

Charge Transfer Dynamics of Inner-Shell Excited States on Organic Films for Photovoltaics

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INTRODUCTION

Organic optoelectronic devices constitute an important class of materials, which can be applied in renewable sources of energy. The fundamental physical process is the charge transfer dynamics of an *exciton* generated after solar radiation absorption. Donor-acceptor polymers, for example, presents moieties with distinct functions in this process.¹ In this work, the structure of thin-films of PFO-DBT and PSiF-DBT are studied by means of inner-shell spectroscopy and *ab initio* methods.

METHODS

Experiments were done at soft X-ray spectroscopy beamline (SXS) at the Brazilian Synchrotron Light Source (LNLS). Spectra in NEXAFS and RAS were measured. Films were deposited by spin coating on indium tin oxide (ITO) coated glass. Charge transfer was evaluated using different temperatures at annealing treatment, which changes the film ordering.

As the excited states are intrinsically localized, the monomer was used as model system to rationalize the polymer inner-shell spectrum. Geometries for monomers were obtained using optimization procedures with DFT methods for systems with five monomer units to represent the polymer structure, from which the monomer is extracted.

The electronic structure was performed with Molpro package. Contracted Configuration Interaction Singles and Doubles excitations method (CISD) was applied to calculate first states at excitation edge for each chemical element. Core relaxation effects on molecular orbitals was obtained by restricted open-shell Hartree-Fock method (HF), constraining the core orbital occupation. We got transition energies and intensities at silicon, nitrogen and sulphur *K*-

edges. Non-adiabatic coupling coefficients between excited states were also evaluated to indicate possible channels for charge transfers.

RESULTS AND DISCUSSION

Calculated transition energies and intensities are in good agreement with spectroscopic experimental data, as exemplified at Figure 1, corroborating our analysis concerning charge transfer in those excited states as will be shown in the symposium presentation.

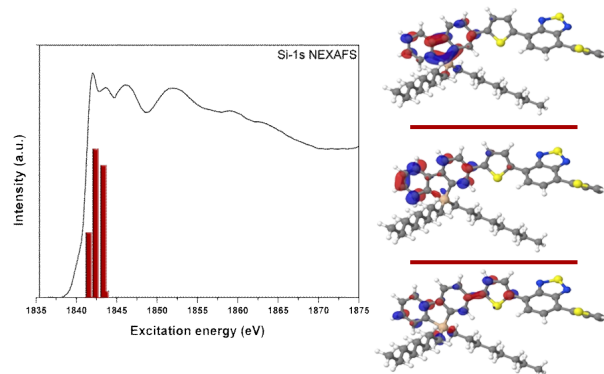


Figure 1. Absorption spectra at Silicon *K*-edge and representation of molecular orbitals involved in three more intense transitions.

CONCLUSIONS

Our methodology presents promising results in order to describe the electronic structure of inner-shell states in polymers. Associated with experiments, it's contributing to understand charge transfer processes in photovoltaics.²

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¹ J. L. Brédas, et al., *Acc. Chem. Res.*, 42 (11), 1691-1699, (2009)

² Y. Garcia-Basabe, et al., *J. Phys. Chem. C.*, 118 (41), 23863-23873, (2014)