Enhanced spectral coverage in tandem organic solar cells

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In order to realize enhanced spectral coverage in organic photovoltaic devices, the authors have stacked a zinc phthalocyanine:C_{60} based cell on the top of a poly-3-hexyl-thiophene:[6,6]-phenyl C_{61}-butyric acid methyl ester layer using a 1 nm thick Au intermediate recombination layer. Such tandem devices comprising active materials with complementary absorption spectra exhibit a short circuit current (I_{sc}) of 4.8 mA cm^{-2}, an open circuit voltage (V_{oc}) of 1020 mV, and a fill factor of 0.45. Measurements of the photocurrent versus wavelength of the incident light show that photons are converted into charge carriers from 400 to more than 800 nm. Further optimization of the respective layer thicknesses may lead to high efficiency devices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2336593]

Organic solar cells have been showing steadily increasing performances during the last ten years,[1] reaching nowadays efficiencies close to 5%.[2] However, their capabilities are still exceeded by the ones of inorganic material based photovoltaic devices.[3] This is explained by the existence of some limiting intrinsic properties of organic semiconductors, such as their relatively low charge carrier transport.[4] The low mobility and the short lifetime of the charge carriers[5] limit the maximum thickness of the active layer and hence the number of photons that can be absorbed and collected. Beyond modifying the properties of the materials, Hiramoto *et al.* proposed a way to bypass this limitation: The authors showed that two identical evaporated cells can be stacked and serially connected by a noncontinuous semitransparent inorganic layer.[6] This layer ensures the recombination of the electrons coming from one cell with the holes coming from the second cell in such a way that the voltage at open circuit (V_{oc}) of the overall device is equal to the sum of the respective V_{oc} of the subcells.[7] Interestingly, it has been shown that the short circuit current (I_{sc}) of the final device, which is given by the smaller current of either cell according to Kirchhoff's law, can be equal to the I_{sc} of an optimized single cell.[8] Thus, this approach based on an optimization of the thickness of the active layer in regard to its transport properties allows to consequently improve the efficiency of small molecules based[8–10] as well as conjugated polymer based organic solar cells.[11]

Apart from their transport properties, organic semiconductors also show limited photovoltaic properties because of their spectrally limited optical absorption.[12] Therefore, a further improvement can be envisaged by realizing real tandem solar cells, based on the superposition of active materials having different band gaps.[13] This concept is employed to achieve high efficiency inorganic solar cells by reducing the energetic losses caused by the thermalization of the charge carriers.[14] But in the case of organic materials, it would allow to increase the photon harvesting by combining semiconductors having complementary absorption spectra. To the best of our knowledge, such devices have not been realized

yet. We have to mention though that Triyana *et al.* have combined different active materials in a fully evaporated structure.[15] The absorption spectra of those organic semiconductors were not significantly different; hence no clear extension of the spectral performances could be measured. In this study, we have stacked efficient conjugated polymer based and small molecules based solar cells, with strongly different absorption spectra, and we show that these tandem devices harvest photons over the entire visible spectrum.

The structure of the tandem cells studied is depicted in the inset of Fig. 1. Indium tin oxide (ITO) coated glass having a sheet resistance about 15 Ω/sq and covered by a 90 nm thick layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (Baytron®, Bayer AG) was used as substrate. Then, poly-3-hexyl-thiophene (P3HT) (1% in weight in chlorobenzene) was spin cast, followed by [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) (1% in weight in dichloromethane). Photoluminescence (PL) investigations performed on that structure revealed a strong PL signal from PCBM, suggesting that some PCBM rich (potentially continuous) environment might be present on the top of the layer: We call this structure *diffused*
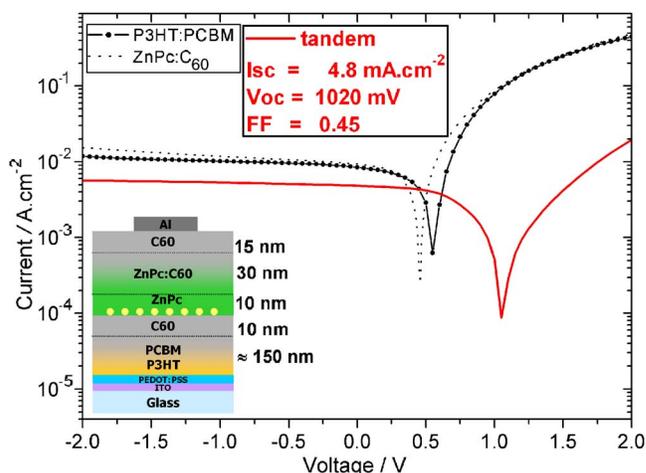

FIG. 1. (Color online) Current vs voltage of (dots) the ZnPc/ZnPc:C_{60}/C_{60} individual cell, (line plus symbol) the P3HT:PCBM diffused bilayer individual cell, and (full line) the tandem cell. The inset describes the structure of the tandem cell.

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bilayer.[16] The rest of the tandem cell was realized by thermal evaporation under a vacuum of 5×10^{-6} mbar. Firstly, a 10 nm layer of C_{60} was evaporated at a rate of 0.03 nm s^{-1}. This was followed by the evaporation of the recombination layer (1 nm of Au) at high rate (0.5 nm s^{-1}) in order to hamper its diffusion in the sublayer. Finally, the second cell, consisting of 10 nm of zinc phthalocyanine (ZnPc, 0.03 nm s^{-1}), 40 nm of a mixture of coevaporated ZnPc and C_{60} (1:1, by weight 40 nm, 0.03 nm s^{-1}), and 15 nm of C_{60} (0.03 nm/s), was realized. The whole structure was closed by an electrode comprising 5 nm of Cr and 95 nm of Al (0.1 nm s^{-1}). The solar cells were characterized under 100 mW/cm^2 (AM 1.5) white light illumination (Steuernagel GmbH). The current-voltage (*I-V*) measurements were carried out under argon atmosphere in a glovebox with a Keithley 236 unit. In order to compare the tandem device to single junction solar cells, ITO/P3HT:PCBM/Al and ITO/ZnPc/ZnPc:C_{60}/C_{60}/Cr/Al were fabricated according to the respective procedures described above.

Figure 1 shows the *I-V* curves of a single P3HT:PCBM cell, a single ZnPc/ZnPc:C_{60}/C_{60} cell, as well as the tandem cell. It can be observed that the P3HT:PCBM diffused bilayer approach results in cells exhibiting good performance despite no post-treatment is used. We measured for this device a I_{sc} of 8.5 mA cm^{-2}, a V_{oc} of 550 mV and a fill factor (FF) of 0.55, yielding a power conversion efficiency of 2.6%. In the case of the single small molecule based cell, an I_{sc} of 9.3 mA cm^{-2}, an V_{oc} of 470 mV, and a fill factor (FF) of 0.50 were recorded, inducing an efficiency of about 2.2%. Thus, the fact that the tandem cell shows an V_{oc} of 1020 mV, equal to the sum of the individual V_{oc}'s of the subcells, suggests that an efficient series connection between the cells is achieved. The FF of the tandem cell is found to be about 0.45, only a little bit lower than the ones of the subcells. However, the tandem device shows a quite reduced I_{sc} equal to 4.8 mA cm^{-2}, which induces an efficiency of 2.3%. We presume that the limitation of the tandem cell performances is mostly due to a lack of optimization of the respective thicknesses of the subcells.[7]

In order to confirm the series connection of the subcells and the extension of the spectral coverage in the tandem device, we have performed I_{sc} versus wavelength measurements. A 900 W xenon lamp combined with a 2 nm resolution monochromator was used as the light source. This one was modulated with a mechanical chopper, and the photocurrent generated by this illumination was recorded using a lock-in technique. Figure 2 exhibits the results obtained for a single P3HT:PCBM cell, a single ZnPc/ZnPc:C_{60}/C_{60} cell, as well as for the tandem cell. The curve related to the tandem device is always lower than the lowest current given by one of the single devices. This is in accordance with the expectations arising from the series connection and Kirchhoff's law. Moreover, it is visible that the current in the tandem device is equal to the current in the P3HT:PCBM device when this cell is the limiting one. However, in the region $375 < \lambda < 630$ nm where the ZnPc/ZnPc:C_{60}/C_{60} cell shows the smaller current, the tandem device exhibits a current which is consequently smaller. This observation can be explained by the structure of the tandem device: The incident light crosses first the P3HT:PCBM cell and then the ZnPc/ZnPc:C_{60}/C_{60} one. Therefore, in the region $375 < \lambda < 630$ nm, a large part of the photons is absorbed in the P3HT:PCBM cell, further reducing the already limiting cur-
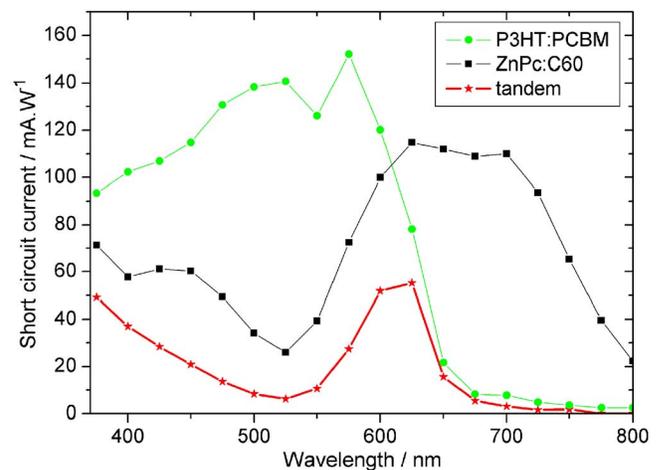

FIG. 2. (Color online) Current at short circuit condition vs wavelength of the incident monochromatic light for (■) the ZnPc/ZnPc:C_{60}/C_{60} individual cell, (●) the P3HT:PCBM diffused bilayer individual cell, and (★) the tandem cell.

rent delivered by the ZnPc/ZnPc:C_{60}/C_{60} cell in this spectral region.

With the spectral coverage enhancement being not clearly demonstrated by the monochromatic $I_{sc}(\lambda)$ measurement, we performed further spectral response experiments on the tandem device. In order to characterize the individual contribution of the subcells, we have added to the chopped monochromatic probe light a continuous monochromatic bias light (xenon lamp with an attached monochromator).[17] While the first light source was swept through the entire visible spectrum and the I_{sc} of the whole tandem device recorded with the lock-in technique, the second light source was fixed to a certain wavelength in order to selectively activate the desired subcell(s). More accurate measurements would need the application of a forward external bias to ensure short circuit condition (and avoid reverse biasing) in the current limiting subcell.[17,18] However, with the respective V_{oc} of the subcells being close to each other and showing only weak light intensity dependence,[19] we presume that the absence of externally applied bias voltage induces only a negligible error in our measurements.[17,18] Figures 3(a)–3(d) gather the results obtained. In the case of Fig. 3(a), a light bias fixed at 500 nm is used, exciting mostly the P3HT:PCBM subcell. When the probe light covers the region below 550 nm, the current measured is small, since only the P3HT:PCBM subcell is active. However, above 550 nm the charge carriers produced in the ZnPc/ZnPc:C_{60}/C_{60} cell can be extracted since the P3HT:PCBM cell is active. An overall maximum is observed at the overlap of the absorption spectra of the subcells. In Fig. 3(b), the light bias has been slightly redshifted (560 nm). The current delivered by the P3HT:PCBM cell at this wavelength is slightly reduced compared to the one collected at 500 nm. Therefore, the current recorded above 550 nm is smaller than in the previous case. In Fig. 3(c), the light bias wavelength is located at the overlap of the absorption spectra (620 nm). Both subcells are activated, and the current from their respective complementary cells can be recorded. Finally, in Fig. 3(d), the situation is exactly opposite to the one in Fig. 3(a). The light bias (700 nm) activates only the ZnPc/ZnPc:C_{60}/C_{60} subcell; hence the $I_{sc}(\lambda)$ of the P3HT:PCBM cell can be recorded. In all cases, a maximum is observed at the overlap of the ab-
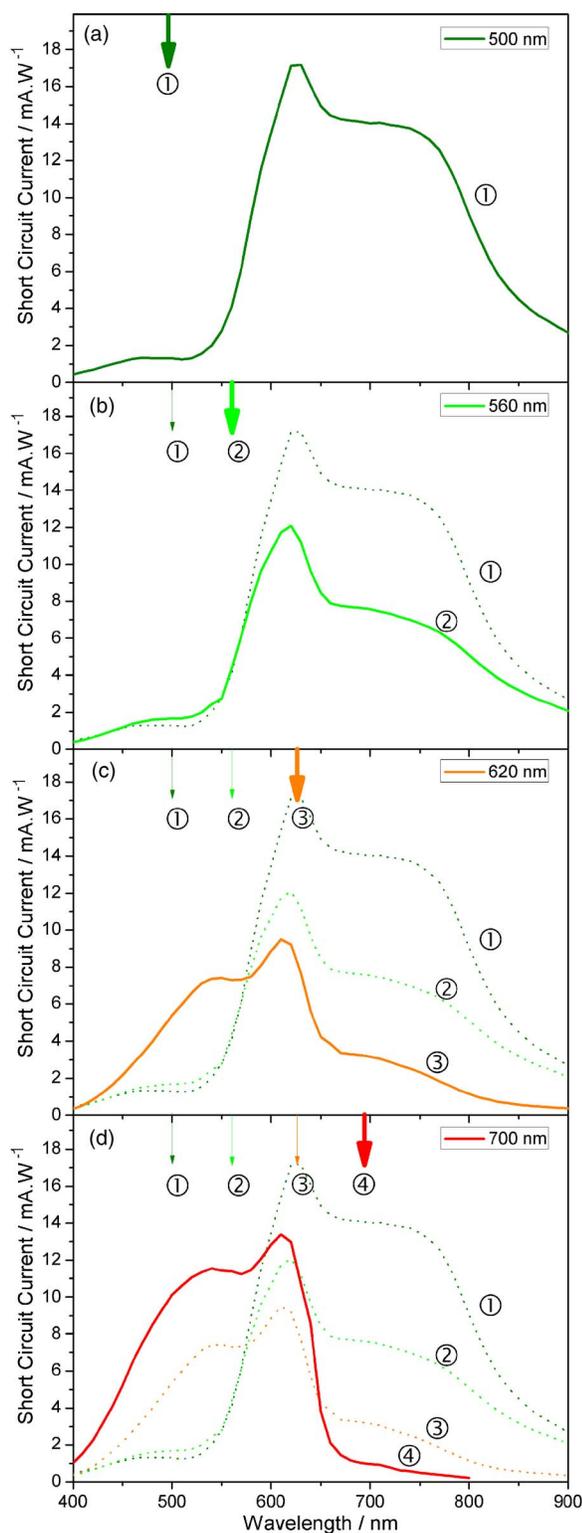
FIG. 3. (Color online) Current of the tandem device at short circuit condition vs wavelength of the incident monochromatic light. In this experiment, a second monochromatic nonchopped light source is used, the wavelength of which is indicated by the arrow: (a) 500 nm, (b) 560 nm, (c) 620 nm, and (d) 700 nm.

sorption spectra of the active materials. Thus, Figs. 3(a)–3(d) confirm that the current delivered by the tandem device is based on the extraction of charge carriers induced by the absorption of photons having wavelength from 400 to more than 800 nm. Moreover, they show that such tandem device based on active materials having complementary absorption spectra can be operated as a two color detector.

In summary, we have stacked P3HT:PCBM and ZnPc:C_{60} based cells in order to realize a real tandem organic solar cells based on active materials having complementary absorption spectra. The tandem device shows a I_{sc} of 4.8 mA cm^{-2}, an V_{oc} of 1020 mV, and a FF of 0.45. Two light source spectrometric measurements of the photocurrent show that the photon harvesting occurs on the entire visible range, from 400 to beyond 800 nm. Although the overall efficiency of this first real tandem organic device is not significantly increased in regard to the individual single cells, an optimization of the respective layer thicknesses may allow the realization of highly efficient devices.

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