Experimental report

17/02/2020

Proposal: 9-11-1902 **Council:** 10/2018

Title: Interfacial studies of charge transport layers in non-fullerene bulk heterojunction organic solar cell blends using neutron reflectivity

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: NiO
MoO3
ZnO
SnO2,
PEDOT:PSS
C94H82N4O2S4 ITIC
(C68H78O2S8)n PBDB-T

Instrument	Requested days	Allocated days	From	To
D17	3	3	15/07/2019	18/07/2019

Abstract:

At Sheffield, we have been testing organic solar cells using a new kind of non-fullerene acceptor, called ITIC, which when blended with polymer semiconductors makes high efficiency devices, 8%-10%. Our device results show a big difference in efficiency according to which surface we spin coat the blend onto. Previous results with fullerene acceptors have shown that these differences can arise from self-stratification of the components during spin coating. Experiments on D17 will confirm or disprove this hypothesis by measuring the depth profile perpendicular to the plane of the film. Neutron reflectivity is key to measuring the vertical composition, and we will also measure the nano-morphology using transmission SANS on our existing beam time at LOQ. Alongside this we will use GIWAXS to measure the crystallinity and orientation of the film components. All together the insight from these measurements will guide further improvement and understanding of how best to process these materials to make high efficiency devices.

Introduction

Organic solar cells (OSC) are a promising clean, inexpensive, scalable renewable energy source. Typical devices consist of a light harvesting blend thin film of conjugated polymer donor (e.g. PBDB-T) and small molecule electron acceptor (e.g. ITIC), sandwiched between tow electrodes. With the development of high performance non-fullerene acceptor materials (NFAs) power conversion efficiencies (PCEs) exceeding 16% are now achievable. At Sheffield, PBDB-T : ITIC based OSCs have been fabricated using various solution-processed charge transport layers (MoO_3, ZnO, PEDOT:PSS, SnO_2 and NiO_x). In this experiment, NR, made possible by the synthesis of deuterated ITIC (d8-ITIC) was used to characterise the vertical composition profile of PBDB-T : d8-ITIC blends (in the plane perpendicular to the substrate) deposited on various solution-processed CTLs. In-situ thermal annealing was performed to track the removal of solvent additives (1,8-diiodooctane) from the blend and to follow temperature-induced interfacial segregation between the donor and acceptor components.

Experimental Details

Materials:

PBDB-T (Ossila Ltd) and d8-ITIC synthesised by colleagues in Wuhan, China were dissolved in a solution of chlorobenzene (Sigma Aldrich) containing 0.5 vol% 1,8-diiodooctane (Sigma Aldrich) in a 1:1 wt% ratio and solid concentration of 20mg/ mL.

Sample Preparation:

PBDB-T : d8-ITIC films were spin-coated onto CTL coated silicon substrates. Films were thermally annealed at either 160°C or 200°C on the beamline in a nitrogen filled heating chamber *(Figure 1)*. The temperature of the sample surface was recorded using a thermocouple attached to the sample.

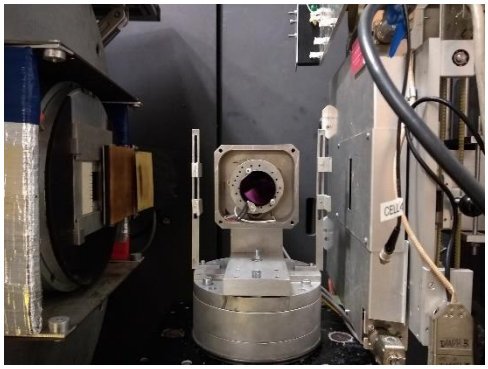

Figure 2: *Nitrogen-filled heating chamber used for in-situ NR measurements during thermal annealing.*

Neutron Reflectivity Measurements:

NR measurements for each sample consisted of three stages:

1. Initial measurement of as-cast film at room temperature prior to heating. Two angles were measured to give a Q range from 0.0059$Å^{-1}$ to 0.29 $Å^{-1}$.
2. Dynamic measurements during heating, taken every 10s for 20min. One angle was measured to give a Q range from 0.0094$Å^{-1}$ to 0.12 $Å^{-1}$.
3. Final measurement at room temperature after cooling. Two angles were measured to give a Q range from 0.0059$Å^{-1}$ to 0.29 $Å^{-1}$.

Results

Initial fitting of a PBDB-T : d8-ITIC blend on PEDOT:PSS has been performed using GenX fitting software. For each layer, a slab model with Gaussian roughness was used.

Fitting Initial and Final Measurements:

Figure 3 shows the initial and final reflectivity curves for a PBDB-T : d8-ITIC blend deposited on PEDOT:PSS and annealed at 160°C along with corresponding SLD profiles. The initial reflectivity curve can be fitted using a single layer for the blend film so that the profile consists of: silicon/ silicon oxide/ PEDOT:PSS/ PBDB-T : d8-ITIC blend. This gives$\chi^2 = 2.85$. The final reflectivity curve could not be fitted well using a single blend layer. The best fit was found by adding a d8-ITIC rich layer at the blend/ substrate interface and PBDB-T- rich layer at the film surface to give a profile that consists of silicon/ silicon oxide/ PEDOT:PSS/ d8-ITIC- rich interface/ Bulk PBDB-T : d8-ITIC blend/ PBDB-T-rich surface. This gives$\chi^2 = 5.22$.

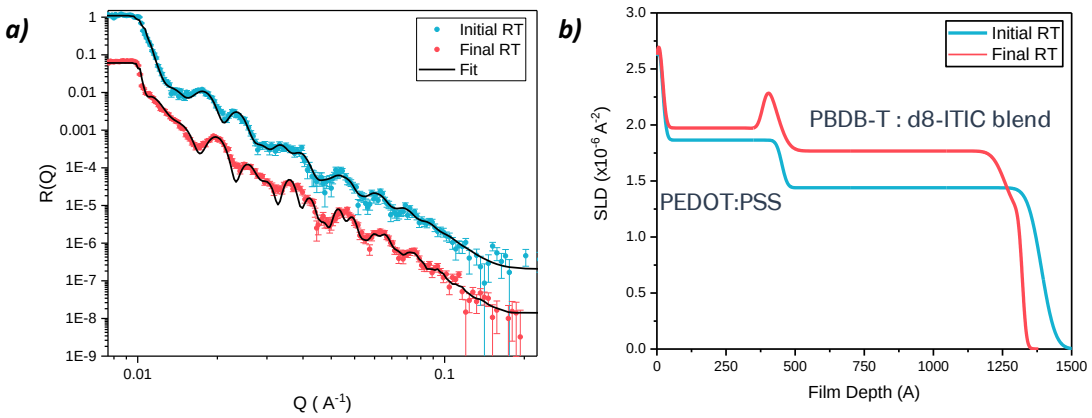

Figure 3: a) *Initial and final reflectivity curves of a PBDB-T : d8-ITIC film on PEDOT:PSS measured at room temperature, before and after thermal annealing at 160°C for 30min (data offset by a decade for clarity).* ***b)*** *Corresponding SLD profiles to the reflectivity curves shown in (a).*

Fitting Dynamic NR measurements:

Figure 4 shows dynamic NR measurements of a PBDB-T : d8-ITIC blend on PEDOT:PSS during thermal annealing at 160°C for 20 minutes. Measurements were taken every 10s then averaged to give 1-minute intervals. For all dynamic measurements the blend layer could be reasonably fit $(1 < \chi^2 < 3)$ using a single layer to give profile consisting of: silicon/ silicon oxide/ PEDOT:PSS/ PBDB-T : d8-ITIC blend. The removal of 1,8-diiodooctane (DIO) from the film during thermal annealing is made clear by plotting blend film thickness and blend SLD as a function of anneal time (Figure 4c). As DIO evaporates from the film, film thickness decreases by $\sim$8nm as expected. This is correlated with a simultaneous increase in the SLD of the blend by $\sim 0.22 \times 10^{-6}\text{Å}^{-2}$. This increase in SLD of the blend as DIO evaporates is also expected due to the low SLD of DIO ($1.18 \times 10^{-7}\text{Å}^{-2}$).

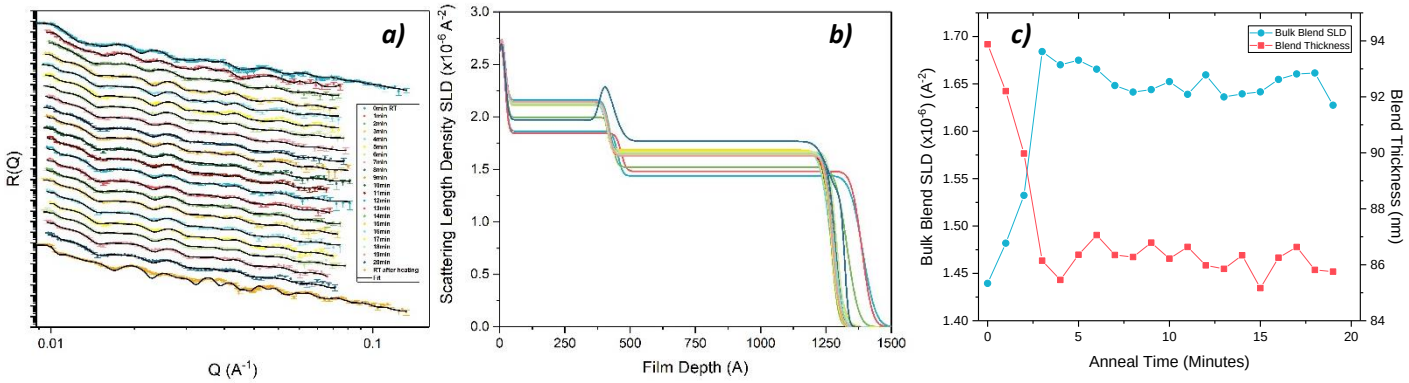

Figure 4: a) *Dynamic NR measurements during thermal annealing of a PBDB-T : d8-ITIC blend deposited on PEDOT:PSS, at 160°C (data offset by a decade for clarity).* ***b)*** *Corresponding SLD profiles to the curves in (a).* ***c)*** *Fit parameters (blend thickness and blend SLD) as a function of anneal time.*

Conclusion

Initial fitting of data from this experiment suggests that PBDB-T : d8-ITIC blends deposited on PEDOT:PSS undergo significant interfacial segregation after thermal annealing. Furthermore dynamic NR measurements track the removal of DIO from the film during thermal annealing. Data fitting for the other solution-processed CTLs remains ongoing but will be used to investigate the self-assembly of PBDB-T : ITIC blends on different surfaces. We intend to publish this data in a suitable high profile journal.

Our local contact for this experiment was Philipp Gutfreund who provided a lot of useful assitance and feedback with measurements. The ILL staff in the workshop and chemistry labs also offered kind support with the heating chamber and use of the spin coater.