The effect of selective interactions at the interface of polymer–oxide hybrid solar cells†

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Received 11th May 2012, Accepted 24th July 2012
DOI: 10.1039/c2ee22212d

The working mechanisms of excitonic solar cells are strongly dominated by interface processes, which influence the final device efficiency. However, it is still very challenging to clearly track the effects of inter-molecular processes at a mesoscopic level. We report on the realization of polymer-based hybrid solar cells made of prototypical materials, namely, poly(3-hexylthiophene) (P3HT) finely infiltrated in a TiO2 scaffold, with power conversion efficiency exceeding 1%. A step-change improvement in the device performance is enabled by engineering the hybrid interface by the insertion of an appropriate molecular interlayer. An unprecedented set of characterization techniques, including time-resolved optical spectroscopy, X-ray photoemission spectroscopy, positron annihilation spectroscopy and atomistic simulations, allows us to rationalize our findings. We show that a suitable chemical structure of the interlayer molecule induces selective intermolecular interactions, and thus a preferential surface energetic landscape and morphological order at the interface which consequently drives a strong improvement in charge generation and a decrease in recombination losses.

Broader context

The development of clean power generation methods based on solar energy conversion is of pivotal importance to guarantee a sustainable economic growth. In particular, those recent technologies which promise low cost and a high level of daily life integration have become extremely appealing. Among the photovoltaic systems developed with this intent, hybrid solar cells, where nanostructured metal oxide scaffolds are interfaced to conjugated polymers, are emerging. They could in principle combine the success of dye-sensitized solar cells (DSC) with that of fully organic solar cells. A conjugated polymer behaves both as light antenna system and hole transporting layer while electrons are injected in the high mobility metal oxide, thus reducing the complexity of the DSC in a solid state device. Then, they should get rid of the limitations of the bulk-heterojunction architectures that suffer from the necessity of compromising between having a high density of exciton splitting interfaces and good percolation paths for the charges. However, hybrid solar cells of this kind have not expressed their full potential yet. This manuscript aims to shed light on interfacial optoelectronic mechanisms, which are fundamental for the optimization of operational processes, with the goal of improving device efficiency.
Introduction

The possibility of taking advantage of characteristics such as high dielectric constant, high electron mobility and good stability has maintained great interest in the development of hybrid solar cells\textsuperscript{1–4} as possible alternatives to fully organic devices (OPV). The research on systems based on polymer–metal oxide nanocrystals has also been very active, thanks to the low cost and easy synthesis of these inorganic compounds. There are essentially two approaches in the device design: the first one consists of a bulk heterojunction (BHJ) structure, like in fully organic solar cells, where metal oxides substitute for the organic acceptor;\textsuperscript{5} in the other, which is inspired by the successful architecture of dye-sensitized solar cells (DSC), the polymer is infiltrated in a metal oxide nanostructured scaffold.\textsuperscript{5} The former has shown poor performances in comparison to all organic BHJ, apparently due to a lack of control on the thin film morphology.\textsuperscript{2,6} The latter, in contrast, could in principle combine the success of DSC with that of OPV. The conjugated polymer behaves both as light antenna system and hole transporting layer, while electrons are injected in the high mobility metal oxide. In principle this system should get rid of the limitations of the BHJ, which suffers from the necessity of compromising between having a high density of exciton splitting interfaces and good percolation paths for the photogenerated charges. In spite of this, however, hybrid solar cells of this kind have not expressed their full potential yet,\textsuperscript{5} and, even more striking, the reason why they are so inefficient is still not clearly understood.

In this work, we present a hybrid photovoltaic cell based on prototypical materials, TiO\textsubscript{2} and P3HT, where the polymer is infiltrated in the metal oxide mesoporous structure. Previous works using nanoporous\textsuperscript{7} or nanorod\textsuperscript{8} structures filled by conjugated polymers could not reach power conversion efficiency above 0.5%. Attention has been paid to the use of interlayers whose main role was to control the energy offset at the oxide–polymer interface.\textsuperscript{9,10} However, the main result has been the improvement of the device open circuit voltage with detrimental effects on the extracted photocurrent or vice versa (see the effect of the 4-tert-butylpyridine (TBP) interlayer on the device performances in Fig. S1†). This highlights that the simple design of the energy levels alignment is not enough to boost the device performances. Another issue that is also currently hotly debated is the effect of incomplete pore filling of the oxide scaffold by the conjugated polymer on the device performances.\textsuperscript{11,12}

We demonstrate that, by modifying the TiO\textsubscript{2} surface through a commercial and inexpensive molecule such as 4-mercaptopyridine (4-MP) (see the inset in Fig. 1), which is optically transparent (ESI, Fig. S2†), we are able to impressively enhance the photocurrent extracted from the nanostructured solar cell, inducing a step change in the overall efficiency of the device which overcomes the 1% limit. We conclude that the pore filling of the oxide mesoporous structure is not the bottleneck in device performances, while the control of intermolecular interactions at the metal oxide-conjugated polymer interface is shown to be a crucial issue. Such interactions induce local order at the molecular level that drives a better functionality of the materials at the interface.

Methods

The photovoltaic cells were prepared as follows. Fluorine doped tin oxide (FTO) coated glass substrates (15 Ω per sq Pilkington) were etched with zinc powder and HCl (2.4 M) in water solution to define the required pattern for the devices bottom electrode. Careful washing of the substrates following the etching step was performed with soap (Hellmanex 2% in water), bidistilled water, acetone and isopropanol. Oxygen plasma treatment was finally performed for 5′ to remove the last traces of organic residues. The substrates were then covered with a compact TiO\textsubscript{2} layer of a thickness comprised between 150 and 200 nm. Deposition of the compact layer was carried out by spray pyrolysis at 500 °C with oxygen as the carrier gas, starting from a 1 : 10 by volume titanium diisopropoxide bis(acetylacetonate) : ethanol solution. The commercial Dysol TiO\textsubscript{2} paste (DSL 18NR-T), previously diluted in ethanol and ultrasonicated until complete mixing, was doctor-bladed by hand onto the TiO\textsubscript{2} compact layer coated FTO substrates to get a mesoporous TiO\textsubscript{2} film of an average thickness of 1 μm. The substrates were then slowly heated to 550 °C (ramped over 1½ hours) and baked at this temperature for 30′ in air. After cooling, the substrates were soaked in TiCl\textsubscript{4} solution (15 mM in water) and oven-baked for 1 hour at 70 °C. After oven-baking, the substrates were rinsed with bidistilled water, dried in air and baked again at 500 °C for 45′. In the case of devices provided with a 4-MP interlayer, after cooling down to 70 °C, the substrates were immersed in a saturated solution of 4-MP in chlorobenzene for several hours (~20 h). Immersion was followed by rinsing with pure chlorobenzene. P3HT (M\textsubscript{w} = 77 500, PD = 2 and RR = 96.3, purchased by Merck and used without further purification) was then spin coated onto the substrates at 1000 rpm for 60′ from a 30 mg ml\textsuperscript{-1} chlorobenzene solution. Spin coater rotation was activated 15 seconds after dispensing the solution onto the substrate in order to promote effective polymer infiltration inside the mesoporous TiO\textsubscript{2} layer. In the case of samples without a 4-MP interlayer, the substrates were re-heated at 200 °C and then cooled down to 70 °C right before spin coating the P3HT, to allow the mesoporous TiO\textsubscript{2} layer to expel residual water. Where scheduled, thermal annealing of samples at 140 °C for 30′ in an inert N\textsubscript{2} atmosphere was
performed following P3HT deposition. Finally, 80 nm thick silver electrodes were thermally evaporated under high vacuum (10^{-6} \text{ mbar}) onto the samples through a suitable shadow mask defining a device active area of $\sim 2 \times 4.5 \text{ mm}^2$. Current density–

voltage ($J-V$) characteristics were measured by a Keithley model 2400 digital source-meter exposing the cell to a class AAA Newport Air Mass 1.5 Global (AM 1.5 G) full spectrum solar simulator. The power of incoming radiation was set at 100 mW cm^{-2} using a NREL calibrated silicon solar cell.

Quasi-cw Photoinduced absorption (PIA) spectroscopy was used to investigate the absorption of photo-generated long-lived species (from $\mu$s to ms). Pump excitation was provided by a diode laser at 530 nm modulated by a mechanical chopper. A 4 mm diameter laser beam was made using a telescope in order to guarantee a good overlap with the probe beam. The probe was generated from a 100 W halogen lamp. The changes in transmission under photoexcitation were detected by a silicon photodiode and measured by a lock-in amplifier referenced to the modulation frequency in order to measure the signal in phase and out of phase with respect to the laser pump. Finally, the modulation frequency in order to measure the signal in phase and out of phase with respect to the reference laser was recorded at 1 kHz repetition rate. The signal was normalized to the un-modulated transmission for every wavelength ($\Delta T/T$).

In order to estimate the lifetime of the absorbing species ($\tau$), the magnitude of the in-phase ($X$) and out-of-phase ($Y$) spectrum has been used according to the expression $\tau = |Y/X|/\omega$, where $\omega$ is the modulation frequency. All samples were measured in a vacuum chamber.

For the transient pump–probe experiment, the samples under study were resonantly photoexcited by a pump pulse and its subsequent dynamical evolution was detected by measuring the transmission ($T$) changes of a delayed probe pulse as a function of pump–probe delay $\tau$ given by the differential transmission $\Delta T/T = (T_{\text{pump-off}} - T_{\text{pump-on}})/T_{\text{pump-off}}$. The laser source was a regeneratively amplified mode-locked Ti:sapphire laser (Clark-MXR Model CPA-1), delivering pulses at 1 kHz repetition rate with 780 nm center wavelength and 150 fs duration. A fraction of this beam was used to pump a non-collinear optical parametric amplifier (NOPA) capable of delivering ultra-broadband pulses in the visible (500–750 nm). Details of the NOPA used can be found elsewhere.$^{14}$ In the present work we used the NOPA in a narrowband configuration to obtain tunable visible pulses with a spectral width of 20 nm and a time-duration of $\sim 180$ fs without the dispersion compensation. Another small fraction of the Ti:sapphire amplified output was independently focused into a 2 mm thick sapphire plate to generate a stable single-filament white-light supercontinuum which serves as a probe pulse. A short-pass filter with 760 nm cutoff wavelength was used to filter out the residual 800 nm pump light thus limiting our probing window to the 450–760 nm region. All samples were excited at 530 nm (10 nJ, 300 $\mu$m beam size) and measured in a vacuum chamber.

Positron annihilation spectroscopy was used to monitor the effect of 4-MP on the penetration of P3HT in the porous TiO$_2$. In order to obtain depth-resolved data, positrons were implanted in the sample at various depths using a variable-energy positron beam (from 0.1 to 17 keV) at the VEPSAS laboratory (LNESS Centre - Politecnico di Milano). The depth resolution of a variable-energy positron beam depends on the positron implantation-profiles of the so-called Makhov distribution$^{15}$ and the exploring region of positron and positronium. The Makhov distribution is sharp at low positron implantation energy and broader at high implantation energy. The exploring region after implantation depends on the positron and positronium diffusion length. In P3HT and porous titania, the components of the studied hybrid solar cells, the positron diffusion lengths are limited to tens of nanometres (see ESI†). Positronium diffusion depends on the pore dimensions and the pick-off conversion,$^{13,16}$ but in the studied elements it is less than a hundred of nanometers. Two hyperpure Ge gamma detectors (Ortec – relative efficiency $\sim$50% at 1.33 MeV) were used to measure the spectrum of the annihilation radiation. The annihilation peak (511 keV) is broadened by the Doppler effect due to the motion of the electrons encountered by positrons. A quick characterisation of the shape of the annihilation peak is given by the so-called ‘shape’ or $S$-parameter, i.e. the fraction of annihilating positron–electron pairs with momenta $p_L \leq 0.456$ atomic units (energy range 511 $\pm$ 0.85 keV). The $S$-parameter corresponds to annihilation of positrons with valence electrons (and para-Ps). The tails of the two-gamma peaks at a high Doppler shift, which come from annihilation with inner atomic shells, are more sensitive than the $S$-parameter to the average chemical composition in the annihilation region and are suitable for quantitative compositional analyses. However, the low counting rate in the high momentum region requires background suppression by adopting the coincidence Doppler broadening technique$^9$ (CDB), i.e. to take both annihilation gammas in coincidence. CDB spectra with about $2 \times 10^7$ total counts were measured with a peak/background ratio of 10$^5$ to 10$^6$. The momentum resolution (FWHM) was 3.5 $\times 10^{-3}$ $m_0c$. The experimental procedure used in this study is similar to those described in ref. 30.

An additional PAS parameter, sensitive to the presence of free volume and to the extension of the inner pore surface, is the positronium fraction. Positronium (Ps) in the ground state exists in two sublevels: 25% singlet (para-Ps) and 75% triplet (ortho-Ps), according to the spins of the electron and positron (antiparallel or parallel, respectively). Annihilation features in a vacuum are different: para-Ps annihilates with emission of two gamma rays (511 keV each, as free annihilation without Ps formation), while ortho-Ps annihilates by emitting three gamma rays producing a continuous energy distribution between 0 and 511 keV, where the sum of the energy of the three photons of the ortho-Ps annihilation is 1022 keV. Ps fraction measurements were performed using the well-known “3$\gamma$ method”.$^{18,19}$ This method is based on the idea of measuring the rate $R(E)$ between a portion of the area under the continuous energy distribution $F$ (from 350 keV up to 500 keV), mainly due to ortho-Ps annihilation, and the peak area $P$ (511 $\pm$ 4.25 keV) mainly due to free and para-Ps annihilation. Thus from the annihilation spectrum it is possible to obtain

$$R(E) = V/1P.$$  \hfill (1)

When there is no pick-off annihilation, i.e. when the positron of the ortho-Ps annihilates with an electron of the material (instead of the ortho-Ps electron) in relative singlet state emitting two $\gamma$-rays (instead of three), the Ps fraction $F(E)$ can be obtained from $R(E)$ using the relationship:

$$F(E) = \frac{1 + P_0(R_1 - R(E))}{P_0(R(E) - R_0)^{-1}},$$  \hfill (2)

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where \( P_0 \) and \( R_0 \) are the parameters when the Ps fraction is nil \( (F = 0) \) and \( P_1 \) and \( R_1 \) are the parameters when 100% of the positrons becomes positronium \( (F = 1) \). The calibration for 0% and \(-100\%\) of Ps in a vacuum was performed using a Ge single crystal \((100)\) at 1000 K.\(^{18}\) The samples investigated by PAS were prepared according to the same procedure shown for the device fabrication, excluding the metal contacts and the TiO\(_2\) compact layer. The PAS measurements were performed at room temperature at a vacuum level around 10\(^{-5}\) to 10\(^{-7}\) Torr.

X-ray Photoemission Spectroscopy (XPS) spectra were generated by excitation with Mg K\(_\alpha\) radiation \((hv = 1253.6 \text{ eV})\). Photoemitted electrons were collected at normal emission and at room temperature with a 150 mm VSW hemispherical electron analyzer operated with pass energy of 25 eV. The overall resolution was about 0.9 eV full width at half maximum (FWHM). The samples for XPS were prepared by the immersion of flat anatase TiO\(_2\) substrates in a solution of 4-MP and chlorobenzene. Both samples were cut from the same TiO\(_2\) substrate and annealed in an oxygen atmosphere before being immersed into the solution. They were cooled down to a temperature of about 80 °C and then immediately immersed into the solution in order to minimize water adsorption by TiO\(_2\). One sample (rinsed) was kept in the solution overnight and then rinsed with clean chlorobenzene. The other sample (not rinsed) was kept in the solution for one more day and then extracted without rinsing. The solution was kept in the dark and at low temperature before the XPS measurements. The thickness of the 4-MP layer in the sample not rinsed was kept as uniform as possible during the solution drying process by gently tilting the substrate. The XPS samples were fixed to a Ta sample holder and inserted into the vacuum chamber. Samples were kept in air for less than 5 minutes before insertion into vacuum. The vacuum level in the analysis chamber was in the low 10\(^{-10}\) Torr range.

The atomistic simulations have been performed using model potential molecular dynamics (MPMD). All calculations have been performed on the anatase \((101)\) surface optimized using density functional theory,\(^{20}\) by freezing the Ti and O positions. Model potentials obtained by combining existing force fields and by adding long-range Coulomb and dispersive interactions to model interactions across the hybrid interface were used. The interatomic potential for TiO\(_2\) is described by the sum of a Coulomb and a Buckingham-type two-body potential\(^{21}\) which has been successfully applied to study nanostructured TiO\(_2\).\(^{22}\)

To describe 4-MP, 2-MP, and P3HT the AMBER force field\(^{23}\) was used that includes either bonding (stretching, bending, torsional) or nonbonding (van der Waals plus Coulomb) contribution. The atomic partial charges were estimated by \(\text{B3LYP}/6-31\text{G}^*\) calculations with the RESP procedure using the Gaussian 09 code.\(^{24}\) The MPMD simulations were performed by using the DL\_POLY-3 code.\(^{25}\) Atomic trajectories were calculated by using the velocity Verlet integrator, with a time step as small as 1.0 fs. Long-range electrostatic forces were evaluated using a particle mesh Ewald algorithm.\(^{26}\) A cutoff as large as 9.5 Å was used in order to accurately calculate the van der Waals interactions. The simulation protocol used for geometry optimization consisted of a combination of 0.1 ns low-temperature molecular dynamics followed by conjugate gradients. The diffusivity of a P3HT single chain was calculated by standard MPMD over 4 ns-long trajectories (1 ns equilibration + 3 ns statistics).

### Results and discussion

In Fig. 1 we show the current–voltage curves for devices tested under AM1.5 conditions. The TiO\(_2\)/P3HT device shows state-of-the-art figures of merit and a power conversion efficiency (\(\eta\)) of about 0.4%.\(^{1,10}\) When the molecular interlayer is added, the photocurrent is doubled and the open circuit voltage is enhanced, as verified over more than one hundred devices tested. In the best case, the photocurrent is pushed from 1.4 mA cm\(^{-2}\) to 3.26 mA cm\(^{-2}\), together with an enhancement of the \(V_{oc}\) from 0.51 to 0.62 V, bringing the power conversion efficiency from 0.37% to 0.95%. Further improvement is observed upon annealing, with an increase in the short-circuit photocurrent to 3.75 mA cm\(^{-2}\) and a rise of the efficiency to 1.13% (see Table 1 for a summary of the devices figures of merit).

This is a remarkable efficiency for such a type of cell, yet the key point is understanding why it occurred and hence how further improvements can be made. To shed light on the role of the interlayer we took into account three critical factors for efficient metal oxide–polymer systems: \(^{2,5,10,12-27,28}\) (i) efficient charge generation at the interface; (ii) reduced charge recombination; (iii) good polymer infiltration throughout the mesoporous structure. We analyzed these points by using different types of spectroscopic techniques. Quasi-cw Photoinduced Absorption (cw-PIA) was used to probe charge absorption in the polymer in the time range of \(\mu\text{s–ms}\)\(^{29}\) (Fig. 2a). When the 4-MP interlayer is introduced, the PIA signal increases by nearly an order of magnitude with respect to the control sample \((\text{TiO}_2/\text{P3HT only})\), especially the broad band peaking at 1.92 eV, which has been assigned to 2D delocalized polarons in the P3HT phase.\(^{29}\) As 4-MP is a bi-functional molecule, we also investigated samples where only thiols or pyridine functionalities are used as interlayers. In the presence of thiols no improvement can be observed. The TBP molecule gives an enhancement of the PIA signal, however it is smaller than in the presence of 4-MP. The PIA signal intensity is proportional to the product of the density of charges photogenerated and their lifetime. In order to disentangle the contribution of these two factors, we separately estimate the charge lifetime (see Methods section). We find a lifetime in the order of 50 \(\mu\text{s}\) for the control sample, while in the presence of the 4-MP interlayer the lifetime is about 150 \(\mu\text{s}\), three times longer. This is an indication of a reduction in charge recombination in the presence of the interlayer, which hampers the electron back-transfer at the interface. However, this does not suffice to account for near one order of magnitude PIA signal enhancement, indicating a comparable improvement in charge generation.

Femtosecond transient absorption (TA) spectroscopy has been used to monitor the charge generation process in TiO\(_2\)/P3HT samples with and without 4-MP (Fig. 2b and c).

### Table 1 Summary of device parameters of TiO\(_2\)/P3HT with and without the 4-MP interlayer and after annealing treatment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(V_{oc} [\text{V}])</th>
<th>(J_{sc} [\text{mA cm}^{-2}])</th>
<th>FF</th>
<th>(\eta [%])</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)/4-MP/P3HT</td>
<td>0.59</td>
<td>3.75</td>
<td>0.51</td>
<td>1.13</td>
</tr>
<tr>
<td>TiO(_2)/4-MP/P3HT + annealing</td>
<td>0.62</td>
<td>3.26</td>
<td>0.45</td>
<td>0.95</td>
</tr>
<tr>
<td>TiO(_2)/P3HT</td>
<td>0.51</td>
<td>1.40</td>
<td>0.50</td>
<td>0.37</td>
</tr>
</tbody>
</table>
respectively). Low pump energy and fluence were used to avoid direct charge generation and recombination in the P3HT phase. The TA spectra of the control sample exhibit two main features at early times after photoexcitation (~500 fs, Fig. 2b). For energies higher than 1.94 eV a positive fractional change in the transmission signal ($\Delta T/T$) can be observed which is assigned to the P3HT ground state photobleaching (PB). At energies lower than 1.83 eV, the sample shows a dominant stimulated emission (SE), followed by a concomitant process of charge generation (appearance of a broad photo-induced absorption (PA) band) and singlet exciton deactivation to the ground state ($S_1 \rightarrow S_0$) which is a clear dominant channel of loss.

In the presence of 4-MP, though part of the photogenerated singlet excitons still recombines to the ground state over the entire time window investigated, the charge absorption band appears instantaneously. In fact no trace of SE can be observed and there is a reduction in intensity of PB vibrionic band at 2.35 eV due to the superimposition with the charge absorption
band in the P3HT. This indicates that excitons generated close to the interface now undergo a very efficient electron transfer. We exclude that the 4-MP molecule itself can be a quenching site for excitons as the same samples were prepared on ZrO$_2$, a high band gap oxide where electron injection from P3HT is inhibited, and we do observe stimulated emission with and without the 4-MP interlayer (ESI, Fig. S3†). We can then conclude that the presence of the interlayer affects the metal oxide–polymer interface, helping the exciton splitting and hampering the electron back-transfer, which leads to a large improvement of the device performances.

In order to investigate if the infiltration of the mesoporous TiO$_2$ with P3HT is influenced by the 4-MP interfacial modification, we have employed Positron Annihilation Spectroscopy (PAS) for the first time in this field. PAS is sensitive to “empty space”, and can directly detect buried, isolated pores of 0.3–50 nm size that are not accessible to conventional probes. In recent years, PAS with a variable-energy positron beam has emerged as a powerful tool for the investigation of thin films, achieving depth-profiles from tens of nanometers up to several μm in thickness (see Methods section). Positrons, the positively charged antiparticles to the electrons, are implanted with a controlled kinetic energy into the porous material and annihilate with free electrons in gamma-rays or in the form of an hydrogenoid atom (bonded state $e^+e^-$) called positronium (Ps). Ps is sensitive to the presence of free volume and to the extension of inner pore surface. An analysis of the resulting gamma-rays allows the deduction of the nature of the annihilation sites (TiO$_2$ pores, polymer, etc.). This enables a nanometer scale mapping of the pore composition over the entire thickness of the device in a non-destructive way. In order to resolve the polymer distribution inside the porous metal oxide the S-parameter was measured. The S-parameter corresponds roughly to annihilation of positrons with valence electrons and bears the chemical signature of the studied material (see Methods section). The S-profiles reported in Fig. 3a display an evolution from the high S-value characteristic of P3HT toward lower values expected for porous TiO$_2$ with or without 4-MP (reference values for the single P3HT and for porous TiO$_2$ and TiO$_2$/4-MP are shown in Fig. 3a). The curves through the experimental points are the result of a fitting procedure (VEPFIT$^{35}$) which identifies four layers in the explored structure: a solid P3HT cap, a thin porous TiO$_2$ layer of about 50–70 nm heavily infiltrated with P3HT, a second thick porous TiO$_2$ region of about 700 nm containing less P3HT and the glass substrate. Following the decrease of the S-parameter we can conclude that there is a P3HT concentration gradient within the oxide in both samples, with and without the interlayer; however, in the presence of 4-MP the degree of P3HT infiltration is reduced in the first layer and enhanced in the deeper region, while the annealing treatment does not induce any change. A quantitative evaluation of this action in the deep region is given from the analysis of coincidence Doppler broadening (CDB) taken at fixed implantation energy, 5 keV (see Methods and ESI†). CDB distributions depend on the electron structure of P3HT and TiO$_2$$^{33,34}$ and, therefore, are sensitive to the average chemical composition at the annihilation sites.$^{33–38}$ In Fig. 3b the CDB spectra $\rho$ are presented in terms of relative change with respect to the reference spectrum of the porous TiO$_2$. The CDB results for TiO$_2$/P3HT and TiO$_2$/4-MP/P3HT samples, taken at a fixed positron implantation energy (5 keV), are fitted using synthetic spectra created as linear combinations of the spectra taken separately for P3HT, for TiO$_2$ and for TiO$_2$/4-MP (see ESI†). Thus it is possible to estimate the fraction of positrons annihilating in P3HT that is a good index of infiltration. This fraction is univocally related to the pore filling factor $f$ (see ESI†).

The values estimated for the pore filling factors are: $f = 16.5 \pm 3\%$ and $f = 22 \pm 3\%$ for TiO$_2$/P3HT and for TiO$_2$/4-MP/P3HT, respectively. The difference observed in terms of $f$ indicates that the presence of 4-MP does not sizably affect the polymer filling factor in such a way as to justify the enhancement in photocurrent observed. This suggests that the pore filling by itself is not the limiting factor controlling the device performances shown in Fig. 1.

Remarkable differences in terms of the positronium (Ps) fraction are found when the 4-MP interlayer is introduced. In fact, the Ps depth profile of Fig. 3c drops drastically when TiO$_2$ is infiltrated with P3HT, especially in the presence of 4-MP (a monolayer of 4-MP in bare TiO$_2$ does not reduce the Ps yield). In particular, the bump in the TiO$_2$/P3HT sample (black symbols) which appears in the deeper region (200–800 nm) is washed out in the presence of 4-MP. The Ps yield reduction can be the consequence of: (i) a better pore filling that favours 2-$\gamma$ annihilation and/or (ii) a larger P3HT covering of the free inner titania surface where Ps is formed. In both cases the polymer induces Ps inhibition and ortho-Ps quenching.$^{39,40}$ The small difference in the filling factors measured in the deeper region by CDB in samples with and without 4-MP cannot explain the large reduction in Ps yield. Moreover, if we look at the shallowest region, the S-parameter shows a lower concentration of the P3HT phase in the presence of the 4-MP layer, while the Ps yield is again reduced. Therefore we conclude that the Ps fraction reduction is due to a reduction of free TiO$_2$ surface, which means a better contact between the oxide and P3HT phases and a closer polymer packing at the interface. In light of this, it is interesting to notice here that there is also a small difference of the Ps-profiles between pristine and annealed samples which is the signature for a reordering of the polymeric chains and closer packing with a reduction of free oxide surface also after annealing. The presented information, inaccessible by optical and electron microscopy techniques previously used, is in perfect agreement with an improvement of charge generation and device photocurrent and, most importantly, moves the focus of the investigation to the most critical point in the system, the nature of the hybrid interface.$^{38,41}$ We proceed with our study by zooming into the interface in order to understand what is driving the materials interaction. Fig. 4 shows X-ray photoemission spectroscopy (XPS) spectra related to the N 1s for TiO$_2$ compact films which were soaked in a 4-MP solution. After soaking, one sample was rinsed (upper row, red spectra) and one was not (lower row, black spectra).

For both samples the measured line shape could be decomposed as a sum of three peaks, labelled as a (characterized by a binding energy $E_{\text{a, b}} = 402.3$ eV), b ($E_{\text{B, b}} = 401.0$ eV) and c ($E_{\text{B, c}} = 399.4$ eV). Peak c is seen to increase when increasing the
4-MP layer thickness. This is a clear indication that it must be related to N atoms in the free pyridine ring, as observed in several other cases.42–45 The presence of peaks at higher binding energies is an indication of chemical interactions of the N atoms with the substrate.43 Therefore, peaks a and b can be assigned to pyridine rings where the N lone pair is involved in intermolecular interactions or even in a bond.42 The observation of more than one bound N state could be explained by different absorption sites on the substrate which can present both Lewis and Brønsted active centers.46 From the XPS results for the N 1s core level we can support the hypothesis that the 4-MP molecules are bounded to the TiO2 surface mainly through the N atoms, while the other molecular functionality, namely the mercapto group, remains unaffected. FTIR spectra taken on the same samples in attenuated total reflection mode confirm this hypothesis probing not bounded thiol groups (see ESI†). This information provides the first key point for a clear understanding of the interface.

To further understand the interaction between the 4-MP and the titania surface, we performed atomistic simulations based on a combination of model potential and first-principles methods. It is found that a single 4-MP molecule efficiently binds to the (101) anatase surface through the active lone pair of the nitrogen atom, confirming the XPS results. In the presence of an ideal surface an N–Ti bond is formed with the titanium atoms of the substrate. In the lowest energy configuration, the molecule is roughly normal to the surface with a N–Ti distance of about 0.2 nm (see the inset in Fig. 4), and it is bound to the surface with an energy as large as \( /C24 \) 1.5 eV. By successively depositing molecules on titania we predict the formation of a 4-MP monolayer exposing a flat surface formed by rows of thiol groups (see Fig. 5a). Each Ti atom of the metal oxide binds to the 4-MP nitrogen atom so that the TiO2 surface is fully covered. Notably, as a result of the \( \pi–\pi \) intermolecular interaction, the monolayer spontaneously forms
an ordered zig-zag pattern stable at room temperature. This arrangement has fundamental effects on the surface thermodynamics. The first remarkable effect of 4-MP coating is to enhance the mobility of the polymer on the TiO2/4-MP substrate. In particular, we find that, at room temperature, the polymer diffusivity on TiO2/4-MP is about one order of magnitude larger than on bare TiO2 3.0 ± 0.3 × 10^{-7} cm^2 s^{-1} and 4.0 ± 0.4 × 10^{-8} cm^2 s^{-1} respectively. The energy barrier for the polymer migration is smaller in the case of TiO2/4-MP since the local charges are smaller and the corresponding electrostatic energy landscape is smoother. Accordingly, the polymer easily migrates on the TiO2/4-MP surface, yielding a larger polymer/substrate interface area. This is nicely consistent with the results shown by PAS and is perfectly in line with the enhancement in coverage area found upon annealing which provides extra energy to the polymer chains. The higher polymer chain mobility on the substrate surface can of course affect its final morphology, due to higher chances for getting its lower energy configuration. Therefore we have tried to investigate the actual polymer chain morphology on the different substrates. The bare TiO2 surface shows positive and negative ions alternate at different heights, thus modulating the local electrostatic landscape. When the conjugated polymer chain is deposited on it, as a consequence of the electrostatic interactions, distortions of the chain can be observed (Fig. 5a). Interestingly, when 4-MP is used to functionalize the metal oxide surface, the substrate results atomically flat, with much smaller atomic partial charges in the external thiol groups. In this case the polymer backbone, spatially separated from the titania by about 1 nm, is planar on the surface and the alkyl chains are aligned along the thiol rows (5b). In the same way, when stacking a second P3HT chain (see Fig. 5) a more ordered configuration is found in the case of TiO2/4-MP where the molecules are planar. These results are in agreement with the optical spectroscopic investigations where a signature of 2D delocalized charges was observed, typically found in P3HT crystalline structures.

To finally validate the importance of the molecular order at the interface level we also consider the alternative case of 2-mercaptopyridine (2-MP). The 2-MP differs from 4-MP only because the thiol group is close to the nitrogen atom. When the molecule is deposited on TiO2, in addition to the Ti–N bond, we predict also the formation of an S–H–O hydrogen bond. The geometry of the bound molecule is consequently affected, preventing the formation of an ordered interlayer (see Fig. 5c) and inducing disorder in the polymer chain when deposited on the surface. In this case, in fact, a slightly lower diffusivity of the polymer on the surface is found (3.0 ± 0.4 × 10^{-8} cm^2 s^{-1}) and an injection barrier is experimentally observed when the 2-MP interlayer is introduced in a working solar cell (see ESI, Fig. S1†).

Conclusions

Summarising the overall characterization we can assert that the presence of an oriented molecular layer, triggered by selective interactions with the TiO2 surface, drives local ordering smoothing the otherwise abrupt interface. These results point out the importance of molecular interactions and local morphology in hybrid interfaces and the implications they have on charge separation and recombination. By tuning the surface properties of the inorganic compounds, we are able to control the polymer chain morphology. This can be translated into better charge generation and separation at the interface not only as a result of the enhancement of the surface contact between the two materials but also as a result of the enhanced delocalization of the polymer photoexcitation, and enhanced local charge mobility. Accordingly, the extracted photocurrent is doubled with respect to the “bare” interface and the overall cell performance improved beyond 1% power conversion efficiency. Investigating the system from a molecular to a mesoscopic level has been strategic to improve the device efficiency to superior and more appealing values, and at the same time to provide some indications for further improvements. We have observed a clear difficulty of bringing all the excitons photogenerated in the bulk of the pore to the donor–acceptor interface, which keeps the external quantum efficiency of the device quite low (see ESI, Fig. S6†). This may indicate a still poor electronic coupling between the two active compounds at the interfaces and/or a localization/trapping of the excitonic species which hampers their diffusion, thus anticipating that a better engineering of the electronic wavefunction at the interface and the possibility of extending the level of order achieved at the interface to a longer range will definitely further boost the device performances.
Acknowledgements

A.P. G.L., E.C. and C.B. thank Fondazione Cariplo (project no. 2009/2527 “Nanostructured MATerials for innovative HYbrid Solar cells – MATHYS”) for funding. F.M., S.A. and R.F. acknowledge Prof. Alfredo Dupasquier for valuable suggestions and stimulating discussions. C.M., G.M. and A.M. thank the Italian Institute of Technology (Project SEED “POLY-PHEMO”) and Regione Autonomia della Sardegna under L.R. 7/2007 for funding and IIT platform “Computation”, CYBER-SAR (Cagliari, Italy), CASPUR (Rome, Italy) and CINECA (Casalecchio di Reno, Italy) for computational support. F.M. thanks the Regione Lombardia (Italy) by NANOSOL project. A.P. and M.B. thank Maria Chiara Mignani for support in device fabrication and Dr Dario Natali for useful discussions.

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