



# Three dimensional analysis of self-structuring organic thin films using time-of-flight secondary ion mass spectrometry

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## ABSTRACT

Selective sub-micrometer structuring of phase-separating organic semiconductor materials has recently got into focus for providing the opportunity of further improvements in optoelectronic device applications. Here we present a 3D-time-of-flight secondary ion mass spectrometry (3D-TOF-SIMS) depth profiling investigation on spin-coated blends consisting of [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) and a cationic cyanine dye (1,1'-diethyl-3,3,3',3'-tetramethylcarbocyanine iodide). TOF-SIMS provides the required lateral and depth resolution to resolve material and molecular inhomogeneities and phase separation in the blend. The data are illustrating the three-dimensional arrangement of the substances involved and confirm results of earlier studies using atomic force microscopy, UV-vis spectroscopy and x-ray photoelectron spectroscopy, and which have shown well distinguishable morphological features. The formation of this domain structure has been found to be dependent on the absolute as well as the individual film thickness, in accordance with models based on thin liquid two-layer films. Honey-comb like primary structures with micrometer dimension were found in samples containing small amounts of dye molecules in the deposition solution. In this case a thin dye deposit on PCBM was detected, which is well separated from the dye layer at the substrate. For this type of sample, we discuss an extended model of film formation based on partial depletion of dye molecules during film solidification, resulting in two individual dye layers.

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## 1. Introduction

Thin films composed of organic donor/acceptor blends find widespread applications due to their photoconductivity [1], as evidenced by photovoltaic [2] and photorefractive [3] results. The final morphology of solution cast films is a consequence from rapid quenching into a two-phase system after solvent evaporation. Several different structures have been reported, as the result of an interplay between film destabilization [4] and phase separation [5]. Recent experiments with cationic cyanine dyes have shown that mobile counter-ions can have a dramatic effect on morphology [6], exciton dissociation [7] and dye aggregation [8]. Models for structure formation in a [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester-dye (PCBM)-dye blend suggest initial formation of a bilayer which breaks up due to destabilizing pressure induced by electrostatic force [6]. This additional way to control morphology and electrical properties of the interface via counter ion properties, together with the strong dependence of domain size from film thickness provide easy access to control parameters for system development and application. The yield of charge generation and charge collection are important device parameters which deter-

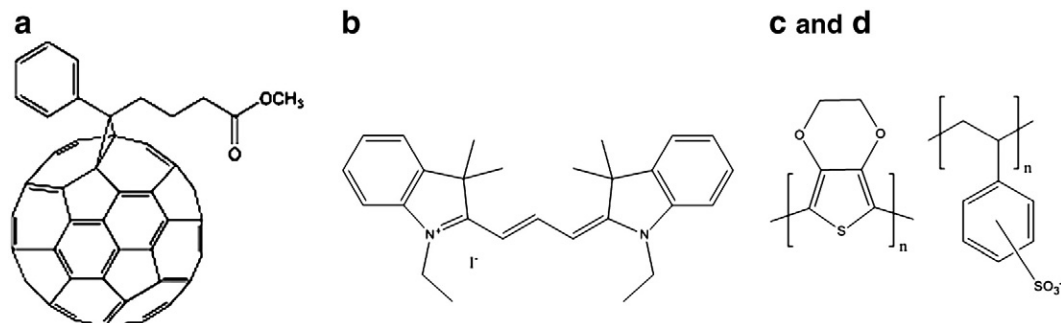
mine the efficiency of semiconductor devices. However, a sensible dimensionality balance between the two values is necessary for optimized performance. In photovoltaic devices charge generation is usually restricted to a very small domain in the blend where the two components meet. The exciton diffusion length, usually in the range of around 10 nm therefore requires morphology with very fine phase separation features. A common system for these solar cells is a blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM). On the other hand, effective charge transport over a relatively large distance to the collecting electrodes of the photovoltaic device is only possible in the presence of continuous charge carrier pathways. This contradicts with a finely spaced phase separation. If the morphological architecture of the blend is too large, however, charge recombination centers and charge traps can reduce system performance.

In this study, spin-coated blends of PCBM ([6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester) and a cationic dye (1,1'-diethyl-3,3,3',3'-tetramethylcarbocyanine iodide) have been investigated with time-of-flight secondary ion mass spectrometry (TOF-SIMS). Depth profiling data revealed the three-dimensional arrangement of the substances involved. We aim at investigating the possibility of obtaining chemical information on a relatively small length scale to confirm previous theories about the parameters affecting the morphology of blend structures in spin coating films.

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**Table 1**  
 Compilation of the samples investigated: Left section: topography plots from AFM topography images, values for the total layer thickness  $h$  (not including a PEDOT/PSS base-layer on some samples), the ratio  $r$  between CyI and PCBM (both values determined by means of absorption spectroscopy) and feature size  $f$  (determined from the dominant wavelength of the Fourier analysis of the AFM images). Middle section: TOF-SIMS image of the distribution of iodine at the surface. Right section: Structure drafts as suggested from combined information of TOF-SIMS and AFM-measurements, respectively.

	Morphology by means of AFM	$h = h_{\text{CyI}} + h_{\text{PCBM}}$ $r = h_{\text{PCBM}}/h_{\text{CyI}}$ $f = \text{feature size}$	TOF-SIMS surface image of mass 127 ( $\text{I}^-$ )	Structure draft				
				Cross section	Top view			
<b>A</b>  <b>B</b>  <b>C</b>  <b>D</b>  <b>E</b>					None  Suggested by means of AFM			
					$h = 13.76 \text{ nm}$ $r = 0.156$ $f = 0.298 \text{ μm}$	None	Suggested by means of AFM	
					$h = 55.4 \text{ nm}$ $r = 0.894$ $f = 0.93 \text{ μm}$		Suggested by means of AFM	
					$h = 142 \text{ nm}$ $r = 1.12$ $f = 1.00 \text{ μm}$		Suggested by means of AFM	
					$h = 192.7 \text{ nm}$ $r = 2.286$ $f = 1.6 \text{ μm}$		PCBM - islands on top of the CyI - pillars have only been seen in AFM-measurements	
$h \sim 215 \text{ nm}$ $r \sim 2.0$ $f \sim 13.5 \text{ μm}$		Suggested by means of AFM						



**Fig. 1.** Molecular structures of the soluble fullerene derivative PCBM (a), the cyanine dye CyI with the free anion  $\text{I}^-$  as charge compensation (b), and both monomer parts of the ionic polymer PEDOT:PSS (c and d).

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