Experimental report

13/09/2022

Proposal:	**9-11-1898**	**Council:**	10/2018
Title:	Dynamical study of organic photovoltaics: extending the study from the ps to the ns timescale and investigating effect of composition		
Research area:	Materials		

This proposal is a continuation of 7-04-139

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Samples:
$C_{72}H_{14}O_2$
$C_{73}H_{36}(SO_2)_4$
$(C_{10}H_{14}S)_n$
$C_{72}H_9D_5O_2$
$(C_{10}D_{14}S)_n$

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	5	4	05/07/2019	09/07/2019
IN11	7	7	03/07/2019	10/07/2019

Abstract:

The dynamics of organic semiconductors used in organic photovoltaics (OPV)impacts the different mechanisms involved in the solar energy conversion process. We propose to continue our work on the dynamics of the model system poly(3-hexylthiophene-2,5-diyl)(P3HT) and Phenyl-C61-butyric acid methyl ester (PCBM) by extending the timescale from picosecond to nanosecond and also by investigating different polymer:fullerene ratios. We have already observed on the picosecond timescale that P3HT is frustrated upon blending while PCBM is plasticized by P3HT. We have carried out molecular dynamics simulation on both hydrogenated and deuterated samples and the simulations reproduce the observed trend.We have shown that the partial wrapping of P3HT around PCBM explains this behaviour on the picosecond timescale and we predict that it should impact P3HT dynamics on the nanosecond timescale. We propose to study P3HT dynamics in blend on longer timescale. We would like to study P3HT and PCBM dynamics in blend of different concentration on the picosecond timescale.

CHEMISTRY OF MATERIALS

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Structural Dynamics of Polymer:Non-Fullerene Organic Solar Cell Blends: A Neutron Spectroscopy Perspective

Mohamed Zbiri,* Peter A. Gilhooly-Finn, Peter Fouquet, Christian B. Nielsen, and Anne A. Y. Guilbert*

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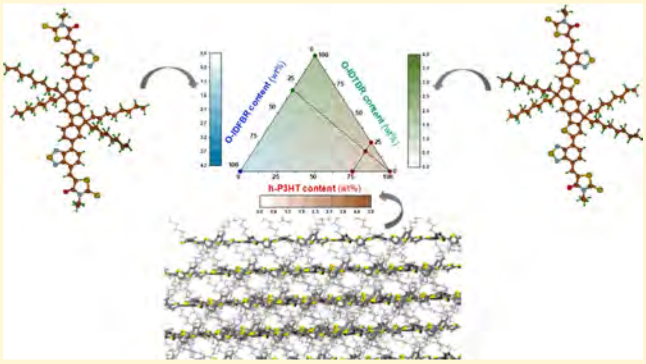

ABSTRACT: Organic solar cells (OSCs) based on ADA-type (acceptor−donor−acceptor) non-fullerene acceptors (NFAs) exhibit improved power conversion efficiency (PCE) compared to the conventional fullerene-based analogues. The optoelectronic properties of the OSC active layer are correlated to the underlying structural dynamics of the active layer blend and therefore influence the device performance. Using synergistically different neutron spectroscopy techniques, we studied the dynamics of binary and ternary blends made of the non-fullerene acceptors O-IDTBR and O-IDFBR and the regioregular donor polymer poly(3-hexylthiophene) (P3HT). Considering key factors like structural relaxation, miscibility, and morphology, within a chosen temperature range, we probed the dynamical responses of the neat phases and the blends using time-of flight quasi-elastic neutron scattering and neutron spin echo measurements, complemented by neutron vibrational spectroscopy. We cover the femtosecond to nanosecond time window directly relevant to the operating active layer molecular processes. Blends of protonated O-IDTBR and O-IDFBR with either deuterated or protonated P3HT were considered for a contrast variation purpose. Our study confirms the observation of the hypomiscibilty of O-IDTBR in the binary P3HT:O-IDTBR compared to O-IDFBR in P3HT:O-IDFBR and points toward a molecular alloying character of the NFA blend O-IDTBR:O-IDFBR, not observed in the ternary P3HT:O-IDTBR:O-IDFBR. A main outcome of this work is the evidenced similar dynamical response of the donor and acceptor components in both the binary and ternary blends, within the accessible experimental picosecond−nanosecond time window and up to 400 K. This finding is in contrast with our previous neutron spectroscopy and molecular dynamics studies of the fullerene-based blend P3HT:PCBM (PCBM: phenyl-C61-butyric acid methyl ester), where we highlighted distinct behaviors of P3HT and PCBM in the blend in terms of the vitrification/frustration of P3HT upon blending and the plasticization of PCBM by P3HT. Alike P3HT vitrification is not presently observed, which we ascribe to the resemblance of the chemical structures of O-IDTBR/O-IDFBR and P3HT. The absence or the weak vitrification evidenced here is in line with recent reports and is likely related to the improved PCE exhibited by the ADA-type NFA-based OSCs.

■ INTRODUCTION

The active layer of polymeric organic solar cells (OSCs) is composed of an electron-donating polymer and (an) electron-accepting small-molecule semiconductor(s). The electron-accepting organic semiconductors, which have been developed to date, can be broadly separated into two classes: (i) fullerene acceptors and (ii) non-fullerene acceptors (NFAs). Although NFAs were developed early on for vacuum-deposited OSCs, fullerene acceptors have been dominating the field since the introduction of the first solution-processed bulk heterojunction due to their compatibility with a large range of donor materials and relative ease of processing.[1] Early NFAs were suffering from a strong tendency to aggregate due to strong π−π interactions stemming partially from their 2D planar shape. Thus, large domains and aggregates of acceptors were forming in the active layer leading to poor efficiencies in comparison with fullerene acceptors. Fullerene acceptors are, however, poorly harvesting the solar energy. Recently, ADA-type (acceptor−donor−acceptor) NFAs started to compete with fullerene acceptors.[2] ADA-type NFAs exhibit three structural elements: the core, the end units, and the side chains enabling controlling the energy levels, optical properties, solubility, crystallinity, and electron mobility. In particular, the excessive aggregation observed in earlier NFAs could be controlled by using twisted cores leading to "3D-like" molecules and by engineering bulky "out-of-plane" side chains. The acceptor groups (end units) can be chosen to ensure good π−π stacking. Recent efforts have made it possible to synthesize

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Quantitative insights into the phase behaviour and miscibility of organic photovoltaic active layers from the perspective of neutron spectroscopy†

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We present a neutron spectroscopy based method to study quantitatively the partial miscibility and phase behaviour of an organic photovoltaic active layer made of conjugated polymer:small molecule blends, presently illustrated with the regio-random poly(3-hexylthiophene-2,5-diyl) and fullerene [6,6]-phenyl C_{61} butyric acid methyl ester (RRa-P3HT:PCBM) system. We perform both inelastic neutron scattering and quasi-elastic neutron scattering measurements to study the structural dynamics of blends of different compositions enabling us to resolve the phase behaviour. The difference of neutron cross sections between RRa-P3HT and PCBM, and the use of deuteration technique, offer a unique opportunity to probe the miscibility limit of fullerene in the amorphous polymer-rich phase and to tune the contrast between the polymer and the fullerene phases, respectively. Therefore, the proposed approach should be universal and relevant to study new non-fullerene acceptors that are closely related – in terms of chemical structures – to the polymer, where other conventional imaging and spectroscopic techniques present a poor contrast between the blend components.

Introduction

Excitons, generated upon light absorption in conjugated polymers, are known to dissociate into free charges in the presence of an electron acceptor material. Bulk heterojunctions made of polymer donor and small-molecule acceptor materials constitute the active layer of organic solar cells. The microstructure of such blends is complex with most likely three phases, a small-molecule rich phase, an amorphous polymer-rich phase and if the polymer is semi-crystalline, a pure crystalline polymer phase.[1] Only few polymers such as poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] (PBTTT)[2] are known to co-crystallise with fullerene acceptors. Because of the asymmetry of the donor and acceptor molecular weights, the small molecule rich phase is nearly pure. The amorphous polymer-rich phase is beneficial for charge separation[3] while the presence of nearly pure percolated donor and acceptor domains are beneficial for the transport of charges generated at the donor:acceptor heterojunction to the electrodes.

If crystallinity is relatively simple to monitor by methods such as X-ray diffraction, the composition of the amorphous mixture of the blends[4,5] as well as changes in conformation with respect to the neat materials is more difficult to access.[6,7] Although crystallinity has been shown to improve charge transport[8] and potentially lead to extra driving force for charge separation by lowering the electronic energy levels,[2] a spinodal-type decomposition emerged as a new picture for phase separation at length scales directly relevant to the operation of the devices,[9–11] with the coarsening of this phase separation directly linked to burn in degradation mechanisms.[10] The crucial role of the Flory–Huggins interaction parameter (χ) in controlling phase behaviour, *i.e.* miscibility in the amorphous phase has been emphasised and related to solar cell efficiency.[11,12] χ is both composition- and temperature-dependent, and is related to the thermodynamical stability of the blend. However, the formation of the bulk heterojunction proceeds through solution processing.[13] Thus, the final microstructure is not thermodynamically stable but kinetically trapped. Crystal seeds of small molecules and more or less large crystals of the polymer may form in the solution depending on the quality of the solvent for each component of the blend.[14–16] Moreover, liquid–liquid demixing may occur during solvent evaporation which could contribute to enhance phase separation.

Previously, we used a combination of quasi-elastic neutron scattering (QENS) measurements[17] and molecular dynamics

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Mapping Microstructural Dynamics up to the Nanosecond of the Conjugated Polymer P3HT in the Solid State

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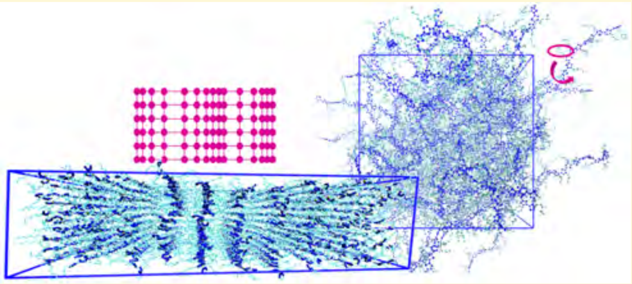
Supporting Information



ABSTRACT: We present a detailed microscopic study of the structure−dynamics relationship of both regioregular (RR) and regiorandom (RRa) poly(3-hexylthiophene) (P3HT) using synergistically different elastic, quasi-elastic, and inelastic neutron scattering techniques. The length scale and the time scale covered by the study is tens of angstroms and the femtosecond to nanosecond, respectively. Deuteration is employed to modulate the coherent and incoherent cross-sections of the materials, beyond a contrast variation purpose, allowing particularly access to both self-motions and collective dynamics of the materials. The neutron scattering measurements are underpinned by extensive quantitative numerical simulations using large-scale classical molecular dynamics (MD) simulations, as well as molecular and periodic first principles quantum chemical (QC) calculations. MD simulations reproduced well the main structural features and slow motions. Further, MD results shed light on differences in collective dynamics between Q-values linked with the $\pi-\pi$ stacking and the lamellar stacking of the polymer, with the crystalline phase being the most impacted. However, MD led to a limited description of molecular vibrations. In this context, first principles molecular QC calculations described well the high-energy vibrational features (>900 cm^{-1}), while periodic QC allowed description of the low- and midenergy vibrational range ($200-900$ cm^{-1}). The midenergy range is predominantly associated with both intramolecular and intermolecular mode coupling, which encloses information about both the polymer conformation and the polymer packing at short range. We show that the presented combined approach of neutron-based measurements and multicomputational calculations allows the full mapping out the structural dynamics of conjugated polymers such as P3HT. One of the outcomes of this study is the validation of the common assumption made that RRa-P3HT is a good approximation for the amorphous phase of RR-P3HT at the macroscopic level, although some differences are shown at the molecular level. The present work helps to clarify unambiguously the latter point which has been largely overlooked in the literature. By comparing the neutron vibrational results with available Raman and IR data in the literature, we highlight the importance to complement such optical spectroscopy techniques with inelastic neutron scattering. The latter offers the advantage of being insensitive to the delocalized π-electron system and, thus, enables relevant quantities such as conjugation lengths to be inferred.

■ INTRODUCTION

Conjugated polymers have attracted keen interest over the past decade for their potential applications as semiconductors in various types of devices: organic light emitting diodes, organic solar cells, organic field-effect transistors, etc. Because polymers are soft materials, a range of dynamics occurs over an extended time scale, from femtosecond to millisecond, and are likely to impact the optoelectronic properties of the material.

Femtosecond dynamical processes like vibrations have been evidenced to impact absorption,[1] inner reorganization energy,[2] charge transfer between molecules of the same types[3] and between different molecules at a heterojunction,[4] delocalization,[5] and so more generally charge transport[6] and charge separation processes.[7] Slower dynamics, on the picosecond to

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