Experimental report

13/02/2023

Proposal:	**9-11-1957**	**Council:**	10/2019
Title:	Understanding the Role of Solvent Additives in Organic Solar Cells		
Research area:	Physics		

This proposal is a new proposal

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Samples:
PEDOT:PSS
$(C_{68}H_{78}O_2S_8)_n$ PBDB-T
$C_{94}H_{82}N_4O_2S_4$ ITIC
$C_{82}H_{14}O_2$ PC70BM

Instrument	Requested days	Allocated days	From	To
D17	3	3	11/02/2021	13/02/2021

Abstract:

At Sheffield, organic solar cells (OSCs) have been made using a new class of materials called non-fullerene acceptors (NFAs) producing high efficiency devices (9-11%) in polymer blends. For OSCs containing ITIC, a NFA, the inclusion of solvent additives (e.g. 1,8-diioodocatane (DIO)) in the blend solution increases efficiency at a detriment to stability, an effect which is not observed in OSCs containing PCBM, a more traditional material. From spectroscopic ellipsometry, we suspect this is due to a greater amount of residual DIO in ITIC-based devices after thermal annealing. NR on D17 will confirm this, allowing us to track DIO removal and characterise the vertical segregation in the plane normal to the film; a phenomenon that has been observed from previous measurements on D17. NR is essential to characterise the vertical profile and is made possible by using deuterated ITIC. We will also assess the crystallinity, grain size and orientation of individual components using GIWAXS in Sheffield along with larger lengthscales using SANS at ISIS. In combination, these measurements will help us achieve the optimum method for producing high efficiency OSCs with real-world stability.

NOTE: This experiment was performed during the Covid-19 pandemic. As a result, ex-situ samples were prioritized and the experiment was simplified considerably to reduce workload on beamline staff. The experiment was combined with experiment 9-11-1988.

Introduction

In this experiment, we used neutron reflectivity to investigate the impact of DIO processing on the vertical chemical composition of two polymer : acceptor blend systems; an NFA-based system (PBDB-T : ITIC) and a fullerene-based system (PBDB-T : PC$_{71}$BM). For PBDB-T : ITIC systems, there is insufficient neutron scattering length density (SLD) contrast between PBDB-T and ITIC. Neutron reflectivity measurements were made possible by the synthesis of a deuterated ITIC analogue (d8-ITIC). (Note, in PBDB-T : PC$_{71}$BM systems, the intrinsic neutron SLD contrast is sufficient and deuterium substitution of one component is not necessary).

Experimental Details

Materials : PBDB-T and PC$_{71}$BM were purchased from Ossila Ltd and used as received. The deuterated ITIC analogue (d8-ITIC) was synthesised by colleagues in Wuhan, China. PEDOT:PSS solution was purchased from (batch Al083) and was stored in a refrigerator at 5 ° C. and filtered immediately before use, using a PVDF 0.45um microdisc filter. Chlorobenzene and DIO were purchased from Sigma Aldrich.

Sample Preparation: Reference solutions of neat materials (PBDB-T, PC$_{71}$BM and d8-ITIC) were dissolved in chlorobenzene and spin-coated onto bare silicon substrates. PBDB-T : d8-ITIC (1:1, w-w%) and PBDB-T : PC$_{71}$BM (1:1, w-w%) active layer solutions were prepared in chlorobenzene and DIO (0, 0.5, 1 and 3 volume concentration) at a solid concentration of 18mg/mL (PBDB-T : d8-ITIC) and 15mg/mL (PBDB-T : PC$_{71}$BM). Blend films were deposited via spin-coating onto PEDOT:PSS coated silicon substrates in ambient conditions at 2000 rpm (PBDB-T : d8-ITIC) and 1500rpm (PBDB-T : PC$_{71}$BM) for 40s. Films were thermally annealed at 160 ° C for 10 minutes under ambient conditions. All films were prepared approximately 1 week prior to measurement. Samples were wrapped in aluminium foil and shipped to ILL in nitrogen-filled plastic bags to prevent further degradation via light or oxygen.

Neutron Reflectivity Measurements: The accepted proposal for this experiment proposed to do *in-situ* neutron reflectivity measurements during thermal annealing to track morphological changes of the blend films. Unfortunately, due to the Covid-19 pandemic, the experimental team was unable to travel to ILL and the experiment was performed remotely. To reduce the complexity and workload required for this experiment, all films were prepared in Sheffield and measured *ex-situ* at ILL without *in-situ* thermal annealing measurements.

D17 was used in time-of-flight (TOF) mode. The reflectometry measurements in this work were collected using incident angles of 1° and 4° for 30 min and 100 min respectively, generating a Q range of 0.0076 – 0.3430 Å^{-1}. For data modelling, a fixed resolution of 2% was used. Specular neutron reflectivity curves were extracted from the raw incident and reflected neutron beams using the COSMOS data reduction program. Data were fitted using GenX software.

Results

Neat Films : Before measuring blend films, reference films of each pure material were measured to characterise their respective SLDs (Figure 1). All film thicknesses were measured by spectroscopic ellipsometry before shipping to ILL and these values agreed well with those extracted from fitting the neutron reflectivity data. Neutron reflectivity of neat reference films (Figure 1), were modelled using a three-slab-layer system of Si/SiO$_2$/PEDOT:PSS/reference film/Air using the fixed parameters shown in (Figure 2). Here, β_n is scattering length density (SLD), L is thickness and σ is roughness. Instrument resolution was fixed at 2%. Fit parameters are provided in Table 1. Fits are evaluated based on a chi-squared χ^2 value normalized to the number of data points (N_{pts}).

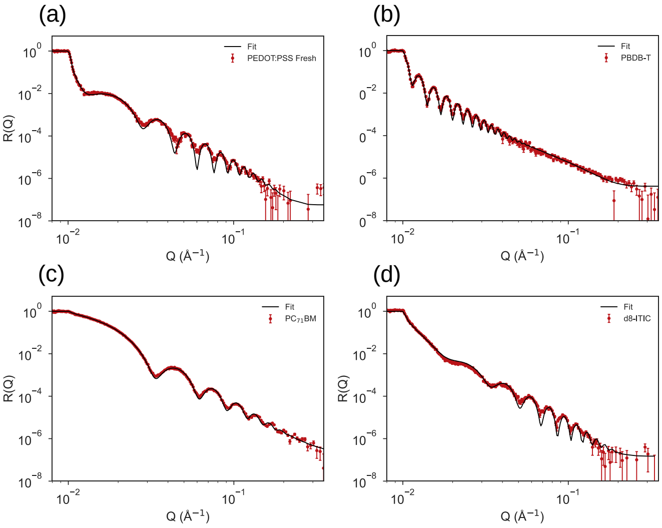

Figure 1: Neutron reflectivity curves from of neat films of (a) PEDOT:PSS (b) PBDB-T (c) PC$_{71}$BM and (d) d8-ITIC with corresponding fits (black line).

Blend Films: Neutron reflectivity of PBDB-T : PC$_{71}$BM and PBDB-T : d8-ITIC blend films processed from chlorobenzene with 0-3 Vol% DIO are plotted as $R(Q)$ versus Q in Figure 3a and Figure 3d respectively. All blend film NR data was modelled as a stack of Si/SiO$_2$/PEDOT:PSS/OPV blend film/Air where each layer in the sample represents a slab characterised by a thickness

Pure Material	I_0	B	SiO_2	Film			χ^2/N_{pts}
			L (Å)	L (Å)	σ (Å)	β_n ($\times10^{-6}$Å^{-2})	
PEDOT: PSS	0.833	0.10	10	385	11	1.68	2.41
d8-ITIC	0.854	3.04	12.5	344	13	2.15	5.81
PC71BM	0.958	0.45	20	201	5	4.67	3.68
PBDB-T	0.923	1.79	11	1886	29	1.15	2.38

Table 1: Neutron reflectivity fit parameters of the pure reference film data shown in Figure 1. I_0 is the scale factor and B is background.

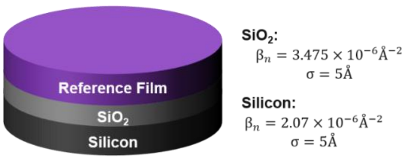

Figure 2: An illustration of the three-slab-layer system and corresponding fixed parameters used to model the pure material reference films.

L, roughness σ and SLD β_n (Figure 4). For the OPV blend film, a single homogenous slab layer was insufficient to appropriately model the data. After trialling various models (single layer, acceptor-rich surface layer), an acceptor-rich layer at the film/PEDOT:PSS interface was required to model all blend films. Fit parameters relating to the OPV blend layer are summarised in Table 2. In Figure 3c and Figure 3d, the SLD profiles corresponding to the modelled NR data are plotted as a function of OPV blend thickness such that the midpoints of the air/film interface and the film/PEDOT:PSS interface are positioned at 0 and 1 respectively.

For PBDB-T : $PC_{71}BM$ systems, the SLD of the buried interface layer increases from 2.81×10^{-6}Å^2 for 0% DIO to 3.52×10^{-6}Å^2 for 3% DIO suggesting the concentration of $PC_{71}BM$ at the film/PEDOT:PSS interface increases with increasing DIO concentration (Figure 3c). To quantify this, the volume concentration of the acceptor ϕ_A as a function of OPV blend thickness was calculated for each sample using Equation 1 (Figure 3e,f): $\phi_A = \frac{\beta_n - \beta_D}{\beta_A - \beta_D}$ (1). Where β_A and β_D are the SLD of the acceptor and donor components extracted from the neutron reflectivity of pure reference films of each material (Table 1). Here, a two-phase blend is assumed such that $\phi_A + \phi_D = 1$. For PBDB-T : $PC_{71}BM$ films processed without DIO, the bulk layer is ~44% $PC_{71}BM$ by volume and there is a small enriched layer at the film/PEDOT:PSS interface, which is composed of ~48% $PC_{71}BM$. As DIO concentration is increased, the acceptor volume concentration at the film/PEDOT:PSS interface rises to ~61%, ~64% and ~68% for films processed with 0.5, 1 and 3 Vol% DIO respectively.

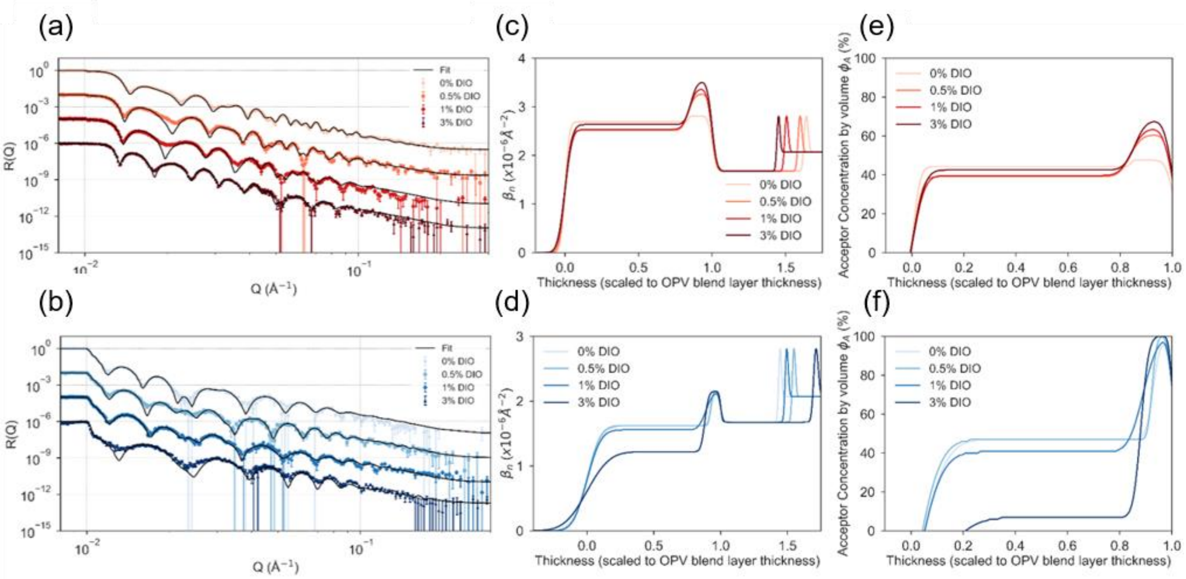

Figure 3: Neutron reflectivity of (a) PBDB-T : $PC_{71}BM$ and (b) PBDB-T : d8-ITIC blend films processed with various concentrations of DIO (0-3 Vol%) on PEDOT:PSS coated silicon substrates. Data has been offset by two decades for clarity. SLD profiles corresponding to the data fitting in parts (a) and (b) for (c) PBDB-T : $PC_{71}BM$ and (d) PBDB-T : d8-ITIC. Acceptor concentration by volume as a function of film depth for (e) PBDB-T : $PC_{71}BM$ and (f) PBDB-T : d8-ITIC blend films.

For PBDB-T : d8-ITIC blends, the NR data was modelled reasonably well for films processed from 0, 0.5 and 1 Vol% DIO with $\chi^2/N_{pts} < 4$ (Figure 3b, Table 2). For each PBDB-T : d8-ITIC sample, it was necessary to fix the upper-bound of the buried interface SLD to the SLD of pure d8-ITIC to ensure fit parameters were physical. For each sample, the fitting program progressed to the upper SLD bound for each sample suggesting the buried interface is composed entirely of pure d8-ITIC. The SLD profiles of blend films processed from 0 and 0.5 Vol% DIO are very similar with the OPV film composed of a ~60Å pure d8-ITIC buried interface layer and a ~700Å mixed bulk layer (Figure 3d). The bulk layer is composed of ~53% PBDB-T and ~47% d8-ITIC by volume which is close to the weight ratio of the materials in solution (1:1) (Figure 3f). For the blend film processed from 1% DIO, the interfacial width of the buried interface broadens and the composition of the bulk layer changes to ∼59% PBDB-T and ∼41% d8-ITIC. As DIO concentration is increased further to 3 Vol% DIO, the vertical segregation between components becomes more severe, with the volume concentration of PBDB-T in the bulk layer increasing to ∼93%.

Blend Film	DIO (Vol%)	Bulk Layer			Interface Layer			χ^2/N_{pts}
		L (Å)	σ (Å)	β_n ($\times10^{-6}$Å^{-2})	L (Å)	σ (Å)	β_n ($\times10^{-6}$Å^{-2})	
PBDB-T : d8-ITIC	0	376	15	1.62	60	19	2.15	2.8
	0.5	723	59	1.62	59	11	2.15	3.73
	1	692	86	1.56	86	34	2.15	2.19
	3	462	70	1.22	62	12	2.15	6.15
PBDB-T : $PC_{71}BM$	0	566	16	2.69	109	5	2.81	5.04
	0.5	597	21	2.52	115	24	3.26	17.50
	1	635	29	2.53	117	28	3.38	16.68
	3	754	35	2.64	127	29	3.52	6.20

Table 2: Neutron reflectivity fit parameters corresponding to the data and SLD profiles shown in Figure 3. Here, the OPV blend layer has been modelled with an acceptor-rich buried region at the film/PEDOT:PSS interface.

Conclusion

In summary, we find that the DIO processing of OPV blend films results in increased vertical segregation between donor and acceptor components. For PBDB-T : PC71BM systems, the blend film consists of a bulk mixed layer and an acceptor-rich buried interface layer at the film/PEDOT:PSS interface. As DIO concentration is increased, the acceptor concentration at the buried interface layer increases from 48% when processed without DIO to 68% when processed with 3 Vol% DIO. In comparison, the vertical phase segregation PBDB-T : d8-ITIC systems is much more severe when processing with the same DIO concentrations. For all DIO concentrations, there is a pure d8-ITIC layer at the film/PEDOT:PSS interface. As DIO concentration is increased, the relative thickness of the pure d8-ITIC layer increases and the SLD of the bulk layer decreases indicating migration of d8-ITIC from the bulk to the interface.

We therefore conclude that although DIO processing leads to vertical stratification in both fullerene and NFA based systems, the severity of phase segregation is considerably different. The findings from this experiment have helped us to understand the PV performance of OPV devices made in Sheffield, allowing us to optimise our processing methodologies for optimum device efficiency. Additionally, the results will guide the design of alternative processing routes for organic photovoltaic blend films to fabricate PV technologies which are both high efficiency and stable. Such technologies are crucial to achieving net-zero CO2 emissions.

This work formed part of a PhD thesis (R.C. Kilbride, *Self-Assembled Nanostructures in Organic Electronics*, December 2022) and a manuscript is currently in the late stages of preparation which the authors intend to submit to a suitable high impact journal. We are grateful to the ILL for allowing this experiment to take place remotely due to Covid-19 restrictions. In particular, our local contact for this experiment, Philipp Gutfreund was invaluable. Philipp performed all measurements remotely, kept the entire experimental team updated on progress and provided excellent assistance with data fitting