Experimental report

16/12/2019

Proposal:	**9-11-1810**	**Council:**	10/2016
Title:	Vibrational Spectroscopy to study organic photovoltaics		
Research area:	Soft condensed matter		

This proposal is a new proposal

Main proposer:	**Anne GUILBERT**
Experimental team:	Mohamed ZBIRI Anne GUILBERT
Local contacts:	Mohamed ZBIRI

Samples:	SC10H14 SC10D14 C72H14O2

Instrument	**Requested days**	**Allocated days**	**From**	**To**
IN1 LAG	5	4	26/03/2018	30/03/2018

Abstract:

The dynamics of organic semiconductors used in organic solar cells impacts the different mechanisms involved in the solar energy conversion process. In a previous experiment, we have measured the dynamics of poly(3-hexylthiophene-2,5-diyl) (P3HT) and Phenyl-C61-butyric acid methyl ester (PCBM). Using deuterated materials to increase the signal of one of the blend material, we have observed the frustration of P3HT 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. Furthermore, we have carried out Raman spectroscopy measurements and test inelastic neutron scattering that points towards coupling between polymer and fullerene in the blend. We would like to continue the study by investigating different polymer:fullerene ratio to pinpoint the mechanisms responsible for the frustration of the polymer and plasticization of the fullerene and elucidate the coupling between polymer and fullerene in the blend. We are already carrying out molecular dynamics simulation and density function theory calculations to try to understand these observations.

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

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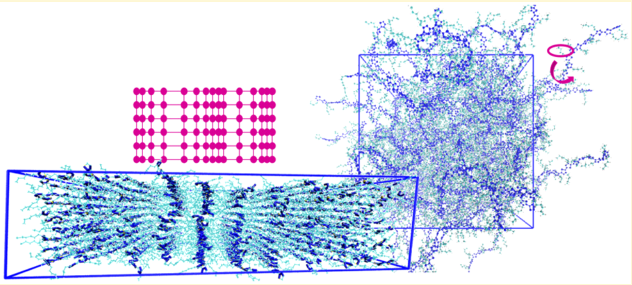
Supporting Information



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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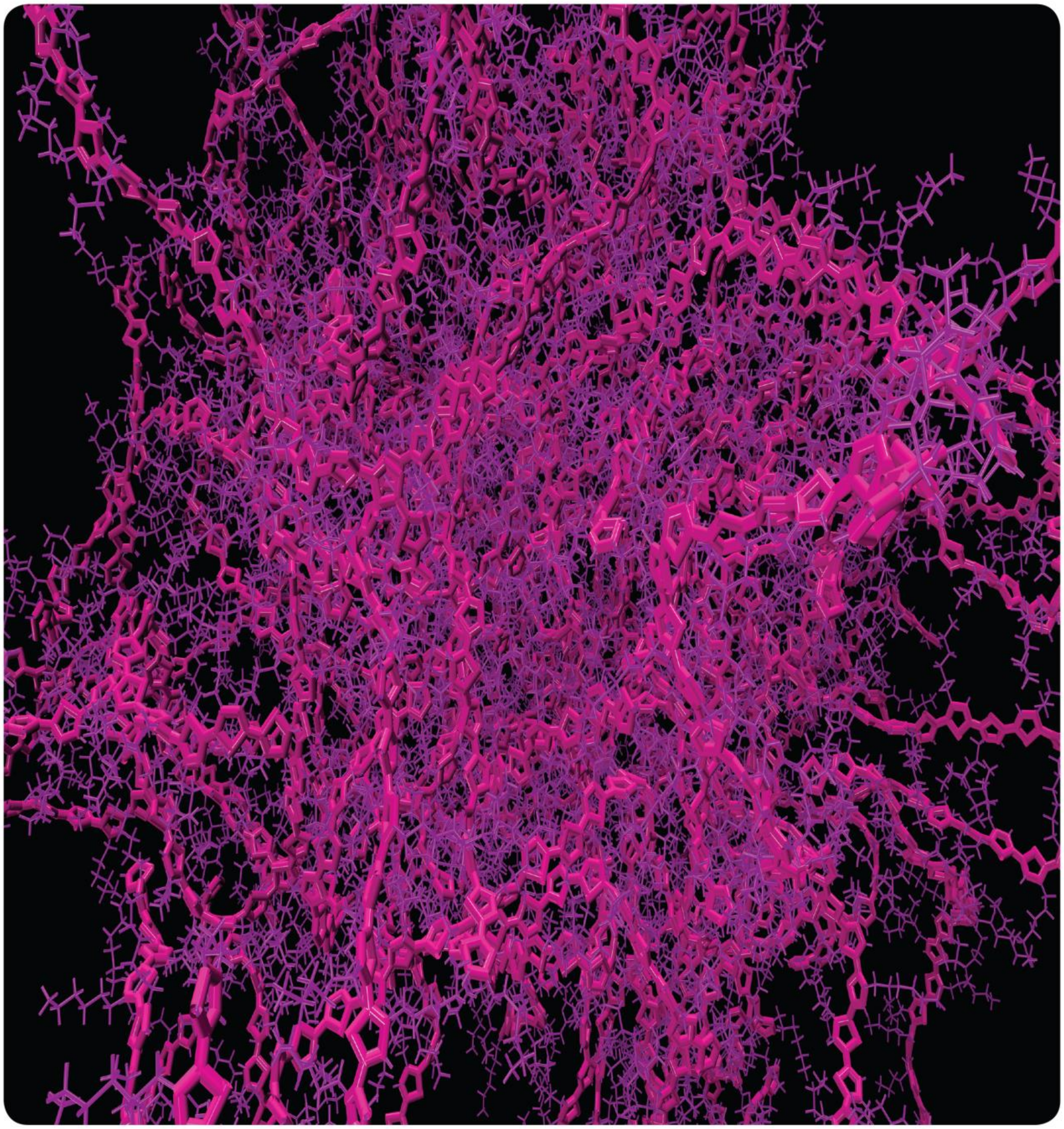

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