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Temperature effects on polarons mobility in nonfullerene organic heterojunction

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Abstract
In this work, we studied electronic transport in organic solar cells (OSC) with the aid of the open-source program Excimontec, which uses the kMC algorithm and Marcu's theoretical model to model the transfer rate of charge. The aim of the study was to simulate the effect of temperature variation on the rate of mobility of charge carriers in heterojunctions composed of non-fullerene acceptor units BYG-1/SMD and BYG-2/SMD together with a small molecule donor (SMD) appropriate.

Introduction
The Small Molecule Donors (SMDs) have several potential advantages and applications compared to their polymer equivalents. In this context, Fullerene Fred Small Molecule Acceptors (NFAs) have become a prominent research area in CSOs. Inmost CSOs, based on non-fullerene materials, the mobility of electrons to acceptor the material is generally less when compared to holes in the donor material [1].

To use non-fullerene acceptors in solar cells, it is necessary to design them to have high electronic mobility. NFAs that have a fraction of material with a strong tendency to remove electrons (such as perylene diimide) have high electronic mobility that increases with the addition of more materials with the potential to extract electrons.

The present work proposed to investigate electronic transport inorganic solar cells (OSC) in the structure of a model based on the kMC algorithm, where we implemented Marcu's theoretical model to calculate charge transfer rates. We performed the simulations with the aid of the open-source programs Excimontec.exe and Ising_OPV.exe, with the focus on studying the mobility of charge carriers in heterojunctions composed of non-fullerene acceptor units BYG-1 and BYG-2 (materials manipulated on a molecular scale using an electron donor fluorene unit as the central nucleus, connected on both sides to the 2-ethyl hexyl naphthamide group which removes electrons through the linking groups formed by strong electron acceptors *5-fluorobenzo [c] [1,2,5] thiadiazole* and *benzo [c] [1,2,5] thiadiazole*, respectively) (**Figure 1**) together with a small molecule donor (SMD) appropriate [2].

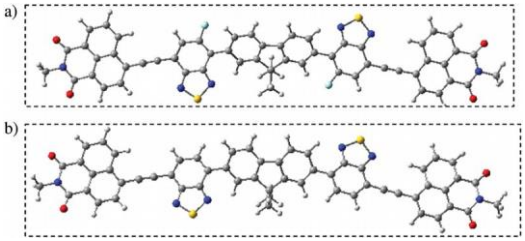

Figure 1 - Optimized structures of (a) BYG-1 and (b) BYG-2 molecules [2]

Methodology

To make up the SMDs portion of the heterojunction, we use the organic molecule know as *1,8-naphthylamide* (NAI) at the terminal sites of the designed molecules that can drive trends in molecular self-assembly and help weaken intermolecular interactions that can control aggregation.

Tabela 1: Parameters Donor / Acceptor

	Doador		Aceitador
	BYG-1	**BYG-2**	**SMD**
HOMO	-5,89 *eV*	-5,84 *eV*	-5,28 *eV*
LUMO	-3,40 *eV*	-3,39 *eV*	-3,26 *eV*
	μ_e	μ_h	**PCE**
BYG-1/SMD	$2,87 \times 10^{-4} cm^2 V^{-1} s^{-1}$	$9,93 \times 10^{-5} cm^2 V^{-1} s^{-1}$	8,67 %
BYG-2/SMD	$1,9 \times 10^{-4} cm^2 V^{-1} s^{-1}$	$9,93 \times 10^{-5} cm^2 V^{-1} s^{-1}$	7,12 %

The simulations were carried out from a set composed of 10 morphologies generated in Ising_OPV.exe and executed in the Excimontec.exe parameter file, which were configured to represent a cubic structure of 50x50x50 times sites with 1 nm away from each other and with periodic limits established in all directions, but activated only in x and y orientations, and deactivated in z. Then, we set the value of 0.5 for the volume fraction of the mixtures that make up the BHJs (used to initialize a random mix) and 0.4 for the value of the interaction energies to control the rate of the phase separation process. We assume the fixed value of the Internal Potential to be -0.1 V and use 200 Monte Carlo steps to control the number of iterations in the program. The HOMO and LUMO parameters of the BYG-1, BYG-2, and SMD compounds that served as input for the simulations and the output (mobility values got experimentally) are in **Table 1** [2].

Results and Discussions

Using Marcu's Theory to describe the interdependence between temperature and mobility, we can assume that transfer integrals and reorganization energy do not change with temperature. We can assume that transfer integrals and reorganization energy do not change with temperature. We can express the relationship between mobility and temperature through the equation $\mu = T^{-3/2}\exp(-\lambda 4k_BT)$, where the term λ is the energy of the organization. The exponential term $\exp(-\lambda 4k_BT)$ predominates at low temperatures, while the power $T^{-3/2}$ dominates at high temperatures. This means that mobility increases for temperatures above T [3,4]. Directly relates maximum mobility to the term $\lambda/4$. Thus, we see that Marcu's theory works best for high-temperature values.

We observed a notable peculiarity regarding the shape of the graph that describes the electron mobility in the heterojunctions BYG-2/SMD as a function of temperature (**Figure 2**). In this graph, we see clearly that the mobility rate decreases sharply within T≈200K and increases again at T≈250K.

The high electronic mobility in the compound based on BYG-1 is because of incorporating the fluorine atom in the electron-donating structure of the molecule, significantly improving intermolecular interaction through C-F⋯S and C-F⋯H. Thus, we can conclude that the lack of fluorine in the *benzo [c][1,2,5] thiadiazole* that makes up BYG-2/SMD show that the intrinsic physical phenomena responsible for delaying the increase in electronic mobility (such as recombination polarization, for example) manager, by increasing the temperature to values above T≈250K, the system gains energy to overcome the effects that impair mobility.

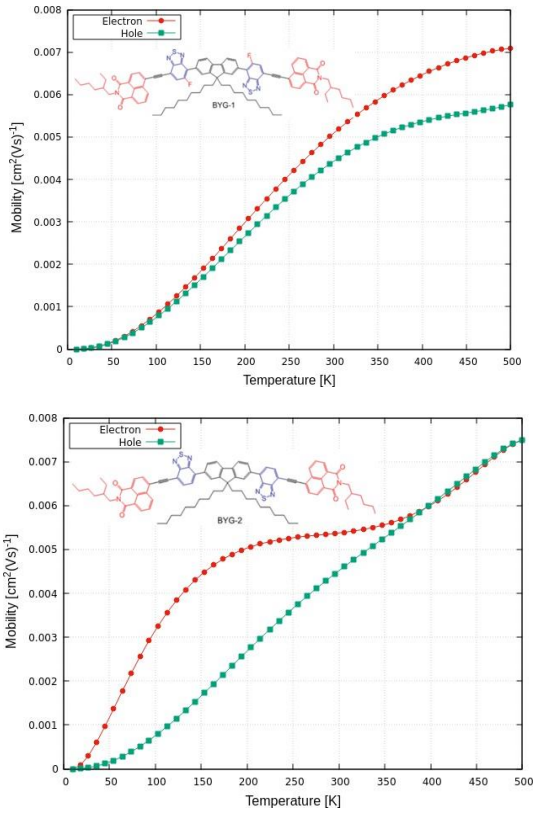

Figure 2. Analysis showing the dependence between temperature of electrons and holes mobility in heterojunctions BYG-1/ SMD and BYG-2/ SMD.

Conclusions

The set of simulations aimed to research the relationship between Temperature [K] and Mobility of the polarons [$cm^2 V^1 s^{-1}$]. The methodology used by Excimontec proved to be effective for this study in devices subjected to high-temperature values, since mobility presented an increasing behavior in the heterojunctions BYG-1/SMD and BYG-2/SMD with increased temperature, between 50K and 500K. We observed an exception to this behavior when simulating electron mobility in the BYG-2/SMD structure, where we see an abrupt reduction in mobility in the temperature range between T≈200 K and T≈250K because of the absence of fluorine atoms in the electron donor structure of the molecule, a fact consistent with the theoretical prediction.

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