Experimental report

16/12/2019

Proposal: **7-04-153** **Council:** 10/2016

Title: Probing dynamics in organic photovoltaics under light excitation

Research area: Soft condensed matter

This proposal is a continuation of 7-04-139

Main proposer: **Anne GUILBERT**

Experimental team:
Mohamed ZBIRI
Anne GUILBERT
Nicholas SIEMONS
Jenny NELSON

Local contacts:
Bernhard FRICK
Mohamed ZBIRI

Samples:
SC10H14
SC10D14
C72H14O2

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	0	4	19/10/2018	23/10/2018
IN6	6	0		
IN16B	6	4	08/12/2016	12/12/2016

Abstract:

The dynamics of organic semiconductors used in organic photovoltaics (OPV) impacts the different mechanisms involved in the solar energy conversion process. Very little attention has been paid to the impact of light absorption on the organic semiconductor. Some experimental and computational studies evidenced that light exposure impacts the dynamics of OPV blends modulating the polymer conformation and by fullerene dimerization . We propose to study the dynamics of the model system poly(3-hexylthiophene-2,5-diyl) (P3HT) and Phenyl-C61-butyric acid methyl ester (PCBM) under light exposure. We have already measured in a previous experiment the ground state and observed 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 are further analysing the trajectories to pinpoint the mechanisms responsible for the frustration of the polymer and plasticization of the fullerene. We propose to study the impact of the light absorption on the observed frustration and plasticization.

CHEMISTRY OF MATERIALS

Article

Cite This: *Chem. Mater.* 2019, 31, 9635−9651

pubs.acs.org/cm

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

Anne A. Y. Guilbert,*[,†] Mohamed Zbiri,*[,‡] Peter Anthony Finn,[¶] Maud Jenart,[§,∥] Peter Fouquet,[‡] Viviana Cristiglio,[‡] Bernhard Frick,[‡] Jenny Nelson,[†] and Christian B. Nielsen[¶]

[†]Department of Physics and Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, United Kingdom

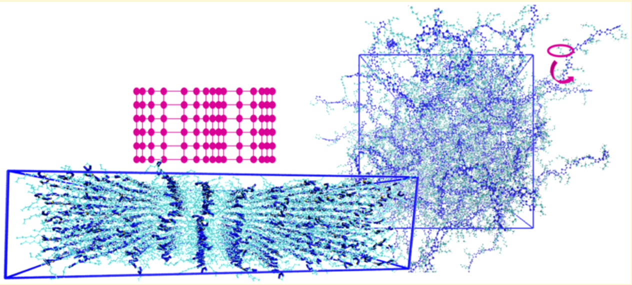
[‡]Institut Laue-Langevin, 71 avenue des Martyrs, Grenoble Cedex 9, 38042, France

[¶]Materials Research Institute and School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

[§]Department of Chemistry and Centre for Plastic Electronics, Imperial College London, South Kensington, London SW7 2AZ, United Kingdom

[∥]AGC Glass Europe SA, Avenue Jean Monnet 4, 1348 Louvain-la-Neuve, Belgium

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 π−π 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.

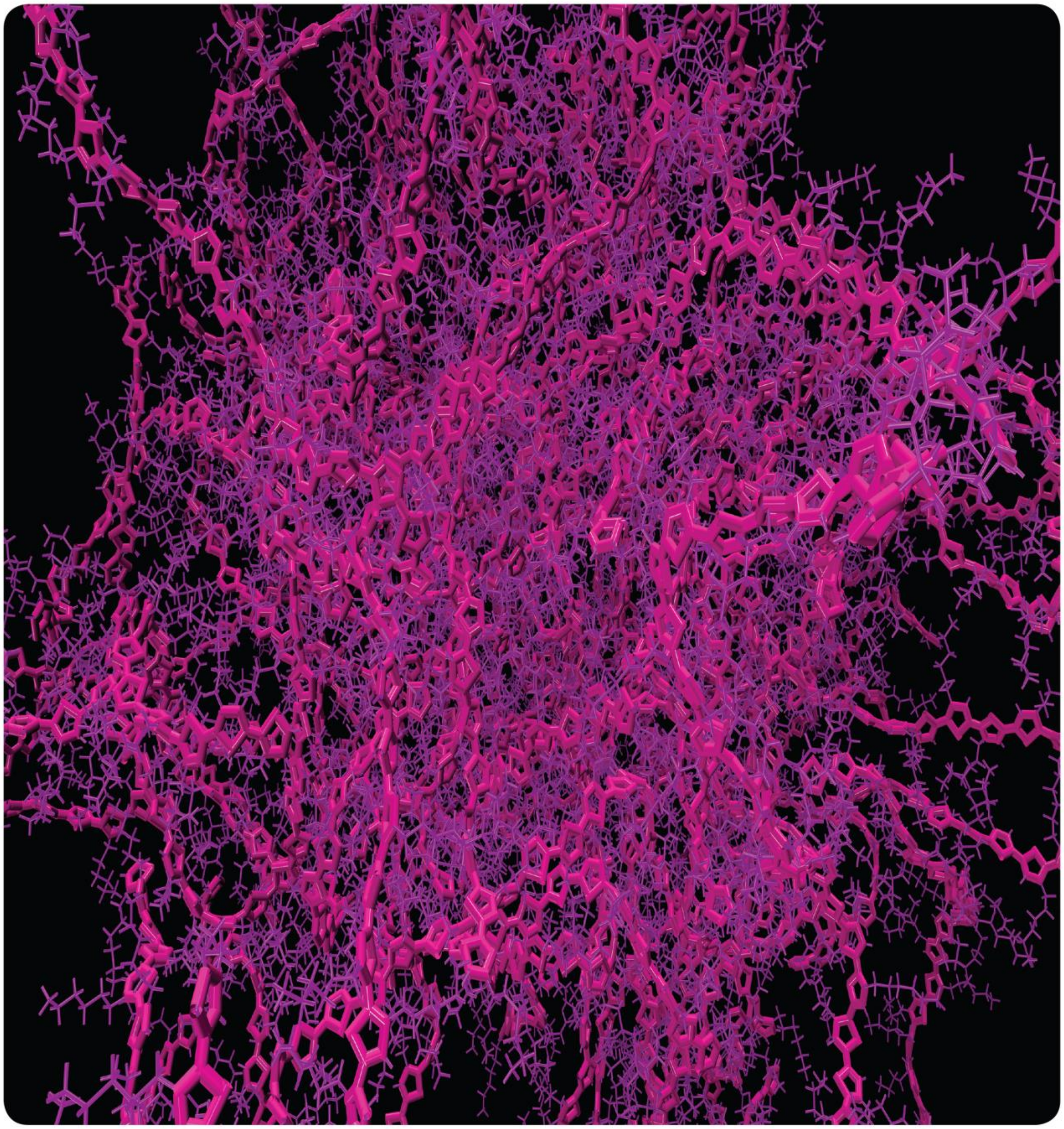
Femtosecond dynamical processes like vibrations have been evidenced to impact absorption,[1] inner reorganization energy,[2] charge transfer between molecules of the same types[3] and between different molecules at a heterojunction,[4] delocalization,[5] and so more generally charge transport[6] and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

Received: July 22, 2019
Revised: September 26, 2019
Published: September 30, 2019

DOI: 10.1021/acs.chemmater.9b02904

cm CHEMISTRY OF MATERIALS

DECEMBER 10, 2019 | VOLUME 31 | NUMBER 23 | pubs.acs.org/cm



ACS Publications
Most Trusted. Most Cited. Most Read.

www.acs.org