1.



Figure S2: Normalised absorption spectra of $TiO_2/P3HT$, $TiO_2/4$ -MP/P3HT before and after annealing.



Figure S3: fs Transient Absorption spectra of P3HT infiltrated in mesoporous films of ZrO_3 a) without interlayer and b) with a 4-MP interlayer. Excitation at 520nm. In both samples there is no quenching of the stimulated emission band and the photo-induced charge absorption band in P3HT cannot be observed.

	Voc [V]	Jsc [mA/cm ²]	FF [%]	PCE [%]
P3HT only	0.49	1.55	54	0.43
2-MP IL	0.30	0.47	21	0.03
TBP IL	0.59	0.55	49	0.17
4-MP IL	0.59	3.75	51	1.13

Table S1: Summary of the devices figures of merit

Coincidence Doppler Broadening

The CDB spectra presented in Fig. 3.b in the manuscript for the infiltrated porous oxides with P3HT (TiO₂\P3HT and TiO₂\4-MP\P3HT) were measured at a fixed positron implantation energy of 5 keV. At this energy more than 87% of the positrons annihilate in the porous film containing P3HT and about 13% in the capping layer as shown in Fig. S4. 5 keV is the maximum implantation energy that allows to avoid the glass substrate contribution (<0.5%). It is possible to observe two effects in the CDB distributions presented in Fig. 3.b for TiO₂\P3HT with and without 4-MP in terms of the relative difference $\Gamma = (\rho - \rho_{TiO_2}) / \rho_{TiO_2}$: a) lowering of the valence electron density, which leads to a narrowing of the central part of the momentum distribution (Γ >1), and b) reduction of the positron wavefunction overlap with atomic cores, which reduces the relative intensity of the CDB spectrum at high momentum (Γ <1). These effects are highly remarked for the P3HT distribution. The CDB momentum distributions of the reference samples are used as well differentiated fingerprint to characterize each material inside the prototype cells. These distributions depend on the electron structure of P3HT and TiO₂ 1,2 . The continuous lines through the experimental points in Fig. 3.b represent a linear combination fit following eq. S1.

$$\rho = w \rho_{P3HT} + (1 - w) \rho_{TiO_2}^*, \tag{S1}$$

where w is the weight of the P3HT contribution, ρ_{P3HT} and $\rho_{TiO_2}^*$ are the momentum distributions of P3HT and the porous TiO₂ oxide, respectively. Note that $\rho_{TiO_2}^*$ was different for TiO₂\P3HT and TiO₂\4-MP\P3HT. In each case it was used the reference oxide with and without 4-MP, as the sample contains or does not contain mercaptopyridine. The fitting procedure

reproduces the experimental results at low and high momentum and gives *w* values of 0.37 ± 0.02 and 0.44 ± 0.02 in TiO₂\P3HT and TiO₂\4-MP\P3HT samples, respectively. *w* is univocally related to the filling factor *f*, but an experimental calibration is not available. Thus, we make an estimation based on the hypothesis that the probability of annihilation in P3HT and the oxide is proportional to the mass fraction times the decay rate of the free positron population λ_{free_i} as obtained from annihilation lifetime spectra.

$$w = \frac{\lambda_{free_{P3HT}} m_{P3HT}}{\lambda_{free_{P3HT}} m_{P3HT} + \lambda_{free_{TiO_2}} m_{TiO_2}},$$
(S2)

where m_{P3HT} and m_{TiO_2} are respectively the masses of P3HT and TiO₂ inside the porous composite. The free positron annihilation rate for a porous TiO₂ layer with the same characteristics to the studied here (nanoparticles of 20 nm in diameter of the anatase phase) was recently determined³ as $\lambda_{free_{TO_2}} = 5.52 \times 10^9 \text{ s}^{-1}$. In the case of P3HT it was possible to estimate $\lambda_{free_{P3HT}}$ by assuming that part of the implanted positrons were trapped into defect sites in the polymeric matrix. Following the standard trapping model⁴

$$\lambda_{free_{P3HT}} = \lambda_{P3HT} \left(\frac{L_{P3HT}}{L_{D_{P3HT}}} \right)^2,$$
(S3)

where λ_{P3HT} is the characteristic decay rate in P3HT ($\lambda_i = \lambda_{P3HT} = 2.43 \times 10^9 \text{ s}^{-1}$ [5]). L_{P3HT} and $L_{D_{P3HT}}$ are respectively the positron diffusion lengths measured in P3HT without defects ($L_{P3HT} = 79\pm3$ nm) and in the defected thin capping layer studied here ($L_{D_{P3HT}} = 20\pm5$ nm). Therefore, $\lambda_{free_{P3HT}}$ is about $3.79\times10^{10} \text{ s}^{-1}$.

Considering that the porosity p of the studied TiO₂ oxide is 60% ($p=V_E/V_T$, initial free volume with respect to the total volume) and using eq. S2 it was possible to estimate the filling factor f ($f=V_{P3HT}/V_E$, volume of P3HT inside the pores respect to the initial free volume).

$$f = \frac{\rho_{TiO_2}}{\rho_{P3HT}} \frac{\lambda_{free_{TiO_2}}}{\lambda_{free_{P3HT}}} \frac{w}{(w-1)} \frac{(1-p)}{p},$$
(S4)

where $\rho_{TiO_2} = 3.84 \ g \ cm^{-3}$ and $\rho_{P3HT} = 1.33 \ g \ cm^{-3}$ are the mass densities. The calculated filling factors are: $f = 16.5 \pm 3\%$ and $f = 22 \pm 3\%$ for TiO₂\P3HT and for TiO₂\4-MP\P3HT, respectively.



Figure S4. Positron implantation fraction as a function of the implantation energy obtained in $pTiO_2\4-MP\P3HT$ by means of the VEPFIT model⁶. The curves indicate the percentage of positrons that are implanted and thermalized at each energy. The vertical dashed line represents the implantation energy used to study TiO_2\P3HT and TiO_2\4-MP\P3HT devices by means of CDB. The continuous blue line is the sum of the contribution of the two oxide layers infiltrated with P3HT, where the main contribution is given by the second layer.



Figure S5. FT-IR spectra of 4-MP in film (red line) and onto a TiO_2 flat layer, after rinsing (black line), in the region 2400-3100 cm⁻¹. The arrow indicates the band assigned to the S-H stretching, whose normal mode is sketched in the inset, that results unaffected by the interaction between 4-Mp and TiO₂.



Figure S6. External Quantum Efficiency (EQE) of a $TiO_2/4$ -MP/P3HT solar cell. The current was measured using a lock-in amplified; the monochromated light was modulated at 21Hz. Convolution of this spectral response with the AM1.5G solar spectrum provides an estimated current density of 2.5 mA/cm². This reveals an underestimation of the actual EQE values due to slow device time response respect to the light modulation frequency.

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