# Experimental report

02/09/2016

**Proposal:** **7-04-139**

**Council:** 10/2014

**Title:** Vibrational and local dynamics as a tool to better understand the microstructure-charge generation relationship in organic photovoltaics

**Research area:** Materials

**This proposal is a new proposal**

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**Local contacts:** Mohamed ZBIRI

**Samples:** phenyl-C61-butyric acid methyl ester
poly(cyclopentadithiophene-alt-benzothiadiazole)

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| IN1 LAG | 4 | 0 | | |
| IN6 | 5 | 5 | 12/05/2015 | 17/05/2015 |
| IN16B | 4 | 0 | | |
| IN5 | 4 | 0 | | |

## Abstract:

In organic photovoltaic devices, the photocurrent generation results from the dissociation of excitons into free charges that happens at the interface between a polymer donor material and a fullerene acceptor material. We propose to study the relationship between molecular packing and local dynamics close to a donor acceptor interface on the efficiency and rate of charge separation. There is some indirect experimental evidence for a relationship. But this is hard to probe experimentally because of the difficulties in probing structure in small domains and in unambiguously identifying excited state species formed following photoexcitation. However the different phases of material will generally express different vibrational modes and these modes are moreover modulated under excitation. We propose to probe the vibrational and local dynamic behaviour of the different phases of material, and later on their behaviour under photoexcitation, combining inelastic and quasi-elastic neutron scattering in order to determine the relationship between presence of different phases and the efficiency of charge pair separation.

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Letter

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# New Insights into the Molecular Dynamics of P3HT:PCBM Bulk Heterojunction: A Time-of-Flight Quasi-Elastic Neutron Scattering Study

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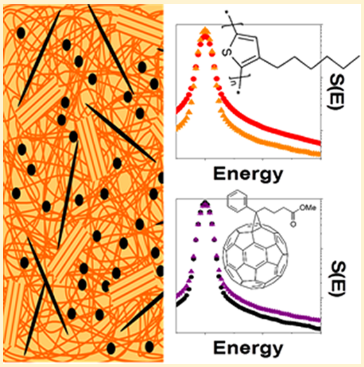
*Supporting Information*

**ABSTRACT:** The molecular dynamics of organic semiconductor blend layers are likely to affect the optoelectronic properties and the performance of devices such as solar cells. We study the dynamics (5−50 ps) of the poly(3-hexylthiophene) (P3HT): phenyl-C61-butyric acid methyl ester (PCBM) blend by time-of-flight quasi-elastic neutron scattering, at temperatures in the range 250−360 K, thus spanning the glass transition temperature region of the polymer and the operation temperature of an OPV device. The behavior of the QENS signal provides evidence for the vitrification of P3HT upon blending, especially above the glass transition temperature, and the plasticization of PCBM by P3HT, both dynamics occurring on the picosecond time scale.



Organic photovoltaic (OPV) devices have attracted a keen interest over the past decade for their potential low-cost, light weight, flexibility, and ease of use and processing. In contrast to inorganic solar cells, the photocurrent generation results from two consecutive processes consisting of the dissociation of photogenerated excitons into free charges at a donor:acceptor (D:A) interface, followed by the transport of those free charges to the relevant electrodes. Transient optical spectroscopy has been used extensively to probe the radiative decay of the different states on time scales from a few femtoseconds up to milliseconds to infer the mechanisms of such processes.[1] If processes occurring at both time scales are not fully understood yet, there is some evidence that the separation of excitons into free charges occurs on tens of femtoseconds to picoseconds time scales.[2]

The influence of the microstructure of the D−A blend on the efficiency of such processes has been highlighted.[3] However, only a few reports exist on the effect of both polymer[4] and fullerene dynamics on these processes.[5] The impact of adding a fullerene derivative on the polymer dynamics has been inferred by showing an increase of the glass transition temperature as a function of the fullerene addition, using differential scanning calorimetry.[6] However, extensive studies on nonconjugated polymers highlight the occurrence of various dynamical behaviors within the broad time scale of femtoseconds to milliseconds. The latter reflect different dynamics ranging from vibrations of atoms, through rotations of the side chain groups (picoseconds to nanoseconds), to backbone motions at longer time scales (>nanoseconds). Therefore, these dynamics are likely to impact the photoelectric processes.

Furthermore, under practical operational conditions, OPV devices operate within a temperature range from ambient temperature up to 360 K (at a maximum sun exposure).[7] Therefore, studying the temperature-dependence of such dynamics is of considerable importance.

Recently, a few computational studies attempted to capture the impact of the D−A microstructure by using molecular dynamic simulations as an initial structure to study charge separation.[8] However, the simulated structures were not validated experimentally, neither were the dynamics studied. Reducing the dimensionality from atom coordinates to few degrees of freedom is needed to carry on more detailed quantum chemistry calculations from those initial structures, and is a demanding task.

Paternó et al. studied the dynamics of the hydrogenated poly(3-hexylthiophene) (P3HT):phenyl-C61-butyric acid methyl ester (PCBM) blend, using different solvents, within a

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