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# Determination of vertical phase separation in a polyfluorene copolymer: fullerene derivative solar cell blend by X-ray photoelectron spectroscopy†

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**A vertical phase separation is evidenced using high-kinetic-energy X-ray photoelectron spectroscopy at different photon energies in a polyfluorene copolymer:C<sub>60</sub> derivative blend relevant for photovoltaic application.**

The development and optimization of organic photovoltaic devices based on three-dimensional heterostructures (bulk heterojunctions) have been a captivating research topic for more than 15 years. These devices are composed of a light absorbing and hole conducting polymer, and an electron conducting fullerene derivative. Recently achieved power conversion efficiency values of 5–6% strongly indicate that this class of solar cells has a promising industrial future.<sup>1,2</sup> Nevertheless, several open questions concerning the functioning mechanism still remain. One of them regards the morphology of polymer:fullerene solar cell blends, which is one of the most important parameters determining the efficiency of the devices. The most common way to prepare the active layer of such solar cells is to spin- or blade-coat the film from a solution of polymer:fullerene blend. The morphology of these films depends on the solubility and surface energies of the components and of the substrate and can change over time due to fullerene diffusion.<sup>3</sup> For efficient solar cells there should be a trade-off between achieving an efficient charge separation on account of the diffusion of the photoinduced exciton towards the fullerene interface, which requires good intermixing of the two components, and a continuous path for the photo-generated carriers. Several techniques have been used to determine the morphology of the blends; each of them gives complementary information and only taken together a full picture emerges: optical techniques<sup>3</sup> have high contrast but lack spatial resolution, electron microscopy<sup>4</sup> has high resolution but does not have the chemical sensitivity to distinguish between the two components of the blend,<sup>5</sup> atomic force microscopy<sup>6</sup> has high lateral resolution but gives information only about the

surface. Besides the in-plane composition of the blend, the composition as a function of depth is extremely important for the understanding of the interface with the electrodes. Evidence for vertical phase segregation has been found in polymer-fullerenes blends by electron microscopy, though the exact composition of the two phases could not be unequivocally determined.<sup>7,4</sup> Recently, dynamic secondary ion mass spectrometry (ToF-SIMS) has been used to harvest chemical information on the blend composition and details of the degradation process.<sup>8</sup> However, despite the superb chemical sensitivity, the destructive character of this technique may be considered a drawback.

In the present study we employed for the first time synchrotron-based hard X-ray high-kinetic-energy photoelectron spectroscopy to probe vertical phase segregation in polymer:fullerene derivative solar cell blends. We studied a blend which has been shown to have an excellent performance as active layer in photovoltaic devices.<sup>9</sup> It consists of a mixture of polyfluorene copolymer F8DTBT and PCBM, depicted in Fig. 1a and b, respectively.

Photoelectron spectroscopy at high kinetic energy is a technique that allows the study of the bulk properties of materials and deeply buried interfaces in a non destructive manner. It has been successfully applied in studies of layered materials and it is a promising technique for the study of the properties of real devices.<sup>10</sup>

The samples were prepared on indium tin oxide (ITO) coated glass. Ortho-dichloro-benzene was used as the solvent. Typically, 10 mg of poly((2,7-(9,9-(di-*n*-octyl)fluorene)-*alt*-5,5-(4',7'-di-thienyl-2',1',3'-benzothiadiazole)) (F8DTBT) were dissolved in 1 ml of solvent and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was added to achieve a ratio of 1:1 polymer/fullerene (in wt%). Films of 50–100 nm in thickness were deposited by blade-coating.

Photoemission spectra were collected at the HIKE experimental station on the KMC-1 bending magnet beamline<sup>11</sup> of the synchrotron radiation source BESSY in Berlin, Germany. This beamline delivers X-rays in the range 1.7–12 keV. The HIKE end station is equipped with a Gammatdata Scienta R-4000 hemispherical electron energy

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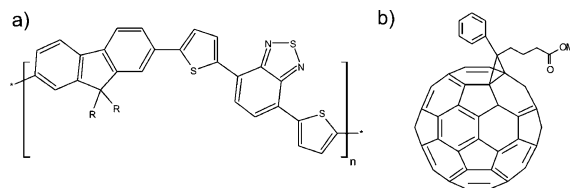
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† Electronic supplementary information (ESI) available: TM-AFM height and phase images of F8DTBT:PCBM thin film, and X-ray photoemission spectrum of the C1s core level region of pure F8DTBT. See DOI: 10.1039/b906297a

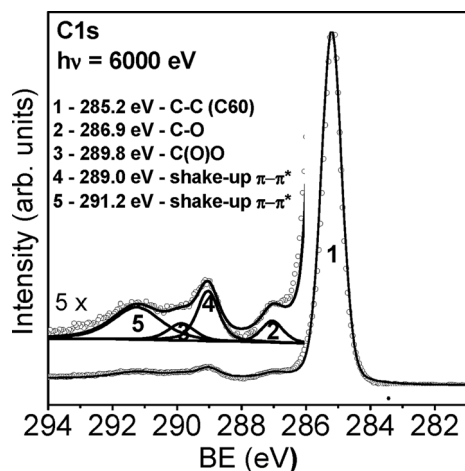


**Fig. 1** Chemical structures of (a) poly((2,7-(9,9-(di-*n*-octyl)fluorene)-*alt*-5,5-(4',7'-di-thienyl-2',1',3'-benzothiadiazole)) (F8DTBT) and (b) [6,6]-phenyl-C61-butyric acid methyl ester (PCBM).

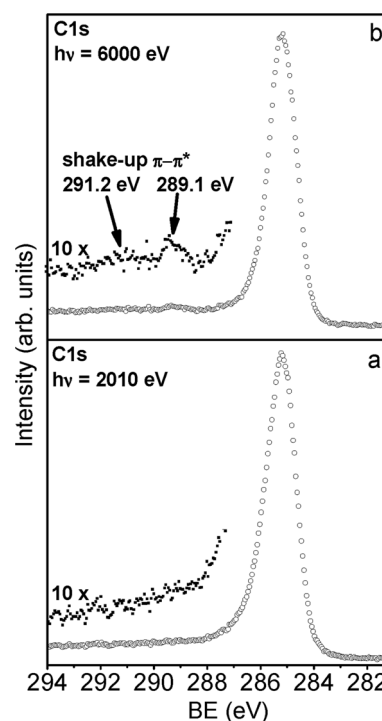
analyzer modified for high transmission and kinetic energy resolution of photoelectrons with energies up to 10 keV. For further details of the experimental set-up see ref. 12. The samples were studied using excitation energies of 2010 eV and 6000 eV; the base pressure in the spectrometer chamber was in the  $10^{-9}$  mbar range. All spectra were collected in normal emission with an overall resolution of 0.32 eV. Binding energies for pure PCBM were referenced to the C1s core level of the C<sub>60</sub> cage at 285.2 eV.<sup>13</sup> For the blend the unsaturated non-functionalized carbon with C1s binding energy set to 285.0 eV was used as in ref. 14. Spectral analysis included a Shirley background<sup>15</sup> subtraction and peak separation using Gaussian–Lorentzian functions<sup>16</sup> in a least square fitting program (Winspec) developed at the LISE laboratory, University of Namur, Belgium.

X-Ray photoelectron spectroscopy performed with different photon energies allows variation of the probing depth in a non destructive way. To obtain the exact fingerprint of PCBM in high-kinetic-energy photoemission spectra, we first measured a 100 nm thick PCBM film spin-coated onto ITO. Fig. 2 shows the C1s core level photoemission spectrum of this film recorded with  $h\nu = 6000$  eV; the spectrum collected with  $h\nu = 2010$  eV (not shown) is identical. The spectrum shows a main peak at 285.2 eV binding energy, which is attributed to both aliphatic and aromatic carbon, and two smaller components: one at 286.9 eV, assigned to the carbon of the methyl group and another one at 289.8 eV, associated with the carbonyl group. Additionally, the shake-up features associated with the C<sub>60</sub>-cage atoms are identified at 289.0 eV and 291.2 eV binding energy.<sup>17</sup>

In Fig. 3 we present the C1s core-level spectrum for a F8DTBT:PCBM blend with (1:1) polymer:PCBM ratio, collected with  $h\nu = 2010$  eV and  $h\nu = 6000$  eV. The more surface sensitive spectrum, collected at lower photon energy, basically coincides with the spectrum collected with the laboratory spectrometer and shows only one rather broad and slightly asymmetric peak at 285.0 eV binding energy but none of the characteristic C<sub>60</sub>-cage shake-up features. This fact indicates that PCBM is not present in the top layers of the solar cell blend. This first evidence supports the behaviour already observed by other authors of the segregation of the fullerene component to the inner layers of polymer:fullerene solar cell blends.<sup>3,8,18</sup>



**Fig. 2** X-Ray photoemission spectrum of the C1s core level region of PCBM collected with 6000 eV photon energy.



**Fig. 3** X-Ray photoemission spectrum of the C1s core level region of the polyfluorene copolymer:PCBM blend collected with (a) 2010 eV and (b) 6000 eV photon energy.

At  $h\nu = 6000$  eV, on the other hand, the C1s core-level spectrum of the blend clearly evidences the characteristic shake-up satellites of the C<sub>60</sub>-cage (Fig. 3b), which proves beyond any doubt that the topmost layer of the spin-coated thin film is not a blend but contains only pure polymer (compare also with the C1s of pure F8DTBT in the ESI†) and a phase enriched in the C<sub>60</sub> derivative is found at a deeper level in the material. By estimating the probing depth for the two photon energies from the inelastic mean free path (IMFP) of electrons in the polymer, it is possible to infer the depth at which the PCBM is found in the solar cell blend and therefore to get a more precise insight into the morphology of the blend thin film without applying any invasive or destructive analysis methods.

The IMFP of electrons is defined as the average distance that an electron travels between the successive inelastic collisions.<sup>16</sup> The IMFPs for conductive polymers such as polycetylenes,<sup>19</sup> polyanilines<sup>20</sup> and polythiophenes<sup>21</sup> have been determined by means of elastic peak electron spectroscopy (EPES). In EPES, the IMFP is determined from the comparison of measured and calculated elastic backscattering probabilities. Lesiak and co-workers determined the IMFP for a series of polythiophenes and stated a statistical error of about 17% for the IMFPs obtained using EPES in the electron energy range from 200 to 5000 eV.<sup>21</sup> At an energy of 1721 eV (equivalent to the kinetic energy of the photoelectrons excited with 2010 eV) the IMFPs for polythiophenes studied by these authors amount to values between 5 and 6 nm and for the highest electron energy (5000 eV) the IMFPs are equal to ~20 nm. Taking into account the similarities in the main structure and density between these polythiophenes and the polymer of our study, these values can be regarded as a good estimate of the IMFPs for F8DTBT for similar electron energies.

In our experiment, as already mentioned, the signature of the C<sub>60</sub> cage does not appear in the photoemission spectrum taken at 2010 eV, which made us conclude that PCBM segregates at a depth which goes beyond a few nanometers. In fact, only when we collected spectra with  $h\nu = 6000$  eV it was possible to observe the characteristic shake-up features of the C<sub>60</sub> cage and we can therefore state that a PCBM enriched phase lies below a F8DTBT layer with a thickness of  $6 < x \leq 20$  nm. Björström *et al.* studied the composition of similar solar cell blends by means of dynamic ToF-SIMS and found a homogeneous composition throughout the whole thickness of the film for a (1:1) polyfluorene:PCBM blend spin-coated on Si and Au-substrates.<sup>3a</sup> However, for higher blend ratios (1:2, 1:3 and 1:4) the authors found a layered structure with alternating polymer and PCBM enriched strata. The fact that it is possible to detect the segregation of PCBM for the (1:1) polymer:PCBM blend in our measurements shows the better sensitivity of our method. The depth profile analysis by ToF-SIMS was performed by sputtering off successive layers of the material, and a depth sensitivity of 10 nm was reported. It is possible to conclude, based on our results, that in the (1:1) ratio blend a vertical phase separation also occurs, and a topmost layer of pure polymer is present followed by a phase enriched in PCBM lying deeper in the film.

The phenomenon of vertical phase segregation is of great interest for the understanding and further development of polymer:PCBM solar cells. The charge collection in bulk-heterojunction solar cells would benefit from a vertical segregation with enrichment of the electron-donating component at the hole-collecting contact and the electron accepting material at the free surface. Instead, the segregation taking place in the investigated sample implies that the polymer and not PCBM will be in contact with the top electrode, since our sample corresponds to the device before contact deposition. Given the performance of solar cells with this blend, this raises the interesting question of whether optimal charge transport is achieved despite polymer segregation at the electrode surface because the interface with the electrode is not abrupt or because electrode deposition causes PCBM diffusion and restores a homogeneous blend at the interface.

In conclusion, we have proven that it is possible to depth profile polymer:fullerene solar cell blends in a non destructive way by high-kinetic-energy photoelectron spectroscopy performed with different photon energies. This has been achieved by tracing the characteristic shake-up satellite features of the C<sub>60</sub> cage. The comparison of the obtained results with values of the inelastic mean free path of electrons in polythiophenes reported in the literature enabled us to estimate the depth at which an enriched PCBM phase is found in the investigated blend. Our results have shown superior depth sensitivity than other depth analysis methods for polymer solar cell blends previously described in the literature and prove that this technique can be applied to obtain unique information on the vertical morphology of real devices.

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