Enhanced performance of single and double junction plastic solar cells
Moet, Date Jan David
Chapter 5

High work function transparent middle electrode for polymer tandem cells

Abstract

Series-connected tandem polymer solar cells can be processed from solution by spin coating a composite middle electrode of ZnO nanoparticles and modified PEDOT:PSS between the two subcells. Since ZnO dissolves in acidic solutions, a modification of the pH of PEDOT:PSS is required. In this chapter, we investigate the effects of a deliberately increased pH of PEDOT:PSS on the performance of double-junction solar cells. It is shown that the work function of PEDOT:PSS layers drops more than 0.5 eV when the acidity is varied from pH 1.8 to 8.5 by addition of 2-dimethylaminoethanol. The use of such a modified middle electrode in polyfluorene-based solar cells results in a significant decrease in open-circuit voltage. This loss can be circumvented by covering the modified PEDOT:PSS middle anode with a thin layer of a perfluorinated ionomer prior to spin coating of the second photoactive layer. Such a middle electrode is demonstrated in a PF10TBT:PCBM double-junction cell, which produces an open-circuit voltage as high as 1.92 V.

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5.1 Introduction

Most device architectures used for polymer multijunction solar cells contain two subcells connected in series. Efficient operation of these tandem cells relies on the adopted middle electrode. A series connection requires the middle electrode to be conductive and (semi)transparent and to simultaneously act as an anode and cathode for the two respective subcells. Furthermore, as low-cost processing is a major asset of organic photovoltaics, the focus in research has recently shifted towards fully solution-processed solar cells. Metal oxides are particularly suitable for use with such techniques, as evidenced by reports on tandem cells containing interlayers of sol-gel processed TiO$_x$\textsuperscript{[1]} and ZnO nanoparticles dispersed in acetone.\textsuperscript{[2]} The latter approach has the advantage that the inserted interlayer is entirely solution-processed from stable dispersions without the need for thermal annealing steps. It was demonstrated that covering a ZnO layer with a modified PEDOT dispersion yields a transparent and conductive interfacial contact, suitable for interconnection of multiple solar cells based on P3HT and MDMO-PPV. To prevent the ZnO layer from dissolving upon application of acidic PEDOT:PSS, a dispersion at neutral $\rho$H was used.\textsuperscript{[2]} It was shown that the neutral PEDOT-based middle anode provided an ohmic hole contact for the P3HT:PCBM back cell. However, since P3HT has a rather low ionization potential of 4.9 eV, an important question is whether neutral-$\rho$H PEDOT:PSS is an appropriate electrode for polymers having high ionization potentials as well. If this is not the case, the open-circuit voltage and thus the efficiency might decrease.\textsuperscript{[3]}

In this chapter, we investigate the influence of $\rho$H on the conductivity and work function of PEDOT:PSS layers and its effect on the performance of polymer:fullerene tandem solar cells. We find that at increased $\rho$H the conductivity remains sufficiently high, but a drop in the work function of PEDOT:PSS strongly limits the open-circuit voltage of single-layer and tandem cells made of PF10TBT:PCBM. To solve this problem, we include a thin layer of a perfluorinated ionomer, which raises the work function of the middle electrode and eliminates the limitation of $V_{oc}$.

5.2 Modification of the acidity of PEDOT:PSS

Commonly used electronic grade PEDOT:PSS dispersions are strongly acidic due to an excess of the polyelectrolyte PSS, which enables the formation of a waterborne dispersion and acts as a charge-compensating counterion for oxidized thiophene units in the PEDOT chains. Ultraviolet photoemission spectroscopy (UPS) studies have demonstrated that an increased $\rho$H by addition of NaOH results in a decrease of the work function of electronic-grade PEDOT:PSS.\textsuperscript{[4,5]} Concomitantly, the ionization energy is unaffected, which indicates that the Fermi level is separated from the HOMO level upon increasing $\rho$H, i.e., the material undergoes a transition from metal-like to semiconductor-like behavior. At high
A large injection barrier with a light-emitting polyfluorene derivative was found, as evidenced by a large decrease in the measured hole-only current. The observed effects on the surface and interface characteristics of PEDOT:PSS layers, resembling those of dedoping, were attributed to deformation of PEDOT chains in the bulk and formation of polaron states on the doped thiophene, induced by changes in the PEDOT surroundings.

In order to systematically alter the $pH$ of PEDOT:PSS (see Figure 5.1a for its chemical structure), we added small amounts of a 1:8 dilution of 2-dimethylaminoethanol (DMAE) in water to a commercially available PEDOT:PSS dispersion (Clevios Baytron PH500, H.C. Starck). Figure 5.1b shows the resulting titration curve. The obtained acidity ranged from $pH$ 1.8 for unmodified PH500 to a slightly basic $pH$ 8.5 after addition of 3.0 vol % DMAE:H$_2$O. As DMAE is a relatively weak base, the equivalence point is found at a $pH$ lower than neutral (2.7 vol %, $pH$ 5).

It is relevant to know to what extent the acidity of PEDOT:PSS should be modified in order to keep the underlying ZnO layer intact. As an indication, the UV-VIS absorbance of a pristine ZnO layer was measured and its value at $\lambda = 350$ nm was compared to that of layers on which PEDOT:PSS of varying $pH$ was applied via spin coating. The measurements were performed versus a glass reference and were scaled to the transmittance at $\lambda = 400$ nm, where no ZnO absorbance is present. The results are shown in Figure 5.2. Due to dissolution in acidic PEDOT:PSS, the absorbance of ZnO strongly decreases below $pH$ 3. Additionally, a major loss in wetting quality and film formation properties of PEDOT:PSS on ZnO is observed at low $pH$. When applied in multilayer solar cells using ZnO, the PEDOT:PSS dispersion should therefore have a $pH \leq 3$. In the remainder of this chapter, we will refer to such dispersions as M-PH500.
Figure 5.2: Absorbance at $\lambda = 350$ nm of initially 75 nm thick ZnO layers on glass, after application and spin coating of PEDOT:PSS of varying pH. Below pH 3, PEDOT:PSS starts to dissolve ZnO, as evidenced by a decrease in absorbance and a concurrent loss in wetting quality.

5.3 Device operation of tandem cells before and after photodoping of ZnO

Tandem solar cells comprising a ZnO/PEDOT:PSS middle electrode usually exhibit an inflection point in the $J - V$ curve around $V_{oc}$ when the illumination source has no or little UV in its spectrum. This has been attributed to a non-ohmic contact between ZnO and neutral PEDOT:PSS, which can be alleviated by sufficient photodoping of ZnO using UV light.\cite{2} The proposed mechanism involves photogeneration of electron-hole pairs in ZnO upon exposure to UV and subsequent desorption of chemisorbed oxygen radicals after capture of photoinduced holes.\cite{6,7} This leaves excess electrons in the conduction band, which enhances the $n$-type character of ZnO. In a porous nanoparticulate film, the surface-to-volume ratio of ZnO is large and the effect of adsorbed oxygen can be considerable.

Figure 5.3 shows the effect of UV exposure on the current–voltage characteristics of a PF10TBT:PCBM double-junction cell.\cite{6} The device was measured under illumination with a metal-halide lamp filtered with a UV cut-off filter, resulting in a spectrum with $\lambda > 385$ nm. In between measurements the filter was removed and the sample was illuminated for time periods indicated in the legend, allowing photodoping of ZnO with UV photons from the same light source. With increasing UV exposure times the $J - V$ curves gradually cease to be S-shaped.

In the discussion below, we assume that ZnO prior to UV illumination is a low-conductive $n$-type semiconductor and PEDOT:PSS is highly $p$-doped and can be treated as a high work function metal. When these materials are brought into contact, a Schottky barrier forms at their interface as electrons flow from ZnO to PEDOT:PSS until the Fermi levels line up. The barrier height is roughly equal to the work function difference, which amounts to $\Phi_{\text{PEDOT:PSS}} - \Phi_{\text{ZnO}} = (5.2 - 4.4) \text{ eV} = 0.8 \text{ eV}$. UV exposure results in a large in-
Increasing UV exposure

Figure 5.3: The effect of UV exposure on the photovoltaic performance of a PF10TBT:PCBM double-junction cell with a ZnO/PEDOT:PSS middle electrode.

crease of the amount of free electrons in ZnO,\cite{8} which reduces the Schottky barrier width such that it becomes virtually transparent to charges due to the possibility of tunneling. As a result, the counterdiode between the two subcells vanishes and the inflection point in the curve disappears.

In order to understand the origin of the S-shaped $J - V$ curves prior to UV illumination, we now focus on the current-voltage characteristics of a tandem solar cell in the dark and under illumination, which are plotted in Figure 5.4. For comparison, the characteristics after UV exposure are given as well. Several notable biasing conditions are indicated

Figure 5.4: Measured current-voltage characteristics of a polymer tandem solar cell with a ZnO/PEDOT:PSS middle electrode, (a) in the dark and (b) under illumination with UV-filtered light. The inset shows the same data on a semilogarithmic scale.
Figure 5.5: Approximate electronic band diagrams of a tandem cell with ZnO/PEDOT:PSS interlayer prior to photodoping. The labels A–E correspond to the various biasing conditions depicted in Figure 5.4.
of which the corresponding energy band diagrams are given in Figure 5.5. At high forward bias (A), a considerable current flows through the cell both before and after UV doping. When there is an ohmic contact between highly doped ZnO and PEDOT:PSS, injected charges that arrive from the photoactive layers can readily flow through the middle electrode without obstruction. In the ‘undoped’ interlayer, the onset of the dark current occurs at a higher voltage since an additional voltage drop is needed to break down the counterdiode. Since the latter is strongly biased in reverse at high forward bias of the tandem cell, electrons injected from the LiF/Al contact can tunnel through the increasingly depleted Schottky barrier and, subsequently, exit the device at the anode of the front cell. If the field is increased even further, holes will eventually be able to pass the interlayer as well. The same obviously holds for the device under illumination, as in this case the current at high forward bias is governed by injection of dark carriers. In the following, we define \( V_{bi} \) as the voltage that is required to have dark conductivity of the doped device. At a slightly higher voltage \( (V = V_{bi} + \delta, \text{line B}) \), the Schottky diode experiences a smaller reverse bias than at A and now prohibits flow of injected charges through the undoped device. For the same reason, a negligible current flows at voltages close to \( V_{oc} \) of the undoped cell under illumination. The band diagram corresponding to line D \( (V = V_{oc} - \delta) \) shows that under these conditions the few photogenerated electrons arriving from the front cell cannot overcome the barrier in order to recombine with holes from the back cell. This changes for decreasing applied voltages, as an increasing amount of photogenerated electrons pile up in the ZnO layer and holes arriving from the back cell are blocked at the ZnO/PEDOT:PSS interface. As the quasi-Fermi level in the ZnO layer is increased relative to that of PEDOT:PSS, the diode effectively sustains an additional forward bias that enables a substantial amount of electrons to pass and recombine with holes at the ZnO/PEDOT:PSS interface (line E). As as result, the short-circuit current in the device is the same before and after photodoping. In the dark, no current flows at zero bias in both cases since the direction of the electric field opposes charge carrier injection (line C).

5.4 P3HT:PCBM tandem cells with ZnO/M-PH500 middle electrodes

To assess the usability of our pH-modified PEDOT:PSS as constituent of a middle electrode in tandem solar cells, we fabricated single-junction and double-junction P3HT:PCBM solar cells. The non-optimized subcells were interconnected with layers of ZnO nanoparticles and a M-PH500 dispersion at pH 3.4. A single thermal annealing step was carried out under nitrogen atmosphere after all solution-processed layers were applied. The current–voltage characteristics of P3HT:PCBM single-layer and tandem devices under illu-

* Please note that these diagrams are only illustrative, as the actual potential distribution in the device depends on the (unknown) relative conductivity of the constituent layers. Furthermore, the amount of band bending indicated in the photoactive layers and in ZnO is somewhat arbitrary.
The current–voltage characteristics of a single-layer P3HT:PCBM solar cell (open circles) and a tandem solar cell based on two P3HT:PCBM subcells (filled circles). Each photoactive layer was approximately 120 nm thick. The single-layer device gave $V_{oc} = 0.55$ V, $FF = 0.64$ and $J_{sc} = 48.1$ A/m$^2$, whereas the tandem device showed $V_{oc} = 1.10$ V, $FF = 0.67$ and $J_{sc} = 22.6$ A/m$^2$. The reduction in $J_{sc}$ is caused by a redistribution of the internal optical field due to an interplay of transmission and reflection inside the device. Strikingly, the open-circuit voltages exactly add up and the fill factor of the tandem cell is even slightly higher than that of the single-junction device. As a result, both cells have an approximate power conversion efficiency of 1.9%.

As a means of constructing tandem solar cells based on P3HT:PCBM, the interlayer combination of easy-to-process ZnO and PEDOT:PSS is very suitable. Featuring high transparency, adequate conductivity and orthogonal solvent compatibility, the approach appears to inflict no compromises on device preparation and performance. However, in the specific case of P3HT:PCBM the requirements on electronic properties for modified PEDOT:PSS are not very stringent. Even if the work function of PEDOT:PSS would be considerably reduced from its usual value of 5.2 eV, ohmic hole contact could still be established with P3HT. Clearly, it is important to find out to what extent this remains valid for polymers with higher ionization potentials.

5.5 PF10TBT:PCBM tandem cells with ZnO/M-PH500 middle electrodes

Many new conjugated polymers used in present-day solar cells have a large ionization potential (IP), often due to the incorporation of fluorene units. Designed to enable high $V_{oc}$ and air stability, these polymers are particularly prone to electronic limitations due

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*The fact that even the single-layer device produces a low current is related to the fact that (a) the P3HT:PCBM layers used in this study were tentatively made rather thin to allow a sufficient amount of light to reach the back cell and (b) the P3HT batch was not purified prior to use, which is known to negatively affect device performance.
5.5 PF10TBT:PCBM tandem cells with ZnO/M-PH500 middle electrodes

Figure 5.7: Experimental $J - V$ curves of a single-junction PF10TBT:PCBM cell (open circles) and a tandem device (closed circles) under illumination (UV filtered, light intensity $\sim 1.2$ sun). The dashed line represents the constructed curve from the characteristics of the single-junction cell, assuming no additional losses. The discrepancy in $V_{oc}$ between experiment and theory amounts to 0.5 V.

One of these materials is the polyfluorene derivative PF10TBT, which was introduced in Chapter 2 of this thesis. This polymer has been used in conjunction with PCBM to create efficient solar cells with $V_{oc}$ close to 1 V.\[^{10}\] With its HOMO energy level at 5.4 eV, PF10TBT is an appropriate model compound for investigation of the $V_{oc} - \Phi_w$ relationship.

According to Kirchhoff’s law, a series-connected double-junction solar cell of PF10TBT:PCBM should produce an open-circuit voltage close to 2 V. However, using the ZnO/M-PH500 interlayer, we found a rather large spread in $V_{oc}$ for such devices with a maximum of only 1.5 V. This is shown in Figure 5.7, together with the predicted $J - V$ curve of a double-junction device as constructed from the experimental data of the single-layer cell.\[^{11}\] The calculation is only approximate as the entire $J - V$ curve was scaled to give a $J_{sc}$ similar to the experimental value. Still, it is evident that a ZnO/M-PH500 interlayer in PF10TBT:PCBM tandem cells imposes a considerable limitation to device performance.

We ascribe the reduction in $V_{oc}$ of PF10TBT:PCBM double-junction cells to a lowered work function of the pH-modified PEDOT:PSS anode. The effect of a non-ohmic hole contact for the back cell on the open-circuit voltage of a tandem device is depicted schematically in the simplified energy band diagrams of Figure 5.8. In the case of ohmic contacts on both the anode and cathode side of the front (F) and back (B) subcells, the open-circuit voltages are determined by the difference in energy between the HOMO of the donor and the LUMO of the acceptor\[^{3}\] and the tandem (T) device will have $V_{oc,T} = V_{oc,F} + V_{oc,B}$. The maximum attainable open-circuit voltage of the back cell decreases when the work function of the middle anode is reduced, which results in an equal loss in the open-circuit voltage of the tandem device.
5.6 Conductivity and work function of M-PH500

To investigate the influence of acidity on the conductivity and work function of PEDOT:PSS, several pH-modified PEDOT:PSS dispersions were spin coated on glass substrates with and without sputtered ITO patterns. The films on plain glass were used to determine the sheet resistance in a collinear four-point probe setup using the appropriate geometric correction factor. The conductivity shows a strong decrease up to pH 2.8, where it reaches a value of $3.3 \times 10^{-3}$ S/cm (see Figure 5.9a). Films of PEDOT:PSS at higher pH showed no further decrease in conductivity. Since standard electronic-grade dispersions of PEDOT:PSS (1 : 6 w/w) form layers with a conductivity between $2 \times 10^{-4}$ S/cm and $2 \times 10^{-3}$ S/cm, this effect is not relevant in the solar cells under study.

Using the non-destructive Kelvin probe method, the work function of each PEDOT:PSS layer on ITO was determined in a nitrogen atmosphere. Subsequently, a composite layer of PF10TBT and PCBM (1:4 w/w) was applied on the substrates, followed by thermal deposition of a LiF/Al cathode to obtain complete solar cells. The only intentional difference between the photovoltaic devices was the acidity of the applied M-PH500 dispersion. The fill factor and open-circuit voltage of the devices were extracted from the current–voltage characteristics recorded under white-light illumination. The $J - V$ curves (normalized at $V = 0$), fill factor, work function and $V_{oc}$ are shown together as a function of pH in Figure 5.9b-d. Although the shapes of the $J - V$ characteristics are dissimilar at different pH due to process variations, there is no systematic effect of pH on the fill factor. The observed decrease in conductivity of PEDOT:PSS thus has no significant effect on device performance.
Figure 5.9: (a) The influence of pH on the conductivity of PEDOT:PSS layers (squares). Indicated by the hashed area is the range of conductivity of standard electronic-grade (EG) PEDOT:PSS (Clevios VP AI4083) with pH 1.5 – 2.5.\(^{[13]}\) (b) \(J - V\) curves of PF10TBT:PCBM single-layer cells on PEDOT:PSS anodes with varying pH. (c) Fill factor of the same cells. (d) Open-circuit voltage of these cells (closed circles) and the work function of the PEDOT:PSS layers before deposition of the photoactive layer (open circles).

However, the work function of PEDOT:PSS is found to strongly decrease with increasing pH. At pH 3.4 it has dropped by more than 0.5 eV compared to that of unmodified PH500. This is consistent with the loss in \(V_{oc}\) from 2 to 1.5 V in double-junction cells made from PF10TBT:PCBM (Figure 5.7). An even further decrease of the work function is observed for higher pH. Clearly the open-circuit voltage of PF10TBT:PCBM cells follows the same trend and is reduced markedly by the pH-induced work function change. Consequently, the ZnO/M-PH500 middle electrode is only suited in combination with back cells based on a donor that has an ionization potential of 4.8 – 4.9 eV, such as P3HT.

5.7 Surface modification of ZnO/M-PH500 electrodes

In order for the back cell to produce the expected photovoltage, a method is needed to recover the work function of the back cell anode. Electronic grade PEDOT:PSS can be
Figure 5.10: Current-voltage characteristics of a PF10TBT:PCBM reference cell (open circles) and a tandem solar cell from two PF10TBT:PCBM subcells (filled circles). Each photoactive layer was approximately 80 nm thick. The two subcells were interconnected with a ZnO/M-PH500/Nafion middle electrode. Equivalent light intensity is 0.9 sun.

reformulated by addition of a 5 wt % Nafion® perfluorinated resin solution in a water/alcohol mixture to obtain a work function of 5.7 eV.\textsuperscript{[14]} Addition of a Nafion solution to pH-modified PEDOT:PSS dispersions is considered less feasible, since it introduces an additional acidic component to the formulation. It is, however, possible to apply a thin Nafion-only layer that raises the work function of the underlying PEDOT:PSS anode. Lee et al. have reported that the work function of ITO increases with 0.5 eV when it is covered with a thin Nafion layer\textsuperscript{[15]} Moreover, using density-functional theory (DFT) calculations, they showed that the ionization potentials of Nafion-like compounds are systematically higher than those of polystyrene sulfonic acids.

Here, we incorporate an interfacial layer of Nafion in a double-junction solar cell of PF10TBT:PCBM, by spin coating Nafion perfluorinated resin solution, highly diluted in ethanol, on top of the M-PH500 (pH 3.4) anode before applying the second photoactive layer. An ohmic hole contact between M-PH500 and PF10TBT is thus restored, without compromising the compatibility with the underlying ZnO layer. As shown in Figure 5.10, this method results in a well-performing double-junction PF10TBT:PCBM solar cell with $V_{oc} = 1.92$ V, FF = 0.61 and $J_{sc} = 34.9$ A/m$^2$ when illuminated with white light at an intensity of 0.9 sun. The single-junction reference device, processed on electronic grade PEDOT:PSS, has $V_{oc} = 0.98$ V, FF = 0.66 and $J_{sc} = 56.0$ A/m$^2$. Now, due to the inclusion of a thin layer of Nafion, the double-junction cell has an open-circuit voltage virtually twice as high as the single-junction device. Altogether, the approximate power conversion efficiency of the double-junction cell amounts to 4.5%, which is higher than that of the optimized single-layer cell ($\eta = 4.0\%$). The physical origin of this effect is discussed in the next chapter.
5.8 Conclusions

Polymer tandem solar cells of P3HT:PCBM and PF10TBT:PCBM were fabricated using solution-processed interlayers of ZnO nanoparticles and PEDOT:PSS at modified pH. The effect of pH on film quality, conductivity and work function of PEDOT:PSS layers was investigated by systematic tuning of the acidity by addition of DMAE in an aqueous solution. In order to leave the underlying ZnO layer intact, PEDOT:PSS dispersions with pH 3 or higher were required. Using a dispersion with pH 3.4, P3HT:PCBM tandem cells were made that showed addition of V_{oc} of the subcells and a maximum power point equal to that of the single-layer cell.

Up to pH 2.8 the conductivity of PEDOT:PSS layers was found to decrease strongly. At higher pH, it stabilizes to a level comparable to that of electronic grade PEDOT:PSS. The work function of PEDOT:PSS decreases with more than 0.5 eV upon neutralization, which yields a significant potential barrier when PF10TBT is contacted. A reduction in V_{oc} of solar cells based on this material results, which reduces the performance of the upper cell in a double-junction stack and, consequently, strongly limits the performance of the complete tandem device.

The introduction of a thin layer spin coated from a diluted perfluorinated resin solution recovers the work function of the modified PEDOT:PSS anode, as evidenced by the high open-circuit voltage of 1.92 V of a PF10TBT:PCBM tandem cell. Together with a fill factor of 0.61 and a decent short-circuit current density, the tandem device outperforms the optimized single-layer cell with an absolute efficiency increase of 0.5%.

5.9 Experimental

Processing of PEDOT:PSS. Glass substrates, with and without ITO patterning, were thoroughly cleaned with soap water, acetone, isopropanol and a UV ozone treatment before application of the PEDOT:PSS layers. The acidity of PEDOT:PSS (Clevios PH500, H.C. Starck) was tuned by addition of a 1:8 dilution of 2-dimethylamino-ethanol in water. The pH was measured, after vigorous stirring, with a Mettler-Toledo FE-20 pH meter using a Hamilton LIQ-GLASS electrode, calibrated with pH 4.01 and pH 7.00 buffer solutions. PEDOT:PSS layers were spin coated in air at high rpm, assisting evaporation of water and eliminating the need for successive thermal treatment. Conductivity measurements were performed with a collinear four-point probe method using the appropriate geometric correction factor (square substrate, width of sample = 6 × electrode spacing, correction factor = 3.77).

ZnO synthesis. ZnO nanoparticles of 5 to 10 nm diameter were synthesized in methanol via hydrolysis and condensation of zinc acetate dihydrate by KOH, as described elsewhere.\(^{[16,17]}\) After centrifugation, the ZnO gels were dispersed in acetone,\(^{[2]}\) followed by sonication and filtration.

Device fabrication. Regioregular P3HT (Rieke Metals, \(M_w \approx 5 \times 10^4\) g/mol, regioregularity \(\sim 90 - 93\%\)), PF10TBT (TNO, \(M_w = 1.9 \times 10^5\) g/mol, PDI \(\sim 3.5\)) and PCBM (> 99.5%, Solenne) were used as received. Photoactive layers were spin coated under ambient conditions from hot chlorobenzene solutions of PF10TBT:PCBM in a 1:4 weight ratio. P3HT:PCBM (1:1 w/w) layers were cast from a chloroform solution under nitrogen atmo-
sphere and annealed before application of a 1 nm LiF / 100 nm Al cathode. Nafion perfluorinated resin solution (Aldrich, 5 wt % in a mixture of lower aliphatic alcohols and water) was diluted 1:20 with ethanol before spin coating at high rpm on top of pH-modified PEDOT:PSS layers in a nitrogen-flushed compartment under ambient atmosphere.

**Characterization.** Current-voltage characteristics were recorded with a Keithley 2400 SourceMeter. Unless stated otherwise, the devices were illuminated with white light from a Steuernagel SolarConstant 1200, corrected for spectral mismatch ($M = 1.40$, for both P3HT:PCBM and PF10TBT:PCBM)\[^{18}\] and filtered with a GG385 UV filter, resulting in a light intensity equivalent to 0.9 sun. Contributions to the photocurrent from regions outside the overlap of ITO and aluminum contacts were eliminated using illumination masks with apertures slightly smaller than the overlap area.

IPCE spectra used for mismatch determination were measured at wavelengths from 400 to 1100 nm using a custom-built setup comprising a 50 W quartz tungsten halogen lamp (Newport Research Series) with a highly stable radiometric power supply, 28 narrow bandpass interference filters (CVI Laser), a custom-built transimpedance amplifier and a Stanford Research Systems SR830 lock-in amplifier. The spectral response was measured without bias illumination but with room lights on, relative to that of a calibrated Si photodiode (Newport 818-SL) with known spectral response.

Layer thickness measurements were done with a Veeco Dektak 6M or 150 profilometer. Optical absorbance was measured with a Perkin-Elmer Lambda 900 spectrophotometer. Conductivity measurements were performed with a custom-built collinear four-point probe setup.
References
